BENEFICIATION OF LOW GRADE TITANIUM ORES FROM SELECTED SITES IN MERU, MURANG'A AND THARAKA NITHI COUNTIES, KENYA

BY

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DECLARATION

I hereby declare that this is my original work and has not been presented for a degree in any other University or any award.

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DEDICATION

This work is dedicated to my mother Agnes Muthoni, my wife Christine Gacheri, my daughter Julienne Muthoni and my son Richmond Kariuki.

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ABBREVIATIONS AND ACRONYMS

AAS	Atomic Absorption Spectroscopy
AES	Atomic Emission Spectroscopy
GDP	Gross Domestic Product
HM	Heavy Minerals
HMC	Heavy Mineral Concentrate
KNBS	Kenya National Bureau of statistics
SPSS	Statistical Program for Social Scientists
SY-3	Syenite
t_{cal}	t-calculated
t_{crit}	t-critical
THM	Total Heavy Mineral
U.S.E.P.A	United States Environment Program Agency
U.S.G.S	United Nation Geological Survey
WHO	World Health Organization
XRD	X –Ray Diffraction

ABSTRACT

Titanium occurs in more than 70 minerals, but only ilmenite and rutile are used for extraction of titanium dioxide and subsequent extraction of titanium metal. Due to decrease in rutile deposit, ilmenite is used as the alternative source of titanium dioxide. Ilmenite exists as a low grade titanium bearing mineral with less than 5 percent titanium dioxide composition by mass, this percentage is not commercially viable for the extraction of titanium. For it to be used to extract titanium, it must be concentrated to improve the levels to 5 percent and above. Recent geological survey shows that titanium oxide exists as an iron-rich ores in Kenya. Occurrence of these iron-rich titanium ores in laterites has also been documented to be in huge amounts in Kenya. Titanium ores remain largely unexploited in Kenya since the current technology in use is very expensive and often requires a lot of water, a scarce resource, thus limited to only where we have large water bodies, in Kwale. Kenya is composed of 80 % of arid and semi-arid whereas titanium ores spread across the country. These research project show results of the study undertaken to find out whether low grade titanium ores in laterites, can be beneficiated to extractable levels above 5% by heating the raw laterites sample with *lantana camara* and separate using a strong magnet. The samples were obtained from selected regions of Meru, Murang'a and Tharaka Nithi counties in Kenya. Chemical analysis carried mainly focused on titanium levels in both the raw and heat-treated samples using Atomic Absorption Spectroscopy (AAS). The mineralogical content in raw and thermally reduced laterite samples was done using Brucker D2 Phaser Diffractometer. The results showed that percentage of titanium dioxide in Mbeu and Kaharate ranges from 3 to 7 percent while those from Tharaka Nithi is between 1.6 to 1.77 percent. The beneficiation of the titanium was done by heating raw biomass-sample in the ratio of 1:10 at temperature range of 500 to 800 ^{o}C in closed ceramic crucibles. When heated, iron-rich titanium (ilmenite ($2\theta = 33.12^{o}$)), goethite ($2\theta = 21.51^{o}$) and haematite ($2\theta = 54.11^{o}$) were converted to maghemite ($2\theta = 35.6^{o}$). On further heating of the magnetically separated products to 1000 ^{o}C, the tailing after magnetic separation was observed to have a peak of rutile ($2\theta = 27.4^{o}$), a clear indication that maghemite contains titanium dioxide in its structure. Magnetically separated products from Mbeu and Kaharate contained between 4.7 to 5.82 % and from Tharaka Nithi contained over 5% of titanium dioxide. Bio-waste is a source of syngas which provide heat and reducing agents. Low grade titanium bearing mineral was upgraded to levels that was more than 5 % which is required for extraction of titanium dioxide and subsequent titanium metal. The proposed method of titanium ore concentration introduces local technology that can be used to beneficiate the ores for commercial exploitation.

CHAPTER ONE

INTRODUCTION

1.1 Background Information

Titanium is widely used as titanium dioxide (TiO_2) for production of white pigment (Gambogi, 2005). The oxide is used in paints (Linak and Inoguchi, 2005), plastics and paper. The pigment is of high refractive index thus used in thin-film optics. It is used in metallurgical and electronic applications and extensively in surface coating (Fisher, 1997). Ti has extensive use in aerospace industries due to its lightness, strength, corrosion and heat resistance. It is used in making artificial hip joints, heart pace makers and spectacle frames (Hanson, 1986). Materials that are manufactured locally will reduce the government expenditure in importation of goods. Similarly surplus locally finished products can be exported to earn foreign currencies to Kenya. This will increase GDP.

In 2013, approximately 1.20 million tons of titanium dioxide was produced worldwide. According to (Bedinger, 2014), China was the top producer of Ti ore with at least a third of the total world share, followed by Australia, India and South Africa. Kenya remains an importer of titanium dioxide products.

Kwale mineral survey by Tionim Kenya Limited technical report of February 2006 indicates the existence of low grade Ti ores in large quantities. The ore exist in a mixture of other minerals with high density. This mixture is known as total heavy metal (THM) or sand formations and is composed of ilmenite, rutile and zircon. Zircon is very expensive. Ilmenite composes of 2.1 percentages on average. 2 percent of ilmenite yields about 50 percent of titanium dioxide that is normally required for commercial exploitation (Abuotha, 2003).

Kenya imports Ti and titanium based products such as bicycle frames used by tourists, toothpaste, quality paint and rubber, ceramics, fabric, soap, cosmetics, and more recent multibillion aeroplane (KNBS, 2011). Kenya incurs a lot of expenses despite her having multibillion wealth still not mined (Mathu and Davies, 1996). Mining of Ti will provide raw materials for the manufacture of such expensive products hence reduce the expenses of importing some of the same.

In Kenya, titanium mining activities are undertaken by Base Resource Limited in Kwale. They mine Zircon ($ZrSiO_4$), Rutile (TiO_2) and Ilmenite ($FeTiO_3$), (MEMR., 2010). The sand formations in Kwale contain averagely 3.4 percent of Ilmenite which constitutes 1.7 percent of TiO_2 before concentration. These sand formations are ilmenite-rich, with 30 percent to 40 percent titanium dioxide (Roy *et al.*, 2000). They are locally concentrated as heavy metal concentrates using Wet Concentrator Plant that produces up to 90 percent heavy mineral (MEMR., 2010). Table 1.1 shows the levels of major components of THM in Kwale and the vicinity.

Table 1.1: Levels of THM in Kwale and its Vicinity

Location	Mombasa		Kwale		Mambrui		Kilifi North		Kilifi South	
Ore (Mt)	500		200		700		1700 (combined total)			
Mineral value	Q'tity (Mt)	Grade (%)	Q'tity (Mt)	Grade (%)	Q'tity (Mt)	Grade (%)	Q'tity (Mt)	Grade (%)	Q'tity (Mt)	Grade (%)
Ilmenite			4.3		6.2	2.3	7.0	1.5	3.6	1.4
Rutile			1.1		0.3	0.1	0.62	0.14	0.33	0.13
Zircon			0.6		0.3	0.12	0.62	0.14	0.36	0.14
Total coastal deposits: 3.1 billion tonnes										

Key: Mt = million tonnes; shaded cells = data unavailable
Source: based on information from Tiomin's web site, www.tiomin.com (2006)

Current method of concentrating Ti ores, that is, gravity separation requires a lot of water and also high-intensity magnetic separator (Dunn *et al.*, 2007; Babu *et al*., 2009) which is very expensive. Kenya is composed of 80 % of arid and semi-arid areas (Kirkbride and Grahn, 2008). Owing to this fact, Kenya remains challenged with water shortage in most parts, and especially those areas that has been reported to have iron-rich titanium ores. The current method used in Kenya for pre-concentration of titanium ores requires a lot of water. Water is a scarce resource in large part of Kenya and especially places documented to have titanium bearing minerals and therefore the methods are unsustainable.

Research has shown that laterites, commonly known as "murram", contain titanium (Keru, 2011; Mutembei *et al*., 2014; Njoroge *et al.*, 2014). Keru (2011), while working on laterites in Ruiru area in Kiambu County, Kenya, reported the presence of Titanium in the sample collected. The author, (Keru, 2011) makes no reference to the titanium dioxide improvement in his work. Mutembei (2014), while working with laterites from Tunyai area in Meru, noted that there was a slight improvement of the titanium levels in the treated sample after magnetic separation. He recommended further investigation on the same.

Njoroge *et al.* (2014) showed improvement in titanium dioxide concentration from raw to heat treated samples. The author, though interested in concentration of iron ores, makes no reference to the titanium dioxide concentration improvement. From the researchers' (Keru, 2011; Mutembei *et al*., 2014; Njoroge *et al.*, 2014) works, it is clear that titanium dioxide concentration is enhanced by thermal reduction of titanium containing laterites. In all cases mentioned above, there was noted low improvement in titanium dioxide concentration, to levels that the ore cannot be used for commercial exploitation, in cases where the ore used has

low concentration of TiO_2 (less than 2 percent). The researchers were thermally treating the ores at temperatures below $700\,^{\circ}C$. This mainly converts iron bearing titanium minerals to magnetite that has a low concentration of Ti in its structure compared to other iron bearing minerals like maghemite. This study investigated the parameters for conversion of the iron bearing titanium minerals to maghemite to enhance improvement of TiO_2 in the ores.

1.2 Problem Statement

Despite many parts of Kenya having titanium dioxide deposits, its mining activity which only includes concentration of the low grade Ti bearing ores is still very low. This has been attributed to high cost of concentration due to expensive methods of extraction. Current method of concentration, by use of gravity, requires a lot of water which is a scarce resource in Kenya. This has limited the concentration, and hence extraction, of the ore to only areas where water supply is in plenty and adequate, around large water bodies, for example Kwale near the Indian Ocean, in Kenya. Alternative methods, which are not limited to water supply will enable concentration, and hence exploitation of titanium as a mineral. The proposed method of concentration of titanium ore, through thermal reduction of the ore using waste biomass, will further rid the environment of obnoxious waste.

1.3 Justification of the Study

Low grade titanium dioxide contains a lot of unwanted materials. Beneficiation is the process of removing unwanted laterites materials in an ore (referred to as gangue) to increase its economic value (in this case, increase the percentage of titanium dioxide by more than 5 percent). Beneficiation of low grade Ti dioxide ores will significantly reduce gangue. Elimination of gangue will reduce transportation cost, such as, the freight and shipping cost of

the ore due to reduction of volume. This research aimed at improving the percentage levels of titanium so as to obtain better value for titanium ores. The resultant ore can be transported to areas of extraction, in a similar manner to the exportation of the titanium ore from Kwale, Kenya

The proposed technique of beneficiating titanium ores uses raw biomass. Biomass for example rice husks are waste. This biomass waste has limited uses in Kenya. It is mainly burnt in open fields creating a lot of smoke and resultant ash. The project has demonstrated it can be economically used to be used to beneficiate titanium ores. This will rid the environment of the waste.

Industrialization of a country needs local available raw materials. This will in turn lead to manufacture of local products and export of finished products thus boosting foreign exchange. This in turn will lead to economic empowerment of our country thus facilitating achievement of the Kenya Vision 2030

1.4 Hypothesis

Thermal beneficiation does not increase percentage of titanium significantly from low grade ores.

1.5 Objectives of the Study

1.5.1 General Objective

To beneficiate thermally low grade titanium ores from selected areas in Meru, Murang'a and Tharaka Nithi County, Kenya

1.5.2 Specific Objectives

i) To determine chemical composition of Ti ore in laterites from selected areas within Mbeu area of Meru, Murang'a and Tharaka Nithi counties, Kenya, using Atomic Absorption Spectrometer (AAS)

ii) To concentrate the Ti ore in laterites through thermal reduction using raw biomass followed by magnetic separation

iii) To determine the mineralogical composition of titanium bearing ores in laterites samples, using X-Ray Diffractometer (XRD), before and after magnetic thermal reduction

iv) To investigate the possibility of converting sampled Titanium ores in laterites samples to maghemite, a product attracted by magnet after roasting the ore mixed with raw biomass in limited amount of air and to determine the percent yield of the concentration method

1.6 Scope and Limitation

The study aims at assessing the levels, mineral occurrence and possible method of beneficiating Ti ores from selected areas in Meru, Tharaka Nithi and Murang'a Counties. It will not cover the whole of Meru County or Tharaka Nithi or Murang'a or the country at large. The research is based in a lab set up. Economic viability in large scale was not done.

CHAPTER TWO

LITERATURE REVIEW

2.1 Laterites

Laterite comes from latin word "*later"* that mean brick (Thurston, 1913). Laterite is restricted to highly weathered material (Cline *et al*., 2002). According to Cline, 1962 it is rich in iron, aluminum, or both but poor in humus. It is depleted of bases and combined silica. It is with or without non-diagnostic substances, such as quartz, limited amounts of weatherable primary minerals or silicate clays and either hard or subject to hardening upon exposure to alternate wetting and drying.

Laterites are also rich in manganese, titanium oxides among many other elements (Lemougna *et al*., 2011). Iron, aluminum and titanium oxides are prominent in lateritic soils, and with the seasonal fluctuation of the water table, these oxides result in the reddish-brown color that is seen in lateritic soils. These mineralogical and chemical compositions are dependent on their parent rocks. Laterites vary significantly according to their location, climate and depth (Hill *et al.*, 2000).

Laterites are formed by leaching of parent sedimentary rocks, such as sandstones and clay, metamorphic rocks such as schists, gneisses, magmatites, volcanic rocks such as granites, basalts, gabbros, periodotites, and mineralized proto-ores (Tardy, 1997). Acid leaching of original mineral lattice is followed by hydrolysis and precipitation of insoluble oxides and sulphates of major elements under the high temperature condition of humid sub-tropical climate (Hill *et al.*, 2000). An essential feature for the formation of laterite is the repetition of wet and dry seasons (Kosei and Yamaguchi, 2010). The reaction zones are in contact with

water from the lowest to highest water table levels is progressive in depletion of the easily leached ions of elements such as sodium(Na), potassium(K), calcium(Ca) and magnesium(Mg) (Kosei and Yamaguchi, 2010).

According to Tardy (1997), one-third of the Earth's continental land area is covered by laterites which are the sub-soils of equatorial forests, of the savannas of humid tropical regions, and of the Sahelian Steppes. In Africa, areas not covered are only southwestern portion of Africa, and the desert regions of north-central region. Other areas of the world without laterites include Arabian Peninsula and the interior of Australia (Tardy, 1997).

Laterites were mainly used for surfacing the roads but recent research showed that laterites contains goethite and haematite, minerals that are thermally reduced into magnetite, a chief ore in extraction of Fe (Keru, 2011; Mutembei *et al*., 2014; Njoroge *et al.*, 2014). The researchers showed that laterites contain Fe ores that can be thermally being reduced to more than 55 percent. These levels can be used for commercial exploitation of Fe. Thus laterites are source of Fe.

2.2 Titanium Occurrence

Titanium is a silvery grey metal in group IVB of the periodic table. It is a member of the first transition series. It is the ninth most common element in the Earth's crust, averaging 0.9 percent Ti (Turekian, 1977). It has an atomic number of 22, relative atomic mass of 47.9 and density of 4.5 g/cm^3 at 20 °C. It has a relatively high melting point of 1668 ^{o}C (Herbert and Revie, 1984).

Titanium has both metallic and non-metallic characteristics (Frost and Lindsley, 1991). Its most common oxidation state is +4 as titanic compounds (Guanglei *et al.*, 2006), but +3 (titanous compounds) and +2 forms are also known. It is also found in oxy forms such as titanyl chloride. The metallic characteristics of titanium are shown in compounds such as titanium chloride, phosphate, sulfate, and nitrate, whereas the non-metallic characteristics are exhibited in a series of titanates, for example, calcium, iron, and sodium titanates (Vinogradov, 1959; Stamper, 1970). Ti is used as a raw material for many industries. It is used, for example, in making motor bike frames, among others. Similarly surplus locally finished products can be exported to earn Kenya foreign exchange, thus increasing GDP.

Ilmenite is present in black magnetite-bearing shore sand extending for a distance of about 8 miles along the Uyoma Peninsula in western Kenya (Dubois, 1966). Analyses of concentrates after removal of magnetite gave a titania content of 13.8 per cent. The reserves are thought to be large. In Malindi prospecting, analysis were carried out on the beach sands and dunes along the coast north of the township and in Formosa Bay in 1953. The sands were found to contain, ilmenite and rutile, together with monazite and various iron minerals. Normal sands usually contain less than 2 per cent of ilmenite, except where they have been concentrated by natural processes. A beach concentrate at Ras Ngomeni was found to contain 3.84 per cent ilmenite while an even higher value of 13.7 per cent ilmenite was recorded from a 5-in band in dark coarse dune sand near the mouth of the Sabaki River.

Ilmenite typically contains around 50 % titanium oxide and around 45 % iron oxide. All the titanium is present as Ti (IV) while around 20 % of the iron occurs as Fe (III) and rest is in the Fe(II) state (Samala *et al.*, 2010). Ilmenite has been used as a commercial ore for producing Ti

(McGee *et al*., 1977). Ti is commonly combined with iron or chromium oxide minerals, and thus ilmenite may contain less TiO_2 than expected. However, leaching of iron from ilmenite during weathering can result in poorly crystalline mineral which lowers its magnetic susceptibility. The term ilmenite also covers the entire range from unweathered ilmenite (TiO_2 content of less than 50 percent) to altered ilmenite (TiO_2 content of more than 60 percent). When the TiO_2 content of altered ilmenite exceeds about 70 percent, it is commonly referred to as leucoxene (Grass *et al.*, 2012). The table 2.1 below shows the composition of oxides of major elements in different samples.

Table 2.1: Average Chemical Compositions of Selected Igneous Rock Types

Rock type / major oxides	**Acidic (Granite)**	**Intermediate (Andesite)**	**Basic (Basalt)**	**Ultrabasic (Peridotite)**
SiO_2	71.3	57.94	49.2	42.26
TiO_2	0.31	0.87	1.84	0.63
Al_2O_3	14.32	17.02	15.74	4.23
Fe_2O_3	1.21	3.27	3.79	3.61
FeO	1.64	4.04	7.13	6.58
MnO	0.05	0.14	0.2	0.41
MgO	0.71	3.33	6.73	31.24
CaO	1.84	6.79	9.47	5.05

Source: (Middlemost, 2013)

2.3 Beneficiation of Titanium Ore

Gangue is the unwanted rock materials in any ore (Daintith, 2000). Beneficiation is the process of removing gangue (unwanted materials from the ore) from an ore so as to increase its economic value (Carter and Barry, 2007). This is done for low grade ores to improve levels to percentage that are used for commercial exploitation. Most mineral including titanium occurs as low grade. Commonly used methods for beneficiating Titanium ores include froth flotation, jigging and magnetic separation (Sharma, 2004).

Beneficiation includes milling (crushing and grinding); washing; filtration; sorting; sizing; gravity concentration; magnetic separation; flotation; and agglomeration (pelletizing, sintering, briquetting, or nodulizing) (USEPA., 1994). Although the literature suggests that all these methods have been used to beneficiate iron, a titanium carrier. Information provided by members of the American Iron Ore Association indicates that milling and magnetic separation are the most common methods used. Gravity concentration is seldom used at existing U.S. facilities (Babu *et al*., 2009). Flotation is primarily used to upgrade concentrates from magnetic separation by reducing the silica content of the concentrate.

Beneficiation improves percentage levels of an element in the ore, especially those whose percentage levels are low, for example titanium among many metals. This removes unwanted materials that make the ore useful for extraction. Titanium ores contain silica as gangue in high amounts. This can be separated by use of a magnet due to magnetic nature of iron rich titanium ore. The levels of the metal of interest goes up in the ore are increased significantly making it possible to extract it at a lower cost (Gehring and Hofmeister, 1994). Low grade Ti ores has so many unwanted materials which include silica and other earthly particles. Beneficiation leads to reduction of freight and shipping cost since less material require less space and resources to be moved from one location to another. These materials are mostly non-magnetic. Removal of these materials makes it possible for the developing countries to manage the transportation expenses.

Titanium mining have not been exploited fully since there are no local industries to absorb the mineral and the freight costs are too prohibitive for an export market (Loupekine, 1968). According to Loupekine (1968), Ti bearing minerals identified in Kenya comprise mainly of

ilmenite, $FeTiO_3$, rutile, TiO_2, ilmenorutile, (Ti, Nb, Fe) O_{26}, titanite, $CaTiSiO_5$ and perovskite, $CaTiO_3$ (Loupekine, 1968). Ilmenite($FeTiO_3$) has a widespread occurrence in Precambrian Basement System rocks as an accessory constituent in gneisses and pegmatites and in detrital rocks derived from them (Hugo, 1993). A feasibility study was carried out in Kwale (Griffiths, 2011) and found Kwale rich in Titanium ore, in addition to zirconia. In Kenya, the mining of titanium is done by Base resource limited as a heavy mineral concentrate.

Njoroge *et al.* (2014), while concentrating iron ore used biomass and temperatures range of 500–700 ^{o}C. Results analysis indicated a low percentage of titanium dioxide in the sample. The researcher used a ratio of biomass to sample ratio of 1:20. This parameter favour conversion of iron bearing minerals such as goethite and haematite into magnetite. Magnetite contains less titanium dioxide. Parameters used therefore could not be used to increase the levels to over 5 % of titanium dioxide which is used for extraction of Ti.

2.3.1 Magnetic Separation

Magnetic separation is popular for beneficiating iron bearing mineral. Magnetic separations are of two types; normal and high density (Harry *et al.,* 1973). Normal magnetic separation is adapted to separate iron ores with high magnetic susceptibility such as maghemite. High density magnetic separation is used to separate iron ores with lower magnetic susceptibilities such as ilmenite. The unit of measurement of magnetic flux density or magnetic induction (B), which is the number of lines of force passing through a unit area of material, in tesla (T). The magnetizing force, which induces the line of force through a material, is called the field intensity (H). The intensity of magnetism or the magnetization (M) of a material relates to the magnetization induced in the material as shown in equation 2.1 (Svoboda, 2004).

$$B = \mu_0 (H + M) \quad \text{.....2.1}$$

In vacuum, M = 0 and it is extremely low in air, therefore equation 2.1 reduces to equation 2.2

$$B = \mu_0 H \quad \text{.....2.2}$$

Magnetic separation is popular for beneficiating iron bearing mineral (Cohen, 1986; Mauricio, 1991). Magnetic separations are of two types; normal and high density (Heiri *et al.*, 2001). Normal magnetic separation is adapted to separate iron ores with high magnetic susceptibility such as magnetite (Morris *et al*., 1985). High density magnetic separation is used to separate iron ores with lower magnetic susceptibilities such as haematite.

Magnetic separation involves use of a strong magnet to remove materials with different magnetic susceptibilities (Svoboda, 2004). Magnetic susceptibility of most material is induced by inclusions or ex-solutions of iron oxides (Borradaile *et al*., 2008). Magnetic susceptibility is affected by temperature change. In low magnetic fields, the permeability of the mixed ferrites increases with increasing temperature (Orlický, 2010). Similar trends have been shown with Ti-rich titanomaghemite (Orlický, 2010).

