

UPGRADING AND CHARACTERIZATION OF SMECTITE FROM SELECTED VOLCANIC SEDIMENTS OF EASTERN UGANDA

*Mukasa-Tebandeke, I.Z¹ .; Ssebuwufu, P.J.M¹.; Schumann, A³ Ntale, M¹. and Lugolobi F²

¹Makerere University, Department of Chemistry, Box 7062, Kampala.

³Makerere University, Department of Geology, Box 7062, Kampala

²Wesleyan University, Department of Earth Sciences, Middletown, USA.

* Person to whom correspondences can be made.

ABSTRACT

Natural clays occur as mixtures of many clay minerals and remains of the rocks that underwent diagenesis to yield the clays. As weathering of clay soils never ceases it may not be possible to mine single clay minerals. The purity of the mineral may increase through hydrocycloning and sedimentation as different clay minerals have different densities, wetting behavior and solubility in water. In this study, information has been accumulated on clays mined from Budadiri, Chelel, Mutufu and Sirron in eastern Uganda which were sedimented to upgrade the content of smectites. The raw clays and fraction the settled from sedimentation mixture after six days were subjected to chemical analysis, differential thermal analysis, Infra-red radiation and X-ray diffraction studies. The data acquired from the various experiments revealed presence of Fe-montmorillonite, illite, kaolinite, K-feldspars, plagioclase and quartz in raw clays. Although smectites and kaolinites may appear similar in color, the alkalinity of aqueous slurries of clay sediments from Budadiri, Chelel and Mutufu showed they were smectites containing nontronite. The clays and clay fractions were made of 40-50% smectite, 20-30% K-feldspars and plagioclase showing they formed from alkaline intrusive granitoids in basic medium. The presence of iron, aluminium, and silicon in approximate percentages of 11, 18 and 60% respectively indicated that sedimentation yielded nontronite and montmorillonite fractions. The IR spectrum absorption peaks at 3600, 3454, 526 and 466cm⁻¹ among others were due to Al-Al-OH, Mg-OH-Al, Si-O-Al and Si-O-Si bond deformations respectively indicated presence of smectites in the clay fractions obtained. DTA showed peaks at temperatures of 100, 250 and 650°C due to presence of smectites.

8.1 INTRODUCTION

Clay is an abundant, naturally occurring, fine-grained mixture of minerals composed predominately of hydrous aluminum silicates. If the surface of Earth was in equilibrium, clay minerals would rule! Clay minerals and clay-sized particles represent the ultimate fate of the crystalline rocks as they interact with environmental conditions at the earth surface, provide the substrate that sustains life and may even have played an essential role in the creation of life, are important constituents of the critical zone, play a key role in global biogeochemical cycling, and are important to humanity with respect to their role in natural hazards swelling clays, slip surfaces of landslides and faults, as a natural resource, as they impact human health, their importance to civil engineering projects, and topical issues such as nuclear waste. Clays fall into six general categories: kaolin, ball clays, fire clays, bentonite, common clays and Fuller's earth. Clays are common all over the world. Some regions produce large quantities of specific types of clay. Ball clays are high quality clays used mostly in pottery, sanitary ware, floor and wall tiles making but are also added to other clays to improve their plasticity. Bentonite is formed from the alteration of volcanic ash. Bentonite is used in pet litter to absorb liquids, as a mud in drilling applications. Common clay is used to make construction materials such as bricks, cement, and lightweight aggregates. Fire clays are all clays used to make refractory products. Fuller's earth is composed of the mineral palygorskite or attapulgite and it is used as an absorbent and pesticide-related products. Kaolinite is clay composed of the mineral kaolin. It is an essential ingredient in the production of high quality paper and refractory porcelain. Montmorillonite or bentonite is a prominent industrial mineral. It is the main constituent of bentonite and the detrimental factor of its properties [1]. Montmorillonite is soft phyllosilicate group of minerals that precipitate from water solution as microscopic crystals. It is a 2:1 smectite clay, having two tetrahedral sheets of silica sandwiching a central octahedral sheet of alumina with plate-shaped particles [1, 2, 3]. It has more than 50% octahedral charge; its cation exchange capacity is caused by isomorphous substitution of magnesium for aluminium in the central alumina plane. The substitution of lower valence cations in such instances leaves the nearby oxygen atoms with a net negative charge that can attract cations [1-4]. Bedeillite is smectite having more than 50% tetrahedral charge originating from isomorphous substitution of aluminium for silicon in the silica sheet.

The crystals of montmorillonite clay are not tightly bound hence water can intervene, causing the clay to swell. The water content of montmorillonite is variable and it increases greatly in volume when it absorbs water. Chemically, it is hydrated sodium calcium aluminium magnesium silicate hydroxide $(\text{Na,Ca})_{0.33}(\text{Al,Mg})_2(\text{Si}_4\text{O}_{10})(\text{OH})_2 \cdot n\text{H}_2\text{O}$. Electrical neutrality of this clay is achieved through cations external to the lattice residing in the inter-laminar region, between the lattice layers. The inter lamellar cations are exchangeable, so bentonite has high cation exchange capacity [1-4]. The inter lamellar cations impart swelling, thixotropy, and adsorptive properties on montmorillonite [2, 5]. Sodium bentonite (Na-montmorillonite) dominantly contains sodium ions in the interlamellar yet Ca-bentonite has calcium ions. Na-bentonite has very high swelling capacities and thixotropic properties when added to water, and is used in drilling fluids. The Ca-bentonite has very low swelling ability; sediments and settles more rapidly than Na-bentonite [6-8]. It occurs in mixtures with chlorite, muscovite, illite, cookeite, and kaolinite.

Several techniques have been developed to enable separation of physical mixtures of clay, density gradient allow a quick identification of the mineral composition to be made. In order to obtain reasonable amounts of pure minerals most efficiently, bulk loading of the gradient with the sample is recommended. Generally 10 hours of spinning at 18,000 revolutions per minute is sufficient to obtain optimum separation [9]. Total, slightly, and highly swelling clay minerals can be separated by centrifuging [10]. A Beckman continuous particle electrophoresis system was reported to be capable of separating mixtures of kaolinite and montmorillonite into five or more fractions by one pass through the instrument [11-13] and recently, procedure was suggested that can accomplish the separation without significantly affecting the character of randomly interstratified illite-montmorillonite, chlorite, illite, or kaolinite when treated at room temperature using acetic acid or hydrochloric acid [14]. It was reported that the major smectite minerals are Na-montmorillonite, Ca-montmorillonite, saponite (Mg-montmorillonite), nontronite (Fe-montmorillonite), hectorite (Li-montmorillonite), and beidellite (Al-montmorillonite). Water molecules and cations occupy the space between the 2:1 layers. The theoretical formula is $(\text{OH})_4\text{Si}_8\text{Al}_4\text{O}_{20} \cdot n\text{H}_2\text{O}$ (interlayer) and the theoretical composition without the interlayer material is SiO_2 , 66.7%; Al_2O_3 , 28.3%; and H_2O , 5%. However, in smectite, there is considerable substitution in the octahedral sheet and some in the tetrahedral sheet. In the

tetrahedral sheet, there is substitution of aluminium for silicon up to 15% and in the octahedral sheet, magnesium and iron for aluminium [1]. If the octahedral positions are mainly filled by Al, the smectite mineral is beidellite; if filled by Mg, the mineral is saponite; and if by Fe, the mineral is Nontronite. The most common smectite mineral is Ca-montmorillonite, which means that the layer charge deficiency is balanced by the interlayer cation calcium and water.

