# IDENTIFICATION OF CLAY MINERALS OF THE EASTERN SOUTHERN REGION OF LAKE VICTORIA BY ETHYLENE GLYCOL AND HEAT: X-RAY DIFFRACTION AND INFRARED SPECTROSCOPY STUDIES

**EHJ Lugwisha**
Chemistry Department, University of Dar es Salaam,
P.O. Box 35061, Dar es Salaam, Tanzania,
Email: elugwisha@gmail.com

## ABSTRACT

*The effect of glycol and heat on some clay minerals of the eastern southern region of Lake Victoria in Tanzania has been studied. First, Whole Rock Powder mount XRD analysis was carried out at the measuring range 2 θ ranging between $2^o$ – $65^o$. Four non-clay minerals found in samples were Na-feldspar, K-feldspar, pyrope and quartz. Oriented clay mineral XRD analysis diffractograms were developed when the air-dried samples were diffracted in measuring range 2θ between $2^o$ – $32^o$. Main clay mineral groups found in the samples were kaolinite, illite and montmorillonite.*

*After glycolating the samples, it was evident that kaolinite diffractograms were inverted while montmorillonite diffractograms peaks were widened and shifted. But on heating to $550^oC$, the peaks for both kaolinite and montmorillonite collapsed. The case was different for illite peaks which showed stability under both treatments. This analysis made it possible to differentiate between kaolinitic and non-kaolinitic clays.*

*IR spectroscopy study was also carried out and the results were presented for comparison to clay minerals identified by XRD analysis. XRD analysis identified kaolinite, illite and montmorillonite as clay minerals in the samples, results which agree with IR. IR absorption bands occurred at 3694, 3825, 694 and ca 430 – 470 $cm^{-1}$ are characteristic of kaolinite mineral. While absorption bands which appeared at 3455, 3463, 3600, 3440, 3610 and 532 – 539 $cm^{-1}$ are characteristics of illite mineral group, and a band at 3432 $cm^{-1}$ signifies the presence of both kaolinite and montmorillonite.*

## INTRODUCTION

The wide industrial applications of clays make their identification an inevitable process. This identification includes not only the constituent clay minerals but also the trace impurities (Wilson 1987)

Although there is a variety of modern equipment to study clays: Infrared, Thermal analysis (TG, DTG, DTA), electron transmission microscope, electron microprobe, Mossbauer spectrometers, nuclear and isotope technology etc – the X-ray diffractometer remains to be a basic tool for clay studies (Tobia and Sayre 1974)

X-ray diffraction techniques can successfully identify clay mineral groups and subgroups on the basis of their reflections. Random powder preparations are used to identify subgroups and polytypes while oriented preparations allow to distinguish layer types and mineral groups. In oriented specimen, clay particles tend to align themselves in one direction from which some series of basal reflections with little or no evidence of hkl reflections are shown best in a diffractometer (Bühman 1998).

Oriented specimen should not only be recorded air dry but also additionally after various treatments that alter the diffraction pattern of the components. This is due to limitations encountered for an analysis basing only on the data of basal reflections from oriented air-dry samples. The large number of mineral phases frequently present in clays, leads to overlapping reflections.

This causes interstratifications of certain clay minerals which posse great difficulties in the identification of different mineral groups present in a particular sample.

Additionally to oriented air-dried samples, this paper presents identification of clay minerals observed after treating the samples with Ethylene Glycol and heated at 550°C so as to allow recognition of the main clay mineral groups (Bühman 1998). This identification is coupled with infrared analysis.

## EXPERIMENTAL

### Samples and Sampling

Clay samples were collected from clay deposits in Mwanza region located in the Eastern Southern part of Lake Victoria. Sampling was done at the locations indicated in Figure 1. Samples were coded OX numbered from 01 to 07. The samples of about 2 kilograms from different sites were taken at about 1m and 4m below the earth's surface. Each sample was then mixed thoroughly.

### Infrared spectroscopy (IR)

The pellet technique, one of the IR techniques used for handling solid samples was employed. 1-2 mg of dried sample was mixed with 100 – 150 mg powdered KBr and the mixture was well grounded and pressed in evacuable die at sufficient pressure to produce a transparent disc (Skooge and West 1980). The disc of sample 03 was analysed using Shimadzu IR 435 specrophotometer while the remaining six samples were analysed using FTIR Maltson 100 spectrophotometer.

### X-rd analysis

X-ray diffraction patterns were obtained by means of D-5005 X-ray Diffractometer, using CuK$_\alpha$ sources at a wavelength, $\nu$ = 1.54056Å

The samples were diffracted in the measuring range 2θ ranging between 2° – 65°. The diffractograms obtained were evaluated by determining the 2θ angles and the intensities of the various peaks. However, the presence of non-clay minerals ranging between 2° – 65° hinders the development of the diffractogram peaks ranging between 2° – 32°. Thus, particles < 2um (i.e. clay particles) from each sieved sample were separated for oriented clay mineral XRD analysis which was run in the latter range (i.e. 2° – 32°)

For oriented clay mineral three XRD analytical procedures were followed. These are: (i) diffraction of air-dried samples, (ii) diffraction of glycolated samples that were solvated with ethylene glycol in an oven at 60 °C for 12 hours. (iii) diffraction of samples that were heated at 550 °C for two hours in the furnace oven.

