



University of Venda

**SCHOOL OF ENVIRONMENTAL SCIENCES**

**DEPARTMENT OF MINING AND ENVIRONMENTAL GEOLOGY**

**MINERALOGY AND GEOCHEMISTRY OF GEOPHAGIC MATERIALS FROM  
MASHAU VILLAGE IN LIMPOPO PROVINCE, SOUTH AFRICA**

**BY**

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**A DISSERTATION SUBMITTED TO THE DEPARTMENT OF MINING AND  
ENVIRONMENTAL GEOLOGY, SCHOOL OF ENVIRONMENTAL SCIENCES,  
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MASTER OF EARTH SCIENCE IN MINING AND ENVIRONMENTAL GEOLOGY**

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## DECLARATION

I, Mashao Unarine, the undersigned student declare that this thesis titled “Mineralogy and Geochemistry of Geophagic Materials from Mashau Village in Limpopo Province, South Africa” for Master of Earth Science in Mining and Environmental Geology degree at the University of Venda, submitted by me, has not been previously submitted for a degree at this or any other institution, and that all reference material contained herein has fully been acknowledged.

.....

Signature

.....

Date

We, the supervisors, certify that this declaration is correct.

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Supervisor's Signature

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Professor JO Odiyo

## DEDICATION

This study is dedicated to my beloved father, Mr R.S. Mashau, in memoriam.

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## ABSTRACT

Literature indicated that several mineralogical identification studies have been carried out on clays but few have focused on the characterisation of geophagic materials from South Africa. Large quantities of earth materials are consumed daily in Mashau Village, however, their mineral content and geochemical compositions had not been determined. Moreover, though the consumption of geophagic materials is very common in the village, the associated health implications had not been addressed. Thus, the main aim of the research was to mineralogically and geochemically characterise geophagic materials commonly ingested in Mashau Village and infer on possible health implications that could result from their consumption. Questionnaires were administered to geophagists in the study area with the aim of generating data on the prevalence of geophagia and the motivations for the practice. Geophagic soils and their parent rocks (for determination of provenance) were sampled and analysed for mineralogical and geochemical content. Geophagic soil samples were subjected to the following physicochemical analyses: colour, particle size distribution, pH, cation exchange capacity (CEC) and electrical conductivity (EC). An x-ray diffractometer (XRD) was used for mineralogical analysis while major oxides and trace elements abundances were determined using x-ray fluorescence (XRF) spectrometry and laser ablation inductively coupled mass spectrometry (LA-ICP-MS), respectively. Furthermore, provenance of the geophagic materials was determined using data obtained from mineralogical and geochemical analysis. Inferred health implications were based on the physico-chemical, mineralogical and geochemical data obtained. Outcomes of the questionnaire survey revealed craving to be the motivation for geophagia in Mashau Village. Although the practice seemed to be prevalent in females of certain ages, it was certainly not limited to gender, age, educational level or socio-economic status. Out of the 20 geophagic samples, 3 samples were brown, 2 had a strong brown colour and another 2 had a light olive brown colour. Other soil colours were less common, as each colour was only observed in one sample. The sand fraction dominated the samples; the clay content was low, giving the samples a sandy clay loamy texture. The pH of the soil ranged from being slightly acidic (5.4) to being slightly alkaline. The CEC values were very high ranging from 17 to 109 meq/100 g.

The EC values were also high (ranging from 11.2 to 245  $\mu\text{S}/\text{cm}$ ) indicating a high amount of soluble salts. Mineralogical analysis of geophagic soils identified quartz, microcline, plagioclase, hornblende, dolomite, muscovite, kaolinite, smectite, talc, anatase, hematite, ilmenite, chlorite and epidote with quartz and kaolinite being the dominant minerals. Actinolite, augite, chlorite, epidote, forsterite, magnetite, muscovite, plagioclase, quartz, sepiolite and microcline were the minerals identified in rock samples. Geochemical analysis for major oxides content ( $\text{SiO}_2$ ,  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{MnO}$ ,  $\text{MgO}$ ,  $\text{CaO}$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{P}_2\text{O}_5$  and  $\text{Cr}_2\text{O}_3$ ) indicated that both geophagic soils and parent rocks were mainly composed of silica and alumina. Trace elements geochemistry showed a depletion of LREEs and an enrichment of HREEs in geophagic soils. The results also revealed that the REEs were enriched in the bulk fraction than in the clay fraction. Relative to the Upper Continental Crust (UCC) compositions, the concentrations of trace elements in geophagic soils were generally low. Provenance determination results showed that geophagic soils in Mashau were derived from basalts and sandstones. Majority of the samples were formed as a result of intense weathering while some were as a result of intermediate weathering. The negative health implications of the studied materials could include perforation of the colon, damage of the dental enamel and anaemia. However, geophagic materials could also be a good source of mineral nutrients and beneficial for reduction of nausea during pregnancy.

**Keywords:** Geophagia, geophagic materials, geochemical compositions, health implications, Mashau Village and mineralogy

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## LIST OF ACRONYMS AND SYMBOLS

|               |   |  |
|---------------|---|--|
| <b>AD</b>     | - | Anno Domini                                |
| <b>BC</b>     | - | Before Christ                              |
| <b>CEC</b>    | - | Cation Exchange Capacity                   |
| <b>CIA</b>    | - | Chemical Index of Alteration               |
| <b>CIW</b>    | - | Chemical Index of Weathering               |
| <b>EC</b>     | - | Electrical Conductivity                    |
| <b>ICP-MS</b> | - | Inductively Coupled Mass Spectrometry      |
| <b>ppm</b>    | - | parts per million                          |
| <b>PIA</b>    | - | Plagioclase Index of Alteration            |
| <b>PSD</b>    | - | Particle Size Distribution                 |
| <b>PWI</b>    | - | Product of Weathering Index                |
| <b>R</b>      | - | Ruxton Ratio                               |
| <b>SPSS</b>   | - | Statistical Package for the Social Science |
| <b>STI</b>    | - | Silica-Titania Index                       |
| <b>UCC</b>    | - | Upper Continental Crust                    |
| <b>V</b>      | - | Vogt's Residual Index                      |
| <b>WIP</b>    | - | Weathering Index of Parker                 |
| <b>XRD</b>    | - | X-ray Diffractometry                       |
| <b>XRF</b>    | - | X-ray Fluorescence                         |

# CHAPTER 1

## INTRODUCTION

### 1.1 Background of the Study

Geophagia is defined as the habitual intended consumption of earthy materials such as soils and clays by humans and animals (Abrahams, 2002; Wilson, 2003; Hooda *et al.*, 2004; Momoh *et al.*, 2015). Soil consumption has been practised for centuries by people from different socio-economic, ethnic, religious and racial groups (Ngole and Ekosse, 2012). Geophagia is practised in almost all the continents in the world, including Africa, Asia, Australia, Europe, North America and South America.

On the African continent, the practice has been reported in Botswana, Cameroon, Ghana, Guinea, Ivory Coast, Kenya, Malawi, Nigeria, Senegal, Sierra Leone, Tanzania, Uganda, South Africa and Swaziland (Young, 2007; Ekosse *et al.*, 2010; Ekosse *et al.*, 2011). However, this practice has been reported to be predominant in Southern African countries; namely Malawi, Zambia, Zimbabwe, Swaziland and South Africa (Walker *et al.*, 1997).

In South Africa, Saathoff *et al.* (2004) reported soil eating among rural school children from the Northern parts of KwaZulu-Natal. The work of Walker *et al.* (1997) amongst South African women revealed that geophagia is more prevalent among rural women than in urban women. In Indian, Coloured and White women the prevalence was much lower than in African women. Geophagia has also been reported in the Eastern Cape Province by Ngole and Ekosse (2012).

Studies undertaken in the rural areas of Free State (QwaQwa) and Limpopo (Sekhukhune) Provinces by Magongoa *et al.* (2011) and Ekosse *et al.* (2010) respectively, showed that the practice of geophagia is still prevalent with persons from rural areas in Southern Africa. Although several mineralogical identification and characterisation studies have been carried out on clays, there are very few studies that have focused on the characterisation of geophagic materials from South Africa (Ngole *et al.*, 2010).

Geophagic behaviour has also been reported in the Vhembe District (Momoh *et al.*, 2015). However, no known studies exist on geophagic practice in Mashau Village. Soil ingestion has both beneficial and detrimental health effects. The positive and negative effects of geophagia may vary, depending on the physico-chemistry, mineralogy and geochemistry of the soils (Diko and Ekosse, 2014). In this study, geophagic soils from Mashau were mineralogically and geochemically characterised in order to ascertain their health implications.

## 1.2 Problem Statement

Large quantities of earth materials are consumed daily in Mashau Village (Figure 1.1). Nonetheless, there is no known documentation of research on the mineral content and geochemical compositions of the consumed materials. Though the consumption of geophagic materials is prevalent in the village, the associated health implications have not been addressed. Furthermore, the motivation for this geophagic behaviour in the study area is unclear.



Figure 1.1: Collection of geophagic materials from Mashau by soil consumers

Geophagists also do not understand the formation of geophagic materials from the study area because they have not been characterised. In addition, the benefits of consuming soils from the study area have not been studied. On the other hand, there is a concern that the mineralogical, geochemical and physical properties of soil may adversely affect individuals ingesting soils from the study area. It is, therefore, important to investigate soils consumed in the area for their mineralogy and geochemistry, as to ascertain the positive and negative effects associated with the consumption of such soils.

### **1.3 Significance of the Study**

Momoh *et al.*, (2015) highlighted that the extent of research on geophagia in the Vhembe District is relatively scarce. The proposed study is the first study on geophagia in Mashau Village which will also provide the mineralogical, geochemical and provenance information on the geophagic materials. It is also the first study to characterise the rocks and soils in the study area. Therefore, the study will provide baseline data for future studies. Currently, serious attention has been devoted to the study of geophagia in medical and geological sciences because of health issues arising from this practice.

The study will assess the role of ingested soils in supplying mineral nutrients; such assessment would be significant for epidemiological and risk assessment studies. It will also help soil consumers understand the characteristics of the geophagic soils they are consuming, as well as their health implications. Findings from the study could equally be applied in educating the community of healthy geophagic practices. There are more social studies done in the area than studies related to the geology, environmental science or environmental geo-health; therefore, the study will contribute positively to this science society.

## **1.4 Objectives**

### **1.4.1 Main Objective**

The main objective of the research was to mineralogically and geochemically characterise geophagic materials commonly ingested in Mashau Village and infer possible health implications that could result from the consumption of these materials.

### **1.4.2 Specific Objectives**

The specific objectives were to:

- Understand geophagia in Mashau Village and motivations for the practice;
- Assess the physico-chemical properties of the materials;
- Characterise the mineralogy of geophagic materials;
- Geochemically characterise the geophagic materials in the area;
- Determine the provenance of consumed geophagic materials; and
- Infer possible health implications from the consumption of geophagic materials.

## **1.5 Research Questions**

- Why do people consume soils?
- Which minerals constitute geophagic materials at Mashau Village?
- What are the geochemical contents of the geophagic materials?
- What are the physico-chemical properties of the materials?
- How were the geophagic materials in the study area formed?
- What are the health implications of consuming geophagic materials from Mashau Village?



## 1.6 Study Area

### 1.6.1 Geographical Location

Mashau (Figure 1.2) is located between latitudes  $23^{\circ}08'00''\text{S}$  and  $23^{\circ}12'00''\text{S}$  and longitudes  $30^{\circ}10'00''\text{E}$  and  $30^{\circ}16'00''\text{E}$  within the Limpopo Province of South Africa (Google Earth, 2016). The study focused on the two sub-villages of Mashau: Mukhoro ( $23^{\circ}09'28''\text{S}$ ,  $30^{\circ}14'00''\text{E}$ ) and Doli ( $23^{\circ}09'30''\text{S}$ ,  $30^{\circ}16'00''\text{E}$ ). The study area is located approximately 19 Km from the Elim Mall and approximately 32 Km from Levubu.

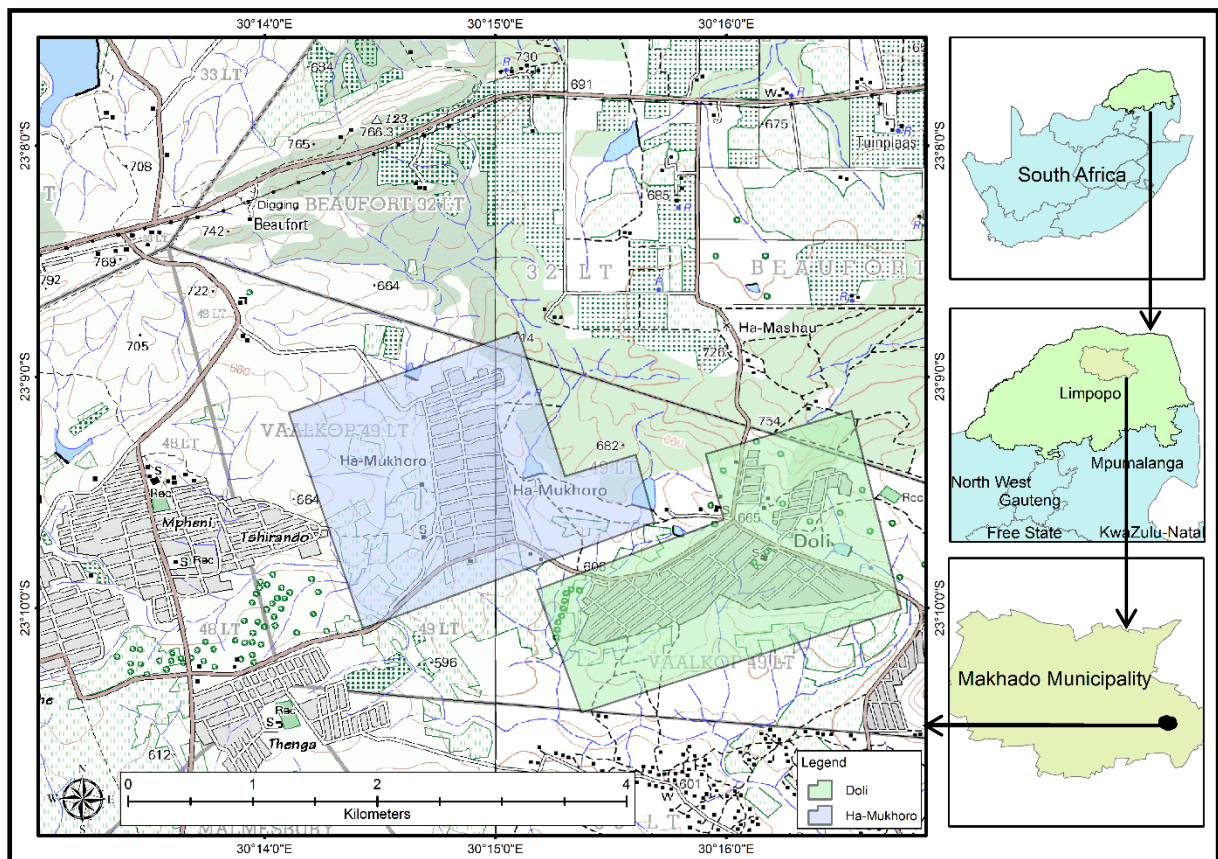


Figure 1.2: Location of Mashau Village (Source: GIS & ENV Services, 2016)

### 1.6.2 Geology of Mashau Village

Geologically, Mashau falls in the Soutpansberg Group. The Soutpansberg Group is a volcano-sedimentary succession which is subdivided into seven formations; namely, Tshifhefhe, Sibasa, Fundudzi, Wyllie's Poort, Nzhelele, Stayt and Mabilingwe (Bumby, 2000).

The Tshifhefhe Formation, which is only a few metres thick, is made up of clastic sediments, including shale, greywacke and conglomerate. The study area falls in the Sibasa Formation, a predominantly volcanic succession of basalts, with intercalated clastic sediments, having a maximum thickness of about 3 000 m (Bumby, 2000). The overlying Fundudzi Formation is developed only in the eastern Soutpansberg, and wedges out to wards the west.

It is up to 1 900 m thick, and consists mainly of arenaceous and argillaceous sediments with a few thin pyroclastic horizons. Near the top of the succession, about 50 m thick layers of epidotised basaltic lava are intercalated with the sediments (Brandl, 1999). The Fundudzi Formation is followed by the Wyllie's Poort Formation, which is an almost entirely clastic succession, reaching a maximum thickness of 1 500 m. Resistant pink quartzite and sandstone, with pebble washes dominate the succession, with a prominent agate conglomerate developed at the base (Barker *et al.*, 2006).

The uppermost unit is represented by the Nzhelele Formation, which consists of a 400 m thick volcanic assemblage (Musekwa Member) at the base, followed by red argillaceous and then by arenaceous sediments. North of the main Soutpansberg outcrop there are two additional units, the Stayt and Mabiligwe Formations (Brandl, 1999).

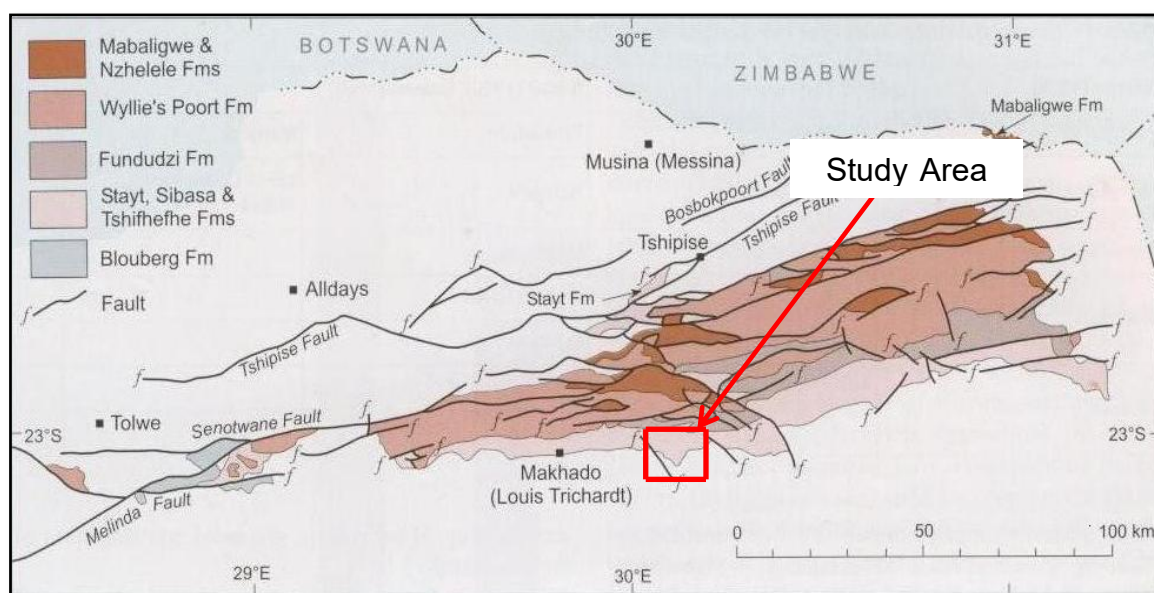


Figure 1.3: Stratigraphy and structural setting of Soutpansberg Group (Barker *et al.*, 2006).

### 1.6.3 Climate

The climate of Mashau is similar to that of Makhado which is strongly influenced by the east-west orientated mountain range. The general climate of the study area can be divided into two seasons: the warm wet season (October to March) and a cool-dry season (May to August) with April and September being the transition months (Kabanda, 2003).

The summer months are warm, with temperatures ranging from 15–35°C. Winter temperatures are mild, ranging from 7–18°C and they seldom drop below freezing point. Due to the East-West orientation of the Soutpansberg, the study area experiences orographic rainfall (Mostert *et al.*, 2008). This phenomenon is due to moisture-laden air from the Indian Ocean, driven by the prevailing south-easterly winds onto the southern scarp of the Soutpansberg (Kabanda, 2003). The average temperatures for the study area are presented in Figure 1.3.

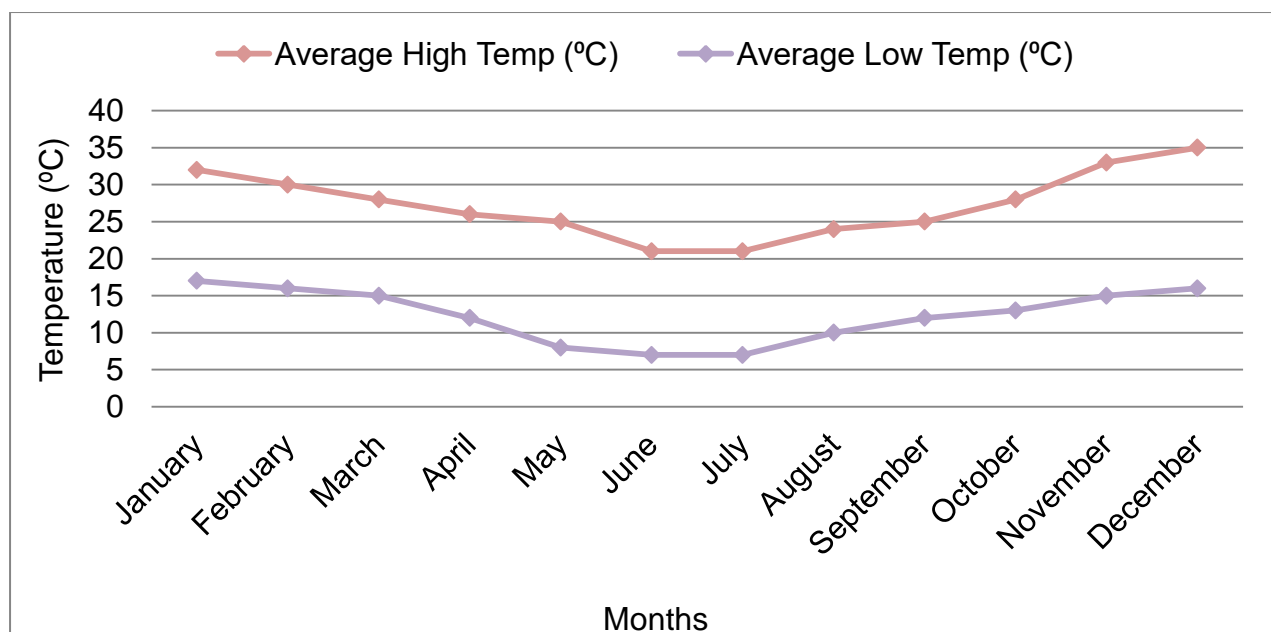


Figure 1.4: Average temperatures for Mashau (Modified from World Weather Online, 2017).

### 1.6.4 Soils

The soils that dominate the study area are derived from sandstone and basalt (Mostert *et al.*, 2008). Soils derived from sandstones are generally shallow, gravelly and well-drained, with low nutrient content and acidic characteristics.



On the other hand, soils derived from basalts are fine-textured, clayey, well-weathered, and generally deep. These poorly-drained soils are prone to erosion along the higher rainfall southern slopes (Mostert *et al.*, 2008). Soils in the study area support the fact that Mashau Village is part of the Sibasa Formation, which is made up of basalts, with intercalated clastic sediments. The general soil types within the village are sandy soils, shallow silty sands, loamy soils and clayey soils which are found within the river valleys.

### **1.6.5 Topography and Drainage**

The study area consists of undulating terrain, with a mountain on the far west, the Thavhayamipfa (Thorn Mountain). The topography at Mashau varies, ranging from approximately 580 m above sea level and reaches an elevation of 1092 m above sea level at the mountain (Google Earth, 2016). Mashau is drained by a non-perennial river, Mutshenzheni, which originates from Thavhayamipfa. The river flows south-eastward and it incised through the hills that form spectacular landscape units.

### **1.6.6 Vegetation**

The vegetation in the study area is known as the Tzaneen Sour Bushveld (Bradenkamp *et al.*, 2000). This is a deciduous, tall open bushveld (parkland) with a well-developed, tall grass layer, occurring on low to high mountains with undulating plains mainly at the base of, and on the lower to middle slopes (Acocks, 1988). The Tzaneen Sour Bushveld (SVI 8) is a very dense, often tall bushveld, merging into forest-like vegetation. This type of vegetation is listed under the Savanna biome and its ecosystem threat status is vulnerable (SANBI, 2004).

### **1.6.7 Land Use Activities**

The land is currently used for various activities, ranging from settlement to agriculture. The land is also used for sand mining and brick making. As a rural area where animals such as cattle, goats and donkeys are still domesticated, the forest serves as grazing land. Commercial farming in the form of cultivation is also one of the land use activities. These activities include the tea and macadamia plantations at Mashau Thondoni, the plant nursery at Mashau Tshirando and the forestry plantations on the mountainous area of Mashau Bodwe.

## CHAPTER 2

### LITERATURE REVIEW

This chapter reviews the literature associated with the main areas of interest in this study, to find a connection between the study area and the accumulated knowledge in the field of the study.

#### 2.1 The Phenomenon of Geophagia

Geophagia is part of pica, a classified eating disorder characterised by abnormal cravings for non-food items and is derived from the two Greek words, geo- (earth) and phag- (eat) (Hooda *et al.*, 2004). The practice has been reported to have been in existence as early as the 1800s by authors ranging from Roman and Greek physicians to explorers. Hippocrates made the first known medical mention of geophagia in the 4<sup>th</sup> century (Young *et al.*, 2010).

During the middle ages (980-1037 AD), imprisonment to cure geophagia in young boys was recommended but more gentle treatment was recommended during pregnancy (Kipel, 1993). Many ancient reports of geophagia indicate that the practice was observed as a symptom of chlorosis. The disease mainly affected pubescent girls and spread widely through Europe during the 16<sup>th</sup> century (Pary-Jones, 1992).

During the 17<sup>th</sup> century, a travelling scientist reported in great detail on the use of *terra sigillata*, the sacred earth, to facilitate childbirth and alleviate disorders of menstruation (Woywodt and Kiss, 2002). Geophagia remained common in Europe during the 18<sup>th</sup> and 19<sup>th</sup> centuries and one of the reports noted geophagical customs in natives of South America. It was observed that dried earth was piled up in heaps to serve as a store during periods of famine (Pary-Jones, 1992).

In Africa, *safura*, a disease of earth-eating among the slaves of Zanzibar, was discovered. Poverty was thought to be the possible explanation for the behaviour but this theory was rejected after observing that wealthy people were also affected. The disorder was a great concern among plantation owners in that slaves who were addicted became inactive and weak until they eventually died. Plantation owners went so far as to have face masks fitted to prevent the slaves from eating earth (Woywodt and Kiss, 2002). Black slaves also used to commit suicide by undertaking geophagia due to a firm belief that after death they would return spiritually to their native home (Abrahams, 2002).

## **2.2 Aetiology of Geophagia**

Some of the reasons advanced by geophagic individuals include the following: nutrient supplementation, detoxification, alleviation of gastrointestinal disorders such as diarrhoea, craving and relief from morning sickness or as part of cultural belief systems (Ngole and Ekosse, 2012).

### **2.2.1 Cultural Expectations**

It is believed that soil consumption is the link between good health, fertility and cultural belief of ancestors' blessings (Msibi, 2014). Soil is eaten openly by women of reproductive age in the Luo people of Kenya. Particular soils from termite mounds are preferred because of their red colour (the colour of blood), intense taste and fertility (Geissler *et al.*, 1999). In Malawi, it is indicated that it is very unusual expecting women not to eat soil because it is believed that it is the way women realise they are pregnant (Mahaney *et al.*, 2000). South African women believe that eating soil while pregnant makes the baby beautiful. Ongoing geophagia in families and communities may be the result of simple mother/daughter-sharing traditions (Msibi, 2014).

### **2.2.2 Medicinal Reasons**

Soil is used to heal common illnesses of the gastro-intestinal tract (GIT) because they possess medicinal properties (Msibi, 2014).

Kaolin and smectite are officially used in modern pharmaceuticals to prevent nausea, vomiting and gastro-intestinal disorders. Other types of clay soils such as termite earth have properties of binding microbes, giving protection to the individuals exposed to the microbes. Smectite clays have the properties of binding mucus in the intestines, causing intestinal linings to be impermeable to toxins and pathogens (Young, 2010).

### **2.2.3 Micronutrients Deficiency**

It has been suggested that geophagia represents a craving generated by a nutritional deficiency. Soil consumption has been shown to supply 17% - 55% of recommended pregnancy supplementation of Ca, Mg, Zn, Fe, Cu, Mn, K and Se (Brand *et al.*, 2009). People eat non-food substances because they are deficient in iron, zinc, calcium, or some other micronutrient and that pica is an attempt to increase micronutrient intake (Young *et al.*, 2008). Individuals who had zinc and iron deficiencies have been reported to abstain from the practice of geophagia after receiving iron and zinc supplements (Young, 2007).

### **2.2.4 Poverty and Famine**

Geophagia is often practised where poverty is prevalent and soil is used as an appetite suppressant and as bulking agent to still hunger during times of insufficient food availability (Msibi, 2014). The relationship between soil consumption, hunger and poverty has been acknowledged (Wywodt and Kiss, 2002).

Young (2010) explained this hypothesis "that hunger motivates pica", in the book, "Craving Earth", and suggests that there are four possible explanations for this practice:

- People who practice pica do not have enough food available;
- People who practice pica do so to fill their stomachs in an attempt to stave off feelings of hunger;
- Non-food substances would not be craved if other food was available;
- People practicing pica would then not choose specific non-food substances, but would eat any available non-food substances.

### **2.2.5 Pregnancy-related Cravings**

During pregnancy, the requirements for nutrients are very high such that expecting women with nutrient deficiencies develop cravings for earth, as the way of supplementing deficient nutrients like iron, zinc and calcium (Young *et al.*, 2010). A study undertaken in Kenya found that 56% of pregnant women that practiced geophagia had low iron status (Geissler *et al.*, 1999).

## **2.3 Characteristics of Geophagic Materials**

### **2.3.1 Physico-chemistry**

The ability of geophagic soil to fulfill the purpose for which they are ingested is also influenced by the physico-chemical properties of the soils. The release of nutrients from ingested soil into the body of the individual ingesting the soil depends on several aspects, including the CEC of the soil. Deficiencies in certain elements like Ca and Fe have also been used to justify the geophagic habits, especially in pregnant and lactating mothers (Ngole and Ekosse, 2015). Electrical conductivity could be used to indicate the amount of dissolved salts in soils. Geophagic soils that exhibit very low EC indicate that the amount of dissolved salts contained in them is low (Ngole *et al.*, 2006).

Geophagic individuals are influenced by the texture of geophagic materials and soil that is soft, silky or powdery is preferred. Geophagic soils from Cameroon studied by Diko and Diko (2014) were predominantly silty, and imparted a gritty feel to the materials. Geophagic soils that are gritty contain fine sand particles of quartz and feldspars, which may negatively affect dental enamel of geophagic individuals (Diko and Ekosse, 2014). Particle size distribution (PSD) of soils could provide clues to the possible health threats that the habit of geophagia may present to an individual (Ngole and Ekosse, 2015).

The pH and dissolved salt content of geophagic soils influences their taste. Generally, the more acidic soils tend to impart a sour taste. The use of soil to control the secretion of saliva during pregnancy, as reported by some women, could be linked to the sour taste of the soil (Diko and Diko, 2014).

Diko and Diko (2014) found the geophagic soils from Cameroon and South Africa ingested for the relief nausea and vomiting during pregnancy to be suitable for use as a remedy. Furthermore, colour could be indicative of mineralogy or presence of organic matter in the geophagic material. The most common shades employed to infer kaolin mineralogy are; white – cream, red, yellow – brown, and grey – green suggesting the presence of kaolinite, hematite, goethite and chlorite respectively (Diko and Ekosse, 2014).

The greyish colour may be attributed to the presence of finely disseminated organic matter (Ngole and Ekosse, 2012). Ngole *et al.* (2010) asserted that preference for reddish or brownish soils is based on the assumption that these materials are rich in iron.

### **2.3.2 Mineralogy**

Minerals in geophagic materials and clays can be quite different from minerals in the parent material from which the material was formed. This is because of the alterations that occur during the weathering process, where primary minerals are altered to form secondary minerals. Primary minerals are deposited or formed at the same time as the rock containing it (Churchman and Lowe, 2012). Minerals in geophagic material are mostly clay minerals formed from the alteration of primary minerals.

Johns (1986) found that four different geophagic clays consumed by Indian people from Bolivia, Peru, and Arizona were dominated by interstratified illite-smectite, sometimes with subsidiary amounts of other clay minerals such as kaolinite and chlorite. In a study by Mahaney *et al.* (2000), the mineralogy of soils consumed by humans in Indonesia was studied. Soils were clay-rich, and low in organic matter. Kaolin minerals, both kaolinite and halloysite, were major components of both the geophagic and control soils.

Ekosse and Jumban (2010) conducted a study on the mineralogy, chemistry and possible human health effects of geophagia and the primary minerals identified were quartz, potassium feldspar and muscovite. Furthermore, the secondary minerals were kaolinite, montmorillonitic smectite, and goethite.

Quartz and kaolinite were conspicuously dominant in the samples. In another study conducted in Kenya by Gichumbi *et al.* (2012), quartz and kaolinite were the dominant phases present in the samples. Other minerals identified included orthoclase, calcite, goethite, hematite, halloysite, gibbsite and smectite. Geophagic soils from selected rural communities in Gauteng and Limpopo Province were studied by Ekosse and Obi (2015). Kaolinite, smectite, talc, muscovite, quartz, calcite, dolomite, microcline, goethite and hematite were the minerals identified.

Two of the most dominant minerals in the geophagic soil samples were quartz and kaolinite. Geophagic clays from Vhembe District, studied by Momoh *et al.* (2015), showed remarkable traces of goethite and hematite minerals. When comparing results from the different studies, it can be concluded that quartz and kaolinite are the most dominant minerals in geophagic materials.

### 2.3.3 Geochemistry

In a study to investigate the geochemical characteristics of geophagic materials from Kenya, the samples had the highest silica content of 54.14% (Gichumbi *et al.*, 2012). The levels of  $Al_2O_3$  were also elevated with values ranging from 11.27 to 27.1%. It was also found that the values for  $Na_2O$  and  $K_2O$  were higher than those of  $CaO$  and  $MgO$  for all the samples (Gichumbi *et al.*, 2012). The values for  $FeO_3$  ranged from 9.20 to 12.7% and the most iron rich samples were obtained from a region where female populations are known to develop exceptional cravings for these materials during pregnancies.

The geochemistry of geophagic soils from Swaziland was studied by Ekosse and Ngole (2012). Chemical composition of the geophagic soils showed the predominance of  $SiO_2$  and  $Al_2O_3$ . Geophagic soil samples with high  $SiO_2/Al_2O_3$  ratio had high sand content which is also related to the high quartz content (Ekosse and Ngole, 2012). The concentrations of major oxides, apart from Al and Si, were generally very low, reflecting very intense weathering of primary minerals.

Odewumi (2013) conducted a study in Nigeria where the geochemical data indicated that geophagic clays composed of  $\text{SiO}_2$  content ranging from 64.40% to 46.30%,  $\text{Al}_2\text{O}_3$  values varied from 36.54% to 20.54%,  $\text{Fe}_2\text{O}_3$  values varied from 4.71% to 1.42%,  $\text{MgO}$  content varied from 0.08% to 0.06%,  $\text{CaO}$  ranged between 1.30% and 0.03%,  $\text{TiO}_2$  values varied from 9.17% to 0.20%, and  $\text{MnO}$  content ranges from 0.631% to 0.09%. These values indicated that the geophagic clays are essentially siliceous aluminosilicates (Odewumi, 2013).

Geochemical analysis results of a study by Olusola (2014), showed the predominance of  $\text{SiO}_2$  (47.14 to 64.92 wt. %) and  $\text{Al}_2\text{O}_3$  (19.47 to 29.39 wt. %) which support the kaolinitic nature of the clay and classifies the clay as aluminosilicates. Other major elements detected were in low percentages. Those include  $\text{Fe}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{K}_2\text{O}$  and  $\text{Na}_2\text{O}$ .

The relatively low  $\text{Fe}_2\text{O}_3$  may be responsible for non detection of iron oxide minerals haematite or goethite from the analysis of the clays (Olusola, 2014). The low percentages of  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{K}_2\text{O}$  and  $\text{Na}_2\text{O}$  suggest the clays are most probably non-expandable/swelling, with low feldspar content (Olusola, 2014). It was then concluded that the main oxide present in geophagic samples is silica (Gichumbi *et al.*, 2012).

Furthermore, the relative abundance of the trace elements (Cu, Pb, Zn, Ag, Ni, Co, Sr, Cd, Ba, Cr, Mo, and Mn) was compared with that of Post-Archean Australian Shale (PAAS), North American Shale Composite (NASC) and Upper Continental Crust (UCC) and a wide variation was observed. The investigated clays were depleted in Zn, V, Cu, Cr, Rb and Sr compared to UCC, NASC. However, the chemical composition was similar to that of the proxy source, the Ilorin Granite. There was not much variation in the trace elements of the samples analysed. The distribution of trace elements in clays and sediments were influenced by weathering processes and nature of the parent rocks (Olusola, 2014).



## 2.4 Genesis of Clay Minerals in Soils

There are three principal mechanisms that account for the genesis of clay minerals in nature, that is, neoformation, inheritance and transformation operating in three geological environments; weathering, sedimentary and diagenetic-hydrothermal (Millot, 1970; Wilson, 1999). A pattern exists relating mechanism to environment (Figure 2.1); however, there are numerous exceptions. Generally, inheritance is dominant in the sedimentary environment where reaction rates are slow whereas transformation, a mechanism that can require large inputs of energy is prevalent in the higher temperature diagenetic-hydrothermal environment (Grim and Kodama, 2016).

The first mechanism, neoformation, is the formation of clay minerals through crystallization of solutions in response to changes in the environmental conditions (Eberl, 1984). The type of clay minerals by neoformation may change as a function of nature of the parent rock, climate, topography, vegetation and the time period during which these factors operated (Grim and Kodama, 2016). Inheritance dominates in sedimentary environment whereby clay minerals are inherited from pre-existing parent rock or weathered materials (Wilson, 1999).

According to Eberl (1984), this happens because either reaction rates are slow or equilibrium has been reached so minimal changes occur in the composition during transportation and deposition. Origin by transformation occurs in the diagenetic-hydrothermal environment where there is deep burial or subjection to an igneous intrusion. Transformation takes place in two forms, that is, ion exchange and layer transformation. In ion exchange, loosely bound ions are exchanged with those of the environment whereas in layer transformation the arrangements of the interlayer cations are modified (Eberl, 1984).

In this mechanism, both aggradation (addition) and degradation (depletion) of alkalis, alkaline earths and other elements influence the formation of clay minerals (Wilson, 1999). Transformed clays carry both the inherited characteristics from the source area and the characteristics from the response to in situ changes in environment.

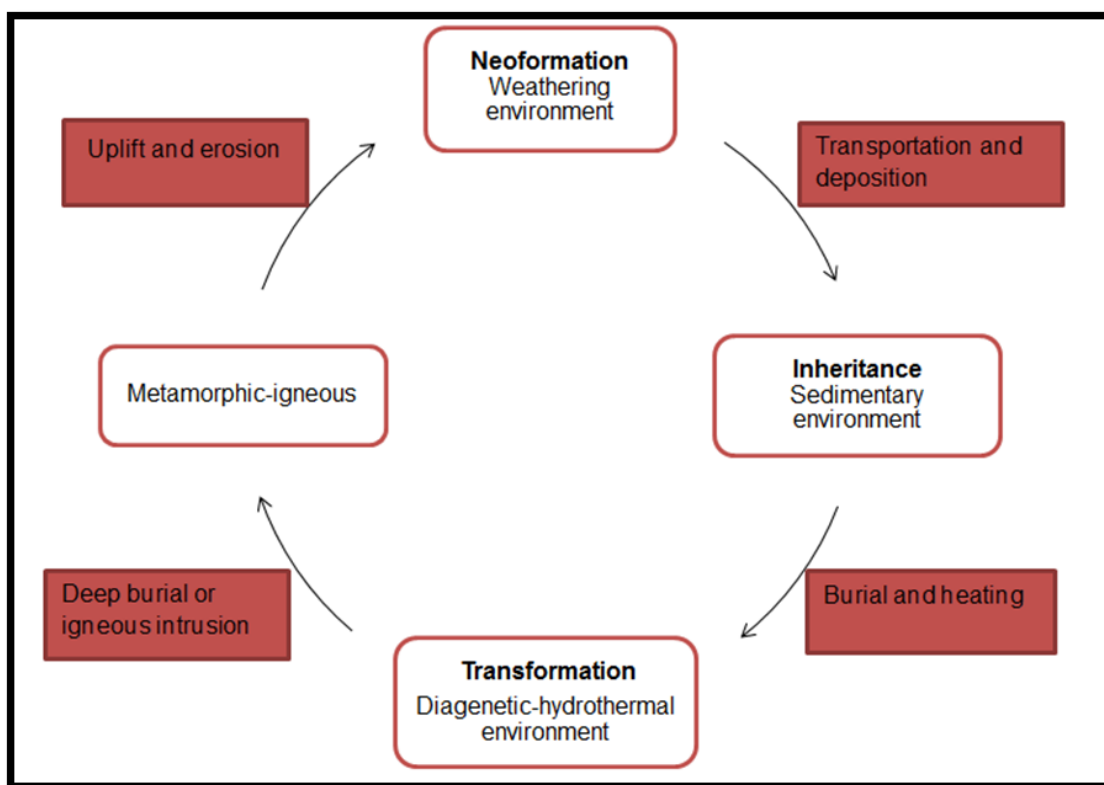


Figure 2.1: Mechanisms and environment for genesis of clay minerals (Modified from Eberl, 1984).

Dixon (1989) reviewed the origin and formation of kaolin minerals and showed that precipitation from solution of kaolinite required acid conditions with moderate silica activity and small amounts of base cations (alkalies or alkaline earths). The micaceous minerals that occur in soil clay fractions have been inherited largely from parent rock or other material, where they originally formed under different conditions from those at the earth's surface (Fanning *et al.*, 1989).

In an open environment, generally unstable olivines easily lose  $Mg^{2+}$ ,  $Fe^{2+}$  or  $Mn^{2+}$  to give first serpentine then smectite and goethite (Churchman and Lowe, 2012). Allen and Hajek's (1989) review referred to several studies where smectites have been identified as products of the alteration of feldspars. The formation of goethite is marked by the oxidation state change of  $Fe^{2+}$  to  $Fe^{3+}$  in iron-rich minerals which allows for goethite to exist at surface conditions. As iron-bearing minerals are brought to the zone of oxidation within the soil, the iron turns from iron(II) to iron(III), while the original shape of the parent mineral is retained.

Vermiculites are mostly formed from the hydrothermal alteration of mica and the main changes that occur are exchange of the interlayer cations and reduction in the charge of the layers (Churchman and Lowe, 2012). In this process, potassium ions occupy interlayer regions of the common micas, biotite and muscovite. Soil composition is greatly influenced by the composition of the parent rock, making the minerals in the soil to have different elemental composition and hence different health impacts (Wilson, 2003). Knowing the origin of geophagic soils is therefore of great importance in studying geophagia and its possible health impacts.

## **2.5 Benefits of Geophagia**

### **2.5.1 Mineral Supplementation**

Soil ingestion in human beings maintains homeostasis in the body by correcting mineral nutrients imbalance because soil contains large quantities of both macro- and micro mineral nutrients (Johns and Duquette, 1991). Clay soils are ingested due to nutrient and mineral deficiency. According to Ekosse and Obi (2015), geophagia could supply a good quantity of supplementation of calcium, magnesium, iron and potassium. Some people believe that zinc and iron are acquired from the eating of clay (Hooda *et al.*, 2004). Red earth has properties used to prevent iron deficiency anaemia, although iron bioavailability is still not clearly understood (Johns and Duquette, 1991).

### **2.5.2 Medicinal Benefits**

Soil minerals have been used in medical practices ever since ancient times, where they were applied in the pharmaceutical and cosmetic industries (Wanzala *et al.*, 2016). Kaolinite acts as a potent antidiarrheal by binding toxins and bacteria and forming a protective coat on the intestines (Young, 2010). Montmorillonite has been used as anti-poison while kaolin (which is commonly found in clay) has the potential to reduce nausea and gastro-intestinal upset (Wanzala *et al.*, 2016). The pH of clays is higher than that of hydrochloric acid in the stomach and because of the alkaline properties of the clays; it could play a role in reducing heartburn (Nyaruhucha, 2009).

### **2.5.3 Relief of Nausea and Vomiting During Pregnancy**

A study by Diko and Diko (2014), to appraise the ability of geophagic soils from Cameroon and South Africa, ingested for the relief of *morning sickness* (Nausea and vomiting during pregnancy) found the samples to be suitable for use as remedy. For these people, the choice of soil over a more conventional alternative treatment for *morning sickness* is based on their belief systems, premised on cultural themes such as, soil represents fertility (Diko and Diko, 2014). Daughters in these tribes will follow the same diet as their mothers because they know that it has been successful in the past (Msibi, 2014).

## **2.6 Health Threats of Geophagic Materials**

Despite the beneficial aspects of geophagia, several studies have associated the practice with detrimental effects such as iron deficiency, anaemia, excessive tooth wear and enamel damage (Magongoa *et al.*, 2011).

### **2.6.1 Dental Damage**

Geophagists can be identified by dentists by the excessive tooth abrasion, cracks, decay and a rare pattern of damage to the tooth surface (Young, 2007). Quartz is the dominant mineral found in geophagic materials because of its resistance to weathering. Quartz particles in studied geophagic clays are very angular and coarse. They are also chemically and mineralogically inert (Ekosse and Anyangwe, 2012). In the mouth, quartz particles easily damage dental enamel because their hardness is more than that of the main dental enamel material, hydroxylapatite (a calcium phosphate mineral with a Moh's scale hardness of 5) (Ngole *et al.*, 2010).

### **2.6.2 Gastro-intestinal Problems**

Radiological examination of geophagists' abdomens may reveal opaque soil masses in the colon. This may lead to constipation, which in turn leads to abdominal obstruction and pain as a result of the soil accumulation in the colon (Abrahams, 2002).

Mechanical bowel problems, constipation, ulcerations and intestinal obstruction, perforation and maternal death have been reported in cases where clay consumption was common (Abrahams, 2002).

