Full Length Research Paper

Characterization and classification of clay minerals for potential applications in Rugi Ward, Kenya

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The applications of various clayey minerals are related to their structural, physical and chemical characteristics. The physical and chemical properties of the clayey minerals dictate their utilization in the process industries and beneficiation required before usage. The study aimed at establishing the potentiality of clayey minerals from the study area, and the possibility of exploring and exploiting them in order to spur industrial development and promote economic self reliance of Kenya as a nation. The plasticity, particle size, surface area, chemical and mineralogy composition, morphological, thermal analysis and other physical properties were studied using various techniques. The clay samples composed of albite (5-16.7%), kaolinite (11.4-36.2%), microcline (15.2-35.3%), quartz (24.3-68.1%), hornblende (7.6% in samples from Ngamwa only), and other mineral impurities in small amounts. Ngamwa clayey materials consist of high impurities of chemical oxides such as TiO_2, MnO, MgO and Fe_2O_3. Generally, quartz and iron were the major impurities present in the samples from the concerned sites. The findings shows that clayey minerals from the study area can be exploited for commercial production of ceramic products after beneficiation using low cost and environmental friendly techniques in order to reduce the levels of iron, quartz, and other impurities to acceptable levels.

Key words: Kaolin, Impurity minerals, shrinkage, plasticity index, surface area, quartz.

INTRODUCTION

Clay is a naturally occurring material composed of layered structures of fine-grained minerals which exhibit the property of plasticity at appropriate water content but becomes permanently hard when fired (Heckroodt, 1991; Njoka et al., 2015). The clay material is formed from chemical weathering processes on the earth's surface, and contributes about 40% of the fine grained sedimentary rocks (mudrocks) which includes mud stones, clay stones and shales. Clay minerals are generally composed of aluminum silicates which are formed by tetrahedral and octahedral sheets that are linked together through sharing of apical oxygen atoms (Madejova, 2003). The formation of clay minerals is dependent on physicochemical conditions of the immediate weathering environment, nature of the starting materials and other related external environmental factors (Wilson, 1999),

thus resulting into various types of clay materials. Consequently, the application potential of any clay mineral type in nature will depend on its chemical composition, structure and other inherent properties (Landoulsi, 2013). On this regard, clay minerals are classified into different groups as follows; Kaolinite, Smectite, Vermiculite Illite and Chlorites.

Kaolinite group which includes clay minerals like kaolinite, hallosite, nacrite and dickite, is a 1:1 type clay mineral. It is composed of one layer of silica and one layer of alumina, which is formed under acidic conditions through advanced weathering processes or hydrothermal changes of feldspars and other alluminosilicates (Miranda-Trevino, 2003). The chemical formula of kaolinite is $Al_2O_3.2SiO_2.2H_2O$ (39% Al_2O_3, 46.5% SiO_2 and 14.0% H_2O) and its structure possesses strong binding forces between the layers which resists expansion when wetted (Miranda-Trevino, 2003; Trickova, 2004). The cation exchange capacity (CEC) of kaolinite is less than that of montmorillonite due to its low surface area and low isomorphous substitution that result from its high molecular stability (Aroke, 2013; Murray, 1999) and this contributes to its low plasticity, cohesion, shrinkage and swelling. However, the material can adsorb small molecular substances such as lecithin, quinolone, paraquat, diaquat polyacrylonitrite, some proteins, bacteria and viruses (Williams and Environmental, 2005). Industrial uses of Kaoline includes; manufacture of paper, paint, rubber, ceramic, plastic and pharmaceutical products, catalyst for petroleum cracking and auto exhaust emission catalyst control devices, cosmetics base and pigments (Olaremu, 2015). Furthermore, kaolin is incorporated as an anti-cracking agent in the manufacture of fertilizer prills, as a carrier for pesticides, manufacture of white cement where it contributes alumina without iron, and in the production of glass fiber as a low-iron and low alkali source of alumina. On pharmaceutical applications for example, Kaopectate and Rolaids are used as the main ingredients for the original formulation of anti-diarrhea medication. Kaolin can be used to decontaminate aflatoxins, plant secondary metabolites, pathogenic microorganisms, heavy metals and other poisons in the animal diets which could be harmful to the digestive system through firm and selective binding of these noxious agents (Trckova, 2004). However, long term exposure to kaolin causes development of radiologically diagnosed pneumoconiosis. Kaolin that is heavily stained with ferric iron results to red or deep red colouration that is evenly widespread on ceramic bodies upon firing in an oxidizing environment. These iron stained clays can be used for coloured clay products but have no potential in high-grade ceramic applications. Therefore, brightness is the critical property in most high-value applications of kaolin (Chandrasekhar, 2006). Naturally, kaolin may be accompanied by other mineral impurities such as feldspar and mica, quartz,

titanoferous, illite, montmorillonite, ilmenite, anastase, haematite, bauxite, zircon, rutile, silliminate, graphite, attapugite, halloysite and carbonaceous materials (Ramaswamy and Raghavan, 2011), thus reducing its industrial usefulness. On this regard, mineralogical analysis coupled with visual assessment of the colour is crucial when sampling for kaolinites, and then complemented by beneficiation trials and product evaluation. However, the later processes are both expensive and time consuming. Preliminary characterization stage ensures that inferior samples are screened out so that resources can be directed towards investigation of samples with most commercial potential. This stage also enables the quantification of toxic elements and/or micronutrients (Fe, Sb, As, Cd, Co, Cu, Pb, Hg, Ni, Se, Te and Zn) whose levels depend on their geological history.

Smectite, which includes montmorrilonite, beidellite, nantronite, saponite and hectorite, are 2:1 layer clay minerals formed from the weathering of soils, rocks (mainly bentonite) or volcanic ash and belongs to a group of hydroxyl alumino-silicate (Erdogan, 2015). The variation of physical and chemical properties of bentonites within and between deposits is caused by differences in the degree of chemical substitution within the smectite structure, the nature of the exchangeable cations present, type and the amount of impurities present (Christidis and Warren, 2009). Minerals associated with smectites include quartz, cristobalite, feldspars, zeolites, calcite, volcanic glass and other clay minerals such as kaolinite (Abdou, 2013). The groups of smectite clays are distinguished by differences in the chemical composition pertaining substitutions of $Al3+$ or $Fe3+$ for $Si4+$ in the tetrahedral cation sites and $Fe2+$, $Mg2+$ or $Mn2+$ for $Al3+$ in the octahedral cation sites. Smectites have very thin layers and small particle sizes which contributes to high surface area and hence a high degree of absorbency of many materials such as oil, water and other chemicals (Marek, 2010; Amel, 2013). Additionally, smectites have higher cation exchange capacities, swelling and shrinkage properties than other clays. The variable net negative charge on smectites structural layers attracts water molecules into the interlayer area thus causing expansion, and the amount of swelling is related to the type of interlayer cation present. For example, the sodium rich smectite clays expand more than those containing calcium ions (Odom, 1984). Na-montmorillonites contain one water layer in the interlayer position and Ca-montmorillonites consists of two water layers which account for the basal spacing on the x-ray diffraction pattern of 15.4 Å for Ca-montmorillonite and 12.6 Å for Na-montmorillonite (Murray, 1999). Soils dominated by these types of minerals form a wide range of cracks upon drying up and the resultant dry aggregates are very hard hence making the soil difficult to till (El-Maarry, 2013).

These soils are stable in arid, semi-arid or temperature

climate and they form smooth gels when mixed with the right amount of liquids. Smectites are valuable minerals for industrial applications due to their high cation exchange capacities, high surface area, surface reactivity, adsorptive capacity and catalytic activity (Odom, 1984). This group of clays has found applications in bonding foundry sands, drilling fluids, iron ore pelletizing, agriculture (as carrier material for pesticides, fertilizers and for coating seeds), paper making, paints, pharmaceuticals, cosmetics, plastics, adhesives, decolorization and ceramics (Christidis, 1998). The material is also used as clarifying agents for oils and fats, chemical barriers, liquid barriers and catalysts (Abubakar, 2014). Preparation of some high technology materials such as pillared clays, organoclays and polymer/smectite-nano ccomposites involves purification and physicochemical modifications of pure smectite (Ray and Okamoto, 2003). However, the commercial bentonites should contain not less than 60% smectite.

