

Minerals, Major and Trace Element Contents of Soils from Termiteria (Ant Mounds) and 10 Meter (10 M) Adjacent Soils in Girei, Adamawa, Nigeria

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Abstract- Geozoological method of prospecting for minerals is one of the easier, cheaper and indirect ways of assessing mineral deposit. The current work assessed the distribution of minerals, major and trace element contents of termiteria and 10 M adjacent soils from Girei local government area of Adamawa state, Nigeria during rainy and dry season. X-ray diffraction (XRD) method of analysis was used for identification of the minerals present in the samples while the elemental contents of the samples were determined by the use of X-ray fluorescence (XRF) method. Six different minerals were identified in the study area which arranged in terms of abundance as follows; quartz > rutile > kaolinite > (anatase and fluorite) > corundrum. Quartz, rutile and kaolinite were the most abundant minerals identified in the study area. Major element determined were: Al, Si, S, K, Na, Ca, Mg, Fe, Mn and Ti, Trace elements include; Ni, Cr, V, Cu, Ba, Zn, Sr, As, Ir, Pb, Ga, Rb, Zr, Yb, Eu, Re, and Ag. The result is presented as mean of three replicate measurements and their standard deviations. Si has the highest value ranging from $(49.6 \pm 0.1 - 46.7 \pm 0.2)\%$ that of adjacent soil is $(65.6 \pm 0.2 - 49.6 \pm 0.9)\%$. Al is the second with range of $(17.0 \pm 0.25 - 13.0 \pm 0.02)\%$ in termiteria while its adjacent soil has range as $(7.77 \pm 0.07 - 4.02 \pm 0.12)$ followed by those of K, Fe and Ti. Trace elements determined were very low even at the ppm levels. Analysis of variance (ANOVA) was used to test for variation between the elemental composition of the termiteria soils and those of 10 M surrounding soils. Generally, statistically there is no significant difference between the elemental composition of the termiteria soils and those obtained from 10 M adjacent soils in the study area ($P < 0.05$). This indicates that the elements are distributed around the termiteria as far as 10 M away. In addition, termiteria can serve as a tool for exploring underground minerals deposit.

Index Terms- Analysis, elemental composition, geozoological method, termiteria

I. INTRODUCTION

Soil is described as a natural body differentiated into horizons of loose unconsolidated minerals and organic matter of variable depth on the earth crust and capable of supporting plant growth and that the contents; air, water, organic matter and minerals are in intimate contact with each other with 96% minerals (Singh, 2009). Mineral is an inorganic substance that occurs naturally in rocks and in the ground and has its own characteristics. More than 30,000 mineral species are known

most of which are characterized by definite chemical compositions, crystalline structures and physical properties, primarily they are classified by chemical compositions, crystal class, hardness and appearance (colour, luster and opacity) and as a rule are restricted to solids with the exception of mercury and water and hence all the metalliferous minerals of economic value which are mined for their metals are described as solid minerals. (Redmond, 2008). Minerals have occupied important place in the lives of modern man that the more available they are in a useful manner the higher the living standard of the users as they determined the status of a country politically, economically, technologically and are keys to the overall total development of our modern societies (Botkins and Keller, 1998). Several authors have shown that there is positive relationship between the economic status of a society and availability of its mineral resources once exploited. Furthermore, a physical need of man is met by agriculture and mining activities (Abaa and Najime, 2006). The fact that solid minerals are not evenly distributed over the earth implies that they are not easily obtainable. It takes time, money and expertise to explore, extract and put them into useful forms. Developing countries especially, Nigeria derives numerous benefits from small scale mineral and material producing operations (Woakes, 1982). Though mineral exploration and extraction is not new in Nigeria for instance, before the advent of the British several communities have been mining mineral resources such as gold, galena, lead, zinc etc and used as cosmetics locally, in fact the recorded production of lead/zinc ore from Enyigba mine was as early as 1925. (Orazulike, 1994). Despite such a long history, statistics shows that solid mineral in Nigeria has been under developed (contributing less than 1% of the GDP) while its counterparts, the fuel mineral resources were developed. Currently, the federal government has acknowledged solid mineral as a potential alternative to the petro-industry for foreign exchange earnings and has set to revitalizing the sector. This is because mineral resources are the foundation upon which an industrialized economy is built, furthermore petroleum industry provides only 6% of Nigeria labour force and over dependence on petroleum industry leaves the economy vulnerable to both international politics and fluctuation in oil prices (Gill, 2011).

