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SCHOOL OF ENVIRONMENTAL SCIENCE

DEPARTMENT OF HYDROLOGY AND WATER RESOURCES

PHYSICO-CHEMICAL, CHEMICAL AND MINERALOGICAL CHARACTERISATION OF EARTHY MATERIALS INDIGENOUSLY USED AS COSMETICS

BY

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Declaration

I, Ibeh Oluebube Sally, hereby declare that this dissertation for the Master of Environmental Sciences degree at the University of Venda, hereby submitted by me, has not been previously submitted for a degree at this or any other institution. To the best of my knowledge and belief, this work contains no material which has been previously published or written by another person except where due reference is made.

Signature ------------------------------------ Date: ------------------------

I hereby certify that the above statement is correct.

Supervisor	Co-supervisor
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Dedication

This work is dedicated to almighty God, the giver of wisdom, knowledge and understanding.

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Abstract

Africa is endowed with various earthy materials, of which each community is uniquely identified. Inspite of the vast knowledge of western cosmetics, application of traditionally used cosmetics have been in existence and will be into practice from generation to generation, this is as a result of their various indigenous knowledge about traditional cosmetics. They are mostly applied during traditional rites and festive periods. Occasionally, earthy materials play a vital role in traditionally used cosmetics. Different reasons have been associated with the use of these earthy materials, they are: for skin cleansing, protection against ultra violet radiation, skin lightening, perfecting the distorted part of the skin and improving beauty. This study is focused on the physico-chemical, chemical and mineralogical characterisation of earthy materials indigenously used as cosmetics.

This is achieved firstly by identifying the various earthy materials applied topically as well as their constituents. Samples for this study were obtained from six (6) different African countries namely: Botswana, Cameroon, Democratic Republic of the Congo, Nigeria, South Africa and Swaziland and were subjected to the following analyses: Scanning Electron Microscope and Electron Dispersive X-ray Spectroscopy for the morphology and elemental analysis, hydrometer method for the determination of particle sizes of each sample and a texture Auto Lookup Software Package (TAL Version 4.2) for the classification of their various textures (%clay, %sand and %silt). The X-ray diffractometry was applied for the identification of their mineral phases (secondary, major and minor). The Brunauer Emmett and Teller (BET) method was used for the physisorption analysis and classifying them according to their isotherm types (Type I, II, III, IV, V and VI). The chemical analysis was achieved by X-ray fluorescence (XRF). The result revealed that the morphology of the various representative samples varies, except CMR 1; 2, SCC 1; 2 and SLW 1; 2 which showed same structure and same elemental constituents, their resemblance indicated that they possess same geological formation. The XRF result indicated the presence of the following trace elements: Al, As, Au, Ba, Bi, Br, Ca, Cd, Ce, Cl, Co, Cr, Cs, Dy, Er, Eu, Fe, Ga, Gd, Ge, Hf, Hg, Ho, I, In, K, La, Lr, Lu, Mg, Mn, Mo, Na, Nd, Ni, Nb, Os, P, Pb, Pd, Pr, Pt, Re, Rh, Ru, S, Sc, Se, Sb, Si, Sm, Sn, Sr, Ta, Te, Tb, Th, Ti, U, V, W, Y, Yb, Zr and Zn, were measured in ppm. For example, Fe – 66.47 (Qwa-Qwa), Al – 4.64 (Swaziland), Si – 6.26 (Democratic Republic of Congo), Ti – 3.75 (Qwa-Qwa) and so on.

From the particle size distribution analysis, some samples were identified to be clay (BTS 1, BTS 2, NG 1, SCC 4, SCC 5, SCC 9, SCC 11, SCC 12, SWL 1 and SWL 2) with their particle sizes < 2µm, whereas other samples showed other properties which are > 2 µm. Ten minerals were identified in the clay fraction samples: albite, goethite, halloysite, hematite, kaolinite (kaolinite-1Md, kaolinite 1) Mica (muscovite), sulphur, talc, chalcanthite and whewellite. The BET method for physical adsorption revealed that BTS 1, BTS 2, CMR 1, CMR 2, DRC A, DRC B, NG 1, NG 2, SWL 1, SWL 2, SCC 1, SCC 4, SCC 5, SCC 8, SCC 9, SCC 11 and SCC 12 countries possess Type II isotherm whereas samples from SCC 2, SCC 6, SCC 7 and SCC 10 had Type III isotherm. The physisorption analysis result also determined the various surface areas and porosity of each representative samples.

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List of Abbreviations

Al – Aluminium
Ca – Calcium
Co – Cobalt
Cr – Chromium
Cu - Copper
Fe – Iron
Ga – Gallium
K – Potassium
Mg – Magnesium
Mn – Manganese
P - Phosphorus
S – Sulphur
Si – Silicon
Ti – Titanium
Rb – Rubidium
V – Vanadium
Y – Yttrium
Zn – Zinc
Zr – Zirconium
As – Arsenic
B – Boron
Ba – Barium
Be – Beryllium
Bi – Bismuth
Cd – Cadmium
Co – Cobalt
Cr – Chromium
Cs – Caesium
Cu – Copper
AIPEA – Association Internationale Pour l'etude des Argiles
BET – Brunauer Emmett Teller
CMS – Clay Minerals Society
EDX – Energy Dispersive X-ray Spectroscopy

IARC – International Agency for Research on Cancer

SEM – Scanning Electron Microscopy

TEM – Transmission Electron Microscope

XRF- X-ray Fluorescence

XRD – X-ray Diffraction

WHO – World Health Organisation

List of Units and Symbols

Å - Angstrom

CEC – Cation Exchange Capacity

Cmol/kg – Centimol per kilogram

g – Gram

K - Kelvin

kV – Kilovolt

mA – Milliamp

meq – Milliequivalent

Kg/m^3 – Kilograms per meter cubed

Ppm - Parts per million

µ - Micro

< - Less than

\> - Greater than

% - Percentage

W% - Weight percentage

Mm – millimeters

nm – Nanometer

Ka- Kiloamp

mg – milligram

µg/d – migrogram per day

m^3 – meter cube

Mol – mole

µm - micrometer

CHAPTER 1:
INTRODUCTION

1.1 Background to the study

Clay Minerals are used in many applications, including the pharmaceutical and cosmetic industries. Clay is among one of the raw materials which its usage for current and new applications will continue to grow (Jovanovic and Mujkanovic, 2013). In manufacturing industries clay materials are used to produce large variety of products such as ceramics, paper, polymers, paint, cosmetics, and many others (Mpuchane *et al*., 2008; Nkoma and Ekosse, 1999; Heckroodt, 1991). In most of these applications, clay materials play a vital and irreplaceable role in which they are present as active or inactive ingredients. They fall within the phyllosilicate group. Clay minerals are known as hydrated aluminium silicates with very fine particle size, usually <2 µm (Moore and Reynolds, 1989). Grim (1962) gave a clear definition of what clay minerals are; classifying them as fine-grained, natural, earthy, argillaceous materials. Brindley and Brown (1980) also defined clay minerals as materials with very small particle size, usually less than 2 µm in diameter, with net negative surface charge.

The term *clay* has been difficult to define*,* because its attribute differ for various disciplines (Heckroodt, 1991). Guggenhein and Martin (1995) termed clay to be a naturally occurring earthy material which comprises of fine grained particle size materials which are generally plastic at appropriate water content but hardened when dried or fired. Clay can be used as a rock term and also can be used as a particle size term in mechanical analysis of sedimentary rocks or soils. As a rock term, it is difficult to specifically define clay because of the wide variety of materials that have been called clays. Clay is a sedimentary rock containing clay size particles and these include claystone, mudstone, bentonite and kaolin.

A general implication of the term ‘clay’ expresses that it is a natural, earthy, fine-grained material that develops plasticity when mixed with a limited amount of water, which was finalised by Association Internationale pour l’etude des Argiles (AIPEA) and Nomenclature committee and the Clay Minerals Society (CMS) (Bailey, 1980). Although clay contains phyllosilicates, it contains other materials which impact its plasticity and they are referred to as “Clay minerals”. The abundance in nature and unlimited potentials of clay minerals has brought wide application (Vaccari, 1998; Kim *et al*., 1998; Ogawa and Kuroda, 1995; Cavani *et al*., 1991; Reichle, 1986 Theng, 1974), particularly in the usage of clay minerals for curative and protective purposes (Robertson, 1996; Carretero, 2002; Veniale *et al*., 2004) and for cosmetic application.

The persistent use of clay minerals as active ingredients in pharmaceutical and cosmetic formulations has been well documented (Viseras *et al*., 2007; Carretero and Pozo, 2007; Del Hoyo, 2007; Lefort *et al*., 2007; Carretero *et al*., 2006; Droy-Lefaix and Tateo, 2006; Love, 2004; López-Galindo and Viseras, 2004; Carretero, 2002; Veniale, 1992, 1997; Galán *et al*., 1985, Bolger, 1995). The structural properties of clay determines its use for cosmetics (Gomes and Silva, 2007; Lopez-Galindo *et al.,* 2007 and Viseras *et al.,* 2004), because clay exists in different forms (Droy-Lefaix and Tateo, 2006; Carretero, 2002). They are popular in the cosmetic industry because of their natural specific properties as well as their remarkable high specific area and adsorption capacity; most of these clay minerals serve as active ingredients and sometimes they are mixed with other plant materials in most traditional and industrial applications (Matike *et al*., 2010).

A field visit was made to some communities in South Africa and it was observed that people still use earthy materials without any treatment for cosmetic purposes. Some common clay minerals which are indigenously applied for skin care are kaolinite, talc and smectites. As stated earlier that clay minerals also contain some non-associated clay minerals, this may in turn mar its utilization. In the case of bentonite it contains large quantity of non-clay minerals, for example feldspar, calcite, gypsum and quartz (Mukasa-Tebandeke *et al.,* 2015).

Clay minerals are used for topical applications and this include their use as dermatological protectors and in cosmetics (Choy *et al*., 2007; Viseras *et al*., 2007; Carretero, 2002). There is so much belief attached to using earthy materials for topical application and this is common to African communities. Some of these beliefs are that it protects them from UV radiation, sunscreening and other dermatological application because ultraviolet (UV) radiation is a real problem to human health. It can harm human skin and can even lead to the extreme case of skin cancer (Hoang-minh, 2010; Matike *et al*., 2010). This knowledge has been passed from generation to generation (Matike *et al*., 2010).

Topical application of earthy materials, are widely dominated by clay minerals. In African communities, clay minerals used for cosmetics are identified primarily by their colour, an inherent property in determining their application. Though white and red clays are the most commonly used in the continent, the use of black, grey, brown, yellow, orange, green, pink and blue clays have also been reported (Mpuchane *et al*., 2008). Africa is endowed with many mineral resources, a field visits to some communities in South Africa shows that there is abundant of this clay minerals and hence making its usage a continuous one.

The use of cosmetics date back to around 10000BC (Price, 2001) and still in existence. Singh, (2010) referred products which are applied to the body for the purpose of cleansing, beautifying or improving the appearance and also for the purpose of enhancing the attractive features of the body to be cosmetics. Some of the cosmetics used contain varying components like amorphous carbon, zincite, cuprite goethite, elemental silicon or talc, hematite, organic compounds (Hardy *et al*., 1998; 2004) and even heavy metals such as lead (Popoola *et al.,* 2013).

This study attempted to investigate the chemical and mineralogical properties in earthy materials from some selected African communities and also to exploit the various clay minerals present in the indigenously used earthy materials through characterisation.

1.2 Statement of problem

A well detailed information on characterisation, chemical and mineralogical compositions of clay minerals present in cosmetic clay used across Africa is still lacking in Africa. Many reasons have been linked to topical application of earthy materials as cosmetics, they are mostly used in facial treatments and are believed to be the best method in the removal of blackheads, spots and acnes without a proper knowledge of the compositions. Earthy materials indigenously applied topically as cosmetics contain various constituents which are not conforming to the standard of cosmetics, hence this work is dealing with the characterisation of the studied earthy materials.

Earthy materials have been known to contain heavy metals which may be useful or detrimental to human health, Some subset of elements; antimony, arsenic, barium, cadmium, selenium, mercury are the most known elements which are classified as heavy metals (*www.perkinelmer.com*), they pose considerable threat to human body. A visit to some markets where these earthy materials are sold indicated that the sellers purchase them from various mines of which their compositions has not been well established. Most of these cosmetic clays contain elements which are essential metals but can become toxic when at high concentration (Glanze *et al.,* 1996). The skin absorb some percentage of these salts of heavy metals and this varies greatly with different physical parameters (Lilley *et al.,* 1988). Heavy metals exposure mostly occur via diet, medications, environments and topical applications (Adal and Tarabar, 2013). Indigenous people who practice the use of earthy materials for topical application generalize them as clay, but in essence they can’t be literally called clay. Their particle sizes were determined to know their classifications using particle size distribution ternary diagram.

Previous studies has shown that earthy materials are made up of clay minerals which fall in class of phyllosilicate, the formation of these clay minerals are as a result of chemical weathering of other silicate minerals at the earth surface. This minerals mostly contains iron oxide, silica, limestone and are peculiar to earthy materials which has yellowish, reddish, or brown colour (Edorgan, 2015).

1.3 Motivation

Earthy materials have been used as cosmetic in many African communities for many decades. This often involve the use of indigenous clays for dermatological purposes (Matike *et al.,* 2010). The chemical, mineral and physico-chemical constituents of these earthy materials are not known. Most earthy materials which are useful for topical application often contain impurities which could present health risk when applied over a long period of time. This includes presence of topical non-natural substances in clay minerals for instance, titanium dioxide (TiO_2), goethite (Fe_2O_3), haematite ($Fe(OH)_2$) and other non-clay materials which are known to produce photo catalytic effect (Hoang-Minh, 2006) and can cause potential threat such as carcinogenic effect, skin irritation to users due to their accumulation (López-Galindo *et al*., 2007). These non-clay minerals are of great concern. Hence in the study, the minerals which are suitable for topical applications will be differentiated from the non-clay minerals.

Furthermore, most earthy materials are coarse in nature, this is as a result of the presence of coarse grain size in the samples. They are not user friendly particularly upon body application. From previous studies, quartz for example appears to be dominant, hence the percentage composition of the unwanted materials (materials required either in less or larger quantities) and this percentage composition of quartz will be determined using a more efficient instrument. A short summary on the assessment of quartz was conducted by IARC (1997) and IPCS, (2000) this shows that bentonite, kaolin and common clay contain large amount of quartz.

1.4 Objectives

1.4.1 The main objective

The main objective of this study was to characterise and to determine the chemical and mineralogical compositions of earthy materials indigenously used topically as cosmetics.

1.4.2 Specific Objectives

The following specific objectives were formulated for the research:

- To identify and characterise the different earthy materials studied.

- To determine the particle size, pore size and surface area present in the studied earthy materials
- To determine the chemical compositions of the studied earthy materials which are used topically.
- To ascertain the level of heavy metals present in each traditionally used cosmetic clay.
- To determine the mineralogical composition of the studied earthy materials.

1.5 Research questions

These questions will assist in attaining the objectives of the study:

- What are the physico-chemical properties of the selected earthy materials?
- What are the chemical compositions of the selected earthy materials?
- What are the trace metals present in the selected earthy materials?
- What are the clay mineralogy of the selected earthy materials?

1.6 Hypothesis

- The physico-chemical, chemical and mineralogical properties of the earthy materials will support the use of earthy materials for cosmeticological application.
- People who use earthy materials for topical application tend to be more susceptible to dermatological infections.

1.7 Study area

The use of earthy materials for cosmetic purposes is indigenous in Africa. In this study, research is built from previous studies conducted on clayey and earthy materials from Botswana, Cameroon, Democratic Republic of the Congo, Nigeria, South Africa and Swaziland. All the countries were chosen according to their geographical regions in Africa. Figure 1 below clearly shows the various countries and locations where the earthy materials were collected. The samples for this study where obtained from localities in these countries where earthy materials are used for cosmetic purposes though not physically substantiated but a field trip was made for cities in South Africa. Sample collection from other localities were from previous studies used for other purposes. Table 1 summarises the various countries, localities and geographical coordinates of the studied earthy materials.

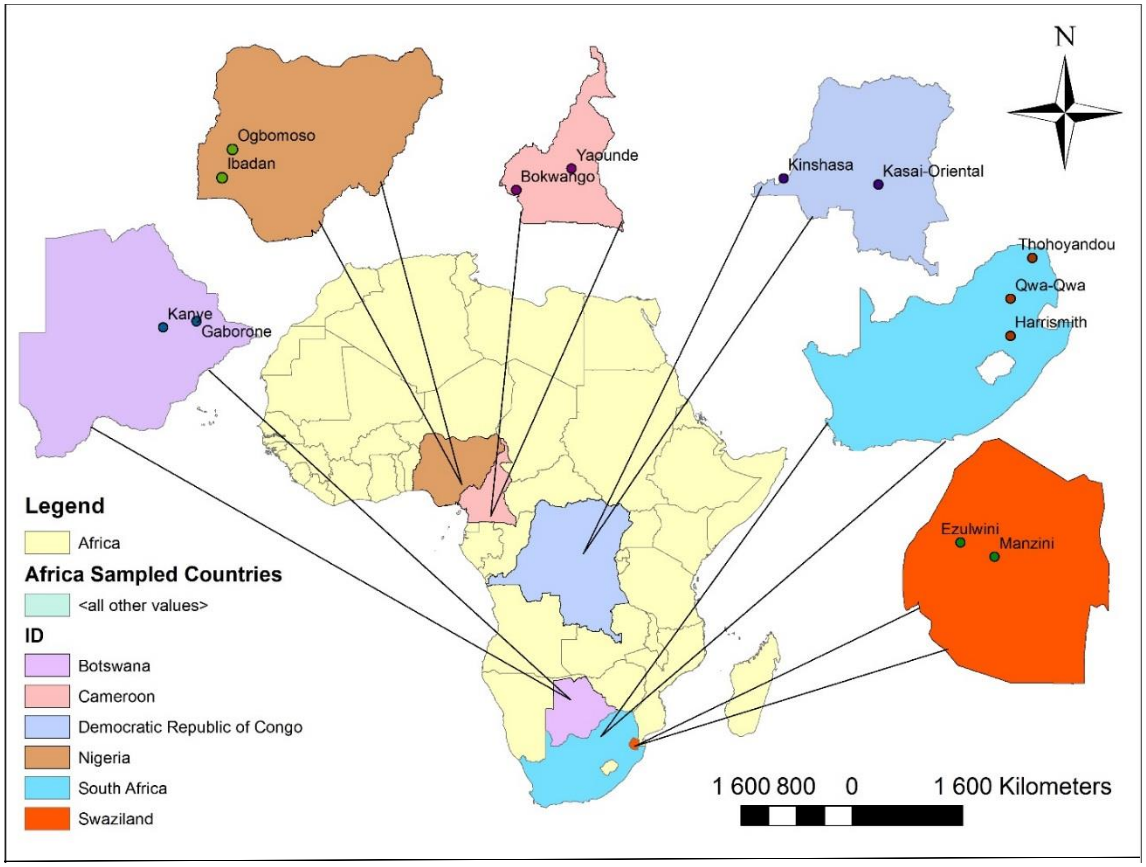


Figure 1: Map of Africa, showing different localities where the studied samples were obtained

Table 1: Countries where the samples were collected with their coordinates.

COUNTRIES	LOCALITIES	GEOGRAPHICAL COORDINATES
BOTSWANA	GABORONE	24.658°S, 25.912°E
	KANYE	24.983°S, 25.912°E
CAMEROON	BOKWANGO	4.139° N, 9.224°E
	YAOUNDE	3.867°N, 11.517°E
DEMOCRATIC REPUBLIC OF CONGO	KASAI- ORIENTAL	5°540’S, 22°27’ E
	KINSHASHA	4.325°S, 15.322°E
NIGERIA	IBADAN	7.396°N, 3.916°E
	OGBOMOSO	8.133°S, 4.250°E
SOUTH AFRICA	HARRISMITH	28.560°S, 29.781°E
	THOHOYANDOU	22.950°S, 30.488°E
	QWA-QWA	28.551°S, 29.080°E
SWAZILAND	EZULWINI	28.609°S, 29.109°E
	MANZINI	26.483°S, 31.367°E

CHAPTER 2:
LITERATURE REVIEW

2.1 Preamble

This chapter vividly explains how clay minerals are formed, their occurrence and origin. Review has been done in the different regions of Africa where topical applications of earthy materials are practiced. Review of chemical, physico-chemical and mineralogical analyses of earthy materials has also been done. The general concept is to review studies which have direct relevance to the present study.

2.2 Historical overview of clay minerals

Clays are among the many minerals used in various industries, they play a vital role in most industrial applications (Murray, 2002). They are naturally occurring earthy materials comprising of finely grained minerals, which are generally plastic at appropriate water content and harden when dried or fired (Guggenheim and Martin, 1995). The earthy material has its particles, usually < 2 µm in diameter and is widely dispersed on the earth's surface (Gomes and Silva, 2007; Ekosse, 2000; Nkoma and Ekosse, 1999; Heckroodt, 1991). Though there has been a great diversity in the definition of clays because of the variation that exist in different fields, clay could be defined on the basis of an assembly of certain specific characters such as plasticity, small particle size, hardening on firing and chemical constituent, they can be referred to as argillaceous sediments or clay sediments or earthy particles which are generally less than 2 µm diameter (Gomez and Silva, 2007; Ekosse, 2000; Nkoma & Ekosse, 1999; Heckroodt, 1991).

The origin of clay minerals has been broadly reviewed over the past half century and formation of soil clay minerals, namely micas, vermiculites, smectites, chlorites and interlayered minerals, interstratified minerals and kaolin (Wilson, 1998) and research is still on in identifying more minerals. Millot (1965) and Jackson (1964) presented an appropriate starting point with regard to the origin and formation of soil clays as assessed principally by the X-ray diffraction and microscopic techniques that were available at the time. Millot (1965) outlined three principal processes to account for the genesis of clay minerals, which may occur at different points in the geochemical cycle including weathering or soil formation at the earth's surface. These processes are:

- Detrital inheritance whereby, for soils, clay minerals are inherited from pre-existing parent rock or weathered materials;
- Transformation where the essential silicate structure of the clay mineral is maintained to a large extent, but with major change in the interlayer region of the structure

- Neo-formation, where the clay mineral forms through crystallization of gels or solutions.

With regard to transformation of clay minerals, a general example would be:

illite -----------> vermiculite -------------->smectite (Wilson, 1998).

This reaction proceeds through a process of depletion and exchange of interlayer potassium (K) and concomitant decrease of layer charge. Millot (1965) distinguished 'degradation' and 'aggradation' as separate forms of the transformation process. The above conversion of illite to montmorillonite (smectite group) involves depletion of elements from illite and is termed degradation, but the reverse reaction (aggradation) involves addition of potassium and other elements. Millot (1965) considered that degradation was characteristic of weathering rocks and soils, but that aggradation was rare in such environments. Table 2.1 shows the weathering processes taking place during clay mineral formation, its mechanism, soil types, chemical names and chemical formula.

Table 2.1: Occurrence of soil clay minerals in relation to weathering process, principal mechanism and soil types

WEATHERING PROCESS	**PRINCIPAL MECHANISM**	**CLAY MINERAL**	**CHEMICAL NAME**	**CHEMICAL FORMULA**
Transformation	Acidolysis (partial)	Smectites	Montmorillonite	$(Na,ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2.nH_2O$
		Vermiculites	Vermiculite	$(Mg_{1.8}Fe^{2+}_{0.9}Al_{4.3}SiO_{10}(OH)_2.4(H_2O)$
		Al-chlorite	-	$Al(ClO_3)_3$
Neoformation	Hydrolysis (partial)	Smectites	Montmorillonite	$(Na,ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2.nH_2O$
			Nontronite	$Na_{0.3}Fe((Si,Al)_4O_{10})(OH)_2.nH_2O$
			Saponite	$Ca_{0.2}Fe((Si,Al)_4O_{10})(OH)_2.nH_2O$
	Hydrolysis (total)	Kaolinite		$Al_2Si_2O_5(OH)_4$
		Halloysite	Endellite	$Al_2Si_2O_5(OH)_4$
		Gibbsite	Aluminum Hydroxide	$Al(OH)_3$

Source: Pedro (1982)

The formation of clay minerals through neo-formation depends upon the appropriate physico-chemical conditions of the immediate weathering environment, such as the pH, composition and concentration of the soil solutions, as well as the nature of the starting material and factors relating to the external environment like temperature, rainfall and percolation rate (Wilson, 1998). Pedro (1964) distinguished two mineral weathering processes implicated in the formation of clay minerals in soils, which he termed 'hydrolysis' and 'acidolysis'. Hydrolysis of minerals occurs through dilute solutions in the pH range 5 - 9.6 and may be total or partial. Total hydrolysis leads to the removal of all elements including silica, and to the precipitation of gibbsite and kaolinite minerals, whereas partial hydrolysis, under different conditions, leads to the formation of smectite minerals (Pedro, 1982).

2.3 Clay minerals formation reactions

Kaolin could be primary (hydrothermal, residual or mixed hydrothermal and residual) or secondary, (sedimentary) depending on their geneses. They are formed by the alteration of feldspar and rocks such as granites and rhyolite (Ekosse, 2011).

$2KAl_3SiO_{10}(OH)_2 + 2H^+ + 3H_2O$ ------> $3Al_2Si_2O(OH)_4 + 2K$------------------------*eqn 2.1*

K-feldspar Kaolinite

$2KAlSi_3O_8 + 2H^+ + 9H_2O$ --------> $Al_2SiO_5(OH)_4 + 2K + 4H_2SiO_4$--------------------*eqn 2.2*

Muscuvite Kaolinite

Ekosse (2011) revealed that the alteration could be due to surface weathering, ground water activity or hydrothermal fluids (primary). Whereas secondary kaolin is obtained from alteration of feldspathicarenite (arkose) coming out from ground water activity, erosion and transportation of the clay size particles, which are mineralogically altered and deposited.

Bentonite is obtained from the alteration of volcanic ash but could also result from transformation of feldspars, micas, various Fe, Mg silicate and silication of detrital phylosilicate (Weaver, 1989).

$3NaAlSi_3O_8$ +4H2O **-------->**$2Na_{0.5}Al_{0.5}Si_4O_{10}(OH)_2 + 2Na^+ + H_4SiO_{(aq)}$ -------------*eqn 2.3*

Albite Montmorillonite

Bentonite is dominated by smectite (mainly montmorillonites) formed as explained in the equation 2.3 above. The deposition and formation occur in low energy environment under temperate climatic condition (low temperature, low permeability, low rainfall, low relief).

2.3.1 Clay minerals

Traditional applications of clay minerals are so many, some which include its use in ceramics, paper, paint, plastics, drilling fluids, foundry bondants, chemical carries, liquid barriers, decolourization, catalysis, even used in cosmetics for topical application (Murray, 2000). The uses of clay have been traced back to 60 BC (Carretero, 2002), but not all clay minerals are used for topical application. Some of the clay minerals which are used are kaolinite, smectite, palygorskite and sepiolite which are among the world's most important and useful minerals for topical application (Murray, 1999).

Application and choice of earthy materials varies, this may be as a result of their structure and their composition. Apart from the structure and composition of earthy minerals there are some additional factors that determine the properties and applications; possibly as a result of the presence of organic material, the non-clay minerals compositions, small amount of exchangeable ions and soluble salts (Grim and Bradley, 1951), texture inclusive too. Table 2.2 summarises some clay minerals that are used for topical applications with their chemical formulas.

Table 2.2: Clay minerals in earthy materials and their chemical formula

Name of mineral	Chemical name	Chemical formula
Kaolinite	Aluminum silicate hydroxide	$Al_2Si_2O_5(OH)_4$
Smectite (Na montmorillonite)	Hydrated sodium calcium aluminum silicate	$(Na,Ca)(Al,Mg)_6(Si_4O_{10})_3(OH)_{6-n}H_2O$
Talc	Hydrated magnesium silicates	$Mg_3Si_4O_{10}(OH)_2$
Goethite	Limonite	FeO(OH)
Hematite	Martite	Fe_2O_3

Source; Ekosse and Mpako (2013)

Presently, there has been an increase in the usage of clay minerals in all spheres of life and this may be as a result of its availability, low cost and good sorption properties, thus making clay mineral a life time resource that cannot be done without. Table 2.3 shows some clay minerals used for different applications, their characteristics, bonding condition and cation exchange capacity (CEC). Matike *et al*., 2011 stated that high CEC values of earthy material will ensure absorption of toxins, bacteria and unwanted substances when applied topically this is also an indication that earthy materials which possess montmorillonite or vermiculite are very good for topical application as presented in Table 2.3. Some clay minerals used for different applications, their characteristics, bonding condition and cation exchange capacity (CEC), these are listed in Table 2.3.

Table 2.3: Summary of 1:1 and 2:1 clay minerals characteristics

Secondary mineral	Type	Interlayer condition bonding	CEC (cmol/kg)
Kaolinite	1:1 (non-expanding)	Lack of interlayer surface, strong bonding	3-5
Montmorillonite	2:1 (expanding)	Very weak bonding, great expansion	80-150
Vermiculite	2:1 (non-expanding)	Weak bonding, great expansion	100-150
Hydrous Mica	2:1(non-expanding)	Partial loss of K, strong bonding	10-40
Chlorite	2:1:1 (non-expanding)	Moderate strong bonding, non-expanding	10-40

Source; Brady and Weil (2008)

2.3.2 Structure of clay minerals

Structurally, clay minerals possess two main units in their lattice, one unit consists of closely packed oxygen and hydroxyls in which some atoms are embedded in an octahedral combination in such a way that they appear equidistant from the six oxygens or hydroxyls (Aluminium, iron and magnesium atoms). The structure is built on silica tetrahedrons, these silica tetrahedron molecules are arranged in such a way that they form a hexagonal formation that are repeatedly indefinitely forming a composition, $Si_4O_6(OH)_4$ (Ralph, 1968).

All of these clay minerals have two basic atomic sheets;

- Silica tetrahedral sheet
- Aluminium octahedral sheet

In silica tetrahedral sheet, silica (Si) occupies the center positions and oxygen ions (O) are strongly bonded to the core atoms. Silica tetrahedral sheet is symbolised with a trapezoid, of which the shorter face holds electrically unsatisfied oxygen atoms and the longer face holds electrically satisfied oxygen atoms.

In aluminium octahedron sheet, aluminium (Al) ion is positioned at the center and hydroxyl ion (OH) is bonded to the core atoms. Aluminium octahedral sheet is symbolised with a rectangle with top and bottom faces having the same characteristics of exposed hydroxyl ions. Figures 2.1 and 2.2 show the structure of the Si-tetrahedral sheet and Al-octahedral sheet.

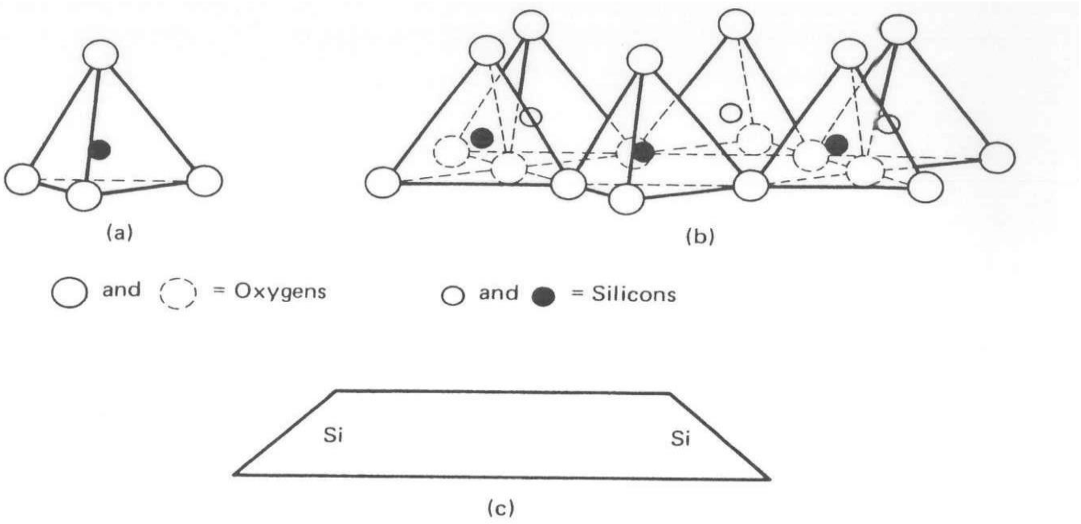


Figure 2.1: Si-tetrahedral sheet (a) Single silica tetrahedron (b) Isometric view of the tetrahedral or silica sheet (c) Schematic representation of the silica sheet (Murray, 2007).

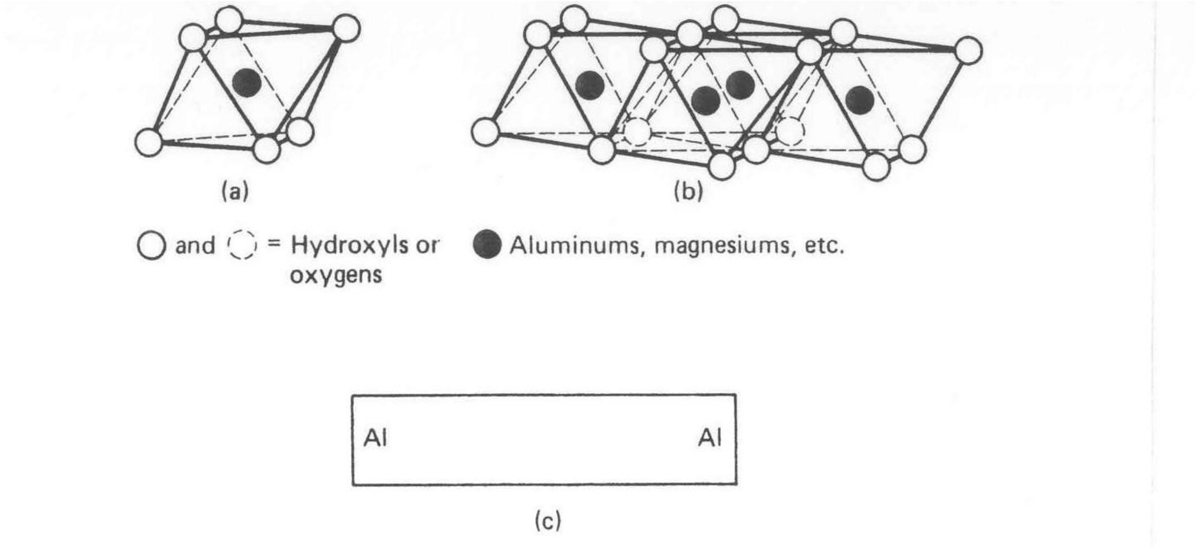


Figure 2.2: Al-octahedral sheet (a) Single aluminium (or magnesium) octahedron (b) Isometric view of aluminium sheet (c) Schematic representation of Aluminium sheet (Murray, 2007).

2.4 Minerals commonly found in clays used for topical application

Relatively few among the many existing minerals in the earth's crust are used as cosmetics (topical application). From various studies, kaolinite, palygosite, smectite and talc are among the few minerals used in cosmetic production. The usage of some of the mentioned earthy materials are due to their high specific area, absorbent and adsorbent properties, rheology and chemical inertness (Fakhfakh *et al.,* 2005).

2.4.1 Kaolinite

Kaolinite is a clay mineral with chemical composition of $Al_2Si_2O_5(OH)_4$. Kaolinite, which is the main constituent of kaolin, is formed by rock weathering (granites and rhyolite). It is also the primary constituent of china clay; which are basically used in the paper, paint and pharmaceutical industries (Pohl, 2011). Kaolinite is one of the most abundant minerals in soils and sediments and its properties are such that it interacts with other soil elements to contribute to the mechanical stability of the soil column (Huertas *et al*., 1999; Chen *et al*., 2000). Kaolinite is a 1:1 layer mineral and a product of advanced weathering processes. One layer of the mineral consists of an alumina octahedral sheet and a silica tetrahedral sheet that share a common plane of oxygen atoms and repeating layers of the mineral are hydrogen bonded together (Bear, 1965). As a consequence of this structure, the silica/oxygen and alumina/hydroxyl sheets are exposed and interact with different components in the soil (Grim, 1968).

The outer groups are situated along the unshared plane of the alumina hydroxyl sheet, while the inner groups are located along the plane that is shared with and borders on the silica oxide sheet (Miranda-Trevino and Coles, 2003). The movement of the inner hydroxyl plane is restricted as a result of chemical bonding between the silica and alumina sheets. As a consequence of its well-packed structure, kaolinite particles are not easily broken down and the kaolinite layers are not easily separated (Miranda-Trevino and Coles, 2003). Hence, most of the sorption activity occurs along the edges and surfaces of the structure. Kaolinite can form a barrier that is not easily degraded and naturally occurring sediments and deposits containing an abundance of kaolinite interspersed with other minerals are effective in controlling the migration of dissolved species (Devidal *et al*., 1996). Clay impurities will depend on the genesis of the mineral and will affect the degree of disorder and the particle size of the clay (Balan *et al*., 1999).

Kaolinite is non-expanding and as a result of its high molecular stability, isomorphous substitution is limited or nonexistent compared to smecitite (Mitchell, 1993). Kaolinite is the least reactive clay (Suraj *et al*., 1998). However, its high pH dependency enhances or inhibits the adsorption of metals according to the pH of the environment (Mitchell, 1993), and this metal adsorption is usually accompanied by the release of hydrogen (H^+) ions from the edge sites of the mineral. Adsorption may also take place on the flat exposed planes of the silica and the alumina sheets (Spark *et al*., 1995). The cation exchange capacity (CEC) is 3-5 mol/kg as shown in Table 2.3. The CEC influences the interaction of the skin with the earthy material. Figure 2.3 shows the structure of kaolinite which is a clay mineral found in cosmetics (adapted from Murray, 2007).

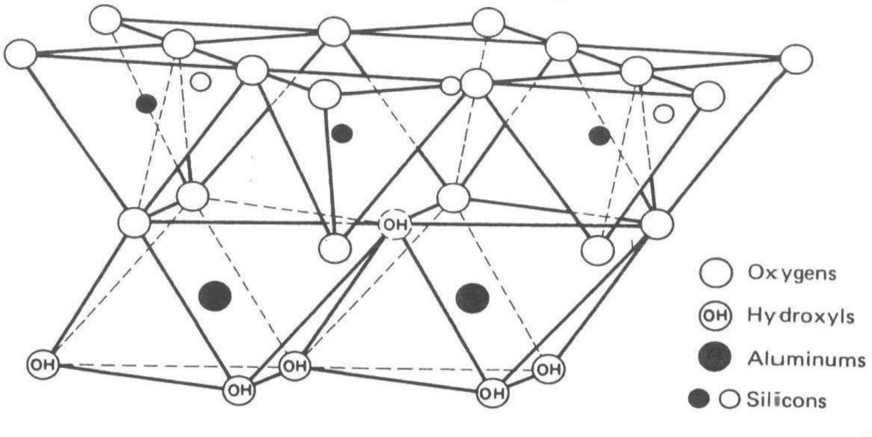


Figure 2.3: Structure of Kaolinite (Murray, 2007)

2.4.2 Smectite

Smectite is one of the largest and most important classes of the phyllosilicate clay-mineral group. They are common in temperate soils and, because of their cation exchange capacities (CEC) and very high specific surfaces, tend to dominate the cationic adsorption chemistry of these soils. Their small particle size (typically < 1µm) and large aspect ratio also allow them to strongly influence the physical properties of soils and sediments (Kloprogge *et al*., 1990). Small size and highly variable composition, however, have led to considerable uncertainty regarding the origin and thermodynamic stability of smectites.

Smectites which have been classified as 2:1 phyllosilicate clays, have a crystal lattice unit formed with montmorillonite as the main mineral. It has one alumina octahedral sheet crammed between two silica tetrahedral sheets. The ion substitution or the site vacancies at the tetrahedral and/or octahedral sheets gives rise to a negatively charged surface. The exchangeable cations between the layers compensate the negative charge and may be easily exchanged by other metal cations, explaining the high ion exchange capacities of these minerals (70–120 meq/100g). Due to this crystalline arrangement, smectites are able to expand and contract the interlayer while maintaining the two dimensional crystallographic integrity. The interlayer between units contains positive cations and water molecules. Montmorillonite is a member of the smectite family (Moore and Reynolds, 1997).

Smectites are major clay minerals in bentonites. The pure forms are often found in nature and can be obtained by purification of bentonites (Grim, 1968). Bentonites comprise of smectitic minerals (usually montmorillonite) with minor amounts of feldspars, quartz (Ekosse and Modisi, 1999) and biotite. Smectites are characterized by a 2:1 layer structure in which two tetrahedral sheets form on either side of an octahedral sheet through sharing of apical oxygens. As the apical oxygens from the tetrahedral sheet form ditrigonal or hexagonal rings, one oxygen from the octahedral sheet is located in the center of each ring and is protonated to yield a structural hydroxyl. In 2:1 phyllosilicates, isomorphous substitution of cations having different valences can lead to charge imbalances within a sheet. These may be partly balanced by the opposite type of charge imbalance in the adjacent sheet, for example a positively charged octahedral sheet may offset some of the negative charge associated with a tetrahedral sheet. The net charge imbalance on a 2:1 layer, if it occurs, is negative. This charge is referred to as the layer charge of the mineral and is balanced by larger cations (example, Na, K, Ca $^{2+}$ and Mg $^{2+}$) that co- ordinate to the basal surfaces of the tetrahedral sheets from adjacent layers. Because these charge-balancing cations are located between adjacent 2:1 layers they are referred to as "interlayer cations". The 2:1 phyllosilicates are distinguished chiefly on the basis of their layer charge. Figure 2.4 shows the structure of smectite adapted by Murray (2007). Properties such as colloidal particle size, crystalline structure, high specific surface area, charge and swelling capacity confer smectites optimum rheological behaviour and excellent adsorption capacities of inorganic and organic substances.

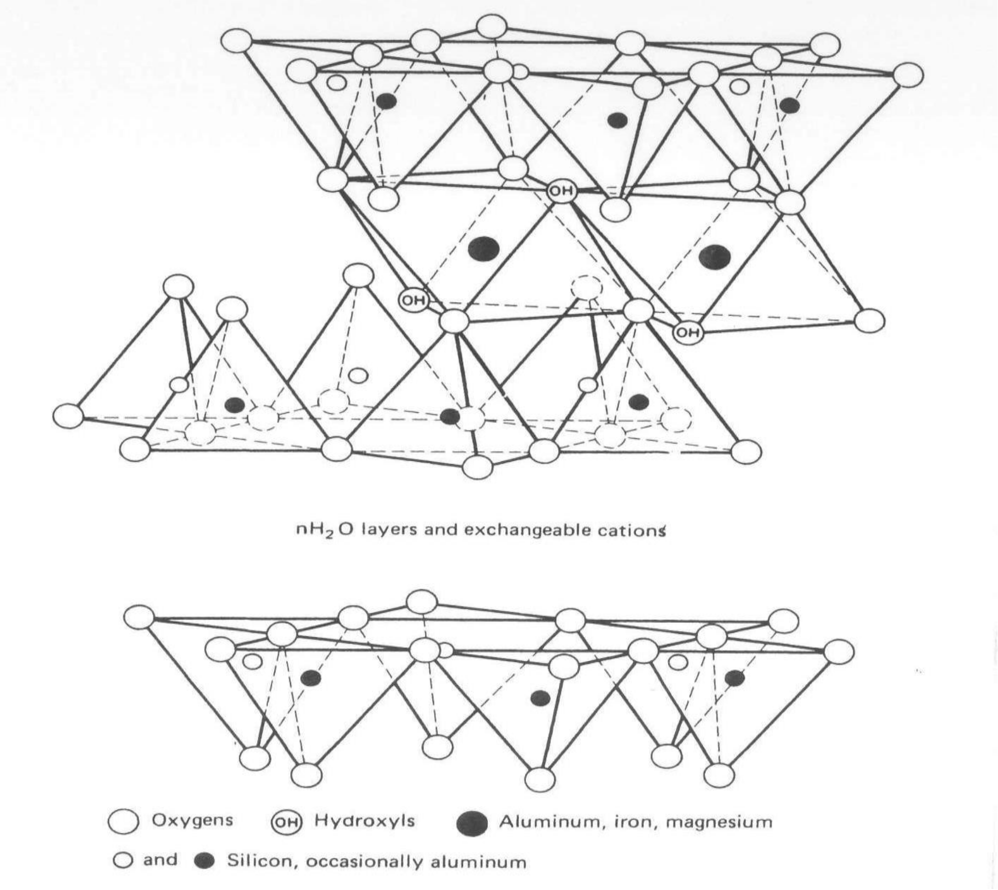


Figure 2.4: Structure of montmorillonite (smectite) (Murray, 2007)

2.4.3 Talc

Talc is a well-known industrial mineral which has the chemical formula of $Mg_3Si_4O_{10}(OH)_2$. It is composed of hydrated magnesium sheet–silicates and belongs to the phyllosilicate family (Boghdady *et al.*, 2005; Fuerstenau and Huang, 2003). Talc has specific gravity of about 2.75 kg/m³; it is relatively inert, and water repellent (Engel and Wright, 1960). Talc is formed by the alteration of serpentine. The resulting talc contains magnesia and water but relatively more silica than serpentine (Andrews, 1985). Talc surface is comprised of two types of surface area, the basal cleavage faces and the edges. The faces surface has no charged group, therefore, it is believed that the talc faces are non–polar and hydrophobic, whereas the edges are hydrophilic due to the presence of charged ions (Mg^{2+} and OH^{-}) (Sarquis and Gonzalez, 1998; Kusaka *et al.*, 1985).The major gangue minerals of talc are carbonates, magnesite, dolomite, serpentine, chlorite and calcite, which contribute to the production of undesirable characteristics. The trace minerals in talc include magnetite, pyrite, quartz and tremolite (Simandle and Paradis, 1999; Sarquis and Gonzalez, 1998; Schober, 1997; Al-Wakeel, 1996; Andrews, 1985). Figure 2.5 shows the structure of Talc adapted by Virta (2001).

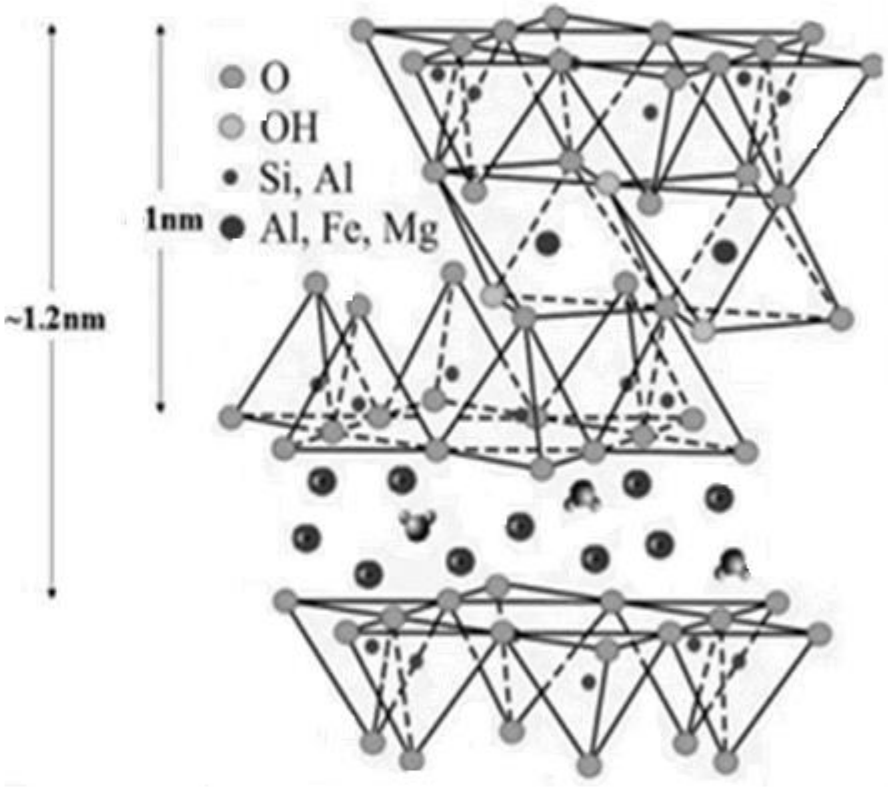


Figure 2.5: Structure of Talc (Virta, 2001)

2.5 Earthy topical materials in some African communities

Clays are not only used for topical application, they are widely used for several purposes, which include brick making, ceramics, pottery, tiles, paint, filling and coating, medicine and cosmetics (Mpuchane *et al*., 2008; Nkoma and Ekosse, 1999; Heckroodt, 1991). The use of clay minerals and non-silicate minerals as active ingredients in pharmaceutical and cosmetic preparations is well detailed (Carretero and Pozo, 2007; Del Hoyo, 2007; Lefort *et al*., 2007; Viseras *et al*., 2007; Carretero *et al*., 2006, Droy-Lefaix and Tateo, 2006; López Galindo and Viseras, 2004; Love, 2004; Carretero, 2002; Veniale 1992, 1997; Bolger, 1995; Galán *et al*., 1985). Daily usage of clay for topical application is a known practice in Africa (see 2.5.1 – 2.5.4). This same practice is still relevant to the present generation.

2.5.1 The use of clays for cosmetic purposes in North Africa

Clays have been in use in Northern Africa and the use started in ancient Egypt where people applied different types of clays on their body for spiritual purposes (Chaudhri and Jain, 2009; Cheryn, 2009; Martel, 2009; Michael and Wheatley, 2009; Aimzster, 2008; DeMello, 2007; Gomes and Silva, 2007; Greene, 2006; Lambert, 2001; Narada, 1998; McNair, 1997). Egyptian men and women blend white clay and scented oils in appropriate proportion for cleansing and spiritual purposes (Greene, 2006; Lambert, 2001; Narada, 1998; McNair, 1997). They extract the white clay from the soil around the Nile River (Chaudhri and Jain, 2009) and apply on specific parts of the body for cleansing purposes (Nelda, 2004). They believe the white colour signifies cleanliness and godliness, as white was perceived to be the colour of the ‘gods’ (Greene, 2006; Lambert, 2001).

Egyptian women later became mindful of their physical appearance and started accentuating the beauty of certain parts of their body with red clay (Chaudhri and Jain, 2009). This made them mix the white clay with the red powder, which was extracted from ferruginous rock (crushed haematitic ochre) (Hirst, 2000) and also it was used to redden the lips and dye the hair (Aimzster, 2008; Nelda, 2004; Lambert, 2001). In the olden days the rich, especially women in Egypt used the procedure stated above to differentiate themselves from women of lower class (Aimzster, 2008). Cleopatra, a noted queen of ancient Egypt, distinguished herself from other Egyptian women by blending red clay with musk and perfume to give her body a smooth bronze appearance (Erman and Tirard, 2003).