Ilmenite is paramagnetic with relatively low magnetic susceptibility (Raieevio *et al*., 1990). Magnetic susceptibility of, iron rich titanium ores such as ilmenite can be increased significantly by heating it in the presence of reducing agents, such as, carbon monoxide and syngas (Ciu *et al*., 2002). These reducing agents are produced by heating raw biomass to temperatures of 500 to 800 ^{o}C. While heating charcoal in the ratio of biomass to sample ratio of 1:10, in controlled air, the researcher increased the magnetic susceptibility of ilmenite. This makes it possible to concentrate Ti in iron rich Ti ores (Steenkamp and Pistorius, 2003) using magnetic separation.

Thermal reduction of ilmenite with carbon monoxide converts FeO in ilmenite ($FeO.TiO_2$) to maghemite (γ-$Fe_2O_3.TiO_2$). Its magnetic susceptibility is high (Ciu *et al*., 2002). Maghemite is also formed as a result of oxidation of magnetite, with less than 2 percent TiO_2 (Morris *et al.*, 1985; Gehring and Hofmeister, 1994). Maghemite loses Fe ions but retain the spinel structure (Brown and Navrotsky, 1993). The roasted ilmenite has a higher magnetic susceptibility and thus can be separated by use of a magnet. Magnetic separation has been used in the concentration of magnetite due to its strong magnetic susceptibility (Mutembei *et al*., 2014). Magnetite can be converted to maghemite (γ-Fe_2O_3) at temperatures above 600 °C (Meizhen *et al*., 2011). The structure of this mineral contains iron enables the concentration of titanium dioxide.

Research concluded recently (Mutembei *et al*., 2014) has shown that Ti is contained in iron rich minerals. These minerals include manganoneptunite, $KNa_2Li(MnFe^{2+})_2Ti_2Si_8O_{24}$, Lindsleyite, $(Ba,Sr)(Ti,Cr,Fe,Mg)_{21}O_{38}$ among others. This clearly indicates that magnetic susceptibility of iron can be used to concentrate Ti. Mutembei used magnetic separation for iron. This suggests that Ti can be concentrated using magnetic separation. Iron and Titanium formations follow a similar trend (Christie *et al*., 2000).

Raw biomass has better reduction properties than charcoal (Goswami, 2014). Biomass materials undergo incomplete combustion at a temperature of 800 ^oC producing hydrogen, carbon monoxide and trace of methane a mixture commonly known as producer gas, which are strong reducing agents. All biomass undergoes gasification (Goswami, 2014), thus can be used as reduction agents when exposed to certain temperature. Rice husks, raw biomass, as shown

in plate 2.1, go into waste rather than being used for concentration of Ti ore. Amount of biomass used in concentration is so small and this reduces problems of introducing silica.

Plate 2.1: Rice Husks Before Burning and One Undergoing Burning
Source: (Osawa and Muchunku, 2006)

A researcher (Mosiori, 2013) conducted a survey on biomass in the Lake Victoria region and found that there is adequate raw biomass that can be gasified to produce synthetic gas (syngas) for use as a reducing agent in the Ti ore beneficiation process. A lot of waste such as rice husks, lawn mowers biomass among others can also be gasified.

2.3.2 Gravity Separation

Gravity separation involves processes where particles of mixed sizes, shapes and specific gravity are separated (Elder *et al.*, 2001). Centrifugal force is used and the particles settle differently depending of their densities. Particles with the highest density settle fast while those with less density follow.

The Wet Concentrator Plant (WCP) concentrates the Very Heavy Mineral (VHM) and rejects most of the non-valuable, lighter gangue minerals. It contains a number of gravity separation

steps, utilizing spiral concentrators. The Heavy Mineral Concentrate (HMC) content of mineral sand ores generally ranges between 3 and 20 percent. The corresponding heavy mineral recovery is generally between 85 and 95 percent at a concentrate grade of 90 percent Heavy Mineral (HM) (Elder *et al*., 2001). Water is reclaimed via a slimes thickener, and re-circulated to the process. Thickened slimes and sand tailings from the spiral plant are pumped to the residue storage areas. Fine material separated from the HM and quartz sand is mixed with flocculent to induce settling. The settled fine material is thickened, remixed with the quartz sand tails and pumped to the mining void and dried. The dried clay is then returned to the mining pit or mixed with topsoil material to enhance the rehabilitation process. Ti is contained in ilmenite, one of the main components of HM.

2.3.3 Froth Flotation

Froth flotation is a highly versatile method for physically separating particles based on differences in the ability of air bubbles to selectively adhere to specific mineral surfaces in a mineral /water slurry (Klimpel, 1995). The particles with attached air bubbles are then carried to the surface and removed, while the particles that remain completely wetted stay in the liquid phase. Froth flotation can be adapted to a broad range of mineral separations, as it is possible to use chemical treatments to selectively alter mineral surfaces so that they have the necessary properties for the separation.

Froth flotation is used to separate a large range of sulphides, carbonates and oxides (DeGennes, 2004) prior to further refinement. The ore is crushed to fine powder, mixed with water to form slurry. Surfactant or collector chemicals (Kawatra and Eisele, 1987) are added to make the

mineral hydrophilic. The slurry is then aerated in a water bath to form air bubbles as illustrated in the figure 2.1

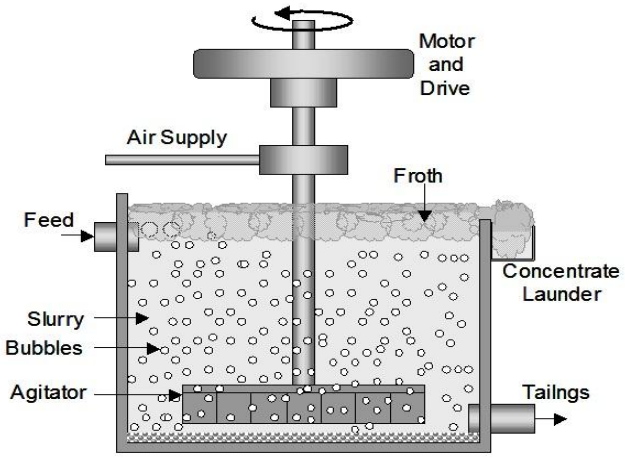

Figure 2.1: A flotation cell
Source: (Kawatra and Eisele, 1987)

Slurry is separated into two, a hydrophilic mineral and hydrophobic gangue. The air bubbles forms a stable froth with the mineral thus reducing its density hence making it possible for it to float and is skimmed off. Where the mineral does not contain Sulphur, a frothing agent is added. According to De Gennes (2004), where bubbles are larger than the ore particle and equal to or less than I millimeter in radius, the particle will rise into the froth layer. Those particles bigger than the air bubble will also rise into the froth but buoyed under similar conditions as those of the fine particles, as shown in figure 2.2 (Kawatra and Eisele, 1987)

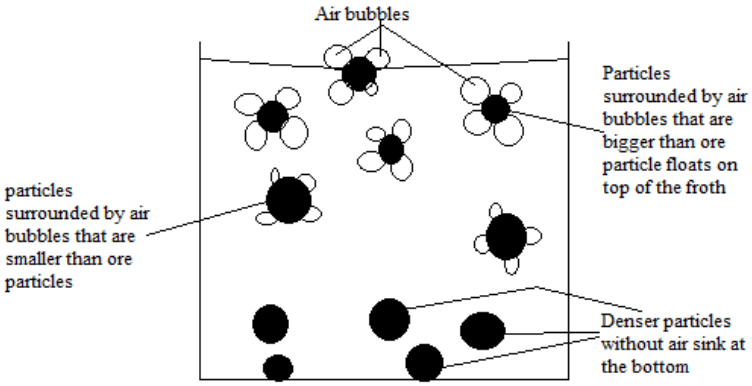

Figure 2.2: Air bubbles of different sizes attached to mineral particles.
Source: (Kawatra and Eisele, 1987)

Froth flotation includes many interrelated components, and changes in one area will reduce compensating effects in other areas. Froth flotation is a good example of an engineering "system", in that the various important parameters are highly inter-related, as shown in figure 2.3.

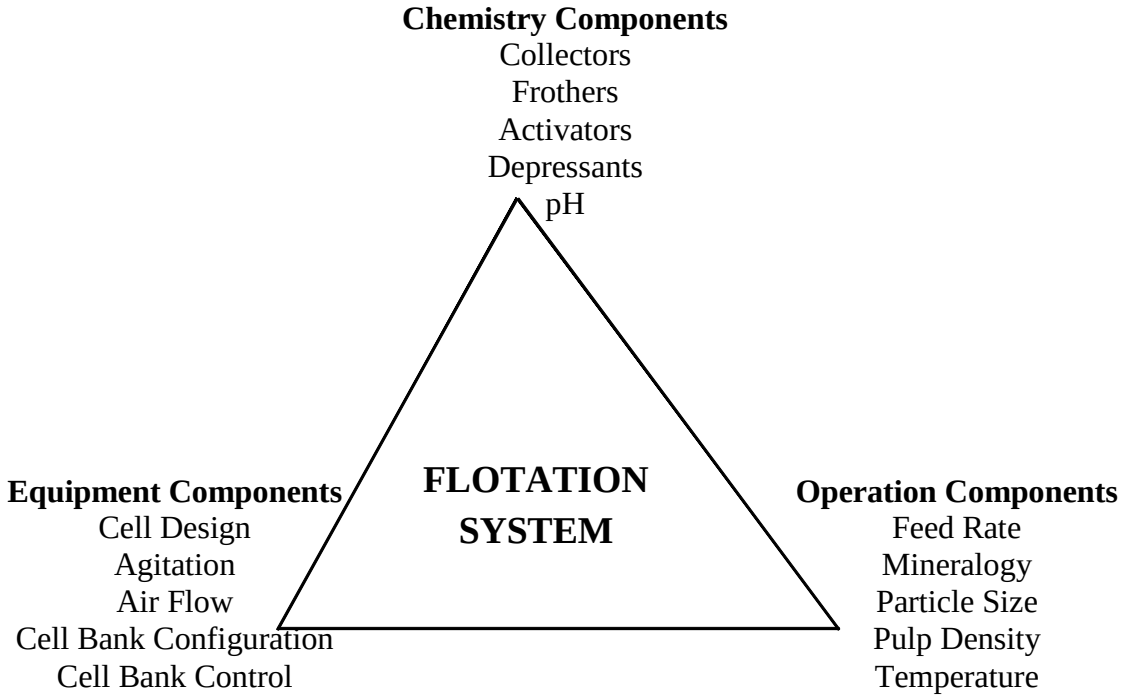

Figure 2.3: The flotation system with all interrelated components

Source: (Klimpel, 1995)

Froth flotation operations take into consideration all these factors. Changes in the settings of one factor (such as feed rate) will automatically cause or demand changes in other parts of the system (such as flotation rate, particle size recovery, air flow, pulp density, etc.) As a result, it is difficult to study the effects of any single factor in isolation, and compensation effects within the system can keep process changes from producing the expected results (Klimpel, 1995). This makes it difficult to develop predictive models for froth flotation, although work is being done to develop simple models that can predict the performance of the circuit from easily-

measurable parameters such as solids recovery and tailings (materials left after magnetic separation) solid content (Rao *et al*., 1995).

Properties of some raw mineral mixtures suspended in plain water are unsuitable for froth flotation thus chemicals are needed both to control the relative hydrophobicities of the particles, and to maintain the proper froth characteristics (Kawatra and Eisele, 1987). Chemicals used are called collectors. Collectors help to selectively adsorb particles onto the surfaces forming a layer on the particle surface that essentially makes a thin film of non-polar hydrophobic hydrocarbons. Collectors increase the contact angle so that air bubbles will adhere to the surface as shown in the figure 2.4.

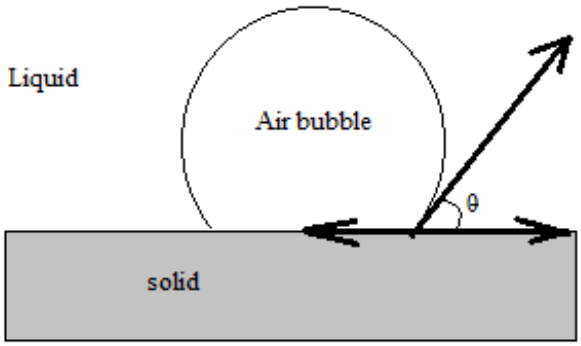

Figure 2.4: Contact angle between air bubble and a solid surface immersed in liquid
Source: (Kawatra and Eisele, 1987)

Selection of the correct collector is critical for an effective separation by froth flotation (Kawatra and Eisele, 1987). Collectors can be classified depending on their ionic charge for they can be nonionic, anionic, or cationic as shown in the figure 2.5.

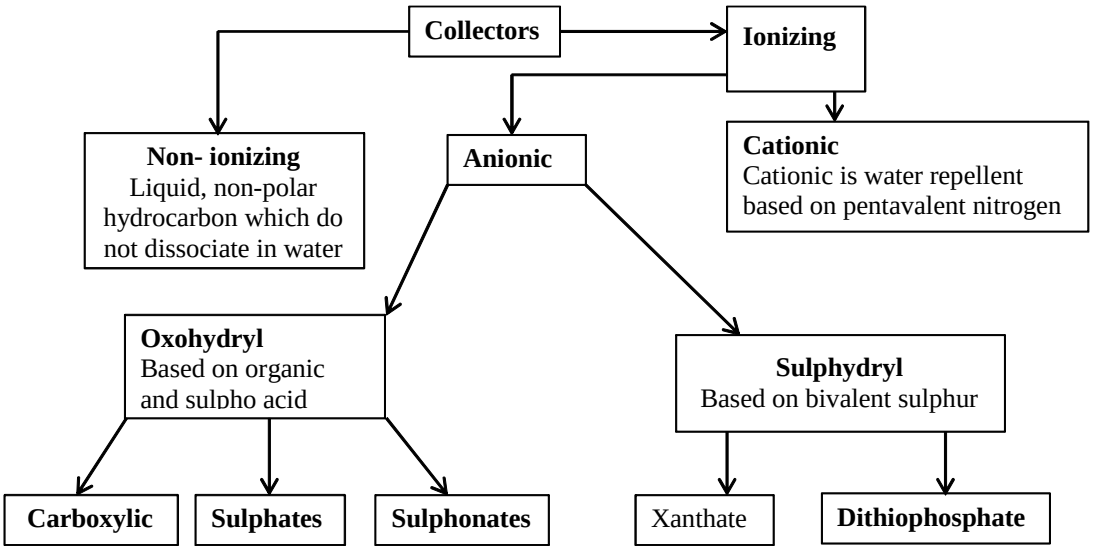

Figure 2.5: Various types of collectors
Source: (Eisele and Kawatra, 1992)

The nonionic collectors are simple hydrocarbon oils, while the anionic and cationic collectors consist of a polar part that selectively attaches to the mineral surfaces, and a non-polar part that consist of a polar part that selectively attaches to the mineral surfaces, and a non-polar part that projects out into the solution and makes the surface hydrophobic. Collectors can either chemically bond to the mineral surface (chemisorption), or be held on the surface by physical forces (physical adsorption).

2.3.3.1 Anionic Collectors

Anionic collectors are weak acids or acid salts that ionize in water, producing a collector that has a negatively-charged end that will attach to the mineral surfaces, and a hydrocarbon chain that extends out into the liquid, as shown in figure 2.6 (Kawatra and Eisele, 1987).

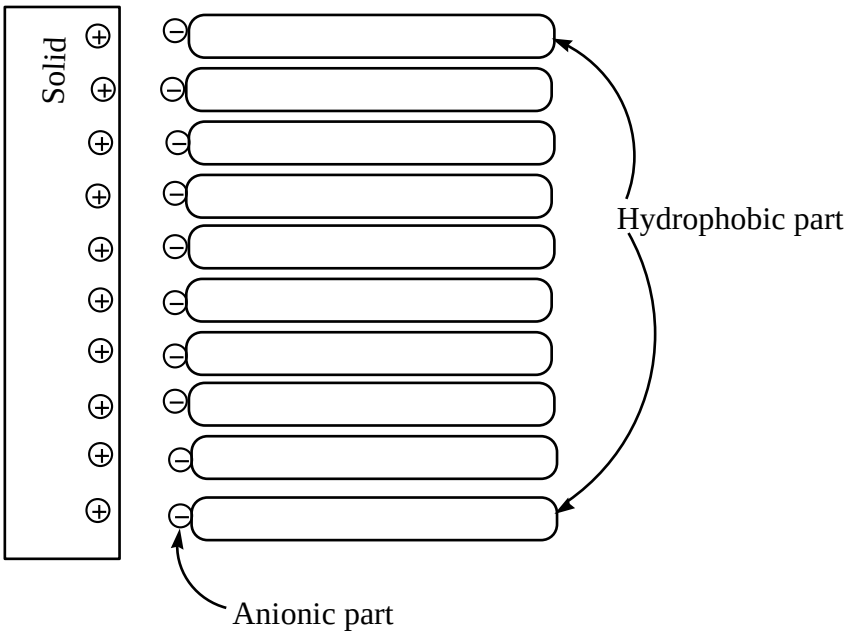

Figure 2.6: Adsorption of anionic collector onto the surface
Source: (Eisele and Kawatra, 1992)

The anionic portion is responsible for the attachment of the collector molecule to the surface, while the hydrophobic part alters the surface hydrophobicity. Collectors for sulfide minerals are the sulfhydryl collectors, such as the various Xanthates and dithiophosphates, Xanthates are most commonly. They are highly selective collectors for sulfide minerals, as they chemically react with the sulfide surfaces and do not have any affinity for the common non-sulfide gangue minerals. Other highly-selective collectors for use with sulfide minerals, such as dithiophosphates, have somewhat different adsorption behavior and so can be used for some separations that are difficult using Xanthates (Eisele and Kawatra, 1992).

Minerals with oxides, for example, titanium dioxide attach to the surface by electrostatic attraction rather than by chemically bonding to the surface (Kawatra and Eisele, 2001). A typical anionic collector for oxide mineral flotation is polystyrene and poly(t-butyl acrylate) shells (Meghann *et al.*, 2008). The anionic group responsible for attaching it to the mineral

surface is poly (t-butyl acrylate) PTBA and polystyrene. PTBA functionalization of TiO_2 allow for the easy hydrolysis with trifluoroacetic acid to generate a polyacrylic acid shell structure, which is now dispersible in alcohols such as methanol and other polar solvents (e.g. water). Incorporated polystyrene and PTBA functionalized TiO_2 into organic electronic devices, demonstrating their potential as new materials.

Particles that are immersed in water develop a net charge due to exchanging ions with the liquid (Kawatra and Eisele, 2001). Chemistry of the solution is changed so that one mineral has a strong positive charge while other minerals have a charge that is either only weakly positive, or negative. Anionic collector therefore will preferentially adsorb onto the surface with the strongest positive charge and render them hydrophobic. Figure 2.7 shows an example on how oleic acid interacts with ilmenite.

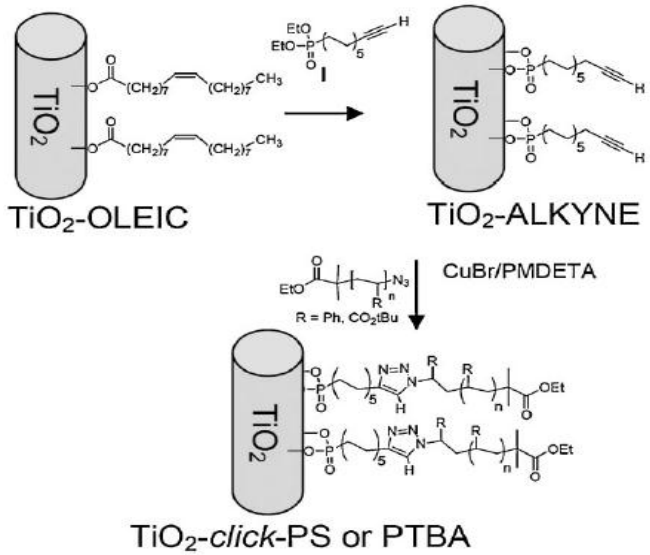

Figure 2.7: Functionalization of TiO_2-Oleic with Dodec-11-ynyl Phosphonic Acid Diethyl Ester
Source: (Eisele and Kawatra, 1992)

The anionic portion is responsible for the attachment of the collector molecule to the mineral surface, while the hydrophobic part alters the surface (Eisele and Kawatra, 1992). Examples of anionic collectors are sodium oleate and fatty acids which occur in vegetable oils, and are found with polar groups such as $RCOO^-$, $ROSO_3^-$, RSO_3^-, $ROCS_2^-$ and $R_2O_2PS_2^-$. They are strong collectors with low selectivity for hematite and other metal oxide minerals (Eisele and Kawatra, 1992). Other chemical reagents used as frothers are methylisobutylcarbinol (MIBC), pine oil and cresylic acid (Klimpel, 1995). Froth flotation works well with minerals that contain sulphur in their structure. Geological surveys shows that titanium bearing minerals are not sulphur based (DuBois and Walsh, 1970; Keru, 2011; Mutembei *et al*., 2014; Njoroge *et al*., 2014). This calls for adaptation of the method to necessitate its use.

2.3.3.2 Cationic Collectors

Cationic collectors use a positively-charged amine group to attach to mineral surfaces (Kawatra and Eisele, 2001). Since the amine group has a positive charge, it can attach to negatively-charged mineral surfaces. Cationic collectors therefore have essentially the opposite effect from anionic collectors, which attach to positively-charged surfaces. Cationic collectors are mainly used for flotation of silicates and certain rare-metal oxides, and for separation of potassium chloride (sylvite) from sodium chloride (halite). Examples of cationic collectors are RNH_3^+, $R_2NH_2^+$ and R_3NH^+ where R is an alkyl group. Frothers are compounds that act to stabilize air bubbles so that they will remain well-dispersed in the slurry (Klimpel, 1995). Frothers form a stable froth layer that can be removed before the bubbles burst. Examples of frothers are alcohols, particularly MIBC (Methyl Isobutyl Carbinol, or 4- methyl-2-pentanol, a branched-chain aliphatic alcohol) or any of a number of water-soluble polymers based on

propylene oxide (PO) such as polypropylene glycols. Polypropylene glycols are very versatile and can give a wide range of froth properties (Tyurnikova and Naumov, 1981).

2.4 Methods of Analysis

Atomic Absorption Spectroscopy (AAS), Atomic Emission Spectroscopy (AES) and X-ray Diffraction Spectroscopy (XRD) are the main methods in the analysis of laterites samples.

2.4.1 X- Ray Diffraction (XRD) Spectroscopy

XRD uses X-rays of a known wavelength that are passed through a sample for identification of the crystal structure. X-rays interact with electrons in the material and are scattered giving diffraction pattern. The position of diffraction peaks by lattice of the crystal, give a unique pattern at different angles and of different intensity. The wave nature of the X-rays diffracted by the lattice of the crystal, gives a unique pattern of the peaks at different angles and of different intensity. This condition is given by Bragg equation 2.4.

$n\lambda = 2d\sin\Theta$…….. 2.4

Where λ is the x-ray wavelength, Θ is the angle between the x-ray beam and these atomic planes and n corresponds to the order of diffraction. The condition for maximum intensity contained in Bragg's equation 2.4 allows us to calculate details about the crystal structure, or if the crystal structure is known, to determine the wavelength of the x-rays incident upon the crystal as in figure 2.8.