### **2.6.3 Nutritional Disadvantages**

Geophagia practices have been suggested to provide nutrient supplementation to the participant. Despite this, bioavailability studies of iron and zinc have, however, indicated that the clay does not actually provide additional zinc and iron. Rather it has been found that it binds with the iron in foods ingested at the same time, reducing the total amount of available dietary iron (Hooda *et al.*, 2004). Therefore, soil ingestion can potentially reduce bio-available nutrient absorption in the human diet and lead to micronutrient deficiencies; for example, anaemia (Hooda *et al.*, 2004; Brand *et al.*, 2009).

### **2.6.4 Source of Heavy Metal Toxicity**

Despite the advantages of geophagia, ingestion of soil may also constitute a health risk for human beings because geophagic materials are mostly contaminated with toxic heavy metals (Fosso-Kankeu *et al.*, 2015). The risk associated with the ingestion of contaminated soil depends on the element of interest, how much is consumed (dose), how often (frequency) and the bioavailability.

Heavy metals include Ag, Al, As, B, Ba, Be, Cd, Co, Cr, Cu, Mo, Ni, Pb, Pt, Rh, Sb, Se, Sn, Ta, Te, Th, Ti, U, V, W, Yb, Zn and Zr but certain heavy metals are of interest toxicity studies. The U.S Environmental Protection Agency (EPA) listed As, Cd, Cr and Pb as the heavy metals of major interest in bioavailability studies (McKinney and Rogers, 1992).

These metals were selected because of their potential for human exposure and increased health risk. In a study conducted in Cameroon, the values of cadmium and lead were above the acceptable thresholds for edible matter. Consequently, people who were consuming kaolin were exposed to the toxicity of these heavy metals (Bonglaisin *et al.*, 2015). There are exposure limits (Table 2.1) set to specify the permissible levels that people can be exposed to over a certain period of time before there can be health implications.

A Minimal Risk Level (MRL) is an estimate of the daily human exposure to a hazardous substance that is likely to be without appreciable risk of adverse noncancer health effects over a specified duration of exposure (Agency for Toxic Substances and Disease Registry, 2016).

Table 2.1: Acute and chronic exposure MRLs for arsenic, cadmium, chromium and lead (Modified from Agency for Toxic Substances and Disease Registry, 2016)

| Heavy Metal | Acute Exposure MRL<br>(mg/kg/day) | Chronic Exposure MRL<br>(mg/kg/day) |
|-------------|-----------------------------------|-------------------------------------|
| Arsenic     | 0.0003                            | 0.005                               |
| Cadmium     | 0.0005                            | 0.0001                              |
| Chromium    | 0.005                             | 0.0009                              |
| Lead        | 0.0003                            | 0.00005                             |

## 2.7 Usage of Questionnaires

Survey research is a commonly used method of collecting information about a population of interest. Questionnaire survey is one of the survey techniques used in research. A questionnaire is a predefined series of questions used to collect information from individuals (Roopa and Rani, 2012; Akinci and Saunders, 2015). The two most common types of survey questions are closed-ended questions and open-ended questions (Roopa and Rani, 2012). In closed-ended questionnaires, the respondents are given a record of prearranged responses from which to choose their answer. The list of responses includes every possible response to the listed questions.

On the other hand, open-ended questionnaires allow respondents to answer each question in their own words (Akinci and Saunders, 2015). Questionnaire surveys collect both qualitative and quantitative data. Qualitative methods of data collection are used to understand the feelings, values and perceptions that underlie a concept of interest (Gratton and Jones, 2004).

Quantitative methods (expressed by means of statistical data) are used for collection of biographical information; for instance, gender, age, education level and income that will be requested from respondents (Msibi, 2014).

Various methods of sampling a population for survey are used; nonetheless, snowball and purposive sampling are the common ones. Snowball sampling is a nonprobability sampling technique (Akinci and Saunders, 2015) which involves identifying respondents who are then used to refer researchers to other respondents, while purposive sampling relies on the judgement of the researcher. In purposive sampling, participants are selected based on the researcher's knowledge about the study, the population and the purpose of the sample; hence the name (Etikan *et al.*, 2016).

## **2.8 Analytical Techniques**

Different methods are used for the analysis of different samples. The commonly-used techniques are Atomic Absorption Spectroscopy (AAS), Inductively Coupled Plasma Mass Spectroscopy (ICP-MS), X-ray Diffraction (XRD) and X-ray Fluorescence (XRF). These techniques complement each other so well that it may not always be clear which one is the optimum solution for a particular application. Selecting a technique requires the consideration of a variety of important criteria, including detection limits, data quality, cost, interferences, ease-of-use and availability of proven methodology (Pandian, 2014).

### **2.8.1 Atomic Absorption Spectroscopy (AAS)**

Atomic absorption occurs when a ground state atom absorbs energy in the form of light of a specific wavelength and is elevated to an excited state. The relationship between the amount of light absorbed and the concentration of analytes present in known standards can be used to determine the unknown sample concentrations by measuring the amount of light they absorb (Khandpur, 2006). Atomic Absorption Spectroscopy requires standards with known analyte content to confirm the linear relationship between the determined absorbance and the analyte's concentration. AAS relies therefore on the Beer-Lambert Law:

$$A = a(\lambda) * b * c \quad (2.1)$$

A is the measured absorbance,  $a(\lambda)$  is a wavelength-dependent absorptivity coefficient, b is the path length, and c is the analyte concentration.

To carry out an atomic absorption spectroscopy, a primary light source, an atom source, a monochromator to isolate the specific wavelength of light to be measured, a detector to measure the light accurately, and electronics to process the data signal and a data display or reporting system to show the results are required (PerkinElmer, 2011).

### 2.8.2 Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

In inductively coupled plasma mass spectrometry, the sample which is usually in liquid form is pumped into the sample introduction system (Jarvis *et al.*, 1992). The sample is converted into an aerosol, which is then ionised. The sample exits the plasma as ground state atoms and ions, representing the elemental composition of the sample (Worley and Kvech, 2000).

Ions move into the mass analyser and then into the detector, which converts the ions into electrical pulses. These are then counted individually. The magnitude of the electrical pulses corresponds to the number of analyte ions present in the sample (Wolf, 2005). After detection, this data is sent to the computer for analysis, where trace element quantitation is done by comparing the ion signal with known calibration or reference standards (Jarvis *et al.*, 1992).

### 2.8.3 X-Ray Diffraction (XRD)

In this diffractometry, a focused beam of X-rays interacts with a sample, and part of it is diffracted (Pandian, 2014). The XRD provides information about the sample by measuring the distances between the planes of the atoms that constitute the sample (d-spacings). This is done by applying Bragg's Law:

$$n\lambda = 2d \sin\theta \quad (2.2)$$

The integer n is the order of the diffracted beam,  $\lambda$  is the wavelength of the incident X-ray beam, d is the distance between adjacent planes of atoms (the d-spacings), and  $\theta$  is the angle of incidence of the X-ray beam (Chacha, 2014).



The angle and intensity of the diffracted beam recorded by a detector forms a diffraction pattern, which provides information about the sample, including types and nature of minerals present. The diffraction pattern for every phase is as unique as a fingerprint. Computers determine what phases are present in a sample by using programs which quickly compare the d spacing of the unknown to those of known materials (Chacha, 2014).

#### **2.8.4 X-Ray Fluorescence (XRF) Spectroscopy**

The basis of XRF is the interaction of X-ray photons from a separate excitation source (X-ray tube) with atoms of the elements of interest found in the sample. When these excitation photons interact with the atoms in the sample, they cause the ejection of inner shell electrons (Jenkins *et al.*, 2000). The atom wanting to restore the original configuration, transfers an electron from an outer shell to the hole in the inner shell.

This results in the emission of energy surplus because outer shell electrons have higher energy than electrons in the inner shell (Brouwer, 2010). The energy of the X-ray is characteristic of the element (Jenkins *et al.*, 2000). The number or intensity of X-rays produced at a given energy provides a measure of the amount of the element present by comparisons with standards (Brouwer, 2010). The XRF spectrometer operates on the principle of Bragg diffraction (Guthrie, 2012) (Equation 2.1).

### **2.9 Geochemical Data Interpretation**

#### **2.9.1 Weathering Indices**

Assessing weathering indices provides a visual representation of changes in bulk chemistry, with presumed increasing (or decreasing) weathering of the parent rock (Fiantis *et al.*, 2010). The following weathering indices, sometimes referred to as indices of alteration, are commonly used for characterising weathering profiles: Chemical Index of Alteration (CIA), Chemical Index of Weathering (CIW), Plagioclase Index of Alteration (PIA), Weathering Index of Parker (WIP), Product of Weathering Index (PWI), Ruxton Ratio (R), Silica-Titania Index (STI) and Vogt's Residual Index (V) (Price and Velbal, 2003).

The CIA was developed by Nesbitt and Young (1982). It is interpreted as the ratio of secondary aluminous minerals (clay minerals) to feldspar (Equation 2.3). It is essentially a measure of the extent of conversion of feldspars to clays such as kaolinite (Price and Velbal, 2003).

$$\text{CIA} = (100)[\text{Al}_2\text{O}_3/(\text{Al}_2\text{O}_3 + \text{CaO} + \text{Na}_2\text{O} + \text{K}_2\text{O})] \quad (2.3)$$

Harnois (1988) developed the CIW. The CIW is identical to the CIA, except that it does not account for the aluminium associated with K-feldspar (Equation 2.4). Most unaltered rocks and primary minerals have CIA and CIW values near 50. By contrast, the secondary products have CIA and CIW values of 70–85 for smectite and illite and 100 for kaolinite group minerals and chlorite (Nesbitt and Wilson, 1992). However, the CIW may yield very high values for K-feldspar-rich rocks, whether they are chemically weathered or not, because it eliminates K<sub>2</sub>O from the equation.

$$\text{CIW} = (100)[\text{Al}_2\text{O}_3/(\text{Al}_2\text{O}_3 + \text{CaO} + \text{Na}_2\text{O})] \quad (2.4)$$

Because plagioclase content in the source rocks is quite abundant, evaluating the PIA (Equation 2.5) is best suited for predicting the changes that may have occurred with the plagioclase feldspar minerals (Fiantis *et al.*, 2010). Fedo *et al.* (1995) proposed the PIA as an alternative to the CIW. The high PIA values indicate most plagioclase has been converted to clay minerals.

$$\text{PIA} = (100)[(\text{Al}_2\text{O}_3 - \text{K}_2\text{O})/(\text{Al}_2\text{O}_3 + \text{CaO} + \text{Na}_2\text{O} - \text{K}_2\text{O})] \quad (2.5)$$

Parker (1970) introduced the WIP, which is based on the proportions of alkali and alkaline earth metals present (Equation 2.6) (Price and Velbal, 2003).

$$\text{WIP} = (100)[(2\text{Na}_2\text{O}/0.35) + (\text{MgO}/0.9) + (2\text{K}_2\text{O}/0.25) + (\text{CaO}/0.7)] \quad (2.6)$$

According to Souri *et al.* (2006), WIP and PWI (Equation 2.7) can be used simultaneously to investigate the mobility of alkaline and alkaline-earth metals and to track movements of less mobile elements. Unlike CIA and CIW, as the values of WIP and PWI decrease, samples are more weathered and assumed to be older (Fiantis *et al.*, 2010).

$$\text{PWI} = [\text{SiO}_2/(\text{TiO}_2 + \text{Fe}_2\text{O}_3 + \text{SiO}_2 + \text{Al}_2\text{O}_3)] \quad (2.7)$$

The Ruxton was proposed by Ruxton (1968) and it relates silica loss to total element loss and considers alumina (and other oxides) to be immobile during weathering. The Ruxton Ratio is the silica alumina (SA) ratio (Equation 2.8); hence, decreasing SA value indicates an increasing intensity of weathering because alumina content increases as the silica content decreases (Ruxton, 1968).

$$SA = \text{SiO}_2/\text{Al}_2\text{O}_3 \quad (2.8)$$

### 2.9.2 Major and Trace Elements

The intensity of the weathering is clearly observable in the mineralogical composition as well as in the distribution of some mobile major elements. Minerals which contain Ca, Na, Mg, Fe and Mn degrade quickly during weathering, breaking down into Al-rich clays, such as kaolinite, and oxyhydroxides (Cox *et al.*, 1995).

The depletion of highly mobile K and Na elements is due to leaching during the formation of clay minerals during increased chemical weathering (Obasi and Madukwe, 2016). Major elements ternary diagrams are useful for evaluating fresh rock compositions and examining their weathering trends because the upper crust is dominated by plagioclase- and K-feldspar-rich rocks (Fedo *et al.*, 1995) and their weathering products, the clay minerals.

Silica-Alumina ( $\text{SiO}_2/\text{Al}_2\text{O}_3$ ) ratios of clastic rocks are sensitive to sediment recycling and weathering process and these are indicators of sediment maturity. This is because quartz survives preferentially to feldspars and mafic minerals (Obasi and Madukwe, 2016). The average  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios in unaltered igneous rocks range from ~ 3.0 (basic rocks) to ~ 5.0 (acidic rocks). Values of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio > 5.0 in sandstones are an indication of progressive maturity (Obasi and Madukwe, 2016). Low values of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios and low values of  $\text{K}_2\text{O}/\text{Na}_2\text{O}$  together indicate a mineralogically immature sediment.

Trace element compositions could potentially be a source of information to determine provenance. Trace elements such as rare earth elements (REE), Th, Sc, Cr, Zr and Co are the most useful for provenance characterization because of their relatively immobile behaviour (Mongelli *et al.*, 2006).

These elements are among the least soluble elements during sedimentary processes and thus preserve the chemical signature of their source rocks (Lopez *et al.*, 2005). The trace elements La and Th are abundant in felsic rocks, while mafic rocks are enriched with Sc and Co.

## 2.10 Summary

This Chapter entailed a brief literature review on aspects associated with the main areas of the study. It covered the phenomenon of geophagia, aetiology of the practice, characteristics of geophagic materials, genesis of minerals in soils, benefits and health threats of geophagia, techniques used for analysis of geophagic materials and geochemical data interpretation.

## CHAPTER 3

### MATERIALS AND METHODS

The research design consisted of two stages of data collection, namely, preliminary work and detailed study, as presented in Figure 3.1. The procedure for the first stage included gathering existing data linked to the topic (desktop study) and inspecting the study area to have an overview of the site (reconnaissance survey). The second stage of the research method involved more precise and specific modes of data acquisition. This chapter discusses various techniques, procedures and summary of the work program which was employed in the investigation of the mineralogy and geochemistry of geophagic materials commonly ingested in the study area.

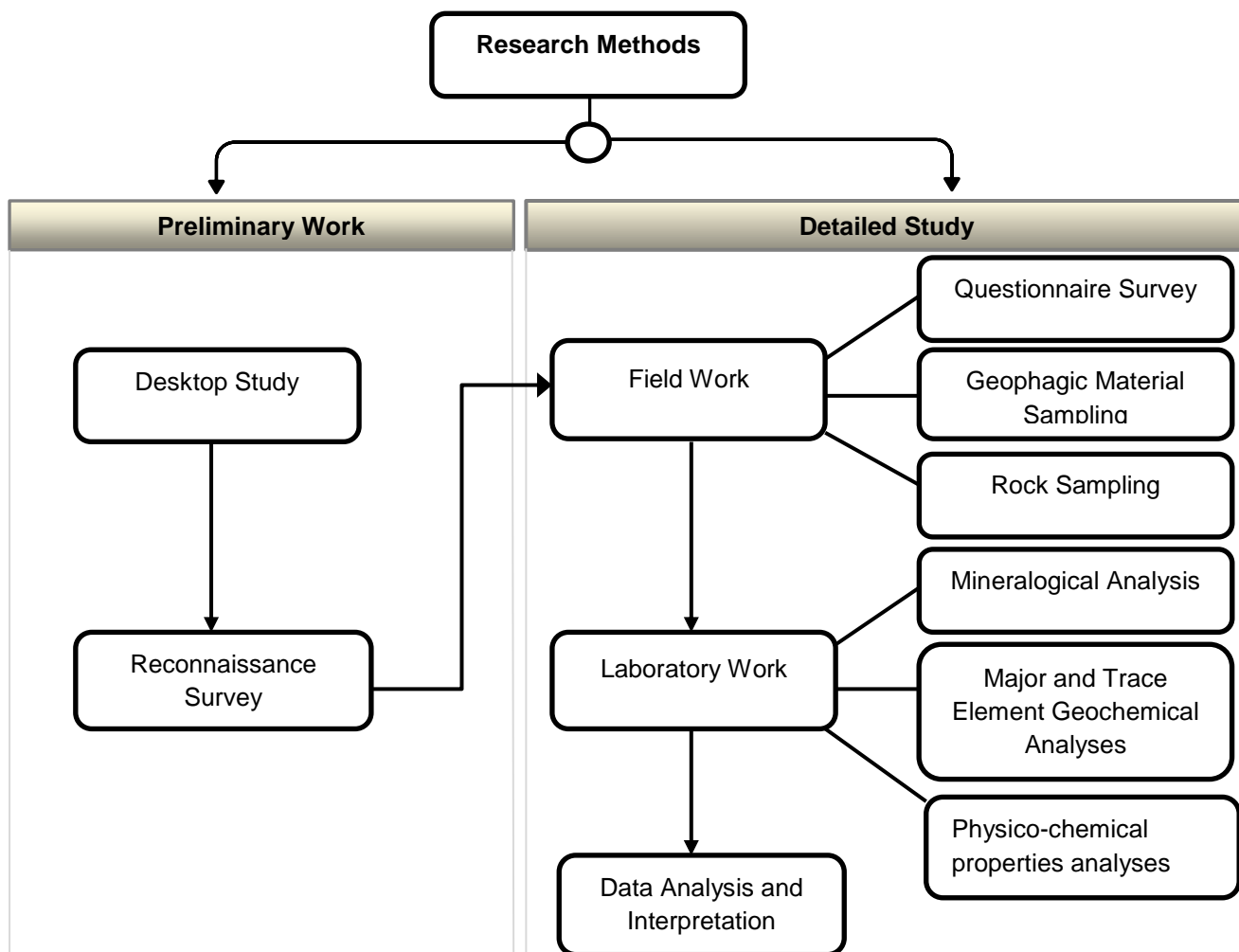


Figure 3.1: Research design

### **3.1 Preliminary Work**

This was the first stage of the investigation and it involved studies undertaken before the actual work. It was composed of two phases, namely; desktop study and reconnaissance.

#### **3.1.1 Desktop Study**

During this phase, existing information associated with the topic and the study area was gathered from materials such as books, documents, internet and journals before the definite work. The mineralogy, geochemistry and health implications of regularly-ingested geophagic materials were evaluated. The different approaches for data acquisition were further reviewed.

#### **3.1.2 Reconnaissance Survey**

Reconnaissance survey involved visiting the study area to get an overview of the area before visiting the location for data collection. Geological information learned from the studied materials was correlated with what was observed on the site. General and non-detailed information about the study area was collected. The survey was crucial as it served to confirm whether the study area is accessible or not and for identifying areas where detailed studies could be conducted.

### **3.2 Field Work**

The field work involved visiting the site for proper and thorough data collection. This was attained through a questionnaire survey, geophagic material sampling as well as rock sampling using relevant methods.

#### **3.2.1 Questionnaire Survey**

A standardised questionnaire developed by Ekosse (2008) was used to collect both qualitative and quantitative data. The questionnaire was developed to characterise human geophagic habits and has been used earlier by the geophagia working group in South Africa, Botswana and Swaziland.

The aim of the survey was to generate data on socioeconomic features, reasons for geophagia, perceptions about the practice, location of the consumed materials as well as the health benefits and consequences derived from geophagia. The questionnaire used during the survey is presented in Appendix 3.1.

Both purposive and snowball sampling were used to identify geophagists in the study area. Purposive sampling was used to select participants based on the researcher's knowledge about their geophagic habit. In snowball sampling, respondents identified during purposive sampling were used to identify other respondents who were then used to refer the researcher to other respondents. A total of 200 questionnaires were administered to the geophagists in the study area.

### **Ethical Considerations**

Ethical considerations were followed and prior to the survey, approval was acquired from the University of Venda Research Ethics Committee (Project no. SES/17/MEG/10/0310). Permission to conduct the survey was also obtained from the traditional leadership after the purpose of the study was explained. The aim of the research was described to the participants orally, in a language they understand. Written consent forms were signed prior to data collection (Appendix 3.2). It was ensured that geophagists understood what their involvement meant and that they voluntarily admit to participate. Participants were allowed to withdraw their consent and participation in the study at any stage, without prejudice. Results of the study, including personal details were anonymously processed into a study report and will remain confidential.

### **3.2.2 Geophagic Materials and Parent Rocks Sampling**

Geophagic samples as well as parent rocks were collected. Samples were collected from three locations in Mashau; that is, two sub-villages where geophagic practice is more prevalent (Doli and Mukhoru) and a traditional geophagic mine site in Matsilele. From the located sites, a total of 20 geophagic and 8 rock samples were collected. From each location where geophagic soils were sampled, representative rock samples were collected. The different locations from where the samples were collected are shown in Table 3.1.

Table 3.1: Sampling locations of the collected samples

| Sample ID                | Location from where the sample was collected | Geographic coordinates |            |
|--------------------------|--|------------------------|------------|
| <b>Geophagic samples</b> |  |                        |            |
| S1                       | Doli   | 23°09'30"S             | 30°16'54"E |
| S2                       | Doli   | 23°09'33"S             | 30°16'02"E |
| S3                       | Doli   | 23°09'40"S             | 30°17'03"E |
| S4                       | Doli   | 23°09'46"S             | 30°16'08"E |
| S5                       | Doli   | 23°09'55"S             | 30°16'74"E |
| S6                       | Doli   | 23°09'53"S             | 30°16'24"E |
| S7                       | Doli   | 23°09'35"S             | 30°16'17"E |
| S8                       | Doli   | 23°09'32"S             | 30°16'34"E |
| S9                       | Doli   | 23°09'41"S             | 30°16'42"E |
| S10                      | Doli   | 23°10'00"S             | 30°15'29"E |
| S11                      | Doli   | 23°09'47"S             | 30°16'52"E |
| S12                      | Mukhoro                                      | 23°09'35"S             | 30°14'51"E |
| S13                      | Mukhoro                                      | 23°09'15"S             | 30°14'43"E |
| S14                      | Mukhoro                                      | 23°09'18"S             | 30°15'04"E |
| S15                      | Mukhoro                                      | 23°09'06"S             | 30°14'52"E |
| S16                      | Mukhoro                                      | 23°09'22"S             | 30°14'51"E |
| S17                      | Mukhoro                                      | 23°09'33"S             | 30°15'06"E |
| S18                      | Matsilele                                    | 23°08'25"S             | 30°13'26"E |
| S19                      | Matsilele                                    | 23°08'25"S             | 30°13'27"E |
| S20                      | Matsilele                                    | 23°08'25"S             | 30°13'26"E |
| <b>Rock samples</b>      |  |                        |            |
| DOL 1                    | Doli   | 23°09'42"S             | 30°16'08"E |
| DOL 2                    | Doli   | 23°09'59"S             | 30°16'18"E |
| DOL 3                    | Doli   | 23°09'57"S             | 30°15'37"E |
| MAR                      | Doli   | 23°09'74"S             | 30°16'29"E |
| MUK 1                    | Mukhoro                                      | 23°09'21"S             | 30°14'53"E |
| MUK 2                    | Mukhoro                                      | 23°09'15"S             | 30°14'51"E |
| MAT 1                    | Matsilele                                    | 23°08'24"S             | 30°13'23"E |
| MAT 2                    | Matsilele                                    | 23°08'24"S             | 30°13'25"E |

Sampling of geophagic materials was random and depended on the location of the consumed material. Parent rocks' sampling depended on the location of the consumed materials and the availability of outcrops. Sampling location maps are presented in Figures 3.2 - 3.4.





Figure 3.2: Location of sampling points in Doli

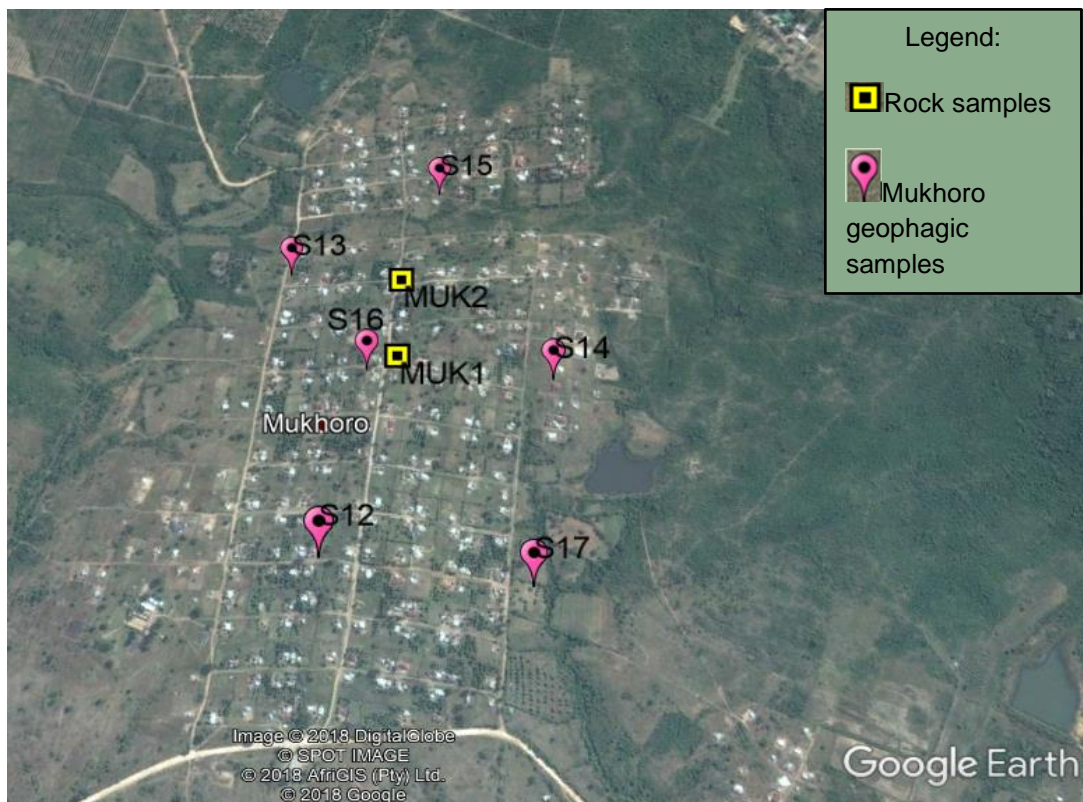


Figure 3.3: Location of sampling points in Ha-Mukhoro

The geophagic mine in Matsilele is approximately 7 Km and 6 Km from Doli and Mukhoro, respectively.

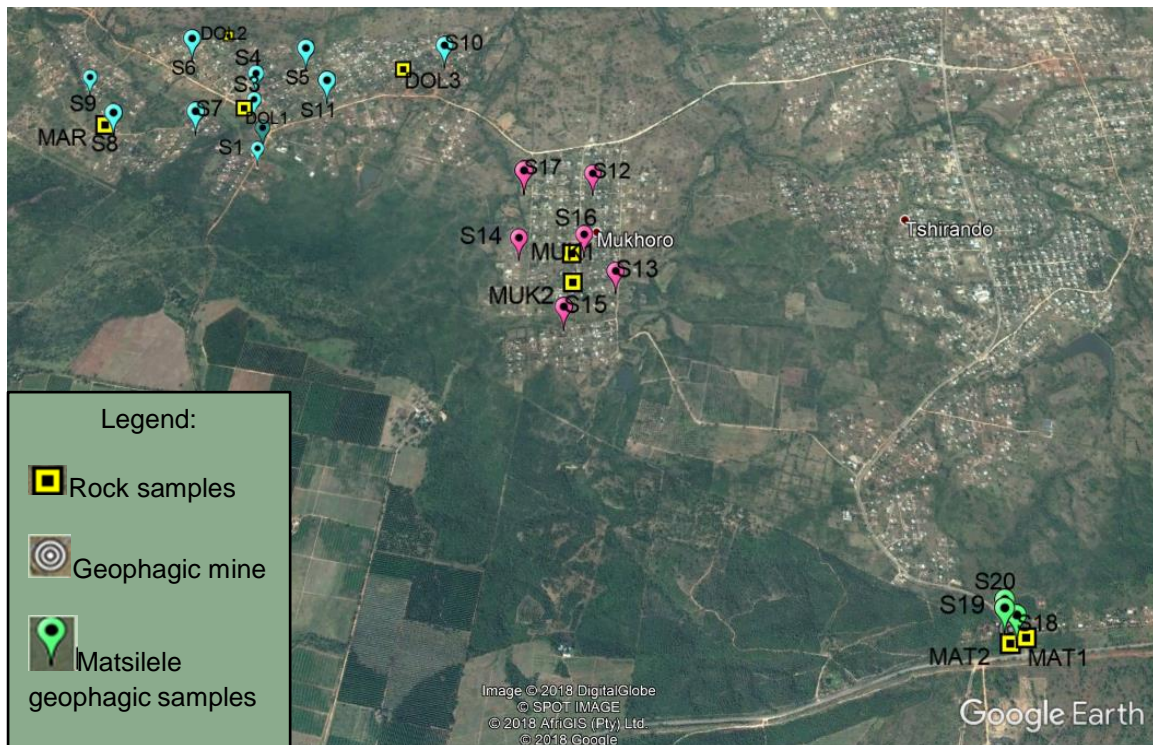


Figure 3.4: Sampling points in Matsilele in relation to other sampling locations

The consumed materials were mainly soil from tree termitaria, mounds and soil from geophagic mine sites; however, other sources included decaying wood and the road side (Figure 3.5-Figure 3.7). Samples from termite mounds, geophagic mine sites and road side were collected by digging with a pre-cleaned hand trowel after removing the overburden. Geophagic samples from trees and decaying wood were scrapped off the tree or wood using a hand trowel. Samples were then transported to the laboratory, where they were air or oven-dried and prepared for various analyses. Rocks were sampled by obtaining a fresh representative sample from the outcrops using a geological and a sledge hammer.





Figure 3.5: Typical geophagic mine site



Figure 3.6: Termitaria geophagic soil





Figure 3.7: Geophagic soil collected from a decaying wood

### 3.3 Laboratory Work

#### 3.3.1 Physico-chemical Analyses

Soil samples were subjected to physico-chemical analyses to determine their colour, particle size distribution (PSD), concentration of hydrogen ion (pH), cation exchange capacity (CEC) and electrical conductivity (EC).

##### 3.3.1.1 Colour

Colour descriptions were obtained by visually comparing the colour of the samples to colours of standard soils recorded in the Munsell Soil Colour Charts (2009) (Figure 3.8a). The charts describe colours in the order of their hue (actual colour), value (degree of lightness), and chroma (strength of colour) as presented in Figure 3.8b. Colour charts were obtained from the Department of Soil Science, University of Venda.

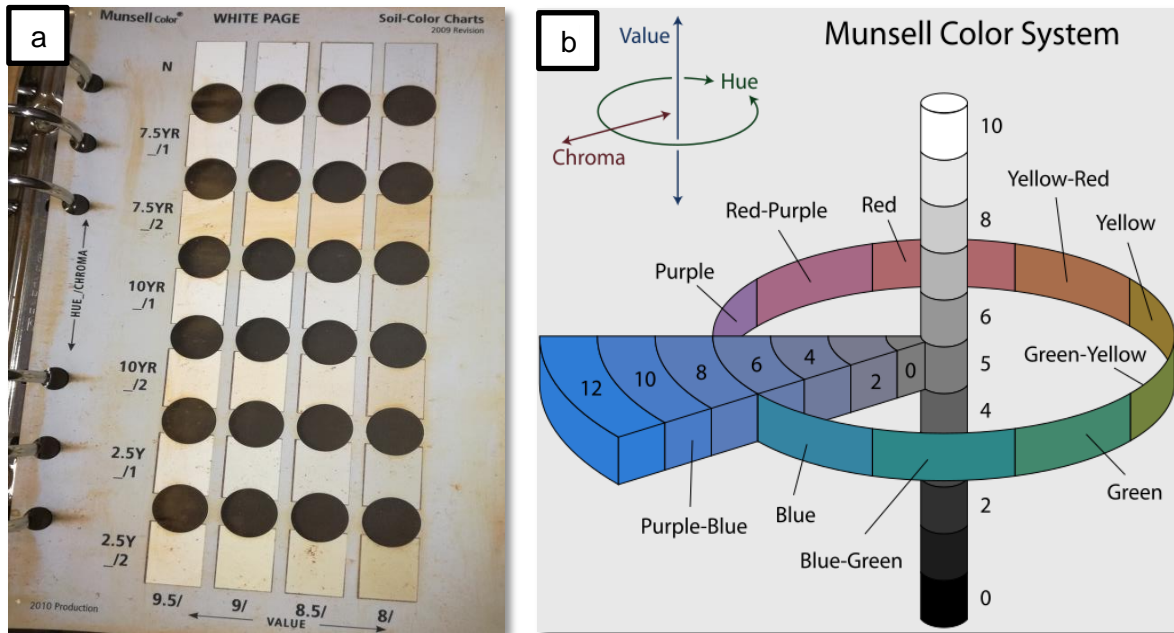


Figure 3.8: a. Munsell colour chart (Source: Munsell Soil Colour Charts, 2009) b. Munsell colour system (Source: Wikipedia, 2007)

The hue refers to the quality by which one colour is discerned from another in the manner they are displayed on the electromagnetic spectrum. This dimension does not reveal whether the colour is dark or light, or strong or weak.

Soils with purer colours have higher hue. The value of a soil colour indicates the amount of light reflected and is used to distinguish a light colour from a dark one. A soil colour value of 10 indicates total reflection (white soil) while the value of 0 indicates no reflection (black soil) (Cleland, 2014). Chroma of a soil refers to the concentration of the hue. Colours of low chroma are referred to as weak while those of high chroma are said to be highly saturated, strong or vivid.

### 3.3.1.2 Particle Size Distribution Analysis (PSDA)

The particle size distribution of the geophagic soils was determined by the hydrometer method following procedures in Brown *et al.* (2016). Particle distribution analysis was done in the Department of Soil Science laboratory, University of Venda. For each sample, 50 g of sieved (passing through a 2mm sieve), oven-dried soil (dried at 40 °C for 48 hours) was analysed.

Prior to analysis, each sample was treated with hydrogen peroxide for organic matter removal. For dispersion of particles, a dispersant was prepared by dissolving 50 g of sodium hexametaphosphate in deionised water and diluting the solution to 500 mL. Organic matter was oxidised by applying 20 mL of hydrogen peroxide and continuing to add until the frothing was minimal (most organic material destroyed).

The procedure was performed on an 80 °C hotplate (Figure 3.9). To obtain dispersion, 20 ml of the dispersion solution was added to the pre-treated soil and stirred with an Eijelkamp mechanical stirrer for 15 minutes. The stirred suspensions were then transferred to 1L sedimentation cylinders, which were filled with deionised water to the 1000 mL mark. The temperature of the suspensions was recorded and the steps were repeated for each sample



Figure 3.9: Organic matter removal

A blank solution was prepared by mixing 100 ml of the dispersing solution and 850 ml of distilled water in a 1000 ml cylinder (the blank is not diluted to 1000 ml; the remaining 50 ml represented the volume occupied by 50 g of soil). Readings were taken by carefully placing an ASTM 152H hydrometer into the suspensions (Figure 3.10).



Figure 3.10: Suspensions in sedimentation cylinders

The first hydrometer reading was taken following 40 seconds of decantation with the second reading taken after two hours. At the beginning of each set, the temperature and the hydrometer readings of the blank were also recorded. After hydrometer readings were taken, density readings were corrected. This was done by subtracting the density of the blank at each reading from the corresponding density readings for the samples.

The following calculations were made to estimate the clay, silt and sand contents:

$$\text{Clay (\%)} = [(R_{2\text{nd}} - R_{C2}) / w] \times 100 \quad (3.2)$$

$$\text{Silt (\%)} = [(R_{1\text{st}} - R_{C1}) / w] \times 100 - \text{Clay (\%)} \quad (3.3)$$

$$\text{Sand (\%)} = 100\% - \% \text{ silt} - \% \text{ clay} \quad (3.4)$$

Where:  $R_{1\text{st}}$  is the first hydrometer reading at 40s,  $R_{2\text{nd}}$  the second hydrometer reading at 2 hours.  $R_{C1}$  and  $R_{C2}$  are the hydrometer readings of the blank, and  $w$  is the weight of soil in the cylinder. The calculated weight percentages of the mineral fractions were plotted in a textural triangle (Figure 3.11) to determine the texture of the samples.



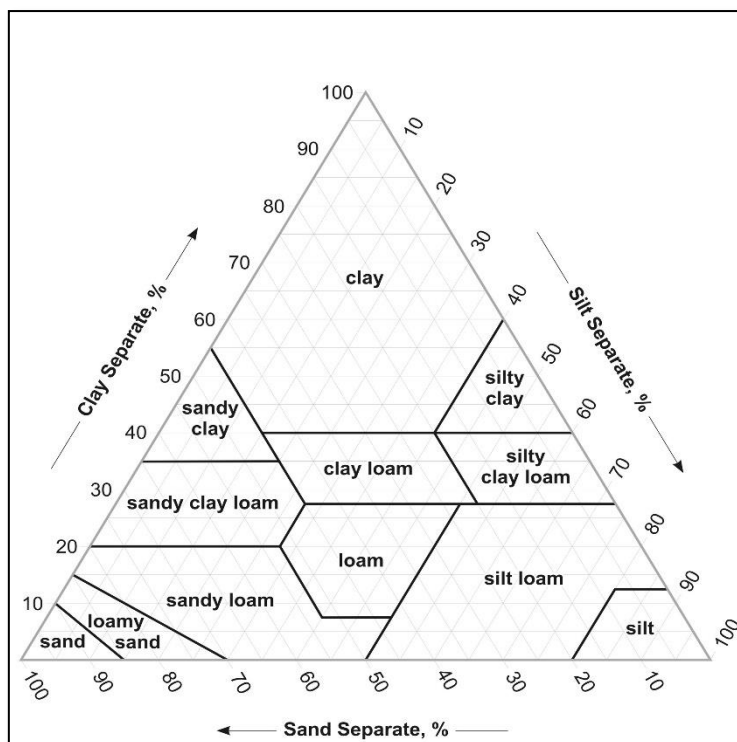


Figure 3.11: Soil texture triangle (Source: Soil Survey Division Staff, 1993)

### 3.3.1.3 Measurement of pH

Soil pH measurements were made with a Thermo Scientific Orion VSTAR90 VERSA STAR Multiparameter meter (Figure 3.12) in the Department of Ecology and Resource Management laboratory, University of Venda. As recommended by Young *et al.* (2008), 10 g of air-dried, sample was mixed with 25 ml of deionised water (soil-water ratio of 1:2.5) in a 250 ml beaker. Soil suspensions were allowed to stand for one hour then the temperature of the mixture was recorded and the meter adjusted to that temperature. Before measurements, the multiparameter meter was calibrated with known buffers of pH = 4.0 and 7.0. Electrodes (rinsed with deionised water) were then immersed in the partially settled sample suspension to measure the pH of soil. The soil suspension was gently swirled while taking the measurement. After each measurement, electrodes were rinsed with deionised water to prevent contamination.





Figure 3.12: Thermo Scientific Orion VSTAR90 Multiparameter meter

### 3.3.1.4 Electrical Conductivity (EC)

For the measurement of EC, procedures described in Young *et al.* (2008) were followed. A 1:2.5 soil-water suspension was prepared by mixing 10 g of air-dried, sieved (passed through a 2mm sieve) soil, with 25 ml of deionised water. Conductivity measurements were made with a Thermo Scientific Orion VSTAR90 VERSA STAR Multiparameter meter (Figure 3.12). Prior to analysis, the meter was calibrated with a conductivity standard of 1413  $\mu\text{S}/\text{cm}$  to obtain the cell constant. Electrodes were rinsed with deionised water before and after calibration as well as between measurements.

### 3.3.1.5 Cation Exchange Capacity (CEC)

Determination of CEC was done using the Ammonium Acetate ( $\text{NH}_4\text{OAc}$ ) method in accordance with procedures in Brown *et al.* (2016). In this method, 1 g of soil was leached with a 1M ammonium acetate solution of pH 7. The  $\text{NH}_4\text{OAc}$ -washed soil was transferred to 50 ml plastic bottles and shaken with a reciprocating shaker for 15 minutes (Figure 3.13a). The exchangeable cations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$  and  $\text{K}^+$ ) in the  $\text{NH}_4\text{OAc}$  extract were determined by ion chromatography in the Department of Ecology and Resource Management laboratory, University of Venda (Figure 3.13b). Values for CEC were expressed as the sum of the exchangeable base cations.

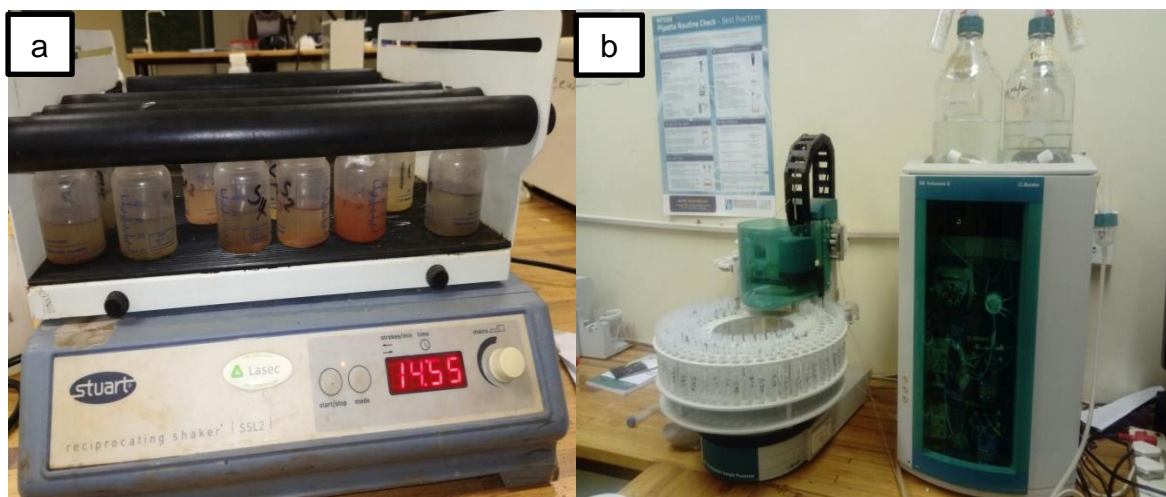


Figure 3.13: a) Shaking of samples with the reciprocating shaker b) measurement of CEC with ion chromatography

### 3.3.2 Sample Preparation for Mineralogical and Geochemical Analyses

For whole-rock and bulk-soil mineralogical and geochemical analyses, samples were crushed, milled and homogenized to a fine powder of approximately 10–15  $\mu\text{m}$  in size. Separation of clay and silt fractions was done by the centrifuge method. The first steps were to remove the organic matter and disperse the samples following Reeuwijk (2002).

For organic matter removal, 20 ml of hydrogen peroxide was added to each sample while dispersion was obtained by adding 20 ml of the dispersion solution to the pre-treated soil and stirred with a mechanical stirrer for 15 minutes. Samples were then transferred to plastic bottles for particle size fractionation by centrifugation in the Department of Hydrology and Water Resources, University of Venda. To separate the clay fractions from the silt fractions, samples were allowed to stand for 3 hours, for the silt to settle out of the suspension.

The supernatants were decanted and transferred into centrifuge tubes while the soil remaining in the bottles (representing clay fraction) was transferred into petri dishes. The soil in the petri dishes was oven-dried at 105°C for 4 hours. Supernatants found in the centrifuge tubes were centrifuged for 30 minutes at a speed of 2500 rpm. The procedure was repeated twice using the Grant-bio LMC 300 centrifuge.

The water was drained off and clay collected at the bottom of centrifuge tubes were transferred to petri dishes and dried at 105°C for 4 hours. Samples were then gently ground and ready for analysis.

### 3.3.3 Mineralogical Analysis

For minerals identification, a PANalytical X'Pert Pro powder diffractometer in a  $\theta$ - $\theta$  configuration (Figure 3.14) was used following Young *et al.* (2008). Whole-rock, bulk-soil and clay fraction mineralogical analyses were performed in the Geology Department, University of Pretoria. Both qualitative and quantitative mineralogical analyses were performed on each sample. Sample preparation was according to the standardised Panalytical backloading system, which provides nearly random distribution of the particles.

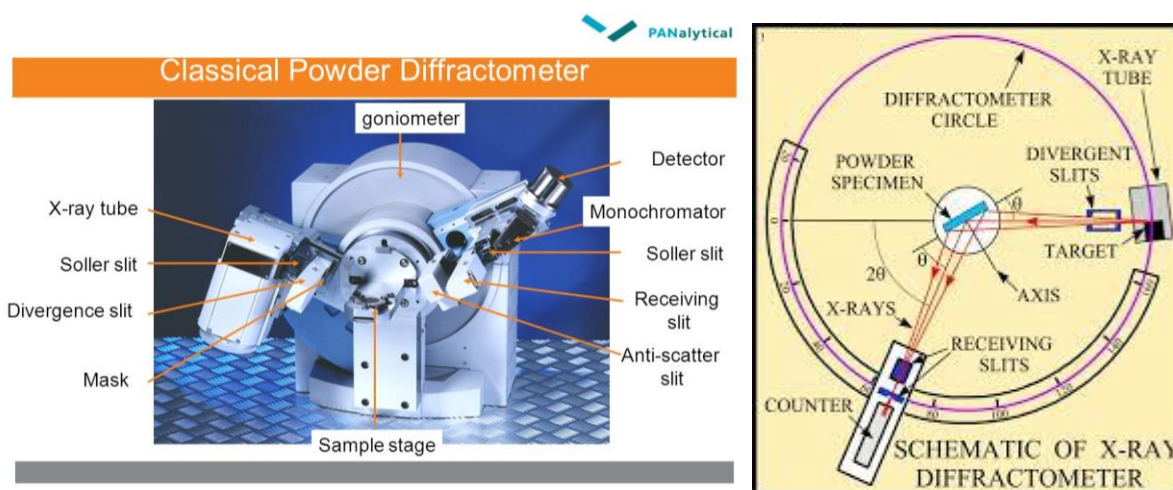


Figure 3.14: Panalytical X'Pert Pro powder diffractometer (PANalytical, 2018)

The diffractometer was fitted with an X'Celerator detector, variable divergence and fixed receiving slits with Fe filtered Co-K $\alpha$  radiation ( $\lambda=1.789\text{\AA}$ ). The phases were established using X'Pert Highscore plus software. The relative phase amounts (weight %) were estimated using the Rietveld method (Autoquan Program).