In Uganda, presence of smectite clays was first reported in 1992 [15]. Years later, the exploratory works [16] indicated presence of montmorillonite in the pitch black soils of the Karamoja region without experimental proof. The clay deposits at Budadiri, Chelel, Mutufu were sampled and analyzed [17, 18] and shown to contain nontronite, a di-octahedral smectite related to montmorillonite. These deposits were formed in the tertiary-quaternary period from volcanic ash. The clays contained 6-50% smectite so they are of very low grade. The impurities present include kaolinite, illite, quartz, K-feldspars and plagioclase. The impurities account for 50-90% of the clay [18]. These smectites showed good response to acid-activation and were successfully used to bleach cotton-seed and sunflower-seed oils [18, 19]. Whereas dioctahedral smectites are made of octahedral alumina placed between two silica tetrahedral sheets; trioctahedral smectites consist of two octahedra alumina held between two silica tetrahedral sheets [20]. Commonly kaolinites contain silica 45-56%, alumina 9-14% iron 0-4 %, calcium or magnesium absent, yet smectites contain silica 20-37%, alumina 10-25% iron 5-16 % calcium or magnesium 5-15% sodium or potassium 5-15% range. It can be asserted that clay fractions mined from volcanic areas near Mt Elgon contain smectites. The major problems facing the utilization of clay deposits at Budadiri, Chelel and Mutufu are low concentration of smectite, high content of impurities, and inconsistent composition. The clays have to be processed and upgraded before utilization. The potential method for this purpose is the wet beneficiation method [2]. It was reported that by subjecting Egyptian Ca-bentonite slurry to a hydrocyclone classifier and treating the over flow with acid removed calcite impurities [21]. Similarly, when slurry of Iraqi Ca-montmorillonite claystone was treated with dilute hydrochloric acid, calcite was eliminated [22]. It was demonstrated that dispersion and sedimentation processes with sodium phosphate as dispersant was very effective in beneficiating China Ca-montmorillonite claystone shown [23] this removed quartz. It was also reported that dispersion sedimentation technique with tetrasodium pyrophosphate was very effective in separating carbonate impurities

from Iraqi attapulgitite – montmorillonite claystone deposit, and the reject was mainly calcite [24]. In this study we have concentrated and analyzed the smectite present in clays mine from Budadiri, Chelel and Mutufu in Eastern Uganda.

X-ray diffraction is important tool for characterization used in solid-state chemistry and materials science. X-rays are short wavelength electromagnetic radiations, about 1 \AA (10^{-10} m), which is similar to size of atom. The discovery of X-rays in 1895 has enabled scientists to probe crystalline structure. X-ray diffraction has been used for the fingerprint characterization of crystalline materials and the determination of their structure. Each crystalline solid has its unique characteristic X-ray powder pattern which may be used as a "fingerprint" for its identification [25]. We can determine the size and the shape of the unit cell for any compound most easily using the diffraction of x-rays. The basal spacing of the Ca-montmorillonite is 14.2 \AA . Na-montmorillonite occurs when the charge deficiency is balanced by sodium ions and water and basal spacing is 12.2 \AA . Ca-montmorillonite has two water layers in the interlayer position and Na-montmorillonite has one water layer [26]. The smectite mineral particles are very small and because of this, the X-ray diffraction data are sometimes difficult to analyze [27, 28].

The infrared (IR) spectrum of a sample is recorded by passing a beam of infrared light through the sample. When the frequency of the IR is the same as the vibrational frequency of a bond or collection of bonds, absorption occurs. Examination of the transmitted light reveals how much energy was absorbed at each frequency or wavelength. The entire wavelength range is measured using a Fourier transform instrument and then a transmittance or absorbance spectrum is generated using a dedicated procedure. Samples of high purity produce spectra with few IR active bonds. More complex molecular structures lead to more absorption bands and more complex spectra. Solid samples can be prepared in a variety of ways. One common method is to crush the sample with an oily mulling agent. A thin film of the mull is applied onto salt plates and measured. The second method is to grind a quantity of the sample with highly pure potassium bromide, finely ground to remove scattering effects from large crystals. This powder mixture is pressed to form a translucent pellet through which the beam of the spectrometer can pass [29].

Differential thermal analysis (or DTA) is a thermoanalytic technique, in which the material under study and an inert reference are made to undergo identical thermal cycles, while recording any temperature difference between sample and reference [30]. The differential temperature is then plotted against time, or against temperature to give the DTA curve, or thermogram. Changes in the sample, either exothermic or endothermic, can be detected relative to the inert reference. The DTA curve provides data on the transformations that have occurred, such as glass transitions, crystallization, melting and sublimation. The area under a DTA peak is the enthalpy change and is not affected by the heat capacity of the sample. The analyzer consists of a sample holder, thermocouples, sample containers and a ceramic or metallic block; a furnace; a temperature programmer; and a recording system. The key feature is the existence of two thermocouples connected to a voltmeter. One thermocouple is placed in an inert material such as alumina, while the other is placed in a sample of the material under study [30].

The hydrocyclone used in solid-liquid separations, serves in rapid de-watering, de-sliming and particle-size fractionation. Where the clay itself is the principal product of a mineral processing plant, the equipment offers a convenient means of effecting a clay/silt/sand split which yields a clay-rich fraction in a suitable state for fine-particle treatment [31]. For precise particle size separation there are a number of constraints on its operation but as a tool for clay investigations in the laboratory several advantages are offered which seldom appear to be appreciated. As in all particle settling operations, the rate at which a specific size of mineral grain travels through a liquid medium is related both to the difference in density between them and to the viscosity of the liquid. For a given size of hydrocyclone, the pressure at which the slurry is pumped through the vessel obviously governs the centrifugal force exerted on a particle in suspension within it and, therefore, the speed with which it travels to the walls in order to be expelled with the underflow discharge [32].

Objective: To concentrate and analyze smectite in volcanic sediments mined near Mount Elgon in Eastern Uganda.

8.2 MATERIALS AND METHODS

8.2.1 Preparation of clays

Composites of raw samples of clays were separately soaked in distilled water, sieved through a mesh 53 μm diameter, dried at 105°C and ground to powder using porcelain mortar and pestle. The powder was stored for future use in desiccators.

8.2.2 Chemical analyses of clays

The analysis for aluminium, iron, calcium, sodium and potassium was determined through fusing the clay powder with sodium carbonate in platinum crucibles [33]. Some elements were from mixtures of clay dissolved in hydrofluoric-perchloric acid mixtures using the Perkin–Elmer 3030 model Atomic absorption spectrometer. Silica was determined by gravimetrically.

8.2.3 Separation of clays

Clay powder (30.0 g) was suspended in distilled water (700.0 ml) in a 1000 mL large plastic beaker. Using an ultrasonic probe the clay was disaggregated for approximately 20 minutes. The beaker containing the suspended sample was removed from the ultrasonic probe enclosure and covered the beaker. The beaker was placed on a vibrationally stable surface and to allow the sample to settle gravitationally without interruption for 47 minutes per cm depth of water. The supernatant solution was decanted off to other plastic beaker and allowed to stand for 2 days. The remaining supernatant solution was decanted off and allowed to evaporate to dryness, ground to powder and used in experiments. The sediment in the beaker was discarded [9, 32].

8.2.4 X-ray diffraction analyses

The clay film supported in the holder by a flat fritted-glass surface was assembled. The filter assembly was connected to a vacuum, and sufficient clay suspension was filtered to deposit the required amount of clay (0.008g) on the membrane. The back of the membrane is rolled gently with a 1" diameter tube, and the membrane is then peeled off, leaving the clay film on the glass

slide. The mount was dried in air or placed over glycerol at 100°C prior to analysis. The length of the samples produced was 40 mm, sufficient to intercept the entire primary X-ray beam at low angles. The mounted clay was subjected x-ray Powder diffraction in Philips diffractometer with PW1710 control unit operating at 40kV and 30mA using the Ni-filtered Cu K α radiation. The XRD patterns were matched with JCPDS-cards in the CD-rom of the computer. Bulk mineralogy was studied with randomly oriented air-dried samples [34, 35].

8.2.5 Infrared spectroscopic studies

The clay powder (3.0 mg) was mixed with highly pure potassium bromide, finely ground to remove scattering effects from large crystals. This powder mixture is pressed to form a translucent pellet through which the beam of the spectrometer can pass [29]. The infrared spectra were run using the KBr discs using B10RD FT540 Fourier Transform IR spectrometer in the frequency range of 3700 – 400 cm⁻¹ [36].