Some believed that application of clay brought protection to the body. White clay powder was mixed with oils and creams (Martel, 2009; Narada, 1998) and used by Egyptian shepherds to protect their skin from the hot Egyptian sun and dry winds. Besides the Egyptians, there are prehistoric reports of the cosmetic use of clays by the Nuba of Sudan. Sometimes the men did not pay dowry when marrying their wives rather they provided marriage services, in which the men decorated their bodies with clay. It was also a sign of love and loyalty to the bride (Royce, 1982). White clay was the main choice of clay, as white signified fidelity; and this practice was maintained throughout the marriage (Royce, 1982).

2.5.2 The use of clays for cosmetic purposes in East Africa

The Baluyia of Western Kenya use clay for cosmetic application, they apply clay on their body during funerals, tribal wars and for beauty purposes (Matike *et al.,* 2010). During funerals, close relatives of the deceased smear white clay over their entire body (Burt, 1982) in an endeavour to associate the dead person with their ancestors. In addition, when Baluyia warriors went into combat, they painted their bodies with clay to achieve a ferocious animal-like appearance. White, blue, red, green and orange hues of clay were used to paint lines and dots on the face and chest of warriors in an effort to intimidate their enemy. Similarly during ceremonies, young Baluyia men and women showed off their youth, vitality and sexuality by decorating their body with different colours of clay. Their women use white clay to supplement their sexuality, equally as the men, who decorated their complete body with white or coloured clays in a diversity of designs to show off their male features (Burt, 1982).

2.5.3 The use of clays for cosmetic purposes in West Africa

According to Kalu (1999), the Igbo community of Nigeria, West Africa, widely uses clay to beautify the body because of the way their women honour their body and value their beauty. In this endeavour, women used *nzu* and *uli* to paint beautiful patterns on their face, arms, legs and body; and *edo* to dye their hair (Ukwu, 2000). They equally use *Uli* to hide imperfections on their body (Willis, 1989). Like the Egyptians, married women in Igbo land distinguish themselves from unmarried women by applying a blend of *uli* and camwood on their body, especially during ceremonies (Ukwu, 2000; Matike *et al.,* 2010).

Topical application of clays has also been reported among the Koma of Nigeria (Eboreime, 1989; Eboreime and Ekefre, 1988, 1986; Birtrus, 1986; Royce, 1982; Netting, 1968). In the prehistoric Koma community, clay was used to celebrate success. Young Koma girls between the ages of 10-14 went through the puberty ritual which involved the extraction of a tooth. After the painful ritual, the girls rubbed themselves with a mixture of red clay and oil to indicate their successful rite of passage from childhood to puberty (Eboreime and Ekefre, 1986).

Clays were also used to differentiate festive days from non-festive days. A significant festive period was the days before and after the harvest. During this period, men and women smeared different colours of clay on their body. Men were mostly associated with dark coloured clays, and women with the bright colours.

The bright coloured clays signified fertility of the land and the role of women as regenerators of society (Eboreime, 1989). Table 2.4 shows the different types of clays used traditionally in African communities for cosmetic purposes.

Table 2.4: Different types of clays used traditionally in African communities for cosmetic purposes

Traditional Names	Colour of clay	Tribe and country where clay is commonly used	Remarks
Nzu Muyuku	White White	Igbo (Nigeria) Senoufo (Cote D'ivoire)	For beautification, sunscreening and identification
Kalaba chalk	White	Cameroon	For beautification
Thriga	Red	Masaai (Kenya), Kikuyu (Kenya)	For beautification
Oritize	Red	Himba (Namibia)	For sunscreening, dermatological application and beautification
Musiro	White	Ilhade (Mozambique)	
Ikota	White	Xhosa (South Africa)	
Ingceke	White	Xhosa (South Africa)	
Umthoba	Yellow	Xhosa, pondo (South Africa)	
Isinouka	Green, Brown, Black and White	Pondo (South Africa)	
Ingwala	Red	Xhosa (South Africa)	
Umdiki	Red	Xhosa (South Africa)	
Imbola	Red	Pondo (South Africa)	
Ibomru	White	Zulu (South Africa)	
Umcako	Red	Zulu (South Africa)	
Letsoku	Red	Pedi (South Africa)	
Luvhundi	Red/white	Venda (South Africa)	

Source; Matike *et al*. (2010)

2.5.4 The use of clays for cosmetic purposes in Southern Africa

Matike *et al.* (2011) reported that Transkei indigenous groups may not have the scientific background related to the use of clays in cosmetics but have through indigenous knowledge been able to identify clays that could be used for different cosmetic purposes. Women from Transkei region of South Africa usually cover their faces with white, yellow or black clay, as cosmetics as well as protection against sun rays. Also, male and female are traditionally initiated by covering their entire body with *ingceke*, a white clay during their annual rite of passage rituals (Ettagale, 1999). Jumbam *et al.* (2013) stated that it is widely believed that clay originating from Isinuka valley about 20 km west of Port St Johns in Eastern Cape are unique in South Africa for their efficacy as cosmetic and therapeutic agents. At Pondo land, children playing in courtyards are often smeared with clay to protect them from dirt, insect bites and adverse effects of the sun (Ettagale, 1999). In Namibia, the Himba tribe particularly the women use *ortije*, red clay to cover their entire body and this is believed to signify ideal Himba beauty and according to Namibia Direct (2006), the clay gives the body a mahogany colour which provides a reddish glow under the desert sun and protect it from ultraviolet radiation.

2.6 Indigenous clays for cosmetic application

2.6.1 Skin protection

Indigenous African tribes use clays to protect their skin from the effects of the sun (Reed, 2007; Ettagale, 1999). Ultraviolet radiation can penetrate deeply into the skin and can cause skin ageing and skin cancer (Juch *et al*., 1994). Clay minerals with high refraction index can be used as solar protectors (Hoang-Minh *et al*., 2010). Kaolinite, talc, and smectites have the ability to form a film that provides the skin with mechanical protection against ultraviolet radiation (Hoang-Minh *et al*., 2010), as they are capable of absorbing or scattering radiant energy (Juch *et al*., 1994). This ability is greatly influenced by their small particle size (Hewitt, 1992). Consequently, clays are included in several cosmetic substances to act as sunscreen (Carretero and Pozo, 2009; Hewitt, 1992). This protective property of clay has also been exploited by indigenous African people.

2.6.2 Cleansing purposes

The Africa communities especially the Himba of Namibia readily use clay for body skin cleansing (Barton and Karathanasis, 2002). The Xhosa and Pondo of Eastern Cape, South Africa smear ingceke on the body of male and female initiates during their annual rite of passage rituals. This application is believed to cleanse their skin from impurities as they progress into the next stage of life (Matike *et al.,* 2010). Clay materials are characterized by high absorption properties that give them the ability to absorb toxins, grease and unwanted substances found beneath the skin, leaving it cleansed, refreshed and free from unwanted substances (Gomez and Silva, 2007).

2.6.3 Beauty Enhancement

Some African tribes use clays to emphasise the beauty of certain body parts (Pallington, 1998). For instance, the Wodaabes of West Africa regard prominent facial features as elements of beauty and attraction (Jefkins-Elnekave, 2006; Beckwith, 1999). Wodaabe men use clays of different kinds to enhance the appearances of their noses, eyes, cheeks, teeth and foreheads (Wood, 2000). Wodaabe have stuck to their traditional cosmetic use of clay despite the emergence of modern forms of cosmetics (Wood, 2000). Their colourful face painting with clay alone makes them different from other African tribes (Jefkins-Elnekave, 2006; Beckwith, 1999).

2.6.4 Tribal uniqueness

Jefkins-Elnekave (2006) and Ettagale (1999) recorded that clays are used by African tribes to establish tribal uniqueness. The Himba of Namibia has been named ‘the Reds’ because of their distinctive red colour derived from daily application of *ortijze* on their entire body (Baeke 2009; Nelda, 2004). In Kenya, the Samburu differentiate themselves from the Maasai and other surrounding tribes by their elaborate cosmetic applications of clays (Zijlma, 2004, 2000). Samburu women apply bright orange clay on their cheeks and around their eyes to enhance their beauty during wedding celebrations. It is this peculiarity that earned them the name Samburu, which means butterflies (Groning, 1998). Also, young Maasai women smear their face and arms with thriga during celebrations such as marriage. This gives them a conspicuous appearance in the midst of other tribes in the region.

2.6.5 Rite of passage

Some African communities apply clays on their body to enhance beauty; others use it to mark transition from one stage in their social life to another (Baeke, 2009; Ettagale, 1999). This practice is common among the Xhosa and Pondo of South Africa. In this community, initiates apply ingceke or ikota on their whole body during the initiation. The aim is to discard the old skin as the initiates are ushered into adulthood (Ettagale, 1999). Similarly, the Maasai boys of Kenya also use clays during rite of passage initiation. Young Maasai men after completing their initiation rite coat their legs with thriga and allow it to dry. This is only washed off after one month. This practice is still in existence. After the thriga is washed off, the legs of the young men appear smooth, beautiful and attractive (Walter *et al*., 2004).

2.7 Some selected trace metals in earthy materials

Trace metals are elements such as arsenic, chromium, cobalt, copper, iron, magnesium, selenium, and zinc, which normally occur at very low levels in the environment but can also be toxic at high concentration. Living things need very small amounts of some trace metals such as zinc, magnesium, iron and so on, while some even at low concentrations can be harmful to the body (WHO, 2005). Below are examples of some trace metals that can be found in an earthy material.

2.7.1 Arsenic

Arsenic is a metalloid, it is believed to have been a naturally occurring element which was developed during Holocene epoch (9560-9300 BC to present) (Saunders *et al.,* 2005). There is prevalence occurrence and toxicity of arsenic in cosmetic products (Hepp *et al.,* 2014), this will also be applicable to earthy materials since they are used for topical application. It exist in various allotropes, but only the gray form are found useful in the industries. Arsenic is a toxic trace element for animals including humans (Goldberg, 2002) and its toxicity strongly depends on its speciation. Similar to Hg and Se, chemical speciation is important in determining mobility and availability of As. Of the two inorganic redox states of As, the As (III) redox state is more acutely toxic than the As (V) redox state (Trivalent and Pentavalent oxidation states) (Penrose, 1974).Trivalent arsenic (arsenite) is about 60 times more toxic than pentavalent arsenic (arsenate). Hence, inorganic arsenic is about 100 times more toxic than organic arsenic compounds (Vu *et al.,* 2003).

2.7.2 Chromium

Chromium is a naturally occurring element that exists in rocks, animals, plants, and soil. Trivalent chromium (Cr (III)) ion is possibly required in trace amounts for sugar and lipid metabolism, although the issue remains in debate. Chromium can be toxic and carcinogenic when absorbed in larger amounts and in its various forms (Cronin, 2004). It exhibits six oxidation states but the most prominent example of toxic chromium is hexavalent chromium (Cr (VI)). Hence since chromium are found to be present in most earthy materials continuous usage may lead to allergies such as dermatitis and may finally lead to the ulceration of the skin, this disease is commonly found in individuals that handle materials that contain chromium (Basketter *et al.,* 2000). The estimated safe and adequate daily dietary intake of Cr was approved by the Food and Nutrition Board of the US National Academy of Science to be, infants (0-1 years) to be 10-40 µg/d, children (1-6 years) as 20-80 µg/d and adults 50-200 µg/d (Krejpcio, 2001).

2.7.3 Cobalt

Cobalt with a symbol of Co is found in small amounts in most rocks, soil, plants and animals. Cobalt is usually recovered as a by-product of mining nickel, silver, lead, copper and iron. Humans also need cobalt because it is part of Vitamin B_{12} due to the presence of the co-enzyme known as hydroxycobalamin (Enghag, 2004). Cobalt is basically required in minute amount, its resultant health effect can lead to contact dermatitis (Donald, 1999). Handling of earthy materials that contain cobalt over a long period of time can be harmful to individuals who practice clay for topical application since the daily dosage is 0.1 milligram per kilogram for body weight (ATSDR, 2004).

2.7.4 Copper

Cu is one of the most important, essential elements for plant and animals, ranking 26th in abundance in the lithosphere. Under normal condition, Cu is a benign agent to humans. The total body requirement of Cu for an adult is 100 – 150 mg, normal diet provides 1-5 mg Cu/day (Alloway, 1995). Cu toxicosis in humans is called Wilson's disease in which the Cu-binding ligands involved in Cu homeostasis are deficient and toxic levels accumulate in several tissues. Until antibiotics became commercially available, inorganic copper formulations were used to treat chronic adenitis, eczema, impetigo, scrofulosis, tubercular infections, lupus, syphilis, anemia, chorea, and facial neuralgia (Dollwet and Sorenson, 1985). The spread of antibiotic resistant bacteria in health care facilities has stimulated a renewed interest in copper and copper alloys as the basis of self-sanitising, solid antimicrobial material (Grass *et al*., 2011).

2.7.5 Iron

Iron is one of the macro nutrients needed by the human body, it plays some vital roles in both plants and animals. Iron amongst other essential elements required for cosmetic application but are toxic at high concentration (Glanze *et al.,* 1996). Iron carries oxygen to the tissues from the lungs and a key component of the heamoglobin, its deficiency can cause anaemia (Robert *et al*., 2013). Though iron is one of the major essential trace metals needed by human, goethite (Fe_2O_3) and haematite $Fe(OH)_2$ are found in most earthy materials, which are known to produce some catalytic effect and they have been identified in substantial quantities (Hoang-Minh, 2006; Ekosse and Modisi, 1999); this in turn can cause a threat to users when accumulated in the human body (López-Galindo *et al*., 2007) and may also have some adverse effect to the physical environment (Ekosse and Modisi, 1999). Research has shown that the total iron needed by both men and women are approximately 3.8 g, and 2.3 g respectively with an estimated minimum daily requirement for iron depending on age, sex, physiological status, and iron bioavailability ranging from, 10 - 50 mg/day (Rimon *et al.,* 2005).

2.7.6 Magnesium

Magnesium is one of the readily available trace elements, it is a macro nutrient. It is relatively nontoxic but high accumulation of it can be detrimental to health. Just like other essential metals, magnesium is required for cosmetic purposes but toxic when they are in high concentration (Glanze *et al.,* 1996). According to research, UK recommended a daily dietary value of magnesium to be 300 mg and 270 mg to both men and women, respectively (Kim *et al.,* 2010).

As stated above that high concentration of magnesium can lead to several health issues such as nausea, vomiting, lowered blood pressure, respiratory paralysis and many others.

2.7.7 Selenium

Selenuim has the symbol of Se, it exists in four oxidation states namely: selenide (Se^{2-}), elemental selenium (SeO), selenite (SeO_4^{2-}) and selenate (SeO_4). Selenium belongs to Group VI of the periodic table having some similarity with sulphur in terms of compounds and forms (Alloway, 1995). Such similarity results in a number of biological interactions evidenced by toxic and deficient responses in both humans and animals. The daily requirement per body weight is 5 micro gram per kilogram. Selenium content in the soil generally reflects the weathering of the parent materials such as atmospheric and anthropogenic inputs influencing their composition. Elevated concentration of Se in the environment is associated primarily with volcanic materials, suphide ore bodies, black shales and carbonaceous sandstones, making continuous application of earthy materials for topical application to seem to be detrimental to human body.

2.7.8 Zinc

Alloway (1995) explains zinc as an essential element for humans and animals, which implies that its deficient intake continuously leads to an impairment of the growth, skin lesions, sexual immaturity and loss of appetite. Owing to its essential properties, Zinc acts as a catalytic or structural component in numerous enzyme involved in energy metabolism and in the transcription and translation (Alloway, 1995). The World Health Organisation (WHO, 2005) safe and adequate dietary intake for adult is 15 mg/day. Otto and Haydel (2003) reported that Zn has some therapeutic abilities especially in the area of promoting wound healing and preventing infections from the entering the body (Lansdown *et al.,* 2007). These findings make zinc suitable for topical application.

2.8 Health concerns of indigenous usage of earthy clay materials for cosmetics

Clay minerals can be beneficial to human health by serving as active ingredients or excipients in pharmaceutical preparations, in spas, and in beauty therapy medicine (Cosmetics). In some cases, however, these minerals can be harmful to human health. Both the beneficial and harmful effects of clay minerals will, however, be discussed below.

Bowes *et al*. (1977) reported in their findings that out of the 27 consumer talcum powders, purchased in the USA, 11 contained tremolite and anthophyllite in proportions ranging from 0.5 to over 14%. This makes the use of palygorskite as a dermatological protector not advisable. Kaolinite, talc, and smectites are used as dermatological protectors. These clay minerals can stick to the skin, forming a film that instinctively protects the skin against external physical or chemical agents, by absorbing the skin's secretions, and creating an enormous surface for their evaporation.

Knowledge of mechanisms controlling the distribution of trace elements in clays is scarce and contradictory, investigations carried out on the geochemical behaviour of some trace elements used in geological reconstruction are referred to as "geochemical indicators" (Fiore *et al*., 2003). It is well known that clays contain trace elements that literature indicate as toxic and/or micronutrients (antimony, arsenic, cadmium, cobalt, copper, lead, mercury, nickel, selenium, tellurium, thallium, zinc) whose concentrations are widely variable, depending on their geological history. These trace elements may be in the clay (or accessory) mineral structure as well as adsorbed on clay particles, which play the most important role in controlling their distribution and abundance.

General population exposure to low concentrations of montmorillonite and kaolinite, the main components of bentonite and kaolin, respectively, and other clay minerals is ubiquitous. There is no information on the possible effects of such low-level exposure. Long-term occupational exposures to bentonite dust may cause structural and functional damage to the lungs. However, available data are inadequate to conclusively establish a dose–response relationship or even a cause-and-effect relationship due to limited information on period and intensity of exposure and to confounding factors, such as exposure to silica and tobacco smoke (WHO, 2005).

Long-term exposure to kaolin causes the development of radiologically diagnosed pneumoconiosis in an exposure-related fashion. Clear cut deterioration of respiratory function and related symptoms have been reported only in cases with prominent radiological findings. The composition of the clay that is its quantity and quality of minerals other than kaolinite is an important determinant of the effects. Statistically significant increases in the incidence of or mortality from chronic bronchitis and pulmonary emphysema have been reported after exposure to quartz (WHO, 2005). No report on local or systemic adverse effects has been identified from the extensive use of bentonite or kaolin in cosmetics (WHO, 2005).

2.9 Some reviewed characterisation, mineralogical and elemental analyses

2.9.1 Charaterisation of earthy materials

Various methods of characterisation, chemical and mineralogical analyses (XRD, XRF, SEM and BET) have been applied on earthy materials for different applications (cement, cosmetics, paper and pharmaceutical). These methods are applied in order to attain a certain specification. Ruiz and Gonzalez (2006) beneficiated and characterised kaolin and some other clay minerals which were used in the cement industry in Argentina, though it has been noted that these earthy materials contain impurities, they improved the quality of the clays by the removal of iron and titanium through chlorination, using X-ray fluorescence, X-ray diffraction and spectrophotometric methods of analysis.

Saikia *et al*. (2003) conducted research on the characterisation and beneficiation of clay used for the production of ceramics, filter materials and other materials, incorporating different techniques, which are; chemical constituents by wet chemical method and XRF analyses; mineralogical compositions by XRD analysis of random powder samples (Joel X-ray diffractometer, model ZDX-11P3A, using Cu K_a radiation), FTIR analysis (Perkin Elmer System 2000 FTIR spectrometer using KBr pellet method), Thermal analysis (computerized TA instrument, model STD 2964 simultaneous DTA TGA) under dynamic conditions in air atmosphere using a-Al_2O_3 as the reference material and particle size analysis (laser particle size analyser, model Cilas 1180). Though most of the sources of earthy materials are from natural sources, they may geologically or through weathering processes contain minor to significant amounts of mineral impurities. For utilisation of earthy materials, it is important to characterise such materials so as to determine the mineral content. Carreterro and Pozo, (2010) conducted a study which classified clay minerals in their groups and Table 2.5 below summarises the mineral groupings.

Table 2.5: Mineral groupings of clay minerals

Groups	Minerals
Oxides	Rutile, perclase, zincite
Carbonates	Calcite, magnesite, hydrocincite, smithsonite
Sulphates	Epsomite, mirabilite, melanterite, chalcnthite, zincosite, goslarite, alum
Chlorides	Halite, sylvite
Hydroxides	Brucite, gibbsite, hydrotalcite
Elements	Sulphur
Sulphides	Greenockite
Phosphates	Hydroxyapatite
Nitrates	Niter
Borates	Borax
Phyllosillicates	Smectite, palygorskite, sepiolite, kaolite, talc, mica

Source; Carretero and Pozo (2010)

2.9.2 Brunauer, Emmett and Teller (BET) technique

The physical properties of earthy materials such as determining their surface area or porosity of solid phase is one of the key factors in cosmetics (topical). Emphases is on the gas adsorption analysis of the materials. BET is one of the commonly used techniques applied in determining the surface area and the porosity of different materials. As stated in Chapter 3, BET equation is applicable for the calculation of surface area and pore sizes relating it graphically. The classification of the pore size of materials was first classified by the International Union of Pure and Applied Chemistry (Sing *et al.,* 1985). The pore volume and pore diameter is evaluated from the adsorption arm of isotherm based on Barrett–Joyner–Halenda (BJH) model. Materials for topical application may vary in pore diameter (Table 2.6). The larger the pore diameter (pore size) the more readily perspiration would take place. If this is the case, the material applied topically could be washed off during perspiration.

BET is a widely used method for the determination of the specific surface area and determination of pore size of finely dried porous solids. The method is aimed at explaining the physical adsorption of gas molecules on a solid surface (Walton and Snurr, 2007; Brunauer *et al.,* 1938). Adsorptive gases (non-corrosive gases such N, Ar and CO_2) are applied on the surface of the reference material and as a result of adsorption, the amount of gas adsorbed at a given pressure helps in the determination of surface area. Probe molecules such as nitrogen which is the commonly used gas are applied during the analysis, requires the exposure of liquid nitrogen over a solid material at a condition of 77 K (Sing, 2001). Surface area, pore size and pore volume are the major physical properties that influences the quality and efficacy of earthy materials, with an interpretation of the studied earthy materials according to their isotherm linear types and the BET surface area is always allied to the particle diameter or radius and the porosity is classified according to IUPAC standard. The pore sizes are divided into three categories: micropores (< 2 nm), mesopores (2 nm – 50 nm) and macropores (> 50 nm) (Sing *et al*., 1985). Figure 2.6 indicates the classification of the various types of adsorption isotherm. Isotherm graphs comes in different shapes and are denoted in the form of Types (I – VI) and these are explained in Table 2.6.

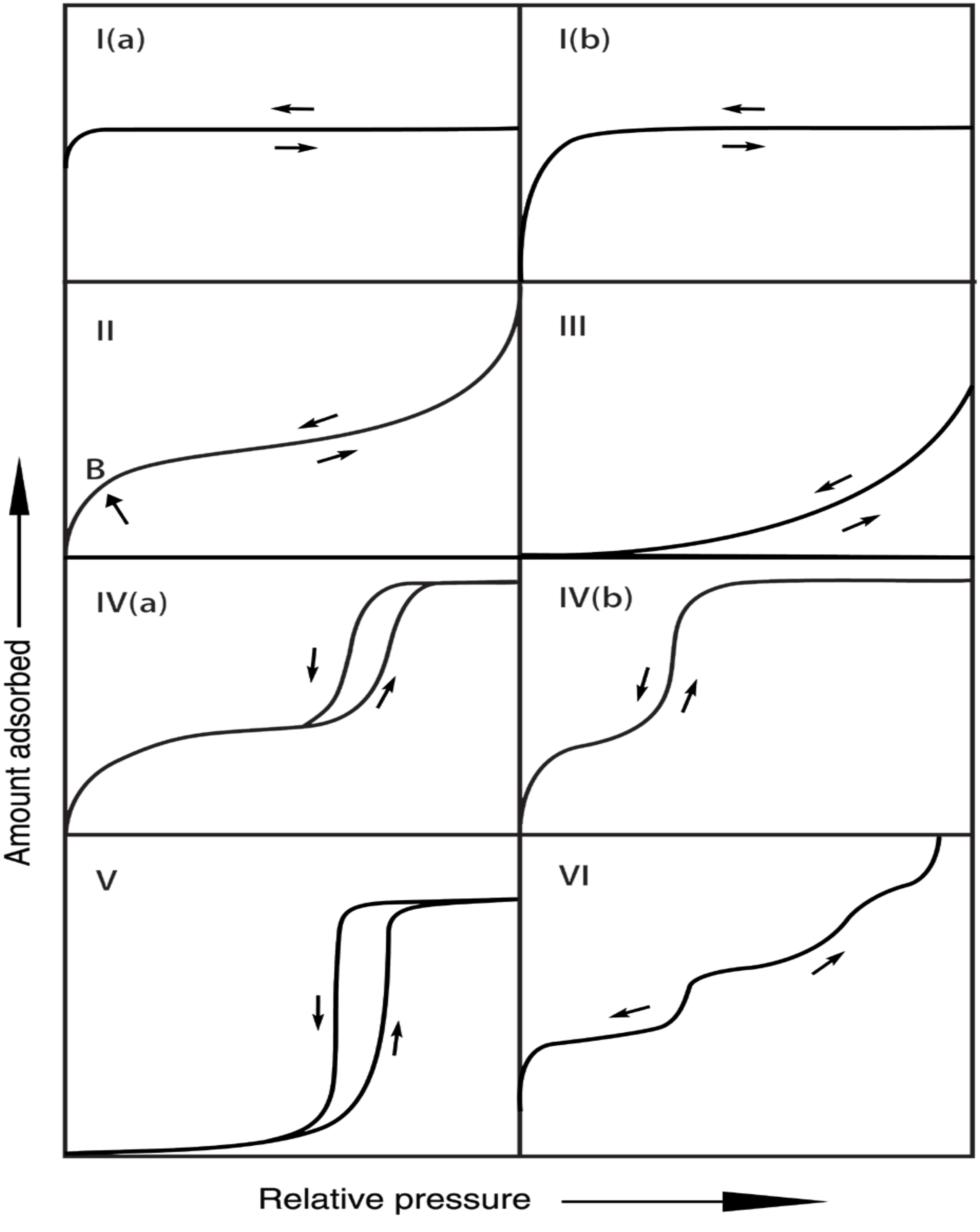


Figure 2.6: IUPAC classifications of physisorption isotherms (Sing *et al.*, 1985)

Table 2.6: Classification of adsorption isotherm adapted from Condon (2006) and Thommes *et al*. (2015)

Isotherms Types	Description of the different types of adsorption isotherm
I	It results in micro-porous surfaces, with monolayer formation. The resultant graph follows Langmuir adsorption isotherm curve with a saturation limit {Fig 2.6(Ia)}.
II	Type II isotherm obeys Langmuir equation but ends with BET equation. They occur on non-porous or macro-porous surfaces with no saturation limit {Fig 2.6(II)}. The formation is multilayer.
III	Type III isotherm shows no monolayer formation but multilayer formation. It only applies to macro-porous surfaces, with low adsorption at low gas pressure. Gas adsorption is infinite {Fig 2.6(IIIa&b)} as vapour pressure approaches saturated vapour pressure ($P \longrightarrow Ps$).
IV	There's slight similarity with Type II at low pressure. Type IV isotherm forms monolayer formation on a mesoporous surface followed by capillary condensation. The surface of the solid/ liquid material saturates before pressure approaches saturated vapour pressure, this is due to the capillary condensation.
V	Type V and Type IV operates on same platform (mesoporous surfaces) with no monolayer formation. There's capillary condensation {Fig 2.6 (V)}.
VI	This forms on non-porous surfaces on a multilayer formation, due to the over laying of the solid. It has no saturation limit {Fig 2.6 (VI)}.

2.9.3 Scanning Electron Microscopy (SEM)

SEM analysis is an instrumental method that gives a general overview of the host material, in essence it is the most widely used analytical method in most laboratories basically for characterisation of physical properties of materials (morphology, shape, size or size distribution) at micro or nano scale (Hodoroaba *et al.,* 2014). The SEM analysis is incorporated with Electron Dispersive X-ray Spectroscopy (EDX).

2.9.4 Electron Dispersive X-ray Spectroscopy (EDX)

The elemental compositions of any studied sample is ascertained with the aid of Electron Dispersive X-ray (EDX). Walton and Snurr (2007) reported that surface area is one of the most important quantities required in characterising porous materials. A study by Hodoroaba *et al.* (2014) revealed that the operation of SEM at a high-resolution, enables a quick and accurate morphological inspection (imaging) and systematic characterisation using EDX. Standard methods of chemical analyses by Scott (1961) were adopted for the study.

2.9.5 Particle size distribution analysis of earthy materials

There are several methods attributed to particle size analysis, some are: laser, sieving, hydrometer pipette. Earthy materials consist of an assembly of particles of different sizes and shapes and the main reason for determining the particles sizes of materials is to group them into their separate various sizes and to determine the relative proportion by weight of each size range (Gee and Bauder, 1986). Hydrometer method is best used method in the determination of particle size <2 μm (Alan, 1997). The method can be used to classify the samples according to their percentages (clay, silt and sand). United States Department of Agriculture (United State Soil Salinity laboratory Staff, 1954) defines sand, silt, and clay as particles with sizes from 2 to 0.05 mm, 0.05 to 0.002 mm, and less than 0.002 mm, respectively.

Relatively, the proportion of clay, silt and sand are determined using textural diagram. The United States Department of Agriculture Textural Triangle is an internationally accepted tool used for textural classification of soils (earthy materials). Soil textural compositions (%sand, %clay and %silt) helps in categorising the regions. Figure 2.7 below shows the various classifications of soil.

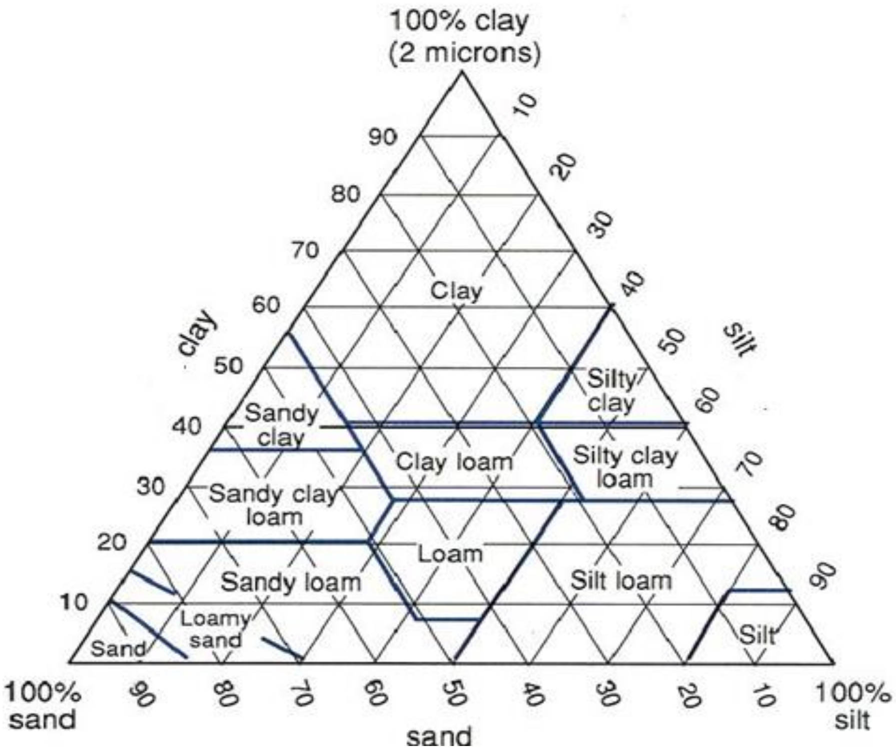


Figure 2.7: A ternary diagram of the soil texture triangle showing the different USDA-based soil texture classifications (Soil Division Staff, 1993).

2.10 Summary

In this chapter, the origin of clay, formation of clay, various practices of earthy materials for topical application were reviewed and were duly delved with. Methods of characterization, BET and SEM were also discussed in details leading to the methodology of the study.

CHAPTER 3:
RESEARCH METHODOLOGY

3.1 Research design

This research is aimed at characterisation and determination of the physico-chemical, chemical and the mineralogical constituents of the earthy materials commonly used as cosmetic in some selected African communities. Several complementary techniques required for the analyses are explained. The data was collected in a standard way or measured numerically for appropriate statistical analyses and interpretation. Graphical displays which contain graphical depictions of experimental data and analyses were drawn to aid the interpretation of the results.

3.2 Sampling and sample collection

3.2.1 Sampling

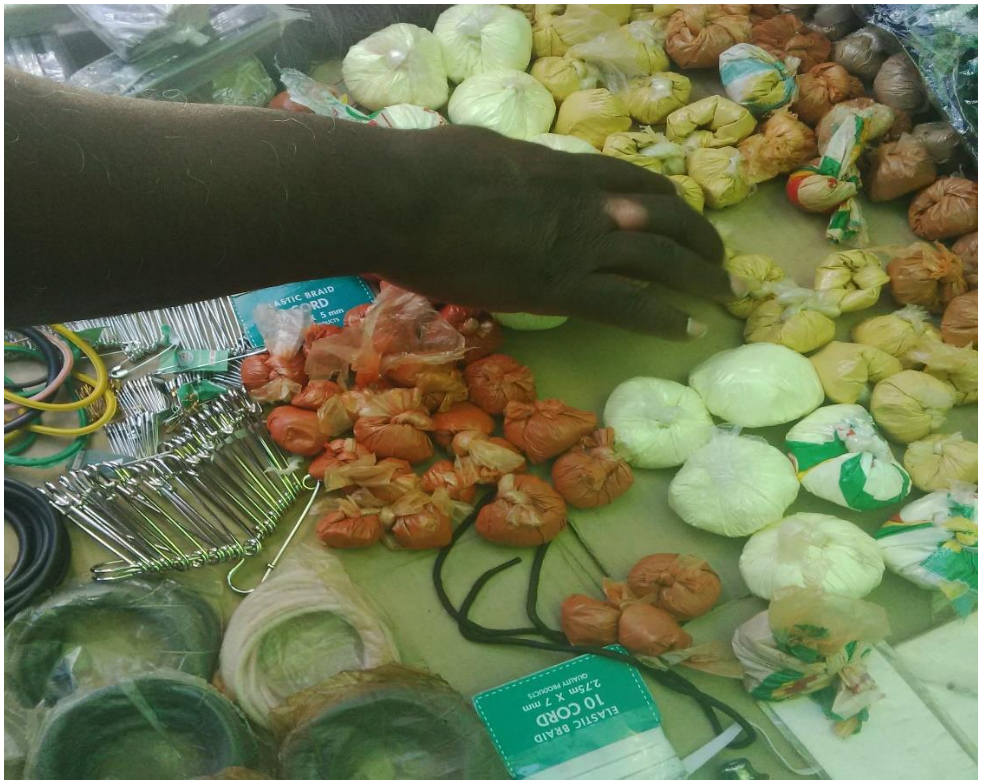
A total of 22 samples were collected for the analyses. Botswana, Cameroon, Democratic Republic of the Congo, Nigeria and Swaziland were the countries were these samples were collected. A field trip was made to various communities in South Africa (Ladysmith, Thohoyandou and Qwa-Qwa), and a total of 12 samples were purchased from open markets in those localities. All the collected samples were packaged in plastic bags until further analyses. Figures 3.1 (A-D) below shows some of the markets where the samples were purchased.


[redacted]
[redacted]

A – Researcher buying earthy materials at Qwa-Qwa open market

[redacted]

B – Researcher buying earthy materials at Thohoyandou open market



C- Display of samples at Qwa-Qwa open market

D- Researcher buying earthy materials at Harrismith open market

Figure 3.1(A-D): Display of different markets where some of the samples were obtained

3.2.2 Coding of samples

The samples for the study were collected from 6 different countries (Botswana, Cameroon, Democratic Republic of Congo, Nigeria, South Africa and Swaziland) and were obtained from different localities within those countries. Codes were used in the identification of the packaged samples and they were labelled thus as follows: BST 1, BST 2, CMR 1, CMR 2, DRC 1, DRC 2, NG 1, NG 2, SCC (1-12) and SWL 1, SWL 2 (Figure 3.2) all making a total of 22 representative samples. Table 3.1 summarises the countries, localities, colour, traditional names and different reasons why these earthy materials are applied topically. The colour of the samples were determined by mussel colour chat, (1992).

Figure 3.2: Labeled samples, using codes to denote the countries of origin

Table 3.1: Sample code, countries, colours, traditional names of where the samples were obtained

Countries	Country Code	Localities	Colour of clay	Traditional Names	Remarks
Botswana	BST 1	Gaborone	Yellow	letsoku	For beautification
	BST 2	Kanye	Pale yellow		
Cameroon	CMR 1	Yaounde	white	Kalaba chalk	For beautification
	CMR 2	Bokwango	Light brown		
Democratic republic of Congo	DRC 1	Kinshasha	Light brown	Mabele Lupemba	It is applied for sunscreening
	DRC 2	Kasai-Oriental	Strong brown		
Nigeria	NG 1	Ogbomoso	White	Amo	For beautification, sunscreening and identification
	NG 2	Lagos	Light brown		
South Africa	SCC 1	Qwa-Qwa	Brown	Mobu	It aids healing of black acnes/cleansing.
	SCC 2		Yellow	Sebabole	
	SCC 3		Black	Sekama	They are applied during festive periods and also to make marks on the body.
	SCC 4		Reddish brown	Letsoku	
	SCC 5		Light yellow	Keketsa	
	SCC 6		Orange	Maknalingela	They are mixed with gentle magic , to enhance complexion
	SCC 7		Brown	Sefate	
	SCC 8		Light blue	Blue stone	For beautification
	SCC 9	Harrismith	Reddish brown	Letsoku	It is applied for sunscreening
	SCC 10		Light brown	Umemzi	
	SCC 11	Thohoyandou	Light brown	Munyaku	For beautification
	SCC 12				
Swaziland	SWL 1	Manzini	Light brown	Libumba	For cultural identification/cleansing and beautification
	SWL 2	Ezulwini	Strong brown		

3.2.3 Sample pretreatment

The visible foreign particles and coarse particles were removed by hand picking (manually). The earthy materials were air dried for 24 hours and then ground using an agate mortar. The finely grounded powder were kept in a cool dry polythene bag until further analyses.

3.3 Laboratory analyses

The laboratory analyses encompasses physico-chemical, chemical and mineralogical techniques. The physico-chemical analysis were determined by Brunauer-Emmett-Teller (BET) analysis. The corresponding techniques are further listed below. The chemical analysis were for the determination of possible chemical constituents present in the samples using X-Ray Fluorescence, whereas the mineralogical analysis were for the identification and characterisation using X-Ray Diffractometry. The research was reported according to physico-chemical, chemical and mineralogical characterisation.

The physico-chemical analyses for the determination of colour, particle size, surface area and SEM are reported below:

3.3.1 *Colour analysis*

The colour of each representative sample was determined using Munsell Soil Colour Charts (1992) (Figure 3.3). The samples were placed on white A4 paper and were compared visually with standard soil colours in Munsell Soil Colour Charts (Munsell Soil Colour Book, 1992 and Ekosse *et al*., 2008). This aids the classification of the representative samples in terms of hue, value and chroma (Munsell Soil Colour Charts (1992).

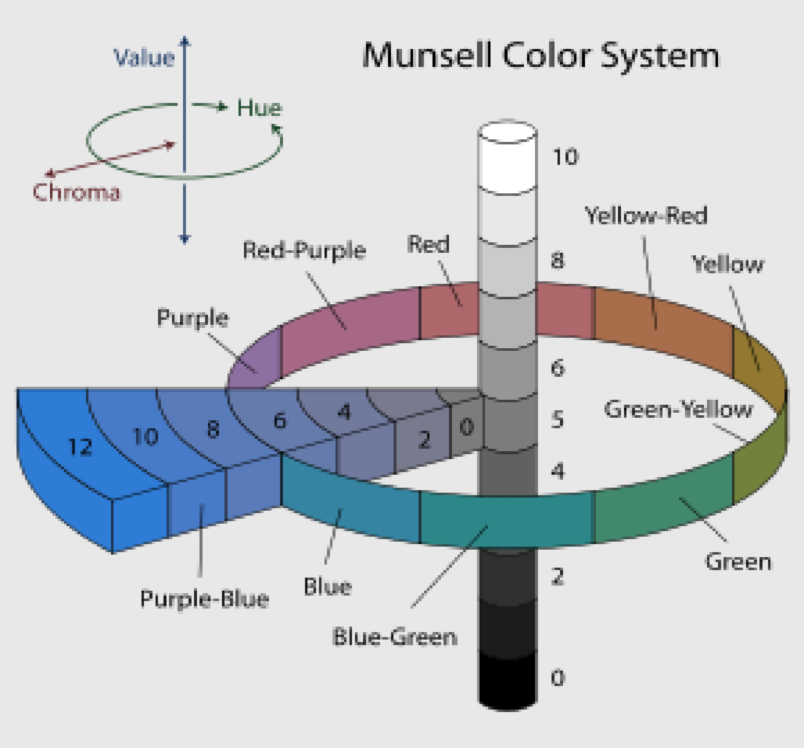


Figure 3.3: Munsell colour system showing Hue, Value and Chroma

3.3.2 Particle size distribution analysis

Removal of organic matter

Earthy materials possess some constituents which cannot be easily removed by mere dispersion, these include: organic matter, carbonate minerals, soluble salts and some oxides. Hence these constituents can only be removed by pretreating the samples (Sheldrick and Wang, 1993; Gee and Bauder, 1986). 10 g of each representative samples were weighed into a 500 ml beaker, 10 ml of hydrogen peroxide was added (using pipette) to burn off all the organic matters present in the samples. This was done in a fume cupboard. Distilled water was added to the beaker up to the 300 ml mark. The sample was placed on the sand bath with interval stirring for 3 hours so as to burn off the remaining hydrogen peroxide and any carbonaceous materials present (Mikutta, 2005; Gee and Bauder, 1986).

Dispersion of the solution

The heated samples were allowed to cool for some minutes. 20 ml of Calgon solution (sodium hexametaphosphate) was added to each sample so as to disperse the particles. With the aid of a Milkshake mixer (Eijkelkamp Mechanical Analysis Stirrer) the solution was allowed to mix for 15 mins as to obtain an even mixture, a method adopted from Laker and Dupreez (1982). The solution was poured into a 1 dm^3 sedimentation cylinder (measuring cylinder), this was done for the whole studied samples. Vigorous shaking was done for the solution and the reading was taken after 5 minutes of allowing the solution to settle in the sedimentation cylinder. The second reading was taken after 2 hours with the insertion of the hydrometer (hydrometer soil ASTM 152H). A blank solution was prepared for the experiment, this was a mixture of 20 ml calgon solution and deionised water filled up to the mark. The stop watch was used to monitor the hydrometer reading, this was set at 15 minutes interval timing for the mechanical shaker, this is to ascertain if the samples fell in the range of < 2 µm, 5 minutes timing for first reading with hydrometer and 2 hours reading for 1st and 2nd readings of the samples (hydrometer). The temperature of each solution (alcohol and mercury thermometer) was taken immediately after the first shake of the cylinder and before the final reading. Figures 3.4 – 3.7 shows the preparation of the analysed samples down to the hydrometer reading for the particle size analysis determination.

Figure 3.4: Weighed samples for particle size distribution analysis

Figure 3.5: Sand bath heating for the removal of carbonaceous and organic matter present in the samples

Figure 3.6: Sedimentation cylinder with samples settling at different layers

Figure 3.7: Hydrometer reading for each representative sample

3.4 Determination of properties of Earthy materials

3.4.1 Morphology of Earthy materials using Scanning Electron Microscope and Energy Dispersive X-Ray

Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray (EDX) analysis were actualised using the procedure of Ruiz-conde *et al*. (2002). The morphology of the studied samples were determined by scanning the earthy materials with Scanning Electron Microscope (SEM) and Energy Dispersive X-Ray (EDX) at University of Cape Town, Electron Microscope Unit. Little quantity of carbon dust and gum were thoroughly mixed and were smeared on the sample holder. Very minute quantity of the finely ground powder of earthy material (Figures 3.8) was spread on the sample holder which was labelled according to the sample codes; this was attached to an SEM sampling plugins (6 samples per analysis), a method adopted from Desbois *et al.* (2009). All the labelled samples (22) were analysed accordingly. The shapes of each of the samples were analysed using EDX detector and INCA software (Figures 3.8 – 3.11).

Figure 3.8: Display of samples for SEM at department of Molecular Biology, University of Cape Town

Figure 3.9: Arrangement and setup of instruments for SEM analysis

Figure 3.10: FEI Nova nanoSEM 230 with a field emission gun

Figure 3.11: EDXS detector of 20 mm square Oxford X-max and INCA software which is used for image acquisition

3.4.2 Determination of surface area of the Earthy materials

Brunauer- Emmett-Teller (BET) method was adopted for the determination of the surface area and the pore size of the earthy materials. Fagerlund (1973) method of determination of surface area, using BET method was adopted for the analysis, which was carried out at University of Cape Town, Chemical Engineering Department. The BET analysis following the underlisted procedure: with the aid of analytical balance, the BET tube, rubber stopper and Styrofoam holder were all weighed. The mass, sample information and tube number were noted before the commencement of the analysis. Approximately. 15 g of each of the samples were outgassed by heating at 90 ºC for 24 hours in a vacuum to remove the moisture content and the physisorbed gases. Then, the sample was transferred to a sample cell and a known amount of nitrogen at its boiling point of 77 K was admitted into the cell. The amount of gas absorbed is the difference of the gas admitted and the amount of gas filling the dead volume. Below is an equation of what happens in Micrmeritics BET analyser, it is an automated instrument.

Dry mass of sample (g) = SPL_{Degas} - $TUBE_{Empty}$

Where: SPL_{Degas} = mass of BET tube containing degassed sample

$TUBE_{Empty}$ = mass of empty BET tube.

The adsorption isotherm is the plot of the amount of gas adsorbed (mmol/g) as a function of the relative pressure of nitrogen, Walton (2007). Brunauer, Emmett and Teller (BET), is the most common method used to describe specific surface area: Its equation is given as:

$$\frac{1}{W((P_o/P)-1))} = \frac{1}{W_m\,C} + \frac{C-1}{W_m\,C}\left(\frac{P}{P_o}\right) \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \; eqn\;3.1$$

Where: W= weight of gas adsorbed

P/P_o = relative pressure

W_m = weight of adsorbate as monolayer

C = BET constant

N = total amount of gas admitted

M = molar mass of the adsorptive

A_{cs} = Area covered by the samples

BET equation requires a linear plot of 1/[W(P/P_o)-1] against P/P_o

Slope (s) Intercept (i):

$$s = \frac{C-1}{W_m\,C} \qquad\qquad i = \frac{I}{W_m\,C} \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \; eqn\;3.2$$

W_m (weight of monolayer):

$$W_m = \frac{1}{s+i} \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \; eqn\;3.3$$

Total Surface Area (S_t) is derived as:

$$S_t = \frac{W_m\;N\;A_{cs}}{M} \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \; eqn\;3.4$$

Specific Surface Area (S) is then determined by total surface area by sample weight:

$$S = S_{t/W} \text{ ………………………………………… } eqn\ 3.5$$

The pore sizes of the studied samples were also obtained, Total pore volume is derived from the amount of vapour adsorbed at a relative temperature close to unity and the equation is given as:

$$V_{liq} = \frac{P_a V_{ads} V_m}{RT} \text{ ………………………………………… } eqn\ 3.6$$

Where: V_{liq} = Total volume

V_m = Pore volume

RT = Constant

V_{ads} = Volume of the adsorbate

Figure 3.12 below shows BET, Tristar II 3020 instruments and Nitrogen gas, of which were used in the determination of the surface area and the pore size of the studied samples.

Figure 3.12: Micromeritics BET, Tristar II 3020 and N_2 (g) used in the determination of surface area and pore size of the studied samples

3.5 Chemical and mineral analyses of earthy materials

3.5.1 X-ray fluorescence (XRF) analysis

The XRF analysis is a multi-elemental analytical technique which is basically used for the determination of all the detectable elements present in a sample, it has a very high precision and accuracy. XRF analysis working principle is the measurement of wavelength or energy and the characteristic X-ray photons emitted from the given sample being analysed. This allows the identification of the elements present in a sample and determining the mass concentration. The earthy material samples were ground until the grain size was lower than 2 µm because the grain size is a critical factor in X-ray fluorescence (XRF) elemental analysis (Saat and Hamzah, 2008). The analysis followed a standardless procedure whereby the XRF explored all the wavelengths in order to identify all the elements present in the studied samples and the instrument’s instructions were followed. This was carried out at University of Cape Town, Chemical Engineering Department. Figure 3.13 below is Bruker ASS S4 pioneer instrument, which is an automated sequential X-Ray fluorescence spectrometer (XRF) which is equipped with an automated sampling system that takes up to 60 samples at a go in the sample holder (A) below, 5 g of the representative samples were weighed into a sample holder and was fed into the instrument. The start button was pressed as the samples were allowed to run for 1 hr and the reading was taken. This is a vital tool for qualitative and quantitative chemical analyses of materials because of its ability to detect the smallest elemental concentration of 10 ppm and ability to analyse most biological and powdered geological samples. This X-Ray fluorescence spectrometer (XRF) was used in the study for the determination of the trace metal concentration of the studied samples.

Figure 3.13: Bruker AXS S4 Pioneer used for elemental analysis (a) sample holder (b) start button (c) off button

3.5.2 X-ray diffraction (XRD) analysis

X-ray diffraction is a characterisation technique which makes use of the interaction between X-rays and the periodic arrangement of atoms in a crystalline angle, this allows any phase present in a solid material to be identified (Ekosse and Mulaba-Bafibiandi, 2008). XRD analysis is basically a non-destructive technique, it identifies the crystalline phases and the orientation of the earthy materials; it is also used in determination of the structural properties which are the size, phase composition, thermal expansion and so on. The X-ray analysis investigates qualitatively different minerals and their compositions. A thin film of the sample was mounted on the glass slide and was mounted on the sample stage and the shutters were closed. Precautions were taken to ensure that the shutters were properly closed. The start button was clicked on the computer as the sample was allowed to run for 30 mins for each representative samples (Figure 3.14). Proper observation was taken on the software as the sample was running in order to ensure that the intensity of the peaks were smooth (Figure 3.14), the points labelled A is the sample stage, B the X-ray tube and C the Vantec X-ray detector. Table 3.2 below explains the working condition of the instruments.