Vermiculite is a hydrated magnesium aluminium-iron silicate which possesses 2:1 type of clay minerals (Tang, 2012). It has a layer charge of 0.9-0.6 per formula unit, and contains hydrated exchangeable cations primarily Ca, and Mg in the interlayer (Schulze, 2005). The high charge per formula unit gives vermiculite a high cation exchange capacity and causes this clay type to have a high affinity of weakly hydrated cations such as K^+, NH_4^+ and Cs^+. Upon rapid heating at a temperature of 900°C or higher, the water in raw flakes vermiculite flashes into steam and the flakes expand into accordion-like particles (Hillier, 2013), a phenomenon known as exfoliation (Belhouideg and Lagache 2014). The expanded or exfoliated material is low in density, chemically inert and adsorbent has excellent thermal and acoustic insulation properties, is fire resistant and odourless. The common applications of exfoliated vermiculite include making of friction light weight aggregates, thermal insulator, brake linings, various construction products, animal feeds and in horticulture (Chad and Stachowiak, 2004; Ucgul and Girgin, 2002; Lescano, 2013). Incorporation of vermiculite in fertilizers makes them more efficient in releasing nutrients and hence making the fertilizers more economical to the consumers (Abdel-Fattah and Merwad 2015). The layered structure and the surface characteristics of vermiculite enable them to be used in products such as intumescent coatings and gaskets, treatment of toxic waste and air-freight. The expansion of vermiculite on heating generates sufficient internal pressure which can be utilized to break hard rock during tunneling work (Ahn and Jong, 2015). Vermiculite ores contain variable amounts of other minerals such as feldspars, pyroxenes, amphiboles, carbonates and quartz that are formed along with vermiculite in the rock and occur as major components, as well as minor components such as phosphates, iron oxides, titanium oxides and zircon (Lescano, 2013). Some impurities like asbestiform amphibole minerals found in vermiculite have toxicity impact on human health as they lead to development of diseases such as malignant mesothelioma, asbestosis or lung cancer; hence, characterization of clays is important in order to identify such impurities.

Illite clay mineral group is also called clay micas. Mica is a group of phyllosilicate minerals with crystalline structure that can be split or delaminated into thin sheets that are platy, flexible, clean, elastic, transparent to opaque, resilient, reflective, refractive, dielectric, chemically inert, insulating, light weight and hydrophilic (Unal and Mimaroglu, 2012). The atoms of mica minerals are bonded together into flat sheets which allow a perfect cleavage of the minerals to produce tough sheets that occur in a variety of colours including brown, green, black, violet or colourless and often with a vitreous to pearly luster (Amrita et al., 2011). Studies have shown that there are over 30 members of mica group, but six forms that are found in nature and commonly used in microscopy and other analytical applications consist of muscovite, biotite, phlogopite, lepidolite, fuchsite and zinnwaldite (Orlando, 2002).Three members (illite group) which includes illite, glauconite and muscovite are referred to as clay minerals because they exhibit characteristic properties of clay, with illite mineral being the most common. Illite is formed from weathering of potassium and aluminum rich rocks like muscovite and feldspar under alkaline conditions. Illite group is a 2:1 layer silicate clay mineral which is non expansive because the space between the crystals of individual clay particles is filled by poorly hydrated potassium cations or calcium and magnesium ions which hinder water molecules from entering the clay structure. The cation exchange capacity of Illite ranges between 20-40 meq per 100 g. The colour of the minerals ranges from grey white, silvery white to greenish grey. The illites find application in structural clay industry and in agro minerals due to high potassium content (Njoka et al., 2015; Van, 2002). Mica clay ores contain a variety of impurities which includes quartz, feldspar, kaolin and pyroxene (Capedri et al., 2004). Presence of these minerals in mica ores will impact upon the industrial value of these deposits and the processing complexity thus reducing or increasing its value depending on the applications (Gaafar, 2014).

Chlorites are hydrous aluminosilicates that are arranged in a 2:1 structure with an interlayer (Wiewiora, 1990). They incorporate primarily Mg, Al and Fe cations and to a less extent Cr, Ni, Mn, V, Cu and Li cations in the octahedral sheet within the 2:1 layer and in the interlayer hydroxide sheet. They also exhibit a large substitution of Si by Al cations in the tetrahedral sheet (Ako, 2015). The colour of chlorites varies from white to almost black or brown with a tint of green where these optical properties are coupled to the chemical composition of chlorite (Saggerson, 1982). Knowledge of

Figure 1. Locally made clay products.

the chemical composition of chlorite is important in the study of phase relationships in low and middle grade metamorphic rock (Albee, 1962).

Considering the diversity of clay mineral groups in nature, the initial mineralogical and chemical examination of clay ores can be used to indicate the suitability of the material for different applications. In Kenya, there are several industries which can utilize the readily available and cheap clay raw materials after beneficiation in order to support industrial growth and relieve the government off the burden of importing such products. The improved industrial utilization of clay minerals in the country will depend mainly on the quality and durability of the material, and for this to be realized, there is need for rigorous studies on this resource. Unfortunately, very little attention has been given to clay characterization and mineralogy in Kenya despite the growing demand for clay products and the possibility of creating jobs through cottage industries. Currently, the local communities in Kenya are relying on the indigenous knowledge to make some clay products whose quality is hard to determine and neither does it meet the export standards as shown in Figure 1.

The objective of this study was to carry out the mineralogical, physical and chemical characterization of Rugi clay deposits in order to highlight its potential application and encourage more studies on this unexploited field.

MATERIALS AND METHODS

Study area

The ceramic clays occur in Tabaya-Karundu Valley in Rugi ward

which is lowland in Nyeri County. The valley has a west-east orientation and covers an area of about 38 ha. The region experiences average temperatures ranges of 12 - 27°C with low temperatures in the month of June and July and highest temperatures in the months January-March and September-October. The average rainfall lies between 500 mm and 1500 mm per annum with bimodal rainfall pattern where long rains occur between March and May and short rains between October and December. Within the valley, there are two major excavation sites for ceramic clay that are close to each other but fall in different administrative units namely, Mweru and Karundu. The former site (Mweru) lies in Mweru sub location at an altitude of 1441 m above sea level on latitude 0° 36.474' S and longitude 37° 6.828' E, whose soil appearance is black/brown (Figure 2).

Karundu lies in Karundu sub location at an altitude of 1445 m above sea level, latitude 0° 36.400' S and longitude 37° 6.799, and the soil appearance is grayish white (Figure 3).

The two sites are located less than 200 m off the Nairobi-Mukurwe-ini highway, and both lie on a swampy ground. The soils within the sites are typically waterlogged with the water bearing viscous appearance and issuing a smell characteristically indicative of the presence of humic acids. Phagmites (*Typha* spp.) are the dominant vegetation on the sites, and in areas where excavation was abandoned, the local community grows a thriving crop of arrowroots. A third excavation site locally known as Ngamwa lies a little lower than Mweru and Karundu sites. Ngamwa lies at an altitude of 1427 m above sea level on latitude 0° 36.504' S and longitude 37° 7.913 E, with soils bearing a light brown coloration and coarse texture. This site is farther (2 km) off the highway than the first two sites, it is impassable and inaccessible due to the poor terrain, and there was virtually no evidence of recent excavation activity compared to the other sites.

Sampling techniques

Three sites namely, Karundu, Mweru and Ngamwa were chosen using purposive sampling technique to collect samples. The collection and preparation of clayey samples was carried out as described by Njoka et al. (2015). The quality and resolution of the obtained results was improved by performing pretreatment of the samples in order to remove the organic matter and other unwanted materials. Spectroscopic grade chemicals were used in the present investigation.

Instruments used and procedures

The following instruments were used in the present work. PG-990 Atomic absorption spectrophotometer, Analytikjena model contra 700, IRAffinity-1 FTIR Spectrophotometer, Shimadzu, Perkin Elmer Model TGA7, Thermal gravity analyzer, Transmission Electron Microscope JOEL.JEM-1210 (120KV, MULTISCAN CAMERA), Bruker AXS D8 Advance diffractometer, Quantachrome NOVA 1200 Gas sorption analyzer. The procedures used by Njoka et al. (2015) and El-Geundi et al. (2014) were adopted in the present study, and the Atterberg limits were determined as described by Melo et al. (2012).

RESULTS AND DISCUSSION

Table 1 presents the consistency limits and physical properties of clayey raw materials from Rugi ward. The consistency limits were determined in order to identify,

Figure 2. Mweru site.

