Characterization of vermiculites from the Mozambique Belt of Tanzania for agricultural applications

By

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DECLARATION

I declare that the work presented in this thesis has been composed by myself and has not been accepted for any other application for a degree. All sources of information quoted have been duly acknowledged by means of references.

Ernest Melkiory Magesa Marwa

Date.....14/08/2009.....

DEDICATION

To the farmers of Tanzania who rely on subsistent rain-fed agriculture for their livelihood

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PUBLICATIONS FROM THIS STUDY

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ABBREVIATIONS

Al	Aluminium
ANOVA	Analysis of variance
As	Arsenic
Ba	Barium
Ca	Calcium
Cd	Cadmium
CEC	Cation exchange capacity
cmol $_{(+)}$/kg	Centimolar of cations per kilogramme
cm	Centimetre
Cl	Chlorine
Co	Cobalt
Cr	Chromium
Cu	Copper
d	Day
DM	Dry matter
DNA	Deoxyribonucleic acid
DTPA	Diethylene triamine pentaacetic acid
EDS	Energy dispersive X-ray system
EPMA	Electron probe microanalysis
Fe	Iron
Ga	Gallium
h	Hour
Hg	Mercury
ICP-MS	Inductively coupled plasma-mass spectrometry
K.	Potassium
La	Lanthanum
MB	Mozambique Belt
Mg	Magnesium
Mn	Manganese
Mo	Molybdenum

Na	Sodium
Nb	Niobium
N	Nitrogen
Ni	Nickel
P	Phosphorus
Pb	Lead
pH	Negative logarithm of the hydrogen ion concentration
Rb	Rubidium
R1	*Reichweite* (50/50 stacking order of mineral components)
S	Sulphur
Sc	Scandium
SEAMIC	Southern and Eastern African Mineral Centre
SEM	Scanning electron microscopy
Si	Silicon
Sn	Tin
Sr	Strontium
TEC	Total exchangeable cations
$t\ ha^{-1}$	Tons per hectare
Th	Thorium
Ti	Titanium
*TMV*1	Tanzania maize variety number one
U	Uranium
V	Vanadium
v/v	Volume by volume
Wt %	Weight percentage
XRD	X-ray diffraction
Y	Yttrium
Zn	Zinc
Zr	Zirconium

ABSTRACT

Crop productivity in Tanzania is generally low and this is partly due to inadequate and poor retention of plant nutrients and moisture by some soils. The country has several vermiculite deposits, but none of them are exploited to improve the soil properties because of lack of information on their potential suitability. The aim of this research was to establish the suitability of vermiculites from Tanzania as soil improvers for crop production through characterization. The study involved five samples from Tanzania and one from South Africa, which was included for comparison purposes. Mineralogy of the samples was studied by a combination of X-ray diffraction (XRD) and scanning electron microscopy (SEM) fitted with energy dispersive system (EDS), whereas electron probe microanalysis (EPMA) and inductively coupled plasma-mass spectrometry (ICP-MS) were used to establish elemental compositions. Extractability of some heavy metals in vermiculites was assessed by diethylene triamine pentaacetic acid extraction (DTPA), whilst extractable P was determined by acetic acid extraction. The pH, water release characteristic, and cation exchange capacity (CEC) were among the physical and chemical properties assessed. Pot and field studies were then carried out in Tanzania to assess maize response and retention of macronutrients in a sandy soil amended with vermiculites. Maize was used as a test crop. The results found indicate that not all samples are vermiculites, some are hydrobiotites. Analysis shows that none of them contain hazardous accessory minerals. However, some have elevated concentrations of Cr and Ni, but these heavy metals are insignificantly plant available and do not inhibit the uptake of essential plant nutrients. Hence, the studied vermiculites are safe to exploit for crop production. In addition, all are slightly alkaline with high CEC and, thus, they are suitable as a growing medium with ability to retain plant nutrients from leaching. However, heating above 600 °C should be avoided as it reduces the CEC of vermiculites by more than 90 % and makes

some of the exfoliated products strongly alkaline and, thus, unfavourable for crop production. The Tanzanian vermiculites can retain plant-available water but their ability is less than vermiculite from South Africa. The P in these vermiculites is extractable and extractability increases on heating to 400 °C. Further heating makes P insoluble and less extractable. Maize vegetative growth, dry matter yield, and nutrient uptake were significantly enhanced by adding vermiculite to the soil over the control. In addition, it retained and fertilized the soil with P. Pre-heated vermiculite at 600 °C performed better than unheated vermiculite and it inhibited the fixation of the applied K and N. It was concluded that the Tanzanian vermiculites have a recommendable potential of improving soil properties for crop production when heated at a temperature of not more than 600 °C. However, more field trials are recommended on other types of soils and crops other than sand and maize used in order to widen the scope of their utilization in Tanzania.

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CHAPTER 1

INTRODUCTION

1.1 PROBLEM STATEMENT AND JUSTIFICATION OF THE STUDY

Tanzania is an agricultural country and the livelihood of nearly 80 % of Tanzanians depends directly or indirectly on subsistence rain-fed agriculture (Mkapa, 2005). Agriculture contributes about half of Tanzania's gross national product (GNP) and provides about 90 % of the rural employment (Mmbaga and Lyamchai, 2001). The main food crops grown in Tanzania are maize, rice, cassava, banana, sorghum, and beans, while cash crops are cotton, tea, coffee, and sisal. Although agriculture is the backbone of the economy, crop productivity is generally low as a result of a number of factors; among them, is inadequate rainfall and poor soil water retention (Ley *et al.*, 2002; Mutiro *et al.*, 2006). The onset and distribution of that rainfall is also unpredictable with most parts of the country experiencing low and erratic rainfall accompanied by long dry spells during the rainy seasons (Mbilinyi *et al.*, 2005; Mapande and Reason, 2005).

The average annual rainfall over the entire country is about 1042 mm (Agrawala *et al.*, 2003) with only half of the country receiving more than 762 mm annually (Mwandosya *et al.*, 1998). The result is soil water stress conditions during the growing season and, thus, reduction in crop productivity. Plant growth is retarded due to insufficient water content in the leaf tissues for plant metabolic activity (Kaya *et al.*, 2006). Apart from the low and unreliable rainfall, the low crop productivity is also compounded by inadequate content and retention of plant nutrients by some soils under crop production (Mwakalila, 2006). Plant nutrients in the soil are lost easily through leaching due to poor retention capacity. The outcome is frequent food

insecurity not only to the farmers but also to the nation. Importation of food from outside the country is sometimes inevitable.

Use of vermiculite in agriculture and horticulture can be one of the alternative means of assisting the farmers in Tanzania to improve soil productivity. Vermiculite can be used in agriculture and horticulture with a marked improvement in soil properties and increase in crop yields. Records show, for instance in Saudi Arabia, Sabrah *et al.* (1993) have found that the application of 4 % w/w vermiculite to the sandy soil improved its physical and chemical properties and, consequently, enhanced the N-uptake and increased wheat yield as well as grain protein content. This was because vermiculite in the soil increased moisture and nutrient retention and, consequently, their availability to the plant.

Laboratory and pot experiments carried out by Suganya and Sivasamy (2006) using 1 % (20 t ha^{-1}) of vermiculite mixed with sandy soil in growing finger millet indicated a significant improvement in water retention of up to 80 % over the control and an increase in the cation exchange capacity by 64 %. Similarly, Jacobs *et al.* (2003) have found an increase in mean height growth for seedlings grown on soil with applied vermiculite as compared to soil with no vermiculite. In India, Jayabalakrishnan (2007) has similarly found an increase in grain yield of sunflower of nearly 1.68-fold when 5 t ha^{-1} of vermiculite was used as a soil amendment. Vermiculite enhanced the cation exchange capacity (CEC) and improved the physical condition of the soil for the productivity of sunflower.

In the State of Minas Gerais in Brazil, the use of vermiculite in 1988/98 significantly increased the yields of soybean, maize, and coffee by 56, 15 and 13 % respectively (Schundler, 2008). In another farm at Fazenda Rio Bonita in Brazil, the application of vermiculite increased

sorghum yield by 29 % (Schundler, 2008). All this was because vermiculite has the favourable properties of growth medium including high CEC and high water retention capacities (Tisdale *et al.*, 1993). In addition, when vermiculite undergoes decomposition (weathering) substantial amounts of macronutrients such as of K^+ and Mg^{2+} and a number of micronutrients are released into the soils, resulting in an improvement in the fertility status of the soils (Kužvart, 1984).

There is the potential of increasing soil productivity in Tanzania by utilizing the country's vermiculite deposits (Harris, 1961; Williams and Skerl, 1940). The deposits are currently not exploited. In the late nineteen fifties an attempt was made to mine 200 tons of vermiculite from the Mikese area in the Mozambique Belt of Tanzania and an exfoliation plant was set up in Dar es Salaam (Harris, 1961). Unfortunately, mining did not last long due to a lack of a satisfactory local market, and no mention is given for what purpose it was used. Kwekivu is another area in the same belt that has been reported to have high quality vermiculite that has never been exploited (Williams and Skerl, 1940). At the time it was discovered during regional geological mapping, the deposit was inaccessible by road or train, but currently the area is accessible. Other deposits that are present in the Mozambique Belt are just mentioned in the geological reports without any further note.

The absence of adequate information on the potential suitability of vermiculites from Tanzania for various applications, particularly in the sector of agriculture which is the backbone of the country's economy, could be among the reasons that are hindering their exploitation. No characterization has so far been done to establish their actual compositions and properties as well as their performance in improving soil properties for crop production. Lack of those

essential data makes vermiculites in the Mozambique Belt of Tanzania non quantifiable resources.

The Tanzanian vermiculites are widely distributed and occur near the surface in the rural areas where the majority of the farmers are living; thus, exploitation and distribution to the farmers will not be costly. In addition, mining of vermiculites would provide employment to the rural community as well as being a source of revenue to the government. However, they require characterization to assess their suitability for agricultural applications and to ascertain whether or not they contain hazardous minerals and elevated concentrations of trace elements, which could be of health and environmental concern. Characterization could also provide baseline data for further studies and comparisons with other vermiculites produced elsewhere in the world. Thus, it will assist in marketing the Tanzanian vermiculites.

1.2 AIM AND OBJECTIVES

The aim of this study was to characterize and establish whether or not vermiculites from the Mozambique Belt of Tanzania are suitable as soil improvers for agricultural applications. In order to fulfil the above aim, a range of studies was carried out with the following specific objectives:

1. To identify and quantify the mineral phases in vermiculites and evaluate their safety records in handling as well as for agricultural applications.
2. To establish the chemical compositions of vermiculites and quantify the total concentrations of the elements they contain with respect to agricultural applications.
3. To assess the extractability of trace elements in vermiculites and their response to heating.

4. To establish the physical and chemical properties of vermiculites which are of agronomic significance and to assess their variation in response to heating.
5. To assess the growth performance and nutrient uptake by maize grown on soil amended with vermiculite under the Tanzanian environment.
6. To assess the ability of vermiculites to retain plant nutrients when added to soils under the Tanzanian environment.

1.3 ORGANIZATION OF THE THESIS

The remaining part of the thesis is divided into seven chapters. Chapter Two is mainly a literature review. It gives an overview of vermiculite with an outline of the location of Tanzania and the geological setting of the Mozambique Belt where vermiculites were sampled. The third chapter deals with the mineralogical and chemical characterization of the studied vermiculites with respect to their suitability for agricultural application. It provides the identification and quantification of minerals in those vermiculites as well as an assessment of their safety records. In addition, it presents their chemical compositions. Chapter Four presents the determination of the physical and chemical properties of vermiculites, which are of agronomic importance and gives an assessment of their variability on heating.

Assessment of the extractability of some trace elements in the studied vermiculites and their response to heating are provided in Chapter Five. Chapter Six reports the performance of maize grown in Tanzania on soil amended with varying amounts of heated and unheated vermiculites. The findings on growth performance, nutrient uptake, dry matter yield, and moisture retention are presented and discussed. Chapter Seven provides the findings of the field experiment carried out in Tanzania to assess the ability of both heated and unheated vermiculites to retain applied plant nutrients in the soil. The last chapter presents the general

discussion (synthesis) and conclusions with recommendations on issues that require further studies and follow-up. References cited together with the appendices are provided at the end of the thesis.

CHAPTER 2

LITERATURE REVIEW

2.1 TANZANIA

2.1.1 Location

Tanzania is situated in East Africa, south of the equator, between latitudes 1-12° S and longitudes 29 - 40° E (Fig. 2.1). It borders Kenya to the north and Mozambique to the south with the Indian Ocean to the east. It is the largest country in East Africa with a total area of 945,000 km^2 and an estimated population of 38.3 millions people (UN, 2004). The country has a tropical climate in most areas and a temperate climate in a few isolated highlands (Agrawala *et al.*, 2003).

2.1.2 Mozambique Belt

Vermiculite deposits, from which the studied samples from Tanzania were taken, occur in the Neoproterozoic Mozambique Belt (Fig.2.1). The belt extends from Ethiopia through Kenya and Tanzania to Mozambique (Sommer *et al.*, 2003). Holmes (1951) was the first to recognize the belt and it is believed to have formed by the collision of East and West Gondwana between 640 and 550 Ma (Tenczer *et al.*, 2006). In Tanzania, it is approximately a 1000 km–long discontinuous linear belt (Sommer *et al.*, 2005) stretching in a N-S direction from Masasi, in the southern part of Tanzania to Kalalani in Tanga Region, in the north of the country. The belt lies between the Tanzanian Craton, which is on the west and Palaeozoic to Cainozoic sediments, on the east. On the eastern and southern margin of the Craton, it is separated from the Craton by the Paleoproterozoic Usagaran Belt. The Usagaran Belt has the same age as the Ubendian Belt, which is on the west of the Tanzanian Craton.

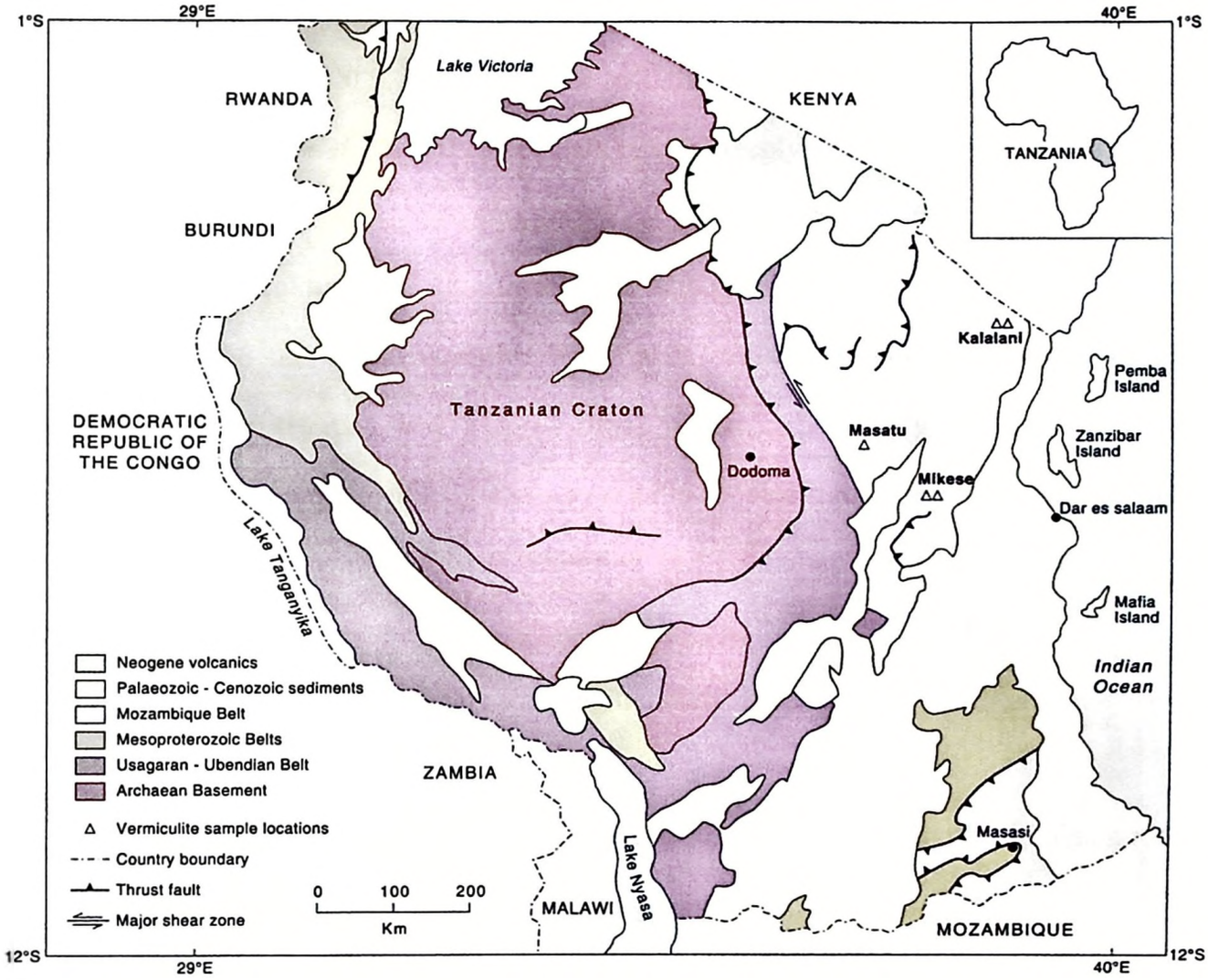

Fig. 2.1: Simplified geological map of Tanzania showing the Mozambique Belt and locations where vermiculite samples were taken (Modified after Pinna *et al.*, 2004). The insert shows the position of Tanzania in Africa.

Geologically, the Mozambique Belt (MB) is polymetamorphic with complex and poorly understood structures (Tenczer *et al.*, 2006). It largely comprises granitoid orthogneisses of Archaean origin (Stern, 2002). In addition, the belt also possesses post kinematic granites and pegmatites (Muhongo *et al.*, 2001). The pegmatites are steeply dipping and strike obliquely to the general trend of the belt with sharp intrusive contacts with the country rock (Williams and Skerl, 1940). Vermiculites occur adjacent to some of the pegmatites. In areas, such as Kalalani where two of the vermiculite samples were taken, the main rock is metagabbro with serpentinite bodies (Hartley and Moore, 1965). Other rocks are granulites and garnet amphibolites with some marble. The serpentinite bodies are veined with magnesite. Significant bodies of vermiculite with actinolite and corundum are found in areas where pegmatites are cross-cutting the serpentinites (Hartley and Moore, 1965). The distribution of vermiculite bodies is both transversely and longitudinally irregular.

At Mikese and Masatu areas, where other vermiculite samples were taken, the dominant rocks are garnet biotite gneisses with some kyanite and graphite bands (Sampson and Wright, 1961). The rocks in the areas are strongly foliated and migmatized with amphibolitic dykes and sills in some places. Here vermiculite occurs in the vicinity of the pegmatites which cross-cut in some areas the amphibolite bodies.

Apart from vermiculite, the belt hosts gemstone deposits and industrial minerals, such as zoisite (tanzanite), kyanite, gold, pyrope, ruby, sapphire, emerald, bauxite, marble, and graphite (Pinna *et al.*, 2004; Harris, 1961). Small scale mining of some of the minerals is currently in progress at a number of places. At Masatu and Kalalani, ruby and sapphire are mined and vermiculite is an unused waste product.

2.2 OVERVIEW OF VERMICULITE

2.2.1 Definition

Vermiculite is a general name given to a group of layer silicate minerals with a net negative layer charge falling between -0.6 and -0.9 per formula unit (Bailey, 1980; Guggenheim *et al.*, 2006). This layer charge is less than that of micas but higher than that of smectites and is both directly and indirectly responsible for many of the useful properties of vermiculite. The mineral is distinguished from other clay minerals by a high Si-Al ratio of 3:1 and a higher layer charge (Hindman, 2006). It has a general chemical formula $(Mg, Ca)_{0.6\text{-}0.9}(Mg, Fe^{3+}, Al)_{6.0}[(Si, Al)_8O_{20}](OH)_4.nH_2O$ (Deer *et al.*, 1992).

Structurally, vermiculite consists of an octahedral sheet sandwiched between two opposing tetrahedral sheets (Abollino *et al.*, 2007). The dimensions of the tetrahedral sheets vary with the size and charge of the cations occupying the octahedral sites (Bailey, 1966). The adjacent tetrahedral sheets (silicate layers) are separated by a double layer of water molecules arranged in a distorted hexagonal pattern around Mg^{2+} ions (Fig.2.2). Its hydration state is defined by the number of layers saturated with water molecules between the silicate sheets (Suzuki *et al.*, 1987). This interlayer water facilitates the exchange and migration of cations in the interlayer space (Douglas, 1989). The basal spacings of the octahedral and tetrahedral sheets as well as the interlayer water for a half-unit cell of vermiculite are shown in Figure 2.2a. Apart from the structural water, the mineral may also occur with a varying amount of non-structural water (Walker, 1951).

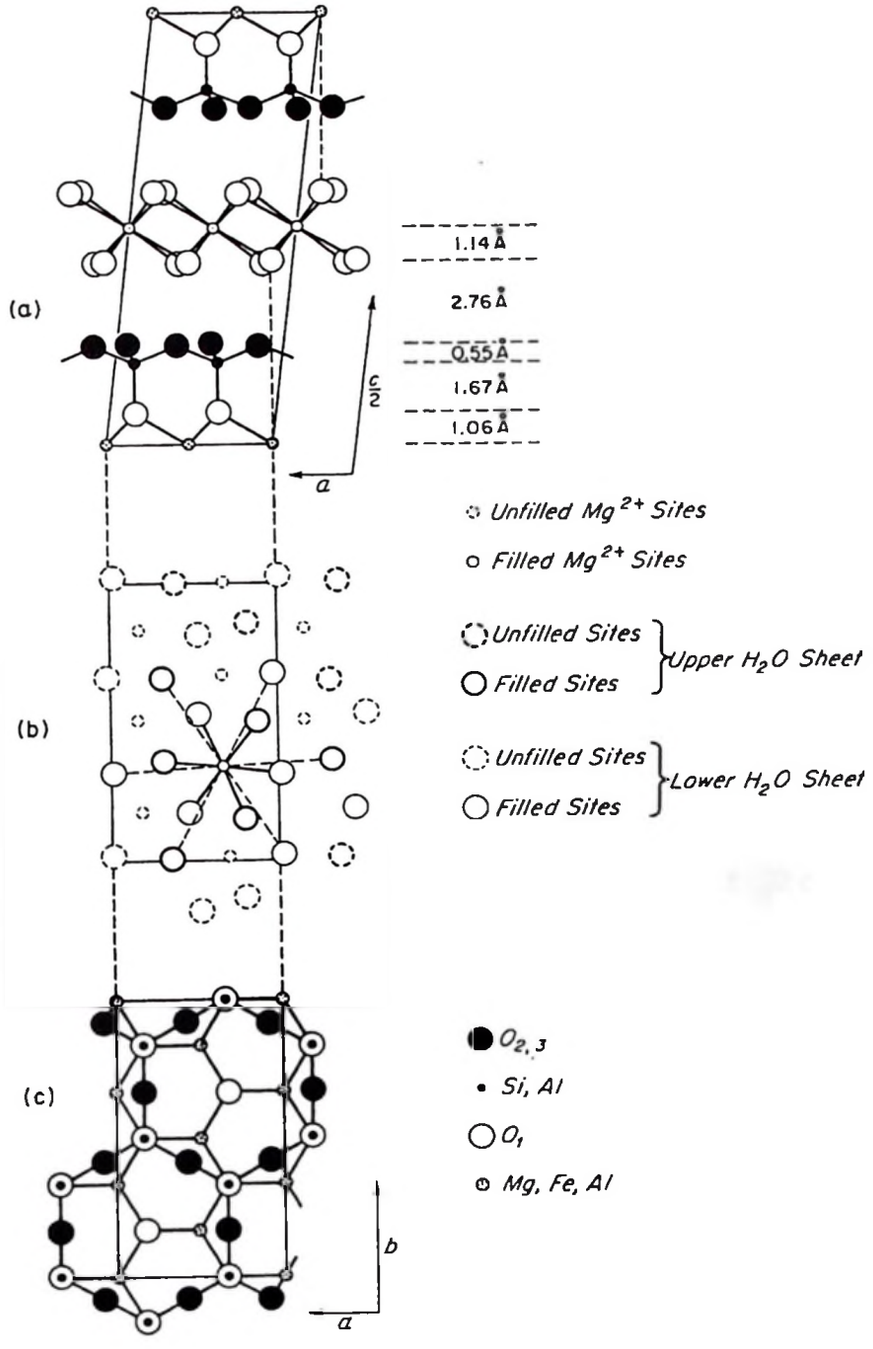

Fig.2.2. The crystal structure of vermiculite with magnesium as the interlayer cation: a) projection normal to the *ac* plane; b) projection normal to *ab* plane showing the interlayer water; and c) projection normal to the *ab* plane showing half of the silicate layer (After Mathieson, 1958).

In macroscopic appearance, vermiculite looks like mica, but it exists in a wide range of colours, such as light yellow, green, brown, and black (Van Gosen *et al.*, 2005). Unexpanded 'pure' vermiculite has a hardness of 1.5, specific gravity of 2.2-2.5, and a perfect (001) cleavage (Walker, 1951). A regularly mixed layer structure of biotite and vermiculite is generally referred to as hydrobiotite (Brindley *et al.*, 1983). When regularly interstratified with phlogopite, it is called hydrophlogopite (Schoeman, 1989). Commercially all are regarded as vermiculite (Frank and Edmond, 2001). Dugarlite, Mondalite, Strong-lite, and Zonolite are among the commercial names also used to refer to vermiculite and related products (Hindman, 2006).

2.2.2 Formation and occurrence

The origin of vermiculite is still a subject of discussion (Tsirambides and Michailidis, 1999). Most studies favour the origin of vermiculite as due to either the action of hypogene hydrothermal solutions or supergene alteration or a combination of the two (Basset, 1963). Association of some vermiculites with minerals and rocks that form as a result of hydrothermal alteration is among the evidence in favour of hydrothermal origin (de la Calle and Suquet, 1988). However, the hydrothermal temperature should be less than 200 °C to favour the formation of vermiculite instead of chlorite (Roy and Romo, 1957; Douglas, 1989). Its formation postdates the high-grade metamorphism of the host rocks (Bush, 1976). According to de la Calle and Suquet (1988), amongst the evidences in favour of supergene alteration is the alteration of biotite and phlogopite in laboratory experiments at room temperature to vermiculite and the increase in the proportion of biotite or phlogopite with depth in major commercial vermiculite deposits.

Vermiculites occur both in dioctahedral and trioctahedral forms (Brindley and Brown, 1984). Most macroscopic trioctahedral vermiculites form generally from the alteration of micas and less commonly from chlorite, olivine, serpentine, pyroxene, and amphibole (Basset, 1963; Bush, 1976). The alteration of micas to vermiculites involves the release of K^+, oxidation of Fe^{2+} to Fe^{3+}, and re-orientation of hydroxyl ions (Douglas, 1989). The dioctahedral varieties which are common in soils originate from the alteration of dioctahedral illite (Brindley and Brown, 1984). In soils, vermiculite is more prominent in *Alfisols, Mollisols*, and *Vertisols* where weathering is less intense (Brady and Weil, 2002).

Economic vermiculite deposits occur in ultramafic igneous or metamorphic complexes with intrusive silicic, alkalic, or carbonatitic rocks (Bush, 1976). Some are found in gneisses and schists along the joints and margins of pegmatites (Simandl *et al*, 1999). Other deposits, according to de la Calle and Suquet (1988), occur in contact zones between carbonate bodies and rocks containing phlogopite. Small deposits of interstratified biotite-vermiculite occur in granitic rocks. The Tanzanian vermiculites belong to those found in ultramafic metamorphic rocks and some are found in gneisses along the margins of pegmatites.

2.2.3 Composition of vermiculite

Mineralogical and chemical compositions of vermiculite are variable depending on the chemistry of the primary rock from which it originates and the degree of alteration it possesses (Suvorov and Skurikhin, 2003). The mineral occurs with an assemblage of other minerals (Hindman, 2006). It is often found in association with interstratified mica/vermiculite or chlorite/vermiculite presumably as transitional phases of mica alteration (Tsirambides and Michailidis, 1999; Wilson, 1970). Common accessory minerals found in vermiculites are quartz, micas, pyroxenes, amphiboles, fluorapatite, corundum, talc, nickel silicates, olivine,

and serpentines (Frank and Edmond, 2001; Simandl *et al.*, 1999). The amphiboles and serpentines in some cases may have microfibrous morphology responsible for causing respiratory disorders and human deaths when inhaled in sufficient amount for a long period (Whitehouse, 2004). Such fibrous minerals are chrysotile, crocidolite, amosite, tremolite, actinolite, and anthophyllite (Van Gosen *et al.*, 2005). Chrysotile belongs to the serpentine group of minerals while the remaining minerals are amphiboles. Commercially, these fibrous minerals are collectively categorized as asbestos minerals (Addison, 1995).

Some vermiculites occur with elevated concentrations of trace elements such as Cr, Ni, Zn, Ti, Mn, Cu, Co, P, La, Y, P and Sc (Frank and Edmond, 2001). Vermiculites acquire these elements from the alteration of the host rocks. Vermiculites localized in ultramafic zones occur with elevated concentrations of Ti, Ni, Cr, and Zn (de la Calle and Suquet, 1988). The trace elements in vermiculites occur in the tetrahedral and octahedral sites while others are found in the interlayer position (Bailey; 1984; Tischendorf *et al.*, 2007). The elements in the tetrahedral and octahedral sites form inner complexes with Si-O and Al-O groups; whereas in the interlayer they are adsorbed by cation exchange (Kraepiel *et al.*, 1999). The adsorption of some elements is pH dependent and varies with their oxidation states (Griffin *et al.*, 1977; Rai *et al.*, 1989). The high ion exchange and retention capacity of vermiculite favours the sequestration of trace elements (Frank and Edmond, 2001). The level of the trace elements in vermiculites is generally variable. Foster (1963) has reported some vermiculites containing as much as 3000 mg/kg Cr and 2000 mg/kg Ni. These trace elements can be toxic to living organisms depending on the species and availability. This is of much concern particularly for the applications of vermiculites in agriculture and horticulture as a soil improver and feed additive to animals. It indicates the necessity of initial mineralogical and chemical characterization before using vermiculite from an unknown source.

2.2.4 Identification of vermiculite and associated minerals

Vermiculite is difficult to identify and quantify because of its broad structural diversity (Środoń, 2006). A number of methods are currently in use, but XRD remains the principal tool commonly employed for identifying clay minerals including vermiculite (Hillier, 2003). With XRD it is also possible to identify and quantify other mineral phases that are present in vermiculite. The use of both random powders and oriented clay fractions is recommended as they are complementary. The random powders provide absolute abundances of different mineral phases while oriented clay fractions enhance the signals from the basal plane (001) which facilitates recognition of individual clay mineral phases (Kahle *et al.*, 2002). Cation saturation with ethylene glycolation and heating are sometimes used in combination with XRD (Thorez, 1976). The ethylene glycol solvation assists in identifying the presence of swelling minerals such as smectite. The smectite swells when solvated with a significant increase in the d-spacing in the XRD patterns (Moore and Reynolds, 1989). According to Moore and Reynolds (1989), vermiculite and other similar layer silicates are not significantly affected by this treatment.

A heating test is used to detect the presence of chlorite in vermiculite (Środoń, 2006). When the sample is heated to 400 °C, smectite and vermiculite usually collapse to 9.6-10 Å while chlorite remains unaffected (Hardy and Tucker, 1988). Further heating of the sample to 550 °C causes dehydroxylation of the hydroxide sheet and the 7 Å component in chlorite is rendered amorphous and the intensity of the 001 reflection is increased (Moore and Reynolds, 1989). Vermiculite at 550 °C shows only a slight collapse or no further collapse (Hardy and Tucker, 1988). Thus, without this prior treatment, it is difficult to distinguish vermiculite and chlorite because they have similar XRD reflection patterns (Walker, 1949).

XRD alone cannot provide conclusive identification of all the mineral phases in vermiculite. Some minerals are present in amounts below the detection limit of XRD, whilst others may cause overlapping of reflections due to interstratifications. Also, XRD cannot determine whether the habit of the mineral is likely to prove harmful, for example, fibres in vermiculite. Thus, additional complementary qualitative and quantitative techniques are necessary (Whittig and Allardice, 1986). Scanning electron microscopy (SEM) when used with an energy dispersive X-ray system (EDS) permits the identification of the individual mineral grains by comparing their characteristic morphologies with elemental compositions (Welton, 1984). Identification of fibrous minerals can also be made with SEM and their dimensions measured. Fibre dimensions are among the factors that determine their toxicity (Lippmann, 1990; Baron, 2001). It has been confirmed that fibres longer than 8 μm and thinner than 0.2 μm are more likely to cause tumours than shorter and thicker fibres (Stanton *et al.*, 1981). Thus, proper identification and quantification of vermiculite and incorporated minerals requires the use of XRD with a range of complementary techniques.

2.2.5 Physical and chemical properties

Exfoliation characteristics

Vermiculite has the unusual property of exfoliating when heated or subjected to chemical treatments, such as steaming or saturation with hydrogen peroxide and sulphuric acid (Walker, 1951). Exfoliation that occurs under both cases is accompanied by a colour change from light green, black, or brown into a silvery white to golden red mass depending on chemical composition and the contained minerals (Suvorov and Skurikhin, 2003). Individual particles when heated to a temperature of 800 – 1100 °C can expand from 6 to as much as 30 times their original volume (Van Gosen *et al.*, 2005). The expansion can produce a light weight material with a density of 90 -110 kg/m^3 (Hindman, 2006). This expansion occurs perpendicular to the

cleavage as a result of mechanical separation of the layers by rapid conversion of contained water to steam (Van Straaten, 2002; Walker, 1961). Both interlayer water and structural OH groups are lost on heating and their release is responsible for the expansion of vermiculite (Justo *et al.*, 1989). The amount of water in pure vermiculite is about 20 wt % and 30 % of that water is in the form of hydroxyl ions (Walker, 1949). Because of strong bonds with Si and Al in vermiculite, the hydroxyl groups are gradually released on heating from about 500 to 850 °C. This release is accompanied by structural changes (Walker, 1951; Barshad, 1950).

Heating provokes metamorphic reactions in vermiculite which lead to the formation of intermediate mineral phases (Marcos *et al.*, 2009). The phase formed depends on the temperature and chemical composition of vermiculite. Previous studies indicate high thermal exfoliation is achieved when vermiculite is regularly interstratified with mica phases (Justo *et al.*, 1989; Midgley and Midgley, 1960). This is true even when vermiculites are treated with chemicals (Ruthruff, 1941). However, no completely satisfactory explanation is offered on the exfoliation mechanism (Heller-Kallai, 2006). Since vermiculites differ in composition and degree of exfoliation, characterization is essential when assessing their potential suitability for agricultural applications.

Cation exchange capacity

Cation exchange capacity (CEC) is a measure of the available quantity of exchangeable cations in a medium that can neutralise the negative charge in the soil at a given pH (Rhoades, 1982). In clay minerals, the CEC is equivalent to the layer charge which is represented by the sum of the exchangeable charge-compensating cations in a mineral (Bergaya *et al.*, 2006). It is widely determined by the displacement of interlayer cations with index cations particularly using the ammonium acetate (pH 7) or sodium acetate (pH 8.2) saturation method (Chapman,

1965). Other methods are also in use. It can also be deduced from the chemical analysis, provided vermiculite is not contaminated with other minerals and its chemical composition is accurately known (Bergaya *et al.*, 2006).

Studies indicate that vermiculites have a high CEC broadly ranging between 50 and 150 $cmol_{(+)}/kg$ (Hindman, 2006; Van Straaten, 2002). Cation exchange capacities of more than 180 up to 210 $cmol_{(+)}/kg$ are also recorded in the literature (Jiménez de Haro *et al.*, 2003). Field experience shows that medium characterized by a high CEC retain nutrients from leaching during irrigation (Tisdale *et al.*, 1993). In addition, it gives an indication of a growing medium with a good fertility potential and a positive response to fertilizer application (Landon, 1991). This implies that vermiculite with a high CEC has a greater ability to retain plant nutrients when applied as a growing medium.

The high CEC of vermiculite is attributed to a number of factors. Among these factors are the surface and interlayer ion exchange associated with the isomorphic replacement of Al^{3+} for Si^{4+} in its tetrahedral sheets and Al^{3+} and / or Fe^{3+} for Mg^{2+} in the octahedral layers (Fitzpatrick, 1983). The isomorphic substitution creates a deficiency of positive charges on the surface of vermiculite which is compensated by exchangeable cations (Ramirez-Valle *et al.*, 2006). It is estimated that isomorphic substitution accounts for 80 % of the CEC of vermiculite and the remaining 20 % is contributed by the broken bonds around the edges of the silica-alumina unit which give rise to unsatisfied charges (Grim, 1953). Thus, the structural and edge charges are the main contributors to the high CEC of vermiculite (Tournassat *et al.*, 2004).

Vermiculites with divalent interlayer cations (Ca^{2+} and / or Mg^{2+}) generally have a higher CEC than those with monovalent cations because they are more hydrated and thus, more

expanded (Grim 1953). Other factors that influence the CEC of vermiculite are the degree of transformation from the parent mineral and the heating temperature it is subjected to during exfoliation (Bergaya *et al.* 2006). Studies in clay minerals show that heating decreases the CEC as a result of the collapse of interlayer space and the destruction of the crystal lattice (Grim, 1953; Heller-Kallai, 2006). In some clay minerals, reduction in CEC on heating is associated with the clogging of exchangeable sites by aluminium and iron oxides (Grim, 1953). Hindman (2006) is of the opinion that, if vermiculite is exfoliated, the CEC can decrease by 5-10 % from the unheated product. Grinding can also change the CEC by altering the crystal structure and particle size (Bergaya *et al.* 2006). Thus, the broad range of the CEC of vermiculite is influenced by a number of factors ranging from natural to human induced. What is not clear is whether or not the decrease in the CEC on heating is a linear function, and how it varies among vermiculites with different chemical composition. This is important in order to establish the appropriate heating temperature based on the response of individual vermiculites.

The pH

The pH measures the negative logarithm of the hydrogen ion concentration in the solution which is in equilibrium with the negatively charged surface of the soil particles (Harrison, 1992). It is an important property that is used to assess the suitability of a growing medium, as it affects the mobility and bioavailability of nutrients as well as the activity of micro-organisms (Brady and Weil, 2002). For instance, a pH of less than 5.5 enhances the mobility and plant availability of bivalent metals; causes toxicity of Al, Mn, and H as well as deficiencies of Ca, Mg, Mo, and P, a phenomenon that is commonly known as 'acid soil headache' (Brady and Weil, 2002). The pH of a growing medium favourable for most plants

and micro-organisms is between 5.5 and 7 (Brady and Weil, 2002). Since vermiculite is used as a growing medium or a soil conditioner, knowing its pH is very important.

Studies done in Korea on imported vermiculites from China and some locally produced varieties for horticultural applications showed a pH range of 6.6 - 8.9 (Kang *et al.*, 2004). This is in agreement with the Vermiculite Association which recognize vermiculites to have a variable pH ranging between 6 and 9.5 (Schundler, 2008). However, most commercially produced vermiculites for agricultural or horticultural applications are usually indicated to be neutral (pH 7). This is true only if during exfoliation, some are amended with other materials to make them neutral. Knowing the pH of vermiculite allows the best use of it to be made in agriculture. Vermiculite which is strongly alkaline could preferably be applied to acid soils in order to improve their acidity towards the optimum range for most crops. Since vermiculites have variable mineralogical and chemical compositions, it is necessary to know how heating affects this important agronomic property.

Water retention

Vermiculite is known to have a high water absorption capacity (van Straaten, 2002). The release of interlayer water and OH groups on heating vermiculite leads to the formation of a porous material with large numbers of pores of different sizes (Marcos *et al.*, 2009). The resulting pores give vermiculite the capacity to absorb and retain a high amount of water. A good variety when exfoliated may have a water holding capacity of six to seven times its own weight (Walker, 1951). Sabrah *et al.* (1993) have found that the application of 4 % w/w of vermiculite to a sandy soil could increase the amount of water retained at field capacity by 23.6 %. This increase was attributed to the large amount of water holding pores of 0.2–9.0 μ, which increased by 132 % over the control as result of applying vermiculite.

Although heating of vermiculite increases the number of pores, sometimes it modifies the pore structure by producing a larger number of closed pores than open pores (Gordeeva *et al.*, 2002). This depends on the composition of vermiculite and the thermal treatment to which it has been subjected. The presence of closed pores in vermiculite inhibits accessibility for air or liquid phases (Aristov *et al.*, 2000) and thus, reduces its ability to absorb water.

In agriculture, particularly for crop production, the most important factor is not the amount of water held by vermiculite, but the amount which is available to growing plants. Thus, the suitability of vermiculite in agriculture is judged by its ability to hold and release water for plant uptake. The water release characteristic gives an indication of that ability (Reeve and Carter, 1991). The release of water usually depends on its matric potential which measures the binding strength of water in a medium (Phene *et al.*, 1992). If the absorbed water is not available to growing plants, then that medium is less advantageous in crop production. In the literature there is no comprehensive information on the water release characteristics of vermiculite, particularly in relation to heating. This justifies the necessity of including this in the characterization of vermiculites from the MB of Tanzania.

2.2.6 Applications in agriculture

USA statistics indicate that 40 % of industrial vermiculite is utilized in the agricultural sector (Simandl *et al.*, 1999). Good liquid absorption and cation exchange capacities as well as light weight, particularly when exfoliated, make vermiculite an excellent product in agriculture, horticulture, and other sectors (Strand and Stewart, 1983). These properties make it a suitable material for use as an additive to mulch, potting soils, and growing mixes (Potter, 2000) and also for seed germination and transplanting trees and other plants (van Straaten, 2002). When applied to the soil it has a high ability to retain moisture and nutrients as well as to release

them gradually to the roots of plants (Potter, 2000). Its high liquid absorption property also makes it suitable for use as a carrier medium in transportation of fertilizers and pesticides as a free-flowing solid (Harben and Kužvart, 1996; van Straaten, 2002). Because of its biological stability, sterility, and chemical inertness, it has found its use as a packing material when transporting fruits and other delicate agriculture produces (Tomanec *et al.*, 1997). Also, it is used as an absorbent in poultry and animal litters. Uncontaminated vermiculite is used as a feed additive for fish, poultry, and animals (Simandl *et al.*, 1999; van Straaten, 2002).

Vermiculite can also be used as an adsorbent in removal of heavy metals from the soil (Abollino *et al.*, 2007) and treatment of metal-contaminated wastewater which is dispersed to the land (Malandrino *et al.*, 2006). However, its ability to adsorb metal ions decreases with the decrease in pH and increase in ionic strength (Malandrino *et al.*, 2006). Thus, the use of vermiculite can assist in reducing excessive accumulation of heavy metals in the soil and prevent groundwater contamination. In addition, it is used in nuclear waste containment and removal due to its high cation exchange potential and layer-silicate morphology (Hindman, 2006). However, it should be noted that the use of vermiculite in the agricultural sector will depend on whether or not vermiculite itself is contaminated with hazardous minerals and heavy metals. This is revealed only after characterization.