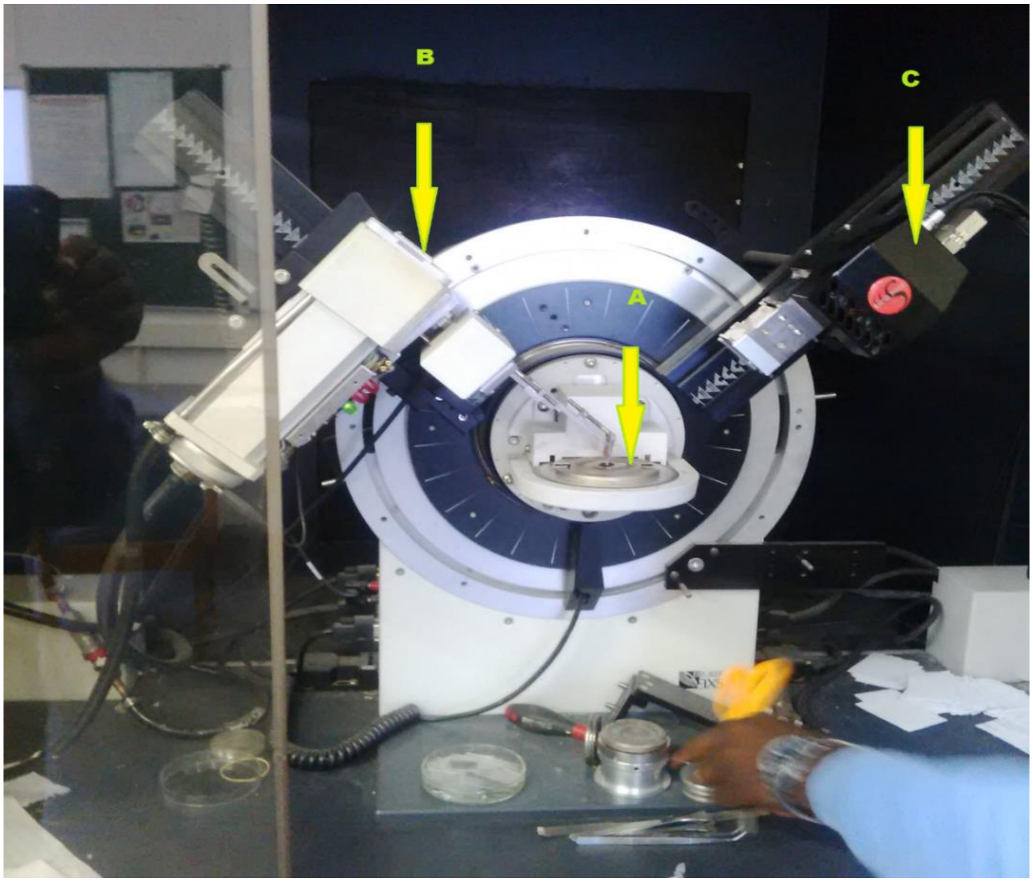


Figure 3.14: D8 Advance Bruker diffractometer showing (a) sample stage (b) X-ray tube (c) Vantec X-ray detector

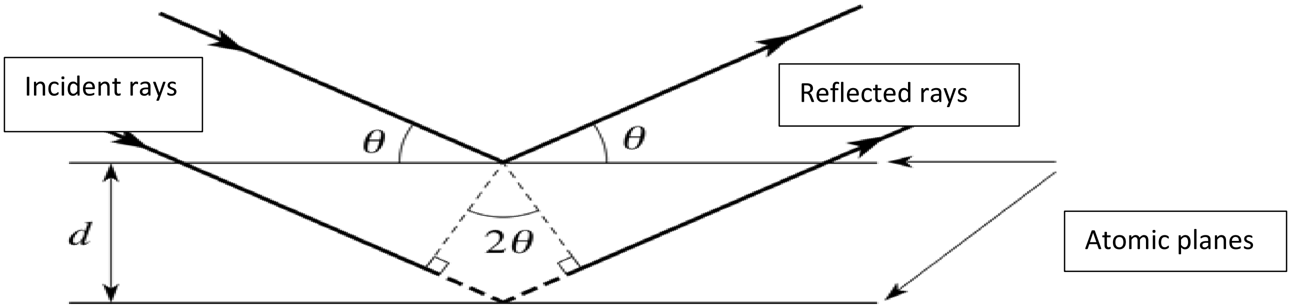


Figure 3.15: Schematic diagram of how XRD works (Bragg's Law)

Table 3.2: Analytical conditions for the XRD instrument

Manufacturer	BRUCKER AXS (Germany)
Diffractometer	D8 Advance
Measurements	Theta-Theta scan in locked coupled mode
Tube	Cu-Kα radiation (1.5406 Å)
Detectors	LynxEye
Tube voltage	40kV
Tube current	40mA
Variable slits	V20
ICDD	PDF database 1998
Data evaluation	EVA software from BRUKER

3.6 Data analysis

Saunders *et al.* (2012) method of data interpretation was adopted in the interpretation of the results. The method explains the suitable research methods applied in the research to ensure the attainment of goals and objectives set out in chapter one. Precautionary measures following each representative analysis were taken to ensure a standardised result. The results were obtained in triplicate to calculate the mean value. The data presentation and statistical analysis was carried out using 2013 Microsoft excel software which was used for the plotting of the data obtained from the XRD and physisorption analysis data. A trial version of OriginLab software was used to plot the histogram for XRF results. The ternary diagram for particle size distribution was drawn using Tal for window version 4.2 (1996-2002). Kruskal-Wallis H test was used to determine the significant values of the mean of the physisorption isotherm.

CHAPTER 4:
RESULTS AND DISCUSSION

4.1 Preamble

In this chapter, the results for the physico-chemical parameters, characterisation, BET, SEM, and other analyses applied to the study are reported and discussed in detail.

4.2 Physico-chemical parameters of the studied samples

4.2.1 Earthy materials colour determination

The identification of colour exhibited by each representative sample was done using Munsell Soil Colour Chats. This determined hue, value and the chroma (Table 4.1)

Table 4. 1: The hue, value, chroma and the colour of the analysed earthy materials

Localities	Sample codes	Hue	Value	Chroma	Colour
Botswana	BTS 1	10YR	7	8	Yellow
	BTS 2	2.5YR	8	4	Pale yellow
Cameroon	CMR 1	5Y	8	1	White
	CMR 2	7.5YR	6	4	Light brown
Democratic Republic of Congo	DRC 1	7.5YR	6	4	Light brown
	DRC 2	7.5YR	5	8	Strong brown
Nigeria	NG 1	10Y	8	2	Light grey
	NG 2	5Y	5	4	Olive
South Africa	SCC 1	5Y	8	1	White
	SCC 2	5Y	7	8	Yellow
	SCC 3	2.5YB	1.7	1	Black
	SCC 4	5Y	3	4	Reddish brown
	SCC 5	7.5YR	8	2	Light yellow
	SCC 6	7.5YB	7	8	Orange
	SCC 7	2.5YR	5	8	Brown
	SCC 8	-	-	-	-
	SCC 9	5Y	2	4	Reddish brown
	SCC 10	5Y	5	8	Light brown
	SCC 11	10Y	4	6	Light brown
	SCC 12	10Y	4	6	Light brown
Swaziland	SWL 1	5YR	4	6	Light brown
	SWL 2	7.5YR	4	6	Strong brown

Table 4.1 showed the colour variation between the representative samples according to Munsell Soil Colour Chats. The characteristic colour values recorded were 2.5-10, 4-8 and1-8 for hue, value and chroma respectively. The classification of hue, value and chroma according to their usefulness in each studied country is reported in Table 4.2. Colour of the analysed samples ranged from white to yellow, red to gray. According to the application in terms of beautification, sunscreening and cleansing, there is no much variation in hue, value and chroma values. The most frequently occurring colours were the yellowish and brownish colours; followed by the greyish, reddish and whitish colours as indicated on Table 4.2.

Table 4.2: Classification of hue, value and chroma in terms of beautification, sunscreening and cleansing

Remarks	Sample codes	Hue	Value	Chroma
Beautification	BTS 1	10YR	7	8
	BTS 2	2.5YR	8	4
	CMR 1	5Y	8	1
	CMR 2	7.5YR	6	4
	SCC 1	5Y	8	1
	SCC 2	5Y	7	8
	SCC 4	5Y	7	8
	SCC 6	7.5YB	7	8
	SCC 7	2.5YR	5	8
	SWL 1	5YR	4	6
	SWL 2	7.5YR	4	6
Sunscreening	DRC 1	7.5YR	6	4
	DRC 2	7.5/YR	5	8
	SCC 11	10Y	4	6
	SCC 12	10Y	4	6
	SWL 1	5YR	4	6
	SWL 2	7.5YR	4	6
Cleansing	NG 1	10Y	8	2
	NG 2	5Y	5	4
	SWL 1	5YR	4	6
	SWL 2	7.5YR	4	6

4.3 Morphological representation of the studied Earthy materials using SEM and EDX

Newbury *et al.* (1995) reported that an EDX analysis is only applicable if it is compared with an appropriate standard otherwise there would be a significant error. The SME imaging and EDX monograph is used to explain the micro-elemental analysis by taking the average of the five spots for each representative samples. INCA software was used in determining the mean average of the spectrums. Chemical components obtained in the studied samples are shown below. Figure 4.1 (a-b) below shows the SEM imaging and EDX monograph. The essence of the analyses is to obtain the topography (morphology) and its elemental compositions.

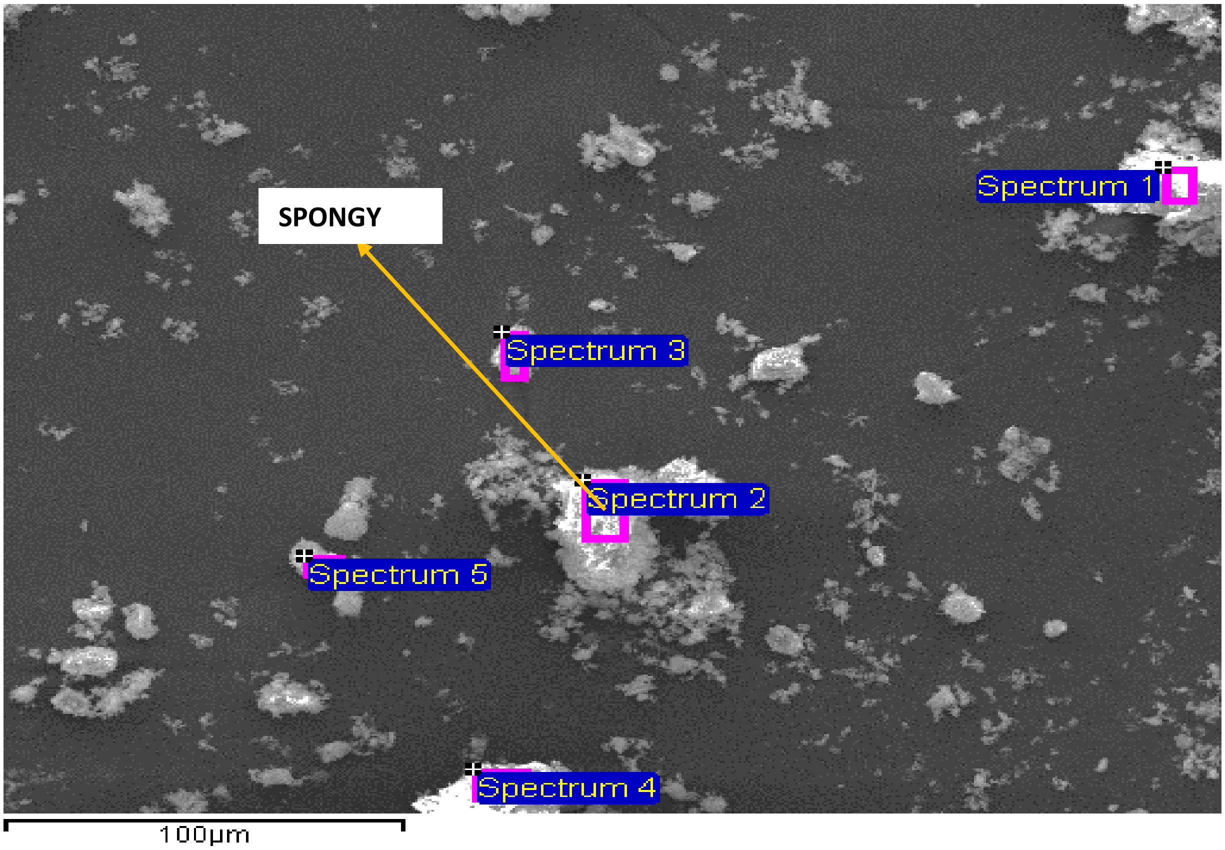


Figure 4.1a: Scanning electron photomicrograph showing spongy morphology of sample BTS 1

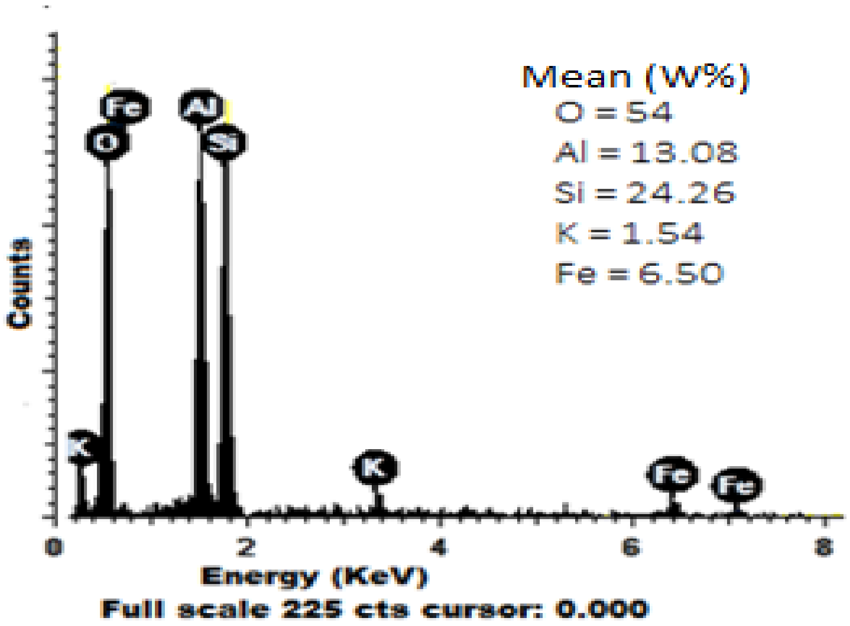


Figure 4.1b: Micro-elemental analysis (EDX) of sample BTS 1

The SEM photomicrograph and elemental compositions (micro-chemical analysis) of the sample above (BTS 1) showed that the material has particle size of 100 µm with spongy surfaces (Figure 4.1a). The major elements present in BTS 1 were identified by EDX analysis (Fig 4.1b, Table 4.3). Al and Si are the two main dominant elements. Aluminium present in the EDX can be substituted by iron. Fe and K are base cations (exchangeable cations), and K is important in cosmetic products (Gomes and Silva, 2007). Table 4.3 below summarises the percentage compositions of sample BTS 1, as analysed in the SEM analysis.

Table 4. 3: Percentage composition of different elements in sample BTS 1

Spectrum	**O**	**Al**	**Si**	**K**	**Fe**	**Total**
Spectrum 1	57.49	16.61	21.65	1.45	2.80	100
Spectrum 2	52.24	13.54	23.72	2.01	8.49	100
Spectrum 3	57.77	17.43	19.60	0.58	4.62	100
Spectrum 4	58.53	9.48	27.06	2.70	2.24	100
Spectrum 5	47.10	8.33	29.25	0.97	14.35	100
Mean	**54.63**	**13.08**	**24.26**	**1.54**	**6.50**	100
Max.	58.53	17.43	29.25	2.70	14.35	
Min.	47.10	8.33	19.6	0.58	2.24	

A spongy surface was observed in BTS 2 (Figure 4.2a). It exhibited same elements as BTS 1 (Al, Si and Fe) except for Ti (Fig 4.2b). This also indicates that the two samples may have the same geological formation. The presence of Ti is an indication that earthy material from BTS 2 is suitable for cosmetic application (topical), because Ti is generally considered a safe metal in cosmetics (Orisakwe and Otaraku, 2013), though not in high concentration. In certain conditions Ti may react with O to form TiO_2.

$$Ti_{(g)} + O_{2(g)} \rightarrow TiO_{2(g)} \text{--} \quad \textit{eqn 4.1}$$

Titanium dioxide has a very high refractive index and strong UV absorbing capabilities. It is one of the major ingredients in most sunscreen products; this is also one of the reasons indigenous communities apply the earthy material. The usefulness of TiO_2 in cosmetic helps in protecting the skin from ultraviolet light. Table 4.4 below summarises the various elements present in the sample with Ti having smallest concentration. Synthetic TiO_2 possesses some brightening agents which makes the skin to have white appearance, though nanosize TiO_2 are extensively used in sunscreen lotions (Jaroenworaluck *et al*., 2006) because of its very small particle size. The elemental analysis (EDX) for sample BTS 2 is shown in Fig 4.2b, were elements such as carbon, titanium, iron, aluminium and silicon were identified.

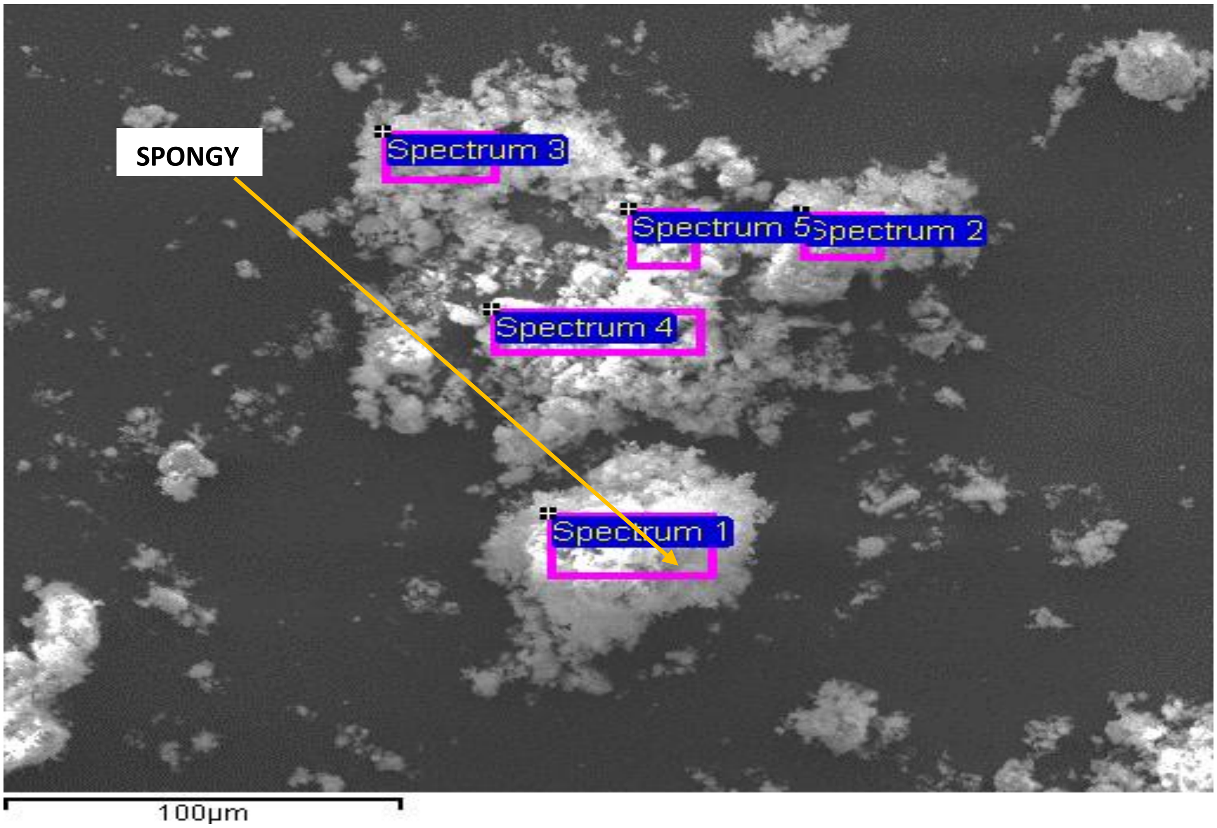


Figure 4.2a: Scanning electron photomicrograph showing spongy morphology of sample BTS 2

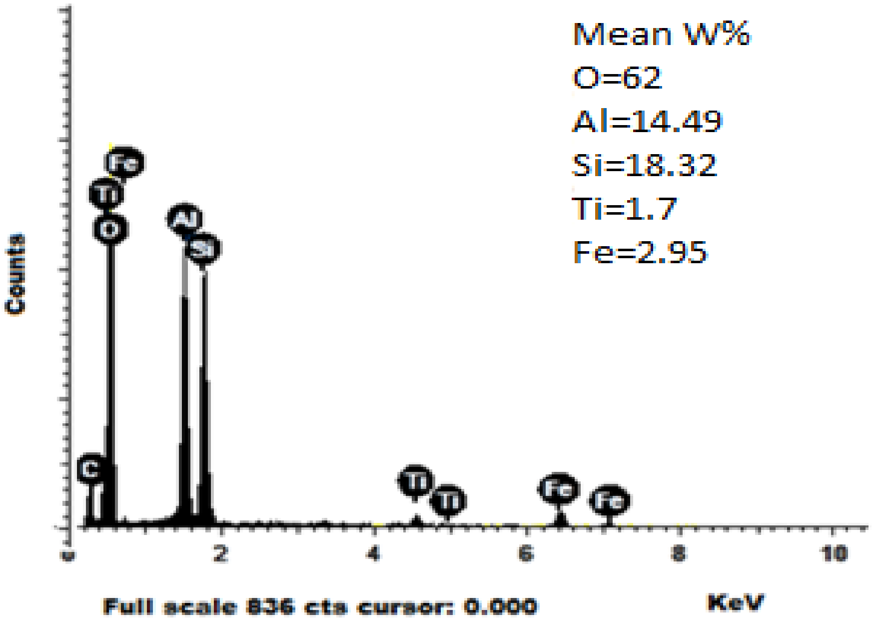


Figure 4.2b: Micro-elemental analysis (EDX) of sample BTS 2

Table 4.4: Percentage composition of different elements in sample BTS 2

Spectrum	O	Al	Si	Ti	Fe	Total
Spectrum 1	61.57	15.45	17.86	1.36	3.75	100
Spectrum 2	60.73	14.92	19.8	1.79	2.76	100
Spectrum 3	65.92	12.1	18.5	0.77	2.72	100
Spectrum 4	59.16	16.65	20.33	1.15	2.71	100
Spectrum 5	65.08	13.32	15.12	3.67	2.81	100
Mean	**62.49**	**14.49**	**18.32**	**1.75**	**2.95**	**100**
Max.	65.92	16.65	20.33	3.67	3.75	

Spot analysis (Figure 4.3a) revealed that the elemental composition of the residues is dominated by Si, O and Al (Figure 4.3b). Fe was also present, possibly due to ion-exchange and it shows a coarse surface. The concentration of Fe was low. Table 4.5 explains the distribution of elements present in CMR 1 sample of various distributions of chemical compositions of the studied sample.

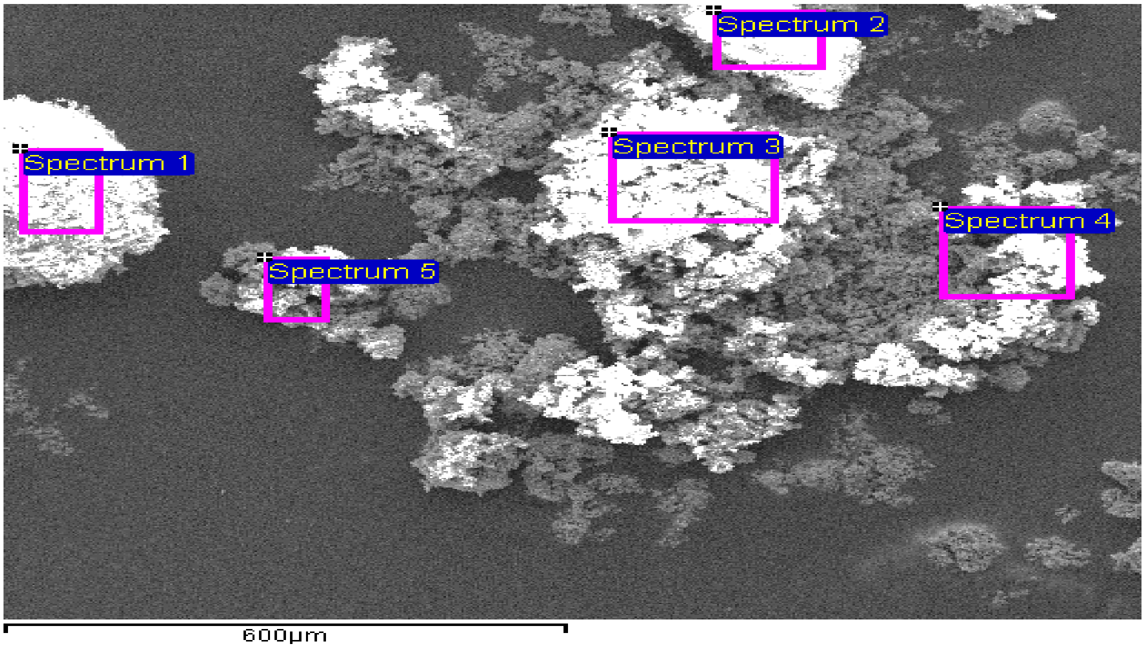


Figure 4.3a: Scanning electron photomicrograph showing coarse morphology of sample CMR 1

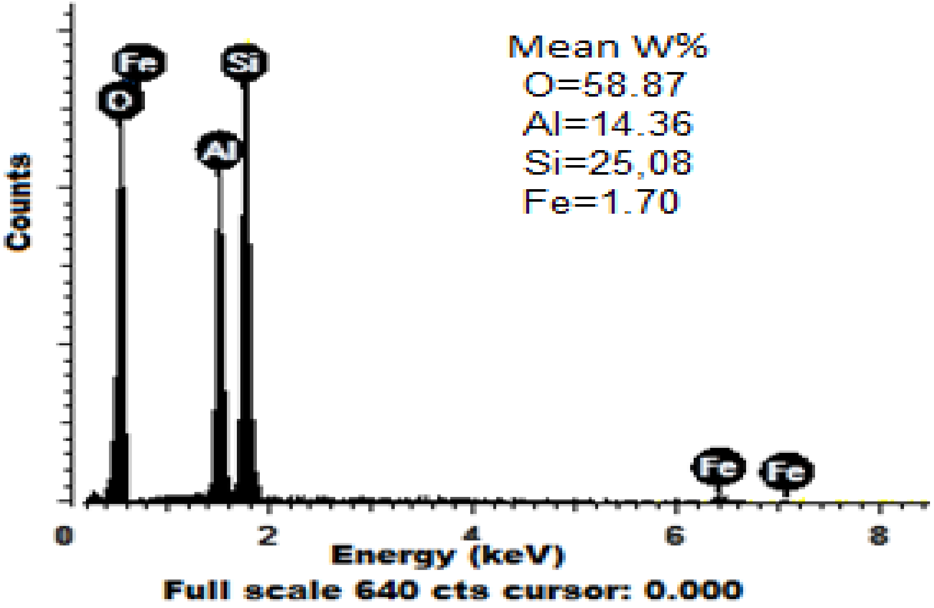


Figure 4.3b: Micro-elemental analysis (EDX) of sample from CMR 1

Table 4.5: Percentage composition of different elements in sample CMR 1

Spectrum	O	Al	Si	Fe	Total
Spectrum 1	59.46	14.18	25.20	1.17	100
Spectrum 2	60.76	15.92	22.07	1.25	100
Spectrum 3	59.31	13.86	24.95	1.87	100
Spectrum 4	57.88	13.95	25.44	2.72	100
Spectrum 5	56.92	13.9	27.72	1.46	100
Mean	**58.87**	**14.36**	**25.08**	**1.70**	**100**
Max.	60.76	15.92	27.72	2.72	
Min.	56.92	13.86	22.07	1.17	

Figure 4.4a, shows the SEM and elemental composition of earthy material obtained from CMR 2 with flaky platelets with swirl-structure (Ekosse and Anyangwe, 2012). Al and Si are the main elements (Figure 4.4b), this is an indication that the material under study is an aluminosilicate. Samples from CMR 1 and CMR 2 were obtained from the same country (Cameroon) but from different localities. They exhibited same chemical compositions except CMR 1 which has notable concentrations of Fe, this might be as a result of ion-exchange on the surface of the material. Table 4.6 summarises the percentage composition (micro-chemistry) occurring in the spectra of CMR 2 sample.

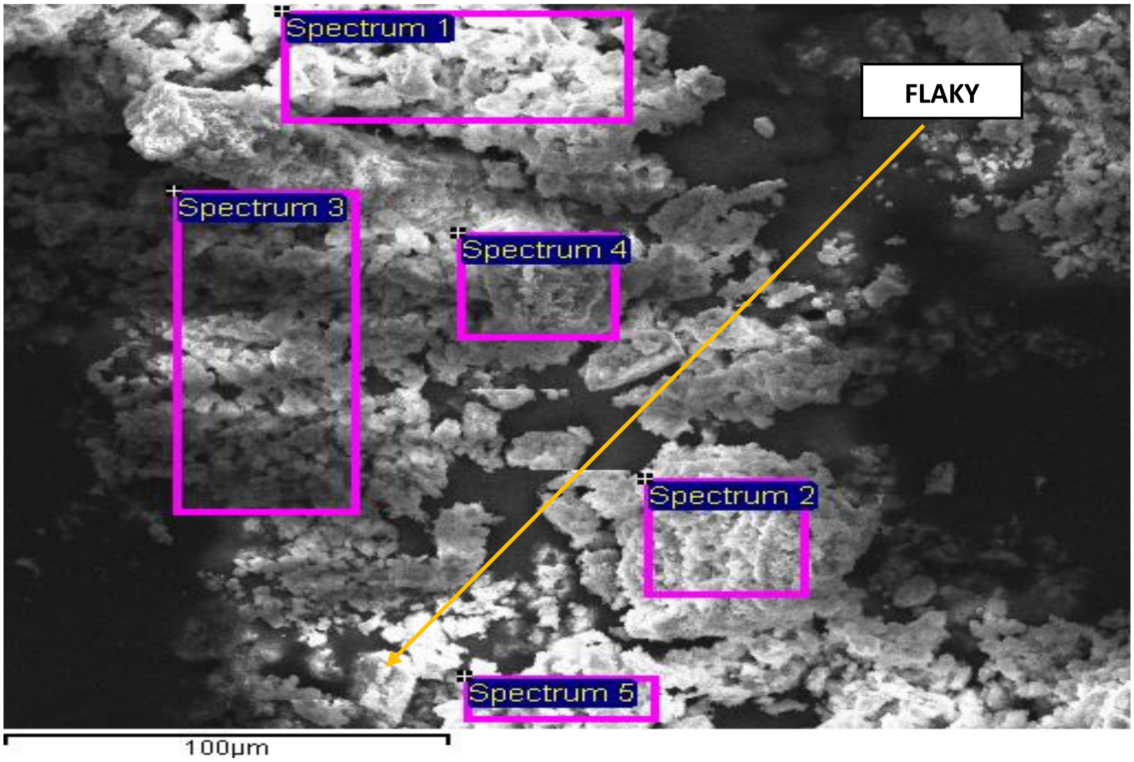


Figure 4.4a: Scanning electron photomicrograph showing flaky morphology of sample CMR 2

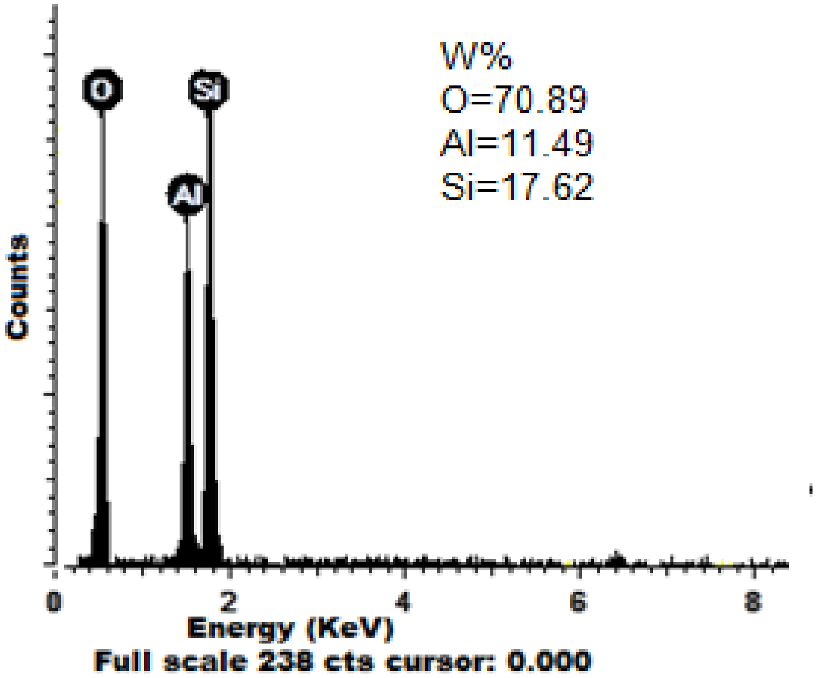


Figure 4.4b: Micro-elemental analysis (EDX) of sample from CMR 2

Table 4.6: Percentage composition of different elements in sample CMR 2

Spectrum	O	Al	Si
Spectrum 1	72.29	10.36	17.35
Spectrum 2	70.54	12.62	16.84
Spectrum 3	68.58	12.09	19.33
Spectrum 4	71.23	10.86	17.91
Spectrum 5	71.82	11.5	16.69
Mean	**70.89**	**11.49**	**17.62**
Max.	72.29	12.62	19.33
Min.	68.58	10.36	16.69

The SEM micrographs showed the presence of amorphous distributions of the studied sample with flaky surface (Figure 4.5a). Other than the presence of Al, Si and Ti, Fe is also present at elevated concentration (Figure 4.5b) and this could be attributed to ion-exchange of base cations on clay interlayers. A base cation (K) was also identified though at a very low concentration. Table 4.7 indicated the different spectrum and the mean concentrations of elements in the studied sample.

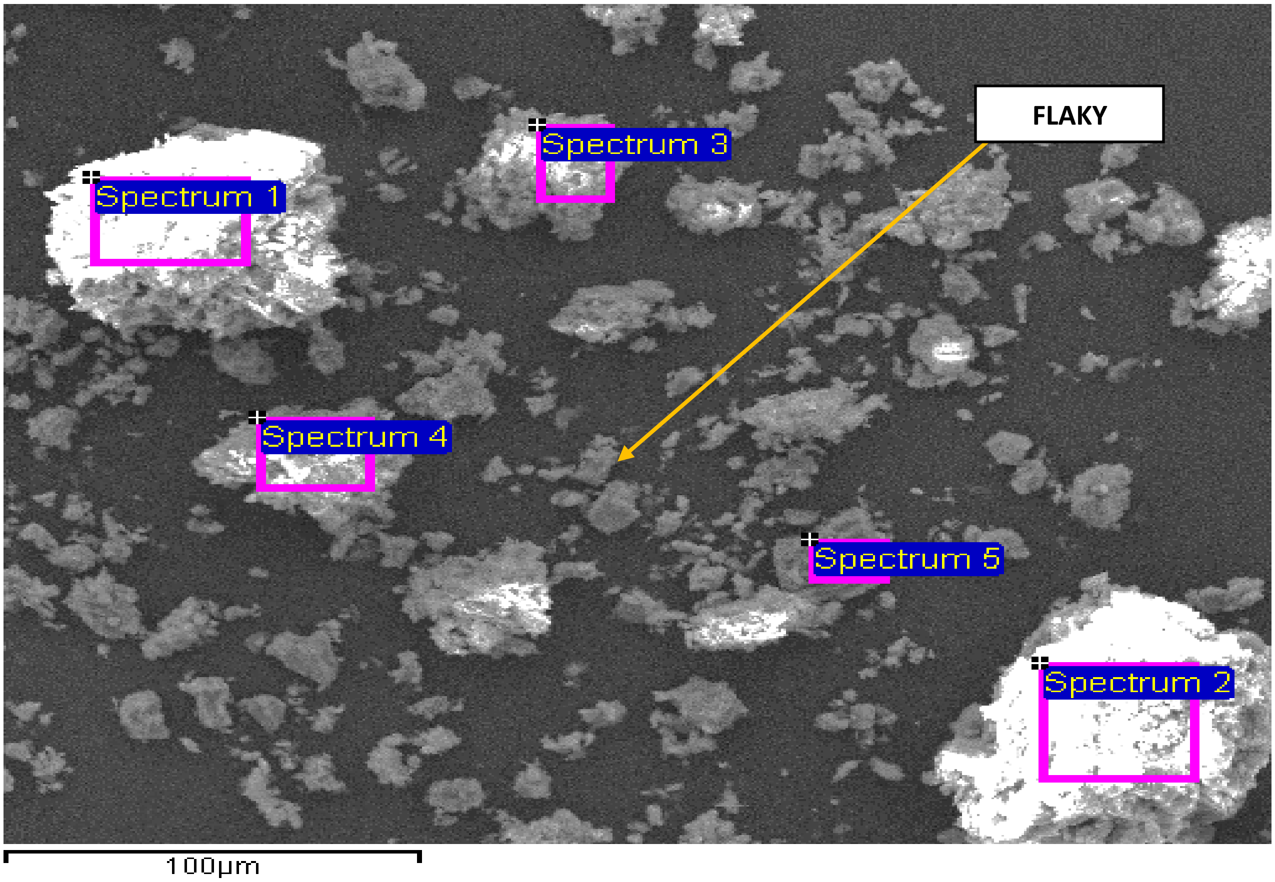


Figure 4.5a: Scanning electron photomicrograph showing flaky morphology of DRC 1

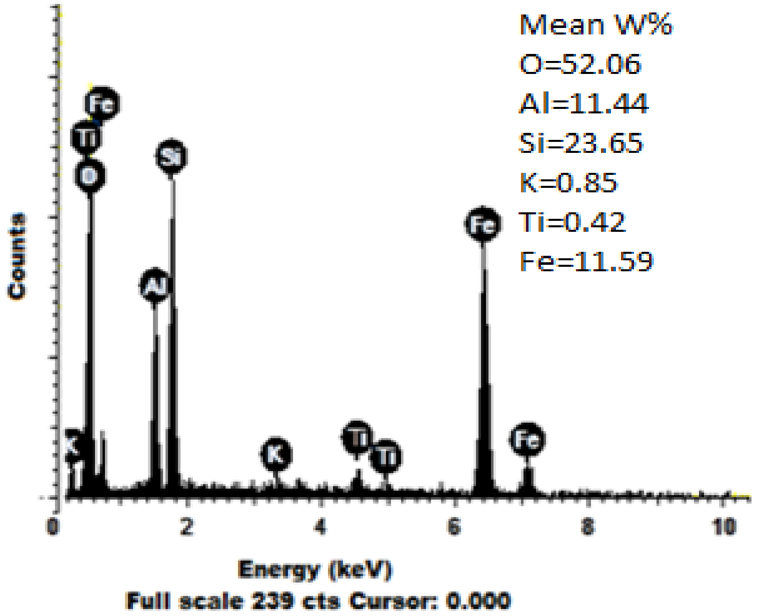


Figure 4.5b: Micro-elemental analysis (EDX) of sample from DRC 1

Table 4.7: Percentage composition of different elements in sample DRC 1

Spectrum	O	Al	Si	K	Ti	Fe	Total
Spectrum 1	37.83	7.73	13.61	0	1.35	39.48	100
Spectrum 2	54.86	9.29	28.89	0.77	0	6.19	100
Spectrum 3	55.06	14.47	22.48	1.69	0.73	5.57	100
Spectrum 4	56.71	5.96	31.35	0.79	0	5.19	100
Spectrum 5	55.83	19.74	21.92	0.99	0	1.52	100
Mean	**52.06**	**11.44**	**23.65**	**0.85**	**0.42**	**11.59**	**100**
Max.	56.71	19.74	31.35	1.69	1.35	39.48	
Min.	37.83	5.96	13.61	0	0	1.52	

The spot analysis (Figure 4.6a - 4.6b) showed uniform chemical composition as BTS 1 (Figure 4.1) and DRC 1 (Figure 4.5b) except for Ti, this is an indication that the sample contains the necessary elements for the cosmetics Table 4.8 below indicated the mean percentages of the studied sample.

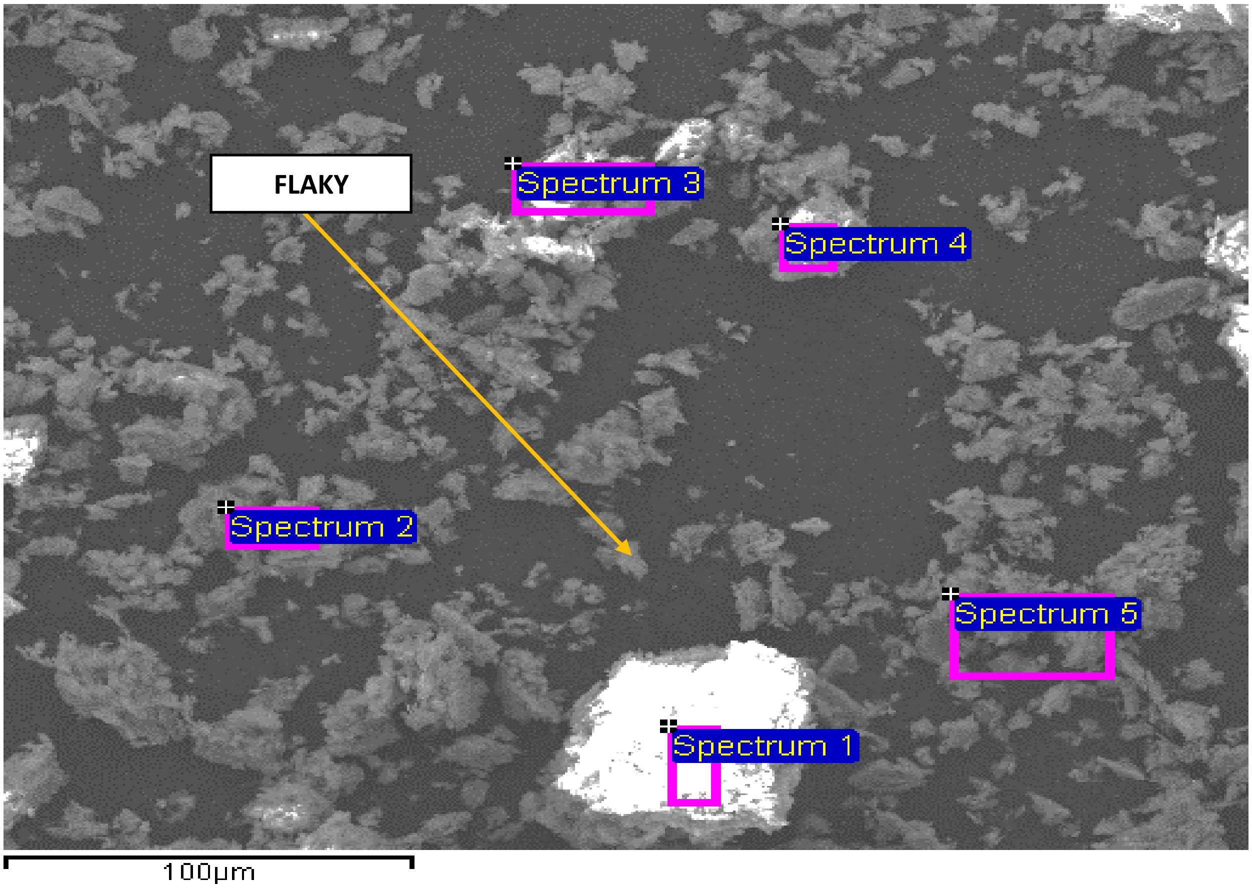


Figure 4.6a: Scanning electron photomicrograph showing flaky morphology of DRC 2

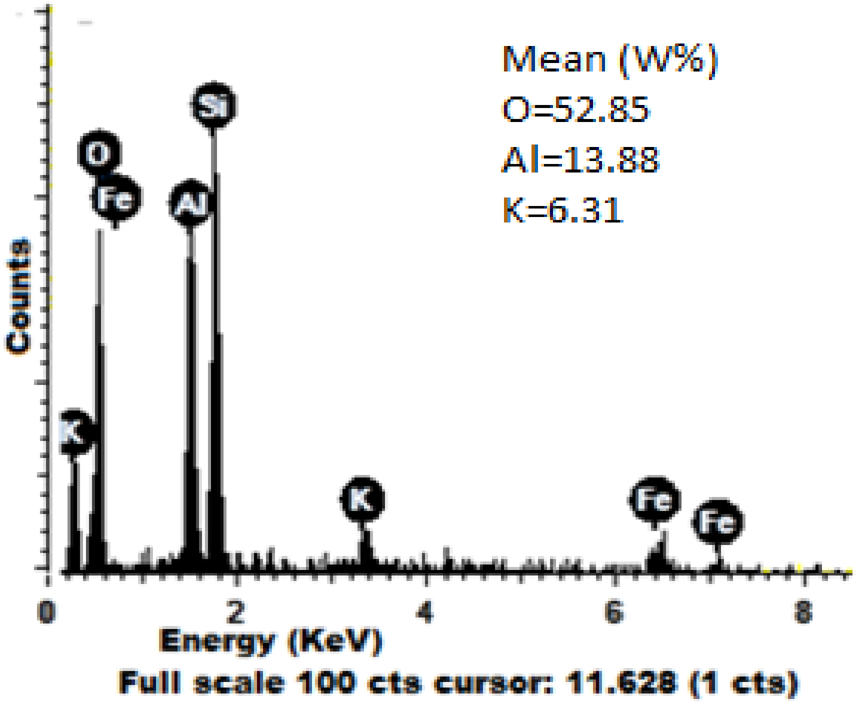


Figure 4.6b: Micro-elemental analysis (EDX) of sample from DRC B

Table 4.8: Percentage composition of different elements in sample DRC 2

Spectrum	O	Al	Si	K	Fe	Total
Spectrum 1	54.85	13.44	21.09	2.20	8.42	100
Spectrum 2	53.26	9.98	30.52	1.80	4.44	100
Spectrum 3	51.59	14.24	22.48	3.10	8.59	100
Spectrum 4	53.02	16.37	23.05	2.73	4.83	100
Spectrum 5	51.53	15.38	24.66	3.17	5.25	100
Mean	**52.85**	**13.88**	**24.36**	**2.60**	**6.31**	**100**
Std. deviation	1.37	2.45	3.67	0.59	2.03	
Max.	54.85	16.37	30.52	3.17	8.59	
Min.	51.53	9.98	21.09	1.80	4.44	

The photomicrograph result showed that the sample has a fibrous surface (Figure 4.7a). The elements were analysed from different spectrum and the mean concentration of each elements was determined (Figure 4.7b). Table 4.9 is the percentage composition of different elements in the sample obtained from Nigeria (NG 1). Spot analysis (Figure 4.7a) revealed that the elemental composition of the secondary residues is dominated by Si, O and Al (Figure 4.7b) which is an indication that the sample is an aluminosilicate. An average concentration of K which is a base cation was also present.

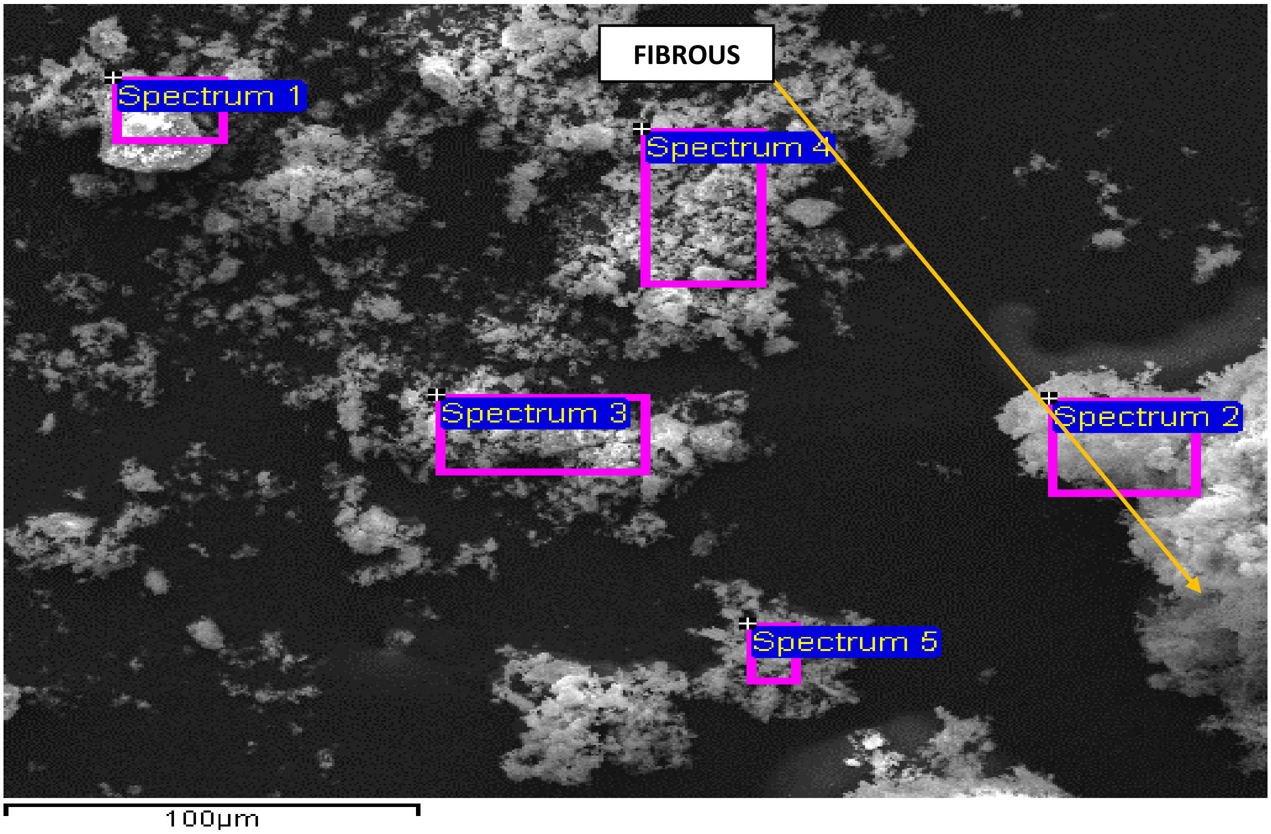


Figure 4.7a: Scanning electron photomicrograph showing fibrous morphology of NG 1

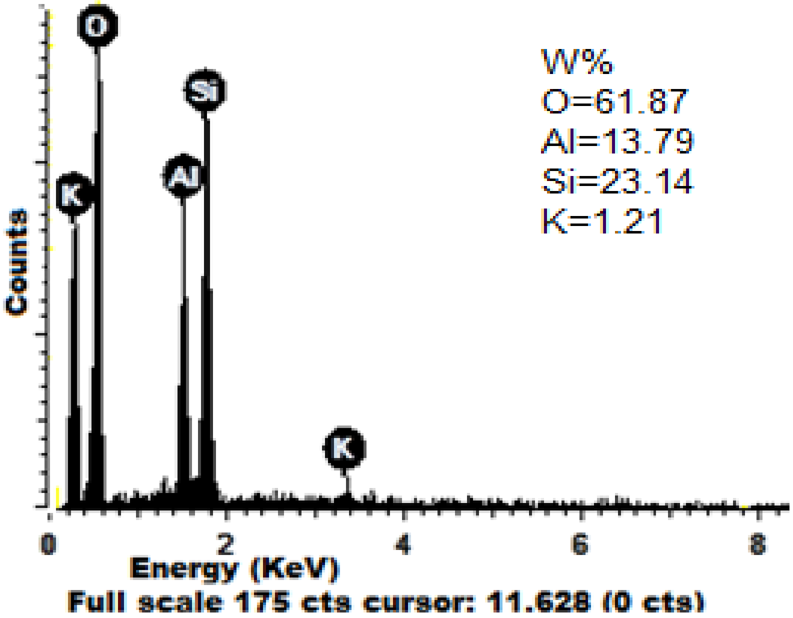


Figure 4.7b: Micro-elemental analysis (EDX) of sample from NG 1

Table 4.9: Percentage composition of different elements in sample NG 1

Spectrum	**O**	**Al**	**Si**	**K**	**Total**
Spectrum 1	59.67	17.81	22.07	0.45	100
Spectrum 2	61.79	14.67	21.92	1.63	100
Spectrum 3	60.62	14.87	23.05	1.47	100
Spectrum 4	66.21	12.44	20.01	1.34	100
Spectrum 5	61.06	9.16	28.64	1.15	100
Mean	**61.87**	**13.79**	**23.14**	**1.21**	**100**
Max.	66.21	17.81	28.64	1.63	
Min.	59.67	9.16	20.01	0.45	

Figures 4.8 (a, b) are the SEM analysis and micro-elemental of NG 2 sample. The same elements exhibited by BTS 1 (Fig 4.1b) and DRC 2 (Figure 4.6b) was also identified from NG 2 (Figure 4.8b). High percentage of Si was observed and this makes the material not suitable for cosmetic application until it undergoes some necessary modification (beneficiation). O which is also present on the clay matrices may have been introduced into the clay surfaces from the atmosphere. Table 4.10 summarises the various mean concentrations of the representative sample.