Figure 3. Karundu site.

classify and predict the fine-grained soil behavior. Liquid limit, plastic limit, plastic index and linear shrinkage of the clayey raw materials collected varied from 40.00-64.00, 19.00-36.00, 18.00-29.00 and 9.00-14.00 respectively. These results showed that the collected clayey materials were inorganic clays except the samples from Karundu site at the depth of 0-20 cm which was inorganic silt. The average values of the plastic index of the samples from

Table 1. Physical properties of clay samples.

| Sample site | Depth (cm) | Atterberg limits (%) | | | | | Texture classes of clay | | | | | |
		Liquid limit	Plastic limit	Plastic index	Linear shrinkage	Inferences	% Clay	% Silt	% Sand	% Gravel	Plasticity ratio LL/PL	Inferences
	0-20	40.0	19	21	11	Inorganic silt	4	21	60	15	2.11	Silty sand
Karundu	20-40	44	26	18	9	Inorganic clays	33	17	48	2	1.69	Clayey sand
	40-60	44.5	25	19.5	9.28	Inorganic clays	49	17	33	1	1.78	Clayey sand
	0-20	44	25	19	10	Inorganic clay	28	15	55	2	1.76	Clayey sand
Mweru	20-40	53	26	27	12	Inorganic clays	25	11	49	15	2.04	Clayey sand
	40-60	53	31	22	10	Inorganic clays	31	20	41	8	1.70	Clayey sand
	0-20	63	32	31	13	Inorganic clay	49	19	29	3	1.97	Sandy clay
Ngamwa	20-40	64	36	28	14	Inorganic clays	56	18	23	3	1.78	Clayey sand
	40-60	60	31	29	14	Inorganic clays	55	17	26	2	1.93	Clayey sand

Karundu, Mweru and Ngamwa were 18.8, 22.7, and 29.33 % respectively. The results revealed that clayey raw material from Karundu have medium plasticity while those from Mweru and Ngamwa possess high plasticity. Furthermore, results from Ngamwa indicated that the clay soil has a finer (more clayer) texture as revealed by its higher value of plasticity index in comparison to the clayey materials from Karundu and Mweru. The high plasticity clayey materials from Ngamwa might be due to high levels of mineral oxide impurities such as TiO_2, MnO, MgO and Fe_2O_3. Clay identification chart using plastic limit and plasticity index parameters was used to identify the type of clayey minerals present in the samples. According to the clay chart, the results obtained in all sampling points were slightly lower in kaolinite than for pure kaolinite clays. The difference might be contributed by the presence of sand and silt in the samples. The plasticity ratio of 5.9, 2.16 and 1.59 indicates montmorillonite, illite

and kaolinite respectively. Results obtained in the present investigation are very close to what is expected for kaolinite clays except those from Karundu samples at the depth of 0-20 cm and Mweru at the depth of 20-40 cm which were close to that of illite clay. However, the obtained results are suggestive of the presence of both kaolinite and illite clayey minerals in the samples in question. The values of linear shrinkage ranged between 9.00-11.00, 10.00-12.00 and 13.00-14.00 for Karundu, Mweru and Ngamwa respectively. High linear shrinkage value in clayey samples from Ngamwa was attributed to the amount of available clay minerals in the samples whereas the slightly low shrinkage values obtained from Mweru and Karundu samples was associated with the presence of high amount of quartz which tends to decrease the magnitude of shrinkage. Clayey mineral samples from the study area consist of 4-56, 11-21, 23-60 and 2-15% of clay, silt, sand and gravel respectively. The clayey

mineral samples which were collected at Karundu (0-20 cm) and Ngamwa (0-20 cm) were silty sand and sandy clay respectively. The high level of gravel from Karundu (0-20 cm), Mweru (20-40 cm) indicated high level of quartz.

The oxides analysis results using XRF and AAS are presented in Table 2. The data obtained for Al_2O_3, SiO_2, CaO, TiO_2 and Fe_2O_3 were used to determine whether XRF and AAS analytical methods produced comparable results. Analysis was done using statistical programme for social sciences (SPSS) version 20 at p= 0.05, and confirmed using excel and manual approaches. The correlation values obtained were as follows; Al_2O_3 (R = -0.16, p=0.968), SiO_2 (R= 0.824, p=0.006), CaO (R= 0.446, p= 0.229), TiO_2(R= 0.173, p=0.655) and Fe_2O_3 (R= 0.609, p=0.081), while the standard errors of the estimates for Al_2O_3, SiO_2, CaO, TiO_2 and Fe_2O_3 were 4.63, 8.58, 0.18, 2.07 and 5.88 respectively. These results revealed that there was no significant

Table 2. Chemical composition of clay samples using XRF and AAS (%). Please provide the respective depths

Sample site	Depth (cm)	XRF									AAS										Conductivity in Hs
		MgO	V$_2$O$_5$	Al$_2$O$_3$	SiO$_2$	CaO	TiO$_2$	MnO	Fe$_2$O$_3$	K$_2$O	Al$_2$O$_3$	SiO$_2$	CaO	TiO$_2$	MnO	Fe$_2$O$_3$	K$_2$O	MgO	Na$_2$O	LOI	
Karundu	0-20	ND	ND	25	71	0.29	1.3	ND	2.3	ND	15.38	78.33	0.28	0.02	0.07	2.30	4.40	0.20	0.28	4.17	28.8
	20-40	ND	0.2	32	45	0.49	5.8	1.9	14.4	1.9	28.34	58.54	0.28	0.47	0.05	1.61	1.44	0.26	0.36	5.12	28.7
	40-60	ND	0.08	40	54	0.51	2.2	ND	4.40	ND	17.18	60.61	0.47	2.28	0.08	6.40	1.66	0.33	0.65	8.97	27.8
Mweru	0-20	ND	0.1ND	27	41	0.53	5.5	0.2	24.40	1.8	20.13	71.02	0.82	2.25	0.10	9.80	2.80	0.60	1.02	8.08	108.8
	20-40	ND	0.1	33	59	0.31	1.2	0.05	6.70	ND	13.50	84.27	0.24	2.62	0.06	2.56	0.76	0.22	0.19	4.08	105.2
	40-60	ND		33	49	0.50	6.6	ND	9.57	1.1	21.64	54.37	0.54	3.10	0.07	4.05	1.10	0.56	0.42	9.63	111.0
Ngamwa	0-20	ND	0.1	34	33	0.1	4.2	ND	17.9	0.33	29.10	49.39	0.54	2.64	0.09	11.60	0.55	0.56	0.35	10.06	21.8
	20-40	ND	0.1	30	30	0.1	3.4	ND	13.9	0.26	27.90	47.15	0.30	3.07	0.08	10.60	0.40	0.41	0.18	14.94	22.0
	40-60	ND	0.08	30	29	0.09	3.2	ND	13.0	0.2	30.30	44.70	0.27	2.41	0.07	11.10	0.40	0.40	0.20	13.80	22.5

correlation for all the oxides since their p- values were above critical value (0.05) except for SiO$_2$ which showed a strong positive correlation (R=0.82) at p-value =0.006 (below critical value). The F-value for SiO$_2$ was 14.81 at p=0.006 (less than critical value) indicating that there was no statistically significant difference in the precision when the two methods are used. The t-value for SiO$_2$ was 3.85 at p= 0.006 (less than critical value) confirming that there was no statistically significant difference in the silica results obtained using the two methods. Also a close scrutiny of the results revealed that several metal oxide were not detected by the XRF analytical method in some samples whereas they were detected in those samples by the AAS method. AAS usually exhibit superior sensitivity and low detection limit than XRF spectroscopic method. Therefore, based on above reasons, AAS results were used for analysis.

The average percentage of Al$_2$O$_3$ in clay mineral samples from Karundu, Mweru and Ngamwa were 18.96, 18.42 and 29.10 respectively and those of Fe$_2$O$_3$ were 3.44, 5.47 and 11.10 respectively. This revealed that the quantity of Al$_2$O$_3$ was less than 30% while that of Fe$_2$O$_3$ was more than 1% in all the samples studied. Clay with a composition of 5% or more of Fe$_2$O$_3$ are used as red firing clays, those with between 1 - 5% Fe$_2$O$_3$ are B tan –burning clay and those containing less than 1% Fe$_2$O$_3$ are used as white firing clays (Murray, 2007). Thus, these clays do not meet the conditions necessary for refractory fired clays, manufacture of high grade ceramic products such as white porcelain and glossy papers and other products that require clay with less than 1% iron content and at least 30% Al$_2$O$_3$. The presence of other oxide impurities like CaO, MgO etc. might also reduce the suitability of clayey mineral samples for refractoriness. The average quantities of Loss on Ignition (LOI) value obtained from clayey minerals from Karundu, Mweru and Ngamwa were 6.087, 7.263 and 12.933% respectively. Notably, there was high values of LOI of clay samples from Ngamwa which might imply that, they possess finer grains, high content

of Al$_2$O$_3$ and could be more compact compared to those from Mweru and Karundu. The relatively higher LOI values in clayey mineral samples from Mweru compared to Karundu were associated with high percentages of impurities, water and organic matter in the samples. The low values of alkaline oxides (K$_2$O, Na$_2$O) in clay mineral samples from Ngamwa in comparison to those from Mweru and Karundu implies presence of low percentage of flux minerals. Ngamwa clayey minerals showed a high percentage of Fe$_2$O$_3$ which might increase the action of alkaline flux that results into a lower melting temperature and an increase in the abundant liquid phases thus making the material difficult to crystallize.

The results of inorganic elements present in clay samples are summarized in Table 3. The average concentration in mg/kg of various elements obtained were; Karundu {Na (0.0243), Ca (0.0229), K (0.0427), Mg (0.0228), Fe (2.207), Mn (0.006), Zn (0.0016), Cu (0.0013), Cr (0.0094), Pb (0.001)}; Mweru {Na (0.0353), Ca (0.0364), K(0.0401), Mg (0.00364), Fe (1.25), Mn (0.0077),

Table 3. Composition (mg/kg) of inorganic elements in the clay samples.