Generally, exploration of solid mineral deposit is an expensive task and the gambling associated with it is discouraging to the mining entrepreneurs, more especially when after spending time, energy and fund the result proves abortive. It is of utmost importance therefore to optimize the exploration expenses and to minimize the risks of mining investment (Fodor

and Bardossy, 2005). According to Orazulike (2012), discovery of mineral deposits is achieved through exploration by geochemical, geological and geophysical methods. In addition, novel methods of mineral exploration have been successfully used to locate prospective mineral deposits, these help to reduce demands associated with the exploration stage of mining. The methods indirectly assess the presence or absence of underground solid mineral deposits, through analyzing plants to determine mineral ore deposit in the soil of a particular area, this method is known as biogeochemical exploration (Dunn, 1995), use of animals and insects, termitaria inclusive (Spore, 1996;). The latter unique method is termed geozoological method of prospecting for solid minerals. Termitaria soils have been analyzed to serve as bio-indicator of mineral deposit (Reddy, 2014).

Termites are small soft-bodied social insects classified at the taxonomic rank order of Isoptera (Adeyeye, 2005). There are conflicting figures in the estimation of species of termites, for instance, there are 2000 species of termites (Ndu, Asun and Aina, 2001; Raven and Johnson, 1995) and 4000 species of termites (Wikipedia, 2013). Termites live in nests built from underground soils, the types of nests are associated with the species of termites that built them. Nests are classified as ground mound, subterranean, pole and tree nests (Adekayode and Ogunkoya, 2009). Anthills, ant mounds, and ant nests are used interchangeably to refer to "termitarium", which is the scientific name (Spore, 1996; Falgariat et al., 2003).

Ecologists view anthills as natural disruptions that maintain heterogeneity in an ecosystem (Bode, Goose and Warpehoski, 2013). But termites and the termitaria are much more than this, this is because of their numerous uses, few among which are: as food, soil amendment, building blocks, ritual clay, tool for mineral exploration, geopathagy (Spore, 1996; Kgomotso, 2007; Adeyeye, 2005). Termites are categorized according to the shapes of their termitaria and methods of feeding for instance; the forager termites *Trinervitermes* build dome-shaped mounds usually less than a metre in height, mushroom-shaped mounds are built by decomposers, *Cubitermes*, (Spore, 1996) and the most prominent in Africa the fungus termites, *Macrotermes* which live in cathedral mound as high as 20 meters dotting many landscape of tropical grassland (Retallack, 1990). The processes involved in building these large epigeal mounds lead to concentration of minerals in the termitaria since soils as deep as 50 M below the earth surface are brought up to the surface (Daniel and Emanu, 2014). Geopathagy is a practice of eating soil more especially clay from termitaria. This habit is practised by over 200 species of animals, including human beings and have been shown to provide some deficient minerals yet, there may be the danger of trace element poisoning if not screened.

X-ray diffraction technique (XRD), has been reported to be a helpful method which relies on sophisticated instruments for identifying phases in crystalline substances quantitatively and or qualitatively including soil samples. (Connolly, 2012). Most of the modern XRF instruments are capable of analyzing solid liquid and thin film samples for both major and trace components in samples to the limit of part per million level. (Ferguson, 2012). The aim of this research work was to assess the mineral and the distribution of the elemental contents of soils from termitaria sampled in Girei local government areas of Adamawa state,

Nigeria during rainy and dry seasons. The objectives were: to identify minerals in the study area, to quantitatively determine both the major and the trace elements and to compare their values with those obtained from 10 meter adjacent soils.