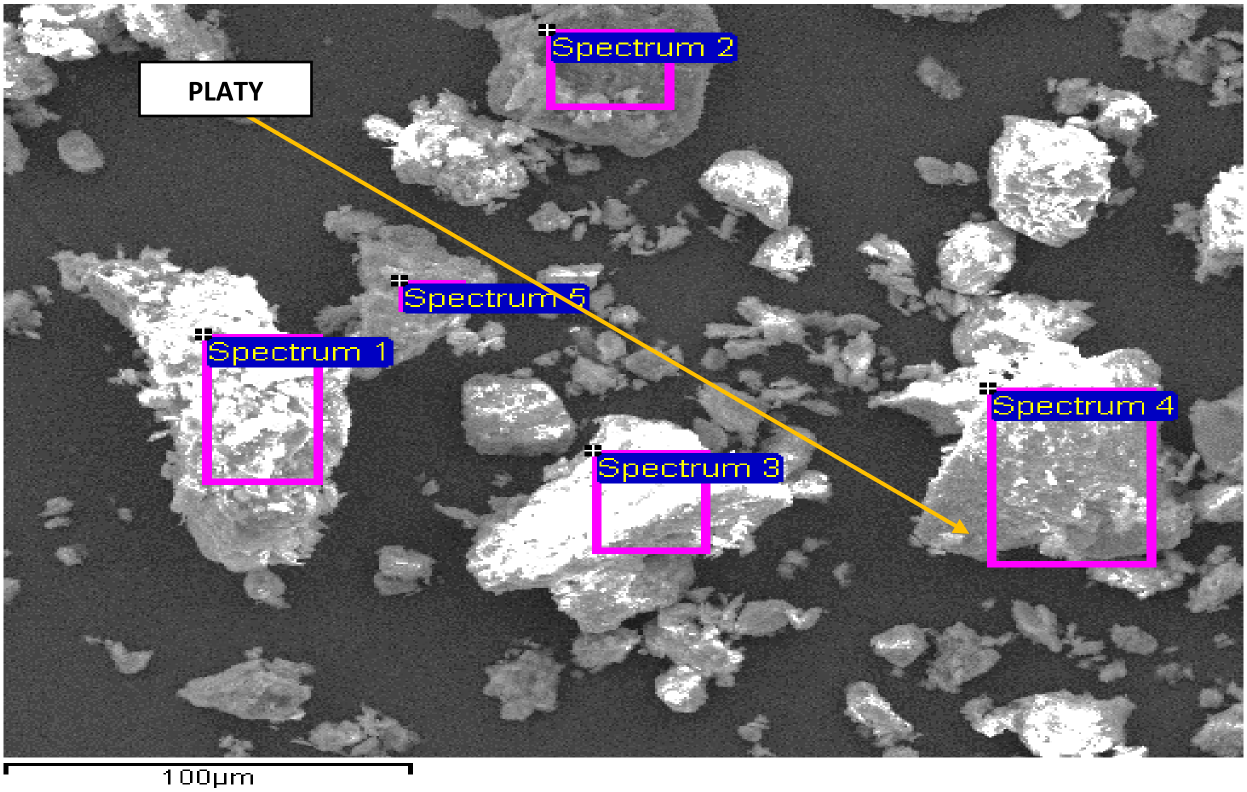


Figure 4.8a: Scanning electron photomicrograph showing platy morphology of NG 2

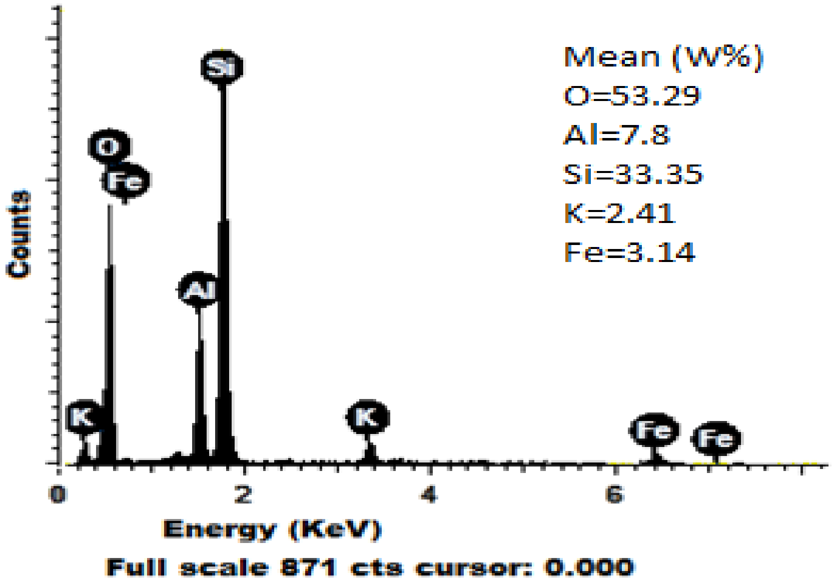


Figure 4.8b: Micro-elemental analysis (EDX) of sample from NG 2

Table 4.10: Percentage composition of different elements in sample NG 2

Spectrum	**O**	**Al**	**Si**	**K**	**Fe**	**Total**
Spectrum 1	54.81	9.13	30.58	2.27	3.22	100
Spectrum 2	47.35	8.06	36.98	3.03	4.58	100
Spectrum 3	54.07	10.06	29.86	3.16	2.85	100
Spectrum 4	51.61	7.4	35.17	2.16	3.66	100
Spectrum 5	58.64	4.34	34.16	1.45	1.42	100
Mean	**53.29**	**7.8**	**33.35**	**2.41**	**3.14**	**100**
Max.	**58.64**	**10.06**	**36.98**	**3.16**	**4.58**	
Min.	47.35	4.34	29.86	1.45	1.42	

The spot shot at SWL 1 and SWL 2 (Figures 4.9a and 4.10a) indicated that the analysed earthy materials contained O, Si and Al as the major components (Figures 4.9b and 4.10b). This indicated that both samples are aluminosilicates. The surfaces of the sample SWL 1 and SWL 2 (Figure4.9a) have coarse surfaces. Fe was also present at elevated concentrations and this could be attributed to ion-exchange of base cations on clay interlayers. Tables 4:11 and 4.12 indicated the percentage composition of different elements in samples from SWL 1 and 2 with their various distributions of elements in their various spectra.

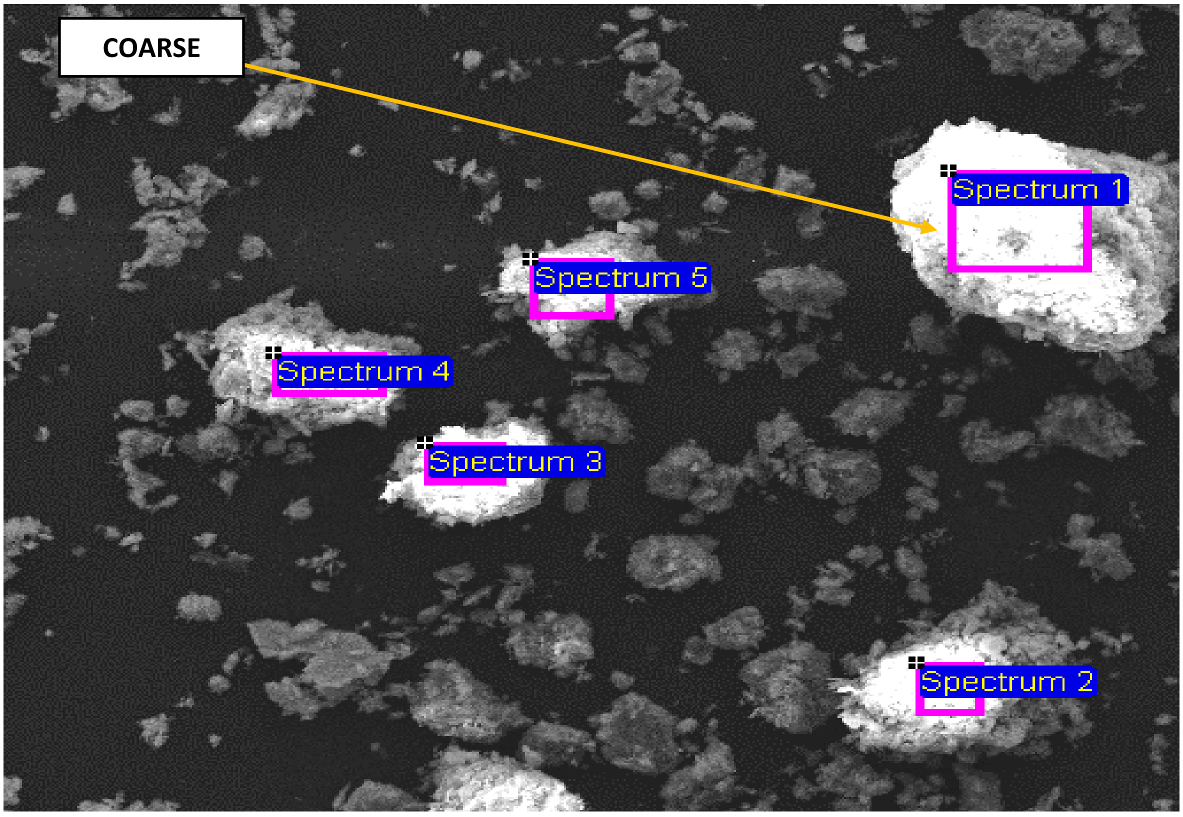


Figure 4.9a: Scanning electron photomicrograph showing coarse morphology of SWL 1

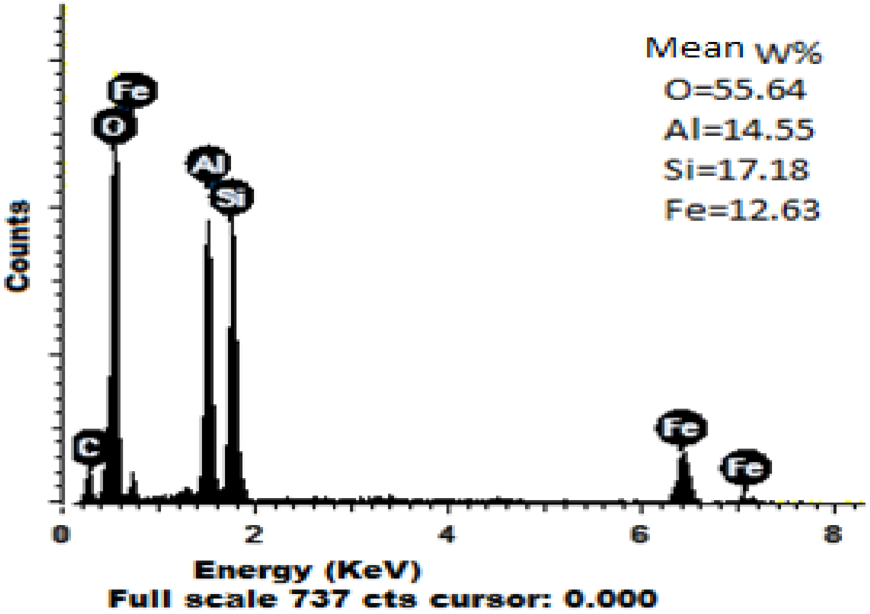


Figure 4.9b: Micro-elemental analysis (EDX) of sample SWL 1

Table 4.11: Percentage composition of different elements in sample SWL 1

Spectrum	O	Al	Si	Fe	Total
Spectrum 1	56.86	14.83	17.09	11.22	100
Spectrum 2	56.04	14.14	16.37	13.44	100
Spectrum 3	54.71	12.53	14.88	17.87	100
Spectrum 4	56.16	15.36	18.86	9.62	100
Spectrum 5	54.41	15.9	18.69	11.01	100
Mean	**55.64**	**14.55**	**17.18**	**12.63**	**100**
Max.	56.86	15.9	18.86	17.87	
Min.	54.41	12.53	14.88	9.62	

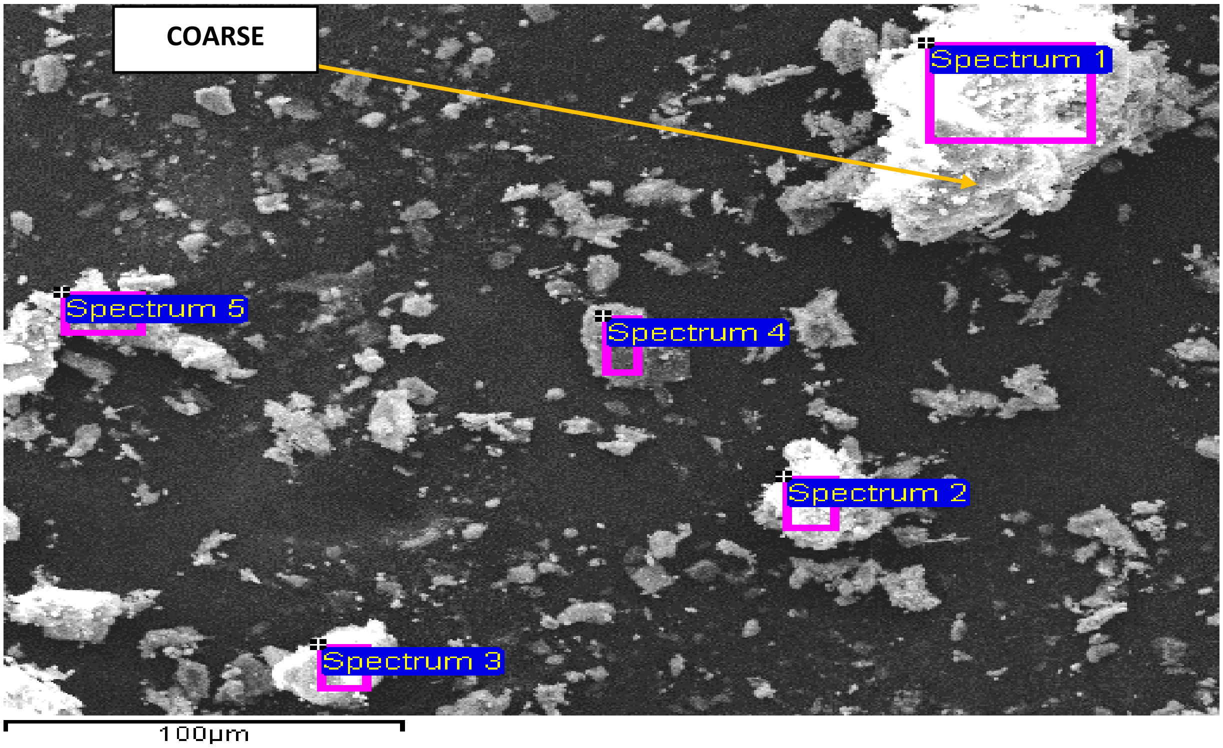


Figure 4.10a: Scanning electron photomicrograph showing coarse morphology of SWL 2

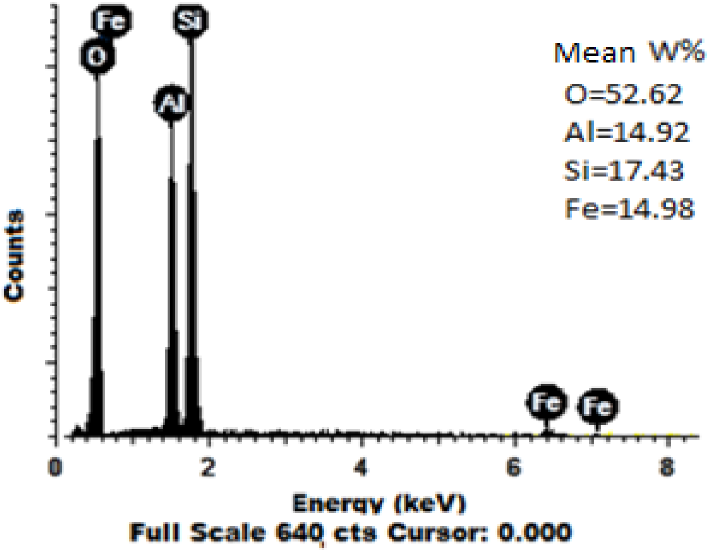


Figure 4.10b: Micro-elemental analysis (EDX) of sample SWL 2

Table 4.12: Percentage composition of different elements in sample SWL 2

Spectrum	O	Al	Si	Fe	Total
Spectrum 1	54.14	15.14	18	12.73	100
Spectrum 2	45.43	12.04	14.42	28.11	100
Spectrum 3	57.13	16.32	18.8	7.75	100
Spectrum 4	57.28	15.87	19.96	6.89	100
Spectrum 5	49.37	15.24	15.96	19.44	100
Mean	**52.67**	**14.92**	**17.43**	**14.98**	**100**
Std. deviation	5.16	1.68	2.23	8.87	
Max.	57.28	16.32	19.96	28.11	
Min.	45.43	12.04	14.42	6.89	

Al and Si are the main elements showing the material under study is an aluminosilicate (Figure 4.11b). The elements present is indicating that presence4. of Al and Mg are required for topical application, whereas the Si present requires beneficiation. Low level of base cations Mg was also present. Fe was present in the studied sample and could have been incorporated during geological deposition and weathering processes. Table 4.13 below summarises various concentrations of the elements (%W). Figure 4.11a showed a coarse surface, this indicated that the material will be unfriendly to the body.

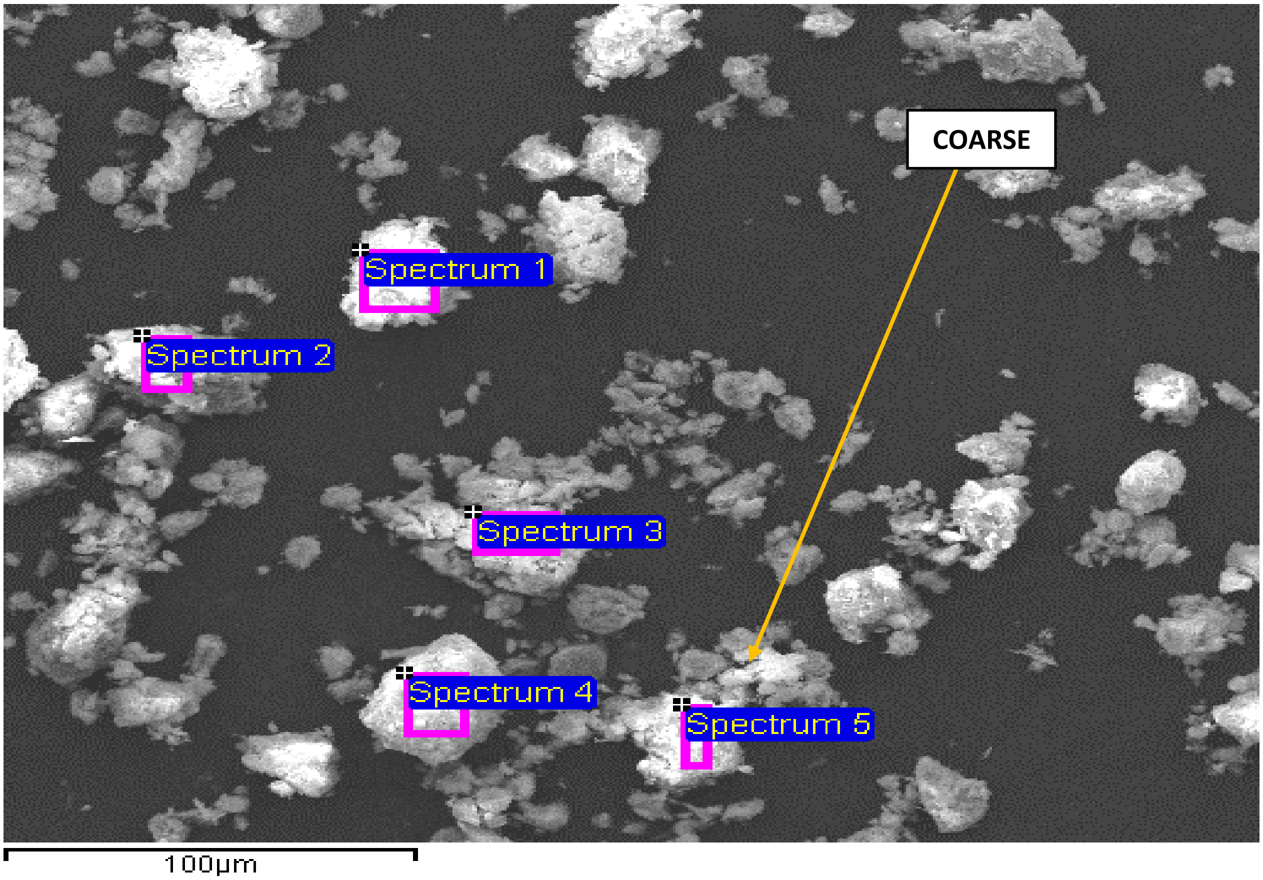


Figure 4.11a: Scanning electron photomicrograph showing coarse morphology of SCC 1

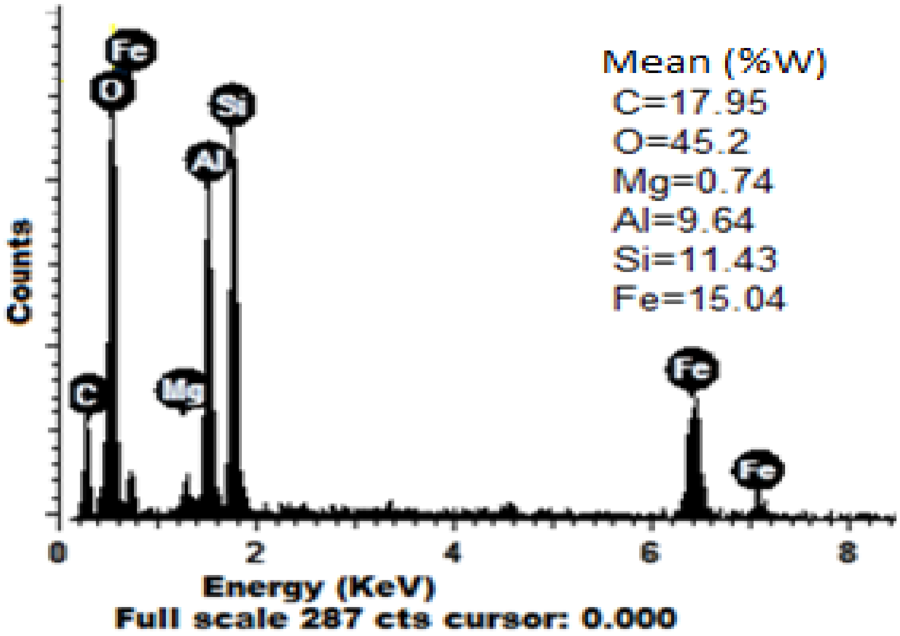


Figure 4.11b: Micro-elemental analysis (EDX) of sample from SCC 1

Table 4.13: Percentage composition of different elements in sample SCC 1

Spectrum	C	O	Mg	Al	Si	Fe	Total
Spectrum 1	21.26	44.86	0.78	8.48	11.18	13.44	100
Spectrum 2	17.2	49.63	0.82	10.63	12.52	9.2	100
Spectrum 3	18.15	43.58	0.76	9.97	13.13	14.41	100
Spectrum 4	14.69	41.48	0.58	7.46	7.32	28.47	100
Spectrum 5	18.44	46.46	0.78	11.66	13.01	9.65	100
Mean	**17.95**	**45.2**	**0.74**	**9.64**	**11.43**	**15.04**	**100**
Max.	21.26	49.63	0.82	11.66	13.13	28.47	
Min.	14.69	41.48	0.58	7.46	7.32	9.2	

The spot analysis of SCC 2 (Figure 4.12a) showed a cloudy image (SEM), indicating the presence of sulphur (81%) and carbon (18.99%) (Figure 4.12b). From the XRD analysis (SCC 2), the sample was confirmed to be sulphur. It has traditionally been in most cosmetic products, though they do not practically get absorbed in the product. Carretero and Pozo (2010) stated that only 1% of topically applied sulphur are systematically absorbed. There has not been any recorded adverse effect of sulphur from topical application because It has been traditionally been in most cosmetic products, though they don’t practically get absorbed in the of its limitation to the skin (Lin *et* al., 1988). It is believed by indigineous communities that cosmetics containing sulphur are beneficial for the cure of eczema and other skin infections. Table 4.14 is the micro-chemistry of SCC 2. Carbon which is also present maybe due to sequestration of atmospheric CO_2.

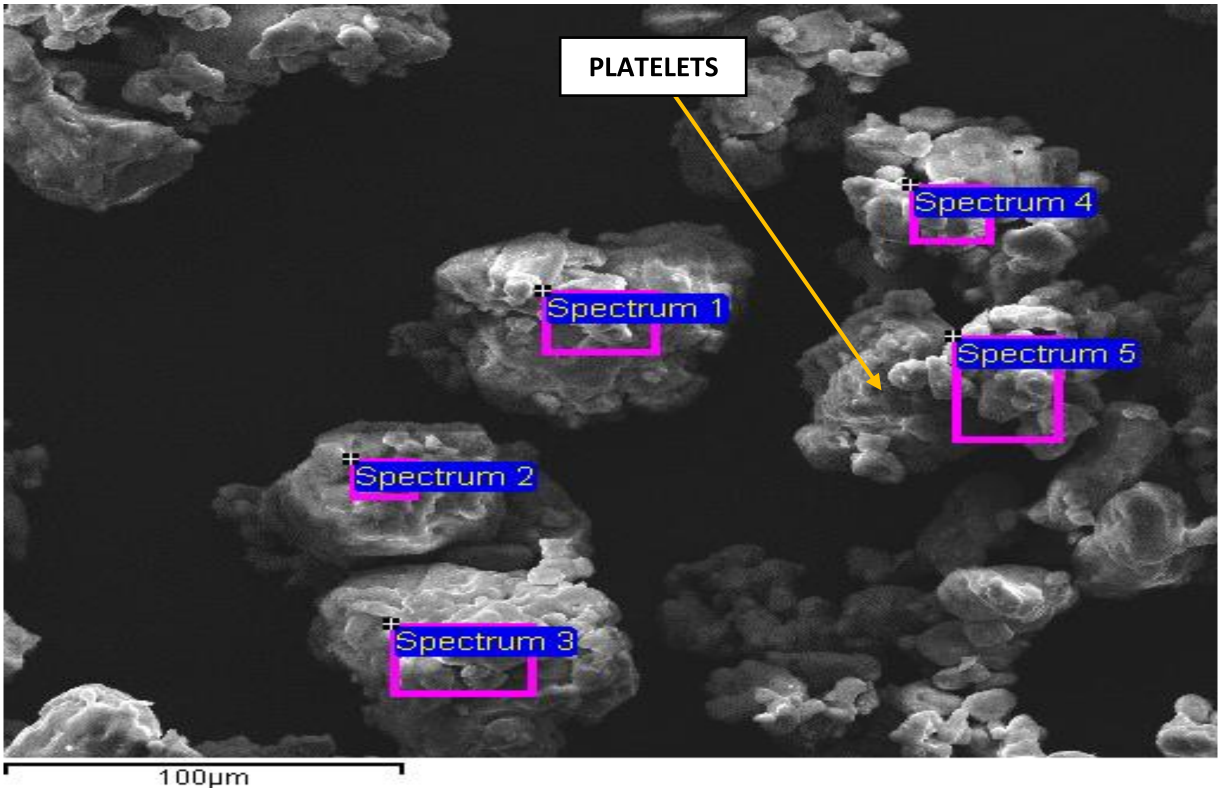


Figure 4.12a: Scanning electron photomicrograph showing platelets morphology of SCC 2

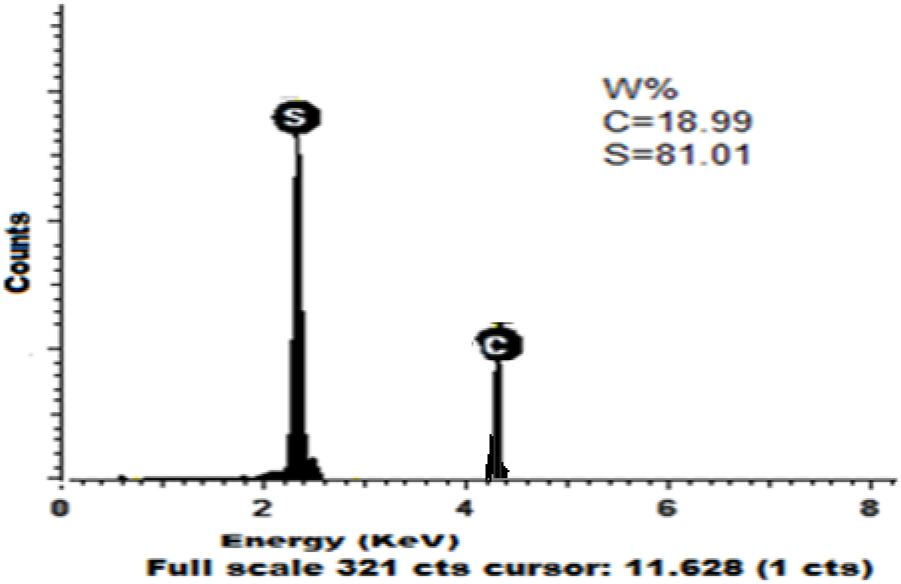


Figure 4.12b: Micro-elemental analysis EDX) of sample from SCC 2

Table 4.14: Percentage composition of different elements present in sample SCC 2

Spectrum	**C**	**S**	**Total**
Spectrum 1	16.94	83.06	100
Spectrum 2	11.01	88.99	100
Spectrum 3	24.74	75.26	100
Spectrum 4	19.85	80.15	100
Spectrum 5	22.39	77.61	100
Mean	**18.99**	**81.01**	**100**
Max.	**24.74**	**88.99**	
Min.	11.01	75.26	

The SEM micrograph (300 µm) above indicated a flappy-plate like image (Figure 4.13a) with several C, O, Mg, Si, Ca, Ti, V and Fe present in the studied sample (Figure 4.13b). Mg and Ca which are base cations were present and may have been incorporated during geological deposition and weathering processes. If Si and V were not present, the usefulness of this material would have been beneficial to man. C and O were also present on the clay matrices and may have been introduced into the clay surfaces from the atmosphere, by hydrolysis or decomposition of organic compounds. Table 4.15 is the percentage composition of different elements in the sample obtained from South Africa (SCC 3).

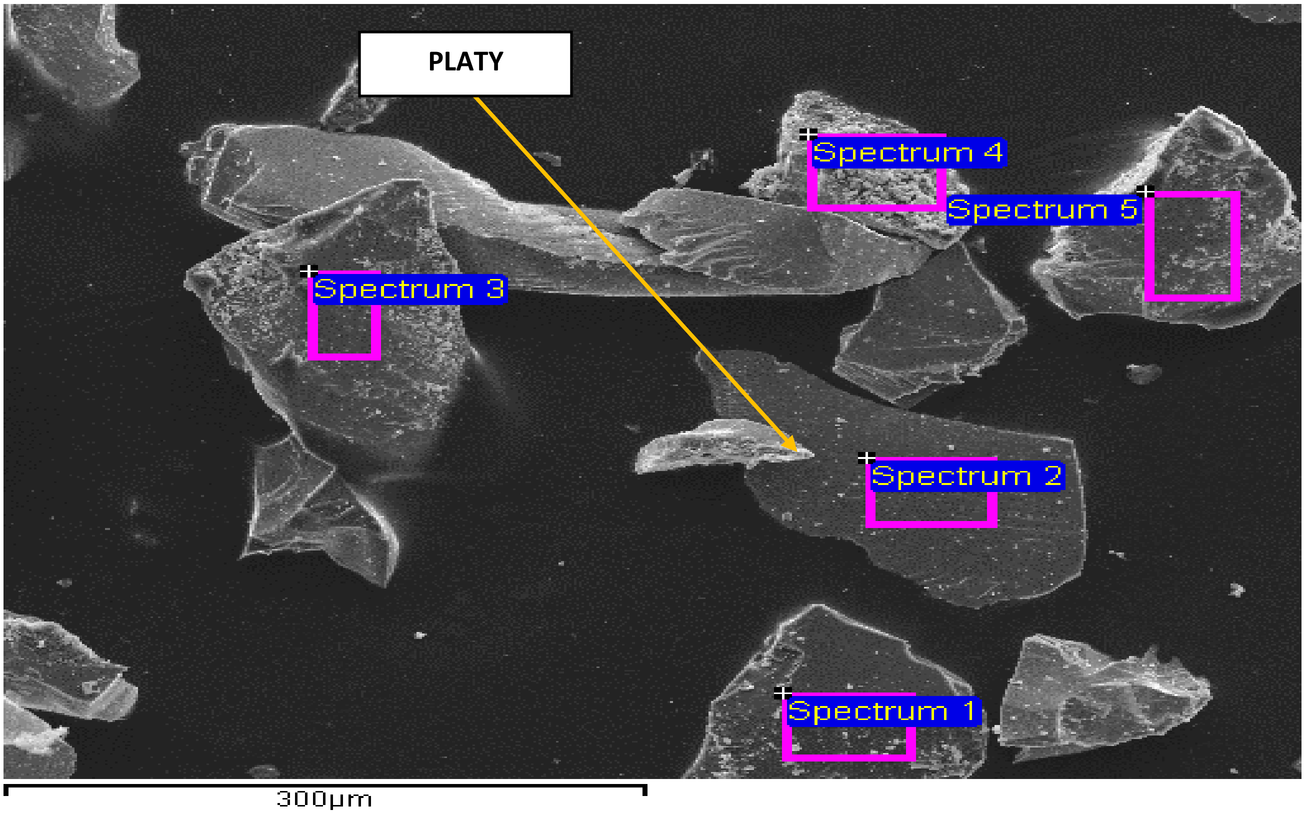


Figure 4.13a: Scanning electron photomicrograph showing platy morphology of SCC 3

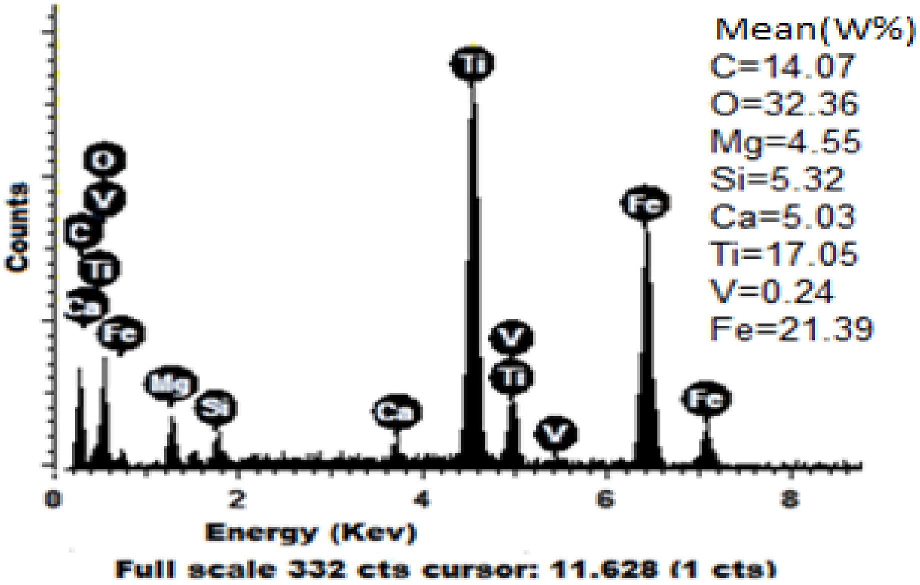


Figure 4.13b: Micro-elemental analysis (EDX) of sample from SCC 3

Table 4.15: Percentage composition of different elements present in sample SCC3

Spectrum	C	O	Mg	Si	Ca	Ti	V	Fe	Total
Spectrum 1	15.85	38.93	9.27	20.55	9.8	0.63	0	4.96	**100**
Spectrum 2	4.45	27.38	3.69	0.32	0	28.99	0	35.18	**100**
Spectrum 3	14.88	30.10	3.42	0.62	0	23.47	0	27.51	**100**
Spectrum 4	19.9	46.51	4.27	4.23	14.6	4.58	0	5.9	**100**
Spectrum 5	15.28	18.86	2.09	0.86	0.74	27.57	1.21	33.39	**100**
Mean	**14.07**	**32.36**	**4.55**	**5.32**	**5.03**	**17.05**	**0.24**	**21.39**	100
Max.	19.9	46.51	9.27	20.55	14.6	28.99	1.21	35.18	
Min.	4.45	18.86	2.09	0.32	0	0.63	0	4.96	

The SEM micrograph (100 µm magnification) showed an amorphous image (Figure 4.14a) with the presence of C, O, Ca and Fe (Figure 4.14b). The earthy materials might undergo some chemical reactions with the present elements to form the following minerals in eqn 4.2 and 4.3.

$$\underset{\text{Calcium oxide}}{CaO_{(g)}} + \underset{\text{Carbon dioxide}}{CO_{2(g)}} \rightarrow \underset{\text{Calcium carbonate}}{CaCO_3} \qquad \textit{eqn } 4.2$$

$$\underset{\text{Iron}}{Fe} + \underset{\text{Oxygen}}{O_2} \rightarrow \underset{\text{Hematite}}{Fe_2O_3} \qquad \textit{eqn } 4.3$$

Calcium carbonate occupies about 99.2% in various mines *(www.congal.com).* The mineral present in calcium carbonate is calcite. The notable high percentage of Fe might also be as a result of ion-exchange on the clay surface. Table 4.16 summarises the various elements present in the sample.

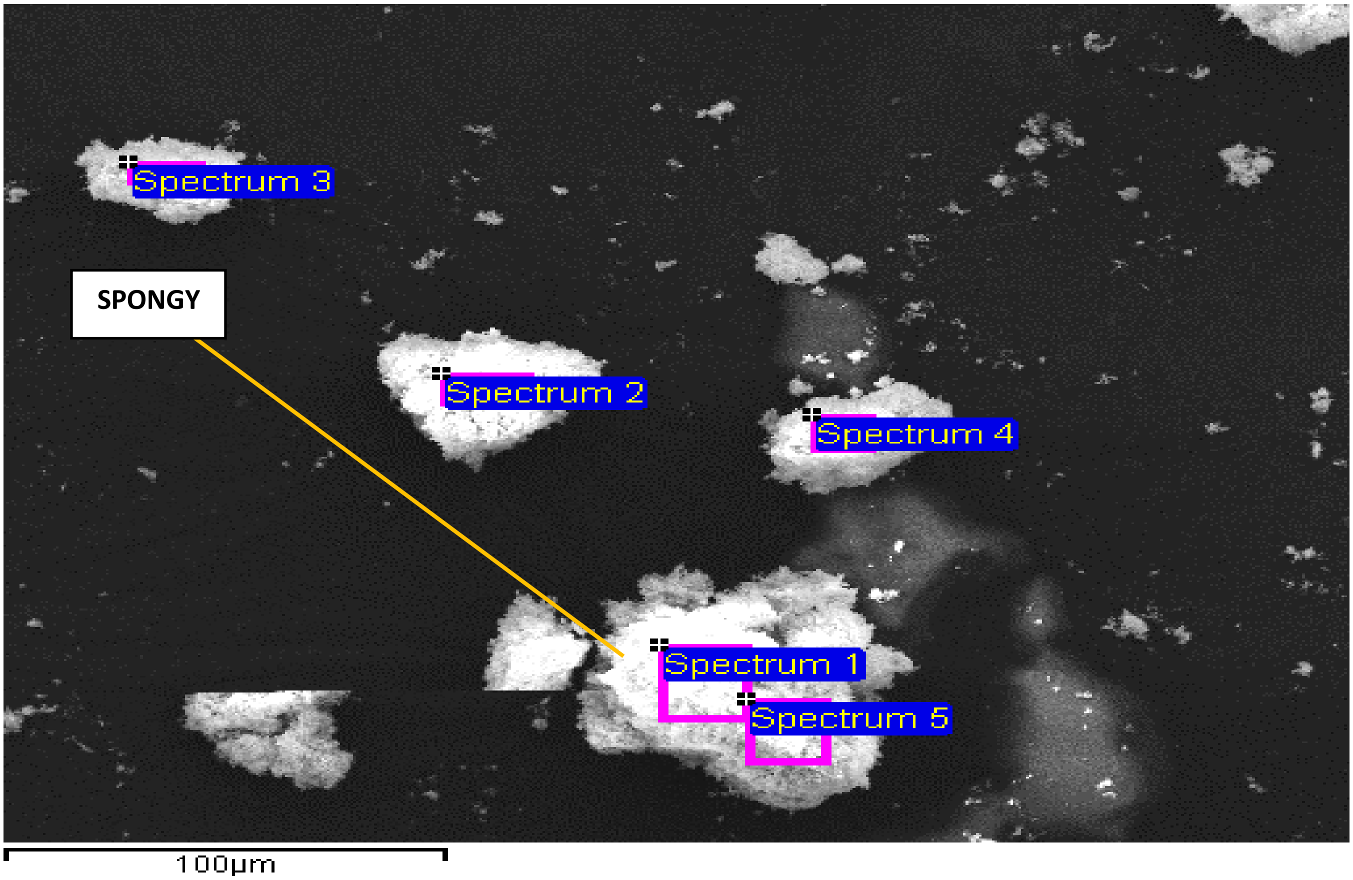


Figure 4.14a: Scanning electron photomicrograph showing spongy morphology of SCC 4

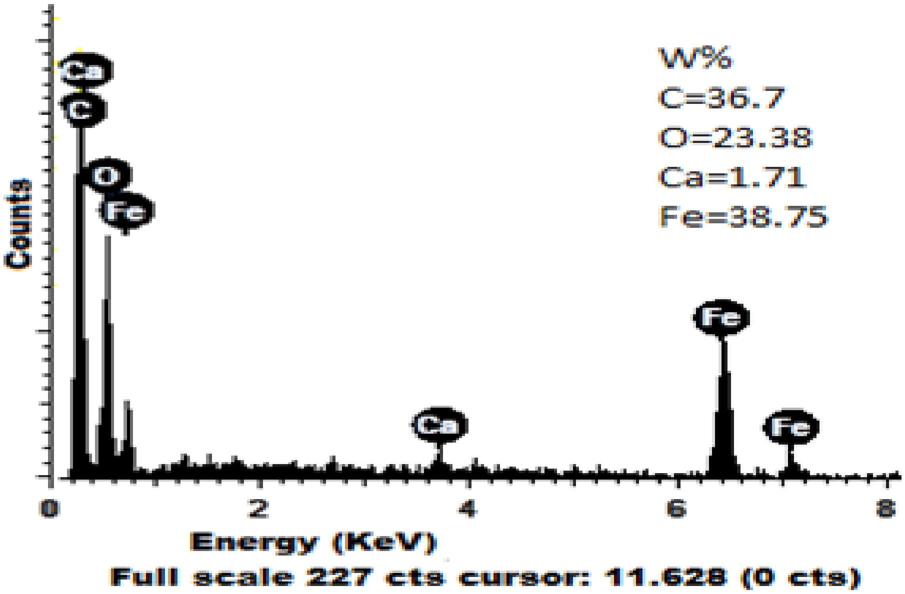


Figure 4.14b: Micro-elemental analysis of sample from SCC 4

Table 4.16: Percentage composition of different elements present in sample SCC 4

Spectrum	C	O	Ca	Fe	Total
Spectrum 1	26.32	14.51	1.19	57.98	100
Spectrum 2	46.19	33.84	0.88	19.09	100
Spectrum 3	34.17	37.23	0.72	27.88	100
Spectrum 4	16.06	7.75	5.29	70.89	100
Spectrum 5	58.09	23.55	0.46	17.9	100
Mean	**36.17**	**23.38**	**1.71**	**38.75**	**100**
Max.	**58.09**	**37.23**	**5.29**	**70.89**	
Min.	16.06	7.75	0.46	17.9	

Spot analysis of SCC 5 sample (Figure 4.15a) revealed that the elemental composition of the major residues is dominated by Si, O and Al (Figure 4.15b) with the presence of amorphous image (Figure 4.15a). Fe was also present, possibly due to ion-exchange.

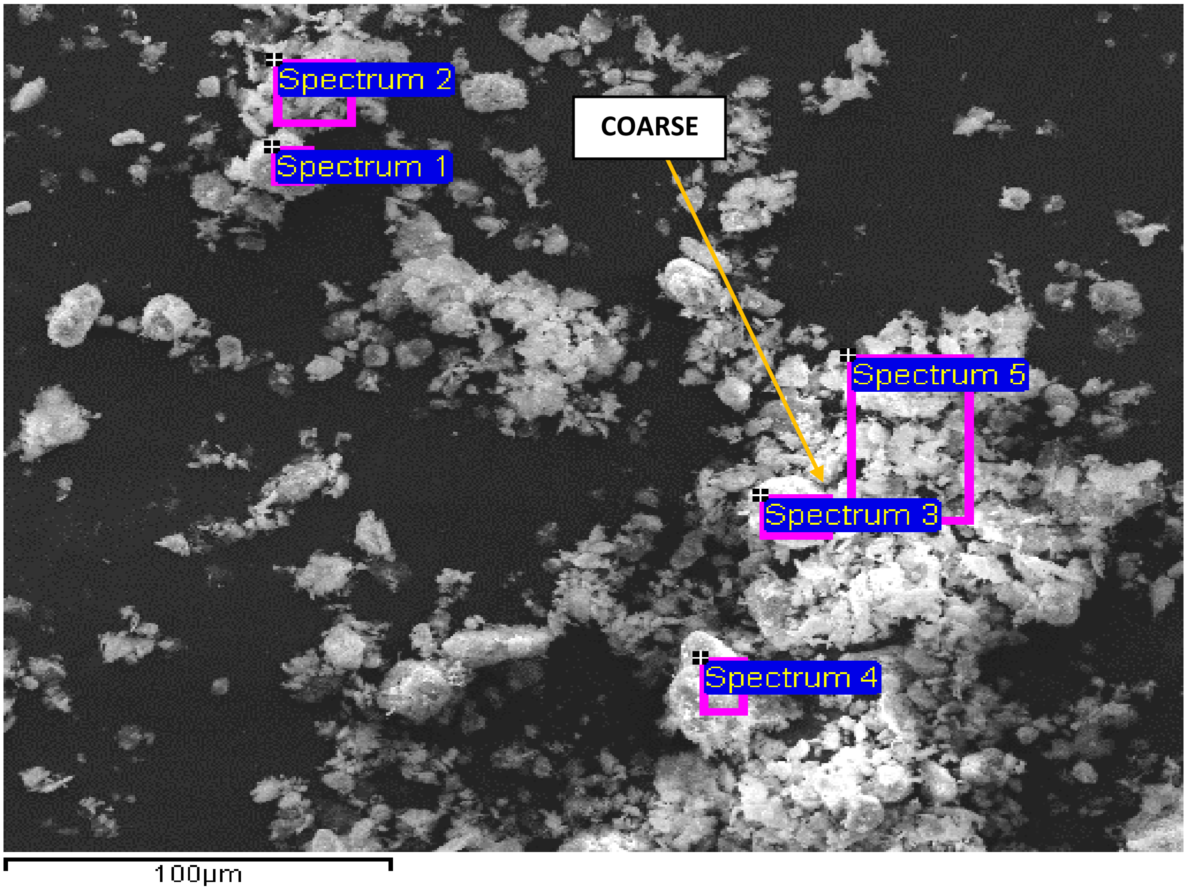


Figure 4.15a: Scanning electron photomicrograph showing coarse morphology of SCC 5

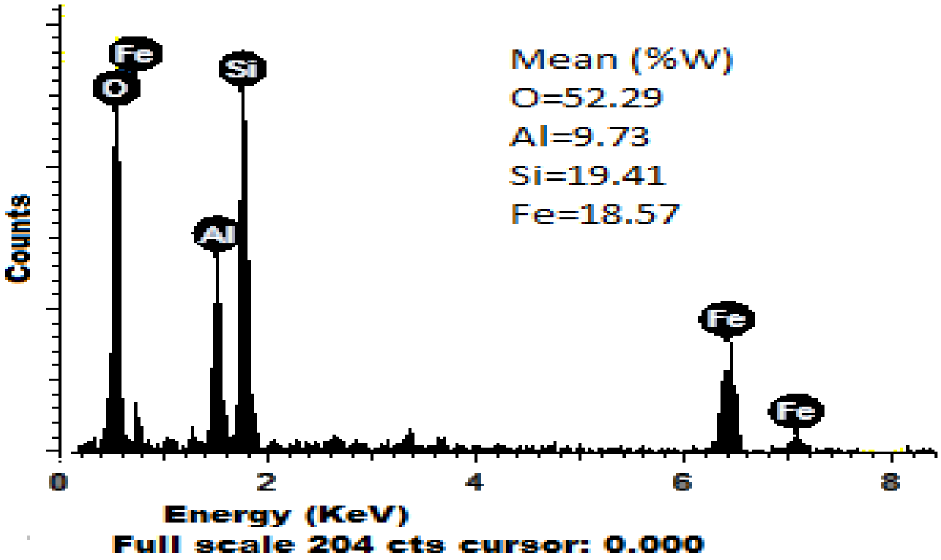


Figure 4.15b: Micro-elemental analysis (EDX) of sample from SCC 5

Table 4.17: Percentage composition of different elements present in sample SCC 5

Spectrum	O	Al	Si	Fe	Total
Spectrum 1	50.77	9.22	19.61	20.4	100
Spectrum 2	50.62	7.73	23.91	17.74	100
Spectrum 3	55.28	12.33	20.98	11.42	100
Spectrum 4	50.35	8.03	13.33	28.29	100
Spectrum 5	54.44	11.33	19.25	14.98	100
Mean	**52.29**	**9.73**	**19.41**	**18.57**	**100**
Max.	55.28	12.33	23.91	28.29	
Min.	50.35	7.73	13.33	11.42	

At 100 µm the spot analysis showed some spherical agglomerates (Figure 4.16a) with the presence of carbon and oxygen (Figure4.16b) which might be introduced into the clay matrices from the atmosphere. Table 4.18 below summarises the level of concentrations of each element.

