# RE-APPRAISAL OF THE GENESIS OF ISHIAGU LEAD-ZINC ORE DEPOSITS, SOUTHERN BENUE TROUGH, NIGERIA

BY

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DEPARTMENT OF GEOLOGICAL SCIENCES,

FACULTY OF PHYSICAL SCIENCES,

NNAMDI AZIKIWE UNIVERSITY, AWKA.

January, 2020

### TITLE PAGE

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### SUBMITTED TO THE

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### FACULTY OF PHYSICAL SCIENCES,

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January, 2020

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### DEDICATION

This work is dedicated to our Lord Jesus Christ, my husband, my parents and my children.

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#### ABSTRACT

The aim of this research work is to use stable isotopes to unravel the genesis of the Ishiagu Lead-Zinc ore deposits. The objectives were to map the study area showing the Lead-Zinc veins, collect samples of ores and rocks associated with the deposit and carry out stable isotope and geochemical studies in order to create a genetic model for the Ishiagu Lead-Zinc deposits. The methods utilized include: geological field mapping, mass spectroscopy for stable isotope geochemistry and X-Ray Fluorescence (XRF) for igneous and carbonate rock geochemistry. Results of geological field mapping identified NW-SE fractured carbonaceous shale, intruded by some basic- ultrabasic igneous rocks. One of the lodes studied cut across the basic intrusive. The  $SiO_2$ ,  $Fe_2O_3$ , and MgO contents of the igneous rock range (in wt%) from 37.7 to 52.1, 8.24 to 16.34 and 4.0 to 14. 93 respectively. The CaO and LOI contents of the carbonate rock range (in wt%) from 48.06 to 49.08 and 37.65 to 38.42 to respectively.  $\delta^{34}$ S of the sulphide ore ranges from  $-8.2^{0}/_{00}$  to  $-2.0^{0}/_{00}$ .  $\delta^{18}$ O and  $\delta^{13}$ C of siderite range from  $20.59^{\circ}/_{00}$  to  $23.19^{\circ}/_{00}$  and  $-1.93^{\circ}/_{00}$  to  $-1.38^{\circ}/_{00}$  respectively. Igneous rock geochemistry established that the intrusive rocks of the area are mainly alkaline gabbros with few ultrabasic varieties. Comparing the  $\delta^{34}$ S,  $\delta^{18}$ O and  $\delta^{13}$ C values from the sulphides to the Natural Sulphur, Oxygen and Carbon Isotope Reservoirs respectively, revealed the similarities between the stable isotope compositions to that from the anchimetamorphosed to unmetamorphosed sedimentary rocks. The range of the sulphur, oxygen, and carbon isotope compositional ratios showed that the ore was deposited under anoxic, slightly acidic and isotopic partial equilibrium conditions. The temperature calculated from isotope geothermometry of the contemporaneous mineral pairs range from 152°C to 240°C with the fractionation factor between the mineral pairs inversely proportional to the temperature of formation. Temperature calculated using carbon isotope is 134 °C. Isotope ratios revealed that one of the lodes was formed in a more reduced condition than the other two. It is therefore proposed from these genetic models that the Ishiagu Lead-Zinc lodes were generated from the anchimetamorphosed to unmetamorphosed shales of the Asu River group of the area and the ores deposited under a reduced, isotopic equilibrium condition, with the temperature of formation ranging between 152°C to 240°C.

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### LIST OF ABREVIATIONS

Δ	Change
<sup>0</sup> / <sub>00</sub>	Per mil
<sup>32</sup> S	Lighter sulphur Isotope
<sup>34</sup> S	Heavier sulphur Isotope
<sup>34</sup> S/ <sup>32</sup> S	Sulphur Isotope partition function
ATMN	Amalgamated Tin Mines of Nigeria
BMS	Base Metal Sulphide
С	Carbon
CaO	Calcium oxide
CI	China Intrusive
Cu	Copper
E	East
Eq	Equation
Fe	Iron
G	Gabbro
GF2	Greenfield Mine 2
GF3	Greenfield Mine 3
GF4	Greenfield mine 4
GFI	Greenfield Mine 1
GI	Greenfield Intrusive
Н	Hydrogen
$H_2S$	Hydrogen sulphide

Ι	Ijolite
Km	Kilometers
Ln	Mathematical log
Mn	Manganese
MVT	Mississippi Valley Type
Ν	North
NaCl	Sodium chloride
NGSA	Nigeria Geological Survey Agency
0	Oxygen
°C	Degree centigrade
ОН	Hydroxyl
Pb	Lead
Pbs	Galena
Ppm	Parts per million
RSP	Palladium Mine
S	Sulphur
$S^1$	South
Sd	Syenodiorite
SiO <sub>2</sub>	Silica
$SO_2$	Sulphate
Т	Temperature
TA	Total Alkalis
TOF	Temperature of Formation

VLF-EM	Very Low Frequency Electromagnetic
W	West
Wt %	Weight Percent
XRF	X-ray Fluorescent
Zn	Zinc
Zns	Sphalerite
ZPE	Zero Point Energy
α	fractionation faction
δ	Isotope compositional ratio

#### **CHAPTER ONE:**

#### **INTRODUCTION**

#### 1.1 Background to Study

One of the main agenda of the current political administration is the diversification of the crude oil monopolized economy into solid mineral development. Nigeria is endowed with vast and varied solid mineral resources among which are galena and sphalerite. Mineral deposits are complex in nature and no two mineral deposits are alike (Jensen and Bateman, 1979). The galena-sphalerite (lead-zinc) mineralogical province of Nigeria stretches across the Benue Trough with the deposit in each part of the trough exhibiting a slight difference in the mineralogy of the ore and the gangue (Olade, 1976; Okezie, 1965). The Ishiagu lead-zinc deposits are located at the southwestern extreme of the trough. The mineralization is hydrothermal in nature and hydrothermal deposits are known for their limited range of minerals, mostly sulphides. (Rose and Hawles, 1979).

The Benue Trough mineralization province therefore affords a good opportunity to examine the detailed characteristics of one of the lead-zinc districts in order to establish its specific origin. The slight variability in habitat noted among the deposits of the Benue Trough may have accounted for the difference in the mineralogy of the ore and gangue. The ore-hosting sediments of the Benue Trough range from deep marine carbonaceous shale in the Southern Benue Trough to platform carbonate in the Central Benue Trough and fluvial to deltaic sandstone in the Northern Benue Trough (Akande *et.al*, 1992). The close proximity of Ishiagu deposits to some intermediate-basic intrusives more than the other deposits of the Benue Trough, should not be overlooked. There is also remarkable difference in the barite content of the Benue Trough deposits from the southwest (Ishiagu district) to northeast (Gabu district) of the Trough (Oha *et.al.*, 2017). Establishing the specific origin and conditions of formation of these deposits is therefore paramount for its characterization and may give an answer to differences mineralogy between the deposits.

Some variants of genetic theories of the deposits have been propounded using trace elements and fluid inclusions (Olade & Morton, 1985: Akande et.al., 1988). Stable isotopic studies have been used on some of the Benue Trough deposits but has not been applied for lead-zinc deposits in Ishiagu. Microthermometry was in some cases used to specifically determine the range of temperatures (Olade and Morton, 1985; Akande et. al., 1988; Christopher and Baldassare, 2014). However, it is a well known fact that temperatures estimated from fluid inclusions can be affected by pressure variability (Barnes, 1979). Hydrothermal deposits are group of deposits which have been investigated and mined far more than any other group and have given rise to many of the great mining districts of the world (Jensen and Bateman, 1979). They are formed when aqueous fluids move through a defined channel and precipitate under favorable conditions to form ore deposits. Hydrothermal fluid can take its source from connate, metamorphic, meteoric and magmatic waters. Though all aqueous solutions are brines of some sort, they vary in their stable isotopic composition which is a function of the different sources of the fluid as well as the conditions of formation of the deposits. Hydrothermal fluids also vary in their major and minor elemental compositions and concentrations and this variance has led to the formation of hydrothermal deposits of different mineralogy (Rose and Hawles, 1979; Jackson, 1979).

This study therefore primarily used stable isotopes to generate a detailed scientific-based genetic model for the Ishiagu Lead-Zinc deposits .The study also looked at the use of an alternative method in estimating the temperatures of formation of each of the deposits. The information got can be harnessed, documented and used for search for more Lead-Zinc deposit.

#### **1.2 Statement of Problem**

The genesis and conditions of formation of the Ishiagu Lead-Zinc deposit has not been properly defined as there are still some controversies trailing the origin of the ore deposit. Establishing the genesis of a deposit is paramount for its characterization. The higher concentration of intermediate – basic intrusives in the Ishiagu area more than other parts of the Benue Trough may have some effect on the origin of Ishiagu deposit. Akande *et. al.*, (1992) suggested that the ore hosting shales in the Southern Benue are slightly more metamorphosed than that of the Middle Benue Trough. Many scholars have studied the genesis of the lead-zinc deposit of Ishiagu but on a regional scale (Central and Southern Benue Trough) (Tattam, 1944 ; Mc-Connel, 1949; Bogue & Renold, 1952; Farrington, 1952; Olade and Morton, 1985; Wright, 1985 ; Akande *et. al.*, 1988). There is therefore need for more detailed study using stable isotope compositions of the deposit. The temperatures of formation of the deposits need to be addressed using a different method (isotope geothermometry). Better understanding of the spatial/trend of isotope distribution and the physico- chemical conditions of ore deposit (Krauskopf, 1967).

### 1.3 Aim and Objectives

The aim of this study is to re-appraise the genesis of the Ishiagu Lead-Zinc deposit of the Southern Benue Trough. The objectives are to:

Carry out geological mapping of the study area Carry out a geochemical study of the intrusives and ore deposit. Carry out sulphur, oxygen and carbon isotope studies on the ore Establish the source and conditions of formation of the ore deposit and Create a genetic model for the Ishiagu deposits

#### 1.4 Scope of Study

The scope of this work includes:

Geologic mapping of the Ishiagu Lead-Zinc Sub-district Southern Benue Trough

Geochemistry of the intrusive rocks.

Establishing the source of the ore fluid using sulphur, oxygen and carbon isotope studies.

Computing the temperature of formation of the deposit using isotope geothermometry.

Use of equilibrium curve to establish the level of isotopic equilibrium attained during the formation of the deposit.

Establishing the effect of the direct host to the deposits using stable isotopes.

Proposing a genetic model for the formation of Ishiagu deposit.

#### 1.5 Significance of the Study

This present work is important considering the fact that:

The deposit is worth studying as hydrothermal deposits have given rise to many of the great mining district of the world and their ores are of good grade.

The understanding of the source and other genetic parameters of the deposit can be of assistance in the development of effective exploration model and thus enable finding of more deposits in the Benue Trough.

The study will also help to widen the already existing academic knowledge on not only the source of the lead-zinc mineralization but also the temperature and conditions of formation This research will contribute in the development of the solid minerals industry in Nigeria by motivating investments in the industry and creating jobs for the youth by finding more deposits in the area.

### 1.6 Location and Accessibility of Study Area

#### 1.6.1 Location of Study Area

The study area lies between latitudes  $5^0 54^1 00^{11}$  N and  $5^0 57^1 00^{11}$  N and longitudes  $7^0 28^1 00^{11}$  and  $7^0 32^1 00^{11}$  E (Fig. 1.1 ). The lead - zinc mines are located precisely in Ihetutu village of Ishiagu town, Ivo Local Government Area of Ebonyi State, Southeast Nigeria. The study area covers approximately 48 square kilometers.

### 1.6.2 Accessibility of Study Area

The study area is about 60 km south – southeast of Enugu City. It is accessible from Enugu via Enugu to Port Harcourt highway to Ishiagu Junction. It is also accessible from Anambra State capital Awka through Awka - Umunze – Isuochi road then to Enugu- Port Harcourt highway and to Ishiagu Junction. 16 km east of Ishiagu Junction is the Community Bank Junction. The study area lies between 5 to 6 km southwest of the Community Bank Junction in Ishiagu town (Fig. 1.1).



Figure 1.1: Location and Accessibility Map of the Study Area

#### **1.7** Climate and Vegetation

Rainfall in the Southeastern Nigeria generally is seasonal. The dry season is from November to March while the rainy season is from April to October, with July as peak of rainfall. The mean annual temperature varies from  $18^{\circ}C - 28^{\circ}C$  and mean annual rainfall of approximately 150 - 230cm are obtainable in the area, together with high humidity (Udo,1970; Dunbar & Udo, 1972). The two prevailing climates results from the two prevailing air masses that blow across Nigeria; the Maritime air mass and the Continental air mass. The maritime air mass originates from the Atlantic Ocean where it picks moisture and enters Nigeria from the south. This air mass is responsible for the rainy seasons. The tropical continental air mass originates from the Eurasia - Arab high pressure belt. This northeasterly wind causes extreme dryness from the month of October to April.

The study area lies within the Guinea Savanna consisting of the high and luxuriant tall grasses and stunted trees (Plate 1.2). The vegetation is controlled by many factors, including drainage, topography, lithology and rainfall. However, a typical vegetation of the area consists of small and slender trees, tall grasses except along the stream valleys which are characterized by dense tropical forests. The common trees in the area include mahogany and palm trees and it is pertinent to point out that this present vegetation (relatively sparse in some areas) does not reflect the true vegetation but resulting from derived savanna forest (Plate 1.2).



Figure 1.1: Map of Nigeria showing the vegetation belts (modified from Iloeje, 1981)



Plate 1.1: Typical Vegetation of the Area

#### **1.8 Relief and Drainage**

The geomorphology of the study area is controlled by the prevalent topographic and geologic factors. The Ishiagu area is generally underlain by sedimentary rocks with pronounced intrusion of igneous rocks (Kogbe, 1989). The area is a gently rolling country of low relief, which forms a part of the Cross River Plain. The general elevation is averagely 300metres above sea level while a few hills such as Ugwuodu and Ugwuajirija stand out reaching above 300m above sea level (Ezepue, 1984). These hills owe their origin to the associated igneous intrusions, all of which are more resistant to weathering than the surrounding shale. In the lead–zinc mineralized zones, resistance to weathering is enhanced by silicification and baking of the country rock (Reyment, 1965).

The area is characterized by a dendritic type of drainage slightly tilting southeast wards. The drainage is controlled by two major rivers; River Ikwo, and River Owa, which have sculptured the landscape (Fig 1. 3). The River Ikwo flows in the West to East direction and drains the northern region of the study area. River Owa, with two tributaries of River Aku and River Ivo drains the southern part of the area. The channels of these rivers constitute the lowest portions of the area while the drainage pattern is dendritic. Some of the rivers are seasonal and therefore dry up during the dry season. The origin of most of the rivers has been attributed to the fractured shale and impervious contact between the shale and the sandstone lenses which characterize the lithology of the study area.



Fig 1.3: Drainage map of the study area showing flow from west to east and the dendritic pattern

#### **CHAPTER TWO: LITERATURE REVIEW**

#### 2.1 History of Mining in the Study Area

The genesis and structure of the lead-zinc mineralization of the Benue Trough have been studied by so many authors as the occurrence has attracted a lot of attention. With respect to geography and mineralization, the Benue Trough of Nigeria hosts three Lead-Zinc mineralization districts: The Abakaliki-Ishiagu Lead-Zinc district in the Southern Benue Trough, the Arufu-Akwana Lead-Zinc district in the Middle Benue Trough and the Zurak-Wase Lead-Zinc district in the Upper Benue Trough (Fig.2.1), (Ofodile, 1975; Akande & Mucke, 1989; Olade and Morton, 1985). Farrington (1952) did a preliminary study of the Nigerian Lead-Zinc fields and discovered that the field covers over 48,000 square kilometers in extent with mineralization at many centers. The deposits in the lead-zinc fields are localized in the Cretaceous sediment along a 600 km long belt within the Benue Trough extending from Ishiagu to Zurak. He recorded that exploitation of galena and sphalerite in the Ishiagu sub-district started as far back as 1925 by the villagers. Bogue & Raynold (1952) admitted that the people of Ishiagu knew of the existence of galena long before 1940 when they started mining it locally for sale and use as cosmetics. Mining of the ore has been carried out for a long time by both the natives for local use as cosmetics and foreign companies for export (Offodile, 1975). From the early 1960's to date, the lead-zinc sub district has been leased to so many mining companies who engaged in both underground and open cast mining. The ores are turned into concentrates (manually) for shipment to foreign countries. Currently, only two companies are engaged in major activities in the area; Greenfield Mine and Palladium Nigeria Limited.



Fig. 2.1 Geologic Map of the Benue Trough Showing the Lead-Zinc Sub Districts (Akande, *et.al.*, 1989)

Series of unpublished research works have been done on the deposit by governmental agencies and some private companies. As early as 1905 the Ishiagu Lead–Zinc deposit was examined by the officers of the then Mineral Survey of Southern Nigeria. From 1922 to 1923, the Russian – Asian Company tested some of the deposits by means of shallow boreholes. In 1947, the area received another attention when Mines Development Syndicate conducted an extensive prospecting programme around Abakaliki, while; McConnell (1949) made a reconnaissance survey of the deposit and wrote short reports. From 1949 – 1952, the Amalgamated Tin Mines of Nigeria Limited (ATMN) carried out a preliminary geological examination of the deposit but did not follow up with the mining.

### 2.1.1 Existing Genetic Models on the Nigerian Lead-Zinc Field

Many scholars have studied the origin as well as the temperature of formation of the Lead-Zinc deposits of the Benue Trough and this has evoked so many genetic hypotheses. Bogue and Raynold (1952) made use of the characteristic features of the deposit as well as its similarities with Lindgren's classification to suggest that the deposit of Ishiagu took its source from magmatic hydrothermal solution from the immediate alkaline intrusive and the deposition is mesothermal. Tattam (1944) believed that the mineralizing solution came from relatively deep seated felsic intrusions which have not been exposed by erosion. Mc Connel (1949) associated the lead-zinc deposit of Nigeria to the telethermal type that originated from low temperature hydrothermal solution associated with the Tertiary to Recent volcanism.

