Full Length Research Paper

Chemical and mineral analyses of Mwea clays

Muriithi, N. T.[1]*, Karoki K. B.[1] and Gachanja A. N.[2]

[1]Department of Chemistry, School of Pure and Applied Sciences, Kenyatta University, P. O. Box 43844 -00100, Nairobi, Kenya.
[2]Department of Chemistry, Faculty of Science, Jomo Kenyatta University of Agriculture and Technology, P. O. Box 62000-00200, Nairobi, Kenya.

Raw clays from Mwea area, Kirinyaga County, in the Republic of Kenya have been analyzed for their major and minor chemical elements. The clays were analyzed after subjection to different heating temperatures, of between 100 and 550°C, cooling and washing them with mineral acids of different concentrations. The results of the study show that the major components of the raw clays, when expressed as the oxides are: silica (SiO_2), 43.5 to 52%; alumina (Al_2O_3), 17 to 22%; iron (III) oxide (Fe_2O_3), 12 to 16%; titanium (IV) oxide (TiO_2), 3.5 to 5.3%; Lime (CaO), 1 to 3%; magnesium oxide (MgO), 0.5 to 1.25%. Elements occurring in very small quantities in the range of 0.1 to 0.9%, again when expressed as oxides are, Na_2O, 0.30 to 0.40%; K_2O, 0.20 to 0.30%; MnO, 0,14 to 0.46%. It was found that when the raw clays were boiled with either H_2SO_4 or HCl of different concentrations, the level of iron was reduced to 7 to 5% Fe_2O_3, depending on the concentration of the mineral acid used. Thus, both 18 M H_2SO_4 and 11 M HCl were found to be the most effective in iron removal. Furthermore, iron-removal was more effective when clay had been heated to a temperature of 400 to 550°C with the effectiveness being higher, the higher the temperature to which clay had been heated. Thus, when clay was heated to 550°C, cooled and washed with 11 M HCl, it contained only 0.08% Fe_2O_3. Very similar results were obtained by using 18MH_2SO_4 instead of11 M HCl. Unfortunately; such a residue contained very little clay if any because, it had nearly 85% SiO_2, and a mere 2.66% Al_2O_3. Mineral determination of the raw clays has shown that Mwea clays are predominantly montmorrillonites. In some sites such as Kandongu, the clays are highly contaminated with quartz. In addition, those elements which could be quantified, there were also elements which occur in only trace amounts and their presence was only shown on the X-ray diffraction spectra. These include copper, zinc, manganese, cobalt, nickel, zirconium, gallliumthallium, selenium, terullium, tantalum, thorium, silver and even gold. The acid-soluble aluminium compound in the raw clay was present as the mineral gibbsite, AlO.OH. There were two sites with relatively high levels of titanium (3.5-5% TiO_2).The titanium in the two sites was present as the mineral ilmenite, $FeTiO_3$ (Cumbiri) and the mineral anatase, TiO_2 (Kiandegwa). Elemental analysis was carried out using atomic absorption spectrophotometry, X-ray fluorescence spectrophotometry and ethylenediaminetetraacetic acid (EDTA) titrations. Within experimental error, the three methods gave very similar results.

Key words: Clay, X-ray fluorescence, atomic absorption spectrometry, X-ray diffraction, ethylenediaminetetraacetic acid (EDTA) titrations.

INTRODUCTION

Chemically, clays are aluminosilicate minerals (Grimshaw, 1971) which have many industrial applications (Murray, 2002). Whereas, for some of these applications the chemical compositions are not very critical, for other applications, the chemical composition of clay is very important. For example, whereas in the production of ceramic products such as roofing tiles or wall bricks the amount of iron in a clay is immaterial, for production of high quality ceramic products such as household crockery, it is recommended that the amount of iron should be less than 1% since larger amounts give undesirable colour to the finished products (Amethyst, 1996).

*Corresponding author. E-mail: muriithi.naftali@ku.ac.ke or ntmuriithi@gmail.com.