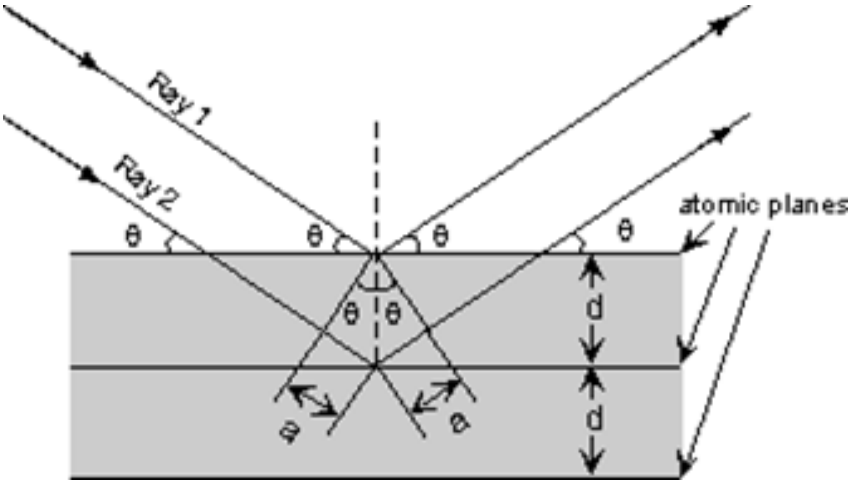

Figure 2.8: Bragg's Law Reflection

Analysis of the diffraction pattern give information on the arrangement of atoms in a given atomic plane: the shape and size of the unit cell is obtained directly from diffraction peak positions while the positions of atoms within the unit cell are related to the relative heights of the diffraction peaks (Myers, 2002). X-rays are useful in determining lattice structures because their wavelengths are on the order of 1 angstrom, the same order of magnitude as the interatomic distances in condensed matter.

A high voltage is applied across electrodes causing electrons to be propelled towards a metal target constituting the anode. Electrons bombarding the metal cause the emission of x-rays with a wavelength characteristic of the metal (Jones and Childers, 2003). Copper is very commonly used metal. X-rays with a wavelength of 1.54 Å are emitted from copper. The x-rays are passed through a slit that collimates the x-rays before they reach the sample chamber. Upon hitting the sample the x-rays are diffracted in all directions. A diffraction pattern is the fingerprint of a mineral or other sample. It records the x-ray intensity at various 2 theta angles. By dividing the angle from the strip readout by two and applying Bragg's equation, we can now calculate the distance between the atoms in the crystal. Smaller diffraction angle show

that the distance between atoms is larger. By use of a handbook of mineral diffraction patterns, the sample can be identified.

2.4.2 Atomic Absorption Spectroscopy

Atomic absorption spectroscopy (AAS) is used for analysis of group two and higher groups elements mainly from solution or solubilized (Muthengia, 2009). The sample solution is nebulized into drops (atomized). It is then fed into a flame. The atoms absorb radiation of specific wavelength. This absorption is measured and interpreted. Atomic absorption exploits different radiation wavelengths absorbed by different atoms. The instrument is most reliable when a simple line relates absorption-concentration. Atomizer/flame and monochromator instruments are crucial in making the AA device work. The technique requires standards with known analytical content to establish the relation between the absorbance and the analytical concentration and relies therefore on Beer-Lambert's law shown in equation 2.5 (Mendham *et al.*, 2000).

$$A = \log_{10}\left(\frac{I_o}{I}\right) = \in .c.L \quad \text{.....} \quad 2.5$$

Where A – Absorbance, I_o – incident radiation at a given wavelength, I – transmitted intensity or attenuated radiations, L – the path length through the sample (cm), c – concentration of the absorbing species ($moldm^{-3}$), $\in$ - molar absorptivity or extinction coefficient ($Lmol^{-1}cm^{-1}$)

Extinction coefficient is a constant which is important molecular property in a given solvent, at a particular temperature and pressure. The method is largely free from spectral and radiation interferences. This is as a result of differences in absorption wavelength. For an unexcited atom, each electron is in ground state, otherwise it is excited.

CHAPTER THREE

MATERIALS AND METHODS

3.1 Sampling Sites and Sampling Design

Sampling of laterites was done randomly from selected sites within Mbeu in Meru County, Kaharate in Murang'a County and Tharaka Nithi County that include Gitongo and Gitara Kianderi. More detailed description in appendix II. Sampling was done on already drilled shallow wells, quarries and walls of seasonal river beds. Within sampling site, three samples were collected at several depths, from the earth surface, of 30 cm, 50 cm and 100 cm below the ground. One kilogram of the laterite samples was packed in a plastic bag labeled A to denote 30 cm, B for 50 cm and C for 100 cm.

3.2 Cleaning of Pulverizer, Glassware and Plastic Containers

The Pulverizer (5E-PCM1x100) was washed using distilled water after each sample was pulverized then dried using gas pump. All glassware used was cleaned by soaking in 1:1 nitric acid solution in water overnight, then cleaned using detergent, rinsed with distilled water and then dried in the oven at 105 ^{o}C. Plastic containers were washed with 1:1 nitric acid, appropriate detergent and rinsed three times with distilled water. They were then dried in an oven at 55 ^{o}C.

3.3 Sample Treatment

150 grams of laterites samples, 100 grams of rice husks and 100 grams of *lantana camara* were dried in an oven at 105 ^{o}C for eight and a half hours, time taken using a stop watch. The three samples were then removed and placed in a desiccator for two hours to cool. They were then ground to 300 microns using a Pulverizer (5E-PCM1x100 Pulverizer).

3.4 Optimization of Biomass to Laterite Sample Ratio

The ground laterites were mixed separately with ground rice husks and *lantana camara* were separately mixed with ground charcoal and raw biomass at ratios of 1:1 to 1:10 in increments of one in clay crucibles. The crucibles were carefully placed on open jiko and pieces of wood as a source of heat. The mixture was then heated in covered ceramic crucibles for 3 hours as shown in plate 3.1. The temperature of the mixture was recorded using a thermocouple (GTH 1160 DIGITALTHERMOMETER NiCr-Ni). The heated sample was then cooled to room temperature in a desiccator.

Plate 3.1: A Charcoal Burner with Samples Heated

The cooled heat treated sample was put into a magnetic separator, plate 3.2. Magnetic portion of the sample was automatically separated from the non-magnetic sample. Both magnetic and non-magnetic samples were packed separately for further analysis.

Plate 3.2: Laboratory Magnetic Separator

Percentage yield of titanium dioxide was calculated using the formula 3.1 and results summarized as shown in the appendix XIX.

$$\%\text{ of titanium dioxide yielded} = \frac{\begin{matrix}\text{Mass of Titanium dioxide}\\ \text{after concentration}\end{matrix}}{\begin{matrix}\text{Mass of Titanium dioxide}\\ \text{before concentration}\end{matrix}} \times 100 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.1$$

The mineralogical compositions were determined using X-ray diffraction (XRD) and an elemental composition for the concentrated samples was determined using atomic absorption spectroscopy (AAS) using the procedure described previously.

3.5 Froth Flotation

500.0 g of ground laterite were weighed and put in a 1000 mL beaker. 500.0 mL distilled water were added to make 1:1 slurry. The mixture was put in a flotation cell shown in plate 3.3 and agitated for 5.0 minutes to make the slurry. 5.0 mL of conditioning reagent was added. The mixture was agitated for 5.0 minutes after adding conditioning reagent. More water was added

to the mixture to make slurry with 30% solid. The pH of slurry was adjusted to between 8 and 9 using sodium hydroxide and 1:1 hydrochloric acid solutions. 30.0 mL of oleic acid was added and the mixture agitated for 10.0 minutes. 3.0 mL of cresylic acid was added and mixture agitated for 3.0 minutes. Air was bubbled through and froth collected in plastic containers. Flotation was done for 10.0 minutes. The results of the chemical analysis on laterites samples using AAS (Behera and Mohanty, 1986) are given in table 4.4.

Plate 3.3: Laboratory Floatation Equipment

3.6 Chemical Analysis

3.6.1 XRD Analysis

10.00 g of the ground sample were put in six sample cell holders. The sample holders were tapped carefully to ensure the particles are parked to avoid displacement which affects peak shifts. They were then loaded for analysis of minerals using data collector software. The results of the analysis of minerals present in each sample were given using a Bruker D2 phaser defractometer for analysis. Data is represented in a collection of single-phase X-ray powder

diffraction patterns for the three most intense D values in the form of tables of interplanar spacings (D), relative intensities (I/I_o), and mineral name (John, 1989b).

3.6.2 Loss on Ignition (LOI)

1.000 g of the ground sample of treated or raw was weighed in a crucible boat using analytical balance Model Mettler AJ150. The sample was heated at 1000 ^oC to a constant weight using muffle furnace. The LOI was determined using equation 3.2 (Heiri *et al*., 2001).

$$\frac{\text{Original weight of the sample} - \text{Final weight of the sample}}{\text{Original weight of the sample}} \times 100 \quad \text{..... 3.2}$$

.

3.6.3 Atomic Absorption Spectrometry

0.100g of the ground sample was weighed in 125 mL plastic beaker. 1 mL of concentrated aqua-regia (mixture of concentrated HCl and HNO_3 in the ratio 3:1) was added followed by 3.0 mL of hydrofluoric acid. The samples were left to digest for 8 hours. 50.0 mL of concentrated boric acid was added in each container and left to digest for one and a half hours. Distilled water was added to make the total volume of 100.0 mL. Syenite (SY-3) and Mount Royal Gabbro (MRG) rock standards were also digested following the same procedure used to digest the samples. Dilutions of the sample solutions were made by transferring 5.0 mL into 100 mL labeled volumetric flask and making up to the mark using distilled water (Abbey and Gladney, 2005). The samples were analyzed using AAS instrument in the usual procedure (SpectrAA.10 model from SEANAC Company) (Mitchell, 1984).

3.7 Data Analysis

The raw data obtained in AAS was analyzed in triplicate and arithmetic mean obtained using the equation 3.3 shown below

$$\bar{x} = \sum_i \frac{x_i}{n} \quad \text{..... 3.3}$$

Where:

$\bar{x}$ - Arithmetic mean of the samples,

x_i - Sample measurements and

n - Population.

Comparison of experimental means of the methods of analysis using AAS was done using significance (t - test) and ANOVA (Harvey, 2000; Miller and Miller, 1988). Standard deviation of the means was calculated using equation 3.4 shown below (Miller and Miller, 1988).

$$s = \sqrt{\sum_i (x_i - \bar{x})^2 / (n-1)} \quad \text{.....3.4}$$

t – Calculated was given by equation 3.5

$$t_{cal} = \left(\bar{x}_1 - \bar{x}_2 \right) \Big/ \sqrt{\left(s_1^2 / n_1 + s_2^2 / n_2 \right)} \quad \text{.....3.5}$$

Bar graphs were used accordingly where necessary.

CHAPTER FOUR

RESULTS AND DISCUSSION

INTRODUCTION

This chapter involves discussion for results for mineralogical and chemical composition for raw and thermally reduced laterites samples using XRD defractometer and AAS respectively, in addition, determination of loss on ignition and percentage yield of titanium dioxide after thermal reduction is also discussed in details. Optimization process of biomass to laterites ratio used for thermal reduction of laterites samples is discussed in details. A statistical data analysis of beneficiation using biomass with other methods that are used to upgrade levels of titanium dioxide, is also focused on in this chapter.

4.1 Mineral Composition of Raw and Heat- Magnetic Treated Samples

Laterites samples were analyzed to determine chemical and mineralogical components. A total of one hundred and seventeen samples were analyzed for chemical analysis and three for mineralogical components. The analyzed data are in form of deffractogram, tables, and bar graphs where appropriate. Comparative statistical data analysis was used where appropriate to test for significance difference.

Table 4.1 shows the mineralogical components of raw and thermally reduced laterites samples from Mbeu in Meru, Kaharate in Murang'a and Gitong'o quarry in Tharaka Nithi County.

Table 4.1: Mineralogical Composition of Raw and Thermally Reduced Laterites Samples from Mbeu, Kaharate and Gitong'o

Area of the Sample	Mineralogical content in raw sample(2θ)	Mineralogical content in Heat-treated sample
Mbeu	Ilmenite, $FeO.TiO_2$ (33.12 ^{o}), Magnetite,Fe_3O_4 (36 ^{o})	Maghemite (γ-Fe_2O_3.TiO_2)(35.6^o)
Kaharate	Goethite ,(FeO) OH) (21.51 ^{o}), ilmenite, $FeO.TiO_2$ (33.12 ^{o}), Magnetite(36 ^{o}), Hematite,Fe_2O_3(54.11^o)	Maghemite, (γ-Fe_2O_3.TiO_2)(35.6^o)
Gitong'o	Goethite(21.51 ^{o}), Ilmenite, $FeO.TiO_2$(33.12^o), Haematite, Fe_2O_3 (33.51^o, 54.11^o), Brammallite,$(Na,H_2O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2,(H_2O)]$(21.51^o)	Manganoneptunite, $KNa_2Li(Mn,Fe^{2+})_2Ti_2Si_8O_{24}$,(63.5^o) Lindsleyite $(Ba,Sr)(Ti,Cr,Fe,Mg)_{21}O_{38}$(58^o), Maghemite, ($\gamma$-$Fe_2O_3$.$TiO_2$) (35.6^o)

XRD Deffractogram obtained from raw laterites samples from Mbeu clearly show the ore is mainly magnetite, quartz and traces of ilmenite (Appendix III). Research concluded recently (Abuga *et al*., 2013) showed that Mbeu area experienced vulcanization process. Magnetite has a very high magnetic susceptibility. Natural processes have been known to convert low-magnetic susceptible iron bearing minerals to more magnetically susceptible minerals. Internal processes that generate heat within the earth crust can also improves magnetic susceptibility of minerals in ores (Sparks and Huppert, 1988). The origin of magnetic susceptibility of soils of volcanic rocks origin in southern Brazil observed that hematite, goethite had been converted to the highly magnetic susceptible maghemite though vulcanization process (Traina *et al*., 1999). This was a reason for the occurrence of the magnetically susceptible minerals in Mbeu since the area is of volcanic origin**.**

On thermal reduction of the raw laterites samples from Mbeu with *lantana camara* at temperature range of 500-800 ^{o}C, the ilmenite and magnetite in laterites samples were converted into maghemite, a highly magnetic susceptible material equivalent to that of

magnetite. On further heating the beneficiated laterites sample to 1000 ^{o}C followed by magnetic separation, the tailing (substance left after magnetic separation) showed a sharp peak of rutile. A clear indication that maghemite contains Ti in its structure. Magnetite contains less percentage of titanium dioxide in its structure compared to maghemite.

XRD deffractogram for raw laterites from Kaharate (Appendix VI) showed the presence of goethite, ilmenite, magnetite and hematite. Magnetic susceptibility of goethite and hematite is very low but that of magnetite is very high. Due to the presence of magnetite, the raw laterites samples were attracted by a magnet before thermal reduction was carried out. Njoroge (2014) reported similar results for raw laterites collected from the vicinity of Kaharate. The sample collected by the researcher contained quartz, goethite, nacrite, hematite and rutile. Due to the presence of large amount of non-magnetic materials in the raw laterites sample were not attracted by a magnet.

XRD deffractogram (Appendix VII) show Thermal reduced laterites samples using *lantana camara* as raw biomass and temperature of 500 to 800 ^{o}C, goethite, hematite and ilmenite were converted to maghemite. Maghemite formation requires very high temperatures. A higher ratio of biomass to laterite sample ratio, that is, 1:10 provided adequate reducing agents that elevated heat to more than 700 ^{o}C to enhance reduction process. Njoroge (2014), while using laterites samples from other sites of Murang'a County used charcoal as a source or reducing agents. The researcher used temperatures of 500 to 700 ^{o}C and biomass to laterites sample ratio of 1:20. Using these parameters, goethite, hematite and ilmenite can only be converted into magnetite. Magnetite contains less percentage of titanium dioxide compared to maghemite. For this reason, the percentage improvement of titanium dioxide was lower.

XRD deffractogram (Appendix VIII) showed that raw laterites in Gitong'o quarry A contain mainly Goethite (FeO(OH), Quartz (overall formula SiO_2), Ilmenite an Iron-Titanium Oxides ($FeTiO_3$), traces of Maghemite (γ-Fe_2O_3) and Haematite (Fe_2O_3) (John, 1989a). The raw ores were therefore not attracted by the magnet since these contain a higher mass of non-magnetic materials. For them to be separated at this stage, a high density magnetic separation is required, which is very expensive if used to concentrate the sample. Mutembei (2014), while working on Tunyai division in the Tharaka Nithi County, observed that raw laterites samples contained traces of magnetite, goethite, Brammallite, magnetite, hematite, shirokshinite, and ilmenite. Goethite, hematite and ilmenite are iron ores that has very low magnetic susceptibility.

Thermal treatment of the raw laterite samples from Gitong'o quarry A (Appendix IX) with *lantana camara* at 500 to 800 ^{o}C, the mineral were converted to a higher magnetic susceptible maghemite. The portion attracted by a strong magnet, contained a high amount of Ti than the raw samples. Mutembei (2014), while using biomass to laterites ratio of 1:10 at lowered temperature of 500 to 700 ^{o}C, converted goethite, hematite and ilmenite to magnetite. The parameters favour the conversion of goethite, hematite and ilmenite into magnetite.

Magnetic nature of the product formed in Gitong'o quarry A can be explained using equations 4.1 and 4.2. Equation 4.1 shows the pre-oxidation of ilmenite and equation 4.2 show thermally reduced of iron-rich titanium ores using a hydrogen, carbon monoxide and traces of methane as reducing agents.

$$2FeTi_2O_{5(s)} + \frac{1}{2}O_{2(g)} \xrightarrow{\text{Below } 800\,^{\circ}C} Fe_2TiO_{5(g)} + 3TiO_{2(s)} \quad \text{.....4.1}$$

$$6Fe_2TiO_{5(s)} + 6TiO_{2(s)} + \frac{1}{2}CH_{4(g)}(CO, H_2) \rightarrow 4Fe_3Ti_3O_{10} + \frac{1}{2}CO_2 + 2H_2O_{(g)} \quad \text{.....4.2}$$

A sharp peak of rutile that was observed (Appendix V) when thermally reduced laterites sample from Mbeu was subjected to further heating to 1000 ^{o}C. The iron-rich titanium ores at a temperature range between 860 to 1,100 ^{o}C decompose to iron and titanium oxide as shown in the equation 4.3 to 4.5 (Cheng *et al.*, 1997; Lobo *et al*., 2013).

$$4Fe_2Ti_3O_{9(s)} \xrightarrow{\text{above } 800\,^{\circ}C} Fe_2TiO_{5(g)} + 2TiO_{2(s)} \quad \text{.....4.3}$$

$$Fe_2TiO_{5(s)} + TiO_2 + CO(H_2, CH_4)_{(g)} \longrightarrow 2FeTiO_3 + CO_{2(g)}(H_2O) \quad \text{.....4.4}$$

$$FeTiO_{3(s)} + CO_{(g)}(H_2, CH_4) \longrightarrow Fe_{(s)} + TiO_2 + 2CO_{2(g)}(H_2O) \quad \text{.....4.5}$$

XRD deffractogram (Appendix VIII) of the thermally reduced laterites samples from Gitong'o quarry A contained other minerals that were attracted by a magnet. In addition to Maghemite, the deffractogram showed that some of iron-rich titanium ores were converted into Lindsleyite and Manganoneptunite. Lindsleyite (Ba,Sr)($Ti_{12}Cr_4Fe_2ZrMg_2$)O_{38}) is one of Ti ore. It contains barium in high amount compared to other elements present (Haggerty, 1983). It is a stable compound of titanium at temperatures below 1300 ^{o}C. According to the researchers (Foley *et al.*, 1994), Lindsleyite contains iron as Fe^{3+}. The presence of Fe^{3+} in the structure makes it attracted by magnet. Manganoneptunite on the other hand is a form of neptunite $KNa_2Li(Mn^{2+},Fe^{2+})_2Ti_2[Si_8O_{24}]$ containing manganese. Manganese has a higher magnetic

susceptibility; also in its structure it contains iron in its lower oxidation state of +2, thus lower magnetic susceptibility. Therefore, the presence of manganese in form of manganese +2 explains why the mineral is attracted by a magnet (Sakamoto *et al*., 2012). Magnetic susceptibility for various manganese compounds have been determined (Fuller *et al*., 1996). Lindsleyite and manganoneptunite, though in small amounts, were attracted by a magnet (Vinogradov, 1959). Data is represented in a collection of single-phase X-ray powder diffraction patterns for the three most intense D values in the form of tables of interplanar spacings (D), relative intensities (I/I_o), and mineral name.

4.2 Optimization of Raw Biomass to Ore Ratio for Ti Concentration

The levels of titanium dioxide in Gitong'o quarry A and Gitong'o quarry B were used to determine the optimal amount of the raw biomass that is required to yield best results of titanium dioxide. The results of optimization are shown in the table 4.2. The results are also represented using bar graphs (Appendix XIV).

Table 4.2: Percentage of TiO_2 in Thermally reduced Laterites at 500 -800 ^oC using different Laterite to biomass Followed by Magnetic Separation

Ratio of biomass to sample	Gitong'o A	Gitong'o B
Raw	1.77±0.08	1.61±0.07
1:1	5.60±0.14	5.49±0.06
1:2	5.65±0.11	5.75±0.09
1:3	5.96±0.09	5.75±0.10
1:4	5.73±0.06	6.15±0.06
1:5	6.17±0.12	6.30±0.04
1:6	6.40±0.08	6.92±0.07
1:7	7.61±0.06	7.10±0.06
1:8	7.87±0.12	7.65±0.14
1:9	7.89±0.07	7.72±0.10
1:10	7.99±0.06	7.69±0.12

Biomass, *lantana camara*, is regarded as a weed whereas rice husks are burnt in open into ashes however this project used them as a source of energy to thermally reduce iron-rich titanium ores in laterites into maghemite. In commercial settings, it is important to determine the optimum ratio of *lantana camara* and rice husks that is required for beneficiation process. Results obtained (Table 4.2) was compared statistically to determine the optimum ratio for beneficiation process using raw *lantana camara* as shown in table 4.3.

Table 4.3: Statistical comparison of the various *lantana camara* to laterite ratios

Ratio of biomass to sample	Gitongo A	Gitongo B
1:1	5.60 ± 0.02^{a}	5.49 ± 0.25^{a}
1:2	5.65 ± 0.03^{a}	5.75 ± 0.41^{a}
1:3	5.96 ± 0.10^{b}	5.75 ± 0.40^{a}
1:4	5.73 ± 0.07^{a}	6.15 ± 0.34^{ab}
1:5	6.17 ± 0.13^{c}	6.30 ± 0.25^{ab}
1:6	6.40 ± 0.20^{d}	6.92 ± 0.27^{bc}
1:7	7.61 ± 0.03^{ef}	7.10 ± 0.17^{bc}
1:8	7.87 ± 0.07^{ef}	7.65 ± 0.25^{c}
1:9	7.79 ± 0.09^{ef}	7.72 ± 0.21^{c}
1:10	7.99 ± 0.07^{f}	7.69 ± 0.20^{c}
p-value	<0.001	<0.001

Mean values followed by the same small letters within the same column don't differ significantly (SNK-test, one way ANOVA, 95% CL).