II. MATERIALS AND METHODS

Materials - The following instruments, equipment and apparatus were used during this work:

X-ray Fluorescence Spectrophotometer (XRF), X-ray diffractometer (XRD), core scoop, hammer, polythene bags, sieve, Pestle and mortar, spade, crucibles, analytical balance.

Sampling and Sample Preparation

Sampling Technique - Geozoological method of prospecting for solid minerals sampling technique was utilized In this method, soils from termitaria were sampled and analyzed for presence of solid minerals which in turn served as an indicator of underground mineral deposits (Pray, 2013).

Sampling area, locations and sites

The study area, Girei is the sampling area of the current work, Girei is the headquarter of Girei local government area, one of the twenty one local government areas in Adamawa state, Nigeria. It is located at the bank of River Benue with coordinates: 9°22'N & 12°33'E. The sampling area was stratifically divided into two locations (east- west) from where a termitarium and its 10 M adjacent soil were chosen as sampling sites in each location.

Sample collection

Method of Bode et al., (2013) was adopted with some modifications, where termitaria were surveyed in the sampling location with the help of the local residents. Termitaria of various sizes were randomly chosen for sampling. Three samples were taken with core scoop to form a composite sample of each sampling site. Control samples were taken from the depth of 0 – 50 cm located at 10 M away from each termitaria in the four cardinal directions as in figure 1. The soil samples were mixed to form composite control sample and stored in properly labeled polythene bags and conveyed to the laboratory.

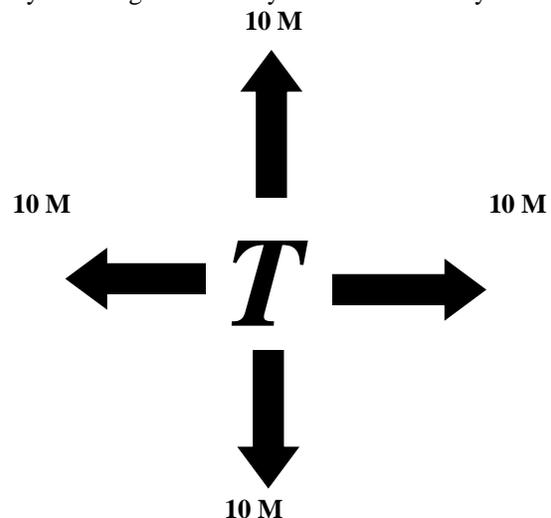


Figure 1: Outline of sampling plan

T = termiteria sampling site

10 M = 10 meter away soil sampling site

Sample Preparation

Soil samples were dried by spreading them on clean polythene sheet in the laboratory for seven days. The dried soil samples were ground using mortar and pestle and sieved to obtain powder form. Gross samples were reduced to test sample sizes through the process of cone and quartering (Okunola et al., 2008). The method involved forming cone shape with the sample and dividing it into four equal portions and taking the two opposite sides of the quarter while the other two quarters were discarded. The retained two quarters were recombined and the process was repeated until about 100g of the sample was obtained.

Analytical Studies of the Samples

X-ray diffraction analysis of the samples were carried out at National Geoscience Research Laboratory Centre, Kaduna (Nigerian Geological Survey Agency) following a modified method outlined by Adesaki and Olunlade (2011). Ground soil sample weighing 0.35g was placed into a sample holder of the computer interfaced XRD instrument and then smeared uniformly on a glass slide to ensure upper surface was flat so as to achieve random distribution of lattice orientation. This was then packed into a sample container and sprinkle on double sticky tape. X-ray of CuK α with wavelength of 1.5418 was used to scan between 2 θ of 10 $^\circ$ and 2 θ of 45 $^\circ$ at increments of 0.04 $^\circ$ with count time of four seconds for each step. Count time of four seconds gave good signal to noise ratio and enabled the analysis to occur at appropriate period. Intensity of the diffracted rays was recorded continuously as the sample and the detector rotated through their respective angles. Peak intensity occurred when mineral containing lattice with d-spacing diffract x-ray at that value of θ . Each peak was made up of two separate reflections k_1 and k_2 , at small values of 2 θ the peak locations overlapped with k_2 and appeared as a hump on the side of k_1 , these combined peaks were considered as one. Higher values of θ yield greater separation of peak where the 2λ position of the diffraction peak was measured at the center of the peak at 80% peak height.

