JMME. Vol. 13, April, 2021
pp. 76 – 83

ISSN: 2006-1919

A STUDY OF TOTAL ORGANIC CARBON OF TARABA, ADAMAWA AND KADUNA GRAPHITE ORES, NIGERIA AND ITS RELATION TO REGIONAL GEOLOGICAL TRANSFORMATION OF ORGANIC SEDIMENTS TO GRAPHITIC CARBON.

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ABSTRACT

The Total Organic Carbon (TOC) of four graphite deposits in Nigeria has been investigated; namely Taraba Upland and Taraba Lowland graphite deposits within Bali mountain locality, Genye in Adamawa and BirninGwari in Kaduna, Nigeria. In each deposit, 100cm deep trenches were dug and samples collected and homogenized. Proximate analysis was done using ASTM reference methods D3172-75 while XRD, XRF, SEM, EDS, FTIR, CHNOS and LOI were carried out on the samples. From CHNO analysis, the TOC values were 45.17mg/kg, 130mg/kg,240mg/kg and 14.09mg/kg respectively; while their minimum graphitic carbon from EDS were 62.55%, 60.15%, 41.65% and 16.98%. These results on a close study follow individual deposit's geological terrain and formation of graphite; even evidenced with LOI test results of 22.5% and 19.5% for Taraba Upland and Taraba lowland graphite deposits. The chemical analysis from XRF results show that there are certain major gangue minerals common among them such as Al_2O_3, SiO_2, Fe_2O_3, Fe_2O_3, TiO_2, K_2O, ZrO_2, etc., while SEM images revealed their morphology to be crystalline flaky except Kaduna graphite that is amorphous.

Key words: *Graphite, Total organic carbon, geological formation*

1.0 INTRODUCTION

Africa has varieties of crystalline and amorphous types of natural graphite distributed within certain geographical locations (Kangkang, et al, 2017); and, Nigeria is fortunate to have been blessed with reasonable quantities of the solid mineral. So far crude oil has been the country's major source of income; contributing to about 80% of her total GDP; and this might have resulted in her negligence of exploration of most of her other natural endowments such as lead, iron, zinc,; except tin-tantalum, manganese, coal which gained early attention because of her foreign relationship with imperialists. Gold, nickel, columbite, tantalum, lead, zinc, copper, etc. are mined privately in small scales; sometimes secretly by individuals. Similarly quarry industries, small scale miners and artisans engage in extraction of such industrial minerals of value and rocks like talc, marble, limestone, barite, phosphate, kaolin, granite, gemstones, which occur relatively in scattered small deposits. Despite the creation of Government organs, there are no adequate database and detailed metallurgical work on Nigeria's graphite ores as could be seen from the geological map inserts of Nigeria (Figure 1) where graphite is not indicated unlike other age-long solid minerals. From extensive tours and observations, the graphite occurring belt of Nigeria is made up of the Basement Complex, the Pan-African-Precambrian older granites and the cretaceous sedimentary basin of Benue Trough (Fatoye F. B. and Gideon Y, B, 2013). The graphite mineralization follows schistosity; with most of them displaying petrographic characterization of strong foliation of rocks defined by parallel orientation of graphite flakes particularly Taraba and Adamawa graphite ores (Havard Gautneb and Einar Tveten, 2000). Figure 2 shows some of the Nigerian graphite ore samples selected from the deposit areas. They contain impurities such as mineral oxides which can be removed through appropriate beneficiation techniques after characterization and particle size analysis (Chelgani Chehreh, et al, 2016, Nivedita, et al, 2009, Patil, et al, 2014). It is quite obvious that intruding hydrothermal fluids in the earth's crust have been some of the sources of these graphite during rock formations in the Mambila Plateau region (Rumble, 2014).

Graphite is a non-metallic mineral of carbonaceous origin and one of the principal crystalline polymorphs of the element, carbon, the other being diamond. It is distinguished by its softness to touch and; conductivity of electricity because its phonons propagate along certain crystallographic planes with its lubricity resulting from structural hexagonal sheet-like layers which slip in lateral directions. The mineral is known to be highly refractory and chemically inert. These properties have endeared graphite to numerous industrial applications such as in iron and steel making, foundry works, automotive parts, oil and gas, renewable energy, Li-ion and dry cell batteries, school pencils, composite materials in aerospace, etc. Graphite is known to occur in metamorphic and sedimentary rocks; and sometimes along coal strata (Simandi, et al, 2016).