Another example that illustrates the importance of the chemical compositions of clay is in the manufacture of Portland Cement. Clay is one of the raw materials used in the manufacture of this commercially very important product. Owing to the relative abundance of magnesium in the earth's crust of about 0.27%, (Greenwood and Earnshaw, 1997), it is virtually impossible to get clay which is totally free of magnesium. However, It is recommended that the level of magnesium in a clay to be used for manufacture of Portland cement must be such that the amount of magnesium in the clinker, expressed as, MgO, does not exceed 5% (Witt, 1966; Troxell et al., 1968). The reason for this is that hydration of MgO to $Mg(OH)_2$ results in very large increase in volume which causes cracking of the concrete. Another reason why presence of magnesium ions is harmful to cement is that when these combine with sulphate ions, the magnesium sulphate formed leads to disintegration of concrete (Troxell et al., 1968).

Since Jaffe' showed that more than 50% of aluminium in kaolinite can be extracted readily with medium sulphuric acid if the clay is first heated to a temperature of 550°C (Jaffe, 1969), clays have become an important source of aluminium and aluminium compounds (Grim, 1981). Indeed, aluminium compounds have been recovered economically from clays with as little as 17% Al_2O_3 (Downa, 1993).

During the year 2008, Kenya imported 963.3 metric tons of kaolinite clays valued at US $400,000 (http://comtrade.un.org/"\t"_blank" United Nations Commodity Trade Statistics Database). Whereas, this is not a large amount of money, it is rather ironical that a country which is struggling even to feed its population can spend this amount of money to import clay which is available locally in terms of millions of tones especially in the rice-growing areas such as the Kano plains in Lake Victoria Basin or Mwea in Kirinyaga County. The reason why manufacturers of high quality ceramics products such as crockery are importing clay is that, whereas the local clays are suitable for manufacture of roofing tiles and wall bricks (and they are being used extensively for that purpose by companies such as Kenya Clay Products located some 20 km from Nairobi on Nairobi-Thika Highway), they are unsuitable for manufacture of high quality products since they contain as much as 17% Fe_2O_3 (Karoki, 2008).

Previously, Mwea Clays have been studied. However, the main interest in these studies was to assess the suitability of the soil for growing rice (Kamoni, 1992; Mohito et al., 2001).

In this paper, we wish to report the results of a study undertaken with three objectives. First, it was of interest to carry out total elemental analysis of Mwea Clays to find out whether they can be used as a source of aluminium and aluminium compounds. The reason for choosing this particular area for study is that should the results show that the clays are a potential source of aluminium, the process of starting an industry in the area should be fairly simple since this is government land leased to people for growing rice.

A second objective of our study was to find out whether the level of iron in the clays could be minimized by washing them with mineral acids of various concentrations. This idea was based on an observation in a previous study that practically all the iron in laterites which contained principally the minerals haematite and goethite was readily removed by washing the pulverized laterites with mineral acids (Muriithi, 1985).

A third objective of our study was actually mooted from the preliminary results which showed iron in Mwea clays was not readily leached with concentrated mineral acids. This behavior was completely different from what was observed during an earlier study of laterites (Muriithi, 1985). In the earlier study, it was observed that, practically all the iron was readily removed when the laterites were treated with concentrated mineral acids. In that study, it was established that the main iron-containing minerals were haematite and goethite (Muriithi, 1985). When the preliminary study of the Mwea Clays showed that very little iron could be extracted even by concentrated mineral acids, it was decided to study the nature of the iron-containing minerals in these clays.

EXPERIMENTAL

Clay samples were collected from eight sites indicated in the enclosed map of Mwea as shown in Figure 1. The area lies within, Latitudes S 0° 38′, S 0° 44′ and Longitudes E 37° 17′, E 37° 23′ and is approximately 50 km². The vegetation in a selected site was cleared with a machete and the top soil which normally contained a lot of organic matter removed. Thereafter, Samples were actually collected twice, one during a wet season and the second, during a dry season. During the dry season, the holes were dug with a steel metal bar and, during the wet season, an auger was used. Samples were obtained from different holes which were several metres apart. In each hole, the samples were got from different depths varying between 20 and 50 cm. For clays collected near roadsides, where deep profiles had been cut during road construction, advantage was taken of this and samples taken from depths of up to two metres. Samples got from different holes within a given site were mixed, dried at 110°C for at least three hours, cooled and ground to a fine powder using an Andrea Wolbring Keramischer Bedarf Ball Mill. The fine powder was put in a desiccator containing P_4O_{10} and left for at least six hour before weighing. The handling of the finely-ground dry sample depended on information being sought.