Sample site	Depth (cm)	Na	Ca	K	Mg	Fe	Mn	Zn	Cu	Cr	Pb	Al	Sb	Co	Cd	Conductivity (µs)	pH
	0-20	0.0117	0.0210	0.0405	0.021	2.38	0.006	ND	ND	0.0126	0.0002	0.752	ND	ND	ND	28.8	5.14
Karundu	20-40	0.0499	0.0213	0.0508	0.0213	2.67	0.0120	0.0044	0.0044	0.0011	0.0011	1.798	ND	ND	ND	28.7	5.17
	40-60	0.0114	0.0263	0.0368	0.0262	1.57	ND	0.0005	0.0005	0.0037	0.0017	1.613	ND	ND	ND	27.8	5.21
	0-20	0.0178	0.0298	0.0460	0.0298	1.23	0.0157	0.0039	0.0066	0.039	0.0008	1.705	ND	ND	ND	108.8	4.45
Mweru	20-40	0.0386	0.0552	0.0258	0.0552	1.49	ND	ND	ND	ND	0.0004	1.107	ND	ND	ND	105.2	4.32
	40-60	0.0496	0.0241	0.0486	0.0241	1.03	0.0073	0.0058	0.0058	0.0058	0.0012	1.701	ND	ND	ND	111.0	4.35
	0-20	0.0140	0.0427	0.0262	0.0427	6.67	0.0146	0.0028	0.0030	0.0030	0.0014	1.942	ND	ND	ND	21.8	5.35
Ngamwa	20-40	0.0076	0.0431	0.0282	0.0431	7.18	0.0162	0.0027	0.0047	0.0047	0.0012	1.93	ND	ND	ND	22.0	5.37
	40-60	0.0162	0.0443	0.0347	0.0443	8.60	0.0181	0.0034	0.0034	0.0034	0.0024	2.84	ND	ND	ND	22.5	5.38

Zn (0.00393), Cu (0.0032), Cr (0.0095), Pb (0.0008)], Na (0.0243), Ca (0.0229), K (0.0427), Mg (0.0228), Fe (2.207), Mn (0.006), Zn (0.0016), Cu (0.0013), Cr (0.0094), Pb (0.001)}; Ngamwa {Na (0.0126), Ca (0.0434), K (0.0297), Mg (0.0434), Fe (7.483), Mn (0.0163), Zn (0.00297), Cu (0.0037), Cr (0.00683), Pb (0.001667)}. The high levels of iron in all clay samples collected might be associated with the black, brown or grayish white colour that was observed in clay mineral samples from the study area. This colouration will have a negative effect on the degree of brightness of the products manufactured using clay minerals from the study area as shown in Figure 1, hence reducing their quality. However, the final product quality can be achieved by reducing the levels of iron and other impurities present to acceptable levels by employing low cost and environmentally friendly techniques. The average pH of clay samples from Karundu, Mweru, Ngamwa were 5.17, 4.37 and 5.36 respectively, and all fall within the pH range of 4.0 to 9.0 for chemically inert kaolinites, implying that the kaolinites present in the studied clay samples are chemically inert. The average conductivity of clay samples from Karundu, Mweru, Ngamwa were 28.4, 108.3 and 22.1 µS respectively. The high value of conductivity of clay samples from Mweru is associated with low pH observed. However, the electrical conductivity has a linear relationship with cation exchange capacity, particle size distribution, mineralogy, organic matter content, porosity and water content of the soil sample. High electrical conductivity relates to clay minerals like the smectite group that exhibits high cation exchange capacity (CEC) thus, the low electrical conductivity observed in the clay samples from Kurundu and Ngamwa imply presence of clay minerals with low CEC like the kaolinite group. Low electrical conductivity can also be brought about by high levels of quartz and low levels of clay mineral content.

The average results of BET (Brunauer, Emmett and Teller) surface area for Karundu, Mweru and Ngamwa were; 35.222, 47.222, and 34.222 m^2/g respectively. The BET surface area for pure kaolinite ranges between 10-20m^2/g. The results obtained in the present investigation suggest the presence of kaolinite in the samples as was observed in the physico-chemical properties analysis. The high kaolinite values obtained compared to those of pure clay is associated with the levels of impurities like quartz, sodium, magnesium ions in the samples. The high level of very small size quartz which are smooth, uniform and non-porous might be present in the region thus contributing to high surface area. This is supported by the high amount of quartz (Karundu, 31.3%, Mweru, 68.1% and Ngamwa, 24.3%) which was present in the samples. Na^+ and Mg^{2+} saturated systems can contribute to a higher surface area compared to other elements. In the present study, the average level of Na^+ in the samples from Karundu, Mweru and Ngamwa were; 0.0242, 0.0353 and 0.0126 respectively while Mg^{2+} values were found to be 0.02283, 0.03636 and 0.04336 respectively. The high values of quartz, Na+ and Mg^{2+} in the samples from Mweru could have contributed to the high surface area

Table 4. BET surface area results.

Sample site	Depth (cm)	BET surface area (m²g)/	Pore volume cm³/g	Pore size (A°)	Nanoparticle size (A°)
			Single point adsorption total pore volume of pores less than 917.424 A° at PP/PO=0.97843255	Adsorption average width	Average particle size
Karundu	0-20	35.222	0.2.601	130.7983	1895.316
Mweru	20-40	47.222	0.11311	130.7915	1890.176
Mweru	40-60	46.6703	0.167204	143.3070	1285.618
Ngamwa	0-20	31.722	0.10301	129.8985	1891.376
Ngamwa	40-60	34.222	0.40201	133.7981	1888.276

observed. The lower BET surface area of the samples from Ngamwa might be associated with high level of weathering of kaolinite in the surface soils or authigeic formation of large kaolinite which could be as a result of less inhibition of crystal growth by organic matter (Melo et al., 2001). The average values of pore volume and pore size for Karundu, Mweru and Ngamwa were 0.20601, 0.167204, 0.40201 cm³/g and 130.7983, 143.307, 133. 7981 Å respectively. The average particle size of nano particles for samples from Karundu, Mweru, Ngamwa are 1895.316, 1285.618 and 1888.276 Å respectively. The high value of pore volume for samples collected from Ngamwa could imply that, the clay from this region have a better crystalline kaolinite in comparison with the other two sites studied (Table 4).

The representative X-ray diffractogram for the clay samples from Karundu site is shown in Figure 4. The d-spacing reflections at; 4.18545, 3.53312, 2.59849, 2.50075, 2.32134, 2.21881, 2.11127, 1.96630, 1.78147, 1.66399, 1.56111 and 1.48185 revealed the presence of kaolinite in the sample. The presence of albite, microcline in the samples was revealed by d-spacing reflection at 3.21200, 3.23012 respectively. The reflection at 3.30796, 2.52836, 2.21881, 2.11127, 1.80485 and 1.66399 showed that quartz was present in the sample. Generally, the reflections of quartz were the strongest in comparison with other peaks thus indicating dominance and high crystallinity of this mineral in the samples compared with other minerals. The peaks of illite and huminic acid at d-spacing 3.32000 to 3.35000 and 3.33000 respectively were not established due to the fact that the principle reflection of quartz (3.30796 Å) occurs almost at the same position.

Clay and non-clay minerals in the samples from Mweru site were identified using XRD method and a representative X-ray diffractogram is shown in Figure 5. The presence of kaolinite clay mineral was revealed by reflection at d- values of 4.17788, 3.52252, 2.31787, 2.21856, 2.10941, 1.96249, 1.66034, 1.5524 and 1.48023. The d-spacing at 3.20419 and 3.24103 revealed the availability of albite and microcline respectively in the sample. Quartz was identified by reflections at 3.30114,

21.21856, 2.10941, 1.96249, 1.80478, 1.66.95.

Figure 6 shows a representative X-ray diffractogram of the clay sample from Ngamwa site. The availability of the kaolinite in this sample was indicated by the reflection at 4.18303, 3.53124, 2.32200, 2.21872, 2.11326, 2.50119, 1.98008, 1.65982, 1.54713 and 4.8144. The d-spacing at reflection 3.21062 and 3.24012 indicated the presence of albite and microline respectively in the sample. Quartz was revealed by reflection at 3.30495, 2.54130, 2.22412, 2.111464, 1.97273, 1.81135 and 1.66119. The percentage composition of the minerals in the clay samples as revealed by XRD results is shown on Table 5.

The percentage composition of Albite was in the range (5.3-16.7), Kaolinite (11.4-36.2), Microcline (15.2-35.3) and Quartz (24.3-68.1). Kaolinite was the only clay mineral detected in the samples with appreciable amounts for industrial applications (greater than 10%). For kaolinite mineral to be utilized industrially, other accessory minerals like albite, microcline and quartz should be reduced to acceptable levels through appropriate beneficiation techniques.