The research investigation was aimed at providing some metallurgical data to highlight the mineralogical qualities of some Nigerian graphite ores so as to encourage their exploration, exploitation and applications in pencils, foundry crucible pots, Li-Ion batteries, renewable energy, etc. which are currently receiving research attentions in the country. Furthermore, a good knowledge from their characterization will enable selection of appropriate beneficiation technique for each graphite deposit.

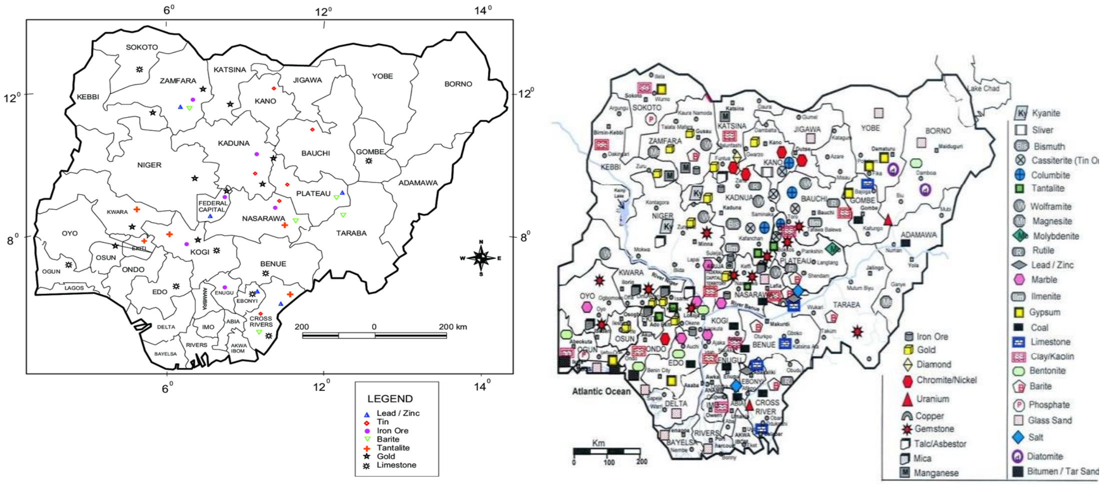


Figure 1 Geological map of Nigeria showing the distribution of major solid minerals; Obaje, (2009).

Taraba Upland Taraba lowland

Adamawa Kaduna

Figure 2. Some lump samples of Nigerian graphite ores collected from the deposits.

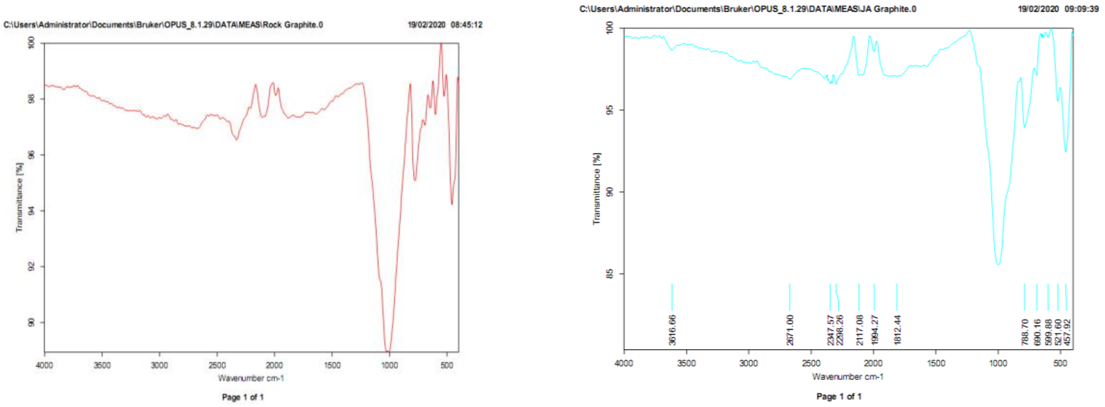
2.0 EXPERIMENTAL

Sample collection: Four graphite deposits were investigated; namely Bali Mountainous region and Bali Lower valley region of Taraba State; Genyegraphite in Adamawa State and Birnin Gwari graphite in Kaduna State. The graphite ores were hard, compact and dark steel gray in colour and came in large lumps usually 25mm to 300mm diameter (Figure 2). They were obtained from the regions with some occurrences stretching over 75 to 140km. At each location, about 150kg of samples were collected from different pocket sites both at the rocky top and swampy thick jungle bottom of the mountains and hills by digging pits or trenches up to 100cm deep at five (5) different sites. Samples were also obtained from surface outcrops.