With respect to the published works on the genesis of the deposit, Farrington (1952) noted that the mineralization is hydrothermal and epigenetic in origin and formed under mesothermal conditions with the hydrothermal fluid taking its source from the surrounding intrusives. Olade (1976) and Olade & Morton (1985) used fluid inclusion studies to show that the sphalerite- galena of the Abakiliki- Ishiagu ore bodies were deposited at relatively

low temperature of  $102^{0}$ C –  $175^{0}$ C with ore fluid salinity mostly in the range of 17-25 equivalent wt.% NaCl. They also predicted that the mineralization is attributed to connate brine set into motion by a high geothermal gradient accompanying continental rifting and the mineral deposition was caused principally by rapid cooling due either to reaction with wall rocks or mixing with meteoric or descending water of low salinity. Akande *et.al.*, (1988) made use of microthermometry of the fluid inclusion to establish a homogenization temperature of  $106^{0}$ C to  $148^{0}$ C and salinity of 15 to 23 equivalent weight percent NaCl for the ore fluid that formed the Central and Southern Benue deposits. He likened the galena-sphalerite mineralization of the Central Benue Trough to sphalerite-galena-fluorite subtype of the Mississippi Valley Type deposit and also suggested that the Lower Paleozoic Basement rocks and their weathered equivalents are the likely source for the Benue Trough ore components. Oxygen, strontium and lead isotope data from the deposit suggested that the ore forming fluid was probably contributed from the Cretaceous evaporite in the trough.

Folorunso & Bale (2015) characterized the mineralizing fluid that formed the Ariki Vein Copper Mineralization, Northern Benue Trough using the oxygen and carbon isotope compositional ratios got from the siderite. He used these compositional ratios to establish that the carbon that formed the deposit took its source from the Cretaceous marine carbonates while the value for the oxygen isotope compositional ratio indicates meteoric water source. He also stated that the significant depletion between the  $\delta^{18}$ O compositions of Akiri siderite when compared to other siderites from some other deposits of the Basin is a function of their differential temperature of formation or fluid composition.

With respect to trace element studies, Olade and Morton (1985) used the trace elemental composition of the sphalerite and galena of the Southern Benue Trough to confirm that the deposit of the study area was formed at a low temperature and that it is of epigenetic origin. This they concluded after comparing it with some other similar deposits of the world. Ezepue

& Dunham (1983) through the trace element studies of sphalerite from the study area concluded that the iron content of Ishiagu sphalerite is very small (0.9 wt% average) to be able to replace zinc in high temperature and iron rich environment. He thereby stated that the trace elemental content of the sphalerite is similar to that from other low temperature deposits of the world. Ezepue (1984) also used XRF to analyze for the minor element composition of the galena and siderite of Ishiagu deposits and detected the presence of Ag and Sb in the galena unlike that of Akande *et. al.*, (1988) who noted the absence of Ag and F in the Southern Benue Trough Lead –Zinc deposit. Ezepue (1985) also reported the presence of Ag, Cd and Sn in the siderite. He used electron microprobe of the major elements found in the siderite to show the substitution of the FeCO<sub>3</sub> by CaCO<sub>3</sub>, MgCO<sub>3</sub> and MnCO<sub>3</sub> and then established that the Ishiagu FeCO<sub>3</sub> is richer in FeCO<sub>3</sub> content (5- 20%) than most siderite from not only the other part of the Benue Trough but also that of Britain and Europe (Bethke & Barton, 1971). He established that the Ag and Sb content and ratio in the galena are also consistent with other epithermal deposits elsewhere.

### 2.1.2 Mineralogy of the Benue Trough Deposits

Akande *et. al.*, (1988) compared the mineralogy of the Central Benue Trough lead-zinc mineralization to that of the Southern Benue Trough and found out that the Central Benue deposits which occur in the carbonate sequence of the Cretaceous Albian contains galena, sphalerite, tetrahedrite, native silver and chalcopyrite unlike the deposit of the Southern Benue Trough which is mainly galena and sphalerite and is hosted by the Albian carbonaceous shales. Akande & Mucke (1989) and Ogundipe & Obasi (2016) stated that the Ishiagu ore deposit consist of massive sphalerite, galena, chalcopyrite, marcasite, siderite, calcite and quartz in descending abundance and proposed the three stages of event in the evolution of the Lead –Zinc deposit to be:

- i. Pre ore fracturing and bracciation of the Albian shales accompanied by the precipitation of pyrite, siderite and quartz.
- ii. Ore stage formation of sphalerite, galena and copper bearing minerals (chalcopyrite, bonite, chalcosite and tetrahedrite).
- iii. Final deposition of octahedral galena, sphalerite, bravoite and marcasite in the hanging walls of the veins.

Oha *et. al.*, (2017) studied the barium content of the mineralization of the Benue Trough and noticed a remarkable increase in their barite content from southwest to northeast with the lead-zinc-barium ratio ranging from approximately 3:1:0 at Ishiagu , 2:1:0 at Enyigba, 1:0:2 at Wanikande and nearly 100% barite at Gabu-oshina,

Olubambi *et. al.*, (2008) use microscopic ore textures to characterize the deposit of Ishiagu as hydrothermal vein deposit. He used X-ray diffraction to show that the sphalerite mineral in the ore consist of fine to coarse grains with less complex intergrowths of the constituent and confirmed that the mineralogy consist of siderite, sphalerite, galena, quartz and traces of pyrite and copper bearing minerals.

Akande *et. al.*, (1992) studied the environment of ore formation and anchizonal metamorphism in the Lead-Zinc-Fluorite- Barite deposit of the Benue Trough, Nigeria and observed that the reflectance (Rm) of finely dispersed vitrinite in the ore-hosting sediments reaches up to 4.3% at the vein centre and decreases to 2.6% at about 2km from the vein in the Southern Benue Trough. The vitrinite reflectance ranges from 0.9 to 1.7 at the Middle Benue veins. He used illite crystallinity indices of these shales in places to suggest anchi to epimetamorphic contact aureole adjacent to the intrusive bodies while he used the vitrinite reflectance (Rm) to suggest that the ore hosting shales in the Southern Benue are slightly metamorphosed than that of the Middle Benue Trough.

#### 2.1.3 Geologic Structures of the Host Rocks

Ezepue & Dunham (1983), Fatoye et. al., (2014) and Obarezi & Nwosu (2013) on different research works stated that the Pb -Zn deposit of southern Nigeria are associated with the folded shales of the Asu River Group and is restricted to a series of closely spaced faults/fractures trending NW-SE. They also reported that the mineralization is exclusively fissure fillings and suggested two episodes of mineralization for the deposit. An epigenetic model of the deposit has also been proposed on the basis of the vein morphology and relationship to the fractures. The lead-zinc mineralization is structurally controlled by the folded, faulted and fractured/jointed host rocks. Fatoye et. al., (2014) established that the mineralization occur in form of disseminations, stockworks and narrow beds with poorly developed wall rock silicifications and that the host lithologies are highly varied ranging from shale to siltstone, sandstone and limestone in the Southern Benue Trough with occasional igneous bodies to shale to siltstone, sandstone, conglomerate ironstone, minor limestone beds and occasional igneous bodies in the Middle Benue Trough. In the Upper Benue Trough, It ranges from shale to sandstone, mudstone, limestone, clay and porphyritic granite. Obarezi and Nwosu (2013) also stated that the joints and fractures that controlled the Enyingba mineralization district trends NW-SE to N-S direction and dip SW.

Okonkwo *et. al.*, (2014) used the Potential Gradient Array Technique of Self Potential method to establish that the ore is a sulphide deposit. He also predicted that the orientation of the anomaly is NW-SE and NE-SW in a cross cutting pattern. Mbah *et. al.*,(2015) used Very Low Frequency Electromagnetic (VLF-EM) studies to suggest that the Lead-Zinc mineralization is structurally controlled. Both ore and gangue minerals occur in successive, symmetrical layers along vertical and/or steeply dipping fractures which often have parallel walls with the host rock indicating fissure filling mode of occurrence.

#### 2.2 Regional Tectonic and Structural Setting

The Nigerian Lead- Zinc - Barite field extends for about 560km in a narrow belt from Ishiagu in the Southern Benue Trough through Azara in the Central Benue Trough to Gidan Dari in the Northern Benue Trough (Fig. 2.1). The study area is at the southwestern tip of the Benue Depression. Murat (1972); Nwachukwu (1972); Olade,1975; Umeji,1978; Obarezi and Nwosu (2013) and Fatoye *et.al.*, (2014) reported that the Benue Trough of Nigeria is an intracontinental Cretaceous sedimentary basin of about 800km length and 150km width. It trends SW-NE from the Gulf of Guinea in the south to the Chad Basin in the north. Burke *et. al.*, (1970) reported that the trough originated as a failed arm of a triple plate margin which evolved by mantle upwelling; crustal stretching during the separation of the West African and the South American continental plates (Fig. 2.2). Benkhelil (1989) proposed transcurrent movement as the basic tectonic mechanism in the formation of the Benue Trough. With respect to tectonic, geographical and stratigraphic features, the Benue Trough is divided into the Northern, the Central and the Southern Benue Trough (Orajaka,1972 ; Nwajide, 2013).

Ages of the basin-fills in the Benue Trough generally decreases southwards from pre-Albian to Conaician (Amajor, 1987) while sediments thickness increases southwards (Reijers, 1996). Resting uncomfortably on the Basement Complex are the arkosic sandstone and shale of fluvial and lacrusrine origin and which were deposited during the Early Cretaceous rift phase (Uzuakpunwa, 1974; Hoque, 1984). The transgressive depositional phase which occurred from the Middle to Late Albian resulted to the deposition of the Asu River Group sediment in the Southern Benue Trough. Hoque (1984) established the prolonged shelf and deep basin deposition of the Southern Trough sediments under predominantly oxygen deficient bottom water condition


Fig. 2.2 Tectonic map of Southeastern Nigeria from Albian to Eocene (modified from Murat, 1972)

The structural pattern of the Southern Benue Trough which resulted from a complex tectonic evolution that occurred during the Santonian Era on the Albian sediments is one of the main factors that made the study area a viable lead-zinc mineralization province. The structures that controlled the mineralization are folds, faults, joints and fractures in which the fracture predominate (Ezepue, 1984; Obarezi & Nwosu, 2013; Fatoye et al., 2014 and Ogundipe and Obasi, 2016). Olade and Morton (1985) and Ezepue (1984) reported that the mineralization occur in a series of successive and symmetrical closely spaced, steeply dipping subparallel fractures which trend NW-SE / N-S and dip SW. The tectonic activities which the study area experienced during Santonian times helped to established its mineralization signatures. It was subjected during it's infilling to slumping, synsedimentary faulting and shearing (Fig. 2.3). Tectonic episodes of compression and faulting also occurred turning the trough into a folded belt i.e the Abakaliki Anticlinorium. The sediments are also locally tightly folded, trending NNE with local deflections traceable to the strike slip transcurrent faulting along a predetermined zone of northeast-southwest trend (Fig. 2.3). This also played a role in the tectonic history of the Benue Trough (Benkhelil and Robineau, 1983). The folding is intense in the core of the Anticlinorium (Benkhelil, 1989).

Ezepue,(1984) stated that the mineralization history, based on field relations of the lead-zinc deposit of the study area is thought to be:

- i. The deposition of the Ivo Shale, a member of the Asu River Group (Albian).
- ii. Intrusion of the intermediate to basic intrusives.
- iii. Folding of the Albian Shale and the intrusive into an anticline with a northeast (NE-SW) axial trend (Fig. 2.3), accompanied by the formation of the NE-SW and NW-SE joints sets.
- iv. Veining of the NE-SW and then the NW-SE joint system by siderite, quartz and subordinate pyrite

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- v. Initiation and development of a NW oriented fault and/ or fracture system by a compressive stress.
- vi. A second phase of mineralization that is structurally and exclusively controlled by the NW-SE striking fault, fracture and joints. Galena and sphalerite accompanied siderite and quartz during this episode of mineralization.
- vii. Uplift and erosion followed by the sedimentation of the Turonian Ezeaku Shale Formation.



Fig 2.3: Structural Map of Southeast Nigeria showing folds and faults around the study area (Adapted from Reyment, 1965)

# 2.2 Regional Stratigraphic Setting of Ishiagu Area

Earlier investigations in the area include those by Tattam, (1944); Reyment, (1965); Orajaka, (1965); Burke *et al.*, (1970); Murat, (1972); Nwachukwu, (1972); Uzuakpunwa, (1974); Kogbe,(1989); Olade, (1976); Petters, (1978); and Benkhelil,(1989). Murat, (1972) subdivided the stratigraphy of Nigeria into the pre-Cretaceous, Cretaceous, Tertiary and the Quaternary . The stratigraphy of the Southern Nigeria sedimentary basins is controlled by three tecno-sedimentary cycles (Murat, 1972; Short and Stauble, 1967; Whiteman, 1982; Obi, 2000; Hoque and Nwajide, 1984). The first cycle started with the opening of the Southern Benue Trough during the Jurassic to Aptian times. Sediments in the trough were deposited from Aptian to Coniacian environments believed to vary from continental to shallow marine. Ojoh (1992) and Okoro and Igwe (2014) noted the presence of deep marine turbidities and mega-slumps in some places. Nwachukwu (1972) noted a minor break in sedimentation during the Cenomanian. These sediments were folded and uplifted during the Santonian epirogeny into Abakaliki anticlinorium

During the second cycle, over 2,000m of sediments were eroded from the Abakiliki Anticlinorium, and deposited in the post-rift subsiding depression of the Anambra Basin from the Late Campanian to the Danian (Murat, 1972). The overall thickness of the sediment deposited was reported to be over 4000 m (Hoque and Nwajide, 1984). The sediment fill include the Late Campanian-Maastrichtian Nkporo group, the Early Maastrichtian Maamu Formation, Late Middle Maastrichtian Ajali Formation and Late Maastrichtian Nsukka Formation.

The third sedimentary cycle started after the filling up of the Anambra Basin and subsequent lateral shift of the depocentre southwards into the modern Niger Delta from the late Paleocene to Recent (Murat, 1972). The Paleocene Imo/Akata Eocene Ameki/Agbada,

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Oligocene Ogwashi Asaba/Upper Agbada and the Miocene to Recent Formations were deposited during this phase

These sediments belong to the Albian Asu River Group, Cenomanian Odukpani Group, Turonian Eze-Aku Group, and the Coniacian Awgu Formation. Each of these sedimentary phases is bounded by sequence boundaries with unconformity surfaces. Figure 2.4 is the stratigraphic map of southeasthern Nigeria while Table 2.1 shows the regional stratigraphic framework from early Cretaceous to Tertiary. The Santonian tectonic episode resulted in the folding, fracturing and uplifting of the Aptian to Coniacian sediment to form the Abakiliki Anticlinorium (Grant, 1971; Murat, 1972; Whiteman, 1982). The Eze-Aku Group occupies both flanks of the Anticlinorium while the Asu River Group is at the crest and overlies the Oban and Bamenda Massifs in Southern Benue Trough (Figure 2.4). A SE to NW polarity relative to the axial fracture system resulted in the subsidence of the Ikpe Platform and the Anambra Platform, east and west of the Abakiliki Anticlinorium respectively (Benkhelil, 1989).



Fig. 2.4 Stratigraphic Map of South East Nigeria showing the formations (modified from Murat, 1972)

	Age	Abakaliki-Anambra Basin	Afikpo Basin		
m.y 30	Oligocene	Ogwashi-Asaba Formation	Ogwashi-Asaba Formation		
54.9	Eocene	Ameki/Nanka Formation/ Nsugbe Sandstone (Ameki Group)	Ameki Formation		
6.5	Palaeocene	Imo Formation Nsukka Formation	Imo Formation Nsukka Formation		
73	Maastrichtian	Ajali Formation Mamu Formation	Ajali Formation Mamu Formation		
83	Camparian	Npkoro Oweli Formation/Enugu Shale	Nkporo Shale/ Afikpo Sandstone		
87.5	Santonian		Non-deposition/erision		
	Coriacian	Agbani Shdstone/Awgu Shale	Eze Aku Grupo		
88.5	Turonian	Eze Aku Grupo	(incl. Amasiri Sandstone)		
93 100	Cenomanian- Albian	Asu River Group	Asu River Group		

 Table 2.1: Stratigraphic Framework for Early Cretaceous-Tertiary Strata in

 Southeastern Nigeria (modified from Nwajide, 2013)

# 2.4 Geology of the Ishiagu Area

# 2.4.1 Shale Unit.

The mineralization is hosted by the Albian shale (Reyment, 1965 ; Kogbe , 1989). The sedimentary rocks are intruded by intermediate to basic alkaline intrusive rocks (Obiora, 2002). The study area is made up of thick sequence of slightly deformed Cretaceous sedimentary rock consisting essentially of Albian shales with subordinate sandstone and limestone of the Asu River Group, The Asu River Group consists largely of bluish-grey shales, sandy shales, with some micaceous sandstone and subordinate limestone. (Reyment, 1965). The Shale is folded into an anticline with a northeasterly axial trend (Ezepue, 1984). The limestone lenses of the Asu River Group are carbonaceous and some part of it is metamorphosed to marble as a result of its association with lead-zinc mineralization of the Lower Benue trough (Kogbe, 1989). The most important unit associated with the lead-zinc

mineralization is the Albian shales into which is intruded some intermediate to basic intrusives of the post Albian- pre-Turonian age.

Reyment (1965) examined ammonite species from the same area and pronounced them to be definitely of Lower Albian. Eburue (1977) collected from the Shale close to the lead-zinc deposit, species of Ammonoidea identical with those described by Reyment (1965) and confirmed them to be Lower Albian. The limestone lenses of the study area is a time equivalent of the Albian shale as shown by the occurrence of Elobiceras, Echinoids and Pelycypods which are fairly common and is believed to have been deposited as shallow-deep marine deposit during the Middle Albian transgression based on diagnostic ammonite fauna (Reyment, 1965). The thickness of the shale ranges from 1500m to 1800m (Cratchley and Jones, 1965).

# 2.4.1 The Intrusive:

The Southern Benue Trough is associated with magmatism during the Santonian more than the Northern Benue Trough. Intrusive bodies and lava flows which are typically of continental alkaline origin are of common occurrence in the Southern Benue Trough. The intrusive rocks include olivine basalt, diorite, gabbro and syenite (Nwajide, 2013; Ezepue, 1984). Tuff are also common. These intrusives occur along the axis of the anticline. They are believed to be of post Albian- pre Turonian in age (McConnel, 1949). The little variations in mineralogy and texture experienced among the intrusives are due to more diverse cooling conditions than to differences in composition of the intruded magma (Farrington, 1952). Radiometric ages of some of the igneous rocks in the Southern Benue Rift are given by Benkhelil (1989) and Umeji (1978). The oldest rock of the lower Benue rift is of Albian to Cenomanian in age. The dates obtained from the igneous rocks in the Okigwe-Ishiagu district are 87ma (Coniacian) for the Leru/Okigwe dolerite and 74Ma (Campanian) for the diorite from Ishiagu. (Umeji, 1978).