The identification of different types of clay minerals was achieved by the use of absorption bands due to structural OH and Si-O groups that were obtained from the FT-IR spectrum. The types of cations that are linked directly to the hydroxyls influences the OH absorption bands and this is important for the determination of cation distribution around hydroxyls. The interpretation of the FT-IR spectrums in Figures 7 to 9 was done using the available literature (Madejova, 2003; Vaculikova and Plevo va, 2005; EmDadul, et al., 2013). A close examination of the obtained FT-IR spectrums revealed the presence of kaolinite clay minerals in all the samples that were investigated and this confirms the XRD results. The four bands in the ranges, 3620.55-3621.39, 3651.92-3653.75, 3670.01-3670.85 and 3690.31-3694.17cm^{-1} confirmed the presence of kaolinite in the samples. The presence of sharp doublets at around 3620.55-3621.39 and 3690.31-3694.17 further revealed the presence of kaolin group in the sample. The absorption bands at the range of 3620.55-3621.39 was assigned to the stretching
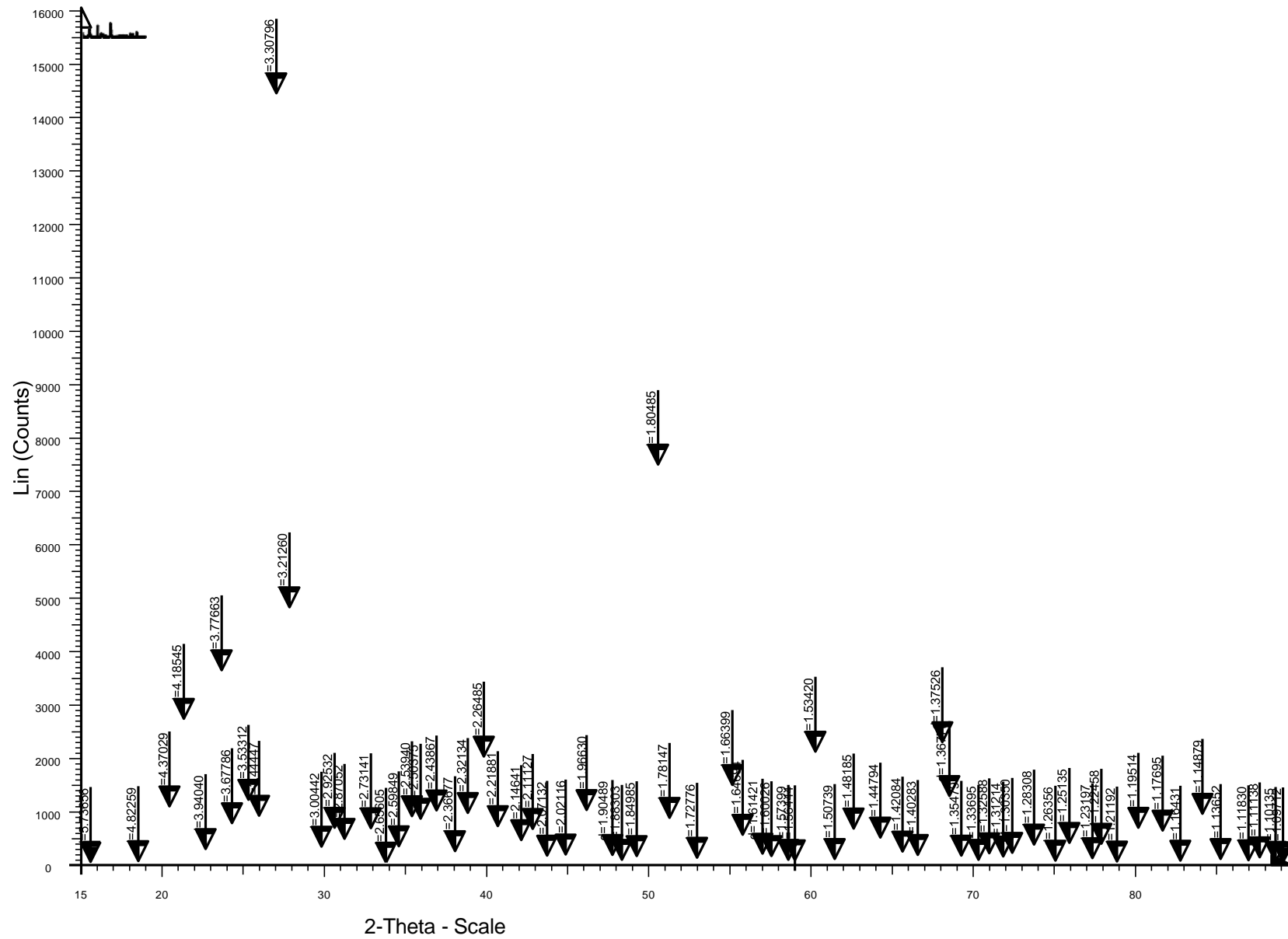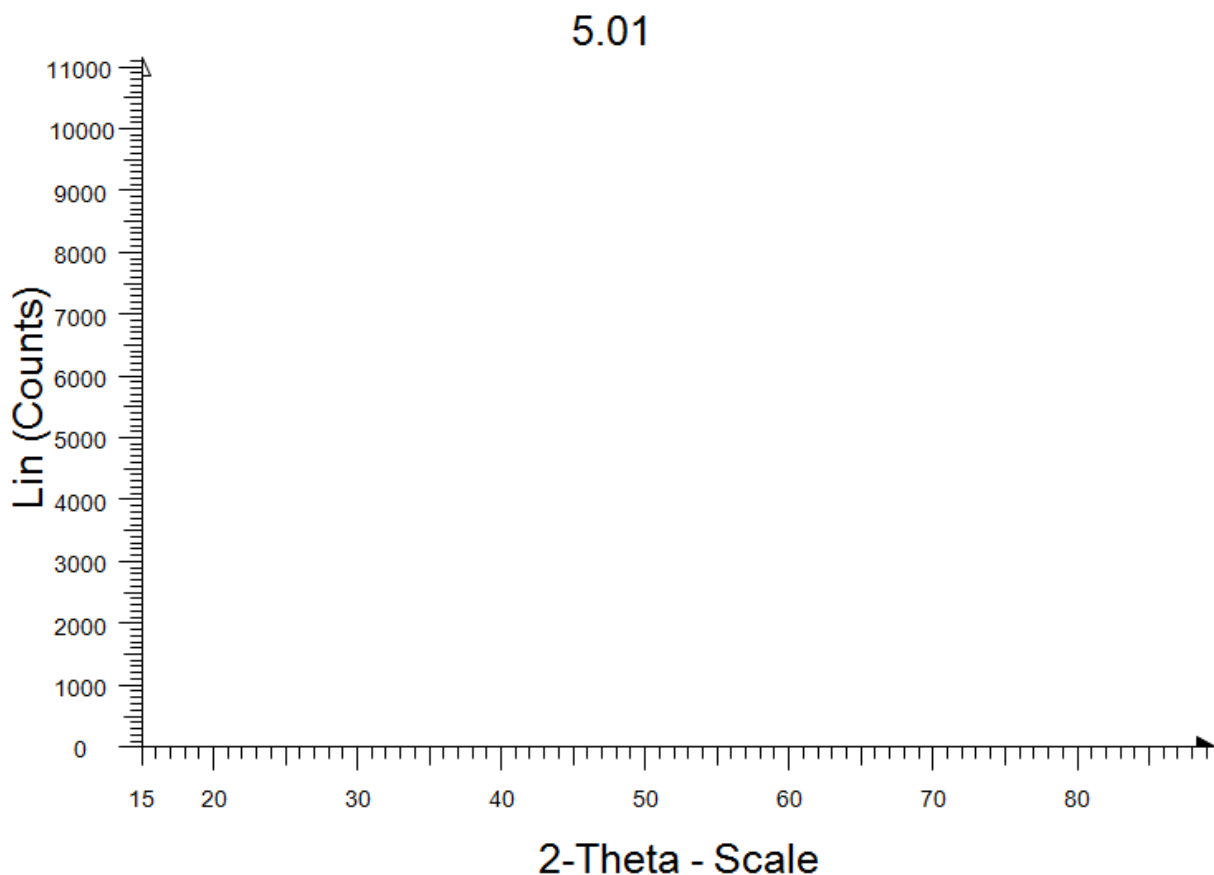
Figure 4. X-ray diffractogram for the clay samples from Karundu site.

