



## Establishing the Conditions of Formation of Ishiagu Galena-Sphalerite Mineralisation, Southeastern Nigeria Using Stable Isotope

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### Authors' contributions

This work was carried out in collaboration between all authors. Author OAI designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Authors ALO and EH managed the analyses of the study. Author OEI managed the literature searches. All authors read and approved the final manuscript.

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### ABSTRACT

The study area is located at southwestern extreme of the Benue Trough of Nigeria. The area is bounded by latitude N5° 57'0" - N5° 54'0" and longitude E7° 32' 0"- N5° 54'0". The Ishiagu galena-sphalerite deposit occurs in the Cretaceous (Albian) carbonaceous shale intruded by basic to ultrabasic igneous rocks. Tectonic events of the Santonian Era led to the folding, fracturing and faulting of the rocks of the Ishiagu area. The study tends to establish the conditions of formation of the hydrothermal deposits of Ishiagu. Establishing the conditions of formation of a deposit is a key to understanding the genesis of the deposit for its proper characterisation. Apart from galena and sphalerite, the ore is composed of chalcopyrite with siderite, quartz and calcite as gangue minerals. Stable isotope of three ore bodies were studied in the area. The  $\delta^{34}\text{S}$  of galena, sphalerite and chalcopyrite range from  $-5.0\text{‰}$  to  $-8.0\text{‰}$ ,  $-2.0\text{‰}$  to  $-4.9\text{‰}$  and  $-5.5\text{‰}$  respectively. Siderite samples have  $\delta^{18}\text{O}$  (PDB) and  $\delta^{13}\text{C}$  (PDB) values ranging from  $-10.01\text{‰}$  to  $-9.5\text{‰}$  and  $-1.93\text{‰}$  to  $-1.38\text{‰}$  respectively. The negative values of the  $\delta^{34}\text{S}$  and  $\delta^{13}\text{C}$  indicates the abundance of reduced sulfur ( $\text{H}_2\text{S}$ ) and carbon ( $\text{CH}_4$ ) respectively in the ore fluid and invariably the reduced nature of the

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hydrothermal system during the formation of the deposit. The range of negative  $\delta^{34}\text{S}$  and  $\delta^{13}\text{C}$  values of the deposit hosted by the intrusive which is  $-4.5^{0}/_{00}$  to  $-8.0^{0}/_{00}$  and  $-1.93^{0}/_{00}$  to  $-1.65^{0}/_{00}$  respectively and that of the shale host which is :  $-2.0^{0}/_{00}$  to  $-6.1^{0}/_{00}$  and  $-1.47^{0}/_{00}$  to  $-1.38^{0}/_{00}$  respectively reveal the more reduced condition of formation of the deposit hosted by the intrusive, the close nature of the geochemical environment and also the effect of the host rocks on the sulfur isotope compositional ratios.

*Keywords: Stable isotope; mineralization; Ishiagu; geochemical environment; hydrothermal system.*

## 1. INTRODUCTION

Nigeria is endowed with an extensive galena-sphalerite metallogenic province. The galena-sphalerite belt is located within the Benue Trough which covers an area of over 4,800 sq km with mineralisation at many centers [1]. The Benue Trough of Nigeria originated as a failed arm of a triple plate margin which evolved by mantle upwelling; crustal stretching and opening of the South Atlantic Ocean [2]. It extends from the northern limit of the Niger Delta to the southern margin of the Chad Basin [3]. With respect to geographical location, it hosts three mineralisation districts: the Abakiliki- Ishiagu district of the Southern Benue Trough, the Arufu-Awkana district of the Central Benue Trough and the Zurak-Wase district of the Northern Benue Trough [4]. The Ishiagu galena-sphalerite prospect is located at southwest extreme part of the Benue Trough. Exploitation of galena and sphalerite by the rural dwellers and foreigners for cosmetics as well as export is dated back to 1925 [5]. For proper characterisation of any mineral deposit the genesis of the deposit which consist of the source of the ore fluid, transportation mechanism and its conditions of formation need to be understood. Many authors have studied the source of the Ishiagu deposit but no studies have been made on the conditions of its formation. Carbon, Oxygen and Sulphur are among the main constituents of geologically important fluid hence the study of its isotopes afford the means of studying the fluid characteristic and reaction mechanism in geologic processes. Understanding the physical and chemical controls on stable isotope fractionation during hydrothermal processes is vital to a correct interpretation of the measured stable isotope ratio. The range of stable isotope ratio of a particular deposit is a function of its condition of formation.