### 3.3.4 Geochemical Analysis for Oxides Determination

The concentrations of oxides in each sample were determined by X-ray Fluorescence (XRF) spectrometry (Figure 3.15) as described by the Council for Geosciences (2011). Soil and rock samples were analysed for  $\text{SiO}_2$ ,  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{MnO}$ ,  $\text{MgO}$ ,  $\text{CaO}$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{P}_2\text{O}_5$  and  $\text{Cr}_2\text{O}_3$ . Prior to analysis, samples were milled and fused beads prepared. This was done by mixing 7 g of high purity trace element and rare earth element-free flux ( $\text{LiBO}_2 = 32.83\%$ ,  $\text{Li}_2\text{B}_4\text{O}_7 = 66.67\%$ ,  $\text{LiI} = 0.50\%$ ) with 0.7g of the powder sample (flux/sample ratio of 10:1).

Oxides concentrations were determined on a PANalytical Axios Wavelength Dispersive spectrometer at the Central Analytical Facilities, Stellenbosch University. The spectrometer was fitted with a Rh tube (2.4kW) and analyzing crystals (LIF200, LIF220, PE 002, Ge 111 and PX1). Gas-flow proportional counter that uses a 90% Argon-10% methane mixture of gas and a scintillation detector were also fitted.

Matrix effects in the samples were corrected for by applying theoretical alpha factors and measured line overlap factors to the raw intensities measured with the SuperQ PANalytical software. The concentration of the control standards that were used in the calibration procedures fitted the range of concentration of the samples. The standards used were NIM-G (Bushveld Granite from the Council for Mineral Technology, South Africa) and BE-N (Basalt from the International Working Group).

Determination of the Loss on Ignition (LOI) was done by oven-drying samples at 105 °C overnight to remove the moisture. After drying, about 2g of each sample was taken in a silica crucible and placed inside a muffle furnace at 1000 °C for 2 hours. Samples were then allowed to cool to room temperature inside a dessicator to avoid adsorption of moisture and weighed again. Equation 3.8 shows the calculation of the LOI (van Reeuwijk, 2002).

$$\text{LOI (wt \%)} = ((W_2 - W_3) / (W_2 - W_1)) \times 100 \quad (3.1)$$

Where:  $W_1$  is the weight of the empty crucible,  $W_2$  is the total weight of the crucible plus sample before keeping inside furnace, and  $W_3$  is the total weight of the crucible and sample after heating to 1000 °C.

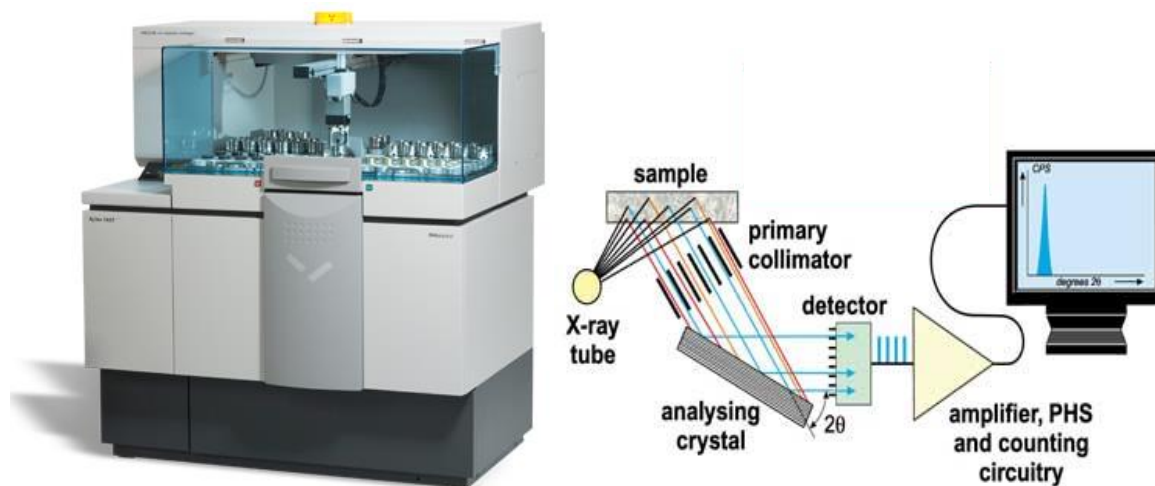


Figure 3.15: PANalytical Axios Wavelength Dispersive spectrometer (PANalytical, 2018)

### 3.3.5 Geochemical Analysis for Trace Elements Determination

Geochemical analysis of trace element concentrations was carried out using an Agilent 7700 ICP-MS at the Central of Analytical Facilities (Stellenbosch University). The spectrometer was connected to a 193 nm Excimer laser from ASI (Figure 3.16). Ablation was performed in He gas at a flow rate of 0.35 L/min, then mixed with 0.9 L/min argon and Nitrogen (0.04 L/min) before being introduced into the ICP plasma. Fusion disks that had been prepared by an automatic Claisse M4 Gas Fusion instrument and Claisse Flux using a sample:flux ratio of 1:10 were crushed. A chip of a sample was mounted along with 12 other samples in a 2.4 cm round resin disk.

For quantification of trace elements, a NIST 612 was used for calibration while the % SiO<sub>2</sub> from XRF measurement was used as an internal standard using standard-sample bracketing. The calibration standard was repeated after every 12 samples. A basaltic glass certified reference standard (BCR-2 or BHVO 2G) was ran in the beginning of the sequence, as well as with the calibration standards throughout. To verify the effectiveness of ablation of fused material, a fusion control standard from BCR-2 was also analysed in the beginning of a sequence. Data was processed using Lolite software v 3.34.



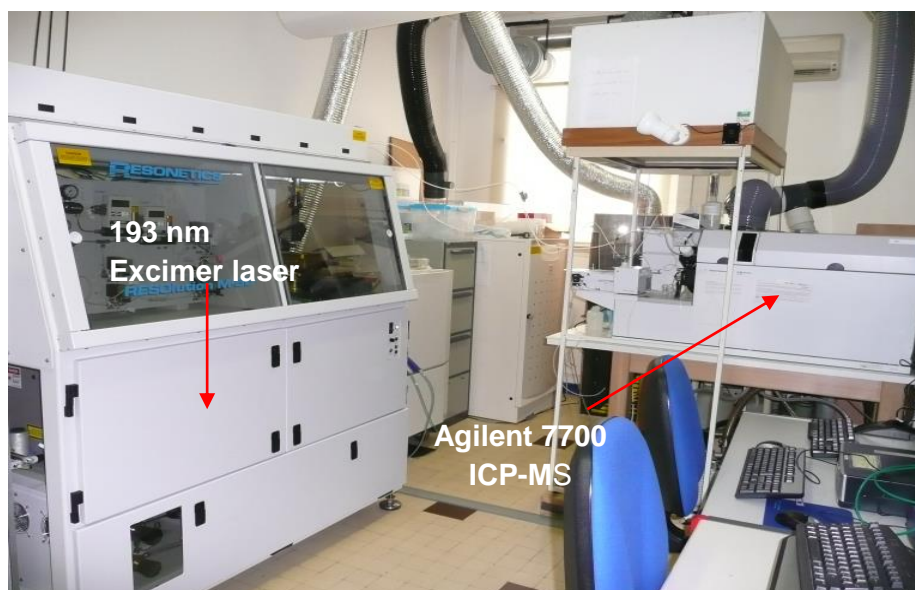


Figure 3.16: Agilent 7700 ICP-MS connected to a 193 nm Excimer laser (Agilent Technologies, 2018)

### 3.3.6 Quality Control

Geophagic materials were sampled with a hand trowel that was pre-cleaned with deionised water before each sample collection. All laboratory apparatus used during analyses were cleaned with deionised water before and after usage. For analyses that were done in external laboratories, duplicate samples were analysed for accuracy.

## 3.4 Data Analysis and Interpretation

### 3.4.1 Analytical Softwares

Data from the questionnaire survey was captured in Microsoft Excel 2013 for statistical analyses which were conducted using the IBM Statistical Package for the Social Science (SPSS) version 23.0. Texture Auto Lookup software package (TAL version 4.2) was used to determine the texture of geophagic samples. Microsoft Excel 2013 and its spread-sheet Tri-plot V14 were used to plot and analyse geochemical and provenance data.

### 3.4.2 Weathering Indices

Calculating weathering indices was important in determining the provenance of geophagic materials. Formulas presented in Table 3.2 were used to calculate weathering indices that were used to track the weathering of parent rocks to form geophagic materials: CIA, CIW, ICV, PIA, WIP, PWI and R.

Table 3.2: Summary of weathering indices (Price and Velbal, 2003; Fiantis *et al.*, 2010)

| Index      | Formula   | Optimum fresh value | Optimum weathered value |
|------------|---|---------------------|-------------------------|
| <b>CIA</b> | $(100)[Al_2O_3/(Al_2O_3 + CaO + Na_2O + K_2O)]$               | $\leq 50$           | 100                     |
| <b>CIW</b> | $(100)[Al_2O_3/(Al_2O_3 + CaO + Na_2O)]$                      | $\leq 50$           | 100                     |
| <b>PIA</b> | $(100)[(Al_2O_3 - K_2O/Al_2O_3 + CaO + Na_2O - K_2O)]$        | $\leq 50$           | 100                     |
| <b>WIP</b> | $(100)[(2Na_2O/0.35) + (MgO/0.9) + (2K_2O/0.25) + (CaO/0.7)]$ | $>100$              | 0                       |
| <b>PWI</b> | $[SiO_2/(TiO_2 + Fe_2O_3 + SiO_2 + Al_2O_3)]$                 | $>50$               | 0                       |
| <b>R</b>   | $SiO_2/Al_2O_3$   | $>10$               | 0                       |

### 3.4.3 Major Oxides and Trace Elements Ratios and Discrimination Diagrams

Major oxides diagrams such as the  $SiO_2$  versus  $Al_2O_3$  binary diagram was used to determine the source area composition. The A-CN-K ternary diagram was used to evaluate weathering and to track changes that took place as parent rocks were being weathered to form the geophagic materials. Trace element binary diagram of La/Sc against Th/Co was also used to constrain initial compositions of parent rocks.

### 3.5 Summary

This Chapter comprised the different techniques that were employed during data acquisition from field work to data analysis and interpretation through laboratory analyses. During field work, a questionnaire was administered to the geophagists in the study area. Geophagic materials as well as rock samples were collected. The collected geophagic samples were analysed for physico-chemical, mineralogical and geochemical characteristics. Samples were analysed for the following physico-chemical analyses: colour, pH, EC, CEC and PSD.

All samples were subjected to mineralogical analysis through XRD. Geochemical analyses for major oxides and trace elements were performed using XRF and ICP-MS respectively. Statistical data collected during the questionnaire survey was analysed using SPSS. Weathering indices were calculated to be used for the analysis and interpretation of geochemical data. To further interpret geochemical data, major oxides and trace elements ratios and discrimination diagrams were plotted. Several precautions listed under quality control were taken to ensure the reliability of results.



## CHAPTER 4

### RESULTS

This chapter comprises the analysis and presentation of the findings resulting from this study, through methods discussed in the previous chapter. The analysis and presentation of data is carried out in two phases; the first phase is based on the results from field work and the second part is based on the findings from laboratory analyses. In this chapter, the captured data is analysed and presented in the form of graphs, tables and pictures.

#### 4.1 Questionnaire Survey

##### 4.1.1 Demographic Information

The survey involved 200 respondents from Doli and Mukhoro, the sub-villages of Mashau. All the respondents (100%) were from rural communities. Majority of the respondents (98.5%) were females and only 1.5% of the respondents were males (Figure 4.1).

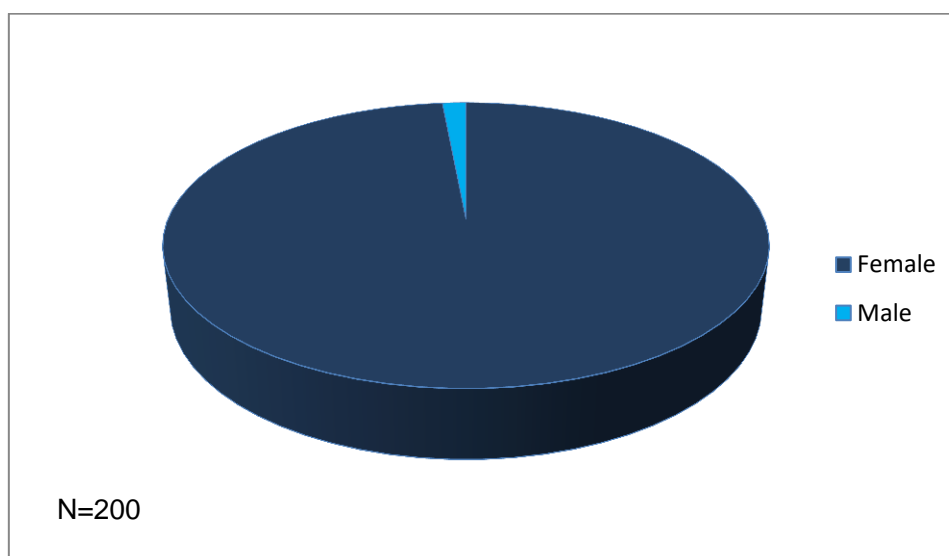


Figure 4.1: Gender of respondents

Of the total sample size (N=200), only 146 respondents indicated their age. The average age of these respondents was 32 years, with the youngest being 7 years old and the oldest 65 (Table 4.1).

Table 4.1: Descriptive statistics of the respondents' ages

| N   | Minimum | Maximum | Mean  | Standard deviation |
|-----|---------|---------|-------|--------------------|
| 146 | 7.00    | 65.00   | 32.28 | 12.33              |

Figure 4.2 proves that the respondents were largely from the 26-35 years age group (27.4%), with those in the 56-65 years age group participating in minority (4.8%).

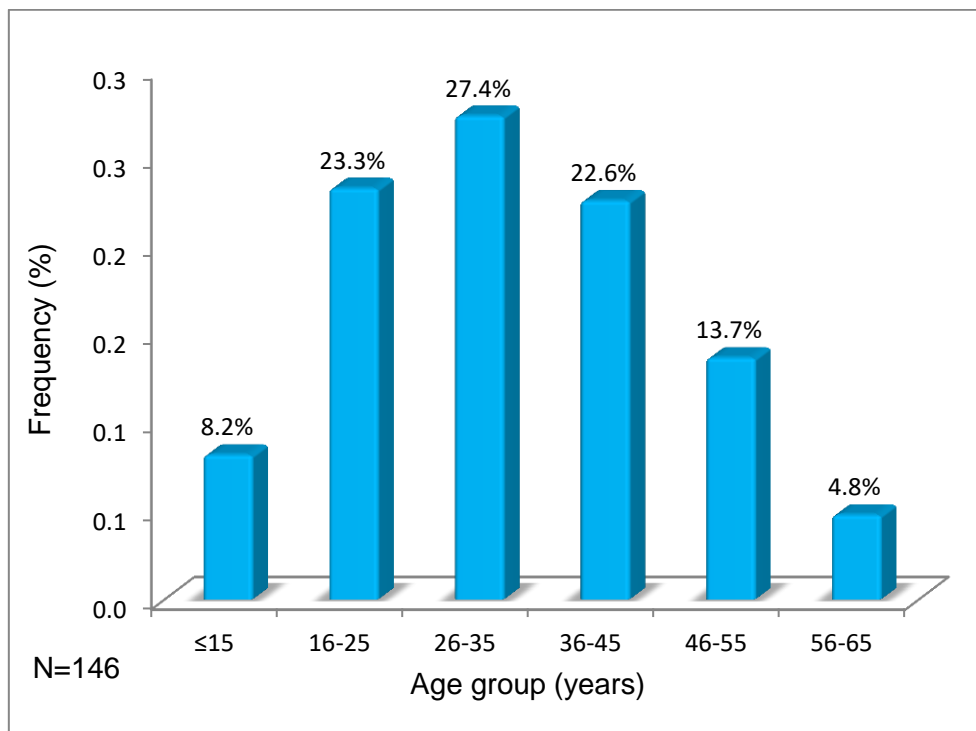


Figure 4.2: Age groups of the respondents

Evidence from Figure 4.3 clearly shows that a greater proportion of the respondents (41.5%) were married, followed by those who were single (40.0%), with the rest of the respondents living with their partners (15.0%), divorced (41.5%) or widowed (1.5%).

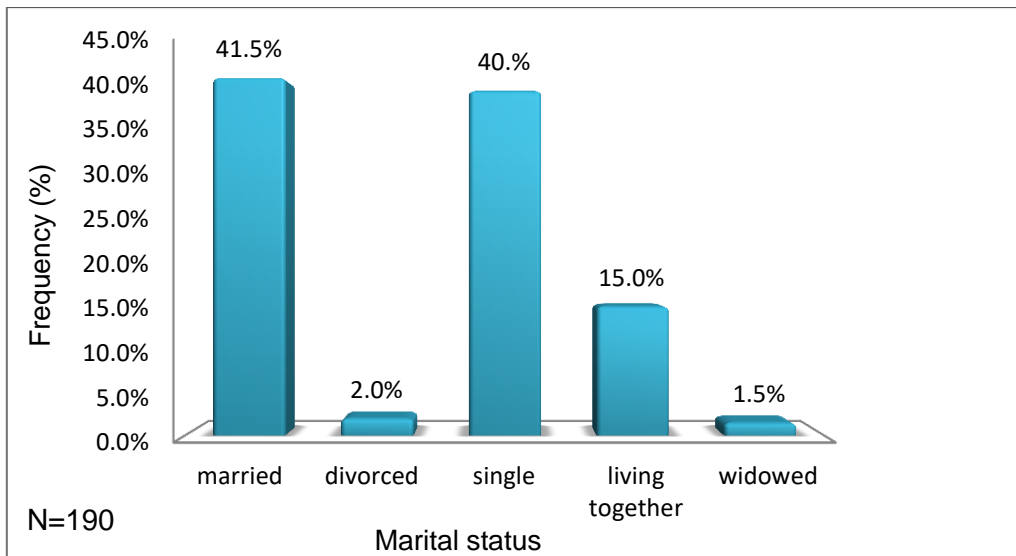


Figure 4.3: Marital status of the respondents

Out of the 200 respondents, 195 revealed their income sources. Majority of the respondents (43.6%) indicated wage employment as their income source and only 17.5% of the respondents depended on non-wage employment. The remaining 39.1% depended on their spouses, parents, children and grants (child and old-age grant) for their income.

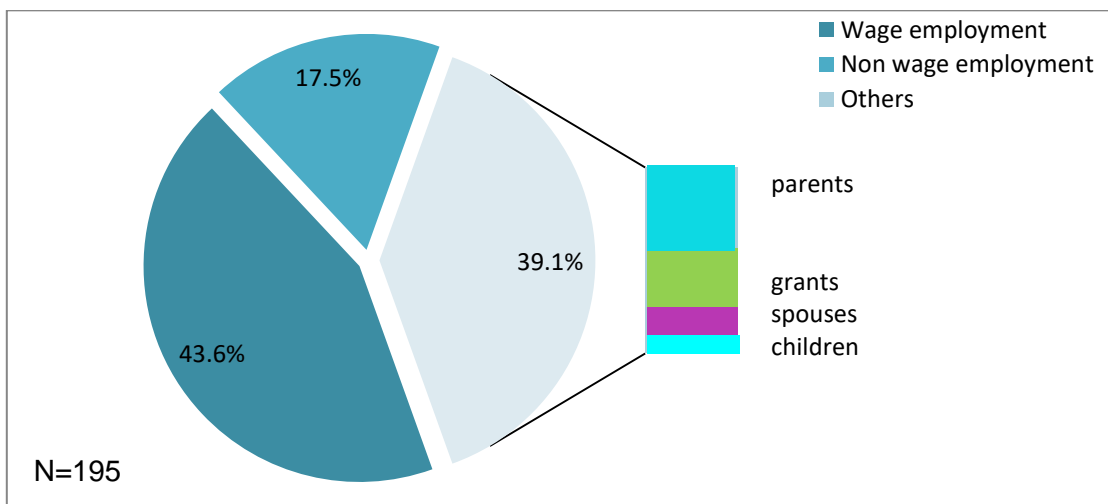


Figure 4.4: Respondents' income sources

The results in Figure 4.5 are clear indication that the majority of respondents were not working, with 20.44% of respondents being unemployed and 19.34% scholars.

This is the group that depended on others for income in the previous response (Figure 4.4). Most of those who were formally employed were having non-professional jobs such as farm workers (10.50%), freelancers (9.39%), domestic workers (5.52%), vendors (4.42%), general workers (3.41%) and other non-professional jobs in minority. It is also clear that those with professional jobs contributed the least, with educators being only 2.21%, nurses were 1.10% and administrators 0.55%.

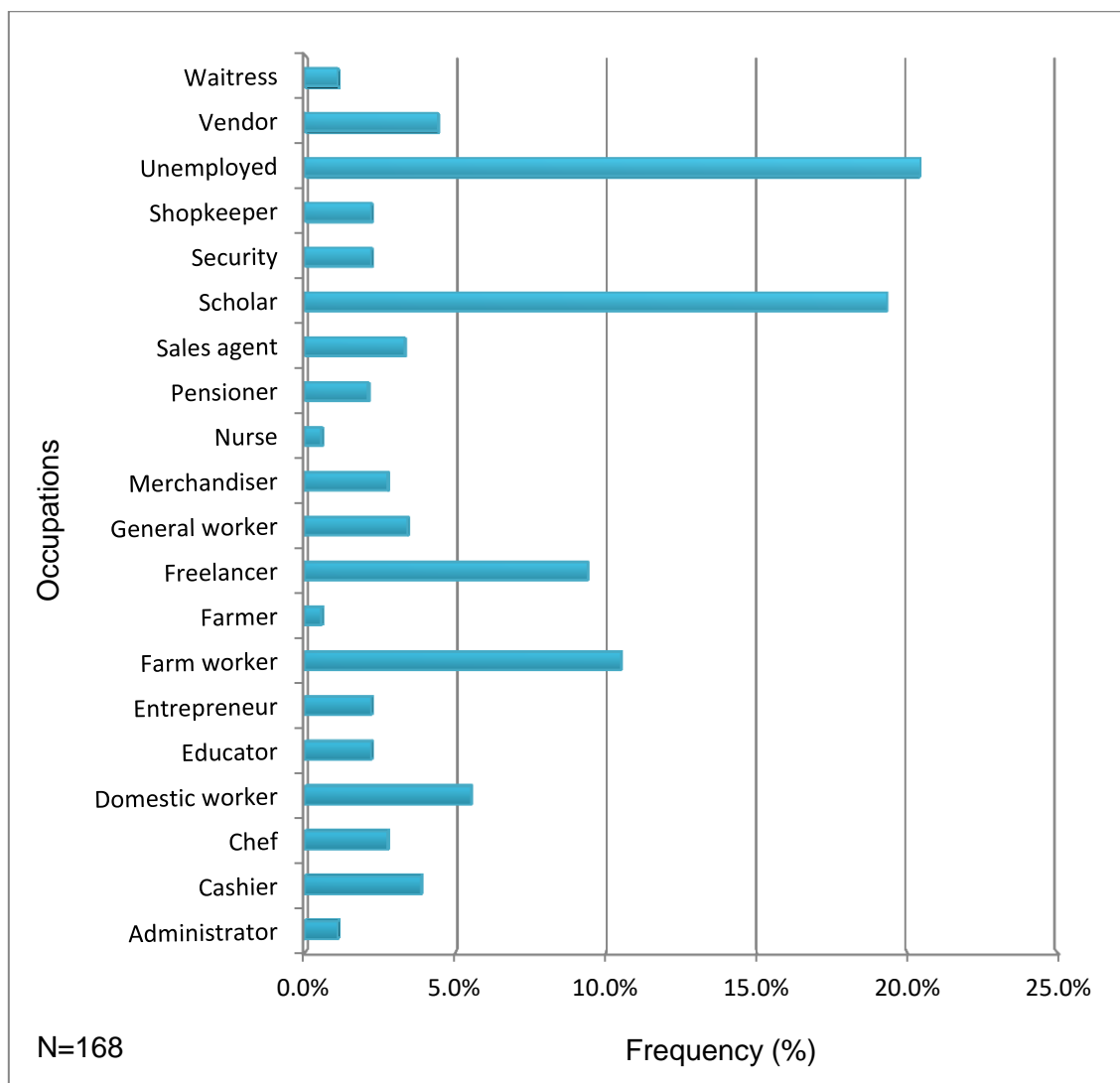


Figure 4.5: Respondents' occupation

In terms of the respondents' highest qualification, more than half of the respondents (78.0%) had progressed up to secondary level. Thirteen respondents (6.5 %) had vocational qualifications, 12 (6%) studied up to primary level and 9 (4.5%) had higher education qualifications (Figure 4.6).

A small proportion of respondents (5, 2.5%) had reached the professional level and only 3 respondents (1.5%) were illiterate. Interestingly, no respondent held a post graduate qualification.

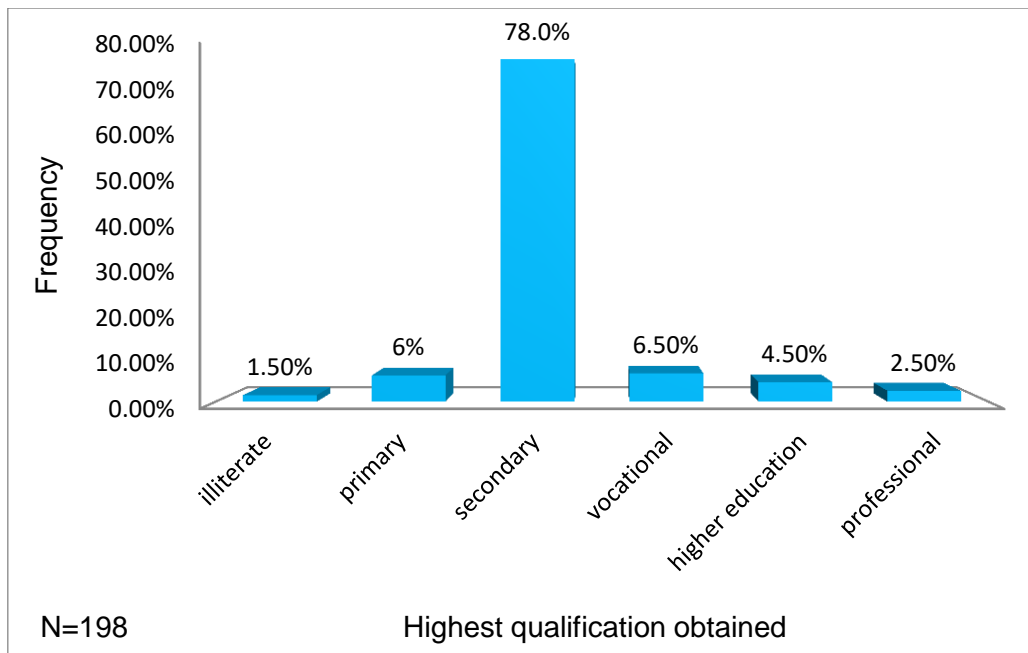


Figure 4.6: Educational level of respondents

#### 4.1.2 Socio-Economic and Cultural Aspects

Out of the total sample size (N=200), 90.5% of the respondents admitted they were consuming soil, 0.5% used to do it and 9.0% had never consumed earth materials. A great proportion (34.8%) of respondents stated that they consumed soil more than once a day, 36.7% indicated that they consumed at least once per day, 21.0% once a week and 17.7% once a month.

From the results in Table 4.2, it is clear that majority (48.07%) of the respondents had been practicing geophagia for a long time (6-10 years). Other respondents had been consuming earth materials for  $\leq 5$  years (22.65%), 11-15 years (18.23%) with those who had been consuming earth materials for more than 15 years being only 11.05%.

Table 4.2: Socio-economic and cultural aspects

|   |                |               |                    |                      |
|---|----------------|---------------|--------------------|----------------------|
| <b>Are you presently consuming soil?</b>                                | yes            | no            | used to            |                      |
| <b>N=200</b>  | 90.5%          | 9.0%          | 0.5%               |                      |
| <b>If yes how often do you consume the soil?</b>                        | one a month    | one a week    | once a day         | more than once a day |
| <b>N=181</b>  | 17.7%          | 21.0%         | 26.5%              | 34.8%                |
| <b>If yes, for how long have you been consuming soil?</b>               | ≤5yrs          | 6-10yrs       | 11-15yrs           | >15yrs               |
| <b>N=129</b>  | 22.65%         | 48.07%        | 18.23%             | 11.05%               |
| <b>What is the reason for consuming soil?</b>                           | craving        | when pregnant | don't know         |                      |
| <b>N=181</b>  | 73.9%          | 23.3%         | 2.8                |                      |
| <b>Do you crave to eat soil?</b>  | once a month   | weekly        | daily              | only when pregnant   |
| <b>N=170</b>  | 17.7%          | 21%           | 58%                | 3.3%                 |
| <b>When pregnant how often do you consume the soil?</b>                 | monthly        | weekly        | daily              |                      |
| <b>N=137</b>  | 6.6%           | 24.1%         | 81.8%              |                      |
| <b>Do you consume other non-food substances?</b>                        | yes            | no            |                    |                      |
| <b>N=168</b>  | 6.1%           | 93.9%         |                    |                      |
| <b>If yes name the substance</b>  | candle wax     | glycerine     | ice                |                      |
| <b>N=10</b>   | 9.1%           | 27.3%         | 63.6%              |                      |
| <b>How often do you consume this substance?</b>                         | daily          | weekly        | monthly            |                      |
| <b>N=10</b>   | 18.2%          | 27.3%         | 54.6%              |                      |
| <b>Do other people know that you consume clay?</b>                      | yes            | no            | don't know         |                      |
| <b>N=177</b>  | 50.3%          | 24%           | 25.7%              |                      |
| <b>If yes who are aware?</b>  | family members | friends       | Family and friends | colleagues           |
| <b>N=91</b>   | 29.7%          | 39.6%         | 17.6%              | 13.2%                |
| <b>How do people perceive this habit of eating non-food substances?</b> | positive       | negative      | don't know         |                      |
| <b>N=93</b>   | 9.7%           | 86%           | 4.3%               |                      |

The outcomes of the survey also showed that craving is the main reason people ingested soil (73.9%) whereas, 23.3% of respondents consumed soils during pregnancy. Five respondents (2.8%) did not know why they indulge in earth materials. Respondents craved to consume soil daily (58%) and some weekly (21%).

Data in Table 4.2 reveal that even when pregnant, respondents consumed earth materials daily (81.8%). Only 6.1% of the respondents admitted they consumed non-food substances with 63.6% consuming ice. These geophagists also disclosed that they consumed glycerine (27.3%) and candle wax (9.1%). It was also made clear that most of the non-food materials were ingested monthly (54.6%), some weekly (27.3%) and few daily (18.2%).

The majority of respondents (50.3%) said other people knew they consumed soil; few respondents (25.7%) did not know if people were aware of their geophagic behaviour and 24% were sure people did not know about their soil consuming habit. Furthermore, people who were aware of this geophagic behaviour were mostly friends (39.6%), family (29.7%), colleagues (13.2%) and in some case both family and friends knew about the habit.

The responses from respondents regarding the people's perceptions about the habit of eating non-food substances revealed that people have different insights about this practice. From the responses, 86.0% indicated that the habit is perceived negatively, 9.7% said it is perceived positively and 4.3% did not know how people viewed this habit (Table 4.2).

Approximately half of the respondents (49%) confirmed that the practice was common among certain members of the community while 30% of the respondents denied it. Of those who admitted, 33.3 % thought the practice was more common among unemployed and freelancing women, 28.6% viewed teenagers and women in 20s as the common group, 23.8 % assumed women aged 30-40 and 14.3 % mentioned farm workers.

From the 165 responses about when respondents craved for the soil, it can be seen that majority (31.2%) craved for the soil upon seeing it, 22.5% during pregnancy and 19.0% craved for the soil when experiencing sleeplessness (Figure 4.7). It is also clear that these are the principal reasons why people craved for the soil.

As displayed, boredom, feeling weak and constipation contributed the least to the craving.

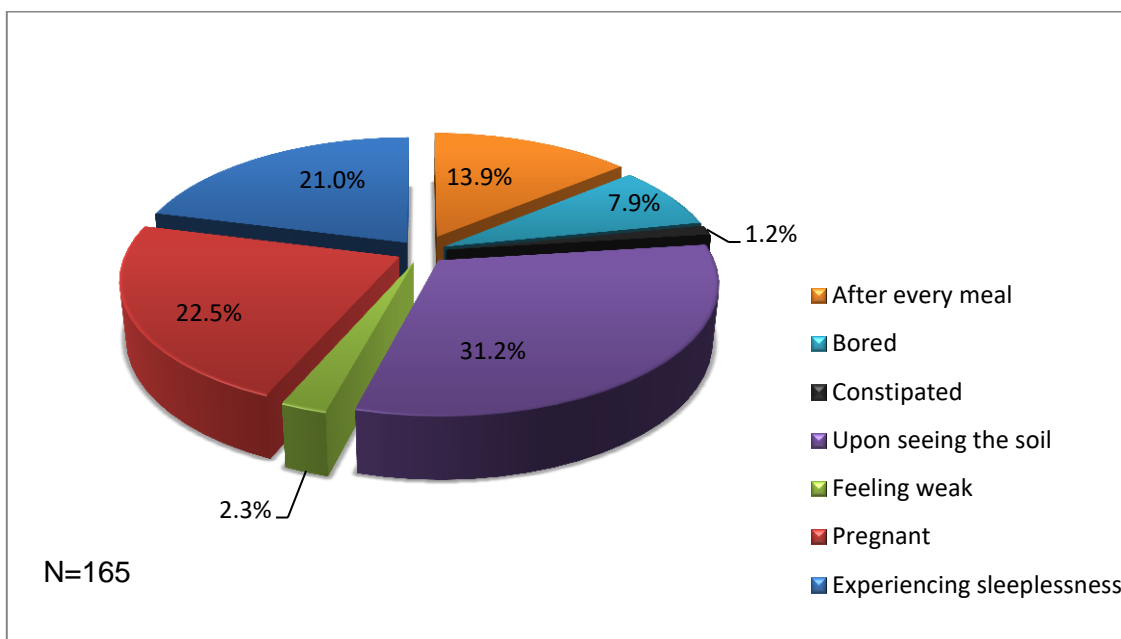


Figure 4.7: Reasons for craving for the soil

Further analyses were run to evaluate if geophagia is associated with certain factors such as age, gender, income source and educational level. To do this, the Chi-square ( $X^2$ ) test was used. Significant association was reflected by  $p < 0.05$ . Chi-square ( $X^2$ ) analyses showed a significant association of educational level with geophagia ( $p < 0.05$ ). There was no association of age ( $p > 0.05$ ), gender ( $p > 0.05$ ) and income source ( $p > 0.05$ ) with the practice of consuming soils (Table 4.3).

Table 4.3: Factors associated with geophagia

|                          | Chi-square          | df* | p-value            |
|--------------------------|---------------------|-----|--------------------|
| <b>Gender</b>            | 0.322 <sup>a</sup>  | 1   | 0.571              |
| <b>Income source</b>     | 2.906 <sup>a</sup>  | 2   | 0.234              |
| <b>Educational level</b> | 15.780 <sup>a</sup> | 5   | 0.008 <sup>†</sup> |
| <b>Age</b>               | 2.939 <sup>a</sup>  | 5   | 0.709              |

\*df=degree of freedom, <sup>†</sup>statistically significant



### 4.1.3 Indigenous Knowledge

The most favoured geophagic substance was soil from termite mounds with 30.6% of geophagists consuming it only, followed by soil (16.0%) and only 1.7% preferred to consume clay only (Figure 4.8). Some earth consumers preferred to consume different geophagic materials with 27.6% preferring to consume both soil and soil from termite mounds while others (24.2%) consumed all the geophagic materials (soil, clay and soil from termite mounds).

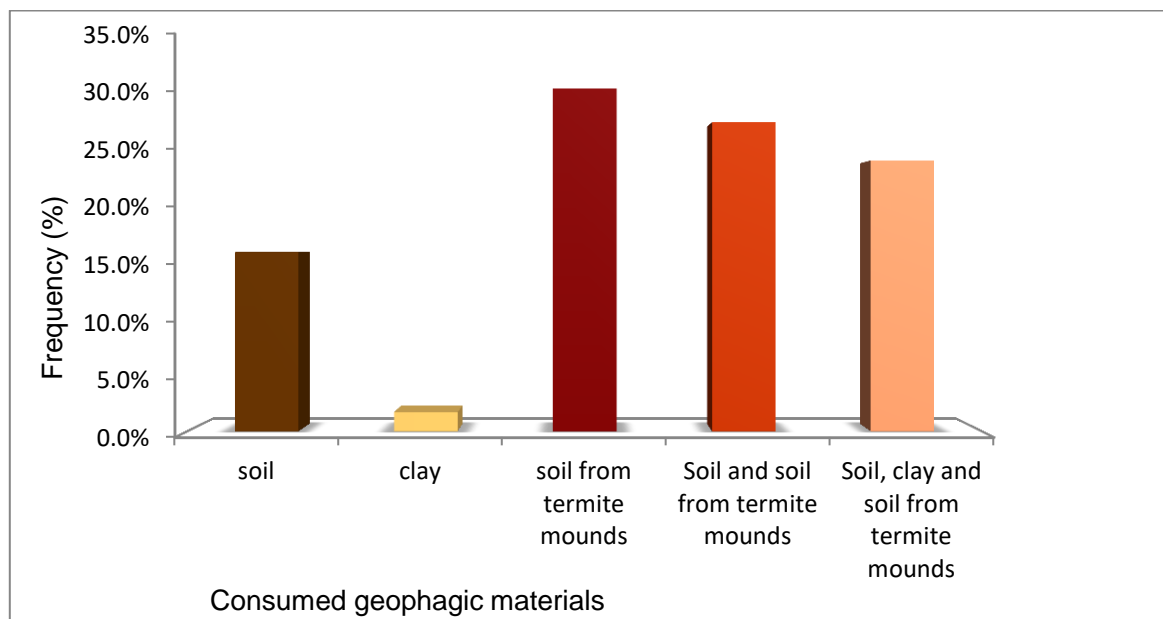


Figure 4.8: Commonly consumed substances

Respondents desired earth materials when dry (98.0%) than when they were wet (2.0%). As presented in Table 4.4, the given traditional names included *mavu*, *munyaka*, *mutwa*, *tshilogo* and *vumba*. The consumed substances were mostly from yards (47.0%), the wild (32.0%), roadside (7.2%) and respondents were seldom given (3.9%) these substances.

The reddish, brownish and khakhi geophagic materials were the most preferred with 49 (43.3%), 38 (26.3%) and 29 (20.1%) people saying they consume them, respectively. Blackish, yellowish, and pinkish soil colours did not dominate the consumed materials. According to respondents, the preferred colours were chosen essentially because of their taste (30.4%), appearance (37.6%), taste and appearance (18.2%) as well as accessibility (13.8%).

It was indicated that geophagic materials are typically stored in plastic bags (36.6% of respondents); however, 25% of the respondents did not store them at all. None of the respondents stored the substances for more than 2 weeks.

Table 4.4: Indigenous knowledge

|  |               |            |                      |                         |                     |        |
|--|---------------|------------|----------------------|-------------------------|---------------------|--------|
| <b>How are substances consumed?</b>                          | wet           | dry        |                      |                         |                     |        |
| <b>N=181</b>   | 2.0%          | 98.0%      |                      |                         |                     |        |
| <b>What are the traditional names of substances consumed</b> | mavu          | munyaka    | mutwa                | tshilogo/mavu a tshiulu | vumba               |        |
| <b>N=180</b>   | 34.3%         | 17.2%      | 35.9%                | 11.0%                   | 1.7%                |        |
| <b>Where do you obtain the substance</b>                     | from the wild | given      | yard                 | roadside                |                     |        |
| <b>N=90</b>  | 32.0%         | 3.9%       | 47.0%                | 17.2%                   |                     |        |
| <b>What is the color of substance consumed</b>               | reddish       | blackish   | yellowish            | brownish                | pinkish             | Khakhi |
| <b>N=143</b>   | 34.3%         | 11.00%     | 2.8%                 | 26.3%                   | 5.5%                | 20.1%  |
| <b>Why do you prefer to consume the specific soil</b>        | taste         | appearance | taste and appearance | ease accessibility      |                     |        |
| <b>N=145</b>   | 30.4%         | 37.6%      | 18.2%                | 13.8%                   |                     |        |
| <b>Method of storage of substance</b>                        | plastic bag   | container  | purse                | spread on floor         | does not store      |        |
| <b>N=169</b>   | 36.6%         | 20.1%      | 5.6%                 | 12.8%                   | 25%                 |        |
| <b>Length of storage</b>                                     | 1 day         | 2-4 days   | 1 week               | 2 weeks                 | consume immediately |        |
| <b>N=127</b>   | 28.00%        | 17.7%      | 6.6%                 | 5.4%                    | 42.2%               |        |

#### 4.1.4 Physico-chemical, Mineralogical, Geological and Chemical Aspects

The environment from which geophagic materials were collected varied but most people obtained the substance from termitaria (38.1%), their yards (27.9%), hilly areas (24.9%), along the road (7.5%) and from river bed (1.7%). More than half (62.5%) of the respondents who consumed soil from mound said it did not matter if the substance was collected from the surface or inside the mound.

Respondents indicated that the consumed materials were not obtained close to rocks (73.5%), although 21.5% was not sure. Those who said the substance was close to rocks also mentioned that very hard rocks dominated (83.3%). The most common ways of collecting the material were digging and scrapping as they were used by 80% of the geophagists while only 20% used selective hand picking (Table 4.4). The preferred depths of digging were 10-20cm, 0-10cm and 20-30cm as chosen by 70.7%, 21.6% and 7.8% of respondents respectively.

Geophagists had different preferences for the feel of the substances; most (41.9%) favoured the powdery, some (21.7%) favoured the silky, while others (5.5%) favoured the gritty. The texture of the material did not matter to 30.9% of the respondents. Almost all the respondents (98.9%) collected the substance when dry, but those who collected them wet (1.1%), said the substance felt sticky.

Findings from the survey showed that those who processed consumed items did so by either grinding (87.5%) or sieving (12.5%). A large portion (87%) of geophagists did not apply any heat treatment before consumption but few (11.3%) did and 1.7% applied only at times. Of those who treated the material, 63.4% baked, 26.6% burned and 10% burned and salted the earth materials.

Table 4.5: Physico-chemical, mineralogical, geological and chemical aspects

|  |               |              |                        |                |       |
|--|---------------|--------------|------------------------|----------------|-------|
| <b>Where does the substance you consume come from</b>                          | hill/mountain | river bed    | termitaria             | road           | yard  |
| <b>N=161</b>   | 24.9%         | 1.7%         | 38.1%                  | 7.5%           | 27.9% |
| <b>If from a mound, where specifically on the mound is substance collected</b> | surface       | inside mound | doesn't matter         | not sure       |       |
| <b>N=29</b>  | 12.5%         | 25%          | 62.5%                  |                |       |
| <b>Are substances obtained close to rocks</b>                                  | yes           | no           | not sure               |                |       |
| <b>N=100</b>   | 5.5%          | 73.5%        | 21.5%                  |                |       |
| <b>If yes, what is the type of rock</b>  | very hard     | hard         |                        |                |       |
| <b>N=6</b>   | 83.3%         | 16.7%        |                        |                |       |
| <b>How is the substance collected</b>  | digging       | scrapping    | selective hand picking |                |       |
| <b>N=177</b>   | 45.2%         | 34.8%        | 20.0                   |                |       |
| <b>If digging how deep</b>   | 0-10cm        | 10-20cm      | 20-30cm                |                |       |
| <b>N=81</b>  | 21.6%         | 70.7%        | 7.8%                   |                |       |
| <b>How does the substance feel when collected?</b>                             | gritty        | silky        | powdery                | doesn't matter |       |
| <b>N=113</b>   | 5.5%          | 21.7%        | 41.9%                  | 30.9%          |       |
| <b>When are substances collected?</b>  | wet           | dry          |                        |                |       |
| <b>N=149</b>   | 1.1%          | 98.9%        |                        |                |       |
| <b>If collected wet, how does the substance feel?</b>                          | sticky        |              |                        |                |       |
| <b>N=2</b>   | 100%          |              |                        |                |       |
| <b>Are substances processed before consumption?</b>                            | yes           | no           | sometimes              |                |       |
| <b>N=167</b>   | 27.0%         | 63.8%        | 9.2%                   |                |       |
| <b>If yes, how are they processed?</b>   | grinding      | sieving      |                        |                |       |
| <b>N=45</b>  | 87.5%         | 12.5%        |                        |                |       |
| <b>Is there any heat treatment of substance before consumption?</b>            | yes           | no           | sometimes              |                |       |
| <b>N=180</b>   | 11.3%         | 87%          | 1.7.%                  |                |       |
| <b>If yes specify type of heat treatment</b>                                   | baking        | burning      | Burning and salting    |                |       |
| <b>N=20</b>  | 63.4%         | 26.6%        | 10%                    |                |       |

#### 4.1.5 Ecological Aspects

Data presented in Table 4.5 revealed that the tree termiteria was mostly (65.9% of respondents) picked over the mound (34.1%). It was also revealed that the conical shaped mounds were more prevalent (67.5%) than the flat topped ones (32.5%). From the 21 respondents who consumed substance from the mound, 5 (25%) preferred the material from old mounds, 2 (10%) preferred the newly constructed and 14 (65%) did not care about the age of the mound.

The mounds were normally found on flat terrain (81.4%) and on hilly areas (18.6%). Those who consumed the earth material from trees, only 14.6% collected the material from specific trees. About 85.4% of the respondents neither collected the material from certain trees (30.6%) nor bother about the type of tree from where it was collected (54.8%). Respondents who were cautious of the tree type preferred soil from *munngo* (66.6%) and *muberegisi* (33.3%) trees.