Presentation of result of x-ray analysis was at peak positions at 2 θ and x-ray counts (intensity) in the form of x-ray plot. Intensity was reported as peak height intensity. Relative intensity was recorded as the ratio of the peak to that of the most intense peak. Thus;

$$\text{Relative intensity} = \frac{I_x \times 100}{I_i}$$

Where I = peak intensity, I_i = most intense peak.

The d-spacing of each peak was obtained by solution of the Bragg equation for appropriate value of λ , that is; $n\lambda = 2d\sin\theta$. when d-spacing was determined, automated/match routines compared the d-spacing of the unknown to the known substance.

X-ray fluorescence procedure for determination of minerals in soil as described by Baranowska et al. (2002) was adopted. 20g of each of the ground soil samples was fused with 0.40g stearic acid in a 20ml platinum crucible and press with hydraulic

press. The fused button was then x-rayed and counted to determine the elements, the excitation source emitted Ag-k x-ray (22.1 KeV) hence all elements with lower characteristics excitation energy were detected in the samples.

III. RESULTS AND DISCUSSION

Results of analysis from this research work were presented and discussed below. Minerals identified by XRD analysis of the samples from Girei local government area of Adamawa State, Nigeria were presented in Tables 1. Results obtained from XRF elemental analysis of the samples were presented in figures 2 and 3. .

Table1 shows the minerals identified by XRD in the samples from the study area. Six different minerals were identified in Girei which could be arranged in terms of abundance as follows; quartz > rutile > kaolinite > (anatase and fluorite) > corundrum . Quartz, rutile and kaolinite were the most abundant minerals identified in the study area, this agrees with the result of a similar work reported by Ptacek et al. (2013). Rutile was identified in all the samples from Girei with the exception of only one site (Tr), on the other hand its polymorph anatase was detected in two locations only (10 M^e and 10 M^w)(table 1). The most abundant form of TiO $_2$ in the study area is rutile this is because it is the most stable polymorph compared to anatase. Both anatase and rutile are oxides of titanium , rutile (TiO $_2$) occupies important place in paint industries because it has high refractive index, strong absorption of UV region of light spectrum and strong reflectance in the visible spectrum which gives it a light scattering properties in addition to particle size which makes it effective pigment for brightness and opacity (Alabi and Omojala,2013). Anatase is the rarest of the polymorphs, it is cherished for its aesthetic value as a jewel .Appearance of fluorite in 10 M adjacent soils in both rainy and dry seasons in Girei west may be due to presence of its ore deposit at sample site or possibly it was leached from its deposit to the present sampling site because it was not detected in any of the termiteria soil samples. CaF $_2$ occurs in hydrothermal veins, cavities in sedimentary rocks, sandstones or hot springs deposits (<http://www.mindat.org/contact.php>). Koalinite was present in all the sample sites in Girei apart from sample sites 10 M east and 10 M west during rainy season (table 1), this may be attributed to the interesting fact which shows that kaolinite clay from termiteria can undergo thermal transformations to result into various compounds culminating into cristoballite. According to Ptacek et al.(2013),

Table 1: Minerals identification in termitera (T) and 10 meter surrounding (10m) soils in Girei Local Government Area.