The stratigraphy of the Southern Nigeria sedimentary basin that is prevalent in the lower part of the Benue depression is controlled by three tecno-sedimentary cycles [6-8]. 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 Cenomanian in environments believed to vary from continental to shallow marine. The presence of deep marine turbidities and mega slumps as well as minor break in sedimentation during the Cenomanian has been identified [9]. 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. The overall thickness of the sediment deposited was reported to be over 4000 m [10]. 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.

Sedimentation in the trough started with the deposition of the intracontinental arkosic sandstone of fluvial and lacustrine origin during the Aptian to early Albian (Late-Early Cretaceous). The Bima Sandstone at the north and the Mamfe Formation at the southern part of the Benue Trough represent this event in the geologic history. This was succeeded by two cycles of transgression and regression which occurred from the Middle Albian to the Coniacian, and filled the southern part of the trough with mudrocks, sandstone and limestone with an estimated thickness of 3500 m [11]. 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. The Santonian tectonic episode resulted in the magmatism. There were also folding, fracturing and uplifting of the Aptian to Coniacian sediment to form the Abakiliki Anticlinorium [12]. The Eze-Aku group occupies both flanks of the Anticlinorium while the Asu River Group overlies the Oban and Bamenda Massifs in Southern Benue Trough. 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 [13]. Transcurrent movement is suggested to be the basic tectonic mechanism in the formation of the Benue Trough [14].

Ages of the basin-fills in the Benue Trough generally decreases southwards from pre-Albian to Conacian [15] while sediments thickness increases southwards. Resting uncomfortably on the Basement Complex are the arkostic sandstone and shale of fluvial and lacustrine origin and which was formed at the early Cretaceous rift phase [16]. The transgressive depositional phase which occurred from the Middle to Late Albian resulted to the deposition of the Asu River Group sediment on the Southern Benue Trough. established the prolonged shelf and deep basin deposition of the Southern Trough sediments under predominantly oxygen deficient environment.

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 galena-sphalerite mineralisation province [17-19]. The

mineralisation occur in a series of successive and symmetrical closely spaced, steeply dipping subparallel fractures which trend NW-SE / N-S and dip SW [20].

This paper is aimed at using the stable isotopes composition of the Ishiagu hydrothermal deposits, Southern Benue Trough to determine the actual source of the hydrothermal fluid and the conditions (pH and fugacity) of formation of the deposits. The stable isotope characteristics of the study area were also compared to that of other deposits of the Benue Trough.

## 2. GEOLOGY AND PETROGRAPHY

The geology of Ishiagu area consists dominantly of cretaceous Albian shale with subordinate limestone intruded by minor basic to ultrabasic igneous rocks. The intrusive are post cretaceous and was formed during the Santonian tectonic episode. CI (Fig. 1) intrusive is located at the Northeastern part of the study area while the GI (Fig. 1) is at the Northwestern part. The names of these intrusive were given with respect to this research work. GF4 deposit is hosted by the GI intrusive which is a gabbro and occurs as melanocratic, medium to large grained igneous rocks comprising essentially of plagioclase