Results from statistical comparison of various ratios showed significantly higher levels of titanium dioxide in ratios of 1:7 up to 1:10. Since the ratio 1:10 contain the lowest amount of *lantana camara*, it gave significantly high levels of titanium dioxide in the material collected by a magnet. This ratio was found to be adequate to beneficiate titanium in iron-rich titanium ores in laterites into maghemite. This implies that the biomass was converted to syngas, a combination of hydrogen, methane and carbon monoxide, which are used as reducing agents. The ratio of 1:10 was therefore used in all the samples in this project. The same ratio was used

when beneficiating the laterites sample with ground rice husks and charcoal. The laterites were also beneficiated using froth flotation.

Ciu *et al.* (2002), increased magnetic susceptibility of titanium ore using carbon, in the ratio of 1:10. The researchers were able to convert iron oxide in ilmenite to maghemite. In this way, Ti is separated using magnetic separation. This method is therefore viable for concentration of Ti in iron bearing ores. The researchers used charcoal from tree which is environmentally unviable. This will bring forth deforestation and thus desertification.

From table 4.3, it is clear that the level of Titanium improved from 1.7 to 8 percent which gives more than 57 percent percentage yield. The amount of titanium dioxide was higher than what was obtained by other researchers. Mutembei (2013) used magnetic separation, but his main focus was iron. He treated the sample using charcoal in the ratio 1:10 and reported improvement of titanium dioxide by between 2 to 3 percent, which gives a percentage yield of 10 to 15 percent. Mutembei observed that heating iron bearing ore, in mix with charcoal converts the mineral to magnetite. The magnetite is attracted by magnet and therefore magnetic separation can be used to concentrate the ore. The parameters used by Mutembei could not convert titanium bearing ores to a more magnetic susceptible material (maghemite) but can only favour conversion of iron bearing ores (haematite and goethite) to magnetite which contain less titanium dioxide.

Keru (2011) showed that when samples containing goethite and haematite are heated between 500 to 700 ^{0}C, at a ratio of 3:20 (approximately 1:7), charcoal to sample respectively, they were reduced to magnetite, $Fe_{2.46}MgO_{0.42}AlTi_{0.03}O_4$. This mineral is attracted by a magnet.

This mineral contains Titanium (Keru, 2011) and therefore, magnetic separation can be used to concentrate heat – treated laterite in a reducing atmosphere. With this ratio the researcher reported an increase in concentration of iron by 17.98 %.

From the results in Table 4.3, it is clear that a ratio of 1:7 to 1: 10 can be used for concentration of Ti in the Tharaka Nithi ore. The ratio would afford sufficient heat generating materials, as well as reducing agents from the burning raw biomass. This in essence could help in management of bio-waste as well as preventing deforestation for charcoal as the source of carbon for concentration of Ti in various ores.

4.3 Comparison of Various Methods of Concentrating Ti

The results for titanium dioxide percentages from froth flotation and magnetic separation using various biomasses after heating laterites sample ores-raw biomass mixtures is shown in figure 4.1.

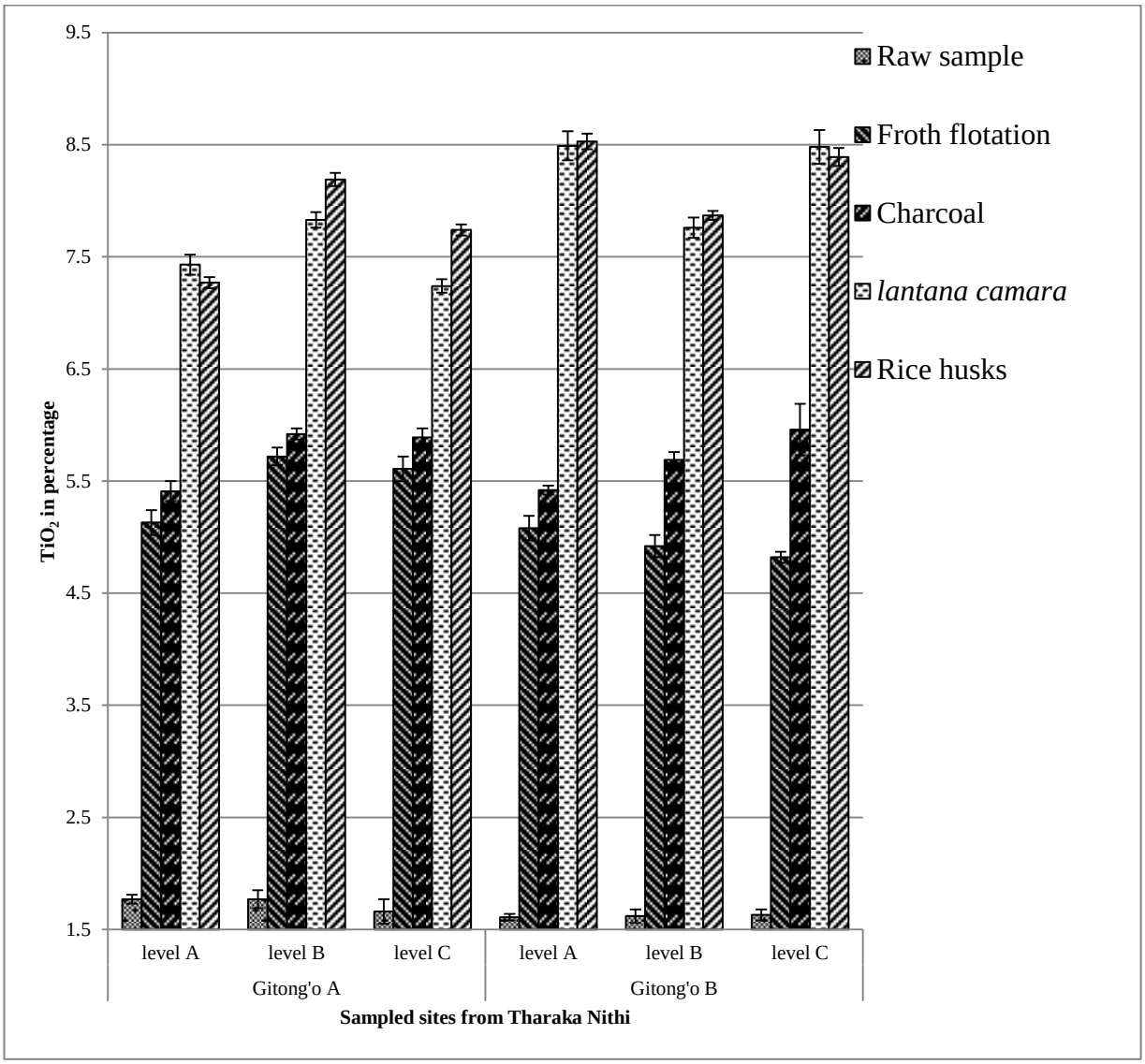

Figure 4.1: Comparison of Percentages of TiO_2 in Samples Upon Mixing with Various Biomass (*lantana camara* and rice husks) at w/w ratio (1:10), Heating at Temperatures of 500 – 800 ^oC followed by Magnetic Separation and Beneficiation by Froth Flotation

Comparison of percentages of TiO_2 in samples upon treatment of froth flotation and charcoal in the ratio of laterites sample to charcoal of 1:10, heating at temperatures of 500-800 ^oC, followed by magnetic separation analyzed by AAS. In Gitong'o level A, comparing concentration using charcoal and froth flotation (Appendix XV), the t_{cal}=3.41 which is greater than t_{crit} = 2.78 thus showing significance difference in the levels of titanium dioxide between charcoal and froth flotation ($p < 0.001, \alpha = 0.05$, one-way ANOVA). Therefore froth flotation

is not preferred over charcoal. Froth flotation works with sulphur or compounds with sulphur (sulphides). Sulphur in sulphides binds with air bubbles thus making it easy for the element/compound of interest to be suspended on water (Kawatra and Eisele, 2001)**.** This property makes it possible to separate mineral and the gangue (Rao, 2004). Ti ore, analyzed using XRD, in the laterites that were in form of oxides not sulphides. Charcoal gave better results than froth flotation as when it heated in controlled air supply; it was converted into carbon monoxide, a reducing agent that converted iron-rich titanium ores into maghemite that is attracted by a magnet.

Results of comparison between rice husks and *lantana camara* gave different amount of titanium dioxide, but of no significance difference. In Gitong'o quarry B, the t_{cal}=2.22 which is lower than t_{crit}=2.78 ($p < 0.001, \alpha = 0.05$, one-way ANOVA). This is because when heated at temperature of 500 – 800 ^{o}C, in controlled air, different raw biomass gave different amount of syngas composition (Mosiori, 2013; Goswami, 2014), but the overall amount of syngas does not vary appreciably and therefore the amount of reducing agent does not vary with the raw biomass. Mosiori (2013) studied various types of raw biomass in the Lake basin region. The researcher found out that although age of raw biomass is important in as far as syngas production is concerned, he found out that the major difference is in the conditions of heating the raw biomass. The major parameters in conditions include temperature and oxygen circulation. This is the reason why the two raw biomass types used in this study did not show much difference with the product formed. Therefore, owing to the above results, any raw biomass can be used in conversion of iron-titanium ores into maghemite a highly magnetic susceptible material, thus upgrading low grade titanium ores into levels of economic exploitation.

In Kenya, rice husks are locally available in large amounts. It is mainly burnt to ashes in the open field (Osawa and Muchunku, 2006). Burning of this raw biomass produces carbon dioxide which creates environmental pollution such as green-house effect and many air borne related effects. Similarly raw biomass is locally available in large quantities as bio-waste. Lantana camara is found in almost all regions in Kenya as weed. Municipal waste is enormous and contains large quantities of raw biomass as waste. This waste can be used effectively for concentrating Titanium minerals and in turn helps in municipal waste management. The concentrated Ti ore will be used to extract Ti.

4.4 Chemical Composition of Samples from the Various Levels before and after Heating with Biomass at Ratio 1:10 Followed by Magnetic Separation

Laterites samples collected from identified sites in Mbeu, Kaharate, Gitong'o quarry A, Gitong'o quarry B and Gitara Kianderi were concentrated using *lantana camara* to laterite ratio of 1:10 at temperatures of 500 – 800 ^{o}C. Table 4.4 gives for iron and Titanium, other elements present in the raw sample were Silicon (Si), Aluminium (Al), calcium (Ca), magnesium (Mg), sodium (Na), potassium(K) and manganese (Mn) (Appendices XV to XVII).

Table 4.4: Chemical Composition of Samples from Level A(30 cm), Level B(50 cm) and Level C (100 cm) after Heating with Biomass at Ratio 1:10 Followed by Magnetic

Sampled Sites	**%(**w/w**) OXIDE CONTENT (**Mean ± SD)					
	Level A		**Level B**		**Level C**	
	TiO_2	**Fe_2O_3**	**TiO_2**	**Fe_2O_3**	**TiO_2**	**Fe_2O_3**
M_1 Raw	**4.85±0.22**	67.19±0.03	**4.75±0.21**	69.63±0.31	**4.80± 0.14**	65.95±0.28
M_1 Conc.	**5.16±0.04**	80.07± 0.08	**4.94±0.19**	76.84±0.15	**5.04±0.09**	79.73±0.07
M_3 Raw	**3.04±0.21**	63.83±0.02	**2.96±0.14**	63.80±0.0	**3.0± 0.21**	63.82±0.06
M_3 Conc.	**4.96±0.05**	77.51± 0.05	**4.85±0.10**	68.80±0.05	**4.28±0.07**	83.09±0.11
M_4 Raw	**4.99±0.17**	53.82±0.20	**4.83±0.12**	52.96±0.05	**4.9± 0.09**	53.94±0.04
M4 Conc.	**5.65±0.09**	76.20± 0.06	**5.67±0.06**	75.15±0.06	**5.56±0.11**	78.83±0.11
M_7 Raw	**5.21±0.11**	60.15±0.22	**5.16±0.09**	57.76±0.11	**5.1± 0.33**	69.88±0.33
M_7 Conc.	**5.57±0.10**	79.30± 0.04	**5.69±0.10**	71.82±0.10	**5.36±0.08**	86.31±0.05
M_9 Raw	**5.66±0.31**	61.22±0.20	**5.62±0.08**	60.92±0.05	**4.60± 0.21**	61.60±0.06
M_9 Conc.	**6.53±0.18**	81.18± 0.04	**5.84±0.10**	68.37±0.05	**4.96±0.05**	75.18±0.07
M_{10} Raw	**4.29±0.09**	70.36±0.05	**4.31±0.21**	70.95±0.08	**3.30± 0.16**	69.54±0.12
M_{10} Conc.	**4.70±0.06**	90.78± 0.09	**4.93±0.12**	76.21±0.10	**4.24±0.08**	79.51±0.09
K_1 Raw	**7.66±0.02**	62.40±0.10	**7.62±0.16**	62.15±0.25	**7.60± 0.24**	62.45±0.05
K_1 Conc.	**7.74±0.10**	79.51± 0.09	**7.82±0.10**	69.19±0.07	**7.87±0.10**	68.87±0.10
K_2 Raw	**4.17±0.26**	62.87±0.25	**4.15±0.09**	62.76±0.17	**4.10± 0.11**	62.87±0.25
K_2 conc.	**5.82±0.06**	82.25± 0.07	**5.67±0.19**	73.21±0.05	**5.41±0.06**	71.44±0.09
K_3 Raw.	**4.50±0.26**	52.10±0.26	**4.50±0.11**	49.13±0.29	**4.50± 0.16**	39.27±0.05
K_3 Conc.	**4.93±0.05**	74.53± 0.04	**5.26±0.06**	68.29±0.10	**5.31±0.05**	73.36±0.07
K_4 Raw	**5.15±0.13**	50.33±0.14	**5.13±0.13**	49.29±0.13	**5.10± 0.02**	48.39±0.11
K_4 Conc.	**5.45±0.10**	78.18± 0.04	**5.85±0.11**	72.33±0.19	**5.69±0.05**	65.10±0.08
GA Raw	**1.77±0.09**	45.61±0.06	**1.77±0.15**	45.39±0.20	**1.6± 0.09**	45.69±0.14
GA Conc.	**7.43± 0.09**	75.28±0.12	**7.83±0.07**	73.55±0.07	**7.59±0.06**	80.67±0.05
GB Raw	**1.61± 0.12**	47.70± 0.14	**1.62±0.23**	47.69±0.04	**1.60± 0.18**	47.58±0.06
GB Conc.	**8.49± 0.13**	77.58±0.13	**7.76±0.09**	81.44±0.04	**8.48±0.15**	79.14±0.04
GK Raw	**1.60±0.09**	46.87±0.07	**1.59±0.15**	46.87±0.12	**1.60± 0.13**	46.81±0.19
GK Conc.	**4.43± 0.09**	82.20±0.12	**5.30±0.08**	86.44±0.11	**4.83±0.05**	79.44±0.09

Key: M-Mbeu, K-Kaharate, GA – Gitong'o quarry A, GK – Gitara Kianderi, Conc. Means thermally reduced ores followed by magnetic separation, Raw means untreated samples

Results from table 4.4 of chemical analysis showed high levels of TiO_2 in raw laterites samples collected from Meru, that is, Mbeu area which ranges between 3 percent to 5.66 percent, and also in Murang'a County (Kaharate) ranged from 4.2 to 7.66 percent. The levels of titanium dioxide from selected sites in the two counties were 5 % and hence can be used for commercial exploitation without concentrating them. Samples collected in Tharaka Nithi, that is, Gitong'o quarry A, Gitong'o quarry B and Gitara Kianderi ranged between 1.6 to 1.77 percent. These levels are less than 5 percent thus cannot be used for commercial exploitation at these concentrations. The percentage levels of titanium in Gitong'o A, Gitong'o B and Gitara Kianderi cannot be used for commercial exploitation. These levels need to be upgraded to 5 % so as to be used for commercial exploitation.

After concentration of titanium dioxide in all samples that were collected, the percentage improved from 4.8 to 5.8 in Mbeu, 5.3 to 7.8 in Kaharate and 1.6 to 8.5 in Gitong'o B. the percentage improvement of the titanium dioxide in Mbeu and Kaharate was about 2 %. Due to natural processes, such as volcanic process in Mbeu, had already converted the titanium ores into magnetite. For the samples collected in Tharaka Nithi, Gitong'o A and B, the levels of titanium dioxide improved from 1.6 percent to 8.5 percent.

Results from table 4.4 showed that titanium dioxide in raw laterite samples within all sampling sites in Mbeu, Kaharate, Gitong'o and Gitara Kianderi. Generally the results of the percentage TiO_2in levels A, B and C are not significantly different ($t_{cal} < t_{crit} = 2.78$) (Appendix XX) except for a few cases. The sites with exceptions included Kaharate 2 and 3, Mbeu 1, 9 and 10 where percentage of titanium dioxide showed significance difference ($p < 0.001, \alpha = 0.05$, one-way ANOVA). This is due to the fact that parent material determines chemical composition of the

ore (Tardy, 1997). This is attributed to the fact that different ores vary depending on location, climate and depth (Schellmann, 1994). Titanium is not concentrated on a particular level in the earth profile. Laterites are formed differently from different parent materials and are distributed in most parts of the world with similar trends of composition depth wise (DuBois and Walsh, 1970).

Results in table 4.4 show that there was significance increase in percentage of titanium dioxide from raw laterites sample to concentrated laterites sample. Generally, in all sampling site titanium dioxide increased significantly, that is , $t_{cal} > t_{crit} = 2.78$, except from Kaharate 1 ($p < 0.001, \alpha = 0.05$, one-way ANOVA). The Levels of titanium dioxide in raw laterites samples vary significantly with those in concentrated laterites samples. This indicates that magnetic separation can be used to improve percentage of titanium dioxide levels from low grade titanium ores. Samples collected from Meru and Murang'a counties did no show much difference between raw and concentrated laterites samples, compared to those samples collected from Tharaka Nithi County which was in fact below 2 percent. The levels in Tharaka Nithi improved to more than 5 percent, thus making it commercially viable.

Results in table 4.4 showed that the levels of iron oxide, before concentration, in the sites of Meru County were between 52 to 71 percent. Murang'a County was between 49 to 62 percent. In Tharaka Nithi sampling sites, the levels of iron oxide was between 45 to 47 percent. The level of iron oxide in Meru was highest, followed by Murang'a and that from Tharaka Nithi was lowest. This was as a result of influence of natural processes that are known to concentrated iron bearing ores such as volcanic activities in Meru and effect of Elnino in Murang'a County. Mutembei (2013) while working in Tunyai Division, of Tharaka Nithi

County, reported that the levels of iron ranged from 40 percent to 43 percent before concentration in mainly lateritic soils. Iron in this form has very low magnetic susceptibility. The researcher was able to concentrate the iron by heating it in a reducing atmosphere to increase magnetic susceptibility.

While working with samples from Ruiru area in Kiambu County, Keru (2011) reported the concentrations of iron oxide ranging from 22 to 40 percent in raw samples, again in lateritic soils. The researcher reported that these levels can be improved by heating the laterites samples in presence of carbon, the reducing agent, to be economically viable. Samples collected from Kamahuha and Juja areas were reported to contain between 45 to 56 percent (Njoroge, 2014). The researcher concentrated iron in the samples by heating the ore in a reducing atmosphere to more than 59.7 %. Therefore samples collected from Murang'a, Meru and Tharaka Nithi Counties could be an alternative source of iron ores.

The results in table 4.4 show both titanium oxides and iron oxide in all levels. Iron is magnetic although magnetic properties depend on its oxidation state. At lower oxidation state of +2, its magnetic susceptibility is low (Svoboda, 2004). At this low oxidation state a high intensity magnetic separator, which is expensive to buy and maintain, is used for magnetic separation. At higher oxidation states low intensity magnetic separators are used, but, in either case iron play a crucial role in magnetic separation (Branch, 1994). Elements contained in an Fe-rich ore can be separated or concentrated as is the case for this study, using magnetic separation (Abubakre *et al.*, 2007; Dunn *et al.*, 2007). Rare earth metals occur in this form, thus making it possible for them to be concentrated using magnetic separation (Abubakre *et al*., 2007; Dunn *et al*., 2007; Kristian *et al*., 2014). Ciu *et al.* (2002) increased the magnetic susceptibility of Ti/Fe

compounds. The increased magnetic susceptibility of Ti in Fe bearing ores can thus be used to increase the concentration of Ti using Magnetic separation.

4.5 Loss on Ignition (LOI)

Table 4.5 shows loss of ignition of the raw laterites samples to test whether raw laterites contain organic matter.

Table 4.5: Loss on Ignition of Raw Samples and Statistical Comparison With Level A and C

	M_1	M_3	M_4	M_7	M_9	M_{10}	K_1	K_2	K_3	K_4	GA	GB	GK
A	13.95 ±0.14	14.31 ±0.19	14.86 ±0.79	13.97 ±0.27	13.30 ±0.52	15.33 ±0.75	14.72 ±0.40	14.38 ±0.48	15.19 ±0.29	13.95 ±0.14	13.95 ±0.04	14.31 ±0.19	15.52 ±0.43
C	15.26 ±0.77	14.12 ±0.39	13.97 ±1.38	14.12 ±0.39	14.12 ±0.39	13.97 ±1.38	15.26 ±0.87	14.92 ±0.08	14.47 ±0.60	14.89 ±0.65	14.72 ±0.41	14.38 ±0.48	15.19 ±0.29
t_{cal}	2.9	0.76	0.97	3.47	0.96	1.73	4.45	1.92	5.93	12.87	3.32	0.23	1.10

Results on loss on ignition showed that different samples has different amount of organic matter. The value of loss on ignition ranged from 6.15 percent to 15.33 percent. This is a clear indication that organic substances vary from one sample to another. The analysis was done using AAS and comparison was done for two levels to test whether there of significance difference in loss on ignition. The t_{cal} is more than t_{crit} in six samples showing significance difference between most of them.

4.6 Chemical Results for Raw and Thermal Reduced and Magnetic Concentrated Ores

The chemical analysis of titanium and iron results, in percentage composition, of thermally reduced laterites samples of the same sampled ores in level A, B and C are given in table 4.4. Results in table 4.4 clearly show the levels of iron increasing from as 45 % to above 53.39 %. In literature, heated biomass in the temperature range of 500 -800 ^{o}C, in limited air is converted to carbon and syngas which are reducing agents. Reducing agents converts less

magnetic iron ores into more magnetic ones. Goethite, haematite, iron-rich titanium and magnetite present were concerted to maghemite. The magnetic susceptibility of maghemite is equivalent to that of magnetite which is known to be highly magnetic. This explains why iron content increases significantly.

Keru (2011), used charcoal as a fuel to heat charcoal-ore mix. The researcher's interest was to concentrate Fe from selected areas in Ruiru division. Mutembei (2014) used muffle furnace for heating. Keru (2011) improved the concentration by an average of 17.98 % across the samples. This could be an expensive method of concentrating the iron ore in addition to the side effects associated with deforestation, a source of wood charcoal. Optimization of charcoal to ore ratio for effective reduction was not done.

Current method of concentrating thermally reduced iron minerals emphasizes on the use of charcoal. Charcoal, a material that is obtained from trees, will lead to cutting down of trees which occupies a small fraction of Kenyan land. According to the Kenya Forest Service, Kenya needs 7.6 billion to reach just 10 % of forest cover by the year 2030. Uses of charcoal may hinder achievement of this target of vision 2030. In addition to this, the World rain forest Movement is concerned about the rate at which Kenyan forest are declining (Matiru, 2010). Each year, about 12,000 ha which is about 0.3 % of the total forest cover is cut down due to population pressure. This is an addition to already effects of deterioration of river sources (Akotsi *et al*., 2006). Thus use of such methods of concentrating iron would be unsustainable.