Table 4.6: Ecological aspect

|   |                   |               |                     |
|---|-------------------|---------------|---------------------|
| <b>If you consume substance from a termiteria, from which one</b>                     | mound             | tree          |                     |
| <b>N=62</b>   | 34.1%             | 65.9%         |                     |
| <b>What is the shape of the mound</b>   | Conical shaped    | flat topped   |                     |
| <b>N=21</b>   | 67.5%             | 32.5%         |                     |
| <b>Do you prefer to consume the substance when</b>                                    | newly constructed | old           | doesn't matter      |
| <b>N=21</b>   | 10%               | 25%           | 65%                 |
| <b>What type of terrain do you normally find these mounds?</b>                        | flat              | hilly         |                     |
| <b>N=19</b>   | 81.4%             | 18.6%         |                     |
| <b>Do you collect the substance from</b>  | mound             | base of mound | distance from mound |
| <b>N=15</b>   | 90%               | 5.6%          | 4.4%                |
| <b>If substance is collected from a tree, do you prefer it from a particular tree</b> | yes               | no            | doesn't matter      |
| <b>N=41</b>   | 14.6%             | 30.6%         | 54.8%               |
| <b>If yes, name the preferred tree type</b>   | munngo            | muberegisi    |                     |
| <b>N=6</b>  | 66.6%             | 33.3%         |                     |

#### 4.1.6 Health Aspects

Outcomes of the survey showed that the majority of the respondents (58.6%) presumed that the consumed substances could be harmful to their health; however, they were not aware (65.7%) of the harmful parasites that could be present (Table 4.6). Out of the total experimental group (181 respondents), only 1 respondent (0.6%) was ever operated upon because of stomach problems.

Respondents did not know (84%) the content of the substance, nevertheless, those who said they knew (16.0%) believed the material contained iron (88.9%) and vitamins (11.1%). Geophagists consumed earth material because it was a tendency to do so (20% of respondents) and for additional nutritional value (14.9% of respondents). The two factors were identified as the main reasons for the consumption although 65.1 % of the respondents did not know why they consumed the earth substances.

Respondents were not regularly infected with flu with 43.6% infected yearly, 38.7% twice in a year and 17.7% once in 3 months. The proportions between those who consumed the substance when infected (30.1%), those who did not (31.5%) and those who consumed at times (38.4%) were almost equal

Table 4.7: Health aspects

|   |                   |                |            |
|---|-------------------|----------------|------------|
| <b>Do you know that the substance could be harmful to your health?</b>              | yes               | no             |            |
| <b>N=181</b>  | 58.6%             | 41.4%          |            |
| <b>Were you ever operated upon for stomach problems?</b>                            | yes               | no             |            |
| <b>N=181</b>  | 0.6%              | 99.4%          |            |
| <b>Are you aware of the harmful parasites that may be present in the substance?</b> | yes               | no             |            |
| <b>N=181</b>  | 34.3%             | 65.7%          |            |
| <b>Do you know the content of the substance?</b>                                    | yes               | no             |            |
| <b>N=167</b>  | 16.0%             | 84%            |            |
| <b>If yes name these contents</b>   | vitamins          | iron           |            |
| <b>N=27</b>   | 11.1              | 88.9           |            |
| <b>Why do you consume substance?</b>  | nutritional value | habit          | don't know |
| <b>N=170</b>  | 14.9%             | 20%            | 65.1%      |
| <b>Do you often get infected (common cold, flu etc)?</b>                            | once in 3 months  | twice per year | yearly     |
| <b>N=155</b>  | 17.7%             | 38.7%          | 43.6%      |
| <b>Do you ingest these substances when infected?</b>                                | yes               | no             | sometimes  |
| <b>N=153</b>  | 30.1%             | 31.5%          | 38.4%      |

| Do you experience chronic illnesses? | yes   | no    |
|--------------------------------------|-------|-------|
| N=129                                | 56.9% | 43.1% |

More than half of the geophagists (56.9%) had chronic illnesses, which are shown in Figure 4.9. The most frequent chronic illness was dizziness with 41.7% of geophagists complaining about it followed by headaches (38.8%), blood in stool (13.6%) and nose bleeding (5.8%) were the infrequent ones.

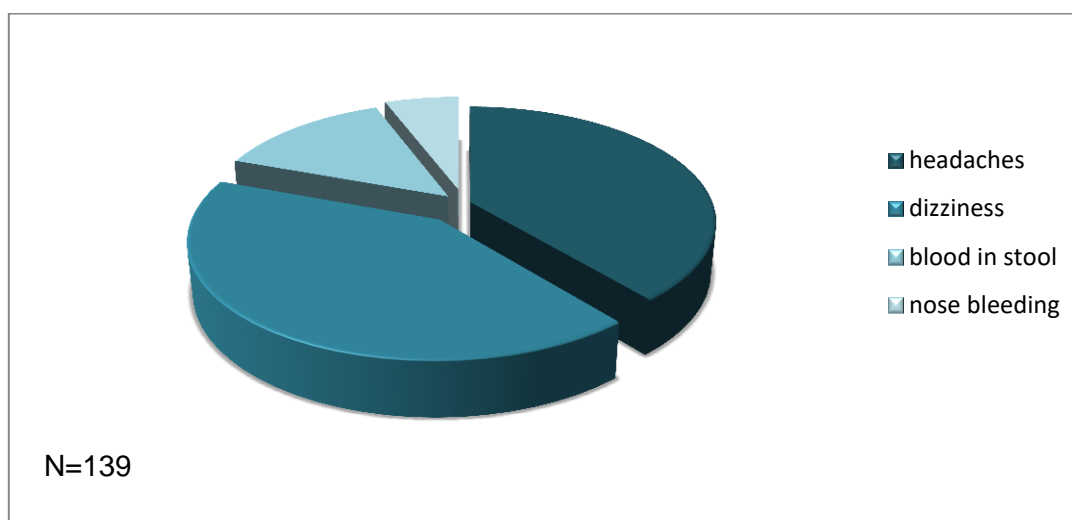


Figure 4.9: Frequent chronic illnesses experienced

None of the 50 respondents had still born except 1 respondent (2.0%) who had 1 still born. Only 2 people had children with abnormalities of which 1 (50%) was cross-eyed and the other (50%) could not defecate when still a baby. It was also mentioned that the cross-eyed child was a premature but the other child (who could not defecate) reached the expected developmental and growth stages. None of the children experienced any pain in the muscles or joints.

Medical conditions diagnosed with or experienced included constant headaches, constipation, high blood pressure (BP), iron deficiency and having low haemoglobin (Hb) level (Figure 4.10). The majority of the geophagists experienced constant headaches (31.6%) and had low Hb level (29.9%). Other respondents experienced constipation (18.8%), others were diagnosed with iron deficiency (12.0%) and some with high Bp (7.7%).



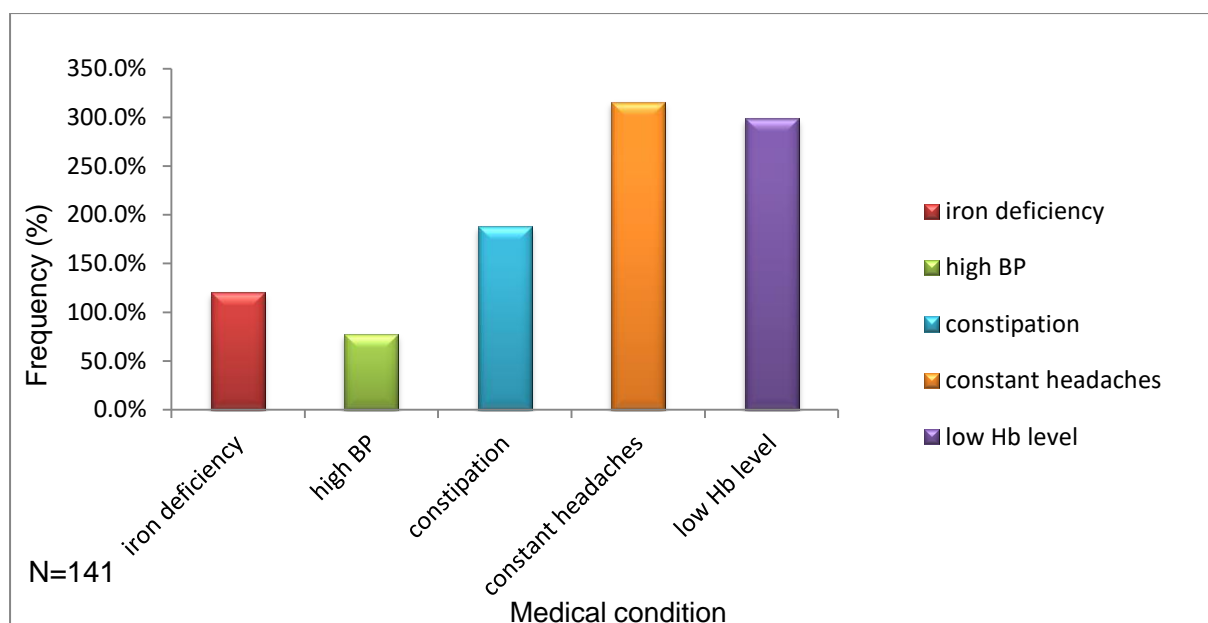


Figure 4.10: Medical conditions experienced/diagnosed

After data regarding health aspects were analysed, the Chi-square ( $X^2$ ) test was used to associate knowledge on the harmful nature of geophagic materials, frequency of getting infections and experiencing chronic illnesses with frequency of consuming soils (Table 4.8). The value of  $p < 0.05$  reflected significance. Chi-square ( $X^2$ ) analyses discovered that there was no association of knowledge of the harmful nature of geophagic materials ( $p > 0.05$ ), frequency of getting infections ( $p > 0.05$ ), and experience of chronic illnesses ( $p > 0.05$ ), with frequency of consuming soils.

Table 4.8: Chi-square ( $X^2$ ) results for health aspects

|   | Chi-square         | df* | p-value |
|---|--------------------|-----|---------|
| Do you know that the substance could be harmful to your health? | 7.775 <sup>a</sup> | 3   | .051    |
| Do you often get infected (common cold, flu etc)?               | 4.051 <sup>a</sup> | 6   | .670    |
| Do you experience chronic illnesses?                            | 1.012 <sup>a</sup> | 3   | .798    |

\*df=degree of freedom, <sup>†</sup>statistically significant

## 4.2 Assessment of Physico-chemical Properties

### 4.2.1 Colour

The first property that appeals geophagists into craving for the soil is colour. Table 4.9 presents a summary of colours of the geophagic soils from Mashau. The colours of the samples were mainly in five groups; red, shades of brown, brown, shades of yellow and pink (Figure 4.11). The majority of samples from Doli contained red and brown colours whereas samples from Mukhoro were mainly brown. The colour of samples from Matsilele varied, with each sample having a different colour.

Table 4.9: Colours of geophagic samples from Mashau

| Sample ID  | Munsell notation |       |        | True colour of samples |
|------------|------------------|-------|--------|------------------------|
|            | Hue              | Value | Chroma |                        |
| <b>S1</b>  | 2.5              | YR    | 5/6    | Red                    |
| <b>S2</b>  | 7.5              | YR    | 6/6    | Reddish yellow         |
| <b>S3</b>  | 2.5              | YR    | 4/4    | Reddish brown          |
| <b>S4</b>  | 5                | YR    | 3/4    | Dark reddish brown     |
| <b>S5</b>  | 7.5              | YR    | 4/4    | Brown                  |
| <b>S6</b>  | 2.5              | Y     | 5/3    | Light olive brown      |
| <b>S7</b>  | 7.5              | YR    | 4/4    | Reddish brown          |
| <b>S8</b>  | 2.5              | Y     | 4/2    | Dark grayish brown     |
| <b>S9</b>  | 2.5              | Y     | 4/2    | Light olive brown      |
| <b>S10</b> | 7.5              | YR    | 4/4    | Brown                  |
| <b>S11</b> | 7.5              | YR    | 3/4    | Dark brown             |
| <b>S12</b> | 2.5              | YR    | 5/6    | Red                    |
| <b>S13</b> | 7.5              | YR    | 4/6    | Strong brown           |
| <b>S14</b> | 7.5              | YR    | 4/6    | Strong brown           |
| <b>S15</b> | 7.5              | YR    | 4/3    | Brown                  |
| <b>S16</b> | 2.5              | YR    | 4/8    | Red                    |
| <b>S17</b> | 10               | YR    | 6/6    | Brownish yellow        |
| <b>S18</b> | 2.5              | YR    | 8/4    | Pink                   |
| <b>S19</b> | 10               | R     | 5/8    | Red                    |
| <b>S20</b> | 10               | YR    | 8/4    | Very pale brown        |

The dominant colour was red which was depicted by 4 samples. Out of the 20 samples, 3 samples were brown, 2 had a strong brown colour and another 2 had a light olive brown colour. Other soil colours were less common, as each colour was only observed in 1 sample. It was clear that geophagists were attracted to red and brown soils.

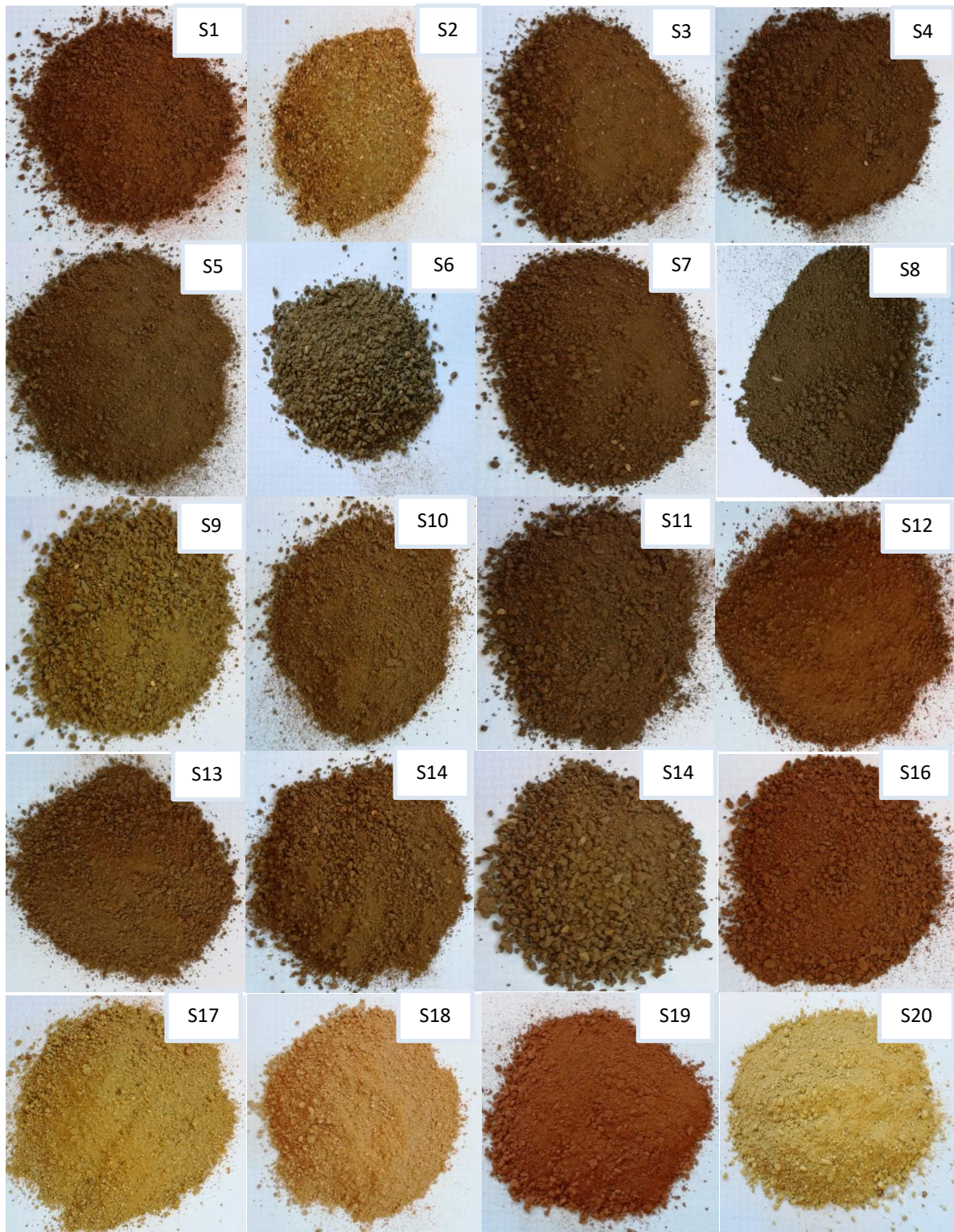


Figure 4.11: Colours of the consumed geophagic materials



#### 4.2.2 Particle Size Distribution (PSD)

Most of the particles in samples had diameters within the sand range ( $50\ \mu\text{m} - < 2000\ \mu\text{m}$ ), whereas the other samples had most of their particles occurring within the silt range ( $2\ \mu\text{m} - < 50\ \mu\text{m}$ ). The particle size distribution of the samples varied as demonstrated in Figure 4.12. The clay contents were  $\leq 40\%$  in all samples while the sand contents ranged from 24-86%. Silt percentages ranged from 2-54% with S20 having the highest silt content. Sample S2 had the highest sand content which was 86% although its clay content was the lowest (0%). Interestingly, the proportions of clay, silt and sand in S13 were equal to those in S9; and the proportions of clay, silt and sand in S8 were equal to those in S10.

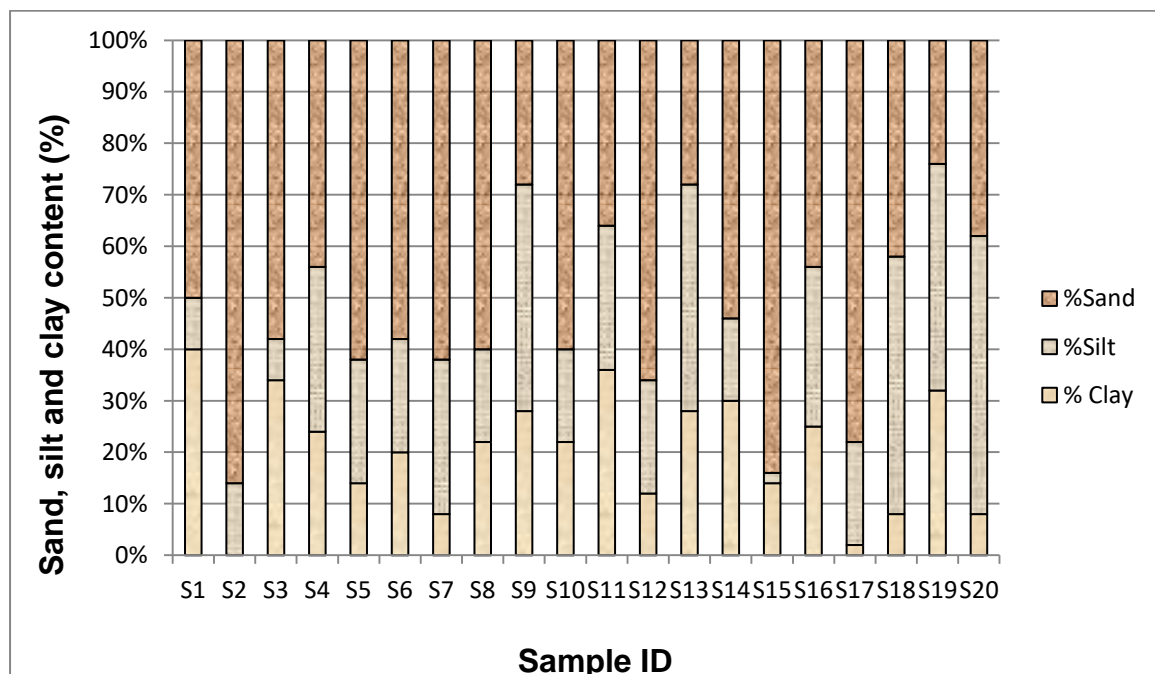


Figure 4.12: Particle size distribution of clay, silt and sand in samples

With the help of Texture Auto Lookup software package (TAL version 4.2), the texture of the samples was determined and their different textural classes are presented in Figure 4.13. Soil samples were classified as sandy clay, sandy clay loam, clay loam, silt loam, loam, sand, loamy sand and sandy loam. Majority of the samples had the sandy clay loam texture (S3, S6, S8 overlapped with S10 and S14).

This group was followed by those which fell into the clay loam textural class (S9 overlapped with S13, S11 and S19). The loam and sandy loam classes were the second dominant textures. None of the samples were clay or silt, nonetheless, S2 was completely sand. Samples S12 and S20 were the only samples in the sandy clay and silt loam classes respectively. The loamy sand texture was only found in S15 and S17.

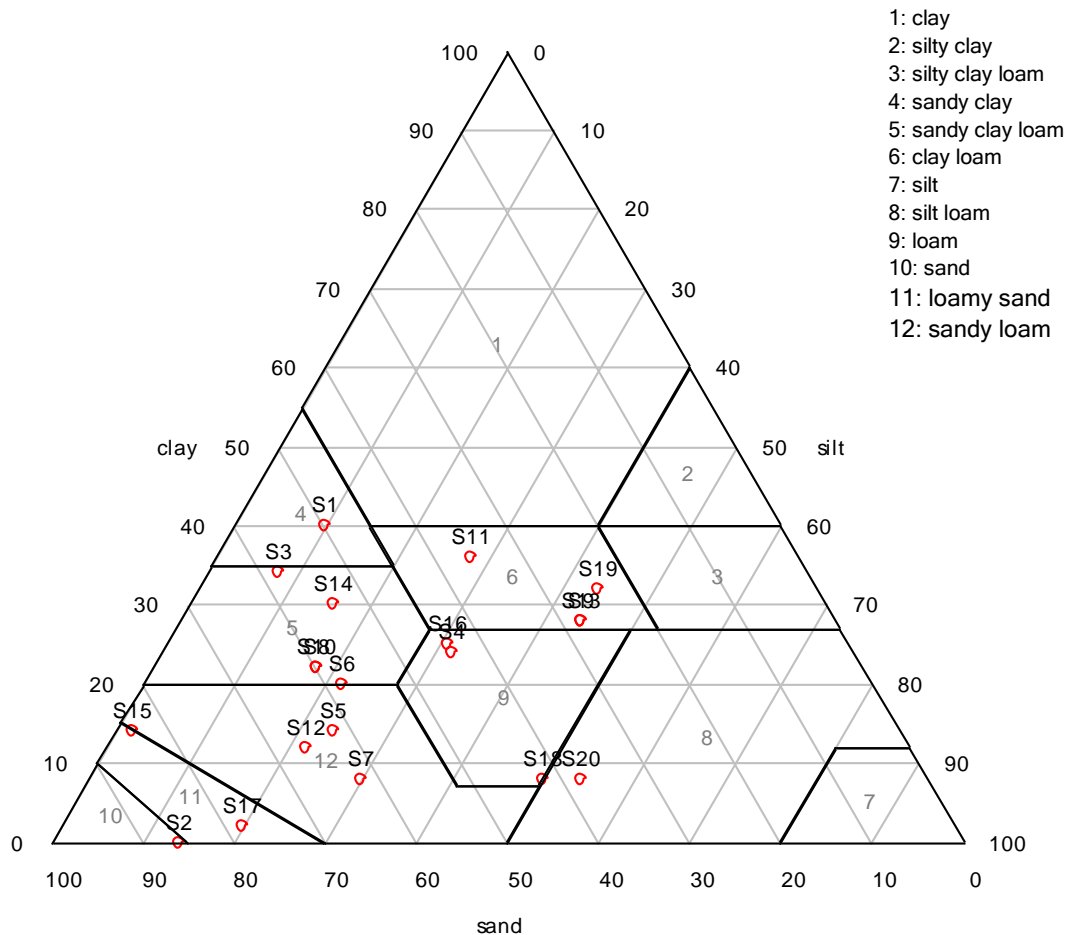


Figure 4.13: Textural classification of geophagic samples

### 4.2.3 Potential of Hydrogen (pH)

The pH values ranged between 5.4 (slightly acidic) in sample S1 to 7.6 (slightly alkaline) in sample S3 (Figure 4.14). Most of the samples had pH values within the slightly acidic range (6 to 6.9). Samples S3, S7 and S13 were the only samples with pH value above 7. Geophagic soils from Doli generally had higher pH values than those from Mukhoro and Matsilele.

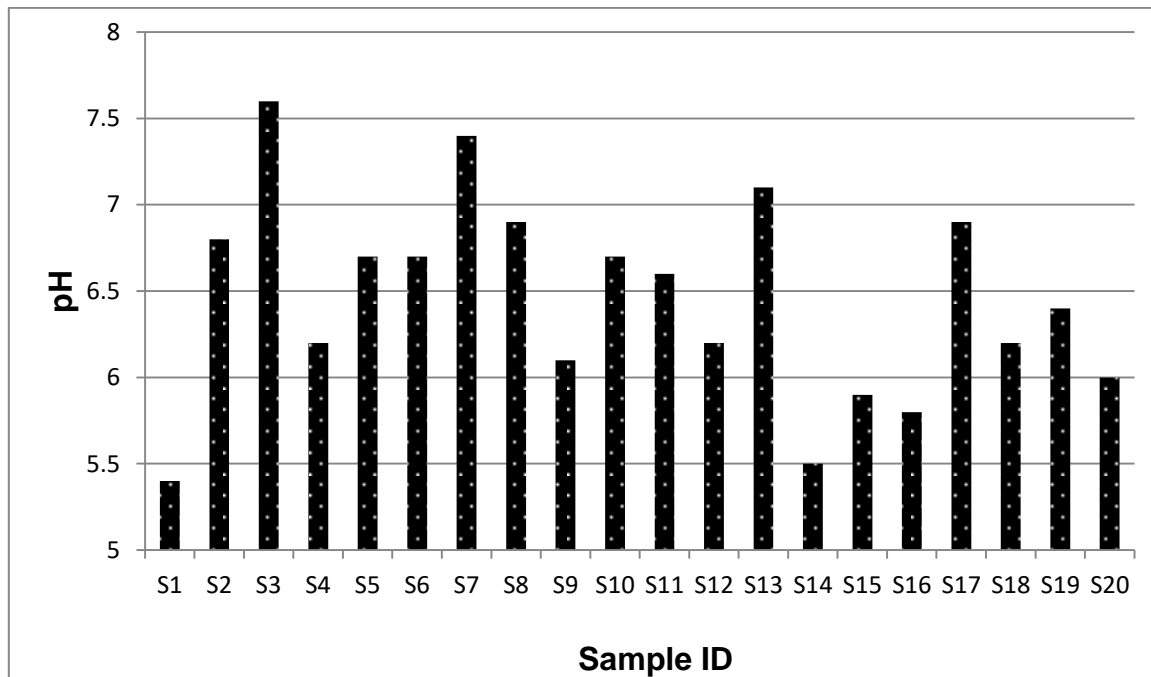


Figure 4.14: pH of soil samples from Mashau

### 4.2.4 Cation Exchange Capacity (CEC)

The CEC of geophagic soils varied, from 17 meq/100 g in sample S11 to 109 meq/100 g in sample S7. Majority of the samples had CEC values of between 50 meq/100 g and 75 meq/100 g (Figure 4.15). Most of the samples that had higher CEC values were from Doli (S10=74 meq/100 g, S3=87 meq/100 g, S4=90 meq/100 g and S7=109 meq/100 g). Sample S13 and sample S17 were the only samples from Mukhoro with higher CEC (>70meq/100 g). The CEC of samples from Matsilele was moderate, ranging from 54 meq/100 g to 67 meq/100 g.

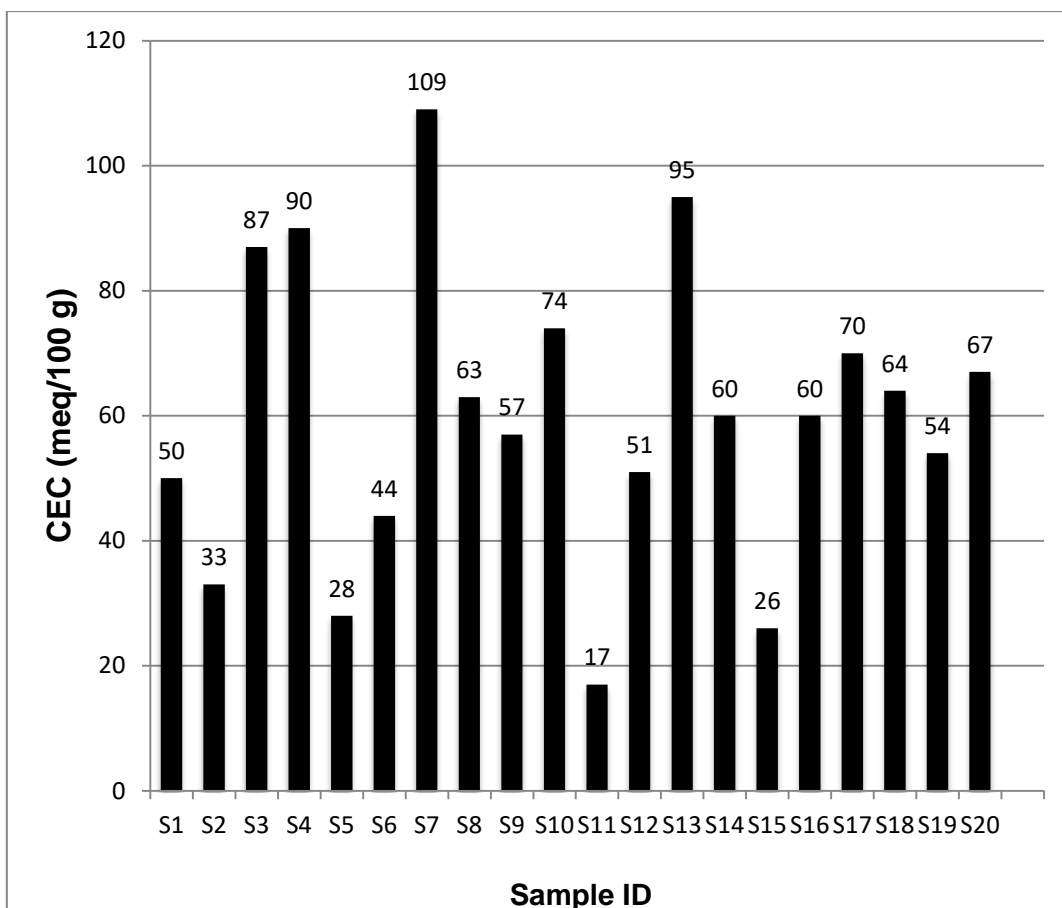


Figure 4.15: Cation exchange capacity of geophagic samples

#### 4.2.5 Electrical Conductivity (EC)

Many samples had moderate to high EC values which indicated a relatively high amount of dissolved salts in some soils. EC values ranged from 11.2 to 245  $\mu\text{S}/\text{cm}$  with sample S7 having the highest value (Figure 4.16). Three samples (S4, S12 and S18) had an equal EC value of 20  $\mu\text{S}/\text{cm}$ . Samples from Doli mostly had higher EC values (average EC = 62  $\mu\text{S}/\text{cm}$ ) compared to those from Mukhoro (average EC = 59  $\mu\text{S}/\text{cm}$ ) which were also higher than those from Matsilele (average EC = 52  $\mu\text{S}/\text{cm}$ ).

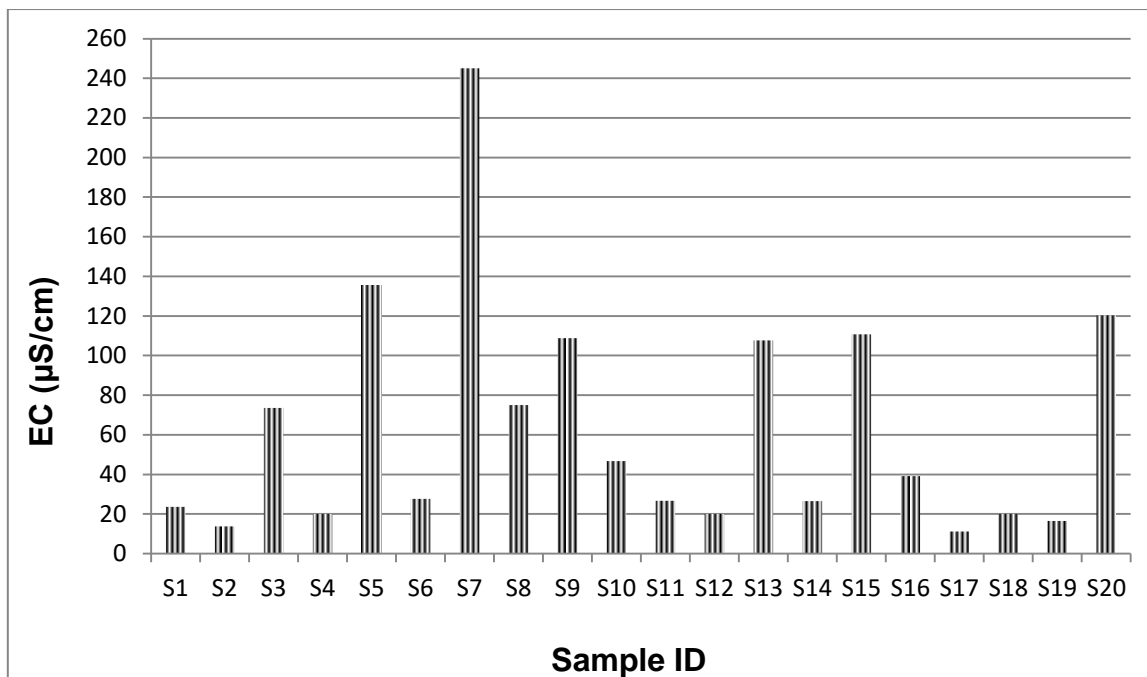


Figure 4.16: Electrical conductivity of geophagic samples from Mashau

### 4.3 Mineralogical Characterisation of Geophagic Materials and Parent Rocks

#### 4.3.1 Mineralogy of Geophagic Materials

The qualitative mineralogical analysis identified fourteen minerals in geophagic materials from Mashau, of which, some were clay minerals and others were non-clay minerals. Non-clay minerals identified included quartz, microcline, plagioclase (albite), hornblende (magnesiohornblende), dolomite and muscovite. Kaolinite, smectite (montmorillonite), talc, anatase, hematite, ilmenite, chlorite (clinochlore) and epidote were the secondary (clay) minerals identified. The mineral phases detected in the 20 geophagic soil samples are shown in Figures 4.17- 4.36.

All samples were mineralogically dominated by both quartz and kaolinite with others in minor to trace abundances being smectite, hornblende, chlorite, haematite, talc, epidote, muscovite, ilmenite, anatase and dolomite. Kaolinite was dominant in samples from Mukhoro; while samples from Doli contained more quartz. Feldspar minerals plagioclase and microcline, occurred in most samples.



Smectite was dominant in samples from Mukhoro and Matsilele than in samples from Doli. Sample S11 was the only sample containing anatase, and ilmenite.