Determination of acid-soluble components from clays

Approximately 100-g sample was accurately weighed, put in a 2-way 500-ml round bottomed flask, about 200 cm³ H_2SO_4 of known concentration was added and the mixture heated for about 2 h using an isomanilte. Thereafter, the mixture was cooled, filtered using a pre-weighed sintered glass crucible of porosity No. 3, the residue thoroughly washed with distilled water, the washings added to the filtrate and the solution made up to a known volume using distilled water. This solution was examined for various elements following standard Analytical Procedures (Medham et al., 2000).
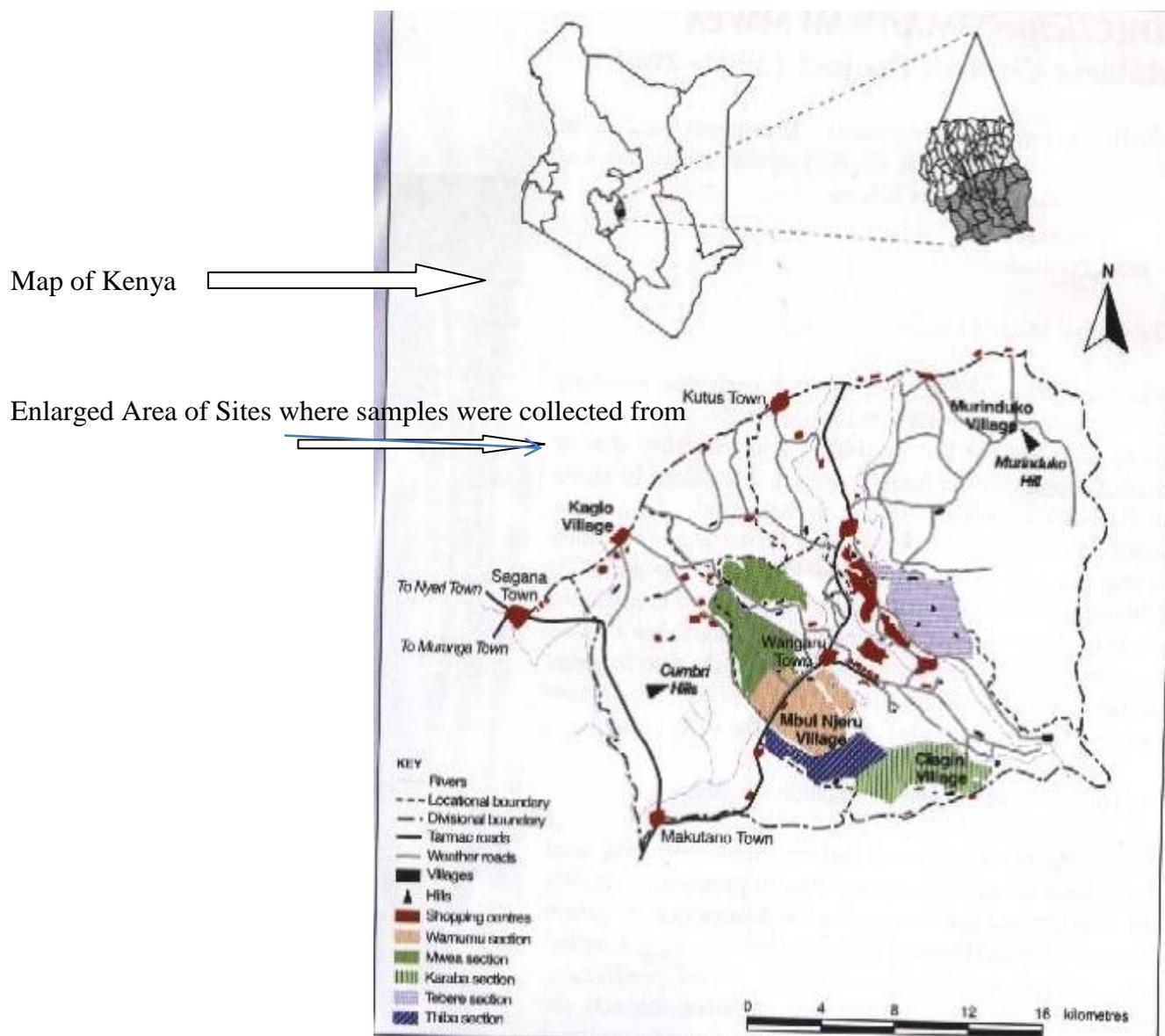
Figure 1. Map of Kenya showing area where samples were collected from.