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# 2.5 The Concept and Theories of stable Isotope Geochemistry

Hydrothermal deposits are formed when hot aqueous solution flow through a defined channel over a restricted portion of the crust and precipitate a localized mass of mineral deposit from its dissolved constituent. The genesis of Ishiagu Lead-Zinc mineralization cannot be well understood without addressing:

- i. The source of the hydrothermal fluid and
- ii. The conditions that existed during its deposition.

Hydrothermal fluid can have a single or multiple sources. The aerial extent of the source can as well be regional or local. Similar hydrothermal deposits can be formed from hydrothermal solution from different sources and a single parentage fluid can also form different types of deposits (Barnes, 1979). Hydrothermal fluid can take its source from four possible geochemical environments:

- i. meteoric waters
- ii. connate and deeply penetrating ground water
- iii. metamorphic waters and
- iv. magmatic waters

## 2.5.1 The Principles of Stable Isotope Geochemistry and Ore Genesis

The definite proof to unlock the dilemma of the source and conditions of formation of any hydrothermal deposit can be provided through sulphur, oxygen and carbon stable isotope studies (Barnes, 1979). Stable isotopes have two main characteristics which are: low atomic number and high / large proportional difference in their atomic mass. This proportional difference in mass between the heavy and light isotopes of the same element e.g ( $^{32}$ S and  $^{34}$ S) leads to a large difference in the vibrational frequency between the heavy and the lighter isotope of the same element. For example, the heaviest hydrogen isotope has the atomic mass which triples the lightest hydrogen isotope. The mass number increases with a factor of 2 unlike the isotope of high atomic number tungsten whose mass difference between its heavier and lighter isotope is about 1.03.

The difference in frequency at which each of the isotopes vibrates in an element is what leads to the fractionation of the isotopes in that element. Fractionation of isotope can be defined as preferential concentration of heavy isotope in an element. Stable isotopes experience different levels and mechanisms of fractionation with respect to different geological and physical processes. This has led to a variation in stable isotope compositional ratios among different geochemical environments thereby causing each geochemical environment (magmatic, metamorphic and sedimentary) to posses a range of isotope compositional ratio which can be used to characterize it, a phenomenon which hardly exists among isotopes of higher atomic number (radioactive isotopes). The use of stable isotope in ore genesis is based on the fact that different ore deposit possesses a range of stable isotope compositional ratio which is a subject to the geochemical process or environment that originates the ore deposit. Fractionation of sulphur and carbon isotopes occurs in a variety of situations in the life of an ore fluid. Fractionation can proceed while maintaining isotopic equilibrium among sulphur bearing compounds in fluids and minerals or may proceed in a non equilibrium manner. Such isotope fractionation may take place in closed or in open system hence observed  $\delta^{34}$ S value of hydrothermal minerals therefore reflect a varied geochemical history of sulphur in hydrothermal fluid and proper interpretation of the significance of the  $\delta^{34}$ S value can be made only through understanding of the many processes of isotope fractionation in hydrothermal system as well as understanding the host geology of the deposit.

In this study, emphasis is laid on sulphur more than oxygen and carbon isotopes because sulphur is one of the major components of hydrothermal fluid as it is present in nearly all natural environments. It occurs as a minor component in igneous, sedimentary and metamorphic rocks, mostly as sulphides and sulfates and can occur as sulfates in evaporites. Sulphur is the dominant nonmetal component of the ore deposit of the study area. It can also occur in every temperature range of geologic interest and most interesting results in stable isotope geochemistry have been established with those elements on which stable gaseous compounds are known (Hoefs, 1973). Different geochemical environments possess different sulphur isotope compositional ratios due to the wide variations in sulphur isotope abundance in nature..

Fractionation can arise from two mechanisms:

- i. Chemical Processes e.g. equilibrium exchange reaction and kinetic processes
- Physical Processes e.g. evaporation, condensation, crystallization, diffusion and metabolic activity of organisms.

The foundation of stable isotope geochemistry was first studied by Urey (1947) when he discovered the isotopes of hydrogen. Urey (1947) found out that the little differences in the chemical properties of isotopes of the elements H, C, O, S and other elements can be calculated by statistical/quantum mechanics, thermodynamic principles and experimental methods. With respect to quantum principles, he established the inverse relationship between

vibration frequency of stable isotopes and their atomic mass. He stated that heavy isotope molecules have a lower vibration frequency and hence lower Zero Point Energy (ZPE) than the light isotopes. This implies that isotopically, heavy molecules are always energetically more stable than their lighter counterpart. As a result of this, all substances are made to stabilize by the addition of heavy isotope on it. The preference for heavy isotope than their light isotope counterpart by substances is termed fractionation. If this results to attainment of chemical equilibrium, then it is called equilibrium isotope fractionation. The amount of heavy isotope added to a substance for its stabilization is determined by the degree at which the molecules vibration energy of that substance is lowered by the heavy isotope substitution. Urey (1947) also found out from the thermodynamical point of view that substances with strong bond has higher vibrational frequency and hence need heavier isotope to be stabilized than substance with weak bond.

Taylor and Epstein (1962) noted that minerals with abundant Si-O bond are enriched in the heavy isotopes of oxygen relative to minerals with fewer Si-O bonds. <sup>34</sup>S enrichment in gaseous and aqueous specie is as such that;  $SO_4^{2-} > SO_3^{2-} > SO^2 > SCO > S_x > H_2S = HS^-$ . With respect to <sup>13</sup>C enrichment in its gaseous and aqueous specie, it is such that  $CO_3^{2-} > HCO_3^- > CO_2^- > C > CH_4$ . These imply that H<sub>2</sub>S is the most depleted of heavy sulphur isotope while  $SO_4^{2-}$  is the most enriched.  $CO_3^{2-}$  is the most enriched of heavy carbon isotope while  $CH_4$  is the most depleted. The O-H bearing minerals on the other hand have abnormally low oxygen isotope ratios due to their very weak bond strength and this suggests that the O-H group is lower in <sup>18</sup>O than the rest of oxygen in the silicate structure. Bachinski (1968) in their studies on the relationship between heavy sulphur isotope enrichment of sulphide and sulfate minerals, found out that under equilibrium conditions, heavier isotopes are enriched in the sulphates than in the sulphides. It is from the facts that +ve  $\delta^{34}S$  values are used to denote the predominance of aqueous sulfate while  $-ve \quad \delta^{34}S$  values are used to denote the

predominance of aqueous sulphides in hydrothermal fluid. Barnes (1979) stated that sulphur can exist majorly as sulfates or sulphides in any hydrothermal fluid while Hoefs (1973) stated that in a suite of coexisting sulphides, the mineral galena has the lowest sulphur isotope compositional ratio followed by chalcopyrite, sphalerite and then pyrite in ascending order. He then estimated the order of sulphur isotope enrichment for various sulphur compounds and this can be used to calculate fractionation factor where experimental data is not available. This means that different compounds of sulphur have different heavy sulphur isotope enrichments hence different sulphur isotope compositional ratio. Sulphur isotope compositional ratio can be defined as the per mil deviation of the <sup>34</sup>S /<sup>32</sup>S ratio of the compound relative to that of the standard given by the Troilite phase of the Canyon Diablo Meteorite (CDT). This can be expressed mathematically as

$$\delta^{34} \mathbf{S} = \left(\frac{{}^{34} S \, {}^{32} S_{sample} - {}^{34} S / {}^{32} S_{s \tan dard}}{{}^{34} S / {}^{32} S_{s \tan dard}}\right)$$
(2.1) *Barnes( 1979)*

$$= \left(\frac{{}^{34}S/{}^{32}S_{samples}}{{}^{34}S/{}^{32}S_{stan\,dard}} - 1\right) \times 1000$$
(2.2) *Barnes(1979)*

Where  $\delta^{34}S$  is the sulphur isotope compositional ratio and  ${}^{34}S/{}^{32}S$ is the partition function (sulphur isotope ratio). Sulphur isotopes ratios are measured with respect to  ${}^{34}S$  enrichment. Positive  $\delta^{34}S$  is used to show enrichment in  ${}^{34}S$  more than the standard while negative  $\delta^{34}S$  is used to denote depletion in  ${}^{34}S$  which is invariably enrichment in  ${}^{32}S$  by the law of material balancing.

When a polymetallic sulphide deposit is in chemical equilibrium there is usually a partial redistribution of isotopes of sulphur among the various species or compounds of sulphur in the deposit. This redistribution of isotopes among coexisting and contemporaneous mineral pairs in equilibrium is termed equilibrium isotope fractionation ( $\alpha$ ). It is defined mathematically as the ratio of the sulphur isotope in one chemical compound (sphalerite) divided by the corresponding ratio of the other chemical specie (galena).

Urey (1947) also used thermodynamic principles to study isotope exchange reaction and found out that isotope exchange reaction is an analogue to cation exchange reaction as they occur in similar way. The two reactions differ in a way that isotope equilibrium constant (equilibrium fractionation factor ( $\alpha$ )) varies significantly with temperature more than ordinary equilibrium constant (K). There is a higher order temperature dependence in isotope exchange reaction i.e. (T<sup>-2</sup>) than in cation exchange reaction which is (T<sup>-1</sup>). With respect to this research work, the kind of fractionation mechanism involved is the one related to the equilibrium isotope exchange reaction between the mineral pairs (sphalerite and galena, sphalerite and chalcopyrite & chalcopyrite and galena). The equations for the exchange reaction in which <sup>34</sup>S and <sup>32</sup>S isotopes are exchanged between the mineral pairs are as thus:

$$Zn^{34}S + Pb^{32}S \leftrightarrow Pb^{34}S + Zn^{32}S$$
(2.3)

$$Zn^{34}S + CuFe^{32}S_2 \leftrightarrow CuFe^{34}S_2 + Zn^{32}S$$
(2.4)

$$CuFe^{32}S_2 + Pb^{34}S \leftrightarrow Pb^{32}S + CuFe^{34}S_2$$
(2.5)

While the fractionation factor between any of the mineral pairs for example sphalerite (M) and galena (N) is expressed as:

$$\alpha_{M-N} = \frac{ratio.of.M}{ratio.of.N} = \left(\frac{{}^{34}S/{}^{32}S_{M}}{{}^{34}S/{}^{32}S_{N}}\right) (2.6) \qquad Barnes(1979)$$

M - sphalerite

N - galena

With respect to the equilibrium exchange reaction process of fractionation, it should be noted that only one atom is exchanged in the above reaction. The isotope fractionation factor is related to cation equilibrium constant K in such that

$$\alpha = K^{1/n}$$
 (2.7) Rollinson (1993)

Where n=1 then

$$K = \alpha \tag{2.8}$$

Values for  $\alpha$  are very close to unity and typically vary in the third decimal place digit (X). Most fractionation factor values are of the form 1.00X. For this reason, fractionation factor are expressed as the third place value i.e the per mil value which is a useful approximation for the fractionation factor.

$$1000\ln(1.00X) \approx X$$
 (2.9)

A stem from the relationship; 1000ln  $\alpha$  is usually used in isotopic studies instead of  $\alpha$ . This 1000ln  $\alpha$  value can also be defined as the difference between the sulphur isotope compositional ratios of the two mineral pairs involved in the isotope exchange reaction (Eq. 2.10).

It has been found that the difference in the  $\delta^{34}S$  value between the mineral pairs (M & N) can be related to fractionation factor as thus:

$$\Delta_{M-N} = \delta^{34} S_M - \delta^{34} S_N = 1000 \ln a_{M-N}$$
 (2.10) **Rollinson (1993)**

Characterization of any mineral deposit is not complete without the information on the temperature of formation of the deposit. This can be computed by the formula given by Ohmoto and Rye (1979) through their experimental studies which provided the relationship

between equilibrium fractionation factor of sulphur isotopes and temperature. The equation was modeled based on the fact that equilibrium fractionation factor (1000ln  $\alpha$ ) which is the partial redistribution of sulphur isotopes between two sulphur species (mineral pairs) at chemical equilibrium is a primary function of temperature (1/T<sup>2</sup>). This is for mineral- mineral and mineral-fluid pairs (Urey, 1947). Fractionation factor is also a function of the difference between the sulphur isotopes compositional ratios ( $\Delta_{M-N}$ ) of the mineral pairs involved in the fractionation (*eq.* 2.10). This give rise to the general relationship for the fractionation factor and temperature as thus:

$$1000 \ln \alpha_{(min1 - min2)} = A(10^{6}/T^{2}) + B \qquad (2.11). \ Rollinson (1993)$$

min 1 and min 2 are the mineral pairs

A and B are constants while temperature is in Kelvin.

Ohmoto and Rye (1979) computed the constants values A for sphalerite and galena to be 0.10 and -0.63 respectively while that of chalcopyrite is -0.05. When two mineral species are involved (mineral-mineral pair), "A" is thereby calculated from the difference between the two constant values mentioned above. For example:

"A" for sphalerite - galena mineral pair is as thus: 0.10 - (-0.63) = 0.10 + 0.63 = 0.73.

For sphalerite- chalcopyrite mineral pair: 0.10-(-0.05) = 0.15

For chalcopyrite – galena pair: 
$$-0.05-(-0.63) = 0.58$$

'B' = 0 for all the mineral pairs involved in this study (Barnes, 1979).

The above relationship is used to calculate the temperature of formation of the sphaleritegalena, sphalerite-chalcopyrite and chalcopyrite-galena mineral pairs. Ohmoto and Rye (1979) originally developed the constant A by plotting the isotope fractionation factor of sphalerite –galena mineral pair from different areas against the temperature of formation determined by fluid inclusion. The curve produced by joining all the points is called the isotope equilibrium curve and the slope of the curve is equal to "(A  $(10^6))/T^{2n}$ . Barnes (1979) stated that equilibrium temperature is got when fractionation factor is plotted against isotopic temperature, superimposed on fluid inclusion temperature. Such a graph can also provide information about the level of equilibrium attained by the deposit of the study area.

From the above information, Ohmoto and Rye (1979) concluded that for a large number of sulphide samples from unmetamorphosed deposit, isotope equilibrium is attained when there is no more change in the sulphur isotope composition ratio of that particular sulphur specie throughout the whole deposit. Temperature in many cases is the single most important variable in controlling isotope fractionation behavior between mineral pairs. Fractionation is not influenced by pressure because pressure has no appreciable effect on isotopic equilibra (Barnes, 1979). Sphalerite –galena mineral pair is chose in predicting the temperature of formation in this research because they are sensitive geothermometers as there equilibrium fractionation factor highly varies with temperature more than some other mineral pairs.

Apart from the temperature studies by Urey (1947), Bigelesen and Mayer (1947), Stern et.al, (1968), Bottinga and Javoy (1973) and Criss (1991) evaluated the temperature dependence of fractionation factor from a theoretical perspective. Criss (1991) developed an equation = A ( $T^2$ ) + B which suggests that at high temperature, fractionation factor vary linearly with respect to temperature  $T^2$ . Clayton (1981) stated that fractionation factor between substances cannot be represented as a simple function of temperature over a broad temperature range. He stated that with increase in temperature, the magnitude of fractionation factor decreases at very low temperature, then increases and finally decreases to approach zero at very high temperature.

None of the plots are linear over the entire temperature range although individual segment of the plot are approximately linear. The exact temperatures at which these limits occur depend on the substance being considered. Because of this complexities, equations describing variation of  $ln \alpha$  with temperature takes a number of forms; for a lower temperature fractionation (T> 100<sup>0</sup>C), the equation is  $ln\alpha = A (T^{-1}) + B$ . At higher temperature  $ln \alpha = A (T^{-2}) + B$ , where A and B are constants normally determined by experiment. The constants are defined as the equilibrium isotope fractionation factor for the distribution of  ${}^{34}$ S between the sulphur species and the fluid (H<sub>2</sub>S).

Clayton (1981) further researched on the relationship between isotope equilibrium constant and temperature  $(1/T^2)$  and found out that the temperature of isotopic equilibrium fractionation between mineral pair can be defined by measuring the difference in their sulphur isotope compositional ratio (eq 2.10; 2.12).

$$\Delta_{M-N} = (A (10^6/T^2) + B)$$
(2.12) Clayton (1981)

Oxygen which is the second stable isotope employed in this study is inherent in water, another major constituent of hydrothermal systems. Oxygen isotope can be used as indicators of origin and history of  $H_2O$  in hydrothermal fluid (Barnes 1979). The principles that govern the fractionation and variation of oxygen isotopes in nature are the same with that of sulphur isotopes. Oxygen in conjunction with carbon isotopes can as well be used to provide information on the evolution of the ore fluid system hence the involvement of carbon isotope studies (Rollinson, 1993). By the above mentioned facts, it could be realized that each of the four types of hydrothermal waters can develop a range of stable isotope (sulphur, oxygen and carbon) compositional ratios from where the source of the sulphur and carbon in the hydrothermal fluid can be determined and knowledge of its origin is fundamental to any theory of ore formation. Barnes (1979

) realized that data from sulphur and carbon isotope compositional ratios of minerals from an ore deposit alone is usually insufficient to define the genesis of ore deposit. It should however be combined with detailed geologic and geochemical studies. Fretwell's law on isotopy states and I quote:

"Stable isotope data can cause severe and contagious stomach upset if taken alone. To prevent upsetting reviewers' stomach and your own, take stable isotope data with a healthy dose of other hydrologic, geologic and geochemical information. Then you will find stable isotope data beneficial" (Kendall & Carldwell, 1998).

Observed isotope compositional ratios therefore reflect a varied geochemical history of the stable isotope in the hydrothermal fluid and the proper interpretation of the significance of these values can only be made through understanding of the geology of the deposit and of the many processes of isotopic fractionation in a hydrothermal system. For example, ore fluid derived from basic magma are usually  $H_2S$  rich unlike that derives from granitic igneous rocks which may be  $H_2S$  or  $SO_2$  rich depending on the fugacity of the environment (Rollinson,1993). The above information has prompted the combination of geologic and geochemical studies in conjunction the stable isotope data to establish the genetic model of the ore deposit of the study area. This work will use isotope geothermometry which has never been applied in Ishiagu area to compute the temperature of formation of the deposit as well as its conditions of formation.