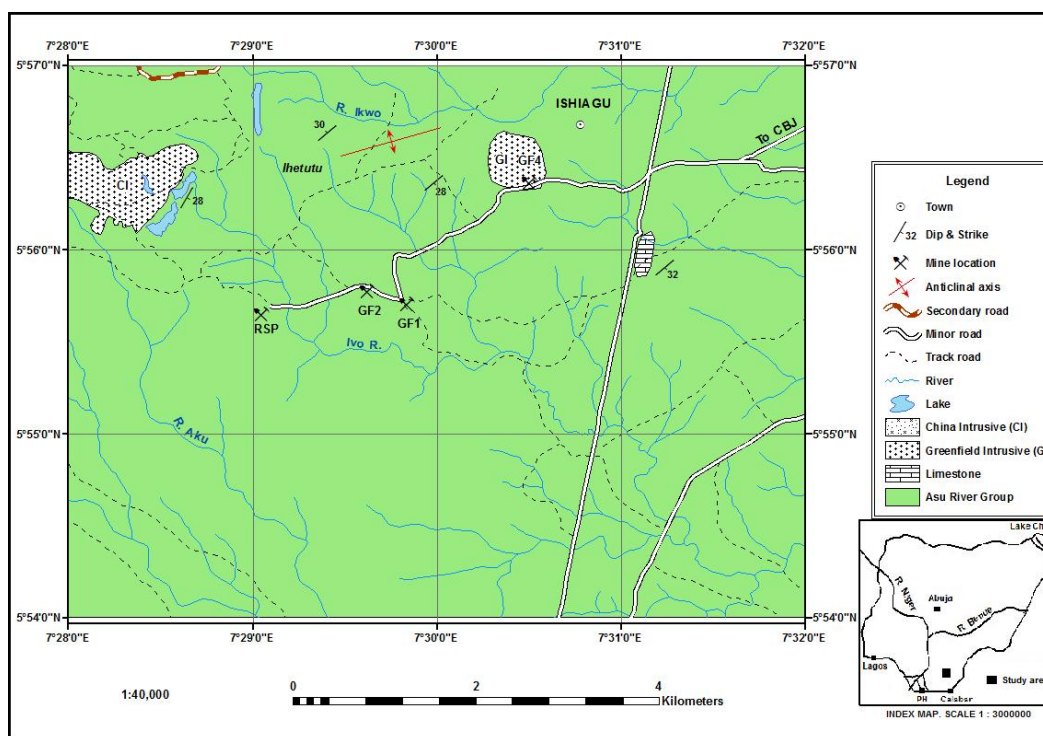


Fig. 1. Geologic Map of the study area

feldspars of labradorite composition, augite and opaque minerals. There are little variations in textural characteristics within each intrusive. Some of the shale unit of the study area is typically dark grey while some are yellowish brown in color. They are finely laminated, with alternating silt and clay bands. It is distinctly fissile. On weathered surfaces, it is grayish or mottled with shades of brown and yellow. GF2 and RSP deposits are hosted by the shale. Fig. 1 shows the positions of the three mines within the study area. GF4 Mine 4 (GF4) with the coordinates N5° 56' 22.9<sup>11</sup> and E 007° 30' 32.5<sup>11</sup> is 6.20 km southwest of the Ishiagu Community Bank Junction which is on the Ishiagu-Afikpo major road. The GF2 Mine 2 (GF2) of the coordinate; N5° 55' 41.5<sup>11</sup> and E 007° 29' 42.4<sup>11</sup> is 2.0 km southwest of GF4 mine while RSP mine (RSP) is 1.3 km west of GF2. RSP mine is of the coordinates; N5° 55' 40.5<sup>11</sup> and E 007° 29' 05.3<sup>11</sup>. GF2 Mine 2 (GF2) comprises of two subparallels, approximately NNW-SSE striking veins. The mineralogy of GF4 and RSP deposit consist of sphalerite, galena, chalcopyrite, marcasite, siderite, calcite and quartz in descending abundance. GF2 deposit has the same mineralogy though sphalerite is lacking. All the veins studied occur in a fracture which trend NW-SE and dip steeply SW to vertical. The lengths of the veins vary from 12 m to 120 m while their widths vary from 2.5 m to 4 m. The mine deposits within the study area are similar in both mineral assemblage and structural orientations except the absence of sphalerite in GF2 deposit.

### 3. MATERIALS AND METHODS

Eight ore samples from three different mines were analysed for their sulfur, oxygen and carbon isotopes compositions. Five out of the eight samples contain contemporaneous galena and sphalerite while one contains contemporaneous galena, sphalerite and chalcopyrite. The two samples from GF2 mine contain only galena while two (GF2B and GF4C) contain siderite intergrowth. Sulphur isotope compositional ratios ( $\delta^{34}\text{S}$ ) were obtained from the galena, sphalerite and the chalcopyrite while oxygen and carbon isotope compositional ratios ( $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ ) were obtained from two of the samples that contain siderite intergrowth. Sample preparations and analysis was carried out at Environmental Isotope Laboratory, Department of Geosciences, University of Arizona. For the determination of sulfur, oxygen and carbon isotope compositional ratios, the