CHAPTER 3

MINERALOGICAL AND CHEMICAL CHARACTERIZATIONS OF VERMICULITES FROM TANZANIA FOR AGRICULTURAL USE

3.1 INTRODUCTION

Mineralogical and chemical characterizations of vermiculites prior to their exploitation for agricultural use are important for a variety of reasons. Studies indicate vermiculite occurs in a wide range of compositions with a number of accessory minerals some of which can be of environmental and health concern to living organisms (Addison and Davis, 1990; Van Gosen *et al.*, 2005). In addition, some occur with elevated concentrations of heavy metals (Frank and Edmond, 2001). The release of some of the metals into the ground when vermiculite is applied as a soil conditioner or as an additive to mulch, potting soil, and growing mixes can be a source of ground pollution and toxicity to plants as well as to other living organisms through the food chain. It is essential to know this basic information when assessing the potential suitability of vermiculites for agricultural applications. Thus, the aim of this chapter is to furnish that information and to assess whether or not any of these vermiculite deposits from the Mozambique Belt (MB) of Tanzania are potentially suitable for agricultural use. In addition, it is aimed at providing baseline data for further more detailed investigations of their potential suitability.

3.2 MATERIALS AND METHODS

3.2.1 Sources of vermiculite

Vermiculite samples were collected from five different sites of potential economic interest in the MB of Tanzania (Fig.2.1). All samples showed the typical appearance of macroscopic vermiculites as defined earlier. The samples marked KL1 (04° 35' 20'' S & 38° 43' 50''E) and

KL2 (04° 34' 37'' S & 38° 44' 14'' E) were taken from separate deposits at Kalalani area in Korogwe District. Similarly, the samples marked MK1 (06° 47' 08''S & 37° 54' 35''E) and MK2 (06° 47' 11''S & 37° 54' 03''E) were collected from two separate deposits at Mikese area in Morogoro Rural District. The remaining sample from Tanzania, which was marked MS, was sampled at Masatu village in Kilosa District (06° 12' 32''S & 37° 10' 24''E). The sixth sample (marked PB) was provided by Palabora Europe Ltd for comparative purposes. The sample originates from the Palabora Vermiculite Mine in South Africa and it was included as an example of a widely available commercial vermiculite product.

3.2.2 Characterization of mineral phases

Vermiculites and other minerals present in the samples were identified and characterized by a combination of X-ray diffraction (XRD) and scanning electron microscopy (SEM). The SEM was fitted with an energy dispersive X-ray system (EDS). The XRD studies were carried out at the Macaulay Land Use Research Institute, Aberdeen, whilst the SEM with EDS studies were conducted at the University of Aberdeen, Department of Geology and Petroleum Geology.

The XRD involved both scanning of oriented mineral specimens and of random powder specimens. The random powder specimens were prepared according to the method of Hillier (1999). The XRD patterns for the random powder specimens were recorded using Co-$K\alpha$ radiation selected by a diffracted beam graphite monochromotor on a Siemens D5000 θ/θ diffractometer. The scans were made over the 2θ range of 2 - 75° with 0.02° steps, counting for 2 second/step. Oriented mineral specimens were saturated with 1*M* $MgCl_2$ to make them homogenous with the same interlayer Mg^{2+} ions. Three XRD patterns were then acquired from the oriented Mg-saturated specimens, namely air-dried; ethylene glycol solvated; and heated

patterns. Procedure for the preparation and scanning of oriented mineral specimens is documented in appendix 3.1.

Semi-quantitative analysis of random powder XRD patterns were thereafter made by a full pattern fitting, normalized reference intensity ratio, method as described in detail by Omotoso *et al.* (2006). Mineral standards were obtained from purified reference specimens, with the exception of sapphirine for which a calculated XRD pattern was used as a standard, based on the structure reported by Higgins and Ribbe (1979). The reference specimens were provided by the Macaulay Land Use Research Institute in Aberdeen, the United Kingdom.

The SEM and EDS were used to assist in the identification of individual accessory minerals incorporated in the vermiculite samples by comparing their characteristic morphologies with their elemental compositions. Both undisturbed samples mounted on stubs and hand crushed mineral grains mounted on glass slides were examined. The samples were carbon coated to prevent the surface from charging. The SEM instrument used was an ISI-ABT55 with energy-dispersive system-LINK AN10/55S. The images were acquired with an ISS-I-SCAN 2000 Digital Image Acquisition System.

3.2.3 Characterization of chemical compositions

Electron probe microanalysis (EPMA) and inductively coupled plasma-mass spectrometry (ICP-MS) were used to establish the chemical composition of the samples. Six representative grains from each sample were randomly selected and analyzed using EPMA. The grains were pre-selected by the aid of EDS on a number of particles prepared from each sample. The EPMA was carried out using a Microscan MK7 equipped with an energy dispersive analyzer (LINK Analytical AN10/25S). The analysis was done using an accelerating voltage of 15kV;

probe current of 3.0 nA; take off angle of 75°; 30 microns electron beam diameter; and counting time of 150 seconds. Standard minerals were used for calibration. Data were acquired and processed using the LINKS ZAF4/FLS software at the University of Aberdeen, Department of Geology and Petroleum Geology. Chemical compositions of major and minor oxides thus obtained were normalized to cation proportions assuming 22 oxygen atom equivalents.

The ICP-MS analyses were carried out by the OMAC laboratories Limited, which is at Athenry Road, Loughrea, in Ireland. The laboratories are accredited to ISO 17025 (the International Organization for Standardization) by the Irish National Accreditation Board. The samples were analysed after digestion using a combination of nitric, perchloric, hydrochloric, and hydrofluoric acids in open polytetrafluoroethene (PTFE) beakers. The multi-acid dissolution technique provides an effective dissolution of the silicate minerals with the silicon volatilizing as fluoride. Certified reference soil (Till-4) and rock (diorite gneiss, SY-4) from CANMET Mining and Mineral Sciences Laboratories in Canada, in-house reference standard (ICP-5), and blanks were incorporated as a quality measure.

3.3 RESULTS AND DISCUSSION

3.3.1 Mineralogical composition

A comparison of the oriented XRD patterns of air-dried Mg-saturated samples with those following ethylene glycol solvation indicates that samples KL1, KL2, MS, and MK2 appear to be vermiculites (Fig.3.1a-c). On solvation with ethylene glycol, the basal spacing (001) of KL1, KL2, and MS all decreased slightly from around 14.4 to 14.2-14.1 Å. According to data tabulated in MacEwan and Wilson (1984), this response to glycolation in the Mg-saturated state is a characteristic of high charge vermiculites, since they only imbibe one layer of

ethylene glycol. However, upon close inspection of the diffraction data a number of differences are apparent amongst these four samples. Thus, sample KL1 shows some indication of heterogeneity indicated by the presence of two close but not identical basal spacings evident by a partial asymmetry and a splitting of the higher order basal peaks. This contrasts with sample KL2, which shows no sign of layer spacing heterogeneity, and instead displays a completely rational series of basal spacings.

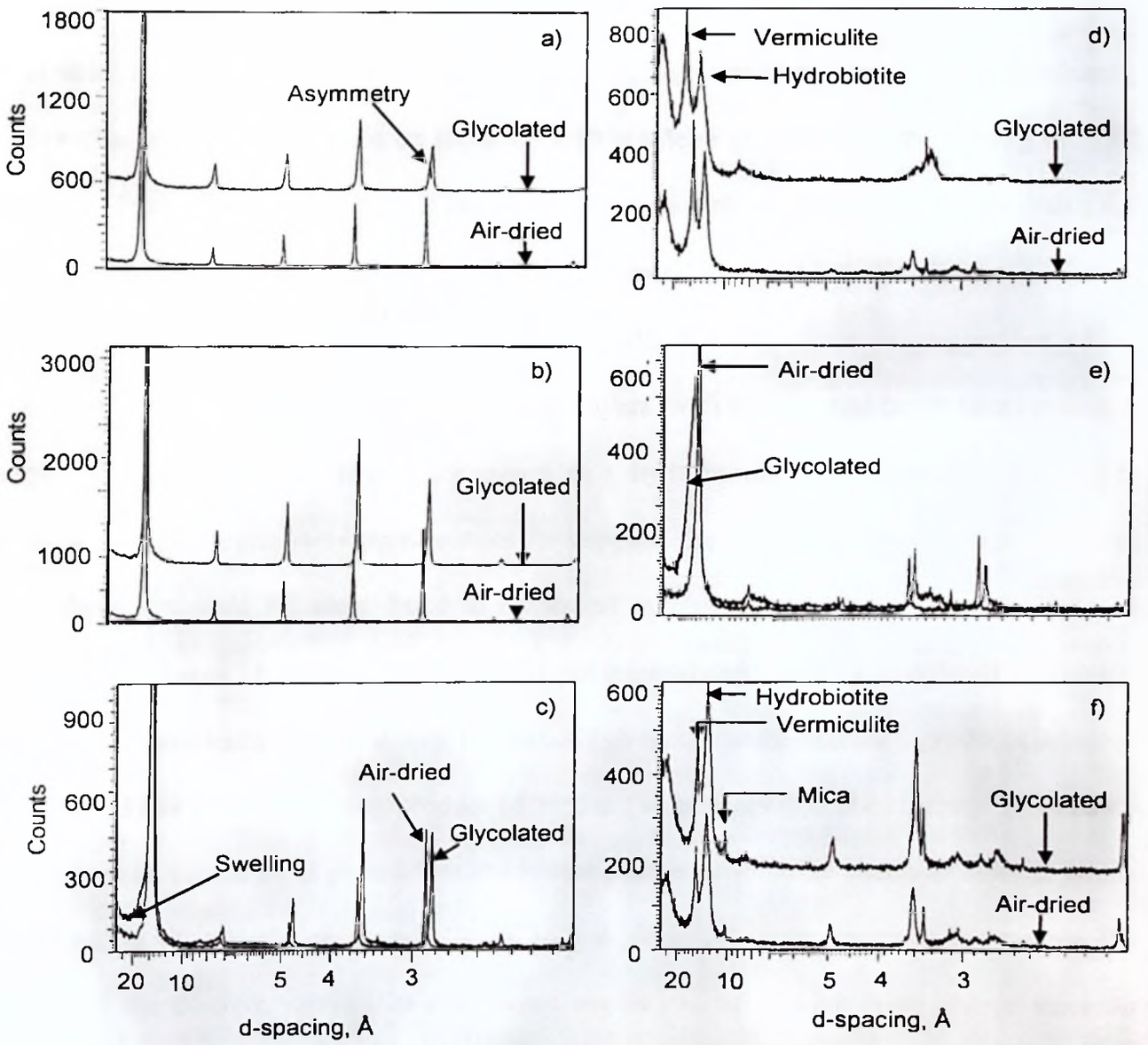

Fig.3.1. Air-dried and ethylene glycol solvated XRD patterns for samples: a) KL1, b) KL2, c) MS, d) MK1, e) MK2, and f) PB. Intensity counts for figures 3.1a, b, d and f are offset for clarity.

Sample MS, records a slightly different form of heterogeneity in that it displays a slight broadening at the base of the main (001) peak towards the larger d-spacings following glycolation. This expansion could possibly be a sign of the presence of a minor component of smectite (Moore and Reynolds, 1989) or of a vermiculite component of lower layer charge, but is not sufficiently resolved from the main vermiculite (001) to determine which is more likely.

In contrast to the previous three samples, sample MK2 appears to be composed predominantly of low charge vermiculite. Thus on solvation with ethylene glycol, the basal spacing of MK2 increased from 14.4 to 15.5 Å (Fig.3.1e). In fact, the peak profile of this vermiculite with a full width at half maximum (FWHM) of 1.134° is very broad compared to those observed for the other vermiculites (KL1 0.169°, KL2 0.105°, MS 0.174°). This is suggestive of an interstratification of high-charge and low charge layers, with smaller and larger basal spacings, respectively. It may also indicate a remnant of a hydrobiotite component (see below). In addition to the four relatively pure vermiculite samples, the remaining two samples MK1 and the reference sample PB were found to consist of mixtures of vermiculite and R1 ordered hydrobiotite phases. Hydrobiotite is a mixed-layer mineral consisting of an ordered alternation of mica and vermiculite layers. It may form as a high-temperature alteration product (Brindley *et al.*, 1983) or as a weathering product of biotite (Wilson, 1970). The discrete vermiculite component in sample MK1 probably is the lowest charge vermiculite observed since it swells most readily on glycolation from 14.4 to 16.3 Å (Fig. 3.1d). In contrast, for sample PB (Fig.3.1f), the discrete vermiculite component appears to be of high layer charge since its basal spacing decreases slightly from its air-dried value of 14.4 Å following glycolation, similar to the responses observed in the essentially pure vermiculite samples KL1, KL2, and MS.

Interestingly, the vermiculite component of the hydrobiotite in each sample mirrors the behaviour of the respective discrete vermiculite component. Thus, whereas the primary basal spacing for both hydrobiotites is around 24 Å, the hydrobiotite in sample MK1 expands to around 26 Å (=10+16 Å) following glycolation but in sample PB it remains effectively unchanged at 24 Å (=10+14 Å). This finding has not been reported before. It implies that the chemistry of vermiculite component in hydrobiotite is preserved when the mineral is altered to vermiculite, resulting in similar response to glycolation.

Based simply on the intensity of the peaks, sample PB has a larger hydrobiotite to discrete vermiculite ratio compared to MK1. In addition, sample PB was found to contain a small amount of trioctahedral mica, a component that is entirely unaffected by glycolation, with a basal spacing of approximately 10.1 Å. Thus, in terms of the overall content of vermiculite as a proportion of the phyllosilicate component, either as a discrete phase or as a component of hydrobiotite, oriented XRD indicates that sample PB contains the least, followed by samples MK1 and MK2 while for samples KL1, KL2, and MS the phyllosilicate component is essentially pure vermiculite.

As expected, *in situ* heating of the Mg-saturated specimens in stages from 25 to 600 °C led to progressive decreases in their (001) basal spacings (Table 3.1). Based on MacEwan and Wilson (1984), the basal spacings of vermiculite of 14.36 - 13.86 Å correspond to a structure containing double sheets of interlayer water. The basal spacings of 11.8 - 11.5 Å indicate vermiculite containing a single sheet of interlayer water whilst a 9.02 Å spacing corresponds to an anhydrous phase. The two samples noted to contain hydrobiotite (MK1 and PB) exhibit the spacings that can be attributed to this phase up to 100 °C. Thereafter, the spacings of both vermiculite and hydrobiotite are unresolved.

Table 3.1. Some XRD (001) basal spacing peak positions (Å) of the heated Mg-saturated samples

Heating	Sample					
Temperature, °C	KL1	KL2	MS	MK1	MK2	PB
25	14.4	14.43	14.37	14.50, **12.49**	14.46	nd*
50	14.34	14.34	14.33	14.26, **12.29**	14.35	14.22, **12.49**
100	11.8	11.69	11.55	11.53, **10.90**	11.55	11.50, **10.98**
200	10.42	10.18	10.21	10.13	10.08	10.4
300	10.13	10.05	9.97	10.07	10.05	10.14
400	10.11	10.04	9.95	9.87	10.01	10.13
500	10.05	9.97	9.88	9.81	9.76	10.11
600	13.8, 9.94	13.8, 9.83	13.8, 9.78	9.58	9.41	10.06

nd* = Not determined. Values in bold indicate peak positions for hydrobiotite in samples containing both vermiculite and hydrobiotite.

Thus, up to 50 °C all specimens contained double sheets of interlayer water whilst heating beyond 100 °C led to the development of phases containing a single sheet of interlayer water (Table 3.1). At and beyond temperatures of 100 °C, the width of most peaks in several of the samples, especially the width of higher orders, is considerable, to the point that broad bands of diffraction are a better description for some regions of the patterns. This most probably indicates the interstratification of vermiculite layers with various integral numbers of water layers (N = 2, 1, 0). Samples KL1 and KL2, show this behaviour most obviously at 100 and 200 °C, and at 600 °C, samples MS and MK1 at 200 and 600 °C, indicating that the dehydration process in the heating experiment is not homogenous, nor entirely consistent from one sample to another. At 600 °C, three peak maxima are resolved across the entire set of samples at approximately 3.3, 3.2, and 3.0 Å (Fig.3.2). These are interpreted to reflect basal spacings of around 9.9, 9.6, and 9.0 which are unlikely to be resolved at lower angles. In each case, this interpretation is supported by the shape of the peak between 9.3 - 10 Å at 600 °C,

which appears to reflect the relative distribution or presence/absence of the peaks observed at higher angles.

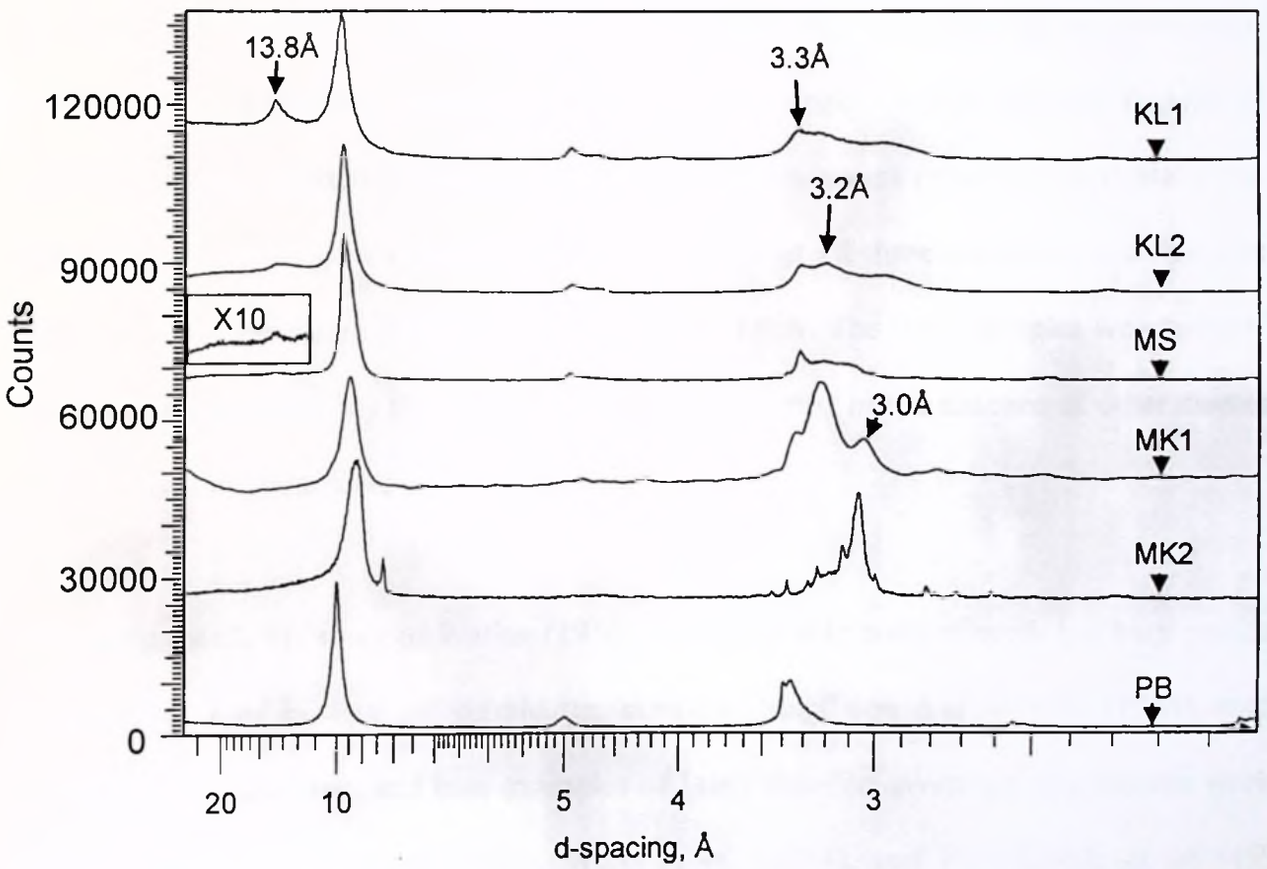

Fig. 3.2. XRD patterns of Mg-saturated samples heated at 600 °C. Intensity patterns have been normalized and offset for presentation purposes and clarity. Inserted box shows a portion of XRD pattern of sample MS enlarged 10 times to show the presence of the 13.8 Å peak.

A further interesting feature of the heating experiments is the clear development of a 13.8 Å peak in three of the vermiculite samples (KL1, KL2, and MS) at 600 °C (Fig.3.2). This is interpreted as evidence of the presence of a small proportion of chlorite or chlorite-like layers in the sample. These layers are most probably present in the samples naturally, and may explain the heterogeneity of the basal spacings in air-dried samples. Alternatively, they may perhaps have developed by migration of exchangeable Mg atoms during the final stages of dehydration such that they have become clustered and organized into specific regions of the interlayer spaces. Certainly, a degree of cation migration seems necessary to explain the 9 Å spacing observed in some samples, and it is notable that all three samples which develop an obvious 13.8 Å peak also develop a peak at around 3.0 Å. The three samples which show this behaviour are also notably the three purest samples in terms of the absence of other discrete or interstratified phyllosilicate components.

Following the classic study of Walker (1956), a considerable body of work has been published on the effects of heating on vermiculite samples. MacEwan and Wilson (1984) made a comprehensive summary and later examples of fairly detailed investigations include work by Von Reichenbach and Beyer (1994), Weiss *et al.* (1994), and Ruiz-Conde *et al.* (1996). Generally, the observations of these and other authors are in broad agreement with those reported herein. For instance, the progressive decrease in the first order basal spacings of vermiculite on heating in stages with the formation of less hydrated phases as found in this study is similar (Walker, 1956; MacEwan and Wilson, 1984; Ruiz-Conde *et al.*, 1996). Similarly, the broad bands of diffraction noted, probably due to coexistence of a number of hydration states at 100 to 600 °C, are in agreement with previously reported observations (Walker, 1956; Von Reichenbach and Beyer, 1994; Ruiz-Conde *et al.*, 1996). However, in the present investigation, a completely anhydrous phase with a basal spacing at 9.02 Å as reported

by MacEwan and Wilson (1984) was not observed; instead phases which are more hydrated with spacings of 9.41 to 10.06 Å were found (Table 3.1).

The evidence observed for the possible formation of chlorite on heating (13.8 Å peak) in what are apparently the purest vermiculite samples is also intriguing, but as yet no satisfactory explanation is available. Although a small fraction of pre-existing chlorite layers are difficult to detect by other means, it is perhaps the most plausible. A small fraction of chlorite is usually masked by vermiculite because they have similar XRD reflection patterns (Walker, 1949; Środoń, 2006). Nonetheless, given that Mg-vermiculite can be transformed into a variety of chlorite-bearing phases by hydrothermal treatment (Moser-Ruck *et al.*, 2003), the possible formation of chlorite-like layers during the experiment may be worthy of further investigation.

The XRD patterns of random, spray-dried, powders for each of the samples are shown in Figure 3.3 and in Table 3.2 details of the minerals detected and quantified by XRD in each sample are presented. Vermiculite sample KL1 was found to contain a moderate amount of opal-CT together with small amounts of quartz and hematite. Sample KL2 was the purest vermiculite sample by far with no obvious impurities detectable in the random powder XRD pattern. Sample MS contained a moderate amount of sapphirine and a trace of quartz, while the accessory minerals detected and quantified in sample MK2 were hematite, calcite, amphibole, pyroxene, rutile, and apatite. For the two samples shown to have large hydrobiotite contents, MK1 contained quartz, rutile, and apatite while PB contained some mica (biotite/phlogopite) and calcite.

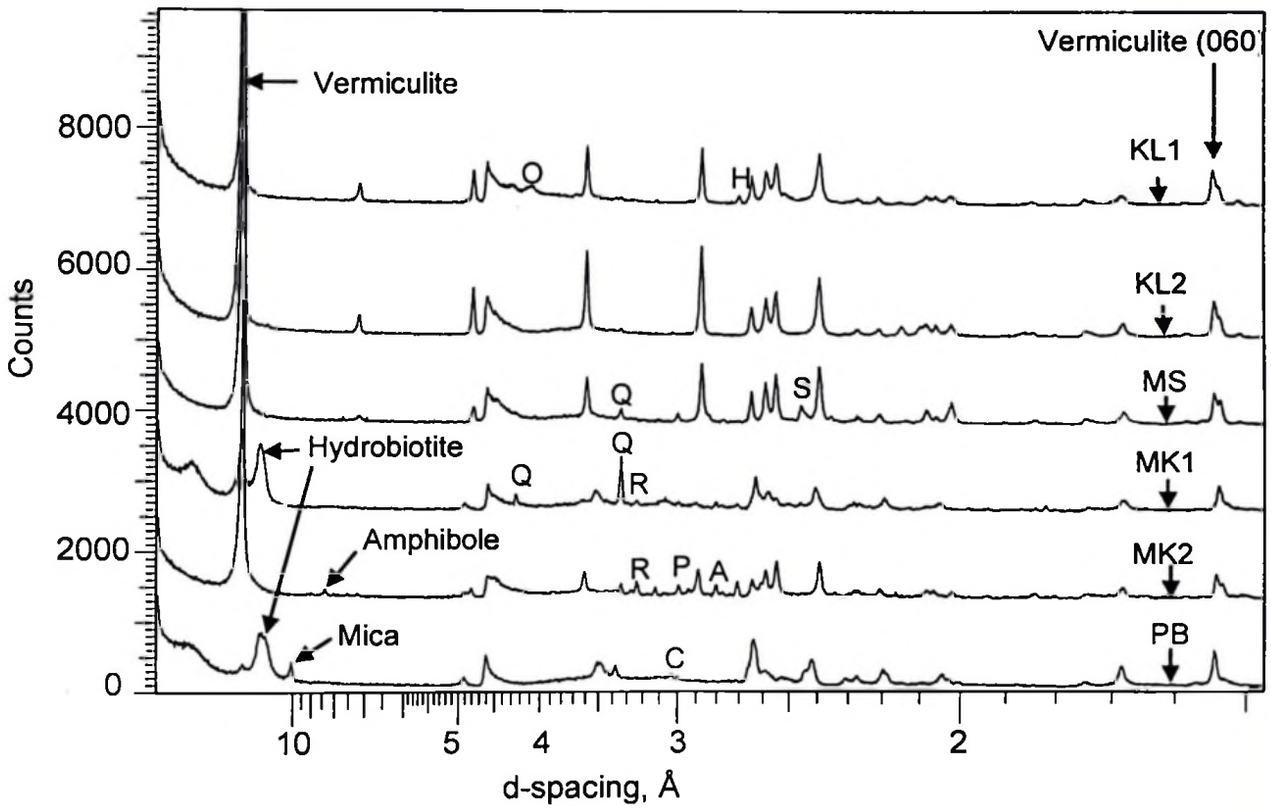

Fig.3.3. Random bulk X-ray powder diffraction showing some of the minerals that are present in the samples. O=Opal-CT, H=Hematite, Q=Quartz, S=Sapphirine, R=Rutile, P=Pyroxene, A=Apatite and C=Calcite. Intensity patterns are offset for clarity.

As was previously indicated by the analysis of the oriented mineral specimens of these samples, PB contained the largest hydrobiotite content, around 87 wt %, while MK1 was around 74 wt % hydrobiotite. Interestingly, the automatic full pattern fitting of sample MK2 for phase quantification fitted a moderate amount of hydrobiotite in this sample, even though the presence of hydrobiotite was not obvious based on the analysis of the oriented mineral specimens. This is an added advantage of the full pattern fitting technique as it complements the normal XRD interpretation by recognizing trace phases which had not been initially identified (Omotoso *et al.*, 2006).

The peak positions for the (060) peak for KL1, KL2, MS, and PB were all found to have values ranging from 1.540 - 1.542 Å while for samples MK1 and MK2 the values were 1.535 and 1.538 Å respectively, thus confirming that all are trioctahedral (Douglas, 1989).

In addition to the impurities identified by XRD, the SEM studies showed that all of the samples contain a variety of other trace minerals (Table 3.3). Appendix 3.2 shows the images of some of the minerals identified by SEM. EDS spectra of some of the trace minerals are also located in Appendix 3.2. Of the minerals identified by the SEM, sepiolite, amphibole, and galena are probably the only three that may be a cause for concern in the context of extraction and agricultural use. Fibrous sepiolite was identified initially in samples KL1 and KL2 (Fig. 3.4a) and later confirmed by XRD of oriented and size fractioned sample (< 2 μm) (Fig.3.5). The sepiolite fibres range from 0.084 to 0.296 μm in diameter, some with a length of more than 8 μm (Fig.3.4b). Many regulatory agencies worldwide treat mineral fibres of less than 3 μm diameter as hazardous to the human respiratory system (Stanton *et al.*, 1981; Cossette, 1984).

Table 3.2. Weight percent of the minerals in the samples as determined by XRD

Sample	Vermiculite	Hydrobiotite	Tri-mica	Quartz	Calcite	Rutile	Hematite	Apatite	Amphibole	Pyroxene	Sapphirine	Opal-CT	Total
KL1	81.8			0.3			1.6					16.1	99.7
KL2	100.0												100.0
MS	78.5			0.8							20.5		99.8
MK1	15.2	74.3		6.5	1.2	0.9		2.0					100.0
MK2	60.0	16.3		2.3	1.0	1.7	1.4	2.7	6.7	8.3			100.4
PB	0.9	87.4	10.7		1.0								99.9

Table 3.3. Accessory minerals in the samples as determined by SEM with EDS

Sample	Pyroxene	Amphibole	Quartz	Rutile	Apatite	Calcite	Hematite	Galena	Zircon	Sepiolite	Gold	Gedrite	Spinel	Högbomite	Ilmenite	Monazite	Sphene	Barite	Feldspar	Sapphirine
KL1			*			*	*		*	*								*		
KL2				*		*			*	*	*							*		
MS			*	*								*	*	*						*
MK1			*	*	*	*	*								*	*	*			
MK2		*	*	*	*	*	*	*	*						*	*	*			
PB	*	*			*	*												*	*	

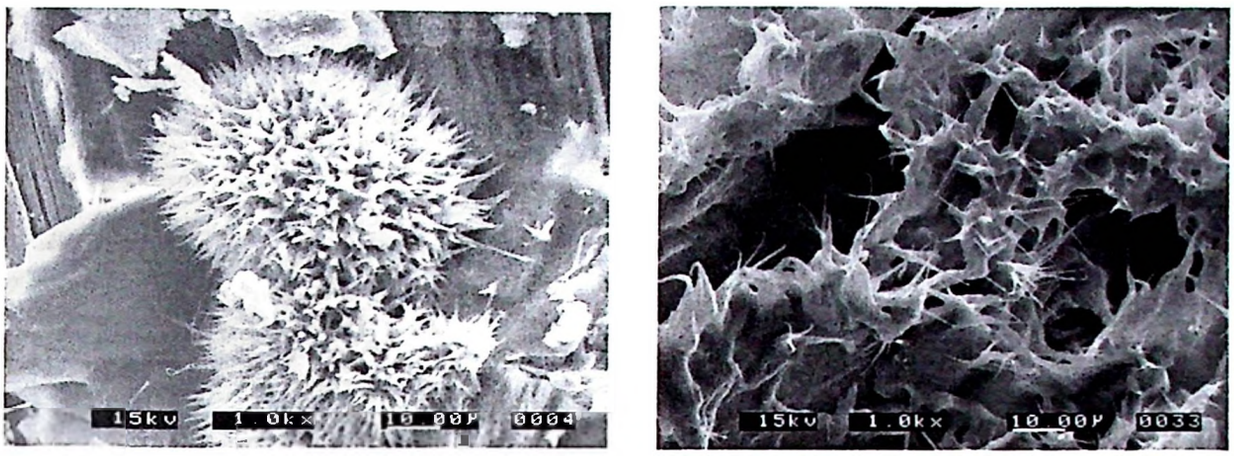

Fig. 3.4a. SEM images of sepiolite in samples KL1 (right) and KL2 (left)

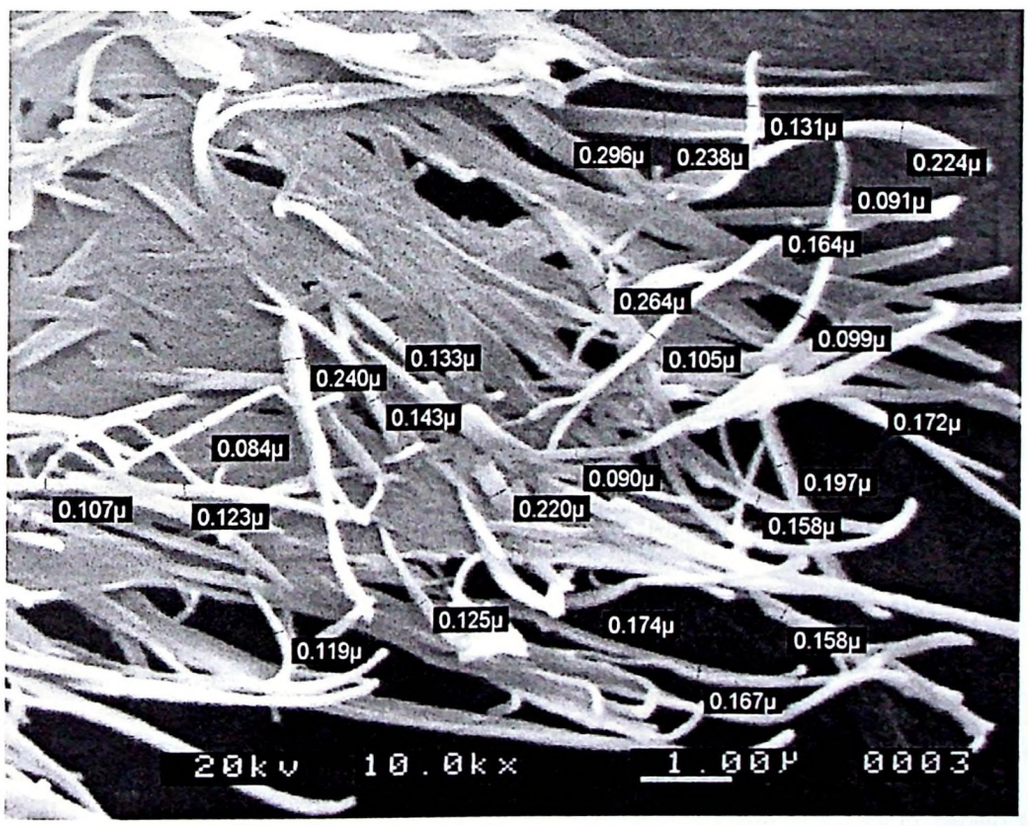

Fig.3.4b. SEM image of sepiolite showing the widths of some fibres in sample KL2.

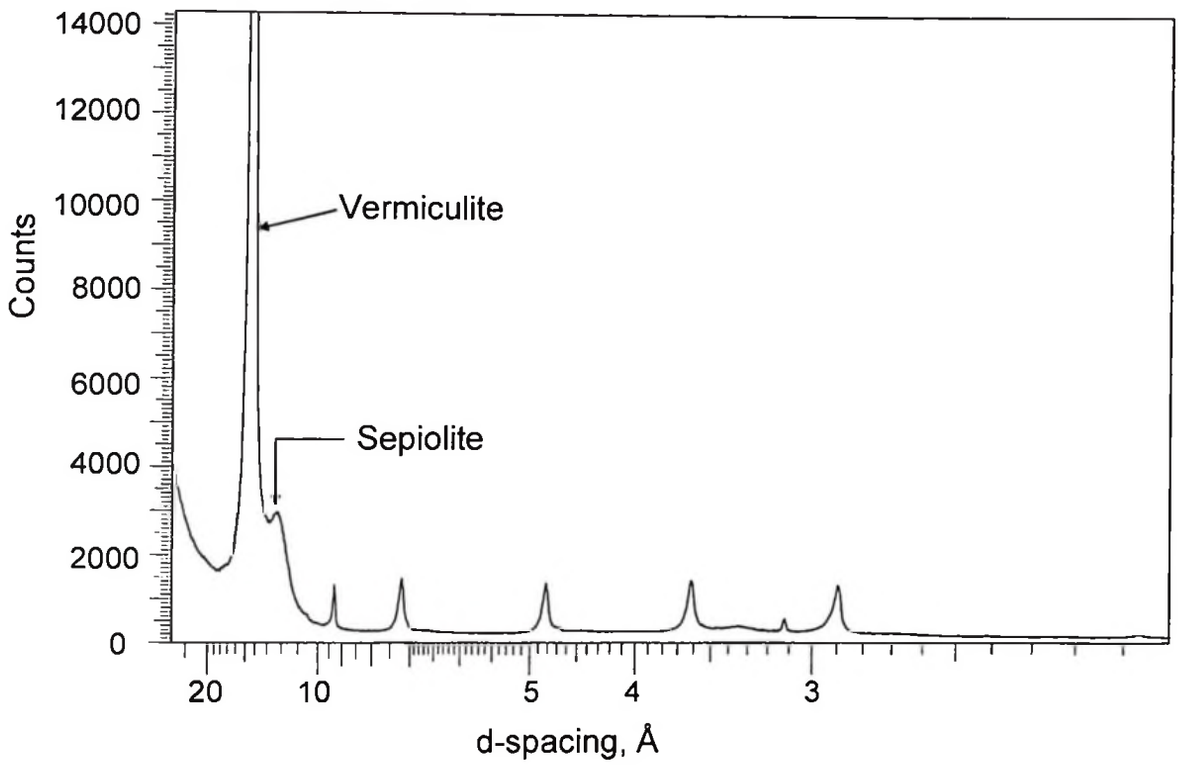

Fig.3.5. Air-dried XRD reflection patterns of oriented mineral fractions (<2 μm) showing a sepiolite phase in sample KL2

Although as yet there is no conclusive evidence for the harmful effects of sepiolite fibres to humans, studies in animal experiments have confirmed high tumour incidences caused by sepiolite fibres with a length of more than 8 μm (Bellmann *et al.*, 1997; HELA, 2005). Apart from known fibrous amphiboles and serpentines, no study other than this has reported the presence of hazardous fibrous sepiolite in vermiculite. However, it should be noted that the amount of sepiolite in these vermiculites is small to the extent that XRD failed to quantify it. Thus, its presence in these vermiculites is unlikely to pose any health risk to humans.

SEM examination of sample MK2, which was shown by XRD to contain about 7 wt % amphibole, indicates the presence of some fibrous forms of amphibole (Fig. 3.6). EDS indicates that the amphibole in sample MK2 could be tremolite or actinolite. Tremolite is among the fibrous asbestiform amphibole minerals known to cause respiratory disorders in humans (Whitehouse, 2004).

Analysis of the fibres in sample MK2 indicates that they are all thicker than 10 μm and thus, cannot be inhaled to cause human lung cancer (Cossette, 1984). However, vermiculite from the deposit where this specimen was collected may require further screening to ascertain whether or not there are thinner asbestiform amphiboles that can endanger human life. Based on this study, this vermiculite is safe for agricultural applications unless proved in the future to contain fibres with a diameter of less than 3 μm, which could preclude it for extraction and processing.

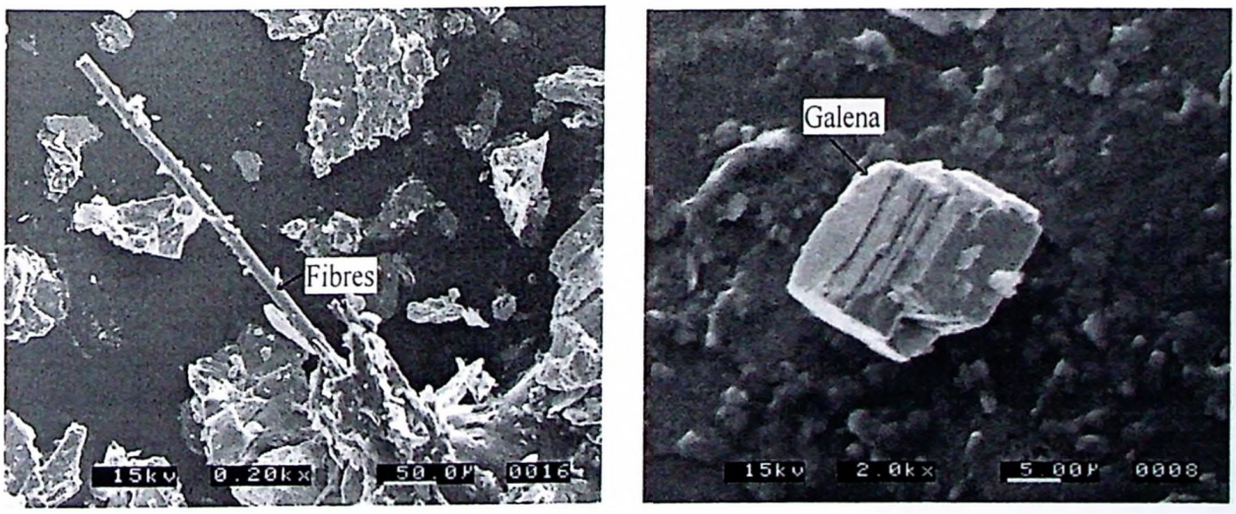

Fig.3.6. SEM images of fibrous amphiboles (left) and galena (right) in sample MK2

Galena was identified by SEM and EDS in sample MK2 (Fig.3.6). Galena is a source of lead, an element that can cause health problems in the human body through inhalation and/or ingestion. Lead is known to affect the brain and the nervous system (Finkelstein *et al.*, 1998). In addition, it is known to inhibit activation of vitamin D and uptake of dietary calcium (Lockitch, 1993). Once it is mined or exposed on the earth's surface, there is no known way to destroy or make it harmless. Since galena was not detected by XRD and Pb content by ICP-MS is low (see below), it implies the amount in this vermiculite is small and its potential health risk to humans is likely to be insignificant.

3.3.2 Chemical composition

The EPMA results showed a significant variation in the chemical compositions of the vermiculites from Tanzania and are also different in a number of respects from that of the Palabora Europe Ltd sample (Table 3.4a). As shown by XRD, the Palabora sample is mainly hydrobiotite not vermiculite and this fact accounts for the high content of potassium observed. Sample MK1, which also has a significant amount of hydrobiotite in it, also shows high potassium, although the amount is not as high as might have been expected based on the XRD results. In this case the analysis may represent a mixture of more and less vermiculitised particles as indicated by its slightly high standard deviation of the mean.

Sample MK1 as well as samples MK2 and KL1 show relatively high titanium values, which tallies with the fact that a variety of titanium-bearing minerals were identified in these samples including sphene, rutile, and ilmenite (Table 3.3 ; Appendix 3.2). In addition, samples MK1 and MK2 showed relatively high percentages of Ca and Fe. The presence of apatite, monazite, and sphene, which are Ca-rich minerals, in these samples is a positive indication that the host rocks from which these samples were formed had Ca- rich minerals.

Similarly, high Al in sample MS reflects its formation in the environment containing Al-rich minerals. The presence of Al-rich minerals in MS, such as sapphirine [(Mg, Fe, Al)$_8$(Al, Si)$_6$O$_{20}$], högbomite [a complex Fe-Mg-(Co-Zn)-Al-Ti oxide], and spinel [$MgAl_2O_4$] (Deer *et al.*, 1992) is supporting evidence (Appendix 3.2).

The small standard deviations of the means obtained from the six independent analyses done for each sample suggest no inclusion was incorporated in the EPMA data. Based on that, attempts were made to calculate their structural formulae. Tables 3.4b and 3.4c includes two such attempts, whereby Fe has been assumed to be all Fe^{3+}, or all Fe^{2+}, and Mg in excess of octahedral occupancy is allocated to interlayer sites. Such calculations indicate clearly that KL1, KL2, MS, and PB have a relatively high layer charge, whereas MK1 and MK2 are significantly lower. This agrees with the observations made independently by XRD in this respect.