## RESULTS AND DISCUSSION

For X-ray diffraction analysis, every crystalline substance has a unique X-ray powder diffraction patterns from which a characteristic set of crystal plane spacing in the crystal lattice "d – spacing", measured by a unit Å and an intensity of reflection at a given diffraction angle $I/I_o$ (where I is an integrated intensity per unity length of diffraction line and $I_o$ is the intensity of the incident beam) can be derived.

Diffractograms obtained from the Whole Rock Powder mount XRD analysis in the region between 2° – 65° revealed five non-clay minerals (clay mineral impurities) [Figures 2a – 8a]. These include Na-feldspar or albite (Sodium aluminium silicate – $Na[A1Si_3O_8]$ found in samples O3 and O4; K-feldspar or microcline (potassium aluminium silicate $K[A1Si_3O_8]$ found in all samples except sample O3; K-Na feldspar or sanidine $[(K,Na)\{(Si,A1)_4O_8\}]$ and pyrope – $Mg_3A1_2(SiO_4)_3$ which were seen in samples O3 and O6 respectively and quartz – $SiO_2$ which was observed in all samples [Figures 2a – 8a].

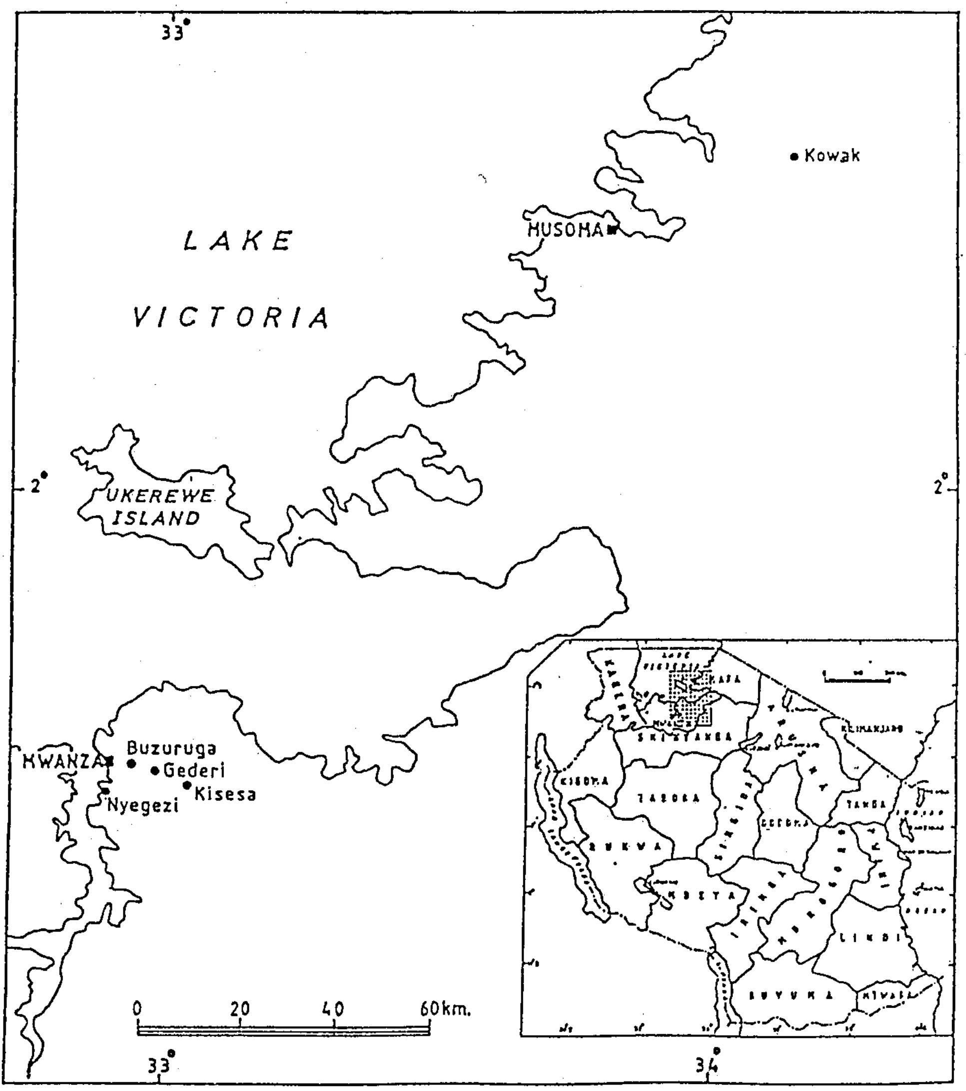
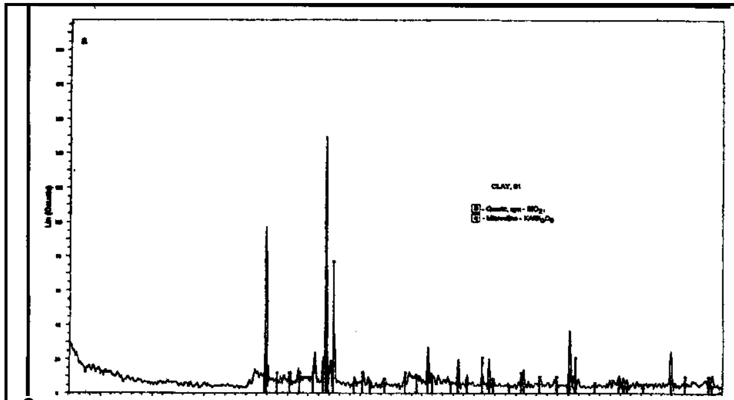
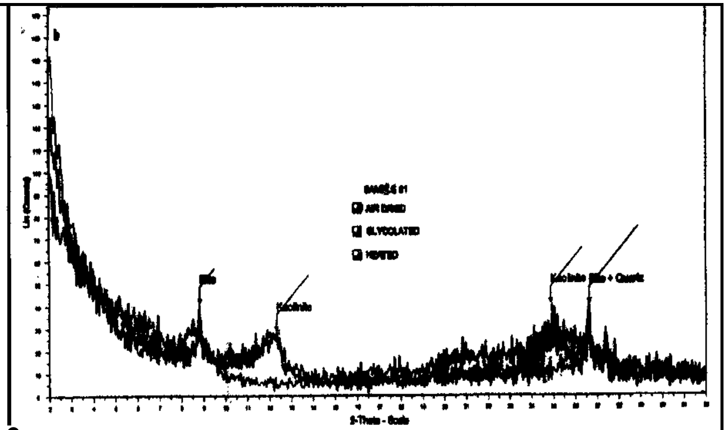