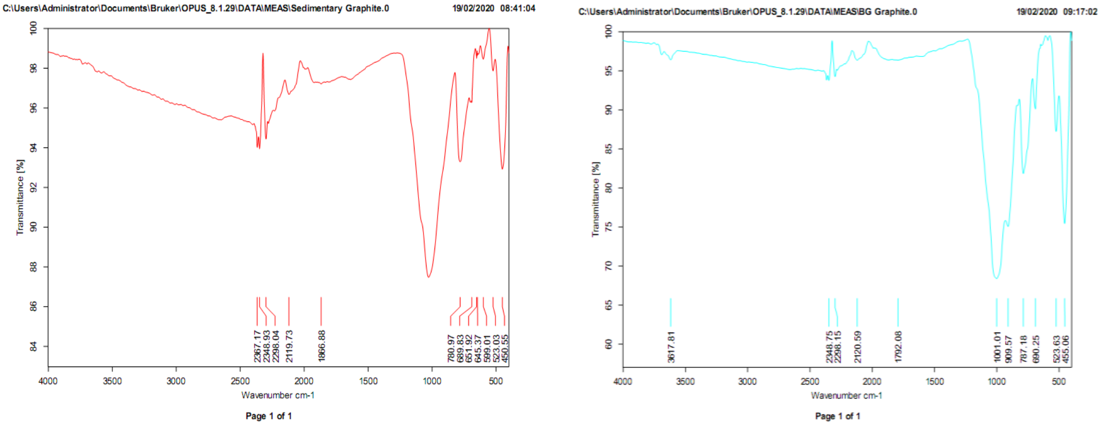
The samples were first dried in open air and then comminution exercises (crushing and grinding) carried out. The crushing was with McLanhan Model 1024 and grinding was with rod milling machine SEPOR Model 17430.00K14. The materials were screened using ASTM E11:87 W.S Tyler’s RO-TAP Model RX-30 which uses 12″ diameter screen sieves and then all materials homogenized. Final samples were drawn from the homogenized ground ores for various analyses and other experiments.

Analysis: The following equipment were used for the analysis:

(a.) Fourier Transform InfraRed (FTIR) - Bruker. Instrument type: INVENIO – R. OPUS Version: Version 8.1, 2920180416. Resolution – 4. Phase correction mode – Mertz; was used for the analysis. The spectra of the four graphite deposits are shown in figure 3 below.



(a.) Taraba Upland (b.) Taraba Lowland



(c.)Adamawa (d.) Kaduna

Figure 3 FTIR Spectra of some Nigerian graphite ores

Each of the deposits has a distinct FTIR spectrum signature with Taraba Upland graphite ore manifesting its crystalline long flake characteristics as evidence in figure 3a.

b.) Carbon Hydrogen Nitrogen Oxygen Sulphur (CHNOS) Analyzer - Analytik Jena. Type: aj-analyzer. Model: multiEA 4000; multiwin 5.4.Serial number: N4-400/R. Soft Ware “Multiwin” was used for the analysis and results shown in table 2 and figures 4.

c.) Scanning Electron Microscope/ Energy Dispersive Spectrometer (SEM/EDS) - Ore Microscope (leitz make), Scanning Electron Microscope SEM (Jeol, Jsm 35 CF). Some of the SEM/EDS images are shown in figures 5, 6, 7 and 8.

d.) X-Ray Diffractometer (XRD) - Phase compositions of the raw ore were identified using an Advance X-ray Diffractometer (D8, Bruker, Larlsrhe, Germany) with C_uK_α radiation (λ = 1.5406mm) at 40kV and 100mA. The mineralogy and morphology of the raw ore was observed using optical microscope see figure 5, 6, 7 and 8.

e.) X-ray fluorescence spectrometer **(XRF):** AXOS, PANalytical B.V, Almelo; The Netherlands.

(MiniPAL 4 Model @2005.Lely weg 1.7602 EA, A/me/O.Pw4025/45B with Rh tub); was used for the analysis. The XRF results showing the gangue oxide minerals of the four deposits are incorporated in table 1.

Table 1: XRF Result Analysis of homogenized of some of the Nigerian Graphite Ores showing associated major mineral gangue oxides.