8.2.6 Differential thermal analysis of clays (DTA)

The clay (0.5g) under study and an inert reference calcined alumina, in cavities of a nickel block were heated in parallel to 1100° C at the rate of 12° C per minute, while recording any temperature difference between sample and reference [30]. The differential temperature is then plotted against time, or against temperature to give the DTA curve, or thermogram. As the temperature is increased, there will be a brief deflection of the voltmeter if the sample is undergoing a phase transition. This occurs because the input of heat will raise the temperature of the inert substance, but be incorporated as latent heat in the material changing phase [37].

8.2.7 Determination of pH of clays

Weighed clay powder (1.0 g) was placed in a beaker, water (20.0 mL) added. The mixture was stirred continuously and allowed to equilibrate for 30 minutes at 25°C. A pH-meter was then used to read the pH of the solution. The method was repeated thrice to get comparing results.

8.3 RESULTS AND DISCUSSION

8.3.1 Location and geological settings of sampled clays

All clays sampled were sedimentary and found along river valleys. Budadiri and Mutufu clay deposits are found in Sironko district. Chelel clay deposits are found in Kapchorwa district near Kapchorwa town. Both Kapchorwa and Sironko lie in areas of past volcanic activity near Mt Elgon.



Figure: 8.1b: Appearance of clay in valley at Chelel

The Chelel clay surface is yellow-orange due chemical alteration of oxides of iron, manganese and titanium to more stable oxidation states when it became exposed to free oxygen in the atmosphere. Gully erosion cut deep transects in the clay show Chelel clay deposits are very deep.

8.3.2 Sampling methods

Six composites of clay from regions suspected to contain smectites were collected. In all cases the clays were dug from virgin mines. The samples were collected at depths in range of 35 – 150 cm from the surface to minimize the effects of weathering and contamination.

The sampled clay deposits were observed to be stratified and contained more than one distinct clay mineral in the different horizons shown in Figure 8.2; having different colors. The

differentiation of the clays into distinct horizons resulted from influence of air, water, solar radiation and plant material, originating at the soil-atmosphere interface. Since the weathering of the clay minerals occurs first at the surface and works its way downwards, the uppermost clay horizons have been altered most, while the deepest layers were most similar to the original parent rock (FAO, 2014).



Figure: 8.2: Representative clay horizons

A clay horizon is a layer generally parallel to the soil crust, whose physical characteristics differ from the layers above and beneath. The clays sampled from Budadiri, Chelel and Mutufu had three horizons. The clay horizons were defined by color and texture. They were described by particle size distribution for texture, and relative to the surrounding material coarser than the horizons above and below. The differentiation of the clay in distinct horizons resulted from influence of air, water, solar radiation and living organisms, operating at the clay-air interface. Since the weathering of the clays occurs most rapidly at the surface and works its way downwards, the uppermost horizons were altered the most and least for the deepest layers. So the deepest layers must be most similar to the unaltered parent rock.

The upper horizons of the stratigraphic column for the clays (Figure 8.2) was yellow or orange in color because it contained iron which became oxidized on exposure to excess air and water [38-40] for a long. Clays from lower horizons are dark grey because iron (II) compounds or there are other minerals and metal ions in lower oxidation states.

The clays in stratigraphic column in Figure 8.2 were formed by diagenesis of glass, volcanic ash, and dickites in the ultra basic media to yield smectites. It is smectites that have extensive substitution with octahedral ions like iron, titanium and manganese which are colored in addition to calcium,

magnesium, potassium and sodium which are white or colorless that show definite color variations in the mines [3, 4]. As clays form in uphill rocky remains, the possibility of in-situ diagenesis of all clays studied has been ruled out on the ground that all clays had been transported and were sampled from a river valleys or/and swamps. The different clay strata shown in figure 2 depict the differences in extent alteration. There were more sand stones in the strata near the bottom the clay pit than that picked from the top. This could have arisen from rate of settling of particle as the clay was eroded from the hills where it formed or weathering effects as the original deposited clay mineral became transformed to other clays and other minerals on changing conditions near the surface from those conditions existing in the deep buried horizons.

8.3.3 Color and pH of clays

Colors and pH of clays suggest presence of characteristic elements upon which predictions about the structural, surface and bleaching properties can be made. The montmorillonite clays have inter lamellar octahedral ions which are exchangeable, [1-4]. Adherence of ions of iron, manganese, titanium and other transition elements imparts color to the clay yet hydrolysis of silicates changes hydrogen and hydroxide ion equilibria in aqueous solutions. Record of average pH and color of clays may serve as reference to nature of environment from which the clay sediments were collected. They also have more than 50% octahedral charge; its cation exchange capacity is caused by isomorphous substitution of magnesium for aluminium in the central alumina plane. The substitution of lower valence cations in such instances leaves the nearby oxygen atoms with a net negative charge that can attract cations [1-4]. As the silicates are formed from a weak acid silicic acid, sodium and potassium aluminosilicates hydrolyze anionically forming excess hydroxide ions in the aqueous slurries of bentonites. The pH a clay slurry can be used to distinguish Ca- and Na-bentonites. The inter lamellar cations impart swelling, thixotropy, and adsorptive properties on montmorillonite [2, 5]. The clay deposits sampled exhibited different colors depicting differences in trace transition elements composition in the clays. The color of clays depends on the quantity and oxidation state of iron and other transition elements present. While clays containing iron in oxidation state +3 are yellow or brown. Green clays contain iron in oxidation state +2 but color could also arise from presence of manganese and titanium compounds in different oxidation states [41-43]. White bentonites lack ions of iron, manganese and titanium. Smectite feels greasy and soap-like to the touch. Freshly exposed bentonite is white to pale green or blue and, with exposure, darkens in time to yellow,

red, or brown. The special properties of smectite are an ability to form thixotropic gels with water, an ability to absorb large quantities of water with an accompanying increase in volume of as much as 12–15 times its dry bulk, and a high cation exchange capacity. Substitutions of silicon by cations produce an excess of negative charges in the lattice, which is balanced by cations (Na^+ , K^+ , Mg^{2+} , Ca^{2+}) in the interlayer space [44].

The colors of selected clays observed in this study are shown in Table 8.1. The orange, brown and yellow clays were mined from near the earth surface and grey and white clays were mined from deeper clay horizons. The differently colored clay horizons were shown to contain various transition elements [42, 45, 46].

Table 8.1: Clay color and pH

Source of clay	Color	pH+0.04
Budadiri	Dark brown	5.60
Budadiri	Dark grey	6.50
Mutufu	Grey	6.90
Mutufu	Dark grey	8.40
Chelel	Whitish grey	7.90

The determination of pH of clay slurries in distilled water was repeated thrice and the average of the three values has been tabulated in Table 8.3 above. Readability of pH was 0.04.

The colors of the clays sampled varied from black to grey through orange in the deposits probably due to presence of iron and other colored metal compounds [47]. Colored clays have interlayer cations as Fe^{2+} , Fe^{3+} , Mn^{2+} , Ti^{4+} and other transition metal ions [42, 43] and some extent these octahedral ions substitute for either silicon in the tetrahedral sheets or aluminium in the octahedral. In all these situations, color is imparted but its intensity will directly depend on quantities of colored ions and their oxidation states.

The white color of the Kimolian bentonites was inversely related to the abundance of iron oxides and anatase [48]. The occurrence of iron in the smectite structures in different oxidation states causes variations in color [49]. The presence of silica imparts high abrasiveness in commercial products [50] and it does not alter the color.

The clays sampled from Budadiri, Chelel and Mutufu showed brown, orange, grey and white colors due to presence of iron, manganese and or titanium ions in different oxidation states as inter layer cations or substituents in the octahedral or tetrahedral sheets of the smectites. The

inter lamellar cations are exchangeable, so bentonite has high cation exchange capacity [1-4]. The inter lamellar cations impart swelling, thixotropy, and adsorptive properties on montmorillonite [2, 4]. The selected clay samples from Mutufu and Chelel had average pH ranging between 7.5 and 8.50 ± 0.034 because the environment where they were mined is ultra basic. The alkalinity of the clay slurries is attributed to presence of alkali and alkaline earth metals whose silicates strongly hydrolyse raising the pH above 7. This showed presence of excess alkali metals like sodium and potassium as well as K-feldspars in these clays. The pH of slurries for Na-bentonites or Na-montmorillonites were reported to lie in the range between 7.8 and 8.5 [51]. As the pH for Chelel and Mutufu clays were as high as those for bentonites from Egypt, Saudi Arabia and Wyoming (USA) it is possible that these clays Na-bentonites.