Minerals	Compound name	Chemical formula	Crystal system	Girei East				Girei West			
				Tr	Td	10mr	10md	Tr	Td	10mr	10md
Anatase	Titanium oxide	TiO ₂	Tetragonal	-	-	-	-	-	-	*	*
Corundum	Aluminum oxide	Al ₂ O ₃	Rhombohedral	-	-	-	*	-	-	-	-
Flourite	Calcium Flouride	CaF ₂	Cubic	-	-	-	-	-	-	*	*
Koalinite	Aluminum silicate hydroxide	Al ₂ Si ₂ O ₅ (OH ₄)	Anorthic	*	*	-	*	*	*	-	*
Quartz	Silicon oxide	SiO ₂	Hexagonal	*	*	*	*	*	*	*	*
Rutile	Titanium oxide	TiO ₂	Tetragonal	-	*	*	*	*	*	*	*

Key: r = Rainy Season, d = Dry Season, — = Absent, * = Present

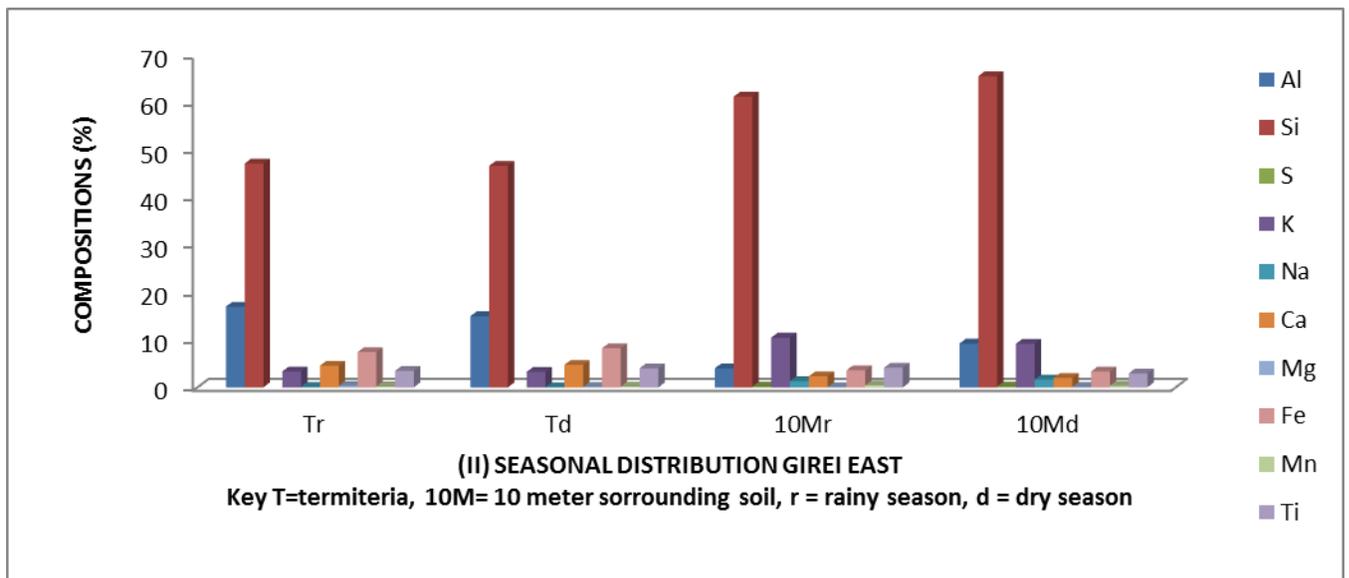
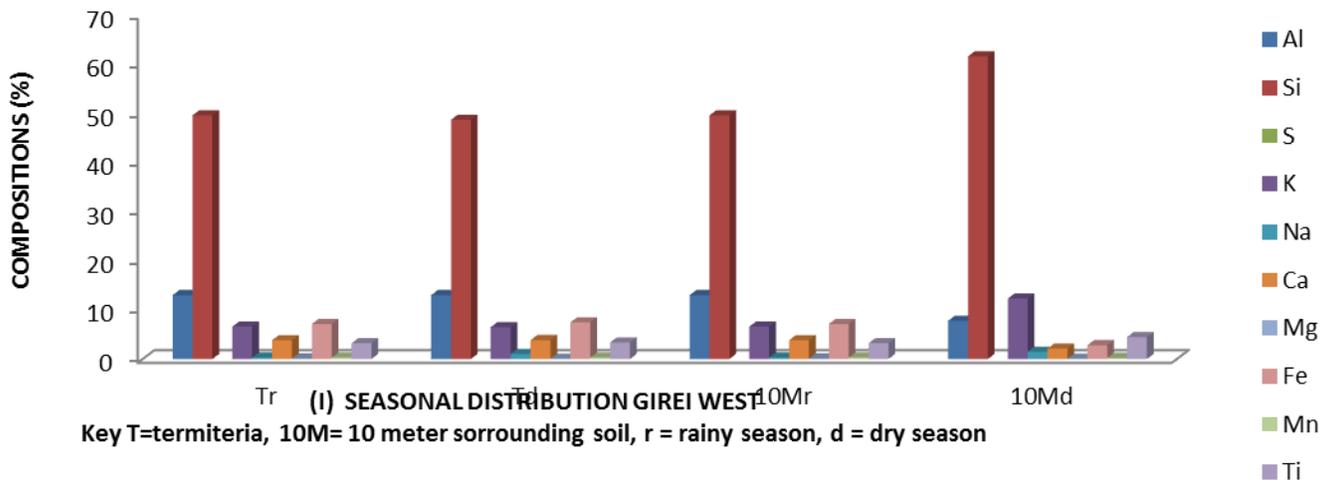