Oxides	Taraba Upland	Taraba Lowland	Adamawa	BirninGwari Kaduna
Al_2O_3	47.39%	22.21	20.21	23.80
SiO_2	37.41%	52.75	47.69	61.53
Fe_2O_3	9.75%	5.38	4.45	1.31
TiO_2	4.59%	4.48	1.69	1.21
K_2O	0.81%	9.99	6.54	8.39
ZrO_2	0.07%	0.10	0.34	-
Na_2O	-	0.50	5.35	0.41
CaO	-	1.02	5.45	-
V_2O_5	-	0.34	0.14	0.04
MgO	-	2.63	3.93	3.28
Cr_2O_3	-	-	0.28	0.04
BaO	-	0.15	0.26	-
P_2O_5	-	-	3.67	-

Table 2: SEM/EDS result of homogenized graphite ores from the deposits and CHNOS analysis of their Total Organic Carbon

Graphite Ore	% Graphitic Carbon	Total Organic Carbon	Peak count value @Aver. 120secs
Taraba Upland	62.55	45.17mg/kg	66
Taraba Lowland	60.15	130mg/kg	283
Adamawa	41.65	240mg/kg	492
Kaduna	16.98	14.09mg/kg	43

3.0 RESULTS AND DISCUSSION

The bulk XRF analyses indicated the following percentage oxide compositions as shown in Table 1, with alumina, silica, hematite, anatase, etc. as being the main oxide minerals in the gangue. There is equally diversity in their gangue compositions; for instance, Adamawa has very high phosphorous content which could pose serious challenges during processing because it has to be reduced to minimum level in most applications; for instance, in iron and steel and foundry works where it is known to be deleterious.

Table 2 shows SEM/EDS results of homogenized graphite ores with percentages of graphitic carbon from the deposits and CHNOS analysis of their Total Organic Carbon; and then figure4 display different peaks of their values. There are other methods of determining Total Organic Carbon (TOC) in soil sediments and materials (Brian S. Schumacher, 2002),

Taraba lowland graphite deposit is in a swampy jungle valley while Adamawa deposit is in flat forest valley land. These environmental locations apart from internal earth geological activities, gave rise to most of the high Total Organic Carbon content values which indicates that they are still undergoing transformations. The Taraba Upland graphite deposit and Kaduna graphite deposit were at the top of mountain ranges over 2000ft above sea level; though at some outcrops, Kaduna graphite ores are seen on lower flat lands and occurring along with gold dusts. Metamorphic activities seemed to be higher here due to rapid changes in temperature and pressure; while in the low valleys or flat beds with thick swampy jungles, organic activities by microbes on sediments are intense with reduced geological pressure and temperature. Organic carbon (OC) of geogenic origins could have been formed when organic compounds in sediments around the lower valleys of Bali Mountains were undergoing transformations or kerogen transformation during diagenesis under high mountain pressure and intense temperature conditions within the region. This process could have continued into the formation of graphite C (OOshashi et al, 2012, Buseck and Beysaac, 2014).

The tables above are interestingly remarkable based on deposit location and geological activities taking place within the Earth’s crust that resulted to differences in the level of organic sediments and rate of transformations to graphite (Buseck P. R and Beyssack O., 2014). It was observed during the study that all the parameters including percentage graphitic carbon (C_g)varied from location to location even 20m apart in a deposit.

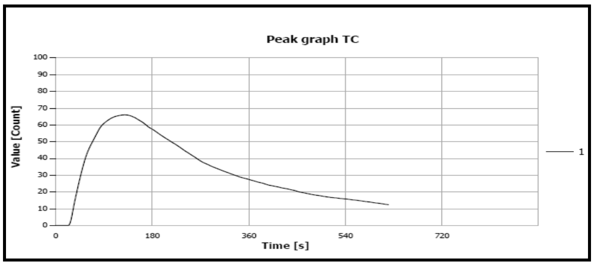


Figure 4a Machine drawn (TOC) graph of Taraba Upland Graphite ore (45.17mg/kg).

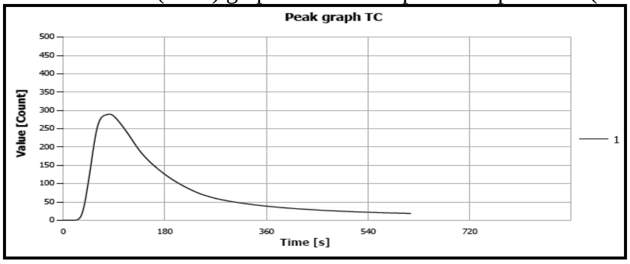


Figure 4b Machine drawn (TOC) graph of Taraba Lowland Graphite ore (0.13g/kg)

