EVALUATION OF *LETSOKU* AND RELATED INDIGENOUS CLAYEY SOILS

by

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DECLARATION

I, Refilwe Morekhure-Mphahlele, the undersigned, declare that the thesis that I hereby submit for the degree PhD in Chemical Technology at the University of Pretoria is my original work. Acknowledgement has been given and reference made in instances where literature resources were used. The work has not been previously submitted by anyone for a degree or any examination at this or any other academic institution.

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ABSTRACT

The nature of *letsoku* and related clayey soils, traditionally used by indigenous Southern African communities for a wide range of purposes, was explored. Thirty-nine samples were collected from Botswana, Lesotho, Swaziland, South Africa and Zimbabwe. They were analysed to determine their composition and physical properties. Structured interviews were used to establish the purpose of use and the location of sourcing sites. The samples were in the form of either powder or rocks, and some were supplied as dry rolled clay balls. Cosmetic applications were almost universally indicated. However, other functions, related to artwork, medicinal use, cultural symbolism and traditional beliefs, were also mentioned. The samples covered a wide range of colours from bright red to yellow, but also from off-white to black, with some having a light grey colour. It was therefore not surprising that the mineral composition of the *letsoku* samples also varied widely. A black sample, and the yellow and reddish pastel-coloured samples, contained significant quantities of the corresponding, colour-imparting iron oxides. Clay minerals featured prominently, although kaolinite and muscovite were more often encountered as the dominant minerals than smectites. All the samples contained silica and in some instances the content exceeded 90 % m/m SiO_2. The presence of high contents (more than 40 % m/m) of gibbsite in the samples from Venda represents a new finding for clayey soils in traditional usage.

Keywords: Clayey soil; traditional knowledge; *letsoku*, composition, clay minerals

Highlights

- *Letsoku* is a mineral product used for cosmetic applications in Southern Africa
- *Letsoku* samples vary greatly in colour and in mineral composition
- Clays, especially kaolin, feature prominently as does silica
- The black and the yellow-to-red pastel colours derive from iron oxides
- Gibbsite (>40 % m/m) detected previously undocumented in traditional cosmetics
- Substantial amounts of muscovite in Botswana and Eastern Cape samples

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

THESIS OVERVIEW

CHAPTER 1: BACKGROUND TO THE STUDY

This is an introductory chapter giving a general description of cosmetics. The evolution of cosmetics using clays and/or minerals as cosmetics from ancient days to the current status is highlighted. The regulations controlling the composition and/or ingredients of cosmetics are also discussed. The global role of clays is outlined and contrasted with the Southern African position involving *letsoku* and related substances. A brief approach on how to explore *letsoku* is presented.

CHAPTER 2: LITERATURE REVIEW OF COSMETICS

This chapter describes cosmetics and introduces the role of the cosmetics regulatory bodies. It provides a review of clays and clay minerals as ingredients in cosmetics in ancient and current times, both globally and locally. It further elaborates on the physicochemical and chemical properties of cosmetic ingredients, their nature and the regulations controlling their inclusion in products. Adverse effects such as toxicity are also accentuated. A comprehensive critique of the techniques that have enabled knowledge about cosmetics and their ingredients to be gained is presented.

CHAPTER 3: RESEARCH DESIGN AND METHODOLOGY

This chapter covers the practical experimental design for assessing the concepts mentioned in Chapter 2. The techniques used are briefly described and presented, together with the methods used for the analyses. The analyses covered chemical composition, physicochemical and structural properties.

CHAPTER 4: RESULTS

This is a detailed presentation of the results of the various analyses undertaken. The results for physicochemical properties are particle size distribution, specific surface area, pH, colour, water content and loss on ignition. The results for the chemical assessments are clay mineral content, metal oxide and trace metal contents. SEM morphological micrographs of the clayey soils are also presented. The results for structural properties are reflected in the thermograms and in the FTIR spectra.

CHAPTER 5: DISCUSSION AND ANALYSIS

Chapter 5 is a critique of the results from Chapter 4 and the key findings. The study contributions and possibilities for future research are also outlined.

LIST OF ABBEVIATIONS

AD	*Anno Domini*- After Christ
ATR-FTIR	Attenuated total reflectance Fourier transform infrared spectrometry
BCE	Before the Common Era or Before Christ Era
BET	Brunauer–Emmett–Teller
BHV01	Basalt Hawaiian Volcanic Observatory standards material or CRM for XRF trace metals (also see glossary)
CEC	Cation exchange capacity
CIR	Cosmetics ingredients review
CRM	Certified Reference Material
CTFA	Cosmetics, Toiletry and Fragrance Association
EBIT	Engineering, Built Environment and Information Technology
EC	European Council of the European Union and **not** the Council of the European Union comprises heads of the member states
EP EC	European Parliament and the European Council,EP&EC (2009)(see glossary)
EP	The European Parliament (about 751 members) is the parliamentary institution of the EU and serves a legislative function of the EU
EU	European Union
FDA	Food and Drug Administration
FD&C Act	Federal Food, Drug and Cosmetic Act
FPL Act	Fair Packaging and Labelling Act
FTIR	Fourier transform infrared spectroscopy
IAM	Institute of Applied Materials
IARC	International Agency for Research on Cancer
INCI	International Nomenclature of Cosmetic Ingredients
IUSS	International Union of Soil Sciences
JNC	Joint National Committee
LOI	Loss on ignition
SARM	South African Reference Material used as a CRM for metal oxides
SEM	Scanning electron microscopy
SSA	Specific surface area
TGA	Thermogravimetric analyser
T:O	Tetrahedral:Octahedral

T:O:T	Tetrahedral:Octahedral:Tetrahedral
UNESCO	United Nations Educational, Scientific and Cultural Organization
UP	University of Pretoria
USDA	United States Department of Agriculture Soil Classification System
UV	Ultraviolet radiation
WRB	World Reference Base International Soil Classification System
XRD	X-ray diffraction
XRF	X-ray fluorescence

GLOSSARY

ANATASE (Ant)

TiO_2

ASTRINGENT

This is derived from the Latin word meaning “to bind fast”. An astringent tends to shrink, dry or constrict body tissues. Examples are calamine lotion and witch hazel.

BELLADONNA

The name means beautiful lady. It is an eye paint made up of lead tetroxide, mercury, sulphur and antimony. The belladonna berry juice was used to enlarge the pupils of women to enhance their appearance. Unfortunately, belladonna is potentially poisonous and may cause dry mouth, blurred vision, red dry skin, spasms, coma, mental problems and many others.

BHVO-1

The BHVO standards material collected from the surface layer of the *pahoehoe* lava that overflowed from Halemaumau in the autumn of 1919. Certificate values are based primarily on international data compilations (Abbey, 1982; Flanagan, 1976; Govindaraju, 1994).

CALCITE (Cal)

$CaCO_3$

CERUSE

Mixture of lead and vinegar

CRÈME CELESTE

Mixture of white wax, spermaceti (from the head of whale sperm), almond oil and rosewater

CHLORITE (Chl)

$Al_4[Si_8O_{20}](OH)_4Al_4(OH)_{12}$

DOLOMITE (Dol)

$CaMg(CO_3)_2$

EPIDOTE (Ep)

$Ca_2Al_2(Fe^{3+},Al)(SiO_4)(Si_2O_7)O(OH)$

ETHNO-PEDOLOGY

Refers to the articulation of indigenous and local cultural knowledge of soils. It has developed as a research platform which attempts to classify soils according to social criteria rather than the physical and chemical criteria as recommended by the United States Department of Agriculture (USDA).

ETHNO-PHARMACOLOGY

The scientific study of folk remedies used as medicines by different ethnic or cultural groups.

EU

The EU is a political and economic union of 28 members located primarily in Europe. It operates as a powerful political and economic group. Cosmetic regulatory control is via Regulation (EC) No. 1223/2009 (the "cosmetics products regulation). The latter harmonizes and simplifies cosmetics regulations across the EU member states. It serves to simplify procedures, update terminology and strengthen the regulatory framework with a view to ensuring a high level of protection for human health.

FAO

The FAO is a specialized agency of the United Nations with 194 member states. It works in 130 countries worldwide. It leads international efforts to defeat hunger. Its aim is to ensure that all people have access to enough high-quality food to lead active healthy lives.

FDA

The FDA is an agency within the US Department of Health and Human Service. It only regulates but does not grant approval. This is exercised via the Federal Food, Drug and Cosmetics Act which forbids the marketing of adulterated or misbranded cosmetics in national commerce. The Fair Packaging and Labelling Act ensures that the ingredients and the finished cosmetics are safe under labelled or customary conditions of use. This includes that the product is properly labelled.

GIBBSITE (Gbs)

$Al(OH)_3$

GOETHITE (Gth)

α-FeO(OH)

GYPSUM

Repeating unit of $CaSO_4.2H_2O$

HAEMATITE (Hem)

Fe_2O_3

HYDROPHILICITY

Refers to having an attraction for water, readily absorbing or dissolving in water.

ILMENITE (Il)

$Fe^{2+}TiO_3$

INCI

The INCI is a system of science-based ingredient names that minimize the language barriers. Examples are iron oxide yellow for which the INCI name is CI 77492 and iron oxide red for which the INCI name is CI 775.

ISOMORPHOUS SUBSTITUTION

The process of replacing one structural cation for another of similar radius. This accounts for the negative and positive charges in clay minerals. An example is the substitution of Al^{3+} for Si^{4+} in the tetrahedron, resulting in a gain of one negative charge.

JEZEBEL

A woman who knows that she is beautiful and will use her looks to “lure in” her next victim. She will do anything and will use anyone to get what she wants.

KAOLINITE (Kln)

$Al_2Si_2O_5(OH)_4$

KOHL

A mixture of metals, lead, copper, ash and burnt almonds for cosmetic application around the eyes to enhance them

MAGNETITE (Mag)

Fe_3O_4expanded as ($Fe^{2+}Fe^{3+}O_4$)

MICROCLINE (Mc)

$KAlSi_3O_8$

MUSCOVITE 2:1 (Ms)

$KAl(Al_2SO_4)(OH)_2$

NETWORK

Refers to proposed specialized laboratories for the certification, after meeting standard criteria of the quality and suitability of peloid muds (similar to the Permanent Thermal Observatory existing in the Abano and Montegrotto spa district, northern Italy) (Veniale *et al.*, 2007).

ORPIMENT

Repeating unit of As_2S_3

PEARL POWDER

Mixture of bismuth chloride and French chalk (talc)

PEDOLOGY

The word is from *pedon*, meaning ground or earth and *ology*, the branch of knowledge or field of study. It refers to the scientific study of soils and their weathering processes in their natural environment. It examines how soils form due to the five soil-forming factors. These are time, climate, parent material, topography and organisms. It involves multiple other disciplines such as ecology, geology, archaeology, hydrology, geochemistry and many others.

PELOID

Mud or clay used therapeutically in health spas

PLAGIOCLASE (Pl)

$CaAl_2Si_2O_8$

QUARTZ (Qz)

SiO_2

RUTILE (Rt)

TiO_2

SEPIOLITE (Sep)

$MgSi_6O_{15}(OH)_2 \cdot 6H_2O$

SMECTITE 2:1 (Sme)

$(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})$

TALC 2:1 (Tlc)

$Mg_3Si_4O_{10}(OH)_2$

TOPOGRAPHY

Involves the study of the structure, shapes and features of the surface of the earth.

UNESCO

UNESCO is a specialized agency of the United Nations. It has 195 member states and ten associate members. It is based in Paris. Its purpose is to contribute to peace and security by promoting international collaboration through educational, scientific and cultural reforms in order to increase universal respect for justice, the rule of law and human rights along with the fundamental freedoms proclaimed in the United Nations Charter. Its aim is to contribute to the building of peace, the eradication of poverty, sustainable development and intercultural dialogue through education, sciences, culture, communication and information. Other priorities include attaining quality education for all and lifelong learning so as to address emerging social and ethical challenges, fostering cultural diversity, a culture of peace and building inclusive knowledge societies through information and communication.

WRB

The WRB is the international standard for the soil classification system endorsed by the International Union of Soil Sciences (IUSS). It was developed by an international collaboration coordinated by the IUSS working group. It replaced the FAO/UNESCO Legend for the Soil Map of the World.

CHAPTER 1 : BACKGROUND TO THE STUDY

1.1 FOREWORD

The evolution of cosmetics over centuries is a captivating story. Their composition has undergone drastic transformation from 10000 BCE to date. The obsession with having a pale, angelic white complexion resulted in the flourishing of dangerous products. White lead, a mixture of $PbCO_3$ and $Pb(OH)_2$, known as *ceruse*, or Venetian *ceruse*, or spirits of Saturn, was the predominant skin whitener among the English, Greeks and Romans. Mixtures such as *ceruse* were found to cause lead poisoning, skin damage, hair loss, facial tremors, muscle paralysis and death. Queen Elizabeth I is reported to have lost so much hair that her forehead appeared enlarged. Pearl powder ($BiCl_3$) and French chalk ($Mg_3Si_4O_{10}(OH)_2$) were also used as skin whiteners. On the other hand, the Egyptian Cleopatra used milk baths, oils and the dead-sea salts to enhance her beauty in a fairly safe way. Unfortunately, this was counteracted by the toxic eye paints of her time. These were mixtures of PbO_4, HgS, antimony (Sb) and cinnabar (α-HgS). The poisonous products were purchased from the pharmacy and deliberately hidden among medicines in the marble chests. *Crème celeste* was an innovative mixture of white wax, spermaceti, sweet almond oil and rose water which emerged during these times. It was a moisturizer, skin lightener, emollient and could hide blemishes. It later became known as cold cream.

This study will review mainly developments concerning clays and minerals, even though other materials were involved, as mentioned before. Kohl was made from galena (PbS), malachite pigment ($CuCO_3{\cdot}Cu(OH)_2$ and ochre (iron oxides with clay). The Egyptians used it on eyelashes, eyelids and eyebrows around 4000 BCE. Around 1000 BCE the Greeks were whitening their complexions with chalk ($CaCO_3$) and lead. Red ochre (Fe_2O_3 in clay) laced with iron oxide was used for their lipstick. During the period from 1400 to 1500 AD arsenic sometimes replaced lead in face powder. Mud baths emerged on the scene among the Romans in 100 AD. White lead paint gained popularity with European women, especially Queen Elizabeth I with her blond hair and pale skin, giving the "the mask of youth" look. The blond "angelic" hair was achieved by applying a mixture of sulphur, alum ($KAl(SO_4)_2.12H_2O$) and honey. This was allowed to stand in the sun prior to use. The Queen had labelled colourful make-up as "vulgar and improper" and suitable for actors only. Around 1800 AD ZnO_2 appeared on the scene as a face powder to replace the toxic lead and copper mixtures. Around

1900 AD make-up became popular again. The French shifted from their perception of "Jezebels" to acceptance of make-up. Men were even using pastes to hide scars and blemishes. Ancient history revealed the numerous pigments generated by the ancient Egyptians (Scott, 2016). Several shades of reds, pinks and yellows were obtained by mixing ochres of different colours. Red (anhydrous iron oxide Fe_2O_3), yellow (hydrated iron hydroxide $FeO(OH).nH_2O$ or limonite) and brown ochres (hydrated iron oxide $FeO(OH)$ or goethite) were mixed with minerals such as calcite ($CaCO_3$), orpiment (As_2S_3) and gypsum (repeating unit of $CaSO_4.2H_2O$). There is emphasis on the distinction between red ochre (a natural substance containing Fe_2O_3) and haematite (Fe_2O_3, a pure version of red ochre). Scott (2016) also mentioned mixtures such as calcite, carbon black (an iron-titanium compound mixed with calcium carbonate) and MnO_2 for eye make-up.

The ancient communities had the freedom to expose their skins to danger because of lack of control, knowledge and regulatory organizations. The current consumers enjoy the benefits of the emergence of various cosmetic regulatory bodies. Cosmetic ingredients are subject to regulations. Aspects covered by these regulations include the terminology used and formulation procedures, with the ultimate aim of ensuring safety for humans. The regulations unambiguously prescribe restrictions on the definition of cosmetics, their properties, the ingredients that may be used, their positive and negative impact on users and the environment. They include aspects such as cosmetic composition as well as the chemical structures, functions and toxicity of the ingredients. The European Parliament and European Council regulate cosmetics via Regulation (EC) No. 1223/2009, (dated 30 November 2009 and the subsequent amendments thereto) of the European Parliament and of the Council on cosmetic products. The FDA defines cosmetics as "articles intended to be rubbed or poured". Most of these are emulsions containing surfactants such as creams, lotions, gels, make-up and products for removing make-up, products intended for application to the lips, products for nail care and make-up, sunbathing products, products for tanning without sun, skin-whitening products and anti-wrinkle products. The variety of products invariably involves a broad spectrum of ingredients, but the focus of this study is on minerals, clays and clay minerals.

The individual chemical ingredients in cosmetics are subject to a review by the Cosmetic Ingredient Review (CIR). The latter operates in association with the Personal Care Products Council (previously the Cosmetic, Toiletry and Fragrance Association, CTFA). It is supported by the FDA and the Consumer Federation of America. The FDA is a non-voting member but observes the CIR activities as it may use their findings in its own safety reviews of cosmetic ingredients. Recommendations are made on the safety and use of the compounds based on the available scientific literature encompassing data. The nine-member steering committee, made up of three dermatologists, two chemists and four pharmacologists or toxicologists, is involved in the general policy and direction of the CIR. The composition of the cosmetics is further subject to the International Cosmetic Ingredient Nomenclature Committee (INC), which is sponsored by the Personal Care Products Council. This is responsible for designating a uniform system, known as INCI names, for cosmetic ingredients that are used globally for consistency in ingredient names. Approved names are published in the *International Cosmetic Ingredient Dictionary and Handbook.* (http://www.cosmeticsinfo.org/Ingredient-dictionary).

Globally, several researchers have reported on the use of some clays and clay minerals as cosmetic ingredients, including their functions (Konta, 1995);(Carretero, 2002);(Carretero and Pozo, 2010);(CIR, 2014), Heckroodt (1991) described clay as the finest fraction, < 2 µm, in the clay, silt and sand triangle based on particle size and structure. Cosmetic physicochemical properties and thermodynamic stability are strongly influenced by the afore-mentioned attributes. The physicochemical properties of clay minerals, e.g. kaolinite, smectites, talc and muscovite, are important attributes in therapeutic applications (Carretero, 2002; Schoonheydt and Johnston, 2006). These authors discussed in detail the oral and topical therapeutic activity, as well as the cosmetic action, of clays in creams, sunscreens, dermatological protectors, anti-inflammatories and gastro-intestinal medications.

Soils and clays also play important cultural and medicinal roles in the life of humankind (Certini and Ugolini, 2013; Hartemink, 2015b; Hartemink and McBratney, 2008). Two approaches, namely the ethno-pedological and ethno-pharmacological, help to capture spiritual, cognitive and practical aspects of the use of clay (Adderley *et al.*, 2004; Barrera-Bassols and Zinck, 2003; De Smet, 1998; Krasilnikov and Tabor, 2003). Soil-derived minerals such as ochre have featured in various cultural products for almost 100 000 years (Carretero, 2002; Hodgskiss and Wadley, 2017; Konta, 1993a; López-Galindo *et al.*, 2007; Viseras *et al.*, 2007).

In essence, ochre is a natural soil-based pigment that ranges in colour from yellow to deep orange or brown. It is essentially a mixture of oxides of iron with varying amounts of sand and clay.

Locally, the Matike *et al.* (2011) study on the Eastern Cape clayey soils highlighted the effect of pH of cosmetics on the acid mantle of skin. The latter study mainly focused on physicochemical properties. Their mineralogical and chemical composition hence their possible cosmetic role, were recommended for future studies. On the other hand the Dlova *et al.* (2013) study identified two traditional types of clays from the Inanda district in Durban, South Africa as low degree UVA protectors. The authors did not examine their safety profile nor their composition. The Jumbam (2014) research on ten clayey soil samples from the Isinuka springs in the Eastern Cape revealed the presence of several clay minerals. Some of them were kaolinite, smectite, plagioclase and halite. The main cosmetic role emphasized was protection against UV radiation and for their effect on pH.

The Sotho clans of Southern Africa have described a number of clayey soils as *letsoku.* These are named differently elsewhere, such as *chomane* in Shangani, *imbola* in Xhosa, *ilibovu* in Swati and *luvhundi* in Venda. There are several other names given by other ethnic groups (Matike *et al.*, 2014). *Letsoku* has also been associated with other materials, e.g. a black manganese oxide (Pahl, 1974b), white clays (probably kaolin) (Bishop, 1984) and the black *sekama* (ilmenite) (Ambrose *et al.*, 2001).

The aim of this study was to explore the clayey soils as potential cosmetic ingredients. Comparison of the clayey soils with well-known topical clay minerals (Carretero, 2002; Carretero and Pozo, 2010; Ekosse, 2000; Favero *et al.*, 2016; Konta, 1995) would aid in confirming the suitability of these soils as ingredients of or as modern cosmetics.

The main custodians of the knowledge of the *letsoku* sampling sites are traditional healers. This added intrigue to the original objective of the research. Subsequently, other functions of and more detailed background information about these clays were investigated. Therefore an interdisciplinary exploratory approach was adopted, resulting in a two-pronged epistemological and a characterization study.

1.2 PROBLEM STATEMENT

The study was inspired by the transition of the cosmetic industry towards more natural ingredients and the quest to reclaim the vanishing cultural practices of Southern African peoples. Clayey soils have been used for eras among Southern African indigenous people.

Topical application is their commonly known function. Several names such as *letsoku (Sotho clans), libovu (Swazi), imbola (Xhosa)* and *chomane (Shona)* have been used to describe these clayey soils. The challenge is to establish a link between the function, nature and composition of the clays. The relevance of mineral composition to the manifold claimed traditional uses of *letsoku* are to be discussed in the context of the known functions that clays and minerals impart to modern formulations, in particular topical cosmetics. Furthermore, to give a scientific account for commonality in function and the differences in the names.

1.2.1 Research questions

The background provided in Section 1.2 raises questions that create a need for some logical or scientific explanation that may justify the continued topical use of *letsoku* by humans. Therefore there is a need to provide answers to the following questions:

- What do people use *letsoku* for?
- What is the nature of *letsoku* and is there a link between its nature and its function(s)?
- Is there justification in the claims made, including the common use of the name *letsoku* for various clayey soils?
- Can *letsoku* compare satisfactorily with the cosmetic ingredients or products currently used?

1.2.2 Objectives

The study could not proceed without actual samples of *letsoku*, hence it was imperative to locate the sourcing sites. Therefore it was essential to do the following:

1. Obtain representative samples.
2. Establish the location of each sourcing site as this was crucial to the research.
3. Seek reliable informants on the use of *letsoku* and the sourcing sites or suppliers of the clayey soil.
4. Determine the physicochemical properties, chemical and mineral compositions of the samples collected to determine commonality amongst the various clayey soils that could substantiate or refute the claims made about these clayey soils.
5. Establish whether there is a correlation between the functions attributable to *letsoku* and the composition and properties of the samples.

6. Assess the actual suitability of the functions of *letsoku* based on the scientific results and information gathered.

1.3 OVERVIEW OF THE RESEARCH DESIGN

The study design included an epistemological study and a comprehensive characterization of *letsoku* samples. The former included a survey conducted through interviews, while the latter involved sample collection and experimental analysis of the attributes of *letsoku*. Ethical clearance for the study was sought from the Faculty of Engineering, Built Environment and Information Technology (EBIT) of the Pretoria University (UP) Research Ethics committee. An overview of the research design is given in Fig. 1.1.

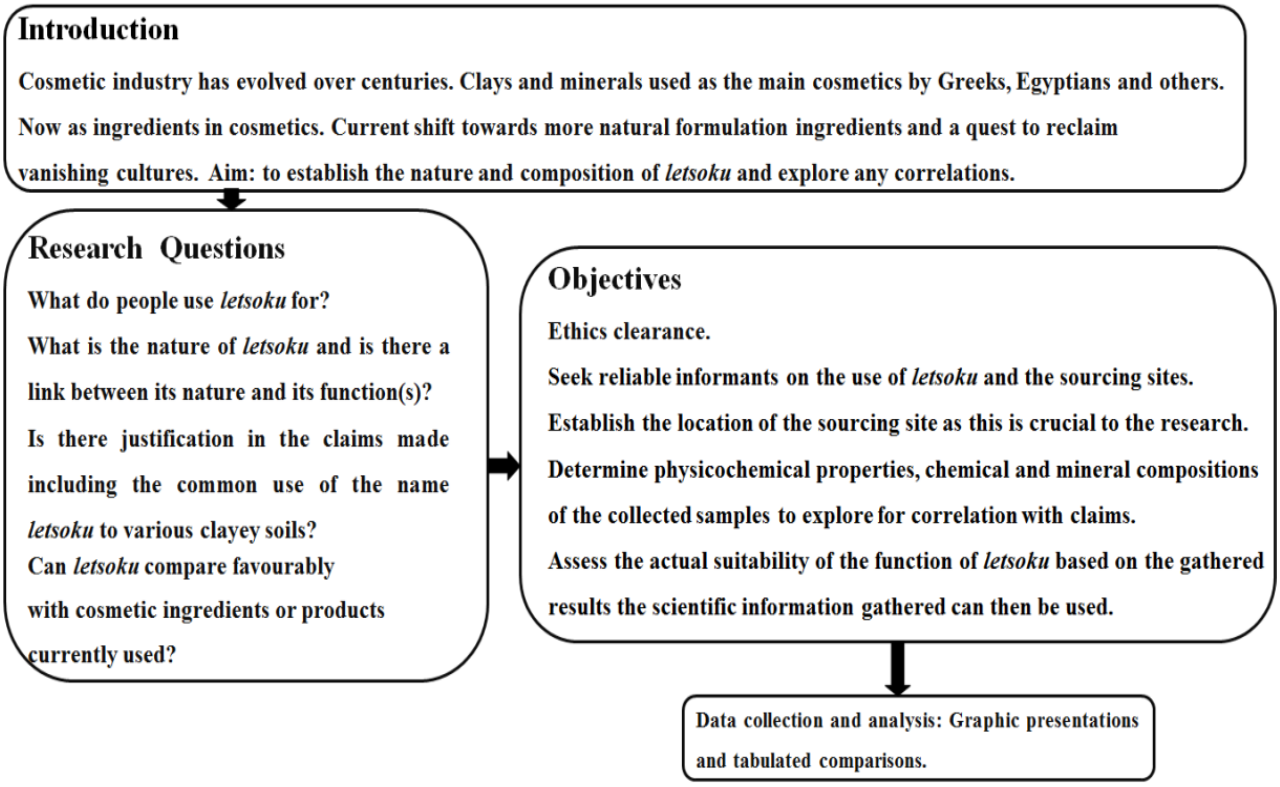


Figure 1.1: Research design flowchart giving an overview of the research process

1.4 DATA COLLECTION AND ANALYSIS

1.4.1 Epistemology

Epistemology was to be done using structured questionnaires and field notes to capture any additional observations not addressed in the questions. Data analysis was to be done using thematic content analysis with the assistance of a biostatistician using structured questionnaires.

1.4.2 Characterization

Characterization included the use of calibrated, specialized and high-performance instruments for:

(a) Physicochemical properties: appearance, colour, BET surface area, particle size distribution

(b) Chemical composition: metal oxide and trace metal analysis

(c) Mineralogical composition: clay mineral composition

(d) Morphological analysis

The above properties were determined using mainly various items of equipment from several departments based at the University of Pretoria.

1.5 RESEARCH METHODOLOGY

This was a branched research project comprising the following steps::

Interviews

Structured interviews in the form of questionnaires were used to obtain information on the use, applications, location of sourcing sites and justification for the use of *letsoku*.

Sample collection

Samples were collected both from the original sites and some were purchased from vendors.

Thematic content analysis

The data collected using questionnaires was analysed to make inferences.

Analysis of the characterization results

The samples were analysed for their physicochemical properties, their mineralogical and chemical composition.

The possibility of a link between the claims and the characterization findings was explored.

1.5.1 Ethical considerations

This involved applying to the Faculty of Engineering, Built Environment and Information Technology (EBIT) of the University of Pretoria to ensure the protection of the informants. Data collection was done on a random Southern African population. A minimum of 40 informants were interviewed according to a document approved by the University of Pretoria.

1.5.2 Determination of clay properties and composition

The physicochemical properties, morphology, clay minerals, metal oxides and trace metal composition content were to be determined. Thermal and spectroscopic analysis were also to be done. The results would then be compared with known market-available or established cosmetic clays.

1.6 CONTRIBUTION

A positive elucidation could lead to devising a means to harness *letsoku* for wider application. It was thought that the study might help undeclared users to share the other positive attributes of *letsoku*. Newly discovered sourcing sites for clayey soils in Southern Africa may enhance poverty alleviation if advanced commercialization takes place.

Formulation opportunities for cosmetologists using *letsoku* may arise from the accurate knowledge of its composition. Academic prospects for researchers are open for the microbiological evaluation of indigenous clays, the isolation of clay minerals and their characterization.

CHAPTER 2 : LITERATURE REVIEW

2.1 INTRODUCTION

According to the US Federal Food, Drug and Cosmetic Act (NIST.IR.8178, 2017), cosmetics are defined as “articles intended to be rubbed, poured, sprinkled or sprayed on, introduced into or otherwise applied to the human body for altering the appearance or cleansing, beautifying and promoting attractiveness”. The main functions of a cosmetic are not to cure but to clean, perfume, change the appearance, correct body odours, protect and keep in good condition. Cosmetics are applied externally on the epidermis, hair, nails, lips, genital organs, teeth and mucous membranes of the oral cavity. Cosmetic products may include skin moisturizers, perfumes, lipsticks, finger nail polishes, eye and facial make-up preparations, cleansing shampoos, permanent waves, hair colours, deodorants and dental products. Soap and drugs are not included.

The European Parliament and the European Commission document (EC (2009) prescribes that a cosmetic product composition should: not contain certain prohibited ingredients (Regulation 1223/2009 Annex II); obey guidelines on restricted substances (these are laid down in Annex III); conform with the requirements connected with colourants (Annex IV); conform with the requirements connected with preservatives (Annex V); and conform with the requirements connected with UV filters (Annex VI).

The complex and sensitive nature of cosmetics has prompted various types of studies. These range from cosmetic composition and application to microbial challenge tests, toxicity and associated health conditions. Various techniques such as surface analysis, particle size distribution analysis, XRD, XRF, electron microscopy, infrared spectroscopy and thermal analysis are essential to address the listed requirements for a cosmetics study.

South Africa is no exception to the rule of nature. The scarcity of specific types of clay presents a challenge concerning clay availability. Kaolin suitable for paper coating is not known to occur in South Africa (Heckroodt, 1991; Ngcofe and Cole, 2014) in spite of the wide spectrum of clay materials available. Approximately 57 different minerals were sourced from 816 mines and quarries in 1995 mainly from the North West, Gauteng, Mpumalanga and the Free State. The discovery of additional sites would benefit the clay industry and probably boost employment. There have been recent discoveries in the Western Cape which encourage similar explorations elsewhere in the country.

2.2 PROPERTIES OF COSMETICS

Cosmetics can achieve the intended purpose(s) as indicated in their definition. This depends on the mixing together of appropriate ingredients in accurate proportions to impart desirable properties suitable to produce the target cosmetic functions. The properties of the individual components invariably play a role in the finished product. Other important aspects include manufacturing risks, ingredient compatibility, stability, product safety, ingredient toxicity and aesthesia.

2.2.1 Physicochemical properties

A primary condition for a cosmetic is that it must adhere to the skin and not "streak or run off" when applied to the skin. Therefore consistency and viscosity should be suitable for application (Viseras *et al.*, 2007) and would vary with the type of product. The high surface area and colloidal nature impart unique properties that enhance their functions. These cosmetics are semi-solid products. They are ointments, pastes, creams, gels and rigid foams which can be deformed and rearranged. These products may contain clays, polymers and other ingredients that may complement their activity. The authors emphasize the need for pre-treatment such as drying, pulverization, sieving and wet separation of the clay fraction and sterilization by heat. Chemical processing may be performed to increase a desired property. Structural properties such as charge distribution affect clay properties. This is demonstrated by comparing 1:1 and 2:1 clay minerals and their swelling and rheological properties.

On clay-like ingredients the authors Carretero and Pozo (2010), Matike *et al.* (2011); Pozo *et al.* (2013), Silva *et al.* (2011), Silva-Valenzuela *et al.* (2013); Viseras *et al.* (2007), Favero *et al.* (2016) and Mattioli *et al.* (2016) concur on the vital role of physicochemical properties such as high adsorption capacity, large specific surface area, particle size, purity, morphology, solubility, low hardness, astringency and high reflectance. This invariably implies appropriate viscosity and hence ingredients that would yield a desirable overall result. High specific surface area is essential for efficient adsorption. Pozo *et al.* (2013) further emphasize the importance of cation exchange capacity (CEC), especially where nutrient delivery is important as in peloids (Carretero *et al.*, 2006) or swelling clays. This aspect should also involve high specific surface area and hence increased adsorption.

According to Fakhfakh *et al.* (2005), plasticity, particle size and cooling kinetics are important clay attributes. Favero *et al.* (2016) elaborate on the role of the clay bioburden and the decontamination process (López-Galindo *et al.*, 2007). The afore-mentioned researchers and Carretero and Pozo (2010) further mention the role of silicon in skin tissue reconstruction. The researchers also reiterate the Al healing activity, pigment dispersion, hydration and melanin adsorption mentioned by Carretero and Pozo (2010). The authors further accentuate the bactericidal, regenerative and antiseptic action of elements such as Si, Al, Fe, Ca, Ti and K. This, according to these authors, should contribute to impurity adsorption, activation of circulation, cell renewal and repair of tissues.

Various resources, rules and regulations concerning the use of clay minerals such as kaolinite, talc and others in pharmaceutical and cosmetic formulations were reviewed by López-Galindo *et al.* (2007). Emphasis was placed on the effect of processing, handling and administration on the safety and stability characteristics. The net charge deficits arising from isomorphous substitution result in different clay technical behaviours.

A comprehensive discussion on peloids requirements was published by Veniale *et al.* (2007). They proposed a coordinated network of laboratories for the control and certification of the quality and suitability of peloid muds for the different pathologies and treatments. This would include their biological activity, cooling rate and bio-adhesiveness. The writers also accede to the need for a high surface area, compatible mineralogy, allowed limits for toxic trace elements and compatible pH for the peloids. Physicochemical properties have proved to be important in peloid preparation where cation exchange capacity, particle size, high adsorption and absorption capacities are crucial for the removal of secretions, oils, toxins and contaminants from the skin. Efficient clay gels and pastes are formed from a balance of the afore-mentioned attributes (Carretero, 2002; Schoonheydt and Johnston, 2006).

Khiari *et al.* (2014) reiterate some of the issues raised by Veniale *et al.* (2007). Their research on the traditional Tunisian medicinal clays led to a serious concern about the alarmingly high amounts of crystalline silica (quartz) contained in these clays.

Schoonheydt and Johnston (2006) accentuated the significance of the edge surface and the planar surface edges as being usually associated with defect sites and being pH dependent. This has an important bearing on the surface area of the clay mineral. The researchers concluded that isomorphous substitution introduces hydrophilicity which may induce the presence of exchangeable cations. This hydrophilicity may also arise from the presence of hydroxyl groups at the surface, such as in kaolinite, and from defect sites. The hydroxyl surface may be an Al−OH surface as in 1:1 kaolinite, 2:1: chlorite or gibbsite and brucite. This surface is known to interact strongly with interfacial water molecules, unlike the siloxane surface. The overall effect is increased chemisorption (Carretero *et al.*, 2013), which concurs with the findings of the previous authors concerning the use of lemnos (Ca^{2+}-smectite) for their astringent and absorbent properties.

2.2.2 Chemical properties

Clay crystal chemistry or chemical composition has a significant influence on the technological properties of the clay raw materials. The latter refer to the drying and firing shrinkage, plasticity index, rheology, resistance and colour after firing (Benea, 2004). The overriding condition is chemical inertness to prevent unexplainable and probably harmful reactions from taking place (Silva *et al.*, 2011). Thermal degradation behaviour (Carretero and Pozo, 2010) may prescribe the suitability of the use of the clays for ceramics or cosmetics (Kpangni *et al.*, 2008).

The chemical nature of the clay minerals present helps in product formulation to achieve desired objectives. The exhaustive review by Carretero and Pozo (2010) gives a detailed outline of the various uses of clay minerals: orally, topically and parenterally. The authors indicate that in cosmetics, minerals may be used as solar protectors, in toothpaste, creams, powders, emulsions, bathroom salts and deodorants.

The chemical structure has a strong bearing on the function of the mineral. For example, solar protection is most likely for TiO_2 compounds. These are sourced from ilmenite. The three main crystalline forms are rutile, anatase and brokite. Smijs and Pavel (2011) presented this inorganic physical sun blocker as being protective against ultraviolet radiation of 290-320 nm (UVB). This is partly attributed to the high refractive index, strong UV-absorbing capabilities and its resistance to discolouration under UV light. UVB has the potential to cause different degenerative skin diseases such as actinic keratoses and skin cancer from epidermal cells. The inorganic UV blockers are considered safer than their organic counterparts. TiO_2 does not cause skin irritation, is chemically inert and has limited skin penetration. Microsized TiO_2 has been used in an attempt to circumvent the opaqueness produced on topical application. This has led to the use of the controversial nanoparticles (NPs) for skin sunscreen (Yang, 2003). TiO_2 may also be used as a pigment and a thickener.

Yang (2003) elaborated on the various mechanisms of TiO_2 as a UV-blocking additive. These range from reflecting and/or scattering of light because of the high refractive index, the absorbance of UV radiation because of the semi-conductive properties and the claim that only the nanoparticles absorb UV radiation. They concluded from their study that TiO_2 absorbs UV radiation irrespective of the particle size and this can be explained by the band theory. This regards TiO_2 as a semiconductor oxide with a large band gap between its low-energy valence band and the high-energy conduction band, namely 3.0 eV and 3.2 eV for rutile and anatase respectively. These correspond to the absorption edges 413 and 388 nm respectively.

Mica (general formula: $X_2Y_{4-6}Z_8O_{20}(OH, F)_4$, where X=K, Na or Ca: Y=Al, Mg or Fe: Z=Si or Al or $K_{<2}Al_4[(Si_{>6}Al_{<2}](OH)_4.nH_2O$ for illite) imparts properties that kaolinite ($Al_2Si_2O_5(OH)_4$) will not be able to impart, that is iridescence. Mica is characterized by a crystal structure composed of aluminium silicate sheets weakly bound by layers of positive ions K^+ and also Na^+. These bonds are so weak that separation into very thin flexible pieces is common. Muscovite is transparent and light in colour. It is a potassium-rich mica with the following general formula:$KAl_2(AlSi_3O_{10})(OH)_2$.

The potassium is sometimes replaced by other monovalent ions such as sodium, rubidium or cesium. Aluminium is sometimes replaced by magnesium, iron or chromium. The ground mineral has a pearly lustre and may be used to impart pearlescence to blushes, eye cosmetics, foundations, hair, body glitter, lipstick, mascara and nail polish.

2.3 SOILS, CLAYS AND CLAY MINERALS

The multi-functional nature of cosmetics invariably involves a variety of simple and complex ingredients which may be organic or inorganic. On the one hand, there are ingredients that impart essential functions such as moisturising, cleansing, exfoliation, preserving and colouring. Colourants such as dyes, iridescent pigments and other ingredients such as minerals may impart aesthetic appeal.

2.3.1 Soils

Soils are mixtures of rocks, minerals and clays. This makes it necessary to have background information on soils to understand clays. Soil taxonomy is varied: for instance in North America the Unified Soil Classification System (USCS) based on engineering properties is used. The criteria used for classification relate to the ultimate use or properties of the soil. This concurs with the conclusion from the study by Adderley *et al.* (2004). They studied the *cesa-goz* soils managed by the Kanuri and Shuwa Arab peoples in northeast Nigeria. Their study revealed that ethno-pedological soil taxonomy can be improved by incorporating it with scientifically defined soil properties and records. Krasilnikov and Tabor (1999) defined ethno-pedology as the study of how people understand, view and manage land at different spatial scales. The definition given by Barrera-Bassols and Zinck (2003) encompasses the soil and land knowledge systems of rural populations from the most traditional to the modern.

The Adderley *et al.* (2004) study implies the incorporation of soil management criteria from both the social and physical sciences into ethno-pedology. The use of optically stimulated luminescence (OSL) revealed the cultural difference in the two soil classification criteria. This accorded with the fact that the soils had been managed differently over a long period. The conclusion was that a robust classification should encapsulate an understanding of both past and present cultural soil activities. Ultimately, this approach would lead to an understanding of the human–environment relationship.

Certini and Ugolini (2013) proposed a soil definition that was considered to have a universal value and is a simple reliable term. They described soil as “a layer of fine-grained mineral and/or organic material with or without coarse elements and cemented portions, lying at or near the surface of planets, moons and asteroids, which shows clear evidence of chemical weathering”.

Hartemink (2015a) emphasized the need for uniform methods of soil analysis and nomenclature for soil classification for the purpose of better understanding and utilization. He also highlights the need to have soil studies of a thematic nature through agricultural production or water purification.

Soil taxonomy may be applied to clays based on the afore-mentioned properties. Clays are characterised by small particles with diameters less than 2 µm. Terms such as solonetz (alkaline soils), durisols (high silica), calcisols (high levels of calcium carbonate) and many others are used to describe them.

Global studies by Certini and Ugolini (2013), (Hartemink, 2015a) and Krasilnikov and Tabor (1999) have highlighted the multi-functionality of clayey soils. These functions include medical/medicinal applications, construction, cementing, painting, food, degradation of contaminants, etc.Adderley *et al.* (2004) and Barrera-Bassols and Zinck (2003) embrace the spiritual, cognitive and practical aspects of soils. They also highlight ethno-pedology as exploring soil and land as “objects of symbolic meanings and values”. This approach attempts to articulate the myths and indigenous cultural knowledge combined with scientific knowledge on soils through ethno-pedology and ethno-pharmacology (De Smet, 1998).

2.3.2 Clays

Clays are components of several cosmetic and pharmaceutical products. Their nature and structure may aid in understanding their role in product formulation.