### **CHAPTER THREE**

# MATERIALS AND METHODS

### **3.1 Materials**

# **3.1.1 Field Work Materials**

The field geological materials and equipment used in the course of this research work include Global Positioning System, Brunton compass, tape, ruler, pencil, biro, geologic hammer, hand lens, sampling bags, field notebook, camera, masking tape and pick axe.

# **3.1.2 Laboratory Materials**

Two analytical methods were used in the course of this research work. The table below shows the different analytical methods with the corresponding materials used.

### 3.2 Methods of Study

# 3.2.1 Field Method

### **3.2.1.a Geological Field Work**

Field mapping is a scientific process of map production. In this study, large scale geological field mapping on a scale of 1:40,000 was done with conventional instruments. A seven day reconnaissance survey of the area was initially done to note the accessibility and general geology of the area and to enable efficient planning for the work. Rock textures and structures were studied onsite followed by the mapping of the ore vein to study the geometry of the ore bodies. The rock types which host the mineralization were also identified. The field/ primary data collected in conjunction secondary data from literature, documents and already existing maps were used for the geologic map production.

## **3.2.1.b Sample Collection**

Ten (10) samples of galena-sphalerite ore minerals and six rock samples were collected from the prospects mapped. The ore samples were used for isotope studies while the rock samples were analysed for geochemical parameters of the rock. Thorough preparations before the initiation of sampling were done by providing good and necessary equipment and sampling materials. These are by:

- i. Ensuring that the equipment were in good conditions.
- ii. Making sure that the sampling bags were properly decontaminated.

# **Ore Sample Collection**

Nine (9) ore samples were collected from the mine pits of the three active mines and one (1) from a decommissioned mine (Table 3.2). The sampling pattern adopted was based on the kind of information/analysis required at the point in time. The interest was to collect well formed euhedral crystals. The lateral intervals of collection were purely dependent on the length of the vein. Measures were taken to make sure that the samples collected are good representative of the whole deposit. The samples were fresh samples from the ore shoot where the highest concentration of galena and sphalerite as well as euhedral textured mineral forms occur. Co-existing and contemporaneous sphalerite and galena samples were selected for isotope geo-thermometry. Table 3.2 shows the number of ore samples collected from each location

Ore Samples	Locations	GPS Co-ordinates		
GFIA	Greenfield Mine 1	N 05 <sup>0</sup> 55 <sup>1</sup> 41.3 <sup>11</sup> E 007 <sup>0</sup> 29 <sup>1</sup> 51.2 <sup>11</sup>		
GF2A, GF2B,GF2C	Greenfield Mine 2	N 05 <sup>0</sup> 55 <sup>1</sup> 41.5 <sup>11</sup> E 007 <sup>0</sup> 29 <sup>1</sup> 42.4 <sup>11</sup>		
GF4A, GF4B, GF4C	Greenfield Mine 4	N 05 <sup>0</sup> 56 <sup>1</sup> 22.9 <sup>11</sup> E 007 <sup>0</sup> 30 <sup>1</sup> 32.5 <sup>11</sup>		
RSP <sub>1</sub> RSP <sub>2</sub> RSP <sub>3</sub>	The Palladium Mine	N $05^0 55^1 40.5^{11}$ E $07^0 29^1 05.3^{11}$		

 Table 3.1 Lists of Ore Samples for Isotope

# **Rock Sample Collection**

Six (6) rock samples were collected from the igneous rocks in the study area. The samples collected were good representative of the whole intrusive. Three (3) samples each were collected from the Greenfield intrusive body [GI] and China intrusive (CI). Table 3.3 shows the rock samples identification numbers and the locations from where they were collected.

Table 3.3 Rock Samples collected for Geochemical Analysis

Rock Samples	Locations	GPS Co-ordinates		
S14a, S14b, S14z	Greenfield Intrusive	N 05 <sup>°</sup> 56 <sup>1</sup> 21.4 <sup>11</sup> ,E 007 <sup>°</sup> 30 <sup>1</sup> 15.7 <sup>11</sup>		
S21a, S21b, S21d	China Intrusive Rock	N 05 <sup>0</sup> 56 <sup>1</sup> 21.4 <sup>11</sup> ,E 007 <sup>0</sup> 30 <sup>1</sup> 15.7 <sup>11</sup>		

### **3.2.2 Laboratory Studies**

The laboratory studies done with respect to this research work are XRF analysis of the intrusive and mass spectroscopy analysis of the ores. Laboratory analysis is impossible without proper sample preparations. The procedures and methods of sample preparation is as important as the analysis itself. Sample preparations and analysis as it concerns mass spectrometry was done by the Environmental Isotope Laboratory, Department of Geosciences, and University of Arizona while the XRF was done by the Nigerian Geological Survey Agency, Kaduna.

### 3.2.3 The Working Principles of the Analytical Methods

### **X-Ray-Fluorescence (XRF)**

XRF was used to determine the major element concentration (chemistry) of the intrusive rocks in the study area. The working principle of X-Ray Florescence Spectrometry is based upon the excitation of a sample by X-Rays. A primary X-Ray beam excites the secondary X-Rays (X-Ray fluorescence) which posses the wavelength characteristics of the elements present in the sample. The intensity of the secondary X-Rays is used to determine the concentration of the elements present by reference to calibration standards.

# **Mass Spectrometry**

With respect to this study, mass spectrometry was used to measure the isotope ratios of sulphur, oxygen and carbon. The measurement was preceded by the chemical separation of the elements of interest (sulphur, oxygen and carbon). Charged ion were generated from the element to be analyzed either by the bombardment of a gaseous sample with electrons (gas source) or by the volatilization of the sample on a glowing filament made of a high-melting-point metal (solid source). The ion beam was filled along a curved tube through a very powerful electromagnet which splits up the atoms according to their mass. A mass spectrum was produced in which the lighter ions are deflected with a smaller radius of curvature than the heavy ions. The quantitative detection of the signals at two or more mass numbers allowed an isotope ratio to be calculated. Gas source mass spectroscopy was used in this study (Stable Isotope studies).

## 3.2.4 Sample Preparation for Isotope Studies

The objective of sample preparation in isotope studies was to homogenize and reduce the grain size in order to make sure that the part analyzed is a good representative of the whole. Any reduction in sample size without prior homogenization will result to bias. The samples collected were cleaned, crushed, and sieved to  $2\text{mm}^2$  sizes to help obtain sulphide separation of 99% purity. They were separated and picked with a thong under binocular microscope after which they were rinsed with deionized water. To avoid contamination, larger blocks of the sample were used for grinding. Grinding from 1cm to smaller sizes was carried out with a mild steel plate to avoid contaminations from Chromium and Nickel. The quality of crushing and pulverizing was routinely checked. It should be noted that the same method of sample preparation was used for the galena, sphalerite, chalcopyrite and siderite used in the isotope analysis in this research. Conventionally stable isotopes are converted into gas (SO<sub>2</sub>, CO<sub>2</sub>) for the purpose of isotopic analysis hence the sample separates were later converted to their gas forms using oxidizing agents after which the mass difference between the isotopes in a sample were measured using mass spectrometer.

# A. Conversion of Sulphur in Galena, Sphalerite and Chalcopyrite to SO<sub>2</sub>

The sample separates were combusted at 1030°C with oxygen and venadium-V-oxide as the oxidizing agents. This was done using an elemental analyzer (COSTECH) coupled to the mass spectrometer.

# B. Conversion of Siderite to CO<sub>2</sub>

The powdered samples were reacted with dehydrated phosphoric acid under vacuum at  $70^{\circ}$ C to convert the siderite to CO<sub>2</sub> for mass difference measurement of the carbon and oxygen isotope compositional ratios.

### **3.2.5 Sample Preparation for XRF Analysis**

The collected rock samples were reduced to less than 63microns size using a Tema vibrating mill. The agate mortar in the mill crushes the samples before sieving them to pass through 63 microns seive is done.

Beads used for the major elemental analysis expressed in oxide weight percent were prepared first by drying the sample powder in an oven at  $110^{\circ}$ C for 24 hrs to remove moisture in the rock powder. About 5.0g of dry rock sample powder was weighed in a silica crucible and then ignited in the furnace at  $1000^{\circ}$ C for 2 to 3 hours for the calcination of impurities in the rock powder. The samples were then removed from the furnace and allowed to cool at room temperature in desiccators. Each ignited rock powder was then weighed again to determine the weight of calcinated impurities i.e.  $H_2O$ ,  $H_2O^+$  and  $CO_2$ . The weighed mixture was mixed properly in a platform dish and ignited in the pre-set furnace (Eggon 2 Automatic fuse bead maker) at  $1500^{\circ}$ C for 10 minutes to form glass bead.

## 3.3 Laboratory Analysis

### 3.3.1 Sulphur Isotope Analysis

The sulphur isotope compositional ratio of the sulphur in  $SO_2$  gas was measured in a continuous flow Gas Ratio Mass Spectrometer (Thermo Quest Fannigan Delta Plus-XL Model). Standardization was based on international standards OGS-1 and NBS+23 and several other sulphide and sulfate minerals. Calibration is linear in the range -10 to +30 per mil. Precision was estimated to be  $\pm 0.15$  or better (1S) based on repeated internal standards.

### 3.3.2 Oxygen and Carbon Isotope Analysis

The oxygen and carbon isotope mass differences were measured on the  $CO_2$  gas using an automated carbonate preparation device (KIEL- III), coupled to a Gas-Ratio Mass

Spectrometer (Fannigan MAT 252). The carbonate preparatory device helped to prepare the sample as stated in section 3.5.1B after which the Gas-Ratio Mass Spectrometer measured the isotope ratios. Measurements were calibrated based on repeated measurement of NBS- 19, NBS-18 and precision is  $\pm 0.10^{-0}$  for d<sup>48</sup>O and  $\pm 0.08^{-0}$  for d<sup>43</sup>C. The values for the oxygen isotope were calculated in SMOW and PDB though the SMOW values were used for the interpretation of the results in this research work since the Natural Oxygen Isotope Reservoir is in SMOW. The values for the carbon isotope ratios were reported in PDB standard.

### 3.3.3 XRF Analysis

The major elemental compositions of the six rock samples collected from the study area were determined using one X-ray tube. Each of the glass beads prepared during sample preparation were labeled and slotted into a computerized XRF (Epsilon 5 Panalytical Model) for major elemental analysis and the results measured in oxides wt% were recorded.

#### **3.4 Data Analysis**

#### **3.4.1 Geochemical Plots**

The compositional data generated from the XRF analysis was analyzed using Oxide-Oxide geochemical plots. The Oxide-Oxide geochemical plots used in this study is the Total Alkalis-Silica Diagram (TAS) which is one of the most useful classification schemes available for igneous rocks studies. Here, the sum of the Na<sub>2</sub>O and K<sub>2</sub>O content (Total Alkalis) and the SiO<sub>2</sub> content (S) are taken directly from the results of rock analysis in wt% oxide and plotted into an existing classification template. This plotted diagram is later superimposed on the TAS diagram of:

i. Cox *et al.*, (1979) to differentiate the alkaline rocks from the sub alkaline rocks and to differentiate the rocks into its specific types.

ii. Kuno (1968) to separate the calc alkaline from the alkaline suites

# 3.4.2 Isotope Data Analysis

## 3.4.2a Sources of the Hydrothermal Fluid

To establish the source of the hydrothermal fluid that formed the deposit. The sulphur, oxygen and carbon isotope compositional ratios were plotted on the Natural Sulphur, oxygen and carbon Isotope Reservoir templates by Hoefs (1973) respectively.

The natural sulphur, oxygen and carbon isotope reservoir histogram help to compare the range of sulphur, oxygen & carbon isotope compositional ratios of the study area to that from different natural geochemical environments.

## 3.4.2b Formation Temperature of the deposit

Mathematical calculations were done with the partition function ratio and/or the sulphur isotope compositional ratio ( $\delta^{34}$ S) using an existing formulae developed by some veteran scholars in stable isotope studies in the course of their experimental works (Urey, 1947).

The steps are as follows:

Establishing the preferential distribution of the sulphur isotope that is, the fractionation factor  $\alpha$  between sphalerite-galena, chalcopyrite-galena and sphalerite-chalcopyrite mineral pairs. This was calculated mathematically using equation equation 2.6. Fractionation factors are always expressed in per mil (1000ln  $\alpha$ ) value. Criss (1991) found out from experiment that 1000ln  $\alpha$  value of the fraction factor  $\alpha$  is equal to the difference between the sulphur isotope compositional ratio of the two mineral pairs and it is a function of  $1/T^2$  (Eq 2.10). Temperatures of deposition of sphalerite- galena,

sphalerite-chalcopyrite and chalcopyrite-galena mineral pairs were estimated using equation 2.10 and 2.11.

1000ln 
$$\alpha(_{\min 1 - \min 2}) = \delta^{34}S_S - \delta^{34}S_G = A(10^6/T^2) + B$$
 .....(2.11 or 2.12).

Rollinson (1993)

# 3.4.2c Level of Equilibrium Attained by the Deposit

The fractionation factor  $\alpha$  in per mil value (1000ln $\alpha$ ) of the mineral pairs and their corresponding temperatures of formation is plotted on a template Bivariate diagram of 1000ln  $\alpha$  Vs Temperature of formation (Barnes, 1979) to show the level of isotope equilibrium attained during the deposition of sphalerite and galena. This is to compare the standard equilibrium curve of the world prominent lead-zinc deposits of Barnes (1979) to the equilibrium level (temperature Vs fractionation factor) attained by the deposit of the study area.

### **CHAPTER FOUR**

# **RESULTS AND DISCUSSION**

# 4.1 Field Results

# 4.1.1 The Geology of the Area

The field studies of the study area (Fig 4.1) revealed that it is underlain by dominantly shale with subordinate limestone. This shale unit was intruded by small to medium sized intrusive rocks (Fig.4.1). Minor faults trending NW-SE and NE-SW directions occured. The three Pb-Zn mineralizations studied occured in the NW-SE trending faults.

# The Shale Unit

The shale unit of the study area typically ranges from dark grey to shades of brown and yellow in colour, finely laminated with alternating silt and clay bands. It is distinctly fissile. It is hard and splintery in some places. The colour is mainly grayish on weathered surfaces. The shale is folded into an anticline with a northwesterly axial trend. West of the anticline the shale, dip  $17^{0}$ - $32^{0}$  in a general northwest direction. East of the anticline, the beds generally dip  $25^{0}$ - $30^{0}$  to the southeast (Fig.4.1). There is a sharp contact between the vein and the shale host in GF2 and RSP mines. The shale adjacent to the veins is lighter in color than the surrounding shale. Some exposed sections contain bed of laminated, medium to coarse grained sandstone. A little subordinate carbonate rock interbeded with the shale is well exposes at the eastern part of the study area around the coordinates: N5<sup>0</sup> 56<sup>1</sup> 002.2<sup>11</sup> and 7<sup>0</sup> 31<sup>1</sup> 06.7<sup>11</sup>(Fig. 4.1). It is apparently of local extent and may not be worth more than the rank of a member. The result of the geochemical analysis of the limestone samples are shown in Table 4.1



Fig. 4.1 Geologic Map of the study area

% oxide composition	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>	CaO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	MnO	Fe <sub>2</sub> O <sub>3</sub>	V <sub>2</sub> O <sub>5</sub>	HgO	BaO	LOI
LS 1	1.60	5.60	-	0.04	48.06	0.79	0.31	0.01	0.540	4.16	0.02	0.30	0.16	38.42
LS 2	1.75	5.35	-	0.05	49.08	0.69	0.40	0.08	0.48	3.95	0.04	0.28	0.20	37.65

 Table 4.1 Major Element Content in Weight Percent of the Carbonate from the Study

 Area

# The Intrusive Rocks of the Study Area:

The shale was intruded by some medium sized igneous rocks. The igneous intrusions are conspicuously exposed within the shale. There are little variations in texture within each of the intrusive. They are majorly micro-phaneritic to phaneritic in texture and mesocratic to melanocratic.

The Greenfield intrusive is located at the northeastern part of the study area. It is quarried by the Greenfield Company and it is not up to 5 meters west of Greenfield Mine 4. The China intrusive is located at the northwestern part of the study area (Fig 4.1). This intrusive is quarried by Chinese Company. The names; China intrusive and Greenfield intrusive were given based on this research work.

## 4.1.2 Geologic Structures

There are fractures trending NE-SW and NW-SE in the study area. Some of these fractures are hosts to the lead-zinc mineralization as the mineralization are restricted to a series of minor, closely spaced, steeply dipping sub parallel fractures and /or joints trending NW-SE to N-S in the shale (Fig.4.2). The NE-SW trending joint sets are also dipping steeply or vertical. A rose diagram of field measurements of fracture orientations taken from both the intrusive and the shale shows a predominance of NW-SE trend and minor NE-SW trend.



Fig 4.2: Rose Diagram of the fractures in the Study Area. The NW fractures host the Pb-Zn ore.

Angle interval	$0^{0} - 30^{0}$	$31^0 - 60^0$	61 <sup>°</sup> - 90 <sup>°</sup>	91 <sup>°</sup> - 120 <sup>°</sup>	$121^{\circ} - 150^{\circ}$	$151^{\circ} - 180^{\circ}$	
frequency	1	2	1	2	4	3	

# 4.2 Geology of the Deposits

Figure 4.1 shows the positions of the three mines within the study area. Greenfield Mine 4 (GF4) with the coordinates  $N5^0 56^1 22.9^{11}$  and E  $007^0 30^1 32.5^{11}$  is 6.20km southwest of the Ishiagu Community Bank Junction which is on the Ishiagu-Afikpo major road. The Greenfield Mine 2 (GF2) of the coordinate;  $N5^0 55^1 41.5^{11}$  and E  $007^0 29^1 42.4^{11}$  is 2.0km southwest of GF4 mine while Palladium mine (RSP) is 1.3km west of GF2. Palladium mine

is of the coordinates; N5<sup>0</sup> 55<sup>1</sup> 40.5<sup>11</sup> and E 007<sup>0</sup> 29<sup>1</sup> 05.3<sup>11.</sup> Greenfield Mine 2 (GF2) is hosted by the yellowish to brown shale. The part of the shale in contact with the vein is light yellowish in colour probably due to bleaching by the hydrothermal fluid while the other shales have different shades of brown. The deposit is structurally controlled in two subparallel, approximately NNW-SSE striking veins. The larger vein covers an area of 31m by 3m while the smaller vein's dimension is 12m by 2.5m. Both veins have a depth of about 12m. The main vein trends 350<sup>0</sup>- 170<sup>0</sup>. An offshoot vein trends 330<sup>0</sup>-150<sup>0</sup>. Vertical to near vertical conjugate joints are common on the walls of the two veins. These joints are oriented in NE-SW and NW-SE directions. The two veins of Greenfield Mine 2 have steep to vertical dip. The main vein has another smaller vein dipping NNW with little mineralization (plate 4.1). Ores in GF2 deposit is dominated by sulphide minerals and capped by thin layer of oxidized ore of malachite and azurite near the surface. The mineralogy includes galena, chalcopyrite, siderite, quartz and calcite. Sphalerite is not readily visible in the deposit. There is no intrusive around Greenfield Mine 2. Wall rock alteration is minimal in the deposit.

