X-Ray Fluorescence (XRF) Characterization of Orile-Oje Archaeological Site, Ogbomosho, Southwestern Nigeria, for Suspected Ancient Ore Smelting Sites.

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ABSTRACT

Geochemical analysis of soil samples from Orile-Oje (or Igbo Oje) archaeological site had been carried out using X-ray Fluorescence (XRF) technique. This was with a view to determining the concentrations of the heavy metals in soils as a means of confirming suspected ancient smelting sites identified from a residual magnetic map.

Eight (8) soil samples (6 from anomalous magnetic zones ad 2 from non-anomalous magnetic zones, as control) were collected with the aid of hand shovel and placed in plastic containers, prepared into thick pellets of 13 mm diameter in Spec-caps and irradiated for 1000 seconds with X-ray using Energy Dispersive X-ray Fluorescence spectrometer with a Ag anode. Qualitative and quantitative interpretations of the sample spectra were done using analytical software for the following elements: K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Sr and Zr.

The concentrations of Fe, Cu, and Zn, from the anomalous magnetic zones are much higher than that from the control zones: 15.1 – 27.0 Wt % as against 4.8 – 5.3 Wt % for Fe; 3.7 – 5.9 Wt % as against 0.32 – 0.36 Wt % for Cu and 2.0 – 5.1 Wt % as against ND – 0.03 Wt % for Zn, respectively. However, the concentrations of iron (Fe) along traverses 3&4 are the highest (23.1 – 27.0 Wt %) followed by the anomalous zone along traverse 6 (15.7 – 17.8 Wt %) and then traverse 5 (15.1 – 15.4 Wt %). The concentrations of the heavy metals in the soil samples collected from anomalous zones along traverses 5 and 6 are relatively high and generally within the range observed in samples collected from the anomalous magnetic closure located along traverses 3 and 4 that coincides with a suspected iron ore smelting site with surface expression of a slag mound. The study concluded that the anomalous magnetic closures are indicative of ancient smelting sites.

(Keywords: XRF, archaeology, characterization, ancient ore smelting site, Orile-Oje, southwestern Nigeria)

INTRODUCTION

Elemental analyses have found useful applications in science-based archaeology. Such applications include but not limited to compositional analysis of synthetic and natural materials (including soils and sediments) and residues to ascertain artifact manufacturing processes and use; chemical and isotopic studies of biological remains and identification of plant and animal residues to investigate ancient diet, nutrition and resource use and other scientific investigations with regard to provenance and in the context of conservation and restoration (Obiajunwa et al., 2002; Pollard and Heron, 2006).

Although several analytical techniques including Spectrometric Methods, Nuclear Techniques, Mass Spectrometry and Chromatography have variously been applied in archaeological studies, the X-Ray Fluorescence Spectrometry (XRF) technique has remained the mainstay of both destructive and non-destructive (in situ) chemical analysis (Caneva and Ferretti, 2010; Gliozzo et al., 2011; and Tykot et al., 2011).

The interpretation of residual magnetic map over an archaeological site at Orile-Oje (or Igbo Oje) via Ogbomosho, Southwestern Nigeria, revealed the presence of magnetic anomalous zones along four out of the six traverses established over the surveyed site (Figure 1) (Eluyemi et al., 2012).

These anomalous zones display typical magnetic anomaly of a dyke-like body in low magnetic latitude (I < 3°) characterized by a magnetic low (negative polarity) flanked on both sides by low amplitude positive peaks. Such anomalous zones were delineated at the extreme north (NW and NE) and south central part and identified in rectangular blocks (Figure 1). The south central negative magnetic closure, identified across traverses 3 and 4, is located on a slag mound (along traverse 4) characteristic of an ancient ore smelting site. Similar anomalies, suspected to be iron ore smelting sites, observed along traverses 5 and 6, have no surface expression of slag mound.

This study involved soil sampling from five suspected iron ore smelting sites and two from non-anomalous magnetic zones serving as control (Figure 1), for elemental analysis with Energy Dispersive X-Ray Fluorescence (XRF). The study is predicated on the assumption that soil samples from an ancient iron ore smelting site will be characterized by relatively high concentration of iron (Fe) than the surrounding environment due to decomposed iron-fillings and other decomposable objects made of metal.

