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Petrology and Geochemistry of Rocks of Ishiagu and Environs Southeastern Nigeria Using Ed-Xrf Method

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Abstract

Geochemistry of rocks of Ishiagu area was carried out using Energy Dispersive X-Ray fluorescence (ED-XRF) method. Twelve samples were analyzed and their geochemical properties determined using Excel-Software. Geological mapping reveals that basalts, dolerites and diorites emplaced in shale and mudrock country hosts are the main lithological units occurring in the area. They have silica content of 40.4–49.2wt.%, indicating they are basic-ultrabasic in character. The dolerite and diorite contain average plagioclase (An70-17.4vol.%), hematite 26.29vol.%, showing enrichment in ferromagnesian minerals and depletion in quartz. The Na_2O and K_2O averaged 1.22wt.% and 1.46wt.% respectively, indicating depletion in alkali, thus corroborating their basic–ultrabasic property. The TiO_2 value is 3.6wt.%, indicating oceanic magma derivation. The industrial metals Pb, Cu, Ni and Zn were relatively similar with average values of 37.13, 23.96, 23.69, and 20.08ppm respectively, showing common protolith. The diorite and dolerite are enriched in trace elements Zr, Sr, with average concentration of 172.49, 109.73ppm, and relatively depleted in As and Au with values of 0.04 and 0.03ppm respectively. Petrogenetic analyses using ternary diagram TiO_2–K_2O–P_2O_5 for discriminating magma type, the dolerites and diorites all plot in continental basaltic field. In the AFM, and P_2O_5 versus Zr plots all the dolerites and diorites fall in the tholeiitic field, corroborating that they originated from tholeiitic basaltic magma, probably derived from lower crust/upper mantle. In the Na_2O/Al_2O_3 versus K_2O/Al_2O_3 diagram the dolerites and diorites all plot in the igneous field, the shale plot in metasedimentary field, while the ironstone fall on the boundary between igneous and metasedimentary fields indicating hybrid provenance.

Keywords: Petrology geochemistry; Ishiagu environs; ED-XRF method; Petrogenesis; Provenance; Protolith.

1. Introduction

Ishiagu and environs lie in the southeastern flank of the Anambra Basin (Fig.1), a sag basin adjoining the Afikpo Syncline of Southeastern Nigeria. The Anambra Basin is generally characterized by sediments of Cretaceous and younger ages mainly sandstones, siltstones, shale and limestones, intruded by various igneous bodies. The chemical compositions of the rocks are used to solve numerous geological problems, including crystallization history of igneous bodies, processes of formation of the sea floor, nature of chemical weathering in various climates, stratigraphic correlation of sedimentary and volcanic rocks, processes of ore genesis, metamorphism and tectonic evolution, alteration processes and many others [1, 2].

1.1. Statement of Problem

The rising population, urbanization and cascading cost of living coupled with the receding GDP resulting from fall in prices of fossil fuel highlights the need to diversify the Nigerian economy and reduce over dependence on oil resources. Hence there is now need for government, companies and individuals to diversify and shift their search for economic resources towards solid minerals and rocks resources exploration and exploitation.

1.2. Background of Study

Although various mineral resources deposits have been reported from Anambra Basin lower Benue Trough Nigeria of which Ishiagu area is a part, some currently undergoing local mining operations, there is still paucity of information about mineral deposits in the area when compared with some international mineral/mining provinces of the world, for example Cape Veldt of South Africa and Ring Complex of northern Nigeria. In particular there has not been intensive and systematic research utilizing combined/integrated petrological and geochemical methods in mineral exploration in the area, perhaps due to inadequate funding by government and lack of state-of-the-art equipment.

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1.3. Justification

The petrology and geochemistry of rocks of Ishiagu and environs in the Anambra Basin and Afikpo Syncline had been studied by some scholars, for example Reyment [3], Ezepue [4], Obi [5], Obioha, *et al.* [6], Obioha [7], Chukwu and Obiora [8], and many others. However, more systematic work covering adjacent/rural areas of Ishiagu and environs is still needed to be done to properly elucidate the complex petrological, geochemical and mineralogical characteristics of the area, using integrated geological mapping, petrological and analytical geochemical approach. This is the goal of the present study. The scope of the study is limited to geological mapping and petrological / geochemical analyses of parts of Ishiagu and environs to elucidate the lithological unit occurrences and a systematic geochemical analysis of the minerals and rocks resources occurrences of the area.

1.4. Significance

The study unraveled the petrology and geochemistry of Ishiagu and Environs Southeastern Nigeria and produced a standard geological map of the area and a report that will serve as guide for future geological exploration in the area.

2. Literature Review

Following the founding of the Geological Survey of Nigeria (GSN) in (1919) and the geological mapping of the Benue valley and Kaduna areas by the GSN [9], there were renewed interests for solid mineral resources exploration and exploitation in Nigeria. Many scholars have worked on the mineralogy, petrology and geochemistry of Ishiagu and environs. They all agree on the occurrence of dolerite, diorite, and basaltic/gabbroic igneous lithotypes emplaced in mainly shale, carbonates, siltstones and mudstones country rocks, which host lead-zinc-barium ores and other minerals in the area. For example, Fayose and Gideon [10] working on geology and mineral resources of the Lower Benue Trough Nigeria, reported the occurrence of over 20 solid mineral resources in the area including coal, lead-zinc, barytes, gypsum, uranium, fluorspar, graphite, cassiterite and manganese etc. Obioha [7] based on trace element geochemistry evidence, reported the occurrence of Ba-Pb in shale and mudrock intruded by diorite – dolerite stocks in Ishiagu area. This report was in agreement with the work of Andrew, *et al.* [11] who reported Pd-Zn-Ba occurrences in Ishiagu area Lower Benue Trough based on contrasting styles of mineralization.