Raw biomass has been used to concentrate iron in laterites in Kenya (Njoroge, 2014). The researcher used saw dust, charcoal among others to concentrate iron. The raw biomass was

mixed with sampled ore in the ratio of 1:20. A current of air was passed through heated biomass- sample mix of 500 to 700 ^{o}C. This temperature range converts biomass to carbon and carbon monoxide. The two are used as reducing agents. The reducing agents converted iron bearing minerals into magnetite which contains little percentage of titanium dioxide. At this temperature range magnetite is formed (Dunlop and Ozdemir, 2000). Fe levels increased by 21 to 23 % (Njoroge, 2014). The percentage of the titanium dioxide obtained increased by 2 – 3 % which lead to between 10 to 20 percent yield.

Laterites samples in Mbeu 4, Mbeu 7 and Mbeu 9 has titanium dioxide levels of area were concentrated naturally through natural processes which are known to increase magnetic susceptibility of iron bearing minerals such as volcanic activities. However, some other regions of Murang'a are known to contain iron bearing minerals that can be concentrated using magnetic separation after thermal treatment of iron bearing ores in a reducing environment (Njoroge, 2014). The Titanium dioxide levels in Mbeu are 5 % these deposits can be used for extraction of titanium.

Ciu *et al.* (2002) studied the effect of temperature change on magnetic susceptibility of iron-rick titanium based sample, in a reducing environment. The researcher used charcoal, in the ratio of 1:10. The researchers observed that the magnetic susceptibility increased on heating the sample in mix with charcoal. The researchers observed that the treated sample was converted to maghemite at 500 to 900 ^{o}C. The maghemite is highly susceptible to magnet. However, the researcher did not determine the percentage yield of the thermally reduced iron-rich titanium ores.

Results (Appendices XV to VII) showed silica in all levels was between 8.86 % and 19.2 % which is high. Silica, which is considered unwanted material in titanium ores, is removed, as non-magnetic material. During separation, it remained as tailing. Presence of silica in ores is mainly considered as a gangue and has necessitated the development of methods of separating it from the required material. Silica, for example, was selectively removed from vanadium-bearing steel slag by use of sodium hydroxide (Zhang *et al.*, 2010). In blast furnace, it is removed as slag. Sarkar (2011) improved the concentration of iron by removing a substantial amount of silica by leaching the ore with 0.5 M NaOH and sulphuric acid at 95 ^{o}C. This improved iron concentration from 58.8 % to 67.5 % (Sarkar, 2011). Mutembei (2013) reduced silica content by 43.3 % by use of magnetic separation. This made the levels of iron increase significantly to 55 – 64 %.

4.7 Percentage Yield

Amount of titanium dioxide was calculated before and after the concentration (Appendix XIX). Results of percentage yield are also shown in figure 4.2. From the results, the TiO_2 obtained after heat treatment was more than 57 percent. The amount of titanium dioxide in the raw sample was calculated by the equation 4.6

$$\text{Mass of } TiO_2 \text{ in raw sample} = \text{percentage by mass of } TiO_2 \times 20 \text{ grams} \quad \text{.....4.6}$$

The mass of titanium dioxide was calculated by multiplying the percentage composition by mass of titanium dioxide in the magnetic separated. The amount of titanium dioxide calculated after use of a magnet was expressed as a percentage of the original mass. Percentage yield of

the titanium dioxide was obtained using equation 4.7 and the calculation represented in figure 4.2.

$$\text{Percentage yield} = \left(\frac{\text{Mass of titanium dioxide after concentration}}{\text{Mass of titanium dioxide before concentration}} \right) \times 100 \text{.....} 4.7$$

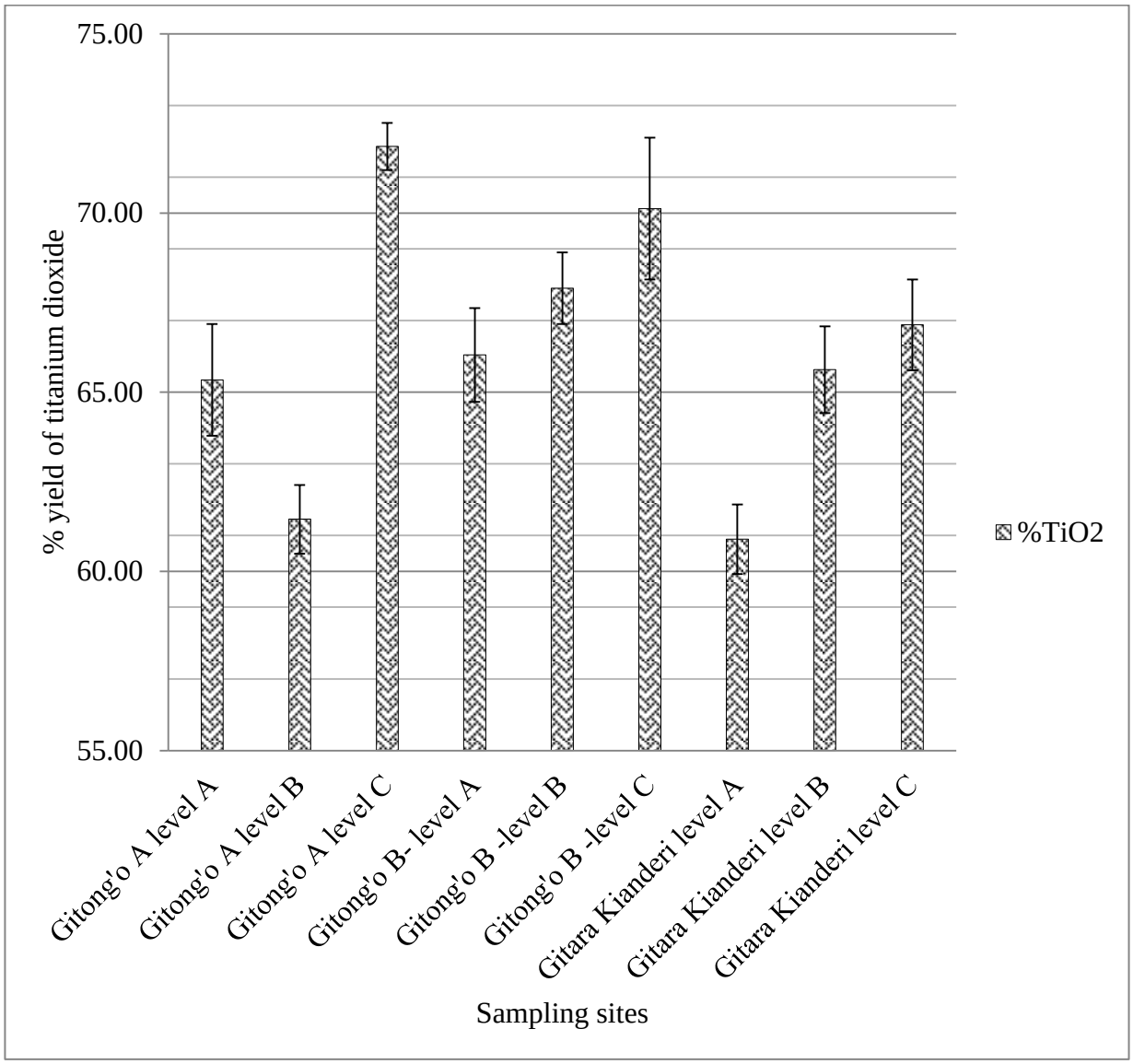

Figure 4.2: Percentage Yield of Ti in heat-treated ore from Tharaka Nithi County

From figure 4.2, titanium dioxide in the material collected by the magnet ranges between 57.7 to 71 percent titanium dioxide percent yield. Waithaka (2014) while working with laterite sample from Juja and Murang'a reported a 2 percent TiO_2 improvement from raw laterites to

concentrated samples. This translates to less than 15 percent titanium dioxide yield. This is a clear indication that maghemite contains more titanium dioxide than magnetite. Dunn *et al.* (2007) used more than one method to concentrate ilmenite from a mixture of rutile, Zircon, Sillimanite, monazite, magnetite among others. They used magnetic separator to remove ferromagnetic materials, gravity concentration to remove non-magnetic fractions (Stamper, 1970). Titanium levels increased by 47.5 % to 47.66 % on the concentrate and tailing contained 7 %. Despite use of strong magnetic separators, the levels are lower compared the ones obtained in this study.

Choi *et al.* (2006) worked with beach sand that contained 0.83 % of titanium dioxide before concentration. Gravity separation using spiral and shaking tables to concentrate the HM enabled them to remove light and coarse particles consisting of quartz. A high-intensity magnetic separator and subsequent use of induced magnetic separator were applied to remove magnetic particles according to their magnetic susceptibility (Choi et al., 2006). The percentage yield TiO_2 using this method was 43.98 %. The researchers managed to separate of Ti using magnetic separation. Concentration of the Ti using raw biomass produced more than 57 percent.

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusion

1. Chemical analysis showed major oxide of elements such as Si, Al, Mn, Ca, Mg, Na, K, Fe, Ti are present. The presence of Fe can be advantageously used to concentrate the Ti

2. Ilmenite was thermally reduced to Maghemite that is attracted by a magnet. Therefore, Magnetic separation can be used to beneficiate Titanium Oxide ores

3. Mineralogical composition showed that raw samples contain Ilmenite and heat-treated product contains Maghemite.

4. Thermal reduction of Ti –bearing minerals in laterites concentrated Ti by > 57 % - Low grade Ti ore can be commercially be exploited

5.2 Recommendations for Further Research

1. More research need to be done on magnetic separation techniques for commercial scales of concentration and/or extraction of Ti, and/or Fe using raw biomass as a reducing agent
2. The study of concentration of other rare elements such as Manganese by use of magnetic separation after heat treatment of the ores in a reducing atmosphere using bio-wastes
3. Explore concentration of Ti (and like elements) in non Fe-rich minerals by mixing the minerals with laterites rich in Fe.

5.3 Recommendation from this Work

Results from this study have shown that thermal reduction of laterites using biomass followed by magnetic separation improves levels of titanium dioxide from low grade to commercial ore grade. Therefore, there is need for cost benefit analysis for commercial scales concentration.

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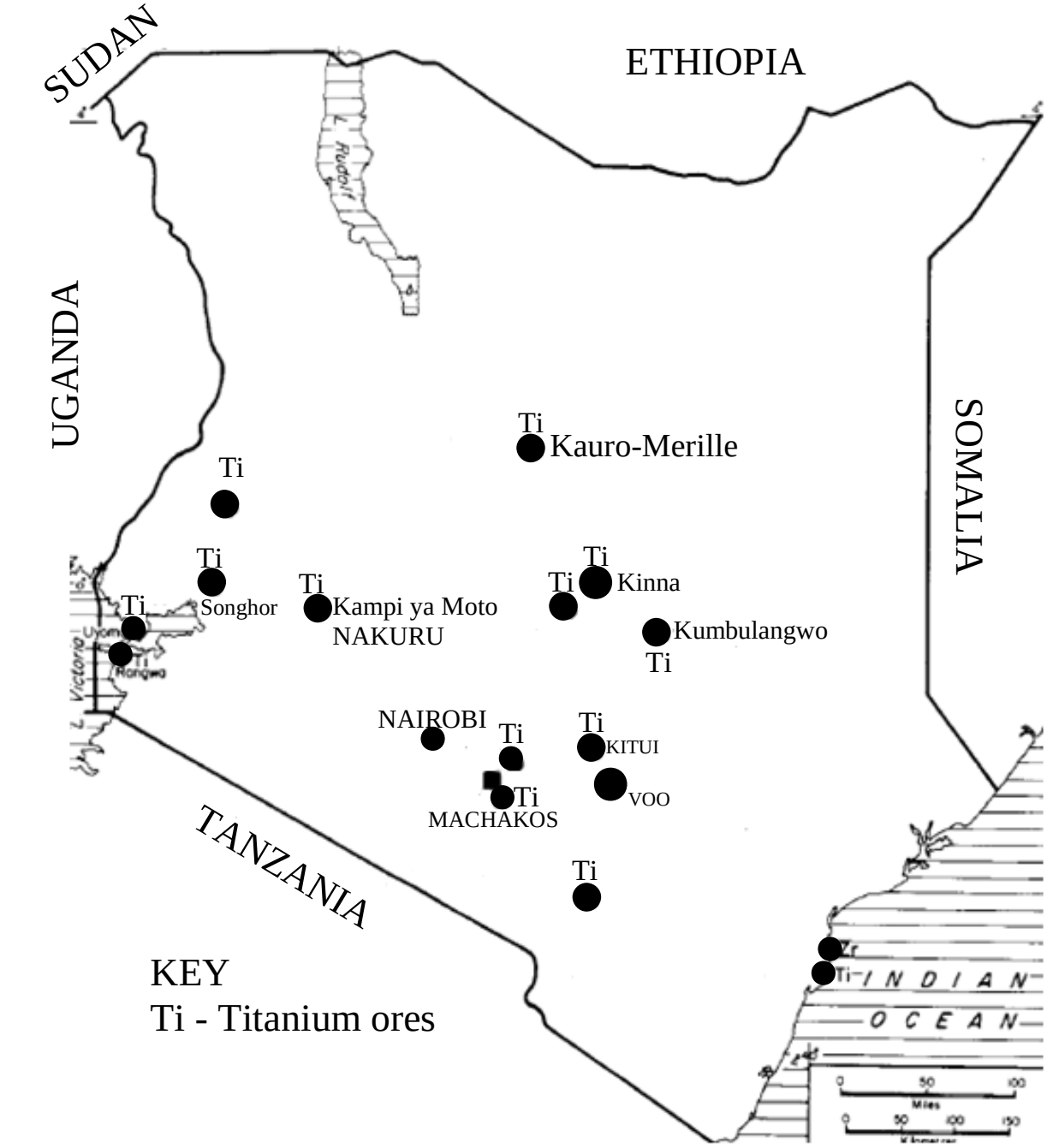
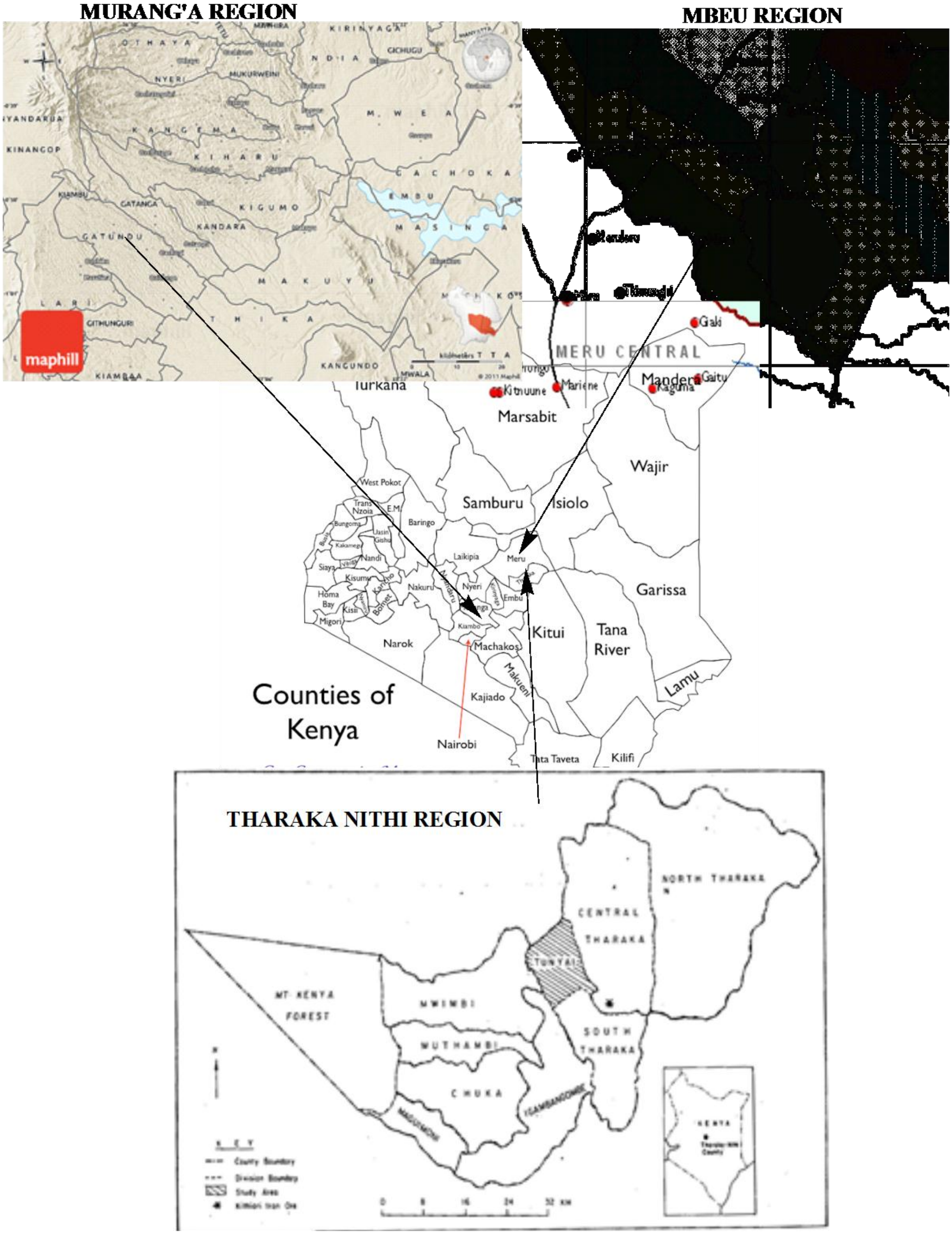
APPENDICES:

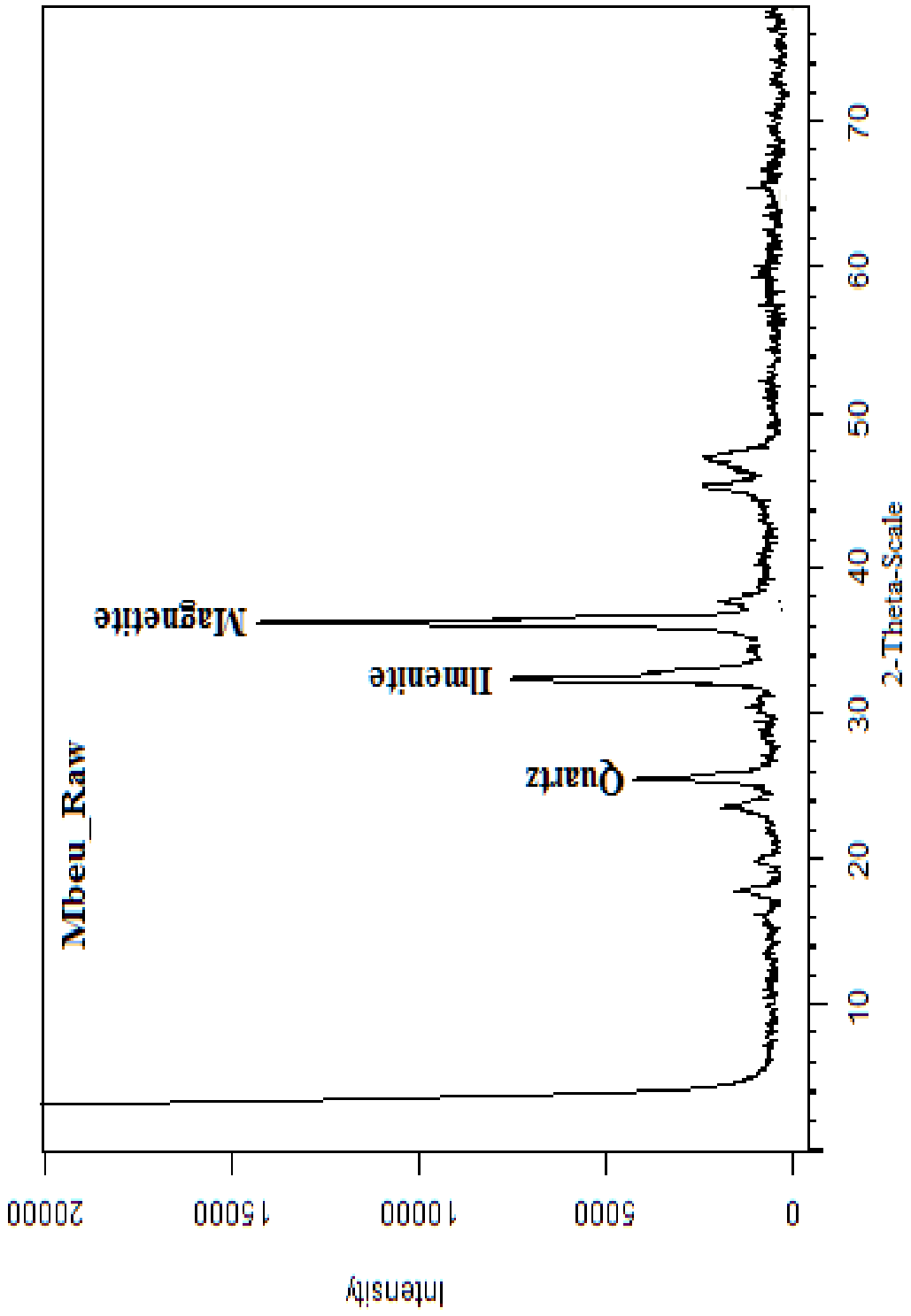
Appendix I: Various Potential Titanium (Ti) Metal Producers