Iron decomposes or corrodes when it is left or abandoned for a long period of time in the presence of moisture, oxygen, and elevated temperature. The process of the decomposition can be expressed with the equation:

$$4Fe + 3O_2 \xrightarrow{H_2O} 2Fe_2O_3.$$

However, the same process holds for copper, zinc, and other metallic objects, but the rate of the decomposition may be a bit slower than in iron. The decomposed metal is found saturated within the environment where it might have been employed in the past thereby changing the natural geochemical composition of that particular environment.

MATERIAL AND METHODS

Geographic coordinates of the centers of the magnetic anomalous zones were read on the residual magnetic map and the locations along the respective traverses were re-occupied using Etrex Garmin GPS (Figure 1).

Eight (8) soil samples were collected with 6 of the samples (A-F) taken from the magnetic anomalous zones while the remaining 2 samples (G &H) were collected from the non-anomalous magnetic zones and used as control (Table 1). The soil samples were collected at a depth of 20 cm and placed inside a sterilized plastic container. The samples were prepared into thick pellets of 13 mm diameter in a Spec-caps (Obiajunwa, 2001) without binder.

A pellet of International Atomic Energy Agency (IAEA) Soil 7 Soil Standard was prepared. Both the soil samples and the standard were then irradiated for 1000 seconds with X-ray, using Energy Dispersive X-ray Fluorescence (EDXRF) spectrometer with a Ag anode. The equipment model is PX 2CR Power Supply and Amplifier for XR-100CR Si Detector, with facilities for spectral acquisition for qualitative and quantitative interpretation (Obiajunwa, 2001). Irradiation of samples was done in irradiation chamber and samples were irradiated for 1000 seconds under X-Ray tube operation condition of 25 Kv and 50 μA.

Qualitative interpretation of the sample spectra was carried out using PMCA Spectral acquisition software. The X-rays energy elements were detected on either the K-lines or the L-lines respectively (Figures 2 and 3). Quantitative interpretation was done with the aid of the XRS-FP analytical software under the Fundamental Parameter analytical method.

RESULTS AND DISCUSSION

Table 2 shows the results obtained from the analysis of standard (soil 7) ran with the samples as a measure of the accuracy of the experimental values and the corresponding certified values.

Table 3 displays the analyzed values for the soil samples collected from the anomalous and non-anomalous magnetic closures. The results of the major heavy metals (Fe, Cu and Zn) within the sampled areas were used to generate a bar chart which shows the concentration of each metal along their respective traverses and stations as well as the concentrations in weight percentage (Wt%) (Figures 4-6).