GF4 deposit is hosted by the GFI basic intrusive rock. The fault which hosts the vein cuts across the southeastern part of the intrusive rock. There is a sharp lateral contact between the intrusive host and the ore (Plate 4.2). The part of the intrusive adjacent to the ore vein has a lighter color which may be as a result of hydrothermal alteration. The elevation of the area is 85 meters.



Plate 4.1: Greenfield Mine 2 showing the ore vein and the surroundng rock



Plate 4.2: Greenfield Mine 4 showing the mined Lead- Zinc vein cutting across the intrusive
The vein covers an area of  $12m \ge 1.5m$  with 10m as its depth. The soil cover overlying the vein has been removed for easy accessibility to the ore vein. The mineralization of GF4 mine occurs within a vein which runs NW-SE Plate (4.2). The vein originated from the surrounding fault hence fractore is a fissure which trends precisely  $330^{0}$ - $170^{0}$  and dips steeply to the SW. The kind of fault system found here is a dip slip fault. Movement along this fault vein raised up the eastern half of the wall rock a little. The downthrown block consists more of shattered rocks with so many vertical to near vertical and horizontal joints orienting both NE-SW and NW-SE. The stress which is restricted to the narrow zones adjacent to the fault has resulted in the formation of some angular rock fragments which were later cemented together by the hydrothermal fluid to form the breccied-filled ores. Sulphide ores in this deposit have filling, massive, disseminated, veined and banded structures. The mineralogy includes galena, sphalerite and chalcopyrite with siderite, quartz and calcite as the gangue minerals.

Palladium mine (RSP) is the largest of all the mines studied in this research work. It is hosted by finely laminated carbonaceous shale which ranges from dark grey to yellowish brown in color (Plate 4.3 & 4.4). This shale is hard and splintery in some places due to effect from burial. The trend of the Palladium Vein is  $340^{0}$ - $160^{0}$  (Fig.4.3). The vein has a vertical dip. The ore body has a limited horizontal extent unlike its vertical extent. Evidence of faulting is noticed by the few breccias filled ores found within the lode. The wall of this mine especially the western part has so many crosscutting as well as vertical to near vertical fractures. The unbaked shale at the northern part have vertical fractures and are striking averagely  $250^{0}$ - $70^{0}$ and is dipping NW. The actual dimension of the deposit is not ascertained as mining activity is still going on in the pit. The already mined vein has a depth of 15m (Plate 4.3). The host rocks to this deposit especially at the eastern side have experienced hydrothermal alteration. There are weathered zones with some oxidized ores at the upper part of the mineral vein (plate 4.5). This has an average thickness of 2.5m. The closest intrusive to the deposit is about 2.5km North West of the mine (Fig. 4.1).



Plate 4.3 Picture showing the mine pit geometry of RSP mine



Plate 4.4: Picture showing the bluish grey unbaked shale host of the Palladium deposit



Plate 4.5: Picture showing the oxidized ore zone overlying the primary ore

#### 4.3 Geochemical Analysis Result.

#### 4.3.1 Intrusive Rocks

Bulk chemical analysis of the intrusive rocks using X-ray Florescence was done to chemically classify the intrusive, specify the rock types so as to predict if they have a common origin. Knowledge of the type of intrusive rock in the study area will helped to infer the kind of sulphur specie (SO<sub>2</sub> or  $H_2S$ ) which will be abundant in the magmatic fluid from such intrusive. Barnes (1979) noted that the kind of igneous rock found in an area can influence the kind of sulphur specie produced and invariably, the sulphur isotope compositional ratio of the magmatic fluid. All the six rock samples from the intrusive were used for geochemical analysis and the results are presented in Table 4.2. The SiO<sub>2</sub> contents of the intrusive range from 37.70% to 52.10% and shows they are generally basic - ultrabasic. The iron, magnesium and calcium content of the rocks range between 8.24% - 16.3%, 4.0% - 16.3%14.3% and 3.6% - 12.6% respectively. The average iron content of the China Intrusive is 14.6% and is higher than that of the Greenfield Intrusive which is 10.34%. Sample 14a from GFI has the highest MgO content while sample 21a of China intrusive has the lowest. The Fe<sub>2</sub>O<sub>3</sub> content is highest in sample 21a followed by 21b. The CaO content of samples 14a, 14b and 21b are higher than others. The weight percent of aluminum in all the samples are also high with the highest being in sample 21a which is 15.4%.

The Total Alkalis (TA) of all the rock samples range from 4.35% to 7.75% (average = 6.44%; n = 6) with the highest being in 21d followed by 14z and the lowest being sample 21b. The Total Alkalis of sample 21a is also high.

	Oxide Composition (wt %)														
Sample Nos	Al <sub>2</sub> 0 <sub>3</sub>	SiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>	CaO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	MnO	TiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	MoO <sub>3</sub>	Ba0	LO1	ТА
14a	13.00	50.10	-	-	12.6	14.93	4.23	1.62	0.17	1.43	10.09	-	2000	9100	5.85
14b	14.5	50.2	1.1	0.9	7.4	4.0	4.2	2.1	0.2	2.6	12.7	-	-	7800	6.30
14z	13.0	43.90	3.00	0.36	6.76	11.34	5.15	2.46	0.19	3.65	8.24	-	3000	6900	7.61
21a	15.4	52.1	1.03	-	1.96	1.32	3.50	3.30	1.21	2.64	16.34	-	1500	8200	6.8
21b	13.31	46.92	0.94	-	8.27	6.08	3.36	0.99	0.27	3.17	14.73	-	3000	9000	4.35
21d	14.00	37.70	2.40	0.35	3.64	12.25	5.18	2.57	2.32	4.54	12.99	900	-	14400	7.75

 Table 4.2. Major Element Content of Intrusive Rocks from the Study Area (in weight percent)

#### 4.4 Results of Isotope Studies

## 4.4.1 Sulphur Isotope

Nine ore samples from four different mines were analyzed for their sulphur isotope compositions. Five out of the ten samples contained contemporaneous galena and sphalerite while one contained contemporaneous galena, sphalerite and chalcopyrite. The two samples from GF2 mine and the one from GF1 mine contained only galena. Results from the six (6) samples with mineral pairs were used to compute the temperature of formation of the deposit of the study area (isotope geothemometry) because they contained contemporaneous galena; sphalerite and chalcopyrite were used to compute for three different formation temperatures. Table 4.3 shows the partition function and the sulphur isotope compositional ratios ( $\delta^{34}$ S) from the galena, sphalerite and chalcopyrite.

Samp. Nos	GPS	Ore type	Host rock	${}^{34}S/{}^{32}S_{sph}$	$^{34}S/^{32}S_{chal}$	$^{34}S/^{32}S_{gal}$	$\delta^{34}S_{sph}$	$\delta^{34}S_{chal}$	$\delta^{34}S_{gal}$
-	Location			spir	chui	gui	spii	enui	Sui
GF1A	$05^{0}55^{1}41.3^{11}$	gal	-						-8.2
	$007^{0}29^{1}51.2^{11}$								
GF2A	$05^{0}55^{1}41.5^{11}$	gal	Shale						-5.0
	$007^{0}29^{1}42.4^{11}$								
GF2B	$05^{0}55^{1}41.5^{11}$	gal	Shale						-5.7
	$007^{0}29^{1}42.4^{11}$								
GF4A	$05^{0}56^{1}22.9^{11}$	sph/gal	Intrusive	0.043953943		0.043798918	-4.5		-8.0
	$007^{0}30^{1}32.5^{11}$								
GF4B	$05^{0}56^{1}22.9^{11}$	sph-gal-chal	Intrusive	0.043934941		0.043799674	-4.9		-8.0
	$007^{0}30^{1}32.5^{11}$								
GF4B	$05^{\circ}56^{\circ}22.9^{\circ}$	sph-gal-chal	Intrusive	0.043934941	0.043909986		-4.9	-5.5	
	$007^{\circ}30^{\circ}32.5^{\circ}$								
GF4B	05°56°22.9°	sph-gal-chal	Intrusive		0.043909986	0.043799674		-5.5	-8.0
	$007^{\circ}30^{\circ}32.5^{\circ}$						4.0		
GF4C	$05^{\circ}56^{\circ}22.9^{\circ}$	sph-gal	Intrusive	0.043935195		0.043805976	-4.9		-7.8
<b>D G D</b>	$00/^{\circ}30^{\circ}32.5^{\circ\circ}$			0.0440.640.01		0.0400000000	•		
$RSP_1$	$05^{\circ}55^{\circ}40.5^{\circ\circ}$	sph-gal	shale	0.044064821		0.043928738	-2.0		-5.1
DOD	$07^{\circ}29^{\circ}05.3^{\circ}$			0.0440.0010		0.040004744	2.0		<i>c</i> 1
KSP <sub>2</sub>	$05^{\circ}55^{\circ}40.5^{\circ}105^{\circ}211$	sph-gal	shale	0.044062013		0.043884744	-2.0		-6.1
DCD	$07^{\circ}29^{\circ}05.3^{\circ}1$	1.	-11-	0.044064921		0.0420074507	2.0		
KSP <sub>3</sub>	$05^{\circ}55^{\circ}40.5^{\circ}105^{\circ}211$	sph-gal	snale	0.044064821		0.04390/458/	-2.0		-3.3
	07/29/05.3								

# Table 4.3 Sulphur Isotope Partition Function and Compositional Ratios of the Samples

## 4.4.2 Carbon and Oxygen Isotopes

Samples GF2B and GF4C contained siderite intergrowth which were used to analyze for their carbon and oxygen isotope compositional ratios ( $\delta^{13}$ C and  $\delta^{18}$ O respectively). Table 4.4 shows the oxygen and carbon isotope compositional ratios of the siderite.

## Table 4.4 Oxygen and Carbon Isotope Compositional Ratios of the Siderite (in $^{0}/_{00}$ )

Host rock	$\delta^{13}C_{(PDB)}$	$\delta^{18}O_{(VPDB)}$	$\delta^{18}O_{(SMOW)}$
	$\pm 0.08$	±0.10	±0.10
Shale	-1.38 Ave -1.43	-7.49	23.19
Shale	-1.47	-7.693	23.04
Intrusive	-1.93	-9.81	20.80
Intrusive	-1.65	-10.01	20.59
	Jost rock Shale Shale ntrusive ntrusive	Host rock $\delta^{13}C_{(PDB)}$ $\pm 0.08$ Shale-1.38Shale-1.47Ave -1.43Intrusive-1.93Ave -1.79	Host rock $\delta^{13}C_{(PDB)}$ $\delta^{18}O_{(VPDB)}$ $\pm 0.08$ $\pm 0.10$ Shale $-1.38$ $-7.49$ Shale $-1.47$ $-7.693$ Intrusive $-1.93$ $-9.81$ ntrusive $-1.65$ $-10.01$

## It should be noted that

 $\delta^{18}O_{(SMOW)} = 1.03091 \, \delta^{18}O_{(VPDB)} + 30.01 \approx (100)$ 

(Barnes, 1979; Rollinson, 1993)

#### 4. 5 Discussion of Results

### 4.5.1 The basic – ultrabasic Igneous Rocks

The chemical composition (Table 4.2) plus the Total Alkalis Vs Silica diagram (Fig. 4.3 and 4.4) of the samples from the intrusive revealed their basic to ultrabasic nature (Read and Watson, 1977). The phaneritic to micro phaneritic textural properties exhibited by the samples picked from the Greenfield intrusive as well as the China intrusive suggests their solidification in hyperbyssal environments. The igneous rocks are high in alkaline and is suggested to be of common origin (Umeji, 1978). The chemistry, texture and colour showed that the igneous rocks of the study area are mainly of basic to ultrabasic clan (gabbro) (Fig 4.3) (Simpson, 1969). This is believed to be a function of fractional crystallization. The ultrabasic parts have very high Total Alkalis Content which is 7.61% and 7.75%.



Fig 4.3. The chemical classification of the intrusive rocks using the total alkalis versus silica (TAS) diagram (Cox et al. (1979).



Fig 4.4: The total alkali versus silica (TAS) diagram (after Kuno (1968)). Separates the subalkali group into calc-alkaline and tholeiitic subgroups

Sample ID	S14a	S14b	S14z	S21a	S21b	S21d
Oxides(wt%)						
SiO <sub>2</sub>	50.10	50.2	43.90	52.1	46.92	37.70
Na <sub>2</sub> O +K <sub>2</sub> O	5.85	6.30	7.61	6.8	4.35	7.75

#### 4.5.2 The Sources of Sulphur in the Hydrothermal Fluid

The sulphur isotope compositional ratio ( $\delta^{34}$ S) in galena in per mil values ranges from -5.0  $^{0}$ /<sub>00</sub> to -8.2 $^{0}$ /<sub>00</sub>, (average: -6.7 $^{0}$ /<sub>00</sub>, n:10, R= 3.2) in sphalerite, from -2.0 $^{0}$ /<sub>00</sub> to -4.9  $^{0}$ /<sub>00</sub> (average: -3.6, n:7, R=2.9) and in chalcopyrite, -5.5 $^{0}$ /<sub>00</sub>. Thus sulphur isotope compositional ratio for all the sulphur specie range from -2.0 $^{0}$ /<sub>00</sub> to -8.2 (R = 6.2) (Table 4.3). The average  $\delta^{34}$ S value in galena from GF2, GF4 and RSP mine are -5.4 $^{0}$ /<sub>00</sub>, -7.9 $^{0}$ /<sub>00</sub> and -5.6 $^{0}$ /<sub>00</sub> respectively while that of sphalerite from GF4 and RSP are - 4.7 $^{0}$ /<sub>00</sub> and -2.0 $^{0}$ /<sub>00</sub> respectively.

The summary of the results obtained are as such;

- i. The  $\delta^{34}$ S from all the minerals studied are negative
- ii. The  $\delta^{34}$ S values for all the sulphur species are relatively wide (i.e variation is  $6.2^{0}/_{00}$ )
- iii. The Greenfield Mine 4 deposit has more negative values than the Palladium Mine.
- iv. The  $\delta^{34}$ S values for the sulphides of the study area increases in the order  $\delta^{34}$ Sgal  $<\delta^{34}$ Schal  $<\delta^{34}$ Ssph
- v. The range of the sulphur isotope compositional ratio from Greenfield Mine 4 (3.7) is narrower than that of Palladium Mine (4.1).

Barnes (1979) and Kendall & Mc Donald (1998) realized that sulphur isotope data needs to be combined with geological and or geochemical data of the host rocks of a study area in order to get sufficient information about the genesis of a deposit. The geology of the study area consists mainly of the carbonaceous shale intruded by the alkaline basic-ultrabasic igneous rocks. Some of the shale units of the Southern Benue area, especially where the ore bodies occur have reached anchimetamorphic conditions (Akande *et. al.*, 1992). The wider range of  $\delta^{34}$ S for the whole sulphur species (galena, sphalerite and chalcopyrite) in the deposit of the study area implies a non-magmatic but sedimentary source of the hydrothermal fluid that formed the deposit. Sedimentary sulphides have a wider range of  $\delta^{34}$ S and are

typically depleted in the heavy isotope unlike magmatic fluid which has a narrow range of values (Barnes, 1979). The  $\delta^{34}$ S value of the olivine alkali basalt are concentrated closely around a mean value of  $1.3^{\circ}_{00} \pm 0.5^{\circ}_{00}$  (Hoefs, 1973; Rollinson, 1993 ; Jia-Xi *et.al.*, 2014). Hoefs( 1973) stated that sulphur probably connected with only magmatism rarely vary in  $\delta^{34}$ S by more than  $5^{0}/_{00}$  even throughout the whole mining district (Jemmali *et. al.*, 2013). Invariably, uncontaminated homogenous ore fluid from magmatic source rarely produces deposits whose sulphur compositional ratios vary by more than  $5^{0}/_{00}$  throughout a mining district. This suggests that the sulphur in the fluid that formed the deposit of the study area is not associated with magmatism since the range is more than  $5^{0}/_{00}$  (6.2<sup>0</sup>/<sub>00</sub>). The above fact is buttressed by the plotting of the  $\delta^{34}$ S on the Sulphur Isotope Reservoir diagrams by Hoef (1973) which suggests a range of  $\delta^{34}$ S value which coincides with the range found in sedimentary and metamorphic rocks. Ore-hosting shale of the Southern Benue are slightly metamorphosed having been heated to an estimated temperature of about 240°C before the Santonian peak of metamorphism with the illite- crystallinity indices suggesting anchi to epimetamorphic contact aureole adjacent to intrusive bodies (Akande *et.al.*, 1992). These imply that the source of the sulphur is from the slightly metamorphosed yo unmetamorphose sedimentary rocks of the study area (Fig.4.5).