In fact, the layer charge of the two MK samples falls out of the current definition of vermiculite and lies within the field of smectites (Guggenheim *et al.*, 2006), irrespective of the assumed oxidation state of Fe (Tables 3.4b and 3.4c). In hand specimen, however, the MK samples have all the characteristics of macroscopic vermiculites (Chapter 2). Furthermore, the XRD response with the Mg-saturated specimens is that of vermiculite (MacEwan and Wilson 1984). It is pertinent to note that the compilation of Foster (1963) includes several vermiculites with comparable layer charge to the MK samples examined. This indicates clearly that the definition of vermiculite and hydrobiotite based on the layer charge needs to be revisited in order to accommodate other lower charge minerals with similar properties and XRD patterns.

Table 3.4a. Microprobe analyses of samples (wt. %), each value is a mean of six individual analyses with a standard deviation. Total wt % is less than 100 because the instrument does not measure H_2O and OH groups. Iron is assumed to be Fe^{3+}.

Main oxides	Sample					
	KL1	KL2	MS	MK1	MK2	PB
SiO_2	37.10 ± 0.64	39.12 ± 0.26	39.64 ± 0.45	42.44 ± 0.49	42.47± 0.64	41.07± 0.17
Al_2O_3	14.54 ± 0.21	16.31 ± 0.16	18.07 ± 0.45	13.97 ± 0.33	14.31± 0.33	10.75 ± 0.57
TiO_2	1.49 ± 0.06	0.53 ± 0.02	0.89 ± 0.15	2.09 ± 0.04	1.30 ± 0.07	1.08 ± 0.15
Cr_2O_3	<0.02	0.21 ± 0.04	0.11 ± 0.05	0.31 ± 0.08	0.06 ±0.04	<0.02
Fe_2O_3	8.12 ± 0.21	4.77 ± 0.15	3.92 ± 0.38	12.08 ± 0.20	11.47± 0.03	7.51 ± 0.71
MnO	0.15 ± 0.01	<0.03	<0.03	0.12 ± 0.06	0.07 ± 0.5	0.06 ± 0.4
MgO	26.28 ± 0.17	26.73 ± 0.27	24.69 ± 0.77	17.31± 0.45	18.20 ± 0.91	25.51 ± 0.58
CaO	<0.02	0.08 ± 0.02	0.46 ± 0.16	1.35 ± 0.18	2.15 ± 0.19	0.03 ± 0.02
Na_2O	0.14 ± 0.12	0.15 ± 0.04	0.15 ± 0.03	0.14 ± 0.03	0.15 ± 0.02	0.14 ± 0.09
K_2O	0.06 ± 0.02	0.09 ± 0.01	<0.06	1.09 ± 0.82	<0.06	5.80 ± 0.71
Total	87.86 ± 0.74	87.97 ± 0.32	87.95 ±1.09	90.91 ± 0.62	90.18 ± 0.62	91.97 ± 1.13

Table 3.4b. Structural formulae of vermiculite and hydrobiotite samples assuming all iron is Fe^{3+}

Element	KL1	KL2	MS	MK1	MK2	PB
Si	5.41	5.61	5.65	6.04	6.04	5.90
Al(T)	2.59	2.39	2.35	1.96	1.96	2.11
∑T	8.00	8.00	8.00	8.00	8.00	8.00
Al(O)	0.00	0.37	0.68	0.38	0.44	0.00
Ti	0.17	0.06	0.09	0.22	0.14	0.12
Fe^{3+}	0.80	0.52	0.43	1.30	1.23	0.52
Cr^{3+}	0.00	0.05	0.02	0.07	0.02	0.00
Mg	5.01	5.00	4.78	3.67	3.86	5.35
Mn	0.02	0.00	0.00	0.02	0.01	0.01
∑O	6.00	6.00	6.00	5.66	5.69	6.00
Exch. Mg	0.70	0.71	0.46	0.00	0.00	0.11
Exch. Ca	0.00	0.01	0.07	0.21	0.33	0.01
Exch. Na	0.04	0.03	0.03	0.03	0.03	0.04
Interlayer K	0.02	0.02	0.00	0.21	0.00	1.07
∑ inter. charge	1.45	1.49	1.09	0.65	0.68	1.34
CEC ($cmol_{(+)}/kg$)	149	152	113	46	71	28

Note: MK1 and PB are essentially hydrobiotites whilst other samples are mainly vermiculites. T=Tetrahedral, O = Octahedral and Σ = Summation.

Table 3.4c. Structural formulae of vermiculite and hydrobiotite samples assuming all iron is Fe^{2+}

Element	KL1	KL2	MS	MK1	MK2	PB
Si	5.52	5.68	5.71	6.23	6.22	6.01
Al(T)	2.48	2.32	2.29	1.77	1.78	1.99
∑T	8.00	8.00	8.00	8.00	8.00	8.00
Al(O)	0.08	0.47	0.77	0.64	0.68	0.00
Ti	0.17	0.06	0.10	0.23	0.14	0.12
Fe^{2+}	0.91	0.52	0.42	1.33	1.27	0.83
Cr^{3+}	0.00	0.05	0.02	0.07	0.02	0.00
Mg	4.82	4.90	4.69	3.70	3.89	5.04
Mn	0.02	0.00	0.00	0.02	0.01	0.01
∑O	6.00	6.00	6.00	6.00	6.00	6.00
Exch. Mg	1.01	0.88	0.60	0.08	0.08	0.53
Exch. Ca	0.00	0.01	0.07	0.21	0.33	0.01
Exch. Na	0.04	0.04	0.04	0.04	0.04	0.04
Interlayer K	0.02	0.02	0.00	0.21	0.00	1.09
∑ inter. charge	2.07	1.83	1.37	0.83	0.86	2.20
CEC ($cmol_{(+)}$/kg)	213	188	142	64	89	115

Note: MK1 and PB are essentially hydrobiotites whilst other samples are mainly vermiculites. T=Tetrahedral, O = Octahedral and Σ = Summation.

The structural formulae can also be used to calculate the CEC of the samples and this has been done assuming that any K is non-exchangeable. The results of this calculation again depend on an assumed oxidation state for Fe, but nonetheless allow the samples to be ranked in order of their CEC (Tables 3.4b and 3.4c). When all iron was assumed to be Fe^{3+}, samples KL1, KL2, and MS, which are relatively pure vermiculite, were found to have a higher CEC ranging between 113-152 $cmol_{(+)}\ kg^{-1}$, while samples with hydrobiotite and/or lower layer charge have CECs of 28-71 $cmol_{(+)}\ kg^{-1}$ (Table 3.4b). A similar trend was found when all iron was assumed to be Fe^{2+} except that the CECs obtained are relatively elevated (Table 3.4c). The higher CECs for vermiculites are due to the fact that their interlayer cations are exchangeable as compared to hydrobiotites which contain micas with the non exchangeable cations (Fanning *et al.*, 1989).

The two samples MK1 and MK2 are clearly more siliceous and have a much higher content of Fe as compared to the other samples whose octahedral sites are mainly filled by Mg. If all Fe in these two samples is assumed to be Fe^{2+}, the octahedral totals fall near to the ideal 6 cations. On this basis, it seems likely that such an assumption may be reasonable, at least for these two samples.

It is also worth noting that, the distinctly different composition of these two samples tallies with a distinct difference in the (060) spacing measured by XRD, which reflects the b-dimension of the unit cell. For the set of vermiculites and hydrobiotites examined, the more Fe-rich MK1 and MK2 samples have smaller b-parameters compared to the more Mg-rich samples (Fig.3.3). This appears counter to observations made on other phyllosilicates as summarized for example in Brown and Brindley (1984), where increased Fe-content tends to correlate with larger b-parameters. However, studies by Radoslovich (1962), Gilkes *et al.*

(1972) and Brindley and MacEwan, (1953) as quoted by Brown and Brindley (1984, pp.334) indicate that the b-parameter decreases with the oxidation of Fe^{2+} to Fe^{3+}. This may be understood if the oxidation results in the ejection of some Fe from the octahedral sites as pointed out by Wilson (1970) resulting in a somewhat more dioctahedral structure and hence smaller b-parameter. Reduction in ionic radius of iron on oxidation of Fe^{2+} to Fe^{3+} could also be the reason for the decrease in the b-parameter. Confirmation of these assumptions requires further investigation using other techniques such as Mossbauer spectroscopy.

3.3.3 Elemental concentrations

Major, minor, and trace elements in the studied samples as determined by ICP-MS are shown in Tables 3.5a-c. Their correlation matrix is located in appendix 3.3. The concentrations of the major and some trace elements are in broad agreement with the analyses made by EPMA with the exception of Cr in all samples and Mn in sample KL1 (Table 3.6). In principle, both analyses might be expected to differ from one another. The ICP-MS results give the total concentration of individual elements in a sample including accessory minerals, whereas EPMA by virtue of the small beam size is more likely to give the actual composition of the vermiculite or hydrobiotite. Their close similarity is an indication that the abundances of accessory minerals in the samples are very low. The difference in the ICP-MS results among the studied samples could be due to the variation in their mineralogical composition (Fig.3.3 and Tables 3.2).

Analysis of the reference standards used is documented in appendix 3.4. The recovery of the elements from the standards was good with the exception of zirconium (Zr), which was poor. It implies that the ICP-MS data was accurately analyzed and thus, the total concentrations of the elements presented are reliable.

The ICP-MS results show clearly that Al is relatively higher in sample MS than in the other samples because of having Al-rich minerals. The concentration of K is similarly high in samples MK1, MK2, and PB. This is probably attributed to the presence of hydrobiotite and / or biotite/phlogopite (Table 3.2). Calcium is also high in MK1 and MK2 because it is the main interlayer cations in these samples other than K. Some Ca and P, Sr, U, Y, La, and Ga in samples MK1 and MK2 could be related to the presence of apatite and monazite (Tables 3.2 and 3.3). According to Belousova *et al.* (2002) and Andrehs and Heinrich (1998), apatite and monazite are capable of accommodating a wide range of trace elements including rare earth elements (REE), Y, U, and Sr. The elements are incorporated in their structures during crystallization. Strong positive linear correlations (Appendix 3.3) among these elements (Ca, P, Sr, U, Y, La, and Ga) also suggest that they are incorporated in the apatite and monazite phases (Baturin and Yushina, 2007).

Observation also show that Pb, As, and Zn are marginally higher in samples MK1 and MK2 than in the other samples. SEM results showed the presence of galena in sample MK2, which accounts for some of the Pb. Galena is a sulphide mineral and can occur with other sulphides such as sphalerite and arsenopyrite, the possible sources of Zn and As in these samples. Williams and Skerl (1940), during regional geological mapping in Tanzania, observed a number of arsenopyrite occurrences in pegmatites bordering these vermiculites. From these pegmatites, As can be mobilized by water into vermiculite (Peters and Blum, 2003) leading to the observed concentrations.

Table 3.5a. Major and minor elements in vermiculite and hydrobiotite samples analyzed by ICP-MS

Sample	Total concentration, wt %									
	Si	Al	Fe	Mg	Ca	K	Na	Ti	P	S
KL 1	n/a*	6.2	4.0	15.9	<0.01	<0.01	<0.01	0.29	<0.01	<0.01
KL 2	n/a	7.9	2.9	16.7	0.09	<0.01	<0.01	0.29	<0.01	<0.01
MS	n/a	9.2	2.9	13.1	0.18	0.01	0.12	0.54	<0.01	<0.01
MK 1	n/a	6.4	7.9	8.0	1.83	2.24	0.04	1.59	0.33	0.02
MK 2	n/a	6.3	7.1	8.3	1.97	2.03	0.07	1.20	0.32	0.01
PB	n/a	6.1	5.1	16.2	0.35	4.95	0.02	0.57	0.04	0.01

n/a* means not determined

Table 3.5b. Trace elements in vermiculite and hydrobiotite samples analyzed by ICP-MS

Sample	Total concentration, mg/kg										
	Cu	As	Cd	Pb	Zn	Mo	Ni	Cr	Zr	Sn	Ba
KL 1	4.8	<0.2	<0.02	1.7	102	<0.05	1208	973	2.4	1.7	9
KL 2	20.0	<0.2	<0.02	8.8	42	<0.05	1457	1008	2.1	0.1	19
MS	3.6	<0.2	<0.02	5.5	33	<0.05	95	202	10.7	0.1	59
MK 1	8.7	3.40	0.02	25.1	221	0.44	587	1935	21.1	3.2	1551
MK 2	5.8	2.60	<0.02	15.9	218	0.58	559	1706	4.4	2.6	1562
PB	14.6	<0.2	<0.02	<0.2	82	0.21	172	240	5.8	0.3	679

Table 3.5c. Trace elements in vermiculite and hydrobiotite samples analyzed by ICP-MS

Sample	Total concentration, mg/kg											
	Nb	Rb	Sr	Sc	V	U	Y	Th	La	Ga	Mn	Hg
KL 1	2.9	2	<2	2.1	27	<0.1	0.1	0.2	<0.5	15.2	549	0.11
KL 2	0.5	1	3	1.3	14	0.1	<0.1	0.2	<0.5	12.6	161	0.10
MS	0.9	1	11	13.0	147	<0.1	1.1	0.9	<0.5	10.5	204	0.06
MK 1	2.8	180	368	15.9	194	2.3	28.0	1.1	63.0	30.0	912	0.08
MK 2	0.3	157	285	14.6	178	2.0	23.7	0.7	63.4	27.2	812	0.06
PB	1.3	585	26	4.8	12	0.1	0.6	0.9	2.7	17.5	338	0.09

Table 3.6. Concentrations of some elements in the studied samples as computed from the EPMA results in Table 3.4a

Sample	Concentration, wt %								Concentration, mg/kg	
	Si	Al	Fe	Mg	Ca	K	Na	Ti	Cr	Mn
KL1	17.34	7.70	5.68	15.85	<0.02	0.05	0.10	0.89	<108	1145
KL2	18.29	8.63	3.34	16.12	0.06	0.07	0.11	0.32	1464	<230
MS	18.53	9.56	2.75	14.89	0.33	<0.05	0.11	0.53	741	<230
MK1	19.84	7.39	8.45	10.44	0.97	0.91	0.10	1.25	2134	955
MK2	19.86	7.57	8.02	10.97	1.54	<0.05	0.11	0.78	393	519
PB	19.20	5.69	5.26	15.39	0.02	4.81	0.11	0.65	<108	497

Strong positive correlations of Pb, As, and Zn among themselves and with elements such as Ca, P, Sr, U, Y, La, and Ga (Appendix 3.3) could link these elements to apatite and monazite which are present in MK1 and MK2. Apatite often occurs with the sulphides as inclusions which may lead to high levels of As, Zn, and Pb (Belousova *et al.*, 2002). In apatite, inclusions of sulphides give a cloudy-grey appearance under the binocular microscope (Belousova *et al.*, 2002).

Although Fe-bearing accessory minerals, such as hematite and /or ilmenite, were observed in samples KL1, MK1, MK2, and PB, a strong negative correlation between Fe and Mg (Appendix 3.3) suggests that most of the Fe is substituting for Mg in the octahedral sites of vermiculite and hydrobiotite (Abollino *et al.*, 2007).

The elements Mn, Ti, and V show strong positive correlations among themselves and Fe (Appendix 3.3). In addition, the elements have a strong negative correlation with Mg. In micas as in vermiculites, according to Tischendorf *et al.* (2007), these elements occur in octahedral sites. Their negative correlations with Mg suggest they are incorporated in these sites by

replacing Mg. Some of these elements can also occur in a trace amount in apatite (Belousova *et al.*, 2002). High Fe and Ti in MK1 and MK2 (Table 3.5a) is an indicator that the host rocks where the samples were taken are enriched in those elements.

High concentrations of Ni and Cr in samples KL1, KL2, MK1, and MK2 (Table 3.5b) also could be linked to the chemistry of the host rock. The host rock for samples KL1 and KL2 is a metagabbro with serpentinite bodies (Hartley and Moore, 1965). Similar elevated concentrations of Ni and Cr are common in soils derived from serpentinite bodies (Oze *et al.*, 2004). High concentrations of Cr and Ni in samples MK1 and MK2 are possibly associated with amphibolitic bodies, which are in contact with these vermiculites (Chapter 2). The occurrence of amphibolites with high Cr and Ni is common, and is used as a proof of their magmatic origin (Meli and Bertolo, 1998). In vermiculite and some micas, Cr occurs in the octahedral sites (Tischendorf *et al.*, 2007). Its weak correlation with other elements that are common in octahedral sites such as Mg and Fe as well as Ni which occur together in amphibolites and serpentines could be due to the small data set used in this correlation.

Barium and Rb are higher in hydrobiotite samples (PB, MK1, and MK2) than in samples composed of pure vermiculite (KL1, KL2, and MS). The elements are common in mica, a constituent of hydrobiotite, as interlayer cations substituting for K (Tischendorf *et al.*, 2007). Globally, micas in Proterozoic pegmatites of the same age to those in the Mozambique Belt of Tanzania are rich in Rb (Quéméneur *et al.*, 2007). An increase of K and Rb with the increase in the amount of hydrobiotite and tri-mica (biotite/phlogopite) in the sample (Tables 3.5a, 3.5c and 3.2) is a proof of their association.

Pegmatites cross-cutting amphibolite bodies in the vicinity of the vermiculite deposits where samples MK1, MK2, and MS were taken could be the source of high V and Sc. Pegmatite fluids mobilize the elements and enrich mafic minerals such as amphibole and biotite (Kempe and Wolf, 2006). Formation of vermiculite might have incorporated the elements from mafic minerals. In micas, including vermiculites, V occurs in octahedral sites (Tischendorf *et al.*, 2007). A strong negative correlation between V and Mg suggests that V substitutes for Mg in octahedral sites (Appendix 3.3). Mining of emerald, a green variety of beryl, from where sample MS was collected, gives clear evidence for the presence of V in the area. Chromium and /or V replace Al in beryl to form emerald (Groat *et al.*, 2005).

The element Zr is marginally higher in samples MS and MK1 than the others and this could be linked to trace amounts of zircon in the samples, well below XRD detection. Similarly, in samples KL2 and PB, Cu is marginally higher than in the other samples for reasons unknown. The remaining elements, Na, S, Sn, Cd, Mo, Hg, Nb, and Th do not show marked differences among the studied samples and their concentrations are generally low.

It should, however, be noted that due to low concentrations of some trace elements in the studied samples and the small data set, some strong correlations reported in Appendix 3.3 could be spurious.

Further inspection of the ICP-MS data shows that the concentrations of Ba, Cr, and Ni in these vermiculites and hydrobiotites can be used as a tool for identifying their source. When the elements are plotted in a triangular diagram, samples from the same locality cluster together (Fig. 3.7). Hydrobiotites from the Mikese area (MK1 and MK2) are grouped together as are

vermiculites from the Kalalani area (KL1 and KL2). The Palabora hydrobiotite (PB) from South Africa is also separated from those from Tanzania.

The tri-plot gives the proportions of Ni, Cr, and Ba in each sample and adds to 100 %. Gunter *et al.* (2005) found that Cr, Ba, and V clearly distinguish Libby vermiculite from other vermiculite products that are used in the USA. In this study, V did not show a clear distinction among the studied samples. Nickel and Cr provided the best discriminants for vermiculites that are hosted by serpentinite. Vermiculites and soils that form in areas underlain by serpentinite and other ultramafic rocks usually have high concentrations of Ni and Cr (Oze *et al.*, 2004). Typical examples are samples KL1 and KL2 which are hosted by serpentinite.

Thus, from this study I can say, a plot of Cr, Ba, and Ni gives a finger print of the source of vermiculites and hydrobiotites in the Mozambique Belt of Tanzania. The plot can be used as one of the criteria in differentiating their products from other sources.

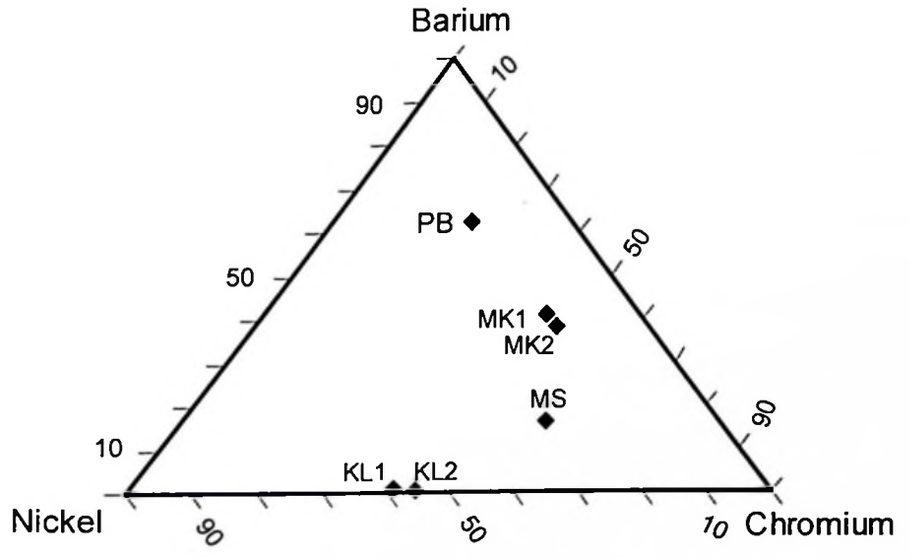

Fig.3.7. Tri-plot of barium, chromium, and nickel (wt %) for the studied samples. PB = Palabora, KL = Kalalani, MK = Mikese and MS = Masatu

3.3.4 Consideration for agricultural application

The elements that could be released into the soil when the studied vermiculites are applied as soil amendments are shown in Tables 3.5a-c. Some of the elements are beneficial to plants whilst others can be toxic. For instance, Ni is an essential micronutrient for higher plants, but in excess is toxic (Brown *et al.*, 1987; Yang *et al.* 1996). The total Ni concentrations in all samples are above the acceptable threshold value of 70 mg/kg recommended in the UK (Alloway, 1999) and 75 mg/kg set by the EEC for agricultural soils (Pasquini, 2006).

Similarly, the total Cr concentrations in samples MK1, MK2, KL1, and KL2 are above the threshold level set for the UK (600 mg/kg) and the Netherlands (800 mg/kg) in soils for growing vegetables (Alloway, 1999). The total Zn concentrations in vermiculite samples MK1 and MK 2 are relatively high but are within the EEC maximum allowable level of 150-300 mg/kg set for agricultural soils (Pasquini, 2006). The element Zn is not hazardous to human health, but when in excess it can cause phytotoxicity in soils (Silanpää, 1982).

Chromium and Ni can be toxic depending on their availability, and species (Zayed *et al.*, 1998). Thus, the potential use of vermiculites and hydrobiotites containing the elements will depend on the oxidation state of individual elements together with their concentrations and availability in the ground for plant uptake. It needs to be established by experimentation, and given that elevated concentrations of Cr and Ni appear to be common in vermiculites generally (Foster, 1963); it may be an aspect that requires more widespread investigation.

3.4 CONCLUSIONS AND RECOMMENDATIONS

The study has established that the samples from the Mozambique Belt of Tanzania are tri-octahedral vermiculites and hydrobiotites with a number of accessory minerals as inclusions. Of the accessory minerals that have been identified, galena and fibrous amphibole in sample MK2 and sepiolite in samples KL1 and KL2, are minerals that could endanger health and may preclude these vermiculites from agricultural application if they are found to occur in significant concentrations. The proportion of vermiculite is high in the samples from Tanzania as compared with that from South Africa which is essentially dominated by hydrobiotite with small amounts of mica, calcite, and vermiculite.

The XRD and EPMA studies have revealed that vermiculite samples KL1, KL2, MS, and PB are higher layer charge minerals while samples MK1 and MK2 are lower layer charge minerals. The layer charges of the two MK samples fall within the field of smectites, whereas XRD analysis indicates that they are vermiculite and hydrobiotite. Thus, the definition of vermiculite and hydrobiotite based on the layer charge needs to be revisited in order to accommodate other lower charge minerals with similar properties and XRD patterns.

In samples composed of both vermiculite and hydrobiotite, the vermiculite component of the hydrobiotite behaves in a similar way on glycolation to that of discrete vermiculite. For the lower charge vermiculites, both swell readily whereas for the higher charge vermiculites no significant change occurs in their basal spacings following glycolation. Since hydrobiotite is a transition phase of mica alteration to vermiculite, it implies that the chemistry of the vermiculite component is preserved during this transformation. The outcome is the similarity in their response to glycolation.

The study has found that the (060) spacings (b-parameters) of the samples decrease with the increase in the iron content contrary to what has been reported in previous studies. The cause is yet to be established and further investigation is recommended.

In the heating experiments, dehydration led to the formation of less hydrated vermiculite and hydrobiotite phases. The basal spacings and diffraction patterns of the phases formed differed from one sample to another. The phases of vermiculite and hydrobiotite became unresolved when the heating temperature exceeded 100 °C. Hydrated phases with basal spacings of 9.41 to 10.06 Å were observed on heating at 600 °C contrary to reports in many studies of an anhydrous phase at 9.02 Å. In addition, heating revealed the presence of trace amounts of chlorite in the samples KL1, KL2, and MS which could be original or caused by migration of exchangeable Mg^{2+} during dehydration.

Concentrations of Ba, Cr, and Ni provide a diagnostic signature that can be used to discriminate vermiculites and hydrobiotites from Tanzania based on their localities. Samples from the same source cluster together in the tri-plot of these elements.

The levels of Ni in all vermiculites and hydrobiotites and Cr in some are above the critical concentrations permitted in agricultural soils in some countries. Use of these products in agriculture will depend on the availability of these elements for plant uptake and thus, requires further investigation.

CHAPTER 4

EFFECT OF HEATING ON THE PROPERTIES OF VERMICULITES WITH RESPECT TO POTENTIAL AGRONOMIC APPLICATIONS

4.1 INTRODUCTION

Vermiculite is a mineral with a diversity of physical and chemical properties resulting from the variation in chemical composition, layer charge, lamellar structure, ability to dehydrate-rehydrate, and disorder effects (de la Calle and Suquet, 1988; Suvorov and Skurikhin, 2003). Although the above properties are well known and studied, there is still no comprehensive information on the temperature at which vermiculite should be exfoliated for agricultural applications and also how some of the properties relevant to its agronomic applications behave after heating. It is thus necessary, when evaluating the suitability of vermiculites from Tanzania for agricultural applications, to include the assessment of their properties and response to heating.

4.2 MATERIALS AND METHODS

4.2.1 Characterization of physical and chemical properties

The same six samples, one from Palabora Europe Ltd and five from Tanzania were used (Chapter 3). The particle size of the samples used ranged between 5.6 and 10 mm in diameter and was obtained after dry sieving. The samples were air-dried to a constant weight and heated at 15, 200, 400, 600, and 800 °C in a laboratory muffle furnace. Heating was carried out by raising the temperature at a constant rate of 5-7 °C per minute to each level. The temperature was maintained at each level for 1 h followed by cooling in desiccators.

The samples were weighed before and after heating. The difference in weights gave the mass loss. The apparent bulk density was measured by weighing a known volume of the sample determined by tipping the loose fragments into a measuring cylinder without compaction (Justo *et al.*, 1989).

The samples for determination of the pH, water release characteristic, cation exchange capacity, and exchangeable cations were ground by hand to avoid structural degradation (Balek *et al.*, 2007) and dry sieved for a minute through a 2 mm sieve. Coarser fractions were ground by hand and re-sieved. The water release characteristic was determined using a pressure plate apparatus according to Reeve and Carter, (1991). The pH was measured using a pH meter by immersing the electrode into the supernatant fluid with a 1/2.5 dried solid/water ratio (Okalebo *et al.*, 2002).

The CEC and exchangeable cations were determined by the ammonium acetate saturation method buffered at pH 7 (Bain and Smith, 1994). Exchangeable cations in the extract were measured by atomic absorption spectrometry (AAS), while the CEC was determined by flow injection analysis (FIAstar 5023 spectrophotometer). Sodium chloride was used instead of potassium chloride for replacing ammonium ions measured in the extract for determination of the CEC. Potassium chloride was not used because hydrobiotites have potassium as interlayer cation (Chapter 3).

The CEC was repeated using the caesium chloride (CsCl) saturation method after getting low values with the ammonium acetate saturation method in comparison to the total exchangeable cations (TEC). The samples were immersed in a 1 *M* CsCl solution overnight, rinsed thoroughly several times in de-ionized water, and analyzed using electron microscopy

according to the method of Hillier and Clayton (1992). The CEC by this method is determined from the wt % of Cs_2O measured.

4.2.2 Experimental design and data analysis

A full completely randomized factorial design was used, comprising 30 treatments derived from 6 vermiculites and 5 levels of heating temperature. Each treatment was replicated three times to give a total of 90 sub-samples. A standard two-factor linear model as described by Quinn and Keough (2002) was used for data analysis:

$$Y_{ij\kappa} = \mu + t_i + \beta_j + (t\beta)_{ij} + \varepsilon_{ij\kappa}$$

Where: $Y_{ij\kappa}$ = observed response when vermiculite is at i^{th} level and the heating temperature is at j^{th} level for κ^{th} replicate, μ = overall mean effect, t_i = effect of the i^{th} level of the vermiculite, β_j = effect of the j^{th} level of the heating temperature, $(t\beta)_{ij}$ = effect of interaction between t_i and β_j, and $\varepsilon_{ij\kappa}$ = error associated with the κ^{th} replicate.

Analysis of variance (ANOVA) was carried out using the MSTAT-C statistical programme (Freed *et al.*, 1991). Separation of treatment means was done using the Duncan's multiple-range test at 5 % level of significance (Montgomery, 1991).

4.3 RESULTS AND DISCUSSION

4.3.1 Water release characteristic

Heating of vermiculites changed their water release characteristic (Fig.4.1). For instance, heating sample KL1 at 600 °C and sample KL2 at 800 °C, lowered their ability to adsorb water as compared to lower temperatures (Fig. 4.1 a & b). This decrease could be a sign of reduction in open pores in the samples. It has been found that heating causes alteration of macro and micro-porosity in clay minerals (Heller-Kallai, 2006). A study by Gordeeva *et al.* (2002) showed that heating could cause an increase in closed pores rather than open pores during exfoliation of vermiculite. The presence of closed pores in vermiculite will inhibit accessibility for water and reduces its ability to adsorb and release plant available water.

Samples MK1 and MK2 showed a different behaviour from that of KL2 and KL1. Heating increased water adsorption capacity by more than two-fold as compared to KL1 and KL2. However, most of the adsorbed water was strongly held even at high matric suctions (Fig.4.1 d & e). It implies that water adsorbed in MK1 and MK2 is not significantly readily available for plant uptake. This is a common characteristic of clay minerals, particularly smectite (Townend *et al.*, 2001). High degree of disintegration on heating these samples might have increased surface area and adsorption capacity. High iron in these samples (12 wt %) as compared to that in the other samples (4-8 wt %) (Chapter 3) might have facilitated formation of strong bonds with water as reported by Townend *et al.* (2001).

Similarly, sample MS showed a different pattern from that of KL1, KL2, MK1, and MK2. Water held by MS at low matric suction on heating was nearly the same, but the amount released increased with the increase in the suction pressure. This indicates heating did not cause marked increase in pore size for this sample; instead it lowered the water binding force.

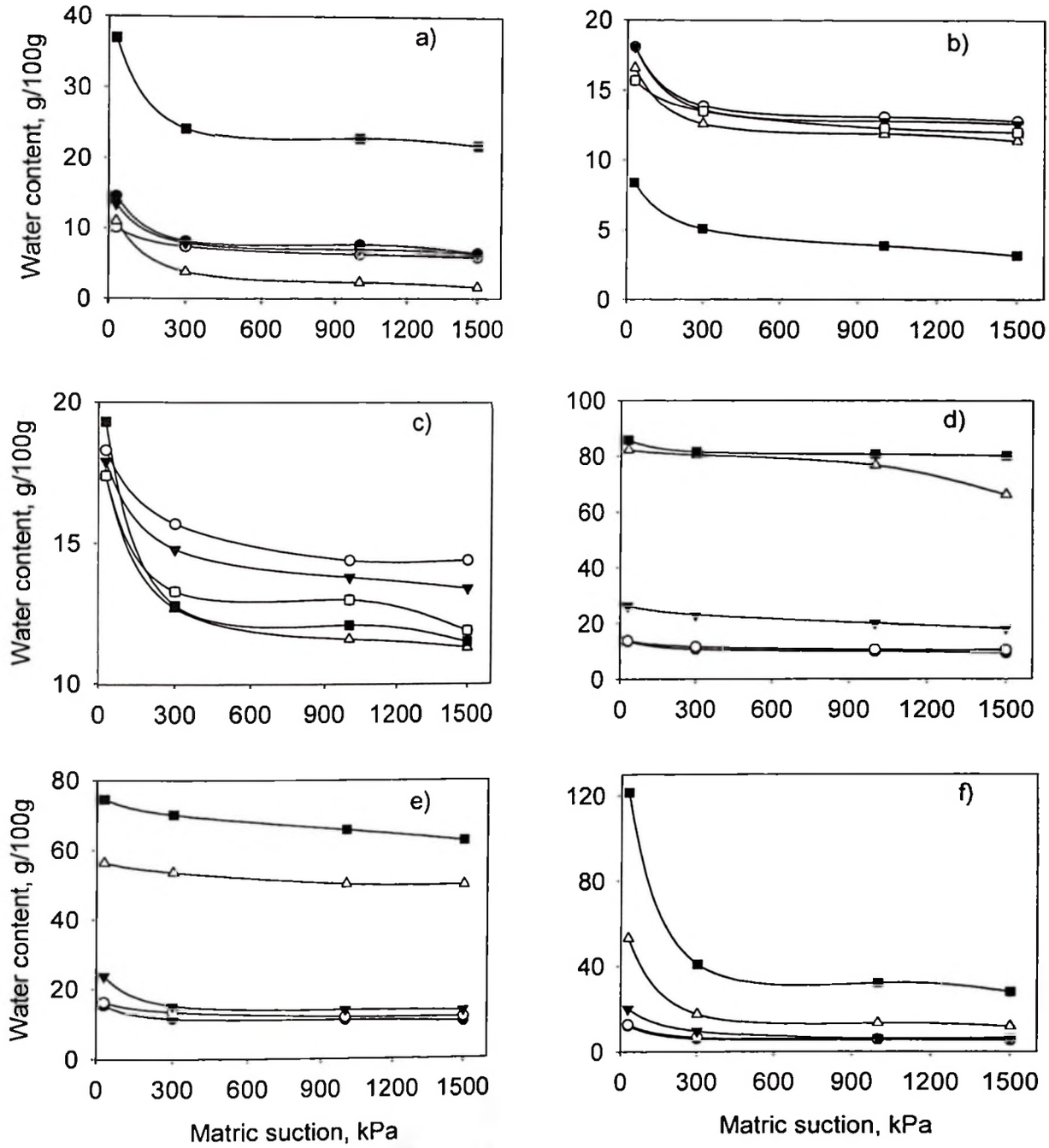

Fig.4.1. Water release characteristic curves for the studied samples: a) KL1; b) KL2; c) MS; d) MK1; e) MK2; and f) PB heated at different temperatures. Shaded squares denote the sample heated at 800 °C; open triangles heated at 600 °C; shaded triangles heated at 400 °C; open circles heated at 200 °C and shaded circles refer to unheated sample analyzed at ambient temperature of 15 °C.

In contrast to samples MK1 and MK2, sample PB showed a high potential to adsorb and release plant available water (Fig.4.1f). The ability to adsorb and release water increased with the increase in the heating temperature. Variation in response to heating could be among the sources of the observed difference between MK samples and PB. For instance, samples MK1 and MK2 disintegrated easily on heating beyond 400 °C, probably this reduced the number of large pores which can hold and release a large amount of water. Heating also indicated that samples MK1 and MK2 have more iron due to the change in colour to brown as compared to sample PB which appeared silvery yellow. The observation is in agreement with ICP-MS and EMPA data obtained in Chapter 3.

In general, when considering all samples together, it shows that heating increased the ability of vermiculites to retain plant available water (Table 4.1). This increase is probably due to the increase in pore size caused by the expansion on heating (Marcos *et al.*, 2009). Expansion leads to the formation of pores to accommodate water pressure associated with the release of interlayer and hydroxyl waters. Excess water pressure is probably suddenly released as pointed out by Walker (1956) through cracks (Gordeeva *et al.*, 2002).

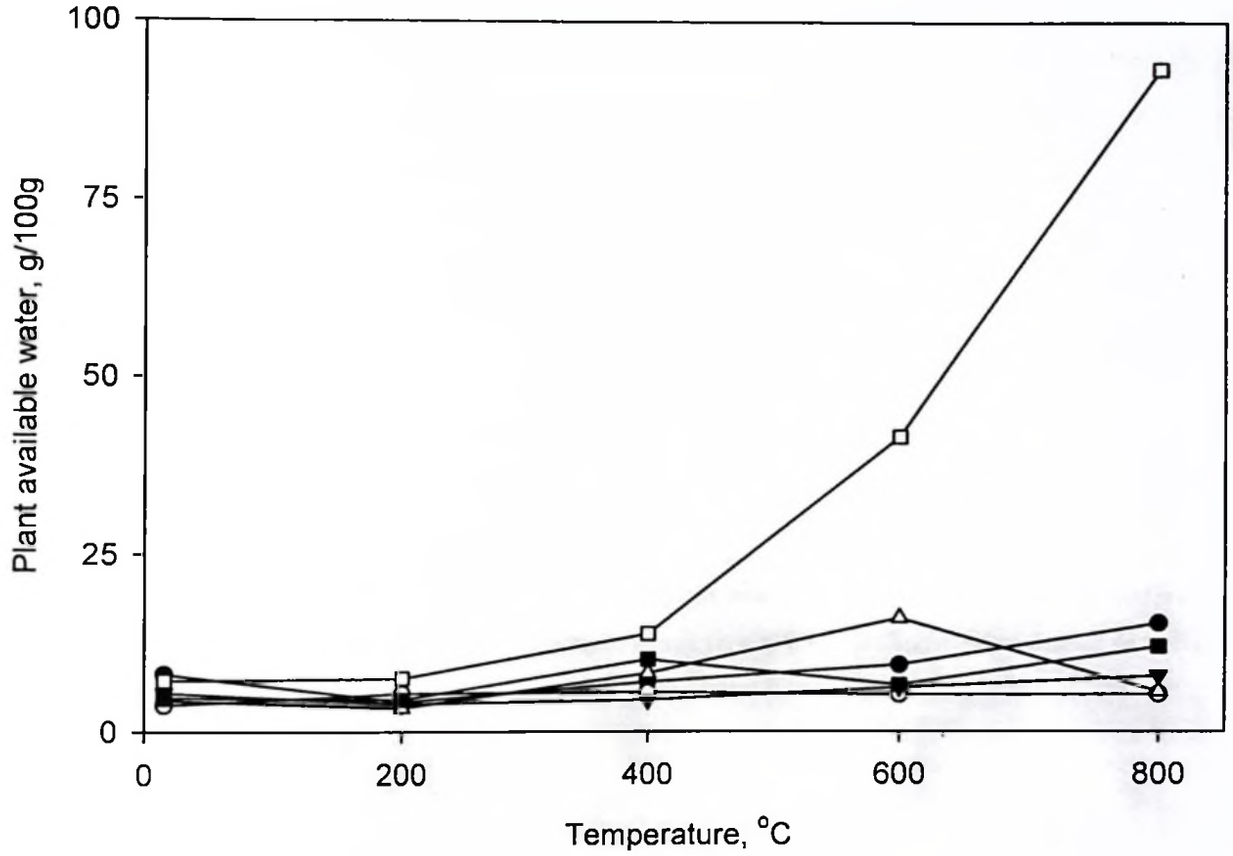

Fig.4.2. Relationship between temperature and retention of plant available water for the six samples: Open squares refer to sample PB, open triangles sample MK1, shaded circles refer to sample KL1; shaded squares sample MK2, shaded triangles sample MS, and open circles (slightly obscured) sample KL2. Each plotted value represents a mean of three replicates. Error bars omitted for clarity.

Table 4.1. Effect of heating on mass loss, bulk density, and retention of plant available water (PAW) for all six samples combined together

Temperature °C	Mass loss g/100g	Bulk density kg/m^3	PAW g/100g
15	0.0e	807a	5.6d
200	8.1d	759b	4.8d
400	11.0c	525c	8.2c
600	11.8b	437d	14.1b
800	14.4a	369e	23.2a
Standard error	0.2	3	0.4
CV, %	8.1	2.2	15.8

Means for each factor in a column followed by the same letter are not significantly different at P < 0.05 according to the Duncan's multiple-range test. CV = Coefficient of variation (a ratio of standard deviation of the data set to the mean).

Table 4.2. Mass loss, bulk density, and retention of plant available water (PAW) for the studied samples

Vermiculite	Mass loss g/100g	Bulk density kg/m^3	PAW g/100g
KL1	6.5d	658b	8.8b
KL2	12.2a	665b	5.0c
MS	11.7a	728a	5.6c
MK1	8.8c	525d	7.5b
MK2	10.5b	545c	7.6b
PB	4.7e	357e	32.7a
Standard error	0.2	3	0.5
CV, %	8.1	2.2	15.8

Means for each factor in a column followed by the same letter are not significantly different at P < 0.05 according to the Duncan's multiple-range test. CV = Coefficient of variation (a ratio of standard deviation of the data set to the mean).

From figure 4.2 and Table 4.2, it is clear that the ability of vermiculites from Tanzania to retain plant available water is significantly lower than vermiculite from Palabora. This may result from the differences in mineralogical and chemical composition (Chapter 3) as well as response to heating as mentioned earlier. Sample PB from Palabora expanded more than vermiculites from Tanzania when heated at a temperature of more than 400 °C. This expansion for sample PB corresponds to the increase in the retention of plant available water and decrease in the bulk density (Figs. 4.2 and 4.4). Low expansion and disintegration of some samples from Tanzania on heating might have affected their ability to retain plant available water.

4.3.2 Mass loss and bulk density

Heating of vermiculites increased the mass loss and decreased the bulk density (Table 4.1; Figs.4.3 and 4.4). The mass loss on heating is attributed to the loss of interlayer water and high-temperature hydroxyl water. Previous studies have shown that the interlayer water is lost when heating at a temperature lower than 550 °C, while dehydroxylation starts at 500 °C and continues up to 850 °C (Barshad, 1950; Walker, 1951). Heating also facilitates the oxidation of iron in vermiculite and micas (Tripathi *et al.*, 1978). Oxidation of iron leads to re-orientation of octahedral hydroxyl ions in order to maintain structural stability (Juo and White, 1969). Hydroxyl water is also lost in the process (Tripathi *et al.*, 1978).

Vermiculites (KL1, KL2, and MS) and hydrobiotites (PB, MK1, and MK2) differ in the extent of lost hydroxyl water when heated between 600 and 800 °C (Fig.4.3). Calculation made revealed that vermiculite samples lost more hydroxyl water (2.8-4.9 %) than hydrobiotite samples (1.5 - 1.7 %). The presence of a larger amount of potassium ions in hydrobiotites has been found to hinder the release of hydroxyl water (Marcos *et al.*, 2009). In contrast, loss of water from vermiculites is facilitated because their crystal structures are more hydrated and expanded because of having bivalent cations with a double layer of water (Tripathi *et al.*, 1978).