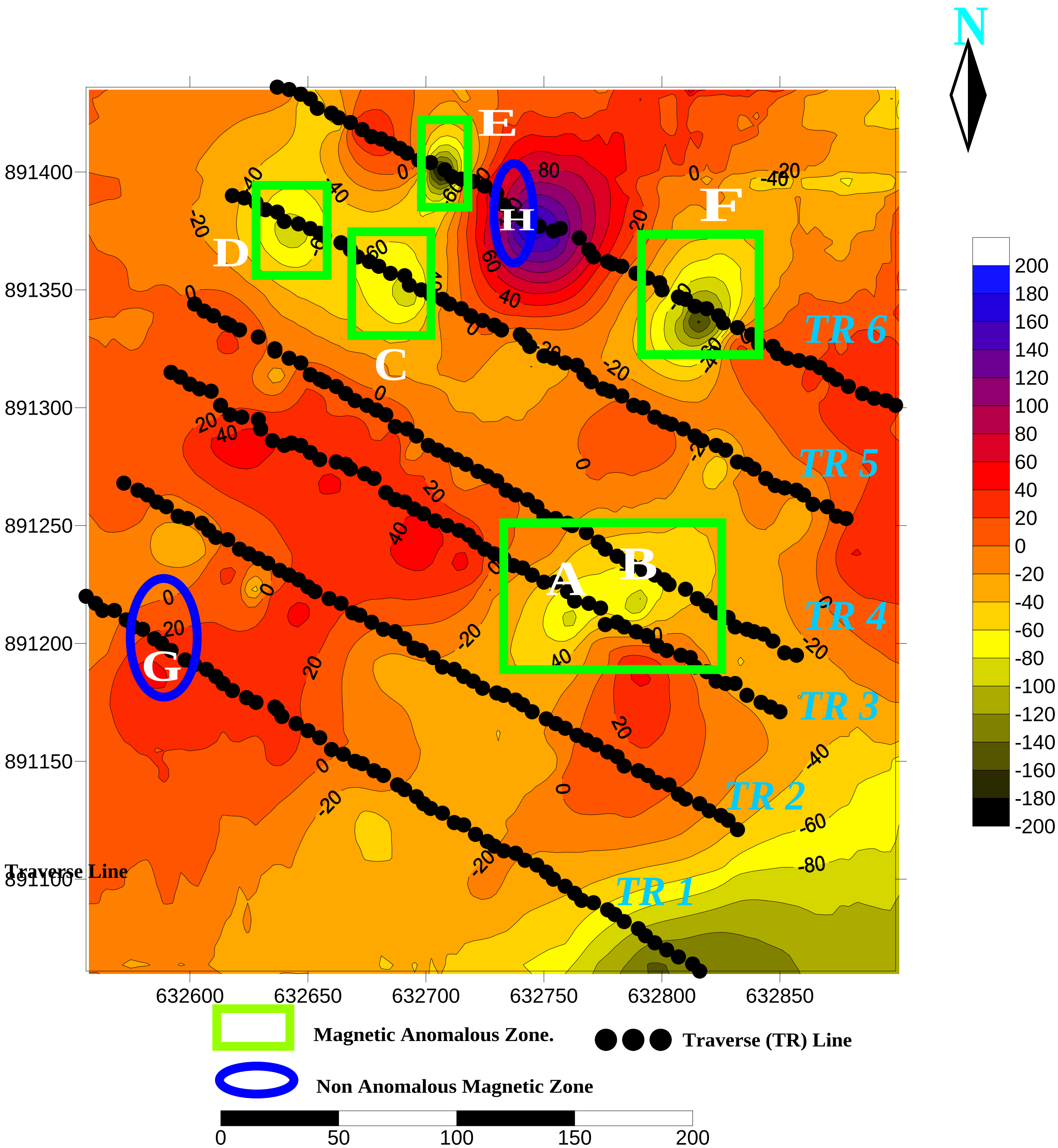

Figure 1: Residual Magnetic Anomaly Map of Orile-Oje Archaeological Site Showing Marked Anomaly Magnetic Closures and Non Anomalous Control Site (Modified after Eluyemi et al., 2012)

Table 1: Location and Coordinates of Soil Samples Collected for XRF Analysis.

Sampling Points	Traverse Number	Station Number	Geographic Coordinate Easting (mE)	Geographic Coordinate Northing (mN)	Elevation (M)
Anomalous Magnetic Zone					
A	Traverse 3	38	0632760	0891226	312
B	Traverse 4	44	0632787	0891233	308
C	Traverse 5	5	0632640	0891379	302
D	Traverse 5	16	0632691	0891356	305
E	Traverse 6	15	0632702	0891404	298
F	Traverse 6	41	0632814	0891343	301
Non Anomalous Magnetic Zone					
G	Traverse 1	10	0632598	0891193	314
H	Traverse 6	24	0632743	0891380	299