Determination of acid-insoluble components of the clays

The acid-insoluble residue was dried at, 130°C for at least 3 h in an oven, cooled in a desiccator, weighed and analyzed for various elements using XRFS (solid) or AAS and EDTA after fusion and preparation of a standard solution technique (Vogel, 2000). Thereafter X-ray fluorescence spectra were recorded on Phillips Model PW4025 Spectrophotometer. The atomic absorption spectra were recorded on Varian Model AA.10 Spectrophotometer. The acid-extract was made up to a known volume and analyzed for various elements. This procedure was repeated for samples which had been heated at 200, 300, 400, 500 and 550°C. The accuracy of the results was assessed by comparing them with those obtained by analyzing SY-2 and MRG rock standards which were obtained from the Canadian Centre for Mineral and Energy Technology (CCMET) through the Department of Mines and Geology, Ministry of Environment Nairobi, Kenya.

Xray-diffraction spectra

X-Ray diffraction spectra were recorded on a PAN analytical X'PERT PRO Diffractometre which was coupled to a computer programme that allows reading of the minerals present in a sample.

RESULTS AND DISCUSSION

The results of elemental analyses for the raw clays are summarized in Tables 1, 2 and 3. Detailed results for each site for example the raw clay after treating it with acids of different concentrations, the clay after heating to various temperatures and extracting with acids of different concentrations, are found elsewhere (Karoki, 2008).

Table 1. Analysis of raw clay from different sites using AAS (Values in %).

Site	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	Na$_2$O	TiO$_2$	CaO	MgO	K$_2$O	MnO	LOIL	Total
A	42.8±1.7	21.0±0.83	14.6±0.3	0.39±0.04	4.43±0.07	1.66±0.02	1.07±0.02	0.21±0.01	0.14±0.01	12.6±0.59	98.88
B	45.1±1.6	18.7±0.61	14.9±0.50	0.46±0.02	4.01±0.03	1.62±0.05	0.99±0.03	0.31±0.02	0.26±0.02	13.2±0.47	101.56
C	46.9±1.2	17.1±0.76	16.6±0.97	0.47±0.03	4.67±0.01	1.93±0.01	1.26±0.05	0.24±0.01	0.37±0.01	9.80±0.63	99.34
D	43.6±1.4	22.7±1.6	11.6±0.53	0.40±0.01	3.29±0.06	2.35±0.03	0.5.26±0.04	0.18±0.01	0.140.03	14.6±0.67	99.36
E	50.1±2.0	14.8±0.9	15.2±0.66	0.360±0.02	4.00±0.12	1.1±0.02	0.90±0.02	0.26±0.03	0.15±0.02	13.4±0.76	101.276
F	47.3±1.7	16.9±0.62	11.7±0.18	0.340±0.02	3.46±0.08	2.54±0.02	1.16±0.02	0.20±0.01	0.22±0.01	15.6±0.81	101.276
G	50.6±2.1	16.2±1.5	11.9±0.37	0.41±0.02	3.21±0.04	3.09±0.07	1.15±0.03	0.23±0.02	0.46±0.02	13.2±0.64	98.05
H	42.0±1.6	20.2±0.83	16.4±0.71	0.37±0.03	4.89±0.02	2.52±0.06	0.87±0.04	0.19±0.03	0.250±0.3	12.6±0.52	100.29

Key: A, Mathangauta; B, Mutithi; C, Kiandegwa; D, Kiamanyeki; E, Nguka; F, Cumbiri; G, Kandongu; H, Kiarukungu.

Table 2. Analysis of raw clay from different sites using XRF (Values in %).