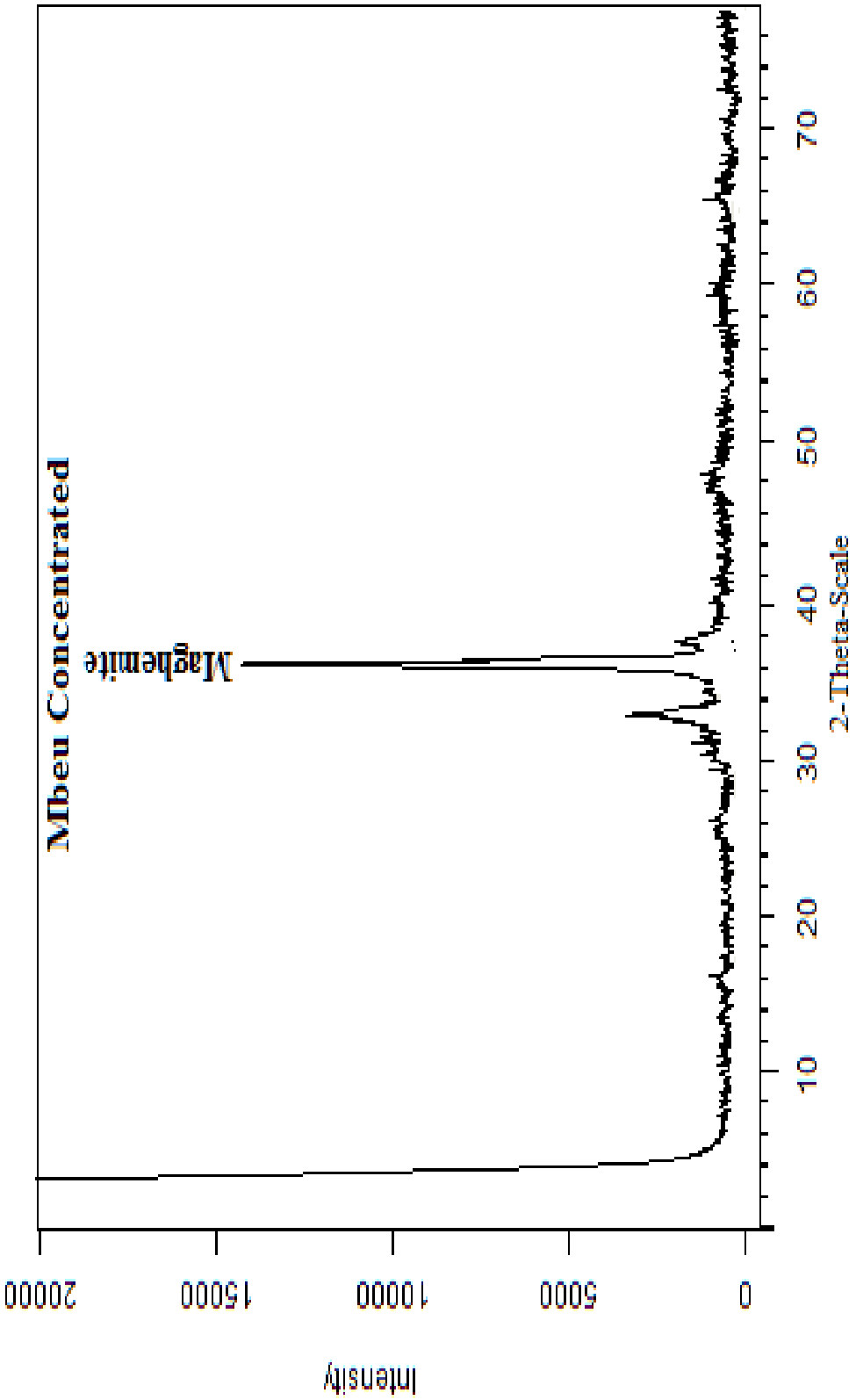
Appendix II: Map of Kenya Showing the Position of Meru, Tharaka Nithi and Murang'a Counties



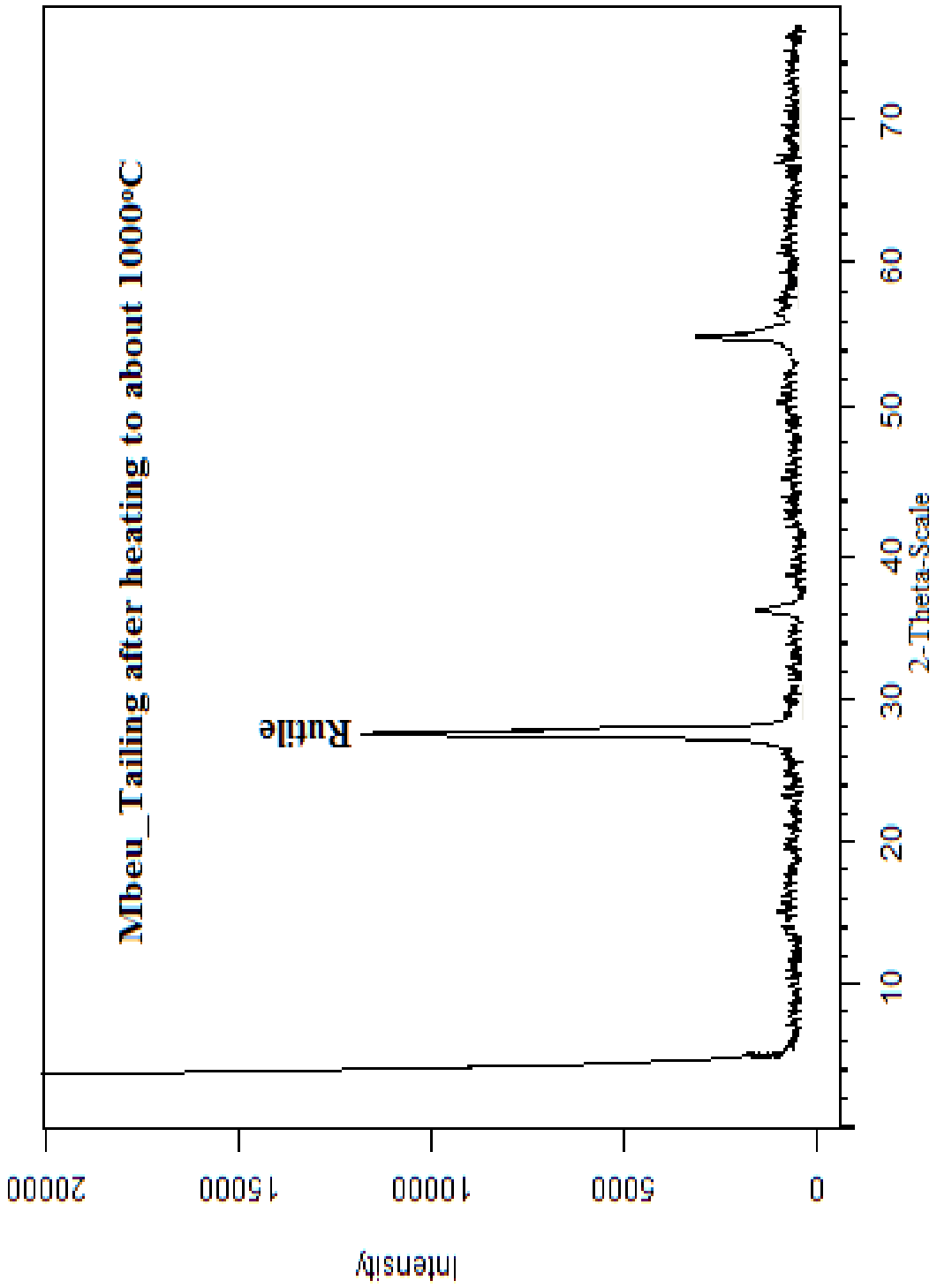
Appendix III: XRD Deffractogram for Raw Laterites Samples from Mbeu area of Meru County



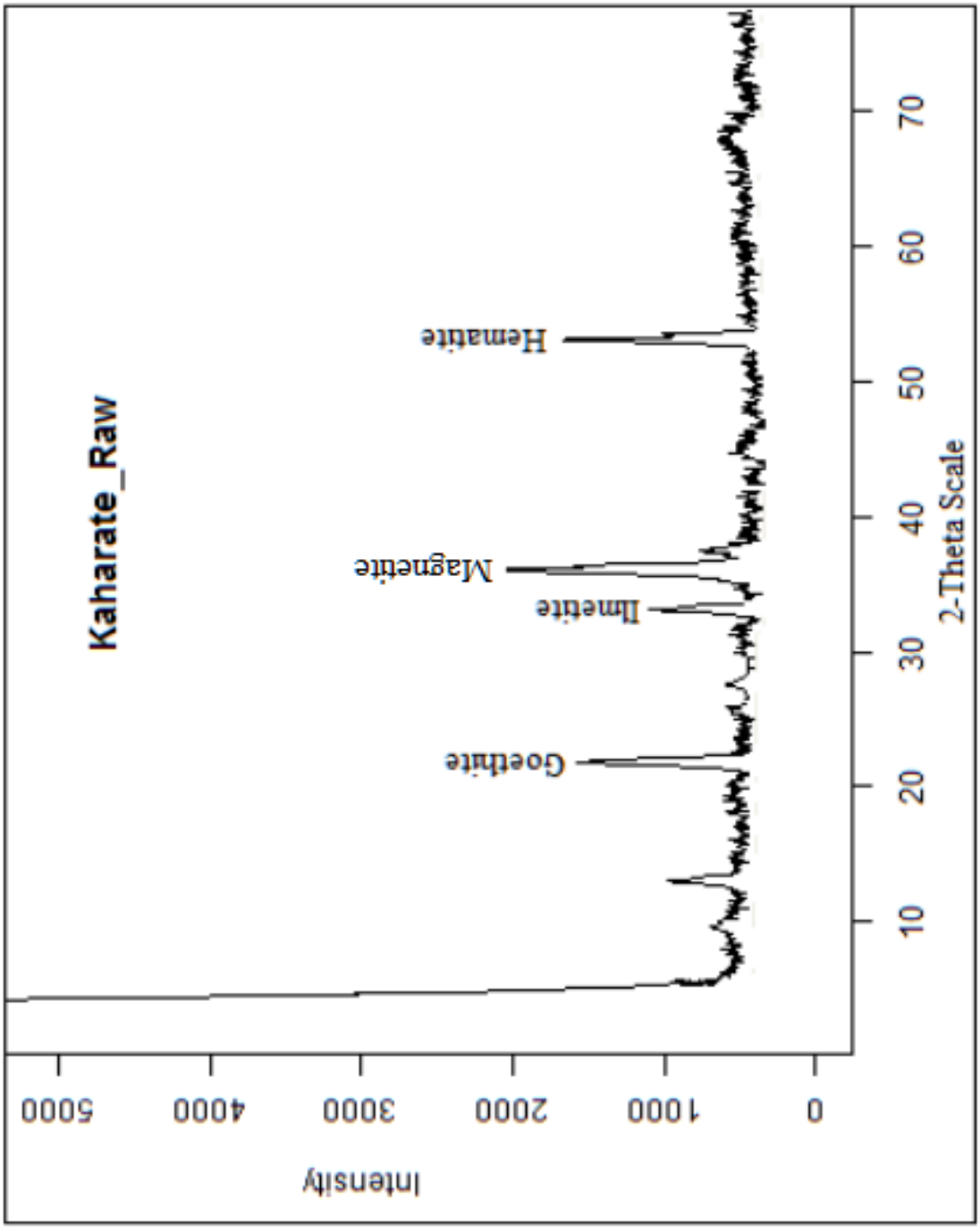
Appendix IV: XRD Deffractogram Thermal Reduced –Magnetic separated Laterite Sample from Mbeu Region



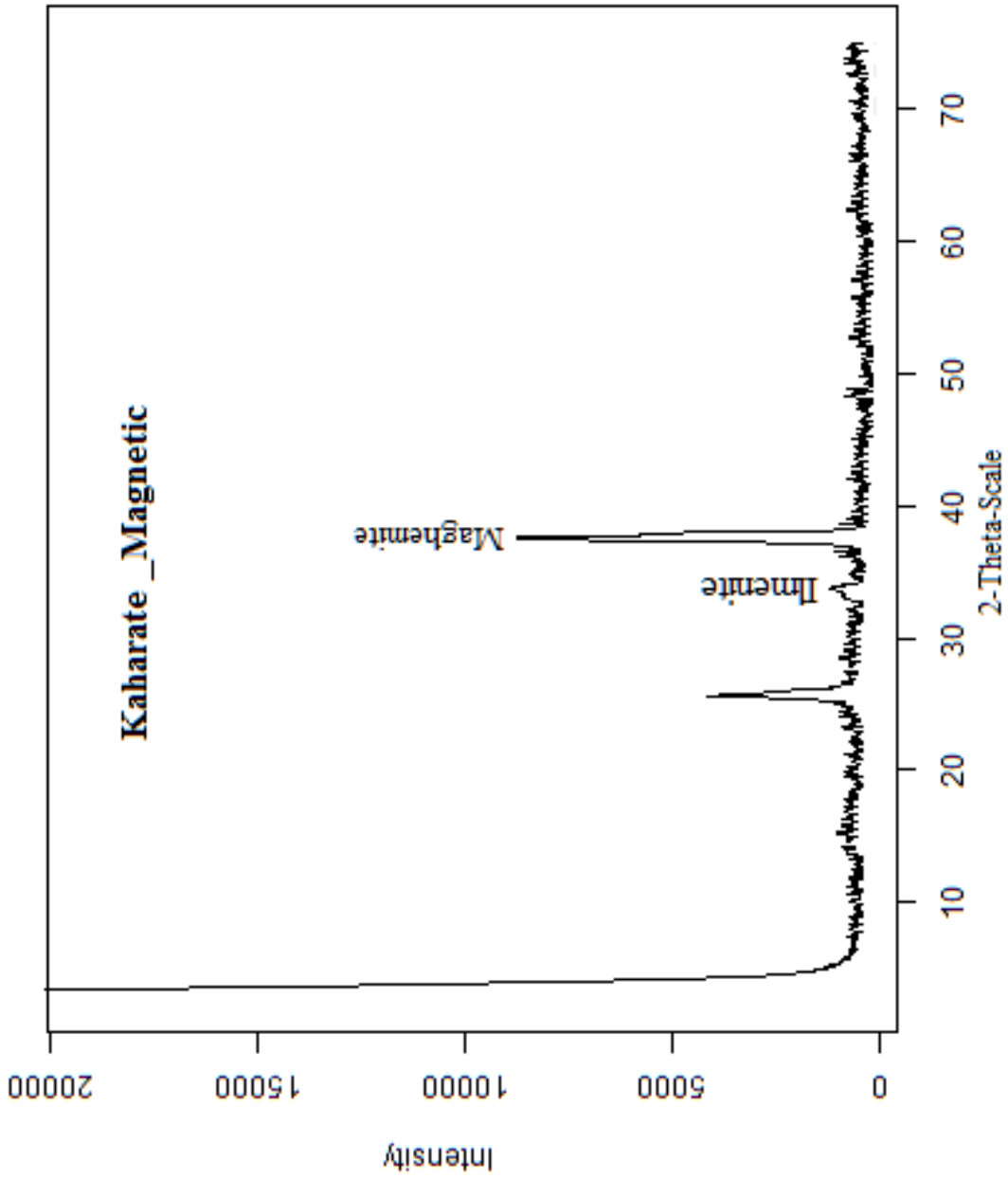
Appendix V: XRD Deffractogram Tailing for Laterites Samples from Mbeu Region at 1000 °C Followed by Magnetic Separation



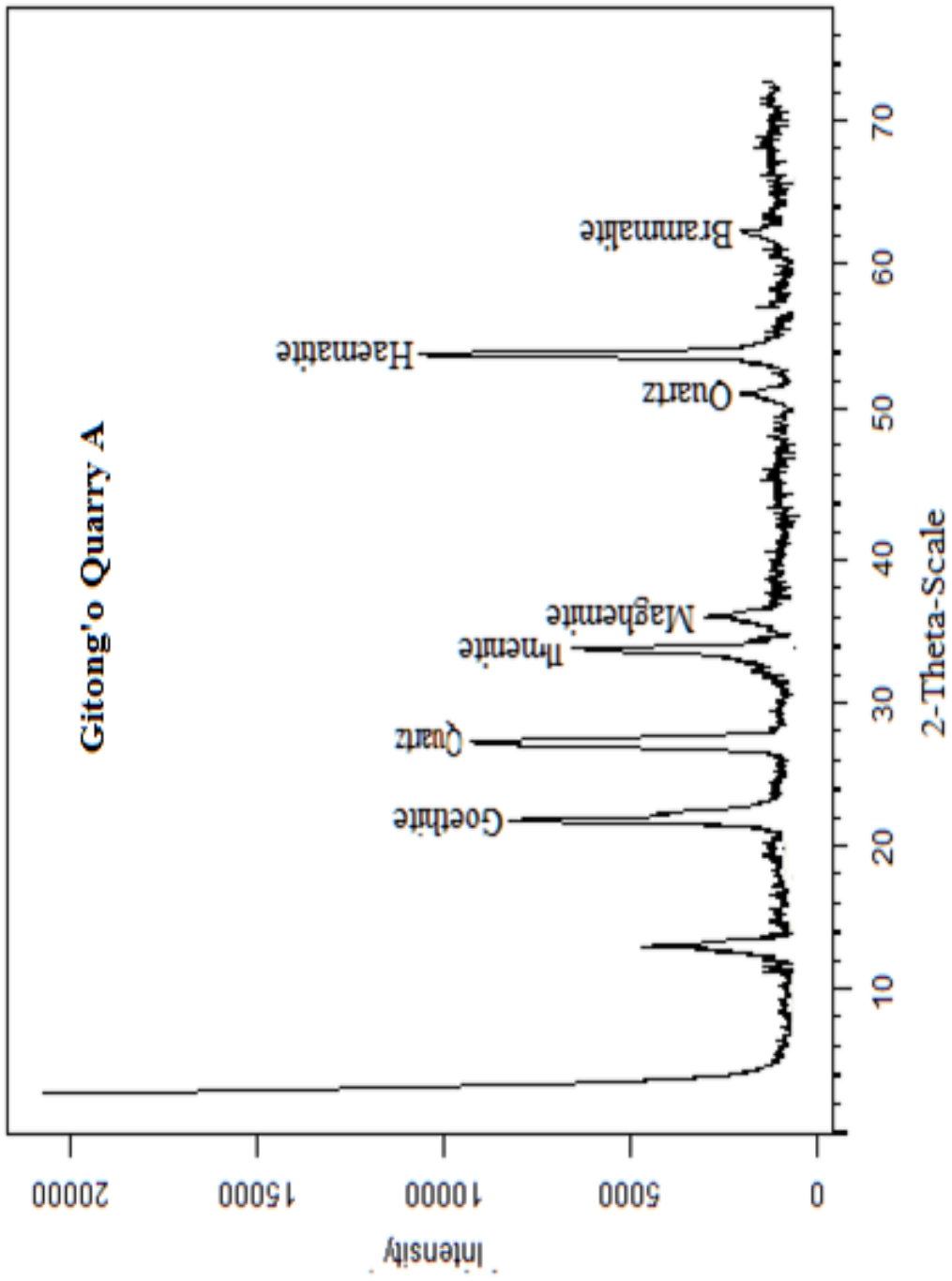
Appendix VI: XRD Deffractogram of Raw Laterites Sample from Kaharate



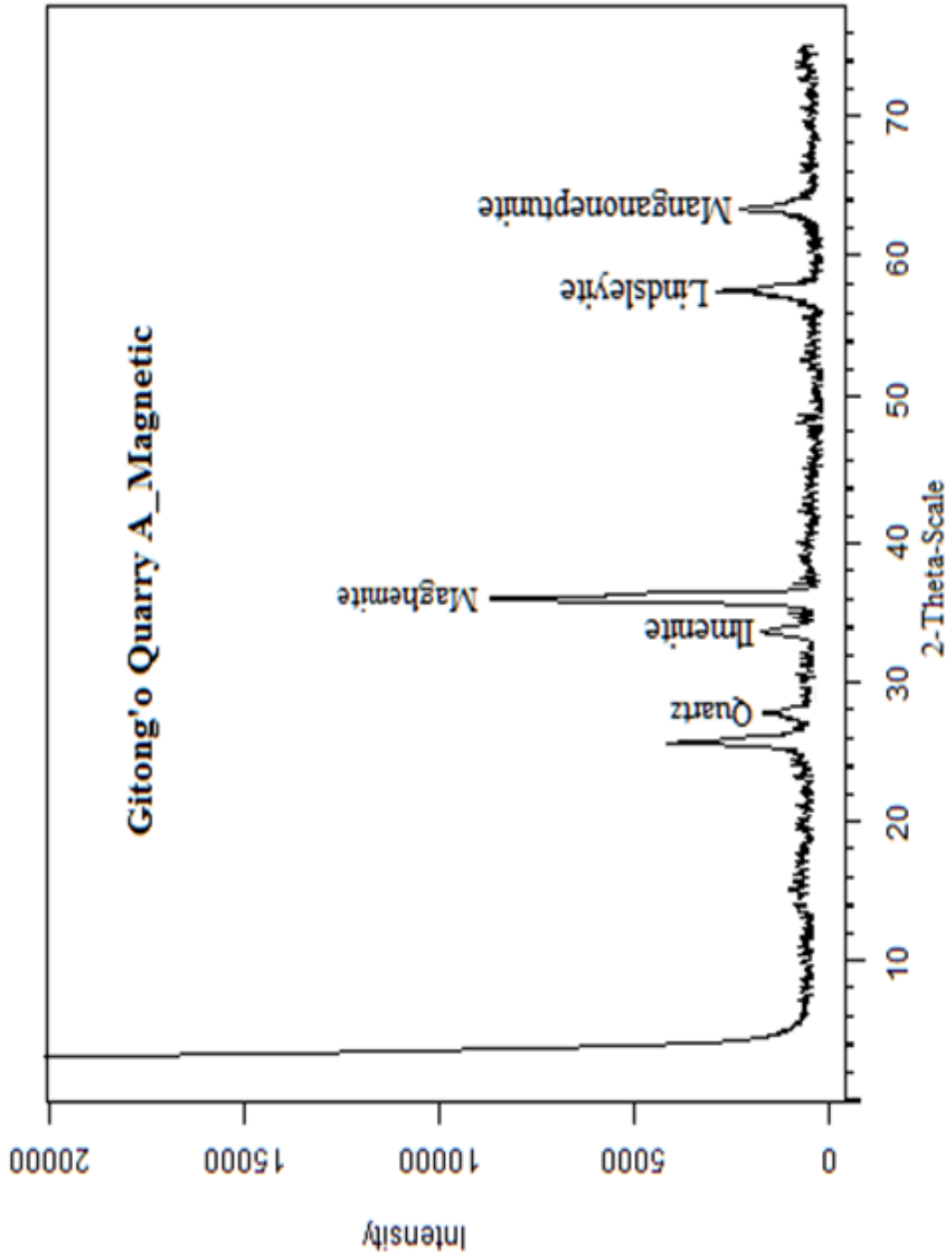
Appendix VII: XRD Deffractogram of Thermal Reduced Magnetic Separated Laterites from Kaharate