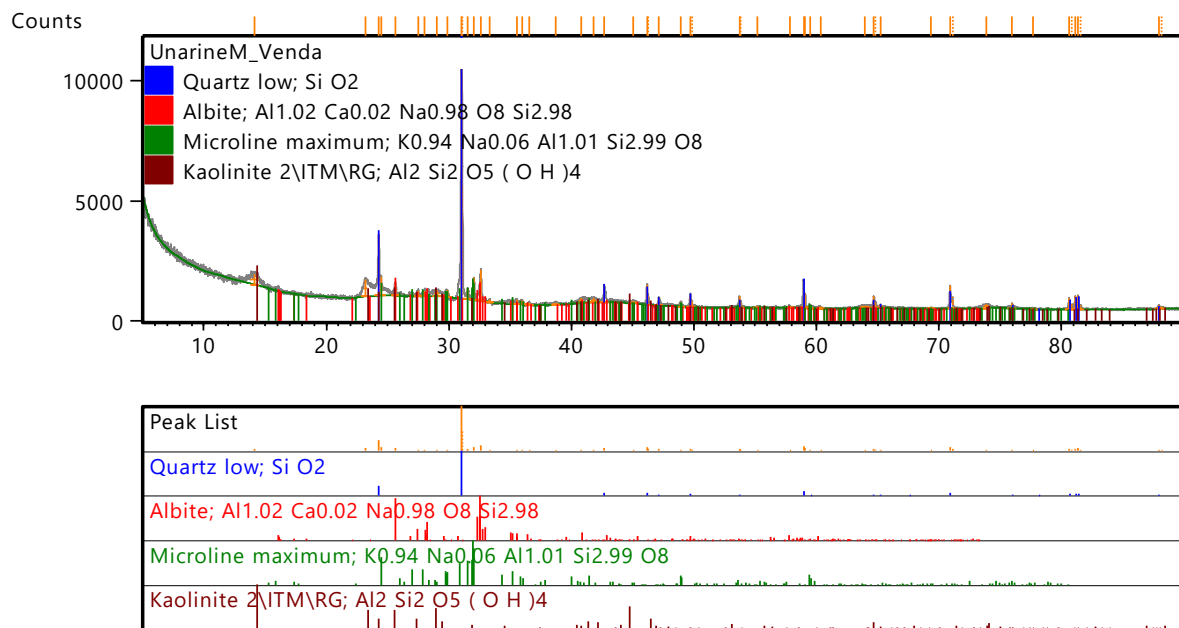


Figure 4.17: Mineral phases in sample S1

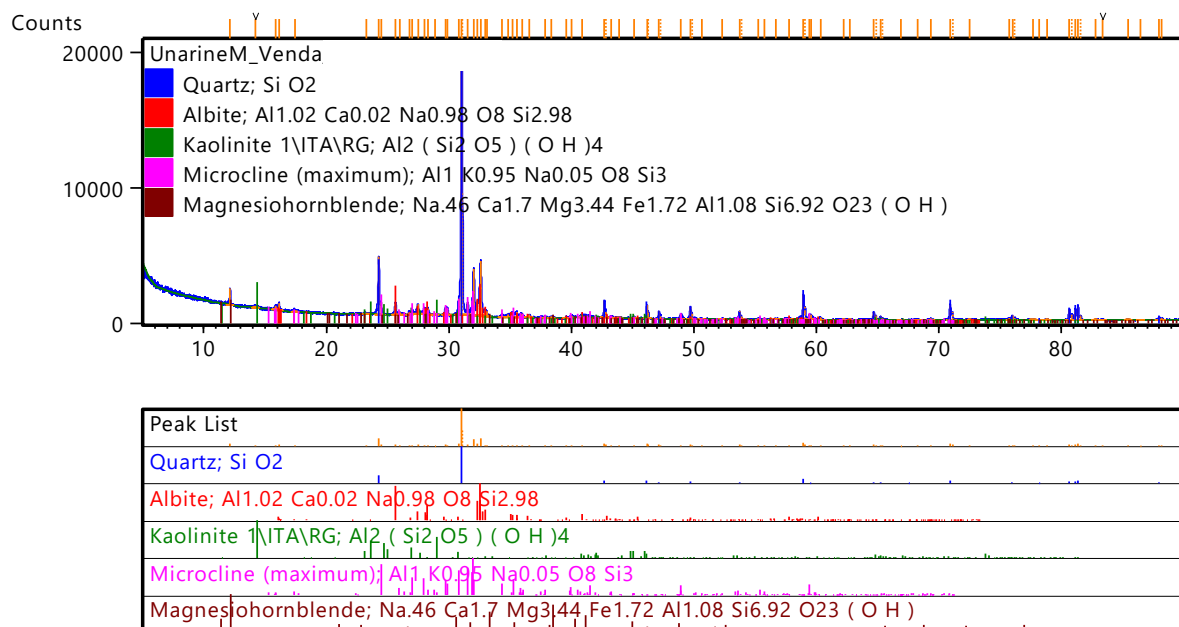


Figure 4.18: Mineral phases in sample S2

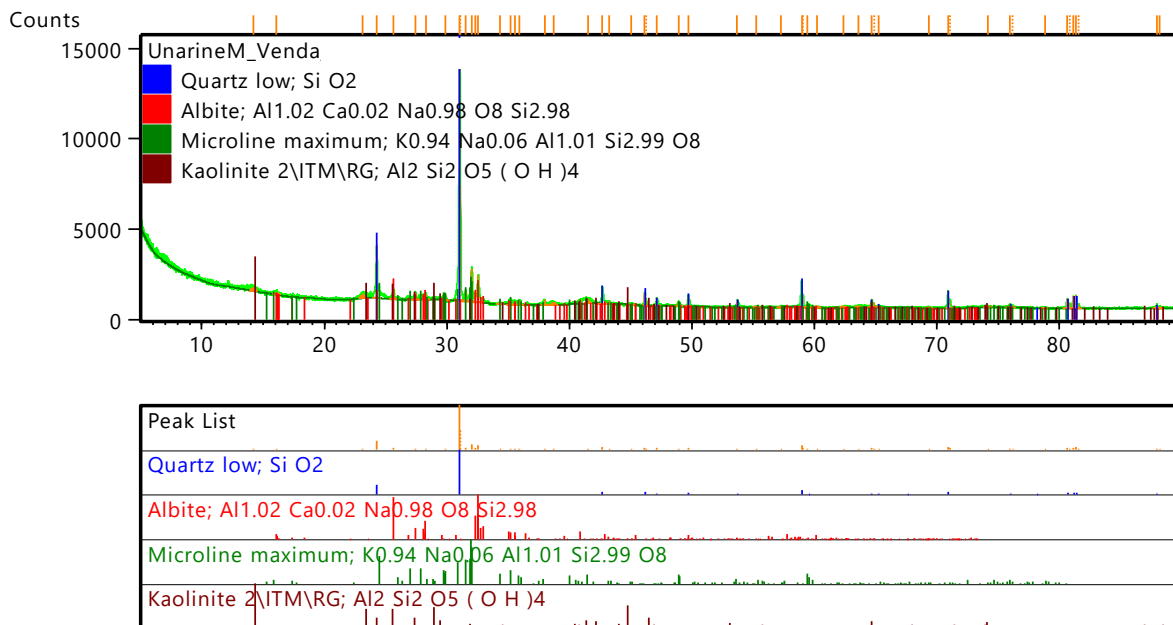


Figure 4.19: Mineral phases in sample S3

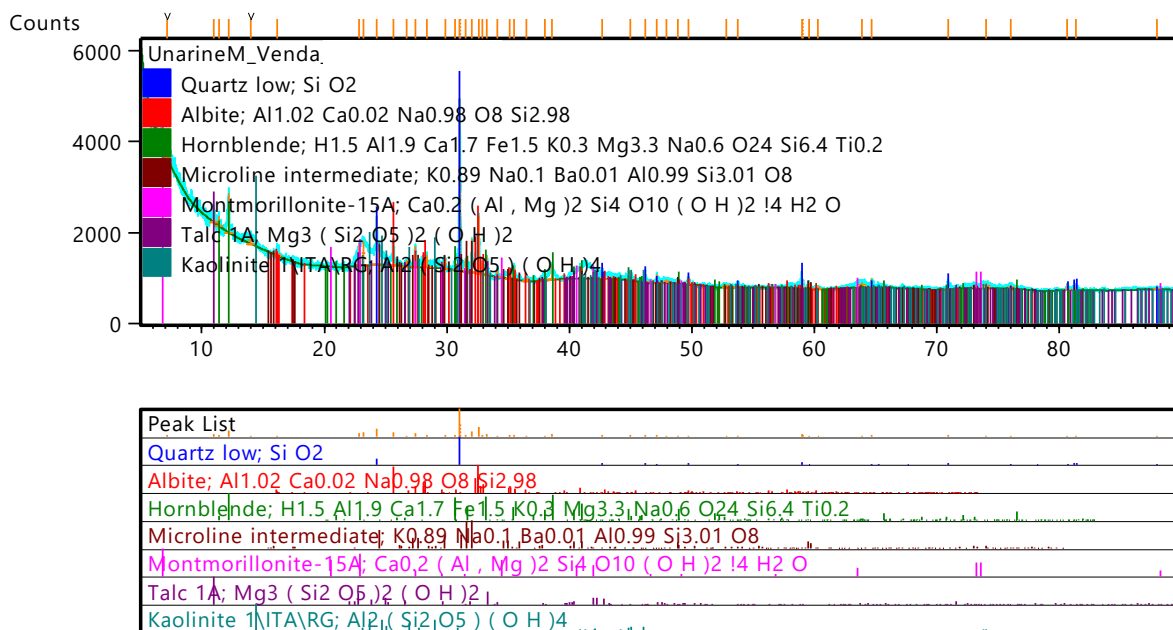


Figure 4.20: Mineral phases in sample S4

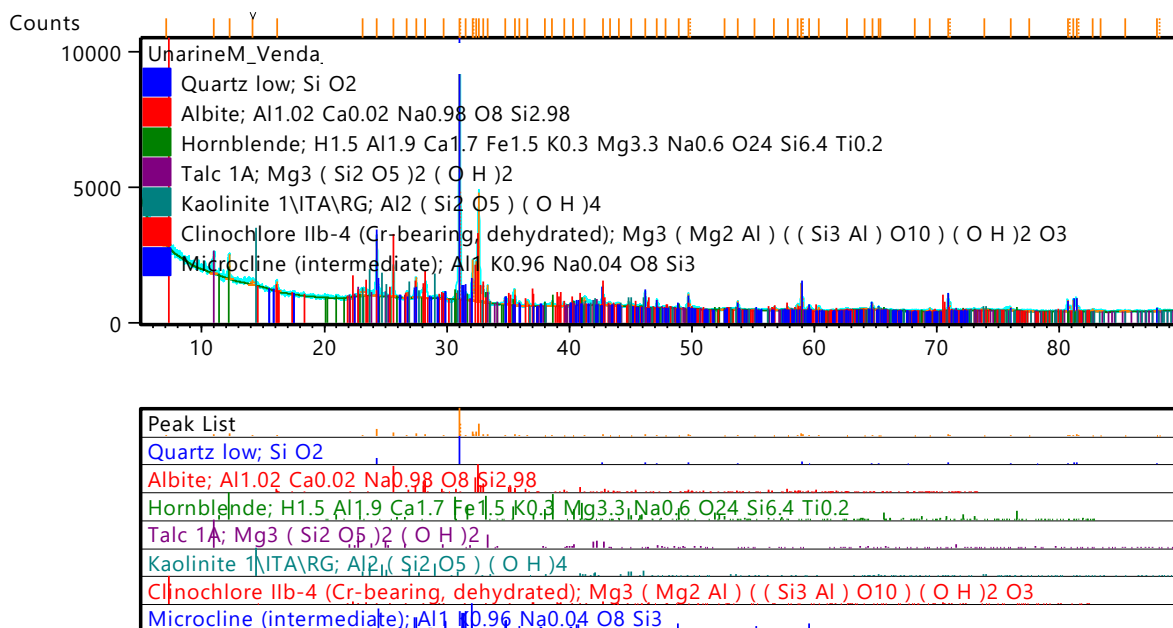


Figure 4.21: Mineral phases in sample S5

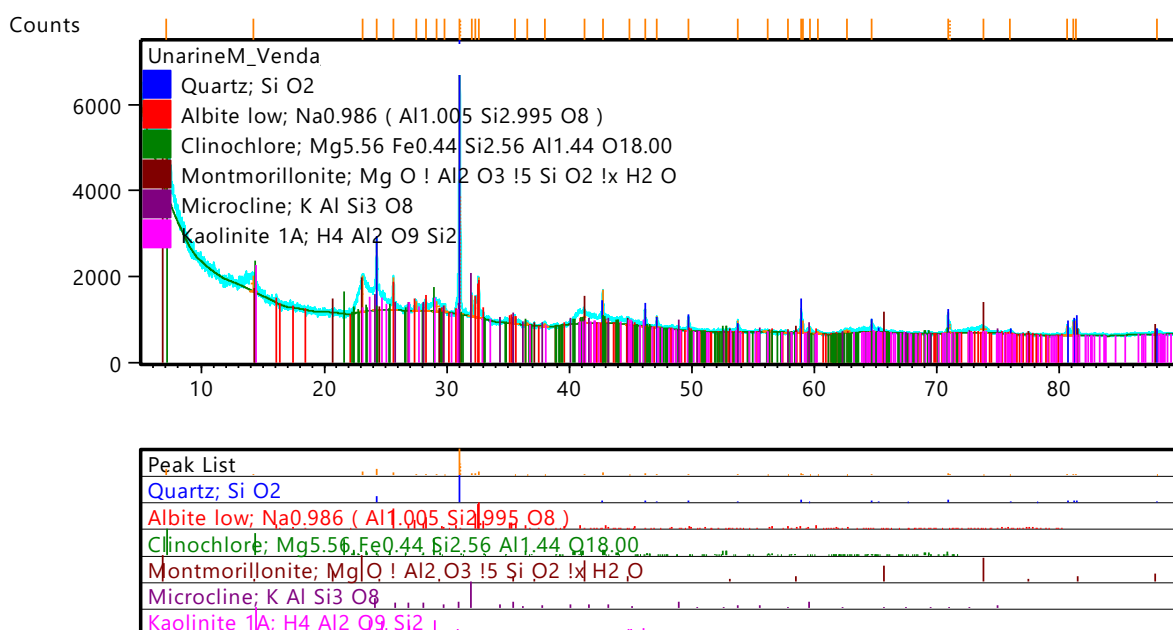


Figure 4.22: Mineral phases in sample S6

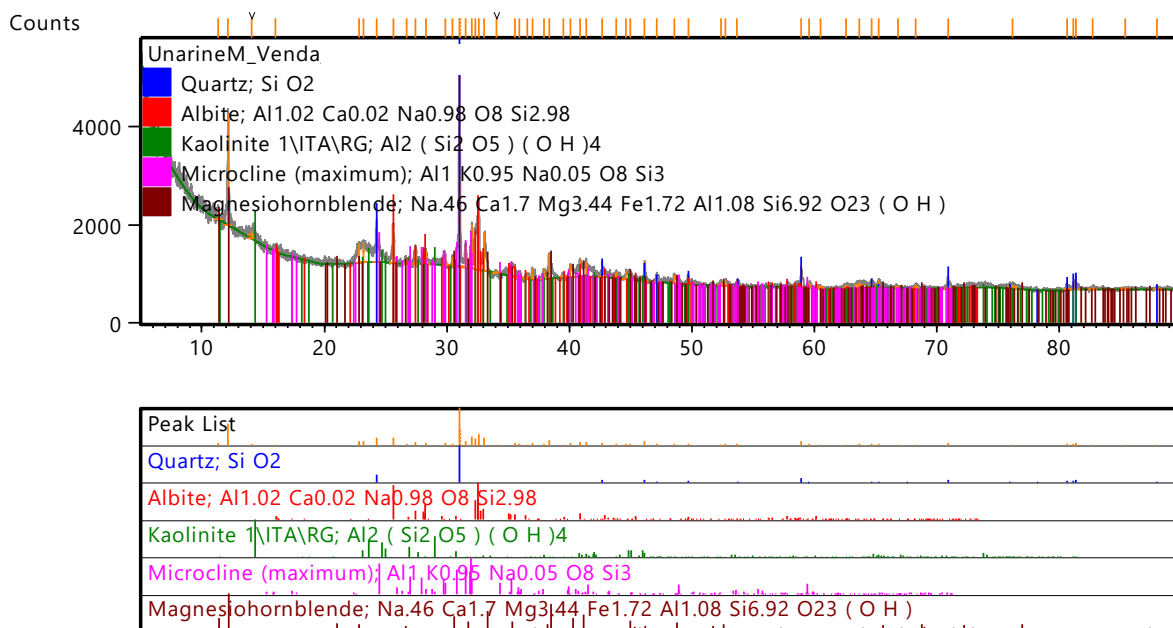


Figure 4.23: Mineral phases in sample S7

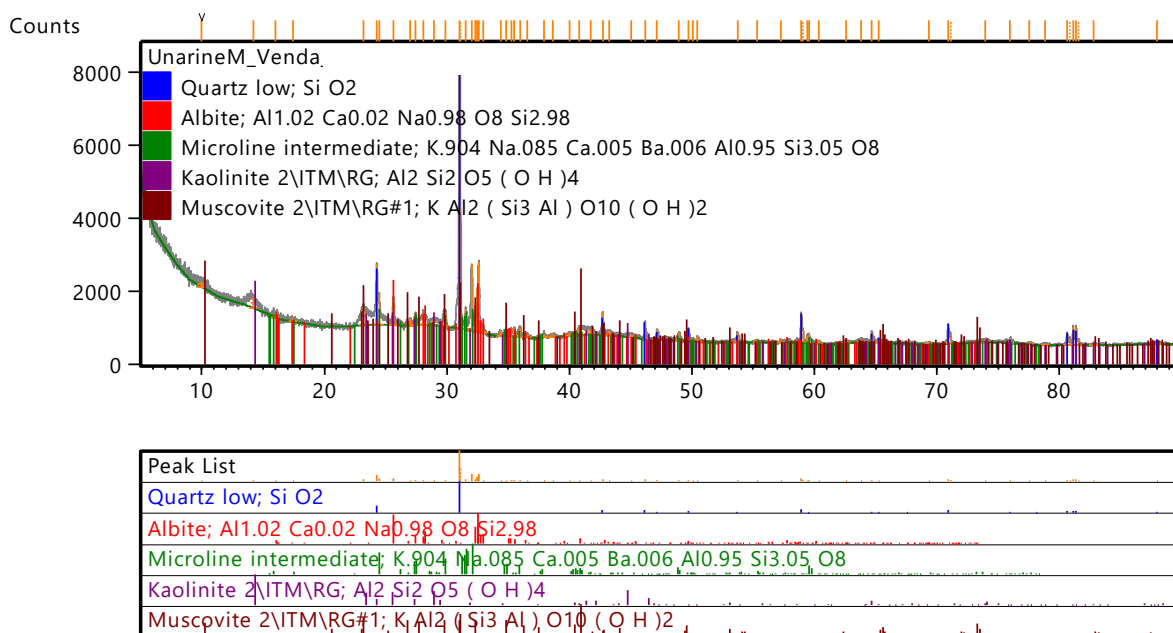


Figure 4.24: Mineral phases in sample S8

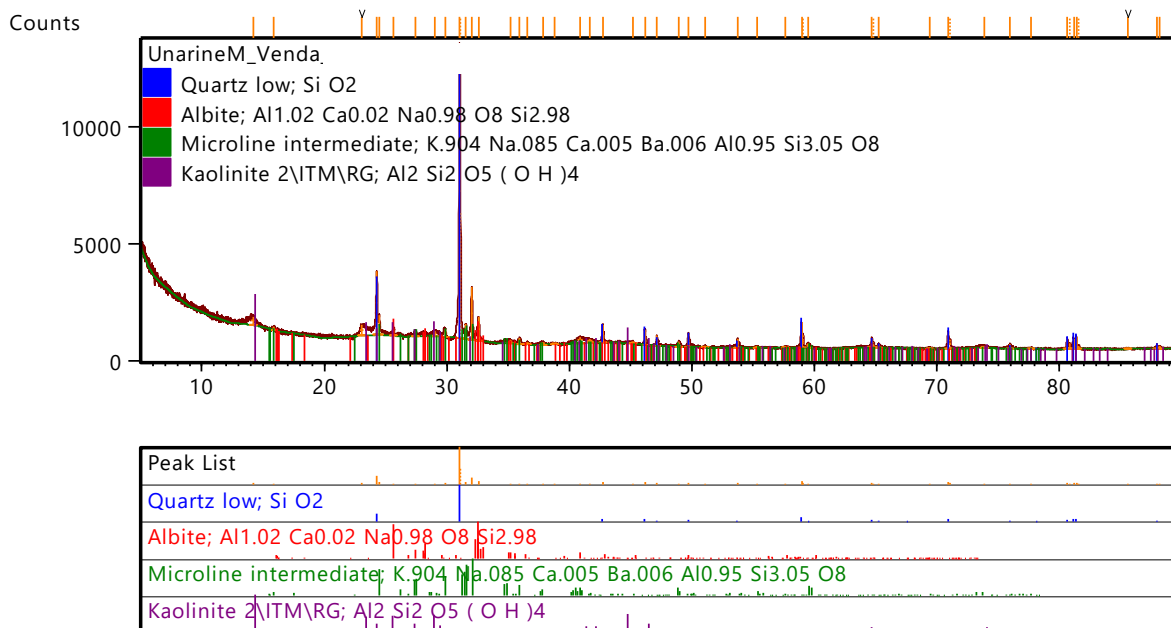


Figure 4.25: Mineral phases in sample S9

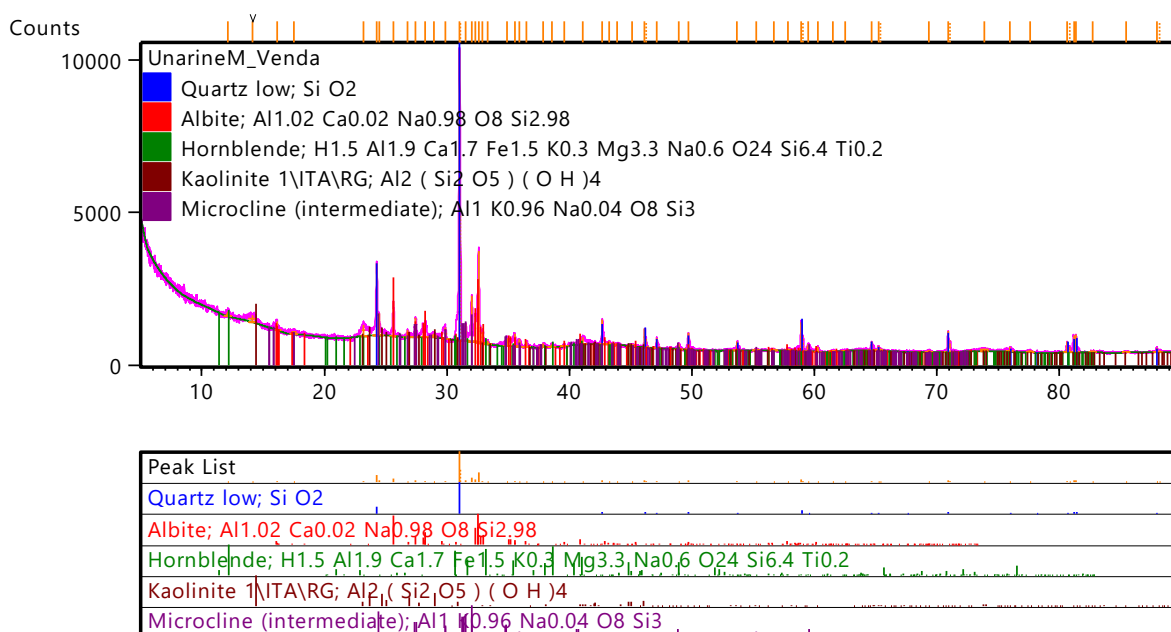


Figure 4.26: Mineral phases in sample S10

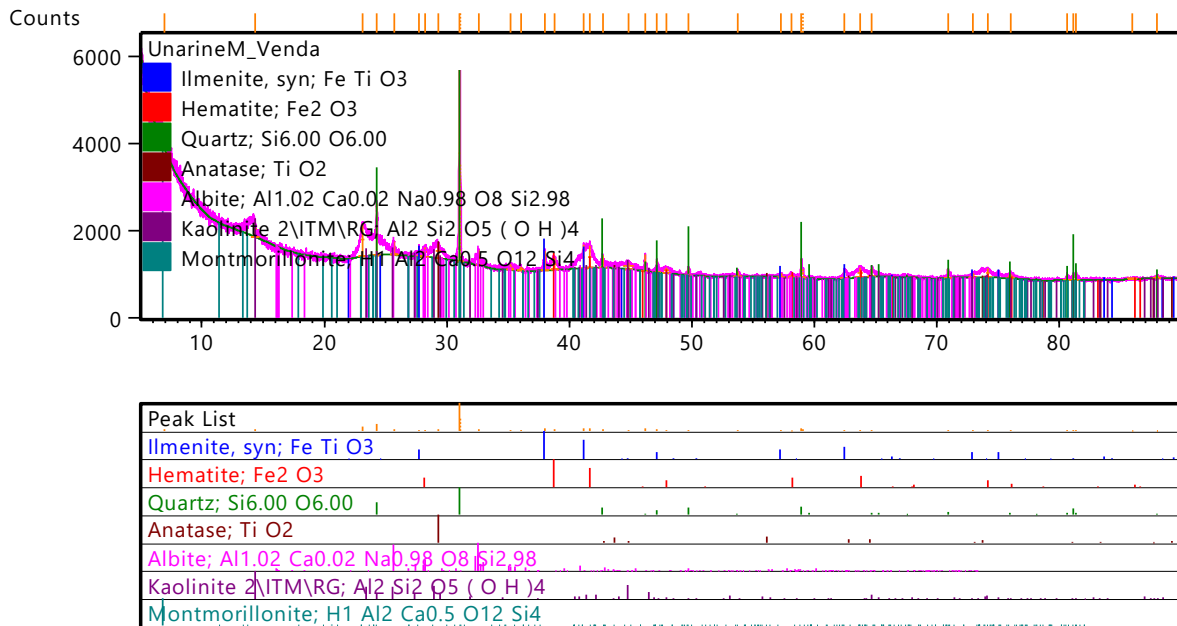


Figure 4.27: Mineral phases in sample S11

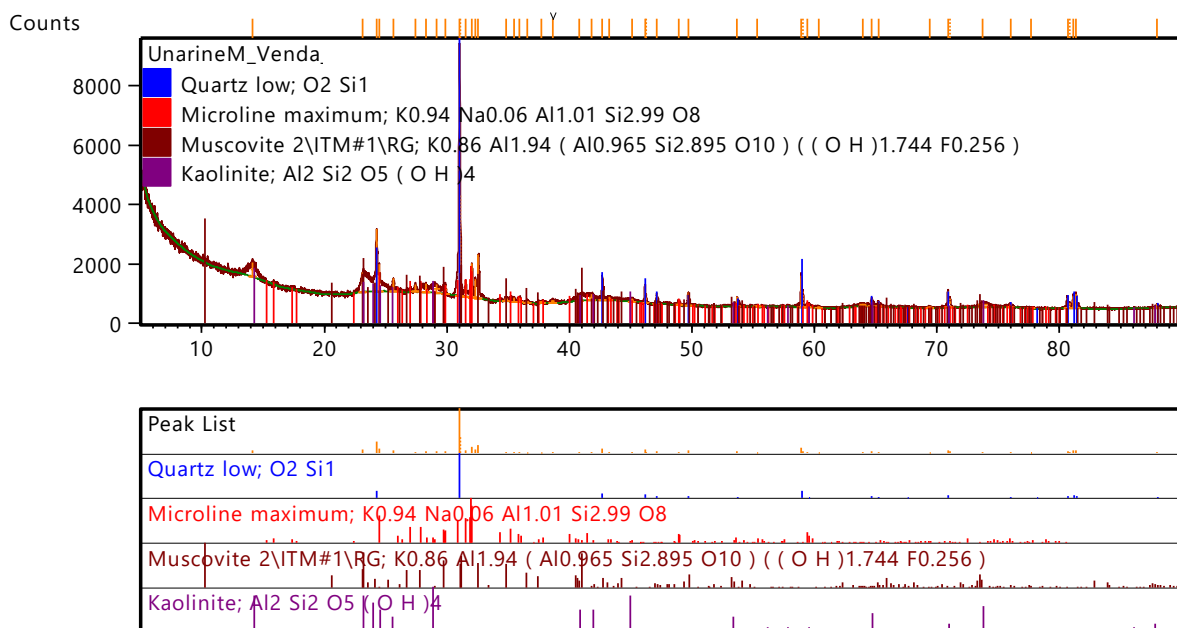


Figure 4.28: Mineral phases in sample S12

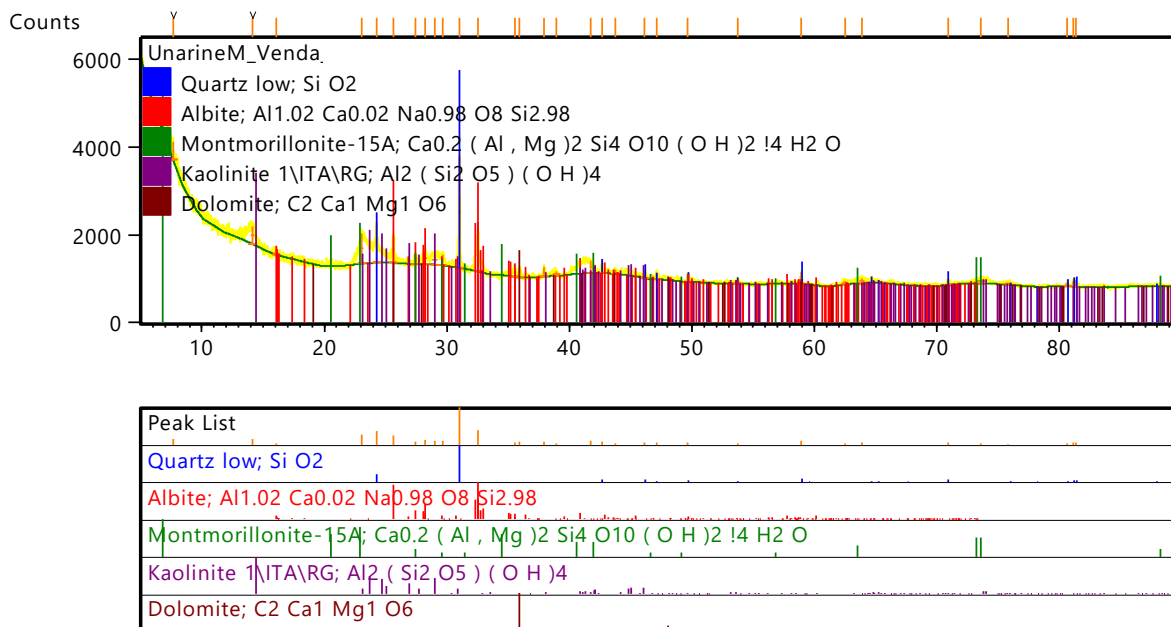


Figure 4.29: Mineral phases in sample S13

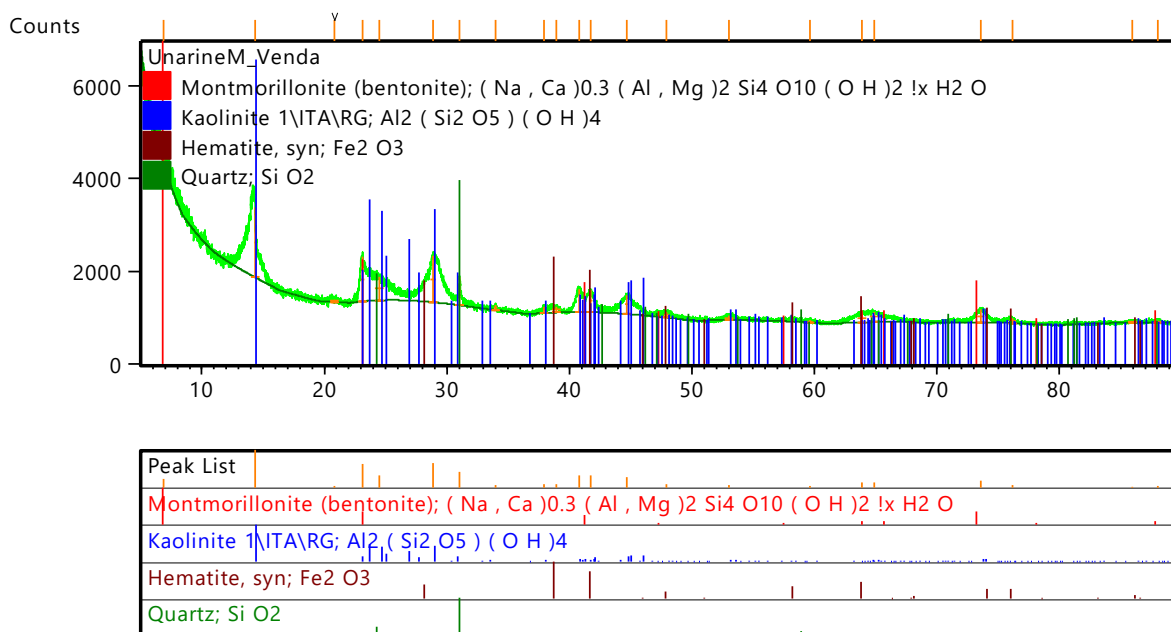


Figure 4.30: Mineral phases in sample S14



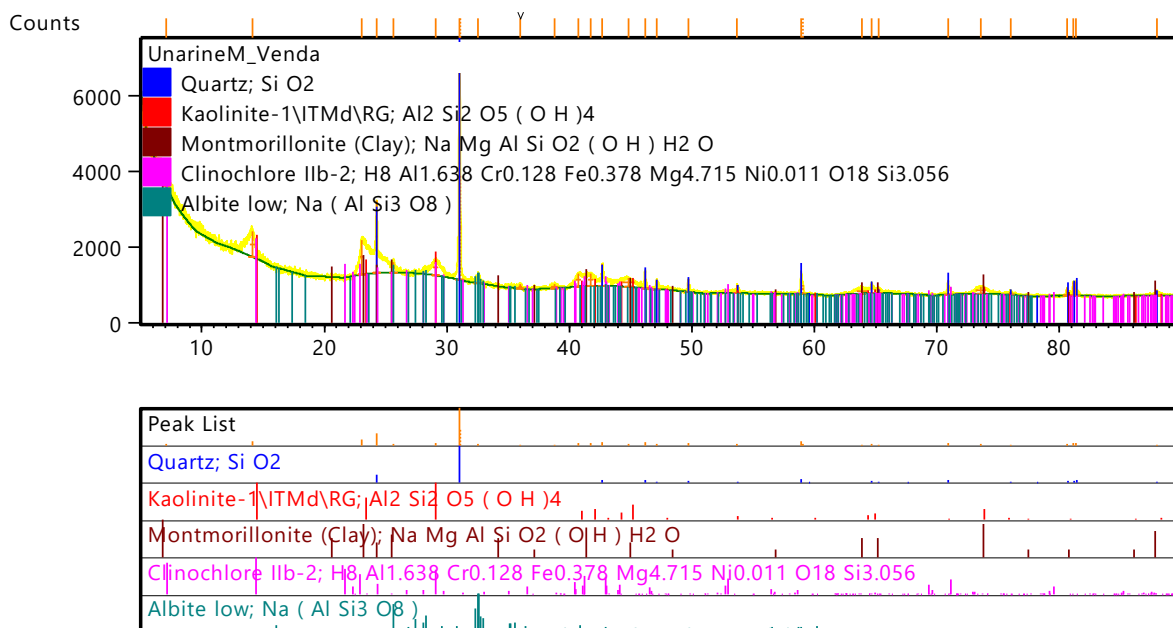


Figure 4.31: Mineral phases in sample S15

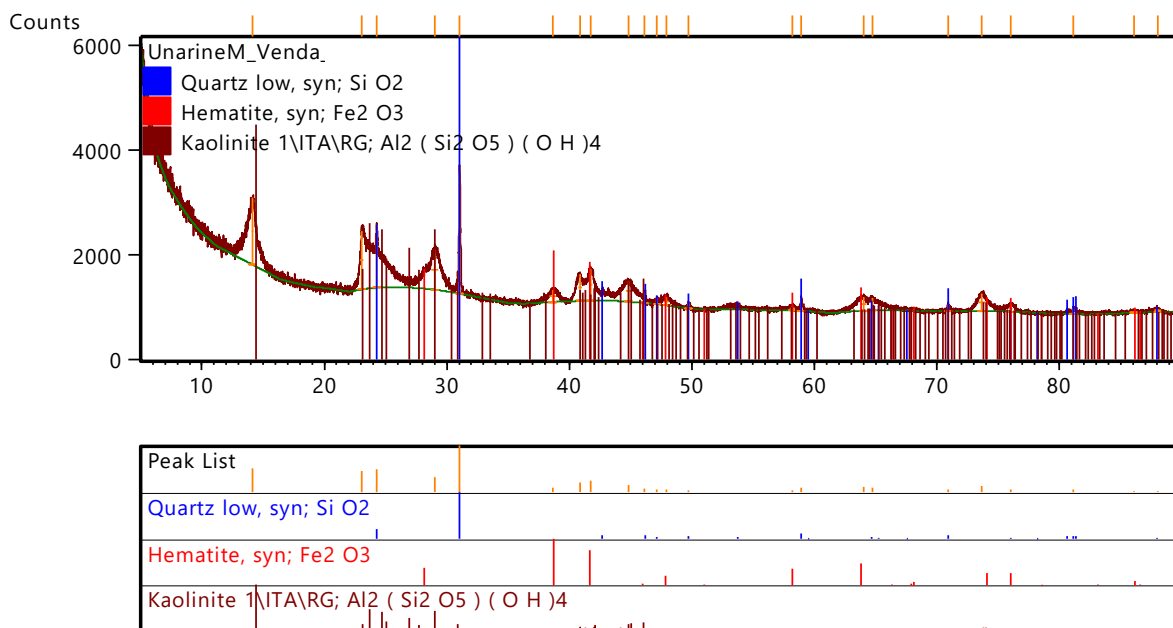


Figure 4.32: Mineral phases in sample S16

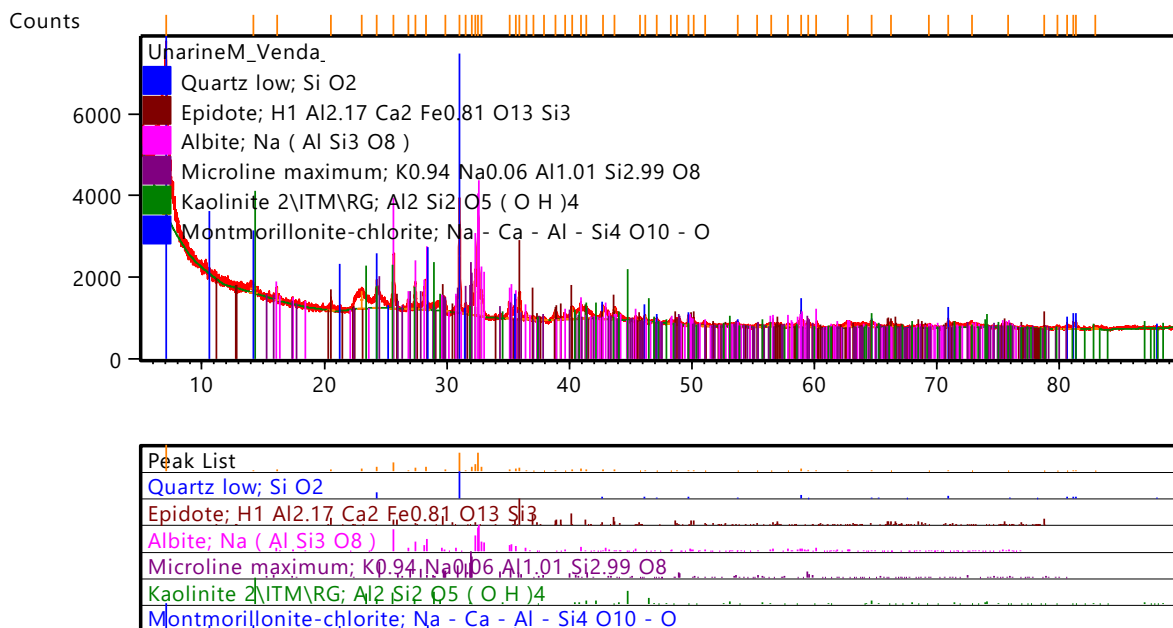


Figure 4.33: Mineral phases in sample S17

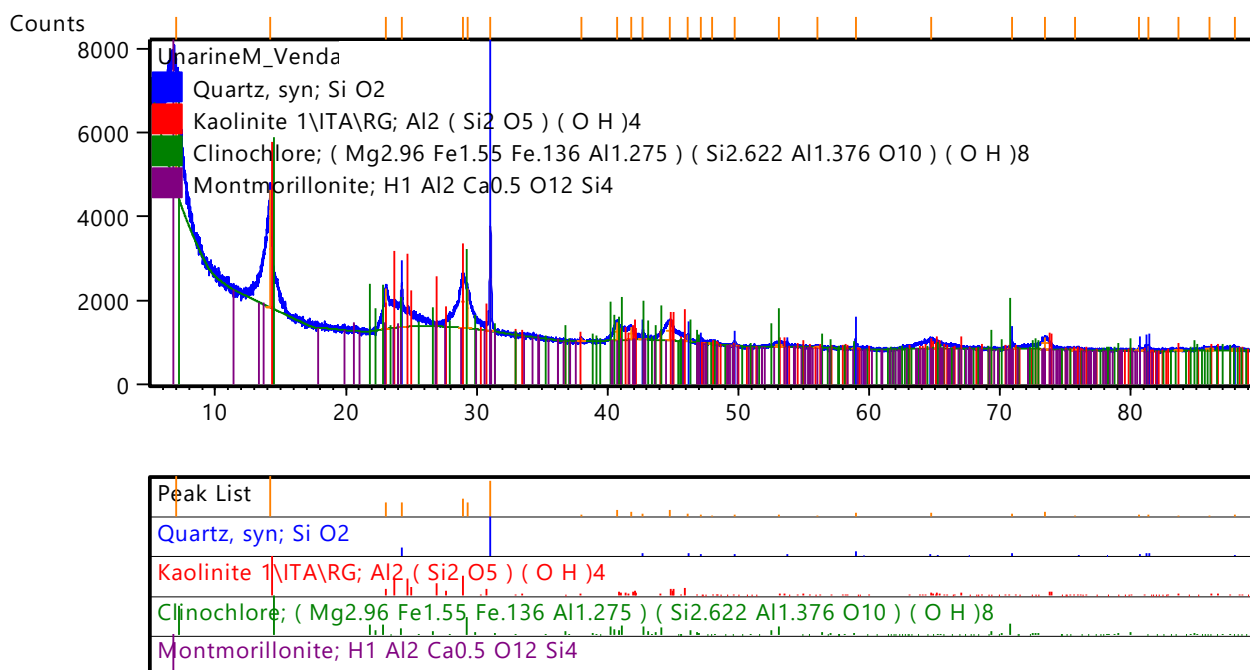


Figure 4.34: Mineral phases in sample S18

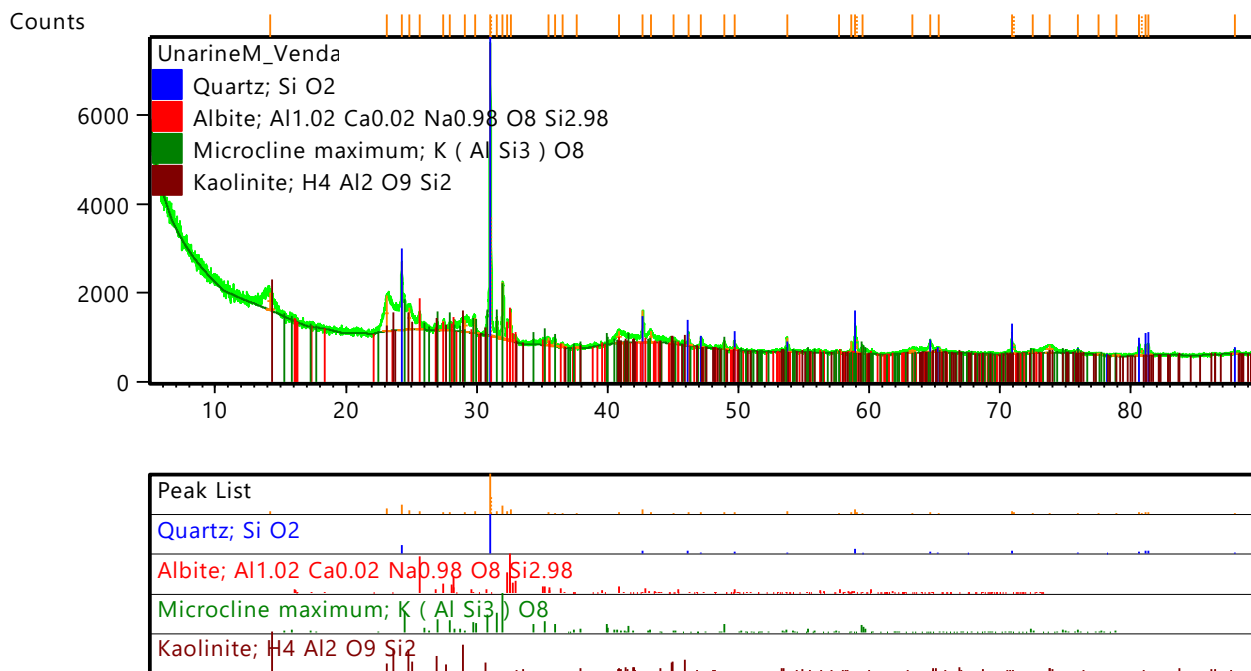


Figure 4.35: Mineral phases in sample S19

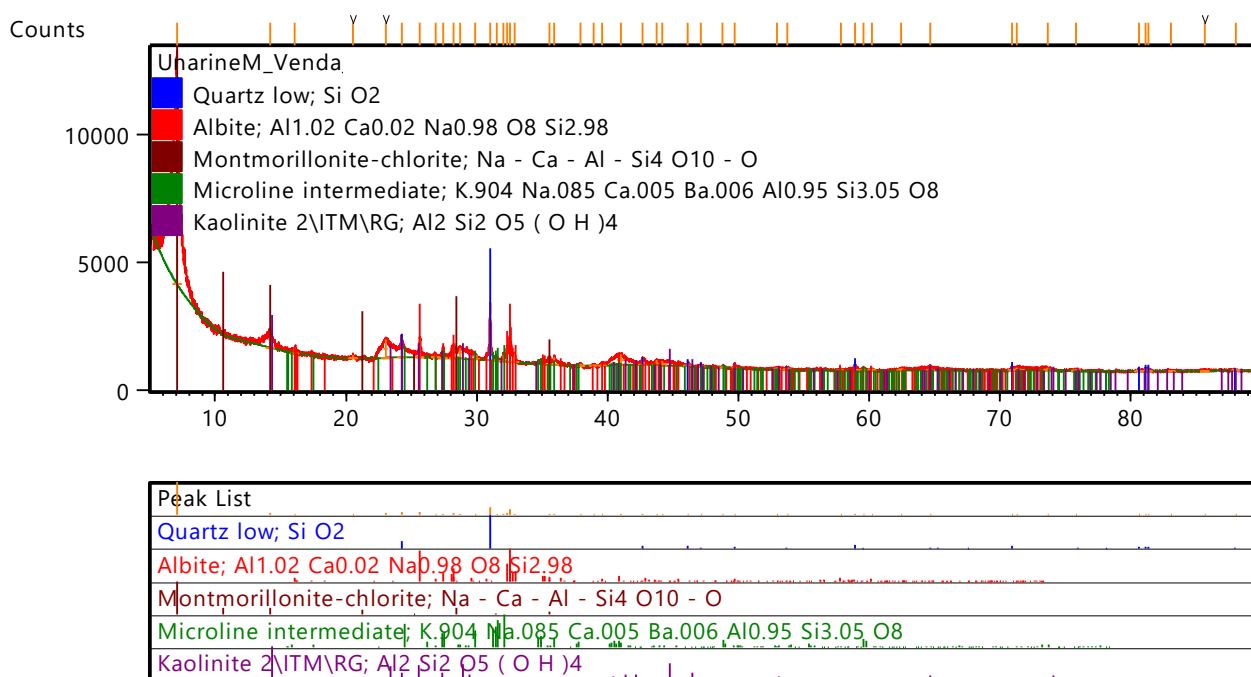


Figure 4.36: Mineral phases in sample S20

Kaolinite and quartz were the major components of the geophagic soils, with abundances ranging from 4 to 90 wt% and 4 to 45 wt%, respectively (Figure 4.37). Samples from Mukhoro had a high content of kaolinite while a high content of quartz was in samples from Doli than the other two areas. More than 80 % of the samples (17 out of 20) contained plagioclase excluding S16, S18 and S14. Microcline was not identified in most samples from Mukhoro (S12-S17) with the exception of the 16 wt% (in S12) and 13 wt% (in S17) contained in two samples.

Hornblende and chlorite were also identified in some of the samples; however, only samples from Doli contained hornblende (S2, S4, S5 and S7). Other minerals (hematite, talc, anatase, ilmenite, dolomite, epidote and muscovite) only occurred in trace amounts with their abundances between 1- 9 wt%. Anatase, ilmenite, dolomite, epidote and muscovite were each present in only one sample with quantitative abundances of 2 wt%, 4 wt%, 1 wt%, 9 wt% and 4 wt% correspondingly (Appendix 4.1).

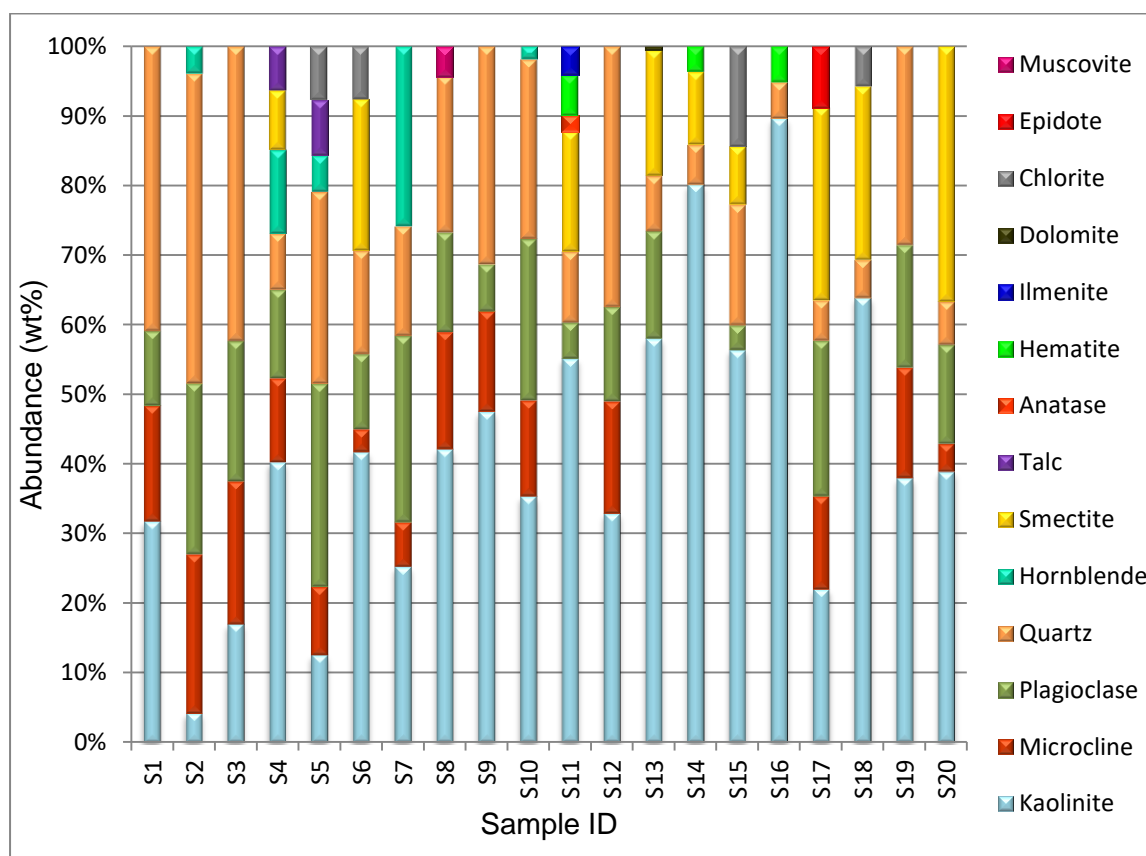


Figure 4.37: Abundances of minerals in geophagic soil samples

The mineralogy of the clay and silt fractions of the geophagic materials was also determined. This was done to compare the minerals in the bulk fraction with the minerals in the clay and silt fractions. To achieve this, representative samples were chosen from the three sites. The mineralogy of the bulk, silt and clay fractions was the same with differing contents. Kaolinite was concentrated in the clay fraction with content ranging from 41.69 to 60.33 wt% while quartz was very low in this fraction (2.6- 5.22 wt%). Quartz dominated the silt fraction whereas kaolinite was very low.

### 4.3.2 Parent Rocks Mineralogy

Mineralogical analyses further revealed that minerals in the eight rock samples were actinolite, augite, chlorite (clinochlore), epidote, forsterite, magnetite, muscovite, plagioclase (andesine), quartz, sepiolite and microcline. Rock samples were dominated by primary minerals with chlorite, epidote, sepiolite and microcline being the only clay minerals. The detected mineral phases of the eleven minerals are shown in Figures 4.38- 4.45. Present in all samples, quartz and plagioclase were the most dominant minerals identified. Almost all samples consisted of actinolite, augite, chlorite, epidote, forsterite, magnetite and muscovite. Microcline, plagioclase and quartz were the only minerals identified in DOL2 and MUK2. Samples DOL1 and DOL3 were the only samples with sepiolite.