Structurally, several scholars have reported the evolution of the Anambra and Afikpo basins as a result of tectonic activities of the Santonian period, which lead to the subsidence of the platforms, flanking west and east of the Abakaliki Trough/anticlinorium [10, 12, 13]. Geophysical techniques by Ofoegbo [14], Cyril [15], using high resolution aeromagnetic survey and spectral analyses had shown a clastic sediment thickness range of 0.5 – 7km in the Lower Benue Trough, a regional structural trend in NE-SW and E–W directions, and three lineament trends in NE – SW, ENE-WSW and NW-SE. Ideozu and Amararu [16], carried out structural analysis of joints and faults in the Lower Benue Trough Nigeria. They reported three (3) joint sets trending NE/SW, NW/SE and E-W. These corroborate the earlier geophysical reports and are inferred as the trend of mineralization of rocks and mineral ores in the Ishiagu area Lower Benue Trough.

The Mamu and Nsukka Formations are Maastrichtian–Paleocene rocks consisting of sequences of shale, sandstone, limestone with coal seams, have thicknesses of about 300-500m in places. The emplacement of igneous rocks in Southeastern Nigeria was sequel to the evolution of the Benue Trough during the Cenomanian-Turonian orogenesis, magmatism, metamorphism, and tectonism [3, 5]. There were three stages of sedimentations; the Pre-Cenomanian deposition of Asu River Group, followed by the Cenomanian-Santonian tectonism and magmatism which resulted in emplacement of intermediate igneous rocks, mainly dolerites and diorites, and some basaltic and gabbroic rocks (Burke…). According to Reyment [3], the inversion tectonics of the Abakaliki anticlinoria which led to the evolution of both the Afikpo Syncline and Anambra Basin, represented the third cycle of sedimentation, which produced the incipient Nkporo shale, Enugu shale and Owelli sandstone.

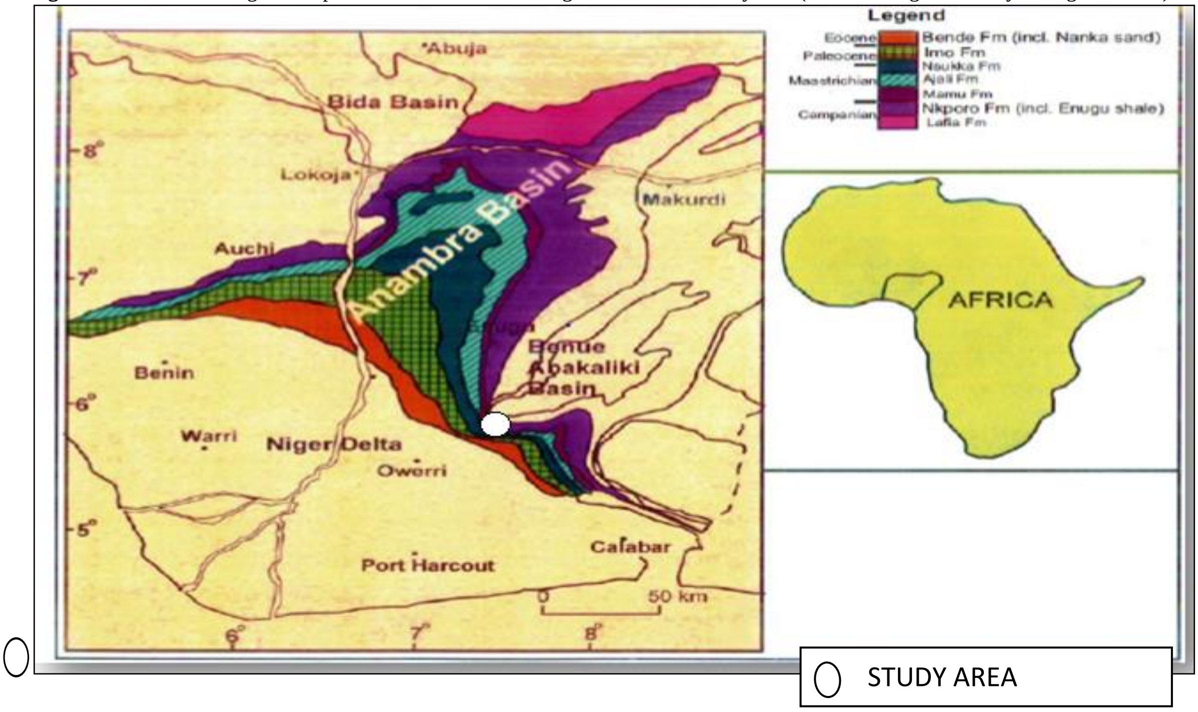
3. Materials and Methods

The study involved both field and laboratory works. The sampling was carried out with the aid of a geographic positioning system (GPS), topographic map and altimeter, which enabled location of outcrops and determination of the coordinates/geometry, thickness of beds, and their dip and strike.