Appendix VIII: XRD Deffractogram for Raw Ore from Gitong'o Quarry A



Appendix IX: XRD Deffractogram for Themally Reduced Ore from Gitong'o Quarry A



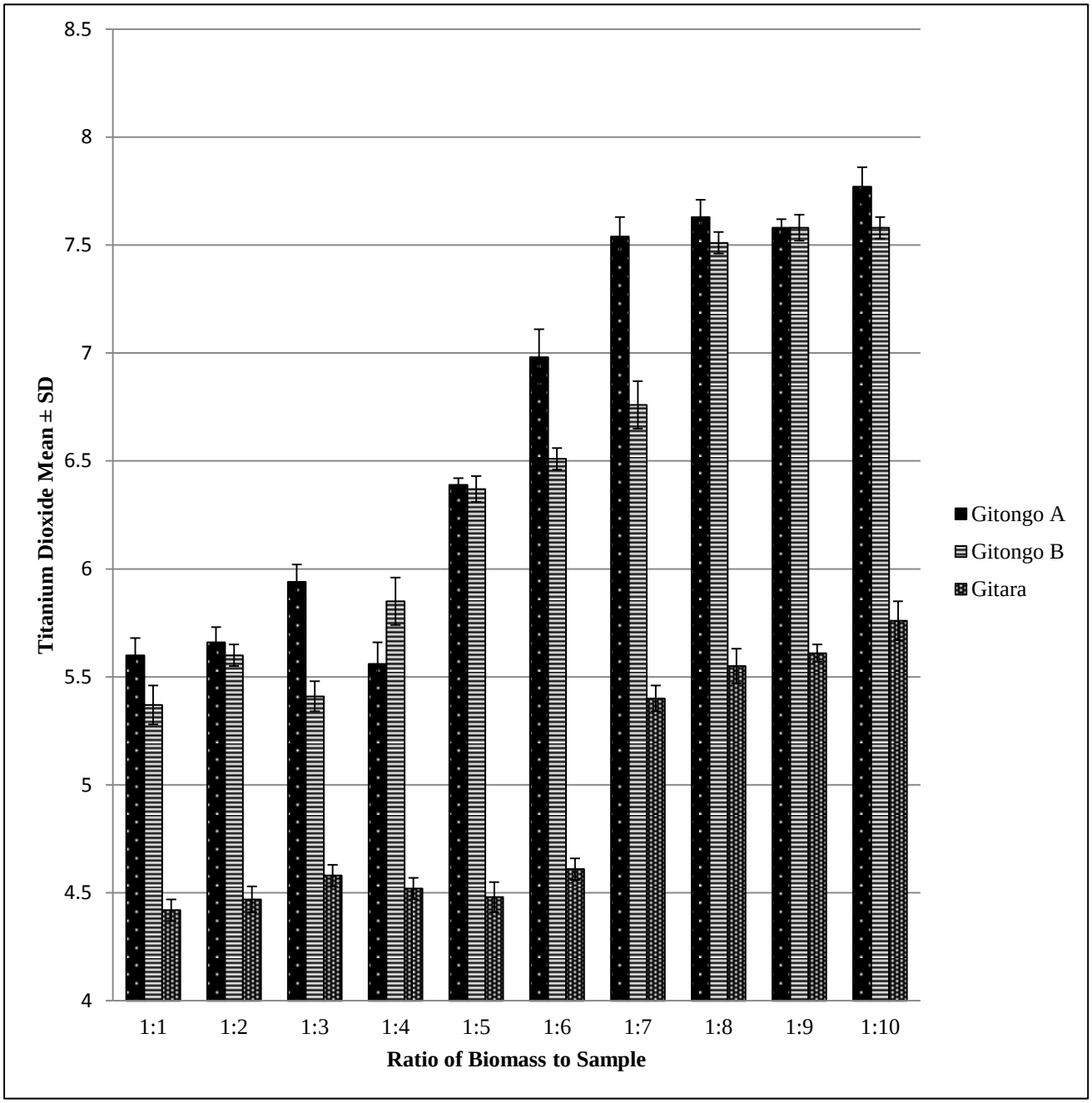
Appendix X: X-Ray Diffraction Table of Minerals (John Weinrich Minerals Auctions)

D_1	I_1	D_2	I_2	D_3	I_3	**Mineral**	**Formula**
Å (2Θ)	%	**Å (2Θ)**	%	**Å (2Θ)**	%		
0.779(162.84)	100	2.180(41.38)	100	0.824(138.39)	90	Sudburyite	(Pd,Ni)Sb
0.787(156.34)	100	0.862(126.66)	80	0.885(121.00)	70	Rhodium	(Rh,Pt)
0.788(155.65)	100	0.777(164.92)	100	3.000(29.76)	100	Bowieite	$(Rh,Ir,Pt)_{1.77}S_3$
0.867(125.36)	100	2.122(42.57)	100	0.802(147.66)	70	Skaergaardite	CuPd
1.019(98.21)	100	1.757(52.00)	100	1.910(47.57)	80	Kalininite	$ZnCr_2S_4$
1.019(98.21)	100	1.081(90.89)	75	1.887(48.18)	63	Nowackiite	$Cu_6Zn_3As_4S_{12}$
1.066(92.54)	100	9.630(9.18)	100	2.050(44.14)	100	Freboldite	CoSe
1.089(90.04)	100	1.846(49.32)	100	2.371(37.92)	90	Ferdisilicite	$FeSi_2$
1.142(84.83)	100	2.180(41.38)	80	1.094(89.51)	80	Chengdeite	Ir_3Fe
1.156(83.57)	100	2.000(45.30)	90	1.003(100.34)	70	Gupeiite	Fe_3Si
1.160(83.22)	100	2.020(44.83)	100	1.430(65.18)	80	Chromferide	$Fe_3Cr1\text{-}x$ (x=0,6)
1.163(82.95)	100	2.228(40.45)	90	1.932(46.99)	70	Isoferroplatinum	$(Pt,Pd)_3(Fe,Cu)$
1.195(80.27)	100	2.240(40.23)	100	0.797(150.24)	90	Tetra-auricupride	AuCu
1.196(80.19)	100	1.991(45.52)	100	1.817(50.17)	90	Fersilicite	FeSi
1.202(79.71)	100	2.295(39.22)	100	1.408(66.33)	90	Rustenburgite/Atokite	$(Pt,Pd)_3Sn$
1.220(78.30)	100	2.130(42.40)	100	1.350(69.58)	60	Osmium	(Os,Ir)
1.299(72.74)	100	2.163(41.72)	100	1.529(60.50)	80	Khamrabaevite	(Ti,V,Fe)C
1.306(72.29)	100	16.000(5.52)	100	4.620(19.20)	100	Perlialite	$K_8T_{l4}Al_{12}Si_{24}O_{72}$•20(H2O)
1.331(70.72)	100	3.070(29.06)	100	1.884(48.27)	80	Maikainite	$Cu_{20}(Fe,Cu)_6Mo_2Ge6S32$
1.335(70.48)	100	3.516(25.31)	90	2.243(40.17)	90	Baotite	$Ba_4(Ti,Nb)_8Si_4O_{28}Cl$
1.375(68.14)	100	3.550(25.06)	100	3.230(27.59)	100	Julienite	$Na_2Co{+}{+}(SCN)_4$•8(H2O)
1.379(67.92)	50	1.717(53.31)	50	2.440(36.80)	50	Oxyvanite	V_3O_5
1.386(67.53)	**100**	**2.750(32.53)**	**100**	**2.880(31.03)**	**70**	**Olkhonskite**	**$(Cr{+}{+}{+},V{+}{+}{+})_2Ti_3O_9$**
1.388(67.42)	100	4.270(20.79)	100	2.190(41.19)	90	Jeremejevite	$Al_6B_5O_{15}(F,OH)_3$
1.390(67.31)	100	10.800(8.18)	100	2.410(37.28)	100	Glucine	$CaBe_4(PO_4)_2(OH)_4$•0.5(H2O)
1.391(67.25)	100	2.390(37.60)	87	2.678(33.43)	71	Zincostaurolite	$4Zn_4Al_{16}(Al,[\ ])_2Si8O40[O6,(OH)2]$
1.400(66.76)	100	1.490(62.26)	100	2.490(36.04)	50	Leadamalgam	$HgPb_2$
1.430(65.18)	100	2.990(29.86)	100	1.620(56.78)	100	Augite	(Ca,Na)(Mg,Fe,Al,Ti)(Si,Al)2O6
1.433(65.03)	100	2.850(31.36)	100	1.582(58.27)	100	Batisivite	$(Ti,V,Cr)_{14}Ba[Si_2O_7].O22$
1.440(64.68)	100	2.140(42.19)	100	2.250(40.04)	90	Mathiasite	(K,Ca,Sr)(Ti,Cr,Fe,Mg)21O38
1.440(64.68)	90	2.840(31.47)	90	1.690(54.23)	85	Romanite	$(Fe{+}{+},U,Pb)_2(Ti,Fe{+}{+}{+})O4$
1.450(64.18)	100	2.480(36.19)	100	2.043(44.30)	90	Bityite	$CaLiAl_2(AlBeSi_2)O_{10}(OH)2$
1.483(62.58)	100	1.057(93.56)	100	3.527(25.23)	100	Ustarasite	$Pb(Bi,Sb)_6S_{10}(Si,Al)4O10[(OH)2$
1.485(62.49)	100	3.170(28.13)	100	9.770(9.04)	100	Brammallite	$(Na,H_3O)(Al,Mg,Fe)_2(H_2O)]$
1.486(62.44)	100	2.150(41.99)	100	2.050(44.14)	100	Niggliite	$PtSnCa_2(Mg,Al)(Cr,Al)_2(SiO4)(Si_2O_7)(OH)_2$•$(H_2O)$
1.494(62.07)	100	2.920(30.59)	80	8.300(10.65)	60	Chrysocolla	$(Cu,Al)_2H_2Si_2O_5(OH)4.n(H2O)$

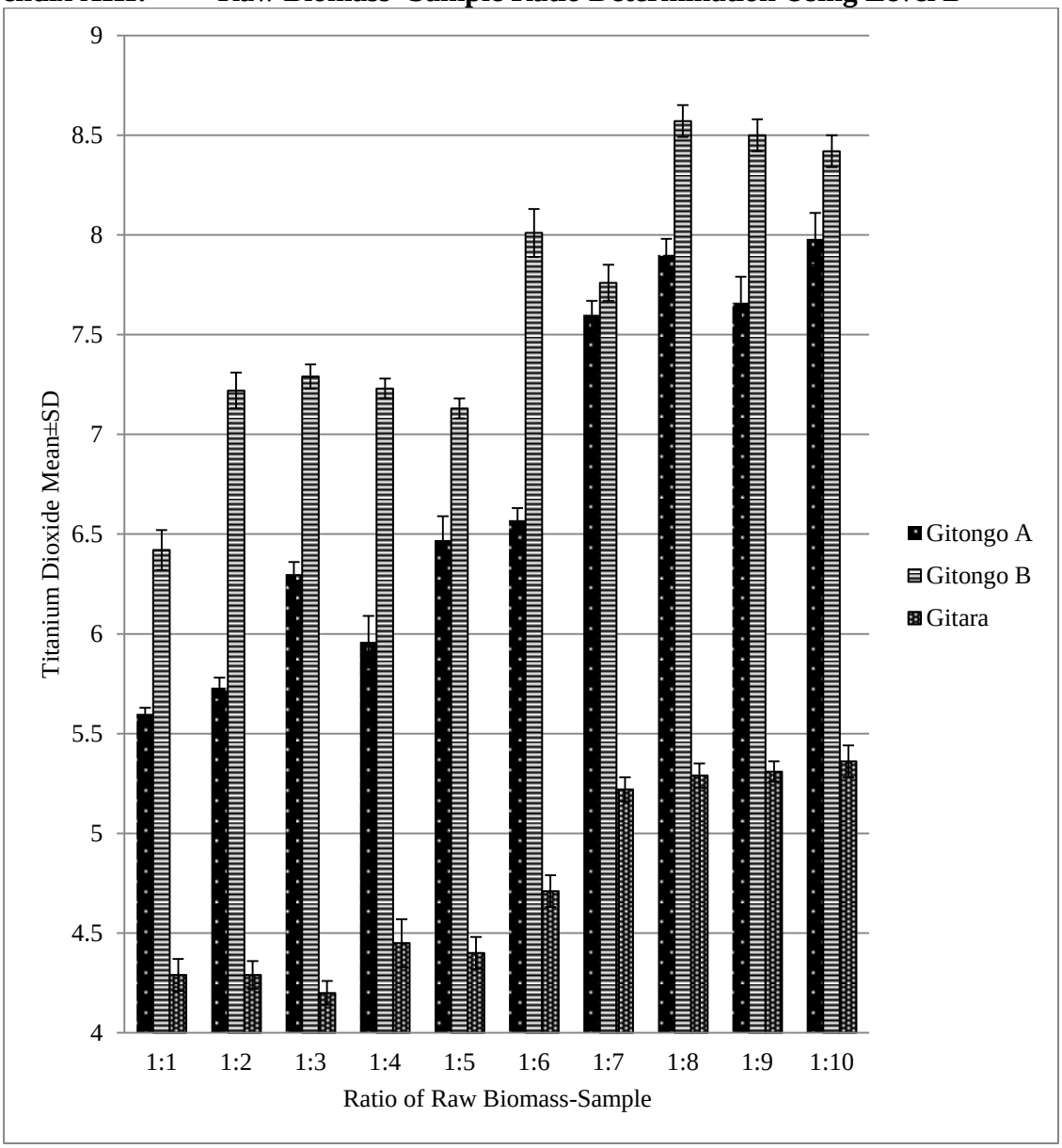
Appendix XI: X-Ray Powder Diffraction of Minerals (John Weinrich Minerals Auctions)

1.495(62.03)	100	1.204(79.55)	90	2.830(31.59)	70	Luanheite	Ag_3Hg
1.503(61.66)	100	2.572(34.85)	100	2.457(36.54)	70	Preiswerkite	$NaMg_2Al_3Si_2O_{10}(OH)2$
1.506(61.52)	**100**	**2.485(36.12)**	**100**	**1.483(63.58)**	**90**	**Manganoneptunite**	**$KNa_2Li(Mn,Fe{+}{+})_2Ti2Si8O24$**
1.508(61.43)	100	3.020(29.55)	100	1.793(50.88)	70	Calciotantite	$Ca(Ta,Nb)_4O_{11}$
1.511(61.30)	100	2.600(34.47)	90	5.200(17.04)	85	Takeuchiite	$Mg_2Mn{+}{+}{+}O_2(BO_3)$
1.516(61.07)	100	3.190(27.95)	100	2.163(41.72)	100	Babefphite	$BaBe(PO_4)(F,O)$
1.519(60.94)	100	2.600(34.47)	100	4.520(19.62)	80	Chromphyllite	$(K,Ba)(Cr,Al)_2[AlSi_{3O10](OH,F)2}$
1.520(60.90)	100	15.400(5.73)	100	4.560(19.45)	100	Nontronite	$NaO.3Fe{+}{+}{+}_2(Si,Al)4O10(OH)2•n(H2O)$
1.522(60.81)	100	2.410(37.28)	100	3.360(26.51)	90	Shirokshinite	$K(NaMg_2)Si_4O_{10}F_2$
1.530(60.46)	100	4.580(19.36)	100	15.800(5.59)	80	Hectorite	$NaO,3(Mg,Li)_3Si_4O_{10(OH)2}$
1.530(60.46)	-	2.610(34.33)	-	3.910(22.72)	-	Kurumsakite	$(Zn,Ni,Cu)_8Al_8V_2Si_5O35•27(H_2O)$
1.539(60.07)	100	2.940(30.38)	100	1.804(50.55)	100	Tazheranite	$CaTiZr_2O_8$
1.540(60.02)	100	2.580(34.74)	100	2.880(31.03)	60	Majorite	$Mg_3(Fe,Al,Si)_2(SiO4)3$
1.540(60.02)	100	2.660(33.67)	60	2.350(38.27)	60	Mcgovernite	$Mn_9Mg_4Zn_2As_2Si_{2O17(OH)14}$
1.540(60.02)	100	3.590(24.78)	100	4.360(20.35)	100	Neotocite	$(Mn,Fe{+}{+})SiO_{3•(H2O)}$
1.540(60.02)	100	2.580(34.74)	100	2.880(31.03)	60	Pyrope	$Mg_3Al_2(SiO_4)_3$
1.540(60.02)	100	15.400(5.73)	100	2.670(33.54)	100	Sauconite	$NaO,3Zn_3(Si,Al)_4O_{10(OH)2•4(H2O)}$
1.544(59.85)	100	2.992(29.84)	100	2.597(34.51)	60	Glagolevite	$NaMg_6[Si_3AlO_{10}](OH,O)8•H_2O$
1.548(59.68)	100	2.940(30.38)	100	1.813(50.28)	100	Lewisite	$(Ca,Fe{+}{+},Na)_{2(Sb,Ti)2O7}$
1.550(59.60)	100	2.522(35.57)	100	1.805(50.52)	92	Sabelliite	$Cu_2Zn(As,Sb)O_{4(OH)3}$
1.552(59.51)	100	2.950(30.27)	100	1.818(50.14)	100	Uranmicrolite	$(U,Ca)_2(Ta,Nb)_{2O6(OH)}$
1.574(58.60)	100	2.620(34.20)	100	2.920(30.59)	90	Calderite	$(Mn{+}{+},Ca)_{3(Fe{+}{+}{+},Al)2(SiO4)3}$
1.587(58.07)	100	3.040(29.36)	100	1.840(49.50)	100	Cesstibtantite	(Cs,Na)SbTa4O12
1.590(57.95)	**100**	**2.130(42.40)**	**100**	**1.800(50.67)**	**100**	**Lindsleyite**	**$(Ba,Sr)(Ti,Cr,Fe,Mg)_{21.O38}$**
1.593(57.83)	100	1.487(62.40)	100	2.900(30.81)	90	Shuiskite	$Ca_2(Mg,Al)(Cr,Al)_2(SiO_4)(Si_2O)(OH)_2•(H_2O)$
1.606(57.32)	-	2.901(30.80)	-	3.414(26.08)	-	Dessauite	$(Sr,Pb)(Y,U)(Ti,Fe{+}{+}{+})_{20}O_{38}$
1.609(57.21)	100	3.159(28.23)	100	2.633(34.02)	80	Cobaltau-stinite	$CaCo(AsO_4)(OH)$
1.610(57.17)	**100**	**2.950(30.27)**	**100**	**2.520(35.60)**	**100**	**Maghemite**	**gamma-Fe+++2O3**
1.618(56.86)	100	2.645(33.86)	100	1.873(48.57)	100	Zavaritskite	BiOF
1.69(54.11)	100	2.59(35.30)	100	**2.69(33.51)**	100	**Hematite**	**Fe_2O_3**
1.72(51.51)	**100**	**2.54(35.44)**	**100**	**2.74(33.12)**	**90**	**Illmenite**	**$FeTiO_3$**
2.45(35.42)	**75**	**2.70(33.53)**	**100**	**4.13(21.51)**	**80**	**Goethite**	**Fe+++O(OH)**

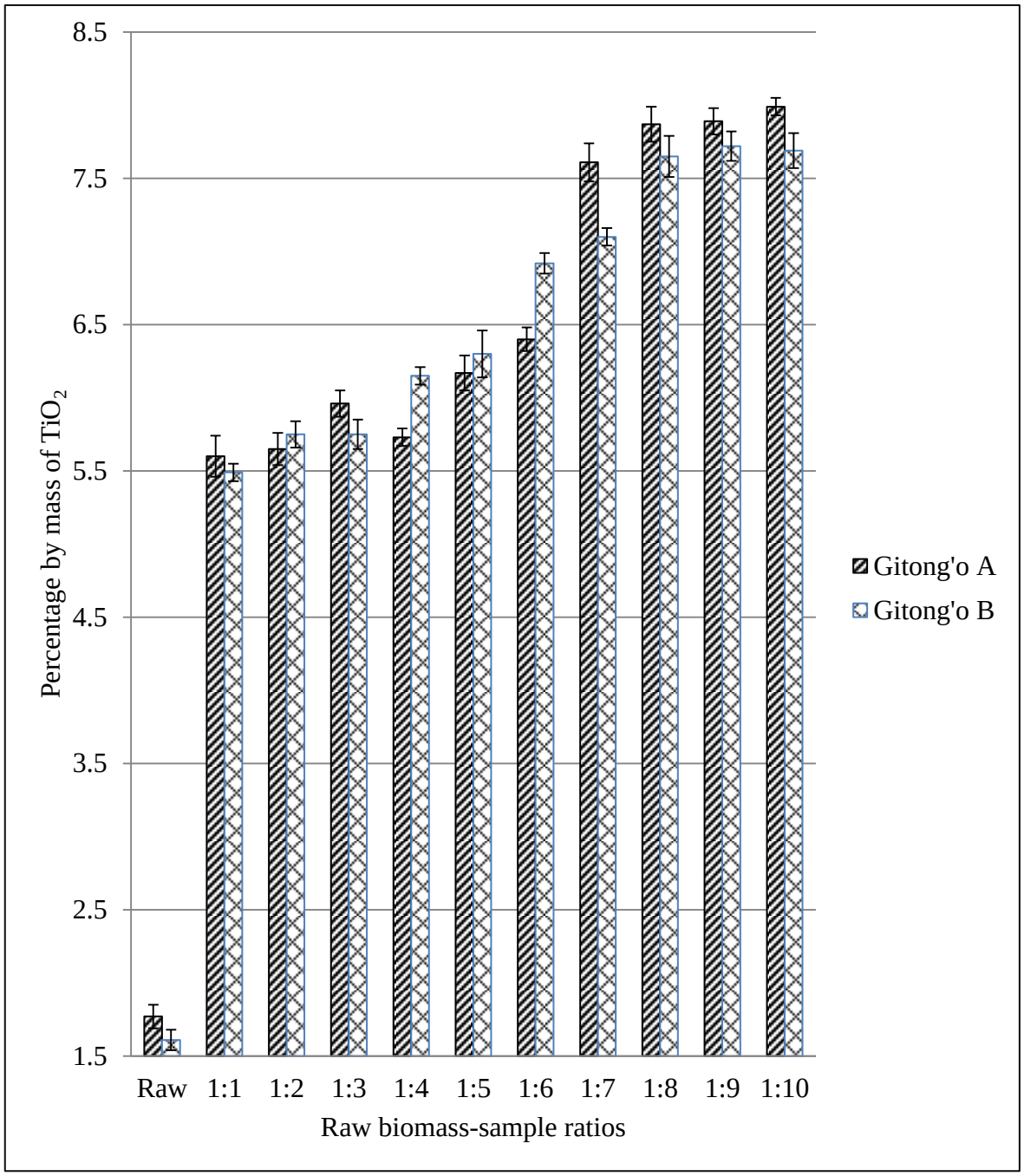
Appendix XII: Biomass Sample Ratio Determination Using Level B



Appendix XIII: Raw Biomass- Sample Ratio Determination Using Level B



Appendix XIV: Percentage of Titanium Dioxide in Different Raw Biomass-Sample ratios



Appendix XV: Chemical Composition of Samples from Level A (30 cm) after Heating with Biomass at a ratio 1:10 Followed by Magnetic Separation