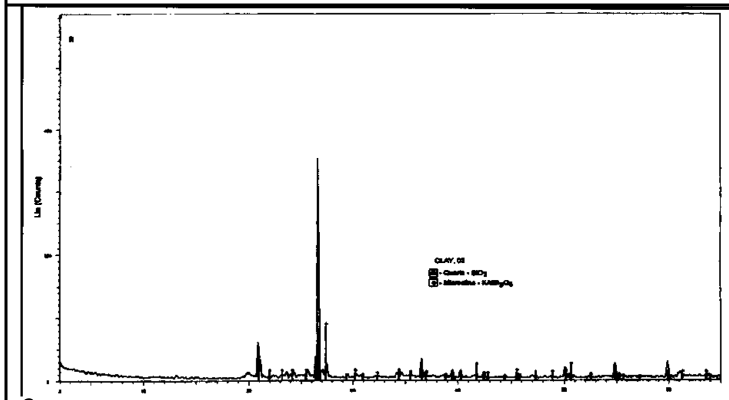
**Figure 1:** A map showing the collection sites for clay samples



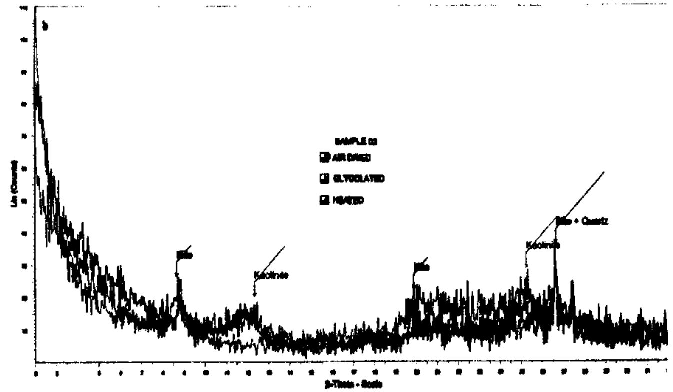
**2a** Random powder XRD diffractogram for sample 01



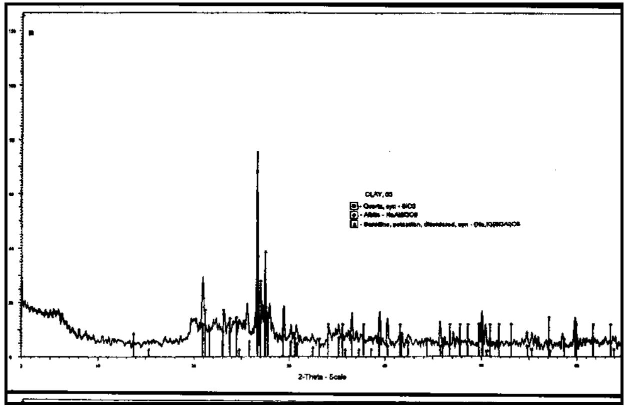
**2** The Oriented XRD diffractogram for sample 01