3.1. Location of Study Area

Ishiagu lies within longitudes 7°34’-411” E and latitudes $5^0$57’-08”N (Figs. 1 and 2). The environs include Okigwe which lies within latitudes $5^0$50’-34”N and longitudes 7°20’-01”E, and Uturu which lies within Longitude 7^o30’-48”E and Latitude 5^o51-’23” N, in the southern Benue Trough. The major roads are the Enugu - Port Harcourt Expressway and the Owerri-Okigwe-Afikpo roads and some footpaths which enhanced accessibility to the outcrop locations. The area is bounded in the north by Awgu and Aniuri in Enugu State, in the south by Ugwuele Isiukwuato areas in Abia State and in the east by Akaeze in Ebonyi State. The Southeastern Nigeria railway line rims from Enugu traversing Ishiagu down to Port Harcourt (Fig. 2). The major physiographic unit is the plateau and escarpment zone, with isolated sandstone hills separated by steep valleys of shale. The area is drained by the Iyiachara, Izeh, Law-Law, Aba-Omega and Ibu rivers. The average rain fall of the area is about 2000mm per annum, with average relative humidity of about 70%, and temperature of 27^0C, with peak intensity of sunshine during January-March [17]. The vegetation is characterized by presence of thick forests with predominance of economic crops such as cassava, plantain, maize and melon.

Fig-1. Generalized Geological Map of Anambra Basin showing location of the study area (After Geological Survey of Nigeria, 1994)



3.2. Geological Setting

The study area is a part of the Anambra Basin in Southeastern Nigeria (Figs. 1 and 2), which evolved after the formation of the Benue Trough [5, 18] during the Cretaceous. The area is underlain by five major Cretaceous-Tertiary lithostratigraphic Formations: The Asu River Group- Albian [12], Eze-Aku Formation, Mamu Formation (Lower Coal Measures- [3, 5]), Ajali Formation (False-Bedded Sandstone- [12]), Nsukka Formation- (Lower Coal Measures, [3]; Table 1). These consist variously of clays, sandstones, shales, coal seams, siltstones, mudstones, lignite and limestones. The Ajali Formation overlies the Mamu Formation with its type locality along the valley of the Ajali River near Enugu [12]. The sandstone is typically white in color but in some cases, iron-stone exhibits significant thickness variation from less than 300 meters to over 1000 meters at the centre of the basin [19].

Figure-2. Location Map of the study area, showing drainage (modified after Nigeria Geological Survey Agency, Report, 1986)

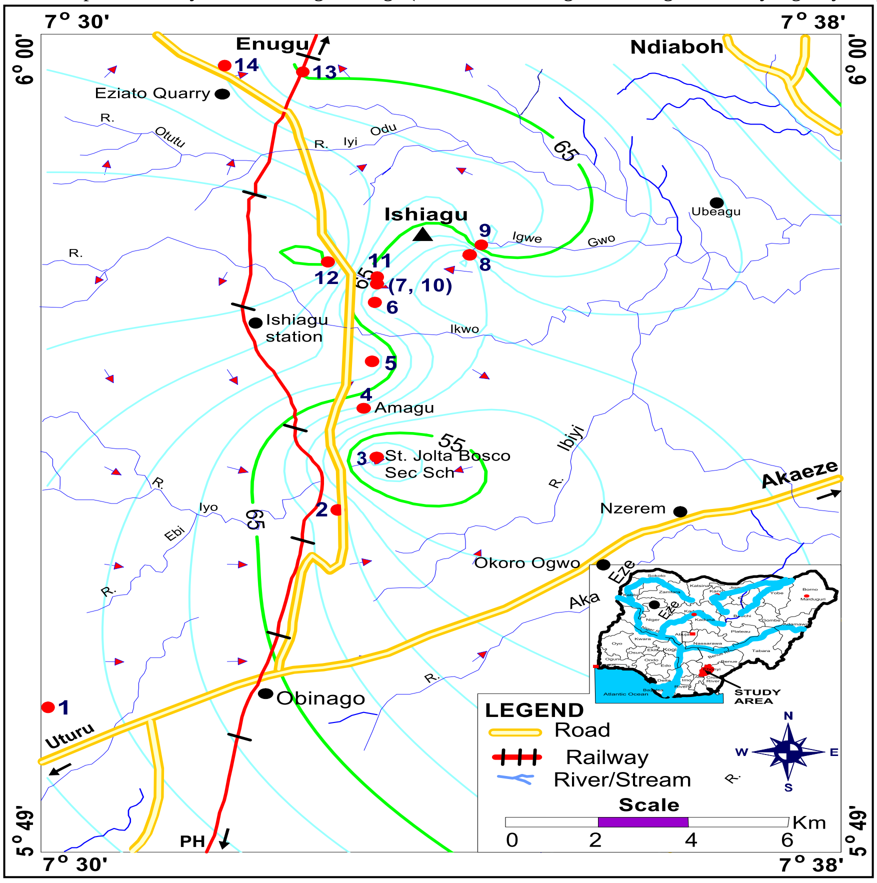


Table-1. Lithostratigraphy of Study Area (Ishiagu and Environs Lower Benue Trough, SE. Nigeria)