Clay as defined by Heckroodt (1991) is an “earthy mixture of fine-grained hydrous aluminium silicates with fragments of colloidal matter and other minerals such as oxides and sulphates”. The Joint National Committee(JNC)of the Soil Science Society (Bergaya and Lagaly, 2006)states (what is well known) that clays exhibit plasticity when wet but harden when heated. Silva-Valenzuela *et al.* (2013) describe them as “natural materials presenting fine granulometry and often exhibiting lamellar structure due to the crystalline arrangement formed by the silicon and aluminium oxides”. The latter authors also highlight the likelihood of the presence of impurities that could invalidate the use of clays in some products such as cosmetics or pharmaceuticals.

Clays are considered to have particle sizes of less than 2 µm, i.e. they are finer than silt. They have various colours from white to dull grey or brown to deep orange-red. They are found in soils and in fine-grained sedimentary rocks such as shale, mudstone and siltstone. Dry clay becomes firm when fired and may undergo permanent physical and chemical changes. Ceramic material may result from these processes to give rise to various products, including bricks, earthenware and porcelain.

Clays can be classified on the basis of their pedology, composition, chemical and physical properties and many other parameters (Heckroodt, 1991) and (Bergaya and Lagaly, 2006). Grain (particle) size may also be considered for classifying sedimentary or secondary deposits. They also contain non-clay mineral components such as oxides, sulphates, organic material, exchangeable ions and salts.

Clays can take the following forms:

a) *Ball clay* or *bentonite* is a sedimentary clay composed of 20–80 % kaolinite, mica and quartz. It is fine grained and plastic in nature.

b) *Common clays* include shales, soil clays and glacial clays which are widespread. They are fine grained and exhibit plastic behaviour when wet. They are used for structural products with rock-like hardness. Products include face bricks, drain tiles, vitrified pipes, pottery, stoneware and roofing tiles.

c) *Fuller's earths* are clays that have enough decolourizing and purifying capacity while remaining chemically inert. They are used to clean wool and also to purify oils.

Clay properties depend mainly on the type and amount of clay minerals and non-minerals present, the particle size distribution and the processing conditions.

2.3.3 Clay minerals

The properties of clay minerals depend on the crystal structure and crystal chemistry according to Konta (1995). Heckroodt (1991) emphasized the importance of particle size distribution, particle shape distribution and that the electrostatic charge of the structural layers also has a significant impact. The negative charge results from the ionic substitutions in the octahedral and tetrahedral sheets of clay minerals. This varies according to whether the charges are on the surface or on the edges. Consequently, clay minerals derive their ability to adsorb cations and anions from the electrostatic charges.

2.3.4 Clay mineral structure

Heckroodt (1991) and Konta (1995) define clay minerals as hydrous layered silicates forming part of a larger family of phyllosilicates. This is a class of hydrated phyllosilicates composed of continuous two-dimensional tetrahedral sheets arranged in structural layers. Clay minerals may be synthetic. Each tetrahedron is composed of a cation T linked to four oxygen atoms such as $[SiO_4]^{4-}$. Other common cations are Al^{3+} and Fe^{3+}. The basic building blocks of clay minerals, silicate tetrahedron and aluminium octahedron, are shown in Fig. 2.1 and Fig. 2.2

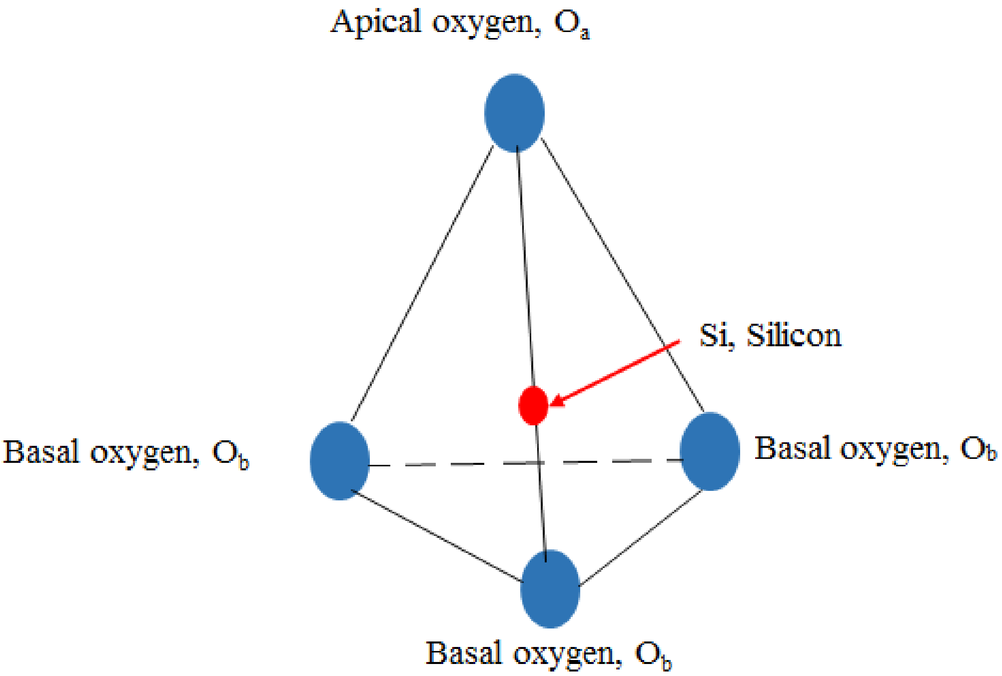


Figure 2.1: Silicate tetrahedron

Other common cations are Al^{3+} and Fe^{3+}. The three basal oxygens, O_b, are linked to adjacent tetrahedra. This results in a continuous two-dimensional structure (Brigatti *et al.*, 2006) along the *a*, *b* crystallographic directions. The free apical oxygens, O_a, point in the same direction and link to the octahedral, O, sheet. The octahedron, O, is composed of a metal oxide coordinated to hydroxide anions such as in $(AlO_3(OH)]^{6-}$(Konta, 1995). The octahedral sheets are formed by connections between the edges of the octahedrons.

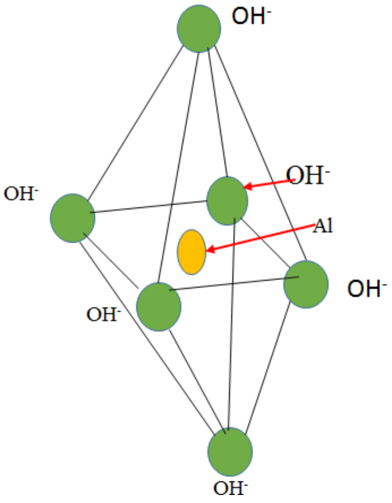


Figure 2.2: Aluminium Octahedron

Tetrahedral apical oxygens, O_a, connect the tetrahedral and octahedral sheets to form a common plane, O_{oct}, with octaheral anionic position O_{oct} (O_{oct} OH^-, F^- and Cl^-). The O_{oct} lies near to the centre of each tetrahedral six-fold ring (Fig. 2.3).

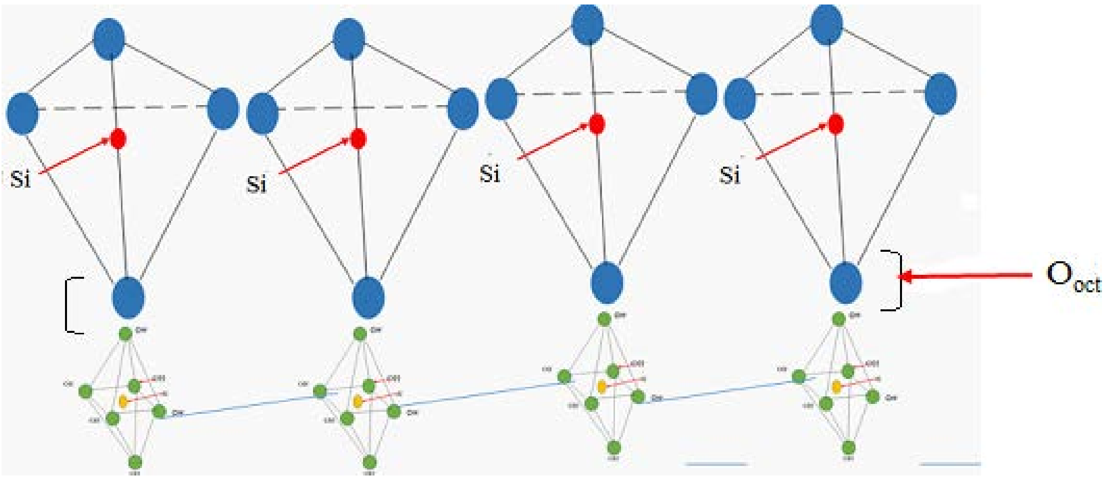


Figure 2.3: A T:O sheet formed by tetrahedra and octahedra

An additional oxygen atom is above the gap in the tetrahedral sheet at the centre of the six tetrahedrals. This oxygen atom is bonded to a hydrogen atom, forming an OH group in the clay structure.

Williams and Haydel (2010) concur with Konta (1995) on the silicate layers. They further propose that the silicate layers are made up of hexagonal SiO_4 stacked on octahedral sheets containing Al, Mg and/or Fe. These are bound to two planes of closely packed O atoms and OH^-. Two M^{3+} or three M^{2+} may fill the edge-sharing octahedra. Some common octahedral cations, namely Al^{3+}, Fe^{3+}, Fe^{2+} and Mg^{2+}, including their ionic radii are presented in Table 2.1 (adapted from (Barton and Karathanasis, 2002).

The total charge balance depends on the structural arrangement and the precise elemental substitutions. These factors explain how a net charge may arise due to the substitution of Al^{3+} for Si^{4+} in the tetrahedral layer for a gain of one negative charge. Similarly, Fe^{2+} may be substituted for Al^{3+} in the octahedral layer due to weathering. In addition , a net negative charge may develop on the basal surface or bottom plane of the tetrahedral layer (Bleam, 1988);(Barton and Karathanasis, 2002).

Table 2.1: Some common elements from the earth's crust and their ironic radii

Ion	Ionic radius (nm)
O^{2-}	0.140
Si^{4+}	0.039
Al^{3+}	0.051
Fe^{2+}	0.74
Zn^{2+}	0.74
Mg^{2+}	0.066
Ca^{2+}	0.099
Na^+	0.097
K^+	0.133

This implies that Si^{4+} may be replaced by Al^{3+} in the centre of the tetrahedron without changing the basic structure of the crystal. Fe^{2+} and Zn^{2+} may also replace Al^{3+} and Mg^{2+} in the octahedra. The above processes of cation replacements are termed isomorphous substitutions. They account for both excess negative (higher valence by lower valence cation) and excess positive charges (lower valence by higher valence cation) in clay minerals.

2.3.5 Classification of clay minerals

The charge of the layers plays a role in their chemical behaviour and serves as a basis for clay classification. Cation substitution in the octahedrons and tetrahedrons takes place into the spaces in the charged areas. The criterion for their classification is also closely linked to the number and the ratio of sheets in a fundamental structural layer (Konta, 1995; Williams and Haydel, 2010). Crystalline clay minerals may be classified into a number of groups– seven plus one according to Konta (1995),the extra one being pigments. The six main ones of relevance here are as follows:

(i) **The kaolinite and serpentine group** minerals are characterized by two-sheet phyllosilicate where the T:O or tetrahedral: octahedral ratio is 1:1 and the apparent charge seems to be zero. However, isomorphous substitution of Al^{3+} for Si^{4+} on the basal surface of the tetrahedral sheet produces a constant structural charge. The additional charge occurs on the edges due to protonation or deprotonation of the exposed OH^- groups (Gunter, 1997; Khawmee, 2010; Schroth and Sposito, 2011), which depends on the solution pH. Repeating units of $Al_2[Si_2O_5](OH)_4$ or $Al_2O_3SiO.H_2O$ form the ideal formula for kaolinite. Halloysite is given by $Al_4[Si_4O_{10}]_2(OH)_8.4H_2O$. Kaolinite may result from the incongruent dissolution or weathering product of feldspar, $2KAlSi_3O_8$.

(ii) A 2:1 clay mineral implies two tetrahedral sheets and one octahedral sheet as in the **smectite group**. The interior of the tetrahedrons and octahedrons contains smaller metal (K^+) cations in the interlayer space. The crystal structure is formed from layers interspaced with the interlayer space which may contain water and/or cations. These are held together by electrostatic or van der Waals forces. Smectites are strongly expanding three-sheet phyllosilicates. The charge of the three-sheet layer equals 0.5 to 1.2.

Examples of ideal formulae of the common smectites are:

montmorillonite	$M^+_{x+y}(Al, Fe^{3+})_{4-y}(Fe^{2+}, Mg)_y[Si_{8-x}Al_xO_{20}](OH)_4.nH_2O$
beidellite	$M^+_xAl_4[Si_{8-x}Al_xO_{20}](OH)_4.nH_2O$
nontronite	$M^+_xFe^{3+}_4[Si_{8-x}Al_xO_{20}](OH)_4.nH_2O$
saponite	$M^+_xMg_6[Si_{8-x}Al_xO_{20}](OH)_4.nH_2O$

where M^+ represents adsorbed alkali cations in the interlayer space (mainly Na^+). The alkaline earth metals, Ca^{2+} and Mg^{2+}, may occur. The product $M_{x/2}^{2+}.M^{+}$ is usually 0.7.

(iii) **The vermiculite group** is the expanding three-sheet phyllosilicates. The T:O ratio equals 2:1. The charge of the three-sheet layer is 1.2 to 1.8. An example of an ideal formula of the trioctahedral vermiculite is $(Mg, Fe^{2+}, Fe^{3+})_6[(Si>Al)_8O_{20}](OH)_4.nH_2O$.

(iv) **The micas** are the three-sheet phyllosilicates where the T:O ratio is 2:1. The overall charge is less than or equal to 2. The formula of a common mica clay is $K_{<2}Al_4[(Si_{>6}Al_{<2}](OH)_4.nH_2O$ for illite. The charge is zero. One subgroup is pyrophyllite $Al_4[Si_8O_{20}](OH)_4$. Another subgroup is talc $Mg_6[Si_8O_{20}](OH)_4$.

(v) **The chlorites** are four-sheet micaceous non-swelling silicates with a T:O of 2:1:1. The charge is 1.1 to 3.3. An example of a dioctahedral chlorite is donbassite: $Al_4[Si_8O_{20}](OH)_4Al_4(OH)_{12}$. Chlorite is also layered but has additional hydroxide sheets such as $Mg(OH)_2$ between the 2:1 silicate layers (Williams and Haydel, 2010).

(vi) **The palygorskite and sepiolitegroup** have a fibrous layered structure. The formulae are $Mg_5[Si_8O_{20}]$ $(OH)_2(OH_2)_4.4H_2O$ and $Mg_8[Si_{12}O_{30}](OH)_4(OH_2)_4.nH_2O$.Sepiolite is fibrous in nature and, unlike the smectites, it is non-swelling. The T:O:T layers are held together by strong covalent bonds with nanometre-dimension separation of the fibres. Fig. 2.4 gives a diagrammatic presentation of the common sheet silicate structures.

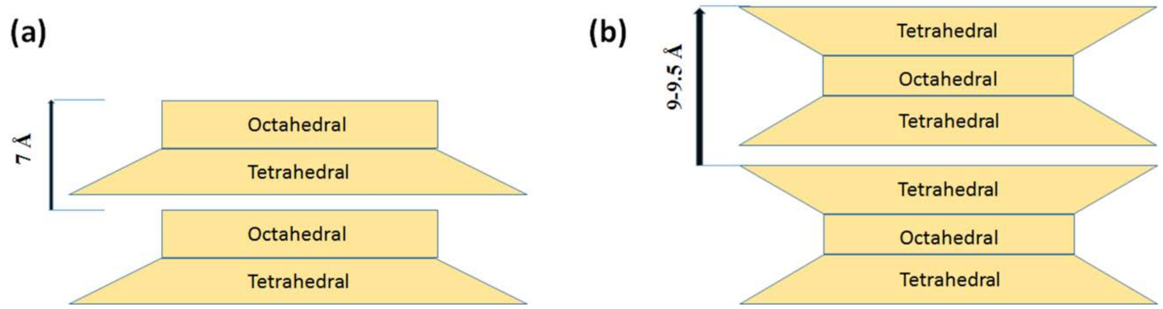


Figure 2.4: Phyllosilicates: a T:O dioctahedral in (a) and a T:O:T trioctahedral in (b)

On the other hand, the T:O:T interlayer may be occupied by cations. The T:O:T silicate may have an additional interlayer octahedral sheet as in chlorite, hence it is described as 2:1:1. This is illustrated in Fig. 2.5.

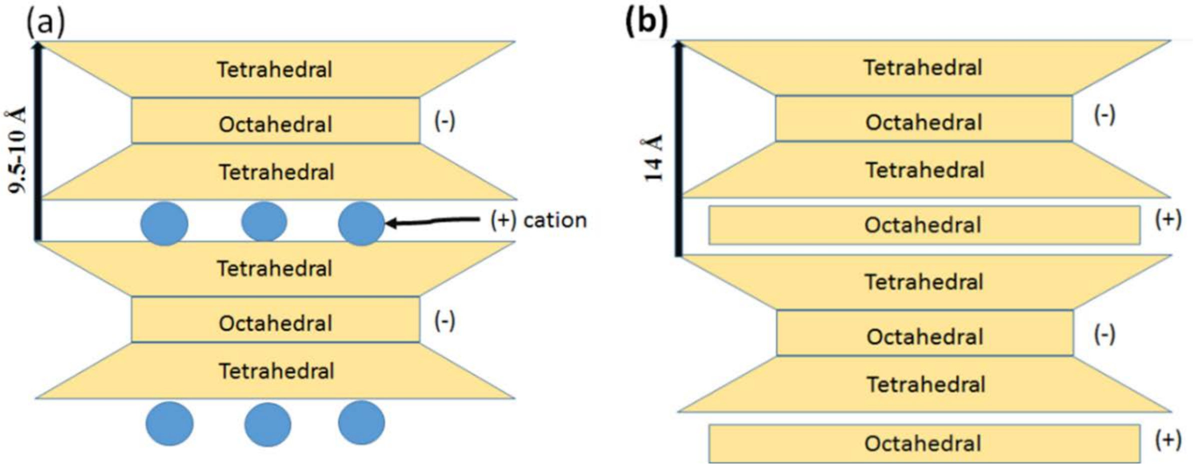


Figure 2.5: A T:O:T plus interlayer cations in (a) and a T:O:T with an additional interlayer octahedral in (b)

2.3.6 Clay mineral properties

The properties of clay minerals are attributable mainly to the net electrostatic charge of the structural layers due to ionic substitutions in the sheets of the clay minerals. These charges may be on the surface or on the edges. Cation exchange capacity (CEC) is the parameter used to gauge this property. It is expressed in milli-equivalents (meq) per 100 grams or centimole (cmol) per kg of material. There is a substantial variation in the CEC values of the various clay minerals: dioctahedral kaolinite is 3–15 me/100 g and trioctahedral smectiteand the minimal exchangeable cations to the surface and the broken edge –OH groups. The cations adsorbed in the interlayer space balance the electrostatic negativity. Common exchangeable cations in the interlayer space are K^+, Na^+, Ca^{2+}, Mg^{2+} and H^+. The latter may be easily replaced by desirable cations in spite of the energy involved. In the three-sheet clay minerals, the ratio of tetrahedral to octahedral sheets equals 2:1; the resultant negative charge varies from 0 to 2 units. The ionic substitutions in the structure are influenced by the chemistry of the environment and the kinetics of reactions occurring during the formation and development of clay mineral

Table 2.2: Minerals and their functions

Mineral	Function
Phyllosilicates	Opacity and high sorption capacity. Examples are smectites, palygorskite, sepiolite, kaolinite, talc, mica
Oxides	High refraction index. Examples are rutile, periclase, zincite
Hydroxides	Brucite, gibbsite, hydrotalcite
Borates	Antiseptic and disinfectant properties as in borax
Nitrates	High water solubility with non-toxic K^+ as in niter (saltpetre)
Phosphates	Act as mineral supplements to hydroxyapatite
Sulphides	Keratolytic reducers such as greenockite
Elements	Antiseptic and disinfectant capacity. Example is sulphur
Chlorides	High water solubility and release of Na, K or Mg.Examples are halite, sylvite
Sulphates	High astringent capacity. Examples are epsomite, mirabilite, melanterite, chalcanthite, zincosite, goslarite, alum
Carbonates	Act as mineral supplements. Examples are calcite, magnesite, hydrocincite, smithsonite

Carretero (2002), Konta (1995),Carretero *et al.* (2013) andMatike *et al.* (2014) gave an exhaustive account of different clay minerals and their functions. Clay minerals feature in various cosmetic products (Carretero, 2002; Konta, 1993a), (López-Galindo *et al.*, 2007). Physicochemical properties are considered important in the use of clay minerals for therapeutic purposes (Carretero and Pozo, 2010; Schoonheydt and Johnston, 2006). The authors also gave an exhaustive account of the therapeutic activity or cosmetic action of the clays. Matike *et al.* (2011) emphasized the permissible cosmetic pH and the resultant effect on the skin's acid mantle.

Carretero and Pozo (2010) also gave a detailed account of the therapeutic effect and cosmetic action of clay minerals varying from cosmetic creams, solar protectors, dermatological protectors, anti-inflammatories to gastro-intestinal protectors. Table 2.3 gives some examples of minerals and clay minerals with their specific functions (compiled from Carretero and Pozo (2010); K. Belaroui (2002); Konta (1995). The therapeutic minerals belonging to the various groups are also indicated in the Table 2.3.

Table 2.3: Physicochemical properties of inorganic and mineral cosmetic ingredients

Mineral	**Activity**	**Physical, physicochemical and chemical features**
Alum	Deodorants	High astringent capacity
Rutile	Solar protectors	High refractive index
Gibbsite	Moisturizers, creams	Flowability, anticaking, compressibility
Kaolinite	Cosmetic creams	Opacity and high sorption capacity
Ca-smectite	Cosmetics	Astringent and absorbent

Engelbrecht (2016) found that the specific surface area (SSA) is affected by the iron oxide content of the clay mineral. The SSA is important in the adsorption by the clay mineral.

2.4 TOXICITY AND SAFETY

There are two aspects of the safety of clays relating to their effect on health. These concern either the use of an ingredient of the product or the whole product itself. Overexposure to clay as a raw material may trigger harmful reactions. This may occur when the raw material is handled during manufacturing or use. On the one hand, some trace metals are essential and may have beneficial effects for humans. Alternatively, a clay-containing product may elicit detrimental or harmful effects.

2.4.1 Toxicity of raw materials and trace elements

Carretero *et al.* (2006) warned about the harmful effects of clay minerals on prolonged inhalation. Several lung pathologies such as cancer, silicosis, pneumoconiosis and mesothelioma may be triggered due to the presence of quartz. Silva *et al.* (2011) state that these clay minerals are typified by high adsorptive capacity which will prove very harmful when in contact with a lung surface. According to the International Agency for Research on Cancer (IARC, 2012), there is sufficient evidence that in humans crystalline silica in the form of α-quartz or cristobalite dust causes cancer of the lungs.

Veniale *et al.* (2007) cautioned about hazardous chemical elements such as As, Cd, Hg, Pb, Se, Tl and others. Passage into the peloid during maturation in waters should be prevented as much as possible. This ensures that none of the harmful elements will pass through during pelotherapy treatment. Recycling of thermal muds is discouraged as this may promote the transmission of ionized radioactive elements which are potentially dangerous for the lungs.

2.4.2 Product safety

Williams and Haydel (2010) emphasized the authentication of product safety and recommend pre-market compliance with the FDA. This action may give safety assurance and authenticity to the product. Silva *et al.* (2011) scrutinized the impact of toxic heavy metals and radionuclides when unintentionally incorporated into cosmetic products. They emphasize that most clay minerals used in formulations may contain some harmful elements, even in trace amounts. These elements may be As, Ba, Br, Cs, Co, Eu, Fe, Hf, Hg, La, Lu, Rb, Sb, Sc, Sm, Ta, Tb, Yb, Zn, Zr and the nuclides are ^{238}U, ^{232}Th, ^{226}Ra, ^{228}Ra, ^{210}Pb and ^{40}K. The authentication may involve identity tests, acidity or alkalinity, microbial limit, water content, amount of acid-soluble substances, amounts of impurities and some chemical limitations and technical properties.

Iwegbue *et al.* (2016) concurred with the former researchers on the heavy metals, but focus on facial products in Nigeria. These include lip products, eye make-up and face powders. Atomic absorption spectrometry (AAS) tests done on these products yielded mean concentration ranges of 3.1 to 8.4 µg g^{-1} Cd, 1 2 to 240 µg g^{-}1Pb, 9.1 to 44 µg g^{-1} Cr, 18 to 288 µg g^{-1} Ni, 1.6 to 80 µg g^{-1} Cu, 7.9 to 17 µg g^{-1} Co, 2.3 to 28 mg g^{-1} Fe, 12 to 230 µg g^{-1} Mn and 18 to 320 µg g^{-1} Zn. The Ni, Cr and Co were higher than the suggested safe limit of 1 µg g^{-1} for skin protection, while the Cd and Pb were above the Canadian specified limits. The researchers recommend regulatory programmes to monitor the contents of metals in cosmetics imported into Nigeria to curb the excesses of harmful metals such as Cd, Pb, Ni, Cr and Co which may endanger lives. They concluded this after establishing that levels of these metals exceeded the Canadian specified limits, especially for the face powders.

Bocca B (2014) warned about the cumulative effect of impurities contained in make-up for eyes, lips and face. The small amounts added daily may add up to unhealthy levels. The review focuses mainly on Sb, As, Cd, Co, Hg, Ni and Pb as they are banned as intentional ingredients in cosmetic formulations. According to the authors, these elements have draft limits as potential impurities in cosmetics and are regarded as toxic.

Siti Zulaikha (2015) emphasized that the intentional or unintentional presence of harmful ingredients needs to be addressed not only by the regulatory bodies, but also through consumer awareness and pro-activeness. Consumers should enlighten themselves about the side-effects of the cosmetics they use, including becoming familiar with banned chemicals. Unfortunate instances may occur where the harmful ingredient(s) is not listed. The writers further advise that the growth of the cosmetic industry and the quest to produce low-cost products should not be allowed to compromise quality and safety.

Siti Zulaikha (2015) further indicated that the “silent” dangers are the ones released by hydrolysis after the product has been formed, such as formaldehyde in rinse-off cosmetics such as shampoo. Some heavy metals may also be released by the breakdown of ingredients or environmental contamination during the manufacturing process. Some noxious substances are allowed at stipulated limits, such as talc with pigments and zinc or magnesium stearate as binder in pressed powder or eyeshadow. The parabens would definitely be included in this category as they are only safe for use in cosmetic products at levels up to 25 % m/m. The list goes on to include metals such as Cu, Al, Au or Ag powders which are deliberately incorporated to produce a specific effect. This includes those heavy metals from metallic devices used during the manufacturing of products. Decorative products such as lipstick and eyeshadow are the most risky. This is aggravated by the inefficient decontamination of raw materials.

2.5 OTHER ASPECTS OF CLAYS OR CLAY MINERALS

The use of clays is not limited to cosmetics. Other applications include medicinal, artwork, cultural symbolism and traditional purposes.

2.5.1 Medicinal applications

According to Carretero *et al.* (2013), in ancient times Greek doctors used clays to treat malaria, stomach and intestinal ailments. In addition, the authors mention that “pink earth” was used for fevers on oral ingestion. Furthermore, in modern pharmaceutical formulations these minerals may be the active ingredients in antacids, gastrointestinal protectors, antidiarrheals, dermatological protectors, anti-inflammatories and local anaesthetics. Alternatively, they may also be used as excipients (often referred to as bulking agents or fillers), as emulsifiers, thickeners, binders and anticaking agents. The authors also highlight their use as peloids to relieve pain due to chronic rheumatic inflammations, to treat cellulite and to manage lipodytrophies.

Davies and Mundalamo (2010) deliberated on the link between an excess or deficiency of trace metals and mineralisation processes. They relate that to the local and regional distribution of diseases in man and animals in South Africa. They propose that future research in medical geology should strive to detect, verify and document such relationships for a better diagnostic spectrum including therapy.

Williams and Haydel (2010) proposed that mud spas may also provide heat to stimulate circulation for rheumatism treatment (Carretero and Pozo, 2010). They quote the untested work of Line Brunet de Courssou (a French humanitarian working in the Ivory Coast of Africa) on the use of clay minerals to treat Buruli ulcer disease. This is known as a flesh-eating infection caused by *Mycobacterium ulcerans*. Nevertheless, the untested work by Brunet de Courssou provided a stimulus for the proposed *in vitro* testing of the effect of “healing” clays on a broad spectrum of human bacterial pathogens. The Fe-smectite-rich clay was associated with healing Buruli. The pH and oxidation state played the role of buffering and controlling the solution chemistry and redox-related reactions at the bacterial cell wall. The researchers differentiate between “healing clays” (using various physical properties) and antibacterial clays. The latter are known to kill pathogenic bacteria, although the mechanism is unknown. The authors also deliberate on geopathy for the remedy of a physiological response to mineral (Fe, Zn) nutrient deficiencies. This may also ease psychological problems, including anxiety, stress and obsessive compulsive disorder (OCD). There is a general consensus that alternative antibacterial agents are needed to overcome the resistance that some bacteria have developed to antibiotics.

2.5.2 Artwork

Pahl (1974a) reported on samples of Iron Age pottery in south-east Botswana. The unique patterns have been useful to archaeologists as a guide to identifying archaeological sites and in some cases for categorizing the different traditional groups. Even broken pieces of pottery have provided leads. According to this author, the pottery was painted black with *letsoku* (powdered manganese ore) and red with *sibilo* (iron oxide). The painting was done along an incised arcade (*sethunya*), with the black and red colours alternating according to the pattern.

Krasilnikov and Tabor (1999) wrote on the use of *kulesta*, defined as ochre used as a painting material in Bulgaria.

2.5.3 Cultural symbolism

Matike *et al.* (2014) presented a comprehensive review on the use of clays by African tribes to establish uniqueness and social status, examples being the red *ortijze* used by the Himba of Namibia, and the white clay used by the Surma and Karo tribes of south-west Ethiopia. In addition, clays may be used to symbolize a change in status. This could be graduation from initiation school. The Xhosa and Pondo use *ingceke* or *ikota* on the whole body during initiation. *Imbola* is used for males' faces and feet and *umdiki* for females' faces and necks at the end of initiation. The Maasai of Kenya use *thriga* at the completion of their initiation.

Bishop (1984) gave an account of the southern Sotho hat called *modianyewe*. Traditionally, *modianyewe* means "he who executes judgement in court". The hat was worn only by older men such as chiefs and kings who could preside during court hearings. On the other hand, there was also a hat called *mosetla* which could serve as a sun hat or rain hat and was worn by all men and women. Young women were bare headed, plaited their hair and covered it with *sekema* (white clay) or *letsoku* (red ochre) to enhance their beauty.

The Baruya people in Papua New Guinea classify certain clays for specific functions (Krasilnikov and Tabor, 1999). The *cheragwaka* is a red ochre that is smeared on the bodies of girls after menstruation. It may also be used on women after childbirth and on traditional practitioners on graduation. The red *eogwaka* is applied to children at the third stage of initiation.

2.5.4 Traditional beliefs

Krasilnikov and Tabor (1999) expounded on the use of clays for traditional beliefs. The Baruya people in Papua New Guinea use the greenish grey *biwaka* soil from the marshes to paint sick body parts. They believe the action will ward off the evil spirits that cause sickness. The *gwegwaka* soil is used in war as a shield for protection.

2.5.5 Aesthesia

Since cosmetics are designed to enhance beauty, they are supposed to have an attractive appeal to the eye and psychologically draw potential users to buy them. Therefore it is imperative that their physical appearance should appeal to the senses, especially sight. Colour is one of the important attributes and entails the appropriate use of colourants, including pigments. The impact of cosmetics that have a "glow" (iridescence or pearlescence) and/or matt effect is to enhance the basic function of the cosmetic.

Goethite and aesthesia have been linked in the analysis of a gothic sculpture (Konta, 1993b). Authigenic quartz dispersed through a matrix of detrital quartz, mica, kaolinite, rutile, anatase and K-feldspar has produced the stone's pleasing golden ochreous colour.

2.6 PIGMENTS

Pigments are substances intended to impart colour to a surface through adhesion. They may be organic (Ribeiro *et al.*, 2015) or inorganic (Scott, 2016). A pigment and a dye are not the same. A pigment performs its function by reflecting or absorbing certain wavelengths of the visible light. Alternatively, electron or charge transfer may be the operative mechanism by which colour is imparted to an object (Scott, 2016). The current study and discussion revolves around inorganic pigments. These have featured in Egyptian history for various functions including artefacts and cosmetics. Pigments are mixtures of minerals such as hydrated iron oxide with various materials to produce colour ranges from pale yellow to orange and red. The ancient Egyptians dispersed inorganic substances in binders or "vehicles" to produce various coloured pigments (Scott, 2016). The binders ranged from plant gums, animal glues, natural resins, egg whites, beeswax, fats and oils. Malachite $CuCO_3{\cdot}Cu(OH)_2$ and galena (PbS) were extensively used by the ancient Egyptians as binders. Red ochre, goethite (α-$FeOOH$), galena, malachite and others were mixed with the binders to produce various colours such as dark red from carbon black, red ochre, red from calcite and haematite (Fe_2O_3), shades of yellow from orpiment (As_2S_3) and goethite (α-$FeOOH$).

Konta (1995) described the eighth group of clay materials as pigments. They impart colour due to the presence of pigment. In ochres, this is due to the presence of chromogenous elements in the crystal structure such as Fe, Ni or Cr. Heat and drying produce colour variations in these pigments. They are used as coatings together with kaolin in the manufacture of oil and other paints. Common samples are clay ochres containing illite and kaolinite and a few with limonite.

Ancient history revealed the numerous pigments produced by the ancient Egyptians (Scott, 2016). Several shades of reds, pinks and yellows were obtained by mixing red, yellow and brown ochres with minerals such as calcite, orpiment and gypsum (repeating unit of $CaSO_4.2H_2O$). Scott (2016) emphasized the distinction between red ochre (natural substance) and haematite (a pure version of red ochre). In fact it was realised that two-thirds of the collected samples contained one or more iron mineral(s) with strong pigmenting properties. Even those samples with a very high quartz content had a reddish colour caused by the presence of iron oxide.

The trend is continuing with modern cosmetics containing mineral pigments made of iron oxide. They also contain “lakes” which are mineral pigments such as aluminium oxide coated with dyes. They are used subject to FDA approval for safety.

2.6.1 Minerals

Ambrose (2001) refuted the confusion of platinum with ilmenite: “no deposit of ilmenite occurs within hundreds of kilometres of Ladybrand”. It was revealed that there are various regions in northern Lesotho with deposits of $FeTiO_3$. These include Koalabata, (Sekamaneng), Kolo (Sekameng), Monastery Mine (Mpokoane), Liphofung, Lentsoaneng, Ntloanatsoana and Ngope-Tsoeu. This ilmenite is known by the ethnic people as *secama* or *sekama*. The locals are believed to grind it into a powder which is then mixed with fat and applied to the hair. Ambrose (2001) reported on ilmenite, mainly kimberlite, being used during female puberty instruction classes for head decoration. The source for kimberlite was mainly from a river as a constituent of dolerite dykes. The sherds from the Rose Cottage Cave also had some quartz grains whose origin still has to be established. The other confusion was Bechuana for South Sotho. Ambrose (2001) also mistook kimberlite ilmenite, $MgTiO_3$ for $TiFeO_3$. The latter is now known to be a source of TiO_2 which has a sunscreen effect. The sourcing sites have already been indicated at the beginning of this paragraph.

2.6.2 Micas

Micas are non-swelling phyllosilicates or sheet silicates. Examples include 2:1 muscovite and 2:1:1 biotite. According to Carretero and Pozo (2010), their inclusion in cosmetic products imparts iridescence to the skin due to their high reflectance. Furthermore, micaceous muscovite produces a luminous effect on skin when added to moisturizing creams. This enhances the cosmetic impact and skin appearance.

2.6.3 Ochre

Tammy Hodgskiss* (2017) gave an account of the ochre pieces more than 96 000 years old, excavated from Rose Cottage Cave. This was a 20 m long x 10 m wide cave in the Eastern Free State, South Africa. The researchers describe ochre as a range of ferruginous rocks made of red ochre containing haematite (Fe_2O_3). On the other hand, yellow ochre contains hydrated iron hydroxide such as goethite (α-FeOOH). They attempt to make a distinction between ochre as a rock which leaves a coloured streak and ochre as a pigment.

According to different geological preferences and processing techniques, ochre application has been associated with this cave for more than 60 000 years. The latter probably refers to rubbing, grinding and scoring. The authors describe ochre as being useful for various purposes. The powder can be mixed with water or other substances to make an adhesive, a sunscreen and for protection against insects. It can also be used for hide tanning and has potential as a colouring agent for symbolic signalling. It has been inferred that the activities that took place in the cave reveal the cognitive complexity of people at the time. They had the ingenuity to refresh the ability of the ochre to transfer the powder through repeated, alternating wetting and grinding.

That, according to the authors, reveals the complex behaviour in Africa almost 100 000 years ago.

2.7 CLAY MINERAL IDENTIFICATION AND QUANTIFICATION

Knowledge about clays has also advanced partly due to the essential methods of investigation such as particle size distribution, XRD, XRF electron microscopy, thermal analysis and infrared spectral analysis(Konta, 1993a; Kundra, 1991).

2.7.1 Particle size

Soil is a complex structure comprising discrete sedimentary and pedogenic layers. The layers have different particle size distribution (PSD) characteristics. Four basic components are found in soil: minerals, organic matter, air and water. The focus of the current study is on minerals. These are divided into three particle size classes: sand, silt and clay. Sand and silt are small particles of rock and are mainly inert. The main difference between them is their water-holding capacity. Clays are mineralogically different and form at or near the surface of the earth. Most belong to the class of minerals called phyllosilicates formed from breakdown products of other minerals (see Section 2.3.4). PSD aids in the knowledge of soil water movement, soil erosion and soil solute migration. Minerals in clays, silts and sands may be of submicron size. Soil categories are defined based on their particle diameter according to two alternative classification systems the United States Department of Agriculture Soil Classification System (USDA) and the World Reference Base International Soil Classification System (WRB) as shown in Table 2.4.

Table 2.4: Soil categories based on particle diameter

Soil category	Particle size range WRB (µm)	Particle size range USDA (µm)
Clay	Less than 2 µm	Less than 2 µm
Silt	2 µm to 50 µm	2 µm to 63 µm
Sand	50 µm to 200 µm	63 µm to 200 µm

The data in Table 2.4 can be portrayed in a ternary plot based on the USDA textural classification isosceles triangle shown in Fig. 2.6. Each of the apices is defined as 100 % sand, silt and clay respectively. Loam refers to the only soil in which neither sand, silt nor clay predominates and has been identified as the ideal soil. The sum of the composition of any coordinates in the triangle is 100 %. The relative proportions of sand, silt and clay account for the soil texture, which has a role in the nutrient-holding and water-holding abilities of a soil. The soil texture is read off from the point of intersection. The three particle size percentages give the soil composition.

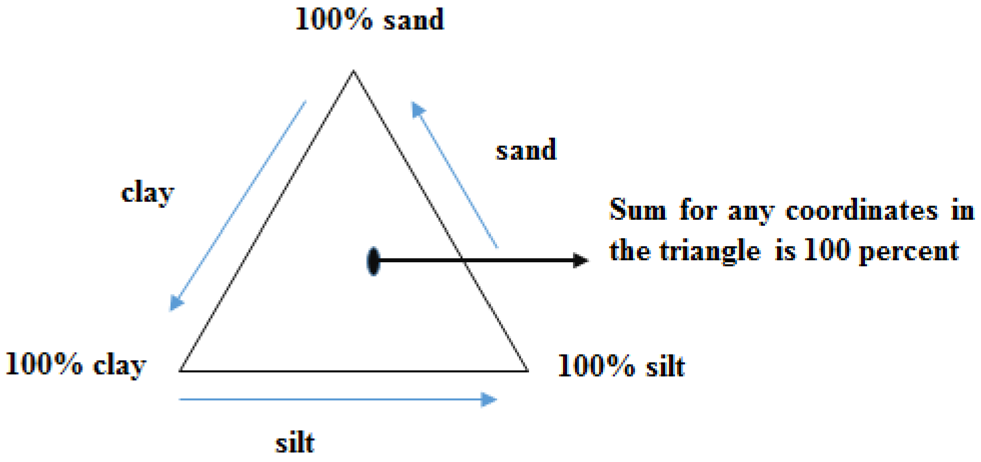


Figure 2.6: Outline of a USDA taxonomy soil textural triangle or ternary plot

Some soil properties are known to result from texture. These are water- or moisture-holding capacity, shrink swell rate and erosion. In addition, the specific surface area (SSA) of each category accounts for their activity. Sand is the least active with the lowest SSA. Pure sand helps to resist compaction and increases porosity. Silt has a higher SSA but it is less than that of clay, which is the most active component. Clay has a large number of chemical charges which may be involved in nutrient retention. Silt is mineralogically like sand but is more chemically and physically active than sand. Quartz (SiO_2), calcium carbonate ($CaCO_3$), feldspar ($KAlSi_3O_8$) and mica-biotite ($K(MgFe)_3AlSi_3O_{10}(OH)_2$ are the typical soil parent mineral materials.

Particle size distribution aids in understanding physical and chemical properties. There is a need to control these aspects tightly in industrial products such as cosmetics and pharmaceuticals. PSD measurements indicate the relative amount and size of particles present according to diameter size.

Laser diffraction such as in a Malvern Mastersizer 3000 may be utilized for particle size measurement. Size distributions of particles from 10 nm up to 3.5 mm are measured. A laser beam is passed through a dispersed particulate sample. The wet dispersion contains a drop of a surfactant which lessens the forces of attraction between touching particles. This gives better particle separation and suspension formation. The angular variation in the intensity of light scattered as a laser beam passed through the wet dispersed sample allows measurement of the particle size distribution. The size of the particles is calculated from the analysed angular scattering density data. The result is reported as a volume equivalent sphere diameter. Smaller angles relative to the laser beam result from scattering by large particles. Conversely, large angles relative to the laser beam result from scattering by small particles, as illustrated in Fig. 2.7 (*Source:* Malvern Mastersizer 3000 brochure: https://www.malvern.com).