The samples with hydrobiotite (PB, MK1, and MK2) show a greater decrease in their bulk density than those mainly composed of vermiculite (KL2, MS, and KL1) (Fig.4.4). This finding is in agreement with previous studies which show more expansion in hydrobiotites than pure vermiculites (Justo *et al.*, 1989; Midgley and Midgley, 1960). This might be due to obstruction of water molecules from the structure by mica layers which facilitate pressure increase. Hydrobiotites show a different trend in the decrease in their bulk densities from that of vermiculite samples (Fig.4.4). The difference between vermiculites and hydrobiotites is clear when heated at a temperature above 200 °C. Among the hydrobiotites, Sample PB lost more weight on heating and registered the lowest bulk density as compared to the other samples (Table 4.2). The lower bulk density for sample PB was due to the high degree of expansion. Observation indicates that heating of hydrobiotites from Tanzania to above 600 °C does not cause significant change in their bulk densities. Also, sample PB showed no marked change in its bulk density on heating to above 400 °C.

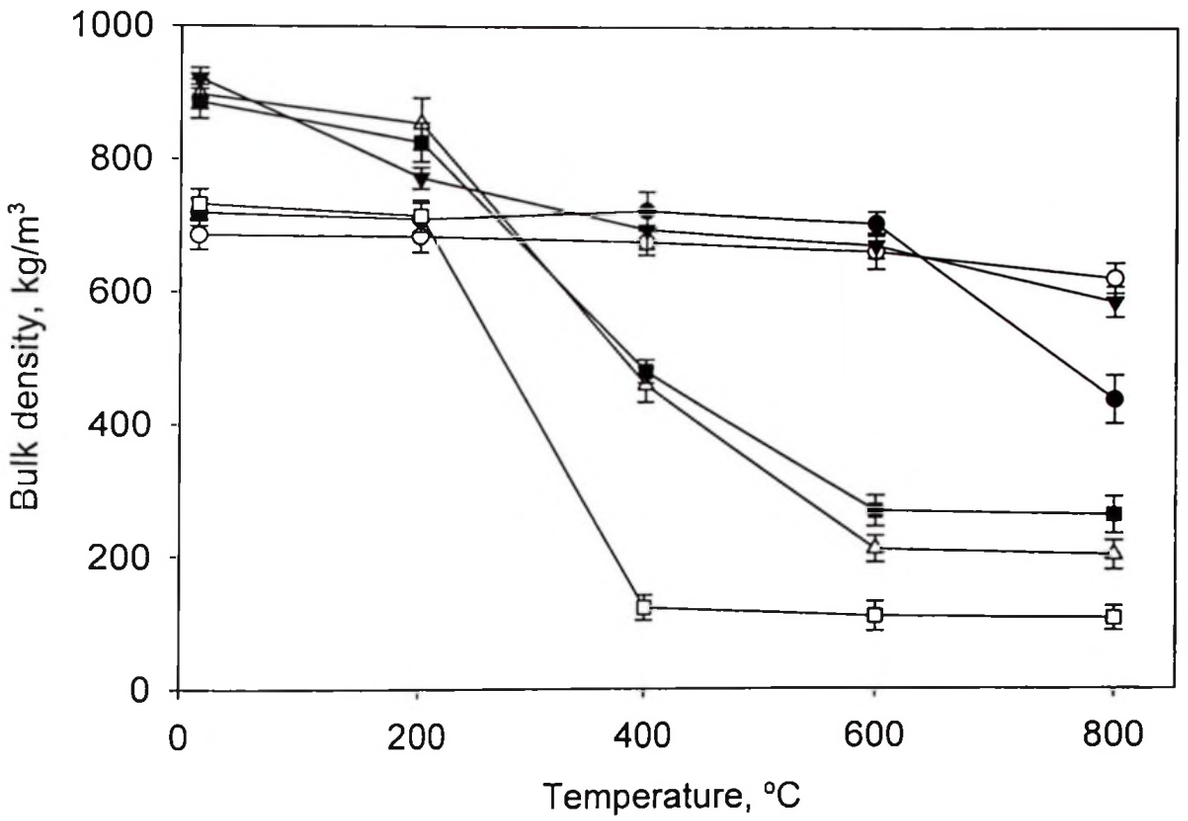

Fig.4.4. Relationship between temperature and bulk density for the six samples: Shaded circles refer to sample KL1; open circles sample KL2; shaded triangles sample MS; open triangles sample MK1; shaded squares sample MK2; and open squares sample PB. Each plotted value represents a mean of three replicates with the standard error shown by a vertical bar.

4.3.3 The pH, CEC, and exchangeable cations

Analysis of the pH of vermiculites and hydrobiotites revealed that they are all slightly alkaline (Tan, 1996). Heating to a temperature of less than 600 °C did not cause significant changes to their pH (Table 4.3 and Fig. 4.5). Heating beyond 600 °C increased significantly the pH for samples PB, KL1, and KL2. The presence of exchangeable Mg^{2+} with a high water affinity (Marcos *et al.*, 2003) might have facilitated hydrogen bonding between H^+ from water and exposed hydroxyl groups. Samples PB, KL1, and KL2 at that temperature had exchangeable Mg^{2+} of 5.3 - 11.2 $cmol_{(+)}/kg$ while for the other samples it was 0.5 - 0.7 $cmol_{(+)}/kg$ (Fig.4.8).

Kawano and Tomita (1991) have revealed that the interlayer Mg cations have an ability to adsorb water molecules rapidly as compared to the other cations due to their high hydration energy. Since heating at high temperature causes re-orientation of hydroxyl ions and hydrogen bonding is possible in clay minerals in the presence of exposed hydroxyl groups (Grim, 1953), this could be the reason for the increase in pH on heating vermiculites and hydrobiotites in the presence of Mg cations.

Thus, from this study, I can say that the increase in the pH of some vermiculites and hydrobiotite on heating at a temperature of more than 600 °C is facilitated by the presence of exchangeable Mg cations. The increase in the pH makes the exfoliated products strongly alkaline and thus, unsuitable for most crops and micro-organisms in soils (Brady and Weil, 2002). For agricultural use, it should be avoided.

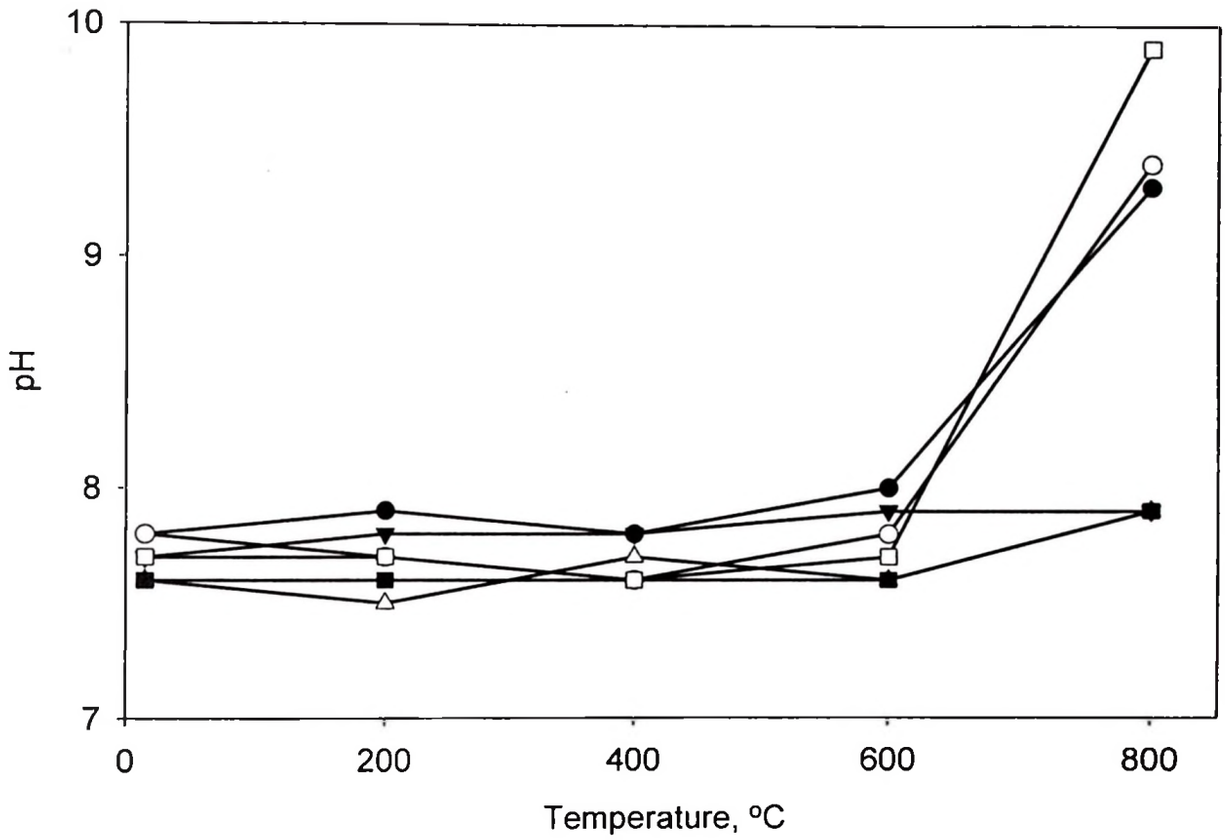

Fig.4.5. Relationship between temperature and pH for the six samples: Open squares sample PB, open circles sample KL2, shaded circles refer to sample KL1; shaded triangles sample MS; open triangles sample MK1; and shaded squares sample MK2. Each plotted value represents a mean of three replicates. Error bars omitted for clarity.

Table 4.3. Effect of heating on the pH, CEC, and exchangeable cations for all six samples combined together

Temperature °C	pH	CEC	Exchangeable cations, $cmol_{(+)}$ / kg				
		$cmol_{(+)}$/kg	Mg^{2+}	Ca^{2+}	K^+	Na^+	TEC
15	7.7b	89.7a	58.0b	14.5a	0.19c	1.14b	73.8a
200	7.7b	68.1b	61.7a	14.5a	0.20c	1.34a	77.7a
400	7.7b	70.5b	51.8c	5.3b	0.20c	1.08b	58.4b
600	7.8b	62.6c	27.3d	2.9c	0.51a	0.44c	31.2c
800	8.7a	16.7d	4.1e	3.1c	0.45b	0.07d	7.7d
Standard error	0.03	1.7	1.3	0.2	0.01	0.04	1.1
CV, %	1.7	13.8	13.1	10.8	13.2	23.0	15.1

Means for each factor in a column followed by the same letter are not significantly different at $P < 0.05$ according to the Duncan's multiple-range test. The CEC was determined by CsCl saturation method and exchangeable cations by ammonium acetate, CV = Coefficient of variation (a ratio of standard deviation of the data set to the mean) and TEC = Total exchangeable cations.

Table 4.4. The pH, CEC, and exchangeable cations for the studied samples

Vermiculite	pH	CEC	Exchangeable cations, $cmol_{(+)}$ / kg				
		$cmol_{(+)}$/kg	Mg^{2+}	Ca^{2+}	K^+	Na^+	TEC
KL1	8.1a	59.7c	23.5c	0.1f	0.04f	0.99b	24.6d
KL2	8.0a	86.6b	93.0a	7.7c	0.12d	0.42d	101.2a
MS	7.8b	102.8a	83.7b	6.8d	0.08e	1.53a	92.1b
MK1	7.7c	21.6e	12.5e	12.1b	0.53b	0.74c	25.9d
MK2	7.7c	62.9c	13.5de	15.6a	0.34c	0.52d	30.0c
PB	8.1a	35.4d	17.3d	6.0e	0.74a	0.67c	24.7d
Standard error	0.04	1.9	1.4	0.2	0.01	0.05	1.2
CV, %	1.7	13.8	13.1	10.8	13.2	23.0	15.1

Means for each factor in a column followed by the same letter are not significantly different at $P < 0.05$ according to the Duncan's multiple-range test. The CEC was determined by CsCl saturation method and exchangeable cations by ammonium acetate, CV = Coefficient of variation (a ratio of standard deviation of the data set to the mean) and TEC = Total exchangeable cations.

The CECs determined by ammonium acetate saturation method for samples KL1, KL2, MS, and MK2 after heating at temperatures less than 600 °C were relatively low (Fig. 4.6) as compared to that obtained by electron microscopy (Fig. 4.7). These are the samples found in Chapter 3 to contain more vermiculite and thus, have more exchangeable cations than hydrobiotite. The lowering of the CECs was probably caused by fixation of some of the ammonium ions during the replacement of the interlayer cations. Ammonium ions may replace the interlayer cations in vermiculite and get trapped, a phenomenon that causes underestimation of the CEC (Bain and Smith, 1994; Møberg, 2001). Similarly, during washing of the excess ammonium acetate with ethanol, it has been found that some of the adsorbed ammonium ions can be replaced by H^+ through hydrolysis or by Ca^{2+} from the dissolution of calcite, gypsum, and silicates (Rhoades, 1982). All samples except MS had traces of calcite/dolomite (Chapter 3) and thus, it is possible that dissolution occurs during washing. In this study, the ammonium acetate saturation method proved unsuitable for determining the CECs of vermiculites.

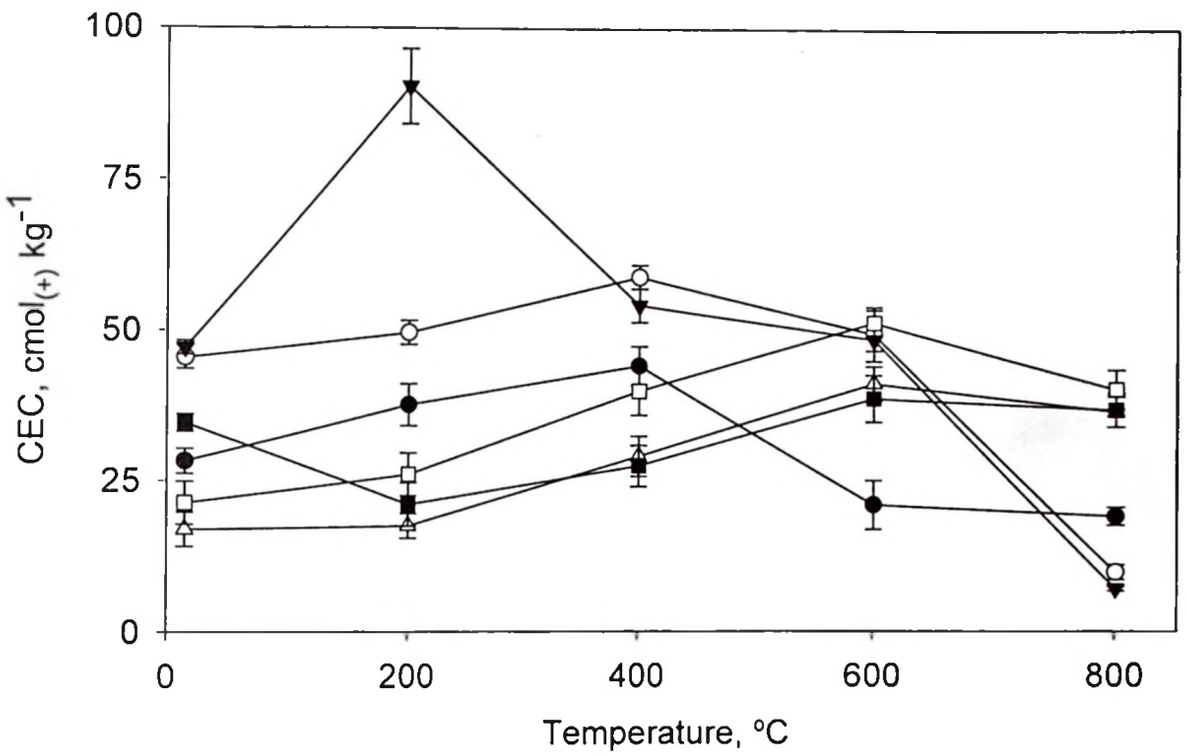

Fig.4.6. Relationship between temperature and CEC determined by ammonium acetate saturation method for the studied samples: Shaded circles refer to CEC for sample KL1; open circles for sample KL2; shaded triangles for sample MS; open triangles for sample MK1; shaded squares for sample MK2; and open squares for sample PB. Each plotted value represents a mean of three replicates with the standard error shown by a vertical bar.

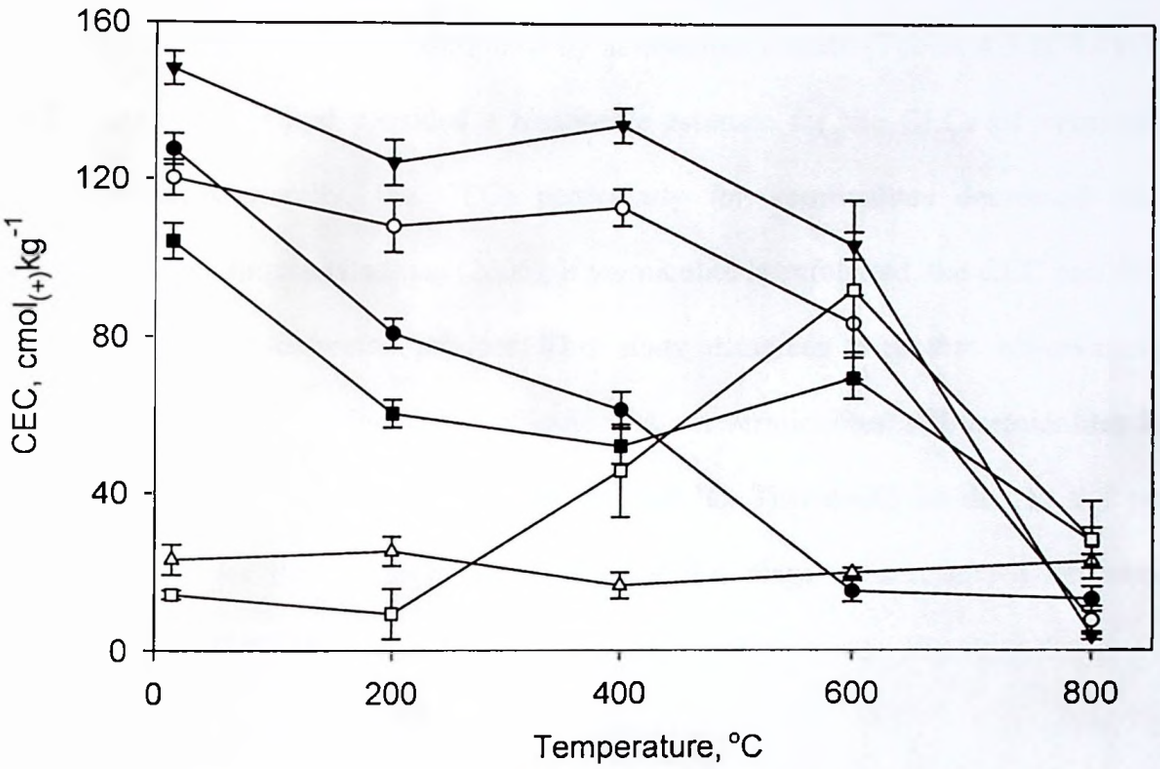

Fig.4.7. Relationship between temperature and CEC for the studied samples determined by CsCl saturation method: Shaded circles refer to the CEC for sample KL1; open circles for sample KL2; shaded triangles for sample MS; open triangles for sample MK1; shaded squares for sample MK2 and open squares for sample PB. Each plotted value represents a mean of four replicates with the standard error shown by a vertical bar.

The CECs determined by CsCl saturation method were broadly comparable to the total exchangeable cations (TEC) determined by ammonium acetate (Tables 4.3 & 4.4). Thus, the CsCl saturation method provided a reasonable estimate for the CECs of vermiculites and hydrobiotites. Generally, the CECs particularly for vermiculites decreased on heating (Fig.4.7). According to Hindman (2006), if vermiculite is exfoliated, the CEC can decrease by 5-10 % from the unheated product. This study disagrees with that observation, unless Hindman (2006) is referring to hydrobiotites but not vermiculites. All vermiculites lost more than 90 % of their CECs on heating above 600 °C. This could be due to the permanent structural changes that occur in vermiculites at this stage as a result of dehydroxylation (Marcos *et al.*, 2009; Walker, 1951).

Loss of hydroxyl ions lowers the negative charges and the ability of vermiculites to adsorb cations. The result is a sharp decrease in the CECs of vermiculites; consequently, their ability to retain nutrients in soils from leaching is also reduced. Heating vermiculites to above 600 °C for agricultural applications should preferably be avoided. Although the CECs of vermiculites decrease gradually on heating to 600 °C, the high values they posses make them suitable as a growing media with a good nutrient retention potential (Van Straaten, 2002).

The CECs of hydrobiotites are less affected on heating because of the increase in the availability of exchangeable K^+ from mica (Fig.4.8). In addition, the presence of exchangeable K^+ retards the release of hydroxyl water from hydrobiotites as mentioned earlier. It implies the lost of the negative charges is less from hydrobiotites during dehydroxylation than from vermiculites. The CECs of the samples containing hydrobiotite (MK1, MK2, and PB) showed a different pattern from those samples with no hydrobiotite in response to heating (Fig. 4.7). For, instance, sample MK1 showed no significant change in the CEC on heating from 400-800

°C; whereas samples MK2 and PB their CECs increased significantly at 600 °C followed by a decrease at 800 °C. Thus, CECs of hydrobiotites do not decrease continuously on heating like vermiculites.

Heating generally decreased the availability of exchangeable Mg^{2+}, Ca^{2+}, and Na^{+} as found in many studies involving clay minerals (Table 4.3; Fig.4.8). The decrease in the exchangeable cations on heating is probably caused by the fixation of the cations in the silicate sheet. The release of the interlayer water destabilizes the interlayer cations. Walker (1956) showed that the interlayer cations on heating could migrate into the hexagonal sites of the silicate sheet and get fixed, while Kawano and Tomita (1991) suggested that they cluster at the centre of the interlayer space and not in the hexagonal sites, because they have the same size. This study disagrees with Kawano and Tomita (1991), because heating caused the (001) basal spacings to decrease as a result of the collapse of the interlayer space (Chapter 3). According to Hofmann-Klemen (1950), the interlayer cations cannot remain without water that is holding them. The decrease in the availability of exchangeable cations is a sign of fixation. The only place where these cations can be fixed permanently is in the hexagonal vacant sites.

Most potassium ions, particularly in hydrobiotites, seem to occur in a non-exchangeable form as found in micas (Zhu *et al.*, 2008; Verburg and Baveye, 1994). Heating of hydrobiotites makes potassium ions more available. Significant increase in exchangeable K^{+} occurred when the hydrobiotite samples were heated to a temperature of more than 400 °C (Fig.4.8c). This is the temperature at which dehydroxylation and structural transformation takes place (Barshad, 1950; Walker, 1951). It implies that the changes that occur at this stage enhance the availability of exchangeable K^{+}.

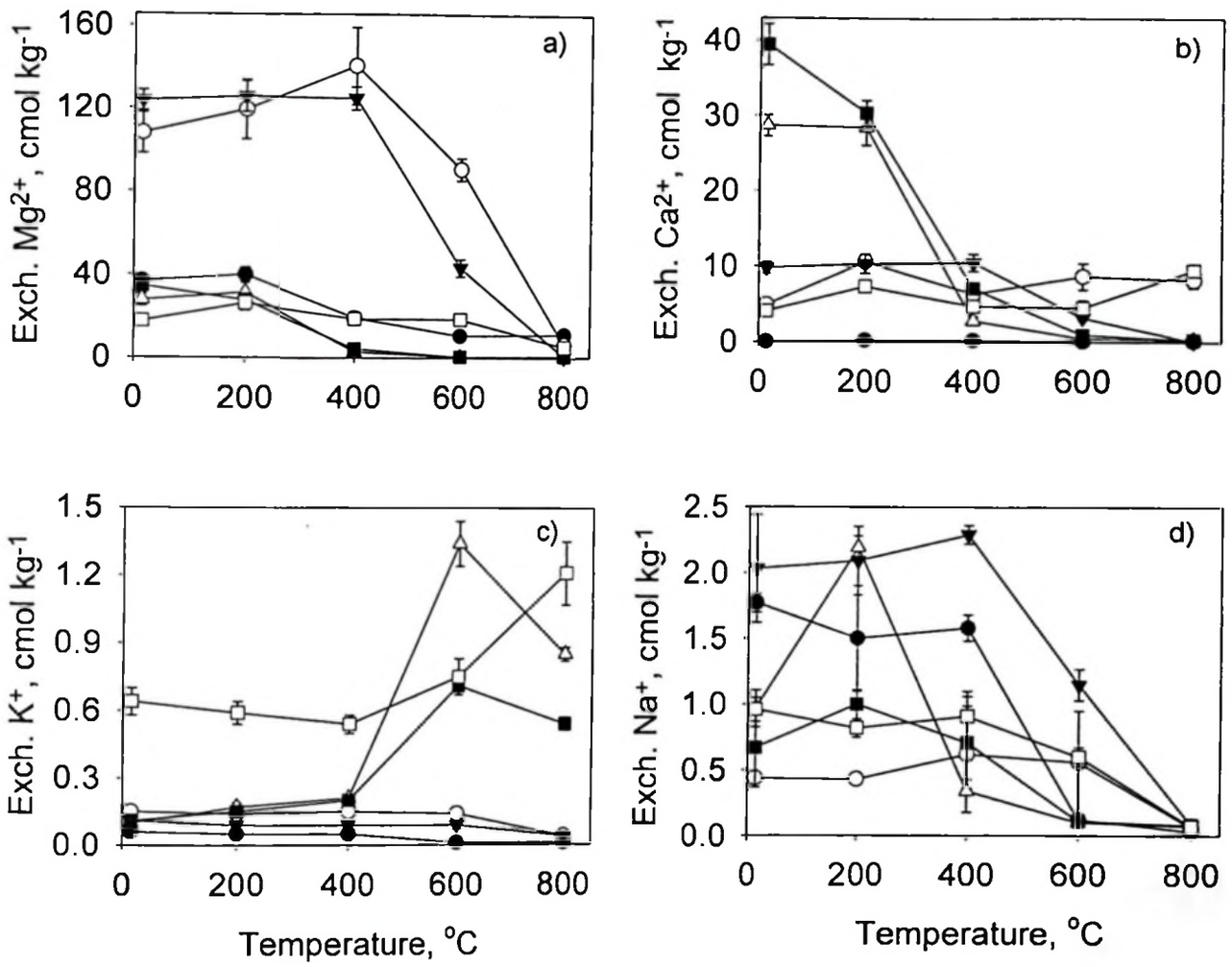

Fig.4.8. Relationship between temperature and exchangeable cations for the studied samples: a) Mg^{2+}, b) Ca^{2+}, c) K^{+}, and d) Na^{+}. Shaded circles refer to sample KL1; open circles sample KL2; shaded triangles sample MS; open triangles sample MK1; shaded squares sample MK2; and open squares sample PB. Each plotted value represents a mean of three replicates with the standard error shown by a vertical bar.

From Figure 4.8, it is clear that the conversion of interlayer K^+ into exchangeable form in hydrobiotites occurs during the dehydroxylation stage. Potassium ions are not fixed in hexagonal sites possibly because of their large ionic radii as compared to the other interlayer cations (Kawano and Tomita, 1991). Potassium ions in vermiculite samples (KL1, KL2, and MS) were not affected by heating because of their low abundance due to the absence of mica phases in these samples (Chapter 3).

The maximum available amount of exchangeable K^+ in hydrobiotites from Tanzania was obtained when heating was done at 600 °C, while that from Palabora was found to increase beyond that temperature. Walker (1951) showed that further heating leads to formation of new mineral phases that probably fix some of the potassium ions in their structure. A number of phases are formed on high temperature heating, depending on the temperature and chemical compositions of vermiculite and hydrobiotite (Stoch, 2004; Marcos *et al.*, 2009).

Analysis of the variances for the studied properties is located in appendix 4.1. Statistically, heating caused a significant effect in varying the physical and chemical properties of vermiculites and hydrobiotites as indicated by their significance levels of $P<0.001$. The mean effect of temperature at each level of heating was based on 18 observations made from the six samples. The studied vermiculites and hydrobiotites showed a significant variability ($P<0.001$) in their physical and chemical properties in regard to the heating level applied. This could be due to variation in the chemical and mineral compositions observed in Chapter 3. Thus, the observed difference in the physical and chemical properties is a contribution of the effects of heating and variations in composition of vermiculites and hydrobiotites. The interaction between temperature and the studied samples also showed a significant variation.

The CEC and exchangeable cations showed a comparable coefficient of variation with the exception of the exchangeable Na^+, which was slightly higher. Other properties showed relatively small coefficients of variation but differ from one another. A high coefficient of variation in exchangeable Na^+ was contributed by a relative high standard deviation. Coefficient of variation gives the precision for the dispersion of the data sets (Mahmoundvand *et al.*, 2007) and it is commonly expressed as a percentage of the standard deviation of the mean.

4.4 CONCLUSIONS

Heating of vermiculites and hydrobiotites decreases exchangeable Mg^{2+}, Ca^{2+}, and Na^+ but increases the availability of exchangeable K^+ in hydrobiotites. Exchangeable K^+ in hydrobiotites is enhanced during dehydroxylation.

The Tanzanian vermiculites have high CECs of 104 - 148 $cmol_{(+)}/kg$ and thus, they have a high potential to retain nutrients from leaching when added to soils. The CECs of hydrobiotites are lower than those of vermiculites. Vermiculites lose their CECs gradually on heating to 600 °C followed by a sharp decrease of nearly 90 % of their original CECs when heated at 800 °C. Thus, heating vermiculites beyond 600 °C for agricultural applications should be avoided. Hydrobiotites are less affected due to the increase in the availability of exchangeable K^+.

The pH of the studied vermiculites and hyrobiotites is slightly alkaline and do not significantly change on heating to 600 °C, but increases in the presence of exchangeable Mg^{2+} at 800 °C. Heating to a high temperature of more than 600 °C should be avoided as it makes the exfoliated products strongly alkaline and unsuitable for crop production.

Water release characteristic of vermiculites and hydrobiotites from Tanzania varies differently from one another in response to heating. Heating does not necessarily increase their ability to adsorb and release plant available water. Thus, initial characterization is essential when assessing unknown products as soil improvers for agricultural applications.

CHAPTER 5

EFFECT OF HEATING VERMICULITES ON EXTRACTABILITY OF PHOSPHORUS AND SOME HEAVY METALS

5.1 INTRODUCTION

The high concentrations of some heavy metals and phosphorus (P) found in some studied vermiculites (Chapter 3) initiated this study to assess their extractability. Since vermiculites are mostly used in expanded state after heating, the effect of thermal exfoliation on the extractability of the incorporated elements was also investigated in a range of samples. No specific study has so far been published on the extractability of P and heavy metals that can be potentially toxic and their response to the heating of vermiculites.

Extractable fractions of heavy metals and other trace elements in soils are operationally assessed by chemical extractions (Grimshaw, 1989). Diethylene triamine pentaacetic acid (DTPA) and acetic acid are amongst the methods used. The methods are widely used despite their limitations (O'Connor, 1988). DTPA extraction was originally developed for predicting plant available concentrations of Cu, Mn, Fe, and Zn (Lindsay and Norvell, 1978). Its use has been loosely extended to cover the assessment of extractable fractions of other trace elements in soils. The levels of DTPA extractable elements are theoretically correlated with plant uptake (Hag and Miller, 1972; Randall *et al.*, 1976) and empirically equated to the plant available fractions (Lebourg *et al.* 1996). Acetic acid extraction is used to determine acid soluble phosphate and is generally appropriate to non-calcareous soils (Grimshaw, 1989). The method was used to extract P because the samples were non-calcareous (Chapter 3).

Although the chemical extractions give a rough and quick estimation of the plant available fraction, under field conditions sometimes it is different. This is due to the fact that field conditions, such as pH and interactions of elements in the soil, can alter the availability and the uptake by plants (Pasquini, 2006). Similarly, the acquisition of the elements by plants in the soil is variable and complex (Hinsinger, 2001).

5.2 MATERIALS AND METHODS

5.2.1 Sample preparation and analysis

The same vermiculites, five from Tanzania and one from the Palabora Europe Ltd, were used. The samples were heated at 15, 200, 400, 600, and 800 °C in a muffle furnace. After heating, the samples were ground by hand and sieved to collect the less than 2 mm fraction. A full factorial design, incorporating 6 vermiculites and 5 levels of heating temperature, was used. Each treatment was replicated 3 times, giving a total of 90 sub-samples.

DTPA extractable Zn, Cr, Fe, Mn, and Ni were determined according to the method of Lindsay and Norvell (1978), whilst the extractable P was assessed using that of Grimshaw (1989). Zinc, Ni, Cr, Mn, and Fe in the extract were measured by flame atomic absorption spectrometry (Perkin Elmer-Aanalyst 100). Extractable P was determined using flow injection colorimetric analysis (FIAstar 5010). The reagents used were all analytical grade.

5.2.2 Data analysis

The data obtained were subjected to analysis of variance and means were compared by the Duncan's multiple-range test using the MSTAT-C software (Freed *et al.*, 1991).

5.3 RESULTS AND DISCUSSION

5.3.1 Extractable P

The results show that high levels of acetic acid extractable P were found in samples MK1, MK2, and PB (Table 5.1). The maximum extractable amounts in samples MK2 and PB were obtained on heating at 200 °C, while in MK1 it was at 400 °C (Fig.5.1). The extractable P in vermiculite samples with no hydrobiotite (KL1, KL2, and MS) were quite low (Table 5.1) and did not show marked changes due to heating (Table 5.2; Fig.5.1). The high extractable P in samples MK1, MK2, and PB was attributed to the presence of apatite and monazite which were absent in samples KL1, KL2, and MS (Chapter 3). A low heating temperature of less than 600 °C seems to facilitate the extractability of P from apatite and monazite. This is an indication that vermiculite is not hindering its release from apatite and monazite and could be a potential source of P when these vermiculites are applied to the soil as growing medium.

Extractability of P from apatite has also been observed by Wallander (2000), but not from apatite which is hosted by vermiculite. A number of studies have found an increase in extractable inorganic P on low temperature heating or drying of soils (Kwari and Batey, 1991; Grava *et al.*, 1961; Serrasolsas and Khanna, 1995). The increase, according to Serrasolsas and Khanna (1995), could probably be due to solubilisation of a readily extractable fraction of the total P. In those studies, however, no mention is given on the source or mode of occurrence of the P in the heated or dried soils.

Table 5.1. Extractable P, Fe, Mn, Zn, Cr and Ni from the studied samples

Sample	Extractable amount, mg/kg					
	P	Fe	Mn	Zn	Cr	Ni
KL1	0.2d	2.7d	1.1e	0.4c	0.7c	0.8a
KL2	2.1d	1.6e	2.4d	0.9a	0.6c	0.8a
MS	1.7d	5.3b	2.6c	0.5b	0.6c	0.3c
MK1	199.8a	5.1b	2.5cd	0.1e	3.3a	0.4b
MK2	135.1b	8.5a	3.4b	0.6b	2.9b	0.5b
PB	50.2c	3.5c	5.8a	0.3d	0.4c	0.1d
Standard error	5.2	0.2	0.1	0.03	0.1	0.04
CV, %	30.9	17.8	9.4	26.3	24.1	30.3

Means in a column followed by the same letter are not significantly different at P<0.05 according to the Duncan's multiple-range test. CV = Coefficient of variation (a ratio of standard deviation of the data set to the mean).

Table 5.2. Effect of heating on extractable P, Fe, Mn, Zn, Cr, and Ni from the studied samples all combined together except for P

Temperature	Extractable amount, mg/kg						
°C	$P_{(i)}$	$P_{(ii)}$	Fe	Mn	Zn	Cr	Ni
15	1.9a	166.5b	1.6d	1.5c	0.5b	0.2d	0.1c
200	1.1b	183.8a	4.4b	0.9d	0.1d	0.7c	0.4b
400	1.7a	172.4b	9.7a	4.8b	0.5b	2.5b	0.8a
600	2.1a	62.6c	4.4b	7.2a	1.1a	3.2a	0.7a
800	1.4b	56.5c	2.2c	0.4e	0.2c	0.6c	0.4b
Standard error	0.1	4.5	0.2	0.1	0.03	0.1	0.04
CV, %	10.5	27.6	17.8	9.4	26.3	24.1	30.3

Means in a column followed by the same letter are not significantly different at P<0.05 according to the Duncan's multiple-range test. $P_{(i)}$ represents the overall response to increase in temperature on extractable P from samples with no apatite and monazite (KL1, KL2 and MS) whilst $P_{(ii)}$ denotes extractable P from samples with apatite and monazite (MK1, MK2 and PB). CV = Coefficient of variation (a ratio of standard deviation of the data set to the mean).

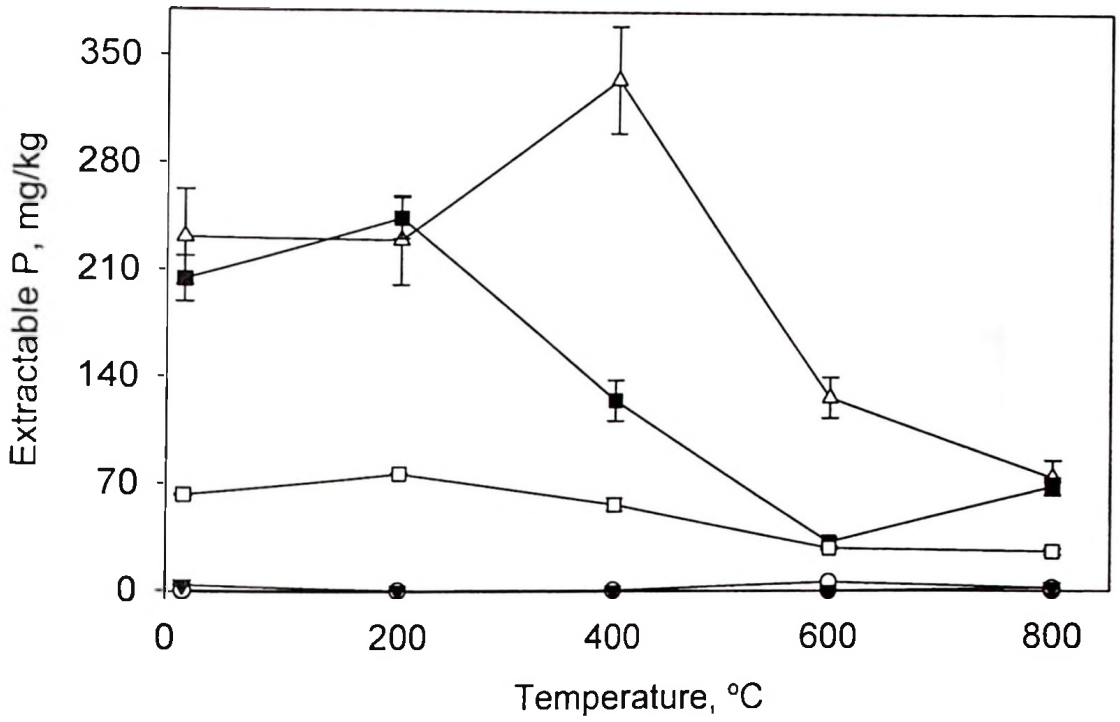

Fig.5.1. Relationship between temperature and acetic acid extractable P for the studied samples. Open triangles refer to sample MK1; shaded squares sample MK2; and open squares sample PB. Extractable P in samples KL1, KL2, and MS are between 0.1 and 6 mg P/kg and plot approximately at the same positions. The shaded triangles represent sample MS; open circles sample KL2 and shaded circles which are completely obscured by shaded triangles refer to sample KL1. Each plotted value represents a mean of three replicates with the standard error shown by a vertical bar.

This study has also found that extractable P is significantly reduced by heating vermiculite to a temperature of more than 400 °C (Table 5.2 and Fig.5.1). Grim (1953) has reported that phosphate ions can replace OH ions by an exchange reaction in clay minerals. In addition, the phosphate ions can be fixed on the edges of the silica tetrahedral sheet because they have the same size and geometry. If that is true, it implies that the phosphate ions are strongly held after replacement of OH and fixation. Observations made by Grim (1953) were followed up by assessing the variation of P in the chemical composition of vermiculites on heating at 15, 200, 400, 600, and 800 °C using EPMA. Major and minor oxides including P were determined in all six samples, but no P was observed in the composition of the heated samples. It was concluded that the phosphates are neither replacing OH ions in vermiculites nor attached on the edge of silica tetrahedral sheet as a result of heating.

Heating at 600 °C and above probably mobilizes phosphate ions and other components of accessory minerals which are in vermiculites to form insoluble compounds. This could be possible because a number of studies have observed formation of new mineral phases in vermiculite on high temperature heating (Stoch, 2004; Walker, 1951). New mineral phases are formed as a result of metamorphic reaction that occurs in association with the loss of structural water and hydroxyl ions (Marcos *et al.*, 2009). Formation of new minerals is a sign of rearrangement of elements in vermiculites. In this process probably phosphate ions are strongly held and made insoluble.

5.3.2 DTPA extractable heavy metals

The DTPA results indicated that extractable Cr, Ni, Mn, Fe, and Zn differ significantly among the studied samples (Table 5.1). The difference reflects the variation in the total concentrations and possibly the difference in the mode of occurrence of individual elements in the samples. Some elements are in vermiculite structures, whilst others are components of the accessory minerals. For instance, EPMA in Chapter 3 showed a substantial amount of Cr, Mn, and Fe in their octahedral sheets. Some of the Fe could be from hematite or iron oxides, accessory minerals identified by XRD and SEM fitted with EDS. Similarly, a number of Mn-rich grains were also identified by SEM and EDS in some samples (Chapter 3).

Although the total concentrations of Cr, Ni, Zn, Mn, and Fe in unheated vermiculites from Tanzania and the Palabora Europe Ltd were relatively high (Chapter 3), the study has found that their DTPA extractable fractions are very low (Table 5.1). In contrast to the unheated samples, heating at 400 and 600 °C significantly increased extractable fractions (Table 5.2 and Fig.5.2a-e). This increase occurred at the temperature range where most of them start to lose hydroxyl ions and begin to undergo structural transformation (Walker and Cole, 1957; Mosser-Ruck *et al.*, 2003). It probably means that the structures of vermiculites are becoming unstable at this stage. The changes that occur during this transition phase could possibly make the elements less strongly held in the structures and thus, increase their extractability.