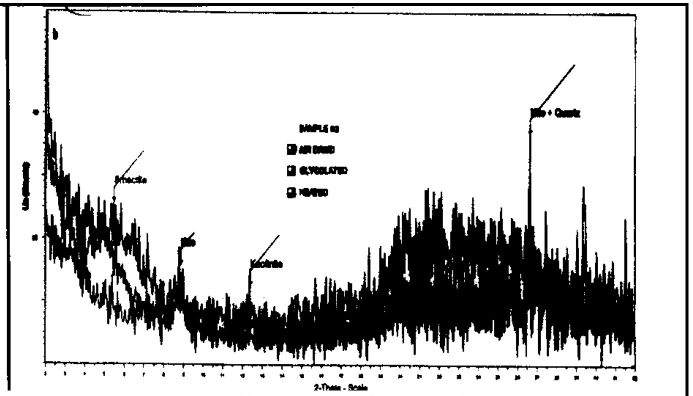
**3a** Random powder XRD diffractogram for sample 02



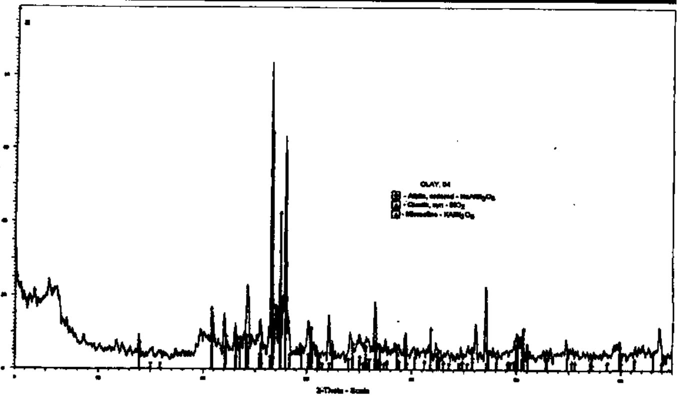
**3b** The Oriented XRD diffractogram for sample 02



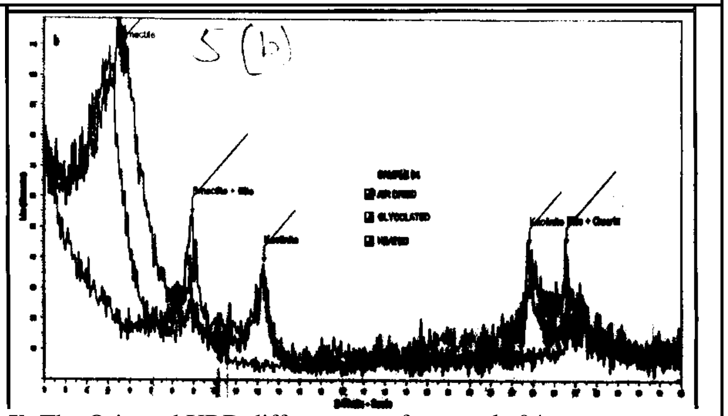
**4a** Random powder XRD diffractogram for sample 03



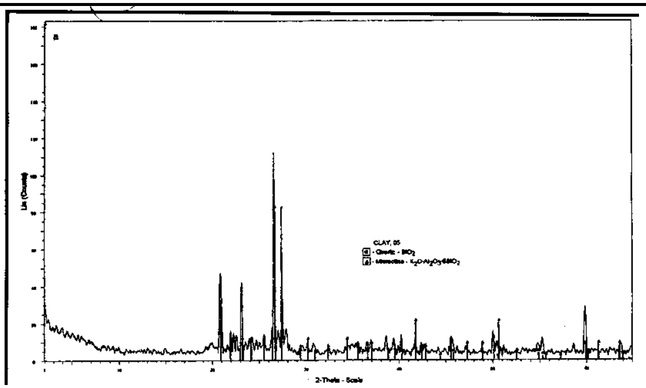
**4b** The Oriented XRD diffractogram for sample 03



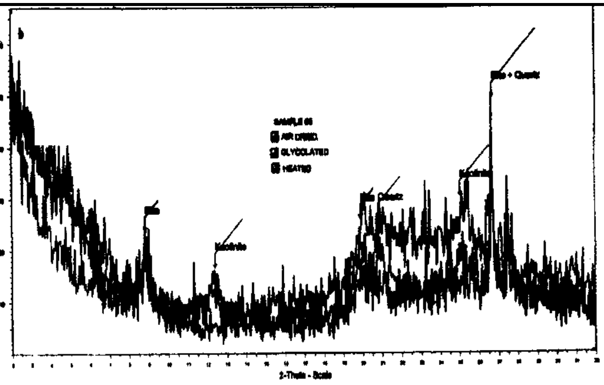
**5a** Random powder XRD diffractogram for sample 04