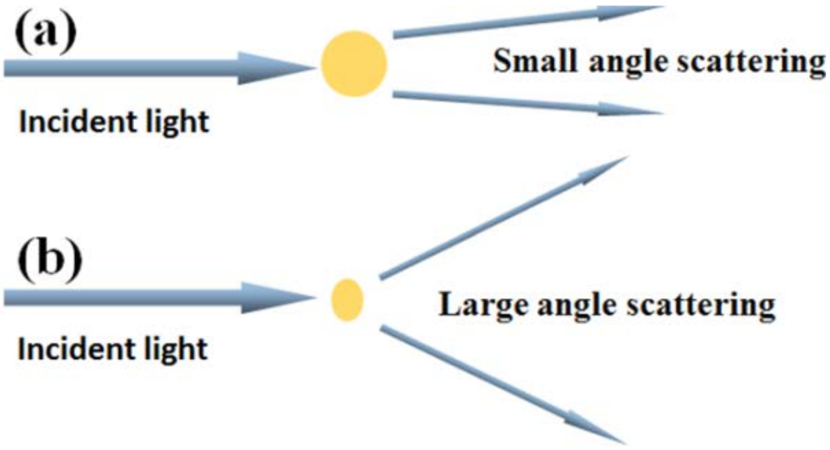
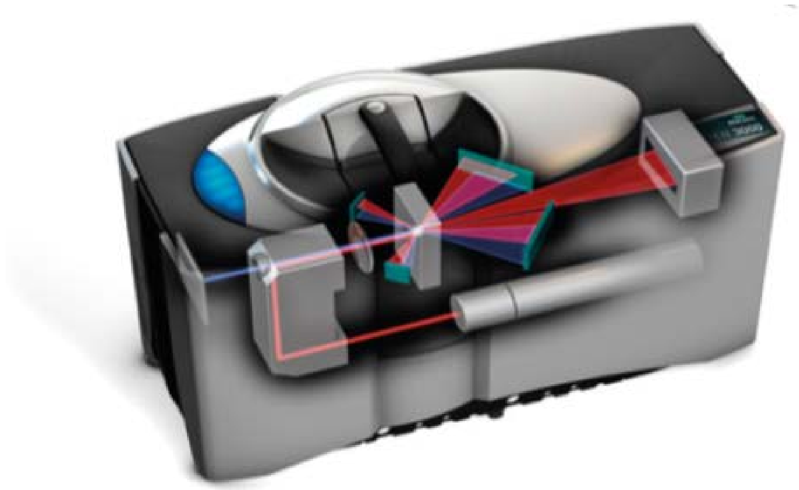


Figure 2.7: Laser beam scattering in large and small particles depicted in (a) and (b) respectively

The Malvern Mastersizer 3000 is equipped to do a sequential combination of measurements with red and blue light sources to measure across the entire particle size range shown in Fig. 2.8 (*Source:* Malvern Mastersizer 3000 brochure: https://www.malvern.com).



Red and blue light sources to measure across the entire particle size range.

Figure 2.8: Advanced focal plane detector in red and the 10 mW solid state in blue light source (*Source:* Malvern Mastersizer 3000 brochure: https://www.malvern.com) and (Institute of Applied Materials, Department of Chemical Engineering, University of Pretoria)

The advanced focal plane detector design is able to resolve very small diffraction angles for large particles. Large diffraction angles for small particles (<100 nm) are measured with a powerful 10 mW solid-state blue light source.

2.7.2 BET (Brunauer Emmet Teller) surface area analysis

Adsorption is the key determinant in the activity of clay minerals. The SSA gives a fair estimation of the extent of adsorption that may take place. Measurement thereof is done using various methods. One of them is the BET surface analyser. This is based on multi-layer adsorption of the nitrogen gas molecules. Furthermore, it is assumed that the surface possesses uniform and localized adsorption sites which behave independently from neighbouring sites as denoted in the Langmuir isotherm. The above allows the determination of the volume of gas that is adsorbed when the surface is covered with a complete unimolecular layer. Nitrogen gas molecules are assumed to be close-packed spheres and each occupies 16.2 Å. This fact and the molar volume are used to calculate the total and specific surface area of the adsorbent or clayey soil as illustrated in the equations that follow:

$$\text{From}: \ S_{total} = \frac{(v_m Ns)}{V}$$

$$\text{Then}: \ S_{BET} = \frac{S_{total}}{a}$$

where S_{total} is the total surface area, v_m the amount of the unimolecular layer of adsorbed gas, N is the Avogadro constant, s is the adsorption cross-section of the adsorbate, V is the molar volume of the adsorbate gas and a is the mass of the adsorbent.

The amount of the unimolecular layer is computed using the BET adsorption isotherm below:

$$\frac{1}{v[(^{P_o}\!/_{P})-1]} = \frac{c-1}{v_m c}\left(^{P}\!/_{P_o}\right) + \frac{1}{v_m c}$$

where P and P_o are respectively the equilibrium and the saturation pressure of adsorbates at the temperature of adsorption, v is the adsorbed gas amount and v_m is the amount of the unimolecular layer of adsorbed gas, and c is the BET constant given by:

$$c = \exp\left(\frac{E_1 - E_L}{RT}\right)$$

where E_1 is the heat of adsorption of the first layer and E_L is the heat of adsorption for the subsequent layers and is equal to the heat of liquefaction, R is the gas constant and T is the absolute temperature.

The BET isotherm may be graphically presented as a linear curve by plotting $\frac{1}{v[(^{P_o}\!/_{P})-1]}$ versus $\left(^{P}\!/_{P_o}\right)$ with the slope given by $\frac{c-1}{v_m c}$ while $\frac{1}{v_m c}$ gives the Y-intercept in the range 0.05 < $^{P}\!/_{P_o}$ < 0.35. This implies that:

$$\frac{1}{v_m c} = y$$

$$\frac{c-1}{v_m c} = m \Rightarrow v_m = \frac{c-1}{mc}$$

2.7.3 Colour test

The Munsell colour system utilizes three attributes of colour, namely hue, value and chroma. These are represented in Fig 2.9 as being mutually perpendicular to each other. The system was adopted by the USDA as the official soil colour system in the 1930s.

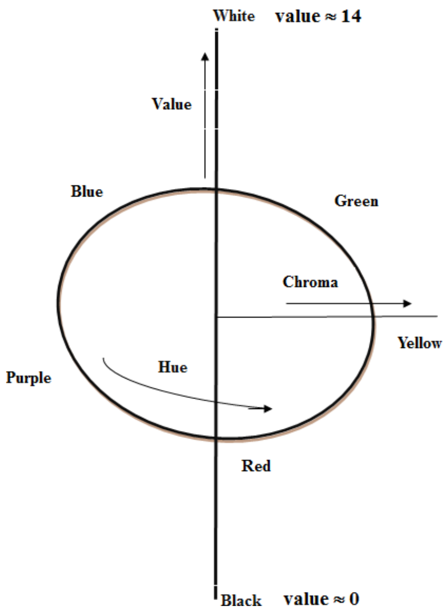


Figure 2.9: Schematic presentation of the Munsell system – hue, value and chroma

The Hue scale is a means of defining differences and overlaps between various fields of colour. Hence every spatial difference on the scale corresponds to the visual difference perceived by the eye. Hue is measured around a horizontal circle made up of five principal hues: red (R), purple (P) and yellow (Y). Intermediate hues are positioned halfway between the main hues, namely RY, YG, GB, BP and RP. Each of these ten steps is broken into ten sub-steps to yield 40+ hues. The main hue is labelled 5 and progresses in increments of 2.5 units such as 5R surrounded by 2.5R, 7.5R and 10R as illustrated in Fig. 2.10.

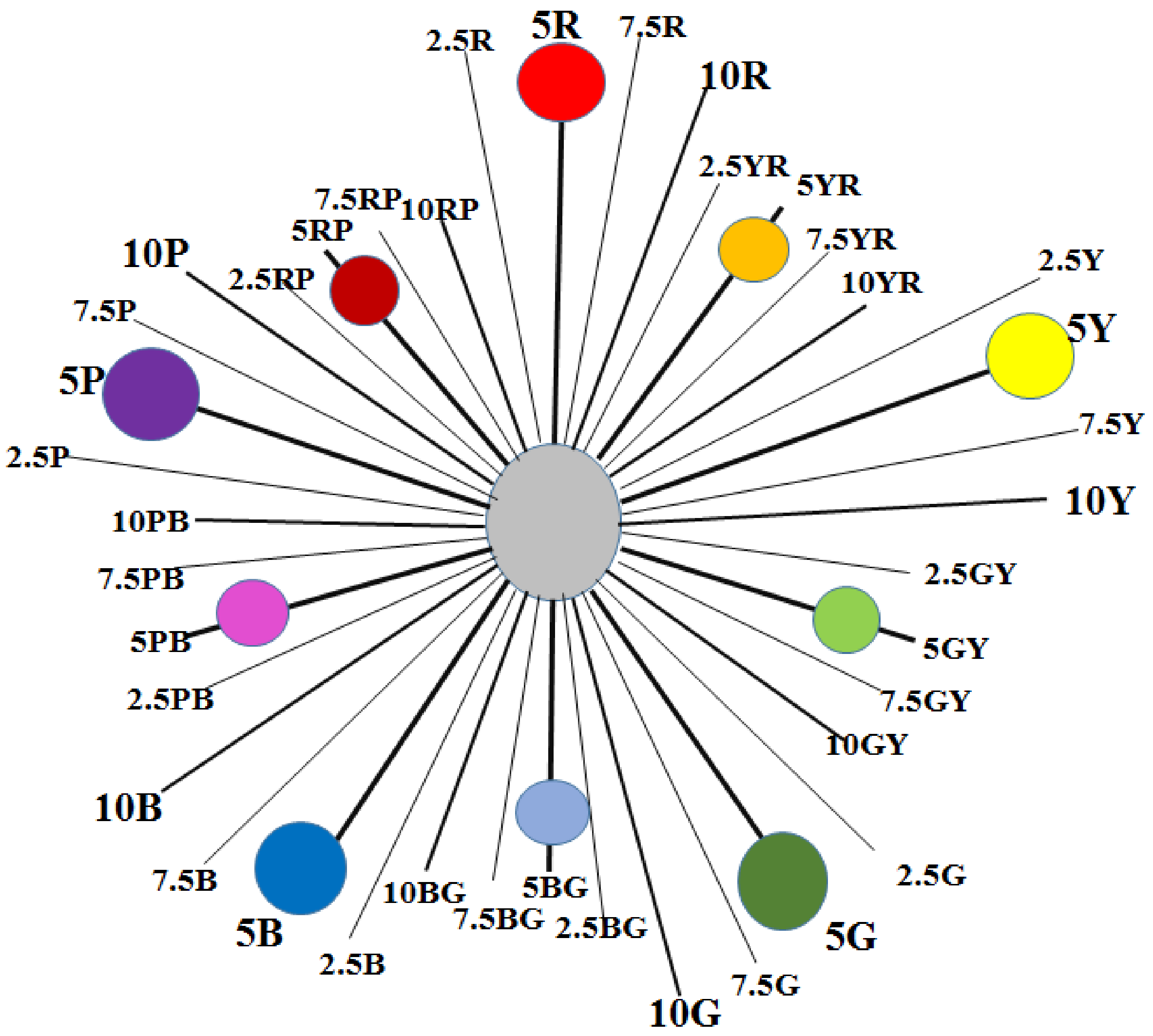


Figure 2.10: A detailed horizontal representation of the Munsell hue component. The central grey area represents a neutral area where complementary colours have been mixed additively with the grey colour

Value refers to the lightness or darkness of a colour. It is measured in a vertical line through the centre of the hue circle. The bottom of the vertical line is equivalent to the colour black which is assigned a value of zero (0). The top is white and is assigned a maximum value of 14. In practice, the above-mentioned values are four and ten respectively.

Chroma refers to the intensity (linked to saturation) and purity of the colour, that is, weak or strong. It is measured radially from the centre or through the radius of the hue circle. Lower chroma implies less pure and more washed-out as in pastels. There is no upper limit for chroma, with the intense vibrant solid colours around 8 and pastels with a lower chroma (around 0 to 4).

A colour is fully specified by listing the three numbers for hue, value and chroma in that order. An example of its application is for a purple of medium lightness and fairly saturated – then the colour is 5P 5/10. This means that the colour is in the middle of the purple hue band, 5/ means medium value and /10 is the chroma. An example of red soil is described by 10 YR 4/6 and Red.

Soil mineralogy has an influence on soil colour. Various soil colours are due to several iron minerals. These result from chemical and biological weathering, mainly redox reactions. Elements combine into new colourful compounds during weathering. Iron forms secondary minerals of a yellow or red colour; organic matter decomposes into black and brown compounds; manganese, sulphur and nitrogen into black mineral deposits. Colour intensity variations may result from different aerobic and anaerobic conditions. Colour may be used to predict soil characteristics, determine the origin of a soil's parent material and as an indication of wetness and waterlogged conditions. It may also serve as a qualitative means of measuring the organic, salt and carbonate contents of soils.

2.7.4 pH measurement

pH is the measure of acidity or alkalinity of the soil. The molar hydrogen ion concentration in an aqueous solution is measured on a pH meter. The latter operates like a voltmeter. It compares the sample voltage with that of a reference standard. The difference between them is used to deduce the difference in pH. The pH meter is composed of a moving coil meter or a numeric digital display on an amplifier and an electrode(s) for insertion into the sample solution. The electrode (modern pH meters) has two probes in one. The glass electrode or silver-based wire in a KCl solution is housed in a glass membrane made from a special glass containing metal salts (mainly Na and Ca). Alongside and inside is the reference electrode which has a KCl wire suspended in a KCl solution. The electrode is insensitive to pH changes.

Prior to use, the pH meter is calibrated with known pH standard solutions to ensure accuracy of measurement. The electrode is dipped long enough into each solution to allow equilibration of solution ions with electrode surface ions for stable measurements. Rinsing with deionized water in between readings prevents cross-contamination. The glass bulb has a built-in sensor selective for changes in H^+ ion concentrations. These are detected by the amplifier as a potential difference. This then is converted to pH according to the Nernst equation:

$$E = E_o - \tfrac{RT}{nF}(\ln Q)$$

where Q is the reaction quotient, *ln* is the natural logarithm, n is the number of moles electrons exchanged, F is the Faraday constant, T is the absolute temperature (K), R is the gas constant, E is the cell potential and E_o is the standard electrode potential at 25°C. At constant temperature, RT/F has a constant value and equals 0.0591 at 25°C when combined with the conversion factor for *ln* to log.

$$E = E_o + 0.0591 \log \tfrac{[H_{inside}]}{[H_{outside}]}$$

The above is the form of the Nernst equation for the full cell from half cells present on the inside and outside of the glass pH electrode. The above equation may be defined in terms of pH where pH = -log $[H^+]$.Then:

$$E = E_o + 0.0591(pH_{outside} - pH_{inside})$$

Since the pH inside is constant, it can be combined with the standard electrode potential:

$$E = E_o^{''} + 0.0591(pH_{outside})$$

The above form of the Nernst equation describes the behaviour of the glass electrode for pH measurements. pH values range from 0 (acidic) to 14 (basic), but for soils the healthy range is narrower, namely 3.5 to 9.5. This means that at 25°C, a pH 0f 9.5 has $10^{-9.5}$moles (pH = -log $[H^+]$) of hydrogen ions per litre of solution. This implies that there are $10^{-2.5}$ moles per litre of OH^-.The role of soil pH is the removal or replacement of certain ions. High acidity corresponds to toxic acid-forming amounts of Al and H. The base-forming cations are expressed as a base saturation percentage. Cation exchange capacity minus acidity equals base saturation in appropriate units. The presence of some cations may impart buffering capacity which is proportional to the soil CEC.

2.7.5 X-ray analysis

The advent of X-ray analysis provided a breakthrough for the qualitative and quantitative analysis of clay minerals. The essential parts of the diffractometer are the X-ray tube which is the source of X-rays, incident beam optics to condition the X-ray beam before it hits the sample. The sample, sample holder and the receiving side optics conditions the X-ray beam after it has encountered the sample. The goniometer which serves as the platform that holds and moves the sample, optics, detector and the tube. The detector which counts the number of X-rays scattered by the sample.

The sample is irradiated by polychromatic X-radiation from an X-ray tube. The elements in the sample are excited to emit their characteristic radiation. This involves several emission lines referred to as K (innermost) and L lines shown in Fig.2.11. The lines in X-ray emission spectra involve electron jumps down to a vacancy or hole in the inner shells of an atom. The hole is created by the emission of an electron on irradiation with polychromatic X-radiation from an X-ray tube.

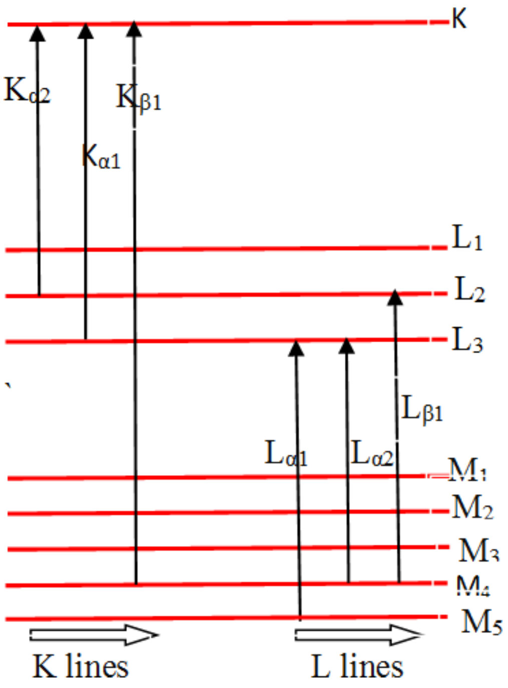


Figure 2.11: Major characteristic lines and their electronic transitions.

The spacing of atoms in crystal lattices is of the same order (0.1 to 100 Å) as the X-ray radiation. This has been used to relate the spacing between atoms, d_{hkl}, in a crystal to the angle

θ, at which X-rays are scattered when they strike the crystal. Constructive interference of beams occurs when A, B and C are in phase or when (DE+EF)/λ = *n*, the order of diffraction as shown in Fig. 2.12. The latter is an integer, *n* 1,2,3…

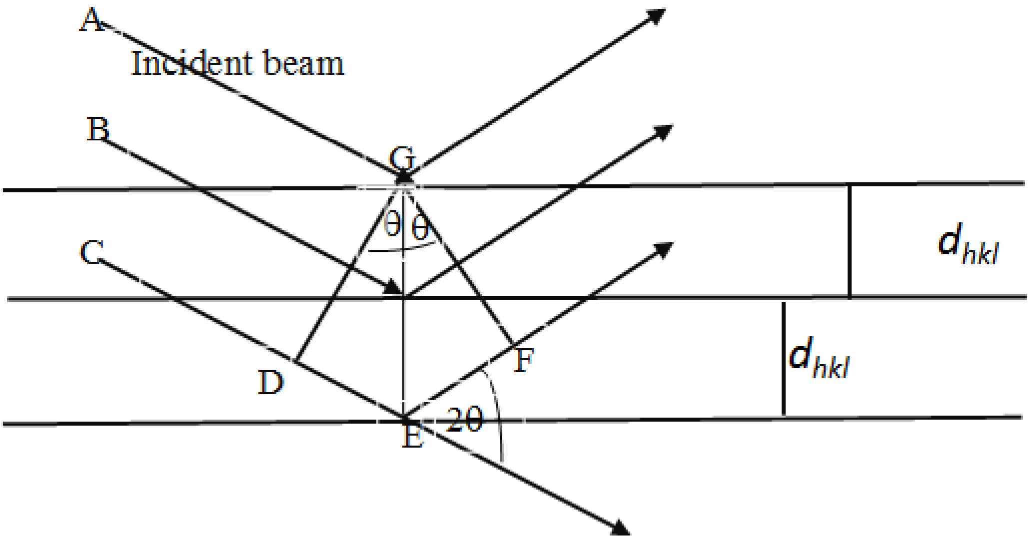


Figure 2.12: Two parallel scattering planes separated by the inter-planar distance d_{hkl}. Three beams (A, B and C) in phase striking the crystal planes.

The beams are separated into individual wavelengths through diffraction by an analysing crystal of suitable d-spacing. The basal spacing or d-spacing between equivalent crystal planes is measured from the specific angle at which they diffract the X-rays of known wavelength. This is done according to Bragg's law. Constructive interference occurs when the conditions satisfy the Bragg or von Laue equation:

$$n\lambda = d\sin\theta$$

where λ is the wavelength of the electromagnetic radiation, *d* the inter-planar distance and θ is the observation angle. The elements are then identified on the basis of their emission lines and hence qualitative analysis is enabled.

The principles underlying **XRD** analysis are detailed in Hillier (2000). These are based on the constructive interference of monochromatic X-rays and a crystalline sample. These rays are collimated and directed to the sample which rotates with the detector in the path of the collimated X-ray beam at an angle θ while the detector is mounted on an arm to collect the diffracted X-rays and rotates at an angle of 2θ in a goniometer to collect data at 2θ angles.

The variation of angle θ has to conform to Bragg's law conditions that no two minerals can have identical inter-planar distances for the angle of diffraction to be used for identification. This implies that each mineral can produce a characteristic set of reflections at values of 2θ corresponding to the inter-planar distance of the prominent atomic planes.

Quantitative analysis involves both the wavelength and the intensity of the emitted radiation. The latter has to be measured accurately using the scintillation or proportional counter. The larger the relative intensity of the emission line, the greater the content of respective element in the sample. Calibration standards are essential to correct for the differential absorption and the inter-elemental excitation effects in the sample. In cases where the matrix of the element is not known, compensation, attenuation and absorption correction methods may be used. These involve external, internal standards, dilution, thin films and scattered intensity and emission transmission methods respectively.

X-ray fluorescence (XRF) has emerged as a valuable physical method for qualitative and quantitative multi-element compositional analysis (Kundra, 1991). In addition, non-destructive and minimal sample preparation is required. The writer lists the XRF components as excitation sources, dispersion devices, detectors and data reduction. The XRF method is supposed to be reasonably sensitive and detection limits for most of the elements are in the low ppm range. Fluorescence refers to a process in which the re-emitted radiation is of a different energy from the absorbed one. XRF is based on the principle that when individual atoms are excited by an external energy source, they emit X-ray photons with a characteristic energy or wavelength. The elements present may be identified and quantified by counting the number of photons of energy re-emitted from the sample.

Moseley expanded on the Bohr model of the atom in which the frequency of light emitted by atoms is proportional to the square of the charge on the nucleus, Z. He further concluded that the K_α line corresponded to the most intense short wavelength line in the X-ray spectrum of a particular element. This yielded Moseley's law:

$f = \left(k_1 \cdot (Z - k_2)\right)^2$ i.e. eiher $\frac{1}{\lambda}$ or $f \propto Z^2$

Where f is the frequency of the observed X-ray line and Z the atomic number

k_1 and k_2 are constants that depend on the type of line i.e. K or L and are fractions of the Rydberg constant. The elements present may be identified and quantified by counting the number of photons of energy re-emitted from the sample.

2.7.6 Scanning electron microscopy (SEM)

Morphological studies constitute complementary methods to X-ray analysis. Bohor and Hughes (1971) indicated that SEM is ideal for studying the shape and structure of clays. The uniqueness of SEM lies in its ability to reveal inter-particle relations, such as interlocking and interpenetration features, aggregate arrangement (face-to-face versus edge-to-face) and shrinkage (drying) features. This SEM feature adds to the speed and ease of operation, and offers a high magnification and great depth of focus for fine-grained materials and surfaces.

SEM is composed of an electron optical column, a vacuum system, a signal detection and a display. The electron optical column consists of an electron source to produce electrons, magnetic lenses to de-magnify the beam, magnetic coils to control and modify the beam, and apertures or holes to define the beam and prevent electron spray. The vacuum system is made up of a chamber which holds vacuum pumps to produce a vacuum, valves to control the vacuum and gauges to monitor the vacuum. Lastly, the detectors collect the signal and electronics which produce an image from the signal.

SEM is based on the thermo-ionic emission of electrons in the inner shells of the sample. The emission is triggered by heating the tungsten filament in a vacuum with an electron gun. The scanned samples are made electrically conductive at the surface and are electrically grounded to prevent accumulation of electrostatic charge. Conductive materials for specimen coating include carbon graphite and gold. The accelerated and finely focused electron beam bombards and scans the sample surface. The electrons interact with atoms in the sample. These produce various signals that contain information about the surface topography and composition of the sample surface. The action causes the secondary electrons to be sent to the detector. These are then processed into a SEM image, referred to as a micrograph. An example of a micrograph is depicted in Fig. 2.13.

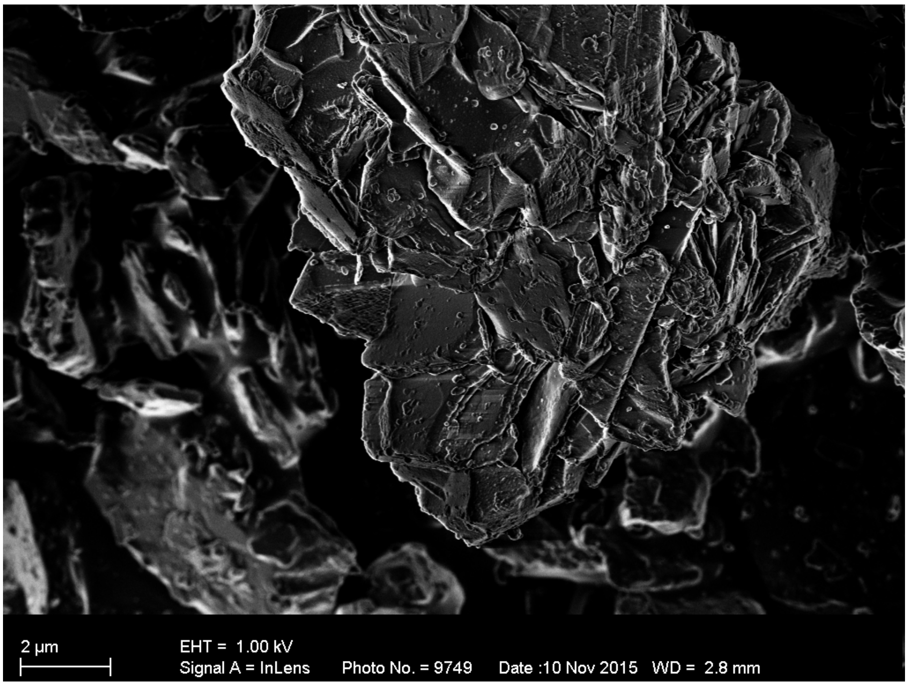


Figure 2.13: An example of a micrograph

2.7.7 Thermal analysis

Thermal methods are based on characteristic temperature regions in which mass loss occurs. An example is when a mineral loses structural water as in thermogravimetric analysis (TGA). TGA can be applied to determine a material’s characteristic decomposition patterns, thermal degradation mechanisms or reaction kinetics, organic content (volatiles) and inorganic content (ash) estimation. A crucible is used such that there is an exchange of materials between the sample and the immediate environment. The results are presented as a thermogravimetric curve with the mass loss or percentage of initial mass on the y-axis versus the temperature or time curve. The plot can also be given as the rate of mass loss versus the temperature curve.

Generally, a TGA curve has the following features: a plateau or horizontal portion indicating constant sample mass, a curved portion whose steepness indicates the rate of mass loss and an inflection at which (dm/dt) is a maximum. The last portion of the thermogram is usually characterized by a stable mass at the maximum temperature where the reaction is considered to be complete. Thermal degradation of clays proceeds via four steps separated by three mass losses. These steps involve loss of H_2O, loss of CO_2 and/or organics, and then loss of inorganic carbonates(Boulingui *et al.*, 2015a). Moisture is assumed to be lost from the onset up to about

100°C. The loss of water of crystallization occurs above 100°C. Heating in air may result in mass loss over the temperature range 200°C to 450°C. This is often associated with the oxidation of organic substances present (Boulingui *et al.*, 2015a; Kristl *et al.*; Smidt and Lechner, 2005). The previously mentioned area may serve as an estimate of the loss on ignition (LOI). However, goethite decomposes into haematite at around 300°C (Song *et al.*, 2014). In addition, this region overlaps with the afore-mentioned inorganics region, implying the possibility of some inorganic degradation. The region ranging between 500°C and 700°C is attributable to the decomposition of inorganic carbonates. The subsequent plateau signals the completion of the thermal degradation. An example of a thermogram is shown in Fig. 2.14.

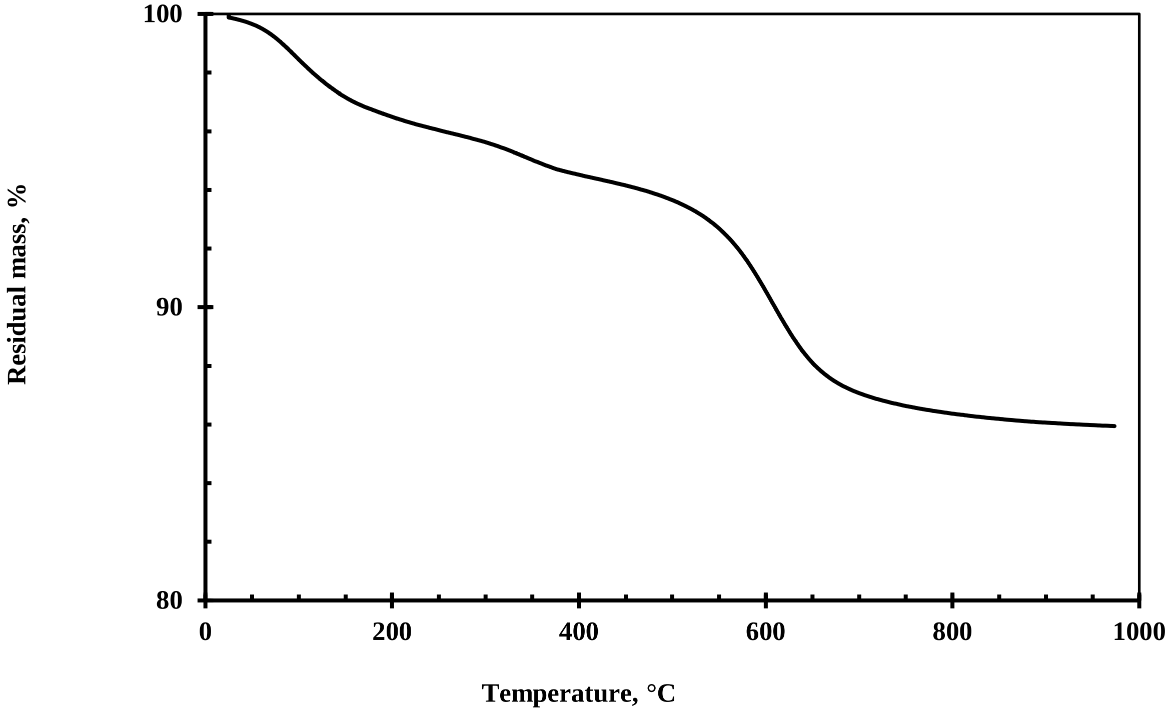


Figure 2.14: Thermal degradative steps in a thermogram

2.7.8 Infrared spectroscopy

According to Petit and Madejova (2013), the vibrations of atoms in a mineral are sensitive to its chemical composition, isomorphous substitution or structural modifications. This attribute makes Fourier transform infrared spectroscopy (FTIR) a most informative technique for probing the chemical composition of inorganic or organic substances. The technique involves the interaction of infrared (IR) radiation with vibrational and rotational transitions in molecules between vibrational energy levels. FTIR is sensitive to asymmetrical stretching or bending and rotations that change the dipole moment (Coates, 1996).

The sample will absorb at characteristic wavelengths providing a spectrum that is unique for every compound. Each compound spectrum has its characteristic fingerprint region, around 500–1500 cm^{-1}, due to intra-molecular forces that are highly specific for each material. The result is then compared with known spectra measured under similar conditions. The detailed underlying principles of attenuated total reflectance Fourier transform infrared spectroscopy, ATR FTIR, are outlined in (Li *et al.*, 2007) and (Pipino *et al.*, 1997). These authors stated that ATR FTIR utilizes the interaction of infrared light with the sample from an internal surface of an ideal crystal with a refractive index from 2.38 to 4.01 at 2000 cm^{-1}. Diamond is the preferred choice of crystal because of its durability and chemical inertness with a refractive index of 2.4 at 1000 cm^{-1}. The ATR-FTIR evanescent wave is depicted in Fig. 2.15.

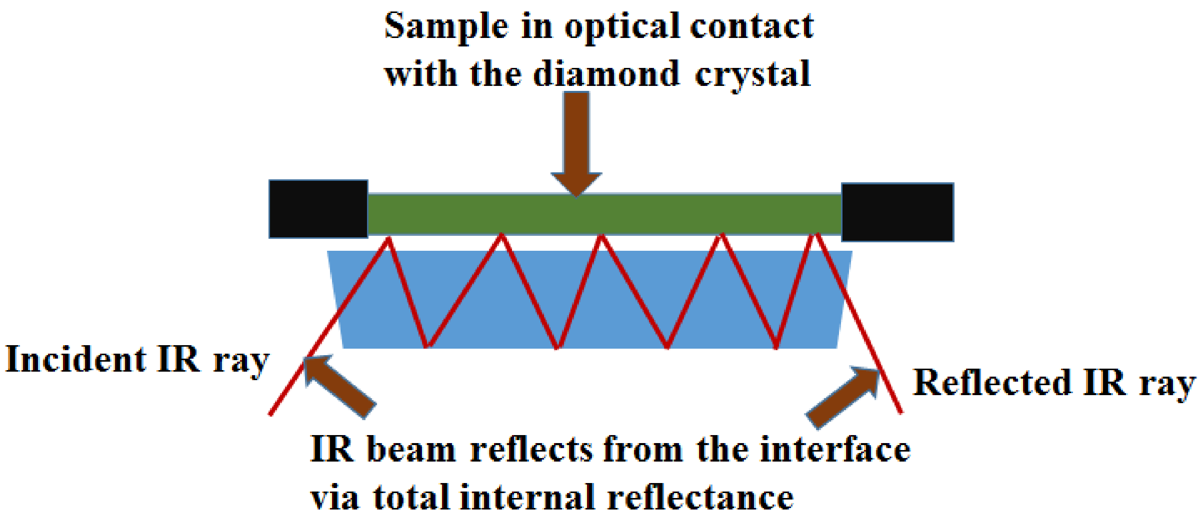


Figure 2.15: The evanescent wave representing total internal reflectance in ATR-FTIR

The refractive indices of the crystal and the sample govern the basic phenomenon of the ATR technique according to the following equation:

$$\theta_c = \sin^{-1}\left(\frac{n_2}{n_1}\right)$$

where n_1 is the crystal refractive index; $n_2$is the sample refractive index and $\theta_c$is the critical angle.

Furthermore, the crystal refractive index must be greater than that of the sample to allow internal reflectance to take place and not light transmission. Five to ten internal reflections may take place depending on the crystal thickness and the angle of incidence. In regions where the sample absorbs radiation, the incident IR beam will be attenuated or weakened and will exit the opposite end of the crystal for processing as an IR spectrum in the IR spectrometer. The crystal requires good optical contact with the sample as the transient IR beam can only extend beyond the crystal depth of 0.5 µ–50 µ into the sample. The detector senses variations in energy versus time for all wavelengths simultaneously and these are converted to intensity versus frequency or wavenumber spectrum.

The IR absorption spectrum results from the interferogram where transmittance or intensity is plotted against the wavenumber or wavelength. The ratio of the radiant power transmitted by the sample (I) relative to the radiant power of incident light on the sample (I_0) results in the quantity of transmittance (T). Absorbance (A) is the logarithm to the base 10 of the reciprocal of transmittance:

$$A = \log_{10}\left(\frac{1}{T}\right) = -\log_{10} T = -\log_{10}\left(\frac{I}{I_0}\right)$$

An infrared spectrum, that is a plot of transmittance against wavenumber, may appear as shown in Fig. 2.16.

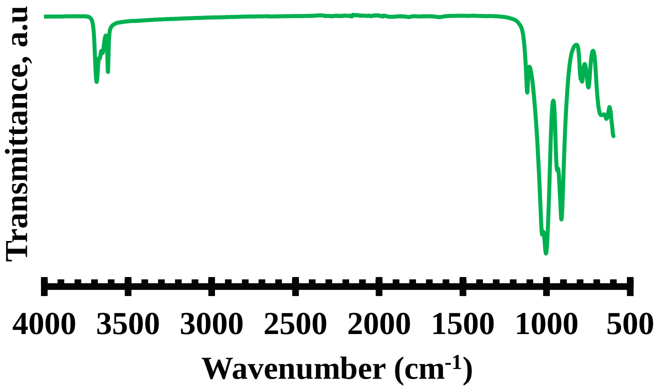
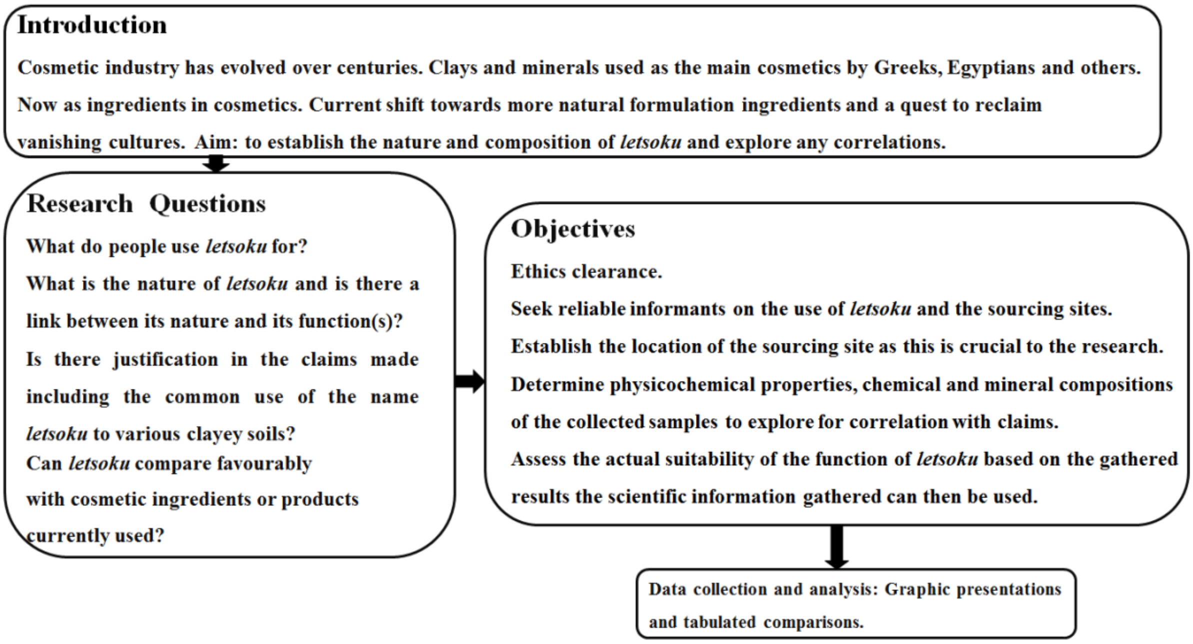


Figure 2.16: An example of an infrared spectrum

CHAPTER 3 : RESEARCH DESIGN AND METHODOLOGY

An interdisciplinary exploratory approach was adopted using structured interviews and characterization. This was an attempt to unravel and justify the claims made about *letsoku* and related clays. The sampling process was preceded by a survey to establish the sourcing sites and the additional applications. Prior to that challenges to obtain the samples were experienced. Legal implications and limited accessibility to these sites resulted in most of the samples being purchased. The structural complexity of clays necessitated the use of multi-techniques to establish the nature and composition of *letsoku*. The above is summarized in Fig. 3.1.



Cosmetic industry has evolved over centuries. Clays and minerals used as the main cosmetics by Greeks, Egyptians and others. Now as ingredients in cosmetics. Current shift towards more natural formulation ingredients and a quest to reclaim vanishing cultures. Aim: to establish the nature and composition of *letsoku* and explore any correlations.

What do people use *letsoku* for?
What is the nature of *letsoku* and is there a link between its nature and its function(s)?
Is there justification in the claims made including the common use of the name *letsoku* to various clayey soils?
Can *letsoku* compare favourably with cosmetic ingredients or products currently used?

Ethics clearance.
Seek reliable informants on the use of *letsoku* and the sourcing sites.
Establish the location of the sourcing site as this is crucial to the research.
Determine physicochemical properties, chemical and mineral compositions of the collected samples to explore for correlation with claims.
Assess the actual suitability of the function of *letsoku* based on the gathered results the scientific information gathered can then be used.

Data collection and analysis: Graphic presentations and tabulated comparisons.

Figure 3.1: Flowchart of the research design

Forty one informants were interviewed. The informants were from various places and backgrounds in Southern Africa. This was made up of a broad respondent population that included traditional healers. Interviews were conducted using structured questionnaires to establish the functions attributed to *letsoku* and to locate sourcing sites. Individuals under 18 years were excluded to enhance the validity of the study. Thematic content analysis was used to analyse the information obtained so as to make inferences. Thirty or more samples for characterization of the materials from various sites in Southern Africa were needed.

GPS coordinates were used to describe the locations of both original and commercial sites. Most of the samples collected were in powder form, some were supplied as dry clay balls, muddy wet clay and others as soft or hard rocks. The collected samples were stored at room temperature in polyethylene jars. Prior to that, the wet muddy samples were dried overnight in a convection oven set at 50°C. A portion of each dry sample was milled into a fine powder of less than 75 µm diameter for analytical purposes.

The completed questionnaires will be kept safe at the home of the researcher in Pretoria East. The informants were assigned study numbers in order to ensure anonymity and confidentiality during the interviews and throughout the research. The names of the informants will not reflect on the data forms but only the study identification number. The reports and articles in scientific journals will not include any information that may violate anonymity. The informant has the freedom to consult with the researcher should there be any sign of breach of confidentiality. There is assurance and reiterated commitment to protect the privacy of the informant.

Characterization involves specific technical quality assurance elements that apply to the technical activities such as policy and procedures for instrument calibration, performance, reference materials and statistical procedures. The planning, control and reporting practices recommended at the start of, during and at the completion of the research form an essential part. This includes the specification and brief description of the experimental instruments used for the characterization.

3.1 ETHICAL APPROVAL AND THE EPISTEMOLOGICAL STUDY

The survey to establish the sourcing sites was subject to ethical clearance. An application was submitted to EBIT accompanied by a researchers declaration form, a designed questionnaire and an informed consent. The relevant documents are attached in Appendix 1. Ethical clearance for this research was granted by the Faculty of Engineering, Built Environment and Information Technology Research Ethics Committee of the University of Pretoria via Record EBIT/116/201.Subsequently the document was used for this phase. Forty one informants with various backgrounds were interviewed in Southern Africa. The inquiry was further challenged with reticence by informants to divulge sensitive information. Nevertheless, the information obtained ultimately assisted towards collecting thirty nine clayey soils for the investigation.