The pH of slurries of smectite-rich clays is greater than 7 due to hydrolysis of sodium or/and potassium silicates. The hydrolysis may be complete or partial. Therefore the interlayer ions are structurally acting as counter ions to the silicate skeleton in Na-bentonite. The aqueous slurries Budadiri clays had pH less than 7 indicating cationic hydrolysis of the clay. This favors kaolinites and Ca-bentonites.

8.3.4 Mineralogy of clays

Clay mineralogy is useful in characterizing the nature of clay minerals and is critical to many geoscience projects and understanding of palaeoclimate. Clay minerals are a group of fine-grained hydrous aluminium phyllosilicates, characterized by two-dimensional sheet structures. Clay minerals can be divided into four major groups: kaolinite, smectite, illite and chlorite. Each of these groups exhibit different characteristics [20]. The mineralogical studies aimed at characterizing, quantifying and interpreting the mineralogy and related physical properties of clay materials. XRD analyses indicated that Budadiri, Chelel and Mutufu clays were composed of illite, kaolinite, K-feldspars, plagioclase, quartz and smectite given in Table 8.2. It is essential to study mineralogy because the properties of clays are determined by their mineralogical compositions [44]. The presence of illite, kaolinite, K-feldspars, plagioclase, quartz and smectite in these clays showed they were polymineralic in nature. Presence of smectites in the selected samples used in this study showed that the clays were phyllosilicates undergoing

weathering to illite and kaolinite as they became exposed to free air and water in the atmosphere [52-54].

The clays studied showed different compositions of the minerals. Despite the efforts to eliminate sand stones and quartz through wet filtering, the clay samples I₁, I₂, J₁, J₂, K and L shown in Table 8.2 still had large quantities of slit. Quartz may represent remains of the unaltered from which the clays being studied were formed by diagenesis; so these clays formed from the similar parent rock compositions.

Table 8.2: Mineralogy of clays

Sample	Kaolinite %	Quartz %	Smectite %	Illite %	Feldspars%	Plagioclase%
I ₁	23.5	23.5	6.0	ND	23.5	23.5
I ₂	23.5	23.5	ND	6.00	23.5	23.5
J ₁	23.5	23.5	5.6	ND	23.5	23.0
J ₂	7.7	15.4	46.2	ND	30.5	ND
K	23.5	23.5	6.0	ND	23.5	23.5
L	7.7	10.4	50.0	ND	30.0	ND

Key:

ND refers to not detected as the peak for the mineral was very low or invisible on the X-ray diffractograms as it was less than 1%. Clay samples designated as I, J, K and L were selected from the respective sediments from Budadiri, Mutufu, Siron and Chelel.

The data in Table 8.2 above was determined using the Reynold's semi-quantitative method [18]. Semi-quantitative assessment is particularly valuable when identifying individual components in polymineralic samples. However, the intensity of peak of a clay mineral may not be directly used to represent the accurate measure of abundance of the mineral in question because quantity of clay mounted and conditions in the X-ray machine vary [55]. Accuracy varies because different clay minerals have differing atomic planes within a clay mineral, and different samples of the same clay mineral may not have the same ability to diffract X-rays [55]. It was reported that useful semi-quantitative comparisons can be made between samples by means of various

ratios of peak areas. These ratios vary in part due to mineralogy and in part due to scattering factors inherent to X-ray diffraction [55]. The dominant smectite from deposits at Budadiri, Chelel, Siron and Mutufu is nontronite or Fe-montmorillonite, and this coincides with studies on clays formed from volcanic sediments. The presence of montmorillonite among clays formed from volcanic sediments the World over was discussed [56]. The proportion of Fe-montmorillonite present in Budadiri clay is low probably due to alteration of the clay to illite, kaolinite and silica. Chemical weathering of montmorillonite takes place when the clay becomes subjected wet atmospheric conditions near the Earth's surface and this is favored by acidic conditions resulting from humic and fulvic acids which occur in the humid vegetations. Generally the amount montmorillonite detectable using x-ray crystallography can be low because its crystal particles are very small.

The high abundance of quartz in all clay deposits sampled showed that the clays must have high silica content; and are bound to be strongly acidic as the silica provides several sites for the hydroxyl groups or water molecules to bind. As Budadiri, Chelel and Mutufu clays were sampled from river valleys where water erosion had transported and deposited them as sedimentary clays, weathering strongly affected the relative quantities of montmorillonite compared to kaolinite and quartz as the clay got exposed to the wet atmospheric conditions. So diminution in montmorillonite concentration proportionately increased illite, kaolinite and quartz. The presence of high silica content in the clays does not serve as evidence for the migration of silica in the mines [54, 57]. However, the high abundance of silica in Aegean clays (Greece) was advanced to show the downward migration of silica in the mines [48, 58]. As more soluble montmorillonite degraded to kaolinite and quartz; the softness of the clay greatly reduced [44]. The abundance of feldspars and plagioclase in the clays from Budadiri, Chelel, and Mutufu is an indication of the partial weathering of the parent rock. The smectite/kaolinite ratios for Chelel, and Mutufu is very low for these alkaline clay showing that kaolinitization may have taken place after diagenesis of the clays uphill [18, 58]. The evidence for the strong alkalinity of the environment where smectites are mined is shown by the high pH of the clay solutions made by suspending these clays in distilled water. The bentonite deposits of Kimolos Island, Aegean, Greece were investigated in order to determine their physical and chemical properties [53] by testing for swelling capacity, pH, rheological properties, green and dry compression strength. These properties were influenced by the smectite content and the degree of disaggregation of the

smectite quasi-crystals due to the nature of the interlayer cation, the presence of mordenite, undevitrified glass shards and the degree of the oxidation of iron. As the smectite-rich clays selected from Chelel and Mutufu contained clay minerals in the ranges of 46-50% Fe-montmorillonite, 23-30.5 % feldspars and 1-25% plagioclase this has been used to propose that these clays have a di-octahedral structure of montmorillonite [14, 18].

8.3.5 Chemical analyses

Chemical analyses of clays and clay fractions have always revealed the class of alumino-silicates to which the analyzed materials belong. In a study involving clays, it is important to establish the elemental constitution of the solid because formulae, surface and bleaching properties of clays and clay material depend on chemical composition of clay. Marine clays formed by digenesis of volcanic ash, glass and tuffs have been reported to be composed of approximately 11% iron; 18% aluminium, and 60% silicon [14]. The averaged chemical composition data obtained in this study on selected clays from region near Mt Elgon in Eastern Uganda are in Table 8.3.

The chemical elements present in clays and clay fractions formed during sedimentation have been presented as relative percentages of the elements expressed as oxides in the entire sample in Table 8.3. Budadiri, Chelel and Mutufu, clays and their fractions had less than 50% silicon dioxide showing that volcanic clays of Budadiri, Chelel and Mutufu, should be are not acidic [15, 16]. The volcanic clays formed from alkaline intrusive granitoids in ultra basic media, contain less silica as it dissolved in alkaline medium. The data in Table 3 shows that there was progressive decrease in quantity of silica present in clay as time taken for the mixture to sediment increased. This has been used to indicate that softness of clay increased. Similarly, the relative proportions of oxides of aluminium, calcium, iron, magnesium, potassium and sodium increased showing the more soluble clays were being collected from the the suspension that sedimented for long time periods.

Clays from magmatic sediments in oceans were reported to contain major elements with relatively high magnesium oxide, ranging from 23.9 to 40.4 % and low silicon dioxide and

aluminium oxide, ranging from 12.8 to 29.0% and their data confirms the data we have adduced in this study on clays from Chelel, Budadiri and Mutufu which are associated with volcanic margins of Mountain Elgon.