The variations in  $\delta^{34}$ S values within the Ishiagu deposits are believed to be a function of different levels of sulphur isotope fractionation arising through

- i. the leaching of sulphide from the surrounding geology through which the hydrothermal fluid moves,
- ii. Cooling of the ore fluid and crystallization of the minerals.
- iii. The close nature of the geochemical system during the formation of the deposit



Fig. 4.5 Natural sulphur isotope reservoir (Adapted from Hoefs, (1973))

Sulphur in any hydrothermal system can exist in the form of sulfate or sulphide (Barnes, 1979 ; Rollinson 1993). The negative value of all the  $\delta^{34}$ S imply that the ore fluid contained more of the sulphide specie than the sulfate (Barnes, 1979; Kendall & Mc Donald, 1998). The sedimentary sulphides were formed by the reduction of the sedimentary sulfates after which they were leached from the Albian shale into the ore fluid as it moved through its channel ways. The kind of sulfate reduction involved in the study area is the non bacterial-inorganic sulfate reduction since the estimated temperature of formation of the deposit of the study area ranges from 152°C to 240°C (Table 4.5). It should be noted that the temperature of formation of the deposits of the study area is above the temperature favorable to sulfate reducing

bacteria (Rollinson, 1993). Barnes (1979) has established that the optimum temperature for the reduction of sulfate to sulphide by sulfate reducing bacteria is  $50^{\circ}$ C (Trudinger *et al.*, 1985). Inorganic sulfate reduction in sediments and ore fluid are triggered by the presence of methane and/ or iron ((Rollinson, 1993; Barnes, 1979). Dewatering and thermal degradation of carbonaceous shales due to overburden can be an effective process for the massive release of methane (Barnes, 2015). Thermodynamically, sulfate-hydrocarbon (methane) reduction is reported to be active in high temperature diagenesis of above  $140^{\circ}$ C or in hydrothermal environments (Machel, 1987).

 Table 4.5. The Computed Temperature of Formation of the Sulphide Mineral of the

 Study Area using Equation 2.12

Sample	GF4A	GF4Bsph-	GF4Bsph-	GF4Bchal-	GF4C	RSP <sub>1</sub>	RSP <sub>2</sub>	RSP <sub>3</sub>
ID		gal	chal	gal			_	2
T(k)	454	486	513	481	497	485	425	455
$T^0C$	181 <sup>0</sup> C	213 <sup>0</sup> C	240 <sup>°</sup> C	208 <sup>0</sup> C	224 <sup>0</sup> C	212 <sup>0</sup> C	152 <sup>0</sup> C	182 <sup>0</sup> C

With respect to the calculated temperature of formation, two processes are involved in the inorganic reduction of the sulfate in the ore fluid and in the surrounding shale (host rock) as stated by Barnes (1979).

Between the temperatures ranges of 75-175°C , the inorganic sulfate reduction took place in the presence of hydrocarbon (methane or Xylene). Barnes (1979) stated that when a carbon bearing hydrothermal fluid or a carbonaceous rock encounter a strongly reducing environment, some of the  $H_2O$  in the fluid and pore spaces respectively will react with the carbon to form different forms of  $CH_4$ . These hydrocarbons will now act on the sedimentary and hydrothermal sulfates to reduce them to sulphides. It should also be noted that the already formed sulphides can equally act as a reducing agent on the organic sulphur in the sedimentary rock and convert them to sulphides. The reaction process operates by the following steps:

 Reduction of sulfate by the reduced sulphur (H<sub>2</sub>S) to form sulphur of intermediate valence state such as

 $2H^+ \ + \ SO_4^{\ 2\text{-}} \ + \ 3H_2S \ \rightarrow \ 4S \ + \ 4H_2O$ 

2. Reduction of sulphur of intermediate valence state by organic compounds such as  $CH_3C_6H_4CO_2H$  (toulic acid) + 3S +  $2H_2O \rightarrow HO_2CC_6H_4CO_2H + 3H_2S$ 

(Source : Barnes, 1979)

Addition of carbonaceous materials from wall rocks can as well cause the reduction of  $SO_4^2$  to  $H_2S$  in ore fluid.

Rollinson (1993) also established that at temperatures above  $250^{\circ}$ C,  $SO_4^{2^{-}}$  in hydrothermal fluids can be reduced to form H<sub>2</sub>S by reacting with Fe<sup>2+</sup> components of the wall rock. This reaction is believed to have been what occurred at the study area especially at the GF4 Mine where the deposit cut accross the basic- ultrabasic intrusive and chalcopyrite was formed at 240°C. The reaction is as such:

 $SO_4^{2-}$  +  $8Fe^{2+}$  +  $10H^+$   $\longrightarrow$   $H_2S$  +  $8Fe^{3+}$  +  $4H_2O$  (Rollinson, 1993)

The fluid entered the fracture in the ultrabasic intrusive and leached out some of the iron which acted as a reducing agent to the fluid and further reduced the sulphur in the fluid to sulphides. This is why the  $\delta^{34}$ S value of the GF4 deposit is lower than that of the RSP deposit.

Table 4.6 compared the stable isotope ratios from the study area to that of some other deposits of the Benue Trough. Akande et. al, (1989) established that the values got from the galena from Arufu (Central Benue) range from  $+2.2^{0}/_{00}$  to  $+2.4^{0}/_{00}$ , the sphalerite got from Eyingba and Ameri (part of Southern Benue deposit) range from -3.7 to  $-7.8^{0}/_{00}$  (mean:  $-5.9^{0}/_{00} \pm 1.5$ ) while that of galena range from -7.1 to  $-10.4^{0}/_{00}$  (mean  $-8.7^{0}/_{00} \pm 1.3$ ) (Table 4.6). The average  $\delta^{34}$ S value of barite from the Northern Benue deposit is +12.8 (Mohammad, 2015).

Table 4.6 Results of the Sulphur Isotope Compositional Ratios of the Deposits of the Benue Trough as compared to that of the Study Area (in  $^{0}/_{00}$ )

Location		$\delta^{34}S_{gal}$	$\delta^{34}S_{sph}$	$\delta^{34}S_{\text{Bar}}$	<b>Pb:Zn:Ba</b> (Oha,2017)
Northern Benue Deposits	Gulani (Muhammad ,2015)	_	_	+12.8	0:0:3%
Central Benue Deposits	Arufu (Akande,1989)	+2.2 to +2.4	_	_	1:0:2
Southern Benue Deposit	Enyingba/Ameri (Akande,1989)	-7.1 to - 10.4	-3.7 to -7.8	-	_
	Ishiagu (This study)	-5.1 to -8.2	-2.0 to -4.9	_	3:1:0

The  $\delta^{34}$ S results got from Arufu, Eyimgba/Ameri when compared to that of the study area, shows that the source of the sulphur for the Central and Southern Benue deposits are almost the same though the fluids that formed the Central Benue deposit contain more of the heavy sulphur isotope (sulphate) than that of the Southern Benue deposits as shown by the positive nature of its value with the intrusive playing more role in the Southern Benue deposits than in the Central Benue deposits. The ore hosting sediments of the Benue Trough range from deep marine carbonaceous shale in the Southern Benue area to platform carbonate in the Central Benue and fluvial to deltaic sandstone in the Northern Benue area. Mineralized vein cutting

through porphyritic diorite have been encountered in the Ihetutu hills near Ishiagu. (Akande *et. al.*, 1992; Oha et. al, 2017).

The  $\delta^{34}$ S values got from Eyimgba/Ameri deposits implies that the ore fluid that formed those deposits contain more reduced sulphur specie (H<sub>2</sub>S) than that of the study area though the values are still within the range found in slightly metamorphosed and un metamorphosed sedimentary rocks (Akande *et. al.*, 1989 & Hoefs,1973). The abundance of sulfate in the Central Benue ore fluid is believed to be a function of the host geology. Reduction of the sedimentary sulfate to sulphide is less effective in the area since the host of the vein is mainly carbonate rock. There is more reduction reaction in compacted shaley rocks of the Southern Benue trough than on the platform carbonates of the Central Benue Trough (Barnes, 1979). The basic intrusive of the Southern Benue Trough also played some role in its more reduced nature and this is the reason for the absence of barite (BaSO<sub>4</sub>) in the Southern Benue deposits unlike in the Central and Northern Benue deposits (Oha, 2013).

#### 4.5.3 The Source of Oxygen in the Hydrothermal Fluid

The  $\delta^{18}$ O value obtained range from 20.59  $^{0}/_{00}$  to 23.19 $^{0}/_{00}$  (mean 21.9 $^{0}/_{00} \pm 0.3$ ; R=2.6 $^{0}/_{00}$ ). All the values obtained are positive. The deposit of GF2 has an average value of 23 $^{0}/_{00}$  while that of GF4 mine has the average of 20.7 $^{0}/_{00}$  (Table 4.4).

The positive nature of the values of the oxygen isotopes (Table 4.4) implies that the hydrothermal fluid that formed the siderite of the study area is slightly more enriched in the heavier oxygen isotope (<sup>18</sup>O) than the Standard Mean Ocean Water (SMOW) (Craig, 1961). Precisely, the siderite of the study area is 2.2% (21.9 parts per thousand) richer in <sup>18</sup>O than the Standard Mean Ocean Water. The small range of value observed (2.6) between the mines shows that the source of oxygen for deposit GF2C is the same with deposit GF4C. That is to

say that the two deposits were formed from the same fluid. The more negative  $\delta^{18}$ O value of GF4 than the GF2 deposit shows that GF4 deposit was formed in a more reduced condition than the GF2 deposit.

With respect to the source of the oxygen in the hydrothermal fluid that formed the deposit of the study area, the  $\delta^{18}$ O value got from the siderite was plotted on the Natural Oxygen Isotope Reservoir Diagram by Hoef (1973) (Fig.4.6) and the values coincided with the range of oxygen isotopes found in metamorphosed and ordinary sedimentary rock. It could be recalled that Albian shale sedimentary rock of the Southern Benue area experienced an anchi metamorphic condition especially where ore deposits occur (Akande *et.al.*, 1992).

Most volcanic and plutonic igneous rocks typically have very uniform  $\delta^{18}$ O values of +  $5.5^{0}/_{00}$  to  $10.0^{0}/_{00}$  and this is the normal isotopic range for magmatic waters while shale's, limestone and charts all tend to be very rich in <sup>18</sup>O with the values of  $+15^{0}/_{00}$  to  $+35^{0}/_{00}$  (Craig,1961).

Barnes (1979) states that a sedimentary rock that was metamorphosed or partly metamorphosed by igneous intrusions on a large part retain their original  $\delta^{18}$ O value during metamorphism and this has made metamorphic waters to have a wide range of values (+ 5 to 25). The  $\delta^{18}$ O value of  $21.9^{0}/_{00}$  from the siderite of the study area thereby implies that the water in the hydrothermal fluid that formed the siderite originated from the surrounding anchi- metamorphosed Albian shales plus that of the sedimentary rocks of the study area. The higher value of  $\delta^{18}$ O from GF2 more than that of GF4 (Table 4.4) is believed to be as a result of the high proximity of GF2 deposit from the intrusive more than that of GF4. GF2 deposit is hosted by only shale which is more enriched in <sup>18</sup>O than the GF4 deposit whose oxygen has been contaminated by the oxygen isotopes from the intrusive hence the variation in  $\delta^{18}$ O value between GF2 and GF4 mine is not a function of only isotopic fractionation but

also of incorporation of lighter / heavier oxygen from the immediate intrusive or shale host rocks respectively.



Fig. 4.6 Natural Oxygen Isotope Reservoir (Adopted from Hoefs (1973))

Comparing the oxygen isotope ratios of the study area to that of other deposits of the Benue Trough (Table 4.7, Fig.4.6), Folorunso & Bale (2015) recorded  $\delta^{18}$ O value of  $-15.42^{0}/_{00}$  to  $-16.2^{0}/_{00}$  (mean: 15.8) for the siderite from Ariki copper deposit, Central Benue Trough while Akande *et. al.*, (1989) recorded  $+19.5^{0}/_{00}$  to  $+21.0^{0}/_{00}$  (mean: 20.2) for the Eyimgba deposits. The  $\delta^{18}$ O values from Enyimgba, Ameri and the study area are similar to each other but quite different from the values from Ariki deposits. This suggests that the source of the oxygen in the hydrothermal fluid that formed siderite in the Southern Benue deposit is different from that of the Central Benue deposits. The oxygen of the Southern Benue is from the anchimetamorphosed and the unmetamorphosed Albian sedimentary rocks of the area while that of the Central Benue deposits is from the meteoric waters in the carbonate host (Folorunso & Bale, 2015).

Table 4.7 Results of Oxygen Isotope Compositional Ratios of the Deposits of the Benue Trough as compared to that of the Study Area (in  $^{0}/_{00}$ )

Location		$\delta^{18}O_{(SMOW)}$ (Ave.)
Northern Benue Deposits	Gulani	_
Central Benue Deposits	Ariki (Foloruso, 2015)	- 15.8
Southern Benue Deposit	Enyingba/ Ameri (Akande, 1989)	+20.25
	Ishiagu (This study)	+21.9

## 4.5.4 The Source of Carbon in the Hydrothermal Fluid

The  $\delta^{13}$ C value for the siderite of the study area range from  $-1.93^{0}/_{00}$  to  $-1.38^{0}/_{00}$  (Mean = -1.66, Range=0.55). The  $\delta^{13}$ C value for GF2B range from  $-1.47^{0}/_{00}$  to  $-1.38^{0}/_{00}$  (Ave = -1.43) while that of GF4C range from  $-1.93^{0}/_{00}$  to  $-1.65^{0}/_{00}$  (Ave = -1.79). The narrow range of values of the  $\delta^{13}$ C from the two mines (Range = 0.55) suggests that the fluid that formed the siderite in the two deposits are the same and have the single source for the carbon (Rollinson, 1993; Kendall and Carldwell, 1998) (Table 4.4). The plot of the  $\delta^{13}$ C of the study area on the Natural Carbon Isotope Reservoir by Hoefs (1973) show that the range of  $\delta^{13}$ C values of the study area coincides with the range of carbon isotopes found in Marine and Fresh Water sediments (Fig. 4.7). Barnes (1979) stated that most marine carbonates regardless of the age of formation have constant  $\delta^{13}$ C value of  $0 \pm 4^{-0}/_{00}$  while carbonate species in fresh water environment however tend to be more negative with the  $\delta^{13}$ C values ranging from  $-10^{0}/_{00}$  to  $-2^{0}/_{00}$ . This implies that the source of the carbon in the siderite is marine sedimentary carbonates. However, Rollinson (1993) stated that marine carbonate has a narrow range of

values between  $-1^{0}/_{00}$  and  $+2^{0}/_{00}$  while marine bicarbonate values range from  $-2^{0}/_{00}$  to  $+1^{0}/_{00}$  hence it can be concluded that the source of the carbon in the siderite of the study area is more of the marine bicarbonate than marine carbonate.

For the formation of carbonate minerals, fluid must contain oxidized carbon species like  $CO_2$ ,  $H_2CO_3$ ,  $HCO_3^{-1}$ , and  $CO_3^{-2-1}$  (Barnes, 1979). The carbonates in the Albian Shales produced these oxidized carbon in the ore forming fluid through:

i. Dissolution of the subordinate limestone of the Carbonaceous Albian Shale. The chemical equation for the reaction is as thus:

$$CaCO_3 + 2H^+ \rightarrow H_2CO_3 + Ca^{2+}$$

Note that the above reaction produces  $HCO_3^-$  (bicarbonate) at surface temperatures and  $CO_2$  at high subsurface temperatures. The  $CO_2$  produced is isotopically similar to the original carbonate (Barnes, 1979)

Oxidation of reduced carbon in organic compounds in the Albian Shales of the
 Asu River group formation can as well give rise to CO<sub>2</sub>



## Fig 4.7 Natural Carbon Isotope Reservoir Adapted from Hoefs, (1973)

Ohmoto and Rye, (1974) stated that a trend of increasing  $\delta^{13}$ C is usually observed for carbonate minerals formed at later stage of mineralization. This explains why there are variations in  $\delta^{13}$ C value within each of the deposit. It also shows that the siderites were formed in a close geochemical system where the lighter carbon isotopes (<sup>12</sup>C) were first used up in formation of the first set of siderite with lower  $\delta^{13}$ C values thereby making the fluid to be more enriched in the heavier isotopes (<sup>13</sup>C) and invariably increased CO<sub>2</sub>/CH<sub>4</sub> ratio (Craig,1966). This is probably what made the later mineralized siderite in GF4B to have a higher value of  $\delta^{13}$ C (-1.65) than the earlier mineralized siderite (-1.93). The variation in  $\delta^{13}$ C values that existed between deposits GF2B and GF4C could be as a result of the different levels of CO<sub>2</sub> and CH<sub>4</sub> incorporation from the host rocks. The carbon in GF4 mine which is being hosted by the intrusive is in more reduced form than that of the GF2 mine. The carbon isotope composition of the carbonates of the Benue Trough is believed to be a record of the

signatures of an integrated amount of carbonates dissolved along the fluid pathway (Akande *et. al.*, 1989).

Rye *et. al.*, (1972) & Xiaofeng et. al,(2016) concluded from experiments that a 100°C drop in temperature can account for approximately 2 of the  $5^{0}/_{00}$  (0.4) increase in the  $\delta^{13}$ C of carbonate minerals. If 100°C drop in temperature can lead to 0.4  $^{0}/_{00}$  rise in  $\delta^{13}$ C value, it means that  $0.36^{0}/_{00}$  i.e. (-1.79-(-1.43)) rise in  $\delta^{13}$ C value between GF4C and GF2B deposit will lead to 90°C drop in temperature of formation. This means that the average temperature of formation in GF2B deposit is less than that of GF4C deposit by 90°C hence if GF4C was formed at an average temperature of 224°C, it means that GF2 was probably formed at an average temperature of 134°C if all things being equal.

Comparing the  $\delta^{13}$ C results from the three groups of deposit in the Benue trough (Table 4.8), Folorunso & Bale, (2015) also recorded  $\delta^{13}$ C value of  $-1.09^{0}/_{00}$  to  $-1.71^{0}/_{00}$  for the siderite from Ariki copper deposit, Central Benue Trough while Akande *et. al.*, (1989) recorded - $2.6^{0}/_{00}$  to  $+2.3^{0}/_{00}$  for the  $\delta^{13}$ C value of the siderite from Enyigba and Ameri deposits (Southern Benue Trough). All the  $\delta^{13}$ C values are within the ranges from marine carbonate sources hence all the deposits of the Lower and Middle Benue Trough has the same source of carbon in the hydrothermal fluid that formed them though Ariki and Ishiagu deposits contain more of marine bicarbonate than ordinary carbonates (Olubambi *et. al.*, 2008).