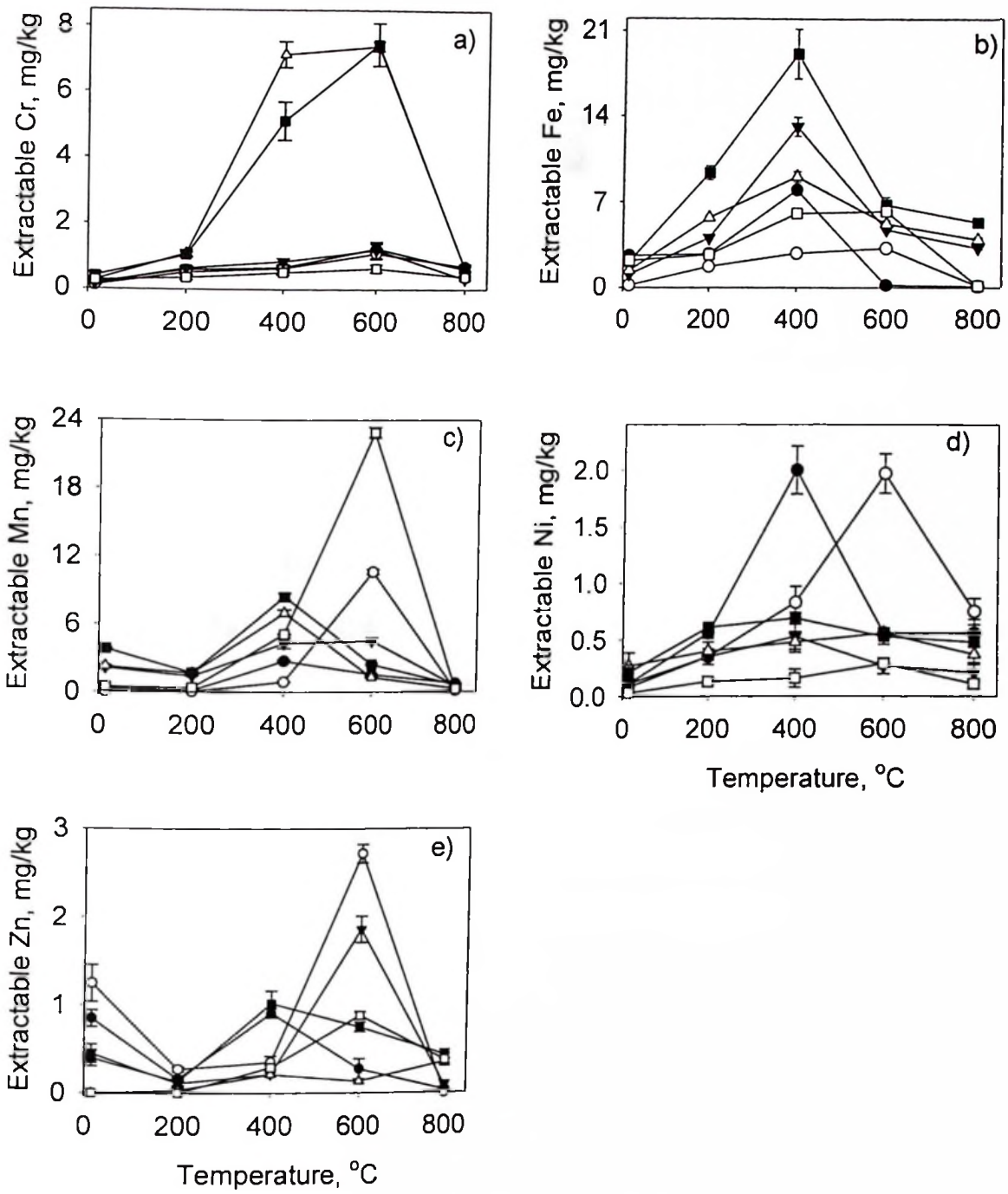

Fig.5.2. Relationships between temperature and DTPA extractable elements: a) Cr; b) Fe; c) Mn; d) Ni; and e) Zn for the studied samples. Open triangles refer to sample MK1; shaded squares sample MK2; open squares sample PB; shaded triangles sample MS; open circles sample KL2; and shaded circles sample KL1. Each plotted value represents a mean of three replicates with the standard error shown by a vertical bar.

Heating at 800 °C, however, decreased significantly the DTPA extractability of the studied elements in comparison to when heated at 400 and 600 °C (Table 5.2 and Fig.5.2a-e). At 800 °C, permanent structural change occurs in vermiculites due to dehydroxylation and new minerals start to form as mentioned earlier. Probably the elements of interest are strongly fixed in the new crystal lattice formed.

Of all the elements, the high DTPA extractable Cr from samples MK1 and MK2 at 400-600 °C is of most concern if these substrates would be used as soil amendments (Fig.5.2a). If we assume that the DTPA extractable value gives an indication of the plant available fraction (Singh *et al.*, 1998), then extractable Cr of 5.1-7.5 mg/kg for samples MK1 and MK2 is relatively high. In the available form, 1-5 mg/kg of either Cr(III) or Cr(VI) in the soil is regarded as critical for most plants (Adriano, 1986). Both Cr species are taken by plants and may cause chlorosis and necrosis depending on their availability and plant species (Skeffington *et al.*, 1976; Zou *et al.*, 2006). However, plant toxicity with Cr(VI) is stronger and occurs earlier than that caused by Cr(III) (Hauschild, 1993). In addition, Cr(VI) is mobile and soluble in water, as such it can leach easily through the soil profile and cause groundwater pollution (Sumathi *et al.*, 2005). In humans, Cr (VI) may cause cancer (Zayed and Terry, 2003). In the presence of MnO_2 which acts as a catalyst and through microbial activity, some extractable Cr(III) can also be oxidized to form highly toxic Cr(VI) (Makino *et al.*, 1998). Generally, a high extractable Cr in soils can suppress the plant uptake of some essential elements due to their structural similarity (Sharma and Pant, 1994).

DTPA extractable Ni from samples KL1 and KL2 at 400 and 600 °C respectively were significantly enhanced as compared to other samples (Fig. 5.2d). Those are the two samples found in Chapter 3 with high total Ni concentrations. Although the Ni extractable fractions for

the two samples were enhanced on heating, the values obtained were still below the frequently quoted DTPA toxicity level of 15 mg/kg extracted from soils (Papadopoulos *et al.*, 2007).

Nickel is regarded as an essential micronutrient particularly to higher plants, but the quantity required is very small (Brown *et al.*, 1987). High levels of plant available Ni in the soil could be a potential source of toxicity (Mishra and Kar, 1974; Papadopoulos *et al.*, 2007). The toxicity of Ni is enhanced when its occurrence is associated with a high Mg-Ca ratio which is common in some vermiculite and serpentines (Proctor, 1971). Thus, heating of vermiculites with high Ni and / or Cr at 400 – 600 °C should preferably be avoided when exfoliating the minerals for agricultural application. It may minimize the potential risk of enhancing the extractable fractions to the toxic levels.

Zinc, Fe, and Mn, like Ni; are essential micronutrients to plants. The DTPA extractable Zn values found for all samples were within the acceptable levels for most crops (Fig.5.2e). Deficiency of Zn is experienced when the extractable fraction is less than 0.6 mg/kg in the soil and it is regarded to be excess when it is more than 20 mg/kg (Silanpää, 1982). DTPA extractable Mn surpassed the deficiency level of 5.0 mg/kg (Silanpää, 1982) when the samples were heated between 400-600 °C. None of the samples reached the excess values of more than 140 mg/kg suggested by Silanpää, (1982). The DTPA extractable Fe increased on heating at 600 °C in all samples, but the maximum values obtained were within the acceptable levels for plants. Lindsay and Cox (1985) consider extractable Fe to be deficient in the soil when it is less than 10 mg/kg.

Deficiency of an element in a growing medium is not a big problem because it can be replenished by the use of inorganic fertilizers. The problem arises when it is in excess and it is

required to be reduced. An excess plant nutrient may interfere with the availability of other nutrients in the soil and the consequence is poor crop yield. From the studied samples, the DTPA extractable fractions of Ni, Fe, Mn, and Zn were all below the maximum allowable limits and thus, suitable for use in soils. As mentioned earlier, in field the extractable fractions found may differ from the actual plant available fractions depending on the soil properties and other site variables (Lindsay, 1972; Pasquini, 2006). Thus, validation by biotests or field trials is essential.

Analysis of the variance is documented in appendix 5.1. It shows clearly that temperature has a significant effect ($P < 0.001$) on the availability of extractable P, Cr, Ni, Mn, Fe, and Zn from the studied samples. Similarly, extractable fractions of these elements vary significantly among the studied samples. Determinations of extractable P, Cr, Fe, Ni, and Zn show a slightly high coefficient of variation of 18-31 % as compared to 9 % of Mn. Observed high coefficients of variation might have been caused by variation in the concentrations of the elements among the studied samples and mode of occurrence (Chapter 3).

5.4 CONCLUSIONS AND RECOMMENDATION

The P in vermiculites is extractable by acetic acid and its extractability increases on heating to a temperature of less than 600 °C. The P is released from apatite and monazite, which occur as accessory minerals in vermiculites. Thus, the use of the studied vermiculites as soil improvers could be a potential source of P fertilization to the soil.

Heating at 600 °C and above decreases significantly the amounts of extractable P. Probably P is made insoluble on heating at higher temperatures. None of the P is replacing the OH or attached to vermiculite structure during heating as previously thought.

The study has established that Cr, Ni, Fe, Mn, and Zn, which are high in some samples, are insignificantly DTPA extractable from the unheated samples. Extractable fractions increase only on heating at 400-600 °C, probably due to destabilization of the vermiculite crystal structure during transition to dehydroxylation. Of all the elements, the high DTPA extractable Cr from samples MK1 and MK2 at 400-600 °C is of most concern as it was above the critical levels permitted in soils for most plants. Other elements were within the acceptable limit. As a follow-up, field trials are recommended to validate these results.

CHAPTER 6

MAIZE RESPONSE TO SOIL AMENDED WITH VERMICULITE UNDER TROPICAL TANZANIAN CLIMATE

6.1 INTRODUCTION

Many attempts have been made to improve the physical and chemical characteristics of the soil using synthetic and natural soil conditioners (Sabrah *et al.*, 1993; Öztürk *et al.*, 2005). However, according to Sabrah *et al.* (1993), the effectiveness of this exercise varies with the soil texture and the type of soil conditioner used. Vermiculite is among the natural soil conditioners that are used to enhance the cation exchange and water storage capacities of soils (Jayabalakrishnan, 2007). Soils with poor water retention occasionally experience water stress conditions during growing season, a condition that retards plant growth and thus, crop yield (Zeng and Brown, 2000). Studies by Sabrah *et al.* (1993) indicate that application of the soil conditioners, such as vermiculite, can enhance seed germination, plant growth, nutrient uptake, and crop yield.

Although many studies have shown that the application of vermiculite to the soils improves their properties, its performance as a soil conditioner under a tropical equatorial climate similar to that of Tanzania for crop production is not known. In addition, availability of trace elements in vermiculite to plants is not well addressed. Thus, to assess the crop response to vermiculite application and the suitability of Tanzanian vermiculite as a soil conditioner, glasshouse pot studies were carried out in Tanzania. Maize (*Zea mays L.*), a staple cereal grown and consumed in Tanzania, was selected as a test crop. Moisture retention, growth performance, nutrient uptake, and dry matter yields as well as trace elements availability to maize plants were among the parameters assessed.

6.2 MATERIALS AND METHODS

6.2.1 Vermiculite and soil descriptions

Vermiculite (MK1) from Mikese area in Tanzania (Chapter 2) was used as a soil conditioner. Other vermiculites were not studied due to time constraints and limited fund. The MK1 was selected because of its favourable pH and slightly higher water holding capacity when heated at 600 °C (Chapter 4). In addition, this vermiculite has high concentrations of Cr and Ni with a small amounts of As and Pb (Chapter 3), which could be toxic, or at least give rise to concerns regarding food contamination, depending on their bioavailability. It was, therefore, a good opportunity to assess their availability and effect on the uptake of micro- and macronutrients by maize.

Vermiculite was excavated from 2-2.5 m depth and air-dried in a glasshouse at the Sokoine University of Agriculture in Tanzania to a constant weight. Half of the sample was expanded for 1h at 600 °C at the SEAMIC Laboratories in Tanzania. Thereafter, both the unheated (raw) and heated (expanded) vermiculites were ground by hand to avoid structural degradation (Balek *et al.*, 2007) and sieved through an 8 mm sieve before mixing thoroughly with sandy soil substrate.

The sandy soil was sampled from 0-20 cm depth, air-dried to a constant weight, and similarly sieved through an 8 mm sieve (Fageria, 2005). The initial properties of the sandy soil used, as determined by laboratory methods of Møberg (2001) and Okalebo *et al.* (2002), are summarized in Table 6.1. Analysis of the soil properties was carried out in Tanzania. Bray – I was used to determine extractable P because it is an ideal method recommended for soils with pH (water) of less 6.5 (Møberg, 2001). The soil used was slightly acidic with a pH of 6.24. It was amended with varying amounts of vermiculite having a pH of 7.6. The pH of the

soil/vermiculite mix made was therefore within the recommended range of 6-7 for maize production (Purseglove, 1988). However, the essential plant nutrients were low to very low (Table 6.1). Hence, addition of supplementary inorganic fertilizers was essential.

Table 6.1. Initial physical and chemical properties of the soil used in pot experiments. Values for the soil parameters are indicated with their standard errors (n=3), where missing it implies the standard error was negligible.

Soil parameter	Value	Rating	Reference to the rating
Soil pH (water)	6.24±0.01	Slightly acidic	Tan, 1996
Soil pH ($CaCl_2$)	5.11±0.01		
Organic carbon (%)	0.21±0.05	Low	Landon, 1991
Total N (%)	0.02±0.01	Very low	Defoer *et al.*, 2000
Bray-1 P (mg/kg)	3.7	Low	Defoer *et al.*, 2000
CEC ($cmol_{(+)}$/kg)	6.67±0.31	Low	Landon, 1991
Exchangeable Ca ($cmol_{(+)}$/kg)	0.54±0.05	Low	Landon, 1991
Exchangeable Mg ($cmol_{(+)}$/kg)	0.13±0.03	Low	Landon, 1991
Exchangeable Na ($cmol_{(+)}$/kg)	0.04±0.03	Low	Landon, 1991
Exchangeable K ($cmol_{(+)}$/kg)	0.05	Low	Defoer *et al.*, 2000
Exchangeable Al ($cmol_{(+)}$/kg)	0.00		
Exchangeable H ($cmol_{(+)}$/kg)	0.05		
DTPA-Extractable Cu (mg/kg)	0.07±0.02	Deficient	Lindsay and Norvel, 1978
DTPA-Extractable Zn (mg/kg)	0.10±0.03	Deficient	Lindsay and Norvel, 1978
Hot water soluble B (mg/kg)	0.36±0.04	Medium	Golov and Bakhova, 1996
Total acidity ($cmol_{(+)}$/kg)	0.05		
Sand (%)	93		
Silt (%)	2		
Clay (%)	5		
Textural class		Sand	

6.2.2 Glasshouse pot experiments

The soil was mixed with 0, 10, 20, 30, 40, and 50 % v/v of raw vermiculite and pre-heated vermiculite at 600 °C. Total treatments were 12 and each one was replicated 4 times. Water holding capacity was determined with the aid of a pressure plate at 30 kPa (field capacity) and 1500 kPa (permanent wilting) prior to the start of the pot experiments. The difference in the water contents at these suction pressures provided the amount of plant-available water a medium can hold during irrigation.

Six kg of soil/vermiculite mix was packed into perforated plastic pots and watered at 100 % field capacity for three days. Watering was then stopped and the soil/vermiculite mix allowed to dry to the wilting point while weighed daily in the morning for the whole period. The aim of this exercise was to determine the retention period of the plant-available water in the soil amended with vermiculite over the control.

Another set of experiments was conducted by growing maize using a similar amount of soil amended with vermiculite. Triple super phosphate (TSP) (160 mg P / kg) and sulphate of potash (200 mg K /kg) were added to the soil/vermiculite mix in accordance with the local fertilization practise. The TSP was ground before application. It should, however, be noted that the pot experiments were conducted before knowing the extractability of P from apatite and monazite in MK1, that is why the normal rate of P was used. Basal applications of the plant nutrients Zn, Cu, B, and Mg were also applied to eliminate deficiencies noted during soil analysis (Table 6.1). The amounts applied were respectively 10 mg Zn/ kg soil, 10 mg Cu / kg soil, 2 mg B / kg soil and 50 mg Mg / kg soil. The fertilizers were thoroughly mixed with the soil by hand prior to the packing into the pots. Nitrogen as sulphate of ammonia (240 mg N /

kg soil) was applied later in split form. The first application as a starter was applied a week after emergence of the maize seedlings and the second application was done three weeks later.

Six maize seeds (variety *TMV-1*) were sown in each pot after saturating the soil at 100 % field capacity (Fageria, 2005). The seedlings were thinned to two per pot one week after emergence. Because of high evaporation rate, watering was done once per day in the morning at 100 % field capacity in order to optimize the availability of trace elements from the added vermiculite. Maize growth performance was monitored by measuring plant heights after every two weeks. In addition, the pots were randomized twice a week to eliminate solar effect (Fageria, 2005). The temperature and humidity in the glasshouse were not controlled and thus depended on the outside weather conditions.

Maize was harvested 8 weeks after emergence of the seedlings because it attained the maximum height that can be accommodated in the glasshouse. Maize was harvested by cutting the stems at 2 cm above the soil surface and washed thoroughly. The soil with the maize stumps was soaked for 10 minutes in a 20-litre container filled with water to loosen the soil. After loosen the soil, the stumps with the roots were gently pulled out and washed several times by spraying water. The maize shoots and roots were oven-dried at 70 ^{o}C and ground to pass through a 0.5 mm for laboratory analyses. The analyses of the dry matter were carried out at the University of Aberdeen, Department of Plant and Soil Science. The sulphuric acid-hydrogen peroxide wet digest method (Allen, 1989) was used for the extraction of N, P, K, Ca, and Mg from the dry matter. Atomic absorption spectrometry (Perkin Elmer-Aanalyst 100) was used to determine K, Ca, and Mg; whilst N and P were measured colorimetrically by continuous and injection flow analyses respectively. The Cr, Ni, As and Pb in the maize dry matter were measured by ICP-MS (Agilent Technologies 7500) after microwave digestion

using nitric acid-hydrogen peroxide. Certified reference rice flour (CRM 1568a) from the National Institute of Standards and Technology, USA, internal standard (indium), elemental spikes, and blanks were incorporated as a quality measure.

In addition, a total of 120 samples of maize shoots, maize grains, and soils were collected from 40 farms randomly selected in 8 districts in Tanzania. The objective was to get an idea of the levels of Cr, As, Pb, and Ni in maize and soils from Tanzania as references to the pot experiments. Sampling involved taking maize shoots, maize grains, and soils from three different sites in each farm at approximately 50 m apart. At each sample location, shoot and grain samples were taken from a single maize plant followed by taking 30 g of soil from 0-30 cm depth. The soil was air-dried and sieved through a 2 mm sieve for laboratory analysis. The maize shoots and grains were oven-dried at 70 °C to a constant weight and ground to pass through a 0.5 mm sieve for analysis. Microwave digestion with nitric acid-hydrogen peroxide was used to extract Cr, As, Pb, and Ni from the maize shoots and flour. The soil samples were block - digested using the same reagents as normally done at the University of Aberdeen, Department of Plant and Soil Science. Analyses of the extracts were carried out by the ICP-MS (Agilent Technologies 7500). Sub-samples of certified reference soil (ZC 73007) from the China National Analysis Centre for Iron and Steel were incorporated in the analysis of the soil samples as quality measure. Elemental spikes, blanks, and indium were also included.

6.2.3 Experimental design and data analysis

The pot experiments were conducted in a randomized complete factorial design comprising 2 main factors. The main factors were raw vermiculite and expanded vermiculite (pre-heated at 600 °C) and amounts of vermiculite (0, 10, 20, 30, 40 and 50 % v/v) added to the soil. The combination of the two factors gave 12 treatments, which were replicated 4 times as

mentioned above. Analysis of variance was done using the MSTAT-C software (Freed *et al.*, 1991) to determine the effects of the treatments on retention of plant-available water, maize growth height, dry matter yield, and uptake of plant nutrients and trace elements. Means were compared by the Duncan's multiple-range test at 5% level of significance.

6.3 RESULTS AND DISCUSSION

6.3.1 Water retention

It was found that the ability of the sandy soil to retain plant-available water was enhanced by the addition of vermiculite (Fig. 6.1). The retention period significantly increased with the increase in the added amount of vermiculite. Both expanded and raw vermiculites showed the capacity to enhance retention of plant-available water in the soil. However, soil amended with expanded vermiculite retained more plant-available water and for a longer period than soil mixed with unheated vermiculite. For instance, the application of 50 % v/v of expanded vermiculite increased the retention period by nearly 3-fold as compared to the control, whereas for the unheated vermiculite, the increase was about 1.5-fold. The ability of the expanded vermiculite to store more water and for a longer period might be due to the possession of more pore volume caused by heating at 600 °C. Pore volume in vermiculite is increased on heating (Marcos *et al.*, 2009).

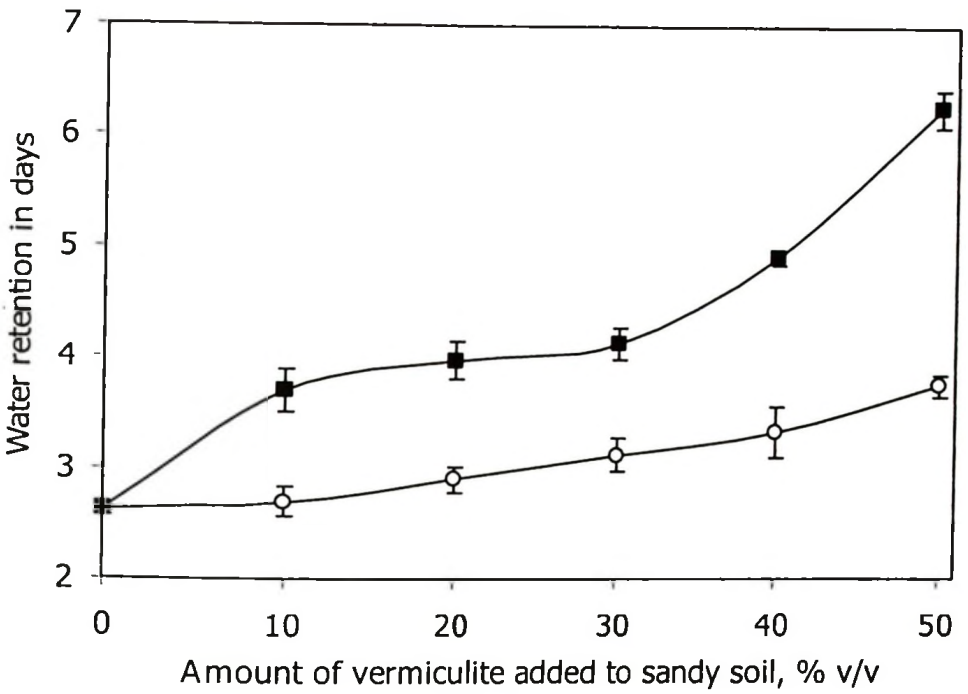

Fig.6.1. Retention of plant-available water in a sandy soil as influenced by the application of raw and expanded vermiculites: Shaded squares represent soil amended with expanded vermiculite, whilst open circles refer to soil added unheated vermiculite. Vertical lines are standard errors (n=4).

6.3.2 Maize growth performance

Application of vermiculite significantly enhanced maize vegetative growth and dry matter yield as compared to the control (Plate 6.1; Tables 6.2 and 6.3). This increase might have been brought about by the improvement in soil moisture retention and probably availability of plant nutrients as it will be seen later. This is possible because vermiculite is capable of improving soil properties and response to fertilization as pointed by Jacobs *et al.* (2003) and Jayabalakrishnan (2007). Both growth heights and dry matter yield increased with the increase in the added amount of vermiculite (Appendices 6.1 and 6.2).

Plate 6.1. Maize growth performances, three weeks after emergence of the seedlings.

Note: exp. = Expanded and verm. = Vermiculite.

Table 6.2. Maize growth height as influenced by the application of vermiculite.

Treatment	Growth height, cm			
	2WAE	4WAE	6WAE	8WAE
Soil without vermiculite (Control)	34.6d	65.0e	73.6f	79.1h
Soil with10% raw vermiculite.	36.5cd	86.3cd	137.8b	157.4cd
Soil with 20% raw vermiculite	36.2cd	86.3cd	144.8ab	166.6b
Soil with 30% raw vermiculite	36.5cd	87.3c	141.1b	152.0d
Soil with 40% raw vermiculite	36.6cd	88.5bc	139.9b	160.6bc
Soil with 50% raw vermiculite	37.8c	94.4b	138.9b	152.5d
Soil with 10% expanded vermiculite	41.1bc	80.4d	93.5e	97.6g
Soil with 20% expanded vermiculite	41.5bc	86.6cd	103.4d	111.5f
Soil with 30% expanded vermiculite	45.4ab	94.9b	128.6c	138.6e
Soil with 40% expanded vermiculite	46.1ab	102.9a	144.8ab	167.8ab
Soil with 50% expanded vermiculite	48.7a	106.0a	149.0a	174.5a
Standard error	1.7	2.1	2.3	2.5
Coefficient of variation (%)	8.5	4.9	3.8	3.7

Means in a column followed by the same letter(s) are not significantly different at P<0.05 according to the Duncan's multiple - range test. WAE = Weeks after emergence of the maize seedlings. Coefficient variation is a ratio of standard deviation of the data set to the mean.

Table 6.3. Maize dry matter yield harvested 8 weeks after emergence of the seedlings

Treatment	8 WAE			Root/Shoot
	Total DM	Root	Shoot	ratio
Soil without vermiculite (Control)	20.4i	6.9f	13.5h	0.51a
Soil with10% raw vermiculite.	78.0e	17.1cd	60.9d	0.28de
Soil with 20% raw vermiculite	86.7cd	17.9c	68.8bc	0.26ef
Soil with 30% raw vermiculite	90.2bc	22.7a	67.5bc	0.34c
Soil with 40% raw vermiculite	95.7b	23.6a	72.0b	0.33c
Soil with 50% raw vermiculite	92.8bc	23.4a	69.4bc	0.34c
Soil with 10% expanded vermiculite	30.0h	8.9f	21.2g	0.42b
Soil with 20% expanded vermiculite	38.2g	9.0f	29.2f	0.31cd
Soil with 30% expanded vermiculite	65.7f	11.7e	54.0e	0.21f
Soil with 40% expanded vermiculite	81.7de	15.6d	66.1c	0.23ef
Soil with 50% expanded vermiculite	106.9a	20.5b	86.4a	0.24ef
Standard error	2.1	0.8	1.7	0.02
Coefficient of variation (%)	6.4	10.0	6.6	9.2

Means in a column followed by the same letter(s) are not significantly different at P<0.05 according to the Duncan's multiple - range test. DM = Dry matter. Coefficient of variation is a ratio of standard deviation of the data set to the mean.

The overall maize vegetative growth in the first 4 weeks after emergence of the seedlings was more on soil-added, expanded vermiculite than on soil mixed with raw vermiculite (Appendix 6.1). The trend changed at 6 and 8 weeks, where more growth occurred in maize grown on soil mixed with raw vermiculite than that with added, expanded vermiculite. The actual reason for this change is unknown. The change contributed to the overall increase in the total maize dry matter yield grown on soil with added raw vermiculite over that grown on soil with expanded vermiculite (Appendix 6.2).

It is clear from this study that increase in the amount of raw vermiculite added to the soil made less difference in maize vegetative growth and dry matter yield as compared to expanded vermiculite (Tables 6.2 and 6.3). Furthermore, vegetative growth 8 weeks after emergence of the seedling and dry matter yield from soil with 10-30 % expanded vermiculite were less than those from soil with 10 % raw vermiculite. It implies that in the presence of less vermiculite, maize grows better on soil with raw vermiculite than expanded vermiculite.

The root/shoot ratio was generally high in maize grown on soil with no vermiculite as compared to soil with added vermiculite (Table 6.3). The amount of water retained by the sandy soil with no vermiculite was relatively small and it was easily lost by evapotranspiration. This was caused by the high temperature in the glasshouse 27-42 °C; average 34 °C with an average relative humidity of 67 %. Loss of water on a daily basis might have created temporary water stress conditions to the maize plants, a state that contributes to a higher root to shoot ratio (Kaya *et al.*, 2006). Under water stress, roots tend to penetrate deeper to search for water, leading to a greater root distribution (Jacobs *et al.*, 2003). This could also be the reason for a low dry matter yield as a result of reduced growth. A similar trend was observed in maize grown on soil with small amounts of expanded vermiculite (Table 6.3).

6.3.3 Uptake and concentrations of plant nutrients

The overall uptake, particularly for N, K, and Ca in the shoot dry matter, increased significantly with the increase in the amount of vermiculite added to the sandy soil (Table 6.4). Increase in shoot growth by the application of vermiculite might have increased the demand for more nutrients from the soil to the shoot. Uptake is driven by the nutrient availability in soils and plant growth (Gastal and Lemaire, 2002). The nutrient uptake by plants and hence, the content in dry matter is a measure of their bioavailability in the soil. This is a clear indication that vermiculite in the soil enhanced the availability of plant nutrients and, thus, the uptake by maize plant over the control. The overall uptake of P and Mg did not show much difference with the increase in the amount of added vermiculite but their uptake was significantly higher than the control.

The overall uptake of N, P and K was significantly higher in maize grown on soil with expanded vermiculite than on soil mixed with raw vermiculite (Table 6.4). The uptake increased with the amounts of expanded vermiculite added to the soil (Table 6.5). Storage of more water due to more pore volume in expanded vermiculite might have caused the observed difference. This is possible because the availability of adequate soil water promotes solubility, mobility, and absorption of plant nutrients (Singh and Singh, 2004).

Table 6.4. Effects of type and amount of vermiculite added to the soil on the concentrations and uptake of N, P, K, Mg, and Ca in maize shoot dry matter yield.

Factor		N	N uptake	P	P uptake	K	K uptake	Mg	Mg uptake	Ca	Ca uptake
		g kg^{-1}	mg pot^{-1}	g kg^{-1}	mg pot^{-1}	g kg^{-1}	mg pot^{-1}	g kg^{-1}	mg pot^{-1}	g kg^{-1}	mg pot^{-1}
Type of	Raw	7.8b	507.4b	3.6b	238.8b	9.8b	664.5b	3.4a	226.1a	1.2a	80.4a
vermiculite	Expanded	22.7a	1013.6a	6.3a	263.2a	18.6a	892.6a	1.3b	66.3b	1.2a	58.1b
Standard error		0.2	11.3	0.2	4.1	0.3	11.5	0.6	3.6	0.0	1.2
Amount	0	33.9a	457.6e	11.9a	160.5c	26.6a	359.7f	1.7d	22.5e	1.7a	23.5e
of	10	21.4b	658.4d	7.6b	261.4ab	15.9b	498.3e	2.9a	147.6ab	1.2bc	48.7d
vermiculite	20	17.3c	639.7d	5.8c	242.4b	14.7bc	604.3d	2.4b	134.3b	1.1c	53.2d
added to	30	13.5d	776.4c	4.0d	241.0b	13.5c	798.4c	2.3bc	145.0ab	1.1c	66.5c
the soil	40	12.3e	834.1b	3.9d	267.0a	13.3c	913.7b	2.0c	143.4ab	1.1c	74.9b
	50	11.1f	893.7a	3.1e	243.0b	13.6c	1078.1a	2.2bc	160.7a	1.3b	103.0a
Standard error		0.4	19.6	0.3	7.2	0.5	19.9	0.1	6.3	0.1	2.0
Coefficient of variation (%)		5.9	7.8	13	8.6	9.0	8.0	12.2	14.2	11.3	9.3

Means for each factor in a column followed by the same letter(s) are not significantly different at $P<0.05$ according to the Duncan's multiple - range test. Coefficient of variation is a ratio of standard deviation of the data set to the mean.

Table 6.5. Concentrations and uptake of N, P, K, Mg, and Ca in maize shoot dry matter as influenced by the added vermiculites to the soil.

Treatment	N g kg^{-1}	N uptake mg pot^{-1}	P g kg^{-1}	P uptake mg pot^{-1}	K g kg^{-1}	K uptake mg pot^{-1}	Mg g kg^{-1}	Mg uptake mg pot^{-1}	Ca g kg^{-1}	Ca uptake mg pot^{-1}
Soil without vermiculite (control)	33.9a	457.6f	11.9a	160.5e	26.6a	350.7i	1.7d	22.5e	1.7a	23.5e
Soil with 10% raw vermiculite.	10.4f	630.8e	5.0d	306.6a	8.2f	500.3h	4.3a	263.0a	1.2b	70.7b
Soil with 20% raw vermiculite	6.8g	466.7f	3.6ef	251.1b	9.0ef	617.5fg	3.3b	224.3b	1.1b	73.4b
Soil with 30% raw vermiculite	8.0g	469.8f	3.4f	229.7bc	10.0ef	676.5ef	3.2b	217.9b	1.1b	77.6b
Soil with 40% raw vermiculite	6.5g	465.0f	3.0f	212.9cd	10.4ef	751.3de	2.8c	203.0b	1.0b	73.8b
Soil with 50% raw vermiculite	7.3g	504.8f	2.8f	193.6d	11.2e	777.0d	3.2bc	222.2b	1.5a	106.7a
Soil with 10% expanded vermiculite	32.4a	685.9e	10.2b	216.2cd	23.6b	496.4h	1.5de	32.2e	1.3b	26.7de
Soil with 20% expanded vermiculite	27.9b	812.6d	8.1c	233.7bc	20.4c	591.0g	1.5de	44.4e	1.2b	33.0d
Soil with 30% expanded vermiculite	20.1c	1082.9c	4.7de	252.4b	17.0d	920.3c	1.3de	72.1d	1.0b	55.4c
Soil with 40% expanded vermiculite	18.2d	1203.2b	4.9d	321.1a	16.2d	1076.0b	1.3de	83.8cd	1.1b	76.0b
Soil with 50% expanded vermiculite	14.9e	1283.5a	3.4f	292.5a	16.0d	1379.1a	1.1e	99.2c	1.2b	99.3a
Standard error	0.5	27.8	0.4	10.1	0.7	28.2	0.1	8.9	0.1	2.9
Coefficient of variation (%)	5.9	7.8	13.0	8.6	9.0	8.0	12.2	14.2	11.3	9.3

Means in a column followed by the same letter(s) are not significantly different at P<0.05 according to the Duncan's multiple - range test. Coefficient of variation is a ratio of standard deviation of the data set to the mean.

Contrary to N, P and K; the overall uptake of Mg and Ca were higher in maize grown on soil with raw vermiculite than on soil mixed with expanded vermiculite (Table 6.4). Probably the availability of exchangeable Mg and Ca in raw vermiculite (see Chapter 4) contributed to the observed difference. Expanded vermiculite had insignificant exchangeable Mg and Ca as most of them are fixed in hexagonal sites on heating vermiculite (Walker, 1956), a condition that reduces significantly their availability to plant uptake. This is the disadvantage of heating vermiculite at a high temperature. The root dry matter also showed the same trend (Appendix 6.3).

With the exception of K and Ca, the uptake of N, P, and Mg did not increase with the increase in the amount of raw vermiculite added to the soil (Table 6.5). The uptake of N, P, and Mg was slightly higher when 10 % raw vermiculite was added to the soil than 20-50 %. This means that addition of more raw vermiculite reduced nutrient uptake; possibly some nutrients were fixed, particularly N as observed in Chapter 4 during the determination of the CECs with ammonium acetate. Contrary to the raw vermiculite, the uptake of N, P, K, Mg, and Ca increased with the amount of expanded vermiculite added to the soil (Table 6.5). More likely, expanded vermiculite does not fix these nutrients but enhances their availability.

Further observation shows that from the initial 1200 mg of K applied per pot to the soil amended with 50 % expanded vermiculite, an increase of about 15 % K was recovered in the maize dry matter. The extra amount might have been contributed by the exchangeable K^+ from the expanded vermiculite. Exchangeable K^+ increased by more than 10-fold on heating this vermiculite at 600 °C (Chapter 4). Zeng and Brown (2000) also noted that exfoliation of vermiculite can facilitate the release of exchangeable K^+. The exchangeable K^+ is plant-available in a similar way to the water soluble K^+ (Carter and Singh, 2004) and

may be sufficient for crop production when it is more than 0.25 $cmol_{(+)}/kg$ (Defoer *et al.*, 2000), a value which was surpassed on heating this vermiculite at 600 °C.

Concentrations of N, P, and K as well as to a broad extent Ca and Mg in the above ground biomass decreased with the increase in the added amount of vermiculite (Table 6.4). This decrease was much pronounced in maize grown on soil with expanded vermiculite than raw vermiculite (Table 6.5). Possibly, it was due to an increase in root and shoot biomass through a dilution effect. Sierra *et al.* (2003) found a similar result when analysing N concentration in maize aerial biomass.

The concentrations of Ca in all treatments were relatively low due to the fact that no Ca-fertilizer was added to the soil as a supplement. However, the overall uptake of Ca was more from soil with raw vermiculite than from soil mixed with expanded vermiculite (Table 6.4). This was probably due to availability of exchangeable Ca from raw vermiculite (see Chapter 4). Similarly, the exchangeable Mg^{2+} from the raw vermiculite supplemented the applied Mg-fertilizer to the extent of increasing its concentration in maize grown on soil mixed with raw vermiculite.

Published critical concentration values for N, P, K, Mg, and Ca in maize tissues at the tasselling stage are respectively 30, 2.5, 19, 2.5, and 4.0 g/kg of dry matter (Melsted *et al.*, 1969). In this study, maize was also grown to the tasselling stage. The average N, P, and K concentrations in aerial biomass for maize grown on soil-added, expanded vermiculite were in broad agreement with the values reported by Melsted *et al.* (1969) (Table 6.4). The N concentrations were also above the average 13 g/kg found in maize silage in USA (Ketterings *et al.*, 2006). The average N and K concentrations in maize shoots from soil

with raw vermiculite were less than that reported by Melsted *et al.* (1969), whereas P was high (Table 6.4).

Studies show that optimum maize yields are obtained when the K concentrations in maize shoots are between 11.4 and 22.9 g/kg (Randall *et al.*, 1977). Jordan-Meille and Pellerin (2004) reported that the common K concentration in maize dry matter is 20 g/kg. The K concentrations in shoot dry matter from the pots with soil-added, expanded vermiculite were within the range reported by Randall *et al.* (1976), while that from the pots with raw vermiculite were slightly low (Tables 6.4 and 6.5).

On the basis of the concentrations and uptake of N, P, and K on the maize dry matter yields, I can conclude from this study that the expanded vermiculite is better than the raw vermiculite in enhancing availability of N, P, and K for maize uptake when applied as a soil amendment. The raw vermiculite does not enhance adequately the availability of N and K in the soil. In the tropical soils of Africa, including Tanzania, N is the major limiting nutrient in maize production followed by P (Kwabiah *et al.*, 2003). Therefore, any material applied as a soil amendment should preferably enhance the availability of N, P, and K to favour maize production. Expanded vermiculite has also an added advantage of increasing the availability of exchangeable K^+ particularly when heated at 600 ^oC and thus, its use could reduce the amount of inorganic K-fertilizers required in the soil. However, heating to get expanded vermiculite and the amount required to improve the soil have cost implications and, thus, will need further consideration in comparison with the use of small amounts of raw vermiculite that provide moderate results.

Statistical analysis of variance for the macronutrients is located in Appendix 6.4. It shows that the heating of vermiculite has a significant effect on the uptake and concentrations of

nutrients in maize. Analysis of the data does not show much variation as indicated by the low coefficients of variation of 6 -16 % (Mahmoundvand *et al.*, 2007).

6.3.4 Availability of trace elements to maize

In Chapter 3, I found that vermiculite MK1 contains high levels of Ni and Cr as well as a small amounts of As and Pb. Pot experiments done in Tanzania have revealed that those elements are insignificantly plant-available (Tables 6.6 and 6.7). The study has found that the increase in the amount of added vermiculite to the soil has little effect on the uptake of those trace elements. However, their concentrations and uptake in maize grown on soil with expanded vermiculite are statistically differently ($P < 0.05$) from those grown on soil with raw vermiculite with the exception of As (Appendix 6.5). The uptake and concentrations were marginally higher in maize grown on soil with expanded vermiculite than in maize grown on soil with raw vermiculite, with the exception of the concentration of As and uptake of Pb (Table 6.6). The observed difference might have been caused by the effect of heating. As observed in Chapter 5, heating at 600 °C destabilizes the crystal structure of vermiculite, making the elements loosely held and, thus, they become easily extractable.

Nevertheless, the concentrations found as a result of adding vermiculite to the soil in all treatments were below the toxicity levels. The level of As found was 0.13-0.18 mg/kg (Table 6.7) less than 0.20 mg/kg in the straw given to cattle in the UK (Nicholson *et al.*, 1999). Similarly, Ni and Pb levels were 1.54-9.44 and 0.06-0.26 mg/kg respectively. The values for Ni and Pb were significantly lower than those from soil with no vermiculite (control). Thus, this vermiculite is safer than the soil. The critical levels for the two elements (Ni and Pb) are respectively 10 and 30 mg/kg above which toxicity effects are likely to occur (Alloway, 1990).

Table 6.6. Effects of type and amount of vermiculite applied to a sandy soil on the concentrations and uptake of As, Pb, Cr, and Ni in maize shoot dry matter

Factor		As	As uptake	Pb	Pb uptake	Cr	Cr uptake	Ni	Ni uptake
		mg kg^{-1}	mg pot^{-1}	mg kg^{-1}	mg pot^{-1}	mg kg^{-1}	mg pot^{-1}	mg kg^{-1}	mg pot^{-1}
Type of vermiculite	Raw	0.13a	0.027a	0.08b	0.005a	0.14b	0.010b	2.29b	0.154b
	Expanded	0.15a	0.007b	0.16a	0.007a	0.25a	0.012a	4.96a	0.212a
	Standard error	0.01	<0.001	0.01	<0.001	0.01	0.001	0.38	0.011
Amount of vermiculite added to the soil % v/v	0	0.17a	0.002d	0.33a	0.005a	0.25a	0.004d	13.49a	0.179a
	10	0.16a	0.006c	0.20b	0.007a	0.23ab	0.008c	6.08b	0.186a
	20	0.14a	0.006c	0.14c	0.006a	0.18c	0.008c	3.06c	0.123b
	30	0.13a	0.008b	0.09d	0.006a	0.19c	0.011b	3.04c	0.177a
	40	0.13a	0.009b	0.09d	0.006a	0.18c	0.012b	3.17c	0.215a
	50	0.14a	0.011a	0.08d	0.006a	0.20bc	0.016a	2.77c	0.215a
	Standard error	0.01	<0.001	0.02	0.001	0.01	0.001	0.07	0.020
	CV, %	13.6	11.1	24.0	26.3	17.0	21.7	30.7	25.2

Means for each factor in a column followed by the same letter are not significantly different at P<0.05 according to Duncan's multiple - range test.

CV = Coefficient of variation (a ratio of standard deviation of the data set to the mean).

Table 6.7. Concentrations and uptake of As, Pb, Cr and Ni in maize shoot dry matter as influenced by the added vermiculite to the soil

Treatment	As	As uptake	Pb	Pb uptake	Cr	Cr uptake	Ni	Ni uptake
	mg kg^{-1}	mg pot^{-1}	mg kg^{-1}	mg pot^{-1}	mg kg^{-1}	mg pot^{-1}	mg kg^{-1}	mg pot^{-1}
Soil without vermiculite (control)	0.17a	0.002e	0.33a	0.005bc	0.25b	0.004d	13.49a	0.179bcd
Soil with10% raw vermiculite.	0.13a	0.008bc	0.14c	0.009a	0.13c	0.008c	2.72c	0.169bcd
Soil with 20% raw vermiculite	0.13a	0.008bc	0.07e	0.005bc	0.12c	0.008c	1.54c	0.105d
Soil with 30% raw vermiculite	0.13a	0.009b	0.06e	0.004c	0.12c	0.008c	2.29c	0.154bcd
Soil with 40% raw vermiculite	0.13a	0.009b	0.06e	0.004c	0.14c	0.010bc	1.90c	0.137cd
Soil with 50% raw vermiculite	0.14a	0.100b	0.08de	0.005bc	0.21b	0.014b	2.99c	0.205bc
Soil with 10% expanded vermiculite	0.18a	0.004d	0.26b	0.005bc	0.33a	0.007cd	9.44b	0.202bc
Soil with 20% expanded vermiculite	0.16a	0.005d	0.21b	0.007abc	0.25b	0.008c	4.58c	0.140bcd
Soil with 30% expanded vermiculite	0.13a	0.007c	0.13cd	0.007abc	0.26b	0.014b	3.79c	0.200bc
Soil with 40% expanded vermiculite	0.13a	0.009bc	0.11cde	0.007abc	0.21b	0.014b	4.43c	0.294a
Soil with 50% expanded vermiculite	0.14a	0.012a	0.09cde	0.008ab	0.20b	0.018a	2.55c	0.224ab
Standard error	0.01	0.001	0.02	0.001	0.02	0.001	0.93	0.027
Coefficient of variation (%)	13.6	11.1	24.0	26.3	17.0	21.7	30.7	25.2

Means in a column followed by the same letter(s) are not significantly different at P<0.05 according to Duncan's multiple – range test.