Table 8.3: Average chemical compositions of clays and fractions

	Mutufu	Chelel	Budadiri	Mutufu	Chelel	Budadiri	Mutufu	Chelel	Budadiri
Clay element	Raw	Raw	Raw	First fraction	First fraction	First fraction	Second fraction	Second fraction	Second fraction
SiO ₂	55.25	51.10	65.00	35.00	32.20	32.00	34.40	32.10	60.00
Al ₂ O ₃	13.20	12.10	12.00	14.00	15.10	13.00	13.20	14.30	20.00
Fe ₂ O ₃	1.30	1.10	4.00	28.00	33.10	34.80	29.80	33.10	3.90
MgO	0.80	1.10	2.00	1.30	1.30	1.20	0.61	0.50	2.60
CaO	10.30	9.50	4.30	3.00	2.80	0.90	2.10	2.10	0.90
Na ₂ O	4.10	5.10	2.50	2.50	2.20	1.50	1.50	1.10	2.60
K ₂ O	3.10	2.80	0.80	0.80	1.00	0.60	1.70	1.10	0.30
LOI	13.00	12.50	7..50	9.00	6.90	6.20	6.70	5.50	7.10

LOI is loss on ignition signifying an estimate of matter lost when the clay was heated.

Readability was 0.05.

The loss on ignition of the selected clays used in this study lie in the range from 6-10% an indication that heating clays to 105°C results in loss of structural water from the clay [59]. The reactions occurring in the clay materials include dehydration and dehydroxylation of soil used.

Interstitial water held in the clay mineral lattice is an additional major factor controlling the plastic, bonding, compaction, suspension, and other properties of montmorillonite-group clay minerals. Within each crystal, the water layer appears to be an integral number of molecules in thickness. Physical characteristics of bentonite are affected by whether the montmorillonite composing it has water layers of uniform thickness or whether it is a mixture of hydrates with water layers of more than one thickness. Loss of absorbed water from between the silicate sheets takes place at relatively low temperatures (100–200 °C). Loss of structural water (i.e., the hydroxyls) begins at 450–500 °C and is complete at 600–750 °C. Further heating to 800–900 °C disintegrates the crystal lattice and produces a variety of phases, such as mullite, cristobalite, and

cordierite, depending on initial composition and structure. The ability of montmorillonite to rapidly take up water and expand is lost after heating to a critical temperature, which ranges from 105 to 390 °C, depending on the composition of the exchangeable cations. The ability to take up water affects the utilization and commercial value of bentonite [1].

The percentages of iron, aluminium and silicon among bentonites worldwide are approximately 11, 18, and 60% respectively. Basing on this, clays from Mutufu, Budadiri and Chelel resemble bentonites. On the basis of relative percentages of aluminium, silicon and alkaline metals or alkaline earth metals[14], the clays studied have been found to satisfy the formulae in Table 8.4. The smectites occur in volcanic sediments of Sironko and Kapchorwa because the areas lie on the foothills of Mountain Elgon, a well known volcanic mountain.

The Budadiri, Chelel and Mutufu clays which were subjected to separation of components were analyzed elementally. The data obtained showed decrease in content of silica of the clay fractions as shown in the Table 8.4 which is a reflection of the surface area increase. So sedimentation can be used to improve adsorptive tendencies for the clays. So hydrocycloning and sedimentation can be used to upgrade or concentrate a smectite [9].

On the basis of relative percentages of aluminium, silicon and alkaline metals or alkaline earth metals, given in Table 8.3, the second clay fraction which settled after six days have been found to satisfy the formulae given below and summarized in Table 8.4.

Mutufu clays settling after six days satisfied the formula for nontronite which is $\text{Ca}_{0.5}(\text{Si}_{7}\text{Al}_{0.8}\text{Fe}_{0.2})(\text{Fe}_{3.5}\text{Al}_{0.4}\text{Mg}_{0.1})\text{O}_{20}(\text{OH})_{4}$ in mixture with silica as its chemical composition consisted of more than ~30% Fe_2O_3 and less than ~12% Al_2O_3 on ignited basis [14].

Chelel clays settling after six days satisfied the formula of montmorillonite, $(\text{Na,Ca})_{0.33}(\text{Al,Mg})_2(\text{Si}_4\text{O}_{10})(\text{OH})_2 \cdot n\text{H}_2\text{O}$, mixed with nontronite as it had more than 14% aluminium and high loss in weight on ignition [14]. Similarly, the final fraction of the Siron clay was a mixture of two phyllosilicates, nontronite and montmorillonite.

The Budadiri clay fraction that settled after six days was nontronite and it satisfies the formula $\text{Ca}_{0.5}(\text{Si}_7\text{Al}_{0.8}\text{Fe}_{0.2})(\text{Fe}_{3.5}\text{Al}_{0.4}\text{Mg}_{0.1})\text{O}_{20}(\text{OH})_4$ because its chemical composition consisted of more than ~30% Fe_2O_3 and less than ~12% Al_2O_3 on ignition basis [14].

Table 8.4: Names and formulae of clay fractions

6th day fraction	Formula	Name
Mutufu	$\text{Ca}_{0.5}(\text{Si}_7\text{Al}_{0.8}\text{Fe}_{0.2})(\text{Fe}_{3.5}\text{Al}_{0.4}\text{Mg}_{0.1})\text{O}_{20}(\text{OH})_4$	Nontronite [14]
Chelel	$\text{Na}_{0.3}\text{Fe}_2(\text{Si}_4\text{O}_{10})(\text{OH})_2 \cdot 4\text{H}_2\text{O}$	Montmorillonite [14]
Budadiri	$\text{Ca}_{0.5}(\text{Si}_7\text{Al}_{0.8}\text{Fe}_{0.2})(\text{Fe}_{3.5}\text{Al}_{0.4}\text{Mg}_{0.1})\text{O}_{20}(\text{OH})_4$	Nontronite [14]

8.3.6 Infra Red (IR) spectroscopy

Infrared spectroscopy Infrared spectroscopy (IR) is widely used to determine and investigate the structure of the various mineral phases. It provides information ranging from the detection and identification of specific or minor mineral constituents, hardly accessible from X-ray diffraction techniques, to the determination of the stacking order and ordering pattern of substituting cations in clay minerals [6]. In the field of clay mineralogy, study of infrared absorption spectra has lately made a remarkable progress, as exemplified by numerous researches on the absorptions in the OH region, on the relationships between the chemical composition and the variation of position of absorption bands, and on the after-heating variation of absorption bands. Concerning the OH region a large number of researches have been made, particularly on absorption of kaolin minerals [61]. The clay minerals powder (0.5gm) were mixed with 300 mg of KBr disk, previously dried at 110 °C and then pressed in vacuum by the oil press.) It was shown that better resolution can be obtain by using KBr instead KI as dispersant for the preparation of the disks [62]. The advantages of IR analysis compared to X-ray powder diffraction in principle, are that with IR technique both the crystalline minerals and amorphous materials can be investigated, especially for minerals that could be found in trace percentage and out of XRD sensitivity. The IR methods are still less widespread for quantitative determination of clay and other minerals. The greatest problem is that the material of equivalent chemical composition but of different

particle size and crystalline state has considerably different spectra [63]. It is remaining best to use the two methods to complement rather than substitute one another [64].

IR studies have been used to identify smectites because they show broad absorption band at 3600cm^{-1} due to OH, 3454cm^{-1} due to inter layer water, 1664 cm^{-1} due to deformational vibration in the HOH group, at 1042 and 798cm^{-1} due to Si-O vibration, the bands at 526 and 466cm^{-1} show presence of Si-O-Al and Si-O-Si deformation vibrations respectively [57]. IR studies on clays helped to identify presence of characterizing groups in smectites [18 ,63]. Knowledge of behavior of clays in the IR region of the electromagnetic spectrum goes a long way to establish the identities of stretching bonds in them. Different groups show different stretching modes at different frequencies in the infra red region of the electromagnetic spectrum as shown on Figures 8.2 and 8.3. The IR spectrum of the clay showed absorption band at 3640 cm^{-1} attributed to stretching vibrations of the OH group while that at 3454 cm^{-1} was due to the presence of interlayer water. The amount of adsorbed water in clays is related to the deformation vibrations of the H–O–H group (1664 cm^{-1}). The bands at 1042 and 798 cm^{-1} are attributed to Si-O stretching vibrations [57]. The bands at 526 and 466 cm^{-1} correspond to deformation vibrations of Si–O–Al and Si–O–Si, respectively [65].