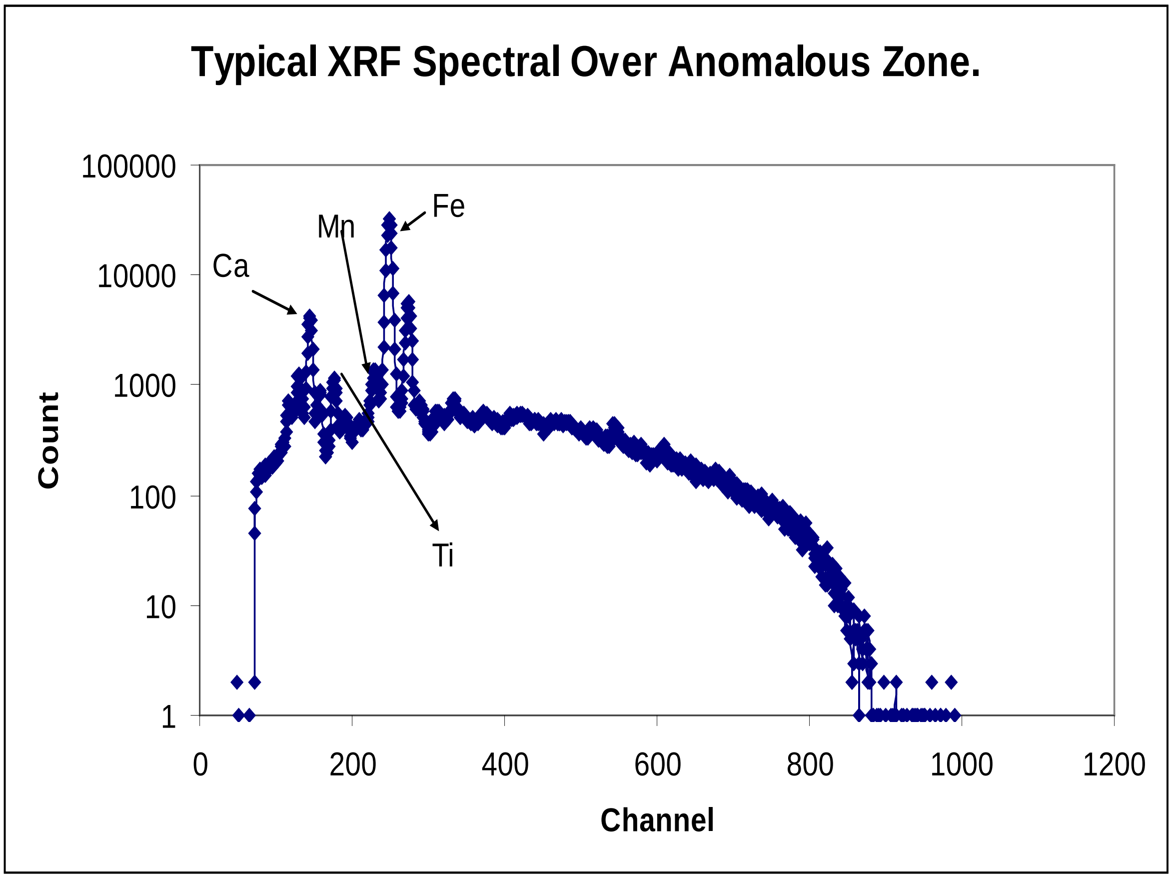

Figure 2: Typical X-Ray Fluorescence Spectral of a Soil Sample from the Anomalous Zones.

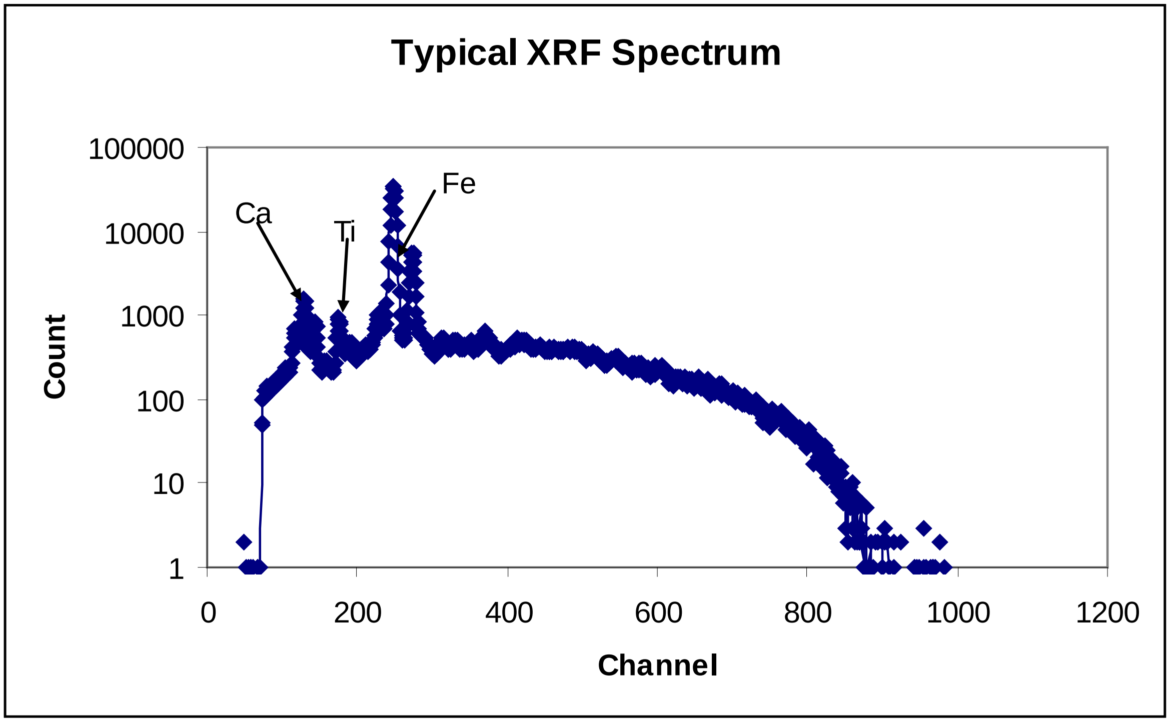

Figure 3: Typical X-ray Fluorescence Spectral of a Soil Sample from the Non Magnetic (Magnetically Quiet) Zones.