procedure of [21] was adopted. Sulfide separates were combusted at 1030°C with oxygen and vanadium-V-oxide as the oxidising agents. This was done using an elemental analyser (COSTECH) coupled to the mass spectrometer. The sulfur isotope compositional ratio of the sulfur in SO<sub>2</sub> gas was measured in a continuous flow Gas Ratio Mass Spectrometer; Thermo Quest Fannigan Delta Plus-XL Model. The powdered samples of siderite were reacted with dehydrated phosphoric acid under vacuum at 70°C to convert the siderite to CO<sub>2</sub> for mass difference measurement of the carbon and oxygen isotope compositional ratios. The oxygen and carbon isotope mass differences were measured on the CO<sub>2</sub> gas using an automated carbonate preparation device (KIEL- III), coupled to a Gas-Ratio Mass Spectrometer, Fannigan MAT 252. All the stable isotope compositional ratios are presented in their per mil values (‰). The  $\delta^{34}\text{S}$  were reported relative to Troilite of the Canyon Diablo Meteorite (CDT) while the  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  were reported relative to Pee Dee Belemnite (PDB).

## 4. RESULTS AND DISCUSSION

### 4.1 Sulfur Isotope Studies

The sulfur isotope results were compared with the Troilite of the Canyon Diablo Meteorite (CDT) standard. The overall range of the sulfur isotope compositional ratio for all the sulfides (galena, chalcopyrite & sphalerite) is from -8.0‰ to -2.0‰. The average  $\delta^{34}\text{S}$  value of galena from GF2, GF4 and RSP mines are -5.4‰, -7.9‰ and -5.6‰ respectively while the  $\delta^{34}\text{S}$  value of sphalerite GF4 and RSP are -4.7‰ and -2.0‰. The  $\delta^{34}\text{S}$  for the sulfur species of the study area decreases in the order  $\delta^{34}\text{S}_{\text{gal}} < \delta^{34}\text{S}_{\text{chal}} < \delta^{34}\text{S}_{\text{sph}}$ .

### 4.2 Oxygen and Carbon Stable Isotope Studies

The  $\delta^{18}\text{O}$  value obtained from GF2 and GF4 mines range from -10.01‰ to -7.49‰ (mean 8.75‰ ± 0.3). The  $\delta^{13}\text{C}$  value for the siderite range from -1.93‰ to -1.38‰ (Mean = -1.66) Table 2.

### 4.3 Conditions of Formation

The  $\delta^{34}\text{S}$  value of the sulfide minerals as well as the  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  from the siderite analysed are all negative. During equilibrium reaction,

**Table 1. Sulfur isotope partition function and compositional ratios of the samples**

Samp. nos	Host rock	GPS location	Ore type	$\delta^{34}\text{S}_{\text{sph}}$	$\delta^{34}\text{S}_{\text{chal}}$	$\delta^{34}\text{S}_{\text{gal}}$
GF2A	Shale	05 <sup>0</sup> 55 <sup>1</sup> 41.5 <sup>11</sup> 007 <sup>0</sup> 29 <sup>1</sup> 42.4 <sup>11</sup>	gal			-5.0
GF2B	Shale	05 <sup>0</sup> 55 <sup>1</sup> 41.5 <sup>11</sup> 007 <sup>0</sup> 29 <sup>1</sup> 42.4 <sup>11</sup>	gal			-5.7
GF4A	Intrusive	05 <sup>0</sup> 56 <sup>1</sup> 22.9 <sup>11</sup> 007 <sup>0</sup> 30 <sup>1</sup> 32.5 <sup>11</sup>	sph/gal	-4.5		-8.0
GF4B	Intrusive	05 <sup>0</sup> 56 <sup>1</sup> 22.9 <sup>11</sup> 007 <sup>0</sup> 30 <sup>1</sup> 32.5 <sup>11</sup>	sph-gal-chal	-4.9	-5.5	-8.0
GF4C	Intrusive	05 <sup>0</sup> 56 <sup>1</sup> 22.9 <sup>11</sup> 007 <sup>0</sup> 30 <sup>1</sup> 32.5 <sup>11</sup>	sph-gal	-4.9		-7.8
RSP <sub>1</sub>	Intrusive	05 <sup>0</sup> 55 <sup>1</sup> 40.5 <sup>11</sup> 07 <sup>0</sup> 29 <sup>1</sup> 05.3 <sup>11</sup>	sph-gal	-2.0		-5.1
RSP <sub>2</sub>	Intrusive	05 <sup>0</sup> 55 <sup>1</sup> 40.5 <sup>11</sup> 07 <sup>0</sup> 29 <sup>1</sup> 05.3 <sup>11</sup>	sph-gal	-2.0		-6.1
RSP <sub>3</sub>	Intrusive	05 <sup>0</sup> 55 <sup>1</sup> 40.5 <sup>11</sup> 07 <sup>0</sup> 29 <sup>1</sup> 05.3 <sup>11</sup>	sph-gal	-2.0		-5.5