Period	Period	Formation	Lithology	Environment	Sedimentation Cycle
C R E	Campanian- Maastrichtian	Nsukka, Ajali, Mamu	Sandstone, Shale, Coal Seam, Clay, Limestone	Regressive; Fluvial-Deltaic	3rd Cycle*
T A C	Santonian- Coniacian	////////////////// Awgu, Nkporo	////////////////////////// Sandstone, Shale, Clay, Limestone	////////////////////// Clay, Limestone Transgressive	2rd Cycle*
E O	Turonian- Cenomanian	Eze-Aku Shale	Shale, Sandstone, Coal Seam, Clay	Transgressive Marine	
U S	Albian	ASU River Group (ARG)	Sandstone, Shale, Limestone, Clay	Regressive	1st..Cycle*

Key: /////// - Unconformity; (Modified after [7]).

3.3. Principle of XRF

The ED – XRF is a non destructive method of quantitative and qualitative elemental analysis of solid and liquid sample materials [20, 21]. In this process, the high energy content of an X-Ray beam causes a sample to generate X-Rays characteristic of the atoms in the sample when inner K, L or M electrons are removed from target atoms and outer electrons fill the vacancies. Elements present in the sample are identified from the energies of the characteristic radiation, and their concentrations are evaluated from the intensity measurements.

3.3.1. Mineral Processing

The mineral processing involved communition i.e. size reduction and pulverization carried out using Jaw roll and cone crushers and pulverizers at the mineral processing plant of the National Metallurgical Development Center (NMDC) Jos. The sampling was carried out using the Don Riff's cone and cutter method in order to obtain a representative fraction of the sample. 200g of the final sample was passed through 200-250 mesh sieves and later dried in an oven at temperature of 105^{o}C for an hour, and allowed to cool. Then mixed with a binder in the ratio of 5.0g samples to 1.0 cellulose flakes binder added. The sample was finally pelletized at a pressure of 10-15 tons/inc^{2} in a pelletizing machine. The pelletized samples were stored in desiccators for analysis.

3.3.2. Sample Analysis

The sample analysis was carried out using Energy Dispersion (ED –XRF- Minipal 4, Model-2005 Machine [21].The machine calibration was performed using Thermo Noran Copper (Cu) calibration standard [20]. Determination of the difference between the measured peak energy value and the ideal value was based on the U.S. National Institutes of Standards and Technology (NIST). The elemental concentrations were reported in percentage (%) concentrations for major elements and parts per million (ppm) for the trace elements.