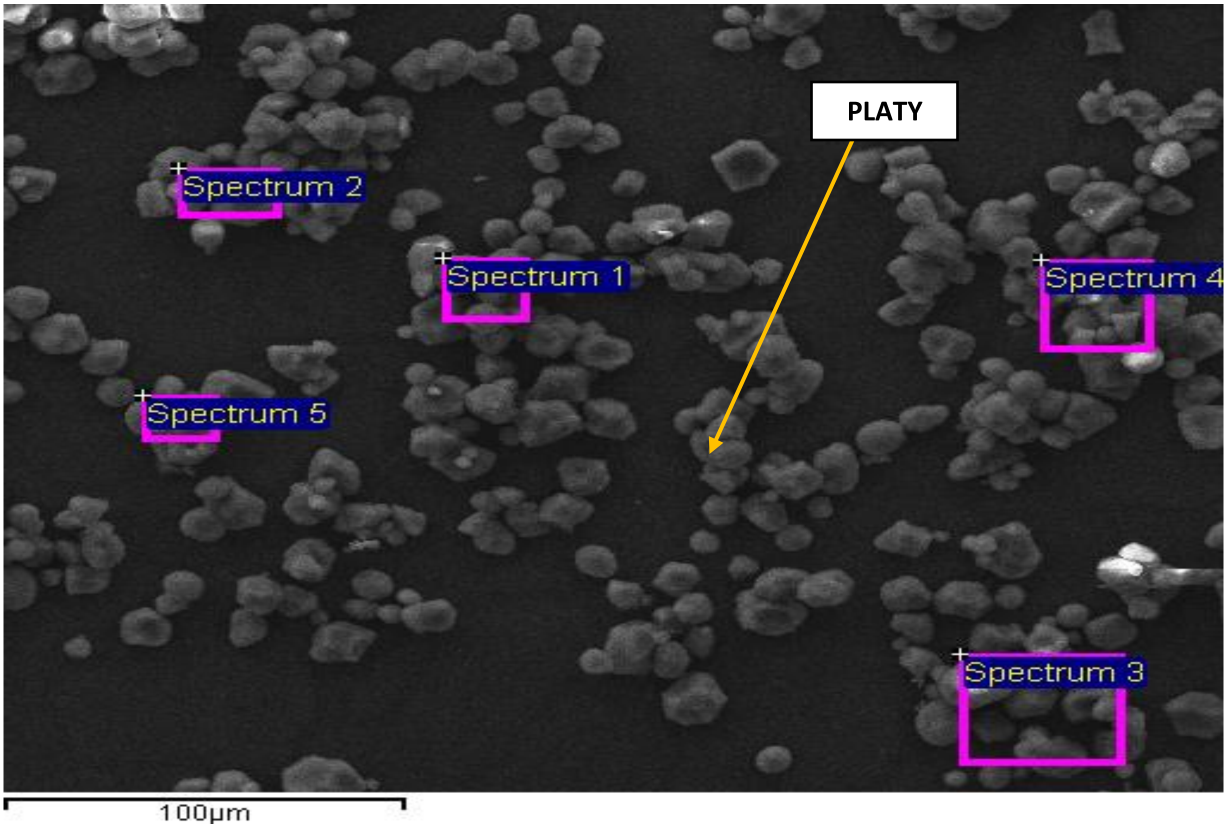


Figure 4.16a: Scanning electron photomicrograph showing platy morphology of SCC 6

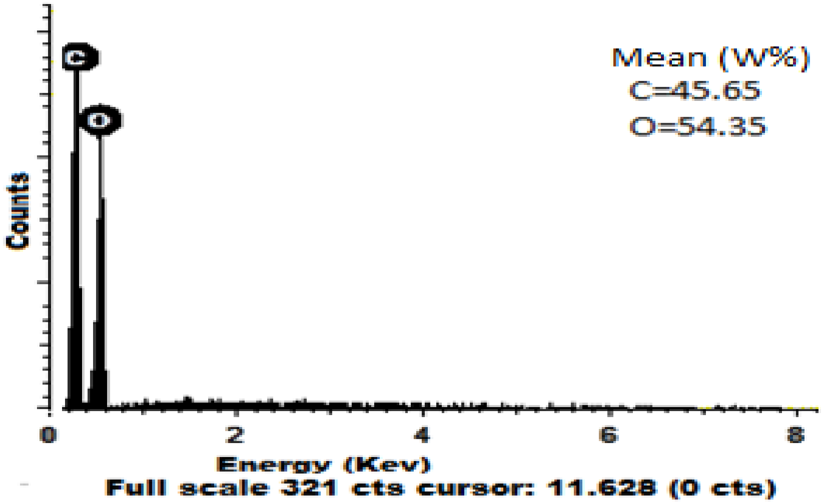


Figure 4.16b: Micro-elemental analysis (EDX) of sample from SCC 6

Table 4.18: Percentage composition of different elements present in sample SCC 6

Spectrum	C	O	Total
Spectrum 1	45.11	54.89	100
Spectrum 2	44.88	55.12	100
Spectrum 3	45.71	54.29	100
Spectrum 4	48.61	51.39	100
Spectrum 5	43.91	56.09	100
Mean	**45.65**	**54.35**	**100**
Max.	48.61	56.09	
Min.	43.91	51.39	

A white patchy flaky image was obtained from the SEM micrograph (Figure 4.17a), indicating that the earthy material contains kaolinitic properties. High levels of base cations (Ca and K) were present, which can be very good exchangeable cation (Figure 4.17b). The mean percentages of the various elements obtained from sample SCC 7 is summarised in Table 4.19.

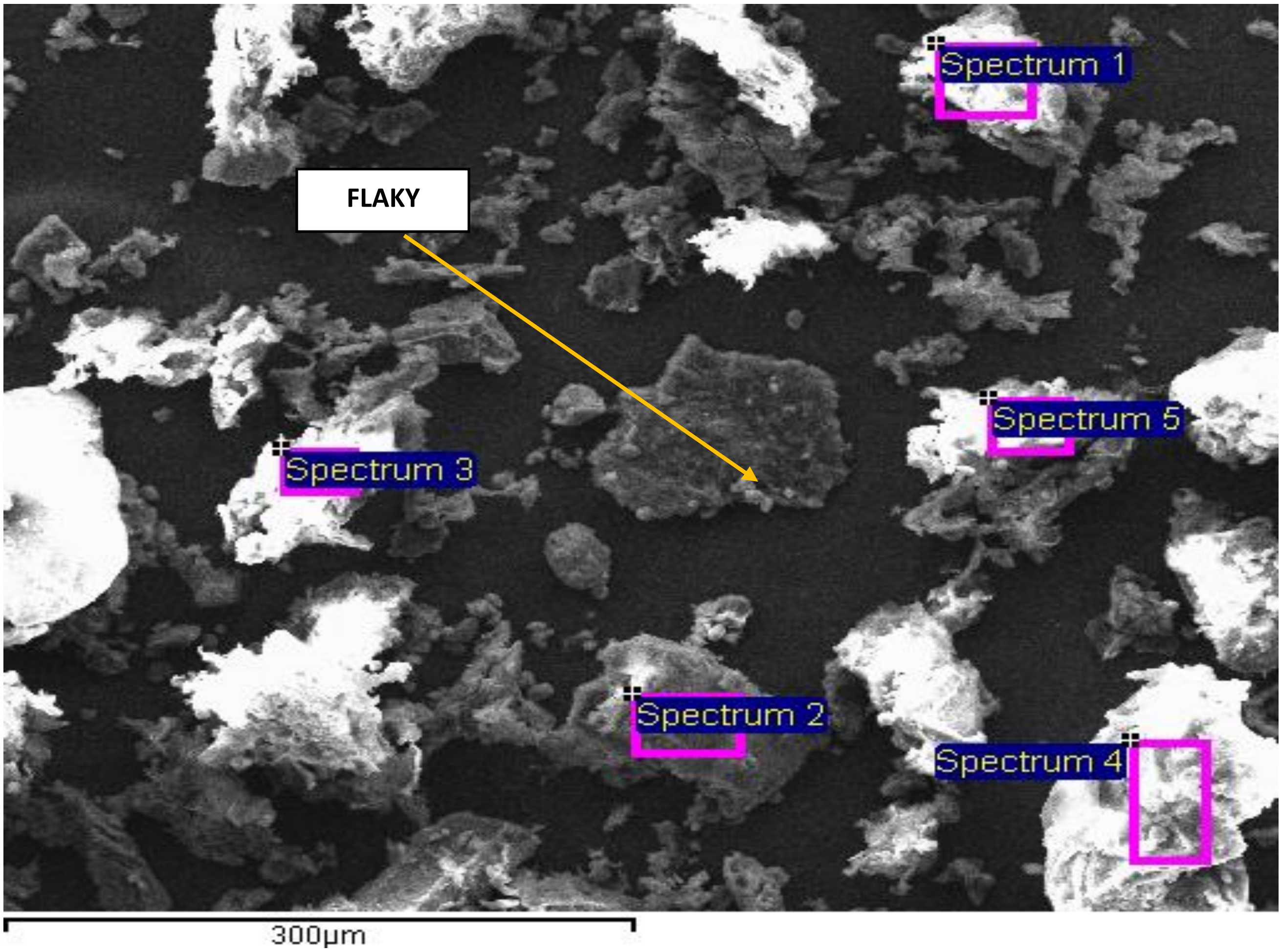


Figure 4.17a: Scanning electron photomicrograph showing flaky morphology of SCC 7

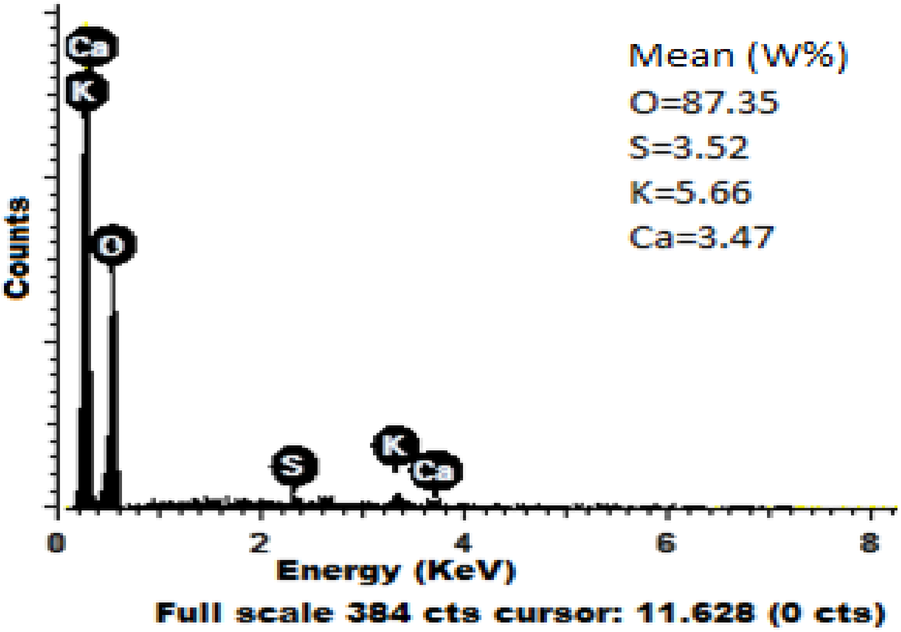


Figure 4.17b: Micro-elemental analysis (EDX) of sample from SCC 7

Table 4.19: Percentage composition of different elements present in sample SCC 7

Spectrum	O	S	K	Ca	Total
Spectrum 1	94.6	2.31	3.09	0	100
Spectrum 2	90.84	2.01	3.52	3.62	100
Spectrum 3	83.35	3.46	5.51	7.68	100
Spectrum 4	81.72	6.51	11.77	0	100
Spectrum 5	86.21	3.33	4.4	6.06	100
Mean	**87.35**	**3.52**	**5.66**	**3.47**	**100**
Max.	94.6	6.51	11.77	7.68	
Min.	81.72	2.01	3.09	0	

The SEM micrograph (Figure 4.18a) showed cylindrical plate like image, with the presence of O, S and Cu present. This is an indication that the material is copper (II) sulphate. Table 4.20 summarises the percentage compositions of the studied sample.

$Cu_{(s)}$ + $S_{(s)}$ + $2O_{2(g)}$ → $CuSO_{4(s)}$ ....*eqn* 4.3

Copper Sulphur Oxygen Copper (II) Sulphate (chalcanthite)

Copper (II) sulphate can occur in either hydrated or anhydrous form depending on the nature and also possess other chemical names or can be referred to with their mineral names. The sample confirmed the XRD result (Figure 4.55), which shows the present $CuSO_4$ is chalcanthite (pentahydrate). U.S Environmental Protection Agency 2009, stated that copper sulfate is not a skin irritant. Hence was classified to be very low in toxicity for dermal irritation but can be detrimental to man when accumulated in the body. Table 4.20 summarises the percentages of the various elements.

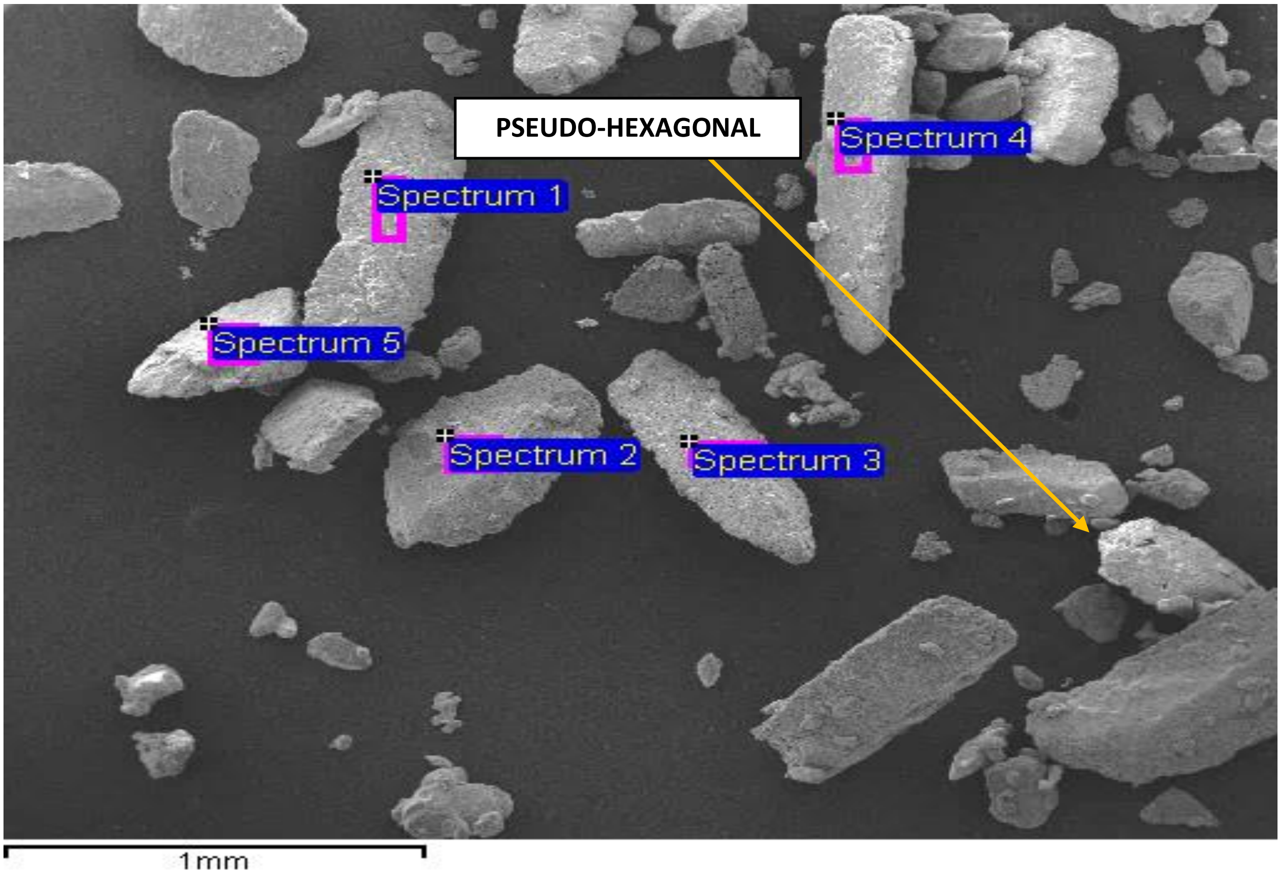


Figure 4.18a: Scanning electron photomicrograph showing pseudo-hexagonal morphology of SCC 8

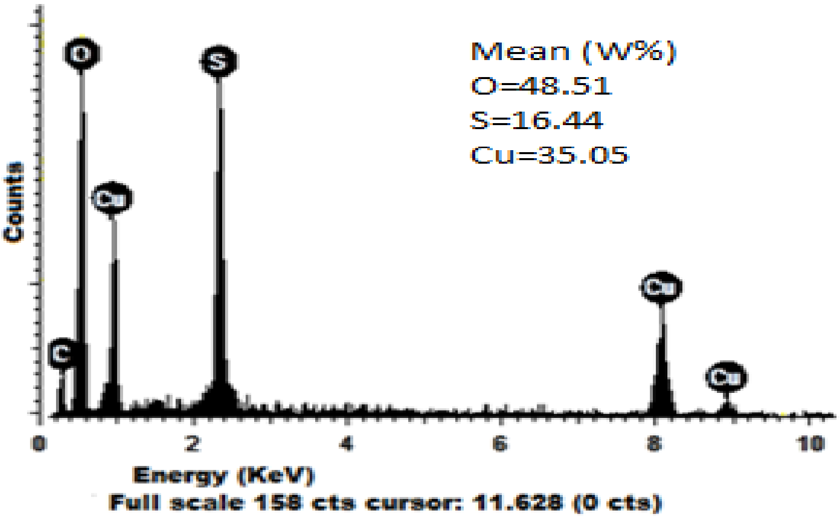


Figure 4.18b: Micro-elemental analysis of sample from SCC 8

Table 4.20: Percentage composition of different elements present in sample SCC 8

Spectrum	O	S	Cu	Total
Spectrum 1	48.08	18.73	33.19	100
Spectrum 2	43.69	16.11	40.2	100
Spectrum 3	54.55	15.86	29.59	100
Spectrum 4	45	13.85	41.15	100
Spectrum 5	51.2	17.65	31.15	100
Mean	**48.51**	**16.44**	**35.05**	**100**
Max.	**54.55**	**18.73**	**41.15**	
Min.	43.69	13.85	29.59	

A coarse structure was obtained on the analysed sample (Figure 4.19a). The SCC 9 sample exhibited the same elemental composition as SCC 1 (Figure 4.19b), which indicates that both materials are from the same country but not from same geology because there were some variations in the percentage compositions of both earthy materials. Some elements present are C, O, Mg, Al, Si and Fe (Table 4.21). The presence of C and O on the clay matrices may have been introduced into the clay surfaces from the atmosphere.

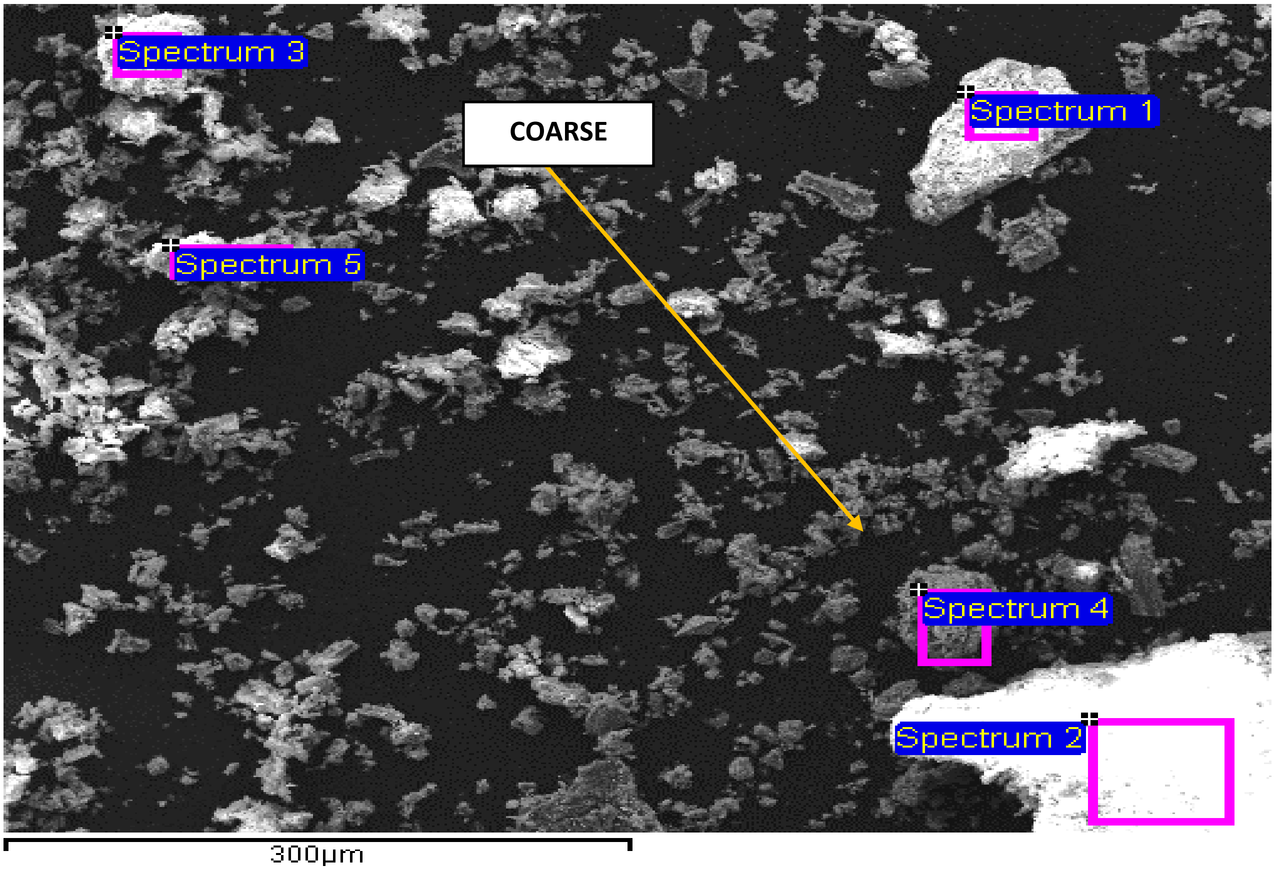


Figure 4.19a: Scanning electron photomicrograph showing coarse morphology of SCC 9

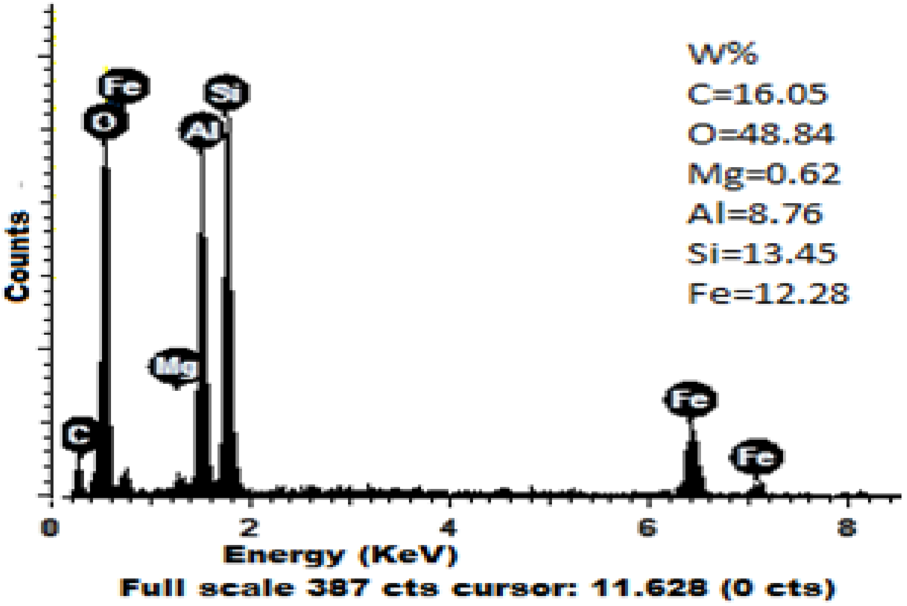


Figure 4.19b: Micro-elemental analysis of sample from SCC 9

Table 4.21: Percentage composition of different elements present in sample SCC 9

Spectrum	C	O	Mg	Al	Si	Fe	Total
Spectrum 1	12.84	48.25	0.43	11.7	14.98	11.8	100
Spectrum 2	8.04	52.75	0.99	8.33	15.53	14.36	100
Spectrum 3	13.84	47.8	1.2	6.75	15.66	14.75	100
Spectrum 4	16.58	47.7	0.48	9.86	12.45	12.93	100
Spectrum 5	28.93	47.7	0	7.16	8.63	7.58	100
Mean	**16.05**	**48.84**	**0.62**	**8.76**	**13.45**	**12.28**	**100**
Max.	**28.93**	**52.75**	**1.2**	**11.7**	**15.66**	**14.75**	
Min.	8.04	47.7	0	6.75	8.63	7.58	

The spot analysis of SCC 10 (Figure 4.20a) showed the same elemental constituents with SCC 7 (Ca, K, O and S) (Figures 4.20b and 4.17b). High levels of base cations (Ca and K) were present indicating that these are the exchangeable cations on the clay interlayers.

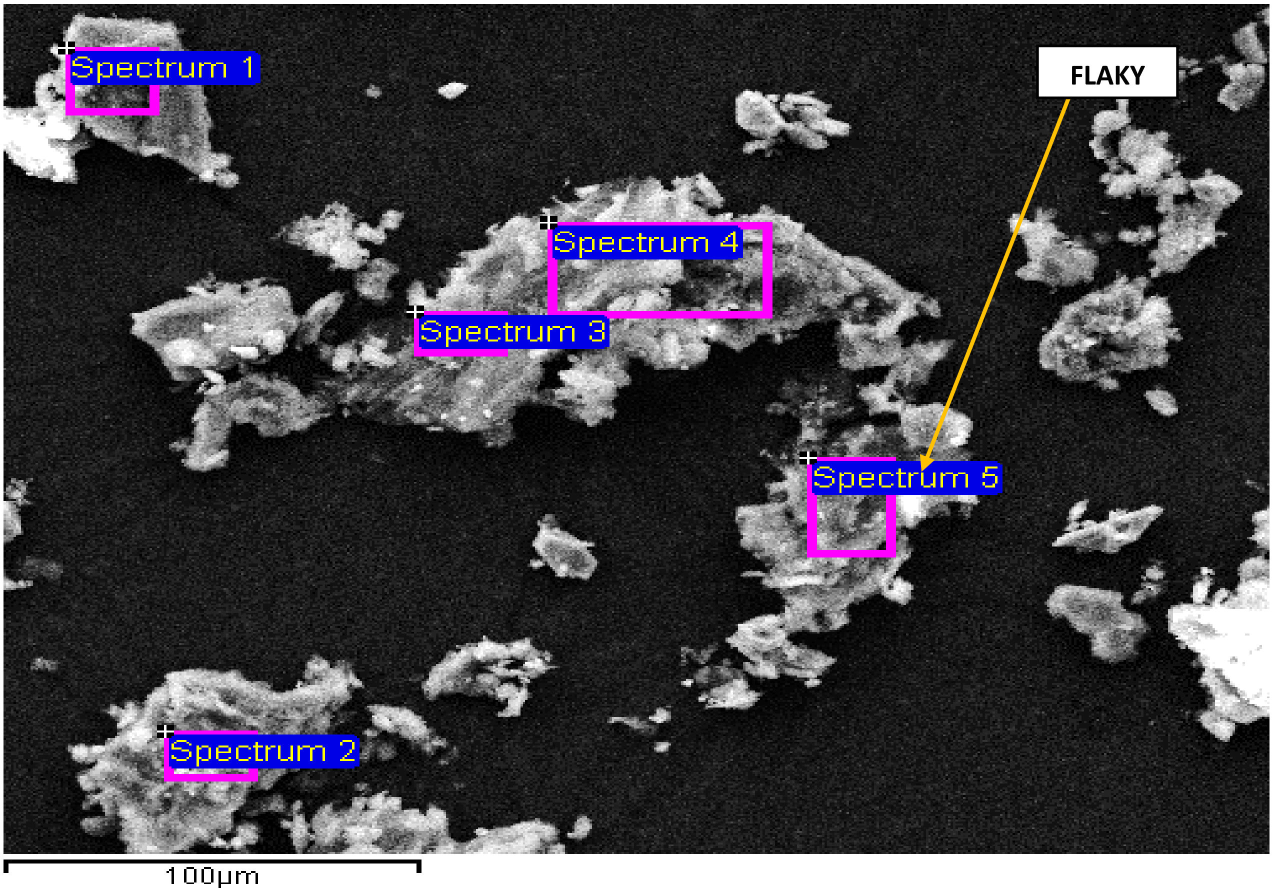


Figure 4.20a: Scanning electron photomicrograph showing flaky morphology of SCC 10

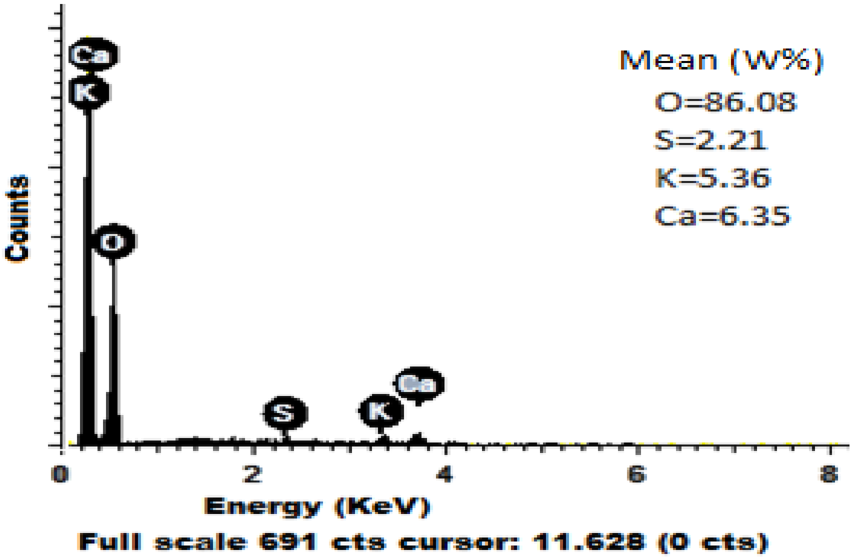


Figure 4.20b: Micro-elemental analysis (EDX) of sample from SCC 10

Table 4.22: Percentage composition of different elements present in sample SCC 10

Spectrum	O	S	K	Ca	Total
Spectrum 1	92.04	1.34	2.31	4.31	100
Spectrum 2	89.04	1.7	4.17	5.09	100
Spectrum 3	77.61	2.71	10.83	8.86	100
Spectrum 4	83.39	2.91	5.31	8.39	100
Spectrum 5	88.35	2.38	4.18	5.09	100
Mean	86.08	2.21	5.36	6.35	100
Max.	92.04	2.91	10.83	8.86	
Min.	77.61	1.34	2.31	4.31	

The SEM micrograph and elemental analyses (100 µm particle size) of samples from Thohoyandou in South Africa (Figures 4.21a and 4.21b, respectively. The spot analysis revealed that the elemental composition of the major residue are dominated by Si, O and Al (Figure 4.12b) and are mostly comparable to those presented (Figure 4.22b). Fe was also present, possibly due to ion-exchange. Same elemental composition was obtained in Tables 4.23 and 4.24 and both samples (SCC 11 and SCC 12) were collected from Thohoyandou, South Africa.

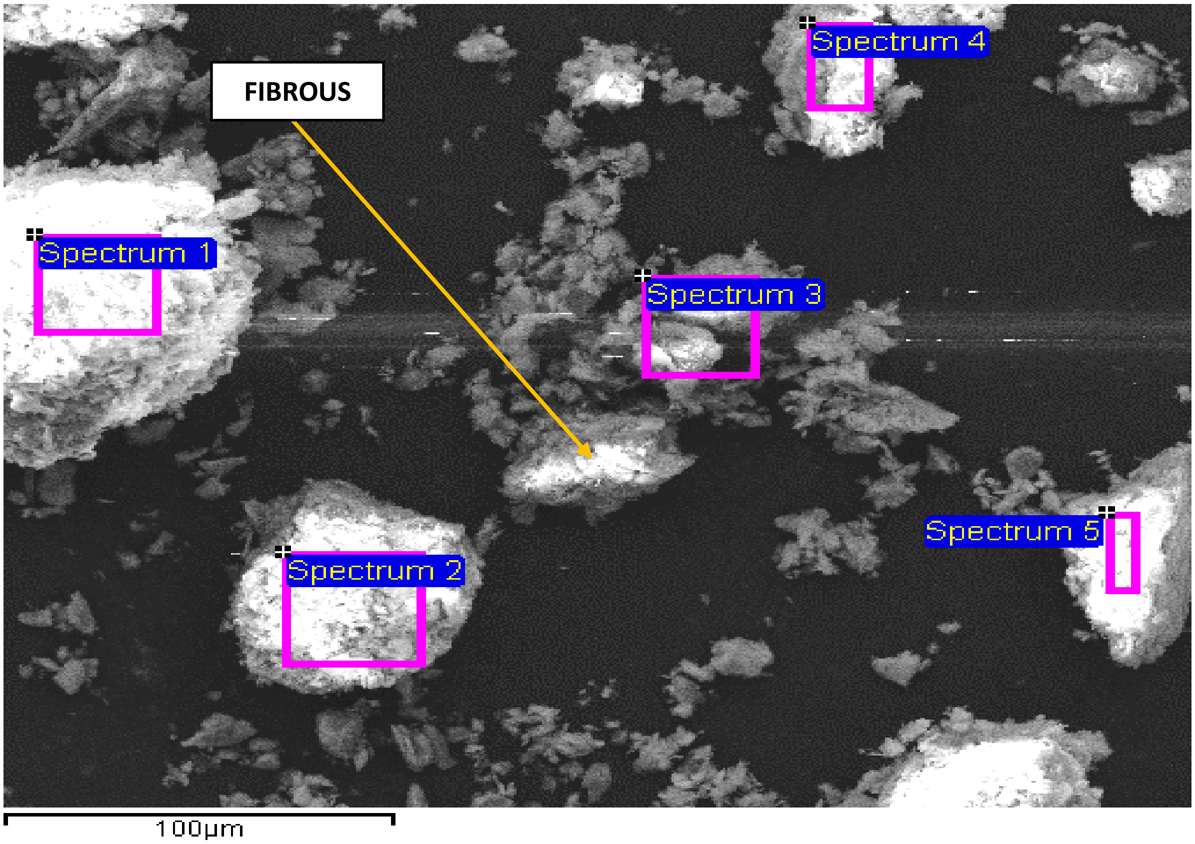


Figure 4.21a: Scanning electron photomicrograph showing fibrous morphology of SCC 11

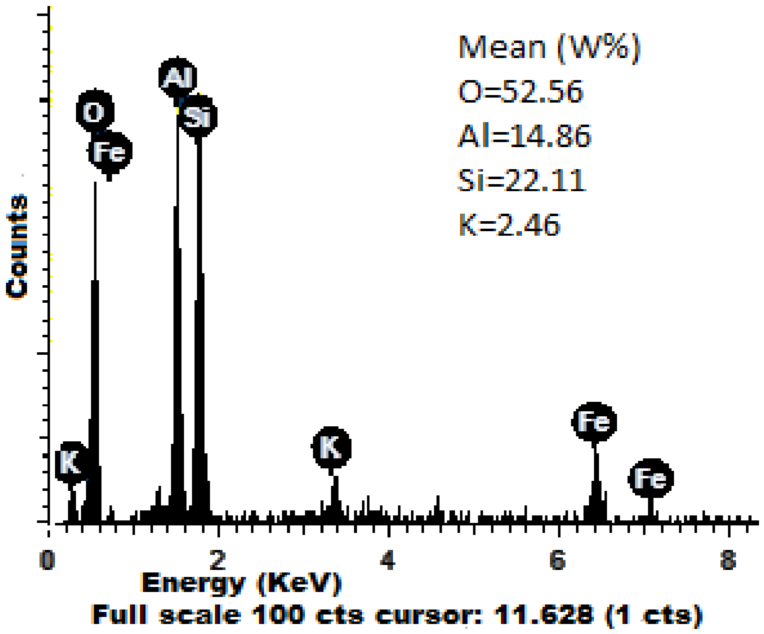


Figure 4.21b: Micro-elemental analyses (EDX) of samples from SCC 11

Table 4.23: Percentage composition of different elements present in sample SCC11

Spectrum	O	Al	Si	K	Fe	Total
Spectrum 1	47.62	16.38	23.33	2.25	10.43	100
Spectrum 2	55.08	14.67	24.15	1.78	4.32	100
Spectrum 3	56.28	13.77	19.45	2.93	7.56	100
Spectrum 4	48.87	15.03	23.04	2.79	10.27	100
Spectrum 5	54.93	14.44	20.6	2.56	7.47	100
Mean	52.56	14.86	22.11	2.46	8.01	100
Max.	56.28	16.38	24.15	2.93	10.43	
Min.	47.62	13.77	19.45	1.78	4.32	

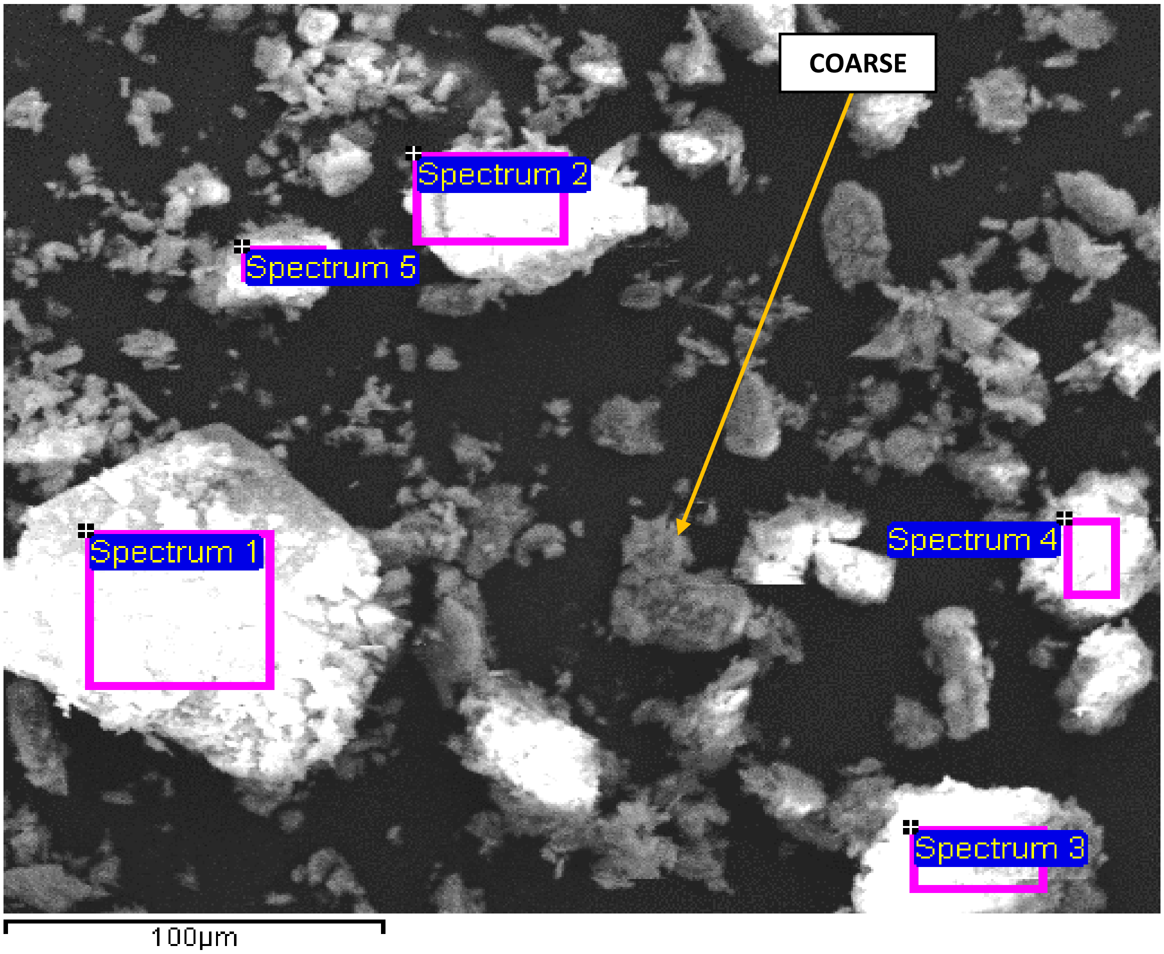


Figure 4.22a: Scanning electron photomicrograph showing coarse morphology of SCC 12

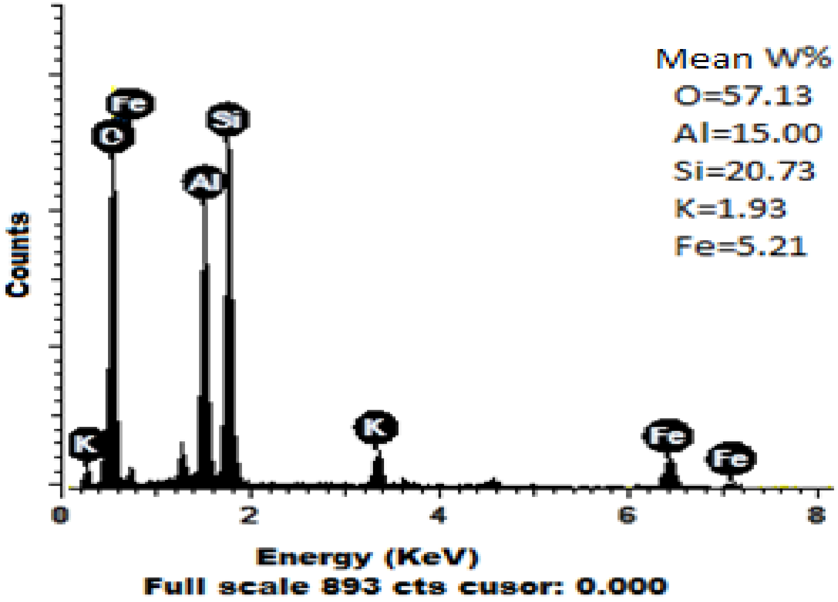


Figure 4.22b: Micro-elemental analyses (EDX) of samples from SCC 12

Table 4.24: Percentage composition of different elements present in sample SCC 12

Spectrum	O	Al	Si	K	Fe	Total
Spectrum 1	57.55	13.60	19.55	2.72	6.57	100
Spectrum 2	57.92	14.53	18.85	2.50	6.20	100
Spectrum 3	58.01	14.99	20.96	1.83	4.21	100
Spectrum 4	55.25	15.98	23.18	1.41	4.18	100
Spectrum 5	56.89	15.90	21.12	1.18	4.91	100
Mean	**57.13**	**15.00**	**20.73**	**1.93**	**5.21**	**100**
Max.	58.01	15.98	23.18	2.72	6.57	
Min.	55.25	13.6	18.85	1.18	4.18	

The Kruskal-Wallis H test (Dunn's multiple comparisons test) on the percentage composition of the different elements from the studied sites showed that there is extremely significant ($P < 0.0001$) (Appendix 1). This implies that the percentage composition of the elements in each samples differs/ varies significantly from one another. Generally, the predominant element are oxygen and silicon which consist quartz in the samples. Hence, making the samples to be harsh/brassy (that is non-user friendly) when applied as cosmetics.

4.4 Physisorption isotherm of the studied earthy materials

There is a great need for complete description of the state of earthy materials which are being applied topically. A total of twenty-two representative samples were analysed for physisorption where BET method was incorporated for surface area and pore diameter (Rouguerol *et al*. 1988). Gregg *et al.* (1982) discussed some isotherm measurements and this was used in the interpretation of the graphs according to their porosity and relating it to the IUPAC standards as discussed in Chapter 2 (Table 2.6). The classification of the studied earthy materials is to determine the isotherm Type each representative sample belongs (Condon, 2006). To expedite the explanation of an adsorption data and the comparison between the studied earthy materials, there is a need to represent the adsorption data graphically. Table (Table 4.25) summarises the various studied samples with their country codes, isotherm types and interpretation. Interpretation and classification of the physisorption of the studied samples were based on overview reported by Condon (2006).

Table 4.25: Classifications of physical adsorption isotherms of the studied earthy materials

Countries	Samples	Adsorption Type
Botswana	BTS 1	II
	BTS 2	
Cameroon	CMR 1	
	CMR 2	
Nigeria	NG 1	
	NG 2	
Swaziland	SWL 1	
	SWL 2	
South Africa	SCC 4	
	SCC 5	
	SCC 8	
	SCC 9	
	SCC 11	
	SCC 12	
	SCC 2	III
	SCC 3	
	SCC 6	
	SCC 7	
	SCC 10	

Figures 4.23 - 4.44 shows N_2 adsorption desorption isotherm values at 90 ºC for 24 hours. The isotherm classification followed a method reported by Bansal and Goyal (2005). Type II isotherm were mostly exhibited in the studied samples as shown in Figures 4.23 - 4.44 they apply to a normal form of isotherm resulting on non-porous or macroporous adsorbent with high adsorption capacity (Sing *et al.,* 1985). This implies that the pore diameter > 50 nm. Hysteresis was not observed in some of the samples implying equal amount of adsorbed to desorbed. However, hysteresis loop occurred in some samples and shows a steep curve of the adsorption (Figures 4.25, 4.28, 4.30, 4.31, 4.33, 4.39 and 4.43), this results when the applied adsorbent are porous in nature (Wu *et al.,* 2005). Samples from South Africa fell under Type III classification (Figures 4.32, 4.33, 4.36, 4.37 and 4.40), this shows that the characteristics of the earthy materials were

not porous, or possibly macroporous, and have low energy of adsorption. There is no monolayer formation because the adsorbed-adsorbent interrelation are weak hence making the adsorbed molecules to cluster on the substrate site. The amount of adsorbed molecule are infinite ($p/p_0 > 1$) unlike Type II isotherm with finite saturation pressure ($p/p_0 = 1$), and the adsorbed monolayer becomes thicker (Thommes *et al*., 2006).

Type I, VI, V and VI isotherms were not observed in the studied materials, Figures 4.23 – 4.44 depicts a typical sorption isotherm with both adsorption and desorption graphs that was measured. The graph below shows an isotherm adsorption plot of quantity of the loaded sample (mmol/g) versus the adsorptive or relative pressure (p/p^o). Isotherms are applicable in the determination of surface area and porosity, most frequently used isotherms are Langmuir, freundljlich isotherm. The hysteresis exhibited by samples CMR 1, CMR 2, DRC A, DRC B, NG 2, SCC 1, SCC 9, SWL 1 and SWL 2 and SCC 3 is as a result of capillary condensation of the pores.