Sampled Sites	**%(w/w) OXIDE CONTENT (Mean ± SD)**						
Level A	SiO_2	Al_2O_3	CaO	MgO	Na_2O	K_2O	MnO
Mbeu 1 Raw	10.83±0.05	0.23±0.02	0.05±.0.01	0.24± 0.01	0.28± 0.02	0.0±0.00	0.60±0.01
Mbeu 1 Conc.	5.40± 0.08	0.15± 0.02	0.04± 0.01	0.17± 0.02	0.33± 0.04	0.00±0.00	0.42± 0.04
Mbeu 3 Raw	10.43±0.06	8.49±0.02	0.11± 0.02	0.38± 0.03	0.40± 0.04	0.8±0.02	1.30±0.02
Mbeu 3 Conc.	5.05± 0.07	6.30± 0.05	0.07± 0.01	0.29± 0.02	0.28± 0.04	0.62±0.05	0.86± 0.06
Mbeu 4 Raw	16.76±0.10	1.55±0.03	0.08± 0.01	0.48± 0.02	0.24± 0.14	0.7±0.01	6.94±0.42
Mbeu 4 Conc.	8.17± 0.04	6.47± 0.05	0.06± 0.02	0.35± 0.03	0.18± 0.04	0.61±0.05	0.60± 0.17
Mbeu 7 Raw	12.69±0.03	6.22±0.01	0.07± 0.01	0.21± 0.02	0.12± 0.03	0.0±0.00	1.10±0.02
Mbeu 7 Conc.	4.25± 0.05	5.54± 0.08	0.04± 0.01	0.16± 0.04	0.07± 0.01	0.03±0.02	0.82± 0.04
Mbeu 9 Raw	16.73±0.05	3.91±0.03	0.15± 0.04	0.33± 0.03	0.22± 0.03	0.0±0.01	0.32±0.00
Mbeu 9 Conc.	3.34± 0.12	3.46± 0.07	0.14± 0.03	0.31± 0.04	0.15± 0.03	0.08±0.04	0.24± 0.03
Mbeu 10 Raw	12.16±0.05	0.22±0.03	0.07± 0.01	0.23± 0.02	0.31± 0.02	0.0±0.00	0.42±0.02
Mbeu 10 Conc.	4.22±0.06	0.16± 0.03	0.06± 0.02	0.16± 0.03	0.25± 0.04	0.03±0.02	0.35± 0.04
Kaharate 1 Raw	8.86± 0.05	7.44±0.03	0.08± 0.00	0.38± 0.00	0.10± 0.00	0.0±0.01	0.41±0.01
Kaharate 1 Conc.	4.26± 0.06	5.19± 0.04	0.06± 0.02	0.32± 0.04	0.06± 0.01	0.05±0.02	0.34±0.04
Kaharate 2 Raw	16.13±0.07	3.24±0.02	0.08± 0.00	0.22± 0.00	0.34± 0.01	0.0±0.00	1.01±0.01
Kaharate 2 conc.	6.52± 0.05	2.21± 0.02	0.06± 0.01	0.15± 0.04	0.27± 0.05	0.05±0.02	0.08± 0.02
Kaharate 3 Raw.	16.72±0.04	9.87±0.03	0.07± 0.01	0.28± 0.00	0.32± 0.01	0.0±0.00	1.86±0.01
Kaharate 3 Conc.	6.35± 0.13	7.68± 0.06	0.06± 0.02	0.15± 0.03	0.19± 0.12	0.06±0.01	1.19± 0.04
Kaharate 4 Raw	19.20±0.03	5.85±0.03	0.16± 0.01	0.30± 0.01	0.23± 0.01	0.1±0.00	2.01±0.03
Kaharate 4 Conc.	7.71± 0.14	5.32± 0.07	0.12± 0.03	0.22± 0.04	0.23± 0.05	0.08±0.01	1.27± 0.04
Gitong'o A Raw	18.42±0.06	19.02±0.08	0.07±0.03	0.03± 0.00	0.68± 0.98	0.0±0.01	0.39±0.01
Gitong'o A Conc.	6.68± 0.03	8.77± 0.06	0.15± 0.02	0.06± 0.01	0.16± 0.02	0.06±0.01	0.47± 0.06
Gitong'o B Raw	16.24±0.06	18.64±0.06	0.09± 0.01	0.27± 0.02	0.12± 0.01	0.0± 0.00	0.43± 0.04
Gitong'o B Conc.	5.22± 0.04	7.60± 0.04	0.24± 0.05	0.35± 0.05	0.09± 0.02	0.06±0.01	0.73± 0.06
Gitara Kianderi Raw	17.53±0.06	15.95±0.05	0.13±0.01	0.30± 0.02	0.14± 0.01	0.0± 0.01	1.02±0.02
Gitara Kianderi Conc.	4.37± 0.06	6.17± 0.05	0.25± 0.05	0.72± 0.11	0.07± 0.01	0.17±0.01	1.30± 0.10

Key: M-Mbeu, K-Kaharate, GA – Gitong'o quarry A, GK – Gitara Kianderi, Conc. Means thermally reduced ores followed by magnetic separation, Raw means untreated samples

Appendix XVI: Chemical Composition of Samples from Level B (50 cm) after Heating with Biomass at a ratio 1:10 Followed by Magnetic separation

Sampled Sites	**%(**w/w**) OXIDE CONTENT (**Mean ± SD)						
Level B	SiO_2	Al_2O_3	CaO	MgO	Na_2O	K_2O	MnO
Mbeu 1 Raw	9.71±0.05	0.19±0.02	0.03±0.01	0.21±0.02	0.25±0.04	0.00±0.00	0.60±0.02
Mbeu 1 Conc.	6.43±0.09	0.21±0.05	0.02±0.01	0.14±0.04	0.14±0.02	0.01±0.01	0.44±0.07
Mbeu 3 Raw	9.87±0.13	8.42±0.10	0.14±0.03	0.35±0.03	0.36±0.03	0.79±0.03	1.31±0.03
Mbeu 3 Conc.	6.68±0.16	7.99±0.13	0.12±0.03	0.26±0.09	0.19±0.11	0.57±0.11	1.11±0.02
Mbeu 4 Raw	18.73±0.05	4.61±0.05	0.05±0.01	0.16±0.03	0.33±0.02	0.34±0.03	6.95±0.13
Mbeu 4 Conc.	8.39±0.14	4.09±0.11	0.05±0.01	0.12±0.03	0.25±0.03	0.26±0.06	5.56±0.11
Mbeu 7 Raw	13.68±0.03	4.62±0.42	0.06±0.01	0.21±0.03	0.13±0.02	0.00±0.02	1.13±0.02
Mbeu 7 Conc.	7.31±0.06	4.59±0.35	0.05±0.01	0.16±0.03	0.08±0.02	0.01±0.01	1.10±0.02
Mbeu 9 Raw	16.72±0.05	3.23±0.04	0.12±0.01	0.28±0.04	0.24±0.02	0.02±0.01	0.32±0.01
Mbeu 9 Conc.	12.45±0.09	3.12±0.04	0.08±0.01	0.23±0.04	0.19±0.04	0.01±0.01	0.29±0.02
Mbeu 10 Raw	9.06±0.05	2.25±0.02	0.66±0.05	0.26±0.02	0.31±0.02	0.00±0.00	0.41±0.02
Mbeu 10 Conc.	6.76±0.08	2.22±0.10	0.56±0.08	0.22±0.03	0.23±0.05	0.02±0.01	0.30±0.06
Kaharate 1 Raw	8.56±0.05	7.44±0.05	0.07±0.01	0.37±0.01	0.09±0.01	0.06±0.01	0.40±0.01
Kaharate 1 Conc.	6.23±0.10	6.88±0.12	0.06±0.01	0.31±0.02	0.06±0.01	0.05±0.01	0.32±0.04
Kaharate 2 Raw	16.05±0.12	2.24±0.02	0.08±0.01	0.21±0.02	0.33±0.01	0.06±0.01	1.01±0.03
Kaharate 2 Conc.	8.32±0.08	2.18±0.06	0.06±0.01	0.15±0.04	0.22±0.05	0.04±0.01	0.87±0.05
Kaharate 3 Raw	16.68±0.03	9.85±0.05	0.08±0.01	0.28±0.01	0.33±0.01	0.07±0.0	1.86±0.03
Kaharate 3 Conc.	7.11±0.08	9.45±0.09	0.06±0.01	0.21±0.03	0.26±0.05	0.06±0.01	1.24±0.09
Kaharate 4 Raw	19.19±0.03	6.84±0.03	0.15±0.01	0.31±0.01	0.23±0.01	0.11±0.01	2.04±0.06
Kaharate Conc.	10.34±0.10	6.39±0.07	0.13±0.03	0.16±0.08	0.14±0.04	0.09±0.01	1.57±0.12
Gitong'o A Raw	18.41±0.09	19.04±0.17	0.06±0.01	0.12±0.15	0.13±0.03	0.04±0.01	0.40±0.02
Gitong'o Conc.	7.22±0.04	9.47±0.08	0.08±0.01	0.06±0.01	0.07±0.01	0.06±0.01	0.39±0.09
Gitong'o B Raw	16.19±0.08	18.73±0.12	0.08±0.02	0.29±0.05	0.13±0.03	0.05±0.01	0.42±0.04
Gitong'o B Conc.	3.71±0.04	5.28±0.06	0.08±0.01	0.38±0.02	0.20±0.02	0.07±0.02	0.43±0.06
Gitara Kianderi Raw	17.55±0.06	16.04±0.08	0.13±0.03	0.30±0.03	0.16±0.02	0.07±0.01	1.04±0.04
Gitara Kianderi Conc.	2.50±0.08	3.57±0.06	0.43±0.06	0.65±0.05	0.04±0.01	0.63±0.06	0.80±0.10

Key: M-Mbeu, K-Kaharate, GA – Gitong'o quarry A, GK – Gitara Kianderi, Conc. Means thermally reduced ores followed by magnetic separation. Raw means untreated samples

Appencix XVII: Chemical Composition of Samples from Level C (100 cm) after Heating with Biomass at a ratio 1:10 Followed by Magnetic Separation

Sampled Sites	**%(**w/w**) OXIDE CONTENT (**Mean ± SD)						
Level C	SiO_2	Al_2O_3	CaO	MgO	Na_2O	K_2O	MnO
Mbeu 1 Raw	10.82±0.04	0.24±0.02	0.03±0.01	0.24±0.02	0.30±0.02	0.00±0.00	0.6± 0.03
Mbeu 1 Conc.	5.27±0.06	0.17±0.05	0.03±0.01	0.16±0.03	0.11±0.03	0.02±0.01	0.42±0.04
Mbeu 3 Raw	7.88±0.05	9.49±0.04	0.13±0.01	0.34±0.02	0.31±0.03	0.81±0.02	1.3±0.03
Mbeu 3 Conc.	4.94±0.09	5.46±0.06	0.07±0.01	0.27±0.04	0.25±0.04	0.51±0.04	0.74±0.06
Mbeu 4 Raw	19.75±0.04	3.56±0.02	0.09±0.02	0.31±0.03	0.06±0.02	0.79±0.02	2.4±0.17
Mbeu 4 conc.	7.62±0.20	2.81±0.08	0.09±0.01	0.22±0.03	0.06±0.02	0.55±0.07	0.65±0.06
Mbeu 7 Raw	12.69±0.03	0.28±0.03	0.05±0.01	0.15±0.01	0.08±0.02	0.00±0.00	0.3±0.53
Mbeu Conc.	3.85±0.13	0.23±0.04	0.04±0.02	0.12±0.04	0.05±0.01	0.01±0.01	0.06±0.02
Mbeu 9 Raw	16.73±0.06	3.93±0.02	0.14±0.02	0.31±0.02	0.23±0.02	0.02±0.01	0.3±0.01
Mbeu 9 Conc.	6.46±0.10	3.55±0.09	0.11±0.02	0.18±0.04	0.15±0.03	0.03±0.01	0.30±0.04
Mbeu 10 Raw	13.19±0.04	1.22±0.03	0.06±0.02	0.25±0.02	0.34±0.01	0.00±0.00	0.4±0.02
Mbeu 10 Conc.	6.66±0.08	1.16±0.04	0.04±0.01	0.21±0.03	0.22±0.08	0.01±0.01	0.31±0.04
Kaharate 1 Raw	8.87±0.02	7.45±0.03	0.09±0.01	0.39±0.01	0.11±0.01	0.07±0.01	0.4±0.01
Kaharate 1 Conc.	6.65±0.13	7.11±0.12	0.06±0.02	0.31±0.04	0.10±0.02	0.05±0.01	0.32±0.04
Kaharate 2 Raw	16.16±0.02	3.24±0.02	0.08±0.01	0.22±0.01	0.34±0.01	0.07±0.02	1.0±0.01
Kaharate 2 Conc.	8.23±0.10	2.13±0.03	0.05±0.01	0.14±0.04	0.30±0.03	0.05±0.01	0.88±0.09
Kaharate 3 Raw	16.73±0.03	9.89±0.02	0.08±0.01	0.29±0.01	0.33±0.02	0.08±0.01	1.8±0.02
Kaharate 3conc.	7.56±0.10	8.83±0.16	0.06±0.01	0.25±0.03	0.25±0.05	0.06±0.01	1.59±0.06
Kaharate 4 Raw	19.22±0.01	7.87±0.02	0.17±0.01	0.32±0.01	0.24±0.02	0.11±0.01	2.0±0.03
Kaharate 4 Conc.	12.32±0.16	6.98±0.13	0.11±0.02	0.29±0.03	0.13±0.09	0.08±0.01	1.86±0.09
Gitong'o A Raw	18.41±0.10	18.90±0.21	0.18±0.16	0.04±0.01	0.46±0.64	0.04±0.01	0.3±0.02
Gitong'o A Conc.	3.54±0.13	6.21±0.03	0.21±0.04	0.30±0.06	0.09±0.02	0.33±0.06	0.38±0.02
Gitong'o B Raw	16.26±0.17	18.60±0.11	0.10±0.02	0.28±0.02	0.12±0.02	0.05±0.01	0.4±0.05
Gitong'o B Conc.	4.29±0.08	5.45±0.12	0.27±0.06	0.56±0.09	0.24±0.31	0.25±0.06	0.56±0.07
Gitara Kianderi Raw	17.40±0.19	16.04±0.07	0.14±0.01	0.23±0.05	0.15±0.02	0.08±0.01	1.0±0.07
Gitara Kianderi Conc.	6.47±0.06	7.29±0.05	0.25±0.03	0.62±0.05	0.06±0.01	0.59±0.06	1.15±0.05

Key: M-Mbeu, K-Kaharate, GA – Gitong'o quarry A, GK – Gitara Kianderi, Conc. Means thermally reduced ores followed by magnetic separation. Raw means untreated samples

Appendix XVIII: Statistical Comparison Between Concentration Using Various Methods

Titanium dioxide percentages from froth flotation and charcoal using magnetic separation

Sample	Level	Raw sample	Charcoal	Froth flotation	**tcal**	**$t_{critical}$**
Githongo A	level A	1.77±0.04	5.41±0.09[a]	5.13±0.11[a]	**3.412**	2.78
	level B	1.77±0.08	5.92±0.05[b]	5.72±0.08[b]	**3.672**	2.78
Sample	level C	1.66±0.11	5.89±0.08[b]	5.61±0.11[b]	**3.566**	2.78
Githongo B	level A	1.61±0.03	5.42±0.04[a]	5.08±0.11[a]	**5.031**	2.78
	level B	1.62±0.06	5.69±0.07[b]	4.92±0.10[a]	**10.93**	2.78
	level C	1.63±0.05	5.96±0.23[b]	4.82±0.05[b]	**8.389**	2.78

Titanium dioxide percentages from Charcoal and *lantana camara* charcoal using magnetic separation

Sample	Level	Raw sample	Charcoal	***Lantana camara***	**tcal**	**$t_{critical}$**
Githongo A	level A	1.77±0.04	5.21±0.09[a]	**7.43±0.09[a]**	**24.67**	2.78
	level B	1.77±0.08	5.82±0.05[b]	**7.83±0.07[c]**	**33.04**	2.78
	level C	1.66±0.11	5.74±0.08[b]	**7.24±0.06[b]**	**21.21**	2.78
Githongo B	level A	1.61±0.03	4.98±0.04[a]	**8.49±0.13[b]**	**36.50**	2.78
	level B	1.62±0.06	5.69±0.07[b]	**7.76±0.09[a]**	**25.68**	2.78
	level C	1.63±0.05	5.96±0.23[b]	**8.48±0.15[b]**	**12.99**	2.78

Titanium dioxide percentages from Charcoal and Rice husks charcoal using magnetic separation

Sample	Level	Raw sample	Charcoal	**Rice husks**	**tcal**	**$t_{critical}$**
Githongo A	level A	1.77±0.04	5.21±0.09[a]	**7.27±0.05[a]**	**28.30**	2.78
	level B	1.77±0.08	5.82±0.05[b]	**7.91±0.06[c]**	**42.91**	2.78
	level C	1.66±0.11	5.74±0.08[b]	**7.34±0.05[b]**	**29.98**	2.78
Githongo B	level A	1.61±0.03	4.98±0.04[a]	**8.53±0.07[c]**	**62.27**	2.78
	level B	1.62±0.06	5.69±0.07[b]	**7.87±0.04[a]**	**29.00**	2.78
	level C	1.63±0.05	5.96±0.23[b]	**8.39±0.08[b]**	**14.11**	2.78

Titanium dioxide percentages from Rice husks and *lantana camara* both using magnetic separation

Sample	Level	Raw sample	**Rice husks**	***Lantana camara***	**t_{cal}**	**$t_{critical}$**
Githongo A	level A	1.77±0.04	**7.27±0.05[a]**	**7.43±0.09[a]**	**2.692**	2.78
	level B	1.77±0.08	**7.91±0.06[c]**	**7.83±0.07[c]**	**1.503**	2.78
	level C	1.66±0.11	**7.34±0.05[b]**	**7.24±0.06[b]**	**2.218**	2.78
Githongo B	level A	1.61±0.03	**8.53±0.07[c]**	**8.49±0.13[b]**	**0.469**	2.78
	level B	1.62±0.06	**7.87±0.04[a]**	**7.76±0.09[a]**	**1.582**	2.78
	level C	1.63±0.05	**8.39±0.08[b]**	**8.48±0.15[b]**	**0.917**	2.78

Appendix XIX: Composition by Mass of Titanium Dioxide Before and after Concentration

Area	Mass of Titanium dioxide after concentration	Mass of TiO_2 in raw sample used
Gitong'o A level A	0.26	0.352
Gitong'o A level B	0.22	0.358
Gitong'o A level C	0.24	0.334
Gitong'o B- level A	0.20	0.318
Gitong'o B -level B	0.27	0.324
Gitong'o B -level C	0.23	0.328
Gitara Kianderi level A	0.18	0.312
Gitara Kianderi level B	0.21	0.32
Gitara Kianderi level C	0.21	0.314

Appendix XX: Statistical Comparison of Titanium Dioxide in the Different Levels

Showing Statistical comparison of Titanium dioxide in level A and B of Raw Laterites Samples

Sample	M_1	M_3	M_4	M_7	M_9	M_{10}	K_1	K_2	K_3	K_4	GA	GB	GK
Level A	4.80± 0.03	3.03± 0.02	4.99± 0.11	5.21± 0.04	5.66± 0.03	4.29± 0.03	7.66± 0.02	4.16± 0.02	4.50± 0.04	5.15± 0.01	1.81± 0.04	1.61± 0.03	1.60± 0.04
Level B	4.75± 0.06	2.96± 0.10	4.83± 0.08	5.16± 0.05	6.62± 0.08	4.31± 0.02	7.62± 0.04	4.15± 0.03	4.51± 0.03	5.13± 0.01	1.77± 0.02	1.62± 0.02	1.59± 0.03
tcal	2.58	1.19	2.04	1.35	0.77	0.96	1.39	1.22	3.12	2.45	1.55	0.48	0.35

Key:
M-Mbeu, K-Kaharate, GA-Gitong'o quarry A, GB – Gitong'o quarry B, GK – Gitara Kianderi

Showing Statistical comparison of Titanium dioxide in level B and C of Raw Laterites Samples

Sample	M_1	M_3	M_4	M_7	M_9	M_{10}	K_1	K_2	K_3	K_4	GA	GB	GK
Level B	4.75± 0.06	2.96± 0.10	4.83± 0.08	5.16± 0.05	6.62± 0.08	4.31± 0.02	7.62± 0.04	4.15± 0.03	4.51± 0.03	5.13± 0.01	1.77± 0.02	1.62± 0.02	1.59± 0.03
Level C	4.87 ± 0.02	3.09± 0.02	4.91± 0.08	5.14± 0.02	4.62± 0.09	3.39± 0.01	7.63± 0.01	4.36± 0.02	4.51± 0.03	5.19± 0.02	1.62± 0.11	1.63± 0.02	1.62± 0.05
Tcal	3.29	2.21	1.22	0.64	14.38	71.26	0.42	12.86	0.41	4.65	2.32	0.61	0.89

Showing Statistical comparison of Titanium dioxide in level A and C of Raw Laterites Samples

Sample	M_1	M_3	M_4	M_7	M_9	M_{10}	K_1	K_2	K_3	K_4	GA	GB	GK
Level A	4.8± 0.03	3.03± 0.02	4.99± 0.11	5.21± 0.04	5.66± 0.03	4.29±0.03	7.66± 0.02	4.16± 0.02	4.5±0.04	5.15± 0.01	1.81± 0.04	1.61± 0.03	1.6±0.04
Level C	4.87 ±0.02	3.09±0.02	4.91± 0.08	5.14± 0.02	4.62± 0.09	3.39± 0.01	7.63± 0.01	4.36± 0.02	4.51± 0.03	5.19± 0.02	1.62± 0.11	1.63± 0.02	1.62± 0.05
tcal	0.96	3.06	1.02	2.71	18.29	49.3	1.64	11.64	2.77	3.1	2.81	0.96	0.54

Appendix XXI: Statistical Comparison of Titanium Dioxide in Concentrated and Raw Samples

Showing Statistical comparison of Titanium dioxide in concentrated and Raw Laterites Samples at Level A

Sample	M_1	M_3	M_4	M_7	M_9	M_{10}	K_1	K_2	K_3	K_4	GA	GB	GK
LEVEL A coc	5.16± 0.04	4.96± 0.05	5.65± 0.09	5.57± 0.10	6.53± 0.18	4.70± 0.06	7.74± 0.10	5.82± 0.06	4.93± 0.05	5.45± 0.10	7.43± 0.09	8.49± 0.13	4.43± 0.09
Level A raw	4.85± 0.03	3.04± 0.02	4.99± 0.11	5.21± 0.04	5.66± 0.03	4.29± 0.03	7.66± 0.02	4.17± 0.02	4.50± 0.04	5.15± 0.01	1.81± 0.04	1.61± 0.03	1.60± 0.04
tcal	10.7	61.8	8.04	5.79	8.17	10.6	1.33	45.2	9.2	5.17	98.8	89.3	49.8

Showing Statistical comparison of Titanium dioxide in Concentrated and Raw Laterites Samples at level B

Sample	M_1	M_3	M_4	M_7	M_9	M_{10}	K_1	K_2	K_3	K_4	GA	GB	GK
LEVEL B conc	4.94± 0.19	4.85± 0.10	5.67± 0.06	5.69± 0.10	5.84± 0.10	4.93± 0.12	7.82± 0.10	5.67± 0.19	5.26± 0.06	5.85± 0.11	7.83± 0.07	7.76± 0.09	5.30± 0.08
Level B raw	4.75± 0.06	2.96± 0.10	4.83± 0.08	5.16± 0.05	6.62± 0.08	4.31± 0.02	7.62± 0.04	4.15± 0.03	4.51± 0.03	5.13± 0.01	1.77± 0.02	1.62± 0.02	1.59± 0.03
tcal	1.65	23.2	14.6	8.21	2.98	8.83	3.22	13.8	19.6	11.3	114.2	115.4	75.21

Showing Statistical comparison of Titanium dioxide in Concentrated and Raw Laterites Samples at Level C

Sample	M_1	M_3	M_4	M_7	M_9	M_{10}	K_1	K_2	K_3	K_4	GA	GB	GK
level C conc.	5.04± 0.09	4.28± 0.07	5.56± 0.11	5.36± 0.08	4.96± 0.05	4.24± 0.08	7.87± 0.10	5.41± 0.06	5.31± 0.05	5.69± 0.05	7.59± 0.06	8.48± 0.15	4.83± 0.05
level C raw	4.87± 0.02	3.09± 0.02	4.91± 0.08	5.14± 0.02	4.62± 0.09	3.39± 0.01	7.63± 0.01	4.36± 0.02	4.51± 0.03	5.19± 0.02	1.62± 0.11	1.63± 0.02	1.62± 0.05
tcal	3.19	28.3	8.28	4.62	5.72	18.3	4.14	28.8	23.8	16.1	82.5	78.4	78.6