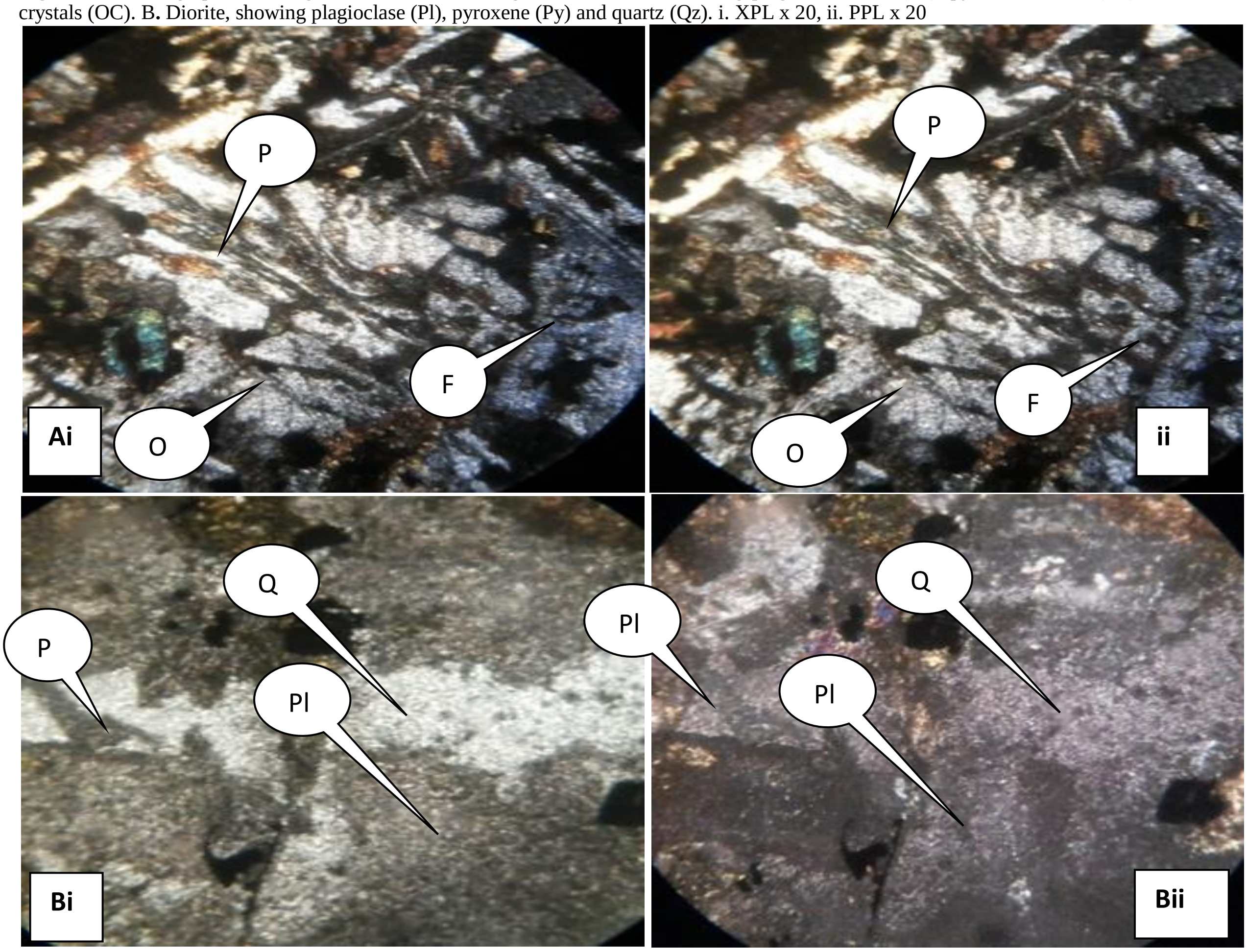
4. Results and Discussion

The field geologic mapping revealed that four main types of igneous rocks occurred in the area: namely, diorite, dolerite, basalt and granite. The igneous rocks were emplaced in shale and mudstone sedimentary and metasedimentary country rocks.

4.1. Dolerite

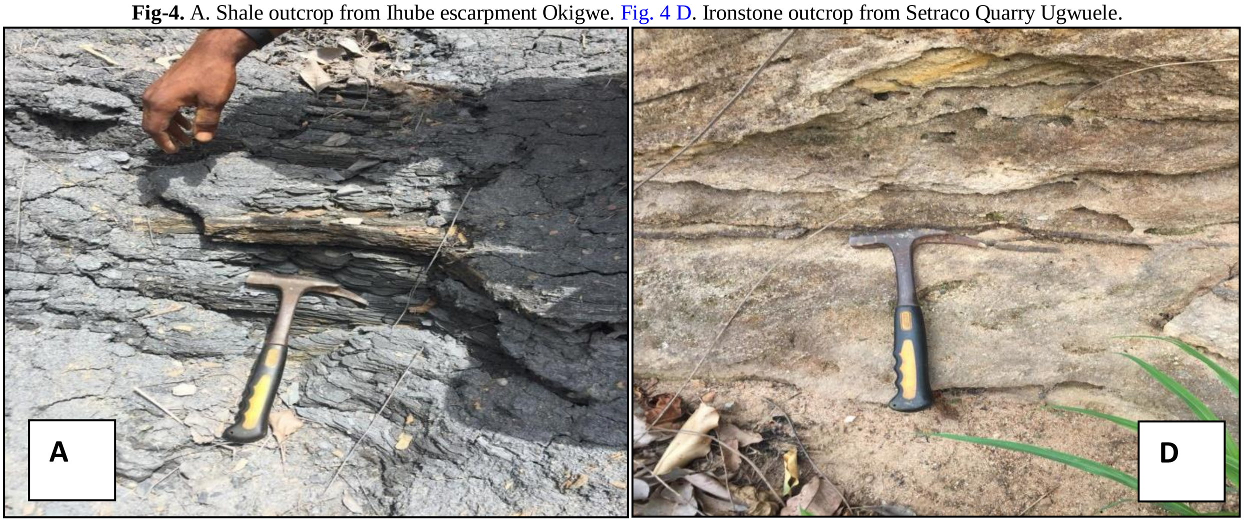
The dolerites (Fig. 3A) are igneous rocks of intermediate hyperbyssal to basic character, composed mineralogically and chemically of similar properties as gabbro and basalt [19]. They occur at the Crush Rock and Setraco quarries Ishiagu and Ugwueleareas respectively.

Fig-3. Photomicrographs of Ishiagu and Environs SE. Nigeria: A. Dolerite, showing plagioclase laths (PL), pyroxene blades (PB), and olivine crystals (OC). B**.** Diorite, showing plagioclase (Pl), pyroxene (Py) and quartz (Qz). i. XPL x 20, ii. PPL x 20



They are dark, hard with interlocking crystalline texture showing high content of ferromagnesian minerals like olivine, pyroxene and plagioclase (anorthite An $_{70}$ – An $_{100;}$ Fig, 3A). They often occur in swarms in some places [22].

Fig-4. A. Shale outcrop from Ihube escarpment Okigwe. Fig. 4 D. Ironstone outcrop from Setraco Quarry Ugwuele.



4.2. Diorite

The diorite outcrops in Crush Rock and Setraco quarries around Ishiagu and Ugwuele area. They showed nearly vertical strike in NE-SW (0-040^o), and dip about (75^o-85^{o}SE). They often show diagonal fractures and faults (Fig, 3B), indicating probable deformation during the Cenomanian and/ or Turonian orogeny. Texturally, they are coarse to medium grained, indicating slower cooling due to deep seated emplacement. They are dark to grayish in color, hard with interlocking crystalline texture corroborating their high content of ferromagnesian minerals, such as plagioclase (An$_{70}$), pyroxene and biotite [23-26]. Fig, 3B shows photomicrograph of the diorite.