Table 2: XRF Analysis of IAEA Standard (Soil 7 Geochemical Standard).

Elements	Percentage Composition of The Elements (Wt%).	
	Certified Values	Analyzed Values
K	1.210	1.2157
Ca	16.300	16.3926
Ti	0.300	0.3022
Cr	0.0002	0.0002
Mn	0.0631	0.0635
Fe	2.570	2.5875
Ni	0.0026	0.0026
Cu	0.0011	0.0011
Zn	0.0104	0.0105
As	0.00134	0.0013
Sr	0.0108	0.0109
Zr	0.0185	0.0186

Table 3: XRF Results of the Soil Samples of the Magnetic Anomalous Zones and Non Magnetic Anomalous Control Site.

Element	Percentage Composition of The Elements (Wt %). Anomalous Magnetic Zone						Non Anomalous Magnetic Zone	
	Traverse 3 Station 38 (A)	Traverse 4 Station 44 (B)	Traverse 5 Station 16 (C)	Traverse 5 Station 5 (D)	Traverse 6 Station 16 (E)	Traverse 6 Station 41 (F)	Traverse 1 Station 10 (G)	Traverse 6 Station 24 (H)
K	2.1646 ± 0.05	2.2084 ± 0.054	6.5800 ± 0.123	7.1470 ± 0.124	6.0302 ± 0.145	2.1570 ± 0.056	4.1946 ± 0.09	3.9247 ± 0.0844
Ca	8.1392 ±0.01	3.3497 ± 0.067	4.3973 ± 0.106	2.5736 ± 0.078	3.0887 ± 0.108	1.6479 ± 0.049	1.8257 ± 0.058	1.8098 ± 0.0584
Ti	0.6690 ± 0.02	0.5649 ± 0.017	1.6711 ± 0.041	0.9353 ± 0.029	0.77 ± 0.0355	0.5179 ± 0.0168	0.6553 ± 0.0212	0.4901 ± 0.0187
Cr	0.0005 ±0	0.0008 ± 0	0.0005 ± 0	0.0005 ± 0	0.0006 ±0.0001	0.0008 ± 0	0.0007 ± 0	0.0008 ± 0.0001
Mn	0.2225 ±0.005	0.2026 ± 0.005	0.2356 ±0.007	0.2865 ± 0.007	0.2829 ±0.0092	0.2375 ± 0.0053	0.2216 ± 0.0057	0.254 ± 0.0062
Fe	23.0907 ±0.04	26.9901± 0.05	15.1008 ± 0.05	15.4025 ± 0.05	17.8379 ± 0.064	15.7101 ± 0.051	5.4907 ± 0.052	4.7886 ± 0.054
Ni	0.0232 ±0.001	0.0325 ± 0.001	0.0341 ± 0.0015	0.0593 ± 0.002	0.0965 ±0.0032	0.0315 ± 0.0013	0.0273 ± 0.0013	0.0373 ± 0.0015
Cu	4.8226 ±0.055	5.9409 ± 0.022	3.746 ± 0.032	5.843 ± 0.01	5.7747 ± 0.035	5.8213 ± 0.013	0.0317 ± 0.017	0.0361 ± 0.018
Zn	3.0418 ±0.02	5.0683 ± 0.021	2.013 ±0.01	5.0324 ± 0.02	4.0712 ± 0.013	2.0318 ± 0.016	ND	0.029 ± 0.017
As	ND	ND	ND	ND	ND	ND	ND	ND
Sr	0.0947 ±0.005	ND	0.2015 ± 0.0099	ND	0.2161 ±0.01	0.0596 ± 0.047	ND	0.0984 ± 0.0066
Zr	ND	ND	0.21 ± 0.01	ND	ND	0.072 ± 0.069	ND	ND