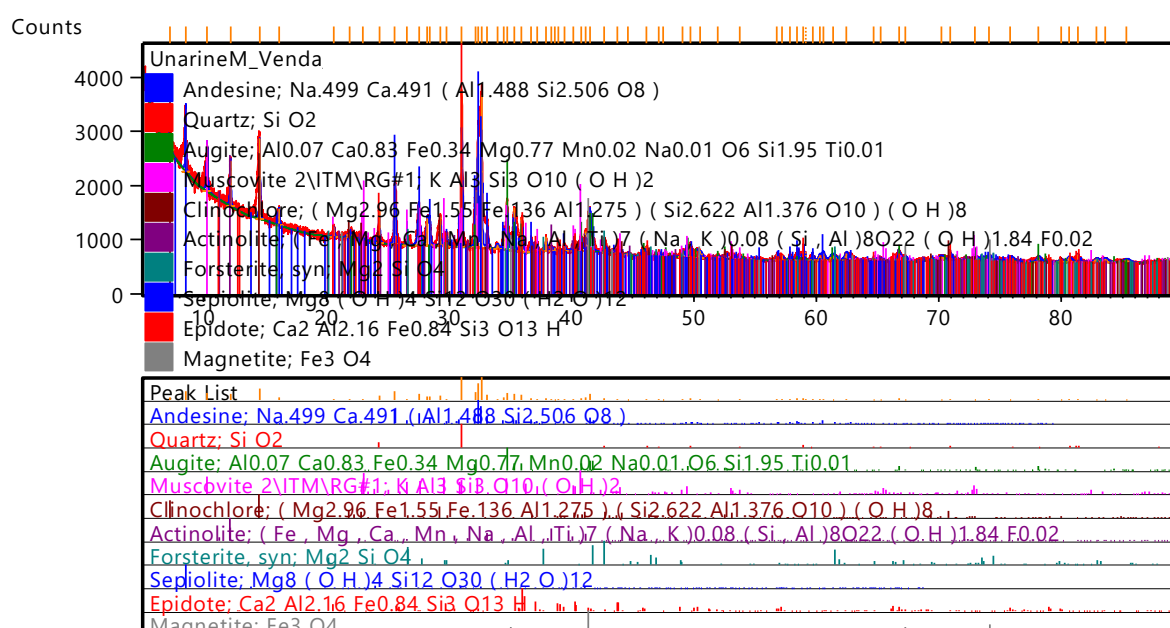


Figure 4.38: Mineral phases in sample DOL1

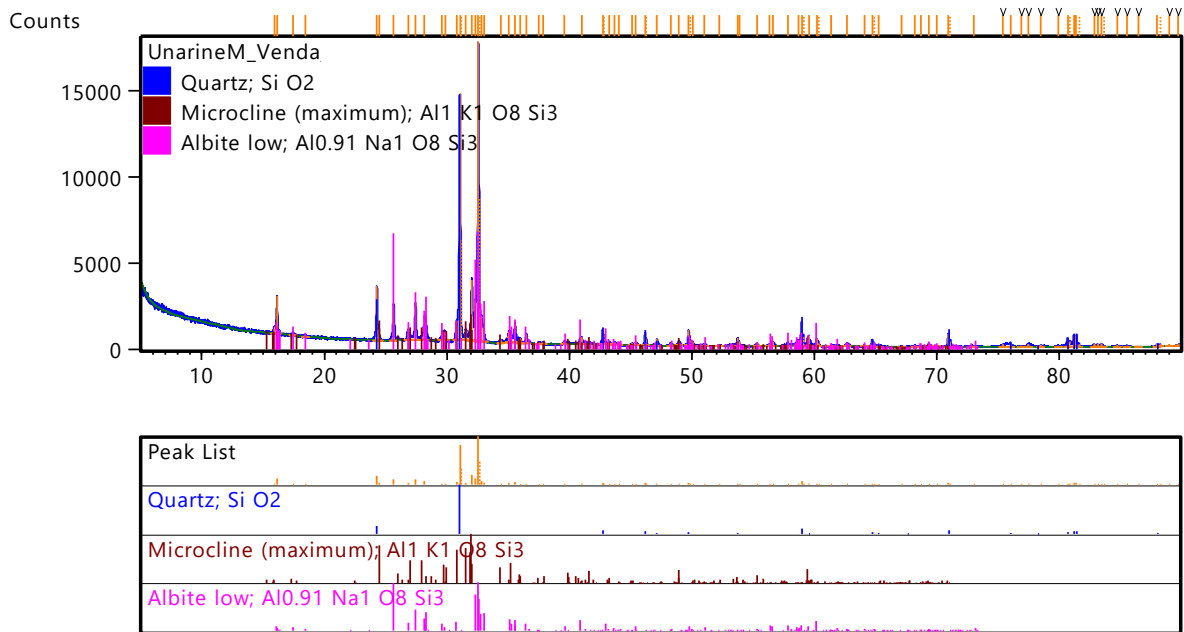


Figure 4.39: Mineral phases in sample DOL2

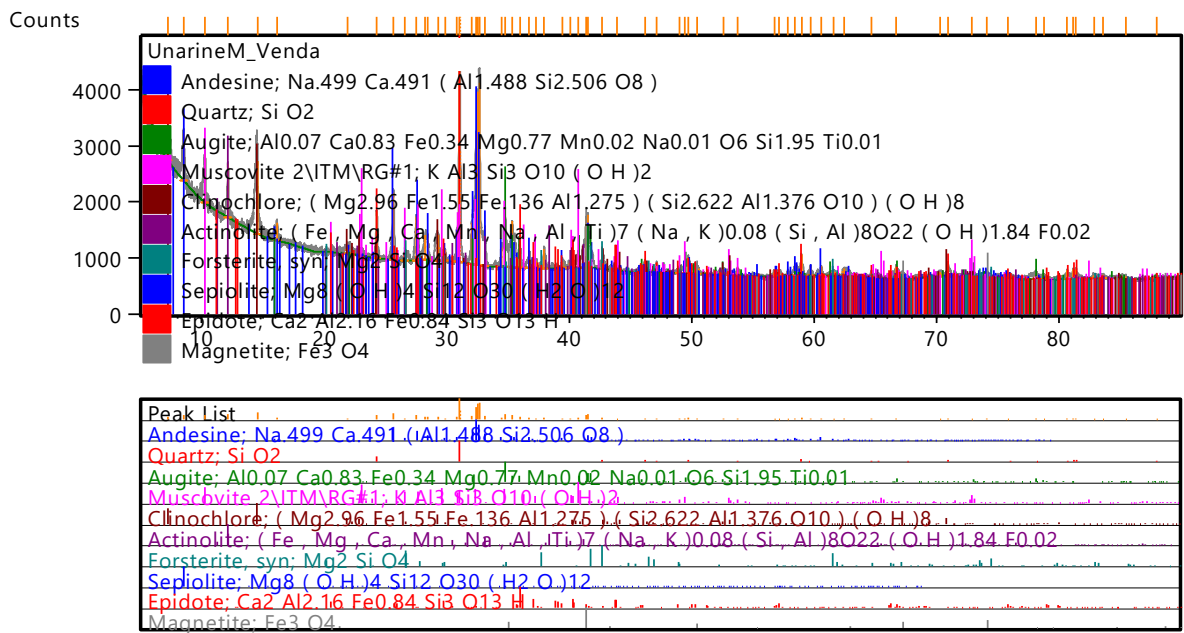


Figure 4.40: Mineral phases in sample DOL3

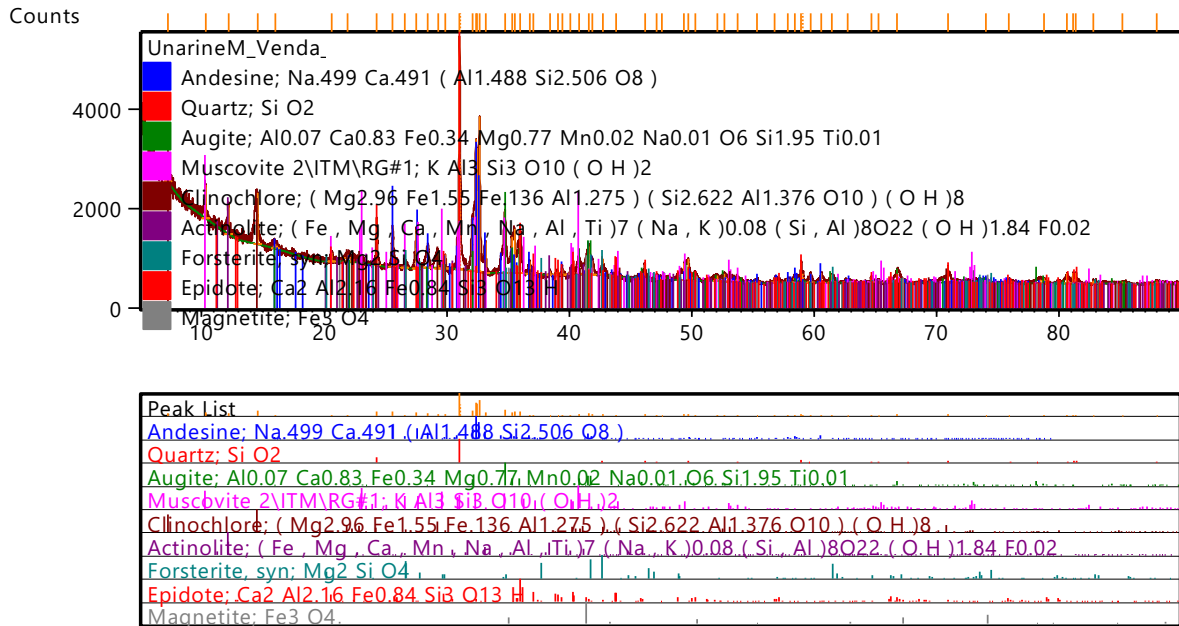


Figure 4.41: Mineral phases in sample MAR

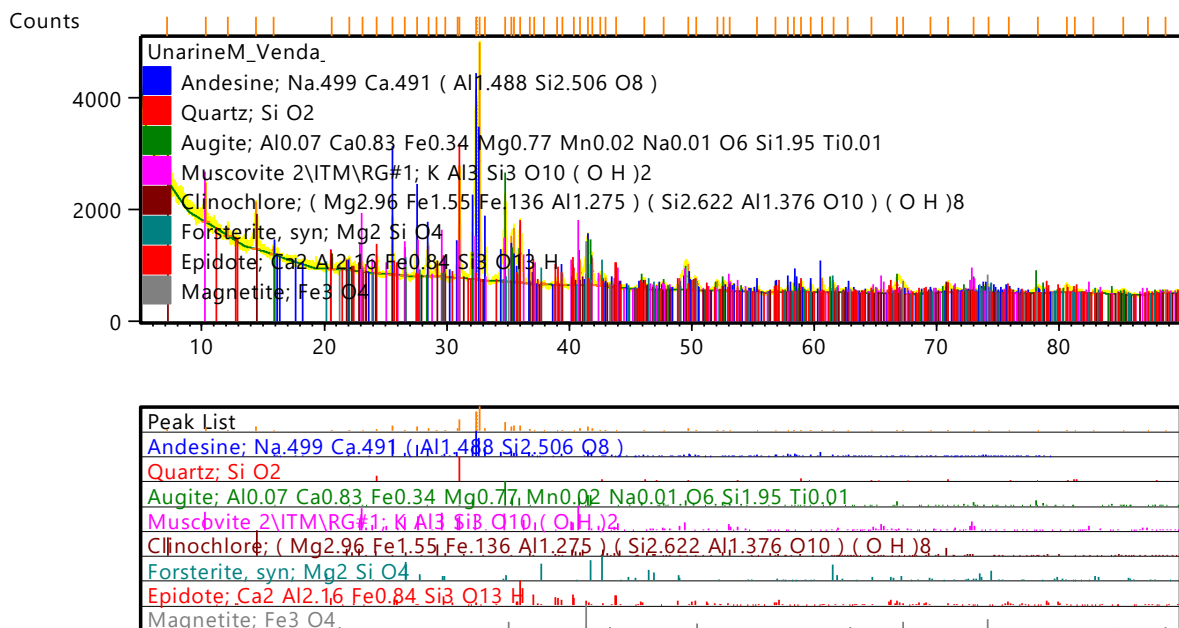


Figure 4.42: Mineral phases in sample MUK1



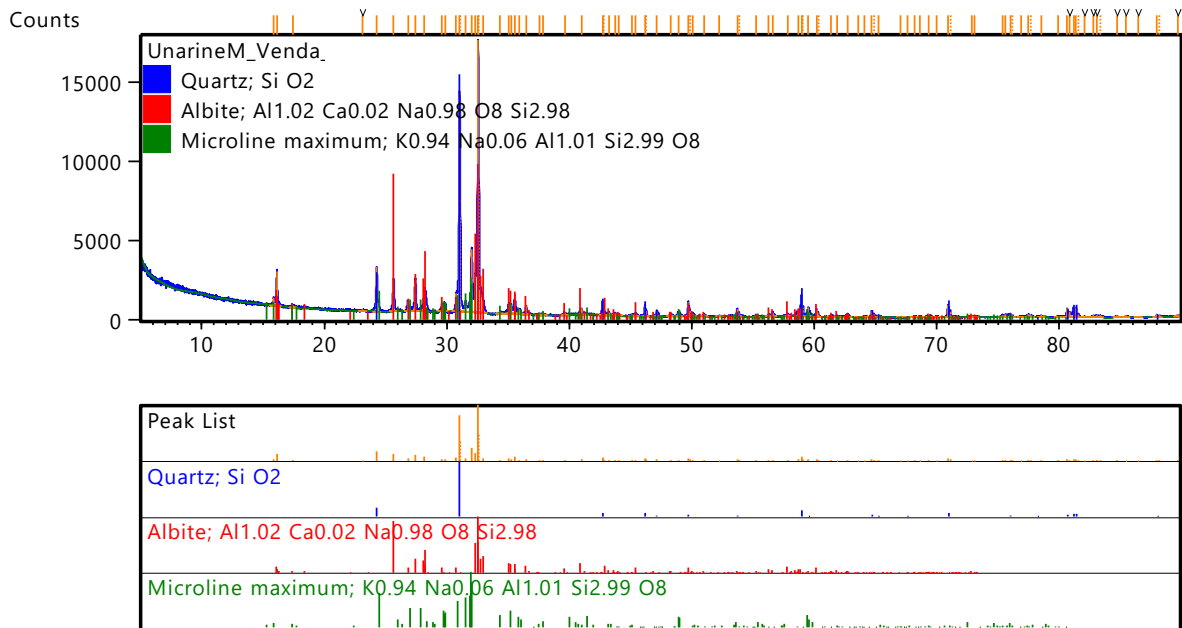


Figure 4.43: Mineral phases in sample MUK2

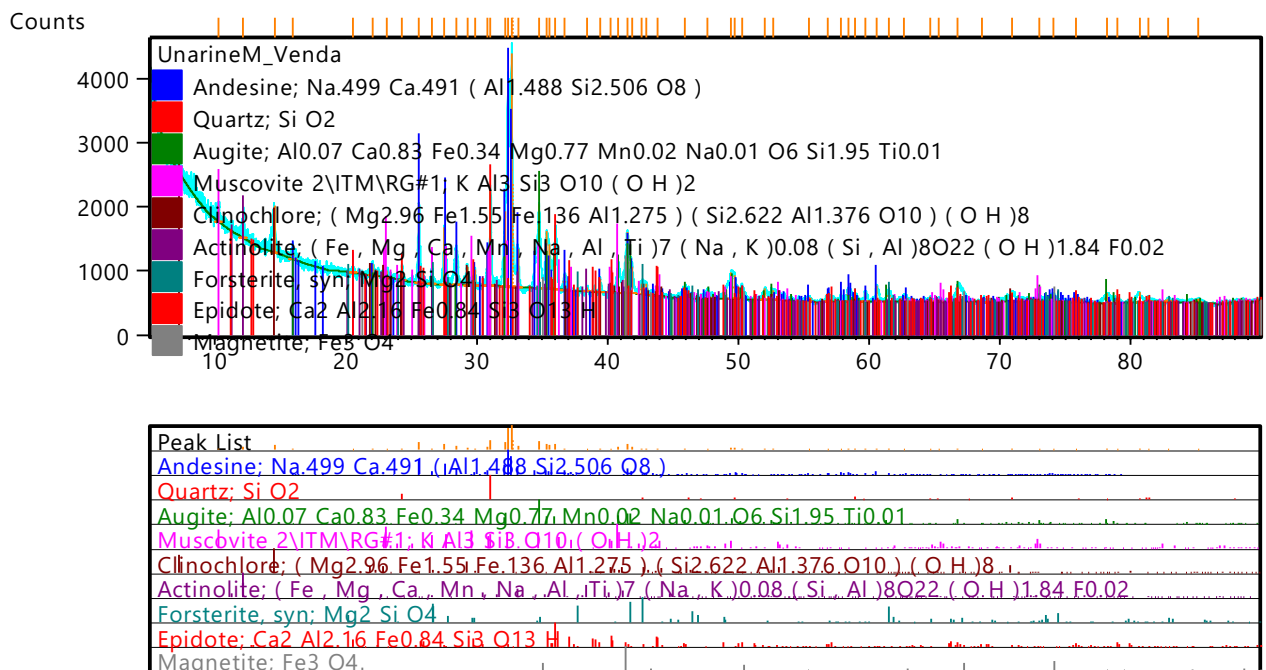


Figure 4.44: Mineral phases in sample MAT1

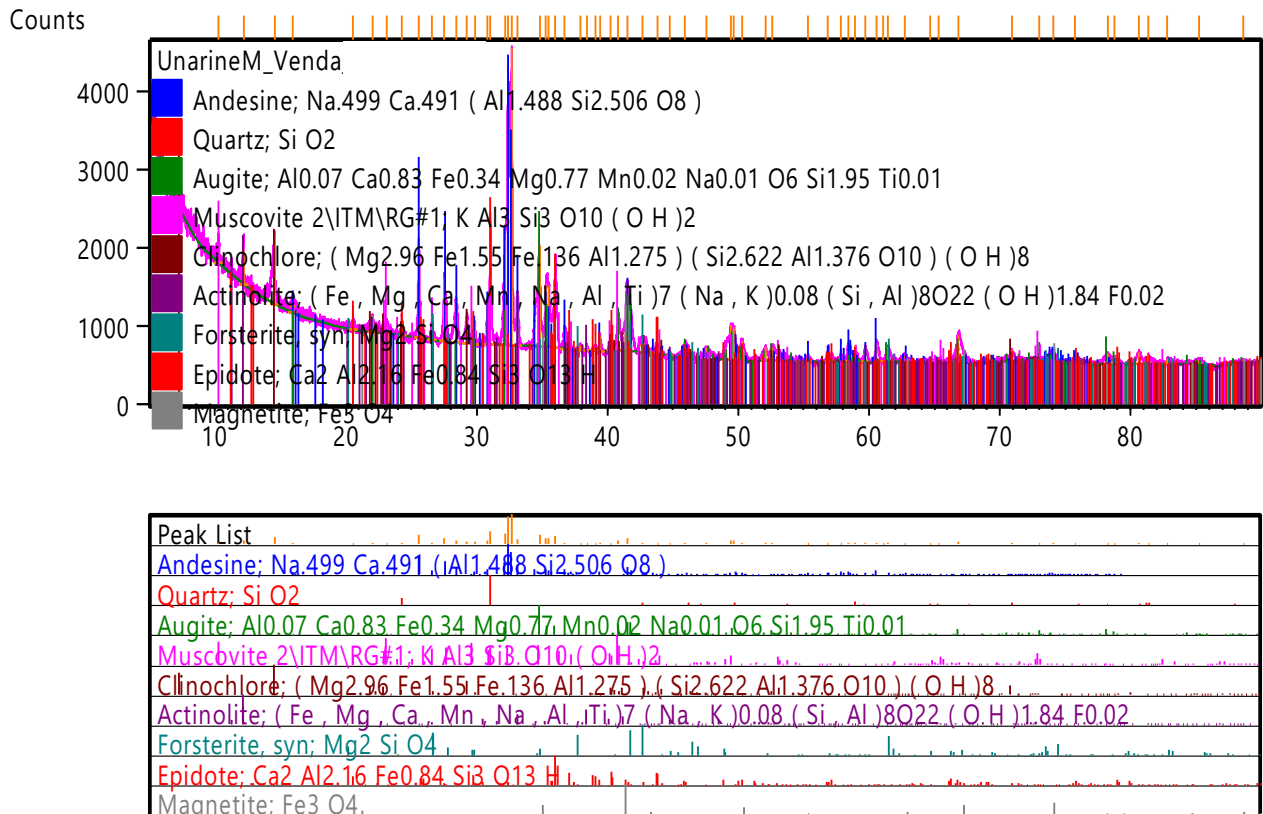


Figure 4.45: Mineral phases in sample MAT2

Semi-quantitative analyses showed that plagioclase was the major constituent of the rock samples with abundances between 41-54 wt% (Figure 4.46). Plagioclase and augite had the highest concentrations in all samples while the combined abundances of other minerals (actinolite, chlorite, epidote, forsterite, magnetite, muscovite, sepiolite, microcline) ranged from 0 to 9 wt%. Although quartz occurred in all samples, its abundance was relatively low (4-29 wt%) compared to augite which had an average concentration of 23 wt%. Samples DOL2 and MUK2 had the highest concentrations of plagioclase (54 wt% for both samples) and quartz (29 wt% and 28 wt%, respectively). A summary of the mineral abundances of the identified minerals in the soil and rock samples is presented in Appendix 4.2.

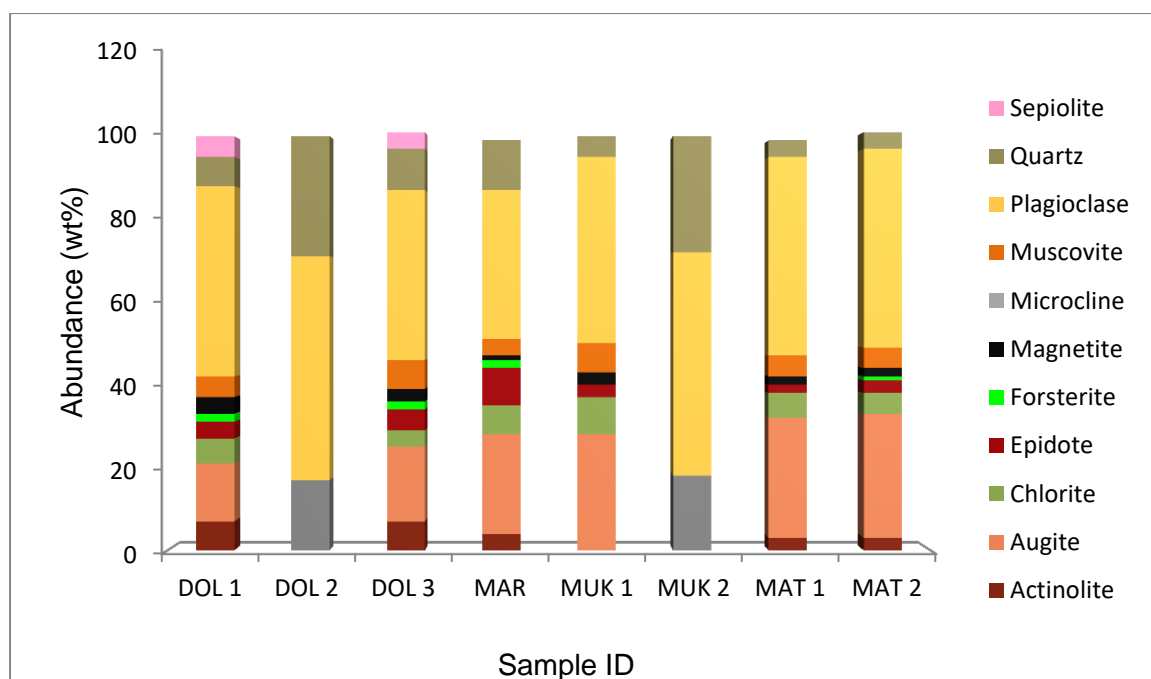


Figure 4.46: Abundances of minerals in rock samples

## 4.4 Geochemical Characterisation of Geophagic Materials and Parent Rocks

### 4.4.1 Geochemistry of Geophagic Samples

#### 4.4.1.1 Major Oxides

As shown in Figure 4.47, geochemical analysis indicated that geophagic soils mainly composed of  $\text{SiO}_2$  (ranging from 37.88% to 72.51%) and  $\text{Al}_2\text{O}_3$  (ranging from 13.18% to 26.36%). The concentration of silica in each sample was higher than the alumina content. Iron oxide was in moderate concentration with an average concentration of 12.38% while  $\text{K}_2\text{O}$ ,  $\text{TiO}_2$ ,  $\text{Na}_2\text{O}$ ,  $\text{MgO}$ ,  $\text{CaO}$ ,  $\text{MnO}$ ,  $\text{P}_2\text{O}_5$  and  $\text{Cr}_2\text{O}_3$  were in traces. Sample S2 had the highest silica content and the lowest content of alumina was contained in this sample. Amounts of  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  were higher in samples from Matsilele than in samples from Doli and Mukhoro. Samples from Doli had the highest silica content (average of 54.29%) followed by samples from Mukhoro (average of 47.45%) then Matsilele samples (43.03%). The abundances of the major oxides in the geophagic samples are shown in Appendix 4.3.

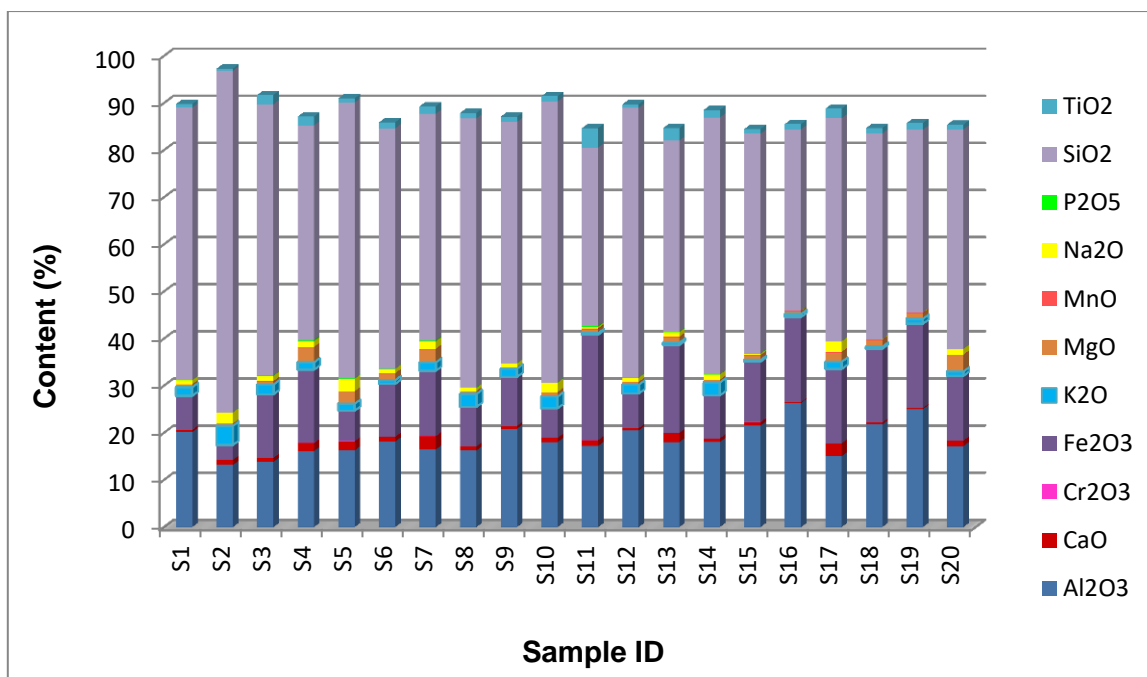


Figure 4.47: Oxides in geophagic soils

#### 4.4.1.2 Trace Elements

In comparison with the UCC, bulk geophagic soils were enriched in transition trace elements (Sc, V, Cr, Co and Ni) with Co having the highest concentrations (Figure 4.48). High field strength elements (Y, Zr and Nb) were also enriched, however, Nb was depleted in all samples.

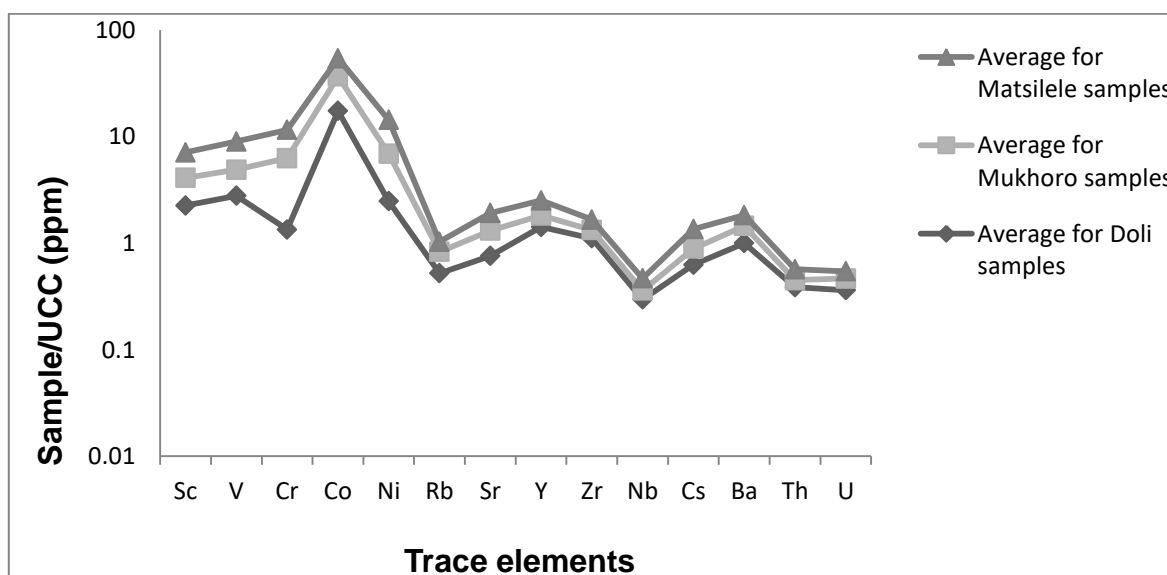


Figure 4.48: UCC-normalised average trace elements concentrations in geophagic soils

With regard to the large ion lithophile elements (Rb, Cs, Ba, Sr, Th and U), geophagic samples were enriched with Cs, Ba and Sr while Rb, Th and U were in depletion. The concentrations of trace elements were in the following order: Doli> Mukhoro> Matsilele.

Two of the eleven geophagic materials from Doli (S6 and S11), four of the six from Mukhoro (S13, S15, S16 and S17) and all Matsilele samples (S18, S19 and S20) were depleted in LREEs and enriched in HREEs. In contrary, the majority of samples from Doli (S1, S2, S3, S4, S5, S7, S8, S9 and S10) and two samples from Mukhoro (S12 and S14) were enriched in LREEs and depleted in HREEs (Figure 4.49). The concentrations of trace and rare earth elements in all geophagic samples are presented in Appendices 4.4 and 4.6 respectively.

The distribution of trace elements in the silt and clay fraction was similar to that of the bulk fraction but with lower concentrations. The clay fraction generally had trace elements concentrations lower than the silt fraction with the exception of DoIA that had higher concentrations in the clay fractions (Appendices 4.5 and 4.7).

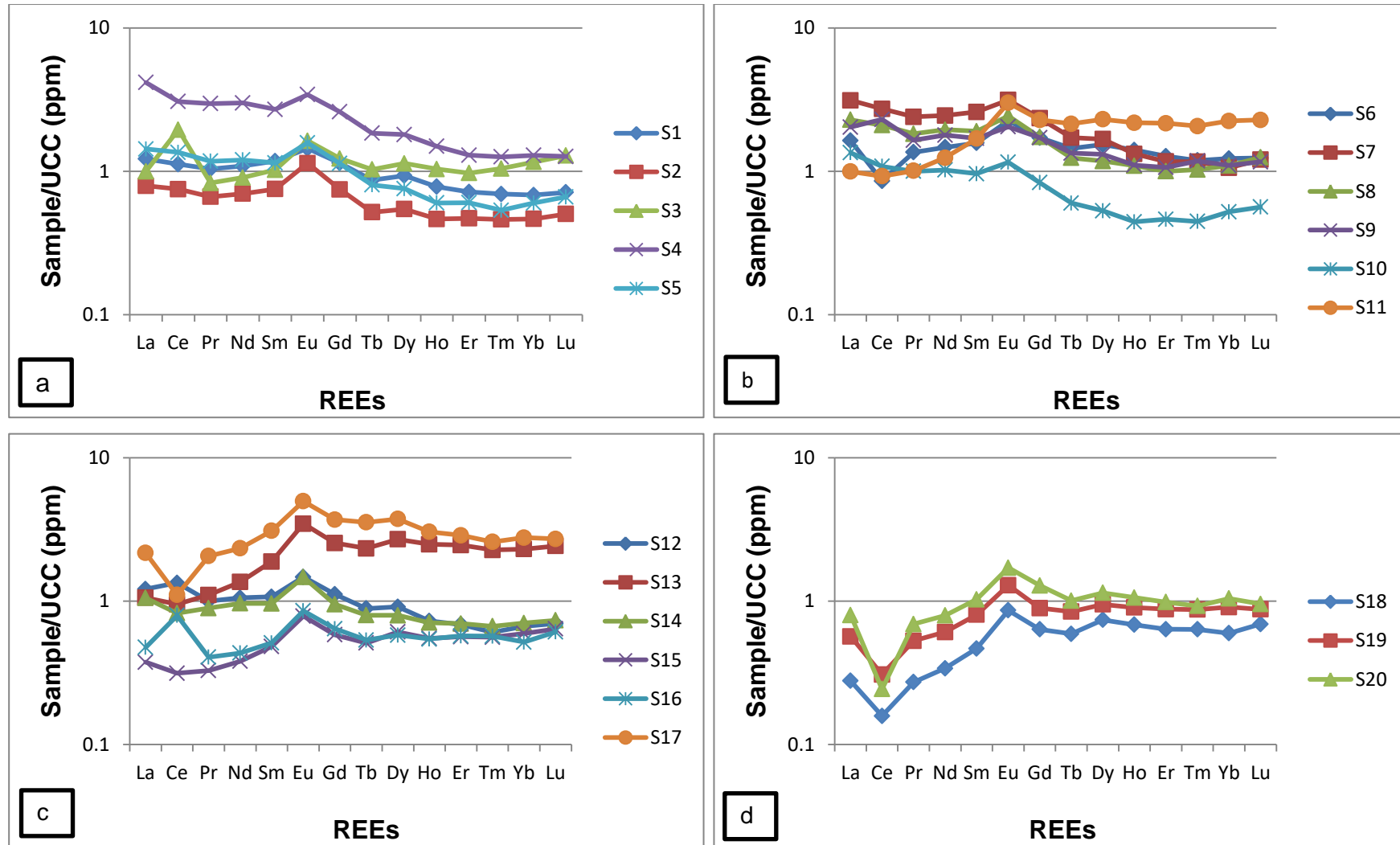


Figure 4.49: UCC-normalised REE pattern of average concentrations of geophagic materials from Mashau Village: a and b-samples from Doli, c-samples from Mukhoro and d-samples from Matsilele.

## 4.4.2 Geochemistry of Parent Rocks

### 4.4.2.1 Major Oxides

Alumina content ranged from 14.57% (in MAR) to 15.79% (MUK2) while the silica content ranged from 48.47% (in DOL1) to 73.56% (in MUK2). The amount of alumina was similar in all samples, with concentrations of about 15% but DOL3 and MAR had lower amounts than the other samples (Figure 4.50). Silica content was higher than the alumina content; it was also noticed that the amount of silica in samples ranged between 48 and 52%. Samples DOL2 and MUK2 had the highest silica content of about 73% in both samples. The concentrations of other oxides ( $\text{Fe}_2\text{O}_3$ ,  $\text{K}_2\text{O}$ ,  $\text{TiO}_2$ ,  $\text{Na}_2\text{O}$ ,  $\text{MgO}$ ,  $\text{CaO}$ ,  $\text{MnO}$ ,  $\text{P}_2\text{O}_5$  and  $\text{Cr}_2\text{O}_3$ ) were slightly higher than in soil samples. The concentrations of the analysed oxides are displayed in Appendix 4.8.

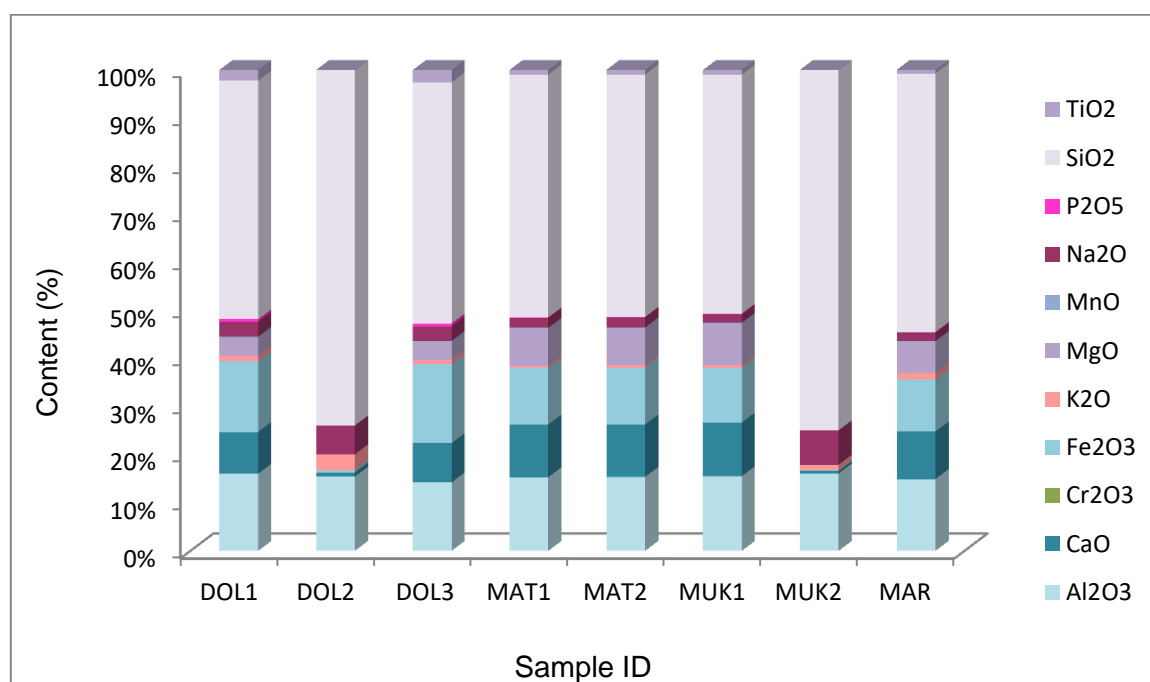


Figure 4.50: Oxides in rock samples

### 4.4.2.1 Trace Elements

Trace elements in rocks were generally lower comparative to the UCC average concentrations. Rocks were enriched in transition trace elements (Sc, V, Cr, Co and Ni) but the concentrations of Sc and V were lower (Figure 4.51). High field strength elements (Y, Zr and Nb) were also enriched; however, Nb was depleted in all samples as in geophagic soils.



With regard to the large ion lithophile elements (Rb, Cs, Ba, Sr, Th and U), rock samples were enriched with Cs, Ba and Sr, Th and U while Rb was in depletion. The concentrations of trace elements in parent rocks were in the following order: Doli > Mukhoro > Matsilele. Rock samples DOL1, MAR, DOL3, MUK1, MAT1 and MAT exhibited the same REE elements distribution pattern (depleted in LREEs and enriched in HREEs) while samples DOL2 and MUK2 were in contrary (enriched in LREEs and depleted in HREEs) (Figure 4.52).

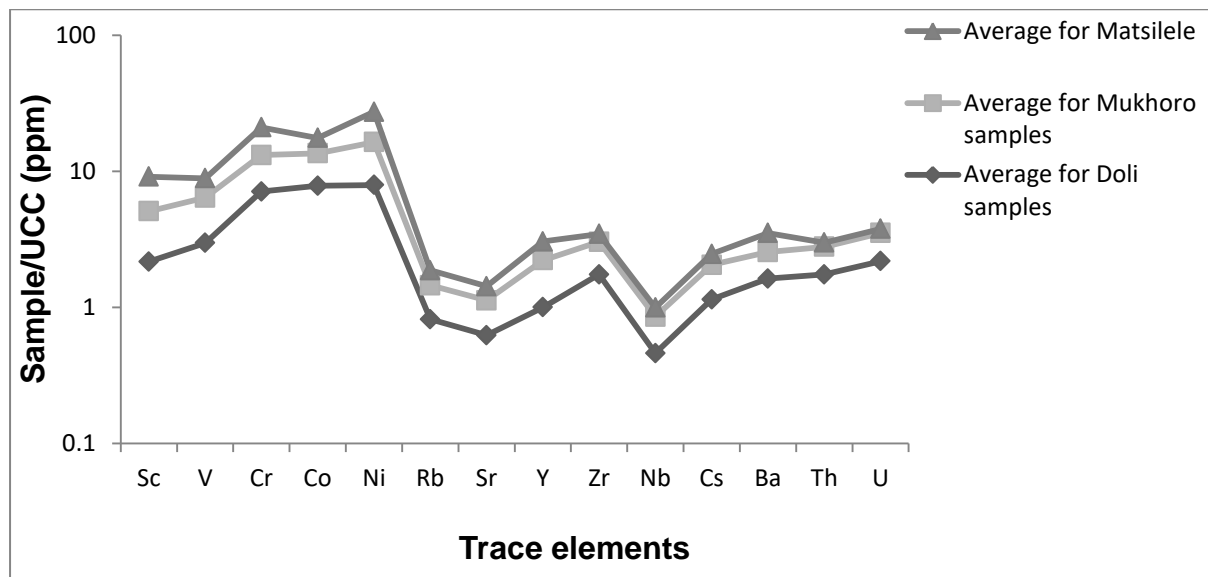


Figure 4.51: UCC-normalised average trace elements concentrations in geophagic soils

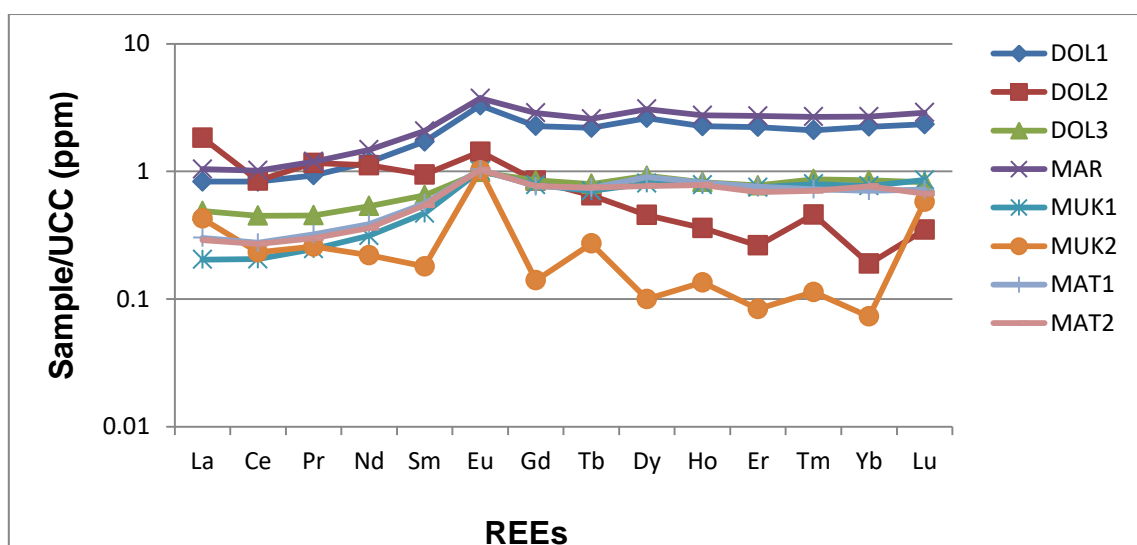


Figure 4.52: UCC-normalised REEs pattern of average concentrations in geophagic soils

## 4.5 Summary

The prevalence of geophagia in Mashau Village was determined. The physico-chemistry, mineralogy and geochemistry of geophagic materials from the study area was characterised. A questionnaire survey undertaken to understand geophagia in Mashau Village and the motivations for the practice revealed the following:

- Majority of geophagists in the study area are females whose geophagic behaviour is influenced by craving. It was also clear that geophagia was not limited to certain age groups, marital statuses, income sources, occupations and educational levels. The motivations for the practice included boredom, constipation, seeing the soil, feeling weak, pregnancy-related cravings and experiencing sleeplessness.

Physico-chemical analyses showed that:

- The colour of the geophagic materials from the study area generally ranged from brown to red with an exception of two samples which had pink and yellow colours.
- Most samples contained a higher percentage of the sand fraction than the silt and clay fraction. This resulted in the majority of samples to have a sandy clay loam texture.
- The pH of the geophagic materials ranged between slightly acidic and slightly alkaline.
- Samples that had higher CEC values were from Doli while samples from other sites had moderate to lower values.
- Majority of the samples had low to moderate EC values which also indicated a low amount of dissolved salts.

With regard to the mineralogy, kaolinite and quartz were the dominant minerals in the geophagic soils. The geochemical composition showed the materials to be generally aluminosilicates since they are dominated by alumina and the silica. It was also clear that trace elements, especially REEs were enriched in the bulk fraction than silt and clay fractions. Rock samples exhibited two different REE elements distribution patterns; there were samples that were depleted in LREEs and enriched in HREEs while others were enriched in LREEs and depleted in HREEs.

## CHAPTER 5

### DISCUSSION

#### 5.1 Geophagia in Mashau Village and the Motivations for the Practice

The geophagic practice in the study area is prevalent among women but few males also practice it. According to Msibi (2014), this may be the result of simple mother/daughter-sharing traditions. Although people from different age groups consumed geophagic soils, the practice was more common in people aged from 26 to 36 years. Geophagia has no educational divides, both the educated and the illiterate indulged in the practice. The study confirms the results of Momoh *et al.* (2015) which also discovered that geophagia was practiced by the educated and illiterate.

The practice of geophagia has been attributed to several reasons; the principal reason people from Mashau ingested soil was because they craved for it. Diko and Ekosse (2014) also reported craving as the main cause of geophagia. Some geophagic individuals indulged in the practice of geophagia because it was a tendency to do so while others consumed soils for additional nutritional value (those who believed the material had iron and vitamins). Young *et al.*, (2010) stated that people who consume soils do so in an attempt to supply the deficient micro-nutrients.

An interesting discovery was made; in addition to soil, other non-food substances consumed included candle wax, glycerine and ice. The practice of geophagia is negatively perceived in the communities of Mashau regardless of its prevalence. As a result, soil consumers hid their geophagic behaviour from their family members and it was mostly their friends who knew about this habit. Though the practice of geophagia is believed to be common among the poor in societies; studies by Ngole *et al.* (2010) indicated the practice to be common among all income and social groups. Outcomes of this study supported this finding.

The income sources of the soil consumers varied, ranging from wage employment, non-wage employment to depending on others. The Chi-square analysis showed no association of income source ( $p > 0.05$ ) with the practice of consuming soils. Geophagists were very cautious of the materials they consumed; the suitability of the soils for consumption was determined by their appearance, their taste or both their appearance and taste. According to Diko and Diko (2014), texture and appearance plays an important role in the selection of the consumed materials.

The texture of the material seemed to make it attractive since powdery and silky materials were favoured. Storing the materials was not preferred but rather most people consumed the material immediately after collection. Geophagic materials are collected when dry although 1.1% of respondents collected them when wet and sticky. Consumed materials were sometimes processed (grinding and sieving) or heat treated (baking, burning, burning and salted) as the materials reported by Smit (2011).

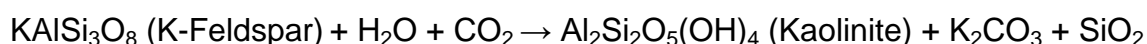
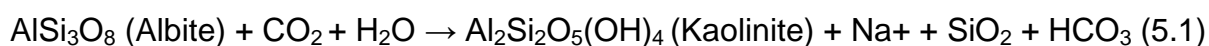
## 5.2 Provenance of Geophagic Materials

### 5.2.1 Mineralogy

The studied geophagic material showed kaolinite and quartz to be the major minerals, as in geophagic soils reported by Wilson, (2003), Ngole *et al.*, (2010), Gichumbi *et al.*, (2012), Ngole and Ekosse, (2012) and Ekosse *et al.* (2017). Kaolinite's dominance was attributed to the alteration of aluminium rich primary minerals to form clay minerals while the occurrence of quartz was a result of its resistance to weathering.

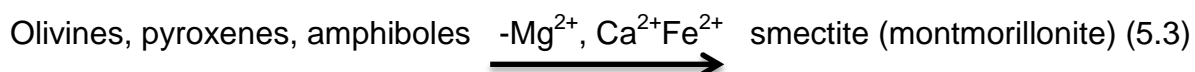
Although these two minerals were present in all samples, they portrayed an inverse relationship. The relationship between kaolinite (K) and quartz (Q) was clearly displayed in samples S2 (K=4 wt%, Q=45 wt%), S6 (K=13 wt%, Q=28 wt%), S14 (K=80 wt%, Q=6 wt%) and S16 (K=90 wt%, Q=5 wt%). As weathering occurs, more quartz is being lost to kaolinite hence the amount of quartz was not as high as that of kaolinite.