CV = Coefficient of variation (a ratio of standard deviation of the data set to the mean).

Concentrations of Cr in maize grown on soil with added vermiculite were 0.12-0.33 mg/kg, whereas the normal level in plants is usually not more than 1 mg/kg (Kabata-Pendias and Pendias, 1992; Pratt, 1966). Katz and Salem (1994) found an average value of 0.37 mg/kg of Cr in maize shoot grown on uncontaminated soils. Thus, from the above results I can say that this vermiculite is safe to use as a soil improver for growing maize in Tanzania.

Although maize in the glasshouse experiments was grown to the tasseling stage, it is worth mentioning that the levels of As, Pb, Cr, and Ni found in the maize shoots were below the median concentrations for maize grown in Tanzania (Appendix 6.6). It proves further that maize grown on soil-added, vermiculite is safer than that grown elsewhere in the country.

Few high levels of Cr and Ni in the maize samples from Tanzania were found in farms that are in the areas dominated by mining activities and, thus, might have been released from the weathering of exposed rocks or tailings. Maize samples with high levels of As of more than 0.6 mg/kg were found from one research farm (Appendices 6.7 and 6.8). The source could be due to the use of pesticides and /or fertilizers containing arsenic.

In cereal grains, As level of more than 0.30 mg/kg is considered to be a serious soil contamination (Williams *et al.*, 2005). The average concentration of As in soils is 10 mg/kg, values greater than 20 mg/kg are regarded as high (Salt *et al.*, 1998). An arsenic level of 34-76 mg/kg in soil was found in a single maize farm near a stone quarry, but the uptake in maize grains and shoots were relatively low, less than 0.17 mg/kg. The source of the elevated As in that farm could be due to the weathering of exposed rocks from the nearby quarry, which contained sulphide minerals.

Samples from three farms, located less than 100 metres from where vermiculite sample MK1 was taken, did not show high concentrations of trace elements in maize shoots and grains. It is an additional proof that vermiculite is not a potential source of plant-available trace elements in comparison with the contamination from uncontrolled mining and quarrying operations as well as use of fertilizers and pesticides.

Analysis of the trace elements from maize farms in Tanzania did not show significant relationships between the concentrations in plant tissues and those in soils. Plots showing plant-soil relationships are located in Appendices 6.7 and 6.8. Zayed and Terry (2003) reported similar observation in the studies of Cr. This could be due to variation in a number of variables in the soil, such as pH, available concentration, oxidation state, redox potential, organic matter content, and interaction with other elements (Pasquini, 2006). All those factors in soils vary from one place to another.

Analysis of As, Pb, Cr, and Ni in the spikes and certified reference material (CRM) is documented in Appendix 6.9. The recovery of the studied trace elements was adequate and, thus, no correction was carried out on the ICP-MS data presented above.

6.4 CONCLUSIONS

The Mikese vermiculite from Tanzania has a potential of enhancing moisture retention to the soil. The moisture retention increased with the increase in the added amount of vermiculite. Expanded vermiculite retained more plant-available water and for a longer period than unheated vermiculite.

Use of vermiculite promoted maize vegetative growth and, consequently, increased dry matter yields. In addition, vermiculite enhanced the availability and, thus, maize uptake of N, P, K, Mg and Ca as compared to the soil with no vermiculite (control). The uptake increased particularly with the amount of expanded vermiculite added to the soil as compared to raw vermiculite. Raw vermiculite contributes exchangeable Mg and Ca to the maize uptake, whilst expanded vermiculite contributed exchangeable K. Vegetative growth and the uptake of P, Mg and Ca were higher in maize grown on soil with 10 % raw vermiculite than from soil with 10-30 % expanded vermiculite. The highest vegetative growth and nutrient uptake was from soil with 50 % expanded vermiculite.

High levels of Ni and Cr as well as small amounts of As and Pb found in vermiculite MK1 are of insignificant concern with respect to maize uptake. The levels found in maize grown on soil with vermiculite were below the median levels in maize grown in Tanzania. Thus, it indicates that vermiculite MK1 is safe to use as a soil conditioner for growing maize in Tanzania.

CHAPTER 7

RETENTION AND FERTILIZATION OF PLANT NUTRIENTS IN A SANDY SOIL AS INFLUENCED BY THE APPLICATION OF VERMICULITE

7.1 INTRODUCTION

Nutrient depletion in most tropical soils is considered to be among the main biophysical factors contributing to decline in agriculture production in many African countries (Sanchez, 2002). It is estimated that 4.4 million t N, 0.5 million t P, and 3 million t K are lost each year from cultivated land in Africa (Sanchez *et al.*, 1997). The loss of nutrients is above the estimated rate of Africa's annual fertilizers consumption (FAO, 1995). The consequence is a decline in crop productivity and food security (Lisuma *et al.*, 2006; Sanchez *et al.*, 1997). The effort done to alleviate the problem is mainly by replenishing the soil with manure and / or mineral fertilisers. However, not all applied nutrients to most tropical soils are retained and made available to plants. Some are lost through crop residue removals, whereas others are lost by leaching or lateral flow, whilst others volatilize as gaseous or get fixed in soil constituents (Sanchez, 2002). Thus, the application of plant nutrients to the soils alone is not a solution to the decline in fertility status of most tropical soils and poor crop yields.

Tropical soils generally have low organic C and total N contents because of low biomass production and a high rate of decomposition (Mokwunye *et al.*, 1996). The low concentration and solubility of P in soils frequently makes it a limiting factor in plant nutrition. The P deficiency is widespread in East Africa and the Sahel (Sanchez, 2002), including Tanzania, where this study was conducted.

This chapter investigates whether or not the use of vermiculite as a soil amendment can assist in enhancing the retention and fertilization of extractable N, P, and K in the Tanzanian soils. The N, P, and K were selected because they are the dominant macronutrients required for plant growth. Of these, N and P are the most limiting nutrients in most tropical soils of Africa (Kwabiah *et al.*, 2003).

7.2 MATERIALS AND METHODS

7.2.1 Site description and soil classification

The study was carried out at Mazimbu area in Morogoro Urban District, Tanzania. The area is located at grid coordinates 06° 47' 02'' S and 37° 37' 34'' E. It is well drained and gently undulating colluvial plain with a uniform slope of 2-3 %. The area is known for its poor fertility potential and crop yield (personal communication with the local residence). Cassava and maize are some of the crops that are usually grown in the area. In the past two years, the area was not cultivated any crop or applied fertilizers.

A soil profile was excavated in the area to a 170 cm depth in order to classify the soil and establish the physical and chemical properties. Excavation was done using a spade and a hoe. After excavation, the soil from top of the profile to the bottom was documented by the aid of the Mussel colour chart. Soil horizons were distinguished and demarcated. Soil samples were taken from each horizon. Sampling was made by taking a small amount of soil from top to the bottom of each horizon. The soil samples obtained were air-dried at a room temperature to a constant weight and sieved through a 2 mm sieve for laboratory analysis. Analysis of the soil properties was done at the Soil Science Laboratories of the Sokoine University of Agriculture in Tanzania using the methods of Okalebo *et al.* (2002) and Møberg (2001). Results found indicate that the soil at the site is loamy sand and is poor in plant nutrients (Appendix 7.1).

The soil was classified as *Ustic Quartzipsamment* based on Soil Survey Staff (1996) and *Orthidystric Arenosol* according to FAO (1998). The soil was ideal for the study because of its poor in plant nutrients and, thus, it was expected to have less interference with the treatments.

7.2.2 Field execution and set-up

The study was carried out from March to June 2007, during the long rainy season, locally known as '*Masika*'. Most crops in the country are grown during that time. The sandy soil documented in Table 6.1, Chapter 6, was mixed with raw vermiculite and pre-heated vermiculite MK1 (600 °C) in varying amounts. The soil and vermiculites were all sieved through an 8 mm sieve before mixing. Amounts of vermiculites added to the soil were 0, 10, 20, 30, 40, and 50 % v/v. A total of 12 treatments were obtained, 6 treatments of soil mixed with raw vermiculite and another 6 treatments of soil mixed with pre-heated vermiculite. Each treatment was replicated three times, giving a sum of 36 samples.

Two sets of samples were made, each with 36 samples. The first set comprised 36 samples from 12 treatments for burying at 0-15 cm from the surface while another set of 36 samples was prepared for burying at 15-30 cm depth. Thus, the total samples used were 72. Each sample weighed one kg. Sulphate of ammonia (240 mg N / kg soil), triple super phosphate (TSP) (160 mg P / kg soil), and sulphate of potash (200 mg K /kg soil) were applied to each soil/vermiculite mix, mixed well by hand, packed into labelled sample bags. The TSP was ground before mixing.

The experimental site was cleared, ploughed, and harrowed to remove all vegetation in order to avoid interference from plant nutrient uptake. Two main plots were made, one for samples

buried at 0 -15 cm and another plot for samples buried at 15 -30 cm from the surface. Each plot was further subdivided into two sub-plots. One sub-plot was for samples with raw vermiculite and another sub-plot for samples with pre-heated vermiculite. Each sub-plot was split into six small plots for the 6 treatments of soil mixed with raw vermiculite and another 6 treatments of soil mixed with heated vermiculite.

Sample burial holes were made using a hoe. A ruler was used to check for the depths (15 and 30 cm from the surface). In each hole, a small litter bag (polyethylene net) with a capacity of carrying about 2 kg of soil/vermiculite mix was inserted. The samples were put into the litter bags and covered by soil. Sample locations were marked using labelled plastic pegs. The samples were spaced 150 cm apart in each sub-sub plots and were buried for 90 d. Weeding was done regularly by hand.

Rainfall and soil moisture at the site were recorded daily during the entire period of the field experiment. The rainfall was recorded using a rain gauge while soil moisture at 0-15 cm depth from the surface was automatically measured using time domain reflectometry (TDR) probes. The instruments were installed at the site by the Department of Soil Science of the Kyoto University from Japan.

After 90 d, the buried samples were carefully excavated, ground by hand, and sieved through a 2 mm sieve for laboratory analysis. Analysis of extractable nutrients retained by the soil/vermiculite mix was carried out at the University of Aberdeen, Department of Plant and Soil Science. The samples were analysed for ammonium and nitrate after digestion with 1*M* KCl (Allen, 1989) by flow injection analysis (Tecator FIAstar 5010 Analyser). The samples for extractable P and K were digested by using acetic acid (Allen, 1989). Extractable P was

determined by flow injection analysis (Tecator FIAstar 5010 Analyser), while the K was analysed by flame emission spectrometry (Perkin Elmer Aanalyst 100). The study did not opt for leachate analysis because its main objective was to determine extractable nutrients that are retained in the soil/vermiculite mix under field condition.

7.2.3 Experimental design and data analysis

A split-split-plot design was used with the depth of burial as the main plot, type of vermiculite as sub-plot and amount of vermiculite added to a sandy soil as sub-sub plot as explained above in detail. Analysis of variance (ANOVA) was done using the MSTATC software (Freed *et al.*, 1991) to determine the effect of burial depth, pre-heating vermiculite, and amounts of vermiculite mixed with the soil on the retention of extractable N (ammonium and nitrate), P, and K in a sandy soil. Comparison of the treatment means was carried out using the Duncan's multiple-range test at 5 % level of significance.

7.3 RESULTS AND DISCUSSION

7.3.1 Rainfall and soil moisture

Rainfall recorded at the site was low and unevenly distributed with several days of dry spells (Fig.7.1). The total precipitation was 216 mm. Daily rainfall distribution was between 0 - 30 mm, with 0.1 mm as the median. The total amount received was far below the average annual rainfall of 1042 mm received in the country (Agrawala *et al.*, 2003). The low and erratic rainfall during growing seasons with periods of dry spells is a common phenomenon in most parts of Tanzania (Mbilinyi *et al.*, 2005; Mapande and Reason, 2005) and, thus, it was not a surprise.

Volumetric soil moisture content at the site was also low and ranged between 0.02 and 0.1 cm^3/cm^3 (Fig.7.1). The moisture content corresponded to the magnitude of precipitation, with high values obtained immediately after heavy rainfalls. Although the soil texture influences moisture content, the low duration and intensity of precipitation experienced at the site might have been the main contributing factors for the low moisture content. Similar observation has also been reported by Pan *et al.* (2008).

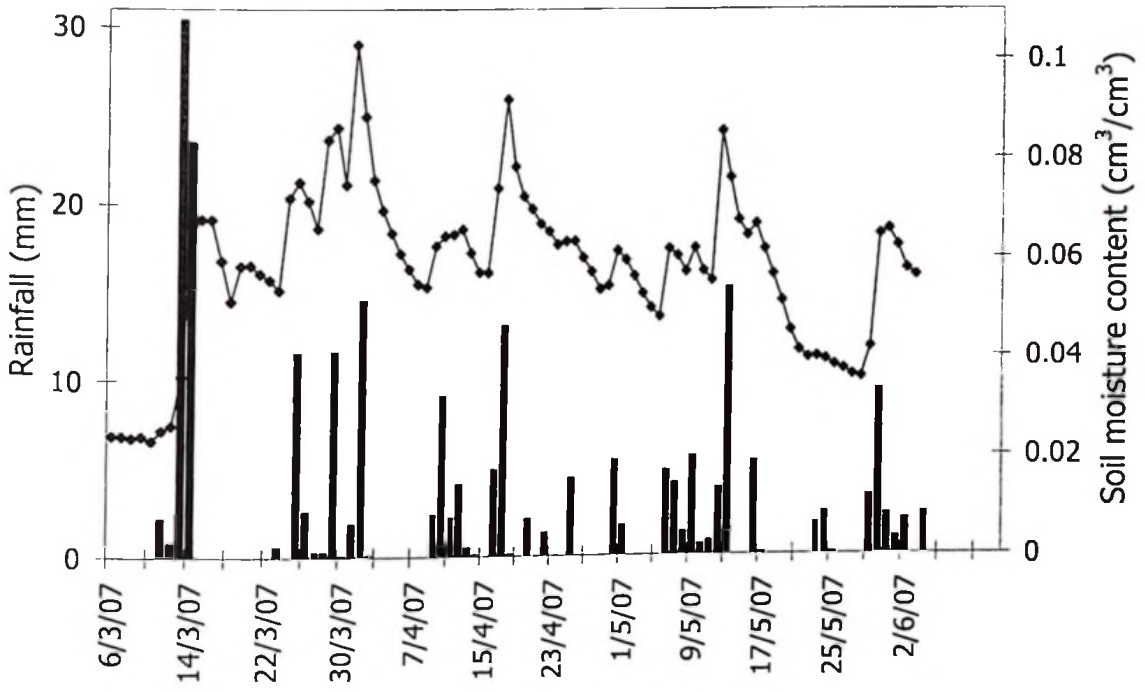

Fig.7.1. Rainfall and soil moisture recorded from 6/3/07 to 6/6/07 during field experiment in Tanzania. The curve represents soil moisture content at 0-15 cm depth from the surface, while histograms denote the rainfall received at the site. (Source: Department of Soil Science, Kyoto University, Japan).

7.3.2 Retention and fertilization of plant nutrients in soil

Vermiculite burial depth caused a significant difference ($P<0.05$) in the retention of extractable nitrate, K, and P but not for ammonium (Table 7.1). As expected, the retention of those nutrients was more at 15-30 cm than at 0-15 cm due to the variation in temperature and rainwater. The temperature and rainwater are usually higher at the surface than at depth; the factors that enhance the solubility and mobility of the nutrients. The temperature enhances P solubility (Kwari and Batey, 1991; Serrasolsas and Khanna, 1995), while more rainwater increases the degree of P saturation and mobility (Casson *et al.*, 2006) and, thus, more leaching of P at the surface than at depth. Similarly, more rainwater at the surface dissolves water soluble K^+ and percolate with it down the soil profile. In addition, surface temperature enhances the availability of exchangeable K^+ (Grava *et al.*, 1961) and leaching during rain.

Table 7.1. Effect of burial depth on the retention of extractable ammonium, nitrate, P, and K in soil amended with vermiculite

Burial depth, cm	Ammonium mg kg^{-1}soil	Nitrate mg kg^{-1}soil	P mg kg^{-1}soil	K mg kg^{-1}soil
0-15 (Control)	2.2a	3.1b	51.3c	50.2c
15-30 (Control)	2.1a	2.6b	51.3c	50.0c
0-15 (All vermiculite)	2.3a	3.6b	94.3b	64.0b
15-30 (All vermiculite)	2.1a	11.4a	114.8a	70.4a
Standard error	0.3	0.4	2.7	2.1
CV, %	44.1	54.9	10.1	14.9

Means in a column followed by the same letter(s) are not significantly different at $P<0.05$ according to the Duncan's multiple-range test. CV = Coefficient of variation (a ratio of standard deviation of the data set to the mean).

The applied N-fertilizer dissolves easily when there is sufficient soil water and undergoes hydrolysis to ammonium, via nitrification it leads to denitrification (Bijoor *et al.*, 2008). Both nitrification and denitrification are microbial processes that operate in the soil at the same time

in varying degree depending on the amount of soil water (Firestone and Davidson, 1989). Apart from the nitrification and denitrification, some of the applied N-fertilizers are lost from agricultural soils by ammonia volatilization (Mughogho *et al.*, 1986; Zhu, 1997). Ammonia volatilization is enhanced with the increase in temperature and water (Fenn and Kissel, 1974; Sigunga *et al.*, 2002), whilst nitrate movement and leaching increases with the increase in soil water (Sànchez-Martìn *et al.*, 2008). Since there were no plants grown at the site for plant off take, leaching by infiltrating water might have been the main mechanism through which P and K were lost, whereas leaching as nitrate and emission to the atmosphere as gas might have been the mechanism behind the loss of the applied sulphate of ammonia.

The soil at the site was loamy sand (Appendix 7.1). Loamy sands have a high proportion of drainage pores and thus, are permeable. When it rains, rainwater and dissolved plant nutrients are rapidly lost from the upper layers (Askegaard and Eriksen, 2000; Eswaran *et al.*, 2005). Interception of some of the infiltrating rainwater in the upper soil horizon and loss through evaporation reduces the amount of water at 15-30 cm depth and thus, loss of nutrients. Similar observation was made by Cai *et al.* (2002) and Freney *et al.* (1983) when studying N losses from buried fertilizers.

Burial depth for the control did not cause any difference in the retention of the applied macronutrients (Table 7.1). In addition, the amount of nutrients retained in the control was significantly lower than that retained in soil with applied vermiculite, with the exception of ammonium. Retention of extractable nitrate, P, and K increased with the increase in the amount of vermiculite added to the soil (Table 7.2). This indicates that vermiculite contributed in enhancing the retention of extractable nutrients when applied to the soil.

Extractable P was highly retained in soil amended with raw vermiculite compared with soil mixed with expanded vermiculite (Table 7.3). The high P in soil mixed with raw vermiculite might be due to the contribution of extractable P from apatite and monazite, which was significantly suppressed in expanded vermiculite as a result of heating (Chapter 5). Contrary to the P, extractable K was marginally higher in soil amended with expanded vermiculite than soil with raw vermiculite, probably due to the increased availability of exchangeable K^+ caused by heating vermiculite (Chapter 4). In Chapter 4, the exchangeable K^+ in expanded vermiculite MK1 heated at 600 °C was found to be 10-fold more than in raw vermiculite, but the observed difference in the amount of K retained between the two products was quite small. Probably, part of the exchangeable K^+ in expanded vermiculite was lost by leaching or fixation.

Table 7.2. Effect of amount of vermiculite added to the soil on the retention of extractable ammonium, nitrate, P, and K.

Vermiculite added to the soil, % v/v	Ammonium mg kg^{-1}soil	Nitrate mg kg^{-1}soil	P mg kg^{-1}soil	K mg kg^{-1}soil
0	2.1abc	2.8c	51.3f	50.1e
10	1.6c	3.5c	61.5e	56.1de
20	1.8bc	5.3bc	83.4d	61.8cd
30	2.1abc	6.9b	97.2c	65.9bc
40	2.6ab	8.0b	119.5b	74.0ab
50	2.9a	13.8a	161.3a	78.2a
Standard error	0.3	1.1	2.8	2.8
CV, %	44.1	54.9	10.1	14.9

Means in a column followed by the same letter(s) are not significantly different at P<0.05 according to the Duncan's multiple-range test. CV = Coefficient of variation (a ratio of standard deviation of the data set to the mean).

Table 7.3. Retention of extractable ammonium, nitrate, P, and K in a sandy soil as influenced by the added raw and expanded vermiculites

Type of vermiculite	Ammonium mg kg^{-1}soil	Nitrate mg kg^{-1}soil	P mg kg^{-1}soil	K mg kg^{-1}soil
Control	2.1a	2.8c	51.3c	50.1c
Raw vermiculite	2.2a	8.6a	126.3a	60.6b
Expanded vermiculite	2.3a	6.4b	82.8b	73.9a
Standard error	0.2	0.6	1.6	1.6
CV, %	44.1	54.9	10.52	14.9

Means in a column followed by the same letter are not significantly different at P<0.05 according to the Duncan's multiple-range test. CV = Coefficient of variation (ratio of standard deviation to the mean).

Retention of extractable N as nitrate and ammonium showed a different pattern from that of P and K. The amount retained was very low compared to P and K. In addition, retention of extractable ammonium did not show any significant difference among the treatments. In proportion, nitrate in expanded vermiculite was slightly more than in soil mixed with raw vermiculite.

The results of the combined effects of the burial depth with the type and amount of vermiculite added to the soil on the retention of the applied nutrients are summarized in Table 7.4. From that table it shows that retention of applied nutrients increased with the depth of burial and amount of vermiculite added to the soil. Ammonium and nitrate were less retained than the other nutrients. The maximum extractable ammonium retained was 4 mg/kg in the soil mixed with 50 % expanded vermiculite and buried at 0-15 cm. The amount retained was less than 2 % of the initial 240 mg/kg of N-fertilizer applied. For the nitrate, maximum retention was 23.8 mg/kg and was found in soil amended with 50 % expanded vermiculite and buried at 15-30 cm. Similarly, this retention was insignificant (< 10 %) when compared to the 240 mg/kg of N-fertilizer applied.

Table 7.4. Combined effects of the burial depth, amount, and type of vermiculite applied to the soil on the retention of extractable ammonium, nitrate, P, and K.

Vermiculite added to the soil % v/v	Ammonium mg kg^{-1}soil	Nitrate mg kg^{-1}soil	P mg kg^{-1}soil	K mg kg^{-1}soil
	Soil mixed with raw vermiculite and buried at 0-15 cm			
0	2.3ab	1.6e	40.3j	49.1f
10	1.8b	1.5e	52.3hij	51.9f
20	2.0b	3.0de	88.8f	57.6ef
30	2.1ab	4.4cde	112.5e	60.0def
40	2.4ab	4.7cde	132.9cd	60.0def
50	2.4ab	4.9cde	176.9b	64.2def
	Soil mixed with raw vermiculite and buried at 15-30 cm			
0	2.0b	4.5cde	62.3hi	51.3f
10	2.1ab	8.8bcde	81.3fg	53.9f
20	2.4ab	11.2bc	121.2de	60.3def
30	1.7b	12.9b	128.3cde	62.5def
40	2.5ab	13.1b	143.3c	67.2cdef
50	2.6ab	21.3a	225.9a	67.9cdef
	Soil mixed with expanded vermiculite and buried at 0-15 cm			
0	2.1ab	1.9e	41.5j	49.3f
10	1.4b	1.7e	47.0ij	57.2ef
20	1.5b	2.8de	57.0hij	62.7def
30	2.7ab	3.6de	66.9gh	65.3cdef
40	3.0ab	4.3cde	91.1f	77.4bcd
50	4.0a	5.2cde	118.0de	83.8abc
	Soil mixed with expanded vermiculite and buried at 15-30 cm			
0	2.0b	3.3de	61.0hi	50.6f
10	1.2b	2.1e	65.3ghi	61.6def
20	1.2b	4.1cde	66.6gh	66.7cdef
30	2.2ab	6.7bcde	80.9fg	75.7bcde
40	2.7ab	10.0bcd	110.6e	91.3ab
50	2.7ab	23.8a	124.2de	96.9a
Standard error	0.6	2.1	5.6	5.5
CV, %	44.1	54.9	10.1	14.9

Means in a column followed by the same letter(s) are not significantly different at P<0.05 according to the Duncan's multiple-range test. CV = Coefficient of variation (ratio of standard deviation to the mean).

In the soil environment, ammonium and nitrate ions are very mobile and biologically labile (Defoer *et al.*, 2000). When applied as mineral fertilisers in soils they can easily be lost by leaching or lost into the atmosphere in gaseous forms (Defoer *et al.*, 2000; Cai *et al.*, 2002). Thus, it is not surprising that the observed recovery was low. The loamy sand at the site might have favoured the leaching of nitrate because of high permeability. Nitrate in agricultural soils is commonly depleted by leaching to the deeper layers below the rooting zone where it accumulates or enters the saturated phase (Fang *et al.*, 2006; Eswaran *et al.*, 2005). From this study, it is clear that vermiculite is incapable of prolonging the retention of extractable N as ammonium or nitrate in the soil for plant growth for more than 90 d.

Although the K retained in the soil increased with the amount of vermiculite applied, the overall fraction retained was low compared to 200 mg K /kg applied to the soil. The K obtained in the control, regardless of the burial depth, was about 25 %. In the soil mixed with raw vermiculite, the K retained ranged between 26-34 %, whilst in soil amended with expanded vermiculite, it was 29-48 %. The observed low K in both treatments might have been caused by leaching. If not by leaching, some might have been fixed in vermiculite as the result of wetting and drying cycles during rains and dry spells (Carter and Singh, 2004; Zeng and Brown, 2000). Contractions of the interlayer space in vermiculite on drying can lead to the entrapment of K (Sparks and Huang, 1985) and, thus, reduction in extractable fractions.

The amount of P–fertilizer applied (TSP) to the soil was 160 mg P/kg. The fraction retained in the control at 0-15 cm depth was 25-26 %, whilst at 15-30 cm was 38-39 %. In soil mixed with raw vermiculite, the P retained at 0-15 cm ranged from 33 to 111 %, while at 15-30 cm it was 51-141 %. It is obvious that raw vermiculite not only retained the applied P, but also fertilized the soil by adding more extractable P. Fertilization might have been attributed to the

extractable P from apatite and monazite as mentioned earlier. The P recovered from the soil mixed with expanded vermiculite was 29-74 % at 0-15 cm and 41-78 % at 15-30 cm. Thus, in comparison with N and K, the P was more retained and in some cases fertilized by the added amount of vermiculite. Vermiculite should preferably be buried at 15-30 cm from the surface for better performance.

The P dynamics in soils is complex. It undergoes slow sorption (fixation) and desorption (release) processes (Sanchez *et al.*, 1997). The presence of organic matter enhances its mobility while the presence of Fe and Al oxides and hydroxides reduces its mobility by fixation (Kwabiah *et al.*, 2003). However, it is considered to be less mobile particularly in fine-textured soils, but leaches in a substantial amount when applied to sandy soils (Brouwer and Powell, 1995; Humphreys and Pritchett, 1971). Since P was applied to the sandy soil and a substantial amount was retained by the soil for more than 90 d over the control, it is a proof that vermiculite enhanced its retention and fertilization. Thus, from this study I can say that this Tanzanian vermiculite has a marked ability of enhancing the retention of extractable P when applied to the sandy soil under tropical climate.

Statistical analysis of the variances is located in Appendix 7.2. It shows the interaction of burial depth with the type and amount of vermiculite added to the soil has no significant effect ($P > 0.05$) on the retention of extractable K and N (as nitrate and ammonium). Also, the burial depth and type of vermiculite did not have marked effect on the ammonium retention. Data for nitrate and ammonium were highly variable, with coefficient of variation of more than 44 % as compared to extractable K and P. This could be due to instability of N in the soil as compared to K and P (Defoer *et al.*, 2000).

7.4 CONCLUSIONS

The study has established that vermiculite is incapable of enhancing the retention of extractable N as ammonium and nitrate, and K in a sandy soil for more than 90 d under tropical Tanzanian climate. Although the retention of these nutrients increased slightly with the burial depth and the amount of vermiculite applied to the soil, the amounts retained were small compared to the initial applied amounts. In addition, part of the exchangeable K^+, which was 10-fold more in expanded vermiculite than in raw vermiculite was also lost.

In comparison with N and K, P was more retained and in part fertilized by the added vermiculites to the soil. Maximum extractable P retained in soil mixed with expanded vermiculite was 78 %, whereas in soil amended with raw vermiculite the amount retained and fertilized was 141 %. Fertilized P came from apatite and monazite in vermiculite. Thus, it was concluded that the vermiculite when added to a sandy soil under tropical condition has a marked ability of enhancing the retention and fertilization of P. More retention occurs when vermiculite is buried at 15-30 cm from the surface than at 0-15 cm. Effective utilization of vermiculite can reduce the burden of replenishing the tropical soils with the same amount of P-fertilizers.

CHAPTER 8

SYNTHESIS

Tanzania is an agricultural country in which 90 % of the rural population gets their earning through subsistent rain-fed agriculture (Mmbaga and Lyamchai, 2001). However, crop productivity is generally low and is compounded, among other factors, by inadequate content and retention of plant nutrients and water (Mwakalila, 2006). The outcome is frequent food shortage and low earnings not only to the farmers but also to the nation. Importation of food from outside the country is sometimes inevitable.

Despite having a number of vermiculite deposits (Harris, 1961; Williams and Skerl, 1940), no attempt has been made to use them to improve the soil properties in order to increase crop production (Schundler, 2008). One reason that is hindering the exploitation of the Tanzanian vermiculites for agricultural purposes is the absence of adequate information on their potential suitability.

The focus of this research was to establish whether or not these vermiculites are suitable for use as soil conditioners for crop production. This goal was achieved through characterization. Characterization was essential because the literature shows that vermiculites occur with a wide range of compositions and variable physical and chemical properties (de la Calle and Suquet, 1988; Van Gosen *et al.*, 2005). In addition, vermiculites occur with a substantial amount of accessory minerals, some of which could be of health concern (Whitehouse *et al.*, 2008).

The study involved five samples (marked KL1, KL2, MS, MK1, and MK2) collected from different sites of economic interest in Tanzania and one sample (PB) from the Palabora Vermiculite Mine in South Africa included for comparison. Preliminary X-ray diffraction (XRD) and scanning electron microscopy (SEM) studies done in Chapter 3 revealed that samples KL1, KL2, and MS are essentially vermiculites, whereas MK1 and PB are hydrobiotites. Sample MK2 contains mainly vermiculite with a small amount of hydrobiotite. Hydrobiotite is a mixed-layer mineral consisting of an ordered alternation of mica and vermiculite layers (Brindley *et al.*, 1983). All vermiculites and hydrobiotites contained a number of accessory minerals. Among these minerals are amphiboles, sepiolite, galena, apatite, and monazite.

Amphiboles with fibrous morphology were found in sample MK2. Published data indicates that the amphibole fibres are very hazardous and may cause lung cancer in humans (Peipins *et al.*, 2003; Whitehouse *et al.*, 2008). However, analysis of the fibres by SEM indicated that they are all thicker than 10 μm. Mineral fibres thicker than 3 μm cannot be inhaled and thus, they are not hazardous to the human respiratory system (Cossette, 1984). Hence, this vermiculite is safe to exploit for agriculture application. However, closer follow-up during mining operations is essential to ensure that there are no thinner fibres that can endanger human life.

Sepiolite was found in vermiculites KL1 and KL2 and had also fibrous morphology (Chapter 3). The mineral has never been reported before in vermiculite. Analysis of the fibres by SEM indicated that their length/diameter ratios are more than 3:1. Studies in animals indicate that sepiolite fibres of these dimensions can cause fibrosis very similar to those caused by

crocidolite amphibole, but in humans no health risk has so far been reported (Bellmann *et al.*, 1997, HELA, 2005).

Quantitative XRD analysis in Chapter 3 failed to detect this sepiolite which implies the mineral is present in these vermiculites in a small amount. Thus, the potential health risk to humans is unlikely to be significant. In agriculture, its presence is advantageous as sepiolite is a potential liming material in correcting soil acidity (Singh and Uriyo, 1976). In addition, sepiolite has considerable absorbent and adsorbent properties which make it an ideal material to remediate soils polluted with metals (Álvarez-Ayuso and Garcia-Sànchez, 2003).

Galena was found by SEM in sample MK2, but again it was undetected by XRD. An independent study done by inductively coupled plasma-mass spectrometry (ICP-MS) in Chapter 3 found Pb levels of less than 25 mg/kg confirming the low concentrations of galena. This concentration is far less than the critical level of 300 mg/kg permitted in agricultural soils in many countries (Li *et al.* 2006; Pasquini, 2006). Although Pb is a toxic heavy metal, it is generally immobile in soils, and the fraction taken by plants is less than 10 % of the total concentration (Kabala and Singh, 2001; Ma and Rao, 1997). Dudka and Miller (1999) have shown that children can take up 300 mg/kg of Pb without a marked effect. Thus, it indicates that this vermiculite is safe to use in agriculture.

Apatite and monazite are sources of the essential plant nutrient P. The minerals were found in samples MK1, MK2, and PB. Operational acetic acid extraction done in Chapter 5 established that the P from these samples is extractable and the degree of extractability increases on heating to 400 °C. Maximum extractable amounts found from samples MK1 and MK2 were respectively 335 and 244 mg/kg, whereas from PB it was 77 mg/kg. If I assume that the

operationally extractable fraction is plant-available, then the use of these hydrobiotites and vermiculites could be a potential source of P - fertilization to the soil and an added advantage in crop production.

Pot experiments in Chapter 6 showed that maize uptake of P from soil amended with raw vermiculite MK1 was not as high as estimated by acetic acid extraction. This could be due to slow natural dissolution of P from apatite and monazite (Grimshaw *et al.*, 1989), whereas acetic acid extraction tends to accelerate the process. Slow dissolution of P might have lowered the extractable fraction in solution and reduced its availability and uptake. Kwari and Batey (1991) and Msola *et al.* (2007) found similar results on P extractability and maize assimilation. Further observation established that heating to above 400 °C reduces extractable P.

Follow-up by EPMA found that the P is not fixed in the vermiculite structure as a result of heating as previously thought (Grim, 1953). The EPMA found no detectable P in the vermiculite structure before and after heating. The decrease in extractable P on heating at a temperature more than 400 °C could probably be due to formation of insoluble compounds with components of other accessory minerals or trace elements in apatite and monazite. This is possible because new minerals are forming on high temperature heating of vermiculite (Marcos *et al.*, 2009), which supports metamorphic reaction and re-arrangement of elements.

Characterization of chemical composition presented in Chapter 3 found that some vermiculites contain elevated concentrations of Cr and Ni. The elements occur in comparable levels to those reported in other vermiculites from other countries (Foster, 1963; Frank and Edmond, 2001). The levels of Cr and Ni found in some samples from Tanzania were above the critical

concentrations of 600-800 mg/kg Cr and 75 mg/kg Ni permitted in agricultural soils in some countries (Pasquini, 2006; Alloway, 1999).

It is well known that Cr and Ni can be toxic and / or essential to living organisms depending on their oxidation state and availability. For instance, Cr(III) is essential to humans and animals for glucose and lipid metabolism, whilst Cr(VI) is a highly toxic carcinogen and can cause death if ingested in large doses (Zayed and Terry, 2003). In plants, both Cr species are not essential and may cause toxicity and/or may inhibit the uptake of essential nutrients because of their structural similarity (Sharma and Pant, 1994). Nickel is an essential micronutrient to higher plants, but in humans and animals may lead to deoxyribonucleic acid (DNA) fragmentation, cell death, and leukemia (Jia and Chen, 2008).

Although Cr and Ni occur in elevated concentrations in the studied samples, a DTPA extraction study done in Chapter 5 revealed that they are non-extractable. Significant extractable fractions were observed only when heated at 400-600 °C. At 400-600 °C, extractable Cr from samples MK1 and MK2 surpassed the maximum level of 5 mg/kg permitted in agricultural soils (Adriano, 1986). However, extractable Ni from all the studied samples did not reach the maximum level of 15 mg/kg that can cause plant toxicity in soils (Papadopoulos *et al.*, 2007).

Follow-up by pot experiments conducted in Tanzania (Chapter 6) found insignificant uptake of Cr and Ni in aboveground maize tissues grown on soil-added, pre-heated (600 °C) and unheated vermiculite MK1. This observation agrees with the DTPA results found in Chapter 5 with the exception of the uptake of Cr from soil-added, pre-heated MK1. The DTPA results showed a high Cr extraction from pre-heated MK1. Insignificant maize uptake of Cr obtained

from pre-heated MK1 is regarded as a sign of poor translocation of Cr to aboveground maize tissues. Dudić *et al.* (2007) reported similar findings. This could be due to the fact that Cr lacks specific plant-uptake mechanisms (Shanker *et al.*, 2005). If Cr is taken up by plants most of it is retained in the roots (Zayed *et al.*, 1998). Accumulation in the roots is possible because it is immobilized in the vacuoles of the root cells and rendered less toxic (Shanker *et al.*, 2004). Insignificant uptake of Cr and Ni by maize is a positive indicator that vermiculites from Tanzania are safe to use as soil improvers for crop production.

The physical and chemical properties of vermiculites from Tanzania with respect to their potential agronomic applications were assessed in Chapter 4. Heating vermiculite samples KL1, KL2, and MS up to 800 °C did not cause a marked decrease in their bulk densities as compared to those composed of hydrobiotite (MK1, MK2, and PB). The reason is that hydrobiotites expand more than vermiculites (Justo *et al.*, 1989). Heating at 600 °C provided a minimum bulk density for samples MK1 and MK2 from Tanzania of about 200 kg/m^3. Further heating did not lead to significant decrease in their bulk densities. Thus, heating at 600 °C is quite sufficient to get the minimum bulk densities for vermiculites and hydrobiotites from Tanzania for agricultural application.

The pH of the studied vermiculites and hydrobiotites from Tanzania is slightly alkaline (pH 7.7-7.8) and remained unchanged on heating to 600 °C (Chapter 4). This was also the case for sample PB from South Africa. Further heating to 800 °C increased the pH of KL1, KL2, and PB to 9.8. This increase in the pH makes the exfoliated products strongly alkaline (Tan, 1996) and unfavourable for most crops and soil micro-organisms. The favourable pH for availability of plant nutrients in soils is between 5.5 and 7 (Brady and Weil, 2002). Thus, to make the best use of vermiculites KL1 and KL2 from Tanzania, they should preferably not be heated to a

temperature more than 600 °C. Since all vermiculites and hydrobiotites from Tanzania are slightly alkaline, the preference should be not to add them to soils that are alkaline unless amended with other materials.

The CECs of vermiculites were found to range between 120 and 148 $cmol_{(+)}/kg$ for samples KL1, KL2, and MS, while for sample MK2 it is 104 $cmol_{(+)}/kg$ (Chapter 4). These CECs are high and fall within the range of good quality vermiculites for agricultural applications (Van Straaten, 2002). The high CEC of the Tanzanian vermiculites gives them a recommendable ability to retain plant nutrients in soils from leaching during irrigation. In addition, the high CEC is a sign of their suitability as a growing medium with good fertility potential and positive response to fertilizer application (Landon, 1991). The CECs for hydrobiotite samples MK1 and PB are 23 and 14 $cmol_{(+)}/kg$ respectively. The CEC of hydrobiotite is less because it is contributed mainly by the vermiculite component (Zhu *et al.*, 2008). Thus, based on the CEC, vermiculites have much more potential for retaining plant nutrients than do hydrobiotites.

Although vermiculites from Tanzania have high CECs, heating to above 600 °C should be avoided as it reduces their CECs by more than 90 %. Most hydroxyl ions are lost when heated to a temperature of more than 600 °C (Barshad, 1950; Walker, 1951). The loss of hydroxyl ions reduces the negative charge and the ability of vermiculites to adsorb cations. The consequence is a sharp decrease in the CECs of vermiculites. Hydrobiotites are less affected due to the increase in the availability of exchangeable K^+ from mica on heating. In addition, the presence of exchangeable K^+, a cation with a large ionic radius, retards the release of hydroxyl ions from hydrobiotites (Marcos *et al.*, 2009). This observation is in agreement with the results of mass loss found in Chapter 4.

Although vermiculites from Tanzania can hold a substantial amount of plant-available water, analysis of water release characteristic curves in Chapter 4 has shown that their ability is less as compared to vermiculite PB from Palabora. The low rate of expansion and disintegration in response to heating as well as the presence of high iron content in some samples were among the factors noted to affect their ability to hold more plant-available water. Some samples expanded on heating, but the ability to adsorb and release plant-available water was found to decrease. This was interpreted as a sign of forming more closed pores rather than open pores as reported by Gordeeva *et al.* (2002). Closed pores hinder adsorption and release of plant-available water (Aristov *et al.*, 2000).

Glasshouse pot experiments and field studies were conducted in Tanzania to assess performance of vermiculite as a soil improver for crop production. Maize, the main staple crop in Tanzania, was used as a test crop. Raw (unheated) and pre-heated vermiculites MK1 at 600 ^{o}C were used as a soil improver. Vermiculite was found to promote maize vegetative growth and, consequently, increase in dry matter yields (Chapter 6). In addition, vermiculite enhanced the availability and, thus, the uptake of N, P, K, Mg, and Ca by maize as compared to the soil with no vermiculite (control). The increase in vegetative growth and nutrient uptake was probably due to the improvement in water retention and CEC (Suganya and Sivasamy, 2006). Availability of adequate soil water might have promoted solubility, mobility, and absorption of nutrients by maize plant (Singh and Singh, 2004).

In comparing raw and expanded vermiculites, raw vermiculite contributed exchangeable Mg and Ca as well as P from apatite and monazite to maize uptake, whilst expanded vermiculite contributed exchangeable K to maize uptake. Vegetative growth and uptake of P, Mg and Ca were higher in maize grown on soil with 10 % raw vermiculite than from soil with 10-30 %

expanded vermiculite, whereas the highest vegetative growth and nutrient uptake was from soil with 50 % expanded vermiculite. The main setback with the raw vermiculite was that it did not enhance adequately the availability of N and K to the optimum levels reported by Randall *et al.* (1977) and Melsted *et al.* (1969).

Furthermore, use of more than 10 % raw vermiculite was found to reduce the uptake of N, P, and Mg. Since there was no leaching during irrigation, this decrease was probably caused by fixation as found in Chapter 4 for ammonium. Contrary to the raw vermiculite, the uptake of N, P, K, Mg, and Ca increased with the amount of expanded vermiculite added to the soil (Table 6.5). More likely, expanded vermiculite does not fix these nutrients, but enhances their availability. Migration of the interlayer cations into the hexagonal voids of the tetrahedral sheet and their fixation as a result of heating (Walker, 1956) seems to block expanded vermiculites from fixing more cations. In addition, loss of hydroxyl ions on heating (Marcos *et al.*, 2009) reduces the negative charges and, consequently, the ability of expanded vermiculite to attract and fix cations.