3.2 MATERIALS AND METHODS

Every attempt was made to control the sampling process to be in accordance with the practices of the traditional healers. Laboratory processing was conducted according to the prescriptions of the relevant equipment for each analysis.

3.2.1 Sample collection

The clayey soil locations were configured from their Global Positioning Locations (GPS) using Google Earth as depicted in Fig. 3.2.

Figure 3.2: Letsoku sourcing sites (Google Earth)

Red markers show the original sourcing sites Makurung in Limpopo and Ntoane, Maleoko hills in Mpumalanga. The yellow markers are for commercial sites where the clayey soils where purchased from herbal shops, vendors and markets. Restricted accessibility to the sourcing sites resulted in the purchasing of most of the clayey soils. Legal implications were also a hurdle.

The decoded thirty nine mixed coloured clayey soil samples that were collected are depicted in Appendix 2. Two sourcing sites and some examples of samples are shown in Fig. 3.3.

Figure 3.3: Sourcing sites and samples

This features two original sourcing sites: a cave in Mpumalanga (Ntoane, Maleoko Hills) and a valley in Limpopo (Makurung) provinces respectively. The rest were purchased from either herbal stores, markets or vendors. The back interior of Mpumalanga reveals a canal leading deeper inside. The left of the entrance shows streaks of the red yellowish clayey soil surrounded by the red orange clayey soil. The Venda, Limpopo clayey soils, za8 and za8b, were very moist and za8b had a green moist interior. Clayey soils in this region are abundant and easily accessible to an extent of being large enough to be used as seats by children in the rural area. The red za1 and white za2 rolled clayey soil balls in Fig.3.3 were purchased from a Pretoria herbal store for at 1 €/ball. Lesotho clayey soils, red les1 and black les2 shown in Fig. 3.3 were purchased from the Maseru market in Lesotho also for 1 €/packet. This is equivalent to a third of what was paid for the Botswana samples. The samples purchased in powder form were applied as obtained. The rocky ones were ground in various ways. One way is grinding (see section 4.1). Alternatively, the rocks were heated dry in an empty pot until it cracked. The ground powder is used without further processing.

Botswana clayey soils prefixed bw were purchased from a vendor traditionally known as *Maletsoku* and based at Gaborone Sun. The following samples were collected: bw1 powder, bw1a rocks, bw2 powder, bw2a rocks, bw3 powder, bw3a rocks, bw4, bw5, bw6, bw6a, bw7 and bw8. The original sourcing site was given as Ramatlabama.

Swaziland red and white clayey soil samples sz1 and sz2 were purchased from Manzini market.

The **Zimbabwe** dark red powdered clayey soil zm1 was bought from a Chiredzi walk about vendor.

The **South African** clayey soils prefixed za were sourced from the listed sites that follow. **Asiatic Bazaar** herbal shop in **Pretoria** supplied commercial red and white rolled balls za1 and za2 respectively. The red powder za12 was purchased from **Kaplan** herbal shop in **Bloemfontein**. **Eastern Cape** (Engcobo,Umtata and Comfimvaba, Queenstown) and clayey soils were donated by a friend za5, za6, za7 and za9. **KwaZulu-Natal** wet greyish green mud donated by a friend: za11a, za11b, za11c (**Mtubatuba**), za13a and za13b **(Nongom**a). The whitish za10 was sampled from a valley in **Makurung, Limpopo**. The orange red clayey soils za8, za8a, za8b, za8b1 and muddy wet grey za8c from **Mbaleni** in **Venda, Limpopo** samples were donated by a colleague. The samples za3, za3b and za3b were sampled from **Ntoane, Maleoko Hills in Mpumalanga**.

3.2.2 Sample processing

The differences in texture and hardness of the collected samples led to a variation of sample processing. Sample preparation was performed as appropriate for each analysis. The hard rocks from Mpumalanga were ground with the jaw crusher shown in Figs 3.4(a) and 3.4(b). The muddy ones from Venda and KwaZuluNatal were dried overnight at 50^{o}C. A portion of each sample together with brittle samples were then milled in a tungsten carbide vessel I Figs 3.4(c) and (d) respectively. Milling was done to produce a fine powder of less than 75 µm. The clayey soils were stored at room temperature in polyethylene jars in the laboratory at the University of Pretoria. Fig. 3.4 shows the inside of the jaw crusher in Figs. 3.4(a) and (b) for grinding hard rocks such as za3, za3a and za3b. Figs. 3.4(c) depicts the tungsten carbide milling vessel which fits into the milling unit in Fig. 3.4(d). The m are used to mill the samples to less than 2 µm.

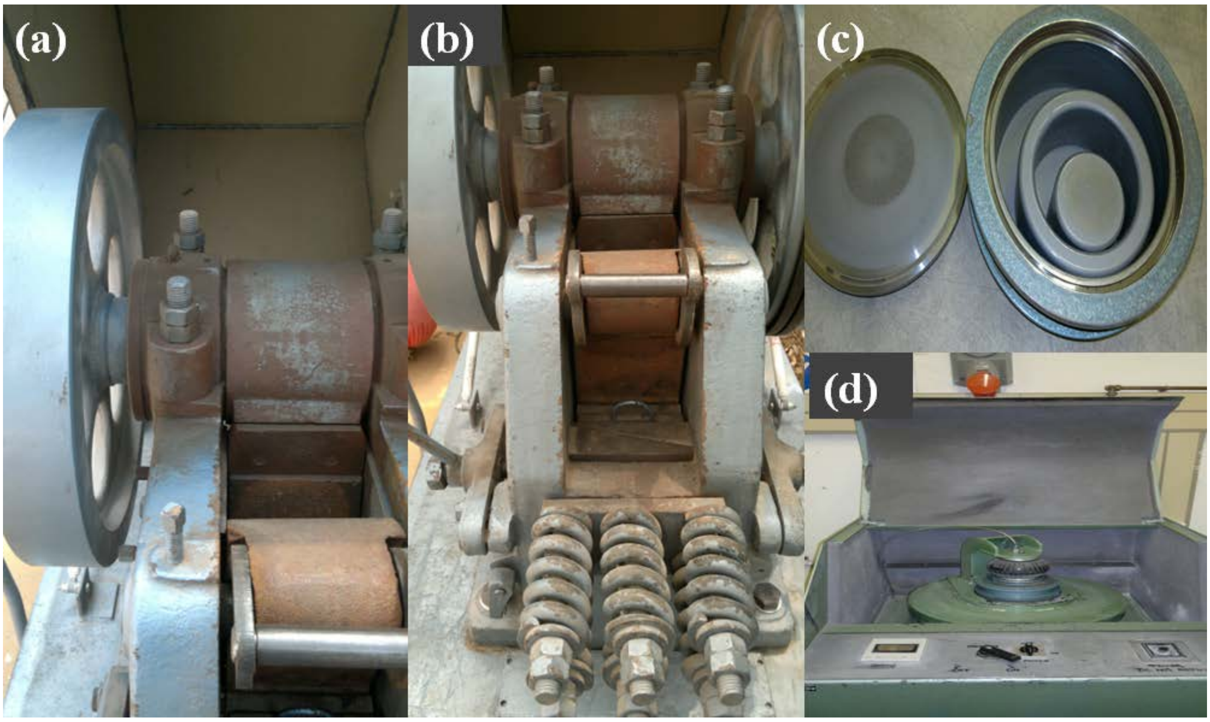


Figure 3.4: Jaw crusher and milling unit (Department of Geology, University of Pretoria)

3.3 CHARACTERIZATION

The multi-functionality of *letsoku* necessitates the use of multiple techniques as already indicated. An account of the techniques and details of the various examinations done is given in the subsequent sections.

3.3.1 Particle size distribution

Particle size is a fundamental property of soil that can provide important clues about the nature of the soil, possible uses and its provenance or origin. Particle size has a significant influence on cosmetics such as lipstick, mascara, foundation, moisturizers, exfoliants and virtually all products. In exfoliants and scrubs the aim is to have the right size of particles to effect the scrubbing. In lipsticks, make-up and products like moisturizers, there is a need to achieve smoothness to prevent abrasion. Stability of emulsions is affected by the wide or narrow particle size distributions. Several methods of particle size distribution are used such as the laser diffraction type, the Malvern Mastersizer, illustrated in Fig. 3.5.

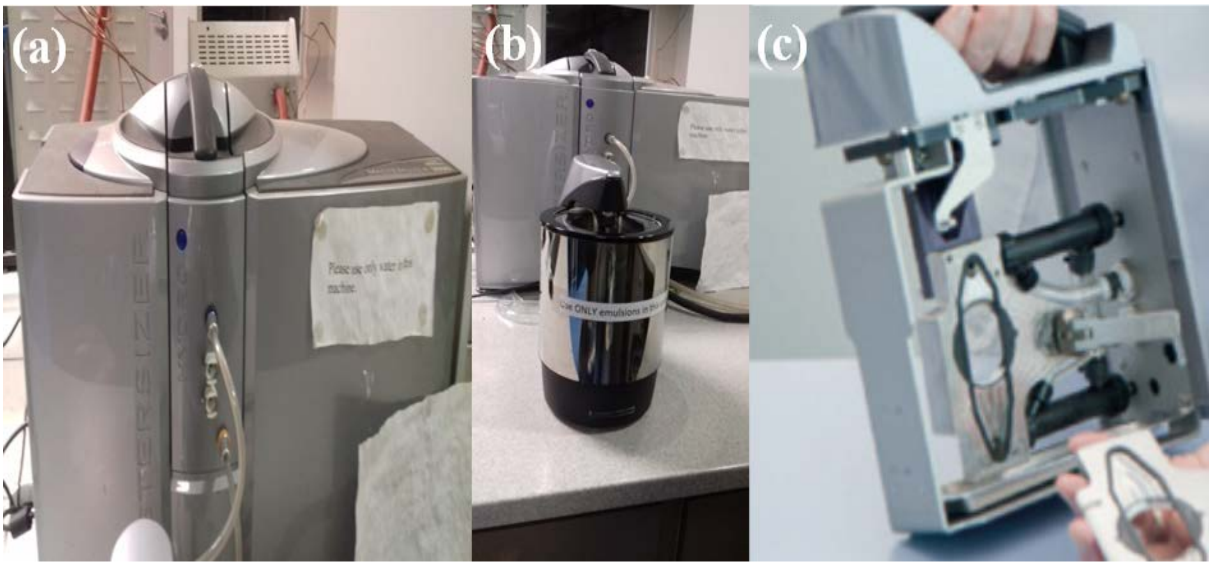


Figure 3.5: Malvern Mastersizer 3000 (Institute of Applied Materials, Chemical Engineering, University of Pretoria)

Fig. 3.5(a) shows the main body with the auto-locking system handle at the top. Fig. 3.5(b) shows the dispersion unit connected by a pipe to the measurement cell of the main body. Fig. 3.5(c) shows the inside of the measurement cell with the windows having a quick-release mechanism; this makes cleaning easier and ensures regular maintenance.

Simple customizable reporting for data presentation makes the system flexible. The results can be processed by defining the distribution width. This involves citing three values or medians on the X-axis: the D10, D50 and D90 where D represents particle diameter, also referred to as average particle size or median diameter. For instance, D50 refers to the diameter where half of the population lies below this value. A D50 of 6.22 µm implies that half of the samples are larger than 6.22 µm and the other half are less than 6.22 µm in diameter. Similarly D_{10} implies that 10% of the samples lie below the given value and 90% above that value. D_{90} would mean 90% of the samples below the given value and 10% above that value. A ternary plot may be drawn using the particle sizes to depict the various soil categories; clay, silt and sand.

3.3.2 BET surface analysis

The analysis was performed on ALL the samples. These were ALL ground and not milled for determining the specific surface area (SSA). Sample preparation was done using the flowing gas method on the VacPrep 061 Degasser. The samples were degassed overnight for adsorbed gases, water vapour and other impurities by drying under vacuum at 100°C. The degassed sample was loaded onto a Micromeritics TriStar II BET analyser. In Fig. 3.6(a) the VacPrep 061 Degasser the black knobs towards the top of the figure are used for vacuum control linked to the glass sample tubes. The picture of the Micromeritics TriStar II BET analyser in Fig. 3.6(b) depicts the liquid nitrogen gas cylinder at the bottom, the central port and the three steel rings (attachment for the glass tubes) from the inside of the top.

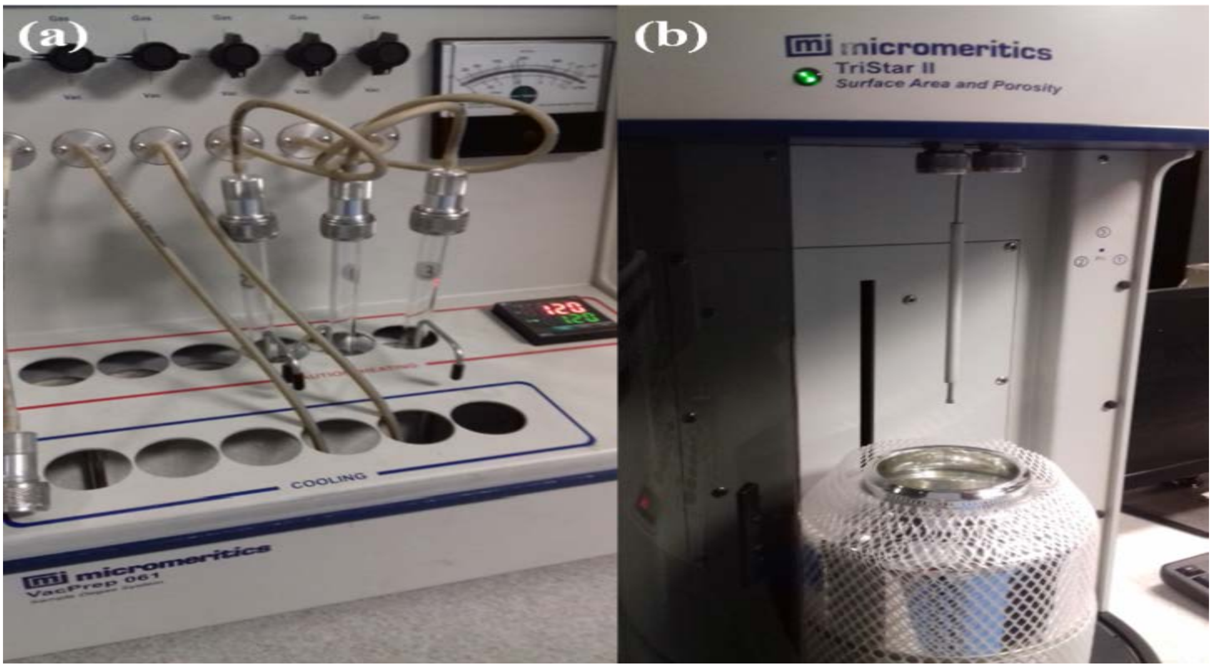


Figure 3.6: The six-port VacPrep 061 Degasser in 3.6(a) and the Micromeritrics TriStar II BET analyzer in 3.6(b) (Institute of Applied Materials, Department of Chemical Engineering, University of Pretoria)

The Micromeritics TriStar II BET analyser is designed to measure a minimum surface area of 0.01 m^2 g^{-1} using nitrogen gas as an adsorbate. Calibration is done using the silica-alumina CRM P/N 004/6821/00 to read 214.8±6 m^2 g^{-1} at P_o=0.990 to 0.998 and pore diameter of 115.5±15Å. The BET analyser measures the saturation pressure on a continuous basis. The central port together with the sample tubes were immersed in liquid nitrogen at -195°C atmospheric P_o of 760 mm Hg.

3.3.3 Colour test

Soil colour is an indicator of the composition of the soil. This may be organic components or the oxidation state of iron present. The former may contain antioxidants. The latter may contribute to the colour and aesthetics of the cosmetic product. A colour test is the visual comparison of the soil or clay colours with the Munsell colour charts depicted in Fig. 3.7.

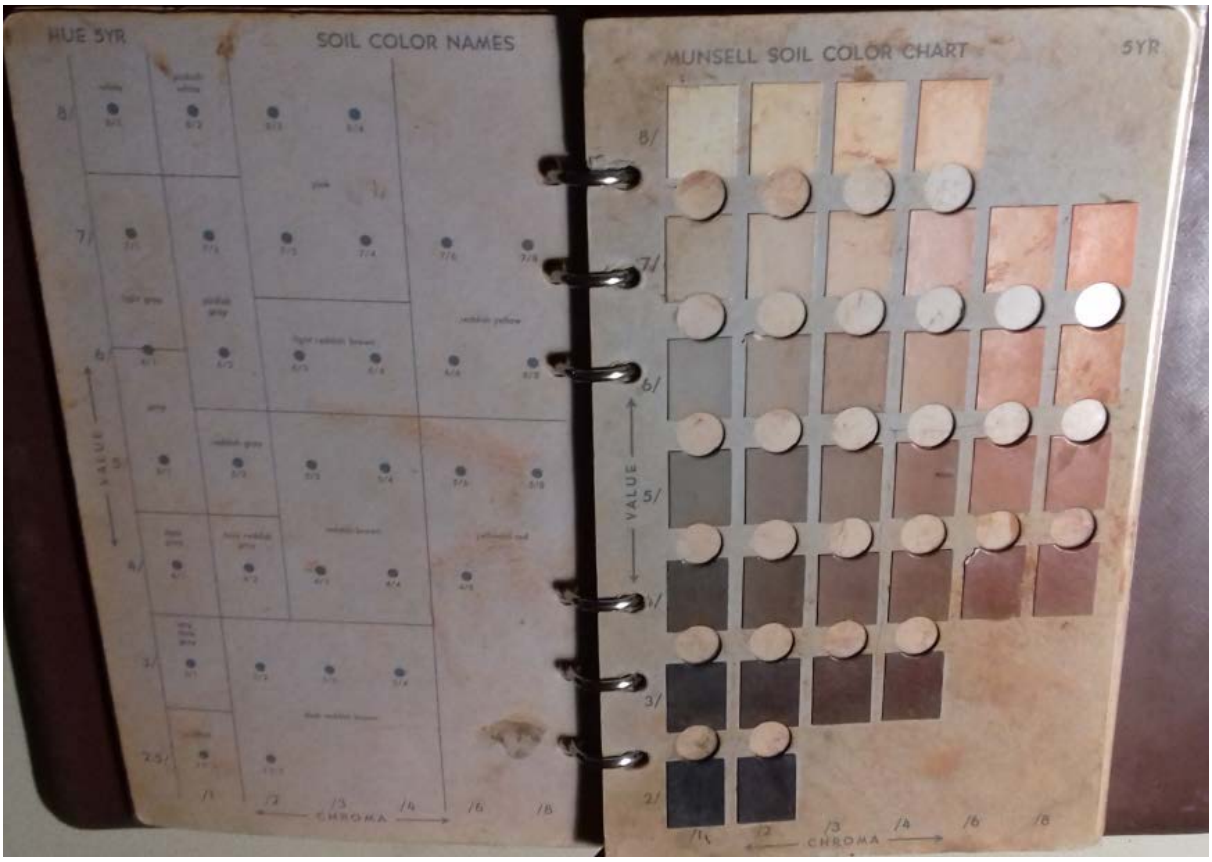


Figure 3.7: Munsell colour charts (Department of Plant and Soil Sciences, University of Pretoria)

The hue is obtained from the top right-hand corner, giving the relative colour position on a scale of 100 different grades of colour. The value from the vertical axis indicates the lightness or darkness of a colour relative to a neutral grey scale. This ranges from black to white. The chroma is from the horizontal axis showing the degree of concentration of hue from a neutral grey with the same brightness: ranges from 4 to about 10. The top of the left page in Fig. 3.7 gives the name of the soil colour and the top right corner of the right page in Fig. 3.7 gives the letter code such as 5 YR. The 5 is the value or how light or dark is the colour and YR stands for yellow-red. Full specification of colour requires the listing of the three numbers for hue, value and chroma in that order.

3.3.4 pH measurement

Calibration was done using the buffers at pH 4.00, 6.00 and 9.00. A Hanna instruments pH meter was used on 1:5 aqueous and 0.01 M $CaCl_2$ slurries of the clayey soils.

3.3.5 X-ray diffraction (XRD) analysis

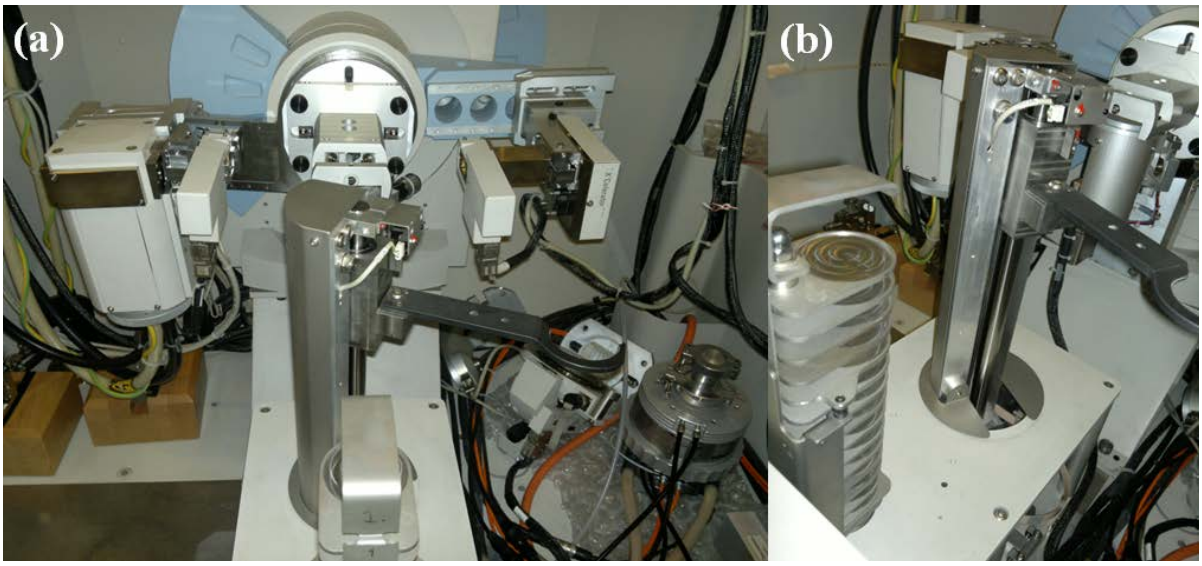


Figure 3.8: Interior of the XRD PANalytical X'Pert Pro powder diffractometer (Department of Geology, University of Pretoria)

The back of the sample carrier with a side arm for transferring the samples onto the sample stage is shown in Fig. 3.8. APANalytical X'Pert Pro powder diffractometer in 2θ configuration with an X'Celerator detector and variable divergence and fixed receiving slits with Fe filtered Co-Kα radiation (λ=1.789Å) was used for analysis. The phases were identified using X'Pert Highscore plus software. The relative phase amounts in % m/m were estimated using the Rietveld method. Errors are on the 3 sigma level.

Sample preparation for both XRD and XRF is briefly indicated in Fig. 3.9. The discs for trace metals, metal oxides and mineral analysis are shown.

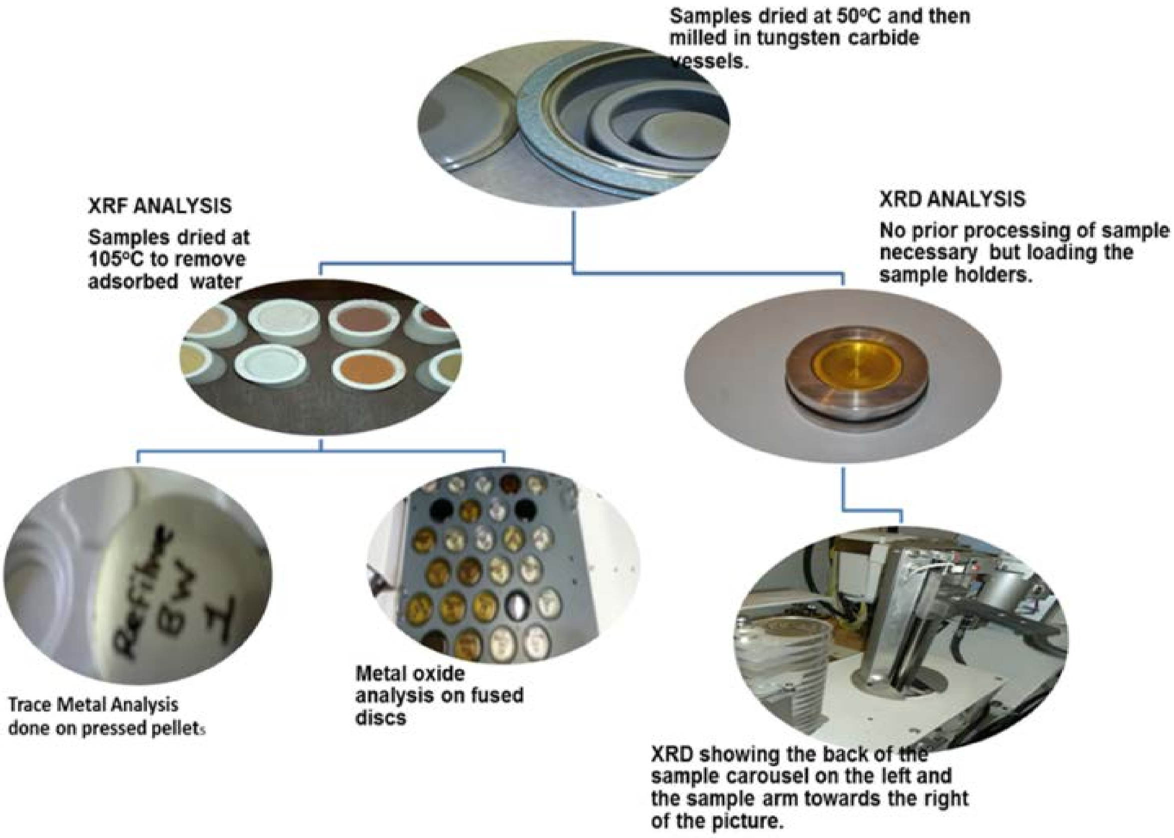


Figure 3.9: XRD and XRF sample preparation (Department of Geology, University of Pretoria)

3.3.6 X-ray fluorescence spectroscopy (XRF) analysis

Fluorescence refers to a process in which the re-emitted radiation is of a different energy from the absorbed one. XRF is based on the principle that when individual atoms are excited by an external energy source, they emit X-ray photons with a characteristic energy or wavelength (Kundra, 1991). The elements present may be identified and quantified by counting the number of photons of energy re-emitted from a sample. Measurements were done on samples milled to particle sizes of less than 75 µm without vaporization and prior digestion. A section of the instrument is shown in Fig. 3.10.

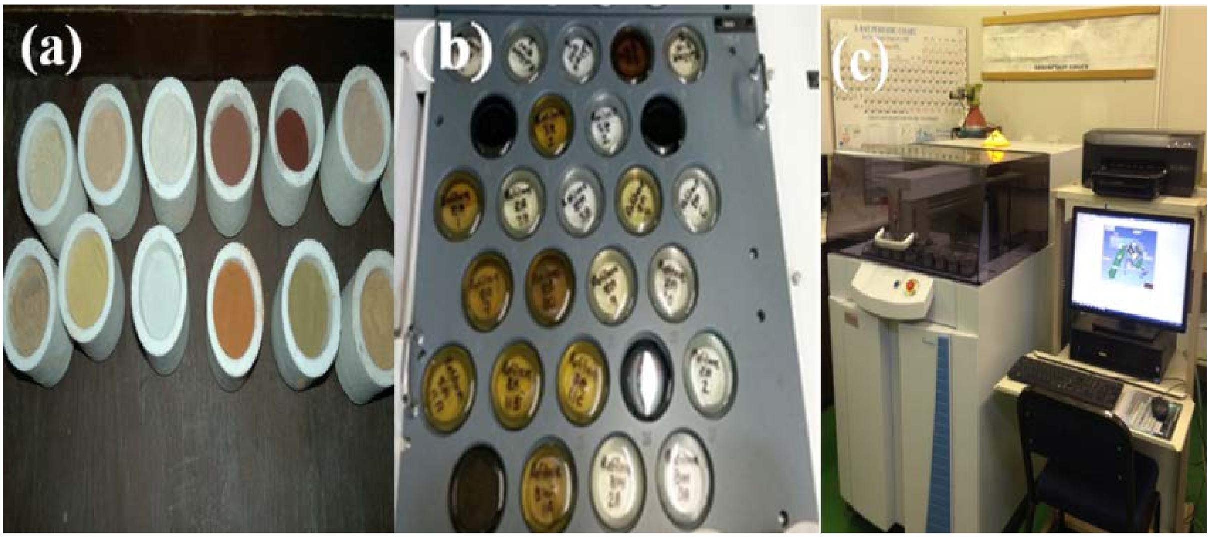


Figure 3.10: Thermo Fisher ARL XRF (Department of Geology, University of Pretoria)

Fig. 3.10(a) shows the dehydrated samples in alumina cups. (b) Lithium borate flux fused glass beads loaded on a tray for metal oxide analysis. (c) Thermo Fisher ARL XRF shows the Thermo Fisher ARL Perform'X Sequential XRF. This was done against certified reference materials (CRMs) referred to as South African Reference Material (SARM) for metal oxides. Samples were prepared with an accurate sample mass of 1 g mixed with 6 g lithium borate flux and fused at 1 050^{o}C to make a stable fused glass bead for metal oxide determination. The instrument is equipped to analyse materials in varied sizes, coatings, layers and heterogeneities. This includes wide elemental coverage, wide concentration ranges and sample matrices with sensitivity and reproducibility. High precision and detection limits for any solid or liquid sample is also enabled with overnight runs. The goniometer provides top speed, accuracy and precision to allow rapid analysis of up to 90 elements in the Periodic Table. It has a security device for dust or liquid collection during accidental breakage and leakage.

During the preparation for stable glass beads the water content was determined by weighing an accurate mass of 3 g of each milled sample into an alumina crucible which was then heated in an oven at 100^{o}C for 2 hours. The dehydrated samples were used to assess the final loss on ignition (LOI) by igniting at 1 000^{o}C overnight.

During the preparation for pellets 10 to 30 g of the milled sample was mixed with moviol or poly(vinyl alcohol) and pressed into a powder in an aluminium cup at about 10 tons for **trace metal** analysis (see Fig. 3.11).

Figure 3.11: Trace metal sample preparation (Department of Geology, University of Pretoria)

3.3.7 Scanning electron microscopy (SEM)

A thin magnetic strip was lightly dipped into the powdered clayey soil sample and mounted onto a double-sided adhesive carbon tape lining a numbered steel plate using a forceps. Compressed air was used to remove excess powder and carbon coating was done using a spluttering coater. The coated samples were placed in the sample chamber in the electron optics column which was evacuated to 3.62×10^{-5} mbar. The electron beam generated by heating the tungsten filament with the electron gun was accelerated by voltage and focused by electromagnetic lenses into a probe of secondary electrons which bombarded the surface of the sample.

Some salient features of the coater and the Zeiss Ultra 55 FESEM field emission scanning electron microscope are shown in Fig. 3.12. The body of the Emitech spluttering coater is shown in Fig. 3.12(a). The inside of the lid of the Emitech coater with the screws for suspending the carbon rods is shown in Fig. 3.12(b). The inside bottom of the coater with the shiny sample stage where carbon coating takes place is shown in Fig. 3.12(c). The front of the Zeiss Ultra 55 FESEM field emission SEM and the side with the side arm at the entrance of the sample chamber in the electron optics column are shown in Figs. 3.12(d) and 3.12(e) respectively.

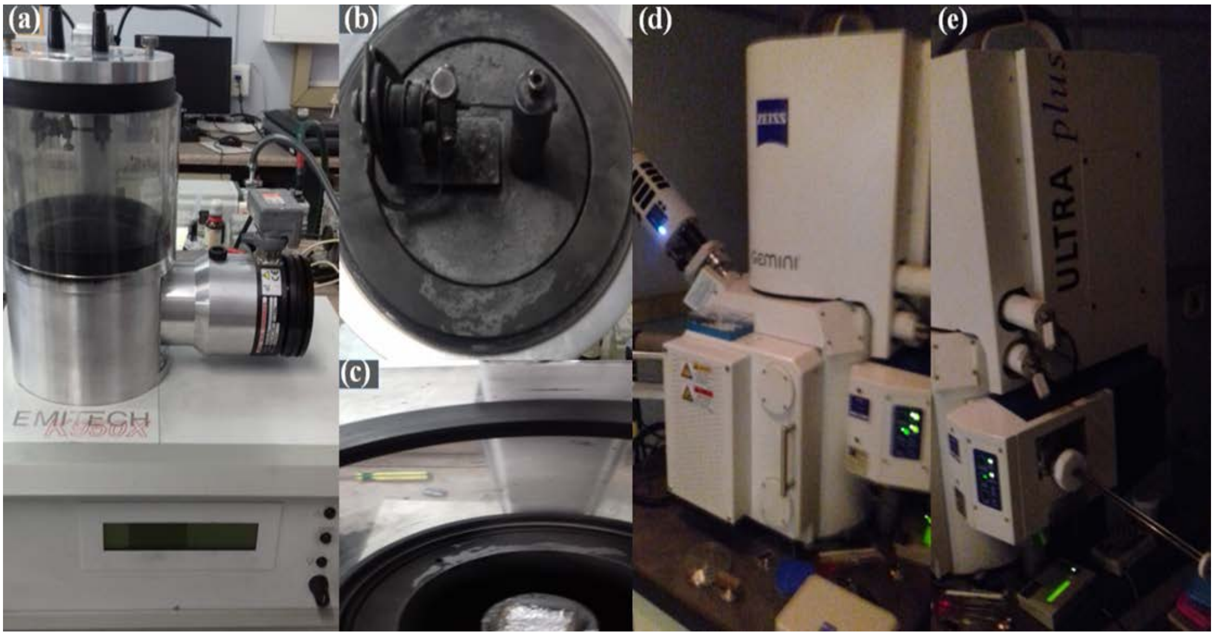


Figure 3.12: The Emitech spluttering coater and the Zeiss Ultra 55 FESEM field emission SEM and the outside of the sample chamber (Department of Physics, University of Pretoria)

In the FESEM a field emission gun provides focused high- and low-energy electron beams. This improves resolution and enables the work to be carried out at very low potentials (0.02-5 kV).This helps to reduce the charging effect of non-conductive specimens and hence there is less risk of damage to the electron beam-sensitive samples. The accelerated and finely focused electron beam bombards the sample surface, causing secondary electrons to be sent to the detector.

In-lens detectors are used in the FESEM. These are optimized to work at high resolution and very low acceleration potential. Hence maximum performance is obtained from the instrument. In the ZEISS ULTRA 55 model the listed detectors are incorporated. A secondary electron in-lens detector (SE2) inside the electron column detector is used for the SEM topography image of the sample surface at medium and low resolutions with high acceleration potential. This detector works with low-energy secondary electrons and provides images with a higher resolution. It is suitable for surface characterization of any material. Low potentials (<5 kV) are ideal for performance and therefore recommended for electron beam-sensitive samples and for minimizing the charging effect on non-conductive samples.

The other possibilities are a backscattered electron detector (AsB) and a backscattered electron in-lens detector (EsB). The purpose of the former is to observe structural contrasts in crystalline materials, while the latter is the only one that can select electrons according to their energy; it is also capable of working at very low voltage. The signal received is then processed into a SEM image referred to as a micrograph.

3.3.8 Thermogravimetric analysis (TGA)

Figure 3.13 shows some of the prominent features of a thermogravimetric analyser.

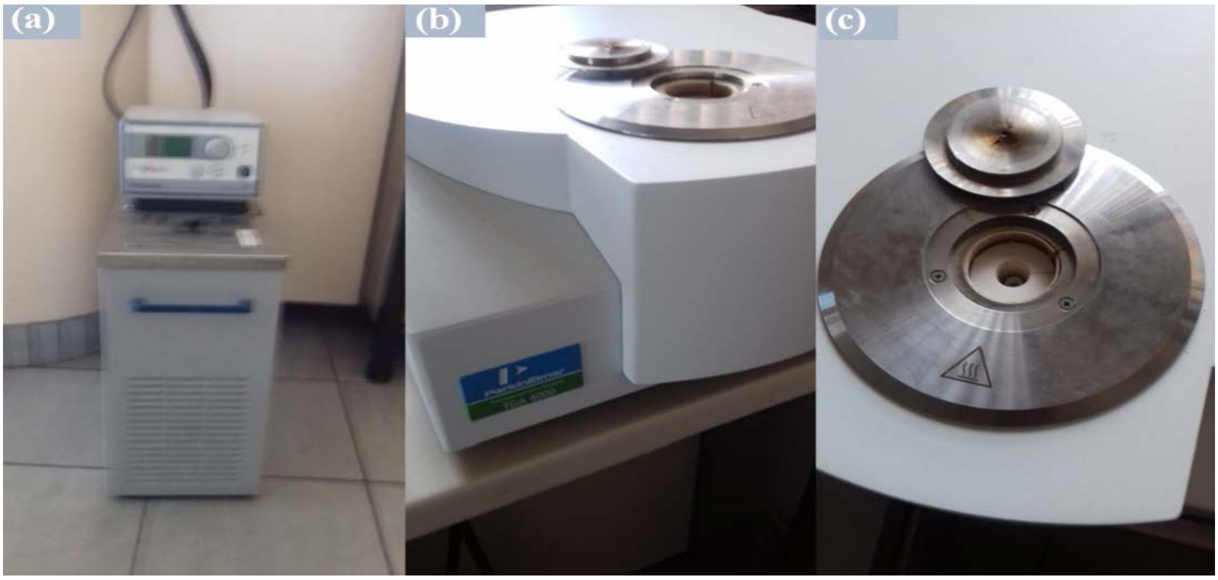


Figure 3.13: Perkin Elmer TGA 4000 (Department of Chemistry, Tshwane University of Technology)

Fig. 3.13(a) depicts the chiller or coolant for the TGA 4000 to ensure shorter cooling down times for the cycles. Figs. 3.13(b) and 3.13(c) show different views of the sample loading port.

The combination of the high performance thermo-balance, sensitive and stable top-loading balance, ceramic balance and other features ensure accuracy and precision. The balance is isolated from operators to protect it from any potential damage. It has an inert corrosion-resistant ceramic furnace and coolant which provides temperature control, fast purge gas and fast cool down time for short cycles. The thick stainless steel walls act as a large heat sink, thermally isolating the balance from the furnace to ensure its stability. The thermocouple measures the heating rate and sample temperature. Samples as large as 1500 mg or 180 µl can be analysed.

The analysis was done on the samples contained in an Al_2O_3 crucible carefully balanced on a precision thermo-balance on a support rod in a furnace equipped with a thermocouple in a calibrated TGA 4000. The thermo-balance was zeroed using the standard operations procedure and a Pyris instrument viewer. The method editor was used to run the samples initially isothermal at 25ºC for one minute. They were then heated from 25ºC to 950ºC at 10ºC min^{-1} using Al_2O_3 crucibles and sample masses of 40 mg to 50 mg at an air flow rate of 50 mL min^{-1}.

3.3.9 Infrared spectroscopic analysis

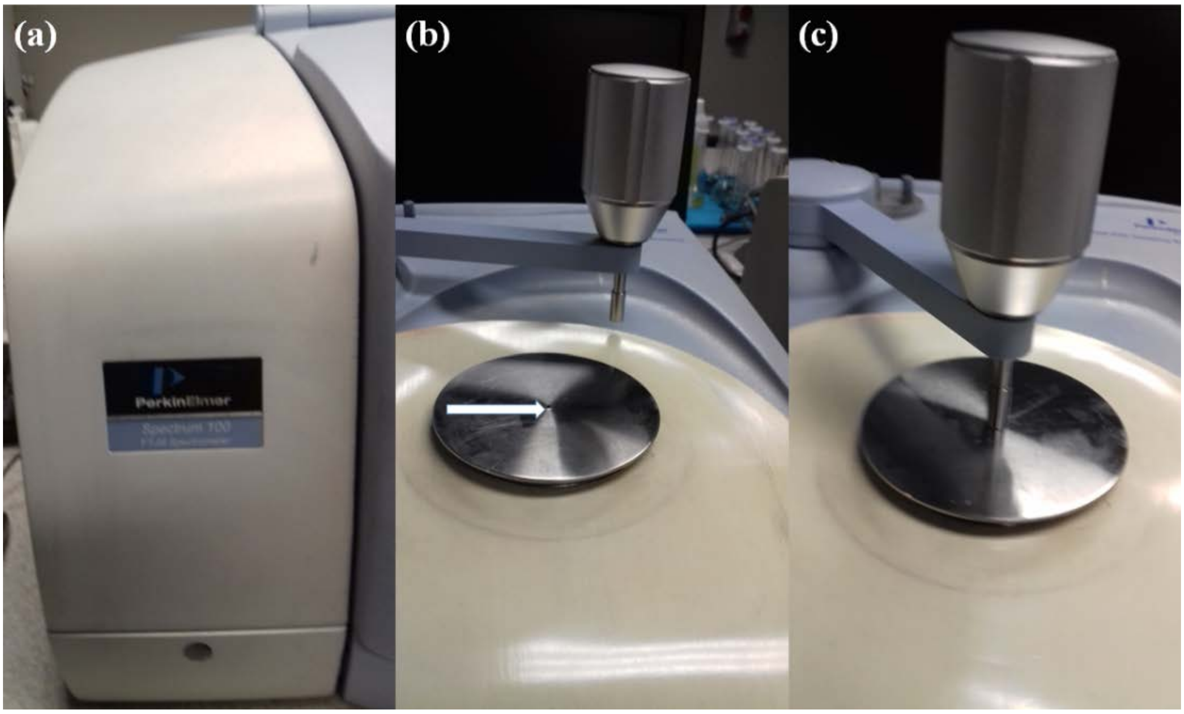


Figure 3.14: Perkin Elmer Spectrum 100 Series ATR-FTIR showing the ATR crystal (Institute of Applied Materials, Department of Chemical Engineering, University of Pretoria)

The white arrow in Fig. 3.14(b) points to a spot corresponding to the location of the diamond crystal within the trough plate. The pressure arm supports the top-mounted prism to ensure good contact between the sample and the crystal. This is achieved by removing the cap and screwing until about 100 N without damaging the accessory parts.