4.3. Sedimentary and Metasedimentary Rocks

Shale, sandstones, limestones, mudstone and Ironstone (Fig. 4a, b), are the major sedimentary and meta-sedimentary rocks [27], into which the igneous dolerites, diorites, basalts, and granitic rocks occurring in the form of dikes, sills and stocks had intruded [28]. They outcrop in almost all parts of the study area. The sandstone outcrops form ridges, while the shale and limestones had been weathered, eroded and washed down forming valleys/depressions in the area. These valleys/flatlands constitute the main agricultural farmlands for rice, cassava, plantain, and palm tree cultivation in the area.

4.4. Geochemistry

The results of the whole rock geochemical analysis of the samples from Ishiagu and Environs Southeastern Nigeria are presented in (Tables 2 and 3). The geochemical data expressed in weight percent of the representative oxides were plotted in various discriminatory diagrams (Figs. 5, 6, 7, 8). Table 2 shows that all the rocks are enriched in SiO_2, Al_2O_3, Fe_2O_3, and TiO_2 with average values of 48.367. 17.40, 26.29, 3.07 Wt.% respectively, except the sample of ironstone from Setraco Quarry Ugwuele (L5-ISQU), which is relatively depleted in Al_2O_3 and TiO_2. Table 2 also revealed a total depletion of MgO_2 in all the analyzed rock samples except the diorite sample from Crush Rock Quarry, Ishiagu (L1- CGD), which has a value of 1.00wt%. The average concentration of the trace elements (TE, Table 3) shows that the values of Zr > Sr > V > Cr > Rb > Cu > Ni = 172.49 > 109.73 > 83.62 > 73.21 > 36.58 > 23.96 > 23.69 ppm respectively, indicating enrichment of Zr, Sr and V and a relative depletion of Rb, Cu and Ni. The V concentration is 83.62ppm which is very close to 80ppm reported by Taylor and McLennan [29] for average composition of Oceanic crust (Table 3). This is further evidence that these rocks are of oceanic environment parentage.

Table-2. Average Results of Whole Rock Major Elements Geochemistry (Wt. %) of Ishiagu and Environs

Major Element (Oxide %)	L1- DCRI	L2-DSQI	L3- DSU	L4-SMFO	L5-ISQU	L6-ISI	∑FN/N
iO_2	42.30	46.50	40.40	49.20	48.60	47.30	48.37
Al_2O_3	9.20	11.00	11.00	23.80	ND	11.00	17.40
Fe_2O_3	22.16	20.58	22.60	7.18	48.41	23.27	26.29
MgO	1.00	ND	ND	ND	ND	ND	0.16
CaO	10.50	6.92	9.25	0.08	0.02	2.83	0.98
TiO_2	3.76	2.49	4.33	6.69	0.29	2.24	3.07
Na_2O	1.82	2.72	2.14	1.07	0.01	2.31	1.13
K_2O	1.85	2.92	2.24	1.06	0.02	2.23	1.10
MnO	0.27	0.29	0.28	0.03	0.05	0.23	0.10
P_2O_5	1.00	ND	1.00	ND	0.50	0.76	0.63
LOI	1.60	1.80	5.60	9.7	3.5	3.8	5.67
TOTAL	95.46	95.22	98.84	98.81	101.4	95.97	104.74
Na_2O+K_2O	3.67	5.64	4.38	2.13	0.03	4.54	3.36
Na_2O/Al_2O_2	0.19	0.24	0.19	0.045	0.0	0.21	0.09
K_2O/Al_2O_2	0.20	0.26	0.20	0.046	0.0	0.20	0.08
K_2O/Na_2O	2.25	1.07	1.04	0.99	2.0	0.96	1.32

KEY: LOI = Loss on Ignition. L1- DCRI = Diorite from Crush Rock Quarry, Ishiagu. L2- DSQI = Diorite from Setraco Quarry, Ishiagu. L3- DCI = Dolerite from Crush Rock quarry, Ishiagu. L4- SMFO = Shale from Mamu Formation, Okigwe. L5-ISQU = Ironstone from Setraco Quarry Ugwuele. L6-ISI = Ironstone from Setraco Quarry, Ishiagu.

4.5. Petrogenesis

The rocks were further analyzed for magma sources/protoliths and tectonic setting using various petrogenetic discrimination diagrams. In the Alkali-Silica diagramNa_20 + K_20 wt% versus $Si0_2$ wt. % [30, 31] Fig. 5, the diorite plotted in the tholeiitic field, while the dolerite plotted in the alkali field. Thus, indicating that these igneous rocks originated from alkali rich tholeiitic basalt magma. The magma must have originated from upper mantle or lower crust and emplaced at the hyperbyssal depth [1, 31].

The plot using the AFM diagram (Fig 6), shows that all the dolerites and diorites fell in the tholeiitic field, thus corroborating the earlier geochemical result. In the TiO_2-K_2O-P_2O_5 ternary discrimination diagram (Fig. 7), all the analyzed dolerite and diorite samples plotted in the oceanic field, indicating that they are of oceanic basalt magma. The TiO_2 values were 3.6 wt. % and 4.33 wt % for the diorite and dolerite respectively (Table 3), which strongly support oceanic origin for the dolerite and diorite igneous rocks.