Feldspar minerals, albite and microcline, were identified in all samples except in 5 samples in which kaolinite's abundance ranged from 56-90 wt%. The presence of feldspar minerals suggested incomplete alteration of majority of samples. The absence of microcline and albite in all samples with considerable amount of kaolinite indicated complete alteration of feldspars to kaolin minerals. The hydrolysis of albite (Equation 5.1) and K-feldspars (Equation 5.2) results in the formation of kaolinite (Diko, 2013).



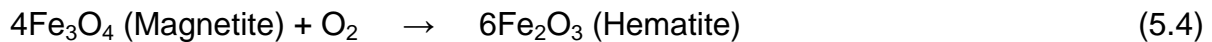
(5.2)

Although samples were made up of more than 50 % of the clay minerals, kaolinite and smectite were the only clay minerals occurring in considerable amounts. Smectites are commonly formed from the alteration of mafic silicates such as olivines, pyroxenes and amphiboles according to Equation 5.3. The smectite  $((\text{Na,Ca})_{0.33}(\text{Al,Mg})_2(\text{Si}_4\text{O}_{10})(\text{OH})_2 \cdot n\text{H}_2\text{O})$  identified in geophagic soils from the study area was probably derived from forsterite  $(\text{Mg, Fe})_2\text{SiO}_4$ , augite  $((\text{Ca,Na})(\text{Mg,Fe,Al,Ti})(\text{Si,Al})_2\text{O}_6)$  or actinolite  $((\text{Ca}_2(\text{Mg}_{4.5-2.5}\text{Fe}^{2+}_{0.5-2.5})\text{Si}_8\text{O}_{22}(\text{OH})_2)$ , which were identified in parent rocks.



Secondary minerals could derive their elemental constituents from the breakdown of more than one primary mineral (Churchman and Lowe, 2012). Therefore, clay minerals, chlorite and talc, have also been reported to form in the same manner as smectite (Equation 5.3). Mafic minerals and feldspars (both plagioclase and K-feldspars) are more susceptible to weathering hence they are usually weathered into clay minerals such as kaolinite and smectite. The presence of hematite in geophagic samples could be as a result of the oxidation of magnetite. According to Kramer (1968), when iron-bearing silicates like pyroxene, dissolve in water, there is a release of  $\text{Fe}^{2+}$  into solution.

The  $\text{Fe}^{2+}$  is then oxidized by  $\text{O}_2$  in the water to  $\text{Fe}^{3+}$ , which in turn combines with oxygen in the water and precipitates out of solution as the iron oxide hematite.



Ferromagnesian minerals magnetite and pyroxene (augite) were identified in all rock samples with the exception of sample DOL2 and MUK2. These minerals could have been the source of the oxidised iron which later formed hematite.

Anatase and ilmenite were also present in geophagic soils. Although anatase and Fe-Ti minerals like ilmenite can all form by neogenesis in intensely weathered soils, anatase is most prone to result from neogenesis (Churchman, 2000; Fitzpatrick and Chittleborough, 2002). However, the titanium minerals in soils are inherited from parent materials.

The major components of the parent rocks were augite and andesine, however, the latter was in substantial quantities. Plagioclase feldspar was identified as andesine in parent rocks but geophagic soils it was present in the form of albite. This could be indicative of the replacement that took place possibly from the surrounding rocks, where  $\text{Ca}^{2+}$  from the Ca-Na rich andesine was substituted with  $\text{Na}^+$  to form the Na rich albite in geophagic soils.

Rong and Wang (2016) explained the albitisation of andesine after being altered by Na-rich hydrothermal fluids whereby andesine becomes sericitised and transformed into albite. This dissolution–precipitation mechanism implies that a new mineral precipitates in the space where an old mineral was without changing the volume of the precipitated mineral.

Based on the mineralogy, rock samples could be divided into two groups; the first group which consisted of actinolite, augite, chlorite, epidote, forsterite, magnetite, muscovite, plagioclase and quartz and the second group which contained microcline, plagioclase and quartz only.

## 5.2.1 Geochemistry

### 5.2.1.1 Major Oxides

Geochemically, geophagic soils were mainly composed of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  in consistence with their mineralogy that showed a high content of quartz and kaolinite. The high content of  $\text{SiO}_2$  was due to the presence of aluminosilicate minerals. Other oxides were in lower amounts because minerals which contain Ca, Na, Mg, Fe and Mn degrade quickly during weathering breaking down into clays (Lopez *et al.*, 2005). Sample S11 had the highest  $\text{TiO}_2$  content because of the occurrence of anatase and ilmenite in the soil. Other oxides such as  $\text{P}_2\text{O}_5$ ,  $\text{Na}_2\text{O}$ ,  $\text{Cr}_2\text{O}_3$  had low concentrations because of chemical destruction under oxidising conditions during weathering (Rong and Wang, 2016).

Figure 5.1 shows UCC (upper continental crust, Taylor and McLennan, 1985) normalised data of major oxides, illustrating that geophagic materials were enriched in  $\text{Fe}_2\text{O}_3$  and  $\text{TiO}_2$  in comparison with UCC. Geophagic materials were clearly depleted in  $\text{MgO}$ ,  $\text{CaO}$ ,  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  which could be attributed to their high solubility (Keskin, 2011). On average, Mashau geophagic materials had lower  $\text{SiO}_2$  abundances relative to UCC. The range and mean values of the major oxides in the Mashau samples and the UCC are shown in Table 5.1.

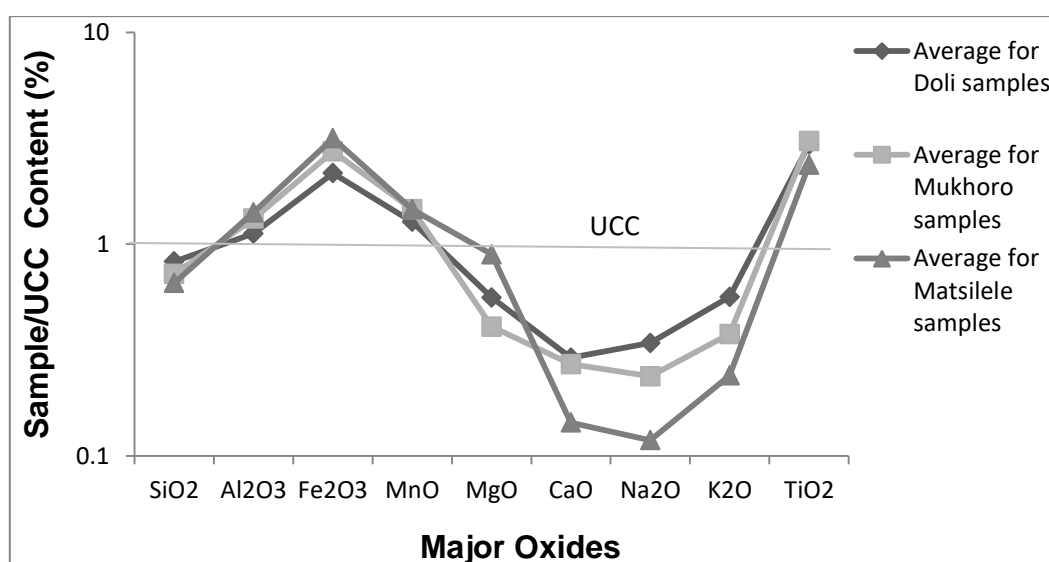


Figure 5.1: Spider plot of major oxides compositions of Mashau samples normalised against UCC values (UCC values from Taylor and McLennan, 1985)



Table 5.1: Major oxides compositions (%) of the geophagic materials from Mashau and for average UCC

| Sampling location |                | SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | Fe <sub>2</sub> O <sub>3</sub> | MnO  | MgO  | CaO  | Na <sub>2</sub> O | K <sub>2</sub> O | TiO <sub>2</sub> |
|-------------------|----------------|------------------|--------------------------------|--------------------------------|------|------|------|-------------------|------------------|------------------|
| Doli              | <b>Average</b> | 0.83             | 1.12                           | 2.16                           | 1.27 | 0.56 | 0.29 | 0.34              | 0.56             | 2.95             |
|                   | <b>Maximum</b> | 72.51            | 20.87                          | 22.4                           | 0.22 | 3.09 | 2.83 | 2.65              | 4.06             | 4.11             |
|                   | <b>Minimum</b> | 37.88            | 13.18                          | 3.2                            | 0.03 | 0.28 | 0.45 | 0.39              | 0.34             | 0.46             |
| Mukhorro          | <b>Average</b> | 0.72             | 1.32                           | 2.74                           | 1.46 | 0.41 | 0.27 | 0.24              | 0.38             | 3.06             |
|                   | <b>Maximum</b> | 57.26            | 26.36                          | 18.67                          | 0.21 | 1.89 | 2.73 | 2.22              | 2.74             | 2.64             |
|                   | <b>Minimum</b> | 38.43            | 15.04                          | 7.35                           | 0.05 | 0.47 | 0.16 | 0.07              | 0.34             | 0.75             |
| Matsilele         | <b>Average</b> | 0.66             | 1.41                           | 3.16                           | 1.46 | 0.89 | 0.14 | 0.12              | 0.24             | 2.37             |
|                   | <b>Maximum</b> | 46.63            | 25.02                          | 17.87                          | 0.13 | 3.42 | 1.17 | 1.22              | 1.05             | 1.4              |
|                   | <b>Minimum</b> | 38.78            | 17.2                           | 13.71                          | 0.11 | 1.12 | 0.25 | 0.08              | 0.44             | 1                |
| <b>UCC</b>        | <b>Average</b> | 65.67            | 15.12                          | 4.98                           | 0.08 | 2.19 | 4.18 | 3.88              | 3.38             | 0.5              |

### 5.2.1.2 Trace Elements

The chemical compositions of geophagic materials represent their primary mineralogy. Concentrations of Na, K, Ca, and Mg are enriched/depleted in the transportation, weathering, and diagenesis stages, whereas Al, Ti, and Zr remain unaffected because of the low solubility of their oxides at a low temperature (Keskin, 2011). The concentration of Zr is used for characterizing the nature and composition of parent rocks (Paikaray *et al.*, 2008). As a result, the Zr/TiO<sub>2</sub> binary diagram was plotted to determine the composition of the parent rocks of the geophagic materials (Figure 5.2)

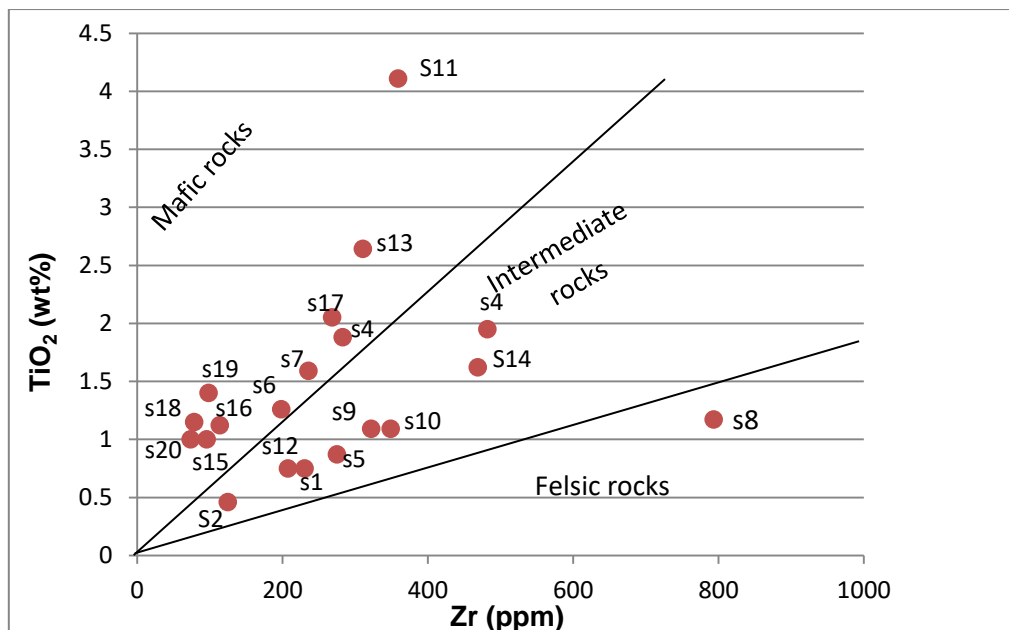


Figure 5.2: Zr against TiO<sub>2</sub> binary plot (After Keskin, 2011)

From the plot, it can be deduced that the geophagic materials were predominantly derived from intermediate to mafic rocks. Only one sample seemed to have been derived from felsic rocks. It was also clear that almost all samples in the intermediate field were from Doli while only two samples were from Mukhoro (S12 and S14). The mafic rocks field was dominated by samples from Mukhoro and Matsilele. All samples from Matsilele (S18-S20) were derived from mafic rocks only.

Rare earth elements (REEs), Th, Sc, Cr, Zr and Co are the most useful for provenance characterization because of their relatively immobile behaviour (Mongelli *et al.*, 2006). Findings from the study showed the REEs to be more enriched in the bulk fraction than the silt and clay fraction. The concentrations of the three fractions were in the following order: bulk fraction > silt fraction > clay fraction. This finding was in accordance with that from Cavalcante *et al.* (2014).

For this reason, provenance determination using REE was based on the REE concentrations in the bulk. The ratios of La/Sc Th/Sc and Th/Cr are significantly different in felsic and mafic rocks and may allow constraints on the average source rock composition (Cox *et al.*, 1995).

The La/Sc, Th/Sc and Th/Cr ratios fall within the range of values obtained for mafic rocks, some within the range for felsic and some within mafic and felsic, indicating intermediate source (Cox *et al.*, 1995).

Table 5.2: Trace elements concentrations (ppm) of geophagic samples from Mashau Village

| Sampling location         |         | Eu/Eu* | La/Sc | Th/Sc | Th/Cr |
|---------------------------|---------|--------|-------|-------|-------|
| Doli                      | Average | 1.35   | 2.33  | 0.87  | 0.14  |
|                           | Maximum | 2.65   | 4.12  | 1.7   | 0.5   |
|                           | Minimum | 0.75   | 0.73  | 0.16  | 0.03  |
| Mukhorro                  | Average | 1.48   | 1.15  | 0.12  | 0.08  |
|                           | Maximum | 3.38   | 2.22  | 1.44  | 0.28  |
|                           | Minimum | 0.53   | 0.3   | 0.12  | 0.01  |
| Matsilele                 | Average | 1.53   | 0.39  | 0.05  | 0.01  |
|                           | Maximum | 1.15   | 0.65  | 0.06  | 0.01  |
|                           | Minimum | 0.54   | 0.34  | 0.03  | 0.01  |
| Felsic rocks <sup>1</sup> | Maximum | 0.83   | 27.7  | 18.1  | 4     |
|                           | Minimum | 0.32   | 0.7   | 0.64  | 0.067 |
| Mafic rocks <sup>1</sup>  | Maximum | 1.02   | 1.1   | 0.4   | 0.045 |
|                           | Minimum | 0.7    | 0.4   | 0.05  | 0.002 |

Eu/Eu\* =  $Eu_N / (Sm_{NX}Gd_N)^{0.5}$ ; <sup>1</sup>Cullers (2000)

Moreover, in the La/Sc, against Th/Co plot (Figure 5.3), majority of the samples plotted in the basic to intermediate fields with few samples in the felsic field. It was again clear that samples in the basic field were mostly from Mukhorro together with all Matsilele samples. Samples from Doli were mostly in between the basic and felsic rock fields suggesting parent rocks of intermediate composition.

The range and mean values of the REEs are shown in Table 5.3. The mean concentrations of the REEs were in the following order: Matsilele > Mukhorro > Doli (decrease in concentrations) (Figure 5.5). In addition, the average LREE obtained from this study were depleted relative to the UCC and they showed enrichment in the HREEs.

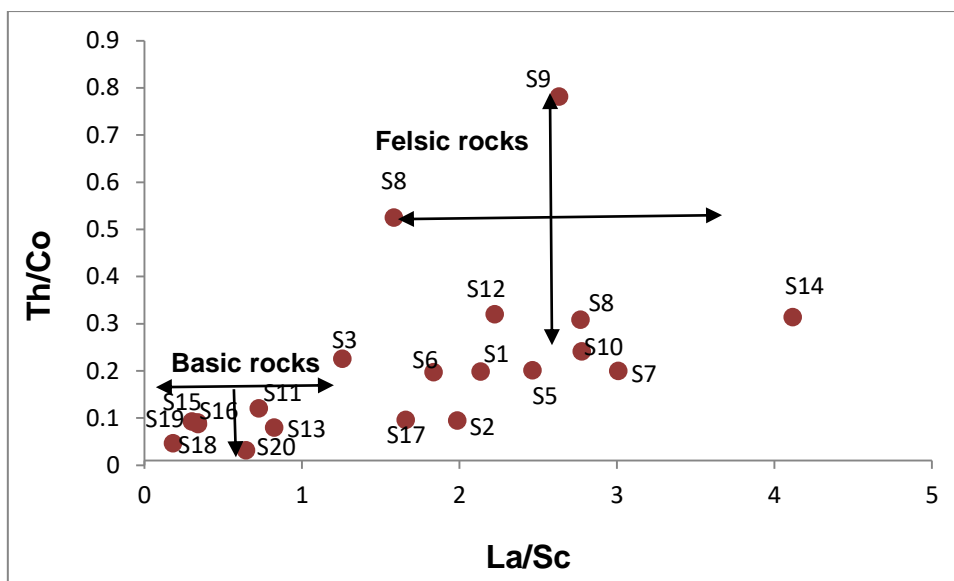


Figure 5.3: La/Sc, against Th/Co binary plot (After Lopez *et al.*, 2005)

The distribution of REEs indicated that geophagic soils were from two different source areas. Although all samples showed a positive Eu anomaly, there were those that were enriched in LREEs and depleted in HREEs and those that were depleted in LREEs and enriched in HREEs (Figure 5.5). According to McLennan *et al.* (1993), enrichment of LREEs reflect felsic provenance compositions whereas their depletion reflect mafic provenance. Based on this hypothesis, samples S1, S2, S4, S5, S7, S8, S9, S10, S12 and S14 were derived from a felsic to intermediate source area composition. Samples S3, S6, S11, S13, S15, S16, S17, S18, S19 and 20 originated from a mafic source.

Table 5.3: Rare earth elements concentrations (ppm) of the geophagic materials in Mashau

| Sampling location |                | La     | Ce     | Pr    | Nd    | Sm    | Eu   | Gd    | Tb    | Dy    | Ho   | Er    | Tm   | Yb   | Lu   |
|-------------------|----------------|--------|--------|-------|-------|-------|------|-------|-------|-------|------|-------|------|------|------|
| <b>Doli</b>       | <b>Average</b> | 54.62  | 106.12 | 10.27 | 39.72 | 7.04  | 1.86 | 6.04  | 0.781 | 4.36  | 0.86 | 2.34  | 0.33 | 2.31 | 0.35 |
|                   | <b>Maximum</b> | 124.95 | 196.35 | 21.07 | 77.9  | 12.15 | 3.01 | 9.87  | 1.37  | 8.06  | 1.74 | 4.97  | 0.68 | 4.98 | 0.73 |
|                   | <b>Minimum</b> | 23.75  | 48.05  | 4.72  | 18.18 | 3.38  | 1.00 | 2.84  | 0.33  | 1.86  | 0.35 | 1.065 | 0.14 | 1.03 | 0.16 |
| <b>Mukhoro</b>    | <b>Average</b> | 31.69  | 56.83  | 6.85  | 28.27 | 6.00  | 1.90 | 6.04  | 0.91  | 5.44  | 1.07 | 3.00  | 0.39 | 2.79 | 0.41 |
|                   | <b>Maximum</b> | 65     | 85.65  | 14.65 | 60.65 | 13.90 | 4.37 | 14.07 | 2.26  | 13.09 | 2.43 | 6.61  | 0.85 | 6.14 | 0.86 |
|                   | <b>Minimum</b> | 11.26  | 20.09  | 2.33  | 9.89  | 2.17  | 0.69 | 2.21  | 0.32  | 2.02  | 0.43 | 1.29  | 0.18 | 1.15 | 0.19 |
| <b>Matsilele</b>  | <b>Average</b> | 16.43  | 15.15  | 3.53  | 15.10 | 3.44  | 1.13 | 3.56  | 0.52  | 3.30  | 0.70 | 1.91  | 0.26 | 1.88 | 0.26 |
|                   | <b>Maximum</b> | 23.95  | 19.71  | 4.91  | 20.65 | 4.62  | 1.50 | 4.88  | 0.64  | 3.99  | 0.84 | 2.26  | 0.30 | 2.31 | 0.30 |
|                   | <b>Minimum</b> | 8.34   | 10.135 | 1.93  | 8.83  | 2.1   | 0.75 | 2.41  | 0.37  | 2.59  | 0.54 | 1.46  | 0.20 | 1.32 | 0.22 |
| <b>UCC</b>        | <b>Average</b> | 30     | 64     | 7.1   | 26    | 4.5   | 0.88 | 3.8   | 0.64  | 3.5   | 0.8  | 2.3   | 0.33 | 2.22 | 0.32 |

### 5.2.1.3 Weathering

Weathering indices of the geophagic soils were calculated to understand their weathering (Table 5.4). The CIA values varied but they were in two categories; first, those that ranged from 60-79 and those that ranged from 80-97. This suggested that geophagic samples were formed from intermediate to extreme silicate weathering. The values of CIW were very high, ranging from 75.24 to 98.69, also suggesting intense weathering. According to Fiantis *et al.* (2010), the PIA is best suited for predicting the changes that may have occurred with the plagioclase feldspar minerals.

Table 5.4 Calculated weathering indices of geophagic soils

| Sample ID | CIA   | CIW   | PIA   | WIP      | PWI  | R    |
|-----------|-------|-------|-------|----------|------|------|
| S1        | 86.60 | 93.95 | 93.38 | 2068.22  | 0.04 | 2.87 |
| S2        | 63.73 | 79.30 | 72.61 | 4799.59  | 0.01 | 5.50 |
| S3        | 77.37 | 87.55 | 85.66 | 2487.65  | 0.03 | 4.16 |
| S4        | 78.21 | 84.64 | 83.27 | 2540.76  | 0.03 | 2.82 |
| S5        | 72.89 | 78.05 | 76.38 | 3255.11  | 0.02 | 3.59 |
| S6        | 87.06 | 90.49 | 90.09 | 1445.97  | 0.06 | 2.81 |
| S7        | 72.64 | 78.76 | 76.80 | 3028.95  | 0.02 | 2.92 |
| S8        | 79.04 | 91.39 | 89.80 | 2788.29  | 0.03 | 3.51 |
| S9        | 87.18 | 94.09 | 93.58 | 1943.40  | 0.04 | 2.46 |
| S10       | 76.92 | 86.10 | 84.22 | 3368.25  | 0.02 | 3.31 |
| S11       | 89.88 | 91.50 | 91.35 | 749.94   | 0.12 | 2.19 |
| S12       | 86.55 | 93.91 | 93.35 | 2110.86  | 0.04 | 2.79 |
| S13       | 83.89 | 86.02 | 85.66 | 1371.46  | 0.06 | 2.25 |
| S14       | 79.67 | 90.62 | 89.13 | 2987.079 | 0.03 | 3.02 |
| S15       | 94.06 | 95.48 | 95.41 | 643.27   | 0.15 | 2.17 |
| S16       | 96.88 | 99.14 | 99.11 | 616.63   | 0.16 | 1.46 |
| S17       | 69.89 | 75.24 | 73.19 | 3092.57  | 0.02 | 3.15 |
| S18       | 96.04 | 97.93 | 97.89 | 600.89   | 0.16 | 2.00 |
| S19       | 94.77 | 98.69 | 98.64 | 1045.87  | 0.09 | 1.55 |
| S20       | 83.78 | 87.79 | 87.18 | 1996.29  | 0.04 | 2.71 |

Majority of samples had very high PIA values (80-90) which implied that most plagioclase had been converted to clay minerals such as kaolinite. This could explain the low plagioclase content that was observed in soil samples even though rock samples had high content of plagioclase. For example, the PIA value of 99.11 was observed in S16, the sample that had the highest kaolinite. The WIP values were low (600-643) in samples that had higher PIA values (95-98). This could be because as the values of WIP decrease, samples are more weathered and assumed to be older (Fiantis *et al.*, 2010). Sample S2, the sample with the lowest kaolinite content and highest quartz content, had the highest WIP value of 4799.59.

Values of PWI were very low, ranging from 0.01-0.16, suggesting extreme weathering. The R ratio ranged from 1.46 (in S16) - 5.5 (in S2) where decreasing SA value indicated an increasing intensity of weathering (Ruxton, 1968). Samples that had lower silica content also had lower R values; while those that had higher silica content had higher R values. Decreasing R value indicated an increasing intensity of weathering while high R values indicated low silicate weathering (Price and Velbel, 2003).

Major elemental variations of sediments are strongly affected by chemical weathering (Obasi and Madukwe, 2016). The A-CN-K diagram in Figure 5.4 displays a substantial loss of Ca, Na and K in geophagic soils as they tend to plot towards the A apex (Lopez *et al.*, 2005). Mukhoro and Matsilele geophagic soils, which are the most evolved sediments according to their CIA, are plotted nearer to the A apex.

The position of majority of Doli samples in the A-CN-K diagram indicates low weathering in the source area. Therefore, the plot of the samples and their CIA values on the A-CN-K diagram indicated that the geophagic materials were generated from two different source areas: the slightly weathered source area and the intensely weathered source area.



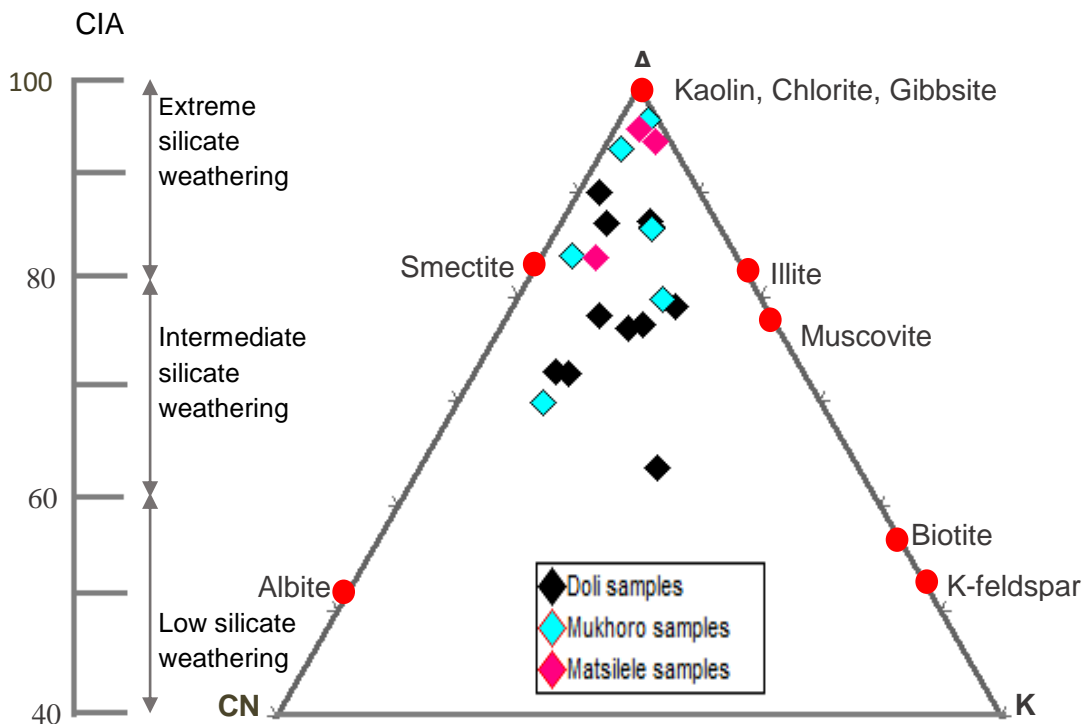


Figure 5.4: A-CN-K ternary plot of the geophagic materials (After Nesbitt and Young, 1982)

To evaluate the degree of weathering of the source area of geophagic samples, a CIA/CIW binary diagram was plotted (Figure 5.5). Majority of samples (11 out of 20) plotted in the extreme silicate weathering while the remaining samples portrayed intermediate silicate weathering. As mentioned earlier, geophagic soils were in two groups; those which were a result of intermediate weathering and those which were formed from extreme weathering.

Apart from S17, all samples that plotted in the intermediate weathering field were from Doli. The presence of hornblende, an amphibole that could be easily weathered was also proof of the low degree weathering (Churchman and Lowe, 2012). These samples also had low content of clay minerals to show alteration. Low weathering condition in the source area may reflect cool and/or arid climate conditions (Etemad-Saeed *et al.*, 2011). Samples that were in the extreme silicate weathering region had higher  $Al_2O_3$  values (>20%) with the exception of S20. The samples also had high kaolinite content than those in the intermediate weathering field with S14 and S16 having 80 and 90 wt% of kaolinite respectively.

The extreme weathering field was dominated by samples from Mukhoro and Matsilele. Strong chemical weathering implied specific humid and warm paleoclimatic conditions in the source area (Lopez *et al.*, 2005).

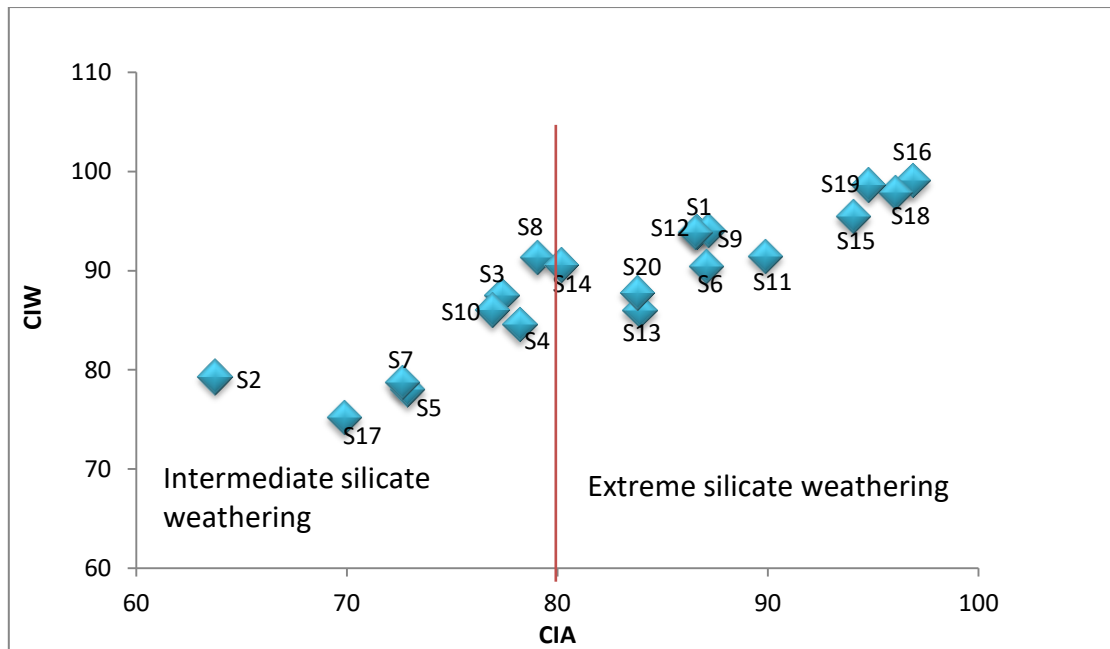


Figure 5.5: Degree of weathering of the source area of geophagic samples

#### 5.2.1.4 Parent Rocks

To conclude on the type of parent rocks geophagic soils were derived from, the Ruxton ratio of the surrounding rocks was calculated (Table 5.2). According to Obasi and Madukwe (2016), the average  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios in unaltered igneous rocks ranged from ~ 3.0 (basic rocks) to ~ 5.0 (acidic rocks). Values of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio > 5.0 in sandstones are an indication of progressive maturity.

The Ruxton ratio ( $\text{SiO}_2/\text{Al}_2\text{O}_3$ ) values were high (approximately 5) in samples DOL2 and MUK2 while other samples had values ranging from 3.09 to 3.52. The average Ruxton ratio of DOL2 and MUK2 showed that they were sandstones. The average  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios of DOL1, DOL3, MAR, MUK1, MAT1 and MAT2 were approximately 3.0, indicating that they are basic rocks (Obasi and Madukwe, 2016).

Mineralogical analysis showed that DOL1, DOL3, MAR, MUK1, MAT1 and MAT2 contained both felsic and mafic minerals but were dominated by mafic minerals' concentration (actinolite, augite and forsterite) while samples DOL2 and MUK2 contained only microcline, plagioclase and quartz.

Table 5.5: Ruxton ratio of rocks

| Rock samples | Ruxton ratio ( $\text{SiO}_2/\text{Al}_2\text{O}_3$ ) |
|--------------|---|
| DOL1         | 3.09  |
| DOL2         | 4.78  |
| DOL3         | 3.52  |
| MAR          | 3.60  |
| MUK1         | 3.19  |
| MUK2         | 4.65  |
| MAT1         | 3.30  |
| MAT2         | 3.28  |

It was thus concluded that samples DOL2 and MUK2 are sandstones whereas DOL1, DOL3, MAR, MUK1, MAT1 and MAT2 are basalts. Bumby (2000) highlighted that the Sibasa Formation, in which the study area falls, is a predominantly volcanic succession of basalts, with intercalated clastic sediments. The findings of this study parallel with the findings in Bumby (2000) and Barker *et al.*, (2006). Based on the mineralogy, major element compositions, weathering indices, literature and what was observed in the field, it was deduced that the rocks from which the geophagic materials were derived are basalts and sandstones.

## 5.3 Health Implications of Consumed Materials

### 5.3.1 Implications of Mineralogical and Physico-chemical Properties

Clay minerals that dominated the geophagic soils were kaolinite and smectite (montmorillonite type). Wanzala *et al.* (2016) reported montmorillonite to have the potential to act as an anti-poison hence it has been used in the pharmaceutical industry since ancient times. Kaolinite-rich soils could be used in reducing the occurrence of diarrhoea since kaolinite in the soil is able to absorb moisture from the gastrointestinal tract (GIT) (Ngole, 2017).

The mineralogical characteristic was consistent with the protection hypothesis by Young *et al.* (2010) which was indicated to account for geophagic practice. A study conducted by Brand *et al.* (2008) concluded that kaolin may interfere with iron absorption in humans, after a patient with anaemia remained anaemic until geophagia was stopped and intravenous iron replacement therapy introduced. Kaolinite does not only reduce the bioavailability of iron but also of other nutrients. In studies by Dominy *et al.* (2004) kaolin adsorbed 30% of the bioavailable fraction of three commonly ingested chemical compounds.

The most preferred soils were brown to reddish brown in colour. Preference to these soil types could be attributed to their inferred Fe content; there is a belief among geophagic individuals that reddish soils are associated with high Fe content. Although the studied geophagic soils were dominated by a sandy clay loamy texture, there was a considerable amount of sand present in the samples which may pose some health risks. Contrary to people's belief, the results indicated that ingested soils are not always clayey in texture. Sand particles are dominated by quartz ( $\text{SiO}_2$ ), a very hard mineral with a hardness of 7 on the Mohs hardness scale. Due to its relatively higher hardness than teeth, sand particles in geophagic soils could cause damage to dental enamel through grinding, cracking and breakage during soil consumption (Ngole and Ekosse, 2015).

Precisely because of the abrasive nature of quartz particles, possible lacerations and perforation of the sigmoid colon may occur. Continuous ingestion of the geophagic clayey soils from Mashau, being more sandy (especially S2, S15 and S17) would pose a greater risk. Perforation of sigmoid colon has been reported by Jahanshahee *et al.* (2004) in a boy after prolonged consumption of sandy material.

Despite being dominated by the sand fraction (sand content ranged from 24-86%; clay content  $\leq 40\%$  in all samples), soils could be used to protect the gastrointestinal (GI) tract through clay flocculation. Ngole (2017) reported that it is not just the amount of clay present in a soil that matters but the minerals that are contained in the clay as soil reactions take place on the surface of these minerals. According to Young *et al.* (2008), this capability is enhanced by their acidic pH values.

Most soil samples were slightly acidic in nature and few were slightly alkaline (pH between 7.1 and 7.6). The ability of the soils to form a coating along the digestive tract mucosa that shields the GI from diarrhoea causing toxins and other toxic substances would be influenced by their pH and EC. The coating protects the intestines from the acidic gastric juice (Ngole *et al.*, 2010) and hence prevents stomach ulcerations. The geophagic soils exhibited low to moderate EC, with the exception of S7 that had a very high EC of 245  $\mu\text{S}/\text{cm}$ . This indicated that the amount of dissolved salts contained in most samples was quite low. The low EC values were attributed to the low content of dissolved mineral salts and also showed that if there is any clay flocculation, it would not be influenced by EC.

The pH and dissolved salt content of geophagic soils influences their taste, that is, the more acidic soils tend to impart a sour taste (Diko and Ekosse, 2014). The taste of these geophagic soils is not likely to have been influenced by the salt content of the soils because it was low. The pH values of most samples analysed were in the acidic range and thus would impart a sour taste. The sour taste may be beneficial during pregnancy to prevent excessive secretion of saliva and reduce nausea. Reduction of salivation and the feeling of nausea during pregnancy is also another reason that women use to justify geophagia (Ngole, 2017).

A study by Diko and Diko (2014), to appraise the ability of geophagic soils ingested for the relief of nausea and vomiting during pregnancy found the samples to be suitable for use as remedy. Hooda (2003) reported that ingestion of clayey soil could also result in deficiencies of certain elements in the human system because soils with high CEC would absorb elements that are already in solution, thereby reducing their availability for absorption in the gastrointestinal tract (GI). Majority of geophagic samples from Mashau had very high CEC values (between 50 and 75 meq/100 g) while some were as high as 80 to 109 meq/100 g. The majority of geophagic individuals believed that the soils they are consuming had iron and were therefore supplementing iron in their bodies.

There is a concern that these soils were actually removing the total available iron that is already in their bodies. The consequence will be anaemia. Geophagists experienced constipation and pain in their stomachs to an extent that one of them had to be operated. This could be the result of soil accumulation in the colon. Abrahams (2002) indicated that radiological examination of these people's abdomens may reveal opaque soil masses in the colon.

Medical conditions geophagists were diagnosed with included iron deficiency and low haemoglobin levels, which could be explained by these high CEC values. Hematite was the only iron bearing mineral identified in geophagic soils in low concentrations (4-6 wt%), thus, even if the CEC values were low, these soils would not be able to supply Fe to the geophagic individuals.

### **5.3.2 Implications of Geochemical Compositions**

#### **5.3.2.1 Major Oxides**

The oxides present in geophagic soils could be a source of mineral nutrients K, Fe, Na, Mg, Ca, Mn, P and Cr. Of these nutrients, Na, K, Mg, Ca, P are classified as macro nutrients while Fe, Mn and Cr are micro nutrients (Teske and Detweiler, 2015). The macro-minerals are required in amounts greater than 100 mg/d and the micro-minerals are required in amounts less than 100 mg/d (Soetan *et al.*, 2010).

Geochemical results showed that soils had high concentrations of Si (average SiO<sub>2</sub> content = 50.55%), moderate concentration of Fe (average Fe<sub>2</sub>O<sub>3</sub> content = 12.38%) and trace concentrations of Mn, P and Cr (average content of their oxides was less than 1%). According to Ekosse and Obi (2015), geophagia could supply a good quantity of supplementation of calcium, magnesium, iron and potassium.

Soils from the study could be a good source of salts indicated by their high EC values. South Africa's Department of Health (2014) established daily nutrient reference values (Table 5.6) which denote the minimum amounts necessary to achieve and maintain optimum nutritional status.

Table 5.6: Nutrient reference values (Source: Department of Health, SA, 2014)

| Mineral nutrient | Daily nutrient reference values (for individuals from the beginning of 37 months and older) |
|------------------|---|
| Calcium          | 1300 mg   |
| Chromium         | 35 µg   |
| Iron             | 13 mg   |
| Magnesium        | 365 mg  |
| Manganese        | 2.3 mg  |
| Phosphorus       | 1250 mg   |
| Potassium        | Not less than 4700 mg per day   |
| Sodium           | Not more than 2000 mg per day   |

The values used in this Table 5.6 were based on Recommended Dietary Allowances (RDAs) which will meet the needs of nearly all (97 to 98%) healthy individuals to prevent nutrient deficiencies. The micronutrient theory of Young *et al.* (2008) implies that people eat non-food substances because they are deficient in micronutrients and that pica is an attempt to increase micronutrient intake. Major oxides such as  $\text{Cr}_2\text{O}_3$ ,  $\text{F}_2\text{O}_3$  and  $\text{MnO}$  could provide the recommended dietary concentrations of Cr, Fe and Mn even though they are in low concentrations. This is because Cr, Fe and Mn are only required in low amounts. The primary roles of the mineral nutrients in the body are presented in Table 5.7.

Of great concern is the high concentration of silica. Soil consumers were frequently exposed to dust that might have a high concentration of silica (quartz), as such, silicosis can be expected. During the collection of consumed soils the material is either dug or scrapped. This can lead to the frequent inhalation of small quantity of silica. The result would be the development of chronic silicosis which does not show symptoms for 15 years or more after an initial exposure (Department of Labour, SA, 2015). Symptoms of silicosis include but are not limited to: coughing, chest pains and fatigue which were also identified in some Geophagists.



The concentration of alumina might not necessarily cause health problems because the body eliminates most of the aluminium in the faeces and urine and some in the sweat (Soetan *et al.*, 2010). In conclusion, the consumed soils could be a good spring of most mineral nutrients; however, the high CEC of the soils could interfere with their adsorption.

Table 5.7: Primary functions of the identified minerals (Source: World Health Organization and Food and Agriculture Organization of the United Nations, 2004)

| Mineral           | Functions in the body  |
|-------------------|--|
| <b>Iron</b>       | Part of the protein hemoglobin which carries O <sub>2</sub> in the body.   |
| <b>Magnesium</b>  | Involved in bone mineralization, the building of protein, enzyme action, normal muscular contraction, and transmission of nerve impulses |
| <b>Manganese</b>  | Involved in the formation of bone, as well as in enzymes involved in amino acid, cholesterol, and carbohydrate metabolism                |
| <b>Phosphorus</b> | A principal mineral of the bones and teeth; part of every cell; maintains acid-base balance  |
| <b>Calcium</b>    | The principal mineral of bones and teeth, also involved in normal muscle contraction (including heart muscle).                           |
| <b>Chromium</b>   | Associated with insulin and required for the release of energy from  |
| <b>Potassium</b>  | Involved in nerve and muscle communication, moving nutrients into cells and waste products out, and regulating blood pressure            |
| <b>Sodium</b>     | Balancing fluids in the body, controlling blood pressure and blood volume, proper functioning of muscles and nerves                      |

### 5.3.2.2 Trace Elements

Of the analysed trace elements, Co, Cr, Cu, Ni and Zn are considered as the essential elements because they are required for the normal functioning of the body (Department of Health, SA, 2014). These elements can however be toxic if they are in amounts exceeding the maximum allowable concentrations. They can be harmful to both the environment and human health (Department of Environmental Affairs, 2010). The South African Department of Environmental Affairs (2010) has established soil screening values for the assessment of contaminated land.

Comparison between these values and the trace element compositions from the present study showed that the study area is not contaminated by trace elements. Furthermore, the values are protective of human health in cases where people are exposed to the specified trace elements orally. From Table 5.8, it can be deduced that geophagic soils from Mashau were a good source of essential trace elements as the soils are not contaminated. The trace elements compositions were very low to cause metal toxicity.

Table 5.8: Trace elements compositions of geophagic materials from Mashau in comparison with the soil screening values that are protective of human health (Source: Department of Environmental Affairs, SA, 2010)

|                     | Co    | Cr     | Cu     | Ni     | Pb     | V      | Zn     |
|---------------------|-------|--------|--------|--------|--------|--------|--------|
| Present study (ppm) |       |        |        |        |        |        |        |
| S1                  | 86.45 | 272    | 54.15  | 189.7  | 37.7   | 99.55  | 40.6   |
| S2                  | 118.8 | 36.05  | 27.2   | 25.2   | 32.915 | 53.45  | 29.05  |
| S3                  | 97.3  | 142.85 | 82.35  | 84.25  | 28.48  | 254.55 | 87.05  |
| S4                  | 75.05 | 804.5  | 120.6  | 504.5  | 36.05  | 224.5  | 130.65 |
| S5                  | 91.95 | 395    | 44.35  | 204.4  | 29.92  | 111.1  | 123.15 |
| S6                  | 57.65 | 267.25 | 163.65 | 186.75 | 19.525 | 176.75 | 71.55  |
| S7                  | 86.35 | 314    | 135    | 212.85 | 43.2   | 216.2  | 127.4  |
| S8                  | 65.55 | 83.3   | 56.15  | 58.75  | 21.165 | 113.95 | 90.2   |
| S9                  | 50.95 | 78.7   | 94.4   | 67.3   | 28.235 | 137.7  | 42.85  |
| S10                 | 74.7  | 190    | 67.35  | 112    | 29.7   | 101.55 | 63.05  |
| S11                 | 56.05 | 153.3  | 125.65 | 102.2  | 10.05  | 474    | 154.45 |
| S12                 | 56    | 272.5  | 54.35  | 186.6  | 37.05  | 105.25 | 42.35  |
| S13                 | 59.1  | 91.65  | 127.45 | 80.15  | 7.825  | 325    | 132.35 |
| S14                 | 54.5  | 102.65 | 71.15  | 67.15  | 26.295 | 155.35 | 66.7   |
| S15                 | 49.25 | 393    | 126.4  | 245    | 13.315 | 197    | 45.35  |
| S16                 | 60.7  | 327    | 220.2  | 255.8  | 22.48  | 189.05 | 63.4   |
| S17                 | 64.6  | 89.05  | 96.95  | 181.2  | 38.25  | 268.35 | 195.25 |
| S18                 | 34.8  | 240.95 | 176.6  | 225.85 | 4.42   | 126.25 | 102.95 |
| S19                 | 32.8  | 312    | 235.85 | 171.25 | 20.045 | 169.95 | 86.9   |
| S20                 | 54.55 | 273.5  | 152.95 | 260.9  | 9.16   | 150.6  | 159.35 |
| SSV2 (mg/kg)        | 630   | 96000  | 2300   | 1200   | 230    | 320    | 19000  |

\*\*SSV2-- Soil Screening Value 2: soil quality values that are protective of risk to human health in the absence of a water resource.