At the onset of taking measurements on the ATR-FTIR, alcohol was used for cleaning the crystal to eliminate contamination. A background correction was done from the clean ATR crystal and platform to accommodate information about the radiation source, the interferometer and the detector at five scans from 500–4000 cm^{-1}. Thereafter, enough sample was transferred to cover the crystal area. The pressure arm was positioned above the sample-crystal area and force was applied to push it onto the crystal surface until the force gauge registered 100 N on the Perkin Elmer Spectrum 100 Series. The sample were analysed at 32 scans from 500 – 4000 cm^{-1} and IR spectra were recorded.

CHAPTER 4 : RESULTS

The findings obtained by analysing the interview data are summarized according to *letsoku* functions in Fig. 4.1. Representative samples of the completed questionnaires are given in Appendix 3. The various themes and categories emanated from the responses of the informants. The emergent themes in descending order from the various responses were: cosmetics, cultural symbolism, medicinal applications, traditional beliefs and artwork, particularly pottery.

4.1 EPISTEMOLOGICAL STUDY

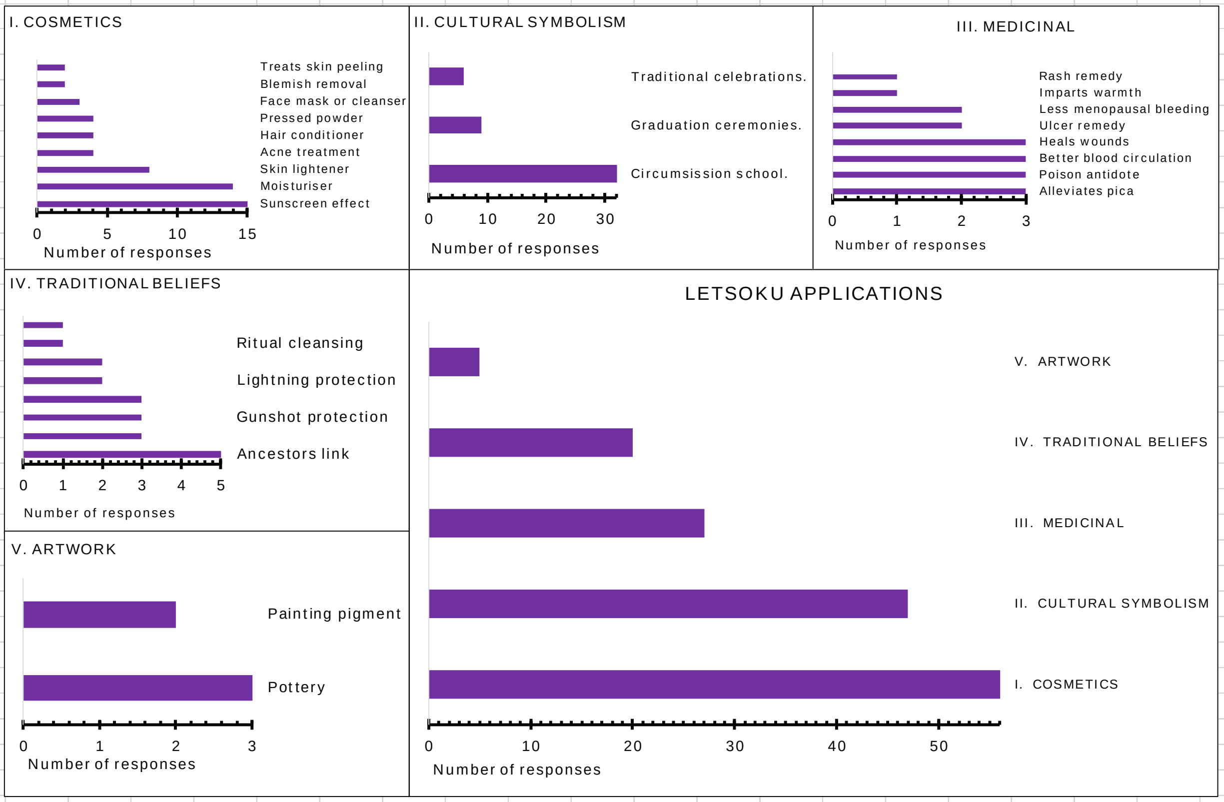


Figure 4.1: Thematic content analysis

The account that follows discusses the information gathered from the various informants who were interviewed. Information includes *letsoku* sourcing sites, sample processing and various *letsoku* functions.

Sourcing sites included Lobatse, Otse, Gaborone, Mmamabule and Mahalapye, Taung, Notwane river, Mogobane, Moshopa, Dinokwe, Serule, Lebung area, Kweneng Laagte, Tsatsu, Kanye, Kgwakgwe, Morupule and Ramatlabama near one of the Botswana borders.

***Letsoku* nature and processing.** According to some informants, *letsoku* has been described as a substance that never solidifies or as a soft stone that is mined in various parts of Africa. Most of the samples were easily powdered and some were supplied as dry clay balls. The raw *letsoku* stones are crushed with a traditional pestle and mortar. Traditionally, this involves pounding on top of a grinding stone (*tshilo*) with another stone. Sieving is done thereafter to yield a fine powder. Some *letsoku* users heat the dry raw stone in an empty pot to disintegrate it into a fine powder. *Letsoku* samples covered a wide range of colours ranging from bright red to yellow but also from off-white to black, with some having a light grey colour. It was therefore not surprising that the mineral composition of the *letsoku* samples varied widely.

4.1.1 *Letsoku* applications

Cosmetics. In cosmetics, each colour is associated with a specific function. Yellow is used as a face powder. Red is mixed with water and used as a mask and a face wash. It is believed to remove pimples and blemishes. Reddish pink and orange is used as a face powder just like the yellow one. White is for general body cleansing and removing bad body and mouth odours. Maroon removes dark patches around the eyes. Purple is for anti-aging. It is mixed with Vaseline and applied to problem areas to eliminate wrinkles. There are no known *letsoku* side-effects.

Sun-screening and moisturising properties were reported for women working outdoors on the farms. Visible *letsoku* layers have been observed on the faces of these women. It is believed that the practice protects the skin against the harmful effects of the sun and makes the skin soft and supple. *Letsoku* has been known to be used as a face mask or cleanser and thereby treat conditions such as acne and greasy skin. Application of *letsoku* is also believed to lighten the skin and remove any dark marks or blemishes present. The clayey soil has been used as a pressed powder or foundation to produce a matt effect. Skin peeling has been known to be treated with a mixture of *letsoku* fine powder and *makhura* (fat skimmed from milk) or petroleum jelly. Its application to hair has been known to promote hair growth.

Cultural symbolism. In some areas of Botswana, the ethnic groups still use *letsoku* to cover the bodies of the initiates. Their caretakers help shave their heads and cover their bodies with a red or maroon *letsoku*. Some informants disclosed that *letsoku* keeps initiates warm at the circumcision school. The girls are covered with enough to ward off winter colds. Young girls used to wear *makgabe* (fringed short skirts) with *letsoku* used to cover each fringe. Among the Ova Herero of Bothatogo in Maun the practice is still ongoing. It is believed to be a symbol of innocence. The graduation ceremonies and other traditional celebrations like welcoming the bride into a new family are marked by application of *letsoku.*

Medicinal applications. Excessive menopausal bleeding in women can be managed or controlled by oral ingestion of an aqueous mixture of red and lighter coloured *letsoku*. Pregnant women who experience pica (abnormal food cravings) may be relieved by oral ingestion of *letsoku*. It is used for the treatment of chicken pox, protection against lightning and witchcraft, luck, spiritual baby calming and ritual cleansing.

It is believed that application of *letsoku* repels dangerous elements such as snakes and lions, and thereby acts as a camouflage for the users in forests. In chicken pox treatment, an aqueous mixture of *letsoku* is used in a manner similar to the use of calamine lotion. Burns may also be healed by applying the dry powder directly to the blister and allowing contact until it has dried up. It is also used for healing wounds and for treating ulcers and rashes. Application to the skin is believed to impart warmth to the body.

Traditional beliefs. Crops in the fields are believed to be protected using *letsoku*. Some farmers mix their seeds with the red or maroon *letsoku* in the ritual called *go gotlha dipeo* (to rub the seed). This is meant to protect the seeds, chase away evil spirits and keep hailstorms from damaging the plants. Farmers rub the seeds scrupulously, using both hands, before planting as a form of nurturing the field in advance. Crops are treated like infants going through the stages of being born, treating the umbilical cord, shaving and smearing the head for protection. Other beliefs include links with ancestors.

Artwork. Potters use *letsoku* to enhance the colour of a finished pot. During the final stage of polishing a pot with a fine stone, *letsoku* is added for adornment. Tanners use either *motsitsana* (a herb) or *letsoku* as a pigment to paint leather skins a bright red colour, especially skin that is used for clothing and shoes. Pigment painting for artwork on walls and caves was also indicated.

4.2 CHARACTERIZATION

A number of techniques were used to evaluate the various aspects in a quest to establish the properties that could account for the composition and cosmetic function of *letsoku*. These properties included particle size distribution, the physicochemical properties, and the chemical and mineral composition.

4.2.1 Particle size distribution (PSD)

The *letsoku* textural composition is depicted on the ternary diagram in Fig. 4.1. The data of some representative samples used to plot the graph are shown in Table 4.1. There is a classic demonstration of heterogeneity. The three Lesotho samples are at the apices of the textural triangle. Les1, les2 and les3 at the clay, sand and silt apices respectively.

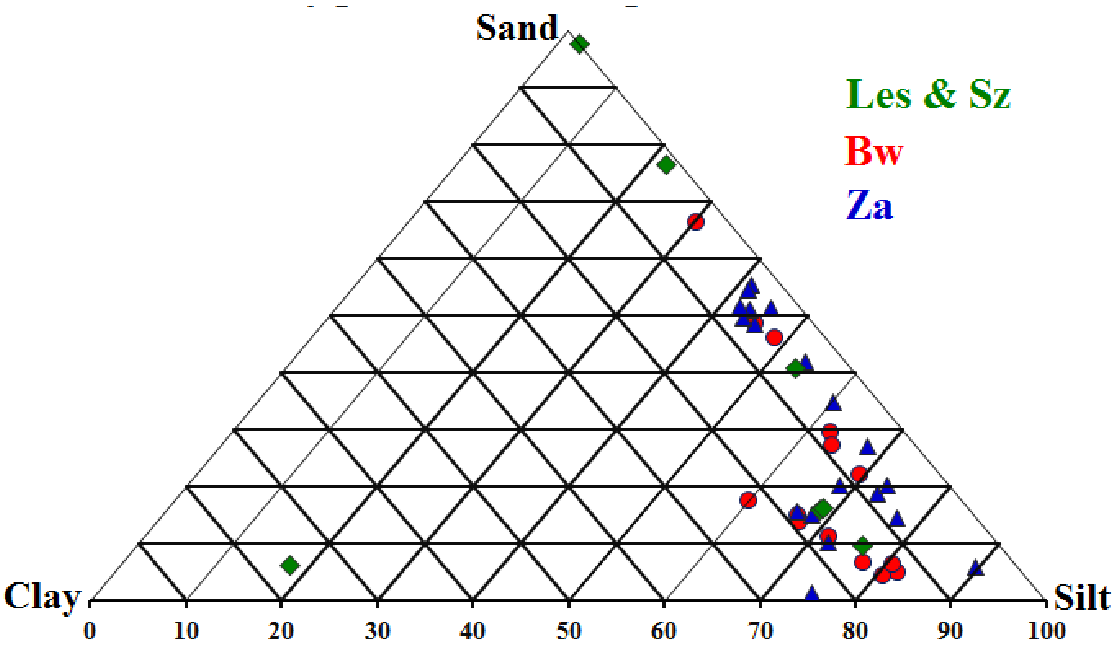


Figure 4.2: Ternary plot for *letsoku* particle size distribution

The PSD of each of the three Lesotho samples has a different mode. Les1 is non-symmetrical with D_{10} = 0.023 µm, D_{50} = 1.22 µm and D_{90} = 32.1 µm. This tallies with its position on the textural triangle on the clay apex. This conforms to the USDA/WRB stipulation of clay particle diameter less than 2µm. On the other hand, les2 has a symmetrical mode with D_{10} = 93.2 µm, D_{50} = 192 µm and D_{90} = 397 µm. This confirms the sandy nature indicated by its position on the apex of the textural triangle. This falls in the sand particle diameter range given as 50 µm to 200 µm or 63 µm to 200 µm according to the USDA and WRB respectively. Similarly, the non-symmetrical bimodal silty les3 has D_{10} = 1.55 µm, D_{50} = 17.4 µm and D_{90} = 58.3 µm. This complies with the USDA or WRB silt particle diameter range of 2 µm to 50 µm or 2 µm to 63 µm. Matike *et al.* (2011) and Jumbam (2014) have emphasized the importance of a high clay or silt content for cation exchange capacity (CEC) or sunscreen effect in cosmetics.

The Eastern Cape samples za5, za6 and za7 exhibit a notable degree of homogeneity. They are together and almost all at the silt apex. Only za9 is slightly different but still located in the silty area with D_{10} = 6.37 µm, D_{50} = 62.0 µm and D_{90} = 229 µm. The heterogeneity trend in the soil categories is demonstrated by the rest of the samples shown in Fig. 4.2. The commercial sample za15 clay and za19 clay mineral are silty and in the vicinity of the Eastern Cape samples on the textural triangle. Furthermore, a pictorial emphasis of the differences in mode of samples from different regions is depicted in Fig. 4.3. There is a drift towards a silt nature especially for bw6, za7 and za11b.

Table 4.1: Calculated normalized values for the three variables and x-axis D-values (µm)

SA ID	Clay	Silt	Sand	X	Y	D_{10}	D_{50}	D_{90}
bw1	19	67	15	74	13	2	8	85
bw1a	3	30	67	63	58	5	152	519
bw2	17	72	11	77	10	2	7	66
bw2a	6	45	49	70	42	3	54	531
bw3	19	67	14	74	12	2	7	76
bw3a	13	82	5	84	4	2	7	33
bw4	16	77	7	81	6	2	7	33
bw5	22	60	18	69	15	1	8	86
bw6a	15	81	5	83	4	2	8	43
bw7	9	69	22	80	19	3	14	162
bw8	9	64	28	78	24	3	14	203
les1	76	18	6	21	5	0	1	32
les2	0	3	98	51	84	93	192	397
les3	14	76	10	81	8	2	17	58
sz1	6	53	41	74	35	2	11	79
sz2	16	68	16	76	14	2	12	82
za1	5	60	35	78	30	5	37	141
za2	18	66	16	74	14	2	7	88
za3a	6	43	51	69	44	3	58	426
za3b	17	68	15	76	13	2	10	75
za5	24	75	2	76	1	1	5	18
za6	18	72	10	77	9	2	9	61
za7	8	73	19	82	16	5	42	187
za8a	5	68	27	81	23	4	22	166
za8b1	12	68	20	78	18	2	12	96
za8c	6	42	52	68	45	4	64	262
za9	3	45	52	71	45	6	62	229
za10	1	12	87	56	76	45	229	620
za11a	3	42	55	69	48	7	70	248
za11c	6	73	20	83	18	3	20	156
za13a	8	77	15	84	13	3	12	125
za13b	4	41	55	69	47	6	70	358
za15	4	90	6	93	5	1	4	30
za19	5	75	25	88	22	4	25	110
zm1	1	22	76	60	66	20	144	432

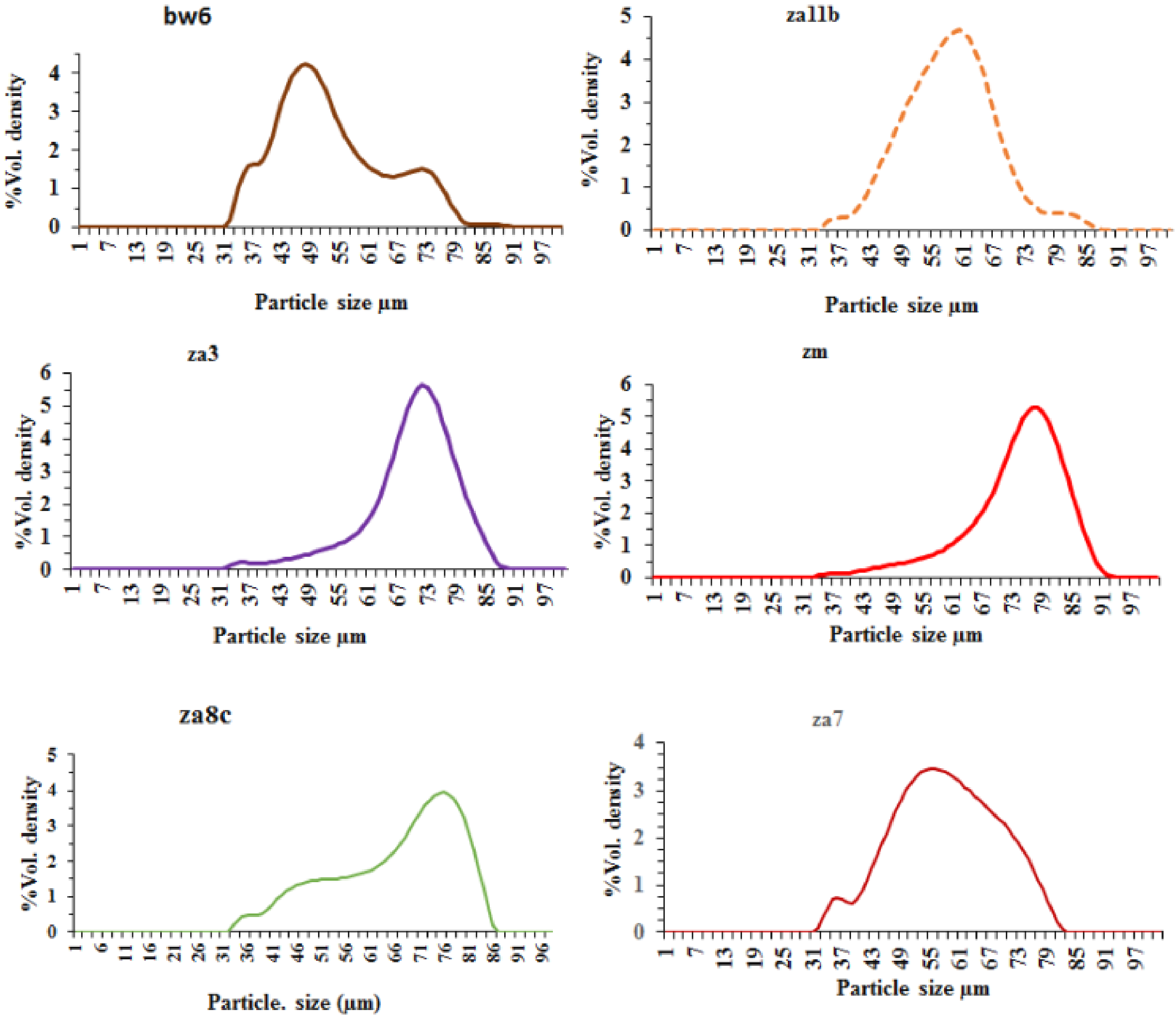


Figure 4.3: A pictorial emphasis of the differences in mode of samples from different regions

4.2.2 Physicochemical properties

Dispersion of *letsoku* samples in water and 0.01 M $CaCl_2$ rendered some slightly acidic but all the others resulted in a slightly basic pH. The results for BET specific surface area (SSA), pH, loss on ignition (LOI) and the Munsell colour of the clayey soils are presented in Table 4.2. Overall, there is a lack of a specific trend. This is further demonstrated in Fig. 4.4 where a lack of correlation is manifested within the same region. However, the SSA was plotted using points arranged in ascending order. Except for samples za5, za6 and za8c, there appears to be a relation between LOI and SSA, although not a rigid one. Moving from left to right of the graph, both LOI and SSA are low (<40 %). The SSA continues and culminates at >90 %, while the LOI is still <40 %. This applies more to the smectitic clays za8c, za10 za11a and za11c.

Lesotho. The poly-disperse sample les1 has the lowest values for the particle size distribution (PSD) evaluation: D_{10}=0.022 µm, implying that 10 % of the particles have a diameter of less than 0.022 µm and 90 %have diameters above that. D_{50}=1.22 µm means that half the particles have diameters less than 1.22 µm, while the other half have diameters greater than 1.22 µm. D_{90} =32.1 is interpreted similarly. There is a potential presence of clay minerals ($\theta < 2$µm) even though the SSA is only 22 m^2 g^{-1}. The above is in agreement with Engelbrecht (2016) and Fakhfakh *et al.* (2005) concerning the high SSA of smectitic clays. Likewise, the T:O (kaolinite) clayey soil les3 has an SSA of 21 m^2 g^{-1} and a pH of 6.7. Les3 has a very high haematite content. Les2 has the lowest SSA of 8 m^2 g^{-1}. There is no haematite or goethite in these samples but they are composed of ilmenite, magnetite, rutile and none of the clay minerals.

Botswana. These samples have a highest SSA of 26 m^2 g^{-1} and a lowest SSA of 5 m^2 g^{-1}. The pH ranges between 6.2 and 7.2. Pastel colours seem to be predominant with only two red coloured samples. Hue varies from 5 YR, 7.5 YR to 10 YR.

Table 4.2: BET SSA pH LOI and Munsell colour test

Sa ID	SSA	pH	LOI	HUE	Value/Chroma	Colour description
za1	68	5.9	14.7	5 YR	6/8	Pinkish white
za7	38	6.2	13.3	5 YR	6/8	Reddish yellow
za11b	73	9.1	15.5	10 YR	6/4	Light yellowish brown
zm1	28	7.6	14.5	5 YR	3/6	Dark red
bw1	23	7.0	4.0	5 YR	8/2	Pinkish white
bw1a	20	7.1	5.5	7.5 YR	8/6	Reddish yellow
bw2	8	6.2	3.8	5 YR	7/3	Pink
bw2a	15	6.2	4.6	5 YR	7/4	Pink
bw3	8	6.9	3.4	7.5 YR	8/2	Pinkish white
bw3a	22	7.0	4.0	5 YR	8/1	White
bw4	22	6.6	4.1	5 YR	4/6	Red
bw5	5	6.8	0.1	10 YR	3/6	Dark red
bw6	26	6.9	1.1	5 YR	7/4	Pink
bw6a	19	7.2	4.5	5 YR	7/3	Pink
bw7	15	6.8	3.6	5 YR	7/6	Reddish yellow
bw8	22	6.9	3.7	5 YR	8/4	Pink
les3	21	6.7	5.1	10 YR	5/8	Red
sz1	59	4.8	15.7	5 YR	4/6	Reddish yellow
sz2	27	5.0	14.0	5 YR	8/1	White
za2	45	5.9	12.6	7.5 YR	8/2	Pinkish white
za5	48	6.4	8.3	7.5 YR	8/6	Yellow
za6	31	7.8	5.7	5 YR	8/1	White (visible grey)
za8	61	6.8	19.6	5 YR	4/6	Yellowish red
za8a	33	7.4	37.4	5 YR	4/6	Yellowish red
za8b	9	7.3	18.0	5 YR	5/6	Yellowish red
za8b1	44	6.8	19.1	5 YR	5/6	Yellowish red
za8c	91	6.1	17.7	10 YR	6/4	Brown
			To	10 YR	5/4	Brown and yellowish/brown
za9	26	6.2	6.0	7.5 YR	8/4	Pink
za10	98	8.4	31.7	10 YR	8/2	Pinkish white
za11a	75	7.9	14.8	2.5 Y	5/2	Greyish brown
za11c	74	8.0	14.2	2.5 Y	7/2	Light yellowish grey
			To	2.5 Y	6/2	
za12	98	7.0	1.1	10 YR	4/6	Red
za13a	79	8.7	12.0	10 YR	6/3	Pale brown
za13b	45	8.6	4.8	2.5 YR	6/4	Light yellowish brown
les1	22	5.2	3.6	10 YR	4/6	Red
les2	8	7.3	0	5 YR	8/1	Very dark grey
za3	4	7.0	0.9	5 YR	5/4	Reddish brown
za3a	20	7.0	2.1	5 YR	5/4	Reddish brown
za3b	18	7.4	1.0	5 YR	7/4	Pink
za15	65	8.0	8.2	5 YR	8/1	White
za19	95	8.7	15.2	5 YR	8/2	Pinkish white

Limpopo. The highest SSA of 98 m^2 g^{-1} was obtained for the basic smectitic za10 sample (Makurung), a natural clayey soil. This was followed by 91 m^2 g^{-1} for the wet, muddy natural smectitic za8c. The rest of the samples had SSAs ranging from 9–61 m^2 g^{-1}, pH 6.09–7.43 and LOI 17.7–37.4 % m/m.

KwaZulu-Natal. TheSSA values for the smectitic clayey soils (za11a and za11c) are 75.2 m^2 g^{-1} and 74.3 m^2 g^{-1}respectively. The T:O clayey soils, za11b and za13a have values of 73.4 m^2 g^{-1} and 79.2 m^2 g^{-1} respectively. The basic micaceous za13b has 45.4 m^2 g^{-1} and a quartz content of 84.5 % m/m.

Eastern Cape. Thecolour variation is from white to pink, then yellow, accompanied by hues of 5 YR and 7.5 YR. The SSA varies between 26 and 48 m^2 g^{-1}. This is slightly higher than the literature value for kaolinite. The discrepancy can be attributed to the smaller particle size.

Gauteng. The SSA of 45–67.7 m^2 g^{-1} in the absence of a smectite is suggestive of a very fine particle size. Even though the two samples have different hues, values and chromas, they have the same pH value of 5.9.

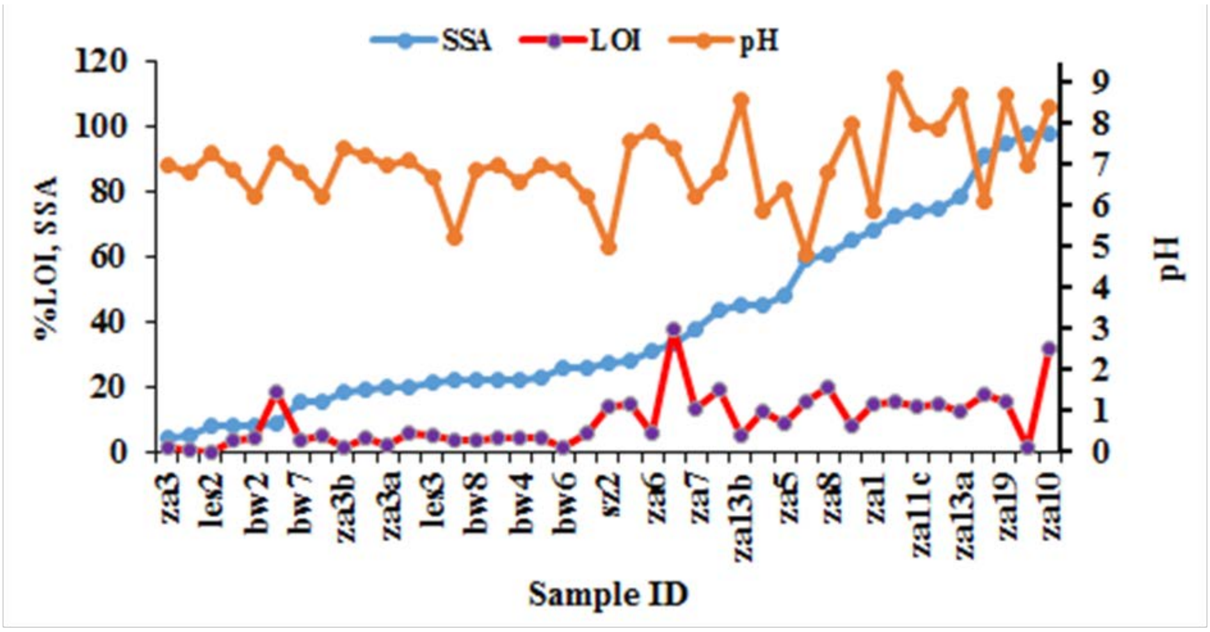


Figure 4.4: Physiochemical properties

Free State. The commercial sample, za12, has a SSA of 97.6 m^2 g^{-1}. Since this is synthetic it could have been intentionally synthesized to small particles which account for the large SSA.

Swaziland. The red sz1 has 73.9 % m/m kaolinite and a SSA of 59.1 m^2 g^{-1} while the white sz2 has 81.2 % m/m kaolinite and a SSA of 27 m^2 g^{-1}. This is an exhibition of heterogeneity within the same region.

Zimbabwe. The SSA result tallies with the literature kaolinite and the result of 90.2 % m/m kaolinite in zm1.

4.2.3 X-ray analyses

4.2.3.1 XRD mineral analysis

Table 4.3 depicts XRD clay mineral results revealing varying quartz content which is very minimal for les1. Les2 is the only sample that contained 32.8 % m/m magnetite and 61.9% ilmenite. On the other hand the Venda 8c is the only sample that contained epidote at 6.0 % m/m. Heterogeneity in mineralogy is a predominant feature not only for the different regions but even amongst samples from the same region. Mpumalanga has the highest quartz content of 99.2 % m/m while Lesotho has a least value of 1.5 % m/m. Kaolinite was highest for Gauteng at 92.3 % m/m and least for Botswana 1.2 % m/m.

The highest non-swelling 2:1:1 muscovite was for Botswana at 59.0 % m/m and the least for Swaziland 3.6 % m/m and Botswana 2.4 % m/m, Venda had the highest 2:1 smectite of 67.3 % m/m and Makurung the least of 16.0 % m/m smectite. The two extremes for haematite were 98.5 % m/m for Lesotho and 0.8 % m/m for Mpumalanga. Gibbsite was only detected in the Venda samples with a highest of 45.1 % m/m.

Botswana had the micaceous non-swelling 2:1 muscovite in all the samples. Trace amounts of the 1:1 kaolinite were detected in 75 % of the samples. The highest quartz content was 59.0 % m/m in bw8. Only one sample had a trace amount of the oxide, rutile. Haematite was detected, up to 93.9 % m/m, in 41.7 % of the samples.

The **Lesotho** samples all had quartz, with the highest value of 45.4 % m/m in les3 and the lowest value of1.5 % m/m in les1. Trace amounts of rutile were detected in les2 and les3. An exceptionally high amount of 98.5 % m/m haematite was reported in les1 but none in les2. However, les2 presented 61.9 % m/m ilmenite and 32.8 % m/m magnetite. Goethite was only detected for les3 and this also had 1:1 kaolinite and the micaceous non-swelling 2:1 muscovite.

The **Swaziland** samples had no swelling clays in the two clayey soil samples. Amounts of more than 73 % m/m 1:1 kaolinite were detected. Micaceous non-swelling 2:1 muscovite and 2:1 talc in minimal amounts were detected, accompanied by trace amounts of haematite. Quartz was present at less than 13 % m/m.

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The **Eastern Cape** had no swelling clays. Significant amounts of 1:1 kaolinite were found in za7 and za9 with trace amounts in za5. Only za7 had no muscovite and only za5 had microcline. Anatase was detected in samples za7 and za9. All samples contained quartz up to 64.9 % m/m. Traces of goethite and haematite were detected in za5 and za7.

The **Free State** commercial za12 had 10 % m/m of the micaceous non-swelling 2:1:1 chlorite. Quartz and goethite are present at less than 20 % m/m each. Haematite content of 58.8 % m/m was reported. The Free State commercial za12 was packaged as iron oxide but perceived as *letsoku* by indigenes. It had 10 % m/m of the 2:1:1 chlorite micaceous clay. Low levels of quartz, 58.8 % m/m of haematite and significant amounts of goethite were also reported.

In the **Gauteng** samples, amounts greater than 84 % m/m of 1:1 kaolinite were detected. There were no swelling clays in the commercial Gauteng za1 and za2. Trace amounts of microcline and quartz were found in both samples. Only za2 had 0.3 % m/m calcite.

The **KwaZulu-Natal** results from the two regions of Mtubatuba, za11b and za11c had swelling smectite at 58 % m/m and 61.2 % m/m respectively. Traces of 2:1:1 swelling chlorite were noted in the Nongoma za13b. Plagioclase and kaolinite are randomly distributed in the two clayey soils. Quartz in za13b was at 84.5 % m/m. The titanium dioxide polymorphs, anatase and rutile, are present in varying degrees in all five samples. The hydrated iron oxide, goethite, is absent only in za13b.

Limpopo sample za8c (Venda) had the highest smectite content of 67.3 % m/m as did za10 from Makurung also in Limpopo. Low levels of kaolinite and muscovite were noted in 60 % of the Venda samples. All the samples had quartz, with the highest value of 89.9 % m/m for za8b. Anatase and goethite were found in 67 % of the Venda samples. The peculiar presence of gibbsite was noted in 67 % of the Venda samples. This was not detected in any other clayey soil from the other regions. Only za10 reflected 54 % m/m dolomite and 4.5 % m/m of sepiolite.

Table 4.3: XRD mineral content in % m/m on fixed receiving slits with Fe filtered Co-Kα radiation (λ=1.789Å)

Sa ID	Mc	Pl	Kln 1:1	Ms 2:1	Tlc 2:1	Sep 2:1	Sme 2:1	Chl 2:1:1	Qz	Ant	Rt	Hem	Mag	Gth	Gbs	Cal	Dol §
za1	-	-	92.3	-	-	-	-	-	7.7	-	-	-	-	-	-	-	-
za7	-	-	76.7	-	-	-	-	-	16.5	3.5	-	3.3	-	-	-	-	-
za11b	-	-	34.4	-	-	-	-	-	47.3	5.5	-	-	-	12.8	-	-	-
zm1	-	-	90.2	-	-	-	-	-	7.3	2.6	-	-	-	-	-	-	-
bw1	3.2	-	-	43.7	-	-	-	-	53.1	-	-	-	-	-	-	-	-
bw1a	1.9	-	4.5	40.5	-	-	-	-	39.8	-	-	-	-	-	-	-	-
bw2	1.3	-	2.8	46.1	-	-	-	-	48.8	-	-	-	-	1.1	-	-	-
bw2a	1.8	-	5.1	59.0	-	-	-	-	34.1	-	-	-	-	-	-	-	-
bw3	1.4	-	-	50.6	-	-	-	-	48.0	-	-	-	-	-	-	-	-
bw3a	3.7	-	3.9	53.8	-	-	-	-	37.8	-	0.8	-	-	-	-	-	-
bw4	-	-	1.2	30.0	2.8	-	-	-	36.5	-	-	29.5	-	-	-	-	-
bw5	-	-	-	2.4	-	-	-	-	3.7	-	-	93.9	-	-	-	-	-
bw6	-	-	4.3	50.0	-	-	-	-	44.0	-	-	1.7	-	-	-	-	-
bw6a	-	-	1.4	57.7	-	-	-	-	40.9	-	-	-	-	-	-	-	-
bw7	-	-	4.7	53.4	-	-	-	-	40.1	-	-	1.8	-	-	-	-	-
bw8	-	-	5.7	35.9	-	-	-	-	57.2	-	-	1.3	-	-	-	-	-
les3	-	-	10.4	7.5	-	-	-	-	45.4	-	2.2	28.7	-	5.8	-	-	-
sz1	-	-	73.9	11.2	1.1	-	-	-	10.7	-	-	3.1	-	-	-	-	-
sz2	-	-	81.2	3.6	0.4	-	-	-	12.1	-	-	2.7	-	-	-	-	-
za2	-	-	84.1	4.0	-	-	-	-	11.7	-	-	-	-	-	-	0.3	-
za5	5.4	-	12.7	16.0	-	-	-	-	58.6	-	-	-	-	7.4	-	-	-
za6	-	-	-	41.9	-	-	-	-	58.1	-	-	-	-	-	-	-	-
za8	-	-	-	9.6	-	-	-	14.1	14.8	1.9	-	-	-	16.1	43.5	-	-
za8a	-	-	17.4	7.0	-	-	-	-	14.4	2.1	-	-	-	17.7	41.3	-	-
za8b	-	-	-	-	-	-	-	5.3	89.9	-	-	-	-	-	4.9	-	-
za8b1	-	-	18.2	4.6	-	-	-	-	11.7	2.7	-	-	-	17.7	45.1	-	-
za8c	-	-	7.9	-	-	-	67.3	5.6	11.0	2.2	-	-	-	-	-	-	-
za9	-	-	23.6	9.6	-	-	-	-	64.9	1.9	-	-	-	-	-	-	-
za10	8.6	12.6	-	-	-	4.5	16.0	-	4.2	-	-	-	-	-	-	-	54.2
za11a	-	5.1	4.3	-	-	-	58.0	-	26.1	1.1	-	-	-	5.5	-	-	-
za11c	-	10.7	-	-	-	-	61.2	-	23.7	1.1	-	-	-	3.3	-	-	-
za12	-	-	-	-	-	-	-	10.0	19.1	-	-	58.8	-	11.1	-	-	1.0
za13a	-	-	35.9	-	-	-	-	-	46.9	5.4	2.7	-	-	9.0	-	-	-
za13b	-	7.0	-	-	-	-	-	7.4	84.5	-	1.2	-	-	-	-	-	-
Za15	-	14.5	0	-	-	-	78.0	-	4.9	-	-	-	-	-	-	-	-
Za19	-	-	-	-	-	-	96.2	-	3.8	-	-	-	-	-	-		
les1	-	-	-	-	-	-	-	-	1.5	-	-	98.5	-	-	-		
les2	-	-	-	-	-	-	-	-	3.8	-	1.5	-	32.8	-	-	-	-
za3	-	-	-	-	-	-	-	-	99.2	-	-	0.8	-	-	-	-	-
za3a	-	-	-	-	-	-	-	-	93.9	-	-	1.5	-	4.5	-	-	-
za3b	-	-	-	-	-	-	-	-	99.2	-	-	0.8	-	-	-	-	-

§ *Clay mineral IUGS standard abbreviations used according to Whitney and Evans (2009) and Siivola and Schmid (2007)* Abbreviations used of the studied clays (Ep = epidote, Mc = microcline, Pl = plagioclase, Kln = kaolinite, Ms = muscovite, Tlc = talc, Sep = sepiolite, Sm = smectite, Chl = chlorite, Qz = quartz, Ant = anatase, Rt = rutile, Il = ilmenite, Hem = haematite, Mag = magnetite, Gth = goethite, Gbs = gibbsite, Cal = calcite, Dol = dolomite) -*Clay mineral not detected*

Mpumalanga had no swelling clays. All the clayey soils reported 93.9 % m/m to 99.2 % m/m quartz. Haematite ranged from 0.8 % m/m to 1.5 % m/m. Za3a also had 4.5 % m/m goethite.

The **Zimbabwe** samples had no swelling clays. The kaolinite content was found to be 90.2 % m/m while anatase was 2.6 % m/m. The quartz amount was 7.3 % m/m.

4.2.3.2 XRF elemental analysis

Metal oxides were determined in all the samples shown in Table 4.4. As expected, all samples contained significant SiO_2 and Al_2O_3. Iron was present in all samples with the highest measured for a Lesotho sample (94.0 % m/m Fe_2O_3) and the lowestfor bw3 from Botswana (1.1 % m/m). Titanium dioxide was highest for a sample from Swaziland (3.3 % m/m TiO_2), but none was detected in some other samples, e.g. those from Mpumalanga and Venda.

Table 4.4: XRF metal oxide content in % m/m

Sa ID	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	Cr_2O_3
za1	40.7	1.5	27.4	16.7	0.1	0.6	0.0	0.0	0.5	0.1	0.1
za7	43.6	1.6	23.3	19.8	0.1	0.1	0.0	0.0	0.2	0.1	0.1
za11b	47.6	2.1	18.2	16.8	0.1	0.8	2.6	0.9	0.1	0.0	0.0
zm1	18.0	0.2	4.7	61.9	0.1	1.7	1.0	0.0	0.3	0.1	0.0
bw1	69.5	0.8	18.3	2.6	0.0	0.4	0.0	0.1	5.1	0.1	0.0
bw1a	54.7	0.7	16.4	20.0	0.0	0.1	0.0	0.2	3.8	0.1	0.0
bw2	66.9	0.8	18.6	3.2	0.0	0.4	0.0	0.1	5.3	0.1	0.0
bw2a	60.6	1.0	22.2	4.4	0.0	0.4	0.0	0.1	6.3	0.1	0.0
bw3	69.4	0.8	18.8	1.1	0.0	0.3	0.0	0.1	5.5	0.1	0.0
bw3a	65.9	0.8	21.0	0.8	0.0	0.3	0.0	0.1	6.2	0.1	0.0
bw4	50.6	0.6	13.5	29.1	0.4	0.2	1.1	0.2	3.1	0.1	0.0
bw5	68.6	0.9	19.9	3.2	0.0	0.3	0.0	0.1	5.6	0.1	0.0
bw6	5.4	0.2	2.3	86.4	1.3	0.0	0.0	0.0	0.4	0.1	0.1
bw6a	66.0	0.9	21.0	1.2	0.0	0.3	0.0	0.1	6.3	0.1	0.0
bw7	63.2	0.9	20.0	4.4	0.0	0.4	0.0	0.1	5.8	0.1	0.0
bw8	67.9	0.7	16.5	5.3	0.0	0.3	0.0	0.1	4.2	0.1	0.0
les3	41.3	0.8	7.3	44.0	<0.01	<0.01	0.1	<0.01	0.9	0.2	0.0
sz1	44.3	0.6	26.7	16.7	0.1	0.6	0.0	0.0	0.3	0.0	0.0
sz2	46.2	3.3	34.9	0.6	0.0	0.1	0.0	0.0	0.1	0.2	0.0
za2	47.9	1.7	34.0	1.7	0.0	0.1	0.0	0.0	0.6	0.0	0.1
za5	60.6	0.8	18.8	9.4	0.0	0.5	0.0	0.0	2.5	0.1	0.0
za6	69.0	0.7	17.6	3.1	0.0	0.9	0.4	0.4	4.3	0.2	0.0
za8	78.1	0.0	0.3	1.8	0.0	0.0	0.2	0.0	0.0	0.0	0.0
za8a	24.8	2.8	33.4	32.1	0.1	0.7	0.5	0.0	0.6	0.3	0.1
za8b	72.6	0.6	6.6	4.5	0.0	1.0	0.1	0.0	0.5	0.1	0.0
za8b1	18.5	2.4	31.2	30.6	0.2	0.3	0.0	0.0	0.3	0.2	0.1
za8c	42.4	2.0	19.6	21.9	0.1	1.0	1.8	0.1	0.1	0.1	0.1
za9	62.5	0.8	18.7	6.7	0.0	0.5	0.0	0.0	3.6	0.1	0.0
za10	25.5	0.1	6.8	2.8	0.1	13.4	20.4	0.5	0.2	0.0	0.0
za11a	52.8	1.8	14.3	16.5	0.1	1.3	2.2	0.4	0.2	0.0	0.0
za11c	53.9	1.7	15.1	16.7	0.1	1.4	0.9	1.1	0.2	0.1	0.0
za12	5.9	0.1	2.2	87.3	0.8	0.0	0.0	0.0	0.2	0.1	0.1
za13a	48.8	2.2	20.4	15.8	0.1	0.7	0.8	1.1	0.1	0.01	0.0
za13b	78.2	0.8	7.8	5.3	0.1	0.5	0.8	0.7	0.8	<0.01	0.0
za15	64.3	0.1	17.1	3.6	0.1	1.7	1.6	2.5	0.6	0.0	<0.0
za19	54.6	0.3	18.0	5.5	0.0	3.8	1.8	0.2	0.5	0.0	0.0
les1	1.3	0.3	0.3	94.0	0.0	0.0	<0.0	0.0	<0.0	<0.0	0.1
les2	44.5	0.8	7.2	46.2	<0.01	0.1	0.1	<0.01	0.9	0.0	0.0
za3	23.6	2.9	36.3	34.6	0.0	0.3	0.4	0.0	0.4	0.2	0.1
za3a	91.1	0.0	0.9	5.4	0.4	0.2	0.0	0.0	0.0	0.0	0.0
za3b	96.0	0.0	0.3	2.3	0.1	0.1	0.0	0.0	0.0	0.0	0.0

The highest crystalline SiO_2 of 91.1 % m/m and 96.0 % m/m were reported for za3 and za3a from Mpumalanga and Lesotho, with the lowestof 1.3 % m/m for les1. Fe_2O_3 is present in all samples, but is highest for Lesotho at 94.0 % m/m and lowestfor Botswana at 1.1 % m/m. Al_2O_3 was detected in all samples with a peak of 36.3 % m/m for Mpumalanga and the lowest contents of 0.3% m/m for Lesotho, Mpumalanga and Venda. TiO_2 ranges between 3.3 % m/m for Swaziland and 0% m/m for Mpumalanga and Venda.