Source	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	TiO$_2$	CaO	K$_2$O	MnO	LOI	Total
A	43.9±1.57	22.1±1.1	14.1±0.24	4.52±0.11	1.74±0.09	0.20±0.06	0.14±0.01	12.6±0.59	99.3
B	44.9±2.2	19.4±0.92	13.6±0.62	4.11±0.09	1.57±0.02	0.36±0.03	0.21±0.01	13.2±0.47	97.35
C	47.5±1.4	17.9±1.2	15.1±0.75	4.81±0.10	1.76±0.03	0.21±0.04	0.14±0.02	9.8±0.63	97.49
D	44.6±1.7	22.4±0.83	12.4±0.87	3.61±0.07	2.21±0.04	0.23±0.06	0.18±0.03	14.6±0.67	99.93
E	49.5±1.0	15.7±0.64	14.4±1.20	3.35±0.09	0.89±0.03	0.34±0.04	0.21±0.03	13.4±0.76	97.79
F	48.6±1.9	17.5±0.96	12.6±0.70	3.72±0.05	2.05±0.01	0.27±0.05	0.19±0.05	15.6±0.81	100.42
G	51.6±0.97	16.5±1.1	13.1±0.68	3.86±0.06	2.81±0.02	0.23±0.04	0.42±0.02	13.2±0.64	100.05
H	43.3±1.2	19.1±0.09	15.9±0.54	5.17±0.08	2.69±0.04	0.16±0.04	0.29±0.01	12.6±0.52	99.21

Key: A, Mathangauta; B, Mutithi; C, Kiandegwa; D, Kiamanyeki; E, Nguka; F, Cumbiri; G, Kandongu; H, Kiarukungu.

Chemical composition of raw clays

The results of the current study show that Mwea clays are typical clays in which, silica is in the range of 42 to 50% and alumina is in the range of 17 to 22%. The major contaminant of these clays is iron, which, when expressed as iron (III) oxide, Fe$_2$O$_3$, occurs in the range 12 to 16%. Titanium occurs in all sites. Two of these are, however, of particular interest since the elements occurs in concentrations of, TiO$_2$, 3.5 to 5.3%; and Lime (CaO) 1 to 3%. Minor components namely, those oxide values of about 1% are:- magnesium oxide, MgO (0.5 to 1.25%), Na$_2$O (0.30 to 0.40%), K$_2$O (0.20 to 0.30%) and MnO (0.14 to 0.46%). The two major minerals of titanium with TiO$_2$ of about 5% would be of special interest if further studies can confirm large enough distribution because, according to Knitell (1983), SUN Corporation has recovered titanium economically with ores, with as little as 0.35%TiO$_2$ from ores titanium and more studies may yeild titanium from ilmenite, FeTiO$_3$, (Cumbiri) and Anatase, TiO$_2$ (Kiandegwa). The acid-soluble aluminium compound was the mineral, gibbsite, AlO(OH).
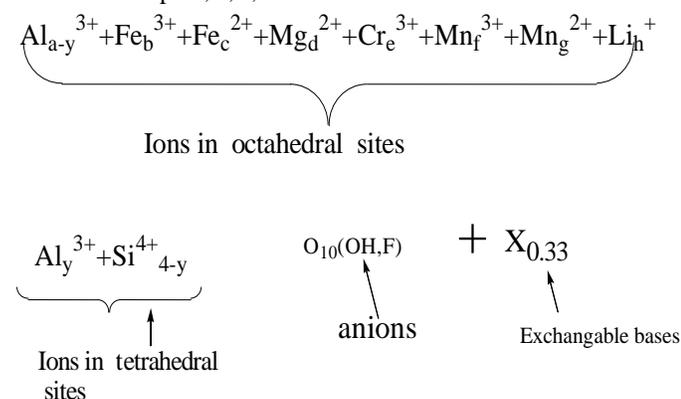
The most reasonable explanation for failure of iron to be extracted with mineral acids appears to be the structure of the clays. The X-ray diffraction spectra showed that the major minerals in Mwea clays are montmrillonites, detailed studies of

Table 3. Analysis of the raw clays for Al_2O_3 and Fe_2O_3 using EDTA method.