Table-3. Average Results of Trace Element Geochemistry (Wt. % and PPM) of Rocks of Ishiagu and Environs, SE. Nigeria, compared with reports of other tectonic settings from other parts of the world

PRESENT STUDY										OTHER TECTONIC SETTINGS			
TE-% Oxide	L1- DCRI	L2- DSQI	L3- DSU	L4- SMF	L5- ISQ	L6- ISI	∑FN/n	TE-A PPM*	TE Ppm	ACC TM	AOC TM	AGRW LM	AC PM
Cr_2O_3	0.11	0.12	0.12	0.09	0.15	0.08	0.107	73.210	Cr	1	270	4	3011
V_2O_5	0.15	0.09	0.16	0.25	0.03	0.09	0.123	83.620	V	230	80		8.3
CuO	0.03	0.03	0.03	0.03	0.03	0.03	0.030	23.964	Cu	75	8.6		28.5
NiO	ND	ND	0.09	0.03	ND	ND	0.030	23.694	Ni	105	135	5	2018

ZnO	0.02	0.03	0.03	0.01	ND	0.04	0.025	20.083					
Ga_2O_3	ND	ND	ND	0.02	ND	ND	0.020						
Rb_2O	0.02	0.02	0.02	0.0.1	0.05	0.03	0.040	36.576	Rb	185	2.2	170	0.55
SrO	0.32	0.13	0.27	0.08	ND	0.16	0.120	109.72	Sr	11	250	100	82
ZrO_2	0.21	0.22	0.19	0.27	0.18	0.25	0.233	172.49	Zr	11	250	175	82
Nb_2O_5	0.03	0.04	ND	0.04	ND	0.04	0.040		Nb	20	2.2		0.56
PbO	ND	ND	ND	0.04	ND	ND	0.040	37.13					
Au	ND	0.03	0.04	ND	ND	0.03	0.030						
As_2O_3	ND	ND	ND	0.04	ND	ND	0.040						
SO_3	0.10	ND	ND	4.27	0.08	ND	0.780	312.39					

KEY: TE APPM* = Trace element average parts per million (After 1969 International Atomic Weight; [31]). ND = Not Detected / Determined. **L1 – L6** Rock description remain as shown under Table 2. A**CC-TM =** Average composition of Continental crust [29]. **AOC-TM =** Average composition of Oceanic crust [29]. A**GRW-LM =** Average composition of Granitic rocks from worldwide localities [32]. **AC-PM =** Average composition of Primitive mantle [29].

In the $Si0_2$ wt. % versus $Na_20 + K_20$ wt. % (Fig. 8), all the analyzed diorite and dolerite samples plotted in the basalt field, except the sample of dolerite from Crush Rock Quarry Ishiagu, which plotted in the tholeiitic basalt field. This further supports tholeiitic basalt magma protolith for the dolerite and diorite.

Fig-5. K_2O+Na_2**O** versus SiO_2 diagram for discrimination of the mafic-ultramafic rocks of Ishiagu and Environs, Southeastern Nigeria (After [30, 31])

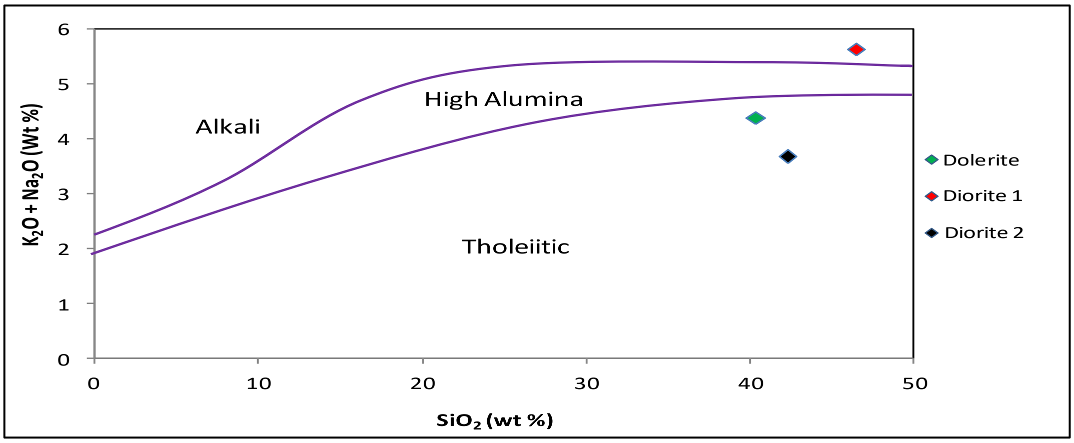


Fig-6. AFM diagram for discrimination of rocks of Ishiagu and Environs Southeastern Nigeria (After [33])

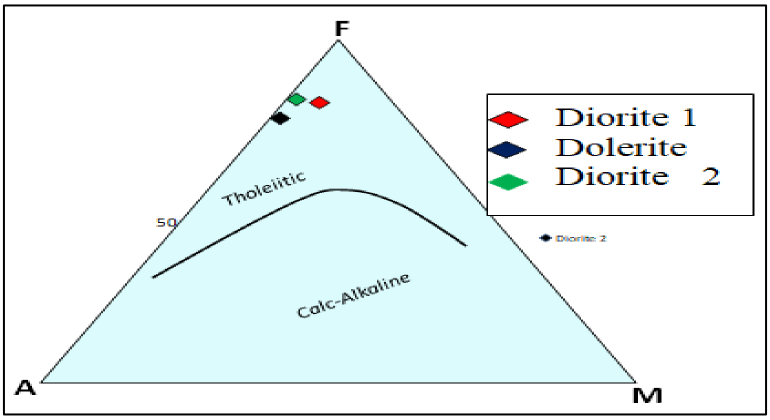


Fig-7. AFM diagram for discrimination of rocks of Ishiagu and Environs Southeastern Nigeria (After [33])