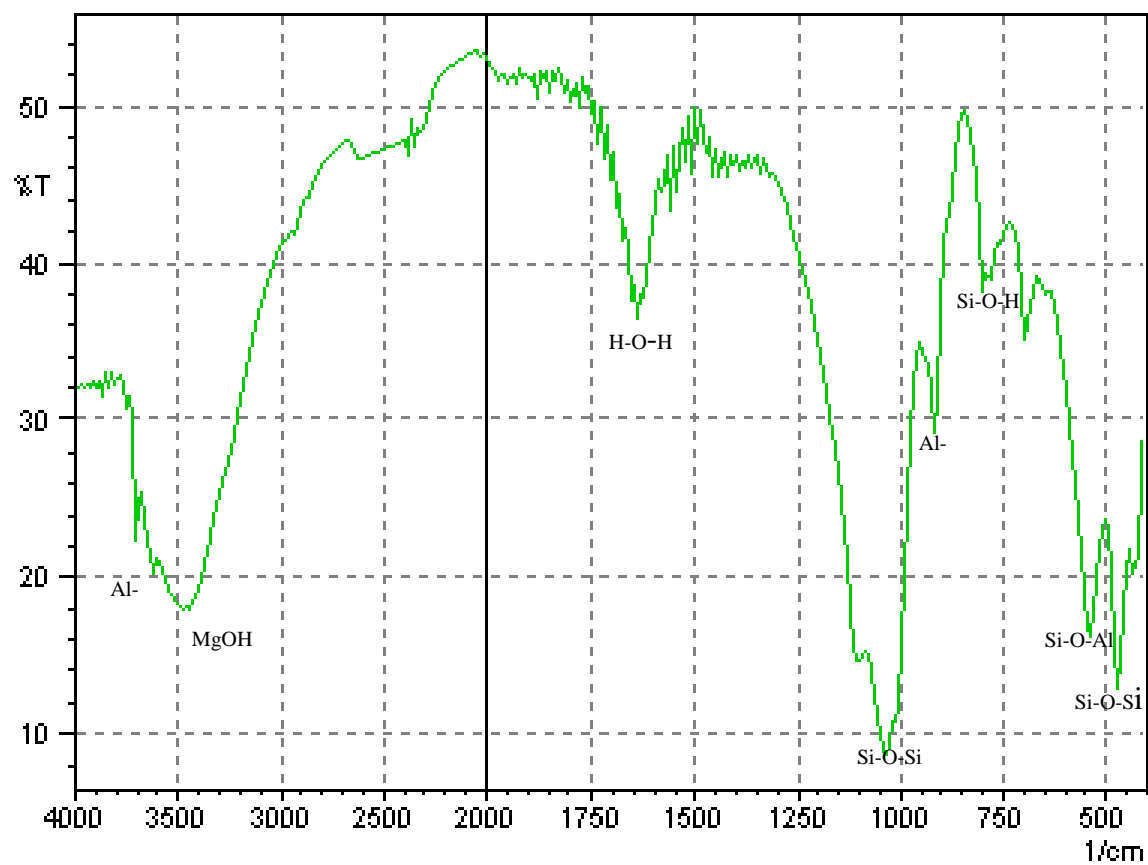


Figure 8.2: IR spectrum for Mutufu clay

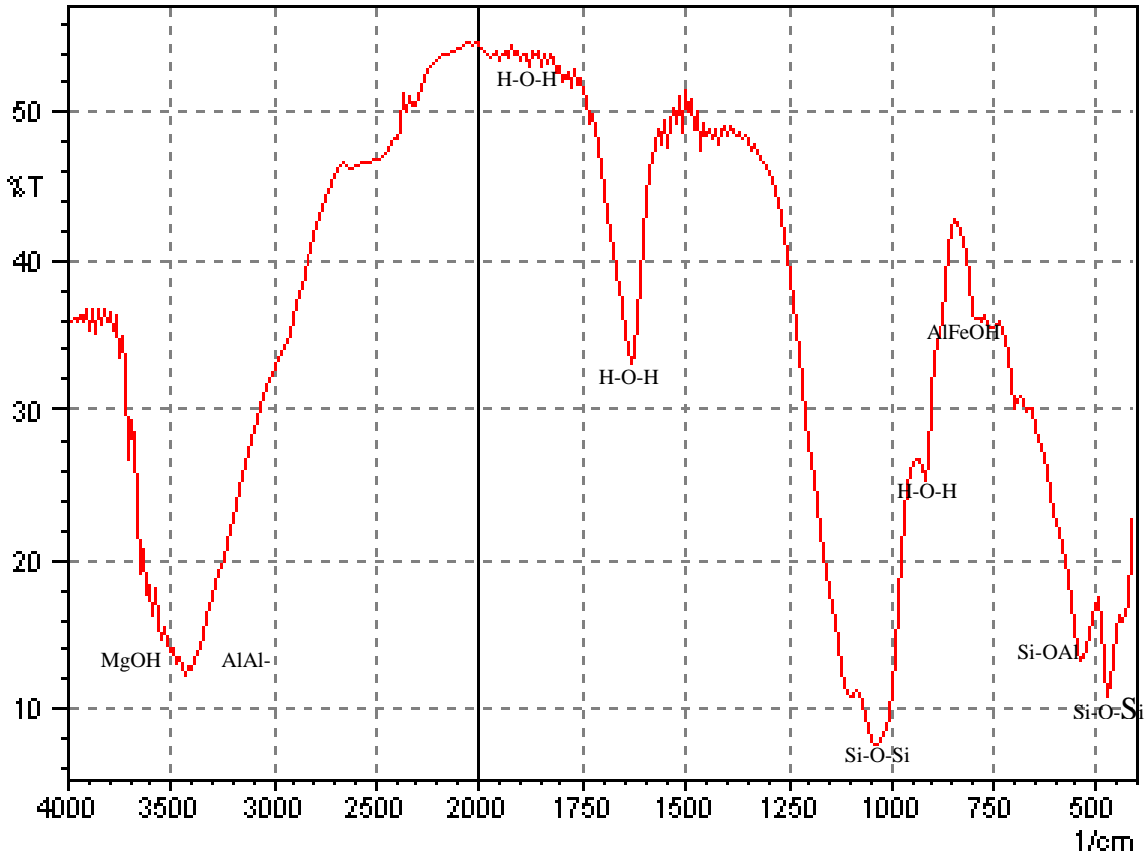


Figure 8.3: IR spectrum for Chelel clay

The band at 1040 cm^{-1} is assigned to (Si-O). The band at 3454 cm^{-1} is due to adsorbed water, and that at 3640 cm^{-1} is due to (Al-Al-OH, Mg-OH-Al). The absorption bands at 918 and 879 cm^{-1} in Figures 8.2 and 8.3 in the representative spectra for the clay deposits at Mutufu and Chelel characterize smectites but the band at 800 cm^{-1} is obscured by Si-O mode which is broadened. These bands are due to the bending mode of Al-Fe-OH bonds. The smectites are also expected to show absorption bands at 845 cm^{-1} [57].

Since the IR spectra for smectite-rich clays selected from Budadiri, Chelel and Mutufu showed peaks due to Mg-OH-Al stretch at 3490 cm^{-1} , Al-Al-OH stretch at 3480 cm^{-1} , H-O-H at 1800 cm^{-1} and 1620 cm^{-1} , Si-O-Si at 1100 cm^{-1} , Al-Fe-OH at 800 cm^{-1} , Si-O-Al at 600 cm^{-1} and Si-O-Si at 490 cm^{-1} it has been proposed that these clay fractions conform to the structure of montmorillonite [66].