5.01

Figure 5. X-ray diffractogram for the clay samples from Mweru site.

vibration of internal surface OH groups which is located between the tetrahedral and octahedral surface of the layers and it forms hydrogen bonds with the oxygen of the Si-O-Si bonds on the lower surface of the next layer which is weak. The strong band at around 3690.31-3694.17 cm^{-1} was attributed to the in-phase symmetric stretching vibrations while the two weak bands at around 3651.92-3653.75 and 3670.01-3670.85 cm^{-1} were due to the out-of plane stretching vibrations. The bands observed at the range of 911.40-914.30 cm^{-1} were either due to vibrations of the inner surface or OH bending groups which is common to kaolinite containing samples, while occurrence of bands at 936.48-936.58 cm^{-1} are as a result of surface OH groups. The bands at the ranges 691.15-695.37 cm^{-1} and 752.27-754.20 cm^{-1} are attributed to the surface hydroxyls while the ones at 1006.89-1113.94 cm^{-1} can be associated with Si-O stretching vibrations of kaolinite. The bands occurring at the ranges 3645.36-3652.75 (OH stretching), 911.40-913.33 (shoulder), 780.24-795.67 and 747.86-753.23 (doublets) cm^{-1} indicated the presence of illite in the sample and they represent Al-Mg-OH deformation. The

strong stretching bands ranging between 909.06-1112.97 and slightly less intense bending bands at406.97-794.95 cm^{-1} revealed the presence of Si-O bonds in all the samples studied. The bands observed at 460.35-4621.87 and 522.96-524.96 cm^{-1} (Si-O asymmetrical bending vibrations), 692.47-695.37 (Si-O symmetrical bending vibrations) 780.24-789.06 and 794.95-795.67 cm^{-1} (symmetrical stretching vibrations) and 1081.15-1099.47 cm^{-1} (Si-O symmetrical stretching vibrations due to Al for Si substitution) indicated the presence of quartz in the samples. The bands ranging from 590.92-604.03 cm^{-1} can be attributed to O-Si-(Al)-O bending vibrations and revealed the presence of microcline feldspar in the samples which accords the results from XRD. The four OH stretching bands (3669.00, 3656.00, 3642.00 and 3623.00cm^{-1}) were associated with the presence of hornblend in the sample. The bands observed at the ranges of 3411.10-3417.43, 2851.88-2957.97, 1031.96-1102.37, 1633.59-1650.36 and 1338.84-1350.17 cm^{-1} indicated humic acid was present in the sample which is in line with observation at the sampling sites. The bands recorded at the range of 2852.88-2957.97 was attributed
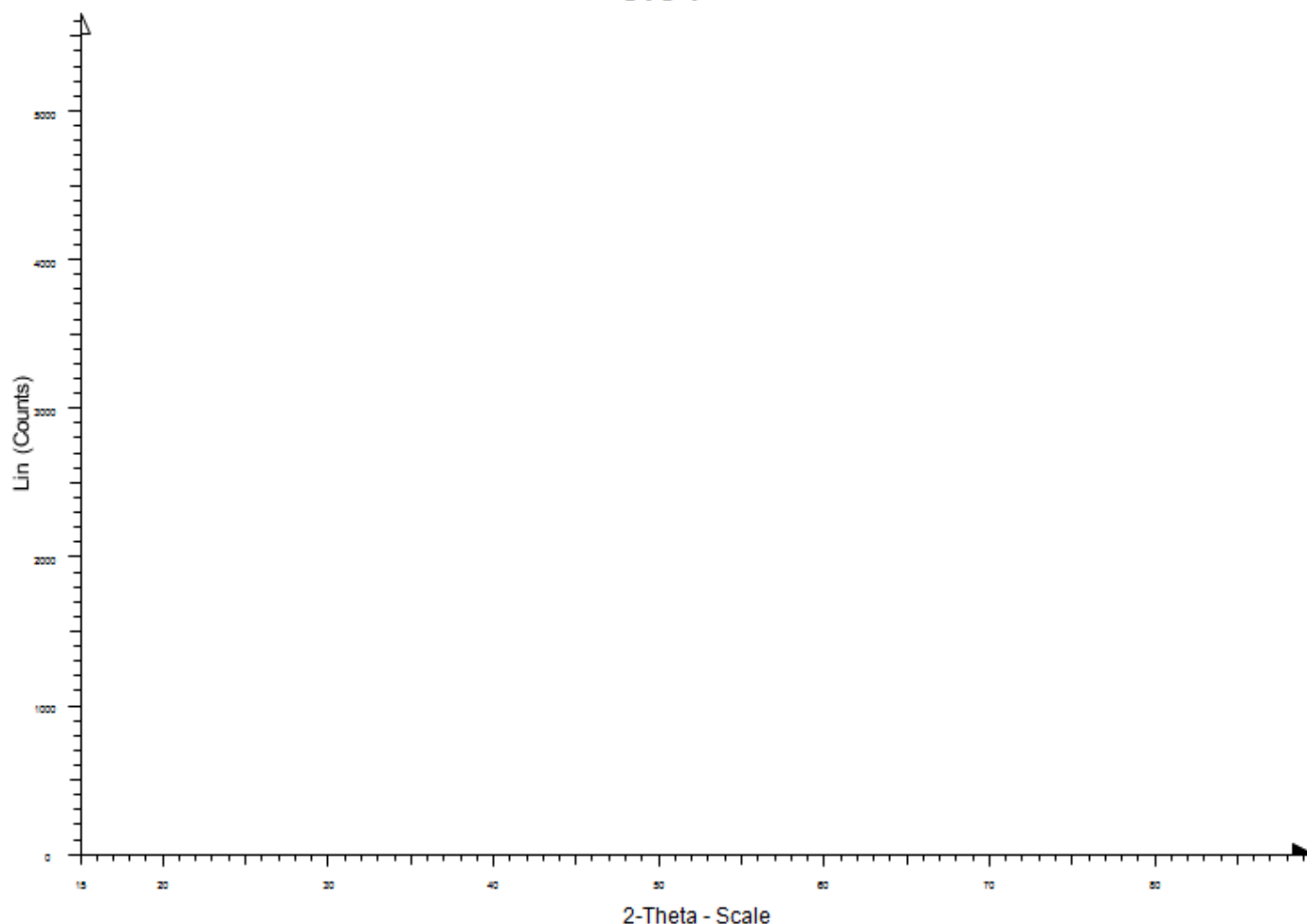
6.01

Figure 6. X-ray diffractogram for the clay samples from Ngamwa site.

Table 5. Percentage composition of clay and non-clay minerals in the sampled clays.

Site	Albite	Clinochlore	Hornblende	Hematite	Kaolinite	Magnetite	Microcline	Quartz
Karundu	16.7	-	-	-	16.6	-	35.3	31.3
Mweru	5.3	-	-	-	11.4	-	15.2	68.1
Ngamwa	11.4	-	-	-	36.2	-	20.4	24.3

to CH_2-CH_3 stretching, while those at 1633.59-1650.36 and 1338.84-1350.17 cm^{-1} indicated humic acid was present in the sample. The bands which appeared at the range of 2851.88-2957.97 was attributed to CH2-CH3 stretching while those at 1633.59-1650.36 and 1338.84-1350.17 cm^{-1} was attributed to COO- asymmetric and symmetric stretching respectively. Presence of the humic acid could contribute to the decrease in the amounts of Si

and Al contents in the clay structure due to decomposition of the Si-O-Si by acidolytic attacks.