In most tropical countries including Tanzania, after N, P is the most frequently deficient element that leads to poor crop yields (Kwabiah *et al.*, 2003). Application of vermiculite MK1 to the field under the Tanzanian climate revealed that it has a better ability to retain P-fertilizer for more than 90 d and to fertilize the soil with P from accessory minerals apatite and monazite (Chapter 7). Retention and fertilization of P increased with the amount of vermiculite added to the soil and the burial depth. A maximum of 140 % of the applied P was retained and an additional amount was fertilized by 50 % by volume of raw vermiculite added to the soil. Normal plant uptake of P from soils applied inorganic P-fertilizer is between 10 and 40 % of the original amount (Aulakh and Garg, 2007), which is far less than the amount of

P retained in soil with added vermiculite MK1. The amount of P retained and fertilized is quite sufficient for growing crops.

In the control, which comprised a sandy soil with no vermiculite, more than 70 % of the applied 160 mg/kg P as triple super phosphate was lost by leaching. Leaching of P from sandy soils is facilitated by the large number of macropores and efficient drainage (Haygarth and Jarvis, 1999). Ozanne *et al.* (1961) reported a loss of about 81 % of P in a sandy soil through leaching below the plant roots in Australia.

The good recovery of P obtained in this study is an additional indication of the suitability of vermiculite from Tanzania as a soil improver. Use of vermiculite as a soil improver may guarantee the availability of adequate P for plant growth and increase in crop yields. What is not known from this study, and which requires further follow-up, is the long-term dynamics of the P which is retained and fertilized by vermiculite and its availability to crops.

Further observation revealed that the addition of vermiculite to the soil does not adequately enhance the retention of N and K for more than 90 d. More than 90 % of the N and 52 % of the K applied as inorganic fertilizers to the soil were not recovered. This could be due to fixation, leaching, and / or loss as gases for N (Cai *et al.*, 2002; Conti *et al.*, 2001). From this study it is clear that vermiculites from Tanzania have no ability to adequately retain N and K in a sandy soil for more than three months under tropical condition.

Conclusions

- The study has established that the samples from Tanzania are not all vermiculites, some are hydrobiotites. All contain a number of accessory minerals, among them are sepiolite, apatite, and monazite. None of the accessory minerals are hazardous to living organisms and the environment. Thus, these vermiculites and hydrobiotites are safe to exploit for agricultural use. Apatite and monazite in the studied samples proved to be the potential source of P-fertilization in soils. Sepiolite was found for the first time in some vermiculites in a small amount. Its presence is an added advantage as it can assist in reducing soil acidity and enhancing the adsorption and absorption properties of vermiculites when added to the soil.

- Although Cr and Ni are present in elevated concentrations in some vermiculites and hydrobiotites, the study has revealed that they are insignificantly plant-available and do not inhibit the uptake of essential plant nutrients. Thus, it is safe to use these vermiculites and hydrobiotites with elevated levels of Cr and Ni as soil improvers for crop production.

- All vermiculites have a high CEC and, thus, they are suitable as growing media with good fertility potential and positive response to fertilizer application. In addition, their high CEC gives them a recommendable ability to retain plant nutrients in soils from leaching during irrigation. However, the CECs of hydrobiotites are relatively lower than those of vermiculites.

- All vermiculites and hydrobiotites from Tanzania are slightly alkaline and their pH is not affected by heating to 600 °C. The pH they possess is suitable for crop production, but to provide a conducive environment for micro-organisms and to optimize the availability of plant nutrients, they should preferably be applied to non-alkaline soils.

- Heating vermiculites to a temperature of more than 600 °C should be avoided as it reduces the CEC by 90 %. In addition, in some samples it makes the pH strongly alkaline and unfavourable for most crops and soil micro-organisms. Similarly, extractable P is significantly reduced and the bulk density does not change much.

- Although vermiculites from Tanzania can adsorb and release a substantial amount of plant-available water, this ability is generally low when compared to vermiculite PB from Palabora. In part, this is caused by their low rate of expansion and disintegration in response to heating as well as their difference in mineralogical and chemical compositions.

- Use of the Tanzanian vermiculite MK1 as a soil conditioner has revealed that it has recommendable qualities of promoting maize vegetative growth, dry matter yield, and nutrient uptake. Vegetative growth, dry matter yield, and nutrient uptake increased with the amount of vermiculite added to the soil. Pre-heated MK1 at 600 °C performed better than unheated vermiculite in enhancing the uptake of N and K. The P was significantly retained and fertilized by the application of vermiculite as compared to K and N. The amount of P retained and fertilized after 90 d was sufficient for growing crops. Thus, use of this vermiculite would provide relief to farmers on the amount of P applied to the soil.

Further research

It is clear from this research that further studies are required to complement what has so far been found during characterization of vermiculites from Tanzania for agricultural applications. The following studies are recommended:

- Field trials by growing crops to maturity and assessing yields following the application of vermiculites to the soil were not done in Tanzania due to the time constraints. Since vermiculites and hydrobiotites differ in their CECs and mineralogy, field performance could also be different. It is, thus, worthy to assess both of them by conducting a series of field trials to establish their suitability under the Tanzanian climate. Crops in Tanzania are not grown only on sandy soils; thus, field trials are essential to ascertain the performance of vermiculites and hydrobiotites on other soils. The outcome of these trials may widen the scope of utilizing vermiculites and hydrobiotites in Tanzania.

- The study has established that Tanzanian vermiculites and hydrobiotites have elevated levels of Cr and Ni, but the elements are not plant-available. Regular application of these vermiculites and hydrobiotites to the ground will continue to add these potentially toxic metals to the soil. What is not known is the fate of Cr and Ni in the ground after complete decomposition of the applied vermiculites or hydrobiotites. This is worthy of further investigation.

- Although the fibres of amphibole in sample MK2 are too thick for human inhalation, further studies are recommended to ascertain whether the whole deposit has no thinner fibres that can endanger human life.

- Vermiculites and hydrobiotites are bulk materials; as such the economics of using these materials needs to be known. To start with, it is essential for the minimum amount required per hectare to be established and the operational costs involved from mining to application on the field assessed critically. In addition, after applying these vermiculites and hydrobiotites to the soil, the study needs to establish the frequency of re-applying on the same field.

- It is also essential to establish the actual available quantity of vermiculite for each deposit. This will give an indication for their sustainability for commercial exploitation.

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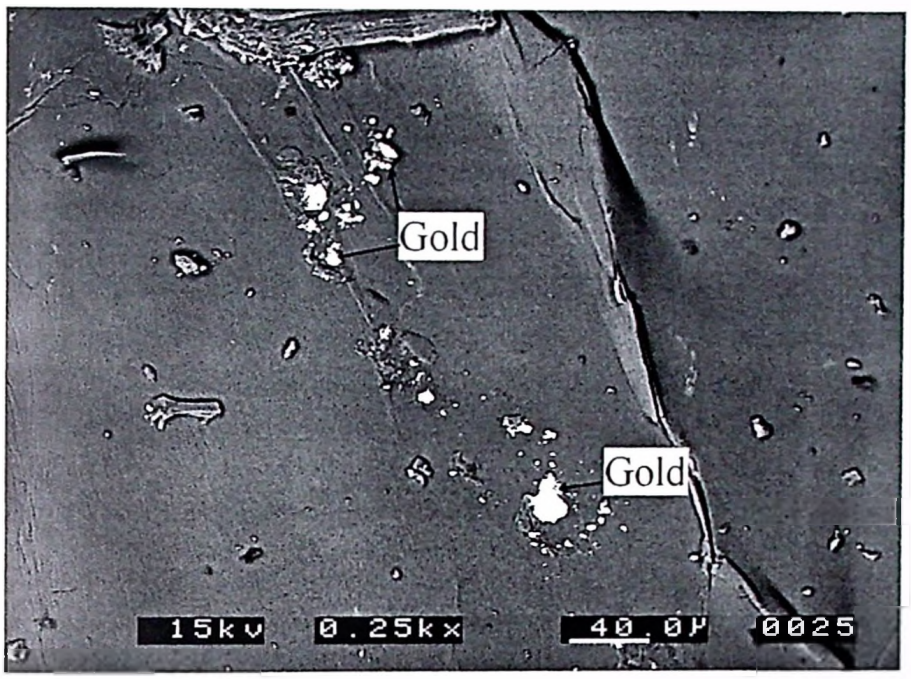
APPENDICES

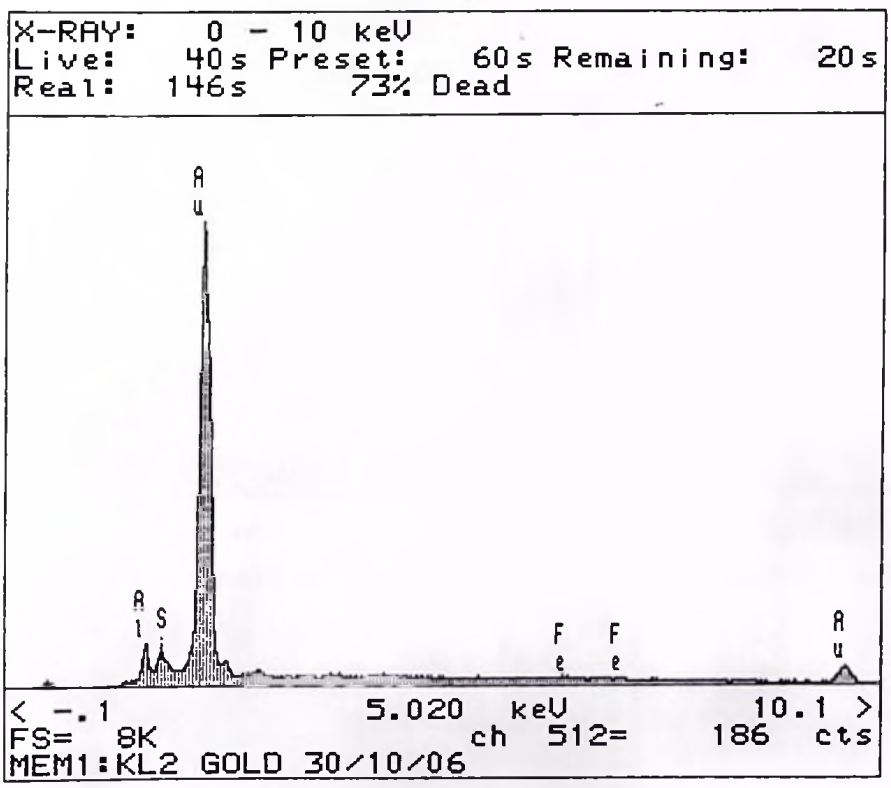
Appendix 3.1. Procedure for preparation and XRD scanning of oriented mineral specimens

Highly oriented mineral specimens were prepared by McCrone milling 3 g of samples for 12 minutes to reduce the particle size. The samples were mixed with water at a ratio of between 4:1 and 5:1 (water: solid) before milling. The resulting slurry was oven-dried overnight at 105 °C, and followed by three washes with 1*M* $MgCl_2$, to obtain homoionic Mg-saturated clay fractions. Each $MgCl_2$ wash involved shaking for 15 minutes by Clifton shaker. After shaking, the samples were centrifuged for 3 minutes using an Accuspin 400. Excess chloride was removed by washing 4 times with de-ionized water. The slurry obtained was pipetted onto glass slides and also onto 'Macor' stubs. The samples were left to settle and dry undisturbed at room temperature for 24 hours. Three types of XRD patterns were acquired from the oriented Mg-saturated samples, namely air-dried, ethylene glycolated and heated patterns. All patterns of oriented Mg-saturated samples were recorded from 3-45° 2θ for 14 minutes using Ni-filtered Cu-*Kα* radiation on a Philips X'Pert Pro diffractometer with 1/32° divergence slit and 1/16° anti-scatter slit, using a position sensitive X-celerator detector. Air-dried and gylcolated patterns were recorded on the specimens mounted on glass slides. Heated patterns were recorded *in situ* on the specimens mounted on 'Macor' discs at 25, 50, 100, 200, 300, 400, 500 and 600 °C, using an Anton Paar XRK 900 furnace stage. Temperature was raised at a rate of 40 °C per minute, and 5 minutes rest time was allowed following temperature stabilization prior to each scan.

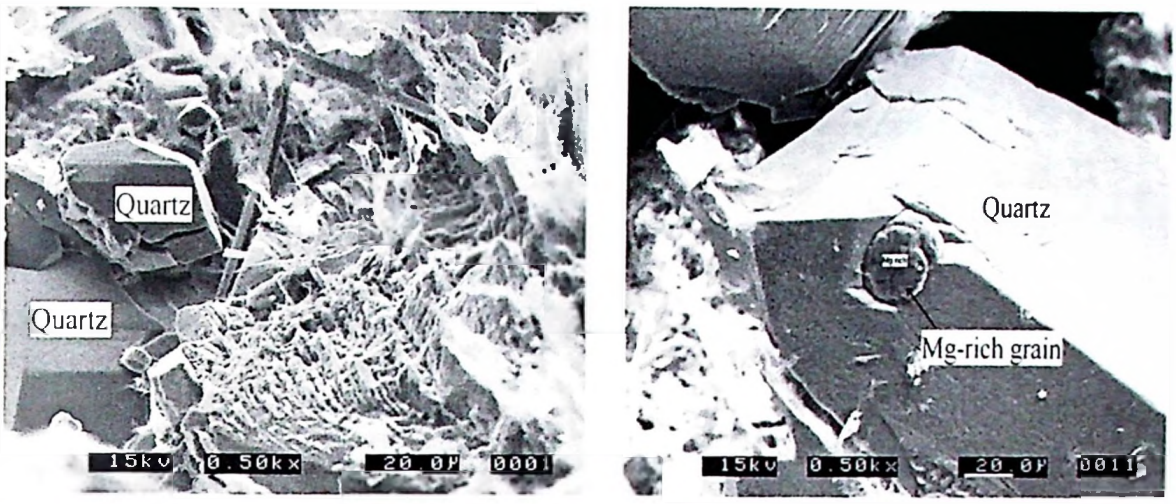
Appendix 3.2. SEM micrographs and EDS spectra of some accessory minerals from vermiculite and hydrobiotite samples



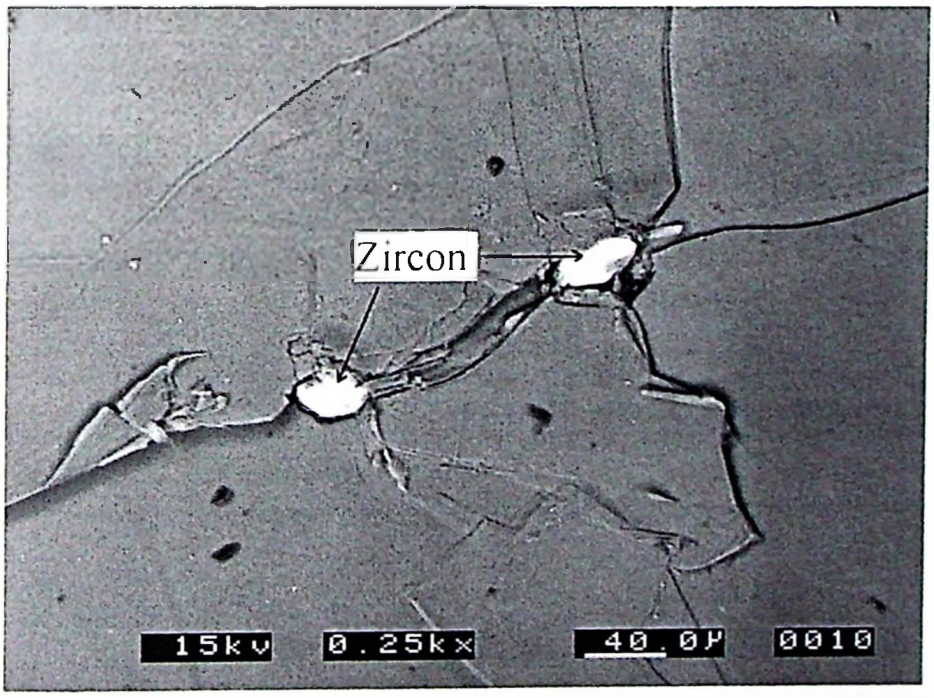
Gold (white) in vermiculite sample KL2. It is very rare for gold to occur in vermiculite. The sample was not contaminated during preparation because it was carbon coated before scanning.



An EDS spectrum of gold from sample KL2

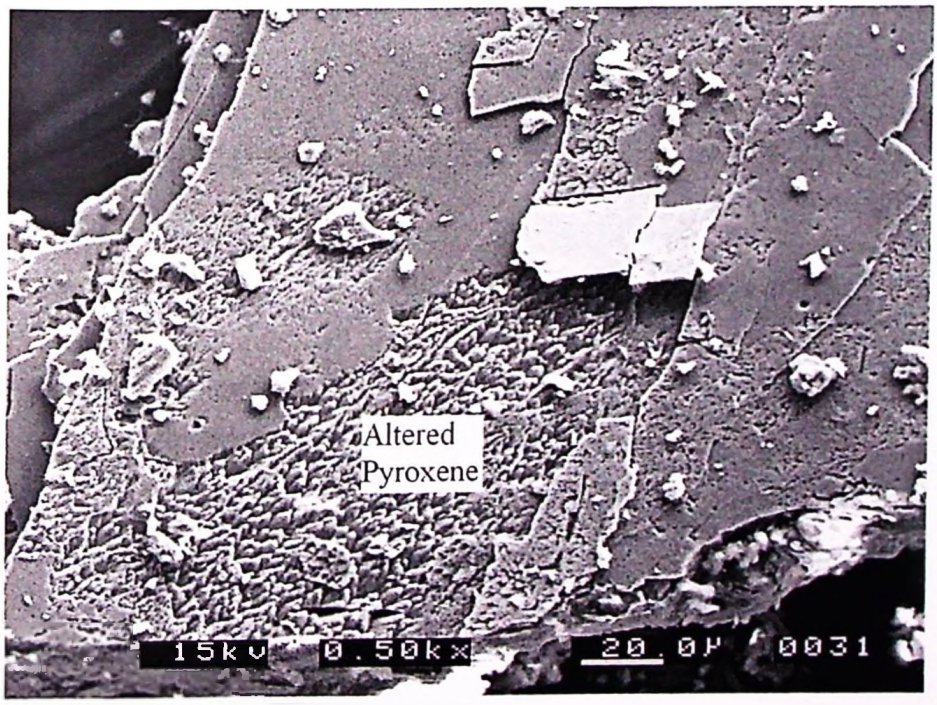


Quartz crystals in sample KL1 (Left) with Mg-rich grain embedded on one of the crystals (right). It indicates that Mg is not only in vermiculite structure, but some are contributed by accessory minerals.

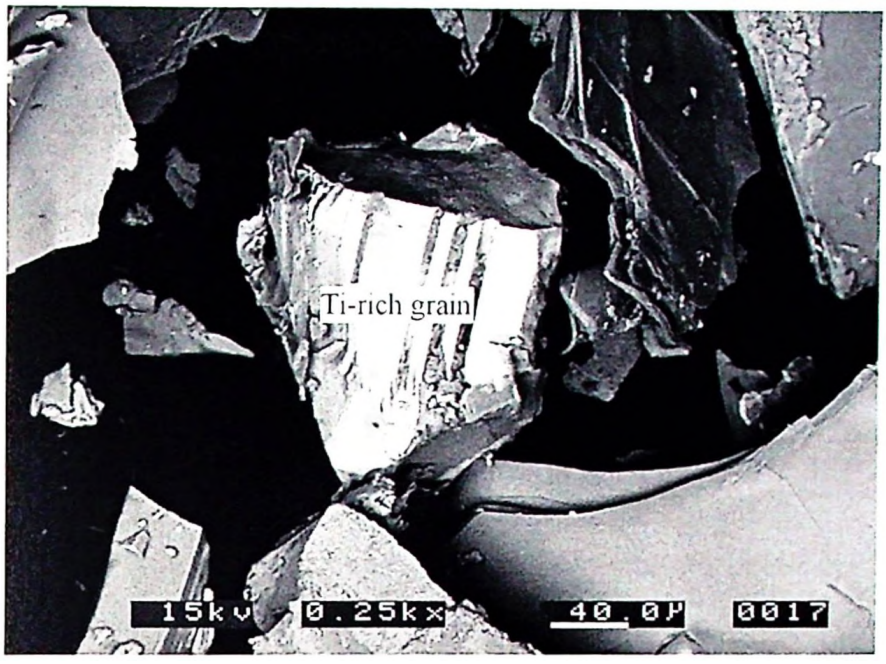


Zircon crystals embedded in micro-fracture of vermiculite KL1. The zircon in the studied samples could be the source of Zr in the ICP-MS results presented in Chapter 3.

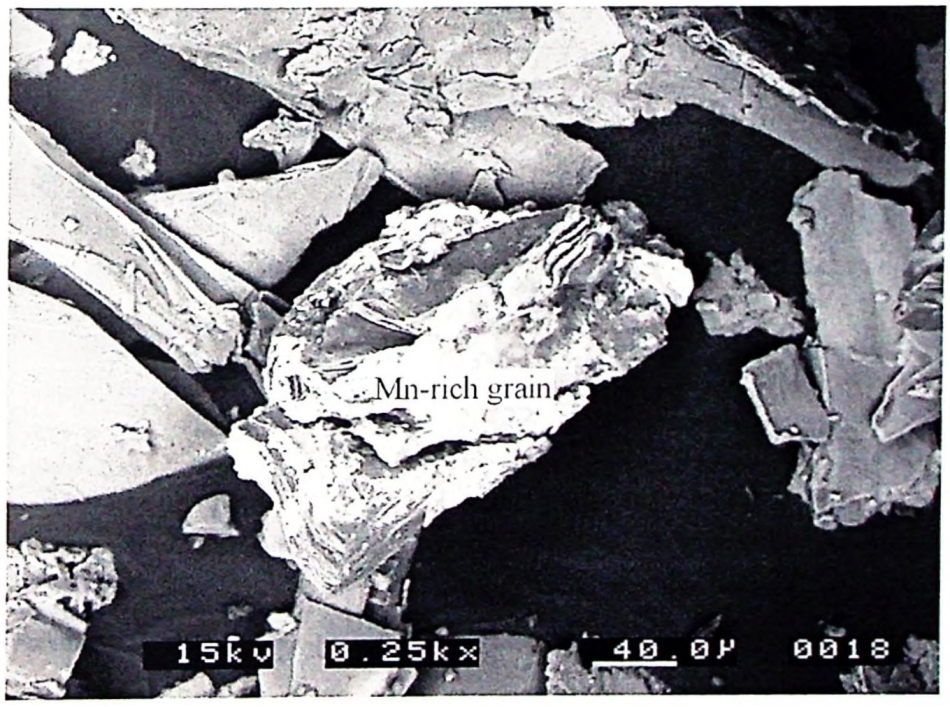
Sepiolite fibres attached on a quartz grain in sample KL1. The fibres pose a potential health risk if inhaled.



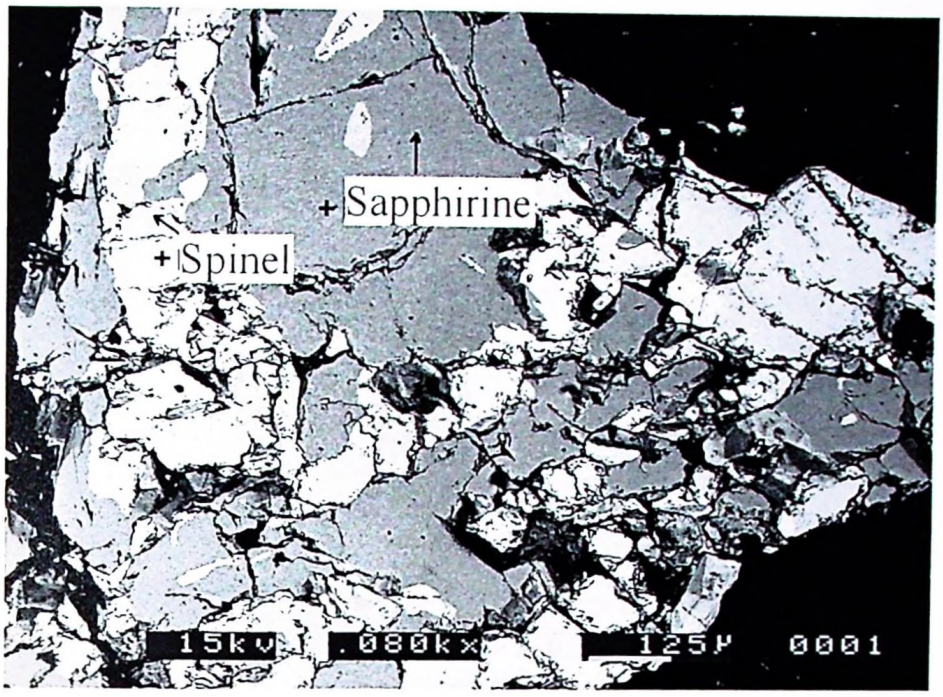
SEM micrograph showing an alteration of pyroxene from sample PB. The EPMA results confirmed the mineral to be diopside. The 'needle-like texture' could be a sign of transformation of diopside to chrysolite (Barrese *et al.*, 1997). Chyrsotile can form as a result of hydrothermal alteration of diopside.

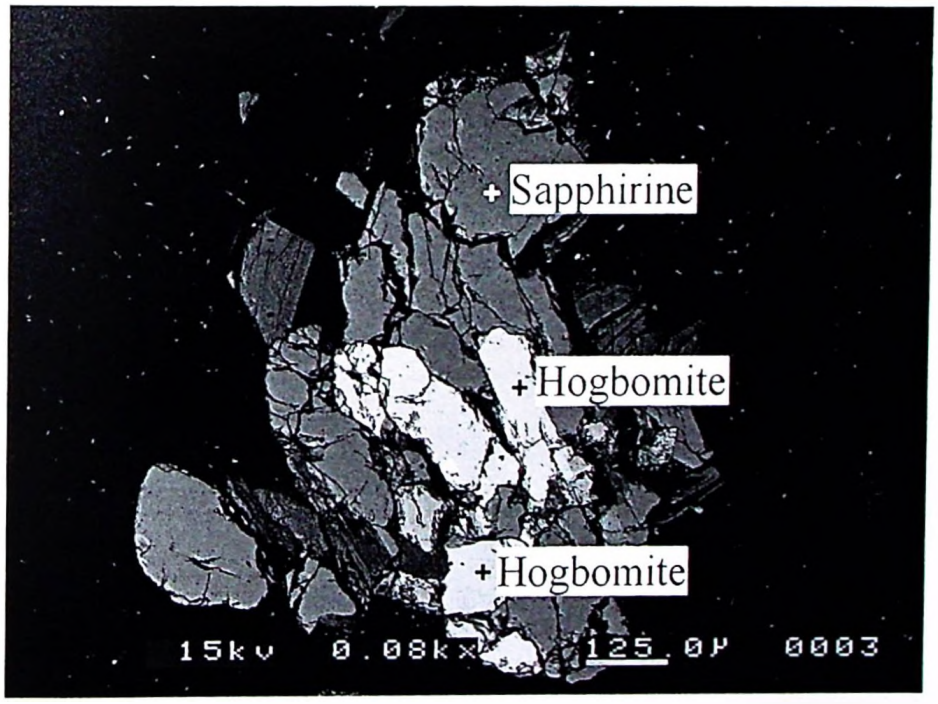


Ti-rich grain (centre) surrounded by several particles of vermiculite MS

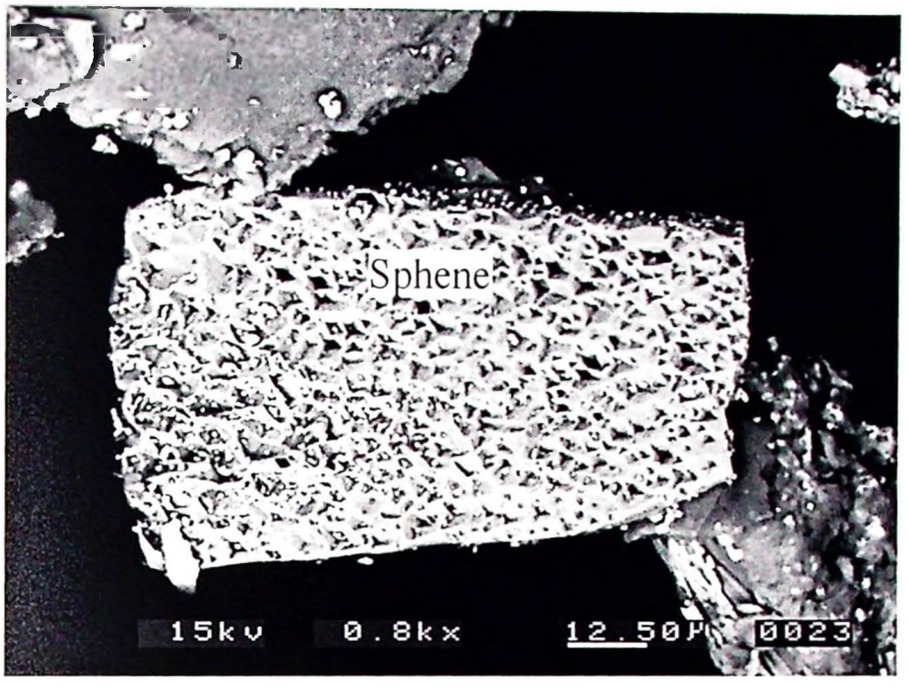


A mineral rich in Mn (centre) in vermiculite sample MS. The mineral could be a carbonate or an oxide.



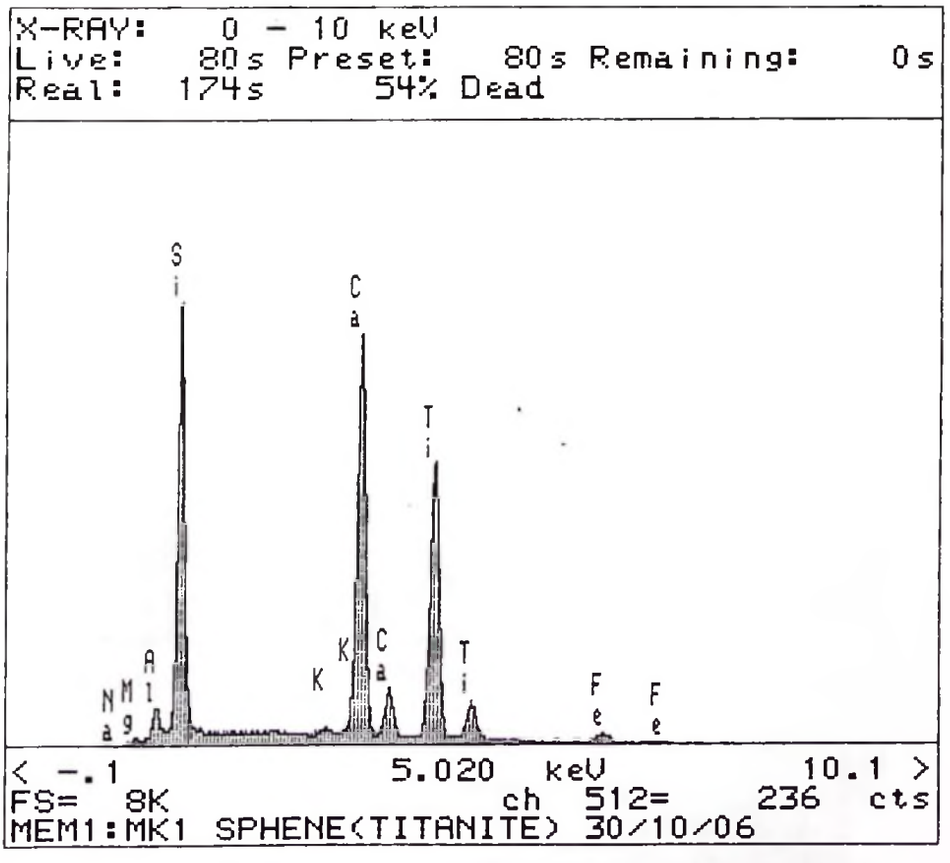


Sapphirine, hogbomite, and spinel minerals in vermiculite sample MS. These are Al-rich minerals and could be the sources for the elevated concentrations of Al in the EPMA and ICP-MS results. The chemical formulae are given in the Chapter 3

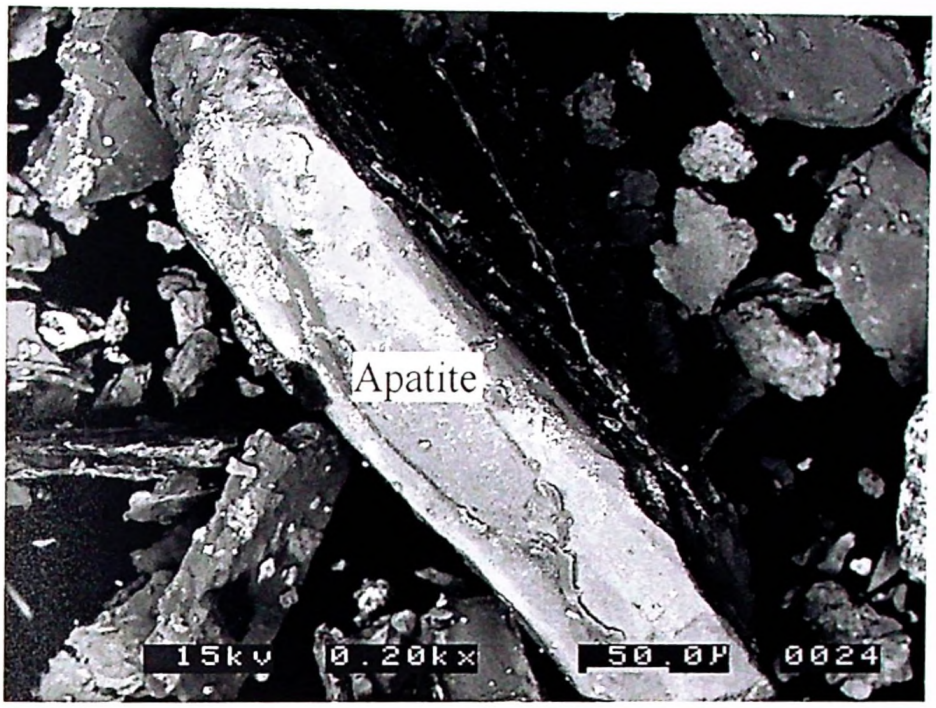


A porous sphene in sample MK1, part of the mineral has been dissolved.

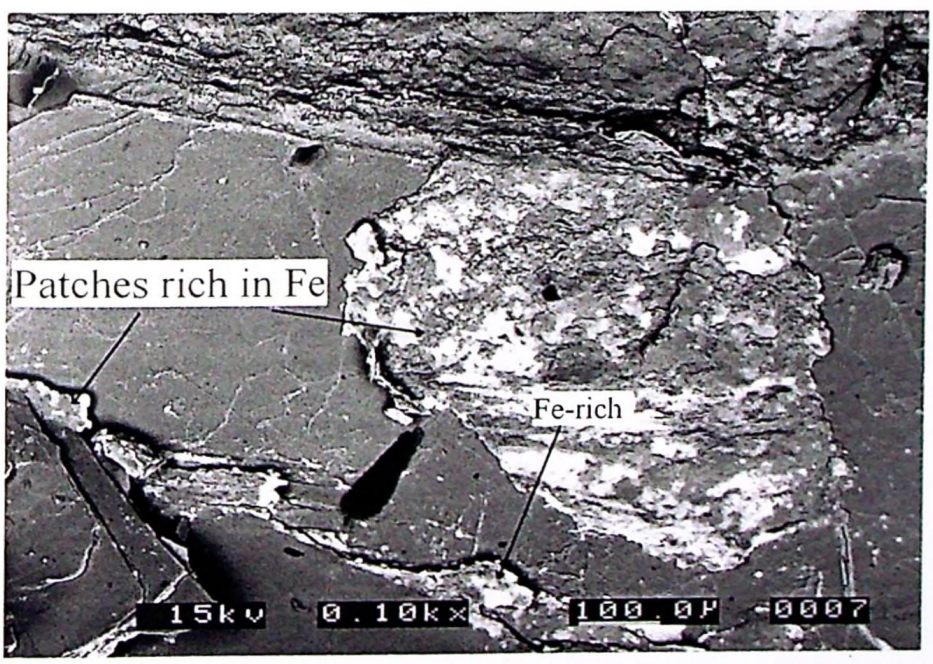
This heterogeneity is interpreted as a sign of differential weathering.



An EDS spectrum of sphene from sample MK1. Sphene is also known as titanite



Apatite with monazite coating (white patches on the surface) in sample MK1.



Fe-rich areas in vermiculite sample MK2 probably representing iron oxide or hydroxide. They show a sign of weathering.

Appendix 3.3. Correlation matrix of some elements in the studied samples

Element	Fe	Mg	Ca	K	Ti	P	S	As	Pb	Zn
Mg	-0.821									
	0.045									
Ca	0.926	-0.943								
	0.008	0.005								
K	0.543	-0.137	0.338							
	>0.050	>0.050	>0.050							
Ti	0.923	-0.940	0.951	0.373						
	0.009	0.005	0.003	>0.050						
P	0.942	-0.937	0.995	0.322	0.961					
	0.005	0.006	<0.001	>0.050	0.002					
S	0.924	-0.717	0.817	0.659	0.909	0.839				
	0.008	>0.050	0.047	>0.050	0.012	0.037				
As	0.919	-0.940	0.970	0.237	0.972	0.986	0.843			
	0.009	0.005	0.001	>0.050	0.001	<0.001	0.035			
Pb	0.737	-0.865	0.857	0.009	0.889	0.880	0.724	0.934		
	>0.050	0.026	0.029	>0.050	0.018	0.021	>0.050	0.006		
Zn	0.965	-0.858	0.939	0.329	0.891	0.959	0.809	0.942	0.779	
	0.002	0.029	0.005	>0.050	0.017	0.003	0.050	0.005	>0.050	
Mo	0.939	-0.850	0.966	0.524	0.887	0.952	0.821	0.891	0.711	0.920
	0.006	0.032	0.002	>0.050	0.018	0.003	0.045	0.017	>0.050	0.009

Values in the first row for each element represents correlation coefficients, whereas in the second row indicate significant levels (P-values). The elements Al, Ni, Hg, Nb, Na, Cd, Zr, and Cu were omitted for lack of significant correlation with other elements.

Appendix 3.3. Continuing

Element	Fe	Mg	Ca	K	Ti	P	S	As	Pb	Zn
Cr	0.757	-0.734	0.809	-0.048	0.743	0.847	0.604	0.877	0.869	0.868
	>0.050	>0.050	>0.050	>0.050	>0.050	0.033	>0.050	0.022	0.025	0.025
Sn	0.882	-0.818	0.842	0.117	0.828	0.882	0.716	0.905	0.782	0.957
	0.020	0.047	0.035	>0.050	0.042	0.020	>0.050	0.013	>0.050	0.003
Ba	0.969	-0.869	0.971	0.547	0.943	0.968	0.902	0.928	0.771	0.929
	0.001	0.025	0.001	>0.050	0.005	0.002	0.014	0.008	>0.050	0.007
Rb	0.383	0.043	0.157	0.982	0.200	0.139	0.524	0.053	-0.164	0.156
	>0.050	>0.050	>0.050	<0.001	>0.050	>0.050	>0.050	>0.050	>0.050	>0.050
Sr	0.931	-0.941	0.976	0.284	0.981	0.990	0.864	0.999	0.923	0.942
	0.007	0.005	0.001	>0.050	0.001	<0.001	0.026	<0.001	0.009	0.005
Sc	0.646	-0.928	0.794	0.148	0.847	0.770	0.618	0.775	0.718	0.636
	>0.050	0.008	>0.050	>0.050	0.033	>0.050	>0.050	>0.050	>0.050	>0.050
V	0.628	-0.953	0.805	-0.026	0.839	0.790	0.558	0.811	0.789	0.670
	>0.050	0.003	>0.050	>0.050	0.037	>0.050	>0.050	0.050	>0.050	>0.050
U	0.927	-0.940	0.984	0.264	0.967	0.995	0.838	0.997	0.919	0.950
	0.008	0.005	<0.001	>0.050	0.002	<0.001	0.037	<0.001	0.010	0.004
Y	0.919	-0.954	0.983	0.241	0.970	0.993	0.828	0.998	0.921	0.945
	0.010	0.003	<0.001	>0.050	0.001	<0.001	0.042	<0.001	0.009	0.004
La	0.924	-0.945	0.994	0.266	0.950	0.998	0.804	0.986	0.887	0.956
	0.009	0.004	<0.001	>0.050	0.004	<0.001	0.050	<0.001	0.018	0.003
Ga	0.990	-0.842	0.948	0.451	0.931	0.967	0.903	0.954	0.808	0.980
	<0.001	0.035	0.004	>0.050	0.007	0.002	0.014	0.003	0.050	0.001
Mn	0.931	-0.824	0.868	0.253	0.850	0.900	0.768	0.903	0.733	0.979
	0.007	0.044	0.025	>0.050	0.032	0.014	>0.050	0.014	>0.050	0.001

Values in the first row for each element represents correlation coefficients, whereas in the second row indicate significant levels (P-values). The elements Al, Ni, Hg, Nb, Na, Cd, Zr, and Cu were omitted for lack of significant correlation with other elements.

Appendix 3.3. Continuing

Element	Mo	Cr	Sn	Ba	Rb	Sr	Sc	V	U	Y	La	Ga
Cr	0.710											
	>0.050											
Sn	0.772	0.900										
	>0.050	0.014										
Ba	0.985	0.724	0.799									
	<0.001	>0.050	>0.050									
Rb	0.360	-0.216	-0.051	0.381								
	>0.050	>0.050	>0.050	>0.050								
Sr	0.906	0.855	0.892	0.944	0.102							
	0.013	0.030	0.017	0.005	>0.050							
Sc	0.700	0.441	0.581	0.731	0.002	0.785						
	>0.050	>0.050	>0.050	>0.050	>0.050	>0.050						
V	0.674	0.560	0.658	0.700	-0.185	0.810	0.977					
	>0.050	>0.050	>0.050	>0.050	>0.050	>0.050	0.001					
U	0.918	0.874	0.895	0.945	0.080	0.998	0.770	0.802				
	0.010	0.023	0.016	0.004	>0.050	<0.001	>0.050	>0.050				
Y	0.910	0.865	0.897	0.938	0.057	0.997	0.794	0.828	0.999			
	0.012	0.026	0.015	0.006	>0.050	<0.001	>0.050	0.042	<0.001			
La	0.942	0.862	0.887	0.952	0.081	0.986	0.774	0.805	0.994	0.994		
	0.005	0.027	0.018	0.003	>0.050	<0.001	>0.050	>0.050	<0.001	<0.001		
Ga	0.937	0.838	0.910	0.966	0.281	0.960	0.640	0.647	0.960	0.951	0.955	
	0.006	0.037	0.012	0.002	>0.050	0.002	>0.050	>0.050	0.002	0.003	0.003	
Mn	0.832	0.847	0.987	0.853	0.088	0.897	0.606	0.652	0.900	0.900	0.899	0.940
	0.040	0.037	<0.001	0.031	>0.050	0.015	>0.050	>0.050	0.015	0.015	0.015	0.005

Values in the first row for each element represents correlation coefficients, whereas in the second row indicate significant levels (P-values). The elements Al, Ni, Hg, Nb, Na, Cd, Zr, and Cu were omitted for lack of significant correlation with other elements.