Trace metals

All samples were analyzed for trace metals except za3b which proved recalcitrant or unmanageable. The results are given in Table 4.5. The highest As content of 355 ppm was obtained for Botswana and the lowest value of 0 ppm also for Botswana, Eastern Cape, Gauteng, KwaZulu-Natal, Makurung, Lesotho, the Free State, Swaziland, Zimbabwe and Venda.

Table 4.5: Trace metals content (ppm)

SA ID	As	Cu	Ga	Mo	Nb	Ni	Pb	Rb	Sr	Th	U	W	Y	Zn	Zr
za1	0	8	33	0	8	19	0	50	5	0	0	1	49	85	177
za7	0	38	25	0	2	25	0	11	9	0	0	1	10	66	131
za11b	7	107	29	0	14	87	0	8	38	0	0	9	44	41	387
zm1	0	6	0	0	0	49	0	0	383	0	0	1	4	158	96
bw1	**50**	12	33	6	32	20	0	206	20	12	0	94	82	30	711
bw1a	**355**	75	34	14	22	61	0	177	25	1	0	14	83	31	607
bw2	**63**	10	34	6	35	21	0	216	19	18	0	47	104	34	714
bw2a	**80**	13	40	10	44	29	0	254	13	24	4	26	166	16	909
bw3	**31**	6	32	5	34	12	0	218	20	15	0	61	83	14	684
bw3a	**35**	5	37	7	40	12	0	247	24	20	0	26	116	9	801
bw4	**9**	13	20	0	13	24	0	105	75	0	0	128	44	21	434
bw5	0	0	0	0	0	30	0	0	162	0	0	1	0	0	64
bw6	**66**	9	35	7	35	17	0	224	20	15	0	38	97	23	755
bw6a	**57**	6	39	9	41	12	0	249	20	22	1	19	115	9	833
bw7	**66**	11	36	7	35	24	0	232	17	18	0	31	105	12	761
bw8	**55**	0	30	62	68	0	73	194	35	46	95	56	122	21	616
les3	0	2	15	0	2	4	0	17	23	0	0	27	3	9	255
sz1	0	61	23	0	2	133	0	9	0	0	0	30	12	71	107
sz2	13	3	37	19	75	12	104	11	64	94	4	1	60	9	1160
za 2	8	2	29	0	6	0	0	21	0	0	0	1	0	8	182
za5	20	29	24	0	14	18	0	144	32	10	0	5	33	84	173
za6	11	15	23	0	16	12	23	216	86	13	0	15	40	56	267
za8	0	386	34	3	10	285	37	6	0	0	0	1	0	40	188
za8a	0	463	36	0	2	247	0	11	20	0	0	9	1	50	193
za8b	0	102	8	0	8	62	0	19	12	4	0	151	1	41	137
za8b1	0	372	29	0	1	281	0	2	0	0	0	1	0	29	182
za8c	0	226	25	0	4	133	0	0	60	0	0	1	31	71	172
za9	1	20	24	0	16	13	14	173	22	13	0	5	32	47	218
za10	0	5	3	0	0	37	0	8	424	0	0	1	0	16	38
za11a	0	97	19	0	8	111	0	9	57	0	0	9	29	50	279
za11c	0	92	22	0	8	71	0	9	98	0	0	1	34	49	350
za12	0	0	0	0	0	22	0	0	198	0	0	1	0	0	52
za13a	0	122	27	0	11	88	0	6	30	0	0	6	41	43	351
za13b	2	38	7	0	6	31	0	34	44	0	0	88	10	29	317
les1	0	50	0	0	0	46	0	0	0	0	0	1	0	933	1
les2	0	0	26	0	779	566	0	0	0	0	0	197	0	281	532
za3	120	6	0	0	0	56	0	0	11	0	0	114	0	23	2
za3a	70	0	3	49	37	18	54	22	32	24	74	135	28	18	32
za3b	U	N	S	T	A	B	L	E		S	A	M	P	L	E
za15	0	1	20	0	18	0	8	16	149	19	0	1	17	59	166
za19	0	5	14	0	8	9	0	33	88	18	0	1	14	48	142

Pb was detected in six samples only (bw8, sz2, za3a, za8, za6 and za9) with the highest of 104 ppm for Swaziland. Rb was 254 ppm for Botswana with the lowest value of 0 ppm for Botswana, Lesotho, Mpumalanga, the Free State, Venda and Zimbabwe. U was 74 ppm in za3a, 4 ppm in bw2a and sz2, and 1 ppm for bw6a. The rest of the samples had 0 ppm each.

Zn the highest value of 933 ppm for Lesotho and the lowest value of 0 ppm for Botswana and the Free State. Zr peaked at 1160 ppm for Swaziland and was lowest for Lesotho at 1 ppm. Botswana had a high range of Zr, 434–909 ppm and an odd low of 64 ppm for bw5.

The heterogeneous nature of the clays is more pronounced in Fig. 4.5 which complements Table 4.5.

The high Zr level in all the Botswana samples is very conspicuous. This also applies to the sz2 sample. Nb and Ni are exceptionally high for les2 and les3 and so is the Zn, but it is much less than that for les1.

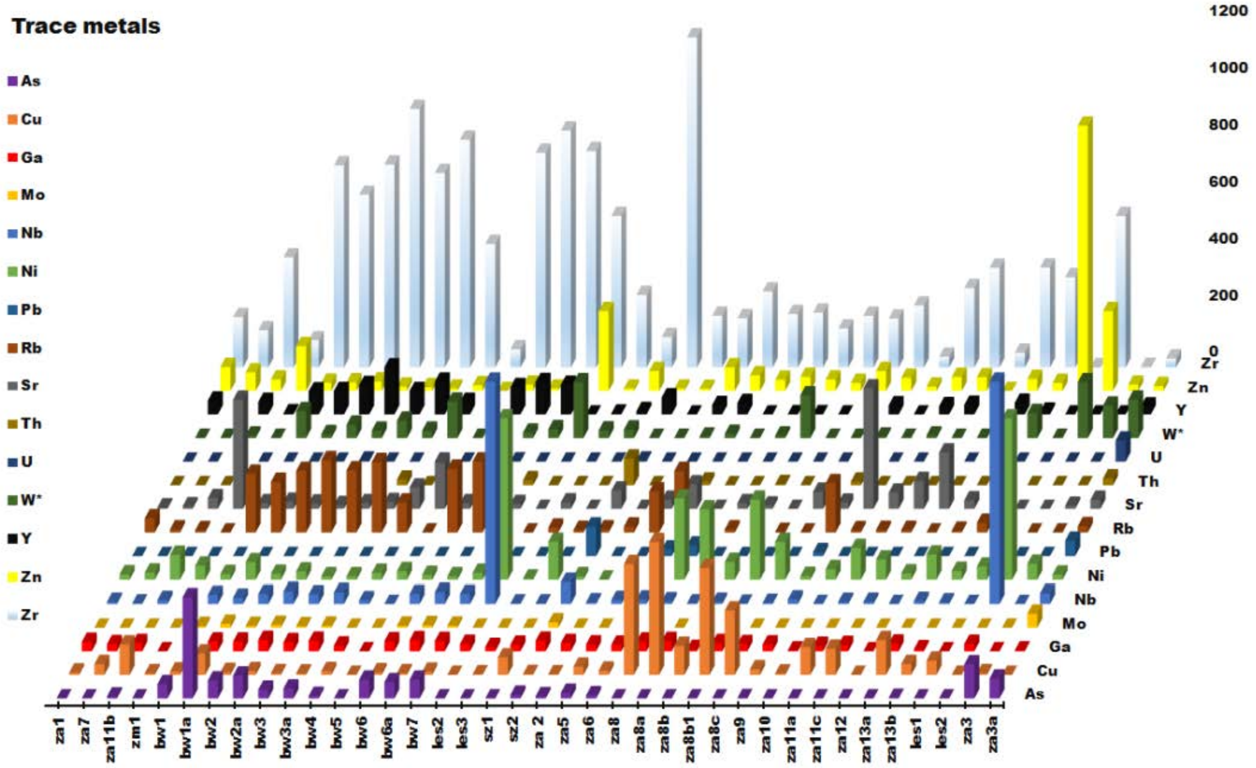

Figure 4.5: XRF trace metals 3-D graph

4.2.4 SEM morphological analysis

Figure 4.6 shows micrographs of representative samples from the various regions in Southern Africa. The particle heterogeneous morphologies range from agglomerated structures of small spherical sub-particles to fibrous forms and platelets.

Botswana sample bw2a has a prevalence of densely bladed muscovite with overlying quartz bubbles. No swelling clays were detected in the 12 Botswana deposits. Trace amounts of micaceous microcline were detected in 50 % of these samples. There were significant amounts of non-swelling 2:1 muscovite in 75 % of the samples. Trace amounts of the 1:1 kaolinite were detected in 75 % of the samples. The highest quartz content was 57.2 % m/m in bw8. Only one sample contained trace amounts of rutile. Haematite (1.3–93.9 %) was detected in 42 % of the samples.

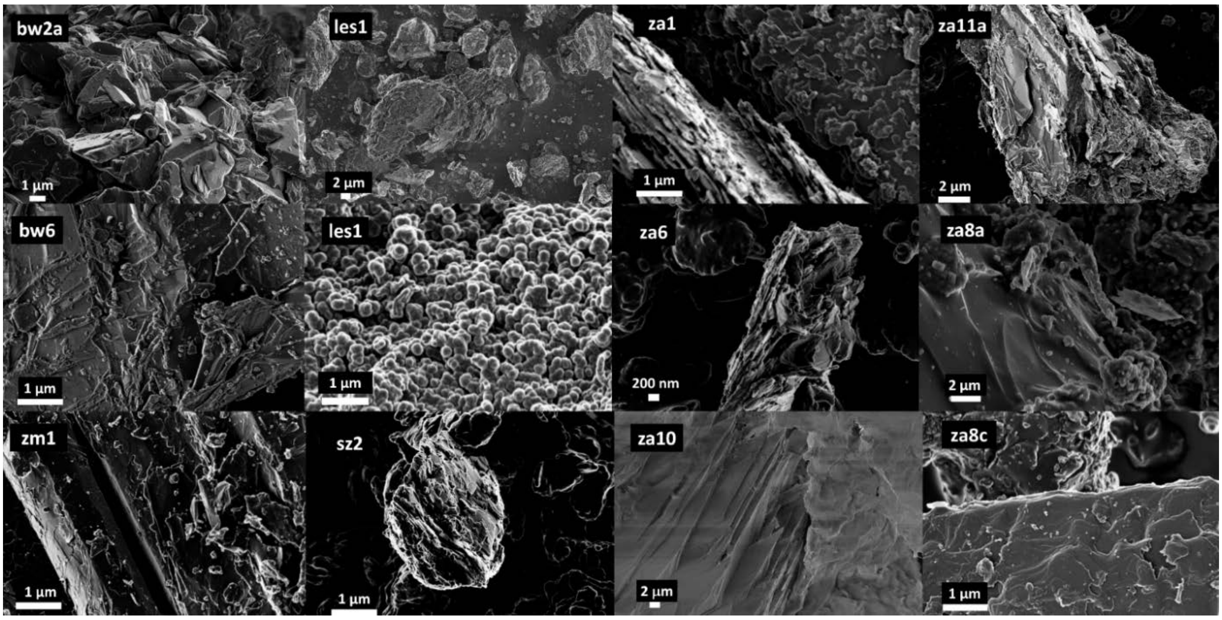

Figure 4.6: SEM micrographs of selected samples

Lesotho les1 shows hexagonal platy black haematite. The swelling clays were not present in the two Swaziland deposits but high amounts of 1:1 kaolinite were detected. Micaceous non-swelling 2:1 muscovite and 2:1 talc in minimal amounts were detected accompanied by trace amounts of haematite. Quartz was present in the two deposits at 10.7 % m/m and 12.1 % m/m.

The second les1 micrograph reflects what appears to be agglomerated nanoparticles. Only les3 of the three Lesotho deposits contained clay minerals or phyllosilicate 1:1 kaolinite and the micaceous 2:1 muscovite. Quartz was detected in all samples with the highest value of 45.4 % m/m in les3 and the lowest 1.5 % m/m in les1. Trace amounts of rutile were detected in les2 and les3. An exceptionally high amount of 98.5 % m/m of haematite was reported in les1 but none in les2. However, les2 contained 32.8 % m/m magnetite and 61.9 % m/m ilmenite while goethite was only detected for les3.

The **Gauteng** za1 depicts the conspicuous prevalence of hexagonal kaolinite platelets and overlying bubbles of quartz.

The **Mtubatuba, KwaZulu-Natal,** za11a has a few hexagonal kaolinite platelets resting on a mesh of quartz.

The **Engcobo, Eastern Cape,** za6 shows the predominance of dense bladed muscovite with conspicuous overlying quartz. None of the other samples contained swelling clays. Significant amounts of kaolinite were found in za7 and za9 with trace amounts in za5. All the clayey soils except for za7 had muscovite and only za5 contained 5.4 % microcline.

The **Zimbabwean** zm1 has conspicuous kaolinite platelets (90.2 % m/m while the anatase content was 2.6 % m/m. Quartz levels were 7.3 % m/m with overlying quartz bubbles. Sz2 shows a trace of muscovite overshadowed by the predominant kaolinite platelets swelling clay was detected in the single sample from Zimbabwe that was found to be clayey soil.

The **Makurung, Limpopo,** sample za10 shows dolomite rhombohedral crystals visible on the fibres of smectite. This is interspersed with fine quartz crystals.

The **Venda, Limpopo,** za8c shows kaolinite platelets and quartz bubbles on the surface of smectite fibres. Za8a has a prevalence of kaolinite and quartz crystals on the surface of smectite and sepiolite fibres.

High amounts of kaolinite were detected with no swelling clays in the commercial **Gauteng** za1 and za2 deposits. Trace amounts of microcline and quartz were found in both samples. Only za2 had 0.3 % m/m calcite.

The results from the two **KwaZulu-Natal** regions are reported as follows. **Mtubatuba** za11b and za11c exhibited swelling character with 58 % m/m and 61.2 % m/m smectite respectively. Traces of 2:1:1 non-swelling chlorite were noted in **Nongoma** za13b. Plagioclase and kaolinite are randomly distributed in the two clayey soils. High levels of quartz were detected, particularly in za13b at 84.5 % m/m. The titanium dioxide polymorphs, anatase and rutile, are present in varying degrees in all five samples. The hydrated iron oxide, goethite, is absent only from za13b.

Swelling clays were detected in za8c from **Venda, Limpopo** and za10 from **Makurung** also in **Limpopo**. The highest was 67.3 % m/m 2:1 smectite for za8c, a wet greyish green sample. Low levels of kaolinite and muscovite were noted in 60 % of the Venda samples. Microcline and non-swelling 2:1 plagioclase reflected only in za10. All the deposits had quartz, with the highest value of 89.9 % m/m for za8b. Anatase and goethite were found in 67 % of the Venda samples. The peculiar presence of gibbsite was noted in 67 % of the Venda samples. This was not detected in any other clayey soil from the other regions. Only za10 reflected 54 % m/m dolomite, 16 % m/m smectite, 12.6 % m/m plagioclase and trace amounts of sepiolite.

No swelling clays were detected in the **Mpumalanga** samples. All the clayey soils reported 93.9 % m/m to 99.2 % m/m quartz. Haematite ranged from 0.8 % m/m to 1.5 % m/m. Only za3a also had 4.5 % m/m goethite.

4.2.5 Thermogravimetric analysis (TGA)

Thermal analysis of the clayey soils was performed and the results of representative samples from Botswana, Lesotho, Swaziland, Zimbabwe and South Africa (Pretoria) are portrayed in Fig. 4.7.

There is an apparent similarity between the thermal degradative patterns of the Botswana samples in Fig. 4.7(a). An expanded version of the same thermogram in Fig. 4.7(b) reaffirms the heterogeneity already noted in the mineralogy. Note that the thermogram label keys for the individual samples are the same for Fig. 4.7(a) and Fig. 4.7(b). The samples za15 and za19 are commercial clay mineral controls which yield steeper gradients than those of the research samples, as expected.

Similarly, the random samples from different regions in Fig. 4.7(d) confirm the heterogeneity which is initially not so evident in Fig. 4.7(c). The thermogram label keys for the individual samples are the same for Fig. 4.7(c) and Fig. 4.7(d).

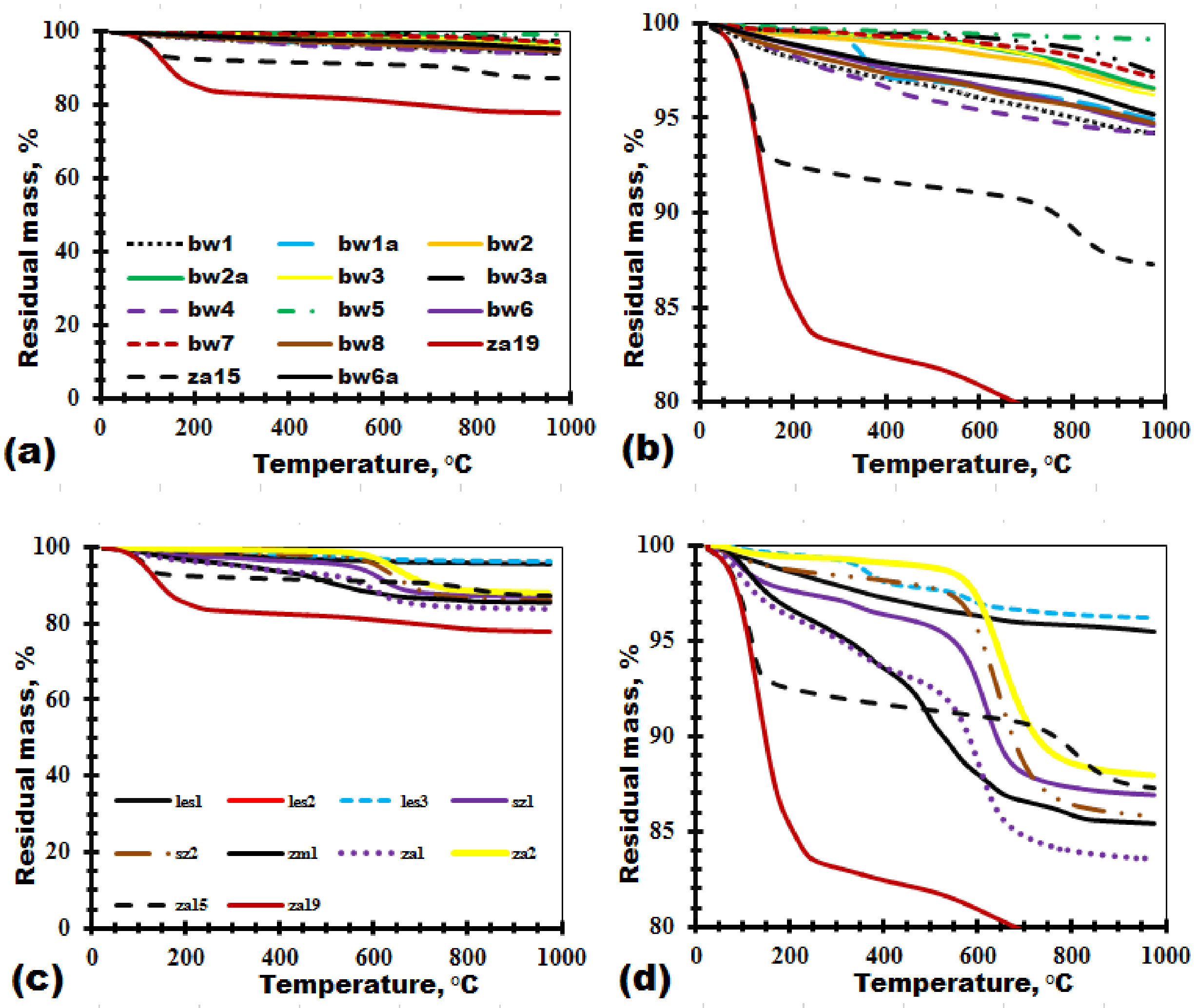

Figure 4.7: TGA thermograms from runs of the samples initially isothermally at 25°C for one minute and then heated from 25°C to 950°C at 10 °C min^{-1} (Department of Chemistry, Tshwane University of Technology)

Botswana samples along with commercial controls of a clay (za15) and a clay mineral (za19) are shown in Figs. 4.7(a) and 4.7(b). Thermograms for the Lesotho, Swaziland, Zimbabwe and South Africa (Pretoria) samples with commercial controls of a clay (za15) and a clay mineral (za19) are shown in Figs. 4.7(c) and 4.7(d).The apparent organic content, estimated from the LOI results (Table 4.1), varied from 0 % m/m for les2, 1 % m/m for za3b to 31.7 % m/m and 37.4 % m/m for samples za10 and za8a respectively. The LOIs for za15 and za19 were 8.2 % and 15.2 respectively. The other Venda samples varied between 17.7 % m/m to 19.6 % m/m. Dehydration of the clayey soils may occur above 450°C.

4.2.6 Infrared spectroscopic analysis

Attenuated total reflectance Fourier Transform infrared (ATR-FTIR) spectra of the clay minerals were obtained. Fig. 4.8(a) are spectra from the Botswana region. Fig. 4.8(b) is a random selection of samples from various regions. Commercial clay za15 and clay mineral za19 are used as controls in this study. Les1 is totally different from the rest of the samples.

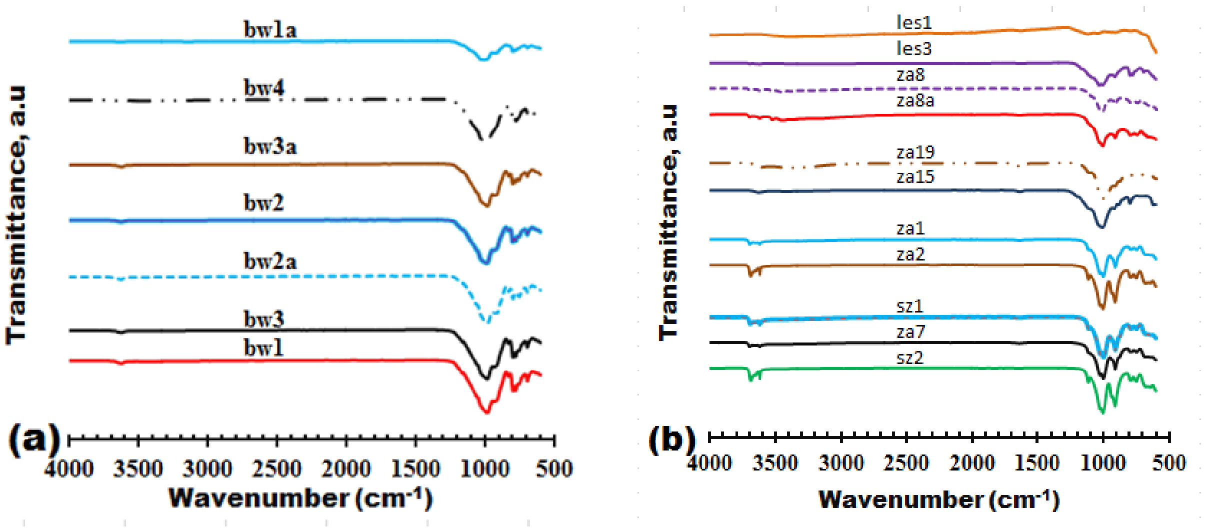

Figure 4.8: ATR-FTIR spectra obtained from runs at 32 scans from 500–4000 cm^{-1} in air

The absence of any bands near 3000 cm^{-1} in the FTIR spectra shown in Fig. 4.8 suggests that very little, if any, organic material is actually present. This negates any implication of the LOI results indicating the presence of organic material. There is a conspicuous absence of a band at 1230–1280 cm^{-1} in virtually all the selected samples except for the very slight hump in les1. This implies the absence of amorphous silica.

The spectra can be fully explained by the presence of inorganic components in terms of previous observations (Fadil-Djenabou *et al.* 2015; Akyuz *et al.* 2008; Russell *et al.* 1994; (Boulingui *et al.*, 2015b). The O-H asymmetric stretching in Al_2O–H occurs around 3700 cm^{-1} probably due to the surface OH groups and the internal OH groups due to the Al-OH in the octahedral sheet at 3650 cm^{-1}. This band is missing in the spectrum for les1, confirming the XRD result of the absence of kaolinite. The band at 3660 cm^{-1} is attributed to water OH bending vibrations(Boulingui *et al.*, 2015b), but there is only a very shallow dip in the spectrum of sample les3.Si-O stretching vibrations are observed at 1000 cm^{-1} (Boulingui *et al.*, 2015b). The band near 920 cm^{-1} is typical for Si–O stretching and Al_2O–H deformation in the alumina silicate, i.e. kaolinite (Fadil-Djenabou *et al.*, 2015).The bands at 1100 cm^{-1} are assigned to Si-O and those at 1025 cm^{-1} to Si-O planar stretching. The bands around 775 cm^{-1} and 750 cm^{-1} can be attributed to the Al-O-Si inner surface vibration. The bands at 800 cm^{-1}, 775 cm^{-1} and 690 cm^{-1} are typical for quartz (Akyuz *et al.*, 2008). There is a slight dip due to the 1.5 % m/m quartz reported in les1.

CHAPTER 5 : DISCUSSION AND ANALYSIS

5.1 ANALYSIS OF RESULTS

The XRD analysis revealed a surprising variability in the mineralogical composition of these soils, even in samples obtained from the same region. This implies that the actual applications must be robust with respect to clay composition. The wide-ranging diversity in the mineral composition was rather eccentric. *Letsoku* versions containing kaolinite and muscovite occurred more frequently than those comprising smectite clays. Some samples were exceptionally profuse in quartz. In fact, some amount of quartz was present in each and every sample collected. The main mineral present in the various samples was not even the same. In decreasing frequency, the main constituents were quartz (37 %), muscovite (18 %), kaolinite (16 %), haematite, gibbsite and smectite each at 8 %, and ilmenite and dolomite each at 3 %. Kaolinite and muscovite were present in 61 % and 56 % of the samples respectively.

Colour varies widely for all clayey soils. It is affected by mineral composition, the iron oxidation state, the presence of organic matter and the moisture content. The variation of colour with Fe(II), Fe(II, III) and Fe(III) oxidation states is illustrated by the oxides in grey-brown ilmenite, black magnetite, red haematite and brownish yellow goethite respectively. The highest Fe(III) content was detected in the haematite sample les1 which had a pH of 5.22. The hydrated iron oxide goethite features as a pigment in cosmetic products such as lipstick and foundations.

Cosmetic applications were indicated as the principal *letsoku* function. In this, colour is usually an important factor as demonstrated by the various pigments generated by the ancient Egyptians (Scott 2016). Several shades of reds, pinks and yellows were obtained by mixing red, yellow and brown ochres with minerals such as calcite, orpiment and gypsum Scott (2016) emphasized the distinction between red ochre (natural substance) and haematite (a pure version of red ochre). This links with the realization that two-thirds of the samples collected contained one or more iron mineral with strong pigmenting properties. Even those samples with a very high quartz content had a reddish colour caused by the presence of iron oxide. In addition, the gritty quartz particles present in some of the samples could provide an exfoliation function suitable for skin cleansing.

Clay minerals were the main constituents in most of those samples that were essentially free of iron minerals. In these materials the adsorption properties may account for the desired function. These two aspects are explored in more detail below.

The colloidal nature of the clays, with the associated high surface area of the platelets and the nature of the surfaces, determines the clay adsorption properties. BET surface area values of 56–119 $m^2 g^{-1}$ were recorded for the *letsoku* smectite-containing samples. They accord with those reported by Fakhfakh *et al.* (2005). In retrospect, the utility of **kaolinite** as a major ingredient in some *letsoku* samples is not that unusual as it finds application in modern cosmetics, e.g. facial masks. Furthermore, kaolinite's heterogeneous pH-dependent surface charges have a significant role in adsorption (Gunter, 1997). These minerals provide opacity to cover, for example, blemishes or to remove grease and toxins from the skin(Carretero and Pozo, 2010) Favero *et al.* 2016). Kaolinite also has extensive application in various products, including creams, toothpaste, cosmetics, facial masks, soaps and as a dermatological protector.

A similar argument holds for the presence of micaceous **muscovite** in some of the *letsoku* samples. Modern creams include it as an ingredient to produce a luminous skin effect. Muscovite emulates the mica that is used for its high reflectance and iridescence in eyeshadows and lipsticks (Carretero and Pozo, 2010).

The TiO_2 polymorphs anatase and rutile have high refractive indices and therefore good light-scattering properties which make them ideal for sun protection. Sample les2 contains mostly ilmenite, $FeTiO_3$, which is familiar to the Basotho people as the black pigment *sekama* (Ambrose *et al.*, 2001). This is a natural source of TiO_2 which is used for sun protection.

Gibbsite, also known as hydrargillite, is an ore of aluminium and makes up one of the minerals of bauxite. It is a natural variety of the amphoteric aluminium hydroxide, α-$Al(OH)_3$ and hence can act as a buffer. $Al(OH)_3$ has been known to bond (coat) onto the TiO_2.This leads to enhanced broad-spectrum sun protection and anticaking and hence even dispersion of the TiO_2(CIR, 2014). Gibbsite is known to be currently present in more than 500 modern cosmetic products. These include eye cosmetics, suntan products, lipsticks and various other skin care products (CIR, 2014). The above results add to the plausibility of *letsoku* and related substances being likely candidates for use in cosmetics, subject to decontamination before use. This introduction of *letsoku* may offer formulation advantages.

The natural **pH of the skin** acid mantle is about 5.5. Skin pH cosmetics should approximate that value (Carretero *et al.*, 2006) to maintain the integrity of the acid mantle. The highly basic pH values measured for samples les2, zm1, za11a and za13 could therefore be a problem for topical applications. This would especially be the case if they are left in contact with the skin for lengthy periods (Carretero *et al.*, 2006; Matike *et al.*, 2011). The variability in pH of the slurries containing iron minerals is remarkable. The les1 haematite slurry had a pH of 5.2, whereas it was 7.3 for the black sample les2 that contained Fe(II, III).

As previously mentioned, the typical supply forms for *letsoku* are rolled balls and fine powders. The latter may produce dusts under certain circumstances. The US Occupational Safety and Health Administration (OSHA) prescribes limits for nuisance dusts and those generated by specific substances. The recommended limit for nuisance dusts, e.g. kaolinite, is 15 mg m^{-3} total dust and 5 mg m^{-3} respiratory exposure over an eight-hour workday. However, prolonged exposure or even inhalation of silica dust poses a high risk of developing silicosis and cancer (Fubini *et al.*, 1995). All the samples contained quartz which, in view of this classification, implies that *letsoku* dust may have a propensity to be carcinogenic, hence limits to exposure are recommended.

Trace metals may be allowed in cosmetics provided they do not pose a potential health hazard. Control may be exercised by complete exclusion or by limiting the amounts to comply with stipulated levels. The latter are recommended by regulatory bodies such as the International Cooperation on Cosmetic Regulation (ICCR) comprising the US FDA, the Japan Ministry of Health, the European Directorate General for Enterprise and Industry and Health Canada. Carretero *et al.* (2013) warns about the dangers of dermal absorption of the trace metals which, in addition, is exacerbated by high quartz levels (Khiari *et al.*, 2014). Orisakwe and Otaraku (2013) reported how topically applied cosmetics may inadvertently gain access to mucous linings of the mouth (lipstick) or the eye interior (eyeshadow). However, a distinction must be made between free metals and those trapped or fixed in other mineral lattices. In addition, cognizance should be taken of the natural abundance of elements in soils (Shacklette and Boerngen, 1984). Toxic heavy metals refers in particular to cadmium, mercury, lead and arsenic. They appear in the World Health Organization's list of the ten chemicals of major public concern (Andrade *et al.*, 2017).

XRF analysis showed that the samples were free from radioactive elements and the toxic elements Hg, Cd, Se and Sb. However, some samples did contain unacceptable levels of some heavy metals, e.g. As, Pb, Cu, Zn, Ni, etc. Another disconcerting discovery is the high silica content, as high as 96.0 % m/m. Even though the intended purpose relates to topical applications, these levels may pose a certain health risk to users. No cadmium or mercury was detected in any of the *letsoku* samples. The maximum level for lead as an impurity in cosmetic products is 10 ppm (Al-Saleh *et al.* 2009). Only sample sz2 contained a measurable amount of lead at 115 ppm. The recommended limit for arsenic is just 3 ppm and 15 % of the present *letsoku* samples exceeded that level. The arsenic content of 41 % of the *letsoku* samples exceeded the Health Canada limit of 3 ppm. Only sample bw8 contained uranium (95 ppm), an element linked to cancer with the potential to damage DNA and the lungs.

Nickel can cause allergic contact dermatitis. The natural abundance in US soils is 19 ppm (Shacklette and Boerngen, 1984) and quite a number of *letsoku* samples exceeded that level by more than an order of magnitude.

Copper promotes hair growth, hence its inclusion in eyelash-enhancing serum. However, high copper levels cause acne and may even result in hair loss. The copper content was highest for the Venda samples za8 (372 ppm) and za8c (226 ppm). The KwaZulu-Natal samples also registered fairly high results in za11a (97 ppm) and za13a (122 ppm). Unusual contrasting results were found for two sets of samples obtained from the same region: les1 (50 ppm) and les2 (0 ppm) from Lesotho and sz1 (61 ppm) and sz2 (3 ppm) from Swaziland. The natural abundance of copper in US soils is 25 ppm(Shacklette and Boerngen, 1984) and similar or lower levels were found in sample za5 (29 ppm) and Botswana samples bw4 (13 ppm), bw1 (12 ppm) and bw3 (6 ppm).

The natural abundance of **strontium** in US soils is 240 ppm and most of the present samples featured significantly lower concentrations than that. Exceptions were samples zm1 and za10. Addition of strontium salts to topical formulations can decrease the signs and symptoms of irritant skin contact dermatitis (Hahn (1999). Relatively high values of **zirconium** were found in the *letsoku* samples, especially those from Botswana. However zirconium compounds are generally considered to be of low toxicity and therefore the high values are not alarming.

The oxide Al_2O_3, also known as **alumina,** is known to function as an abrasive, absorbent, anticaking, bulking and opacifying agent (CIR, 2014). This oxide is present in virtually all the samples (0.3–36.3 % m/m agent). The highest percentage is for za3.

Rationalizing **traditional beliefs** is a highly challenging problem as subjective components of indigenous knowledge are difficult, if not impossible, to justify (Barrera-Bassols and Zinck, 2003). The present study did not take into consideration the socio-cultural contexts from which the traditional beliefs and practices are derived. In order to do justice to this topic, an integrated approach is required and it is necessary to consider the relevance of the cultural context and to elaborate on concepts such as the “body sick parts”, “evil spirits”, and different stages in initiation (Barrera-Bassols and Zinck 2003, Krasilnikov and Tabor 2003). These ideas most likely also play a role in the application of *letsoku* in the cultural context. Artwork, similarly, is a common activity which dates back to the Middle Stone Age era (Pahl, 1974b) and ancient Egypt (Scott 2016).

The **thematic content categories** included aspects such as chickenpox treatment, ulcer remedies and blood circulation improvement. These also raise validity challenges related to potential modes of action. Current studies in medical geology delve into the impact of clays on human health (Buck *et al.*, 2016; Londono and Williams, 2016). For example, Fe(II) in goethite has been linked to some form of transmission mechanism (Mustafa *et al.*, 2006). Whether *letsoku* involves any of the above-mentioned is a matter for further investigation.

Adsorption seems to be the most likely explanation for most of the cosmetic categories. This could be attributed to the colloidal nature of the clays and the charged surfaces. The constant structural charge on kaolinite has been emphasized by (Gunter, 1997), Khawmee (2010) and Schroth and Sposito (2011). Furthermore,Johansson (1999) has demonstrated that the adsorption on OH^- of kaolinite is pH dependent.

Some of the categories under **medicinal application** may require a different justification besides inter-layered structure and charged surfaces. Wound healing may be explained in terms of wound debridement reported by Otto and Haydel (2013). This is also emphasized by

(Carretero *et al.*, 2013). The previous authors include the cure of wounds by muds or the *terras* as astringents and absorbents, malaria and stomach/intestinal ailments and control of excessive bleeding.

Clayey soils with higher values of specific surface area (SSA) and those with higher values of loss on ignition (LOI) tend to have higher adsorption capacity. Adsorption is essential for cosmetics to adhere to the skin to form mechanical protection and promote skin oil retention (Carretero and Pozo, 2010). High SSA is linked, among other factors, to anticaking or suspending ability (Viseras *et al.*, 2007)which hinders sedimentation and flocculation.

Informants from random parts of Southern Africa point to the common use of these clayey soils as cosmetics, medicines and as objects of cultural symbolism, traditional beliefs and the making of clay pots. Further study of other aspects of the clayey soils might shed light on the authenticity of some of these claims.

5.2 KEY FINDINGS OF THE RESEARCH

- The study revealed that the justification for the use of the common name *letsoku* against the common cosmetic functions does not lie in uniformity in mineral composition.
- It also revealed that the value of *letsoku* reaches beyond a red pigment used on initiates and clay pots.
- Moisturizers, sunscreens, blemish removers and ulcer remedy are some of the other benefits of *letsoku.*
- The ochre nature was confirmed
- Gibbsite (>40 % m/m) detected previously undocumented in traditional cosmetics
- Substantial amounts of muscovite in Botswana and Eastern Cape samples

5.3 CONCLUSIONS AND RECOMMENDATIONS

The heterogeneous colours of the clayey soils pose questions about the validity of the multiple use of the name *letsoku*. Nevertheless, the presence of clay minerals such as kaolinite, smectite, muscovite, sepiolite and others that are currently used to make modern cosmetic products justifies common topical application in cosmetics. In addition, the persistent common use over the past eras and positive comments by various informants from different regions cannot be disregarded.

The unusual discovery of the presence of gibbsite in traditional cosmetic clayey soils may add to the economic viability of the clayey soils more so since gibbsite features in more than 500 modern cosmetic products. Harnessing of this discovery may ultimately help to improve the economy and alleviate poverty, especially for the rural communities, through advanced marketing and distribution.

The study may help the undeclared users to share the other positive attributes of *letsoku*. This way, the search for more economical natural materials will be enhanced and hopefully alleviate poverty by way of job creation in commercializing the clayey soils where possible.

5.4 CONTRIBUTIONS

A successful exposé of the Southern African clayey soils concerning the safety aspect, quality, structure and properties could help to understand the nature and actions of *letsoku*. In the process this may augment the existing sources of clayey soils in Southern Africa. This would ultimately aid in poverty alleviation for rural communities through advanced marketing and distribution. Formulation opportunities for cosmetologists using *letsoku* may arise from the accurate knowledge of its composition.

5.5 FUTURE RESEARCH

The advent of medical geology is imminent in spite of the risks of toxicity and kidney overload on oral ingestion of clays. Further studies for the elucidation of the mechanism of action of these clayey soils may be helpful in reaching their full understanding and appropriate application as they contain minerals that are known to have medicinal benefits. Decontamination of the clayey soils, isolation, characterization and formulation using the clay minerals can provide further research opportunities besides economic advancement.

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APPENDICES INCLUDING PUBLICATION(S) AND CONFERENCE(S)

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UNIVERSITY OF PRETORIA

FACULTY OF ENGINEERING, BUILT ENVIRONMENT AND INFORMATION TECHNOLOGY

FACULTY COMMITTEE FOR RESEARCH ETHICS AND INTEGRITY

(EBIT Ethics Committee)

APPLICATION FOR APPROVAL OF A RESEARCH PROJECT

This application form must be read with the Regulations for Research Ethics and Integrity. By completing and submitting this form, you declare that you have read and understand the Regulations.

Important: Each item must be completed.

Complete the form in your word processor. Forms completed in handwriting are not accepted.

Where applicable, underline the correct answer (e.g. Yes or No).