Thermal analysis

The representative thermographic curves for the samples studied are shown in Figures 10 and 11. These curves
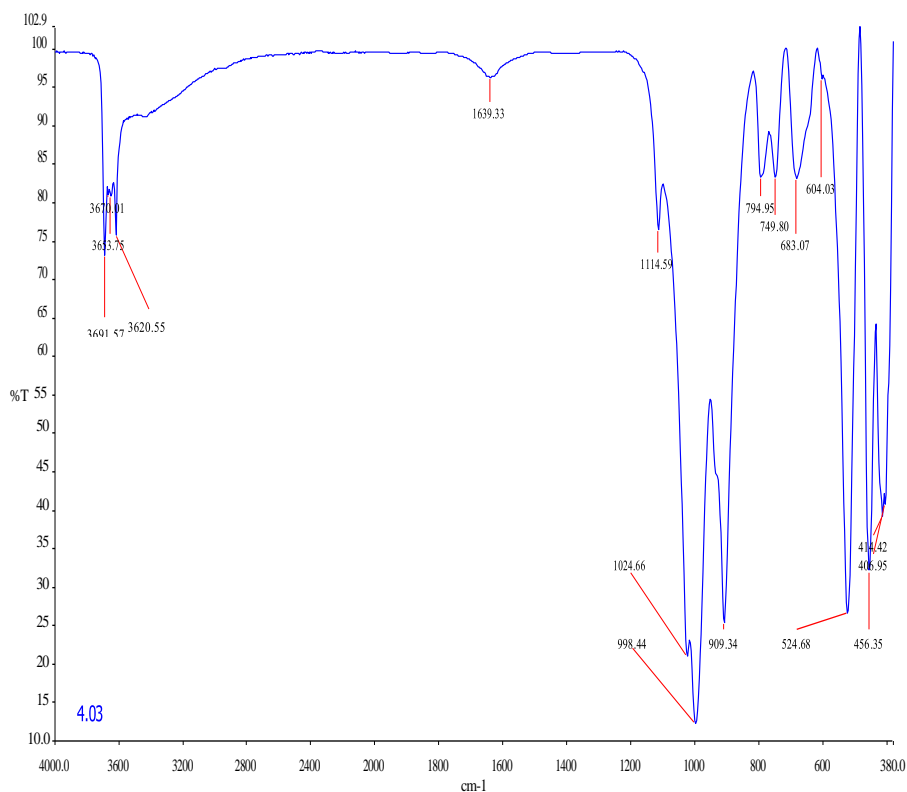
Figure 7. FT-IR Spectrum (Karundu site).
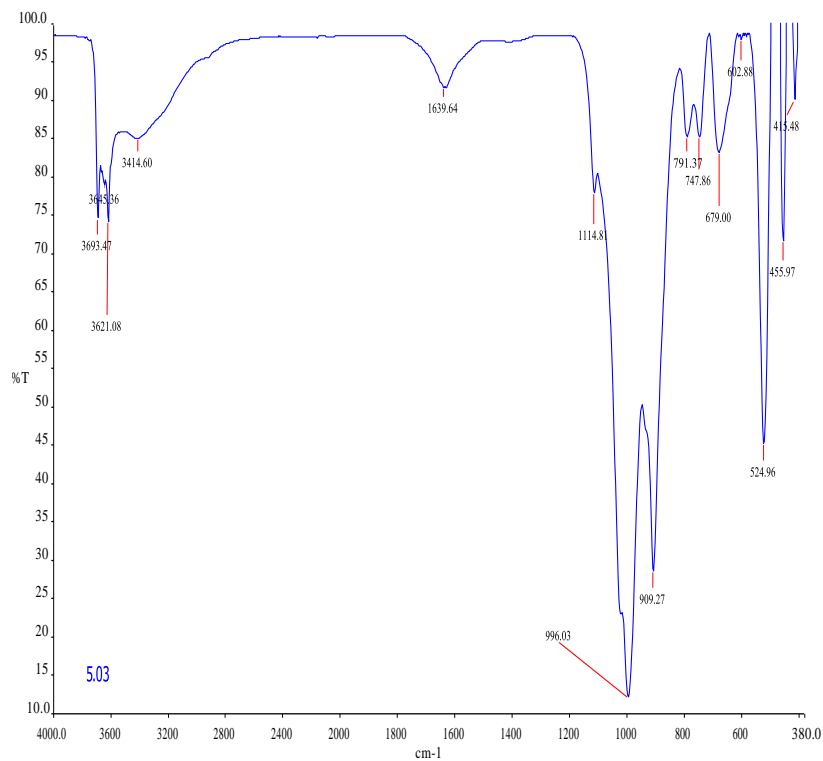
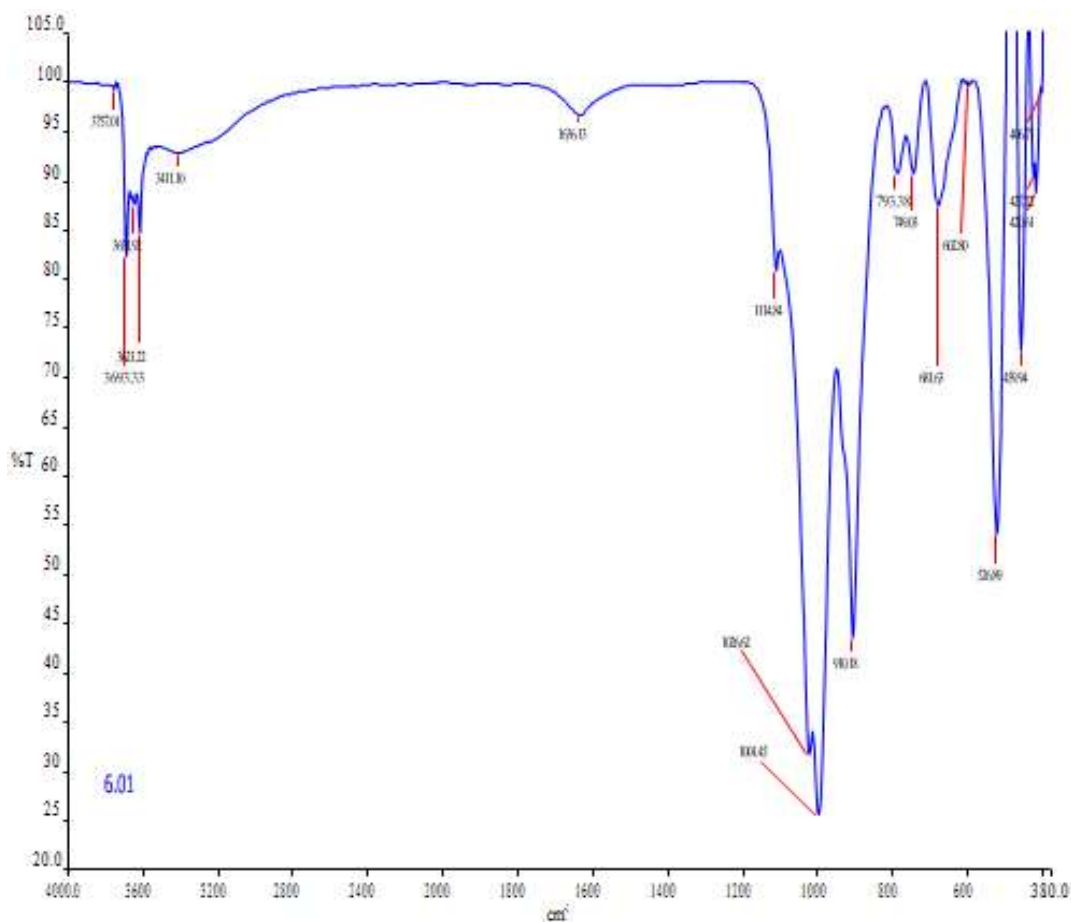**Figure 8.** FT-IR Spectrum (Mweru site).

Figure 9. FT-IR Spectrum (Ngamwa site).

contain useful information regarding various temperature ranges which is indicative of where the processes of dehydration, dehydroxylation and phase transformation of various clay minerals studied takes place. A close examination of the curves revealed that only 3.125% of free water, adsorbed water and volatile products are lost between the temperature ranges of 25-200°C. The loss in weight of 10.625% between the temperature ranges of 200 to 500°C was attributed to the loss of the products resulting from organic reaction. The dehydroxylation process which resulted to the loss of 0.875% of structural water took place between the temperature range of 500 to 800°C. About 0.625 of hydroxyl water was lost from 800 to 900°C which completed dehydration process. A combustion reaction between inorganic oxygen and organic carbon took place from 900 to 1000°C. The symmetrical and smooth thermal curve in the interval from 400 to 800°C suggested the presence of kaolinite in the samples. The representative of SEM micrographs of the clay minerals samples is presented in Figures 12 and 13. The presence of almost pseudo hexagonal shapes and very small flattened platelets observed in these

figures shows the presence of kaolinite. On further examination of SEM micrographs, the larger clay mineral particles seems to consist of much smaller platelets which indicates that the clay sample is made up of very fine particles. The presence of quartz was revealed by almost rounded and also V-shaped platelets with brighter luminescing and this confirms the results of XRD and FT-IR.