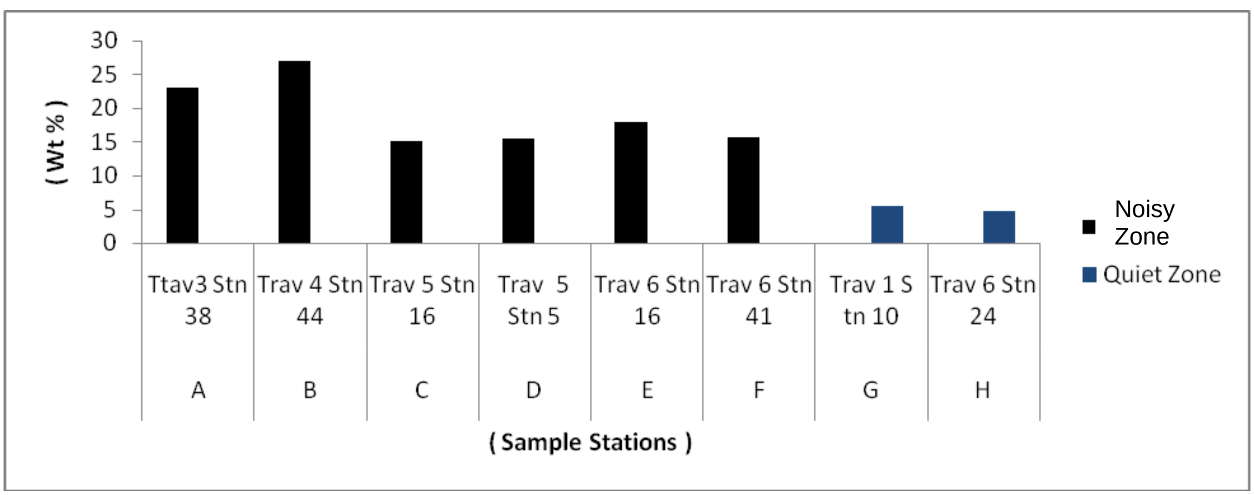

Figure 4: Concentrations of Iron (Fe) Over the Magnetic Noisy and Quiet Zones.

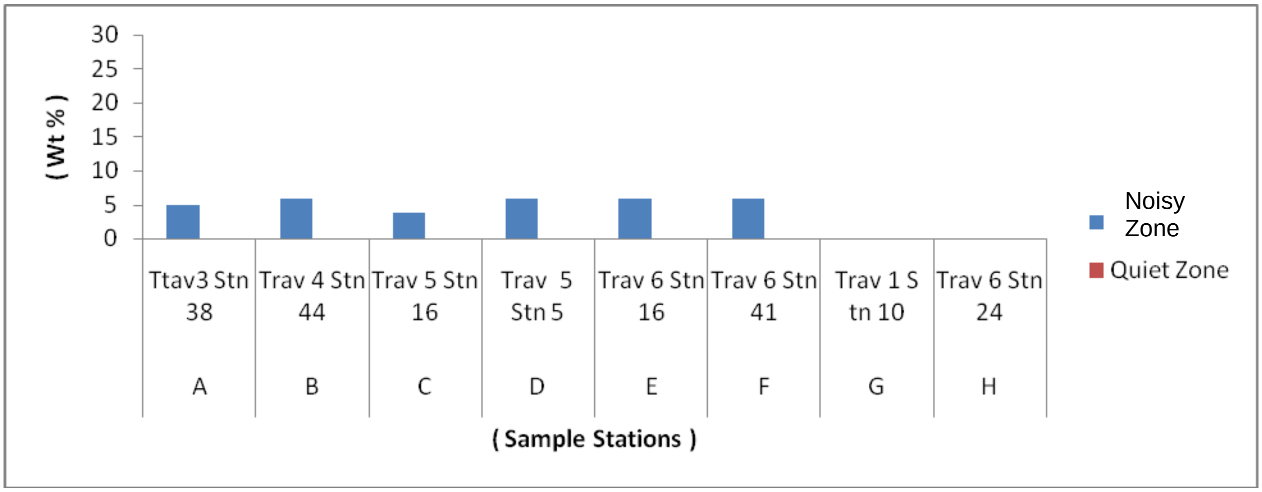

Figure 5: Concentrations of Copper (Cu) Over the Magnetic Noisy and Quiet Zones.