Figure 2: (i) & (ii), Comparisons of Major Elemental composition of termiteeria (T) and 10 M surrounding soils in Girei local government area for the two seasons

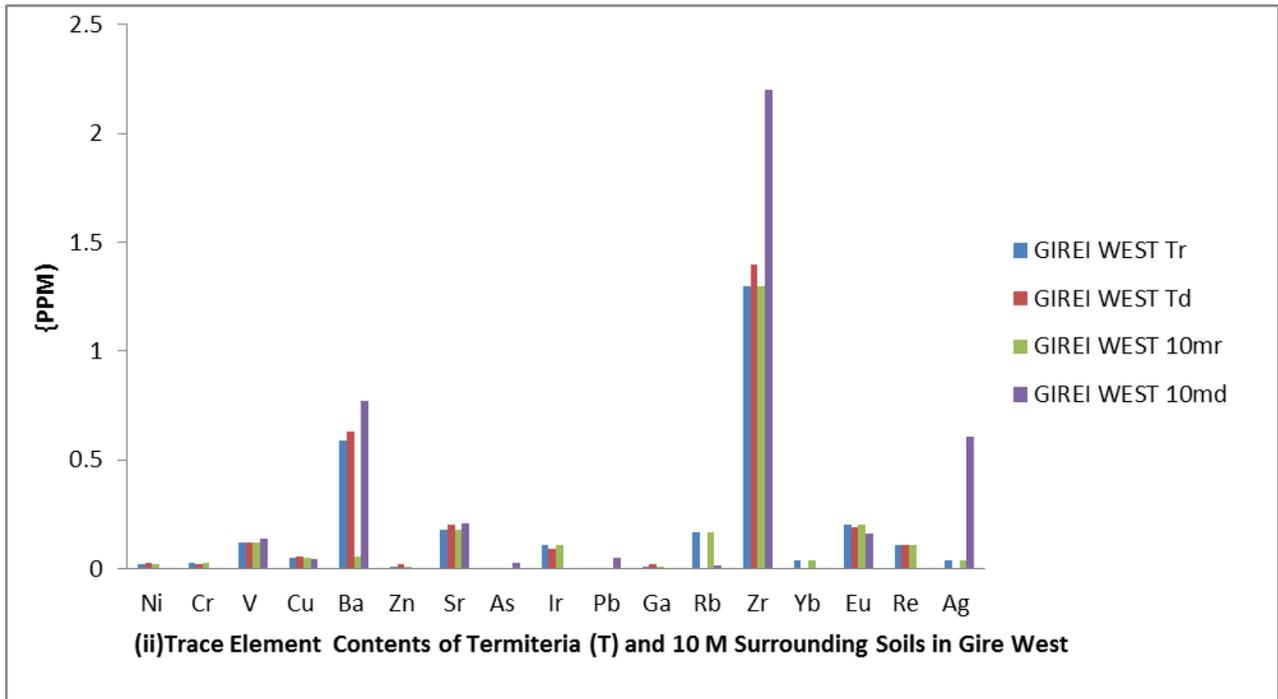
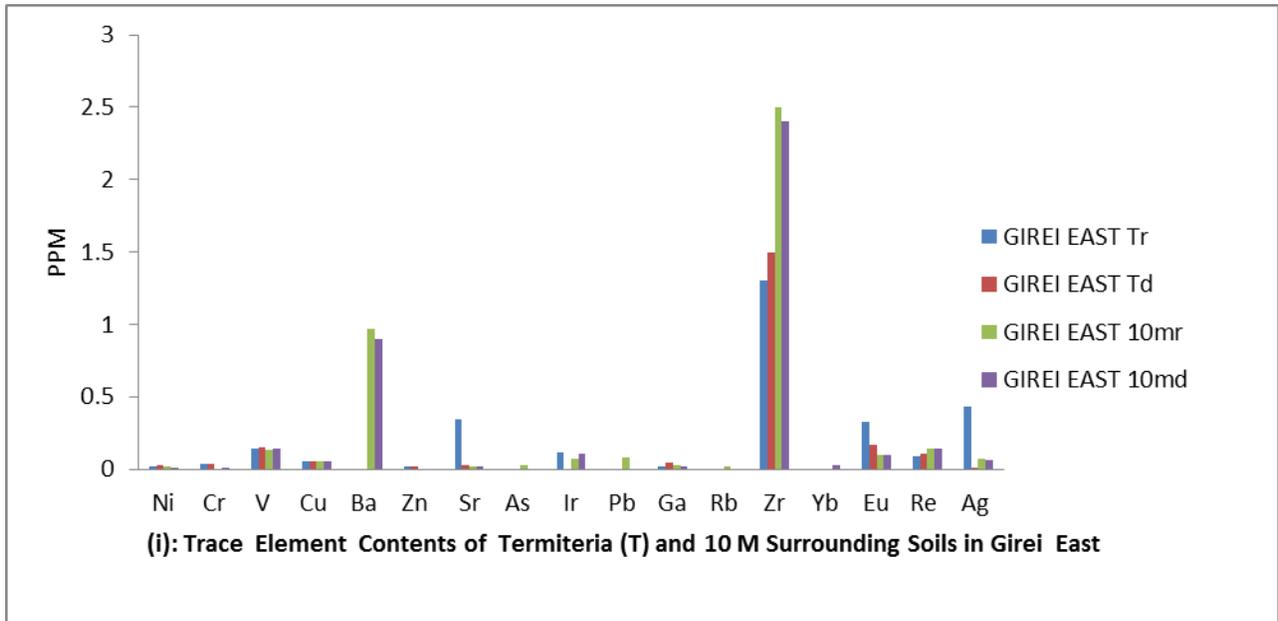
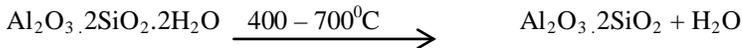


Figure 3 : (i) & (ii) Trace Element Contents of Termiteria and 10 M Surrounding Soils in Girei

The stages involved in the thermal transformation of kaolinite are:

Dehydroxylation of Kaolinite into Metakaolinite;



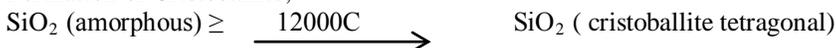
Formation of the Al- Si spinel phase;



Formation of the Mullite:



Formation of Cristoballite;



Among the several industrial uses of kaolin, its use as an alternative to TiO_2 as pigment in paints when it is calcined (alabi and Omojola, 2013).

Detection of corundum and abundance of quartz may be associated with the kaolinite thermal transformation.