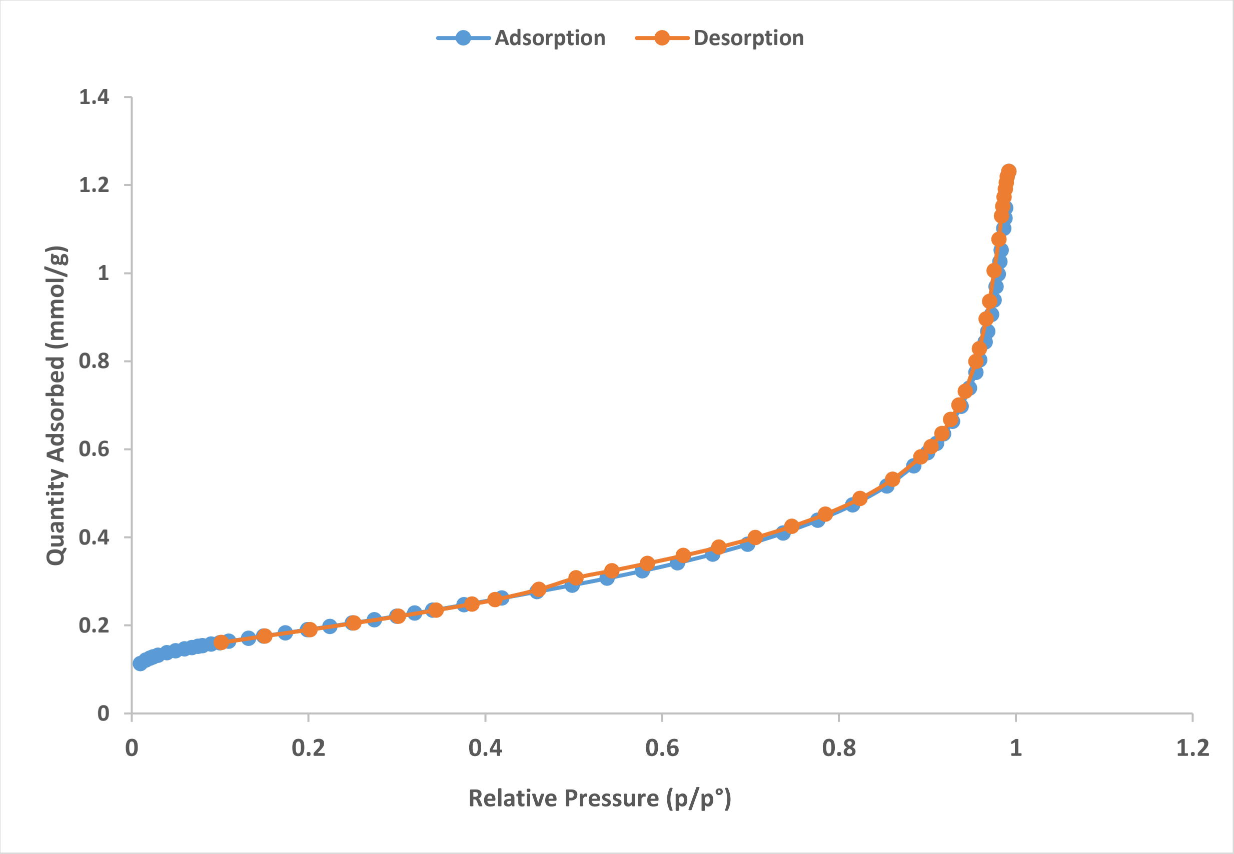


Figure 4. 23: Typical N_2 adsorption/desorption isotherm measured at 77 K of BST 1

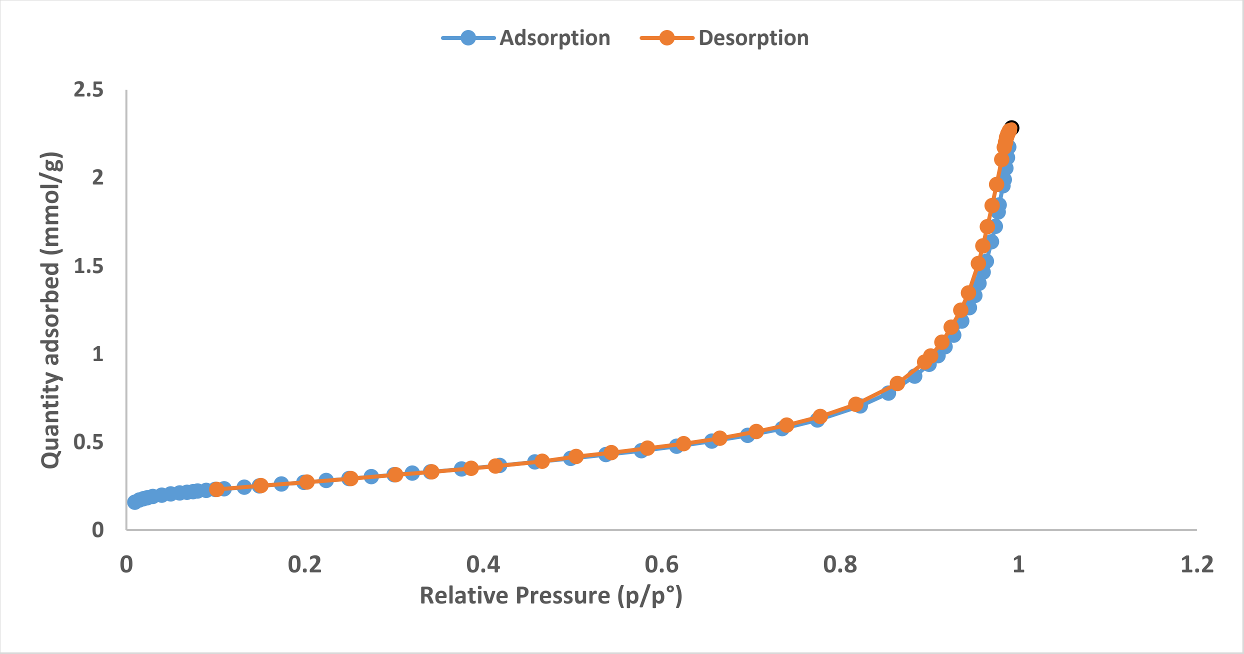


Figure 4. 24: Typical N_2 adsorption/desorption isotherm measured at 77 K of BST 2

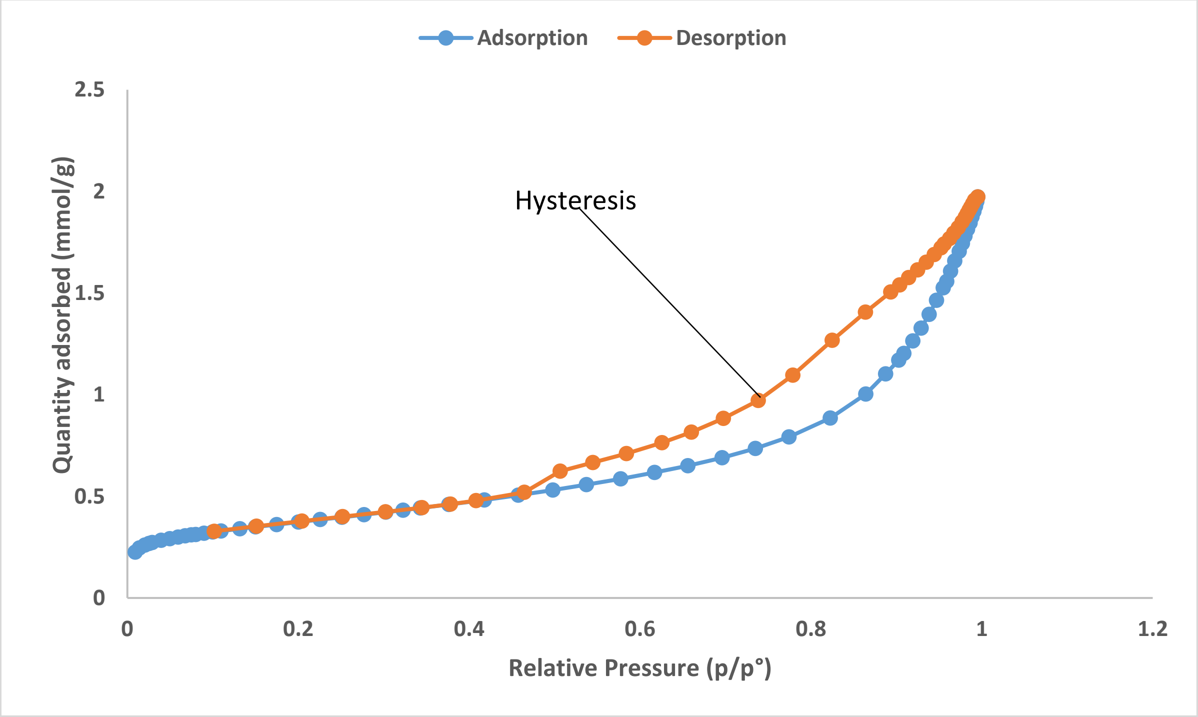


Figure 4. 25: Typical N_2 adsorption/desorption isotherm measured at 77 K of CMR 1

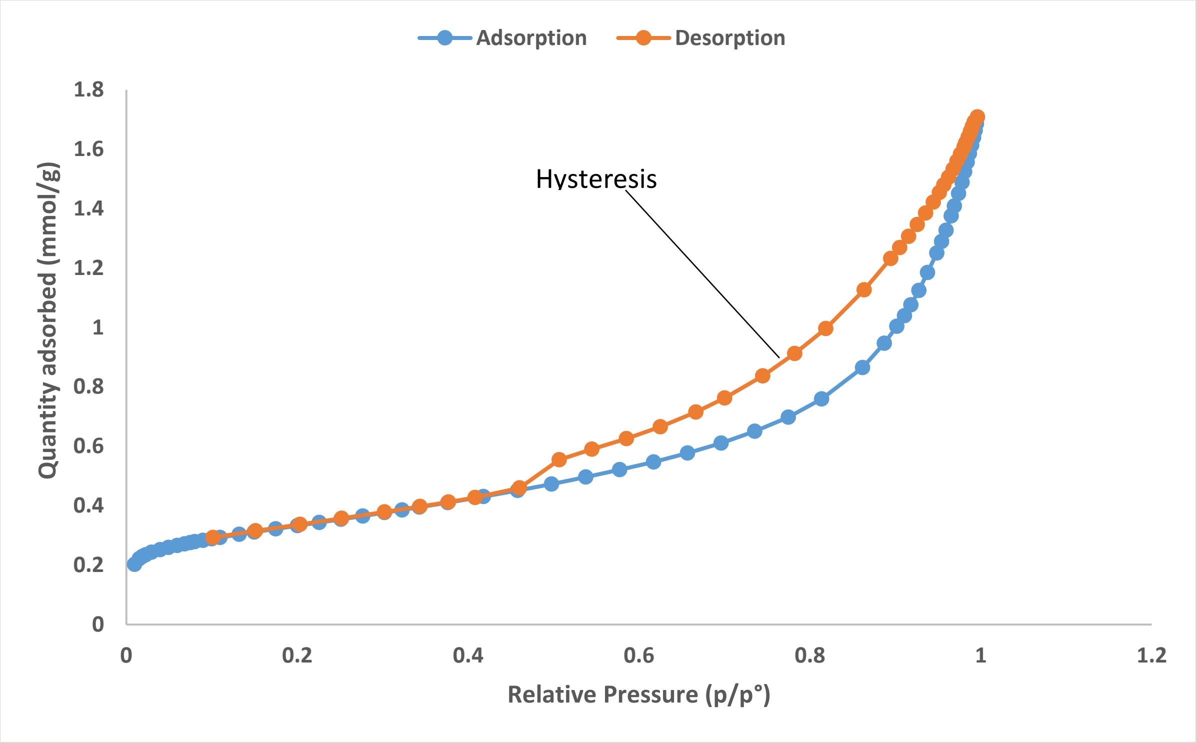


Figure 4. 26: Typical N_2 adsorption/desorption isotherm measured at 77 K of CMR 2

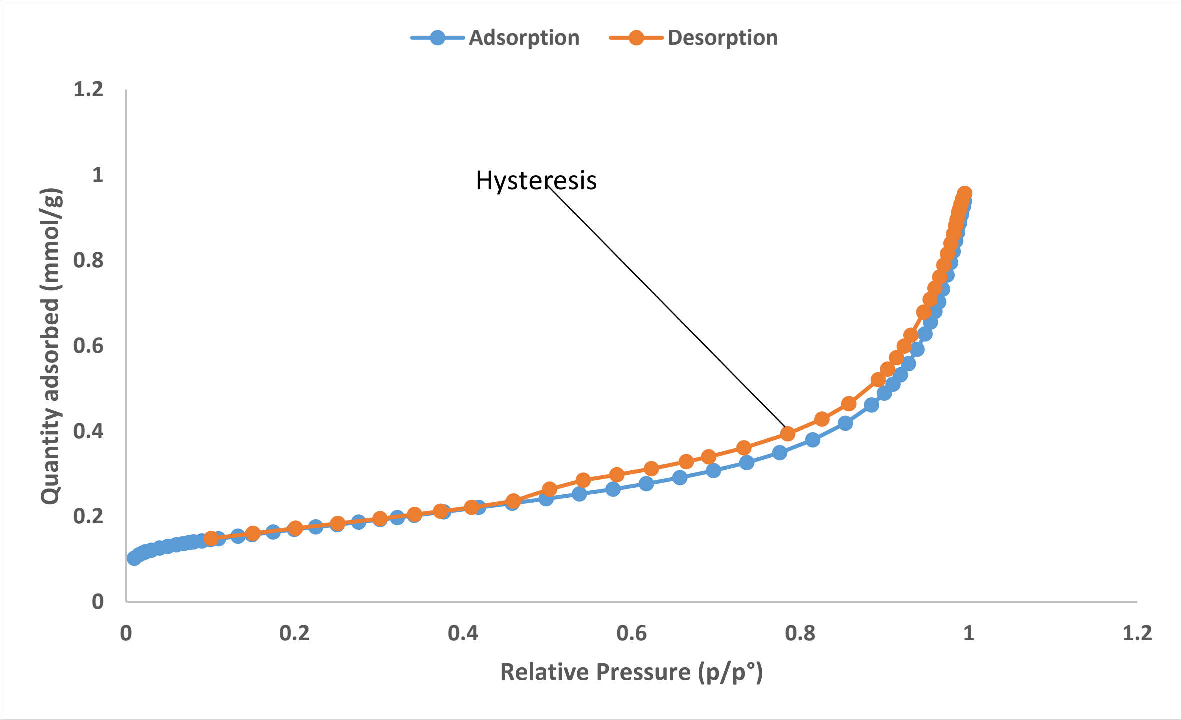


Figure 4. 27: Typical N_2 adsorption/desorption isotherm measured at 77 K of DRC 1

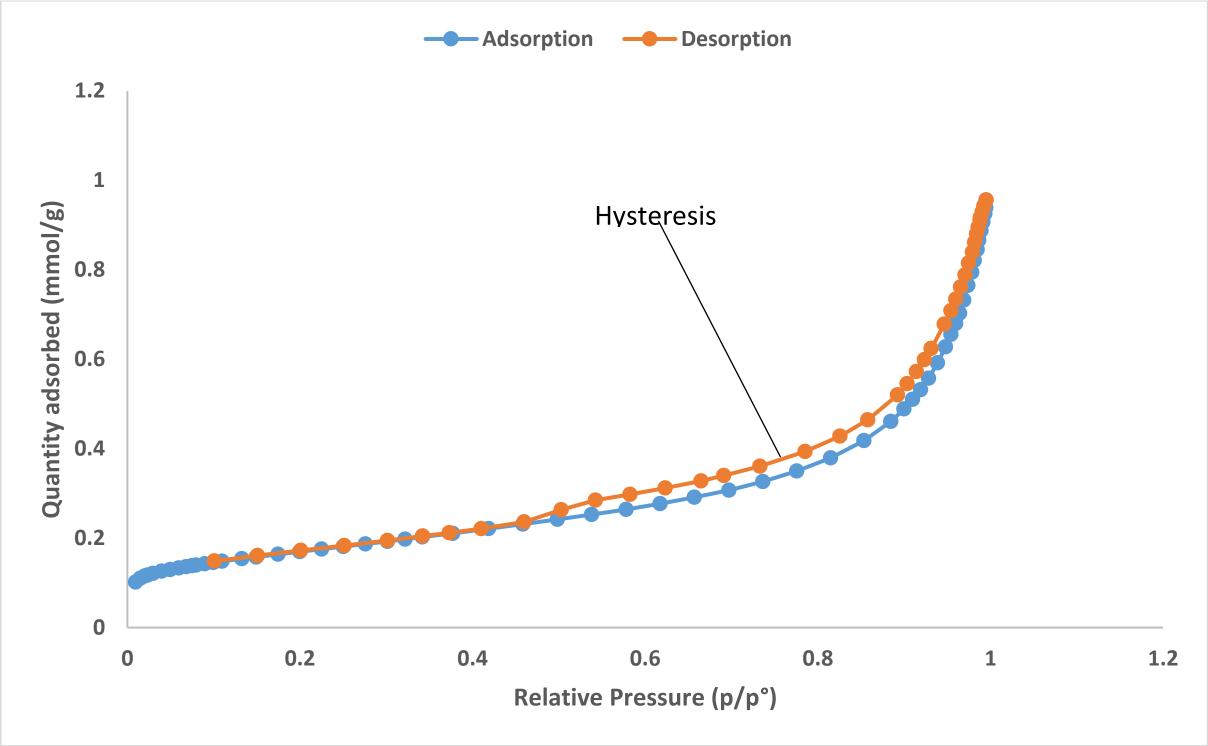


Figure 4. 28: Typical N_2 adsorption/desorption isotherm measured at 77 K of DRC 2

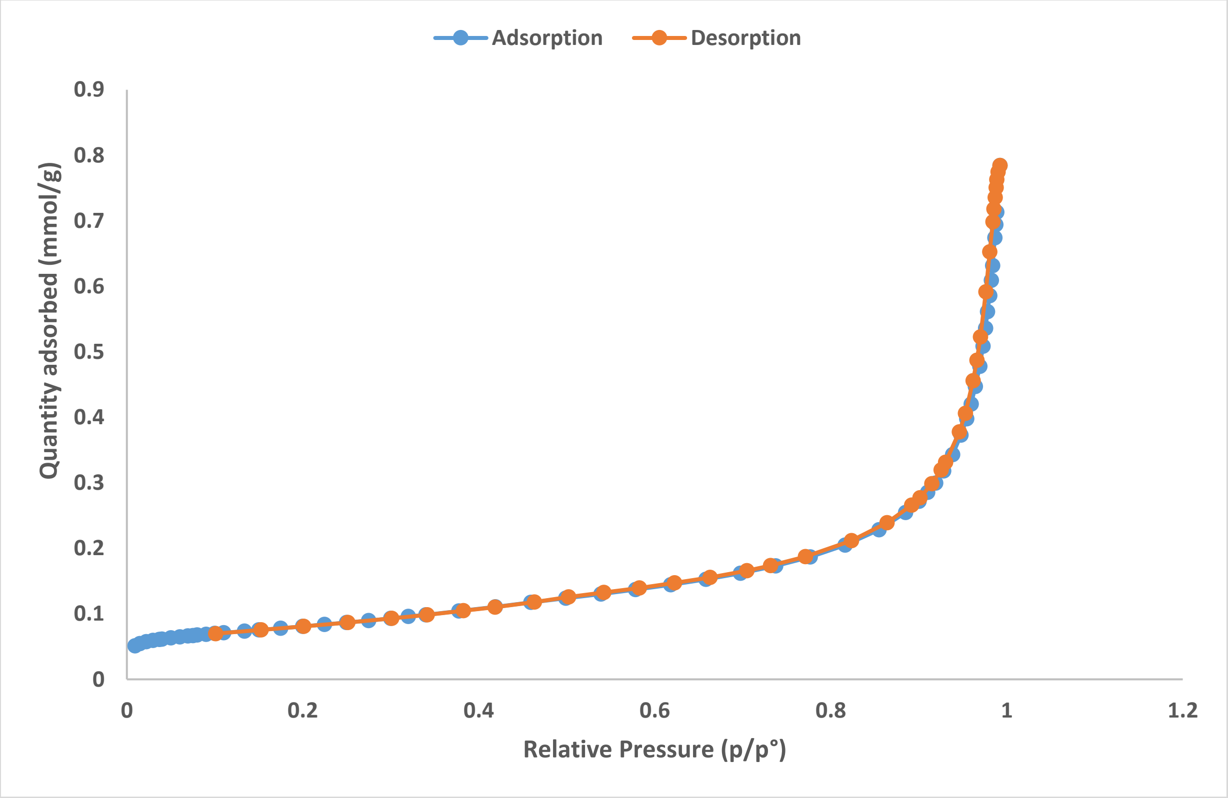


Figure 4. 29: Typical N_2 adsorption/desorption isotherm measured at 77 K of NG 1

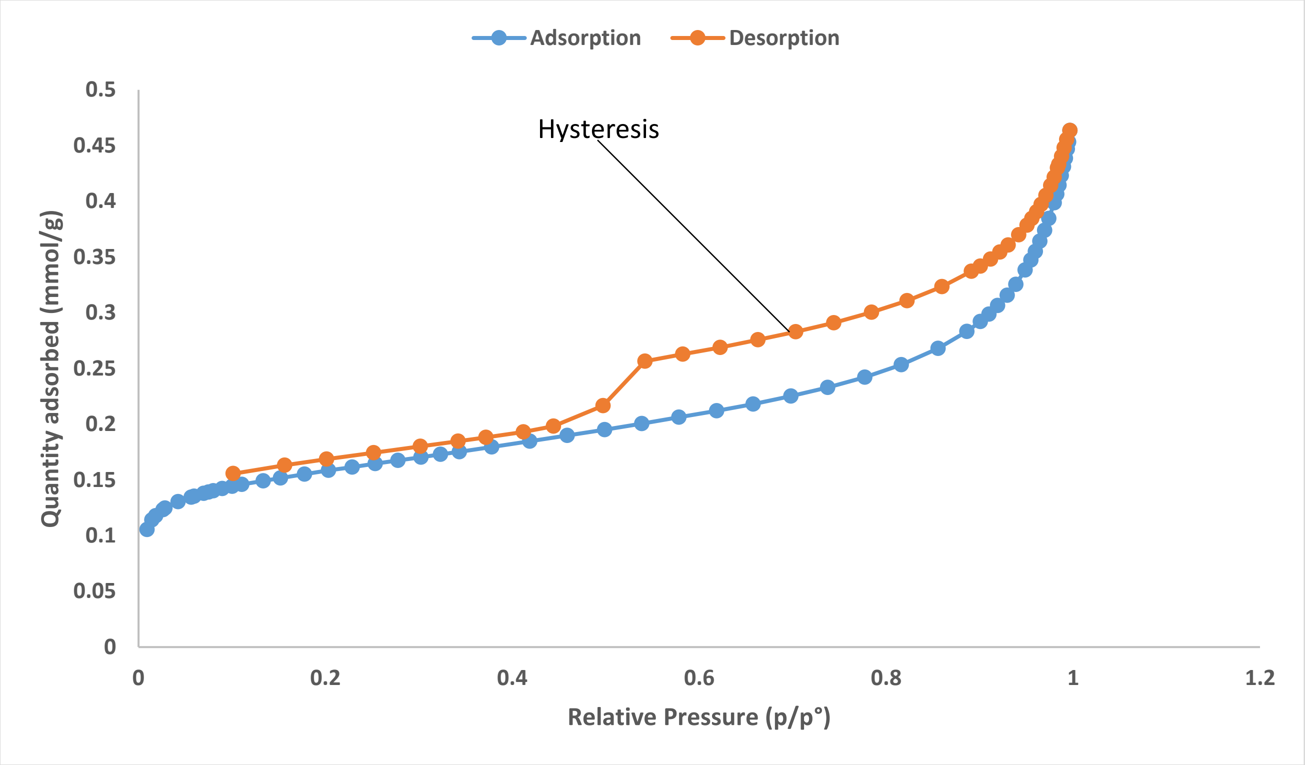


Figure 4. 30: Typical N_2 adsorption/desorption isotherm measured at 77 K of NG 2

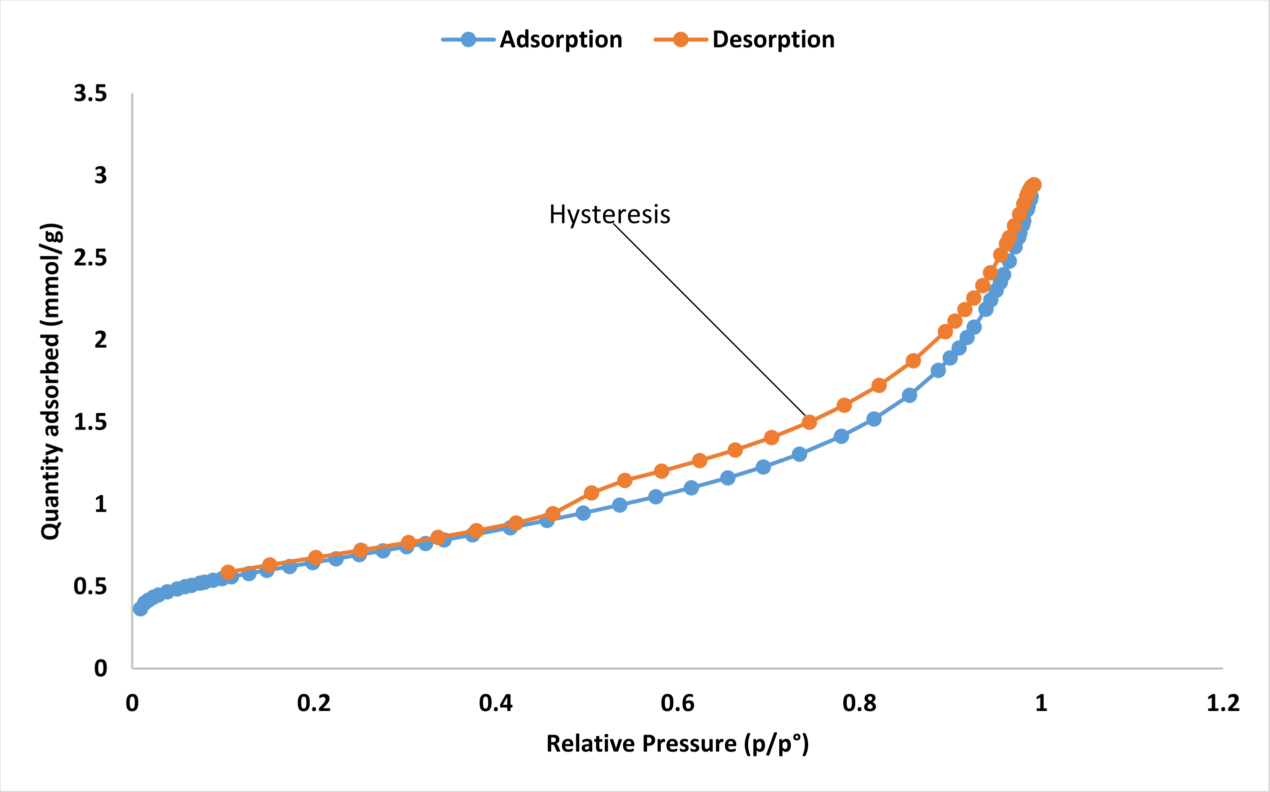


Figure 4. 31: Typical N_2 adsorption/desorption isotherm measured at 77 K of SCC 1

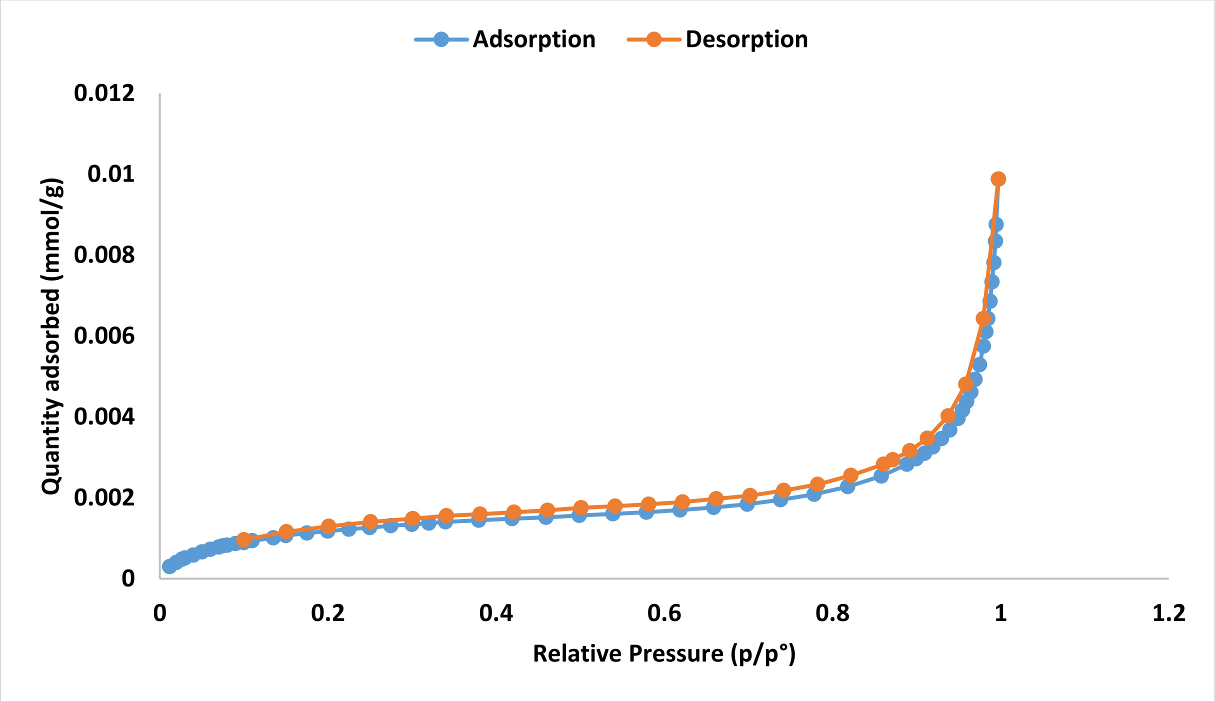


Figure 4. 32: Typical N_2 adsorption/desorption isotherm measured at 77 K of SCC 2

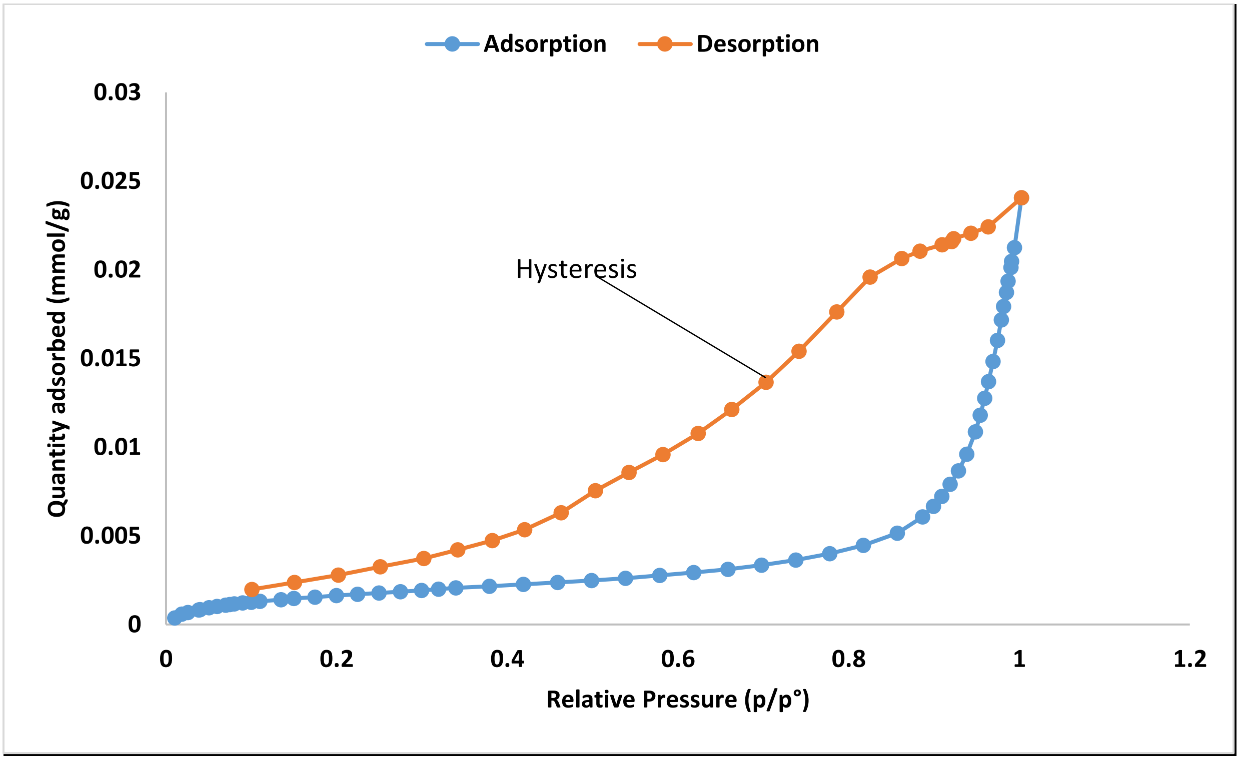


Figure 4. 33: Typical N_2 adsorption/desorption isotherm measured at 77 K of SCC 3

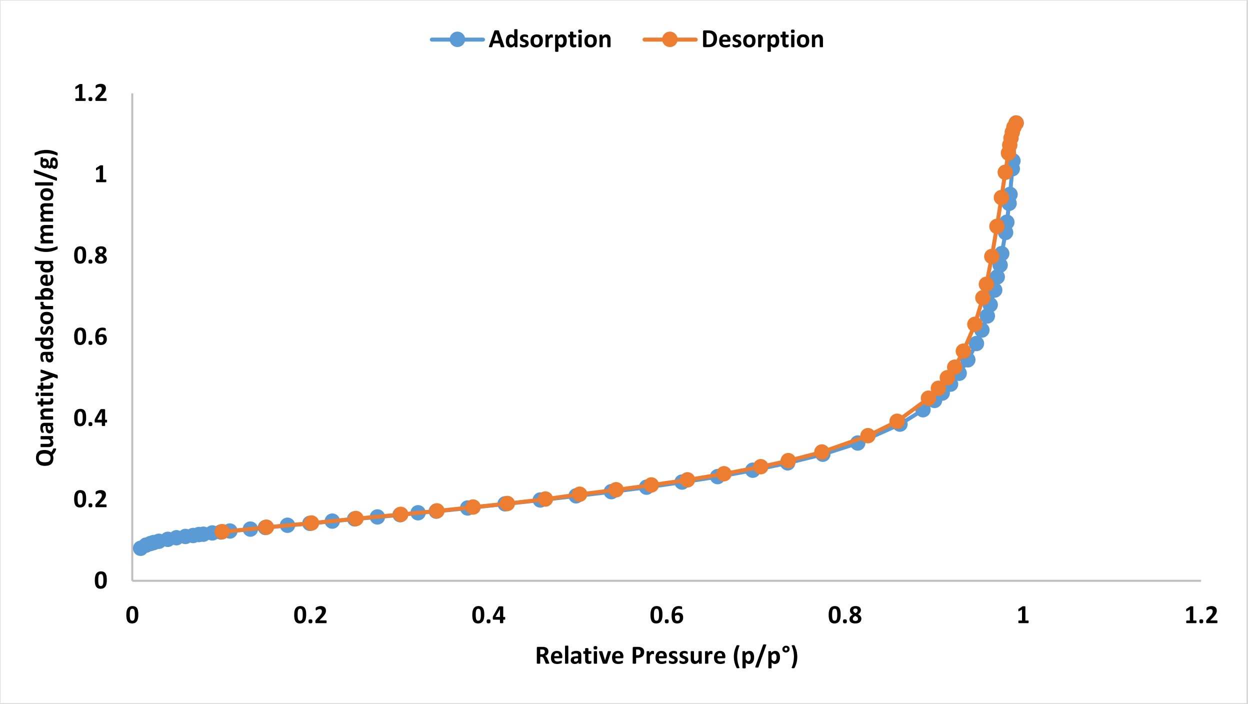


Figure 4. 34: Typical N_2 adsorption/desorption isotherm measured at 77 K of SCC 4

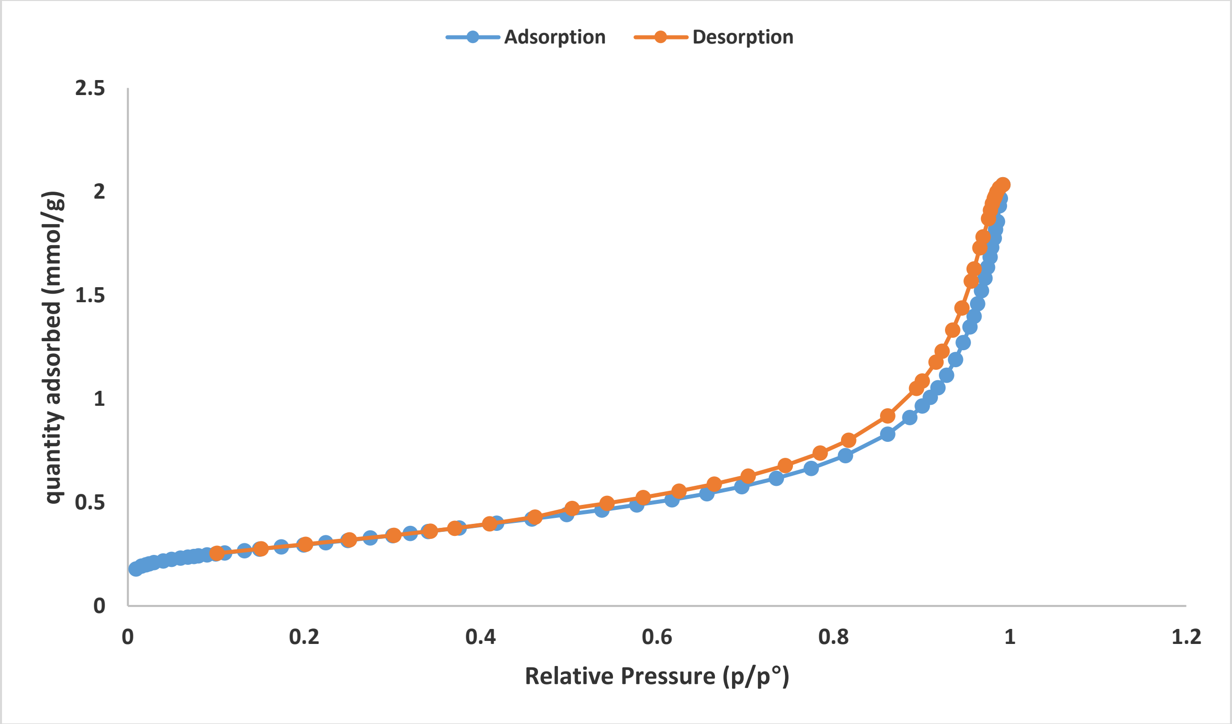


Figure 4.35: Typical N_2 adsorption/desorption isotherm measured at 77 K of SCC 5

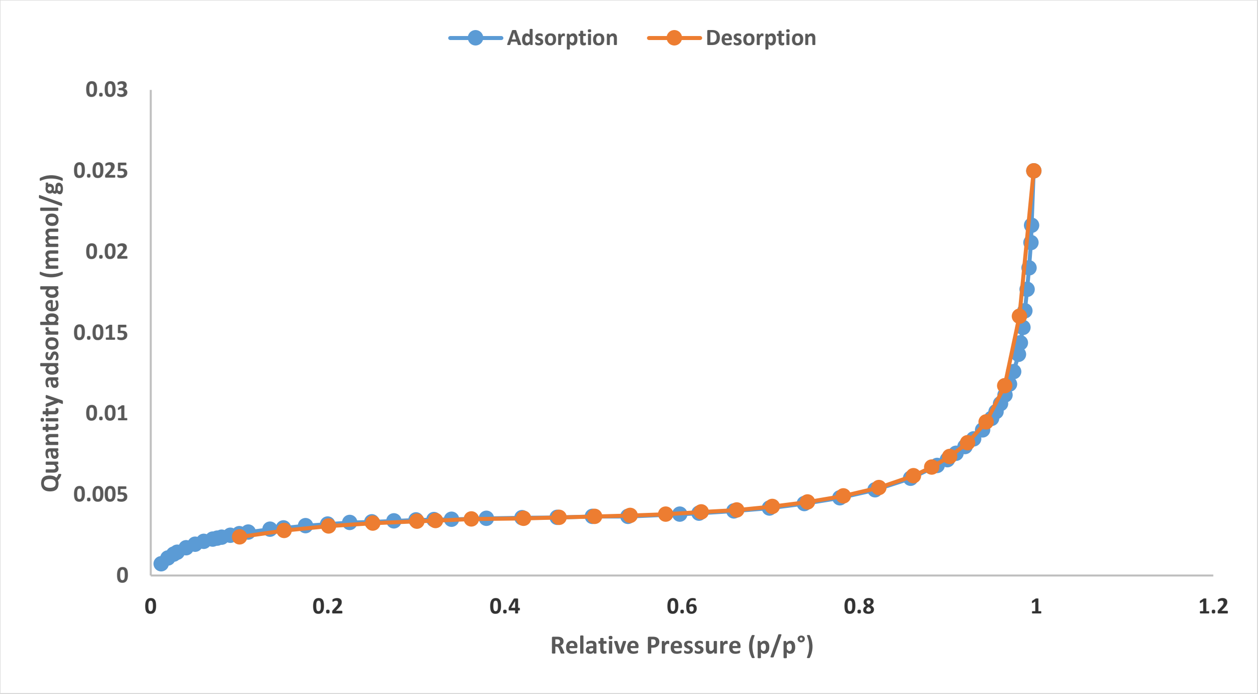


Figure 4. 36: Typical N_2 adsorption/desorption isotherm measured at 77 K of SCC 6

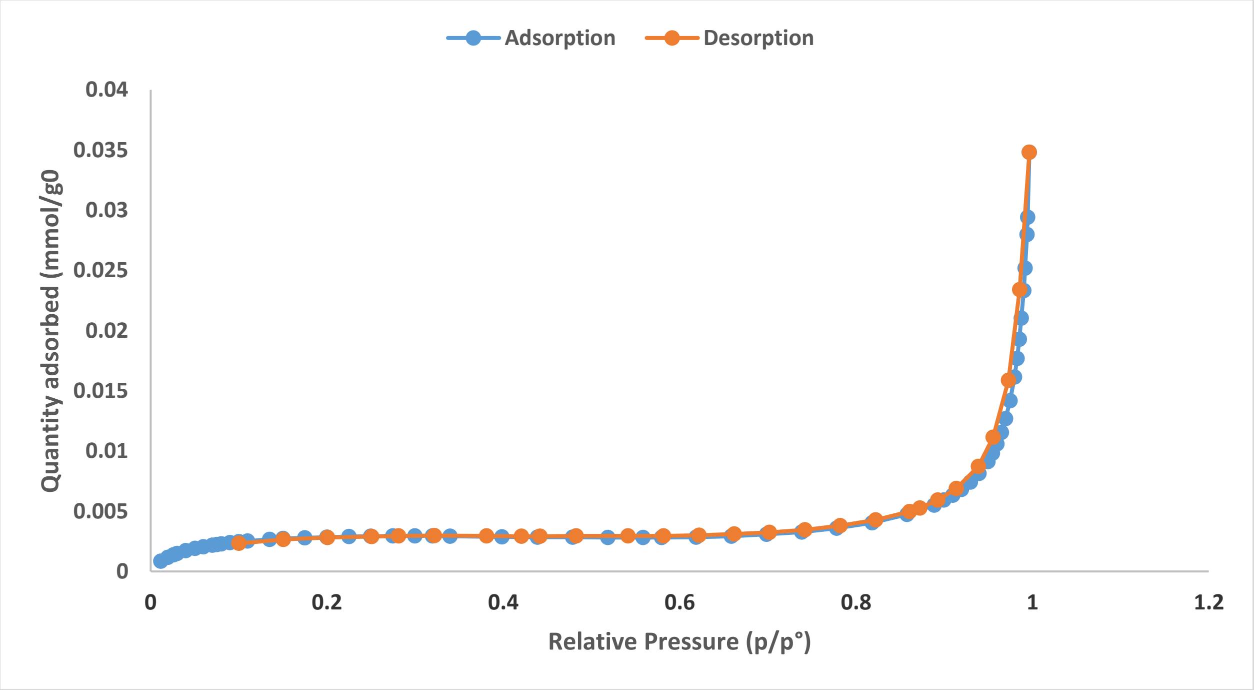


Figure 4. 37: Typical N_2 adsorption/desorption isotherm measured at 77 K of SCC 7

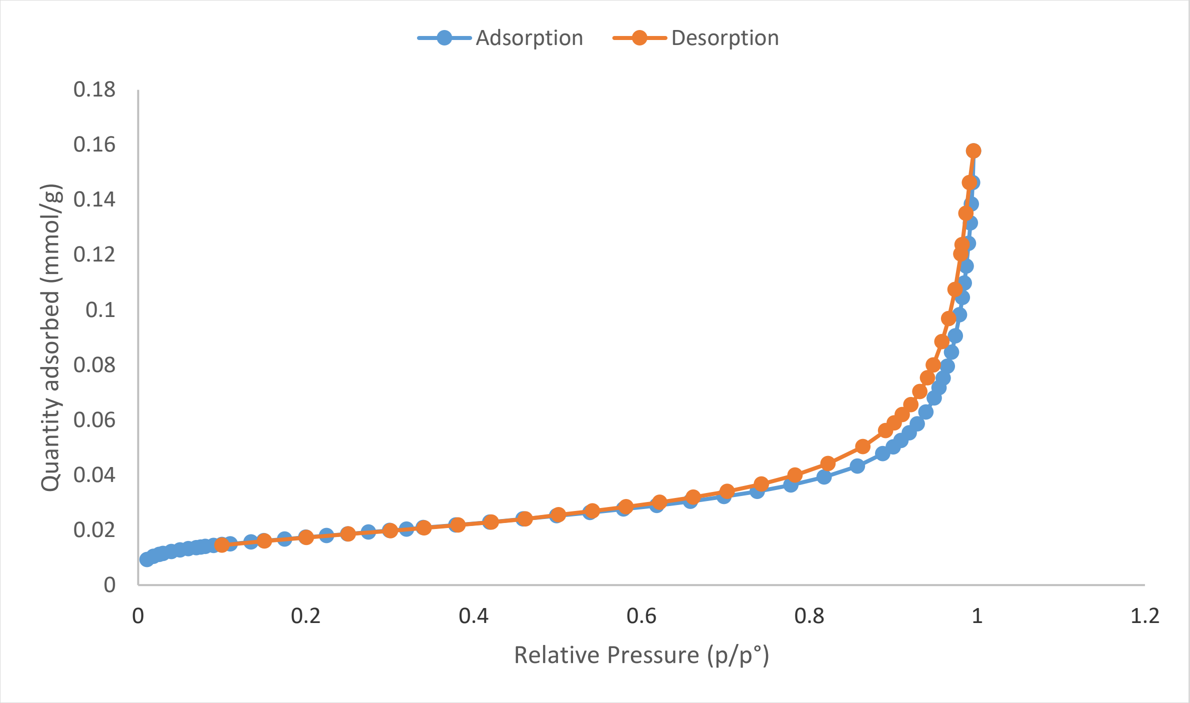


Figure 4. 38: Typical N_2 adsorption/desorption isotherm measured at 77 K of SCC 8

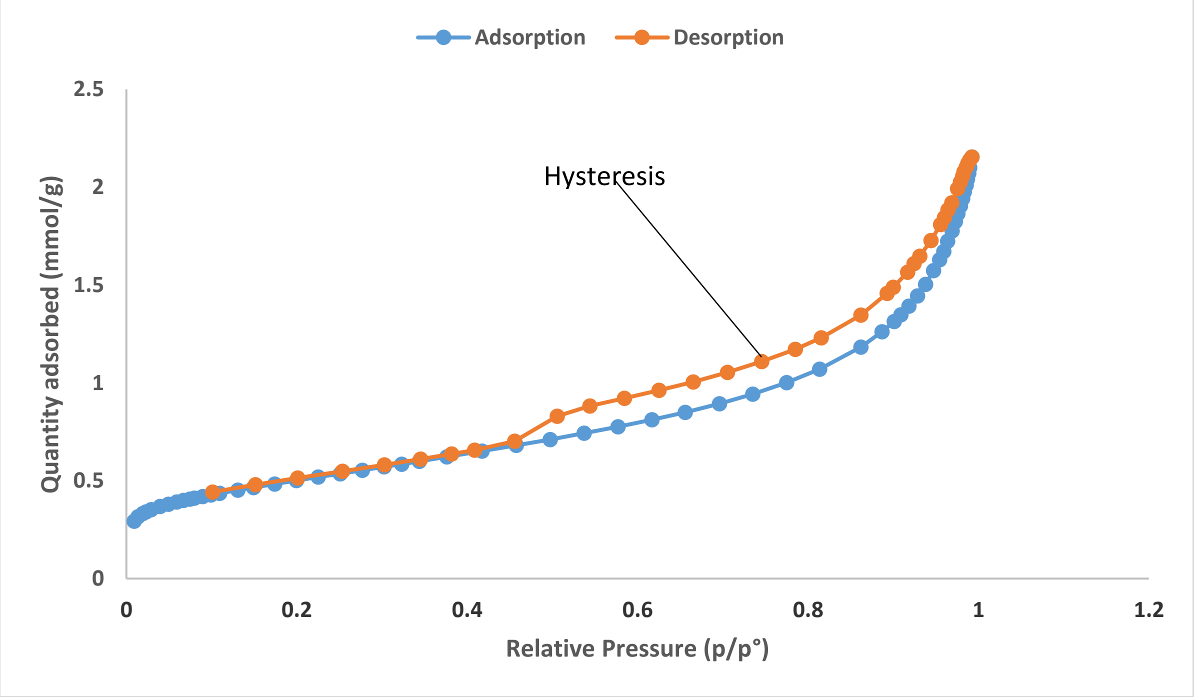


Figure 4. 39: Typical N_2 adsorption/desorption isotherm measured at 77 K of SCC 9

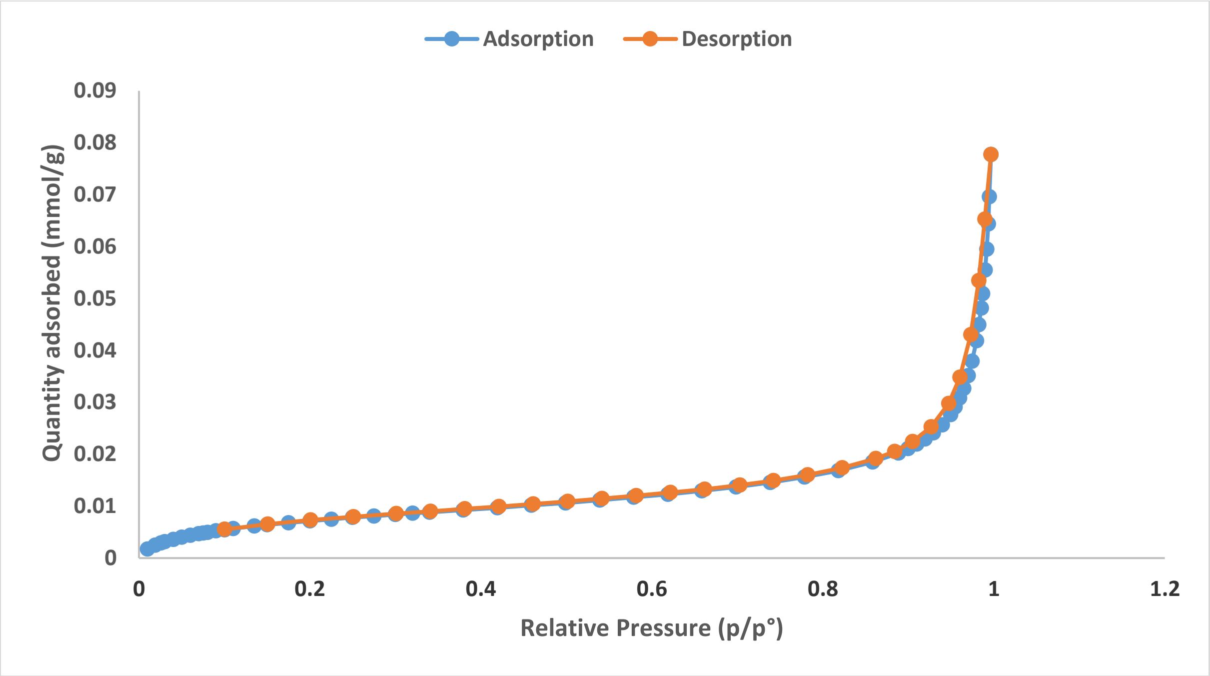


Figure 4. 40: Typical N_2 adsorption/desorption isotherm measured at 77 K of SCC 10