Conclusion

The clayey mineral samples are kaolinitic in nature, having more than 10% kaolinite and contain different types of impurities which make it less useful. The major impurities species are quartz and iron with minor ancillary cations such as Mn^{2+}, Mg^{2+}, Na^+ and K^+ etc. The identification and quantification of impurities in the clay samples from the study area makes it easier for future researchers in the selection or modification, and sequentialization of beneficiation process with the objective of reducing impurity levels to acceptable limits
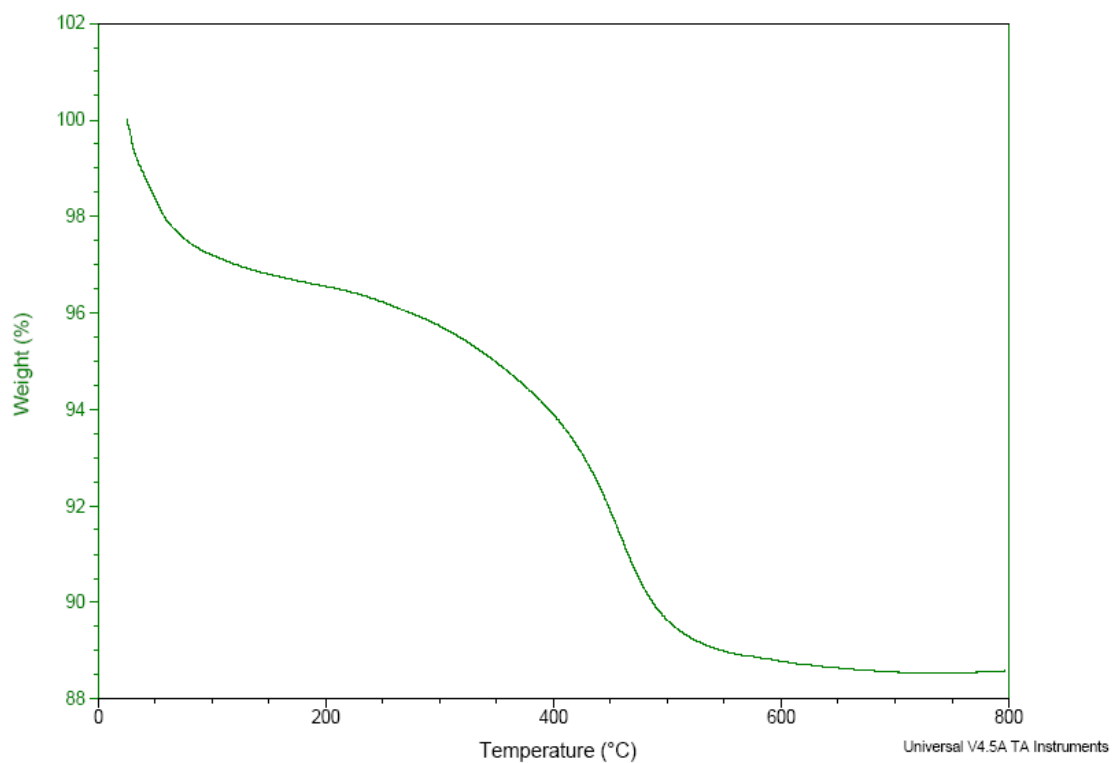
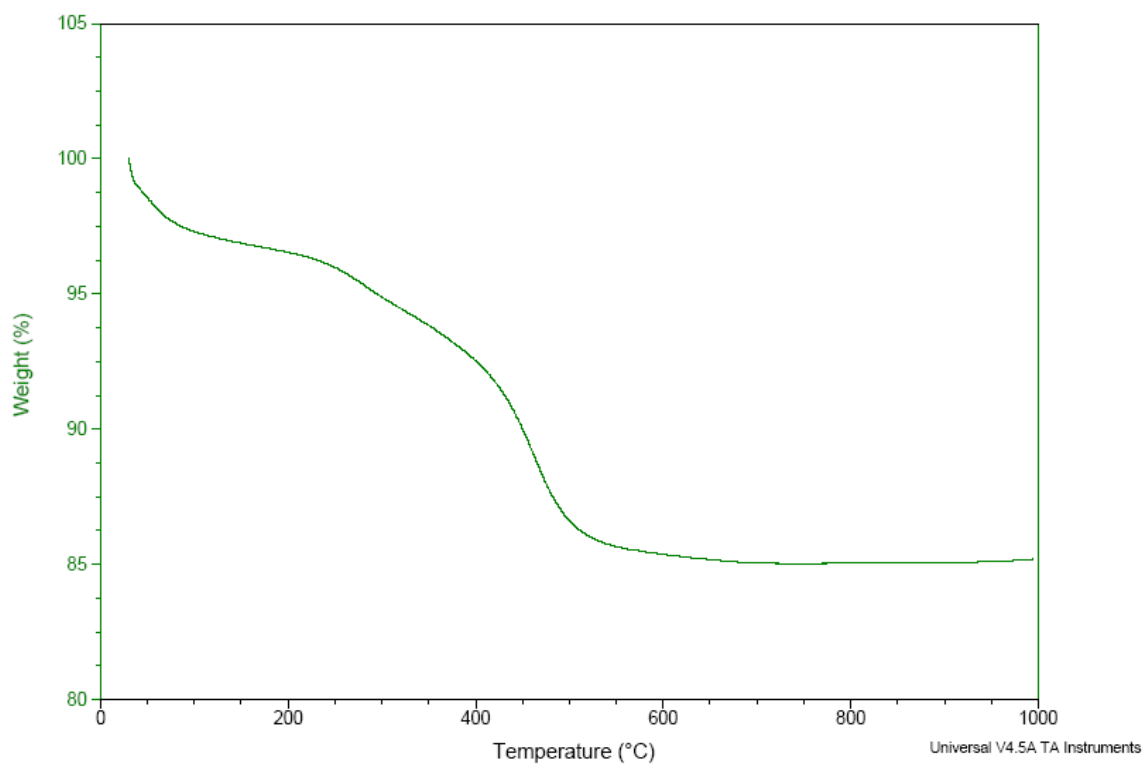**Figure 10.** Representative thermographic curve A.

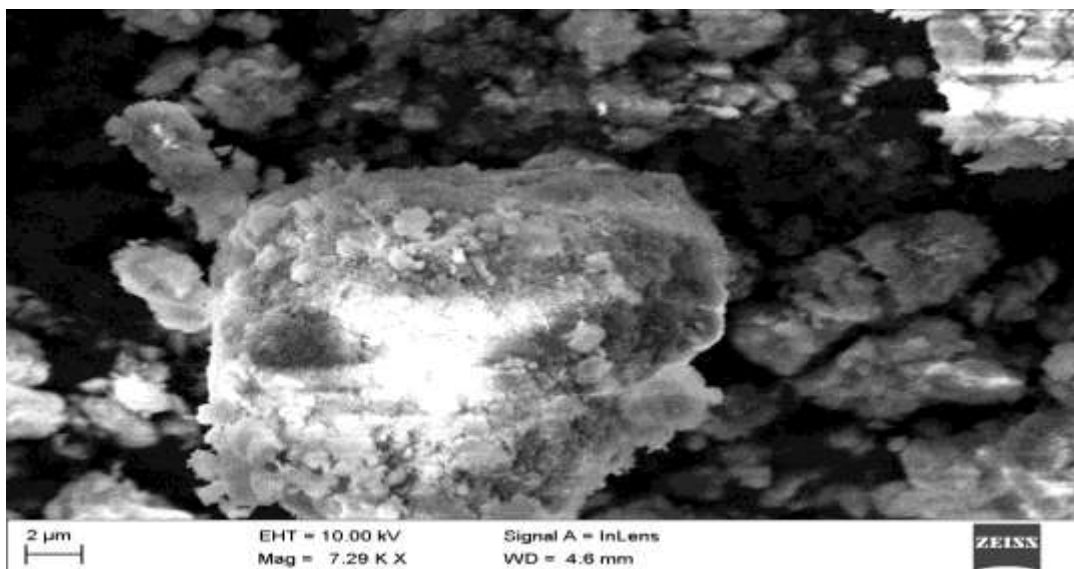**Figure 11.** Representative thermographic curve B.
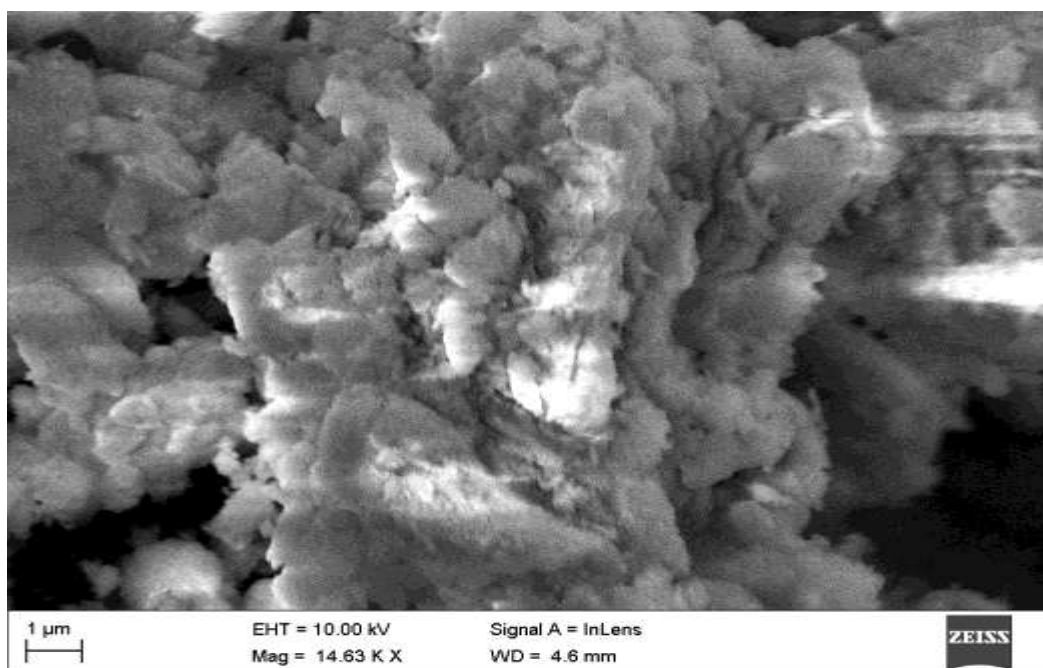
Figure 12. SEM micrograph A.

Figure 13. SEM micrograph B.

hence rendering the raw materials useful for commercial production of ceramic products and eventually maximizing its potential utilization.

Conflict of interests

The authors have not declared any conflict of interests.

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