The distribution of the elements as indicated by figures 2 and 3 generally supports the theory that eight elements accounted for 99% of the earth's crust by weight, these elements also known as rock forming elements are: O_2 46.6%, $\text{Si} = 28.2\%$. $\text{Al} = 8.2\%$, $\text{Fe} = 5.6\%$, $\text{Ca} = 4.2\%$, $\text{Na} = 2.4\%$, $\text{K} = 2.1$ and $\text{Ti} = 0.6\%$ (Botkin and Keller, 1998).

Al contents of termiteria soil fall within the range of $(17.0 \pm 0.3 - 13.0 \pm 0.0)\%$ while that of adjacent soil is $(13.0 \pm 0.1 - 4.0 \pm 0.1)\%$. The disparity between values of Al in termiteria and its 10 M adjacent soil is expected because kaolinite (compound of Al) was detected in all the termiteria soils while in 10M soils it was not detected in the two 10M sample sites (table 1). Si contents of termiteria soil has range of $(49.6 \pm 0.1 - 46.7 \pm 0.2)\%$ that of adjacent soil is $(65.6 \pm 0.2 - 49.6 \pm 0.9)\%$. Si contents of termiteria soil is slightly low compare to its adjacent soil this may be due to high clay contents of termiteria, nevertheless, Si has the highest value amongst the minerals this is because Si and Al are the second and third most abundant elements in the earth's crust, they naturally exist as aluminosilicate – minerals (Pinkas, 2005). K has range of, $(7.0 \pm 0.5 - 3.3 \pm 0.3)\%$ and $(12.3 \pm 0.5 - 6.6 \pm 0.0)\%$ in termiteria and 10 M adjacent soils respectively. Values of K in 10M sample doubled those obtained in the termiteria samples, this may be attributed to the natural deposit of K since minerals are not evenly distributed in the earth's crust (Botkin and Keller, 1998). Fe was detected in the range of $(8.2 \pm 0.2 - 7.1 \pm 0.1)\%$ in termiteria and $(7.5 \pm 0.1 - 2.8 \pm 0.7)\%$ in its 10M adjacent soil. Fe is the fourth most abundant element in the earth's crust. High content of Ti in the sample compare to its natural content in the earth can be attributed to its mineralization in the study area as TiO_2 (tables I). Generally, Mg and Ca contents of termiteria are slightly higher than the ones in the adjacent soils. This trend is usual because Ca, Mg, and K contents of termiteria have been reported to be higher than for soil unaffected by the termiteria soil, furthermore, most of the elements fall within the reported values for termiteria as; ($\text{Si} = 46.5$, $\text{Al} = 18.6$, $\text{Mg} = 1.6$, $\text{Fe} = 6.7$, $\text{Ti} = 1.4$, $\text{Ca} = 6.3$, $\text{K} = 2.0$ and $\text{Na} = 1.6$) % (Ptacek, 2013).

Seventeen trace elements were determined in the samples (figure 3, i & ii) at part per million levels. Quantitatively, these can be presented in the following sequence; $\text{Zr} > \text{Ba} > \text{Ag} > \text{Sr} > \text{Eu} > \text{V} > \text{Re} > \text{(others)}$. Zr ranges as $(1.5 - 1.3)$ ppm in termiteria, $(2.5 - 1.3)$ ppm in 10 M soils. Range for Ba is $(0.9 - 0.7)$ ppm, highest values for; $\text{Ag} = 0.6\text{ppm}$, $\text{Sr} = 0.3\text{ppm}$, $\text{Cr} = 0.04\text{ppm}$, $\text{Ni} = 0.01\text{ppm}$, $\text{V} = 0.13\text{ppm}$, $\text{Eu} = 0.3\text{ppm}$, $\text{Pb} = 0.08\text{ppm}$, $\text{As} = 0.03\text{ppm}$. Most of the trace element are under the class of alien substances to the body hence their presence in the body may cause damage to the organs hence the practice of geophagia has to be done cautiously.

Though there are slight variations between the values obtain for elemental contents of termiteria soils and those of the adjacent soils, statistically there is no significant difference $p < 0.05$. This indicates that the elements from the termiteria have distributed to the surrounding soils as far as 10 M away. This further explains reason for exceptionally good growth of plants around termiteria environment.

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