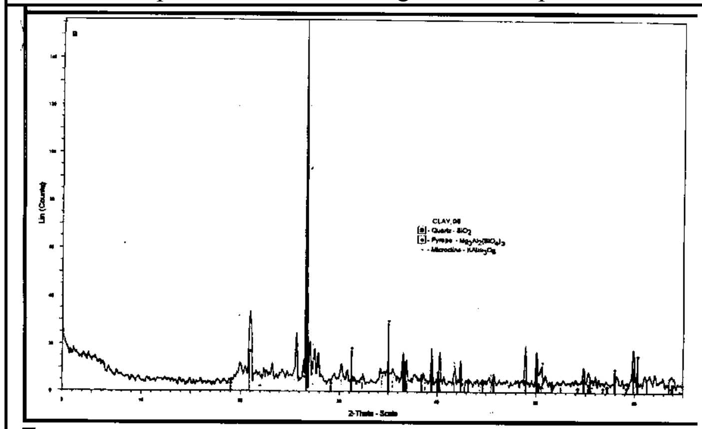
**5b** The Oriented XRD diffractogram for sample 04



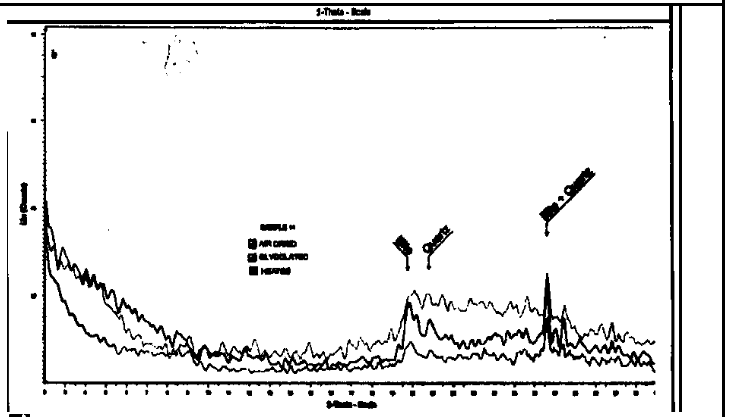
**6a** Random powder XRD diffractogram for sample 05



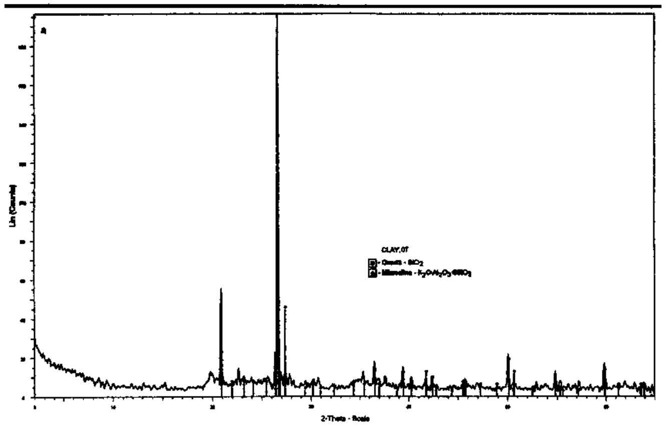
**6b** The Oriented XRD diffractogram for sample 05



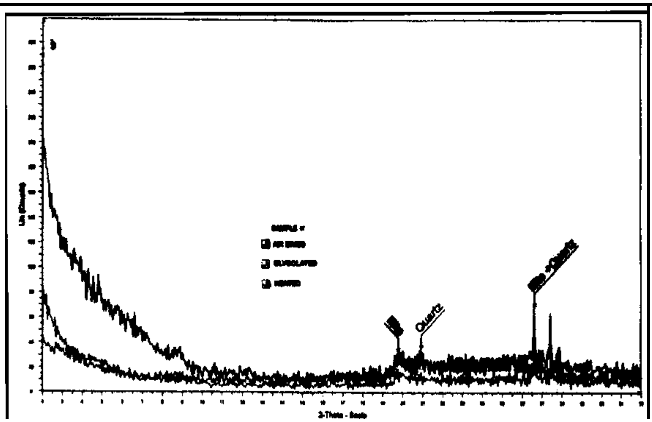
**7a** Random powder XRD diffractogram for sample 06



**7b** The Oriented XRD diffractogram for sample 06



**8a** Random powder XRD diffractogram for sample 07



**8b** The Oriented XRD diffractogram for sample 07

In Oriented Clay Mineral XRD analysis at the measuring range 2θ ranging between 2° – 32°, diffraction results were obtained after the samples were (i) air dried (ii) glycolated and dried up and (iii) heated at 550°C. When the air-dried samples were diffracted, peaks were developed on the diffractogram. These diffractograms revealed three main clay minerals namely illite which appeared in all samples, kaolinite which was seen in all samples except samples 06 and 07 and montmorillonite which appeared in samples O3 and O4.