Table 4.8 Results of the Carbon Isotope Compositional Ratios of the Deposits of the Benue Trough as compared to that of the Study Area (in  $^{0}/_{00}$ ) (Jalo Muhammad,2015 and the Study area)

Location		$\delta^{13}C_{(PDB)}$
		(Ave.)
Northern Benue Deposits	Gulani	_
Central Benue Deposits	Ariki (Foloruso,2015)	-1.4
Southern Benue Deposit	Enyingba/ Ameri (Akande,1989)	-2.6 to 2.3
	Ishiagu (This study)	-1.7

#### 4.5.5 Effect of the Immediate Host Rock on the Source of the Ore Fluid.

The direct host of a mineral deposit can influence the mineralogy and stable isotope chemistry of the ore as well as that of the surrounding (Rose & Hawles, 1979 & Zack, 2015). The  $\delta^{34}S$  data variations which occur between RSP and GF4 deposits are believed to be as result of their different host rocks. The average sulphur isotope compositional ratios ( $\delta^{34}$ S) for GF4 mine is  $-6.35^{\circ}/_{00}$  while that of RSP mine is  $-3.7^{\circ}/_{00}$  (Table 4.3). The average carbon isotope compositional ratio for GF4 deposit is  $-1.79^{\circ}/_{00}$  while that of GF2 is  $-1.43^{\circ}/_{00}$  (Table 4.4). It should be recalled that the GF4 is hosted by the intrusive while the GF2 and RSP deposits are hosted by the shale. The more negative  $\delta^{34}$ S value of GF4 deposit simply imply that the hydrothermal fluid that formed the deposit contain more H<sub>2</sub>S than that of the RSP deposit. This variation in their values can be attributed to the more reduced condition of formation of the GF4 deposit than the GF2 and RSP deposits which resulted to the incorporation of reduced sulphur and carbon (<sup>32</sup>S & <sup>12</sup>C) in the GF4 deposit. The shale surrounding the Greenfield intrusive possess more sedimentary sulphide and methane than the other shales due to the high level of inorganic reduction which has occurred in the shales converting majority of its sedimentary sulfates to sulphides. In the temperature range of 75°C-175 °C, inorganic sulphate reduction can take place in the presence of hydrocarbon

(CH<sub>4</sub>) while at temperature 250 °C and above, sulfate reduction can be achieved by reduction with ferrous iron. (Barnes , 1979; Rollinson, 1993). GF4 deposit is being host by a basic intrusive rock which normally has high iron content. The iron also acted as a reducing agent to the hydrothermal fluid that flowed into the fractures of the intrusive to reduce its sulfate to sulphides. The heat from the intrusive provided the elevated temperature condition in the surrounding shale for the inorganic reduction of its sulfate to sulphides. At high temperature, water in carbonaceous shale is usually converted to hydrocarbon. These two processes helped to increase the amount of reduced sulphur and carbon in the hydrothermal fluid that formed the GF4 deposit than that of the RSP deposit.

#### 4.5.6 Conditions of Formation of the Hydrothermal Deposit

#### 4.5.6.1 Condition of the Ore forming fluid.

The negative values obtained from the sulphur isotope compositional ratios ( $\delta^{34}$ S) in all the sulphide minerals imply that the hydrothermal fluid that formed the deposit of the study area contains lighter sulphur isotope than the heavier counterpart (Table 4.3). It also means that the fluid has lighter isotope than the standard, which is the Troilite of the Canyon Diablo Meteorite (Kendall & Carldwell, 1998).

The two sulphur species that exist in hydrothermal fluid at temperature below 350  $^{\circ}$ C is H<sub>2</sub>S and SO<sup>2-4</sup> while that of carbon are CH<sub>4</sub> and CO<sub>3</sub><sup>2-</sup>(Barnes, 1979). At equilibrium, heavier isotopes accumulate more in substances of higher interatomic bond strength while lighter isotopes accumulate more in substances of lower interatomic bond strength (Kendall & Carldwell ,1998). Lighter stable isotopes (<sup>32</sup>S & <sup>12</sup>C) are highly embedded on reduced sulphur and carbon specie while heavier isotopes (<sup>34</sup>S & <sup>13</sup>C) are highly embedded on the oxidized sulphur and carbon species respectively (Bachinski ,1968). This implies that <sup>34</sup>S and

<sup>13</sup>C denotes the presence of  $SO_4^{2-}$  and  $CO_3^{2-}$  respectively while <sup>32</sup>S and <sup>12</sup>C denotes the presence of H<sub>2</sub>S and CH<sub>4</sub> respectively. Stable isotopes are measured with respect to its heavy isotope enrichment or depletion. The negative  $\delta^{34}S$  and  $\delta^{13}C$  values of the isotope compositional ratio in the study area hence suggests the depletion of the heavier isotopes and invariably, enrichment of the lighter isotopes (by law of material balancing). The above explanation implies that the hydrothermal fluid that formed the deposit contain more of H<sub>2</sub>S than  $SO_4^{2-}$ . The abundance of H<sub>2</sub>S in the ore fluid that formed the deposit of the study is also noticed by the absence of sulfate minerals (barite) in the deposit. It should be noted that some other deposits of the Benue Trough contain barite unlike that of Ishiagu deposit.

This intrusive acted directly and indirectly for the thermochemical sulfate-hydrocarbon / inorganic reduction of the sedimentary sulfates to sulphides. The Fe<sup>2+</sup> also helped to further reduce the ore fluid especially in the GF4 deposits which is the reason for the more negative  $\delta^{34}$ S value of the deposit. From Table 4.5 ,Southern Benue Deposits has  $-v \delta^{34}$ S values and contain no barite mineral unlike the Central Benue deposits whose  $\delta^{34}$ S value is positive and it contains lead : zinc: barite in the ratios of 1:0:2 (Oha et. al., 2017)

With respect to carbon isotope, the negative values of the carbon isotope compositional ratios strongly suggest that the fluid is depleted of heavier carbon ( $^{13}$ C) than the standard which is the American Belemnite from the Cretaceous Pedee Formation, South Carolina (Rollinson, 1993). The negative value also imply that the ore fluid contain more of the reduced carbon than the oxidized carbon. Barnes (1979) stated that the kinetic processes involved in the conversion of atmospheric CO<sub>2</sub> to organic carbon and then to reduced carbon (CH<sub>4</sub>) entails the preferential concentration of the lighter carbon isotope in the organic and reduced carbon hence methane is the most depleted of  $^{13}$ C in nature. Just as in sulphur isotope, oxidized carbon (Craig,

1963). The above explanations imply that the negative  $\delta^{13}C$  of the study area means that CH<sub>4</sub> is more in the fluid than the oxidized carbon.

Summarily, the abundance of  $CH_4$  and  $H_2S$  in the hydrothermal fluid as well as the absence of barite strongly suggested that the geochemical system during the formation of Ishiagu area is slightly acidic and reduced.

## 4.5.6.2 The Close Nature of the Hydrothermal System of the deposit

The little variation in  $\delta^{34}$ S which occurred within each of the deposit suggests that the deposit of the study area was formed in a system that is close to SO<sub>4</sub><sup>2-</sup> (Rollinson, 1993; Barnes, 1967). There were little or no more incorporation of sulfate during the time of precipitation of the minerals. In a close system i.e. in environments where the rate of sulfate reduction is faster than rate of sulfate supply, the  $\delta^{34}$ S value of the sulphides minerals produced depends on the extent of reaction between the reduced sulphur (<sup>32</sup>S) and the available metal (Shafaroudi & Mohammad,2015). Here <sup>32</sup>S in the ore fluid attaches itself to the available metals (Pb, Zn, Cu and Fe) which make the residual fluid to be a bit richer in <sup>34</sup>S. This fluid enriched in <sup>34</sup>S later produces sulphide minerals with a higher  $\delta^{34}$ S value hence the variation in  $\delta^{34}$ S values and a distribution that skewed towards positive value. This is why in GF4 deposit, the  $\delta^{34}$ S value for galena vary from -8.2<sup>0</sup>/<sub>00</sub> to -7.8<sup>0</sup>/<sub>00</sub> and sphalerite vary from -4.9<sup>0</sup>/<sub>00</sub> to -4.5<sup>0</sup>/<sub>00</sub> while in Palladium mine,  $\delta^{34}$ S galena vary from -6.1<sup>0</sup>/<sub>00</sub> to -5.1<sup>0</sup>/<sub>00</sub>. There is no variation in  $\delta^{34}$ S for the sphalerite in RSP mine because the system for its formation is a partially a closed one. The system is also open to H<sub>2</sub>S since there are available metal ions to continuously remove the aqueous sulphide from the system to form sulfate (Barnes, 1979).

#### 4.5.6.3 Temperature of Formation of the Deposit

By the use of co-existing mineral pairs, the temperature of formation of the minerals were calculated based on the Model generated by Clayton (1981) (see equation 2.12). The temperature of formation computed from chalcopyrite-galena mineral pair of sample GF4B was compared with that of the sphalerite-galena mineral pair of the same sample. The closer the two temperatures of formation, the higher the level of equilibrium attained (Barnes, 1979). The estimated temperatures are shown in Table 4.9.

The computed temperatures of formation for the lead-zinc sulphides of the Greenfield Mine 4 (GF4) deposit range from 181°C to 224°C (Average :206 °C ,Range : 44) while that of Palladium Mine range from 152°C to 212°C (Average: 182 °C, Range: 60). The temperatures calculated using sphalerite-chalcopyrite mineral pair in GF4 deposit is 240°C while that calculated using chalcopyrite-galena mineral pair is 208°C (Table 4.8). The temperature estimate using carbon isotope for the GF2 deposit is 134°C. The range of temperature of formation revealed the epithermal to mesothermal nature of Ishiagu deposit while the overlap in temperature of formation among the deposits studied suggests that they were deposited at the same episode of mineralization. The temperature range helped to buttress the fact that the sedimentary H<sub>2</sub>S was formed by thermo chemical sulfate-hydrocarbon / inorganic sulfate reduction of the sedimentary sulfate using hydrocarbons and iron as reducing agents (Valley et. al., 1986). The effect of the intrusive on the formation temperature of the deposits manifested itself in the temperatures of formation of Greenfield Mine 4 (GF4) deposit which range from 180°C to 224°C (Ave 206°C) and that of Palladium Mine deposit (RSP) which range from 152°C to 212°C (Ave 182). Formation temperature of ore deposits can be a function of the geology of the host rocks of the deposit (Bateman, 1950). The GF4 deposit occurs in a vein found in the Greenfield intrusive while the RSP deposit occurs in the shale. Jensen & Bateman, (1979) has shown that sedimentary rocks absorb heat more than igneous

rocks hence deposits formed in veins which occur in sedimentary rocks has a lower temperature of formation than the same deposits formed in a vein found in igneous rock. The RSP deposit is about 0.7 km from the China intrusive and 1.5km form the Greenfield intrusive.

Sample ID	$\alpha_{sph/gal}$	$\alpha_{sph/chal}$	$\alpha_{chal/gal}$	$\Delta_{sph/gal}$	$\Delta_{sph/chal}$	$\Delta_{chal/gal}$	1000Ina	T(k)	T <sup>0</sup> C
GF4A	1.003539			3.5			3.53	454	181 <sup>0</sup> C
GF4Bsph-gal	1.003088			3.1			3.08	486	213 <sup>0</sup> C
GF4Bsph-chal		1.00056			0.6		0.57	513	240 <sup>0</sup> C
GF4Bchal-gal			1.00252			2.5	2.52	481	208 <sup>0</sup> C
GF4C	1.002949			2.9			2.95	497	224 <sup>0</sup> C
RSP <sub>1</sub>	1.0030978			3.1			3.10	485	212 <sup>0</sup> C
RSP <sub>2</sub>	1.0040394			4.1			4.04	425	152 <sup>0</sup> C
RSP <sub>3</sub>	1.00352			3.5			3.52	455	182 <sup>0</sup> C

 Table 4.9. The Estimated Fractionation Factor and Temperature of the Sulphide

 Mineral Pairs From the Study Area

Comparing the temperature of formation of the deposit to other deposits of the Benue Trough and that of the world at large, it was observed that the temperatures estimated from the Ishiagu deposit overlaps with the temperature of formations: 102 °C -175°C (Olade and Morton, 1985) and 104°C -172°C (Akande *et. al.*, 1992) calculated without pressure correction for the deposits of the Lower Benue Trough. The scholars made used of microthermometry to compute the temperature of formation while in this research, isotope geothermometry were used. It should be recalled that temperature of formation estimated from fluid inclusion can be affected by pressure. Farrington (1952) and Nwachukwu (1975) predicted a maximum sedimentary cover of ca, 1000m at the time of ore formation in the study area. A depth of formation of ca, 1km would require a pressure correction of  $30^{\circ}$ C to be added to the homogenization temperature (Akande *et. al.*, 1989). This will bring the temperatures of formation to be  $132^{\circ}$ C –  $205^{\circ}$ C (Olade and Morton, 1985) and  $134^{\circ}$ C –  $202^{\circ}$ C (Akande *et. al.*, 1992).

The formation temperature of Mississippi valley type deposit is similar to that of some part of the deposit of the study area especially those that were deposited below 200°C (Barnes, 1979). It should be recalled that the source of hydrothermal fluid that formed the MVT deposit is from the carbonaceous limestone host.

#### 4.5.6.4 Fractionation between the Mineral Pairs.

The estimated fractionation factors between the sphalerite and galena in Greenfield Mine 4 (GF4) ranges from 1.002949 to 1.003539 (average: 1.003192, Range: 0.0006) and that of the Palladium Mine (RSP) range from 1.0030978 to 1.0040394 (average: 1.0035524, Range: 0.0009416). Fractionation can simply be defined as the preferential concentration of a particular isotope in a mineral. It leads to the concentration of sulphur isotopes cans occur at different stages in the life of an ore fluid. With respect to this study, fractionation occurred (1) during the evolutionary history of the hydrothermal fluid involving reduction of sedimentary sulfate to sulphide (2) during the leaching out of the sedimentary sulphides by the moving fluid, (3) during cooling of the fluid and (4) during the precipitation of minerals. The first two forms of fractionation are what led to the accumulation of sedimentary sulphides in the ore fluid hence its negative value. The third form is brought about the variation in  $\delta^{34}$ S values among the sulphide minerals. The two mechanisms of fractionation (Equilibrium Exchange Reaction and Kinetic Isotope Processes) were involved in the

preferential concentration of the isotopes of sulphur in sphalerite, chalcopyrite and galena and isotopes of oxygen/carbon in the siderite. The kind of mechanism that is paramount with respect isotope geothermometry is the Equilibrium Exchange Reaction mechanism of fractionation which occurred between the mineral pairs used in the calculation. Urey (1947) established that this mechanism of fractionation is a function of temperature. Equilibrium Exchange Reaction involves the exchange of the two sulphur isotopes <sup>32</sup>S and <sup>34</sup>S between the two mineral pairs leading to the more concentration of <sup>34</sup>S in the sphalerite than in the chalcopyrite and invariably the galena. The mineral-mineral isotope equilibration of the Urey's Principles of Quantum Theory (ZPE) states that there is normally more heavy isotope substitution on substances with higher vibration energy or rather minerals with higher inter atomic bond strength than that of lower vibration energy (lower atomic bond) (Hoefs, 1973; Waring, 1988 and Valley & Cole, 2001). From Table 4.9, the estimated values of the fractionation factors are more than unity (1) in all the mineral pairs. All the values of the fractionation factors ( $\alpha$ ) between sphalerite and galena mineral pair in the deposit of the study area is greater than unity meaning that heavier sulphur isotopes is more in the sphalerite than in galena (eq. 2.6) (Hoefs, 1973).

The reactions involved in the exchange of the two isotope  ${}^{34}S$  and  ${}^{32}S$  between sphalerite and galena mineral pairs in this study is represented by the chemical equation below:

$$Zn^{34}S$$
 +  $Pb^{32}S$   $\longrightarrow$   $Zn^{32}S$  +  $Pb^{34}S$ 

It should also be noted that the fractionation factors for sphalerite - chalcopyrite mineral pair is also more than unity (Table 4.9) implying that heavier isotopes  ${}^{34}S$  are more concentrated in sphalerite than in chalcopyrite. The equation for the reaction is expressed as:

$$Zn^{32}S + CuFe^{34}S_2$$
  $Zn^{34}S + CuFe^{32}S_2$ 

The value of the fractionation factor between chalcopyrite – galena mineral pair is also more than unity implying that the heavier sulphur isotopes are more concentrated in chalcopyrite than in galena (Table 4.8). The reaction for the fractionation is as follows:

The fractionation factor between sphalerite-galena mineral pair is greater than that between chalcopyrite-galena and sphalerite-chalcopyrite mineral pairs. This makes the sphalerite-galena mineral pair the best pair to be used in the isotope geothermometry since the mineral pair with the highest fractionation factor serves better as the most sensitive thermometer (Rollinson, 1993).

With respect to temperature - fractionation relationship, Hoefs (1973) stated that the magnitude of the different between the isotope compositional ratios of mineral pairs. sphalerite and galena ( $\Delta_{sph-gal}$ ) decreases with increase in temperature (Fig.4.8). It could be seen from Table 4.9 that the mineral pair with the highest temperature of formation has the lowest fractionation factor while the mineral pair with the lowest temperature of formation has the highest fractionation factor. The temperature-fractionation relationship of the study area is in agreement to that of Urey (1947), Ohmoto and Rye (1979) and Criss (1991) who through theoretical and experimental studies developed the inverse relationship between equilibrium fractionation factor and temperature of formation (eq. 2.11). Figure 4.8 is the diagram of the plot of the fractionation factor in per mil value against the temperature of formation of the sphalerite-galena mineral pair in the deposit of the study area.



Fig. 4.8 The Plot of Fractionation Factor against Temperature of Formation of the Sphalerite – Galena Mineral Pair in the study area

## 4.5.6.5 Isotopic Equilibrium Nature of the Deposit

The main mineral pair involved in this study is the sphalerite -galena mineral pair. Isotopic equilibrium was achieved between the two mineral pairs when there is a state of no more change in the partition function values of the minerals involved or rather when the  $\delta^{34}$ S values are the same at every point in a deposit. Three methods were used to check the level of isotopic equilibrium attained between the sphalerite- galena mineral pair (sec.3.6.3).

i. The plot of the equilibrium fractionation factor of the mineral pairs against their corresponding temperature of formation revealed a very little deviation of some of the points from the standard equilibrium curve line (Barnes,1979) (Fig.4.9). The mineral pair whose point did not fall on the curved line showed apparent disequilibrium while the mineral pairs whose points fell on the curve showed complete isotopic equilibrium.