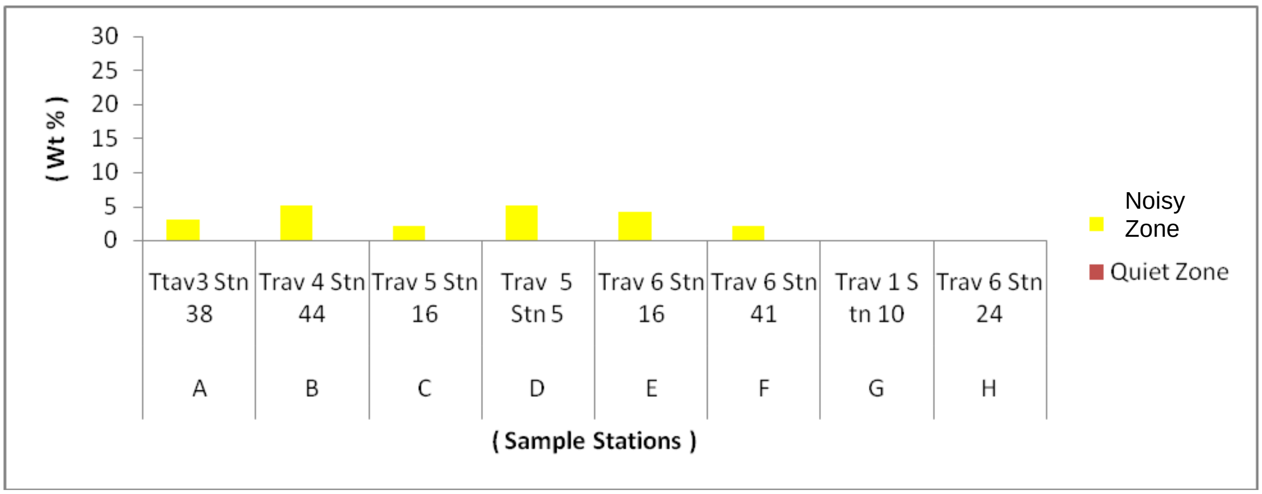

Figure 7: Concentrations of Zinc (Zn) Over the Magnetic Noisy and Quiet Zones.

The qualitative interpretation from the spectral of the samples analyzed reveal an average of 9 elements from non-anomalous magnetic (control) zones and an average 10 elements from the anomalous magnetic zones (see Table 3). The concentrations of Fe, Cu, and Zn, from the anomalous magnetic zones are much higher than that from the control zones – 15.1 – 27.0 Wt % as against 4.8 – 5.3 Wt % for Fe; 3.7 – 5.9 Wt % as against 0.32 – 0.36 Wt % for Cu and 2.0 – 5.1 Wt % as against ND – 0.03 Wt % for Zn, respectively. However, the concentrations of Iron (Fe) along traverses 3&4 are the highest (23.1 – 27.0 Wt %) followed by the anomalous zone along traverse 6 (15.7 – 17.8 Wt %) and then traverse 5 (15.1 – 15.4 Wt %). Iron (Fe) has the highest concentration of 27 Wt % in the analyzed samples while copper (Cu) and zinc (Zn) have relatively lower peak concentrations of 6 Wt % and 5 Wt %, respectively.

The concentrations of the heavy metals in the soil samples collected from anomalous zones along traverses 5 and 6 are relatively high and generally within the range observed in samples collected from the anomalous magnetic closure located along traverses 3 and 4 that coincides with a suspected iron ore smelting site with surface expression of a slag mound. The anomalous magnetic zones have relatively higher concentrations of iron (Fe) than the non-anomalous magnetic (control) zones.

CONCLUSION

Geochemical analysis of soil samples from Orile-Oje (or Igbo Oje) archaeological site had been carried out using X-ray Fluorescence (XRF) technique. This was with a view to determining the concentrations of the heavy metals in soils as a means of confirming suspected ancient smelting sites identified from a residual magnetic map.

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ACKNOWLEDGEMENT

The elemental analysis of the soil samples was carried out at the Centre for Energy, Research and Development (CERD), Obafemi Awolowo University, Ile-Ife, Osun State, Nigeria. The authors are grateful for access to the Centre's XRF facilities.

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SUGGESTED CITATION

Eluyemi, A.A., M.O. Olorunfemi, and B.A. Ogunfolakan. 2012. "X-Ray Fluorescence (XRF) Characterization of Orile-Oje Archaeological Site, Ogbomosho, Southwestern Nigeria, for Suspected Ancient Ore Smelting Sites". *Pacific Journal of Science and Technology*. 13(2):428-436.

Pacific Journal of Science and Technology