**Table 1:** XRD reflections (d) in Å of oriented clay minerals after Ethylene glycol and heat treatment at 550 °C.

| D spacing of air-dried sample. Å | D spacing after Ethylene Glycol-treatment Å | D spacing after heated to 550 °C-Å | Mineral |
|---|---|---|---|
| **Sample 01** | | | |
| 10.082 | 10.082 | 10.082 | Illite |
| 3.342 | 3.342 | 3.342 | Illite |
| 7.185 | 7.185 | - | Kaolinite |
| 3.574 | 3.574 | - | Kaolinite |
| **Sample 02** | | | |
| 10.221 | 10.221 | 10.221 | Illite |
| 3.337 | 3.337 | 3.337 | Illite |
| 7.185 | 7.185 | - | Kaolinite |
| 3.579 | 3.579 | - | Kaolinite |
| **Sample 03** | | | |
| 9.947 | 9.947 | 9.947 | Illite |
| 3.342 | 3.342 | 3.342 | Illite |
| 7.297 | 7.297 | - | Kaolinite |
| 4.437 | 4.437 | - | Kaolinite |
| 16.078 | Shifted | - | Montmorillonite |
| 3.024 | Shifted | - | Montmorillonite |
| **Sample 04** | | | |
| 10.037 | 10.037 | 10.037 | Illite |
| 3.342 | 3.342 | 3.342 | Illite |
| 7.185 | 7.185 | - | Kaolinite |
| 3.574 | 3.574 | - | Kaolinite |
| 15.081 | shifted | - | Montmorillonite |
| **Sample 05** | | | |
| 10.082 | 10.082 | 10.082 | Illite |
| 3.333 | 3.333 | 3.333 | Illite |
| 7.094 | 7.094 | - | Kaolinite |
| 3.562 | 3.562 | - | Kaolinite |
| **Sample 06** | | | |
| 4.481 | 4.481 | 4.481 | Illite |
| 3.333 | 3.333 | 3.333 | Illite |
| **Sample 07** | | | |
| 4.481 | 4.481 | 4.481 | Illite |
| 3.342 | 3.342 | 3.342 | Illite |

The results from oriented air dried samples above were not enough to confirm the clay mineral groups obtained. Identification and hence confirmation of these clay minerals was achieved from the differences on the diffractograms obtained by glycolating the samples, drying them, then diffraction process carried out; and by heating the samples at 550 $^{o}$C for two hours prior to the diffraction process. Presentation of these results is given in figures 2b to 8b and Table 1 for all samples.

Diffraction results [Figs 2b – 8b & Table 1] show that some of the diffractogram peaks in all samples were not affected by the two prescribed treatments. This behaviour of stability in chemical treatment (glycolated) and heat transformation (at 550 $^{o}$C) was shown by illite. This happened at d-spacing equals to 10.082 Å and 3.342 Å (sample 01) 10.221 Å and 3.337 Å (sample 02); 9.947 Å and 3.342 Å (sample 04); 10.082 Å and 3.333 Å (sample 05); 4.481 Å and 3.333 Å (sample 06); and 4.481 Å and 3.342 Å (sample 07).

When the samples were glycolated, dried and diffracted some peaks were shifted in some samples. But on heating the samples at 550 $^{o}$C followed by diffraction, these shifted peaks collapsed. This characteristic of altering the diffraction patterns which is a characteristic of kaolinite group (Lagaly 1981) was observed in samples 01, 02, 03, 04 and 05. This was observed at d-spacing values of 7.185 Å and 3.574 Å (sample 01); 7.185 Å and 3.579 Å (sample 02); 7.297 Å and 4.437 Å (sample 03); 7.185 Å and 3.574 Å (sample 04); and 7.094 Å and 3.562 Å (sample 05).

For samples that were glycolated and dried, the diffraction patterns showed that peaks of samples 03 and 04 were widened and shifted (Table 1). But on heating the samples at 550 $^{o}$C, the peaks collapsed. This occurred at d-spacing values of 16.078 Å and 3.024 Å (sample 03) and 15.081 Å (sample 04). Such observations are typical characteristic of montmorillonite clays (Lagaly 1981). Kaolinite a non-swelling mineral in water can be made to swell by using intercalation compounds (Bühmann *et al.* 1985). The intercalation compounds are compounds, which insert atoms or molecules as guest molecules between the layers of the host structure without disrupting the chemical bonds of the host materials. Ethylene glycol in this case is the intercalation compound which inserts its molecules into the interlayer of kaolinite. X-ray diffraction results show inverted diffractogram peaks for samples that were glycolated and dried.

The observation potrayed by kaolinite after both chemical and heat treatment is a tool to distinguish minerals of kaoline subgroups. For instance kaolinite –serpentine group minerals are characterised by 7Å reflections (Bühman 1998). The heat treatment (550 $^{o}$C) causes the collapse of the kaolinite structures, while serpentine structures are not affected. As a consequence an X-ray pattern recorded after the treatment of kaolinite will show no reflection but serpentines will do. So in this case a kaolin mineral is kaolinite since no reflection was observed. (Table 1 and Figures 2b -8b).