Source	Al_2O_3	Fe_2O_3
Muthangauta (A)	19.6±0.13	12.9±0.03
Mutithi ((B)	18.2±0.11	13.1±0.04
Kiandegwa (C)	16.6±0.05	14.7±0.02
Kiamanyeki (D)	19.6±0.06	13.6±0.03
Nguka (E)	13.4±0.02	13.9±0.03
Cumbiri (F)	15.9±0.04	13.8±0.01
Kandongu (G)	16.7±0.02	12.4±0.05
Kiarukungu (H)	18.8±0.06	14.7±0.02

montmorrilonites by other workers (Ross and Fredricks, 1945; Ross, 1960); of over 100 montmorillonite minerals have shown that these have the complex structure of the type shown thus:

Note: Montimorrilonites have number of ions, indicated by the subscripts a, b, c, d.. etc

$$Al_{a-y}^{3+}+Fe_b^{3+}+Fe_c^{2+}+Mg_d^{2+}+Cr_e^{3+}+Mn_f^{3+}+Mn_g^{2+}+Li_h^{+}$$

Ions in octahedral sites

$$Al_y^{3+}+Si_{4-y}^{4+} \qquad O_{10}(OH,F) \qquad + X_{0.33}$$

Ions in tetrahedral sites

anions

Exchangable bases

Key: The subscripts, *ab,c* etc inndicates variable number of the ions, 1,2, 3, etc

In such a structure, the cations of various metals are embedded in the rather complex structure shown. In our opinion, the very high resistance of iron to go into solution even in hot mineral acids can be attributed to this complex structure of montimorrillonites.

Loss on ignation

The data on this column represent loss of chemically-combined water and combustion of organic matter. As may be expected, these two parameters varied widely because the amount of organic matter in the clays is not uniformly distributed. Even the amount of combined water is not, by any means constant in clays.

REFERENCES

Amethyst GT (1996). The mineral Chlorite. Clay Miner. Soc. J. TOC37: 5.

Downa AJ (1993). Chemistry of Aluminium, Gallium, Indium and Thallium. Blackie Academic and professionals. pp. 81-87.

Greenwood NN, Earnshaw A (1997). Chemistry of the Elements 2nd Ed 1997, Butterworth, Heinmann Amsterdam, London, New York Elsevier, P. 1294.

Grim RE (1981). Technology of Clay. J. Am. Ceramic. Soc. 64: 90.

Grimshaw RW (1971). The Chemistry and Physics of Clays and Allied Ceramic Materials. Ernest Benn Ltd, 4th Ed 1971. 1:29.

Jaffe WD (1969). The Effect of Heat Treatment on Reactivity of Minerals, PhD Thesis, University of Leeds.

Kamoni PT (1992). Detailed Soil Survey of Mwea Irrigation Agricultural Development Project Report No D56, December.

Karoki KB (2008). Analysis and Treatment of Clays from Mwea to Assess their value of Aluminium and Ceramics Product. M Sc. Thesis Kenyatta University.

Knittel D (1983). in "Kirk-Othmer Encyclopedia of Chemical Technology Wiley Interscience '3rd Ed. P. 100.

Medham J, Denney RC, Barnes JD, Thomas M, Sivasankar B (2000). Textbook of Quantitative Inorganic Analysis including Elementary Instrumental Analysis 5th Ed, Longman Group Limited, London and Longman INC, New York. pp. 124-125.

Murray HD (2002). Industrial Clays: Case Study. International Institute for Environment and Development (IIED). England. pp. 1-4.

Mohito K, Ota T, Wanjogu R (2001). Physical and Chemical Properties of Vertisols and Soil Nutrient Management for Intensive Rice Cultivation in the Mwea Area in Kenya. Jpn. J. Trop. Agric. 45:126-132.

Muriithi N (1985). Iron Content of Some Samples of the Black Murrams and Red Ochres from different parts of Kenya. Kenya J. Sci. Technol. A, 6(2):103-110.

Ross CS (1960). 7th Nat. Conf. Clays and Clay Minerals (Pergamon Press 1960).

Ross CS, Fredricks SB (1945). US Geological Survey, Prof. Paper No. 205-B 1945.

Troxell GE, Davis HE, Kelly JW (1968). "Composition and Properties of Concrete, 2nd Ed McGraw Hill Book Company, 1968 Chapter 2.

Vogel AI (2000). Textbook of quantitative Chemical Analysis. 6th Ed. 2000, Pearson Chenai Delhi Chardigah. pp. 316-324.

Witt JC (1966). Portland Cement Technology,Chemical Publishing Company, Inc. 2nd Ed 1966, Chapter 3.