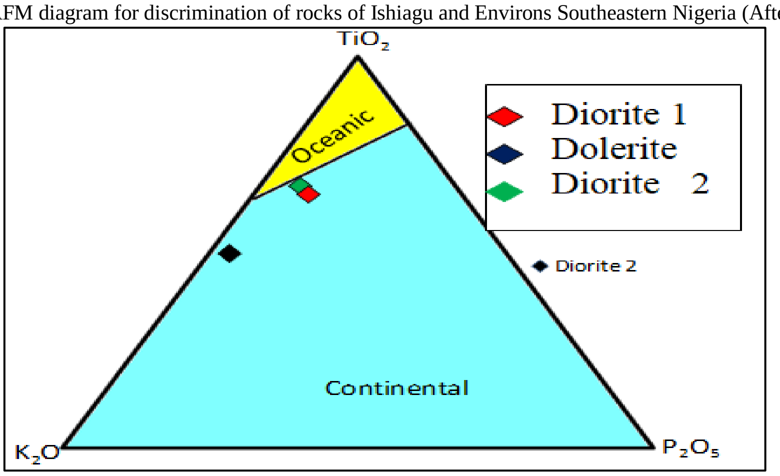
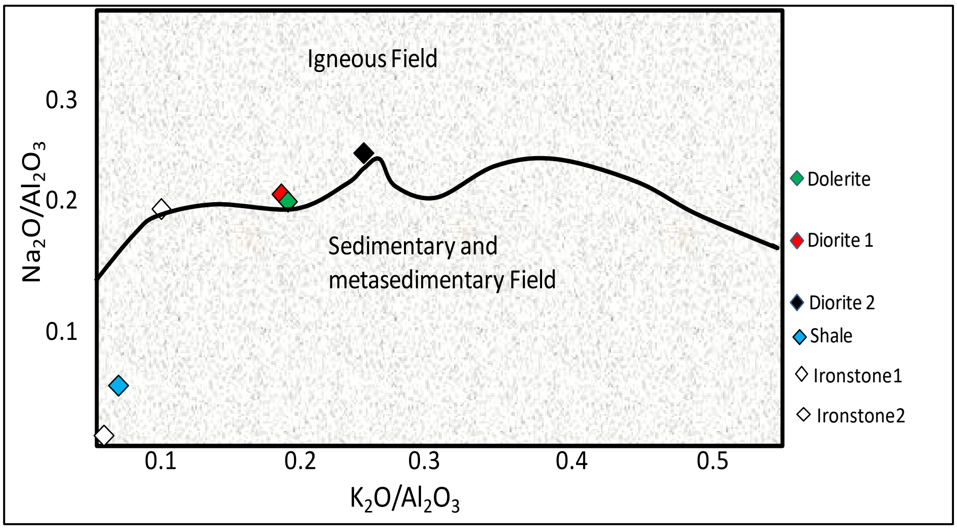


Fig-8. Na_2O/K_2O versus K_2O/Al_2O_3 ternary diagram for discriminating rocks of Ishiagu and Environs Southeastern Nigeria ([30])



The above results all agree with those of Ekwueme [2] in the study of rocks of Uwet area and Obioha [7] in the study of rocks of Ishiagu area both of Southeastern Nigeria. Petrological characteristic analysis using Na_2O/K_2O versus K_2O/Al_2O_3 ternary diagram Fig. 8 [30], all the dolerites and diorites plotted in the igneous field, the shale plotted in the sedimentary / metasedimentary field, the samples of ironstone from Ugwuele plotted in the boundary between igneous and sedimentary / metasedimentary field, indicating hybrid provenance for the ironstone.

5. Conclusion

Systematic study of rocks of Ishiagu and environs showed that dolerite and diorite of tholeiitic basalt composition were the main igneous rock outcrops in the area. These were emplaced in shale and mudrocks sedimentary / metasedimentary host rocks. The SiO_2 content of the rocks ranged from 40-49wt.%, indicating basic to ultra-basic origin. The industrial metals Zn, Pb, Cu, and Ni show narrow concentration range of 20-24ppm, pointing to a common protolith. Petrogenetic discriminant (Na_2O/K_2O versus K_2O/Al_2O_3), showed that the dolerite and diorite plotted in the igneous field corroborating their magmatic origin,the shale plotted in the sedimentary/metasedimentary field, indicating sedimentary provenance. One sample of ironstone plotted in the igneous field, and one in the boundary between igneous and sedimentary fields (Fig. 8), showing hybrid origin. The TE composition, AFM ternary discriminant and K_2O+Na_2**O** versus SiO_2 binary diagram, all corroborated tholeiitic basalt magma, emplaced within oceanic environment for the diorite and dolerite.

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