Similarly the same happened in montmorillonite (Smectite) which is a swelling mineral (Brindley 1966, Byrne 1954), on glycolating the mineral, dried up followed by X-ray diffraction the diffractogram peaks were shifted and widened. But on heating at 550$^{o}$C the peaks collapsed. The difference between kaolinite and montmorillonite is observed in chemical treatment that is when samples are glycolated, where kaolinite diffractogram peaks are shifted while montmorillonite peaks widen and shift (Table 1). But when clays are subjected to heat treatment at 550 $^{o}$C they both collapsed. The reasonable explanation for this is that heat treatment at 550 $^{o}$C collapses swelling minerals by dehydrating the interlayer material. As a result the swelling clay minerals are destroyed or transformed. Apparently, illite is a clay minerals which is not easily affected by chemical and heat treatments (Bühman 1998) For example, it is less subjected to transformation. This is why the diffractogram peaks of the three processes namely drying the sample in air, glycolating and heat treatments revealed by X-ray analysis are almost the same.

The results for the identification of minerals by ethylene glycol and heat treatment from the XRD analysis are supported by Infrared analysis (Table 2). The absorption bands due to OH stretching vibration at 3694 and 3825 $cm^{-1}$ are found in all samples except sample 03, 06 and 07, this is a characteristic property of kaolinite group mineral (Nakamoto 1962; Newmann 1987). However, for reasons which are yet to be investigated the 3694 $cm^{-1}$ peak is not observed in sample 01. Other bands, which suggest the presence of kaolinite, appear at 694 $cm^{-1}$ and ca 430 – 470 $cm^{-1}$ in all samples except samples 06 and 07, all these results are supported by XRD analysis.

The broad bands found at 3455 $cm^{-1}$ (sample 01); 3463 $cm^{-1}$ (Sample 02); 3600 $cm^{-1}$ (Sample 03); 3440 $cm^{-1}$ (sample 05) and weak band at 3632 $cm^{-1}$ (Sample 06); 3610 $cm^{-1}$ (Sample 07) are characteristics of illite (Van der Marel and Beutelspacher 1976; Wilson 1987). The presence of illite is also supported by a strong absorption at 532 – 539 $cm^{-1}$ which appears in all samples. These results are confirmed by XRD analysis.

In clay samples 02, 03 and 04 there is one broad band centered at 3432 $cm^{-1}$, which signifies the presence of both kaolinite and montmorillonite. The observation of these minerals (kaolinite and montmorillonite) is suppoted by strong peaks which appear between 1010 and 1033 $cm^{-1}$ in all samples and was also observed by Kirk – Othmer (1879) in his work. Contradictory results are given by XRD analysis which show that montmorillonite is found in samples 03 and 04 only, thus warranting for this peak to be assigned to a different vibration which is not due to montmorillonite.

Weak broad bands in vicinity of 1400 $cm^{-1}$ which due to some impurities present are shifted to 1396, 1411, 1426, 1457, and 1380 $cm^{-1}$ for samples 01, 02, 03, 04, and 05 respectively are due to the presence of nitrate ions (Nakamoto 1962). On the other hand, a peaks centred near 800 $cm^{-1}$, which appears in all samples, represent quartz.

The peaks centred between 2930 $cm^{-1}$ and 2360 $cm^{-1}$ are due to the presence of KBr disc used as a “matrix” and therefore are not diagnostic of any mineral.