8.3.7 X-ray diffraction (XRD) analyses

X-ray diffraction is the primary tool for identifying and quantifying the crystalline compounds. Clay scientists strongly rely on it in asserting the nature of minerals. Powder XRD diffractograms characterize minerals and elements present in solids. Clay powders have been distinguished into smectites and kaolinites basing on XRD patterns. XRD analyses form a core component in elucidating clay structures [34]. The separated particles contained smectite of poorly crystal structure, mixed-layer clays, and the mica mixed with quartz and may not have been suitable for chemical analyses using XRD technique. The XRD patterns of clays and clay fractions from Sironko and Kapchorwa are represented by the Mutufu and Chelel clays respectively (Figures 5a and 5b) which contains smectite (S), illite (I), kaolinite (K), K-feldspars (Kf), plagioclase (Pc) and quartz (Q) [57, 67]. The presence of feldspars and plagioclase in these clays showed that the parent rocks were volcanic ashes.

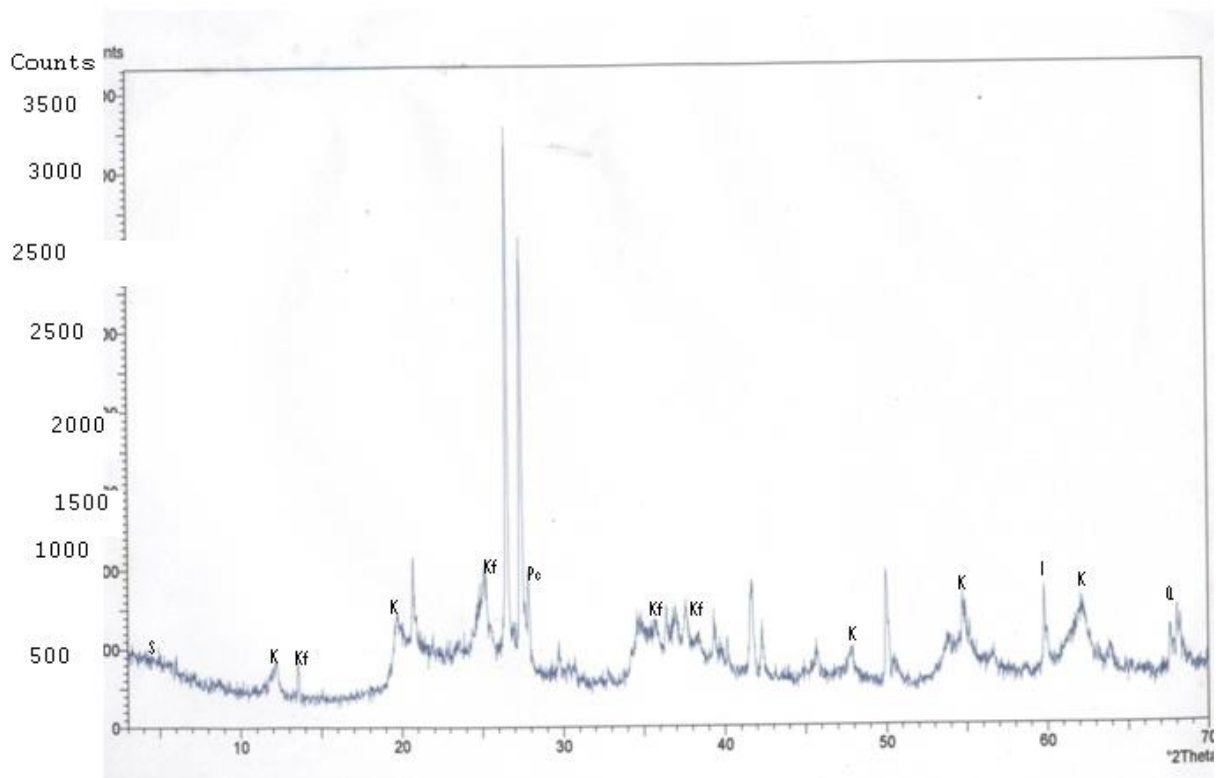


Figure 8.5a: XRD pattern of clay fraction settling after six days for clay from Mutufu

Key: smectite (S), illite (I), (K), K-feldspars (Kf), plagioclase (Pc) and quartz (Qz)

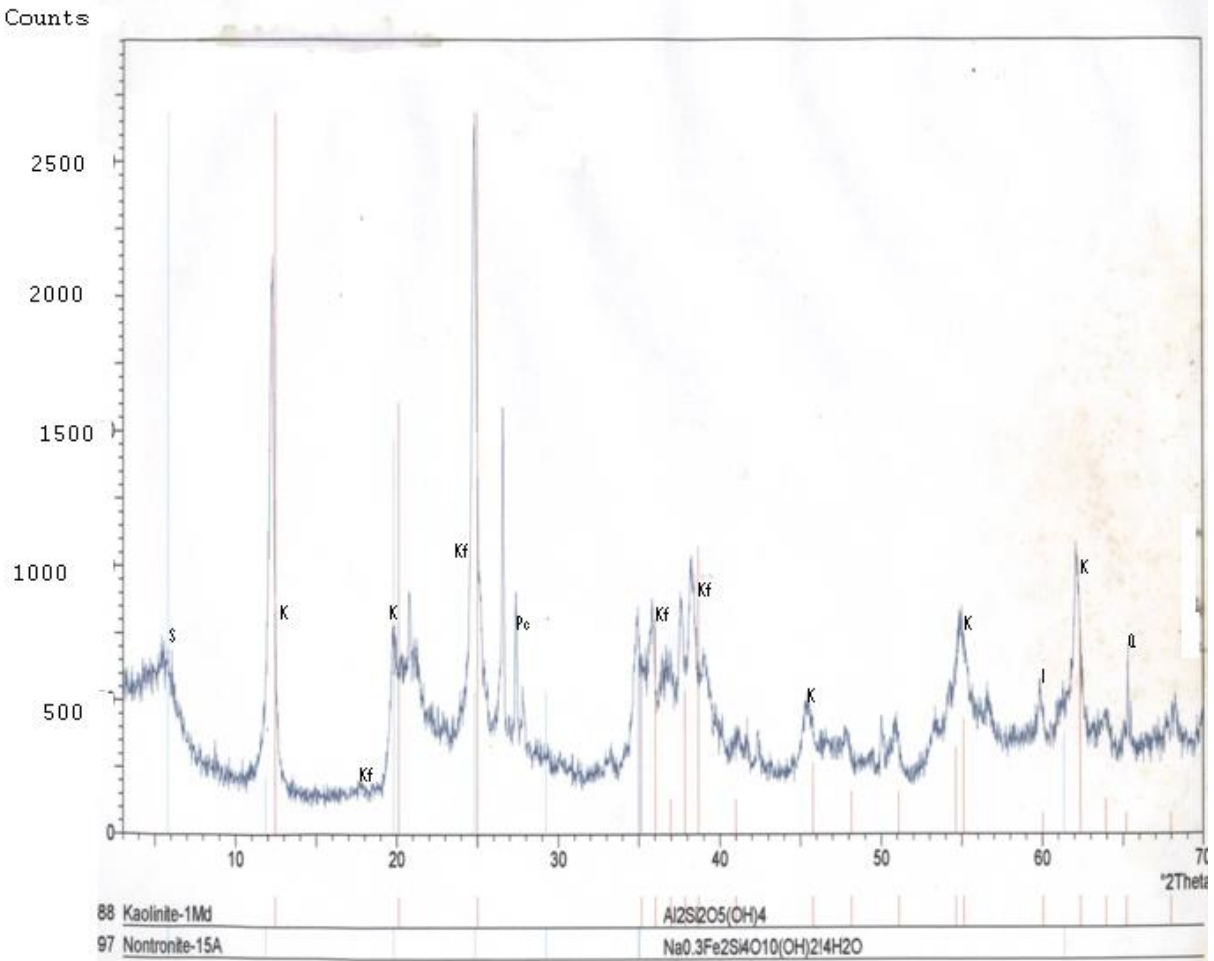


Figure 8.5b: XRD pattern of clay fraction settling after six days for clay from Chelel

Key: smectite (S), illite (I), kaolinite (K), K-feldspars (Kf), plagioclase (Pc) and quartz (Q)

The XRD patterns in Figures 5a and 5b representing selected clay and clay fraction from Mutufu and Chelel showed presence of Fe-montmorillonite (nontronite) mixed kaolinite, K-feldspars, plagioclase and slit even when allowed to sediment in six days. The XRD patterns do not show very large peaks for Fe-montmorillonite because the crystals of this clay are very small [68, 69]. So interactions of the electron clouds of atoms and ions in the smectite with electric dipoles of the X-rays were limited by size crystals leading failure to observe broad peaks even after concentrating the smectite [27, 28].