**Fig.4.9: Establishing the Equilibrium Nature of the Deposit (Modified from Barnes, 1979)** 

- ii. By comparing the estimated temperature of formation of chalcopyrite-galena (208°C) mineral pair of sample GF4B to that of sphalerite-galena mineral pair (213°C) of the same sample, it was seen that the two calculated temperatures of formation were not equal. The closeness of the two temperatures signifies that though the mineral pairs did not attain a complete equilibrium, a high level of equilibration was reached i.e. (apparent disequilibrium). The closeness of the  $\delta^{34}$ S values between the sulphur species also supported that.
- iii. The presence of well developed, contemporaneous galena and sphalerite in the samples also revealed high attainment of equilibrium

Generally, the deposit of the study area did not attain a complete equilibrium state but a high level of equilibrium was reached. The main reason for the partial equilibration or rather apparent disequilibrium of the deposit is believed to be as a result of the little variability/changes in the isotopic composition of the mineralizing fluids and the already formed minerals (galena and sphalerite) as the fluids move through the host rock (Barnes, 1979). These changes can be as a result of the differences in the mechanism and conditions of mineral deposition temperature and closeness of the system. The above fact is in consonance with that of Jensen & Bateman (1979) statement which says that, hydrothermal fluid is always a changing entity especially as it moves through rocks and precipitate minerals which makes it almost impossible for a complete equilibrium to be achieved. The similarity in the equilibrium nature of samples GF4A and RSP<sub>3</sub> as well as samples GF4B and RSP<sub>1</sub> is a function of their condition of mineral deposition precisely temperature (Fig.4.9).

In summary, the equilibrium condition of the deposit of the study area is more of a function of their temperature of formation and this is in agreement with what Ohmoto (1986) predicted that equilibrium fractionation between mineral pairs is a function of only temperature and nothing else. The equilibrium nature of the deposit of the study area is similar to the
equilibrium nature of some part of Kuroko deposit and Upper Mississippi valley deposit (Fig.4.8). The partial equilibrium nature of sample GF4B was also confirmed by the disparity on the temperature of formation between sphalerite-galena mineral pair (213°C) and chalcopyrite- galena mineral pair (208°C).

# 4.6 Genetic Model for the Ishiagu Lead Zinc Deposit.

Ishiagu mineralization is directly linked to tectonic activities of the Santonian and hence associated with the hydrothermal activities a few after that period. The source of the fluid is believed to be from the deeply buried, anchimetamorphosed to unmetamorphosed sedimentary rock of the Southern Benue Trough. Dewatering accompanying overburden pressure, geothermal heat as well as heat from the intrusive to the surrounding shale brought about the formation of CH<sub>4</sub> on the carbonaceous sediment under a reduced condition. The hydrocarbon invariably acted on some of the sedimentary sulfate to reduce them to sulphides. Lithostatic pressure of the compacting Albian sediments as well as the Osmotic pressure which developed across the shale membrane in the trough reduces the sediment's porosity and extrudes basinal brine enriched in metal ions, reduced sulphur and carbon species (H<sub>2</sub>S & CH<sub>4</sub> respectively) from the deeply buried, slightly metamorphosed to unmetamorphosed sedimentary rocks of the Ishiagu area. Local heat source from the intrusive provided a convecting hydrothermal system which also contributed to the force that drove the brine. Brine transport through permeable fractures and pore spaces in both the shale and the intrusive was enhanced by the complexes formed between the metal and ligands in the solution. These complexes acted like shields inhibiting the precipitation of sulphides as the ore fluid moves. The reduced, slightly acidic, closed and undisturbed nature of the geochemical environment of the hydrothermal fluid created favorable conditions for the metallogenic element (Pb, Zn, Cu) to react with the sulphide anions ( $S^{2-}$ ). Mixing of the hot rising solution with the cold near surface water mass as well as adiabatic expansion brought about a drop in the internal energy of the fluid and invariably reduces the solubility and stability of the metal sulphides and their complexes respectively thereby leading to precipitation. Chemical reaction of the moving ore fluid with rock lining as evidenced by the altered wall rock also enhance the precipitation of sulphide minerals in fissures. The slight changes in the stable isotopic compositional ratios of the deposit that formed in the intrusive is as a result of the leached iron from the intrusive wall rock which further reduced the sulphur and carbon species in the hydrothermal fluid to H<sub>2</sub>S and CH<sub>4</sub> respectively. With a continued decrease in temperature and pressure and increase in the concentration of the ore fluid constituents, the ore fluid became more reduced and interacted with the sedimentary and igneous wall rock so that more Pb and Zn sulphides are precipitated from the fluid at the temperatures between 134°C and 240 °C under a closed geochemical system and high equilibrium condition.



Fig. 4.10: Proposed genetic model of Ishiagu deposit

## **CHAPTER FIVE**

# SUMMARY, CONCLUSION, RECCOMMENDATIONS AND CONTRIBUTIONS TO KNOWLEDGE

# 5.1 Summary

The geology of the study area is made up of shale intruded by several small to medium sized mesocratic –melanocratic, phaneritic intrusive which are alkaline in nature with a slight variation in their mineralogical and textural characteristics. Two out of the three lead zinc deposits studied are hosted by the shale while one cut across the intrusive. The mineralization occur in fractures trending NW-SE and dipping steeply to vertical.

The sulphur isotope compositional ratios of the sulphide minerals studied range from  $-2.0^{0}/_{00}$  to  $-8.2^{0}/_{00}$  while that of oxygen and carbon range from  $20.59^{0}/_{00}$  to  $23.19^{0}/_{00}$  and  $-1.93^{0}/_{00}$  to  $-1.38^{0}/_{00}$  respectively. The sulphur isotope values of the study area coincides with the range of values found in sedimentary and metamorphic rocks suggesting that the deeply buried anchi-metamorphosed to unmetamorphosed sedimentary rocks are the source of the sulphur in the deposit with the ore fluid containing mainly H<sub>2</sub>S. The sulphide which was formed by the inorganic / thermal sulfate reduction of the sedimentary sulfate was leached out of the Albian sedimentary rocks at the temperature between  $150^{\circ}\text{C}-240^{\circ}\text{C}$  using methane, Fe<sup>2+</sup> and the prior formed sulphides as the reducing agent.

The changes/ variations in the  $\delta^{34}$ S values found between and within the deposits of the study area is a function of fractionation, the level of H<sub>2</sub>S and Fe<sup>2+</sup> incorporations from the surrounding shale and intrusive respectively, the fugacity and the close nature of the system that formed the deposit. There is averagely less fractionation and more homogenization of isotopes in GF4 deposits than in the RSP deposit. The abundance of  $H_2S$  in the hydrothermal fluids of the study area is the reason for the absence of barite in the deposit unlike other deposits of the Benue Trough.

The ore fluid is enriched in the heavier oxygen isotope more than the Standard Mid Oceanic Waters. The  $\delta^{18}$ O value got from the siderite of the study area coincides with the range of oxygen isotopes found in metamorphosed and ordinary sedimentary rock. The carbon isotope compositional ratio of the siderite of the study area is within the range found marine sediments with the fluids containing more of the reduced carbon (CH<sub>4</sub>) than the oxidized carbon. The temperature of formation of GF2 deposit was estimated to be at 134°C using carbon isotope. The abundance of CH<sub>4</sub> and H<sub>2</sub>S in the hydrothermal fluid as well as the absence of barite has strongly suggested that the geochemical system during the formation of Ishiagu area is reduced and slightly acidic.

The  $\delta^{34}$ S results of Arufu, Eyimgba/Ameri deposits when compared to that of the study area, shows that the source of the sulphur for the three groups of deposits are almost the same though the fluids that formed the Arufu deposit contain more of the heavier sulphur isotope (sulfate) than the lighter one (sulphides). The  $\delta^{18}$  O values from Enyimgba/ Ameri and the study area are similar but quite different from that of Ariki deposits. The oxygen of the Central Benue deposits is from the meteoric waters of their carbonate host. The  $\delta^{13}$ C values of the three groups of deposit in the Benue trough are within the ranges found in marine carbonate source

Sphalerite-galena mineral pair provided the best mineral pair for the isotope geothermometry in this research work.

Computed temperature range for the formation of the deposit is 152°C - 224 °C for sphaleritegalena mineral pair; 240 °C for sphalerite – chalcopyrite mineral pair and 208 °C for chalcopyrite- galena mineral-pair. The TOF in GF4 deposit is averagely higher than that of RSP deposit. The temperature of formation of the deposit is inversely proportional to the fractionation factor. The temperature estimate for the study area is the same with that estimated by Olade and Morton, (1985) and Akande & Mucke (1989) for the other deposits of the Lower Benue Trough despite the difference in the methodology used. The TOF of the deposit of the study area is also similar to the TOF of some part of MVT deposit and Kuroko type deposit.

Though the mineral pairs of the study area did not attain a complete equilibrium, a high level of equilibrium was reached within the deposit i.e. (apparent disequilibrium) which manifested in:

The closeness of the points plotted to the equilibrium curve (Fig. 4.17) and

The closeness of the two calculated TOF for the sphalerite-galena and chalcopyritegalena mineral pairs which are  $208 \,^{\circ}$ C and  $213 \,^{\circ}$ C respectively.

The genetic model of the Ishiagu Lead-Zinc deposit was composed using the information got from the research.

# **5.2 Conclusion**

The geology of the study area consists of the Cretaceous Albian shale intruded by basic – ultrabasic igneous rocks which are of common origin. Some of the lead-zinc deposits of the area are hosted by the Albian shales while others are hosted by the intrusive. There is a close relationship between the mineralization and the geologic structures in the study area. Generally, the deposits of the study area were formed by the same hydrothermal fluid with the ore fluid enriched in light sulphur and carbon isotopes. The ore fluid is believed to be connate brine which originated from the deeply buried sedimentary and anchimetamorphic rocks of the southern Benue Trough.

The intrusive host of the GF4 mine has slight effect on the isotope compositional ratios of the ore fluid due to its basic nature hence the variation in  $\delta^{34}$ S between GF2 and GF4 deposits is as a result of their different host geology. The Pb-Zn ore deposit of the Ishiagu area is epithermal to mesothermal and was formed in an undisturbed, reduced and slightly acidic condition. All the deposits studied were formed at the same episode of mineralization and a high level of isotopic equilibrium was reached during deposition.

The source of sulphur and carbon in the Ishiagu deposit is the same with that of the other parts of the Benue Trough but the source of their oxygen is different. The Northern Benue deposits contain heavier sulphur isotopes followed by the Central Benue deposit. The Southern Benue deposits contain more of the lighter sulphur isotopes than the heavier sulfur isotopes and this is what brought about the absence of barite in the Southern Benue deposits.

## **5.3** Contributions to Knowledge

Outlined here are the contributions of this research work to the body of knowledge. They are:

- i. The production of the detailed geologic map of the study area showing the locations of the deposits studied.
- ii. Production of a detailed stable isotope data for Ishiagu Lead- Zinc deposit
- iii. Using the Stable isotope data to characterize the Ishiagu Lead- Zinc deposit
- iv. Computation of the temperatures of formation of the deposits using isotope geothermometry.
- v. Establishing the source and the evolution of the hydrothermal fluid.
- vi. Establishing the reduced, slightly acidic geochemical environment that existed during the formation of Ishiagu deposit.
- vii. Establishing the reason for the absence of barite in Ishiagu deposits unlike some other deposits of the Central and Northern Benue Trough

viii. Establishing the role and the effect of the surrounding intrusive on the source of the fluid that formed some of the Ishiagu deposits (GF4) using their stable isotope compositional ratios.

# **5.4 Recommendations**

It is therefore recommended that

- i. Detailed isotope studies should be done on the other deposits of the Benue Trough for their proper characterization, documentation and knowledge.
- Trace element studies should be carried out on the deposits to further establish the ore
   host rock relationship

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#### **APPENDIX I**

**Derivation of the Formula for the Calculation of the Fractionation Factor and Temperature of Formation from Isotope Mineral Pairs** 

Partition function =  ${}^{34}S/{}^{32}S$ 

Sulphur isotope compositional ratio ( $\delta^{34}S$ )

$$= \left\{ \begin{array}{c} \frac{{}^{34}S^{32}S_{sample} - {}^{34}S^{32}S_{standard}}{{}^{34}S^{32}S_{standard}} \right\} \times 1000$$

$$= \left\{ \underbrace{\overset{34}{-} S^{32} S_{sample}}_{34S/^{32} S_{standard}} - \underbrace{\overset{34}{-} S^{32} S_{standard}}_{34S/^{32} S_{standard}} \right\} \quad x \quad 1000$$

$$= \left\{ \begin{cases} \frac{3^4 S}{3^2} S_{sample}}{\frac{3^4 S}{3^2} S_{standard}} - 1 \end{cases} \right\} \qquad x \ 1000$$

Where  $\delta^{34}$ S is the sulphur isotope compositional ratio. When a polymetallic

Sulphide deposit is in chemical equilibrium there is usually a partial redistribution of isotopes of sulphur among various species or compound of sulphur in chemical equilibrium in the deposit. This redistribution of isotopes among coexisting and contemporaneous mineral pair is termed equilibrium isotope fractionation ( $\alpha$ ) which is defined as the ratio of the sulphur isotope in one chemical compound e.g. sphalerite divided by the corresponding ratio of the other chemical species e.g. galena.

With respect to this research work, the kind of mechanism involved is the one related to the equilibrium exchange reaction of the mineral pair (sphalerite and galena). The equation of the exchange reaction in which <sup>34</sup>S and <sup>32</sup>S isotope is exchange between the sphalerite and galena is as thus:

$$Zn^{34}S + Pb^{32}S = Pb^{34}S + Zn^{32}S$$

While the fractionation factor between the two mineral pair is expressed as:

$$\alpha_{\text{sph-gal}} = \frac{\text{ratio of sphalerite}}{\text{ratio of gelena}} = \frac{{}^{34}S^{32}S_{\text{sphalerite}}}{{}^{34}S^{32}S_{\text{gelena}}}$$

To show that the difference in the  $\delta^{34}$ S value between the two mineral pairs involved is equal to fractionation factor in per mil value (1000ln  $\alpha$ ) as thus:

$$\Delta_{\text{sph-gal}} = \delta^{34} S_{\text{sph}} - \delta^{34} S_{\text{gal}}$$

$$= \left\{ \begin{cases} \frac{3^{4} S^{3^{2}} S_{sphalerite}}{3^{4} S^{3^{2}} S_{standard}} & -1 \\ \end{cases} x 1000 & - \\ \begin{cases} \frac{3^{4} S^{3^{2}} S_{gelena}}{3^{4} S^{3^{2}} S_{standard}} & -1 \\ \end{cases} \right\} x 1000$$

Let us call

$$\frac{{}^{34}S^{32}S_{sphal}}{{}^{34}S^{32}S_{standard}} = A \text{ and } \frac{{}^{34}S^{32}S_{gelena}}{{}^{34}S^{32}S_{standard}} = B$$

Hence

$$\{(A-1)1000 - (B-1) \ 1000\}$$

$$(1000 \ A \ -1000) - (1000B - 1000)$$

$$1000A \ -1000B + 1000$$

$$1000A - 1000B$$

$$1000 \ (A-B)$$

$$\alpha = \frac{\text{ratio of sphalerite}}{\text{ratio of gelena}} = \frac{A}{B}$$

Then to get the relationship between D sph-gal and fractionation factor we have

Dividing all by B

$$= 1000 \left(\frac{A}{B} - \frac{B}{B}\right)$$
$$= 1000 \left(\frac{A}{B} - 1\right)$$
$$= 1000 (\alpha - 1)$$
$$\Delta_{\text{sph-gal}} = 1000 \ln \alpha$$

From section 2.5.1 of this work, it could be seen that many scholars did study on between isotope equilibrium constant and temperature  $(1/T^2)$  and found out that the temperature of isotope equilibrium between mineral pair can be defined by measuring the difference in their sulphur isotope compositional ratio hence the relationship below ;

 $\Delta_{sph-gal} = \delta^{34}S_{sph} - \delta^{34}S_{gal} = A (10^6/T^2) + B$ 

## **APPENDIX II**

# Computation for the Temperature of Formation of the Mineral Pairs from the Study Area Using the Formula:

 $1000 \ln \alpha = \Delta_{\text{Sph-gal}} = A (10^6/\text{T}^2) + B$ 

$$= T = \sqrt{\frac{A(10^6)}{1000 \ln \alpha}}$$

For GF4A 
$$T = \sqrt{\frac{730,000}{3.54}} = 454K = 181^{\circ}C$$

For GF4B <sub>sph-gal</sub> 
$$T = \sqrt{\frac{730,000}{3.09}} = 486K = 213^{\circ}C$$

For GF4B <sub>sph-chal</sub> 
$$T = \sqrt{\frac{0.15 \times 10^6}{0.57}} = 513K = 240^{\circ}C$$

For GF4B <sub>chal-ga</sub> 
$$T = \sqrt{\frac{0.58 \times 10^6}{2.5}} = 481 \text{K} = 209^{\circ} \text{C}$$

For GF4C <sub>sph-gal</sub> 
$$T = \sqrt{\frac{0.73 \times 10^6}{2.95}} = 497 \text{ K} = 224 \text{ }^{\circ}\text{C}$$

For RSP<sub>1</sub> 
$$T = \sqrt{\frac{0.73 \times 10^6}{3.1}} = 485K = 212 \text{ °C}$$

For RSP<sub>2</sub> 
$$T = \sqrt{\frac{0.73 \times 10^6}{4.04}} = 425^{\circ} K = 152^{\circ} C$$

For RSP<sub>3</sub> 
$$T = \sqrt{\frac{0.73 \times 10^6}{3.52}} = 455K = 182^{\circ}C$$

Note:

For sphalerite-galena mineral pair the constant "A" = 0.73

For sphalerite-chalcopyrite mineral pair the constant "A" = 0.15

For chalcopyrite-galena mineral pair, the constant "A" = 0.58

The values of A were calculated from the equilibrium fractionation factors between the minerals and the hydrothermal fluid and the value of B is zero for all the calculations.