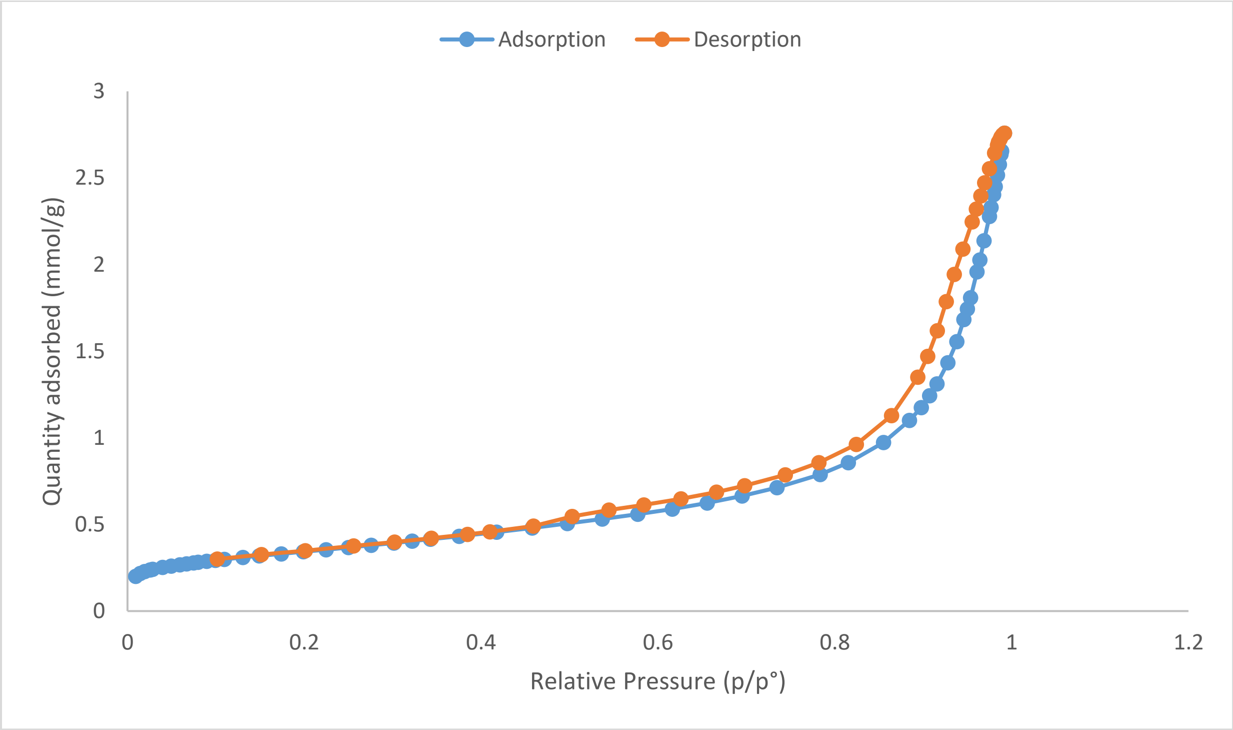


Figure 4. 41: Typical N_2 adsorption/desorption isotherm measured at 77 K of SCC 11

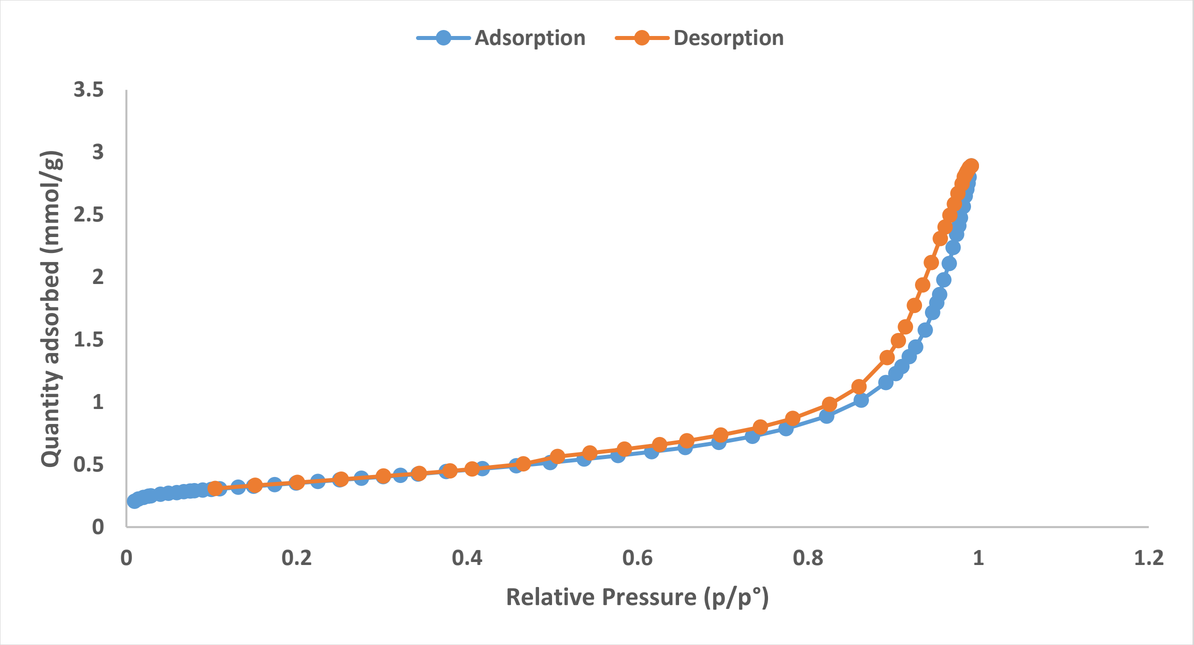


Figure 4. 42: Typical N_2 adsorption/desorption isotherm measured at 77 K of SCC 12

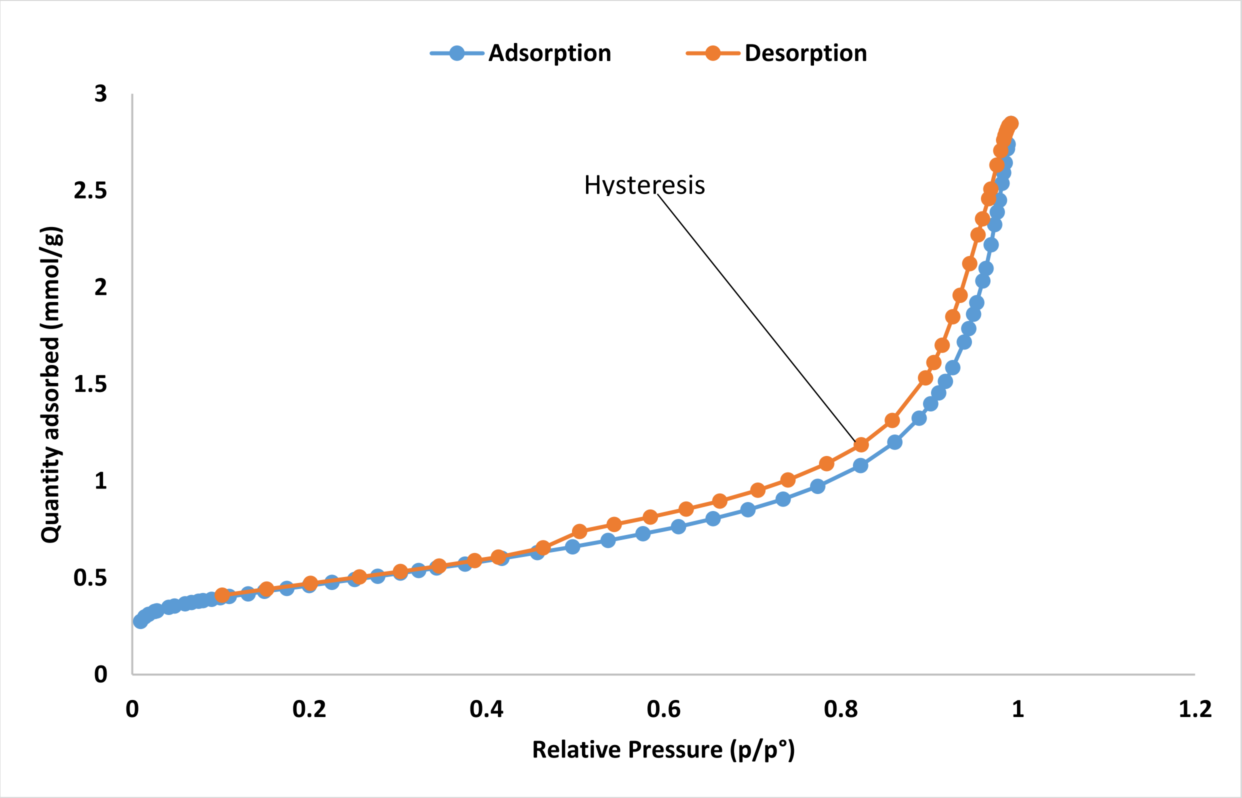


Figure 4. 43: Typical N_2 adsorption/desorption isotherm measured at 77 K of SWL 1

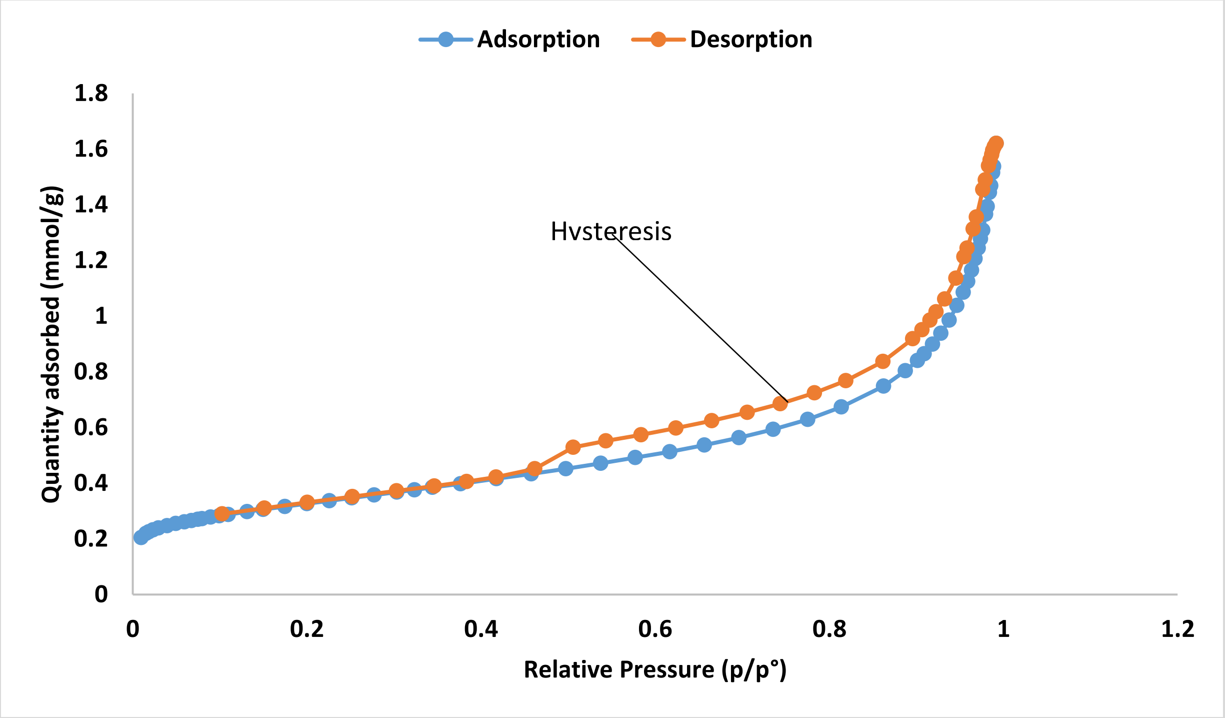


Figure 4. 44: Typical N_2 adsorption/desorption isotherm measured at 77 K of SWL 2

4.3 Particle size distribution analysis

4.3.1 Percentage compositions of clay, silt and sand

A ternary diagram was used to show the various textural distributions of the earthy materials as shown in Figure 4.45 (USDA textural triangle). The results obtained from hydrometer method was plotted using Tal for window version 4.2 (1996-2002). Particle sizes of samples SCC2, SCC 3, SCC 4 and SCC 10 were not determined, this is because the samples did not show any properties of clay minerals. Figure 4.45 shows the classification of the studied earthy materials and their distribution in ternary diagram according to USDA standard.

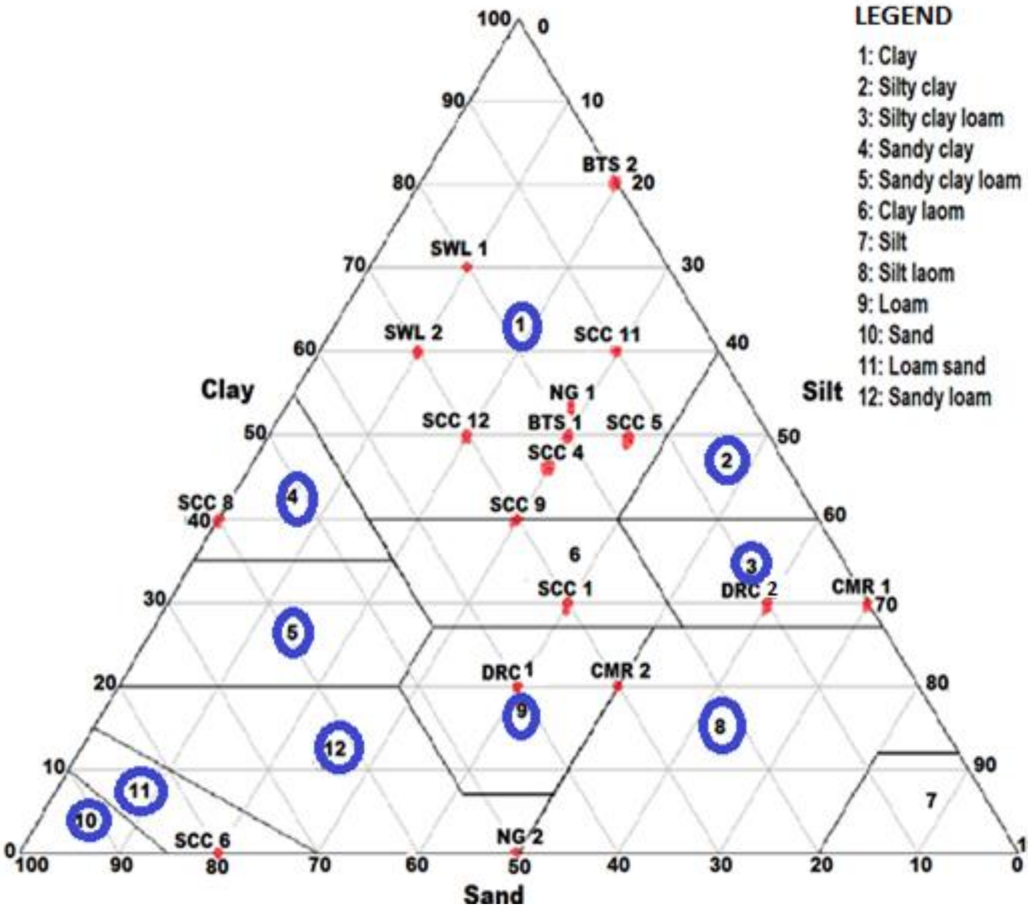


Figure 4.45: Ternary diagram showing the different soil classifications based on USDA standard

Particle size influences water holding capacity of earthy materials. The above classified diagram shows that samples from BTS 1, BTS 2, NG 1, SCC 4, SCC 5, SCC 9, SCC 11, SCC 12, SWL 1 and SWL 2 are clay soil, while sample SCC8 is a sandy clay soil, DRC 2 and CMR 1 are silt clay loam soil, SCC 1 is clay loam, NG 2 is sandy loam and SCC 6 has more of sand in its composition. The above results show that samples which were identified as clay are suitable for cosmetic application, since clay minerals suitable for cosmetic applications have their particle sizes in the range of 0-2 µm(<0.002 mm) (Murray, 2000). Hence samples which do not fall in the range of clay are not suitable for cosmetic applications because they do not meet the cosmetic requirements. The particle size distribution showed that materials in the range of clay are rich in fine grained particles and clay minerals, which greatly affect the physicochemical properties such as the cation exchange capacity, cooling rate, plasticity, adhesiveness, swelling properties (Veniale *et al.,* 2007). The fine grain size distribution obtained from the studied samples will increase the uniformity of pore size between the grains and help in proper smearing of the samples on the body against UV light. Irrespective of the whole representative samples containing different percentages of clay, silt and sand (Fig 4.46), BTS 1 (50%), BTS 2 (70%), NG 1 (50%), SCC 4 (50%), SCC 5 (50%), SCC 11 (60%), SCC 12 (50%), SWL 1 (70%) and SWL 2 (60%) showed a high percentage composition of clay than silt and sand. CMR 1 (70%), CMR 2 (50%), DRC 2 (60%), SCC 1 (40%) in the other hand had high percentage compositions of silt, whereas SCC 6 (80%) and SCC 8 (60%) had only sand and silt without any composition of clay. SCC 9 had 40% of clay, 30% of silt and 30% of sand. The above illustration makes it easier to determine which products are suitable for topical application, since previous studies have proven clay to be one of the major ingredients of cosmetic materials. The texture and the composition of a certain material will help in determining the holding capacity and constituents.

4.4 Trace element concentration of the studied samples

Twenty-two representative samples which were analysed using XRF were identified for their concentration of trace elements. A total of 66 elements were investigated in the studied samples and they are as follows: Ag, Al, As, Au, Ba, Bi, Br, Ca, Cd, Ce, Cl, Co, Cr, Cs, Dy, Er, Eu, Fe, Ga, Gd, Ge, Hf, Hg, Ho, I, In, K, La, Lr, Lu, Mg, Mn, Mo, Na, Nd, Ni, Nb, Os, P, Pb, Pd, Pr, Pt, Re, Rh, Ru, S, Sc, Se, Sb, Si, Sm, Sn, Sr, Ta, Te, Tb, Th, Ti, U, V, W, Y, Yb, Zr, Zn. Amongst all the analysed samples, few of the elements showed high concentration in each independent countries whereas some of the elements showed little or no trace elements. The elements for which their concentrations could not be determined were not included in the analyses. Continuous existence of trace elements in the studied earthy materials are attributed to substitution, replacement or adsorption of trace elements on the surface or across the lattices of the representative samples (Adjia *et al.,* 2013; Ekosse, 2002; 2001).

Van der biji and Van Eyk (2000); Jumbam (2011), reported that substances which are commonly applied to the skin have the possibility of causing local and systemic effects. Some radioactive elements were detected in BTS 1, BTS 2, CMR 1, CMR 2, DRC 1, DRC 2, NG 1, NG 2, and SWL 1 of the earthy materials although some were considerably low. Sr which is present in the analysed samples is a well-known radioactive element, which is used as a radioactive tracer in the treatment of cancer and also serving some purposes in Agriculture, unless when it occurs as strontium chromate, it can be regarded as being harmful due to the presence of chromium (ATSDR, 2004). The harmful effect is in accordance to its accumulation over a long period of time, though The International Agency for Research on Cancer (IARC) and Environmental Protection Agency (EPA) declared radioactive strontium as carcinogenic to humans. Other toxic elements obtained in the analyses were Ga, Rb, Sr, Y, Cr, Ti and V. Some essential elements (major elements) which the body require were also analysed for, they are Mg, Al, P, Ca, Mn, Cu, Zn, S and K. Rare earth elements are considered to be dangerous, moreover there has not been know regulation for the analysed trace elements which are contained in earthy materials for cosmetic application (Lopez-Galindo *et al.,* 2007; Silva *et al.,* 2011). Tables and graphical representations were used to show the ranges/variations in concentrations. Table 4.25 represents the summary of standard-less XRF results according to their countries and localities. Average concentration of each trace element for each representative country was taken to show the differences in the trace elements of different countries based on the sites of analyses. Figure 4.47 below summarises the average concentrations of each trace element taken for each country and their locality.

Table 4.26: XRF results the studied selected countries and their localities, determined in (ppm)

	BOTSWANA		CAMEROON		DEMOCRATIC REPUBLIC OF CONGO		NIGERIA		SWAZILAND		SOUTH AFRICA											
ELEMENTS	Gaborone	Kanye	Yaoundé	Bokwango	Kinshasa	Kasia-Oriental	Ogbomoso	Ibadan	Manzini	Ezulwini	Qwa-Qwa								HarriSmith		Thohoyandou	
	(BTS 1)	(BTS 2)	(CMR 1)	(CMR 2)	(DRC 1)	(DRC 2)	(NG 1)	(NG 2)	(SWL 1)	(SWL 2)	(SCC 1)	(SCC 2)	(SCC 3)	(SCC 4)	(SCC 5)	(SCC 6)	(SCC 7)	(SCC 8)	(SCC 9)	(SCC 10)	(SCC 11)	(SCC 12)
Mg	0.04	-	-	-	-	-	0.04	0.04	0.92	-	0.17	0.03	0.70	0.23	0.03	-	0.02	-	0.04	0.01	0.07	0.10
Al	3.99	4.58	4.54	3.96	3.65	3.50	2.73	0.02	4.64	0.67	3.93	0.01	0.11	0.08	2.07	-	-	-	2.02	0.01	1,.96	3.57
Si	6.12	5.05	6.77	6.25	6.26	5.26	4.87	2.73	4.71	0.66	4.03	0.04	0.79	0.22	3.89	0.01	0.04	0.01	2.13	0.03	2.20	4.69
P	0.11	0.11	0.10	0.09	0.11	0.09	0.06	0.04	0.09	0.03	0.10	0.08	0.10	0.10	0.07	0.05	0.06	0.05	0.05	0.05	0.04	0.08
S	0.02	-	-	-	-	-	-	-	-	-	-	11.26	0.02	0.05	0.01	0.01	0.21	1.24	-	0.21	-	-
K	0.38	0.10	-	-	0.36	0.81	0.34	0.31	0.06	0.01	3.02	-	0.05	0.01	0.25	0.01	0.52	-	0.01	0.32	0.32	0.69
Ca	0.05	0.10	0.06	0.05	0.05	0.07	0.04	0.02	-	0.03	0.05	0.06	1.44	0.78	0.08	0.04	1.10	0.03	0.05	1.56	0.04	0.10
Ti	0.20	1.01	0.09	0.08	0.16	0.15	0.17	0.06	0.01	0.13	0.49	-	3.75	0.01	0.10	-	-	-	0.21	-	0.05	0.12
Cr	0.03	0,05	-	-	0.03	0.04	0.02	0.01	0.06	0.03	0.09	-	0.11	0.03	0.04	-	-	-	0.04	-	0.01	0.01
Mn	0.01	0.04	0.02	0.01	0.02	0.01	-	0.02	0.05	0.08	0.06	-	0.13	0.07	0.01	-	0.03	-	0.12	0.44	0.09	0.07
Fe	12.48	7.21	4.10	3.59	17.56	11.50	0.87	3.40	18.35	15.59	19.27	0.05	11.30	66.47	18.61	0.09	0.17	0.32	17.00	0.25	9.36	8.32
Co	0.02	0.02	0.01	0.01	0.04	0.03	-	0.01	0.05	0.06	0.04	-	0.05	0.11	0.03	-	-	-	0.04	-	0.02	0.02
Cu	0.02	0.01	0.01	0.01	0.02	0.01	0.01	0.01	0.02	0.02	0.03	0.01	0.02	0.02	0.01	0.01	0.01	24.28	0.10	0.01	0.01	0.01
Zn	0.01	0.02	0.04	0.56	0.02	0.01	-	0.03	0.01	0.02	0.02	-	0.02	0.20	-	-	-	0.03	0.02	0.03	0.04	0.03
Ga	0.00	0.02	0.02	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.01	-	0,00	0.25	0.01	-	-	-	-	-	0.01	0.01
Rb	0.03	0.05	-	-	0.02	0.06	0.06	0.08	0.01	-	-	-	-	-	-	-	-	-	-	0.01	0.10	0.08
Sr	0.01	0.06	-	-	0.02	0.05	0.02	0.05	-	-	-	-	0.12	-	-	-	0.26	-	-	0.22	0.03	0.03
Y	0.01	0.05	0.08	0.08	0.02	0.03	0.03	0.06	0.01	0.02	0.04	-	-	-	-	-	-	-	-	-	0.05	0.05
Zr	0.15	0.11	1.27	1.39	0.07	0.03	0.11	0.16	0.06	0.08	0.04	-	0.07	-	-	-	-	-	0.13	-	0.05	0.05

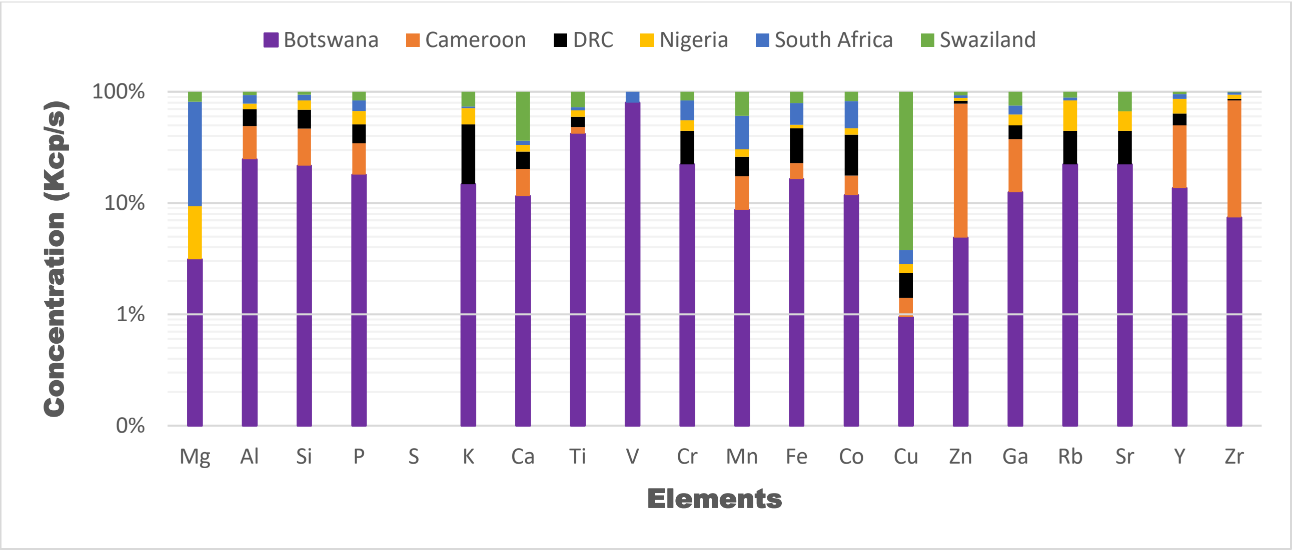
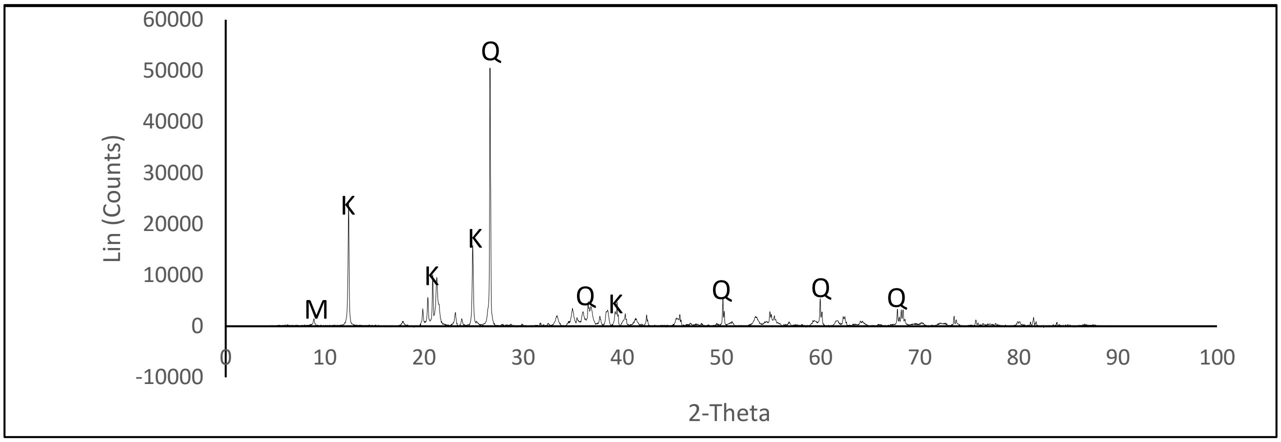


Figure 4.46: Average concentrations of trace elements for each representative countries

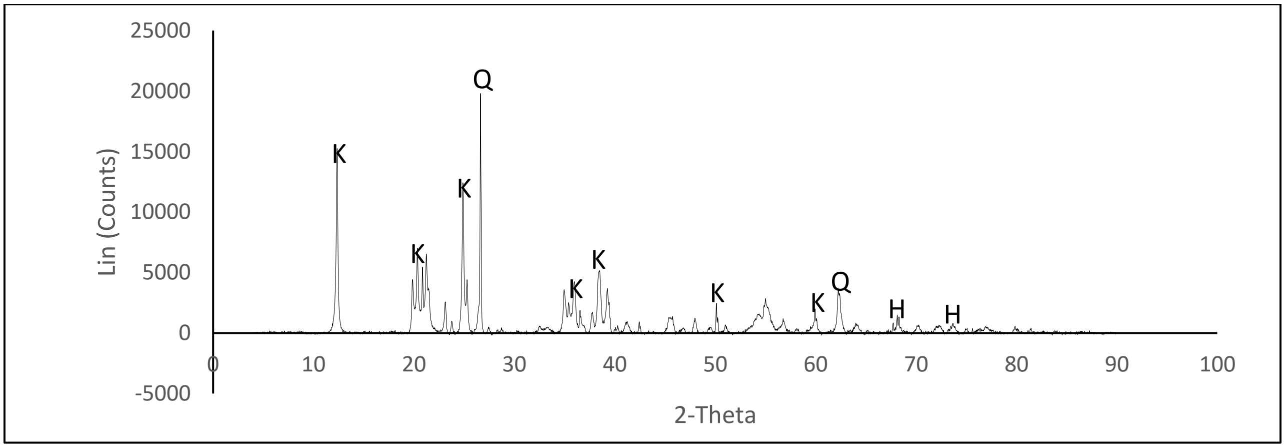
The histogram indicated the different concentrations of trace elements present in the studied earthy materials. As stated above, only trace elements such as; Al, Ca, Co, Cr, Cu, Fe, Ga, K, Mg, Mn, P, S, Si, Ti, Rb, V, Y, Zn and Zr were detected. There are more clusters of iron among all the studied countries, in essence indicating that all earthy materials are rich in Fe, likewise Si. Fe showed the highest concentration of 16.97ppm, in all the representative countries (Fig 4.46). Al and Si were not left out in terms of occurrence in the whole samples. The variation is as follows in their descending order: SWL > DRC > SCC > BTS > CMR > NG. The above histogram showed that earthy materials from NG and CMR are preferably good for topical application because of their relatively low concentration of Fe. Accumulated intake of Fe when it is above 20 mg causes gastrointestinal symptoms. United Kingdom guidiance intake value is 17 mg/day while the United state EPA has not derived any notable toxicity value for Fe (Nnorom *et al.* 2005). Records of trace metal exposure has been well documented and can occurr through diet, medication, environment (Adal and Tarabar, 2013) and through earthy material used for topical applications.

4.5: Mineralogical characteristics of the studied earthy materials

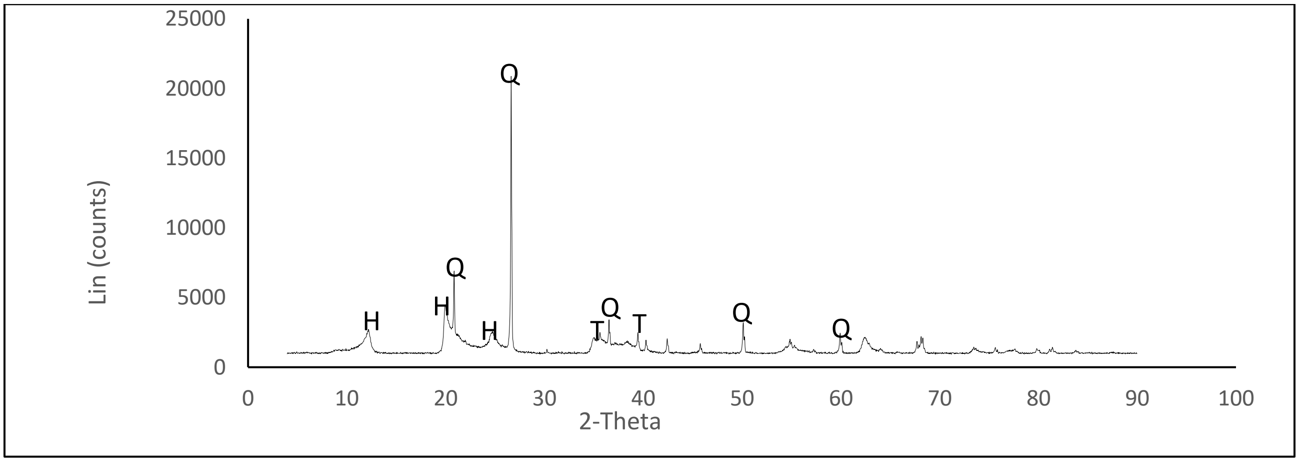
The nature of the different phases and the study of the phases (minerals) of the earthy materials were identified by XRD. Characterised materials mostly occur in three phases, they are: Major, minor and traces. The X-ray Diffraction of the patterns of each of the representative samples were obtained. All the twenty-two representative samples underwent characterisation and the method of identification was adopted from a method used by Ekosse and Mulaba (2008). Figure 4.47 - 4.55 show the different X-ray diffractograms of studied samples. The mineral names were denoted by letters.



Sample BTS 1



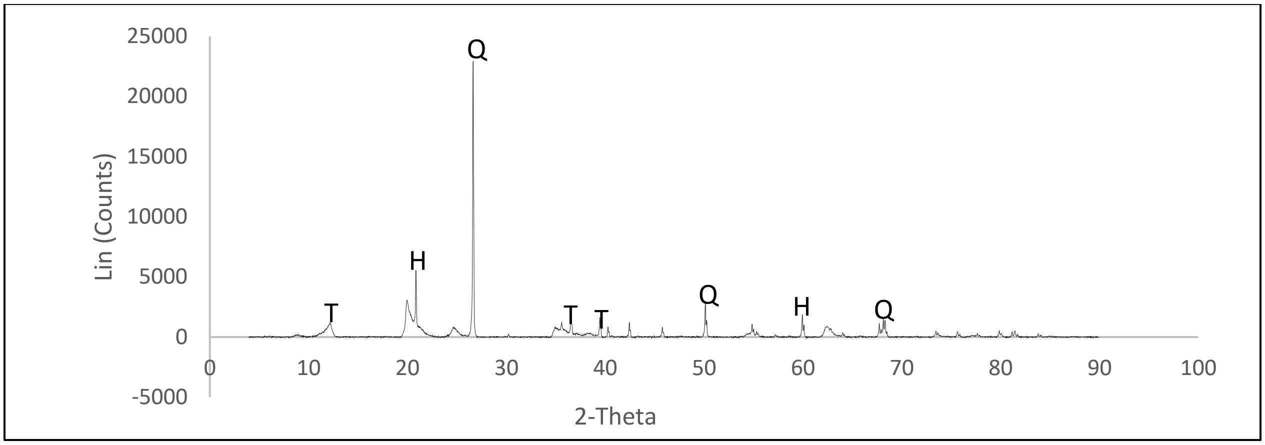
Sample BTS 2



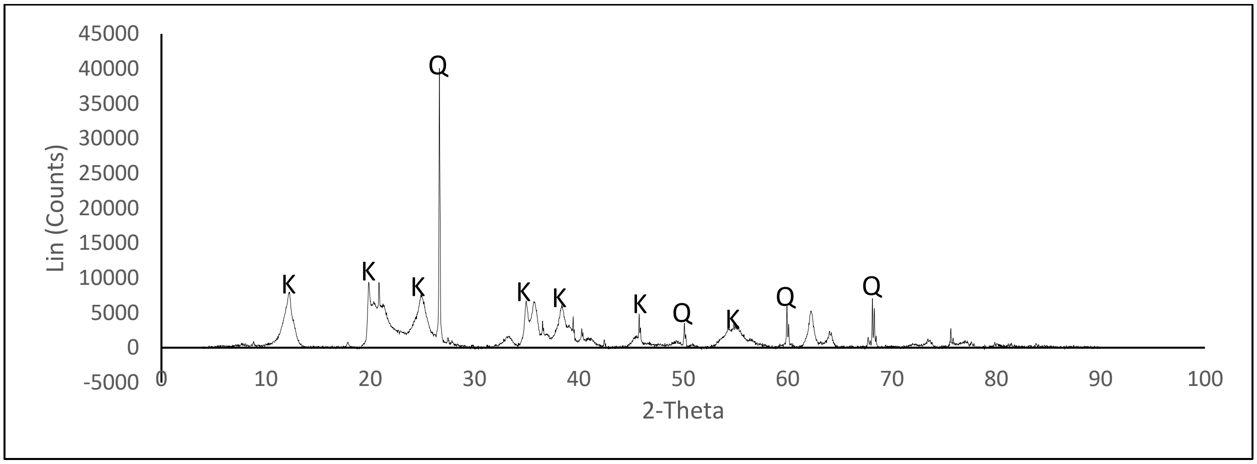
Sample CMR 1

Note: H= Halloysite, M= Muscovite, K= Kaolinite, T= Talc and Q= Quartz

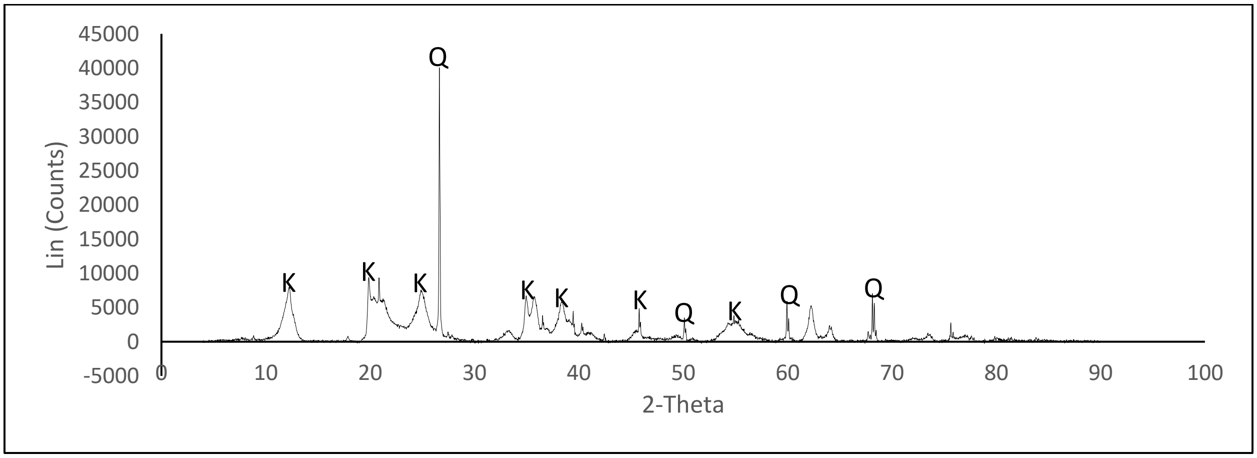
Figure 4.47: X-ray diffractograms of earthy materials used for beautification



Sample CMR 2



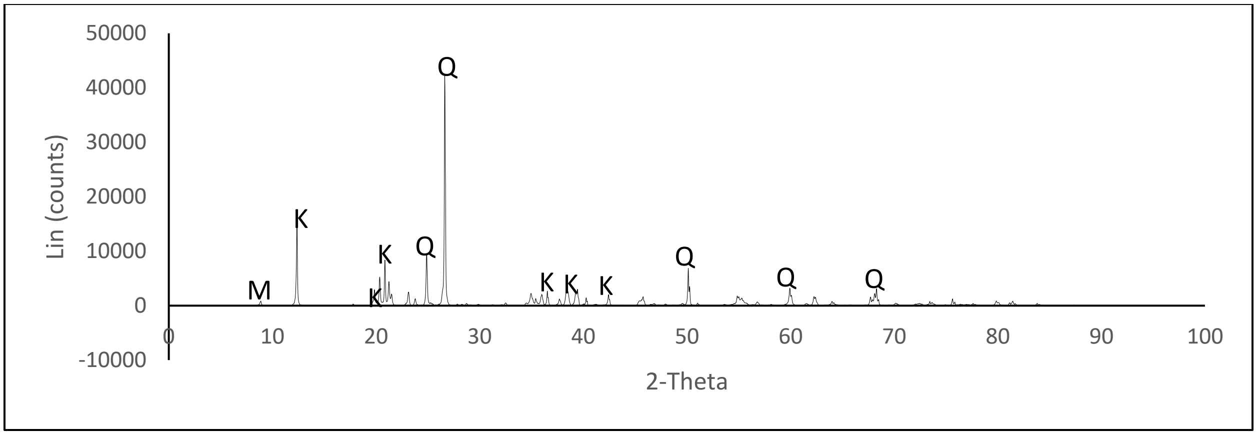
Sample SWL 1



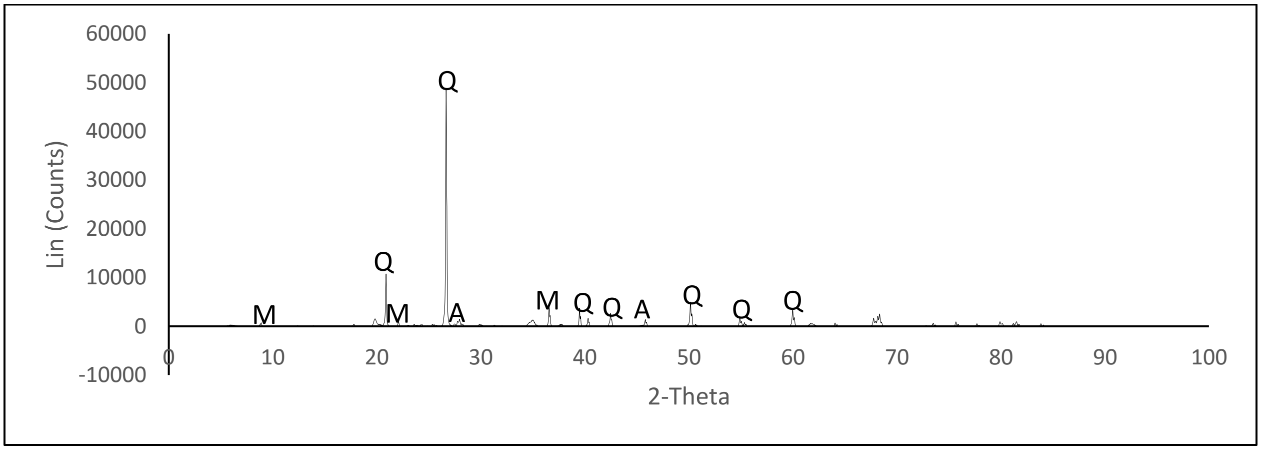
Sample SWL 2

Note: H= Hematite, K= Kaolinite, Q= Quartz and T=Talc

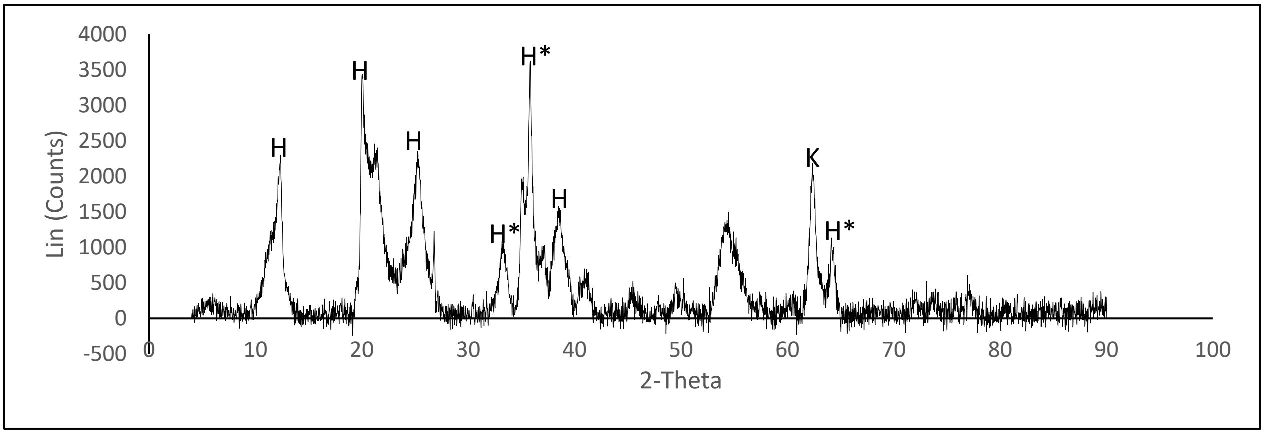
Figure 4.48: X-ray diffractograms of earthy materials used for beautification (cont'd)



Sample NG 1



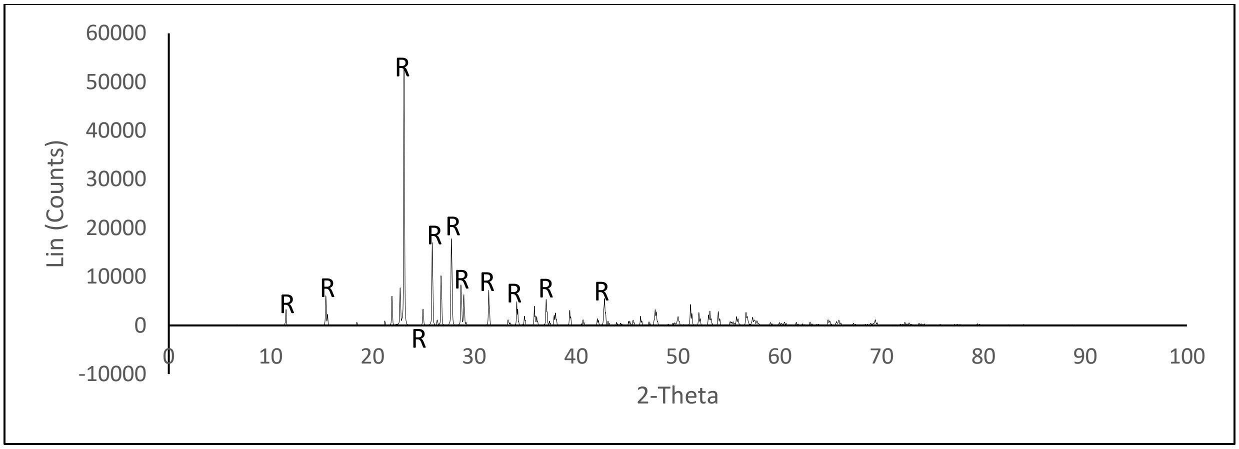
Sample NG 2



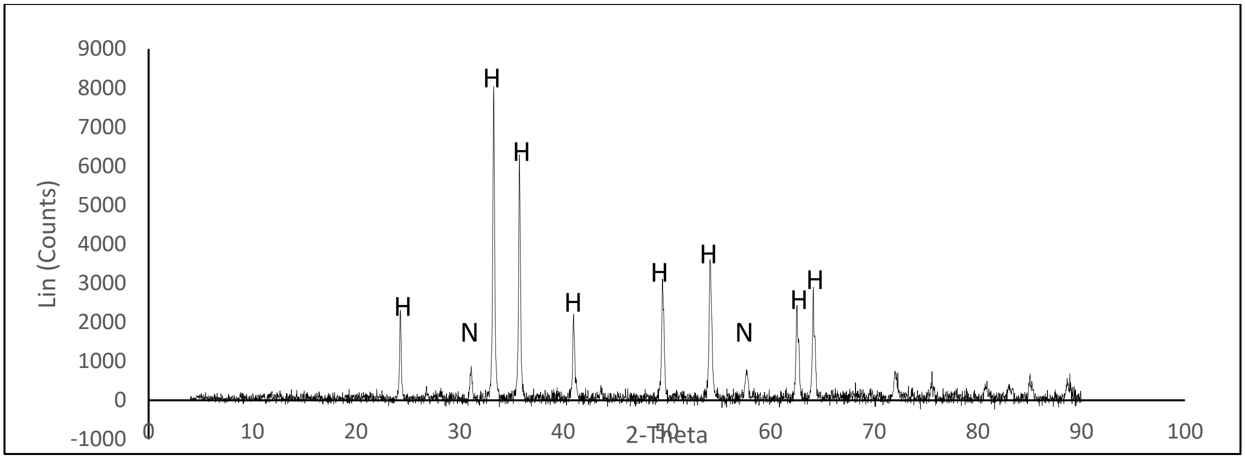
Sample SCC 1

Note: A=Albite, H=Halloysite, H*=Hematite, K= Kaolinite, M=Muscovite and Q=Quartz

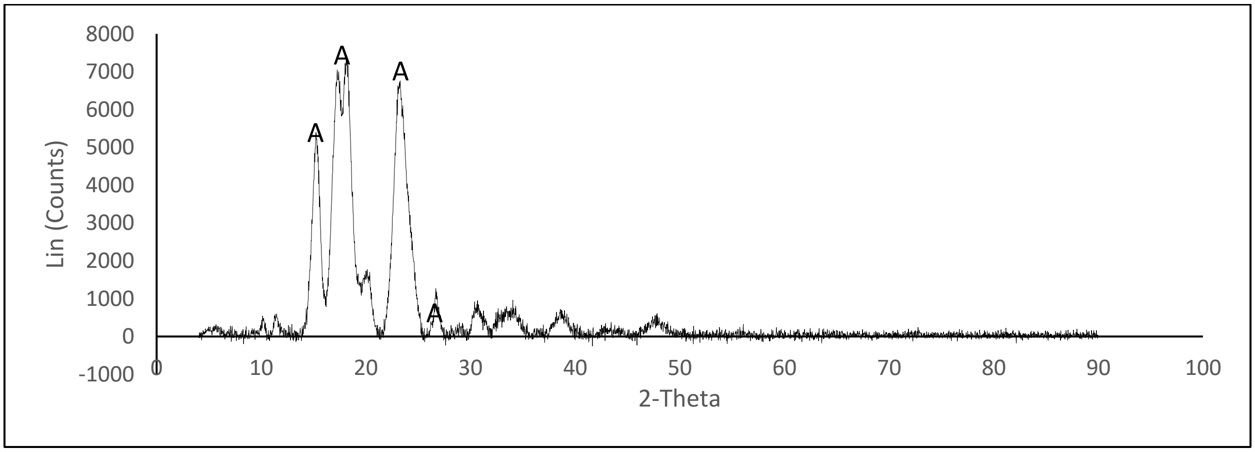
Figure 4.49: X-ray diffractograms of earthy materials used for beautification (cont'd)