**Table 2:** Infrared Frequencies ($cm^{-1}$) of clay minerals observed

| Sample | 01 | 02 | 03 | 04 | 05 | 06 | 07 | Vibration | Assignment |
|---|---|---|---|---|---|---|---|---|---|
| | | 3694.97(m) | | 3694.97(m) | 3694.97 | | | AI-O-H | Kaolinite |
| | | | | | | 3632.13(m) | | A1-O-H | Illite |
| | 3625.55(m) | 3625.55(m) | | 3625.55(m) | 3617.83(m) | | | A1-O-H | Kaolinite |
| | 3455(b/m) | 3463(b/m) | 3600.5(b/m) | | 3440(b/m) | | | A1-O-H | Illite |
| | | 3432(b/m) | 3432(b/m) | 3432(b/m) | | | | H-O-H | Kaolinite/Mont |
| | | 2969(w) | | | | 2968(vw) | | | |
| | | | | | | 29309(w) | | | KBr disc |
| | 2923(w) | 2923(w) | | 2932(m) | 2923(m) | | 2923(w) | | KBr disc |
| | 2854(w) | 2854(w) | | 1635(m) | 2854(w) | 2860(w) | 2861(w) | | KBr disc |
| | | 2645(w) | | | | | | | |
| | 2368(vw) | | | | | | | | |
| | | 2360(w) | | 2360(w) | | | | | KBr disc |
| | 1635(m) | 1627(vw) | 1640(m) | 1635(m) | 1627(m) | | 1635(m) | H-O-H | |
| | | | | | | 1611(m) | | H-O-H | |
| | 1396(vw) | 1411(vw) | 1426(m) | 1454(w) | 1380(vw) | | | | |
| | 1257(vw) | 1257(vw) | | | | 1263(vw) | | | |
| | 1033(vs) | 1022(vs) | 1031(vs) | 1033(vs) | | | 1033(vs) | Si-O-Si | Kaolinite/Mont |
| | | | | | 1010(vs) | 1010(vs) | | Si-O-Si | |
| | 917(w) | 917(w) | | 917(w) | 917(vw) | | 917(vw) | A1-O-H | Kaolinite/Mont |
| | | | | | | 801(m) | | Si-O-A1 | Illite&quartz |
| | 771(m) | 779(w) | 791(m) | 771(m) | 779(m) | | 771(w) | Si-O | Quartz |
| | | | | | 725(vw) | | 725(vw) | Si-O | Quartz&illite |
| | | | | | | 700(w) | | Si-O | Illite |
| | 694(m) | 694(m) | | 694(m) | 694(w) | | 694(vw) | Si-O-A1 | Kaolinite |
| | 647(vw) | 647(vw) | 639(w) | 647(w) | 647(w) | | 647(vw) | Si-O-A1 | |
| | 539(s) | | | | | 538(m) | | | |
| | | 532(s) | 532(s) | 532(s) | 532(m) | 477 | 532(m) | Si-O-A1 | Musco/vite |
| | 470(s) | 470(s) | | 462(s) | 470(s) | | 470(m) | Si-O | Kaolinite |
| | | | 432(vw) | 431(vw) | 431(vw) | | | Si-O | Kaolinite |
| | 416(vw) | 416(vw) | | | | | 416(vw) | | |

**NOTE:** vs – very strong; s – strong; m – medium; w – weak; vw – very weak; b – broad; Mont – Montmorillonite.

## CONCLUSION

The results of this investigation demonstrate how ethylene glycol and heat treatment were useful for the identification of clay minerals in our samples.

Diffraction patterns from oriented specimens in the air-dry condition; after Ethylene glycol treatment and after heating at about 550 °C had lead to the recognition of the main clay mineral groups in the analysed samples. These clay minerals were not revealed in the Whole Rock Powder Mount XRD analysis which was run in the range 2_ between 2° – 65° because of the presence of "impurities" (non-clay minerals) which hinder the development of the diffractogram peaks in region ranging between 2° – 32°. Clay minerals found in analysed deposits are kaolinite, illite and montmorillonite while non-clay minerals found are Na-feldspar, K-feldspar, pyrope and quartz. Infrared studies revealed results, which were complementary to the X-ray results, thus confirmed the observations.

## ACKNOWLEDGEMENTS

I am thankfully acknowledging the financial support from Gender Dimension Programme Committee (GDPC) of the University of Dar es Salaam. I am indebted to Mr. Richard Mhamba and Mr. Charles Maige who were highly involved in the field work. I also want to thank Mr. Matemu of SEAMIC for assisting me in the laboratory work.

## REFERENCES

Brindley GW 1966 Ethylene glycol and glycerol complexes of smectites and vermiculites. *Clay miner* ***6****: 237 – 256.*

Bühmann C, Fey MV and Villiers JM 1985 Aspects of the X-ray identification of swelling clay minerals in soils and sediments *South African Journal of Science* ***81****:505 – 509*

Bühmann D 1998 The Phylosilicates of clays and their X-ray identification. Lecture notes prepared for the X-ray diffraction (XRD) course, 1st – 14th March 1998 at SEAMIC, in Dar-es-salaam

Byrne PJS 1954 Some observations on montmorillonite organic complexes. *Clays miner.* ***2****: 241 – 253.*

Kirk – Othmer 1979 Encyclopaedia of Chemical Technology. John Wiley and Sons Inc. New York.

Lagaly G 1981 characterization of clays by organic compounds *Clay Miner* ***16****:1 - 21*

Nakamoto K. 1962 Infrared Spectra of Inorganic and Coordination compounds. Wiley. New York.

Newman ACD 1987 Chemistry of Clays and Clay minerals Mineralogical Society Monograph 6. London.

Skoog DA and West DM 1980 Principles of Instrumental Analysis 2nd Edn, Holt – Saunders International Editions.

Tobia SK and Sayre EV 1974 Recent Advances and Technology of materials. Bishay A. Edn vol 3. Plenum New York.

Van der Marel HV and Beutelspacher H 1976 Atlas of Infrared Spectroscopy of Clay Minerals and their Admixtures. Elsevier Scientific Publishing Company. New York.

Wilson MJ 1987 A handbook of Determinative Methods in clay Mineralogy. Chapman and Hall, New York.