8.3.8 Differential thermal analyses (DTA)

Differential thermal analysis (or DTA) is a thermo-analytical technique, in which the material under study and an inert reference are made to undergo identical thermal cycles, while recording any temperature difference between sample and reference [30]. The differential temperature is then plotted against time, or against temperature to give the DTA curve, or thermogram. Changes in the sample, either exothermic or endothermic, can be detected relative to the inert reference. The DTA curve provides data on the transformations that have occurred, such as glass transitions, crystallization, melting and sublimation. The area under a DTA peak is the enthalpy change and is not affected by the heat capacity of the sample. The analyzer consists of a sample holder, thermocouples, sample containers and a ceramic or metallic block; a furnace; a temperature programmer; and a recording system. The key feature is the existence of two thermocouples connected to a voltmeter. One thermocouple is placed in an inert material such as alumina, while the other is placed in a sample of the material under study [30].

Generally, DTA curves in Figure 8.6 showed a small change in the endothermic peak corresponding to the loss of adsorbed water (at about 150°C), and peaks corresponding to the loss of structural hydroxyl groups (530 and 600°C) [70, 71]; Lombardi et al, 2002). The endothermic peak in the range of temperatures between 550 and 660°C is attributed to dehydration of the mineral leading to formation of γ -aluminium oxide in kaolinite clays [72]. The differential thermal analysis data presented in Figure 8.6 showed that the clays lost inter layer water molecules in the temperature range between 230 and 210°C. The clay samples studied exhibited endothermic peaks at 140° and 210°C due to loss of hydration water [45, 73](.

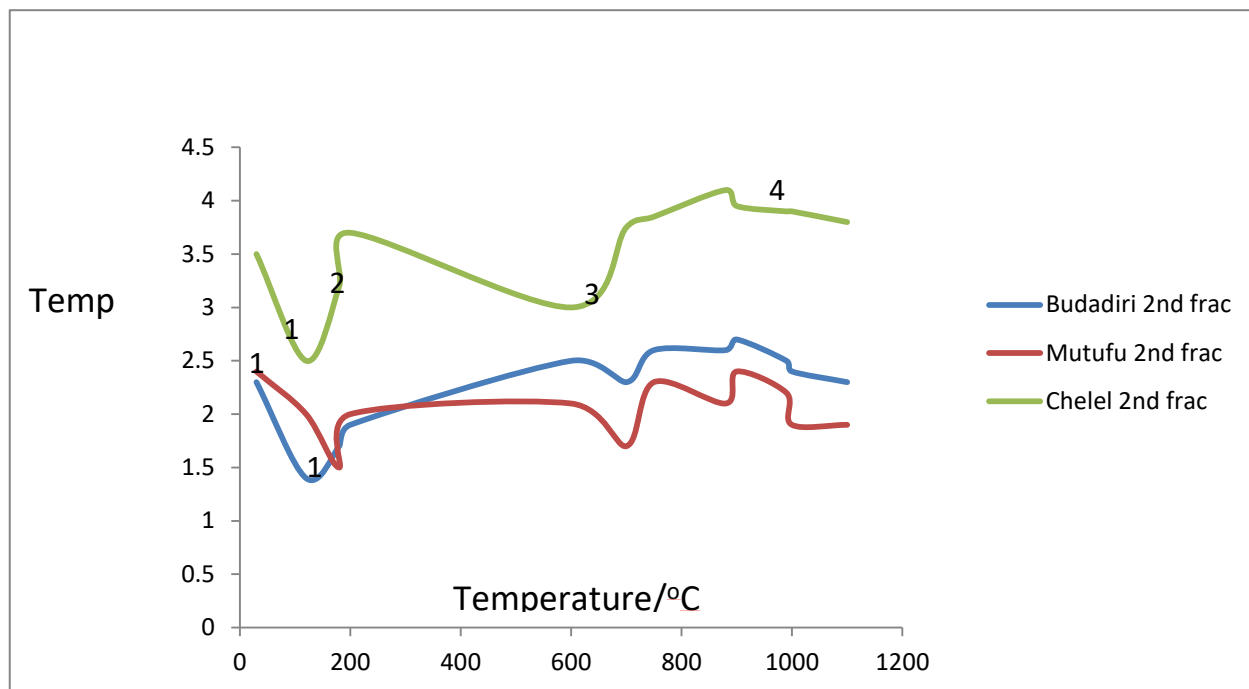


Figure 8.6: Behavior of clay during differential thermal analysis

For the curves above, the respective reactions are; at 1 is dehydration, 2 is dehydroxylation, 3 is calcinations and 4 is recrystallization.

The smectite clays showed exothermic peaks in the range of 900 – 1000°C. Montmorillonite showed initial endothermic peak at temperature between 100 and 250°C due to loss of water held between the basal planes of the lattice structure [74]. The initial peak is large and extended over a wide temperature range, indicating that the clay possessed water molecules other than pore water which causes no thermal reaction above 100°C. Lattice water is lost at temperatures higher than 100°C [75, 76]. So the DTA curves show that clay fractions contained smectites. The thermal stability of montmorillonites is related to crystalline structure [71]. The loss of hydroxide ions from clay material causes irreversible modification of the crystal structure, producing the endothermic peak at temperatures between 650 and 700°C [77]. This has been used to suggest that these clays have high thermal stability.

The deformation in crystal structure of montmorillonite clay is initiated by different isomorphous substitutions which cause a temperature shift of the peak [78]. The higher the degree of octahedral substitution, the lower is the hydroxyl release temperature. The high octahedral substitution of iron in montmorillonite clay caused the shift of the endothermic peak from near 600°C to 544°C because the Fe-montmorillonite suffered 0.60 octahedral isomorphous substitutions [71].

As the curves in Figure 8.6 resembled DTA diagrams published in international journals [71], it has been proposed that the selected clays have similar structure to montmorillonite. Basing on XRD and DTA studies, the distribution of clay minerals in the different fractions have been discussed as follows; the fraction which settled most easily was made of less soluble, high density minerals like quartz, plagioclase and K-feldspars. The main mineral left in the supernatant solution after the first fraction was collected was Fe-montmorillonite because it has low density, high solubility and consequently high saturation point. So it could remain in solution for long.

8.4 CONCLUSION

The results on the chemical and mineralogical composition of clays and clay fractions from the volcanic sediments of the Mt. Elgon showed that they were Fe-montmorillonite, mixed with kaolinites and partially metamorphosed rocks as plagioclase and feldspars. The Budadiri, Chelel and Mutufu clay are tertiary-quaternary volcanic clays. The smectite that sedimented from Budadiri, Chelel and Mutufu clays was Fe-montmorillonite, a dioctahedral smectite.

Sedimentation separated Fe-montmorillonite from illite, kaolinite, K-feldspars, plagioclase and quartz because it is less dense and more soluble than the impurity in the raw clays. The presence of inter lamellar ions and water caused the differences between the smectite and impurities in it.

The DTA, IR, pH and XRD data acquired on Budadiri Chelel and Mutufu clays indicated that they were smectite-rich. Sedimentation separated the nontronite from other clay minerals because of its higher solubility than kaolinites, feldspars and plagioclase. The clay that settled last from sedimentation experiments was nontronite.

8.5 RECOMMENDATIONS

The clay fractions collected through sedimentation experiments from Budadiri, Chelel and Mutufu clay deposits should be analyzed farther using scanning microbe and XRF.

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