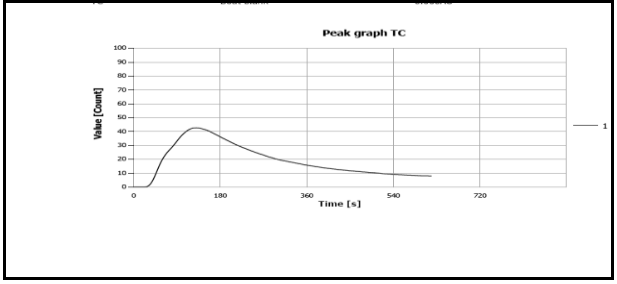


Figure 4cMachine drawn (TOC) graph of Birnin Gwari Graphite ore (14.09mg/kg)

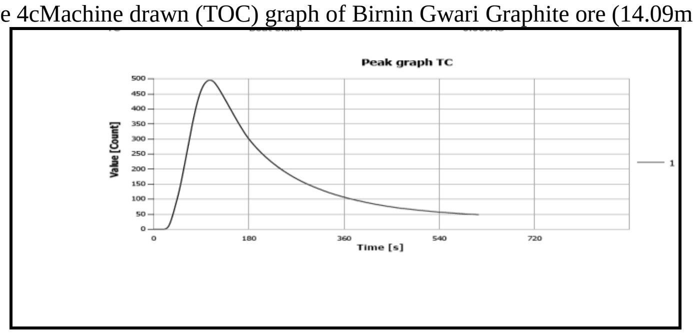


Figure 4dMachine drawn (TOC) graph of Adamawa Graphite ore 0.24g

Figures 5, 6, 7 and 8 are the SEM images of some Nigerian graphite ores investigated. It could be observed that while Kaduna graphite ore (Figure 8) depicts amorphous fibrous nature, Taraba and Adamawa graphite ores are highly crystalline and flaky, though the flake length of Taraba upland graphite is higher. This has drawn attention to its potential numerous applications where long flakes are required; for instance, in Li-Ion batteries, pencils, carbon brushes, etc.

Most of the vital properties for application of graphite in industry; for instance, conductivity, are dependent on flake length and crystalline structure of the graphite; with higher flake length and % purity commanding higher market prices.

Figure 9 is a processed Taraba Upland graphite of 150µm particle size that is currently under investigation for use in many applications such as pencils, Li-Ion batteries, carbon bRushes, foundry crucible pots, gaskets, brake linings, etc.

Figure 5 SEM image of Taraba Upland.

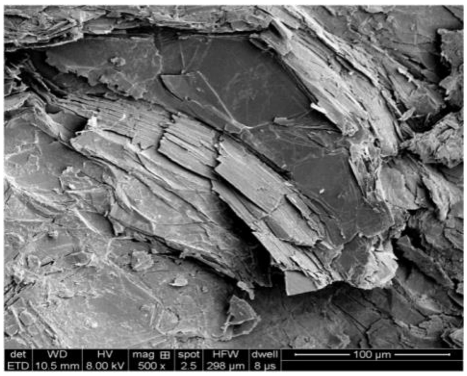


Figure 6 SEM image of TARABA LOWLAND

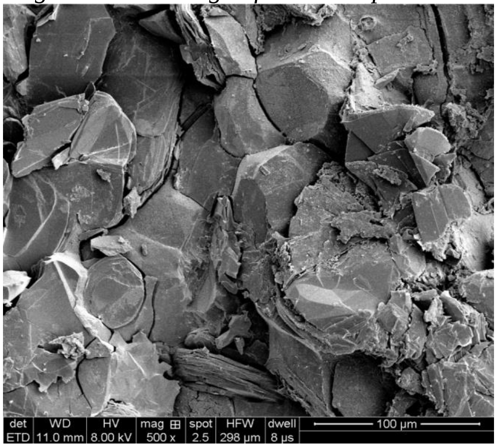


Figure 7 SEM image of Adamawa graphite ore.

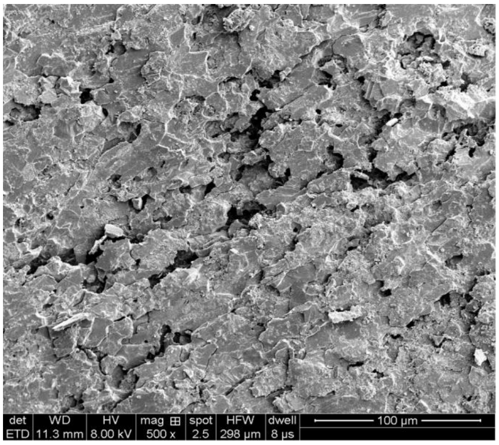


Figure 8 SEM image of Kaduna graphite

Figure 9 Photograph of processed Taraba Upland graphite of particle size 150µm (98.87%FC).