1. RESEARCHER DETAILS: (Please include your Supervisor details in this section if you are a student)

Applicant details:		**Supervisor details:**	
Initials and surname:	R MPHAHLELE	Initials and surname:	WW FOCKE
Title:	MRS	Title:	PROF
Email:	ntirika@gmail.com	Email:	Walter.Focke@up.ac.za
Phone:	082 057 6424	Phone:	083 326 6549 or 012 420 3728
Employee/**student** number:	96276313	Employee number:	2431459
Department:	Institute of Applied Materials Science-Chemical Engineering	Department:	Chemical Engineering
Are you a student (**yes** or no):	Student		Director of the Institute of Applied Material Science

2. RESEARCH PROJECT TITLE (use a descriptive title)

EVALUATION OF LETSOKU AND RELATED SOUTHERN AFRICAN CLAYS

3. RESEARCH PROJECT DETAILS

3.1 Provide a complete but concise description (no more than 5000 characters, including spaces) of the study objectives and study design, so that the relevant ethical aspects can be identified.

- From this, please identify the aspects clearly that you believe require ethics clearance: The underlined sections, highlighted in yellow are the ones which need ethics clearance.
- Please note: do NOT submit a complete research proposal. The Ethics Committee will not consider this, but will only consider the documents required for submission of an application.

3.1.1 Objectives

The chemical composition of the samples from the various locations will be investigated in an attempt to establish any correlation or significant differences amongst the various soil samples that could substantiate or refute claims made about these clays.

3.1.1.1 Primary Objectives

- Collection of samples from various Southern African sites.
- Determination of physicochemical properties: pH, morphology and rheological properties.
- X-ray geochemical analysis, oxides and trace metals analysis for the composition and toxicity.
- Quantitative determination of humic substances.
- Thermal analysis.
- Adsorption properties.
- Microbiological tests.
- Sun protection tests.

3.1.1.2Secondary Objectives

- Establish the sources and perceived functions of the indigenous substances from the locals and explore other possible clay benefits.

3.1.2 Study design and Methodology

A scientific quantitative and descriptive approach was adopted to establish the attributes and composition of the substances and also link to the validity of the claims made.

3.1.2.1 Sample size and population

The aim is to collect thirty or more samples for quantitative analysis and to interview a minimum of forty participants.

3.1.2.2 Exclusion criteria and inclusion criteria

This is more applicable to the descriptive research. Participants eighteen years or older will be consulted with the expectation that the ages defined will help optimize the validity of the study. In addition, avoid ethical issues of involving minors.

3.1.2.3Procedures / frequency of visits

No specific frequency except where information is incomplete or there is a need for more samples but thereafter to inform the participants about the outcome(s) of the research.

3.1.2.4Quality assurance of specific tools to be used

This mainly involves technical quality elements which comprise specific quality assurance elements that apply to the technical activities such as policy and procedures for instrument calibration, performance, reference materials and statistical procedures. The planning, control and reporting practices recommended at the start of, during and at completion of the research form an essential part.

The descriptive information on the questionnaires will be safely stored at home. The participant assigned study numbers will be used to ensure anonymity and confidentiality during the interviews and also throughout the research and the final report.

3.1.2.5Data collection and analysis

The quantitative section includes the use of high precision, specialized and efficient instruments such as:

- pH meter
- Scan Electron microscope (SEM)
- X-ray diffraction spectrometer (XRD) and X-ray fluorescence (XRF) spectrometer,
- Thermo-gravimetric analyzer (TGA),
- Differential scanning calorimeter (DSC)

The qualitative aspect will be done using:

- The questionnaires, field notes to capture other observations not addressed in the questions and
- Where possible a recorder to be transcribed to remove bias and have a permanent record of what was and what was not said during the interview.

The data analysis will be done with the help of a biostatistician for the questionnaires and submitted on a data capturing sheet.

3.1.3 Materials and methods

3.1.3.1 Samples:

Questionnaires, brief notes and recordings where possible will be administered to voluntary participants with the purpose of obtaining information concerning:

- The sampling or collection of the materials from various locations in South Africa, Swaziland, Zimbabwe and Botswana for the research
- Clay samples will be stored in polyethylene jars at room temperature and kept in the laboratory at the University of Pretoria.

3.2 Will a research questionnaire/survey be used? • If Yes, please answer the next question. If No, ignore the next question. • Please submit your questionnaire, survey questions or interview questions with your application. This will be a separate file that should be submitted as a pdf file, using this filename format:	**Yes**	**No**

Questionnaire.pdf or Survey.pdf Questionnaire.pdf		
3.2.1 Does your questionnaire/survey include any personal questions? (including ANY of the following: name, address, email address, any other information by which a respondent can be identified, gender, age, race, income, medical status)?	**Yes**	[✓ **No**]
3.3 Are employees of a firm, organisation or institution questioned as informant in this study? • If Yes, please submit letter(s) of permission from this entity to carry out this study. It should be clear that the person giving permission is authorised to do so and should be on a company letterhead and should include the date and that person's signature. • Where required, your application cannot be considered without this permission. • This letter should be submitted as a pdf file, using this filename format: CompanyPermissionLetter.pdf	**Yes**	[✓ **No**]
3.4 Will you be surveying or questioning UP students or UP personnel in this study? • If Yes, you need to submit a letter or email from the Dean that provides permission for you to include UP personnel or students as participants in your study. • Where this is required, your application cannot be considered without this permission letter. • This letter should be submitted as a pdf file, using this filename format: DeanPermissionLetter.pdf	**Yes**	[✓ **No**]

4. RESEARCH SUBJECTS

Does the project involve people as participants, either individually or in groups? If Yes, please answer questions 4.1 to 4.7. If No, continue to section 5.	[✓ **Yes**]	**No**
4.1 Does the study involve people as informants, or does it involve people as research subjects? ***Informants*** are people of whom you require an opinion, e.g. people that are interviewed or that take part in a survey. ***Research subjects*** are people that actively take part in research, e.g. where biological measurements are made (e.g. heart rate) or where people take part in behavioural tasks (e.g. listening tasks)	[✓ **Informants**]	**Subjects**

4.2 Describe possible safety and health implications that participation in the project may pose.

There are no safety or health implications involved.

4.3 What is the expected duration of participation of people in the project?

This should be once off except where information is incomplete or there is a need for more

samples or clarification but thereafter to inform the participants about the outcome(s) of the research.

4.4 Describe the manner in which confidential information will be handled and confidentiality assured.

- The assurance that the information collected will be kept strictly confidential.
- The participants' names will not reflect on the data forms but only the study identification numbers.
- Reports and articles in scientific journals will not include any information that may violate the participants' anonymity.
- The participant has the freedom to consult with the researcher should there be any sign of breach of confidentiality.
- The researcher's assurance and reiterated commitment to protect the participants' privacy.

4.5 Please explain how and where data will be stored.

The descriptive information on the questionnaires will be safely locked and stored at home for 15 years.

4.6 Is remuneration offered to subjects for participation? If yes, please expand.

No remuneration is offered to subjects for participation.

4.7 INFORMED CONSENT/ASSENT

Informed consent is a requirement for *all* studies. All participants need to be provided with an individual informed consent, which the researcher should keep on record. An example for an informed consent form appears on the website, but this should be adapted to be very specific about your study and what you will require of participants.

Please submit your informed consent form (example) with your application.
This should be submitted as a pdf file, using this filename format: Informed Consent.pdf

4.7.1. Please describe how you will obtain informed consent/assent from your participants (or their caregivers in the case of underage participants).

The minimum sampling age is 18 years implying no underage participants are involved.

4.7.2 Detail the measures you will take to ensure voluntary participation.

It is explicitly stated in the informed consent form to be signed by the participant that:
"I understand my right to choose whether to participate in the project and that information furnished will be handled confidentially. I have been provided with a copy of this consent form."
It is clear that they are not forced to start or continue with the study against their will.

5. ENVIRONMENTAL IMPACT and HAZARDOUS MATERIALS

5.1 Does the project have a potentially detrimental environmental impact, or are hazardous materials used in the project?	**Yes**	**[✓ No]**

- If Yes, you will need to submit a letter of approval from the Department of Facilities and services, Occupational Health and Safety division, before the Ethics Committee can consider your application.
- If section 5 (this section) is the only aspect of your project for which you require clearance from the Ethics Committee (i.e. no people or animals are included in your study), you should not apply to the Ethics Committee, but should apply for clearance directly to the Occupational Health and Safety division.
- If No, continue to section 6.

6. DISSEMINATION OF DATA

6.1 How and where will your results be published and/or applied?

Report(s) about our findings and results will be published in scientific journals. Once the report(s) are complete, the findings will be shared with the participants on a one to one basis or electronically.

7. DECLARATION (Tick the relevant boxes)

√	I accept and will adhere to all stipulations pertaining to ethically sound research as locally, nationally and internationally established.
√	I will conduct the study as specified in the application and will be principally responsible for all matters related to the research.
√	I shall communicate all changes to the application or any other document before any such is executed in my research, to obtain the necessary permissions from the Ethics Committee.
√	I will not exceed the terms of reference of the research application or any other documents submitted to the Ethics Committee.

√	I confirm that I'm not seeking ethics clearance for research that has already been carried out.
√	I affirm that all relevant information has been provided and that all statements made are correct.
√	I have familiarised myself with the University of Pretoria's policy regarding plagiarism http://www.aibrary.up.ac.za/plagiarism/index.htm. Plagiarism is regarded as a serious violation and may lead to suspension from the University.
Please submit the completed Declaration By The Researcher form with your application. Please submit this as a pdf file with this filename format: Declaration.pdf	

8. SUBMISSION CHECKLIST

Each item to be submitted should be submitted as a separate pdf file, using the naming convention given earlier in this document or below.

8.1 Have you submitted your application form (this form)? Please submit as a pdf file with this filename format: ApplicationForm.pdf	[✓ **Yes**]	**No**	
8.2 Have you submitted your survey questions, questionnaire or interview questions (where applicable)?	[✓ **Yes**]	**No**	
8.3 Have you submitted the required Informed Consent Form?	[✓ **Yes**]	**No**	
8.4 Have you submitted the Declaration By The Researcher form?	[✓ **Yes**]	**No**	
8.5 Have you submitted permission letters from firms, institutions or organisations where required?	**Yes**	**No**	**N/A**
8.6 Have you submitted a permission letter from the Dean where required?	**Yes**	**No**	**N/A**

INFORMED CONSENT TO PARTICIPATE IN A RESEARCH STUDY

INSTITUTE:	University Of Pretoria Centre For Material Science Chemical Engineering, Built Environment And Information Technology Faculty Of Engineering, Built Environment And Information Technology
RESEARCH COORDINATOR: **STUDENT**:	Prof WW Focke Refilwe Mphahlele
STUDY TITLE:	Evaluation of letsoku and related indigenous Southern African substances.

1) Introduction

This serves as an invitation to participate in a voluntary research study. Feel free to turn down the invitation or to withdraw from the study at any time if you do participate. You will be asked questions during the period of the study, but you may choose not to answer all the questions. However, any answers from you will hopefully give us knowledge that may help many people in future.

The whole informed consent document will be read out to you. Before you decide to take part, please take as much time as you need to ask any questions and discuss this study with me, the investigators, or your family. The proposal of this pilot study has passed through the University of Pretoria's Faculty of Health Sciences Research Ethics Committee. You will receive a copy of this informed consent form for future reference.

2) What is this research about and why is it being done?

The research is about clays used in Southern Africa. Clays are used internationally for various reasons or applications.

The aim of this research is firstly to identify any clays used in various Southern African locations and thereafter investigate any similarity or relation between them. Secondly, familiarization with any applications of the clays. A successful exposition may benefit humanity by reaffirming and harnessing local raw materials and where possible and essential to improve community awareness, safety and effective usage of the clays.

3) Why are you invited to participate in this study?

The practice of clay usage is growing internationally and the applications are also increasing. This does not necessarily suggest that you use the clays but it is hoped that you might have some knowledge about the clay itself or clay users. The selection is random and aims to include individuals who will help in the quest to obtain the clay samples and are fairly conversant with the materials but this does not exclude those who do not know of any clays.

4) How many individuals will take part in this research study?
We plan to enroll forty participants. This will be divided into some who know about clays and those who are oblivious of the clays.

5) How long will you take part in this research study?
The scientific study will occur over a number of years but the questionnaire will be filled in now and then where information is incomplete or even just once during the study period. At the end of the study you will be informed about the findings.

6) What procedures are involved in this research study?
The survey will involve the use of questionnaires to find out more about obtaining samples, the uses, history, positives and negatives associated with the clays. The scientific study which will take a number of years also forms a part of this study.

7) What are the risks and discomforts of this research study?
By participating in this research you are not supposed to experience any physical discomfort as this just involves answering questions on paper. You will not even be asked to apply the clays on your skin or ingest them.

8) What benefits are there for taking part in this study?
If you participate in this research, you may not get any personal or financial benefits but your participation is likely to help us to determine whether the clays are safe and efficacious for human usage. Where possible and essential, these raw materials will be improved to better or improve humanity’s quality of life.

9) Are there reasons that your participation may end early?
Your participation will end early for two reasons namely when withdrawing yourself from the study or when the researchers decide to withdraw you from the study. If you decide to withdraw from the study you will not be punished and refusing to participate will not affect you or your rights in any way. If you do decide to withdraw, you should contact Prof Walter Focke on 0833266549, or Refilwe Mphahlele on 0820576424 to tell them your decision. We will keep the information collected up to the time you withdraw, and continue to use the information for research unless you tell us differently. The researchers may decide to withdraw you from the study if it is determined that you are no longer able to meet the requirements of the study.

10) What will happen when the research study is over?
We will write a report about our findings and results will be published in scientific journals. Once the report is complete, we will share our findings with you on a one to one basis or electronically.

11) Will you have to pay to take part in this research study?

There will be no cost to or by you to participate. Also the researchers doing this study and the University of Pretoria will not make any money by doing this study.

12) What privacy and confidentiality procedures apply to the information gathered from you in this study?

All information that we collect from this research project will be kept strictly confidential. Information will be collected using a study identification number that will be assigned to you. Your name will not be on any data forms; instead we will use your study number. Your name will only be on the contact information sheet that will be locked away in an office at the University of Pretoria. Reports and articles in scientific journals will not include any information that may identify you. A very small possibility of a confidentiality breach in research studies does exist, but we will make every effort to protect your privacy.

13) Who can answer your questions about the research and your rights as a research subject?

If you have any problems or questions about this study or about your rights as a research participant, you may ask them now or later. If you wish to ask questions later, you may contact Prof Walter Focke on 0833266549, or Refilwe Mphahlele on 0820576424. You may also call Manda Smith at the Health Sciences Research Ethics Committee at the University of Pretoria on 012-354-1330.

14) Consent to participate in this research study

The above information has been read to me before signing this consent form. The content and meaning of this information has been explained to me. I had the opportunity to ask questions and I am satisfied that my questions have been answered. I understand the study will span over a number of years but the questionnaire will be filled in occasionally or even just once during the study period. I understand that it is my choice to participate in this study and that I may withdraw from the study at any time. I understand that the Research Coordinator can exclude me from the study at any time during the study.
I have been provided with a copy of this consent form.

………………………………………	…………………………………	………………
Participant’s signature	Participant’s name	Date
………………………………………	…………………………………	………………
Interviewer’s signature	Interviewer’s name	Date
………………………………………	…………………………………	………………
Witness’ signature	Witness’ name	Date

QUESTIONNAIRE	
INSTITUTE:	University Of Pretoria Institute Of Applied Materials, Faculty Of Engineering, Built Environment And Information Technology,
RESEARCH COORDINATOR: STUDENT:	Prof Walter W Focke Refilwe Mphahlele
STUDY TITLE:	Evaluation of Letsoku And Related Indigenous Southern African Clays.

Interviewer					
Participant assigned Study number					
Date					
Address					
Contact number(s)					
Age range (years) **Indicate with a √**	18-20)	21-30	31-40	41-50	50 upwards

Thank you for voluntarily participating in this study and please note that all information will be kept confidential. You are <u>not</u> obliged to or forced to answer <u>all</u> the questions. The questions have been phrased in such a way as <u>not</u> to take too much of your time.

You will be asked a number of questions which may be easily answered whilst others may be challenging. A recorder may be used for clarity and removal of bias but participant identity will be protected at all times. Any kind of answer or information supplied by you is very important to this research study and will help us and the other community members on the usefulness and nature of these clays. Kindly answer the questions to the best of your ability with detailed explanations or descriptions wherever possible.

1. Have you noticed some people walking around with red or white or any coloured stuff smeared on their faces, hair or any part of their bodies?

   ………

   ………

2. If yes where did you see these people?

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3. Do you know the name of the stuff used in question 1?

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4. Where else have you seen people with stuff visibly smeared on any part of their bodies?

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5. Do you know where the stuff can be obtained?

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6. Do you know if it is free or for sale?

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7. If it is for sale, do you know of or have you heard of places where it can be bought?

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8. Please estimate the price of the stuff if it is not free? Indicate with a √:

Estimate price per 50 g	
Less than R10	
R11 – R50	
R51 – R100	
R110 – R200	

9. If it is free, do you know of or have you heard of places where it can be obtained for free?

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10. Have you or anyone you know ever used the stuff before?

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If yes, describe the appearance of the stuff that was used:

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11. Do you know or have you heard if the colour of the stuff is linked to its specific function?

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12. What was the reason for using it?

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13. Were the results satisfactory or as expected after using it? Explain.

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14. Was the stuff easy to use? Explain.

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15. Was it used alone or mixed with something else?

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16. Do you know or have you heard if it can be used for any other applications? Describe fully.

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17. Do you know or have you heard if there are negative effects or allergic reactions that are linked to the stuff? Describe as best as you can.

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18. Have you noticed or do you know if the stuff is used by both men and women?

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19. Have you noticed or do you know if the stuff is used by people of all ages? If yes please describe fully.

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20. Have you noticed or do you know if the stuff is used by people from specific ethnic groups? If yes, list them please.

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21. Have you noticed or do you know if the stuff is used by people from specific areas or places? If yes please describe or list them.

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22. Have you noticed or do you know if the stuff is used by people who seem to have enough money (affluent), or with money problems (financially disadvantaged people)?

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23. Have you noticed or do you know if the stuff is used mainly by knowledgeable people or graduates (doctors/nurses/teachers) or uneducated (illiterate) people?

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RESEARCHER DECLARATION

APPLICATIONS MUST INCLUDE THE FOLLOWING STATEMENTS

Hereby I, REFILWE MPHAHLELE, in my capacity as THE RESEARCHER, that:

1 Research subjects will be informed, information will be handled confidentially, research subjects reserve the right to choose whether to participate and, where applicable, written permission will be obtained for the execution of the project (example of permission attached).

2 No conflict of interests or financial benefit, whether for the researcher, company or organisation, that could materially affect the outcome of the investigation or jeopardise the name of the university is foreseen.

3 Inspection of the experiments in loco may take place at any time by the committee or its proxy.

4 The information I furnish in the application is correct to the best of my knowledge and that I will abide by the stipulations of the committee as contained in the regulations.

5 Signed: ______ Date: 2015.12.03

APPENDIX 2: Sample identity and site location

Samples for the evaluation of *letsoku & related substances*: Legend: les ~ Lesotho za~ for South Africa: bw ~ Botswana: sz ~ Swaziland: zm~

Sa ID	Sourcing site	Source type	Colour	GPS coordinates
za1	Arula, Asiatic Bazaar, Pretoria, SA	commercial	orange-red	S25^{o}44.248$'$ E028^{o}10.513$'$
za2		commercial	white	’
za3	Maleoko mountain, Ntoane, Dennilton, Mpumalanga,SA	mouth of cave	brick red and yellow	S 25^{o}17.504 E 029^{o}15.808
za3a				
za3b				
za5	Engcobo,Umtata and Comfimvaba, Queenstown.	commercial	yellow imbola	S 31^{o}40$'$30$''$ E 28^{o} 0$'$ 0$''$
za6		commercial	pale green imbola	
za7		commercial	red orange imbola	
za8	Mbaleni, Venda, Limpopo,South Africa	demolished hilltop.	moist reddish medium stones.	S 30.4906^{o} E 22.9603^{o}
za8a				
za8b				
za8b1				
za8c		wetlands	wet greenish gray muddy vumba	
za9	Engcobo,Umtata and Comfimvaba,Queenstown	Commercial ground between hills	red orange medium rocks	S 31^{o}40$'$30$''$ E 28^{o} 0$'$ 0$''$
za10	Makurung, Ga-Mphahlele village, Limpopo		white powder with black spot	S24^{o} 35’ E29^{o} 35$'$
za11a	Mtubatuba, Kwa-Zulu Natal	River	muddy gray greenish clay	S 28.4167^{o} E 32.1833^{o}
za11b		River		
za11c		River		o
za12	Bloemfontein market, OFS	Commercial	maroon red powder	
	Nongoma,Kwa-Zulu Natal	River	wet gray greenish mud	S 27.8833^{o} E 31.6333^{o}
za13a				
za13b		River	wet gray greenish mud	

Appendix 2

Legend: za for South Africa: bw ~ Botswana: les ~ Lesotho: sz ~ Swaziland:

Sample	Sampling Location	Source type	Colour	GPS coordinates
sz1	Manzini market, Swaziland	Commercial	Red orange powder or libovu	26^{o} $29^{'}$ E 31^{o} $22^{'}$
Sz2	Manzini market, Swaziland	Commercial	White medium pebbles	S 26^{o} $29^{'}$ E 31^{o} $22^{'}$
Zm1	Chiredzi, Zimbabwe	Commercial	Maroon shimmering powder chomane	S21.0389^{o} E31.6778^{o}
Bw1	Gaborone Sun	Commercial but originally from Ramatlabama	Yellow letsoku	S $24^{o}39^{'}8.6^{''}$ E 25^{o} $54^{'}$ 45
Bw2			Pinkish letsoku powder	
Bw3			White letsoku powder	
Bw4			Bright red letsoku powder	
Bw5			Maroon powder letsoku	
Bw6			Purple letsoku powder	
Bw2A			Pink white letsoku rocks	”
Bw3A			White letsoku rocks	”
Bw4A			Orange red letsoku rocks	
Bw6A			Off white letsoku rocks	
Bw7			Orange letsoku	
Bw8			Whitish orange centred letsoku rocks	

QUESTIONNAIRE	
INSTITUTE:	University Of Pretoria Institute Of Applied Materials, Faculty Of Engineering, Built Environment And Information Technology,
RESEARCH COORDINATOR: STUDENT:	Prof Walter W Focke Refilwe Mphahlele
STUDY TITLE:	Evaluation of Letsoku And Related Indigenous Southern African Clays.

Interviewer	Refilwe Mphahlele				
Participant assigned Study number	LETSEBIT 01				
Date					
Address					
Contact number(s)					
Age range (years) **Indicate with a √**	18-20)	21-30	31-40	41-50 ✓	50 upwards

Thank you for voluntarily participating in this study and please note that all information will be kept confidential. You are <u>not</u> obliged to or forced to answer <u>all</u> the questions. The questions have been phrased in such a way as <u>not</u> to take too much of your time.

You will be asked a number of questions which may be easily answered whilst others may be challenging. A recorder may be used for clarity and removal of bias but participant identity will be protected at all times. Any kind of answer or information supplied by you is very important to this research study and will help us and the other community members on the usefulness and nature of these clays. Kindly answer the questions to the best of your ability with detailed explanations or descriptions wherever possible.

1. Have you noticed some people walking around with red or white or any coloured stuff smeared on their faces, hair or any part of their bodies?

YES, I HAVE

2. If yes where did you see these people?

I have seen them at home in Swaziland
and on TV

3. Do you know the name of the stuff used in question 1?

I know the red stuff, its called red
"~~oat~~" or libovu in Swaziland
Ochre

4. Where else have you seen people with stuff visibly smeared on any part of their bodies?

I have seen people on the streets
especially those that sell the red stuff.

5. Do you know where the stuff can be obtained?

It is obtained in rural areas around
Swaziland, at the foot of some mountains
or hills around a place called Lwandle

6. Do you know if it is free or for sale?

It is free where it is dug but
it is for sale at the market in Manzini,
Swaziland

7. If it is for sale, do you know of or have you heard of places where it can be bought?

It is found on the streets in
Manzini and at the market place

8. Please estimate the price of the stuff if it is not free? Indicate with a √:

Estimate price per 50 g	
Less than R10	
R11 – R50	✓
R51 – R100	
R110 – R200	

9. If it is free, do you know of or have you heard of places where it can be obtained for free?

it is obtained in the rural area around Swaziland, I am sure of a place called Lwandle in the Manzini region

10. Have you or anyone you know ever used the stuff before?

I have never used it.

If yes, describe the appearance of the stuff that was used:

N/A

11. Do you know or have you heard if the colour of the stuff is linked to its specific function?

Yes I have heard

12. What was the reason for using it?

I know that in Swaziland it is used in traditional weddings called kuteka. It is smeared on the face of the new bride as a symbol of a start of marriage and acceptance in the new home.

13. Were the results satisfactory or as expected after using it? Explain.

No results are expected in the above function

14. Was the stuff easy to use? Explain.

Since I have never used it, I do not know.

15. Was it used alone or mixed with something else?

In the traditional weddings, the red oak is mixed with water.

16. Do you know or have you heard if it can be used for any other applications? Describe fully. YES

Some women use it as a sun screen.
The Xhosa people use it during boy's circumcision ceremony

17. Do you know or have you heard if there are negative effects or allergic reactions that are linked to the stuff? Describe as best as you can.

no I have not heard.

18. Have you noticed or do you know if the stuff is used by both men and women?

It is used by women as suncreen and by boys during circumcision ceremonies

19. Have you noticed or do you know if the stuff is used by people of all ages? If yes please describe fully.

I have not heard of older men using it

20. Have you noticed or do you know if the stuff is used by people from specific ethnic groups? If yes, list them please.

YES, I know it is used by Swazis and Xhosas. Im not sure of other ethnic groups

21. Have you noticed or do you know if the stuff is used by people from specific areas or places? If yes please describe or list them.

Not necessarly. If you decide to wed a woman the traditional way it doesn't matter your background, the new bride will be smeared with it. Area or place does not count.

22. Have you noticed or do you know if the stuff is used by people who seem to have enough money (affluent), or with money problems (financially disadvantaged people)?

I have never seen rich people using it but on the face as it is common in rural places.

23. Have you noticed or do you know if the stuff is used mainly by knowledgeable people or graduates (doctors/nurses/teachers) or uneducated (illiterate) people?

It is used mainly by uneducated people

QUESTIONNAIRE	
INSTITUTE:	University Of Pretoria Institute Of Applied Materials, Faculty Of Engineering, Built Environment And Information Technology,
RESEARCH COORDINATOR: STUDENT:	Prof Walter W Focke Refilwe Mphahlele
STUDY TITLE:	Evaluation of Letsoku And Related Indigenous Southern African Clays.

Interviewer	Refilwe Mphahlele.				
Participant assigned Study number	LETSEBIT 02.				
Date					
Address					
Contact number(s)					
Age range (years) **Indicate with a V**	18-20)	21-30	31-40	41-50	50 upwards ✓

Thank you for voluntarily participating in this study and please note that all information will be kept confidential. You are not obliged to or forced to answer all the questions. The questions have been phrased in such a way as not to take too much of your time.

You will be asked a number of questions which may be easily answered whilst others may be challenging. A recorder may be used for clarity and removal of bias but participant identity will be protected at all times. Any kind of answer or information supplied by you is very important to this research study and will help us and the other community members on the usefulness and nature of these clays. Kindly answer the questions to the best of your ability with detailed explanations or descriptions wherever possible.

1. Have you noticed some people walking around with red or white or any coloured stuff smeared on their faces, hair or any part of their bodies?

Yes.

2. If yes where did you see these people?

Rural areas.

3. Do you know the name of the stuff used in question 1?

Phepa

Letsoku

4. Where else have you seen people with stuff visibly smeared on any part of their bodies?

Botswana — Initiation school.

5. Do you know where the stuff can be obtained?

Yes.

6. Do you know if it is free or for sale?

Some places it's free

Others you can buy.

7. If it is for sale, do you know of or have you heard of places where it can be bought?

- Gaborone mall at the Stalls.
- Arula in Pretoria
- Maseru market in Lesotho.
- Manzini market in Swaziland.

8. Please estimate the price of the stuff if it is not free? Indicate with a √:

Estimate price per 50 g	
Less than R10	
R11 – R50	√
R51 – R100	
R110 – R200	

9. If it is free, do you know of or have you heard of places where it can be obtained for free?

- Mohaleshoek
- Zeerust
- Botswana

10. Have you or anyone you know ever used the stuff before?

Yes

If yes, describe the appearance of the stuff that was used:

Red; powder

Phepa/ White; powdered from granules

11. Do you know or have you heard if the colour of the stuff is linked to its specific function?

White/ Phepa — for spiritual cleansing

Red — protective spiritually
— Sunscreen.

12. What was the reason for using it?

Phepa / White — Spiritual cleansing

Red — Spiritual / physical protection

— Sunscreen.

||| ⇒ helps initiates to blend with the environment for protection against snakes etc.

13. Were the results satisfactory or as expected after using it? Explain.

(Video)

14. Was the stuff easy to use? Explain. Easy.

Not mixed Used as powder

15. Was it used alone or mixed with something else?

Nothing mixed.

16. Do you know or have you heard if it can be used for any other applications? Describe fully.

No

17. Do you know or have you heard if there are negative effects or allergic reactions that are linked to the stuff? Describe as best as you can.

No

18. Have you noticed or do you know if the stuff is used by both men and women?

Yes; both useng

19. Have you noticed or do you know if the stuff is used by people of all ages? If yes please describe fully.

No

20. Have you noticed or do you know if the stuff is used by people from specific ethnic groups? If yes, list them please.

All black people use the clay.

21. Have you noticed or do you know if the stuff is used by people from specific areas or places? If yes please describe or list them.

Blacks from all over Africa.

22. Have you noticed or do you know if the stuff is used by people who seem to have enough money (affluent), or with money problems (financially disadvantaged people)?

Used by anybody irrespective of Status!

23. Have you noticed or do you know if the stuff is used mainly by knowledgeable people or graduates (doctors/nurses/teachers) or uneducated (illiterate) people?

All irrespective of literacy.

QUESTIONNAIRE	
INSTITUTE:	University Of Pretoria Institute Of Applied Materials, Faculty Of Engineering, Built Environment And Information Technology,
RESEARCH COORDINATOR: STUDENT:	Prof Walter W Focke Refilwe Mphahlele
STUDY TITLE:	Evaluation of Letsoku And Related Indigenous Southern African Clays.

Interviewer	Refilwe Mphahlele				
Participant assigned Study number	LETSEBIT 03				
Date					
Address	House # 192, Manamakgotha				
	Mararaneng seetsa				
Contact number(s)	078 6666 084				
Age range (years) **Indicate with a V**	18-20)	21-30	31-40 ✓	41-50	50 upwards

Thank you for voluntarily participating in this study and please note that all information will be kept confidential. You are not obliged to or forced to answer all the questions. The questions have been phrased in such a way as not to take too much of your time.

You will be asked a number of questions which may be easily answered whilst others may be challenging. A recorder may be used for clarity and removal of bias but participant identity will be protected at all times. Any kind of answer or information supplied by you is very important to this research study and will help us and the other community members on the usefulness and nature of these clays. Kindly answer the questions to the best of your ability with detailed explanations or descriptions wherever possible.

1. Have you noticed some people walking around with red or white or any coloured stuff smeared on their faces, hair or any part of their bodies?

   Yes

8. Please estimate the price of the stuff if it is not free? Indicate with a √:

Estimate price per 50 g	
Less than R10	
R11 – R50	✓
R51 – R100	
R110 – R200	

9. If it is free, do you know of or have you heard of places where it can be obtained for free?

Not sure but it look like it is not found in far areas.

10. Have you or anyone you know ever used the stuff before?

Yes

If yes, describe the appearance of the stuff that was used:

Some look like it has sandy soil and redish brown in colour, some are white in colour:

11. Do you know or have you heard if the colour of the stuff is linked to its specific function?

Not sure about that:

~~Not of any.~~
Some are used by traditional doctors on their faces.

17. Do you know or have you heard if there are negative effects or allergic reactions that are linked to the stuff? Describe as best as you can.

Not of any.

18. Have you noticed or do you know if the stuff is used by both men and women?

I have seen both especially traditional doctors

19. Have you noticed or do you know if the stuff is used by people of all ages? If yes please describe fully.

I have seen elders.

23. Have you noticed or do you know if the stuff is used mainly by knowledgeable people or graduates (doctors/nurses/teachers) or uneducated (illiterate) people?

Even If you are educated but Called for traditional healing you use the staFF. Some are uneducated and poor to buy good and healthy staFF.

QUESTIONNAIRE	
INSTITUTE:	University Of Pretoria Institute Of Applied Materials, Faculty Of Engineering, Built Environment And Information Technology,
RESEARCH COORDINATOR: STUDENT:	Prof Walter W Focke Refilwe Mphahlele
STUDY TITLE:	Evaluation of Letsoku And Related Indigenous Southern African Clays.

Interviewer	Refilwe Mphahlele				
Participant assigned Study number	LETSEBIT 02				
Date					
Address					
Contact number(s)					
Age range (years) **Indicate with a V**	18-20)	21-30	31-40	41-50	50 upwards ✓

Thank you for voluntarily participating in this study and please note that all information will be kept confidential. You are <u>not</u> obliged to or forced to answer <u>all</u> the questions. The questions have been phrased in such a way as <u>not</u> to take too much of your time.

You will be asked a number of questions which may be easily answered whilst others may be challenging. A recorder may be used for clarity and removal of bias but participant identity will be protected at all times. Any kind of answer or information supplied by you is very important to this research study and will help us and the other community members on the usefulness and nature of these clays. Kindly answer the questions to the best of your ability with detailed explanations or descriptions wherever possible.

1. Have you noticed some people walking around with red or white or any coloured stuff smeared on their faces, hair or any part of their bodies?

   Yes.

NB Processing of letsoku: heat @ high temp until disintegration

8. Please estimate the price of the stuff if it is not free? Indicate with a √:

Estimate price per 50 g	
Less than R10	
R11 – R50	
R51 – R100	
R110 – R200	

N/A.

9. If it is free, do you know of or have you heard of places where it can be obtained for free? Thaba Moopo next to Leboakgomo

10. Have you or anyone you know ever used the stuff before?

Yes

If yes, describe the appearance of the stuff that was used:

Red powder

11. Do you know or have you heard if the colour of the stuff is linked to its specific function?

Don't know

Dont know

17. Do you know or have you heard if there are negative effects or allergic reactions that are linked to the stuff? Describe as best as you can.

None known

18. Have you noticed or do you know if the stuff is used by both men and women?

All.

19. Have you noticed or do you know if the stuff is used by people of all ages? If yes please describe fully.

All.

23. Have you noticed or do you know if the stuff is used mainly by knowledgeable people or graduates (doctors/nurses/teachers) or uneducated (illiterate) people?

All

Characterisation of *vumba* and *ubumba* clays used for cosmetic purposes

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Walter W. Focke[3]
Wiebke Grote[4]

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ARTICLE INCLUDES:
× Supplementary material
× Data set

FUNDING:
Tshwane University of Technology

Two traditional cosmetic clays bear similar names in different local South African languages: *vumba* (Tshivenda) and *ubumba* (isiZulu). The wet clays are applied topically for cosmetic purposes by the respective indigenous peoples. Six samples from two South African provinces were characterised using X-ray diffraction, X-ray fluorescence spectroscopy, Fourier transform infrared spectroscopy, thermal gravimetric analysis and scanning electron microscopy. It was found that the samples differed widely with respect to mineralogy and chemical composition. This finding raises the possibility that texture characteristics during application on the skin override composition effects. Of concern is the high levels of quartz found in all the samples as it might pose a health hazard; the lowest value for quartz was 11 wt% for *vumba,* while values for *ubumba* ranged from 26 wt% to 85 wt%. All samples contained varying amounts of silicates in the form of smectite, kaolin, chlorite and plagioclase. Minor amounts of anatase and rutile were present in some samples. Three samples also contained goethite. All samples were essentially free from the toxic elements As, Pb, Hg, Cd, Se and Sb. However, they did contain low levels of chromium and heavy metals such as Cu, Zn and Ni. The pH values of *ubumba* slurries were slightly basic, while those of a *vumba* slurry were slightly acidic.

Significance:

- Wide ranges of composition appear to be acceptable.
- The clays do not contain highly toxic or radioactive elements.
- The high levels of quartz present may pose a human health risk.

Introduction

Throughout human history, clays and clayey soils have been used for religious, artistic, cosmetic and therapeutic purposes. For example, the utilisation of ochre, a clay stained by iron oxides, dates back to the Middle Stone Age. South Africa has a rich tradition in this regard. Evidence of human exploitation, also dating back to the Middle Stone Age, has been found at Klein Kliphuis[1], the Blombos Cave[2], Diepkloof Rock Shelter[3] and the Sibudu Cave[4]. The practice of using ochre-like substances for topical cosmetic applications and other purposes persists to the present day. The red clay pastes are known as *letsoku* in Sotho culture and *ibomvu* among Nguni people and are used by both women and men in traditional ceremonies. This and other lighter-coloured clays apparently also serve as sunscreens.[5]

Clays find application as cosmetic products, i.e. applications in which the preparation is placed in contact with the outside of the human body, e.g. the skin, hair and lips.[6] In this context 'clay' can refer to a mineralogical term. However, it may also denote a natural material composed of very fine-grained minerals that show some plasticity when mixed with an appropriate amount of water.[7] The layered structure and colloidal size of the particles constituting the clay give rise to desired rheological characteristics and sorptive abilities, among others.[7] Natural clays typically contain other minerals such as quartz, feldspars, carbonates, sulfates and iron, aluminium or titanium oxides. These minerals may affect the chemical (e.g. stability, purity), physical (e.g. texture, moisture content, particle size) and toxicological requirements specified for each clay application.[7] Particular attention is paid to the presence of silica as there is sufficient evidence to suggest that it is a potential carcinogen. To avoid requirements for labelling that provides safety information, the silica content must be less than 0.1%.[7]

Traditional clays, used among indigenous people in the Eastern Cape Province of South Africa, have been studied extensively.[5,6,8-11] However, there are few reports dealing with the nature and properties of the yellowish-grey clays that are also used primarily for cosmetic purposes. Interestingly, *letsoku* is usually supplied as a dry powder, whereas other clays, colloquially known as *vumba* and *ubumba* in the rural areas, are supplied in a wet form and provide a skin moisturising effect. This communication provides information on the nature and chemical composition of the latter two clays sourced from KwaZulu-Natal and Limpopo Provinces, respectively. This information is relevant for assessing the suitability of these cosmetic clays for more widespread commercial distribution.[12]

Materials and methods

Materials and sample preparation

The wet light brown to grey clay samples were sourced from three different sites in two South African provinces. The clays were supplied by traditional healers and are reportedly sold locally for topical cosmetic applications, although health benefits are also claimed. In some cases, different samples with distinct properties were supplied from the same general deposit. Details of the sampling locations are given in Table 1.

Table 1: Location of the clay deposits sampled

Sample	Location	GPS coordinates
U1, U2, U3	River pond near Mtubatuba (KwaZulu-Natal)	28.4167°S, 32.1833°E
W1, W2	Nongoma (KwaZulu-Natal)	27.8833°S, 31.6333°E
V1	Mbaleni wetlands, Venda (Limpopo)	30.4906°S, 22.9603°E

The wet clay samples were supplied packaged in clear polyethylene bags by the traditional healers who sell the products for topical applications. They were transferred into polyethylene bottles. Portions were dried at 50 °C overnight before being milled into fine powders (<75 μm) in a milling unit fitted with a tungsten carbide vessel.

Characterisation

X-ray diffraction (XRD) measurements were performed at the Department of Geology (University of Pretoria) on a PANalytical X'Pert PRO X-ray diffractometer in *q-q* configuration, equipped with Fe-filtered Co-Ka radiation (λ = 1.789 Å) and an X'Celerator detector and variable divergence and fixed receiving slits. Samples were prepared according to the standardised PANalytical back-loading system, which provides nearly random distribution of the particles. The data were collected in the angular range $5° \leq 2q \leq 90°$ with a step size of 0.008° 2θ and a 10-s scan step time. The phases were identified using X'Pert Highscore plus software.

The relative phase amounts (weight %) were estimated by the Rietveld method using Autoquan/BGMN software (GE Inspection Technologies; Kleeberg & Bergmann) which employs the fundamental parameter approach. Autoquan combines the analytical potential of BGMN with an 'easy to operate' user surface. In the Rietveld method, an observed data pattern is compared with a calculated pattern. By varying all the parameters the difference between the calculated and observed patterns is minimised by a least squares procedure, until the best possible fit is obtained. The background was fitted by the polynomial order which was determined automatically, depending on the angular range.

X-ray fluorescence spectroscopy (XRF) analyses were performed at the Department of Geology (University of Pretoria) on powders milled to a fine particle size (<75 μm). The moisture content was determined by weighing an accurate mass of approximately 3 g of powder into an alumina crucible. The crucible was then heated in an oven at 100 °C for 2 h. Thereafter the dehydrated samples were roasted at 1000 °C overnight. A sample mass of 1 g of the residue was fused with about 6 g of lithium tetraborate at 1050 °C for metal oxide determination. The trace metals were determined on samples bound with poly(vinyl alcohol) and pressed into powder briquettes.

Scanning electron microscopy (SEM) was performed in the Laboratory for Microscopy and Microanalysis (University of Pretoria), on the powders. Sample powders were lightly sprinkled onto small stubs of double-sided adhesive carbon tape. Compressed air was used to remove any excess powder. The morphology of the carbon-coated powders was studied with a Zeiss Ultra-55 field emission scanning electron microscope fitted with an InLens detector at an acceleration voltage of 1 kV.

Attenuated total reflection Fourier transform infrared (ATR–FTIR) spectra were recorded on an in-house Perkin Elmer Spectrum 100 Series instrument. The spectra represent averages of 32 scans over the wave number range 500–4000 cm^{-1}.

Thermogravimetric analysis (TGA) was performed on an in-house Perkin Elmer TGA 4000 unit. Alumina crucibles were used and the sample size was about 40 mg. Temperature was scanned from 25 °C to 950 °C at 10 °C/min with air flowing at 50 mL/min.

The cation exchange capacity of the clays was determined using the pH-dependent methylene blue halo method adapted from Kahr and Madsen[13].

Results and discussion

The X-ray diffractograms presented in Figure 1 indicate that the materials are complex mixtures of various minerals. The mineral compositions derived from the XRD data are summarised in Table 2. According to the main mineral phases present, samples V1 and U1 are smectitic clays with major admixtures of quartz and minor amounts of kaolin and plagioclase. In contrast, all the other samples are composed primarily of quartz with intermediate amounts of kaolinite and plagioclase. All samples contain minor amounts of the recalcitrant titanium dioxide, i.e. rutile and anatase. Only samples U1, U3 and W1 contained goethite, which also explains their yellowish colour. An unexpected and surprising observation is the high compositional variability of the samples. This variability extends to the samples sourced from effectively the same locations. This finding leads one to speculate that factors other than mere compositional aspects determine the suitability of the clays for their intended purposes. Perhaps the subjective texture experience during skin application and use might be more important. In the wet, as-supplied form, all samples had a smooth creamy feel when rubbed between the thumb and index finger. However, they also featured varying degrees of grittiness. Sample W2 was particularly gritty, probably because of the presence of silica particles.