## CHAPTER 6

### CONCLUSIONS AND RECOMMENDATIONS

#### 6.1 Conclusions

This study has characterised the mineralogy and geochemistry of geophagic materials from Mashau Village and inferred on the health implications that could result from their consumption. Themes of the study focused on understanding the motivations for geophagia, characterising the consumed materials (mineralogically and geochemically), assessing their physico-chemical properties, determining their provenance and inferring the health implications that could be derived from the practice. To achieve these objectives, questionnaires were administered, geophagic materials were analysed for mineralogical, geochemical and physico-chemical properties using relevant methods. The findings of the study were interpreted and the following conclusions made:

- The geophagic behaviour in Mashau Village was not influenced by hunger or beliefs (cultural, spiritual and traditional), neither was it ritual. The practice was initiated by craving.
- Geophagic materials are not always clayey in texture; consumed materials from the study area were primarily reddish brown, sandy clay loam soils.
- Kaolinite and quartz are the dominant minerals in geophagic soils. Mineralogical analysis revealed that the studied geophagic materials were mainly composed of kaolinite and quartz; other minerals in subsidiary amounts were microcline, plagioclase, and smectite.
- The geochemical composition showed the materials to be generally aluminosilicates since they are dominated by alumina and the silica. It was also discovered that trace elements, especially REEs are not always enriched in the clay fraction as reported by literature. Trace elements in the geophagic materials were enriched in the bulk fraction than silt and clay fractions. They were also very low relative to the average trace element compositions of the Upper Continental Crust (UCC).

- Geophagic materials in the study area were predominantly the products of intermediate to extreme weathering. Geophagic materials from Mashau were mainly derived from intermediate to mafic source areas. Samples from Doli were mainly formed from intermediate weathering of rocks with intermediate compositions whereas samples from Mukhoro were mostly the products of extreme weathering of mafic rocks. All samples from Matsilele were derived from intense weathering of mafic rocks. Samples were derived from the basalts and sandstones in the study area.
- The relationship between geophagia and its health implications is essentially dependent on the mineralogical, geochemical and physico-chemical properties of the ingested materials. Based on the mineralogical analyses results, the soils can be used to treat diarrhoea as they have a high amount of kaolin which has the potential to absorb water from the GI. Geophagic soils could be a good source of essential trace elements since their concentrations were very low and also lower than the soil screening values that are protective of human health. The slightly acidic nature of the soils can be beneficial since it gives them a sour taste which is mostly desired by pregnant women in overcoming nausea and excess salivation.
- Possible health shortcomings from the ingestion of the geophagic soils in the study area would include dental enamel damage and perforation of the sigmoid colon. This is because of their high quartz content (especially soils from Doli) and sand fraction even though their texture is mostly sandy clay loam. Soils from Mashau cannot be useful as a source of Fe supplement as inferred by many geophagists based on their colour. Due to their high CEC, these soils may adsorb exchangeable Fe and other related cations in the GI, reducing their bioavailability and resulting in micronutrient deficiencies such as anaemia.

## 6.2 Recommendations

The current study inferred the possible health implications that could result from the practice of geophagia in Mashau Village based on the mineralogy, physico-chemical properties and geochemistry. Further studies must be undertaken to assess the bioavailability of essential trace elements in the consumed materials. Considering that the practice of geophagia cannot be eradicated, more studies are required to identify suitable strategies to make the ingested soils safer for those indulging in the practice. The lack of understanding of the health implications deriving from geophagia among geophagic individuals is of great concern. There is a need for educating the geophagic communities about the medical consequences of geophagia.

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## APPENDICES

### APPENDIX 3.1: QUESTIONNAIRE

#### Mineralogy and Geochemistry of Geophagic Materials from Mashau Village in Limpopo Province, South Africa

#### Introduction

Date of interview .....

Name of interviewee (optional) .....

Area (Address).....

#### A. Demographic Information

##### 1. Geographic Information

| Location                | Mark the correct option |          | Specific town or area |
|-------------------------|-------------------------|----------|-----------------------|
| 1. Location             | Rural                   | Suburban | Urban                 |
| 3. Specify town or area | Rural                   | Suburban | Urban                 |

##### 2. Personal Information

|                       |                  |                  |                     |                 |                        |
|-----------------------|------------------|------------------|---------------------|-----------------|------------------------|
| 4. Sex                | Male             |                  | Female              |                 |                        |
| 5. Age                |                  |                  |                     |                 |                        |
| 6. Number of children |                  |                  |                     |                 |                        |
| 7. Ages of children   |                  |                  |                     |                 |                        |
| 8. Sex of children    |                  |                  |                     |                 |                        |
| 9. Marital status     | Married          | Divorced         | Single              | Living together | Cohabating             |
| 10. Income source     | Wage employment  |                  | Non wage employment |                 | Others, please specify |
| 11. Occupation        |                  |                  |                     |                 |                        |
| 12. Income            |                  |                  |                     |                 |                        |
| 13. Educational level | Illiterate       | Primary          | Secondary           | Vocational      | Technical              |
|                       | Teacher training | Higher education | Post graduate       | Professional    | Other (specify)        |

#### B. Socio-Economic and Cultural Aspect

##### 1. Habits

|                                       |     |    |
|---------------------------------------|-----|----|
| 14. Are you presently consuming soil? | Yes | No |
|---------------------------------------|-----|----|

|  |  |                         |                             |                                |
|--|--|-------------------------|-----------------------------|--------------------------------|
| 15. If yes how often do you consume the soil?                            | Once a month   | Once a week             | Once a day                  | More than once a day           |
| 16. If yes, for how long have you been consuming soil?                   |  |                         |                             |                                |
| 17. What is the reason for consuming soil?                               | Standard practice (cultural, traditional, spiritual) | Craving                 | Medical value               | Complement diet                |
|  | Ritualistic  | When hungry             | When pregnant               | Don't know<br>Others (specify) |
| 18. Do you crave to eat soil?  | Regularly once a month                               | Regular weekly          | Regular daily               | Only when pregnant             |
| 19. When do you crave for the soil?                                      | Pregnant   | Lactating               | Both pregnant and lactating | Experiencing sleeplessness     |
|  | Nauseated but not pregnant                           | Constipated             | Feeling weak                | Others (specify)               |
| 20. When pregnant how often do you consume the soil?                     | Once a month   | Weekly                  | Daily                       | Others (specify)               |
| 21. Do you consume other non-food substances?                            | Yes  |                         | No                          |                                |
| 22. If yes name the substance  |  |                         |                             |                                |
| 23. How often do you consume this substance?                             | Daily  | More than a week        | Weekly                      | Monthly                        |
| 24. How much of the substance (handfuls) do you consume                  | Daily  | More than once a day    | Weekly                      | Monthly                        |
| 25. Do other people know that you consume clay?                          | Yes  |                         | No                          | Don't know                     |
| 26. If yes who are aware?  | Family members                                       | Extended family members | Friends                     | Others (specify)               |
| 27. How do people perceive this habit of eating non-food substances      | Positive   | Negative                | Indifferent                 | Don't know                     |
| 28. Is this practice more common among certain members of the community? | Yes  |                         | No                          | Don't know                     |
| 29. If yes, specify  |  |                         |                             |                                |

**C. Indigenous Knowledge**

|   |               |         |                          |                  |
|---|---------------|---------|--------------------------|------------------|
| 30. What substances are consumed?                         | Soil          | Clay    | Soil from termite mounds | Others (specify) |
| 31. How are substances consumed?                          | Wet           | Dry     | With other food          | Others (specify) |
| 32. What are the traditional names of substances consumed |               |         |                          |                  |
| 33. Where do you obtain the substance                     | From the wild | Bought  | Given                    | Others, specify  |
| 34. If you buy, give the brand name                       |               |         |                          |                  |
| 35. If you buy indicate the price per handful             |               |         |                          |                  |
| 36. What is the color of substance                        | Reddish       | Whitish | Blackish                 | Yellowish        |

|  |       |                  |                         |                 |
|--|-------|------------------|-------------------------|-----------------|
| consumed   | Khaki | Others (specify) |                         |                 |
| 37. Why do you prefer to consume the specific color type | Taste | Tradition/belief | It is easily accessible | Other (specify) |
| 38. Method of storage of substance                       |       |                  |                         |                 |
| 39. Length of storage                                    |       |                  |                         |                 |

#### D. Physico-chemical, Mineralogical, Geological and Chemical

|   |               |  |  |                        |                                     |
|---|---------------|--|--|------------------------|-------------------------------------|
| 40. Where does the substance you consume come from                          | Hill/mountain | River bed                                  | Termitaria                                 | valley                 | Others (specify)                    |
| 41. If from a mound, where specifically on the mound is substance collected | Surface       | Inside mound above the surface of the soil | Inside mound below the surface of the soil | Does not matter        | Not sure                            |
| 42. Are substances obtained close to rocks                                  | Yes           |  | No   |                        | Not sure                            |
| 43. If yes, what is the type of rock  | Very hard     | Hard                                       | Soft                                       | Very soft              |                                     |
| 44. How is the substance collected  | Digging       | Hand grabbing                              | Scrapping                                  | Selective hand picking | Other (specify)                     |
| 45. If digging how deep   | 0-10 cm       | 10-20 cm                                   | 20-30 cm                                   | >30 cm                 | Others (specify)                    |
| 46. How does the substance feel when collected?                             | Gritty        | Silky                                      | Powdery                                    | Does not matter        | Don't know                          |
| 47. When are substances collected?  | Wet           |  | Dry  |                        | Does not matter<br>Others (specify) |
| 48. If collected wet, how does the substance feel?                          | Very sticky   | Sticky                                     | Very soapy                                 | Soapy                  | Neither                             |
| 49. Are substances processed before consumption?                            | Yes           |  | No   |                        | Sometimes yes/no                    |
| 50. If yes, how are they processed?   | Grinding      | Pounding                                   | Sieving                                    | Slurring               | Other (specify)                     |
| 51. Is there any heat treatment of substance before consumption?            | Yes           |  | No   |                        | Sometimes yes/no                    |
| 52. If yes specify type of heat treatment                                   | Baking        | Boiling                                    | Burning                                    | Combinations (specify) | Others (specify)                    |

#### E. Ecological Aspects

|  |         |             |             |                      |
|--|---------|-------------|-------------|----------------------|
| 53. If you consume substance from a termitaria, from which one   | Mound   |             | Tree        |                      |
| 54. If substance is collected from termite mound (section C), describe the height of the mound preferred | <0.5 m  | 0.5-1 m     | 1-2 m       | >2 m                 |
| 55. What is the shape of the mound   | Conical | Flat topped | Dome shaped | Others (specify)     |
| 56. Do you prefer to consume the   | Newly   |             | Old         | Does not<br>Not sure |

|  |             |       |                   |                              |
|--|-------------|-------|-------------------|------------------------------|
| substance when   | constructed |       | matter            |                              |
| 57. What type of terrain do you normally find these mounds?                        | Flat        | Hilly | Undulating        | Valley<br>Others (specify)   |
| 58. Do you collect the substance from  | Mound       |       | Base of the mound | Some distance from the mound |
| 59. if substance is collected from a tree, do you prefer it from a particular tree | Yes         | No    | Not sure          | Does not matter              |
| 60. If yes, name the preferred tree type   |             |       |                   |                              |

### F. Human Health Associated With Geophagia

|  |                        |                                  |                               |                    |                  |
|--|------------------------|----------------------------------|-------------------------------|--------------------|------------------|
| 61. Height   |                        |                                  |                               |                    |                  |
| 62. Weight   |                        |                                  |                               |                    |                  |
| 63. Do you know that the substance could be harmful to your health                           | Yes                    |                                  | No                            |                    |                  |
| 64. If yes, in what sense  | Constipation           | Abdominal pains                  | Poison the body               | Causes tooth decay | Others (specify) |
| 65. Were you ever operated upon for stomach problems?  | Yes                    |                                  | No                            |                    |                  |
| 66. If yes, how many times and for what reason?  |                        |                                  |                               |                    |                  |
| 67. Are you aware of the harmful substances/ parasites that may be present in the substance? | Yes                    |                                  | No                            |                    |                  |
| 68. Do you know the content of the substance   | Yes                    |                                  | No                            |                    |                  |
| 69. If yes name these contents   | Vitamins               | Calcium                          | Iron                          | Salt               | Others (specify) |
| 70. Why do you consume substance?  | To clean your body     | For additional nutritional value | To protect against infections | Do not know        | Others (specify) |
| 71. Do you often get infected (common cold, flu etc)   | More than once a month | Once a month                     | Once every three months       | Twice yearly       | Yearly           |
| 72. Do you ingest these substances when infected   | Yes                    |                                  | No                            |                    | Sometimes        |
| 73. Do you experience chronic illnesses  | Yes                    |                                  | No                            |                    |                  |
| 74. If yes, which of these?  | Headaches              | Dizziness                        | Blood in stool                | Fatigue            | Chest pains      |
|  | Coughs                 | Muscle pains                     | Tremors                       | Blood in urine     | Nose bleeding    |
| 75. Number of still born   |                        |                                  |                               |                    |                  |
| 76. Number of children born with abnormalities   |                        |                                  |                               |                    |                  |
| 77. Name the abnormalities   |                        |                                  |                               |                    |                  |
| 78. Did these children reach the   | Yes                    |                                  | No                            |                    | Others (specify) |

|  |                 |                     |                  |                    |       |
|--|-----------------|---------------------|------------------|--------------------|-------|
| expected developmental and growth stages                             |                 |                     |                  |                    |       |
| 79. Did the children experience any pains in the muscle or joints    | Yes             | No                  | Others (specify) |                    |       |
| 80. Children under age of three that experienced parasite infections |                 |                     |                  |                    |       |
| 81. Medical condition diagnosed/ experienced                         | Iron deficiency | High blood pressure | Constipation     | Constant headaches | Other |



## APPENDIX 3.2: CONSENT FORM



**University of Venda**  
*Creating Future Leaders*

**Research Title: Mineralogy and Geochemistry of Geophagic Materials from Mashau Village in Limpopo Province, South Africa.**

Dear Participant

You are invited to participate in a research study conducted by Mashao Unarine, student no. 11613612. The study has been approved by the University of Venda Ethical Committee and the local traditional leadership. Thus, by signing this document, you are stating that:

- The objective of the research has been described to you orally.
- You understand what it means to be involved in the study and that your participation is voluntary.
- You are aware that the results of the study, including personal details will be anonymously processed into a study report and will remain confidential.
- You understand that you may, at any stage without giving reasons, withdraw your participation in the study.
- You declare yourself prepared to participate in the study.

I, the undersigned, hereby consent to be a participant in the questionnaire survey of the above mentioned study.

Printed name of participant

Date

Signature of participant

.....

.....

.....

## APPENDIX 4.1: ABUNDANCES OF MINERALS IN GEOPHAGIC SOILS (wt%)

| Sample ID | Kaolinite | Microcline | Plagioclase | Quartz | Hornblende | Smectite | Talc | Hematite | Chlorite |
|-----------|-----------|------------|-------------|--------|------------|----------|------|----------|----------|
| S1        | 32        | 17         | 11          | 41     | —          | —        | —    | —        | —        |
| S2        | 4         | 23         | 25          | 45     | 4          | —        | —    | —        | —        |
| S3        | 17        | 21         | 20          | 4      | —          | —        | —    | —        | —        |
| S4        | 40        | 12         | 13          | 8      | 12         | 9        | 6    | —        | —        |
| S5        | 13        | 10         | 29          | 28     | 5          | —        | 8    | —        | 8        |
| S6        | 42        | 3          | 11          | 15     | —          | 22       | —    | —        | 8        |
| S7        | 25        | 7          | 27          | 16     | 26         | —        | —    | —        | —        |
| S8        | 42        | 17         | 14          | 22     | —          | —        | —    | —        | —        |
| S9        | 48        | 14         | 7           | 31     | —          | —        | —    | —        | —        |
| S10       | 35        | 14         | 23          | 26     | 2          | —        | —    | —        | —        |
| S11       | 55        | —          | 5           | 10     | —          | 17       | —    | 6        | —        |
| S12       | 33        | 16         | 14          | 37     | —          | —        | —    | —        | —        |
| S13       | 58        | —          | 15          | 8      | —          | 18       | —    | —        | —        |
| S14       | 80        | —          | —           | 6      | —          | 10       | —    | 4        | —        |
| S15       | 56        | —          | 4           | 17     | —          | 8        | —    | —        | 14       |
| S16       | 90        | —          | —           | 5      | —          | —        | —    | 5        | —        |
| S17       | 22        | 13         | 22          | 6      | —          | 28       | —    | —        | —        |
| S18       | 64        | —          | —           | 6      | —          | 25       | —    | —        | 6        |
| S19       | 38        | 16         | 18          | 28     | —          | —        | —    | —        | —        |
| S20       | 39        | 4          | 14          | 6      | —          | 37       | —    | —        | —        |

## APPENDIX 4.2: ABUNDANCES OF MINERALS IN PARENT ROCKS (wt%)

| Sample ID | Actinolite | Augite | Chlorite | Epidote | Forsterite | Magnetite | Microcline | Muscovite | Plagioclase | Quartz | Sepiolite |
|-----------|------------|--------|----------|---------|------------|-----------|------------|-----------|-------------|--------|-----------|
| DOL 1     | 7          | 14     | 6        | 4       | 2          | 4         | —          | 5         | 46          | 7      | 5         |
| DOL 2     | —          | —      | —        | —       | —          | —         | 17         | —         | 54          | 29     | —         |
| DOL 3     | 7          | 18     | 4        | 5       | 2          | 3         | —          | 7         | 41          | 10     | 4         |
| MAR       | 4          | 24     | 7        | 9       | 2          | 1         | —          | 4         | 36          | 12     | —         |
| MUK 1     | —          | 28     | 9        | 3       | —          | 3         | —          | 7         | 45          | 5      | —         |
| MUK 2     | 3          | 31     | 7        | 3       | 1          | 2         | —          | 5         | 42          | 6      | —         |
| MAT 1     | 3          | 29     | 6        | 2       | —          | 2         | —          | 5         | 48          | 4      | —         |
| MAT 2     | 3          | 30     | 5        | 3       | 1          | 2         | —          | 5         | 48          | 4      | —         |

### APPENDIX 4.3: GEOPHAGIC SOILS MAJOR OXIDES CONTENT (%)

| Sample ID | Al <sub>2</sub> O <sub>3</sub> | CaO  | Cr <sub>2</sub> O <sub>3</sub> | Fe <sub>2</sub> O <sub>3</sub> | K <sub>2</sub> O | MgO  | MnO  | Na <sub>2</sub> O | P <sub>2</sub> O <sub>5</sub> | SiO <sub>2</sub> | TiO <sub>2</sub> | L.O.I |
|-----------|--------------------------------|------|--------------------------------|--------------------------------|------------------|------|------|-------------------|-------------------------------|------------------|------------------|-------|
| S1        | 20.17                          | 0.45 | 0.04                           | 7.23                           | 1.82             | 0.56 | 0.04 | 0.85              | 0.05                          | 57.85            | 0.75             | 10.08 |
| S2        | 13.18                          | 1.07 | bdl                            | 3.2                            | 4.06             | 0.4  | 0.04 | 2.37              | 0.04                          | 72.51            | 0.46             | 2.05  |
| S3        | 13.85                          | 0.85 | 0.02                           | 13.48                          | 2.08             | 0.56 | 0.14 | 1.12              | 0.09                          | 57.59            | 1.95             | 7.60  |
| S4        | 16.15                          | 1.71 | 0.12                           | 15.45                          | 1.57             | 3.09 | 0.15 | 1.22              | 0.25                          | 45.57            | 1.88             | 12.86 |
| S5        | 16.29                          | 1.93 | 0.05                           | 6.45                           | 1.48             | 2.53 | 0.09 | 2.65              | 0.09                          | 58.58            | 0.87             | 8.84  |
| S6        | 18.17                          | 1    | 0.04                           | 11.21                          | 0.79             | 1.36 | 0.08 | 0.91              | 0.03                          | 51.06            | 1.26             | 14.31 |
| S7        | 16.46                          | 2.83 | 0.05                           | 13.87                          | 1.76             | 2.67 | 0.18 | 1.61              | 0.18                          | 48.13            | 1.59             | 10.65 |
| S8        | 16.25                          | 0.84 | 0.01                           | 8.42                           | 2.78             | 0.45 | 0.09 | 0.69              | 0.12                          | 57.11            | 1.17             | 11.82 |
| S9        | 20.87                          | 0.57 | 0.01                           | 10.45                          | 1.76             | 0.28 | 0.03 | 0.74              | 0.05                          | 51.27            | 1.09             | 12.88 |
| S10       | 18.03                          | 0.9  | 0.02                           | 6.3                            | 2.5              | 0.82 | 0.06 | 2.01              | 0.05                          | 59.69            | 1.09             | 7.76  |
| S11       | 17.23                          | 1.21 | 0.02                           | 22.4                           | 0.34             | 0.74 | 0.22 | 0.39              | 0.14                          | 37.88            | 4.11             | 15.55 |
| S12       | 20.52                          | 0.46 | 0.04                           | 7.35                           | 1.86             | 0.54 | 0.05 | 0.87              | 0.06                          | 57.26            | 0.75             | 9.95  |
| S13       | 18.03                          | 1.95 | 0.01                           | 18.67                          | 0.53             | 0.98 | 0.21 | 0.98              | 0.17                          | 40.52            | 2.64             | 15.37 |
| S14       | 18.07                          | 0.76 | 0.01                           | 9.14                           | 2.74             | 0.47 | 0.07 | 1.11              | 0.07                          | 54.49            | 1.62             | 11.38 |
| S15       | 21.54                          | 0.74 | 0.06                           | 12.79                          | 0.34             | 0.95 | 0.07 | 0.28              | 0.05                          | 46.68            | 1                | 16.03 |
| S16       | 26.36                          | 0.16 | 0.05                           | 18.06                          | 0.62             | 0.52 | 0.12 | 0.07              | 0.05                          | 38.43            | 1.12             | 15.00 |
| S17       | 15.04                          | 2.73 | 0.01                           | 15.8                           | 1.53             | 1.89 | 0.18 | 2.22              | 0.06                          | 47.32            | 2.05             | 10.75 |
| S18       | 21.8                           | 0.38 | 0.03                           | 15.66                          | 0.44             | 1.34 | 0.11 | 0.08              | 0.01                          | 43.69            | 1.15             | 15.90 |
| S19       | 25.02                          | 0.25 | 0.04                           | 17.87                          | 1.05             | 1.12 | 0.13 | 0.08              | 0.02                          | 38.78            | 1.4              | 19.04 |
| S20       | 17.2                           | 1.17 | 0.04                           | 13.71                          | 0.94             | 3.42 | 0.11 | 1.22              | 0.01                          | 46.63            | 1                | 14.66 |

## APPENDIX 4.4: CONCENTRATIONS OF TRACE ELEMENTS (TRANSITION, HIGH FIELD AND LITHOPHILE) IN THE BULK FRACTION OF GEOPHAGIC SOILS (ppm)

| Sample ID | Sc    | V      | Cr     | Co     | Ni     | Rb     | Sr     | Y     | Zr     | U     | Nb    | Cs   | Ba      | Ta   | Pb    | Th    |
|-----------|-------|--------|--------|--------|--------|--------|--------|-------|--------|-------|-------|------|---------|------|-------|-------|
| S1        | 17.17 | 99.55  | 272.00 | 86.45  | 189.70 | 106.90 | 132.05 | 15.71 | 230.60 | 6.51  | 10.67 | 5.84 | 503.00  | 0.81 | 37.70 | 17.11 |
| S2        | 11.95 | 53.45  | 36.05  | 118.80 | 25.20  | 161.30 | 283.00 | 9.90  | 124.85 | 5.33  | 6.64  | 2.61 | 953.00  | 0.55 | 32.92 | 11.26 |
| S3        | 23.85 | 254.55 | 142.85 | 97.30  | 84.25  | 84.05  | 206.20 | 19.59 | 482.00 | 6.61  | 11.61 | 2.44 | 868.50  | 0.90 | 28.48 | 21.96 |
| S4        | 30.35 | 224.50 | 804.50 | 75.05  | 504.50 | 84.30  | 272.20 | 28.96 | 282.85 | 5.50  | 15.89 | 9.79 | 1233.00 | 1.03 | 36.05 | 23.52 |
| S5        | 17.41 | 111.10 | 395.00 | 91.95  | 204.40 | 65.25  | 330.00 | 13.12 | 275.00 | 3.68  | 6.84  | 2.80 | 774.50  | 0.44 | 29.92 | 18.51 |
| S6        | 26.75 | 176.75 | 267.25 | 57.65  | 186.75 | 66.15  | 123.60 | 28.55 | 198.15 | 2.99  | 9.38  | 7.07 | 553.00  | 0.81 | 19.53 | 11.36 |
| S7        | 31.15 | 216.20 | 314.00 | 86.35  | 212.85 | 89.75  | 298.05 | 26.83 | 235.70 | 4.59  | 10.37 | 4.22 | 1345.00 | 0.96 | 43.20 | 17.26 |
| S8        | 24.77 | 113.95 | 83.30  | 65.55  | 58.75  | 131.90 | 282.10 | 23.79 | 793.50 | 7.95  | 12.97 | 2.43 | 1685.00 | 0.89 | 21.17 | 20.21 |
| S9        | 23.15 | 137.70 | 78.70  | 50.95  | 67.30  | 98.10  | 185.35 | 21.79 | 322.15 | 17.75 | 16.31 | 3.35 | 649.50  | 1.23 | 28.24 | 39.80 |
| S10       | 14.55 | 101.55 | 190.00 | 74.70  | 112.00 | 93.85  | 231.65 | 9.85  | 349.00 | 4.30  | 10.31 | 2.98 | 1046.00 | 0.73 | 29.70 | 18.01 |
| S11       | 41.15 | 474.00 | 153.30 | 56.05  | 102.20 | 25.99  | 60.45  | 44.45 | 358.95 | 2.13  | 15.73 | 3.14 | 231.80  | 1.11 | 10.05 | 6.74  |
| S12       | 16.35 | 105.25 | 272.50 | 56.00  | 186.60 | 118.00 | 136.70 | 15.02 | 207.55 | 6.49  | 10.80 | 5.90 | 527.00  | 0.82 | 37.05 | 17.91 |
| S13       | 38.45 | 325.00 | 91.65  | 59.10  | 80.15  | 22.78  | 95.15  | 51.65 | 310.50 | 1.72  | 10.80 | 2.72 | 305.50  | 0.77 | 7.83  | 4.71  |
| S14       | 19.93 | 155.35 | 102.65 | 54.50  | 67.15  | 133.45 | 204.50 | 14.69 | 469.00 | 7.67  | 14.24 | 3.22 | 728.50  | 1.06 | 26.30 | 28.60 |
| S15       | 37.30 | 197.00 | 393.00 | 49.25  | 245.00 | 22.67  | 56.90  | 10.83 | 95.75  | 1.90  | 5.63  | 1.62 | 225.50  | 0.49 | 13.32 | 4.54  |
| S16       | 42.05 | 189.05 | 327.00 | 60.70  | 255.80 | 46.40  | 19.60  | 10.38 | 113.50 | 1.22  | 4.36  | 2.42 | 259.00  | 0.32 | 22.48 | 5.28  |
| S17       | 39.15 | 268.35 | 89.05  | 64.60  | 181.20 | 83.70  | 541.50 | 58.80 | 268.30 | 3.51  | 13.13 | 4.31 | 1004.50 | 0.89 | 38.25 | 6.19  |
| S18       | 46.15 | 126.25 | 240.95 | 34.80  | 225.85 | 30.84  | 33.50  | 13.65 | 78.30  | 0.40  | 3.34  | 2.22 | 296.50  | 0.21 | 4.42  | 1.62  |
| S19       | 50.25 | 169.95 | 312.00 | 32.80  | 171.25 | 62.00  | 29.19  | 18.00 | 98.20  | 0.76  | 4.38  | 1.38 | 452.50  | 0.30 | 20.05 | 2.96  |
| S20       | 37.10 | 150.60 | 273.50 | 54.55  | 260.90 | 49.40  | 255.00 | 23.23 | 73.45  | 0.98  | 3.10  | 1.03 | 859.50  | 0.20 | 9.16  | 1.72  |

## APPENDIX 4.5: CONCENTRATIONS OF TRACE ELEMENTS (TRANSITION, HIGH FIELD AND LITHOPHILE) IN THE SILT AND CLAY FRACTIONS OF GEOPHAGIC SOILS (ppm)

### Silt Fraction

| Sample ID | Sc     | V      | Cr     | Co     | Ni    | Cu     | Zn    | Rb    | Sr    | Y      | Zr     | Nb     | Mo    | Cs     | Ba     |
|-----------|--------|--------|--------|--------|-------|--------|-------|-------|-------|--------|--------|--------|-------|--------|--------|
| DolA      | 11.685 | 75.05  | 49.05  | 179.25 | 29.3  | 26.55  | 38.55 | 147.6 | 432   | 13.24  | 938.5  | 11.52  | 0.675 | 1.9185 | 2124.5 |
| DolB      | 10.12  | 94.2   | 225    | 224.5  | 82.3  | 22.85  | 46.15 | 76.55 | 335.5 | 10.71  | 1058.5 | 16.09  | 0.755 | 1.45   | 1175.5 |
| MukA      | 9.825  | 75.8   | 163.85 | 204.95 | 68.4  | 23.7   | 45.7  | 97.25 | 372   | 9.6    | 819    | 13.415 | 0.615 | 1.59   | 1401.5 |
| MukB      | 22.15  | 228.55 | 191.75 | 102.15 | 139.9 | 161.65 | 92.4  | 76.55 | 217.3 | 15.5   | 344.3  | 10.77  | 0.755 | 5.69   | 753    |
| Mat       | 42.45  | 140.95 | 303    | 28.175 | 174.5 | 187.25 | 82.4  | 70.9  | 25.7  | 11.075 | 101.35 | 4.58   | 0.435 | 1.66   | 435    |

### Clay Fraction

| Sample ID | Sc    | V      | Cr     | Co    | Ni     | Cu     | Zn    | Rb     | Sr     | Y     | Zr     | Nb    | Mo   | Cs   | Ba      |
|-----------|-------|--------|--------|-------|--------|--------|-------|--------|--------|-------|--------|-------|------|------|---------|
| DolA      | 26.05 | 125.00 | 95.80  | 27.50 | 75.75  | 93.65  | 87.80 | 151.40 | 226.70 | 25.36 | 343.00 | 16.33 | 1.00 | 3.48 | 1622.50 |
| DolB      | 19.84 | 184.90 | 509.50 | 39.40 | 288.50 | 75.95  | 65.35 | 81.10  | 129.60 | 15.33 | 384.35 | 15.87 | 1.52 | 4.72 | 806.00  |
| MukA      | 20.48 | 166.85 | 336.00 | 27.50 | 207.70 | 105.70 | 95.65 | 101.15 | 135.00 | 12.69 | 210.00 | 16.40 | 1.57 | 4.72 | 710.00  |
| MukB      | 28.45 | 181.30 | 311.00 | 31.85 | 257.00 | 180.40 | 89.20 | 83.80  | 108.10 | 13.75 | 257.90 | 13.44 | 1.00 | 7.58 | 588.50  |
| Mat       | 37.20 | 106.50 | 286.00 | 20.92 | 166.70 | 152.50 | 84.05 | 75.55  | 15.16  | 4.65  | 80.20  | 2.83  | 0.29 | 1.96 | 307.50  |

## APPENDIX 4.6: CONCENTRATIONS OF RARE EARTH ELEMENTS (REEs) IN THE BULK FRACTION OF GEOPHAGIC SOILS (ppm)

| Sample ID | La     | Ce     | Pr    | Nd    | Sm    | Eu   | Gd    | Tb   | Dy    | Ho   | Er   | Tm   | Yb   | Lu   |
|-----------|--------|--------|-------|-------|-------|------|-------|------|-------|------|------|------|------|------|
| S1        | 36.65  | 71.80  | 7.38  | 28.30 | 5.31  | 1.27 | 4.35  | 0.56 | 3.27  | 0.62 | 1.65 | 0.23 | 1.52 | 0.23 |
| S2        | 23.76  | 48.05  | 4.73  | 18.19 | 3.39  | 1.00 | 2.85  | 0.33 | 1.91  | 0.37 | 1.08 | 0.15 | 1.04 | 0.16 |
| S3        | 29.96  | 124.95 | 5.89  | 23.51 | 4.61  | 1.44 | 4.67  | 0.66 | 3.98  | 0.83 | 2.24 | 0.35 | 2.58 | 0.41 |
| S4        | 124.95 | 196.35 | 21.07 | 77.90 | 12.16 | 3.02 | 9.88  | 1.18 | 6.31  | 1.19 | 2.98 | 0.42 | 2.87 | 0.41 |
| S5        | 42.90  | 86.85  | 8.35  | 31.20 | 5.15  | 1.39 | 4.31  | 0.52 | 2.65  | 0.48 | 1.39 | 0.18 | 1.34 | 0.21 |
| S6        | 49.10  | 54.85  | 9.65  | 38.20 | 7.10  | 1.99 | 6.53  | 0.92 | 5.38  | 1.13 | 2.93 | 0.39 | 2.73 | 0.40 |
| S7        | 93.75  | 174.40 | 17.04 | 63.60 | 11.66 | 2.77 | 8.92  | 1.10 | 5.87  | 1.06 | 2.70 | 0.39 | 2.35 | 0.39 |
| S8        | 68.55  | 134.20 | 12.97 | 50.75 | 8.56  | 2.14 | 6.59  | 0.79 | 4.12  | 0.88 | 2.30 | 0.34 | 2.44 | 0.40 |
| S9        | 60.95  | 147.40 | 11.70 | 46.45 | 7.64  | 1.80 | 6.53  | 0.86 | 4.60  | 0.88 | 2.45 | 0.39 | 2.44 | 0.37 |
| S10       | 40.40  | 69.35  | 7.11  | 26.55 | 4.33  | 1.02 | 3.17  | 0.38 | 1.86  | 0.36 | 1.07 | 0.15 | 1.16 | 0.18 |
| S11       | 29.90  | 59.20  | 7.16  | 32.30 | 7.62  | 2.65 | 8.68  | 1.37 | 8.07  | 1.74 | 4.98 | 0.68 | 4.98 | 0.73 |
| S12       | 36.36  | 85.65  | 7.10  | 27.40 | 4.83  | 1.30 | 4.25  | 0.57 | 3.20  | 0.58 | 1.58 | 0.20 | 1.48 | 0.22 |
| S13       | 31.71  | 60.80  | 7.84  | 35.35 | 8.50  | 3.05 | 9.66  | 1.49 | 9.44  | 1.99 | 5.65 | 0.75 | 5.12 | 0.78 |
| S14       | 31.55  | 52.80  | 6.34  | 25.05 | 4.34  | 1.29 | 3.62  | 0.51 | 2.79  | 0.57 | 1.61 | 0.22 | 1.56 | 0.24 |
| S15       | 11.26  | 20.09  | 2.33  | 9.89  | 2.18  | 0.69 | 2.22  | 0.33 | 2.14  | 0.44 | 1.30 | 0.19 | 1.32 | 0.21 |
| S16       | 14.29  | 50.85  | 2.89  | 11.29 | 2.30  | 0.75 | 2.44  | 0.34 | 2.03  | 0.44 | 1.32 | 0.19 | 1.15 | 0.20 |
| S17       | 65.00  | 70.80  | 14.65 | 60.65 | 13.91 | 4.37 | 14.07 | 2.27 | 13.09 | 2.44 | 6.61 | 0.85 | 6.15 | 0.87 |
| S18       | 8.35   | 10.14  | 1.94  | 8.84  | 2.10  | 0.76 | 2.42  | 0.38 | 2.59  | 0.55 | 1.47 | 0.21 | 1.33 | 0.22 |
| S19       | 17.02  | 19.72  | 3.76  | 15.84 | 3.62  | 1.14 | 3.40  | 0.54 | 3.32  | 0.72 | 2.02 | 0.29 | 2.02 | 0.28 |
| S20       | 23.96  | 15.61  | 4.92  | 20.65 | 4.63  | 1.51 | 4.89  | 0.64 | 4.00  | 0.85 | 2.27 | 0.31 | 2.32 | 0.31 |

## APPENDIX 4.7: CONCENTRATIONS OF RARE EARTH ELEMENTS (REEs) IN THE SILT AND CLAY FRACTIONS OF GEOPHAGIC SOILS (ppm)

### Silt fractions

| Sample ID | La     | Ce     | Pr    | Nd    | Sm    | Eu   | Gd   | Tb   | Dy   | Ho   | Er   | Tm   | Yb   | Lu   |
|-----------|--------|--------|-------|-------|-------|------|------|------|------|------|------|------|------|------|
| DolA      | 30.99  | 72.45  | 6.54  | 25.96 | 4.33  | 1.28 | 3.60 | 0.46 | 2.37 | 0.48 | 1.40 | 0.19 | 1.56 | 0.25 |
| DolB      | 52.65  | 93.95  | 8.76  | 32.90 | 4.93  | 1.01 | 3.11 | 0.36 | 1.92 | 0.37 | 1.08 | 0.18 | 1.29 | 0.23 |
| MukA      | 58.40  | 110.40 | 10.16 | 37.15 | 5.34  | 0.96 | 3.37 | 0.37 | 2.03 | 0.40 | 1.16 | 0.18 | 1.62 | 0.25 |
| MukB      | 159.30 | 272.35 | 24.43 | 84.75 | 10.75 | 1.82 | 7.07 | 0.74 | 3.62 | 0.64 | 1.86 | 0.26 | 1.95 | 0.27 |
| Mat       | 10.77  | 14.70  | 2.35  | 10.11 | 2.17  | 0.74 | 2.10 | 0.33 | 2.16 | 0.48 | 1.26 | 0.20 | 1.38 | 0.19 |

### Clay fractions

| Sample ID | La    | Ce     | Pr    | Nd    | Sm    | Eu   | Gd   | Tb   | Dy   | Ho   | Er   | Tm   | Yb   | Lu   |
|-----------|-------|--------|-------|-------|-------|------|------|------|------|------|------|------|------|------|
| DolA      | 83.85 | 152.95 | 16.01 | 63.40 | 10.42 | 2.29 | 7.98 | 0.99 | 5.00 | 1.02 | 2.74 | 0.38 | 2.60 | 0.41 |
| DolB      | 30.75 | 62.00  | 5.82  | 22.55 | 3.88  | 1.05 | 3.28 | 0.43 | 2.63 | 0.55 | 1.55 | 0.23 | 1.61 | 0.25 |
| MukA      | 43.20 | 98.70  | 8.49  | 32.80 | 5.46  | 1.31 | 4.27 | 0.58 | 3.14 | 0.61 | 1.83 | 0.27 | 1.94 | 0.31 |
| MukB      | 25.11 | 63.40  | 5.36  | 20.55 | 3.74  | 1.11 | 3.13 | 0.48 | 3.10 | 0.60 | 1.67 | 0.25 | 1.86 | 0.28 |
| Mat       | 4.07  | 10.02  | 1.07  | 4.51  | 0.96  | 0.38 | 1.12 | 0.14 | 1.11 | 0.23 | 0.64 | 0.08 | 0.76 | 0.10 |



## APPENDIX 4.8: PARENT ROCKS MAJOR OXIDE CONTENT (%)

| Sample ID   | Al <sub>2</sub> O <sub>3</sub> | CaO   | Cr <sub>2</sub> O <sub>3</sub> | Fe <sub>2</sub> O <sub>3</sub> | K <sub>2</sub> O | MgO  | MnO  | Na <sub>2</sub> O | P <sub>2</sub> O <sub>5</sub> | SiO <sub>2</sub> | TiO <sub>2</sub> | L.O.I. |
|-------------|--------------------------------|-------|--------------------------------|--------------------------------|------------------|------|------|-------------------|-------------------------------|------------------|------------------|--------|
| <b>DOL1</b> | 15.66                          | 8.48  | bdl                            | 14.33                          | 1.11             | 3.7  | 0.21 | 2.97              | 0.57                          | 48.47            | 2.19             | 1.53   |
| <b>DOL2</b> | 15.23                          | 0.86  | bdl                            | 0.45                           | 3.25             | 0    | 0.01 | 5.88              | 0.03                          | 72.91            | 0.07             | 0.40   |
| <b>DOL3</b> | 13.88                          | 7.96  | 0                              | 15.97                          | 0.91             | 3.62 | 0.23 | 2.95              | 0.61                          | 48.95            | 2.51             | 1.49   |
| <b>MAR</b>  | 14.57                          | 9.63  | 0.01                           | 10.6                           | 1.28             | 6.34 | 0.16 | 1.74              | 0.08                          | 52.57            | 0.72             | 1.31   |
| <b>MUK1</b> | 15.29                          | 10.92 | 0.04                           | 11.21                          | 0.54             | 8.45 | 0.18 | 1.73              | 0.11                          | 48.88            | 0.98             | 1.21   |
| <b>MUK2</b> | 15.79                          | 0.5   | bdl                            | 0.18                           | 1.11             | bdl  | 0.01 | 7                 | 0.01                          | 73.56            | 0.04             | 1.15   |
| <b>MAT1</b> | 15.1                           | 10.79 | 0.02                           | 11.57                          | 0.49             | 7.59 | 0.17 | 2.05              | 0.09                          | 49.85            | 0.96             | 0.83   |
| <b>MAT2</b> | 15.11                          | 10.7  | 0.02                           | 11.62                          | 0.49             | 7.54 | 0.17 | 2.05              | 0.09                          | 49.59            | 0.95             | 0.94   |

## APPENDIX 4.9: CONCENTRATIONS OF TRACE (TRANSITION, HIGH FIELD AND LITHOPHILE) IN PARENT ROCKS (ppm)

| Sample ID   | Sc    | V      | Cr     | Co     | Ni     | Cu     | Zn     | Rb    | Sr     | Y     | Zr     | Nb    | Mo   | Cs   | Ba      |
|-------------|-------|--------|--------|--------|--------|--------|--------|-------|--------|-------|--------|-------|------|------|---------|
| <b>DOL1</b> | 28.40 | 228.20 | 29.30  | 136.80 | 42.20  | 85.80  | 156.70 | 63.20 | 226.20 | 46.10 | 308.10 | 10.65 | 0.97 | 2.98 | 251.00  |
| <b>DOL2</b> | 5.16  | 7.56   | 6.02   | 255.00 | 10.40  | 6.05   | 21.10  | 73.40 | 498.00 | 6.81  | 59.00  | 1.55  | 0.57 | 0.80 | 1366.00 |
| <b>MAR</b>  | 34.30 | 213.00 | 123.40 | 168.30 | 111.60 | 97.30  | 84.30  | 61.50 | 169.30 | 17.13 | 82.90  | 3.75  | 0.57 | 2.50 | 308.00  |
| <b>DOL3</b> | 31.10 | 218.00 | 28.80  | 136.20 | 33.30  | 62.80  | 177.00 | 35.50 | 165.90 | 54.60 | 392.00 | 13.61 | 1.22 | 2.98 | 275.00  |
| <b>MUK1</b> | 36.70 | 247.00 | 335.00 | 177.30 | 137.70 | 120.10 | 101.50 | 36.60 | 159.60 | 16.15 | 55.80  | 2.77  | 0.42 | 1.41 | 133.30  |
| <b>MUK2</b> | 3.88  | 5.27   | 10.20  | 207.40 | 39.60  | 5.46   | 8.50   | 32.50 | 225.90 | 1.44  | 27.70  | 0.36  | 0.28 | 0.53 | 361.00  |
| <b>MAT1</b> | 33.90 | 245.00 | 186.10 | 183.90 | 145.80 | 135.80 | 85.80  | 22.11 | 212.00 | 15.43 | 65.40  | 2.70  | 0.57 | 1.77 | 210.30  |
| <b>MAT2</b> | 32.40 | 247.10 | 183.20 | 168.00 | 151.50 | 137.60 | 88.90  | 22.51 | 211.10 | 15.46 | 61.70  | 2.71  | 0.50 | 1.69 | 211.00  |

## APPENDIX 4.10: CONCENTRATIONS OF RARE EARTH ELEMENTS IN PARENT ROCKS (ppm)

| Sample ID   | La    | Ce    | Pr   | Nd    | Sm   | Eu   | Gd    | Tb   | Dy    | Ho   | Er   | Tm   | Yb   | Lu   |
|-------------|-------|-------|------|-------|------|------|-------|------|-------|------|------|------|------|------|
| <b>DOL1</b> | 24.97 | 53.25 | 6.61 | 30.70 | 7.71 | 2.89 | 8.61  | 1.40 | 9.15  | 1.81 | 5.12 | 0.69 | 4.97 | 0.75 |
| <b>DOL2</b> | 54.95 | 54.15 | 8.24 | 29.00 | 4.25 | 1.25 | 3.22  | 0.41 | 1.59  | 0.28 | 0.60 | 0.15 | 0.42 | 0.11 |
| <b>DOL3</b> | 14.68 | 28.80 | 3.21 | 13.89 | 2.93 | 0.87 | 3.23  | 0.50 | 3.22  | 0.65 | 1.79 | 0.29 | 1.89 | 0.26 |
| <b>MAR</b>  | 31.20 | 64.90 | 8.47 | 38.35 | 9.32 | 3.28 | 10.90 | 1.65 | 10.78 | 2.19 | 6.25 | 0.88 | 5.97 | 0.92 |
| <b>MUK1</b> | 6.11  | 13.16 | 1.75 | 8.15  | 2.11 | 0.89 | 2.97  | 0.45 | 2.82  | 0.62 | 1.73 | 0.26 | 1.71 | 0.27 |
| <b>MUK2</b> | 12.81 | 14.83 | 1.83 | 5.73  | 0.81 | 0.89 | 0.53  | 0.17 | 0.35  | 0.10 | 0.19 | 0.04 | 0.16 | 0.19 |
| <b>MAT1</b> | 9.04  | 17.65 | 2.27 | 10.04 | 2.52 | 0.91 | 2.89  | 0.48 | 3.17  | 0.65 | 1.75 | 0.24 | 1.56 | 0.23 |
| <b>MAT2</b> | 8.66  | 17.30 | 2.13 | 9.36  | 2.44 | 0.90 | 2.91  | 0.48 | 2.69  | 0.62 | 1.59 | 0.23 | 1.69 | 0.21 |