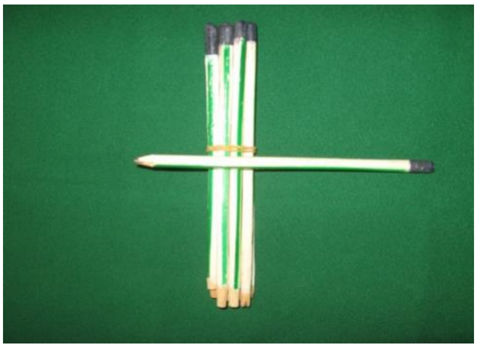


Figure 10 HB Sample Pencils

4.0 CONCLUSION

It is obvious from the work that graphite ores of Taraba Upland, Taraba lowland, Adamawa and Kaduna are not totally occurring as low grade ores; though cannot be used directly without processing. Secondly the graphite ores in Nigeria have good metallurgical properties to attract investment on exploitation; and the formation of these ores were favoured by similar good geological setting existing in those parts of the World where graphite ores exist. Based on various tests on the graphite ores, appropriate beneficiation techniques such as froth and column flotations, leaching or any other method can be selected and applied to upgrade them for maximum use in industries.

REFERENCES

1. Kangkang Sun., Yangshuai Qiu and Lingyan Zhang., (2017). Preserving Flake Size in an African Flake Graphite Ore Beneficiation Using a modified grinding and pre-screening process. www.mdpi.com/journal/minerals. 2017, 7, 115; doi:10, 3390.

2. Fatoye, F . B and Gideon, Y. B. Geology and Mineral Resources of the lower Benue Trough, Nigeria. Adavancesib Applied Science Research. 2013, 4(6)/21-28. Felagia Research Library.

3. Havard Gautneb and Einar Tveten (2000). The geology, exploration and characterization of graphite deposits in the Jennestad area, Vesteralen Northern Norway. NGU BULL 436, 2000. p.67-72.

4. Chelgani Chehreh S., Rudolph M., Kratzsch R., Sandmann D., and Gutzmer J. (2016). A review of Graphite Beneficiation Techniques. *Mineral Processing and Extractive Metallurgy* Review. Vol. 37. No. 1, pp 58-68. http://www.tandfonline.com/loi/gmpr20

5. Nivedita Patrick, Raju K. K. V.S. and BhiwaRao R. (2009). “Characterization, Beneficiation and Utilization of Calcareous Graphite from Tamilnadu, India”. Regional Research Laboratory (CSIR) Bhubaneswar India.

6. Patil, M. R., Ravi, B. P., Rudramuniyappa, M. V., and Kumar. P. s., (2014). Characterization Studies on graphite from Shivaganga Area, Madurai, Dist., Tamilnadu. *International Journal of Innovative Science, Engineering and Technology*, Vol. 1 Issue No 4. www.ijiset.com. pp 460-464

7. Rumble, D. Hydrothermal graphite carbon. Elements.10(6). 427-433; doi.1o2113/gselements.10.6.427, 2014.

8. Obaje N.G. Geology and mineral resources of Nigeria. Springer Verlag Berlin Heldelberg. 2009

9. Sjmandi G. I., Paradis S., Neetz M., and Akam C, (2015). Graphite deposits: origin and economic importance. Symposium on Strategic and Critical materials proceedings. British Columbia Geological Survey, Victoria. Pp 163-171

10. Brian S. Schumacher, (2002). Methods for the determination of Total organic carbon (TOC) in soils and sediments. NCEA-C-1282.EMASC-001. United States Environmental Protection Agency. Exposure Research Laboratory. Ecological Risk Assessment Support Center.

11. Ooshashi, K., Hirose, T., Kobayashi, K and Shimamoto, T. The occurrence of graphite- bearing fault rocks in the Atotsugawa fault system. Japan. Origins and implications for fault creeps. Journal of structural Geology, 38, 39-50.Doi/10.1016/j.jsg.2011.10.011.2012

12. Busseck Peter R. and Beyssac Oliver (2014). From Organic Matter to Graphite: Graphitization. Journal: Elements, Vol. 10. Issue No. 6; Pp 421-426. 2014. asu.pure.elsevier.com