Sample SCC 2



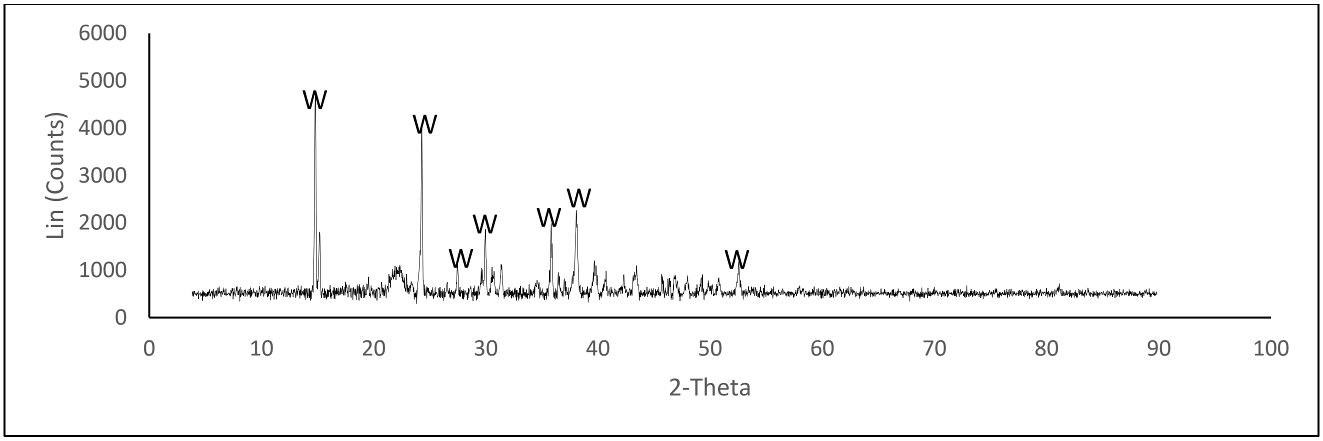
Sample SCC 4



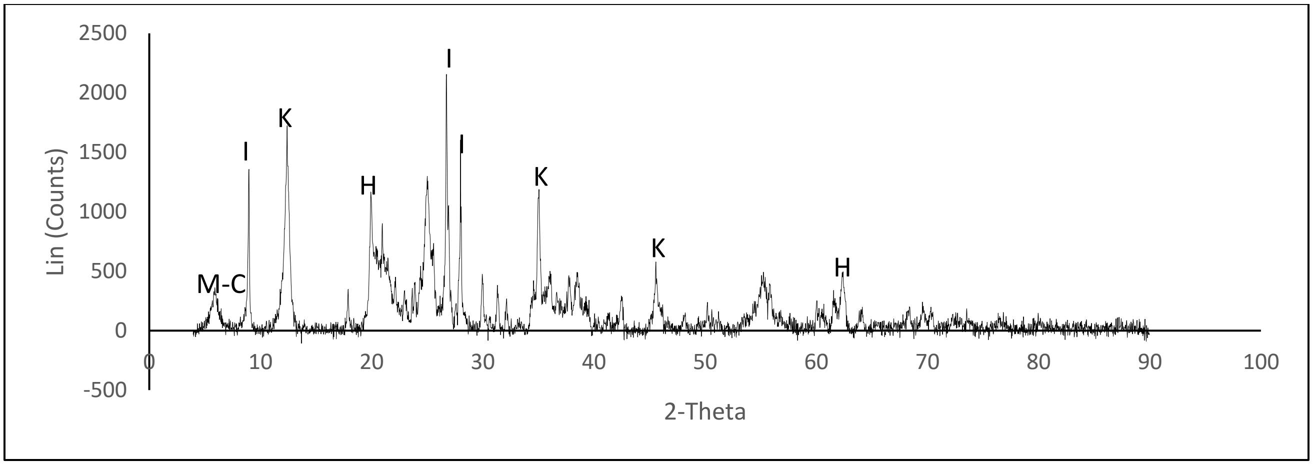
Sample SCC 6

Note: A= Amylum, H= Hematite, N= Nephelinite and R= Rosickyite

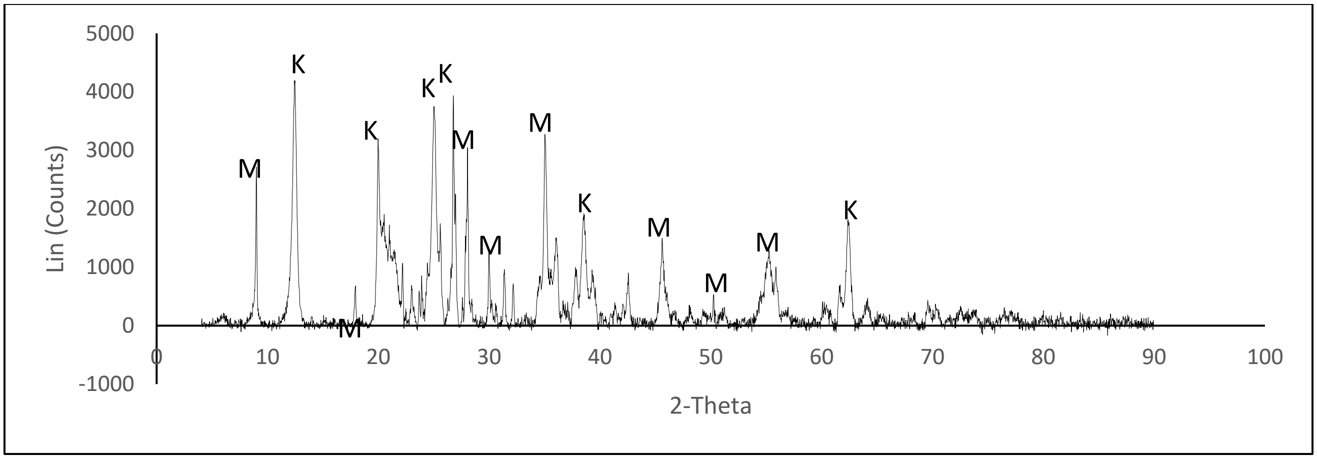
Figure 4.50: X-ray diffractograms of earthy materials used for beautification (cont'd)



Sample SCC 7



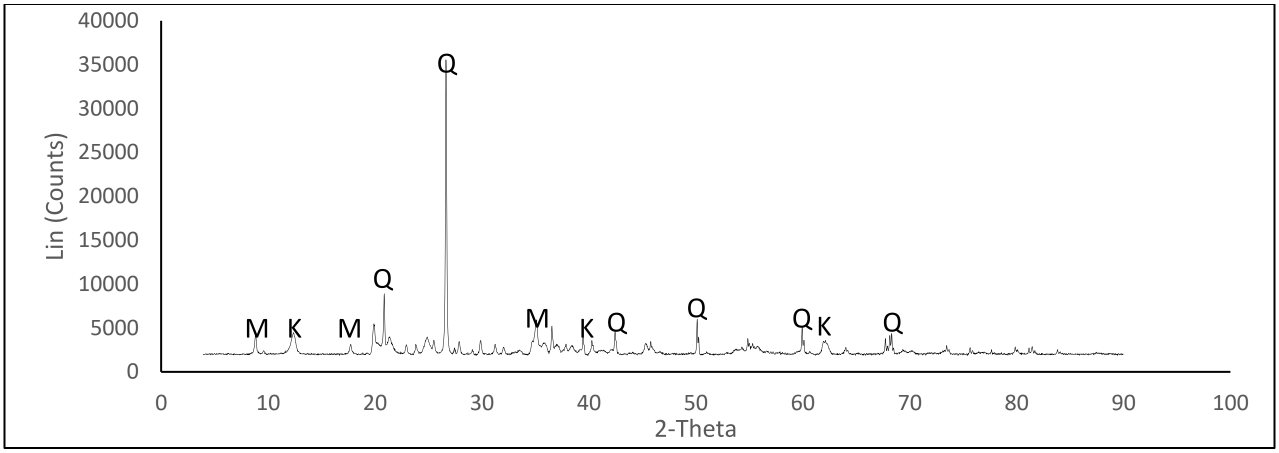
Sample SCC 11



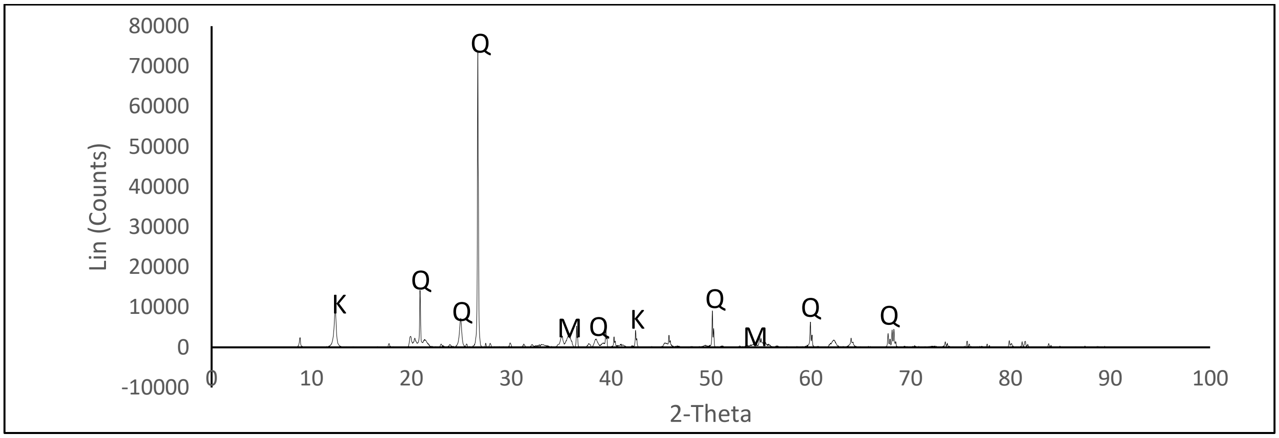
Sample SCC 12

Note: I=-illite, K= kaolinite,M= Muscovite, M-C= montmorillonite and W= Whewellite

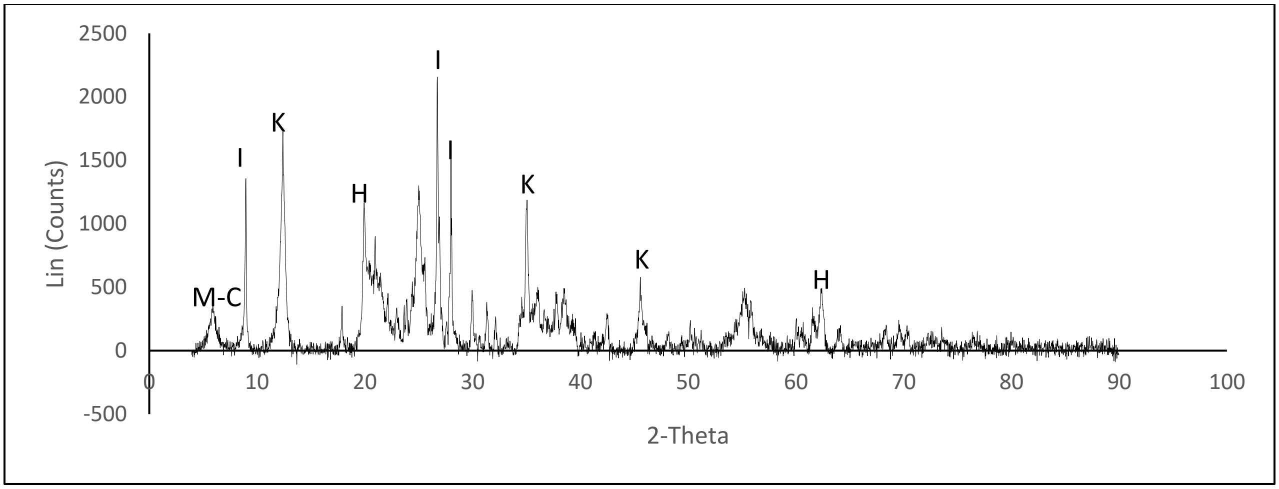
Figure 4.51: X-ray diffractograms of earthy materials used for beautification (cont'd)



Sample DRC 1



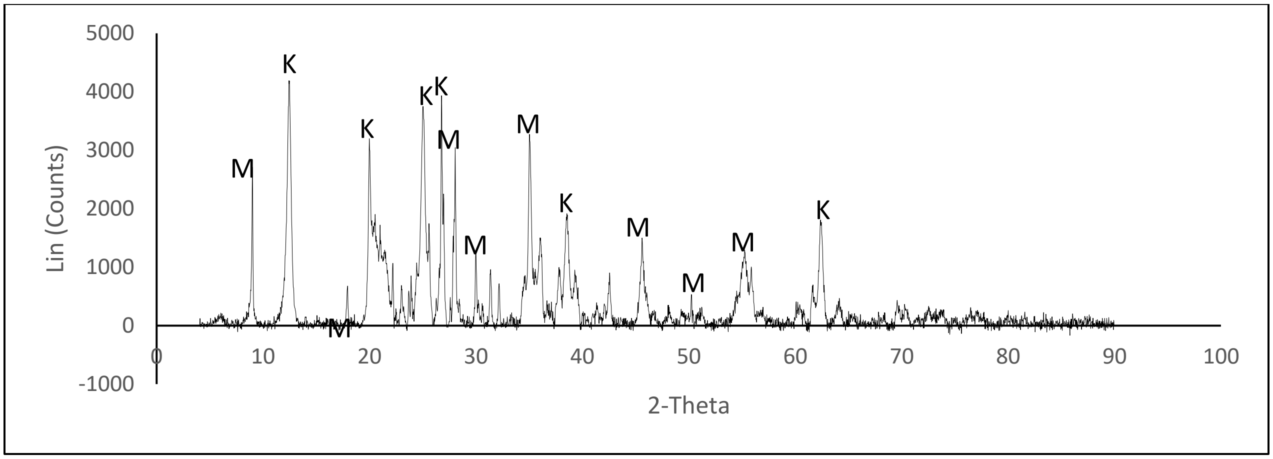
Sample DRC 2



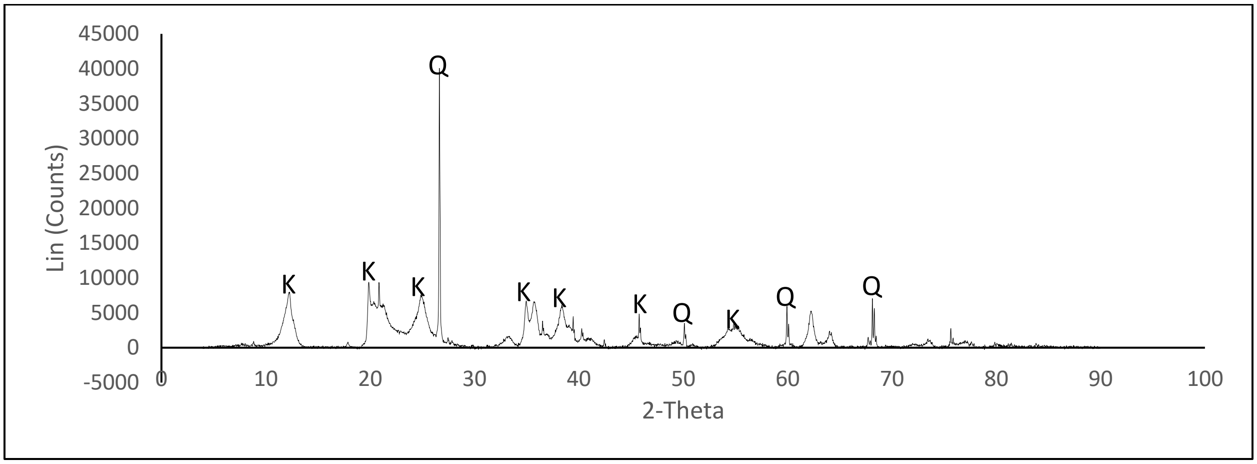
Sample SCC 11

Note: I= Illite, K= Kaolinite, M-C, Montmorillonite, Muscovite and Q= Quartz

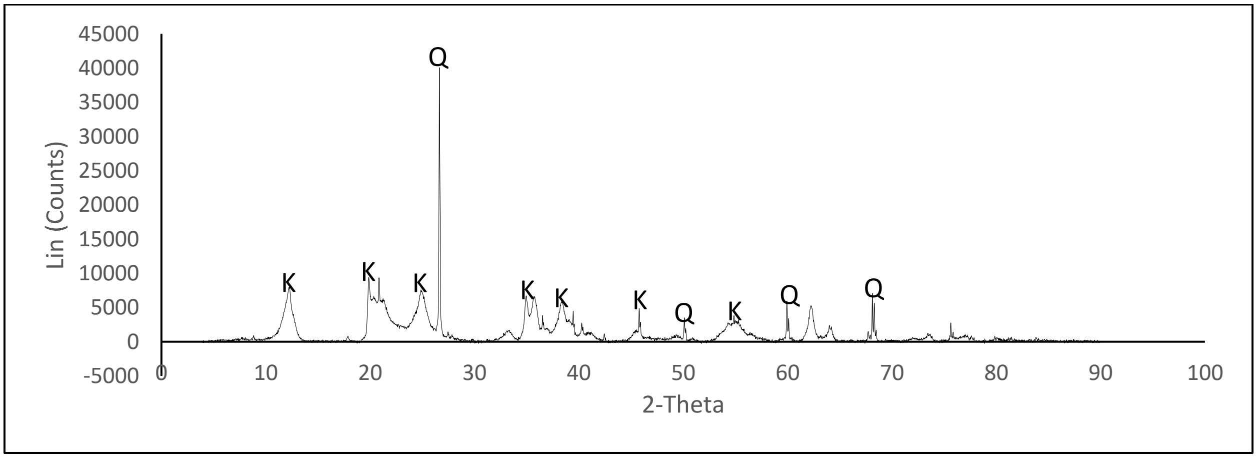
Figure 4.52: X-ray diffractograms of earthy materials used for sunscreening



Sample SCC 12



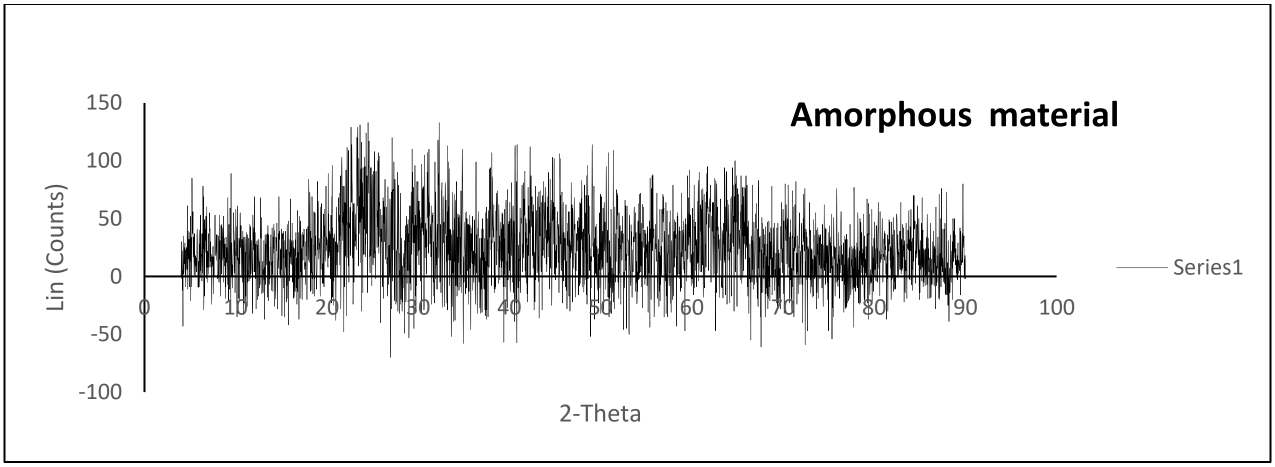
Sample SWL 1



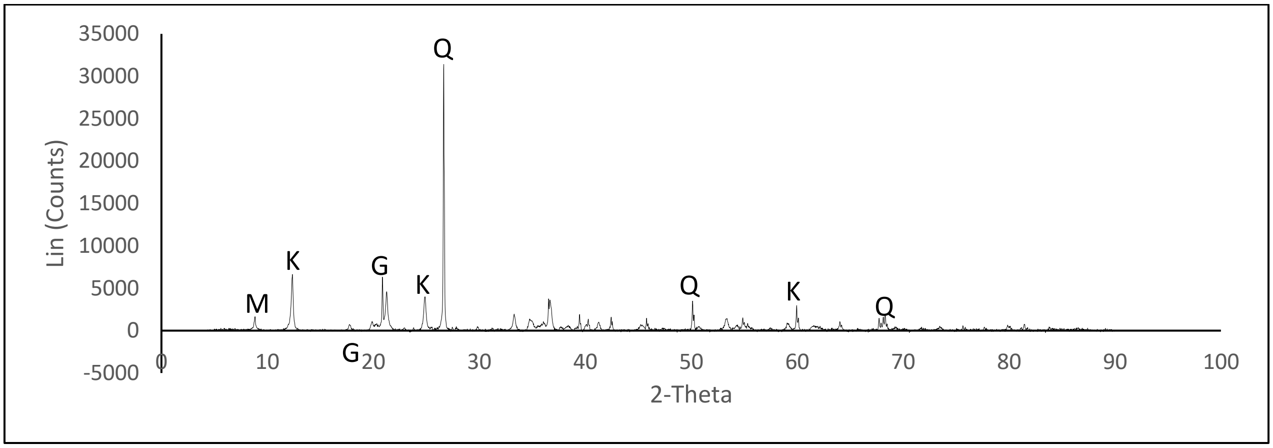
Sample SWL 2

Note: K= Kaolinite,M= Muscovite and Q= Quartz

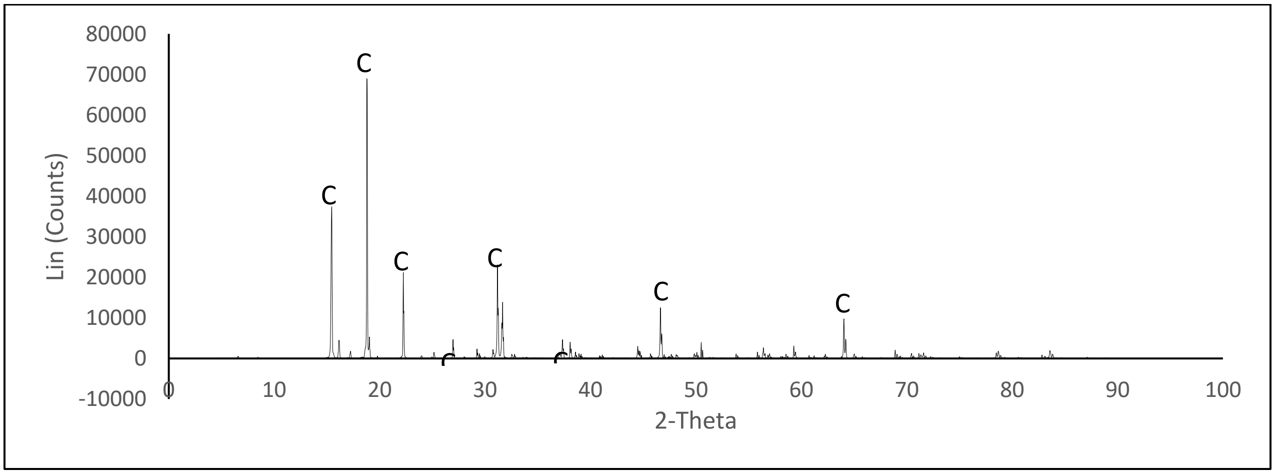
Figure 4.53: X-ray diffractograms of earthy materials used for sunscreening (cont'd)



Sample SCC 3



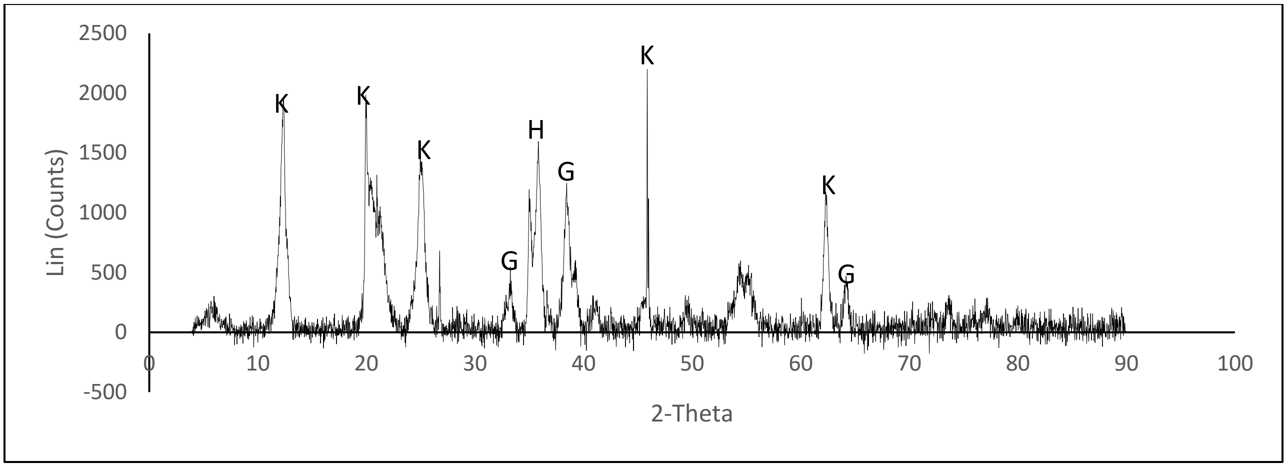
Sample SCC 5



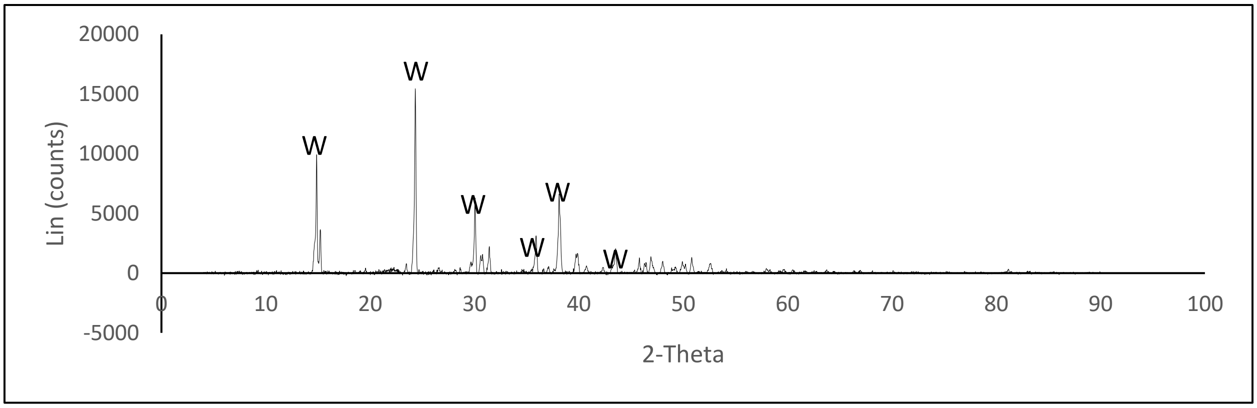
Sample SCC 8

Note: C= Chalcanthite, G= Geothite, K= Kaolinite, M=Muscovite and Q= Quartz

Figure 4.54: X-ray diffractograms of earthy materials used for cleansing/identification



Sample SCC 9



Sample SCC 10

Note: G= Geothite, H= Halloysite, K= Kaolinite and W= whewellite

Figure 4.55: X-ray diffractograms of earthy materials used for cleansing/identification (cont'd)

The minerals present in the samples are: Muscovite, albite, kaolinite, quartz, chabazite (Calcium aluminium silicate hydrate), halloysite, talc, hematite, montmorillonite, nephelinite, rosickyite, whewellite, goethite, hematite and quartz. Some amorphous peaks (phases) were also identified especially Figure 4.54 (SCC 3) and Figure 4.55 (SCC9), this makes the diffractogram to have a noisy background. There is a distinct similarity shown by CMR 1 and CMR 2 (Figure 4.47 and 4.48) and also in SWL 1 and SWL 2 (Figure 4.54). Samples obtained from different localities in South Africa (SCC1-SCC12), indicated different types of clay minerals and non-clay and are most suitable for cosmeticological application. Sulphur (Rosickyite) was present in Figure 4.50 and the mineral is believed by the users to be a good anti-bacteria, anti-fungal and antiseptic material. Sulphur (Rosickyite) is essential especially in skin care products which act as a keratolytic and germicidal agents improving acnes, pimples, seborrhea and psoriasis (Gupta and Nicol, 2004) and also used as therapeutic agent (Careterro, 2002) . However, Chen *et al.* (2011) reported that sulphur is difficult to use in cosmetic products directly due to its poor solubility.

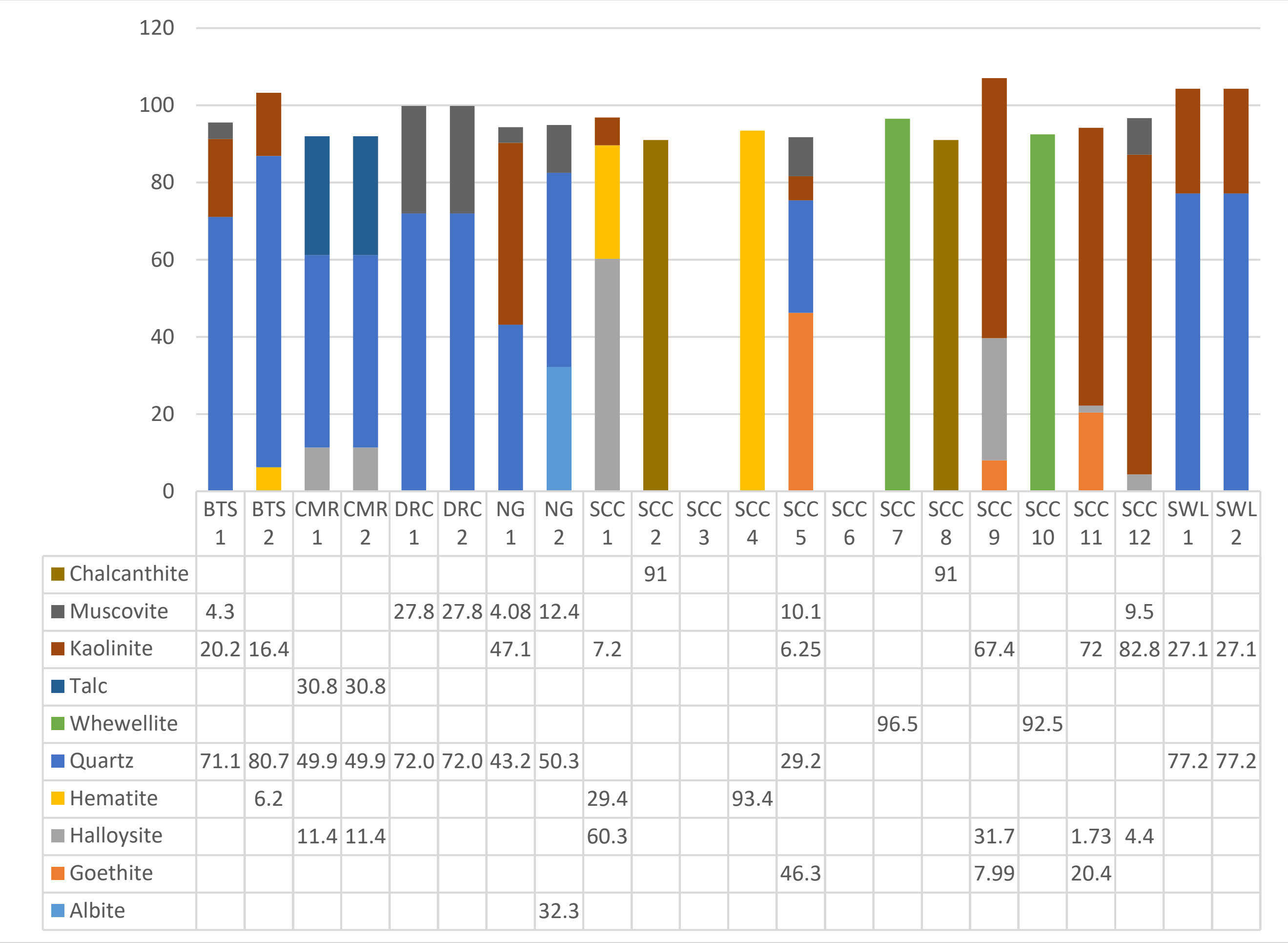
4.6 Characterisation of the studied samples by XRD

4.6.1 Mineralogy of the analysed earthy materials

Ten minerals were identified in the clay fraction samples: Albite, goethite, halloysite, hematite, kaolinite (kaolinite-1Md, kaolinite 1), Mica (muscovite), sulphur, talc, chalcanthite and whewellite. The qualitative identification of minerals present are mostly determined based in terms of their shapes, position and their intensity (Silva *et al*., 2011) and possibly their reproducibility. Samples from BTS 1, BTS 2, CMR 1, CMR 2, SCC 1, SCC 2, SCC 4, SCC 5, SCC 6, SCC 7, SCC 11, SCC 12, SWL 1 and SWL 2 fell in the category of earthy materials used for beautification, DRC 1, DRC 2, SCC 11, SCC 12, SCC 8, SWL 1 and SWL 2 are beneficial for sunscreening, whereas NG 1, NG 2, SWL 1 and SWL 2 are beneficial for cleansing (Table 4.27).The percentage contained in each representative sample was determined using the EVA software. Figure 4.57 summarises the various clay minerals present in the studied samples.

Table 4.27: Minerals identified from the XRD analysis (quantitative)

Sample Remarks	**Sample codes**	**Minerals and Oxides**													
		Albite	Muscovite	chabazite	Halloysite	Rosickyite	Whellite	Chalcancite	Talc	Montmorillonit	illite	Kaolinite	Goethite	Hematite	Quartz
Beautification	BTS 1	-	×	×	-	-	-	-	-	-		×	-	-	×
	BTS 2	-	-	-	×	-	-	-	-	-	-	×	-	-	×
	CMR 1	-	-	-	×	-	-	-	×	-	-	-	-	-	×
	CMR 2	-	-	-	-	-	-	-	×	-	-	-	-	×	×
	SCC 1	-	-	-	×	-	-	-	-	-	-	-	-	×	-
	SCC 2	-	-	-	-	×	-	-	-	-	-	-	-	-	-
	SCC 4	-	-	-	-	-	-	-	-	-	-	-	-	×	-
	SCC 5	-	×	-	-	-	-	-	-	-		×	×		×
	SCC 6	-	-	-	-	-			-	-	-	-	-	-	-
	SCC 7	-	-	-	-	-	×	-	-	-	-	-	-	-	-
	SCC 11	-	-	-	-	-	-	-	-	×	×	×	-	×	-
	SCC 12	×	-	-	-	-	-	-	-	-	-	×	-	-	-
	SWL 1	-	-	-	-	-	-	-	-	-	-	×	-	-	×
	SWL 2	-	-	-	-	-	-	-	-	-	-	×	-	-	×
Sunscreen	DRC 1	-	×	-	-	-	-	-	-	-	-	×	-	-	×
	DRC 2 SCC 11	-	×	-	-	-	-	-	 ×	 ×	-	× ×	-	-	× -
	SCC 12	×	-	-	-	-	-	-	-	-	-	×	-	-	-
	SCC 8	-	-	-	-	-	-	×	-	-	-	-	-	-	-
	SWL 1	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	SWL 2	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Cleansing	NG 1	-	×	-	-	-	-	-	-	-	-	×	-	-	-
	NG 2	×	×	-	-	-	-	-	-	-	-	×	-	-	-
	SWL 1	-	-	-	-	-	-	-	-	-	-	×	-	-	×
	SWL 2	-	-	-	-	-	-	-	-	-	-	×	-	-	×



	BTS 1	BTS 2	CMR 1	CMR 2	DRC 1	DRC 2	NG 1	NG 2	SCC 1	SCC 2	SCC 3	SCC 4	SCC 5	SCC 6	SCC 7	SCC 8	SCC 9	SCC 10	SCC 11	SCC 12	SWL 1	SWL 2
Chalcanthite										91						91						
Muscovite	4.3				27.8	27.8	4.08	12.4					10.1							9.5		
Kaolinite	20.2	16.4					47.1		7.2				6.25				67.4		72	82.8	27.1	27.1
Talc			30.8	30.8																		
Whewellite															96.5			92.5				
Quartz	71.1	80.7	49.9	49.9	72.0	72.0	43.2	50.3					29.2								77.2	77.2
Hematite		6.2							29.4			93.4										
Halloysite			11.4	11.4					60.3								31.7		1.73	4.4		
Goethite													46.3				7.99		20.4			
Albite								32.3														

Figure 4.56: Percentage composition of minerals contained in the earthy materials

From the above figure, there is presence of quartz in many of the samples from each representative country with BTS 2 having the highest percentage. The compositions are present in this order for each country, BTS 2 > SWL1 and SWL 2 > DRC 1 and DRC 2 > BTS1 > NG2 > CMR 1 and CMR 2 > NG 1 > SCC 5. No mineral was identified in SCC3 and SCC6 samples, which shows that these samples are inorganic materials. Muscovite was only present in BTS1, DRC A, DRC B, NG1, NG2, SCC5 and SCC12. Heamatite was identified in BTS2, SCC1 and SCC4. Kaolinite appeared in BTS1-2, NG 1, SCC 1, SCC 5, SCC 9, SCC 11, SCC 12, SWL 1 and SWL 2. The BET surface area of the studied samples were also obtained in terms of their adsorption and desorption capacity (Table 4.28). SCC 1 had the highest surface area of 52.04 m^2/g, this is an indication that smearing of the earthy material will be easily possible as there would not be abrasion whereas SCC 2 has 0.11 m^2/g.

Table 4.28: BET and BJH physisorption analysis (adsorption and desorption)

Samples	**Single point surface area (m^2/g)**	**BET surface area (m^2/g)**	**BJH adsorption cumulative surface area of pores (m^2/g)**	**BJH desorption cumulative surface area of pores (m^2/g)**	**Single point adsorption total pore volume (cm^3/g)**	**BHJ adsorption cumulative volume of pores (cm^3/g)**	**BJH desorption cumulative volume of pores (cm^3/g)**	**Adsorption average pore diameter (BET) (Å)**	**BJH Adsorption average pore width (Å)**	**BJH Desorption average pore width (Å)**
BTS 1	14.74	15.35	18.12	17.46	0.04	0.04	0.04	103.67	92.15	101.62
BTS 2	20.95	21.75	25.33	24.41	0.07	0.08	0.08	138.61	123.50	133.73
CMR 1	29.08	29.60	29.70	34.64	0.07	0.07	0.07	91.35	92.83	83.29
CMR 2	25.93	26.60	26.44	29.71	0.06	0.06	0.06	87.88	88.80	82.47
DRC A	19.72	20.21	16.45	15.00	0.03	0.03	0.03	62.20	72.87	80.85
DRC B	13.18	13.52	13.94	13.90	0.03	0.03	0.03	96.31	94.20	96.00
NG 1	6.29	6.38	7.20	7.17	0.02	0.03	0.03	**155.05**	141.04	155.49
NG 2	12.45	12.95	7.66	7.90	0.02	0.01	0,01	**48.54**	70.96	69.13
SCC 1	50.04	**52.04**	57.18	56.10	0.10	0.10	0,11	76.58	72.87	75.08
SCC 2	0.09	**0.11**	0.12	0.10	-	-	-	113.35	99.27	141.06
SCC 3	0.12	0.15	0.20	0.69	-	-	155.84	58.48	-	-
SCC 4	10.96	11.40	12.82	12.03	0.04	0.04	0.04	137.12	115.62	132.87
SCC 5	22.94	23.79	26.63	26.97	0.07	0.07	0.07	114.69	106.15	108.61
SCC 6	0.25	0.30	0.24	0.17	-	-	-	99.23	120.18	199.19
SCC 7	0.22	0.26	0.08	0.10	-	-	-	154.02	454.19	491.00
SCC 8	1.35	1.42	1.54	1.47	0.01	-	0.01	143.02	127.93	152.47
SCC 9	38.94	40.44	41.10	41.80	0.07	0.07	0.08	71.99	72.73	73.30
SCC 10	0.55	0.65	0.86	0.69	-	-	-	148.35	110.93	160.87
SCC 11	26.62	27.60	30.62	31.57	0.10	0.10	0.10	133.40	124.05	125.47
SCC 12	27.32	28.29	31.02	32.00	0.10	0.10	0.10	137.28	128.85	129.41
SWL 1	35.81	36.90	37.91	38.36	0.10	0.10	0.10	102.93	102.45	105.18
SWL 2	25.42	26.13	24.57	25.32	0.10	0.05	0.06	81.59	87.29	89.59

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

5.1 CONCLUSION

The objectives of the study were to physico-chemically, chemically and mineralogically characterise indigenous earthy materials used as cosmetics, with the view of identifying the various earthy materials and their indigenous names. The study was systematised from the collection of samples, physico-chemical and chemical analyses with the appropriate instrument leading to the interpretation of data responding to the research questions (Chapter 1).

The following concluding remarks was observed in the above study:

PHYSICO-CHEMICAL OUTCOME OF THE STUDIED EARTHY MATERIALS

In the physico-chemical analysis, the morphology, particle size, BET and the physisorption isotherm of the studied samples were obtained, below are the summary of results obtained:

(a) Morphology: With the aid of the scanning electron microscope, the following surfaces were obtained from the studied earthy materials: BTS 1, BTS 2, SCC 4 showed spongy surfaces, flaky surfaces were observed in CMR 2, DRC 1, DRC 2, SCC 7 and SCC 10 whereas NG 1 and SCC 11 are fibrous materials. Platy surface were seen in NG 2, SCC 3 and SCC 6. CMR 1, SWL 1, SWL 2, SCC 1, SCC 5, SCC 9, SCC 12 exhibited coarse surfaces while SCC 2 and SCC 8 showed platelets and pseudo-hexagonal respectively. It was observed from the micro-elemental analysis that some material showed the presence of elements found in clay minerals used in cosmetic application.

(b) Particle size: The particle sizes of each of the representative samples were determined using hydrometer method; the data obtained was used in the classification using ternary diagram. This helped in achieving the processibility, appearance and the performance of the studied earthy materials and it was obtained that samples that fell within the range of clay (<0.0002mm) can be referred to as in terms of minerals as secondary minerals, whereas samples which were determined to be sand or silt have their diameters between 0.002-2.0mm and can be classified as quartz or feldspar.

From the soil textural diagram (Figure 4.45) showed that samples BTS 1, BTS 2, NG 1, SCC 4, SCC 5, SCC 9, SCC 11, SCC 12, SWL 1 and SWL 2 were clay loam soil, DRC B and CMR 1 are silt clay loam soil and SCC 8, SCC 1, NG 2 and SCC 6 are sandy clay soil, clay loam, sandy loam and sand, respectively.

(c) Physisorption isotherm: The classification and the different types of the physisorption isotherm were determined; this helped in knowing the materials which are suitable for application and was classified in terms of their adsorption types (Types I- VI), textural properties (microposity, mesoporosity and macroporosity) and their absorbing capacity. Samples form Botswana (BTS 1 and BTS 2), Cameroon (CMR 1 and CMR 2), Nigeria (NG 1 and NG 2), South Africa (SCC 4, SCC 5, SCC 8, SCC 9, SCC 11 and SCC 12) and Swaziland (SWL 1 and SWL 2) fall within Type II adsorption isotherm, whereas samples SCC 2, SCC 3, SCC 6, SCC 7 and SCC 7 (South Africa) are Type III isotherm.

CHEMICAL CONSTITUENTS OF THE STUDIED EARTHY MATERIALS

Trace elements were determined and the following elements were obtained from the studied samples: Ag, Al, As, Au, Ba, Bi, Br, Ca, Cd, Ce, Cl, Co, Cr, Cs, Dy, Er, Eu, Fe, Ga, Gd, Ge, Hf, Hg, Ho, I, In, K, La, Lr, Lu, Mg, Mn, Mo, Na, Nd, Ni, Nb, Os, P, Pb, Pd, Pr, Pt, Re, Rh, Ru, S, Sc, Se, Sb, Si, Sm, Sn, Sr, Ta, Te, Tb, Th, Ti, U, V, W, Y, Yb, Zr, Zn though some appeared in small concentrations and they aligned with the EDX results. On the other hand, it is necessary to study the existence of hazardous elements such as As, Pb, Hg, Cd, Se, Sb, Cu and their kinesis in the human body to prevent harmful effects to health.

MINERALOGICAL CONSTITUENTS OF THE STUDIED EARTHY MATERIAL

The mineralogy was determined and the following minerals were observed after characterisation with XRD: Albite, calcite, goethite, halloysite, hematite, kaolinite, mica (muscovite), quartz, illite, smectite (montmorilonite) talc and whewellite. Quite a number of the samples contained kaolinite (BTS 1-2, NG 1, SCC 1, 5, 9, 11, 12, SWL 1-2) which is a good dermatological protector including talc and mica which have protective film and luminous effect.

At the end of the study the physico-chemical parameters, chemical constituents and mineralogy associated mineral phases of the earthy materials were appropriately investigated and clearly understood and the study also showed that earthy materials are widely dominated by clay minerals.

5.2 RECOMMENDATIONS

- Feedback should be sent to different communities who apply the studied earthy materials by enlightening them on the effects of long term usage, in terms of the toxicity of the trace elements.
- There is need for modification and beneficiation of the studied earthy materials before topical application, this is to improve the quality of the earthy materials, for instance removal of quartz and other unwanted materials present.

- Nitrogen was used as the adsorbate for the determination of surface area and porosity of this study, it is hence recommended that other gaseous adsorbates (argon, carbon dioxide, ethane, helium, krypton, methane, nitrogen, water vapour and xenon) should also be applied to the earthy materials (gas adsorption) especially samples with high surface area to ascertain the accuracy. This should be determined also at 77 K.

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Appendix 1: Kruskal-Wallis Test (Nonparametric ANOVA)

The P value is approximate (from chi-square distribution) because at least one column has two or more identical values. Kruskal-Wallis Statistic KW = 130.14 (corrected for ties)

```
                         Number    Sum     Mean
                             of     of      of
      Group                 Points   Ranks   Ranks
=============== ======= ======= =======
         O                  22   5319.0   241.77
         Al                 22   3626.0   164.82
         Si                 22   4045.0   183.86
         K                  21   2571.0   122.43
         Fe                 21   3503.0   166.81
         Ti                 22   2114.0   96.091
         C                  22   2663.0   121.05
         Mg                 22   2074.0   94.273
         S                  22   2309.0   104.95
         Ca                 22   2203.0   100.14
         V                  21   1804.0   85.905
         Cu                 22   1960.0   89.091

                Number
                  of
    Group        Points   Median    Minimum    Maximum
=========   ===== ======   ======== ========
         O         22      53.070    0.000      87.350
         Al        22      10.585    0.000      15.000
         Si        22      17.525    0.000      33.350
         K         21       0.000    0.000       5.660
         Fe         21       6.310    0.000      38.750
         Ti        22       0.000    0.000      17.050
         C         22       0.000    0.000      45.650
         Mg        22       0.000    0.000       4.550
         S         22       0.000    0.000      81.010
         Ca        22       0.000    0.000       6.350
         V         21       0.000    0.000       0.2400
         Cu        22       0.000    0.000      35.050
```

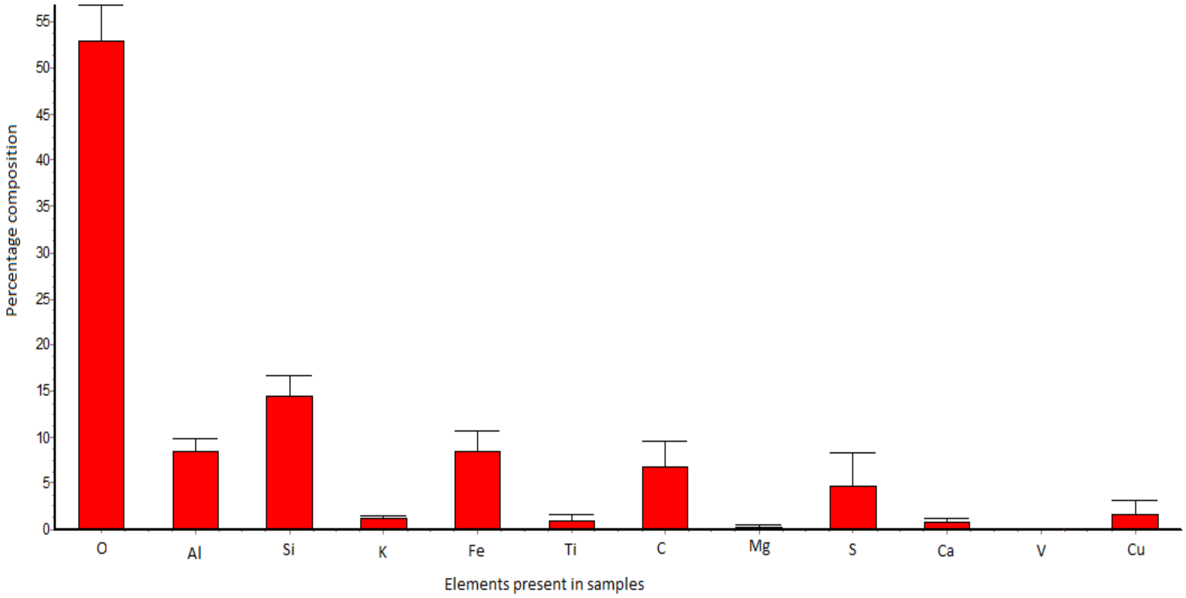

Figure 4.57: Graphical representation of elements present in the samples (XRF) with their percentage compositions.