Appendix 3.4. Results of the elements in the reference standards used during ICP-MS analysis of vermiculite samples at the OMAC Laboratories Ltd. Assigned value, certified value, and measured value for Al, Fe, Mg, Ca, K, Na, Ti, P, and S are in %, whilst for the remaining elements are reported in mg/kg.

Element	Assigned value	Certified value		Measured value			% Recovery		
	ICP-5	SY-4	Till-4	ICP-5	SY-4	Till-4	ICP-5	SY-4	Till-4
Al	1.41	10.95	7.62	1.43	11.08	7.55	101	101	99
Fe	2.69	4.34	3.94	2.77	4.34	3.93	103	100	100
Mg	1.34	0.33	0.76	1.41	0.33	0.84	105	101	111
Ca	9	na	na	8.64	0.04	0.17	96		
K	0.29	1.38	2.70	0.27	1.41	2.49	93	102	92
Na	0.16	5.27	1.82	0.15	5.33	1.75	96	101	96
Ti	10	na	na	10.22	0.36	1.33	102		
P	0.059	0.057	0.087	0.061	0.057	0.102	104	101	118
S	2.80	na	na	2.88	0.02	0.08	103		
Cu	950	7	237	951.7	4.6	258.8	100	66	109
As	630	na	111	660.9	0.9	110.2	105		99
Cd	9	na	na	8.64	0.04	0.17	96		
Pb	1015	10	50	981.8	10.9	51.5	97	109	103
Zn	3175	93	70	3198.7	106.3	76.7	101	114	110
Mo	44	na	16	44.87	1.00	16.77	102		105
Ni	188	9	17	185.9	9.7	18.5	99	108	109
Cr	na	12	53	463	12	53		97	100
Zr	na	517	385	32	66	136		13	35
Sn	13	7.1	na	12.4	8.6	13.9	95	121	
Ba	400	340	395	442	340	405	111	100	102
Nb	na	16	15	22.01	13.00	13.11		81	87
Rb	120	55	161	100.6	59.2	186.9	84	108	116
Sr	160	1191	109	153	1195	118	96	100	108
Sc	10	1.1	10	11.8	1.1	10.9	118	99	109
V	103	8	67	101	5	64	98	57	96
U	40	0.8	5.0	36.1	0.5	3.5	90	59	70
Y	14	119	33	15.2	119.6	14.1	109	101	43
Th	8	1.4	17.4	8.1	1.4	16.0	101	100	92
La	63	58	41	60.7	59.0	40.8	96	102	99
Ga	12	35	na	12.6	36.1	18.0	102	103	
Mn	1138	836	490	1139	836	534	100	100	109
Hg	na	na	0.039	11.55	0.03	0.04			100

Na = not provided

Appendix 4.1. Analysis of variances for mass loss, bulk density, pH, plant available water, CEC, and exchangeable cations for the studied samples

	df	Ss	Ms	F-value	P	NoM	SE
Mass loss							
Vermiculite	5	674.5	134.9	254.5	<0.001	15	0.2
Temperature	4	2211.7	552.9	1043.2	<0.001	18	0.2
Interaction	20	219.4	11.0	20.7	<0.001	3	0.4
Error	60	31.8	0.5				
Total	89	3137.4					
Coefficient of variation: 8.05 %							
Bulk density							
Vermiculite	5	1343994.1	268798.8	1596.2	<0.001	15	3.4
Temperature	4	2725310.0	681327.5	4045.8	<0.001	18	3.1
Interaction	20	1424831.3	71241.6	423.0	<0.001	3	7.5
Error	60	10104.2	168.4				
Total	89	5504239.6					
Coefficient of variation: 2.24 %							
The pH							
Vermiculite	5	3.69	0.74	38.84	<0.001	15	0.04
Temperature	4	14.07	3.52	185.15	<0.001	18	0.03
Interaction	20	8.49	0.42	22.33	<0.001	3	0.08
Error	60	1.14	0.02				
Total	89	27.39					
Coefficient of variation: 1.74 %							
Plant available water							
Vermiculite	5	8458.5	1691.7	545.6	<0.001	15	0.5
Temperature	4	4231.7	1057.9	341.2	<0.001	18	0.4
Interaction	20	12672.6	633.6	204.4	<0.001	3	1.0
Error	60	186.0	3.1				
Total	89	25548.8					
Coefficient of variation: 15.75 %							

Note: df= degree of freedom, Ss= Sum of square, MS= mean square, P= Probability, NoM= Number of observations per mean and SE= standard error.

Exchangeable Mg^{2+}

	df	Ss	Ms	F-value	P	NoM	SE
Vermiculite	5	104533.6	20906.7	736.7	<0.001	15	1.4
Temperature	4	42927.8	10732.0	378.1	<0.001	18	1.3
Interaction	20	39162.0	1958.1	69.0	<0.001	3	3.1
Error	60	1702.8	28.4				
Total	89	188326.2					
Coefficient of variation: 13.12 %							

Exchangeable Ca^{2+}

Vermiculite	5	2143.7	428.7	568.4	<0.001	15	0.2
Temperature	4	2550.7	637.7	845.5	<0.001	18	0.2
Interaction	20	4486.4	224.3	297.4	<0.001	3	0.5
Error	60	45.3	0.8				
Total	89	9226.1					
Coefficient of variation: 10.78 %							

Exchangeable K^{+}

Vermiculite	5	6.00	1.20	718.54	<0.001	15	0.01
Temperature	4	1.71	0.43	255.34	<0.001	18	0.01
Interaction	20	3.65	0.18	109.20	<0.001	3	0.02
Error	60	0.10	0.00				
Total	89	11.45					
Coefficient of variation: 13.17 %							

Exchangeable Na^{+}

Vermiculite	5	12.27	2.45	70.52	<0.001	15	0.05
Temperature	4	20.67	5.17	148.51	<0.001	18	0.04
Interaction	20	11.77	0.59	16.91	<0.001	3	0.11
Error	60	2.09	0.04				
Total	89	46.81					
Coefficient of variation: 22.95 %							

CEC

	df	Ss	Ms	F-value	P	NoM	SE
Vermiculite	5	92222.2	18444.4	257.6	<0.001	20	1.9
Temperature	4	70306.3	17576.6	245.5	<0.001	24	1.7
Interaction	20	80933.5	4046.7	56.5	<0.001	4	4.2
Error	90	6443.6	71.6				
Total	119	249905.6					
Coefficient of variation: 13.76 %							

Note: df= degree of freedom, Ss= Sum of square, MS= Mean square, P= Probability, NoM= Number of observations per mean and SE= standard error.

Appendix 5.1. Analysis of variance for extractable P, Cr, Fe, Mn, Ni, and Zn from the samples

Acetic acid extractable P

	df	Ss	Ms	F-value	P	NoM	SE
Vermiculite	5	532088.9	106417.8	265.1	<0.001	15	5.2
Temperature	4	70855.5	17713.9	44.1	<0.001	18	4.7
Interaction	20	154463.1	7723.1	19.2	<0.001	3	11.6
Error	60	24083.1	401.4				
Total	89	781490.6					
Coefficient of variation: 30.90%							

DTPA extractable Cr

	df	Ss	Ms	F-value	P	NoM	SE
Vermiculite	5	130.32	26.06	220.51	<0.001	15	0.09
Temperature	4	124.34	31.09	263.01	<0.001	18	0.08
Interaction	20	160.94	8.05	68.08	<0.001	3	0.20
Error	60	7.09	0.12				
Total	89	422.69					
Coefficient of variation: 24.07%							

DTPA extractable Fe

	df	Ss	Ms	F-value	P	NoM	SE
Vermiculite	5	445.57	89.11	142.38	<0.001	15	0.20
Temperature	4	737.66	184.42	294.65	<0.001	18	0.19
Interaction	20	345.61	17.28	27.61	<0.001	3	0.46
Error	60	37.55	0.63				
Total	89	1566.39					
Coefficient of variation: 17.80%							

DTPA extractable Mn

	df	Ss	Ms	F-value	P	NoM	SE
Vermiculite	5	188.17	37.63	481.22	<0.001	15	0.07
Temperature	4	616.45	154.11	1970.55	<0.001	18	0.07
Interaction	20	1030.29	51.51	658.68	<0.001	3	0.16
Error	60	4.69	0.08				
Total	89	1839.60					
Coefficient of variation: 9.42%							

DTPA extractable Ni

	df	Ss	Ms	F-value	P	NoM	SE
Vermiculite	5	4.93	0.98	45.41	<0.001	15	0.04
Temperature	4	4.85	1.21	55.94	<0.001	18	0.04
Interaction	20	8.68	0.43	20.01	<0.001	3	0.09
Error	60	1.30	0.02				
Total	89	19.76					
Coefficient of variation:30.34%							

DTPA extractable Zn

	df	Ss	Ms	F-value	P	NoM	SE
Vermiculite	5	5.13	1.03	63.73	<0.001	15	0.03
Temperature	4	10.67	2.67	165.49	<0.001	18	0.03
Interaction	20	16.17	0.81	50.18	<0.001	3	0.07
Error	60	0.97	0.02				
Total	89	32.94					
Coefficient of variation:26.25%							

Note: df= degree of freedom, Ss= Sum of squares, P= Probability, NoM= Number of observations per mean and SE= standard error.

Appendix 6.1. Effect of type and amount of vermiculite added to the soil on maize growth height

Factor		Growth height, cm			
		2WAE	4WAE	6WAE	8WAE
Type of Vermiculite	Raw	36.7b	88.6b	140.a	157.8a
	Expanded	44.60	94.2a	123.9b	138.0b
	Standard error	0.7	0.9	1.0	1.0
Amount of vermiculite applied % v/v	0	34.6c	65.0e	73.6e	79.1e
	10	38.8b	83.3d	115.6d	127.5d
	20	38.8b	86.4d	124.1c	139.1c
	30	40.9ab	91.1c	134.9b	145.3b
	40	41.4ab	95.7b	142.3a	164.2a
	50	43.2a	100.2a	143.9a	163.5a
	Standard error	1.2	1.5	1.7	1.8
	CV, %	8.5	4.9	3.8	3.7

Means for each factor in a column followed by the same letter(s) are not significantly different at P<0.05 according to Duncan's multiple - range test. WAE = Weeks after emergence of the maize seedlings. CV = Coefficient of variation.

Appendix 6.2. Effect of type and amount of vermiculite added to the soil on maize dry matter harvested 8 weeks after emergence of the seedlings

Factor		Dry matter yield, g / pot			Root/shoot
		Total DM	Root	Shoot	ratio
Type of vermiculite	Raw	88.7a	20.9a	67.7a	0.31a
	Expanded	64.5b	13.1b	51.4b	0.28b
	Standard error	0.9	0.3	0.7	0.01
Amount of vermiculite applied % v/v	0	20.4f	6.9e	13.5f	0.51a
	10	54.0e	13.0d	41.0e	0.35b
	20	62.4d	13.5d	49.0d	0.29c
	30	77.9c	17.2c	60.7c	0.28c
	40	88.7b	19.6b	69.1b	0.28c
	50	99.8a	22.0a	77.9a	0.29c
	Standard error	1.5	0.5	1.2	0.01
	CV, %	6.4	10.0	6.6	9.2

Means for each factor in a column followed by the same letter(s) are not significantly different at P<0.05 according to Duncan's multiple - range test. CV = Coefficient of variation.

Appendix 6.3. Concentrations and uptake of N, P, K, Mg and Ca in maize root dry matter as influenced by the addition of vermiculite to the soil

Treatment	N	N uptake	P	P uptake	K	K uptake	Mg	Mg uptake	Ca	Ca uptake
	g kg^{-1}	mg pot^{-1}	g kg^{-1}	mg pot^{-1}	g kg^{-1}	mg pot^{-1}	g kg^{-1}	mg pot^{-1}	g kg^{-1}	mg pot^{-1}
Soil without vermiculite (control)	28.5a	196.4c	7.1a	49.1e	23.1a	158.9c	1.1g	7.8d	1.2d	8.1f
Soil with 10% raw vermiculite.	8.8f	150.5d	5.3bc	90.5bc	3.8g	65.6e	3.8e	65.7c	2.3c	38.4d
Soil with 20% raw vermiculite	6.8g	123.0d	4.9cd	87.5bc	5.3f	94.6d	5.8c	103.5b	2.1c	38.2d
Soil with 30% raw vermiculite	5.9g	135.2d	4.4de	100.6a	7.2e	165.7c	8.8b	223.0a	3.3b	73.8b
Soil with 40% raw vermiculite	5.4g	127.1d	4.0ef	93.6ab	7.2e	170.6bc	9.1ab	215.2a	3.3b	78.5b
Soil with 50% raw vermiculite	6.0g	139.5d	3.5f	82.4c	9.1d	213.2a	9.7a	225.4a	4.0a	94.2a
Soil with 10% expanded vermiculite	28.5a	250.0a	5.8a	51.2e	17.1b	151.5c	1.8fg	15.6d	1.4d	12.4f
Soil with 20% expanded vermiculite	24.3b	218.2bc	4.6b	41.0e	15.9b	142.3c	2.0f	18.0d	1.5d	13.3f
Soil with 30% expanded vermiculite	20.7c	241.2ab	3.5cde	41.3e	12.2c	143.2c	2.5f	28.8d	2.3c	27.0e
Soil with 40% expanded vermiculite	16.3d	254.3a	3.2f	50.2e	10.1d	157.1c	2.3f	36.5cb	2.4c	37.5d
Soil with 50% expanded vermiculite	12.7e	260.1a	3.4f	69.4d	9.5d	194.4ab	4.8d	98.6b	2.4c	48.7c
Standard error	0.7	9.1	0.3	3.3	0.5	9.0	0.2	10.7	0.1	3.1
Coefficient of variation (%)	8.7	9.6	11.2	9.9	8.6	12.0	10.8	24.6	10.7	15.8

Means in a column followed by the same letter(s) are not significantly different at P<0.05 according to Duncan's multiple - range test.

Appendix 6.4. Analysis of variance for macronutrients in maize from pot experiments

N-concentration in maize shoot

	df	Ss	Ms	F-value	P	NoM	SE
Type of verm.	1	1906.2	1906.2	1666.6	<0.001	24	0.2
Amount of verm.	5	2917.3	583.5	510.1	<0.001	8	0.4
Interaction	5	690.8	138.2	120.8	<0.001	4	0.5
Error	36	41.2	1.1				
Total	47	5555.5					
Coefficient of variation: 5.8%							

N-uptake in maize shoot

	df	Ss	Ms	F-value	P	NoM	SE
Type of verm.	1	2133848.4	2133848.4	692.1	<0.001	24	11.3
Amount of verm.	5	998670.5	199734.1	64.8	<0.001	8	19.6
Interaction	5	1163118.6	232623.7	75.4	<0.001	4	27.8
Error	36	110985.8	3082.9				
Total	47	4406623.3					
Coefficient of variation: 7.8%							

K-concentration in maize shoot

	df	Ss	Ms	F-value	P	NoM	SE
Type of verm.	1	657.9	657.9	306.0	<0.001	24	0.3
Amount of verm.	5	1063.6	212.7	98.9	<0.001	8	0.5
Interaction	5	287.0	57.4	26.7	<0.001	4	0.7
Error	36	77.4	2.1				
Total	47	2085.9					
Coefficient of variation: 9.0%							

K-uptake in maize shoot

	df	Ss	Ms	F-value	P	NoM	SE
Type of verm.	1	433352.0	433352.0	136.4	<0.001	24	11.5
Amount of verm.	5	2907783.3	581556.7	183.1	<0.001	8	19.9
Interaction	5	622799.0	124559.8	39.2	<0.001	4	28.2
Error	36	114340.0	3176.1				
Total	47	4078274.3					
Coefficient of variation: 7.9%							

P-concentration in maize shoot

	df	Ss	Ms	F-value	P	NoM	SE
Type of verm.	1	59.6	59.6	96.0	<0.001	24	0.2
Amount of verm.	5	433.4	86.7	139.6	<0.001	8	0.3
Interaction	5	43.9	8.8	14.1	<0.001	4	0.4
Error	36	22.3	0.6				
Total	47	559.2					
Coefficient of variation: 13.0%							

Note: df = degree of freedom, Ss = Sum of square, Ms = Mean square, P = Probability, NoM = number of observations per mean and SE = Standard error of the mean.

P-uptake in maize shoot

	df	Ss	Ms	F-value	P	NoM	SE
Type of verm.	1	4964.4	4964.4	12.1	<0.001	24	4.1
Amount of verm.	5	59433.8	11886.8	29.0	<0.001	8	7.2
Interaction	5	55977.6	11195.5	27.3	<0.001	4	10.1
Error	36	14772.5	410.3				
Total	47	135148.3					
Coefficient of variation: 8.6%							

N-concentration in maize roots

	df	Ss	Ms	F-value	P	NoM	SE
Type of verm.	1	1605.6	1605.6	823.9	<0.001	24	0.3
Amount of verm.	5	1933.6	386.7	198.4	<0.001	8	0.5
Interaction	5	530.6	106.1	54.4	<0.001	4	0.7
Error	36	70.1	1.9				
Total	47	4139.9					
Coefficient of variation: 8.7%							

N-uptake in maize roots

	df	Ss	Ms	F-value	P	NoM	SE
Type of verm.	1	100321.6	100321.6	301.0	<0.001	24	3.7
Amount of verm.	5	4931.9	986.4	2.9	0.024	8	6.4
Interaction	5	21564.4	4312.9	12.9	<0.001	4	9.1
Error	36	11999.6	333.3				
Total	47	138817.5					
Coefficient of variation: 9.6 %							

K-concentration in maize roots

	df	Ss	Ms	F-value	P	NoM	SE
Type of verm.	1	345.4	345.4	324.8	<0.001	24	0.2
Amount of verm.	5	1212.5	242.5	228.0	<0.001	8	0.4
Interaction	5	300.7	60.1	56.5	<0.001	4	0.5
Error	36	38.3	1.1				
Total	47	1896.9					
Coefficient of variation: 8.6 %							

K-uptake in maize roots

	df	Ss	Ms	F-value	P	NoM	SE
Type of verm.	1	2067.1	2067.1	6.3	0.017	24	3.7
Amount of verm.	5	47112.0	9422.4	28.7	<0.001	8	6.4
Interaction	5	19339.6	3867.9	11.8	<0.001	4	9.0
Error	36	11801.3	327.8				
Total	47	80320.0					
Coefficient of variation: 12.0%							

Note: df = degree of freedom, Ss = Sum of square, Ms = Mean square, P = Probability, NoM = number of observations per mean and SE = Standard error of the mean.

P-concentration in maize roots

	df	Ss	Ms	F-value	P	NoM	SE
Type of verm.	1	0.9	0.9	3.3	0.076	24	0.1
Amount of verm.	5	79.2	15.8	56.1	<0.001	8	0.2
Interaction	5	2.6	0.5	1.8	0.127	4	0.3
Error	36	10.2	0.3				
Total	47	92.9					
Coefficient of variation:		11.2 %					

P-uptake in maize roots

	df	Ss	Ms	F-value	P	NoM	SE
Type of verm.	1	13523.3	13523.3	307.9	<0.001	24	1.3
Amount of verm.	5	3704.3	740.9	16.9	<0.001	8	2.3
Interaction	5	5019.8	1004.0	22.9	<0.001	4	3.3
Error	36	1581.1	43.9				
Total	47	23828.5					
Coefficient of variation:		9.9 %					

Mg-concentration in maize shoot

	df	Ss	Ms	F-value	P	NoM	SE
Type of verm.	1	33.52	33.52	447.85	<0.001	24	0.05
Amount of verm.	5	7.03	1.41	18.78	<0.001	8	0.10
Interaction	5	8.51	1.70	22.75	<0.001	4	0.14
Error	36	2.69	0.07				
Total	47	51.75					
Coefficient of variation:		12.17 %					

Mg-uptake in maize shoot

	df	Ss	Ms	F-value	P	NoM	SE
Type of verm.	1	212575.34	212575.34	672.03	<0.001	24	3.63
Amount of verm.	5	105014.67	21002.93	66.40	<0.001	8	6.28
Interaction	5	59808.06	11961.61	37.81	<0.001	4	8.89
Error	36	11387.39	316.32				
Total	47	388785.46					
Coefficient of variation:		14.16 %					

Ca-concentration in maize shoot

	df	Ss	Ms	F-value	P	NoM	SE
Type of verm.	1	0.01	0.01	0.62	>0.50	24	0.03
Amount of verm.	5	2.53	0.51	24.84	<0.001	8	0.05
Interaction	5	0.36	0.07	3.57	<0.001	4	0.07
Error	36	0.73	0.02				
Total	47	3.63					
Coefficient of variation:		11.28 %					

Note: df = degree of freedom, Ss = Sum of square, Ms = Mean square, P = Probability, NoM = number of observations per mean and SE = Standard error of the mean.

Ca-uptake in maize shoot

	df	Ss	Ms	F-value	P	NoM	SE
Type of verm.	1	4175.36	4175.36	127.90	<0.001	24	1.17
Amount of verm.	5	28843.81	5768.76	176.71	<0.001	8	2.02
Interaction	5	4076.22	815.24	24.97	<0.001	4	2.86
Error	36	1175.24	32.65				
Total	47	38270.63					
Coefficient of variation: 9.27%							

Mg-concentration in maize roots

	df	Ss	Ms	F-value	P	NoM	SE
Type of verm.	1	189.29	189.29	829.66	<0.001	24	0.10
Amount of verm.	5	199.17	39.83	174.59	<0.001	8	0.17
Interaction	5	67.12	13.42	58.84	<0.001	4	0.24
Error	36	8.21	0.23				
Total	47	463.79					
Coefficient of variation: 10.83%							

Mg-uptake in maize roots

	df	Ss	Ms	F-value	P	NoM	SE
Type of verm.	1	134559.72	134559.72	291.98	<0.001	24	4.38
Amount of verm.	5	141983.65	28396.73	61.62	<0.001	8	7.59
Interaction	5	56536.77	11307.35	24.53	<0.001	4	10.73
Error	36	16590.67	460.85				
Total	47	349670.81					
Coefficient of variation: 24.63 %							

Ca-concentration in maize roots

	df	Ss	Ms	F-value	P	NoM	SE
Type of verm.	1	8.53	8.53	145.15	<0.001	24	0.05
Amount of verm.	5	24.53	4.90	83.51	<0.001	8	0.08
Interaction	5	2.84	0.57	9.68	<0.001	4	0.12
Error	36	2.11	0.06				
Total	47	38.01					
Coefficient of variation: 10.65 %							

Ca-uptake in maize roots

	df	Ss	Ms	F-value	P	NoM	SE
Type of verm.	1	11308.04	11308.04	286.69	<0.001	24	1.28
Amount of verm.	5	22821.53	4564.31	115.76	<0.001	8	2.22
Interaction	5	3160.27	632.05	16.02	<0.001	4	3.14
Error	36	1419.98	39.44				
Total	47	38709.82					
Coefficient of variation: 15.76%							

Note: df = degree of freedom, Ss = Sum of square, Ms = Mean square, P = Probability, NoM = number of observations per mean and SE = Standard error of the mean.

Appendix 6.5. Analysis of variance for trace elements in maize from pot experiments

As-concentration in maize shoot

	df	Ss	Ms	F-value	P	NoM	SE
Type of verm.	1	0.002	0.002	4.464	0.045	18	0.005
Amount of verm.	5	0.006	0.001	3.281	0.021	6	0.008
Interaction	5	0.003	0.001	1.773	0.157	3	0.011
Error	24	0.009	<0.001				
Total	35	0.020					
Coefficient of variation:		13.63%					

Pb-concentration in maize shoot

	df	Ss	Ms	F-value	P	NoM	SE
Type of verm.	1	0.039	0.039	28.042	<0.001	18	0.009
Amount of verm.	5	0.270	0.054	38.522	<0.001	6	0.015
Interaction	5	0.023	0.005	3.234	0.023	3	0.022
Error	24	0.034	0.001				
Total	35	0.366					
Coefficient of variation:		24.03%					

Cr-concentration in maize shoot

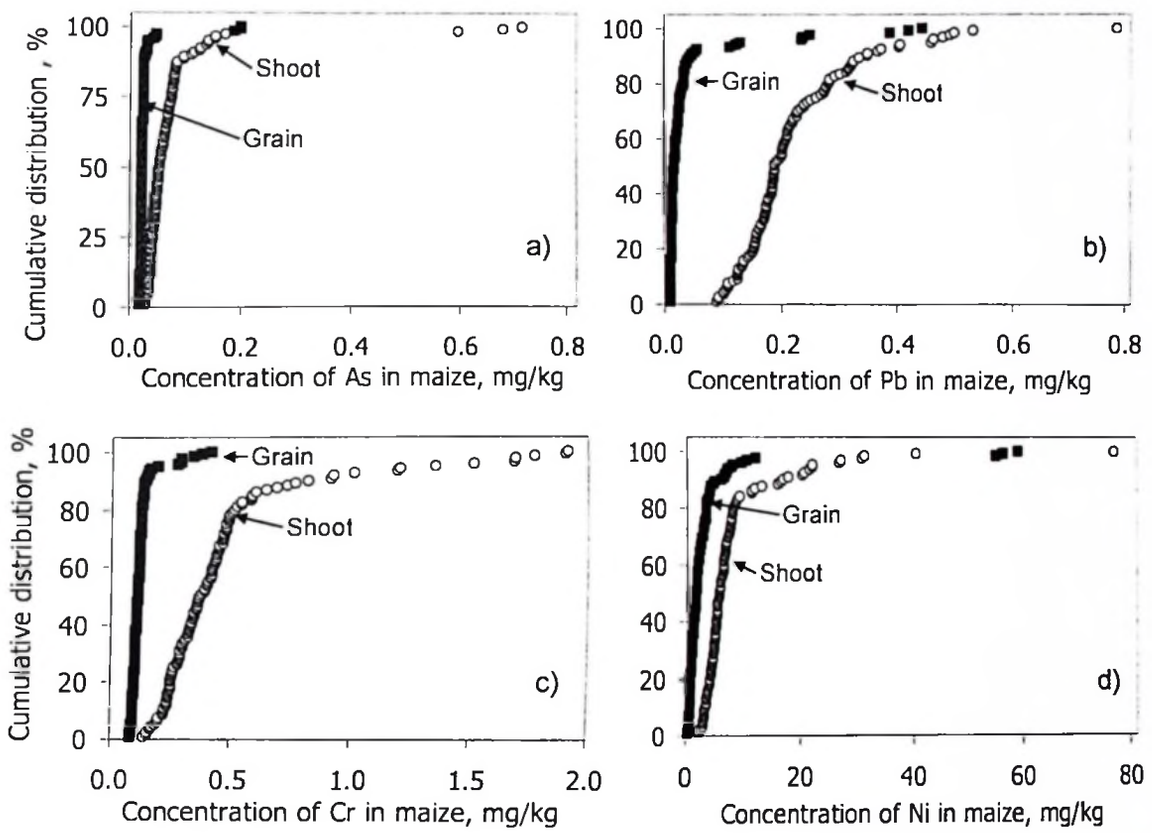
	df	Ss	Ms	F-value	P	NoM	SE
Type of verm.	1	0.073	0.073	59.510	<0.001	18	0.008
Amount of verm.	5	0.027	0.005	4.455	0.005	6	0.014
Interaction	5	0.053	0.011	8.697	<0.001	3	0.020
Error	24	0.029	0.001				
Total	35	0.182					
Coefficient of variation:		16.98 %					

Ni-concentration in maize shoot

	df	Ss	Ms	F-value	P	NoM	SE
Type of verm.	1	44.467	44.467	17.056	<0.001	18	0.381
Amount of verm.	5	532.879	106.576	40.879	<0.001	6	0.659
Interaction	5	50.332	10.066	3.861	0.010	3	0.932
Error	24	62.571	2.607				
Total	35	690.249					
Coefficient of variation:		30.65 %					

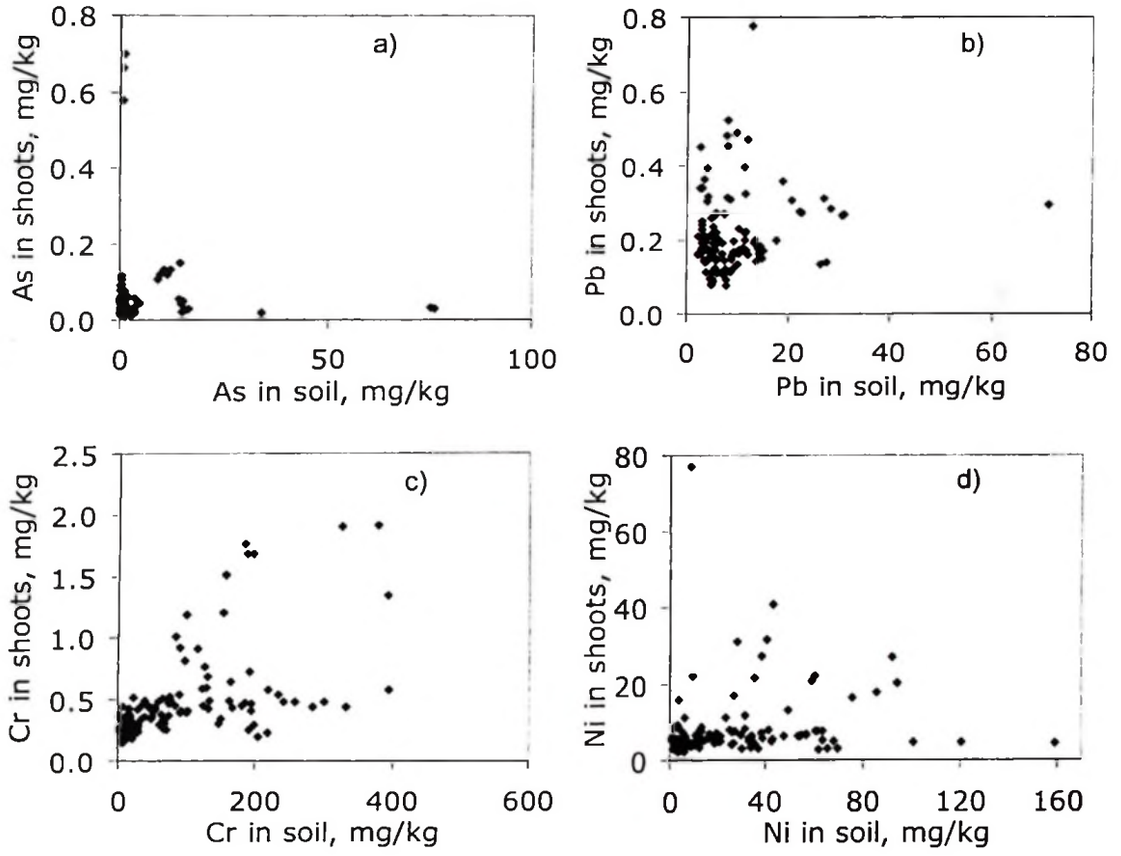
Note: df = degree of freedom, Ss = Sum of square, Ms = Mean square, P = Probability, NoM = number of observations per mean and SE = Standard error of the mean.

Appendix 6.6. Concentrations of trace elements in maize from 40 farms in Tanzania: a) As; b) Pb; c) Cr; and d) Ni

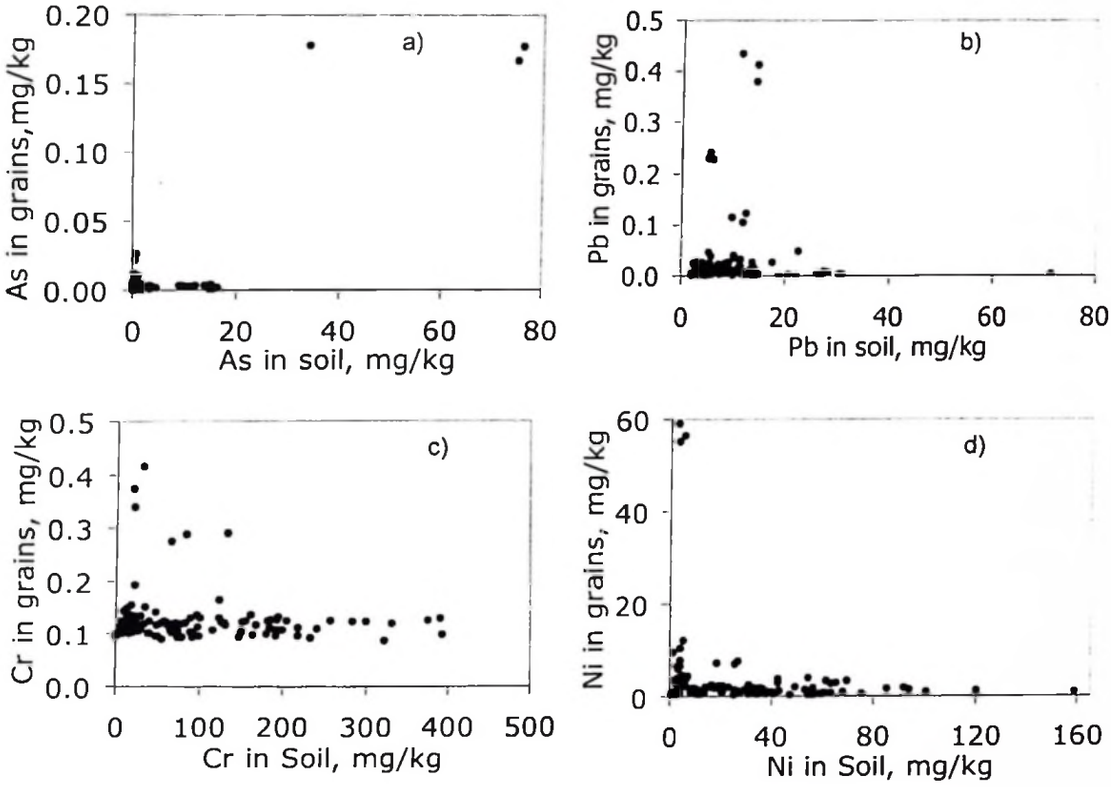


Note: Cumulative distribution gives the ranking in percentage of the concentration of the element from the lowest to the highest out of 120 samples analysed. Shaded squares represent the concentration of an individual element in grains whereas open circles refer to the element in maize shoots.

Appendix 6.7. Relationships between concentration of trace elements in soil and maize shoots: a) As; b) Pb; c) Cr; and d) Ni from 40 maize farms in Tanzania.



Appendix 6.8. Relationships between concentration of trace elements in soil and maize grains: a) As; b) Pb; c) Cr; and d) Ni from 40 maize farms in Tanzania.



Appendix 6.9. Results of As, Pb, Ni, and Cr in the reference standards used during ICP-MS analysis of maize shoots, maize grains, and soils from maize farms in Tanzania. Measured values are means of four replicates with their standard errors. Where the standard error is not indicated it means the value obtained was less than 0.01.

Recovery of the elements from the reference standards during the analysis of maize shoots

Element	Spike			CRM 1568a		
	Actual value µg/l	Measured value µg/l	Recovery %	Certified value mg/kg	Measured value mg/kg	Recovery %
As	1.0	0.91±0.03	91	0.29±0.03	0.30±0.01	103
Pb	1.0	1.00±0.02	100	na	0.01	na
Cr	10.0	10.10 ± 0.07	101	na	0.1	na
Ni	10.0	9.79±0.08	98	na	0.16	na

Recovery of the elements from the reference standards during the analysis of maize grains

Element	Spike			CRM 1568a		
	Actual value µg/l	Measured value µg/l	Recovery %	Certified value mg/kg	Measured value mg/kg	Recovery %
As	10.0	8.37±0.04	84	0.29±0.03	0.31±0.04	110
Pb	10.0	9.87±0.11	99	na	0.02	na
Cr	10.0	10.01±0.09	100	na	0.11	na
Ni	10.0	9.66±0.07	97	na	0.14	na

Recovery of the elements from the reference standards during the analysis of soils

Element	Spike			CRM ZC73007		
	Actual value µg/l	Measured value µg/l	Recovery %	Certified value mg/kg	Measured value mg/kg	Recovery %
As	5.0	4.96±0.13	99	18±2	16.0±0.2	89
Pb	20.0	19.20±0.42	96	61±2	57±4	93
Cr	100.0	100.70±1.03	101	67±3	60±2	90
Ni	100.0	107.32±3.47	107	27.4±0.9	24.3±0.8	89

na = no reference value was given in the reference material ; CRM = Certified reference material

Appendix 7.1. Soil profile at Mazimbu experimental site in Tanzania

1. General information

Profile number:	MAZIMBU-1
Author(s) & Date:	E. M. M. Marwa and A. K. Kaaya, on 14/02/2007
Location:	Mazimbu SUA Farm, Morogoro District, Tanzania.
Coordinates:	06° 47' 02" S and 37° 37' 34" E
Parent material:	Colluvial sands from Mindu Mountains
Topography and Landform:	Gently undulating colluvial plains. Soil profile is located on a uniform slope of 2-3%.
Effective soil depth:	Class 4 – Very deep (> 170 cm).
Drainage class:	Well drained
Land use:	Agriculture – Rain-fed production of annual crops including maize and cassava.
Soil Classification:	*USDA Soil Taxonomy:* Ustic Quartzipsamment (Soil Survey Staff, 1996)
	World Reference Base: Orthidystric Arenosol (FAO, 1998)

2. Description of soil horizons

Horizon	***Depth (cm)***	Description
Ap	0 – 20	Very dark brown (7.5YR 2.5/2) moist; loamy sand; weak fine and medium crumb structure; soft (dry), very friable (moist) and none sticky; slightly plastic (wet); simple packing textural voids; few fine and very few medium roots; few termites/ants channels and nests; abrupt, smooth boundary to AB.
AB	20 - 33	Dark brown (7.5YR 3/2) moist; loamy sand; weak very fine and fine sub angular blocky structure; very friable (moist), non sticky, slightly plastic (wet); simple packing textural voids; very few very fine and medium roots; few termites/ants channels and nests; gradual, smooth boundary to Bw1.
Bw1	33 - 133	Dark yellowish brown (10YR 3/4) moist; loamy sand; moderate fine and medium sub angular blocky structure; very friable (moist), non sticky, slightly plastic (wet); simple packing textural voids; very few fine and medium roots; few termites/ants channels and nests; gradual, smooth boundary to Bw2.
Bw2	133 – 170+	Pale brown (10YR 6/3) moist; sand; very weak medium sub angular blocky structure; very friable (moist), non sticky, non plastic (wet); simple packing textural voids; very few fine and medium roots; few termites/ants channels and nests.

3. Analytical data

Soil parameter	Horizon			
	Ap	AB	Bw1	Bw2
Depth (cm)	0 – 20	20 – 33	33 – 133	133 – 170+
Texture: Clay (%)	7	7	6	5
Silt (%)	7	18	10	4
Sand (%)	86	75	84	91
Textural class	LS	LS	LS	S
pH in H_2O (1:2.5)	6.56	6.55	6.30	6.05
Organic C (%)	0.75	0.31	0.12	0.04
Total N (%)	0.06	0.02	0.01	0.01
EC ($mScm^{-1}$)	0.11	0.11	0.10	0.10
Bray 1 available P (mg/kg)	3.90	5.51	1.03	0.67
CEC NH_4OAc ($cmol_{(+)}/kg$)	13.6	6.8	7.3	8.2
Exchangeable cations:				
Ca^{2+} ($cmol_{(+)}/kg$)	2.48	1.54	1.08	0.95
Mg^{2+} ($cmol_{(+)}/kg$)	1.14	0.87	0.75	0.60
K^{+} ($cmol_{(+)}/kg$)	0.55	0.44	0.26	0.07
Na^{+} ($cmol_{(+)}/kg$)	0.34	0.33	0.34	0.34
TEC ($cmol_{(+)}/kg$)	4.51	3.18	2.43	1.96
Cation saturation (%)	33.2	46.8	33.3	22.7

Note: LS = Loamy sand, S = Sand, EC = Electrical conductivity and TEC = Total exchangeable cations

Appendix 7.2. Statistical analysis of variance for plant nutrient retained in a sandy soil mixed with vermiculite and buried for 90 d.

Ammonium

	df	Ss	Ms	F-value	P	NoM	SE
Burial depth	1	0.72	0.72	0.32	>0.50	36	0.25
Error for randomization	4	9.06	2.26				
Type of vermiculite	1	0.01	0.01	0.01	>0.50	36	0.16
Depth vs Type	1	1.06	1.06	1.11	0.3	18	0.23
Amount of vermiculite.	5	15.00	3.00	3.15	0.020	12	0.28
Depth vs Amount	5	0.73	0.14	0.15	>0.50	6	0.40
Type vs Amount	5	6.64	1.33	1.40	0.02	6	0.40
Depth vs Type vs Amount	5	1.34	0.27	0.28	>0.50	3	0.56
Error for all factors	44	41.83	0.95				
Total	71	76.39					

Coefficient of variation: 44.11%

Nitrate

	df	Ss	Ms	F-value	P	NoM	SE
Burial depth	1	846.32	846.32	178.29	<0.001	36	0.36
Error for randomization	4	18.98	4.74				
Type of vermiculite	1	63.04	63.04	4.63	0.037	36	0.61
Depth vs Type	1	56.66	56.66	4.16	0.047	18	0.87
Amount of vermiculite.	5	953.55	190.71	13.99	<0.001	12	1.06
Depth vs Amount	5	448.70	89.74	6.58	<0.001	6	1.51
Type vs Amount	5	61.32	12.26	0.90	>0.50	6	1.51
Depth vs Type vs Amount	5	47.76	9.55	0.70	>0.50	3	2.13
Error for all factors	44	599.55	13.63				
Total	71	3095.88					

Coefficient of variation: 54.92%

Note: df = degree of freedom, Ss = Sum of square, Ms = Mean square, P = Probability, NoM = number of observations per mean and SE = Standard error of the mean.

Extractable P

	df	Ss	Ms	F-value	P	NoM	SE
Burial depth	1	7546.06	7546.06	28.24	0.006	36	2.72
Error for randomization	4	1068.98	267.24				
Type of vermiculite	1	23751.10	23751.10	252.77	<0.001	36	1.62
Depth vs Type	1	646.20	646.20	6.88	0.012	18	2.28
Amount of vermiculite.	5	97948.23	19589.64	208.48	<0.001	12	2.80
Depth vs Amount	5	367.78	73.56	0.78	>0.50	6	3.96
Type vs Amount	5	12182.55	2436.51	25.93	<0.001	6	3.96
Depth vs Type vs Amount	5	1282.41	256.48	2.73	0.031	3	5.60
Error for all factors	44	4134.40	93.96				
Total	71	148927.71					

Coefficient of variation: 10.13%

Extractable K

	df	Ss	Ms	F-value	P	NoM	SE
Burial depth	1	565.60	565.60	3.49	0.135	36	2.12
Error for randomization	4	647.43	161.86				
Type of vermiculite	1	2204.48	2204.48	24.03	<0.001	36	1.60
Depth vs Type	1	89.33	89.33	0.97	>0.50	18	2.26
Amount of vermiculite.	5	6787.83	1357.57	14.80	<0.001	12	2.76
Depth vs Amount	5	176.15	35.23	0.38	>0.50	6	3.91
Type vs Amount	5	1341.01	268.20	2.92	0.023	6	3.91
Depth vs Type vs Amount	5	63.71	12.74	0.14	>0.50	3	5.53
Error for all factors	44	4035.95	91.73				
Total	71	15911.49					

Coefficient of variation: 14.88%

Note: df = Degree of freedom, Ss = Sum of square, Ms = Mean square, P = Probability, NoM = number of observations per mean and SE = Standard error of the mean.