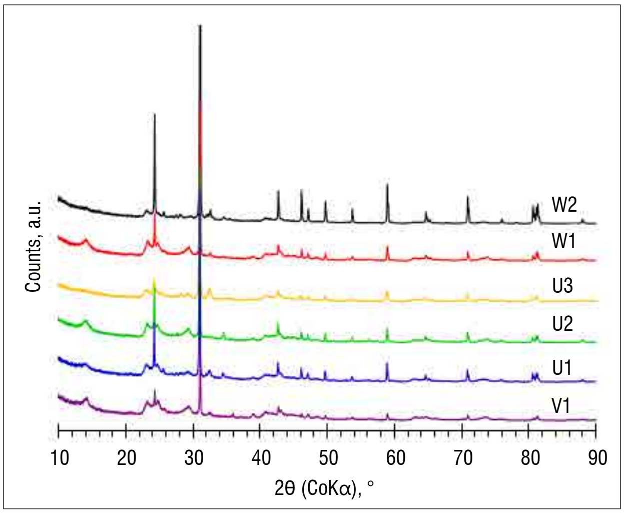


Figure 1: X-ray diffractograms obtained for pulverised clay samples.

Table 2: X-ray diffraction derived mineral content (wt%) estimated using Autoquan software

Mineral	Sample					
	V1	**U1**	**U2**	**U3**	**W1**	**W2**
Kaolinite 1:1	7.9±0.9	4.3±0.6	12.8±1.1	10.7±0.8	35.9±1.4	–
Smectite 2:1	67.3±1.6	58.0±1.1	–	–	–	–
Chlorite 2:1:1	5.6±0.9	–	–	–	–	7.4±0.5
Plagioclase	–	–	–	–	–	7.0±1.0
Plagioclase	–	5.05±0.75	34.4±1.4	23.7±0.7	–	–
Epidote	6.0±0.6	–	–	–	–	–
Quartz	11.0±0.5	26.1±0.6	47.3±1.3	61.2±1.0	46.9±1.3	84.5±1.0
Anatase	2.2±0.2	1.1±0.1	5.5±0.5	1.1±0.1	5.4±0.5	–
Rutile	–	–	–	–	2.7±0.6	1.2±0.3
Goethite	–	5.5±0.4	–	3.3±0.3	9.0±0.8	–

A significant finding is that all samples contained substantial amounts of quartz. The quartz content varied from 11.4 wt% in sample V1 to 84.5 wt% in sample W2. According to Khiari et al.[14], a quartz content above 15 wt% is cause for concern, even for topical applications, as there is sufficient evidence of quartz carcinogenicity.

The chemical composition results in Table 3 confirm the high silicon content expected in view of the silica and the silicate minerals present in the samples. In particular, it confirms the very high quartz content of sample W2. Sample V1 shows the highest iron content, despite the fact that it apparently contains no goethite. At first this appears to be a contradiction. However, iron-rich smectites containing even higher amounts of iron have been reported.[15]

Table 3: Metal oxide content (wt%) determined by X-ray fluorescence spectroscopy and loss on ignition results

Metal oxide	Sample					
	V1	U1	U2	U3	W1	W2
SiO_2	42.4±0.4	52.8±0.4	47.6±0.4	53.9±0.4	46.8±0.4	78.2±0.4
TiO_2	2.00±0.03	1.75±0.03	2.11±0.03	1.73±0.03	2.19±0.03	0.80±0.03
Al_2O_3	19.6±0.3	14.3±0.3	18.2±0.3	15.1±0.3	20.4±0.3	7.76±0.3
Fe_2O_3	21.8±0.3	16.5±0.3	16.8±0.3	16.7±0.3	15.6±0.3	5.30±0.3
MnO	0.13±0.01	0.13±0.01	0.07±0.01	0.10±0.01	0.05±0.01	0.07±0.01
MgO	1.0±0.1	1.3±0.1	0.85±0.1	1.39±0.1	0.66±0.1	0.48±0.1
CaO	1.76±0.07	2.24±0.07	2.58±0.07	0.90±0.07	0.79±0.07	0.84±0.07
Na_2O	0.11±0.11	0.39±0.11	0.90±0.11	1.06±0.11	1.11±0.11	0.70±0.11
K_2O	0.06±0.06	0.24±0.06	0.10±0.06	0.20±0.06	0.11±0.06	0.76±0.06
P_2O_5	0.06±0.08	0.04±0.08	0.03±0.08	0.05±0.08	0.01±0.08	0.01±0.08
Cr_2O_3	0.05±0.01	0.05±0.01	0.04±0.01	0.05±0.01	0.03±0.01	0.02±0.01
V_2O_5	0.07±0.00	0.06±0.00	0.08±0.00	0.06±0.00	0.08±0.00	0.02±0.00
ZrO_2	0.02±0.00	0.04±0.00	0.06±0.01	0.06±0.01	0.05±0.01	0.06±0.01
Loss on ignition	12.06	11.01	11.92	9.63	12.10	4.94

The trace metals detected by XRF are listed in Table 4. Fortunately, all the samples are essentially free of the toxic elements As, Pb, Hg, Cd, Se and Sb. However, they do contain low levels of chromium and other heavy metals such as Cu, Zn and Ni. They do not contain detectable levels of the radioactive elements uranium and thorium. Strontium (Sr) (30–98 ppm), zirconium (Zr) (172–387 ppm) and yttrium (Y) (10–44 ppm) are present in substantial amounts. The stable form of Sr is not radioactive and it does not pose a significant human health risk at the levels detected. However, Zr and Y do pose a radioactive risk. Future studies should investigate whether the potential toxic elements are readily exchangeable or strongly bound to the mineral structures.

Additional data on the materials are presented in Table 5. Dispersion of sample V1 in water rendered it slightly acidic, but all the other samples produced a slightly basic pH. Clays used in cosmetics are usually fairly basic with the pH ranging from pH 7 to 10.5.[7] Literature reports indicate skin pH values ranging from pH 4 to 7, but 'natural' skin actually has a surface pH just below 5.[6,16] Apparently this pH is beneficial for the natural resident flora.[7] Application of clay-based cosmetics could make it too alkaline which could cause the skin to become too dry and sensitive, and may even result in eczema. So care is advised when using the present clays in skin applications for extended periods of time.

Table 4: Trace metal content determined by X-ray fluorescence spectroscopy

Element (ppm)	Sample					
	V1	U1	U2	U3	W1	W2
As	0	0	7	0	0	2
Cu	226	97	107	92	122	38
Ga	25	19	29	22	27	7
Mo	0	0	0	0	0	0
Nb	4	8	14	8	11	6
Ni	133	111	87	71	88	31
Pb	0	0	0	0	0	0
Rb	0	9	8	9	6	34
Sr	60	57	38	98	30	44
Th	0	0	0	0	0	0
U	0	0	0	0	0	0
W*	1	9	9	1	6	88
Y	31	29	44	34	41	10
Zn	71	50	41	49	43	29
Zr	172	279	387	350	351	317

Table 5: Cation exchange capacity, estimate of upper bound for organic content and pH

	Sample					
	V1	U1	U2	U3	W1	W2
pH	6.1	7.9	9.1	8.0	8.7	8.6
CEC (mEq/100 g)	30	31	37	37	35	19
TGA organics (wt%)	8.9	6.3	6.6	6.3	6.2	2.6

CEC, cation exchange capacity; TGA, thermogravimetric analysis

The fairly significant loss on ignition values (9–12%) (see Table 3) suggest the presence of organic material. In some cases, when soil samples were heated in air, mass loss was observed in the TGA traces over the temperature range 200–500 °C (Figure 2). This mass loss often is associated with the oxidation of any organic substances present.[17,18] However, goethite decomposes into haematite at about 300 °C.[19] The mass loss resulting from the corresponding loss of water is 10.0 wt%. Taking this loss into account, an upper bound for the organic content of the materials was determined and these values are listed in Table 5. The apparent organic content varied from 2.6 wt% for sample W2 to 8.9 wt% for sample V1.

However, the absence of any bands near 3000 cm^{-1} in the FTIR spectra shown in Figure 3 suggests that very little, if any, organic material is actually present. The spectra can be fully explained by the presence of inorganic components in terms of previous observations.[20-23] The O-H asymmetric stretching occurs around 3700 cm^{-1}, probably as a result of the presence of the surface and internal OH groups of the Al-OH in the octahedral sheets. This band is lacking in the spectrum of sample W2, confirming the XRD result of the absence of kaolinite. The band at 3660 cm^{-1} is attributed to water OH bending vibrations[23], but there is only a very shallow dip in the spectrum of sample W2. The absence of a band located at 1230–1280 cm^{-1} implies the absence of amorphous silica. Si-O stretch vibrations are observed at 1000 cm^{-1}.[23] The bands near 920 cm^{-1} are typical for Si-O stretching and Al_2O-H deformations in the aluminium silicate, i.e. kaolinite.[20] The bands at 1100 cm^{-1} are assigned to Si-O and those at 1025 cm^{-1} to Si-O planar stretching. The bands around 775 cm^{-1} and 750 cm^{-1} can be attributed to the Al-O-Si inner surface vibration. The bands at 800 cm^{-1}, 775 cm^{-1} and 690 cm^{-1} in the spectrum of sample W2 are typical for quartz.[21]

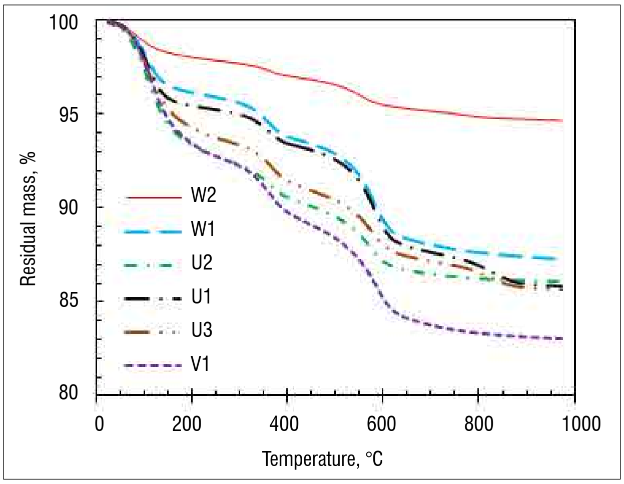


Figure 2: Thermogravimetric analysis mass loss curves for clay samples.

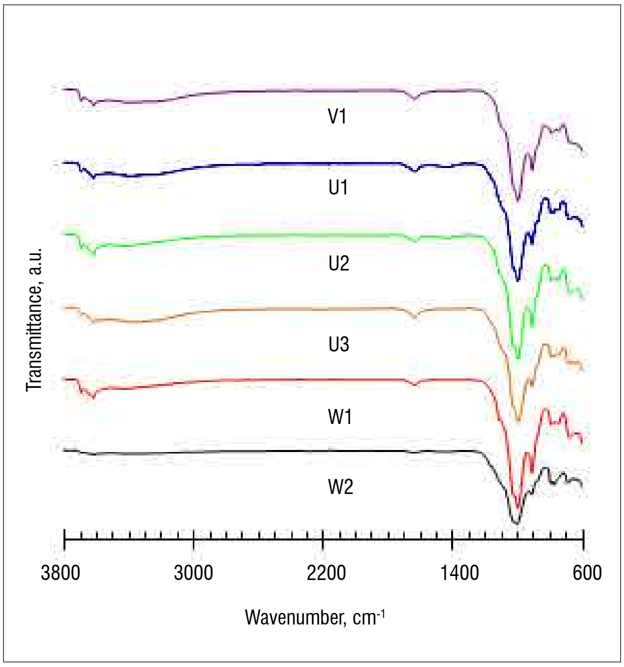
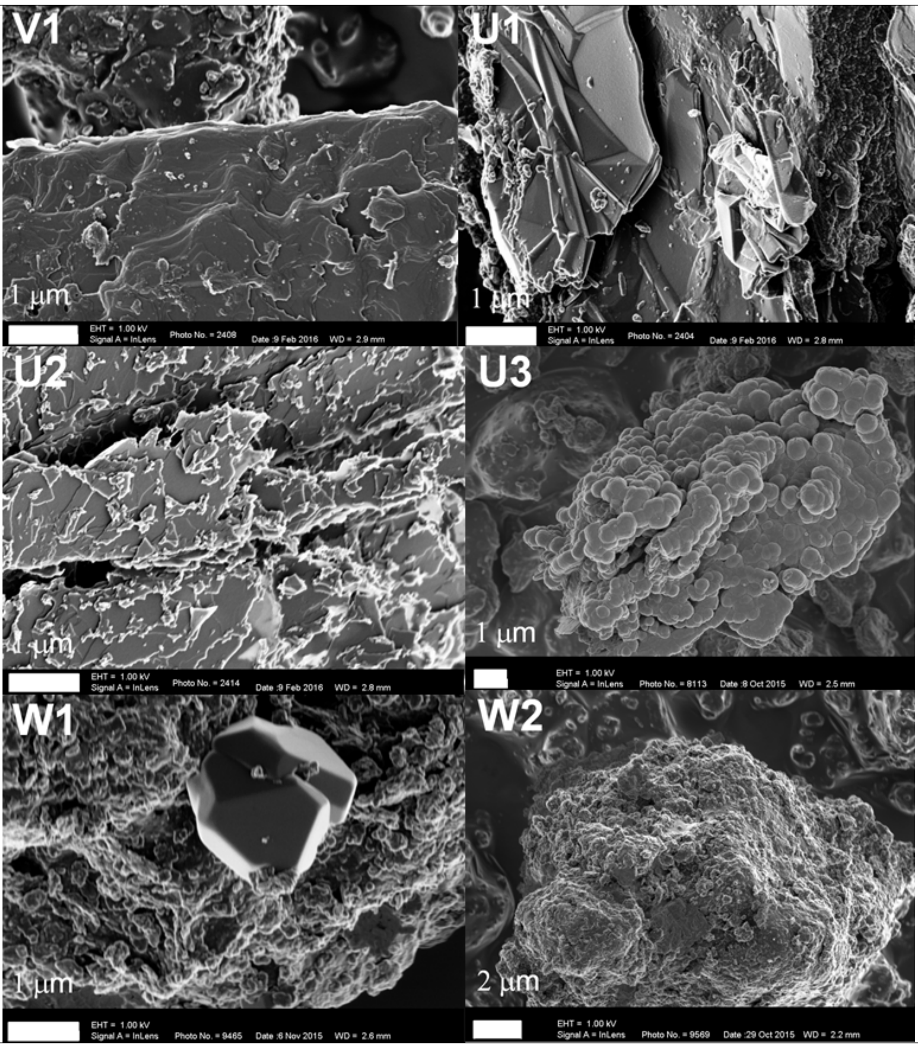


Figure 3: Attenuated total reflection Fourier transform infrared (ATR–FTIR) spectra of clay samples.



V1, U2 and U3: smectite platelets; U3: kaolin flakes; W1: a titanium dioxide crystal on top of quartz agglomerates; W2: quartz agglomerate

Figure 4: Scanning electron micrographs showing the morphology of powder particles.

The powder particles present in each individual clay sample exhibited various morphologies. The scanning electron micrographs in Figure 4 show only some selected particle morphologies found in each of the clay samples. However, in all cases, flake-shaped particles and highly agglomerated structures comprising small roundish sub-particles are present. The former reflect the presence of the phyllosilicates (kaolin, smectites, etc.), while the latter represent the other minerals present (silica, goethite, anatase, rutile, etc.).

Conclusion

We analysed clay samples sourced via traditional healers from Mtubatuba and Nongoma in KwaZulu-Natal and from Mbaleni in Limpopo, South Africa. These clays, known as *vumba* and *ubumba*, are supplied in a wet state and are reportedly used as topical cosmetics with health benefits. XRD analysis revealed a surprising variability in the mineralogical composition of the clays, even in samples taken from the same deposit. This implies that the actual application is robust with respect to clay composition. XRF analysis showed that the samples were free from radioactive elements and the toxic elements As, Pb, Hg, Cd, Se and Sb. However, they did contain low levels of chromium and other heavy metals, e.g. Cu, Zn, Ni. A disconcerting discovery is the high silica content, ranging from 11 to 85 wt%. Even though the intended purpose relates to topical applications, these levels may pose a certain health risk.

Acknowledgements

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Authors' contributions

R.M-M. collected the samples, performed most of the experiments and managed the characterisation done by others, notably the XRD and XRF investigations. She also analysed the results and drafted the manuscript. W.W.F. supervised R.M-M., assisted in evaluating the experimental results and edited the manuscript. W.G. assisted with sample preparation (milling) and performed the XRD analyses.

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Characterisation of *vumba* & *ubumba* clays for cosmetic purposes

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ABSTRACT

- **Two traditional cosmetic clays bear similar names in different local South African languages: *vumba* (Tshivenda) and *ubumba* (isiZulu).**
- **Six samples from two South African provinces were characterized using XRD, XRF, FTIR, TGA and SEM.**
- **Aim: to establish justification for the common usage of the clays as cosmetics by comparing their nature and composition.**
- **Key words: traditional clays, cosmetic purpose, composition, pH, quartz**

KEY FINDINGS

- **Difference in mineralogy and chemical composition.**
- **Clay minerals found in current cosmetic products were present in some samples: Kaolinite (Kln), TiO_2 polymorphs anatase (Ant) and rutile (Rut).**
- **Quartz, a potential carcinogen, was found in all the samples.**
- **No toxic elements As, Pb, Hg, Cd, Se and Sb: low levels of Cr and heavy metals such as Cu, Zn and Ni.**
- **Slightly basic pH values for *ubumba* slurries and slightly acidic for *vumba*.**

HIGHLIGHTS:

- Heterogeneous composition is predominant even though the clays are all used as cosmetics.
- NO highly toxic or radioactive elements.
- High levels of quartz present may pose a human health risk.

INTRODUCTION

Clay minerals:

- Fine-grained cosmetic ingredients that exhibit plasticity when mixed with water
- Layered structure and colloidal particle size impart rheological properties & adsorptive abilities.
- Stability, texture, moisture content, particle size & toxicological requirements may be affected by quartz, iron, sulfates, carbonates & feldspars.

MATERIALS AND METHODS

Table 1: Sampling sites

Sample	Location	GPS coordinate
u1,u2,u3	Mtubatuba, KwaZulu-Natal	28.4167^{o}S, 32.1833^{o}E
u4,u5	Nongoma, KwaZulu-Natal	27.8833^{o}S, 31.6333^{o}E
v1	Mbaleni, Venda	30.4906^{o}S, 22.9603^{o}E

METHODS

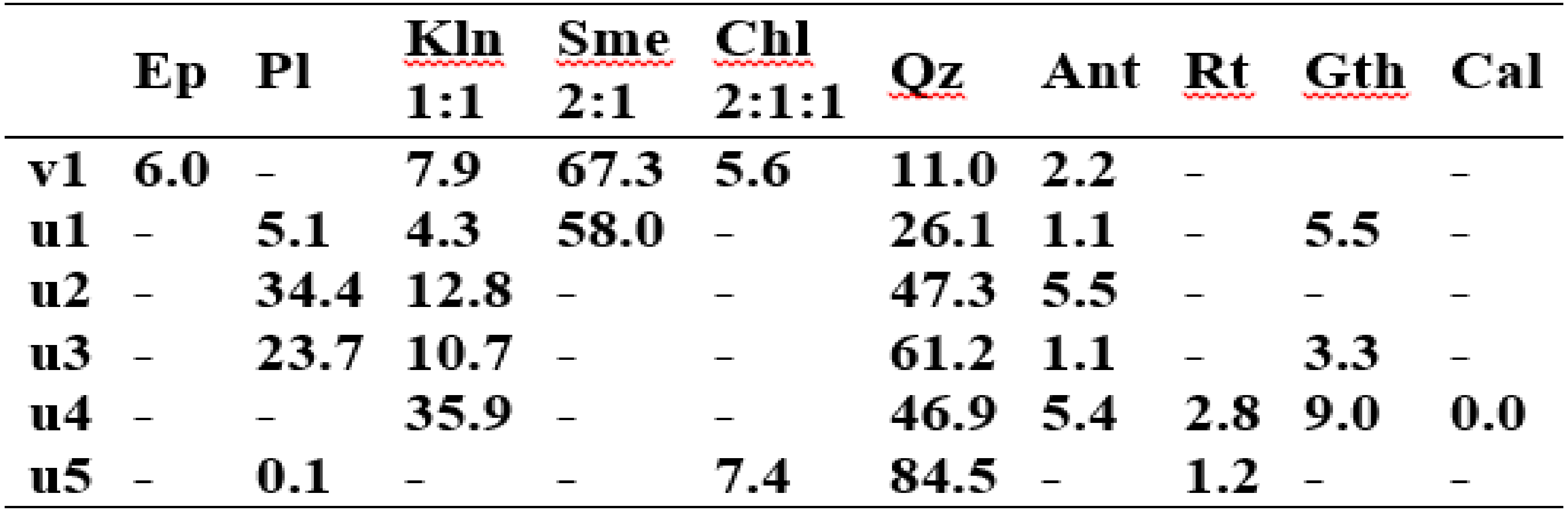
- **XRD and XRF, ATR–FTIR and TGA analyses performed on powders milled to a fine particle size (<75 µm).**
- **SEM and CEC performed on manually ground sample powders.**

RESULTS

- Table 2 reveals the heterogeneity of the clay mineral composition
- More than 55% m/m, of the swelling 2:1 smectitic clay in v1 and u1.
- High levels of quartz, 84.5% (m/m) for KwaZulu Natal.
- Khiari, Mefteh et al. (2014): limit of less than 15% (m/m) as being fairly safe against the even stricter Cosmetic Ingredient Review (CIR 2016) of less than 5% (m/m).
- The presence of the TiO_2 polymorphs, anatase and rutile, justifies use for sun screening if decontamination is done.
- Various amounts of Al_2O_3 and Fe_2O_3 present in all the samples.
- Table 4: conspicuous absence of the toxic metals: As, Pb, Hg, Cd and Sb. None of the radioactive elements U, Th and Rb were detected. High levels of Zr and Y are alarming.
- Notable potential presence of organic material according to Table 3 from the loss on ignition results.
- pH values not in line with recommended values for use on the skin
- (Matike, Ekosse et al. 2011)

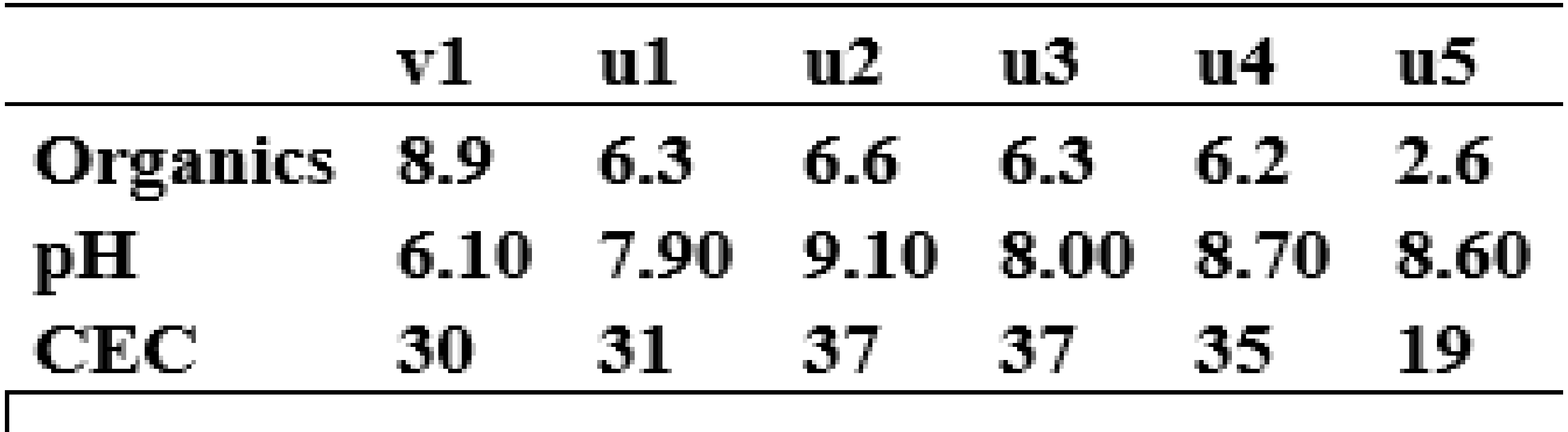
RESULTS

Table 2: XRD estimated clay mineral (% m/m)



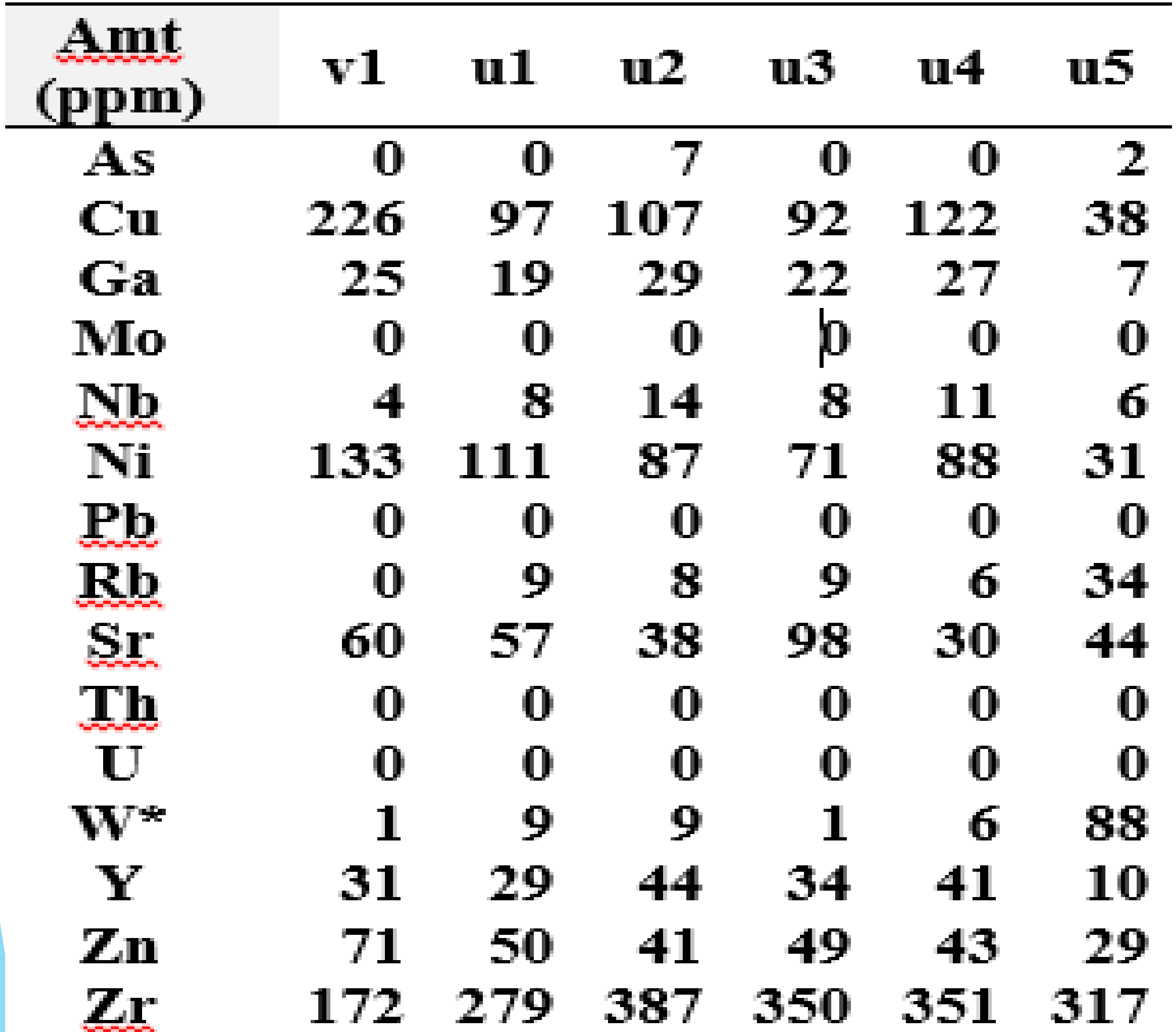
	Ep	Pl	Kln 1:1	Sme 2:1	Chl 2:1:1	Qz	Ant	Rt	Gth	Cal
v1	6.0	-	7.9	67.3	5.6	11.0	2.2	-		-
u1	-	5.1	4.3	58.0	-	26.1	1.1	-	5.5	-
u2	-	34.4	12.8	-	-	47.3	5.5	-	-	-
u3	-	23.7	10.7	-	-	61.2	1.1	-	3.3	-
u4	-	-	35.9	-	-	46.9	5.4	2.8	9.0	0.0
u5	-	0.1	-	-	7.4	84.5	-	1.2	-	-

Table 3: Organic content (% m/m), pH and CEC (mEq 100 g^{-1})



	v1	u1	u2	u3	u4	u5
Organics	8.9	6.3	6.6	6.3	6.2	2.6
pH	6.10	7.90	9.10	8.00	8.70	8.60
CEC	30	31	37	37	35	19

Table 4: XRF trace metals content (% m/m)



Amt (ppm)	v1	u1	u2	u3	u4	u5
As	0	0	7	0	0	2
Cu	226	97	107	92	122	38
Ga	25	19	29	22	27	7
Mo	0	0	0	0	0	0
Nb	4	8	14	8	11	6
Ni	133	111	87	71	88	31
Pb	0	0	0	0	0	0
Rb	0	9	8	9	6	34
Sr	60	57	38	98	30	44
Th	0	0	0	0	0	0
U	0	0	0	0	0	0
W*	1	9	9	1	6	88
Y	31	29	44	34	41	10
Zn	71	50	41	49	43	29
Zr	172	279	387	350	351	317

RESULTS: INFRARED SPECTROSCOPIC ANALYSIS

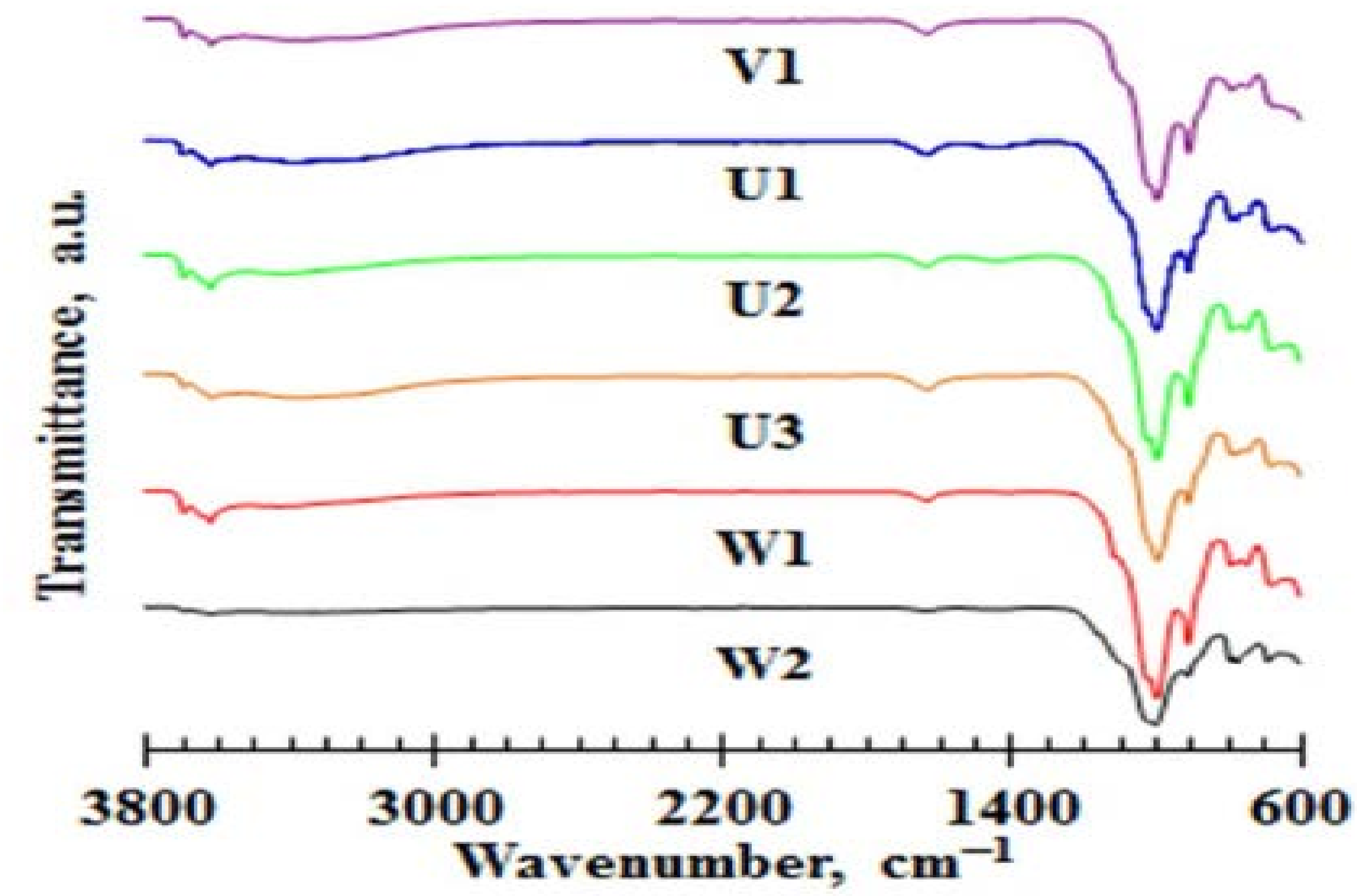


Figure 1: Infrared spectroscopic analysis.

RESULTS: THERMOGRAVIMETRIC ANALYSIS

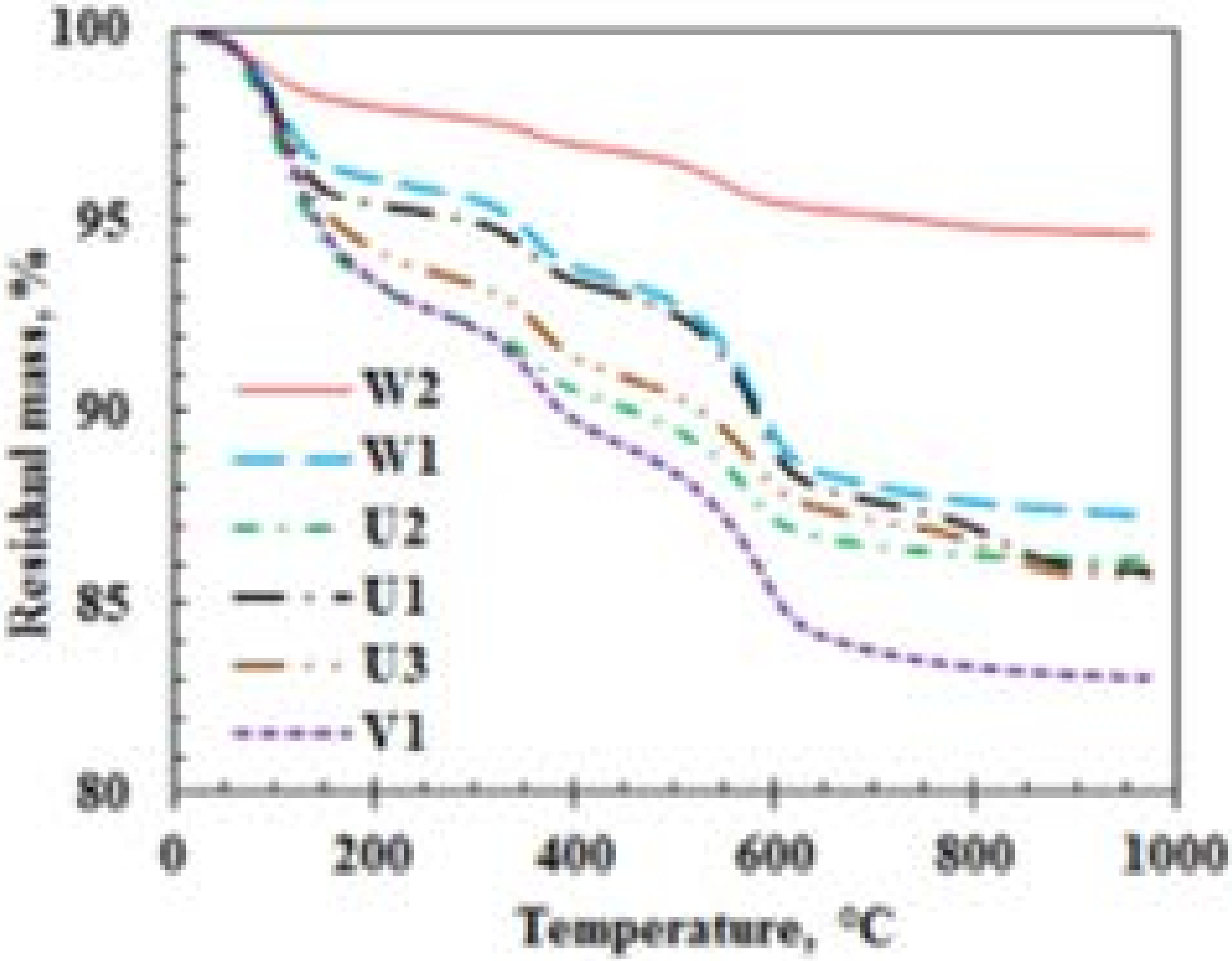


Figure 2: thermogravimetric analysis

RESULTS

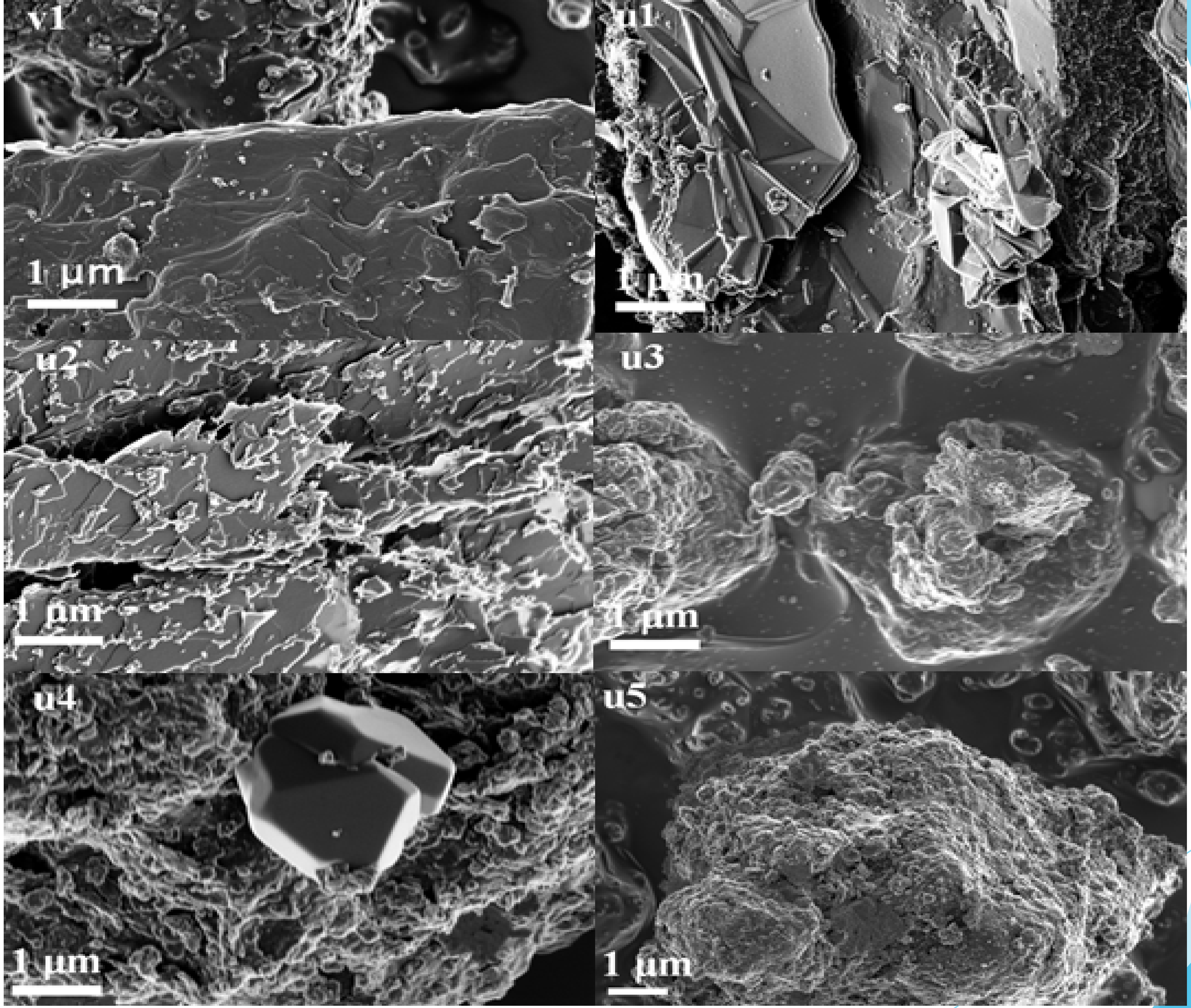


Figure 3: SEM micrographs for morphology

RESULTS

- Presence of crystalline silica is emphasized by the Si—O vibrations at 1000 cm^{-1} in Fig 1.
- Bands near 920 cm^{-1} are typical for Si—O stretching and Al_2O—H deformations in the aluminium silicate (kaolinite).
- Absence of any bands near 3000 cm^{-1} in the FTIR spectra in Fig 1 suggests that very little organics is present contrary to Fig 2 TGA's organic thermal degradation in the range 200-500°C.
- SEM micrographs re-affirm the XRD results in Fig 3 and Table 2 respectively.
- Variability in morphology with kaolinite, quartz & TiO2 prominent

CONCLUSION

- The actual composition is dynamic with respect to clay composition
- Heterogeneous composition poses a question mark on the justification of commonality.
- The absence of toxic elements is a positive factor for safety.
- Quartz poses a health hazard for the users of the clay.

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