**Table 2. Results of oxygen and carbon stable isotope studies**

Sample ID	Host rock	$\delta^{13}\text{C}_{(\text{PDB})}$	$\delta^{18}\text{O}_{(\text{PDB})}$
<b>Analytical precision</b>		$\pm 0.08$	$\pm 0.10$
GF2B	Shale	-1.38	Ave -1.43 -7.49
GF2B	Shale	-1.47	
GF4C	Intrusive	-1.93	Ave -1.79 -9.81
GF4C	Intrusive	-1.65	

the heavier isotope generally preferentially accumulates in the species or compounds with higher oxidation state while lighter isotopes accumulate in species or compounds in their reduced state [22]. During equilibrium isotope fractionation between sulphates and sulphides, heavier Sulphur isotopes tend to accumulate in the sulphate while lighter sulphur isotopes accumulate in the sulphides. It is from this fact that it was established that the isotope compositional ratio for sulphates are positive while that of sulfides are negative [23]. Among different phases of the same compound or different species of the same element, the denser the material, the more it tends to be enriched in the heavier isotope. The negative values of the  $\delta^{34}\text{S}$ ,  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  hence imply that the hydrothermal fluid that formed the deposit of the Ishiagu area contain more of the lighter isotopes ( $^{32}\text{S}$ ,  $^{16}\text{O}$  and  $^{12}\text{C}$ ) than the heavier ones ( $^{34}\text{S}$ ,  $^{18}\text{O}$  and  $^{13}\text{C}$ ). Since sulfur in hydrothermal fluid usually occur either as sulfates and sulfides, the  $\delta^{34}\text{S}$  range of values in the study area depict the presence of more sulfides in the fluid than the sulfate hence a reducing condition of formation for the deposit. Thermochemical sulfate-hydrocarbon reduction is reported to be active in high temperature > 140°C or hydrothermal environment [24-26]. The

same principle also applies for the negative  $\delta^{13}\text{C}$  value whose range depicts the abundance of reduced carbon in the form of  $\text{CH}_4$  in the ore fluid. Dewatering and thermal degradation of carbonaceous shale can be an effective process for the massive release of methane. This implies that the deposit of the study area was formed in a reduced, and slightly acidic environment and this is the main reason for the absence of barite in Ishiagu deposits [27]. The more negative  $\delta^{34}\text{S}$  and  $\delta^{13}\text{C}$  of the deposit hosted by the intrusive (GF4) than that of shale shows that the GF4 deposits was formed in a more reduced environment than the GF2 and RSP. This may be attributed to the iron content from the intrusive that may have acted on the hydrothermal fluid of GF4 deposit to reduce.

The deposit was also formed in a close geochemical system as depicted in the little variation in  $\delta^{34}\text{S}$ ,  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values within each deposit. As  $^{32}\text{S}$  is used up in the formation of the early sulfide mineral, the hydrothermal fluid become more enriched in the  $^{34}\text{S}$  there by making the later formed sulfides to have a higher  $\delta^{34}\text{S}$  value. The same principle also applies for carbon and oxygen isotope ratios. The preferential concentration of heavy sulfur

isotopes in the order; sphalerite > chalcopyrite > galena (Table 1) is a function of the minerals' inter atomic bond strength.

## 5. CONCLUSION

The hydrothermal fluid that formed the deposit of Ishiagu contained more of the lighter isotopes of Sulphur, oxygen and carbon as denoted by the  $\delta^{34}\text{S}$ ,  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values. This has invariably made the fluid to contain more of the reduced species of Sulphur and carbon compound:  $\text{H}_2\text{S}$  and  $\text{CH}_4$  respectively hence the deposit was formed in a reduced condition. The deposit was also formed in a closed geochemical environment as depicted by the slight variation in their  $\delta^{34}\text{S}$ ,  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values.

The different hosts of the deposits have slight effect on their isotope compositional ratios. The variation in  $\delta^{34}\text{S}$  within each deposit is a function of the closed nature of the geochemical system during the mineral formation while the difference in  $\delta^{34}\text{S}$  value which exist among the different sulfur species is a function of the inter atomic bond strength.

## COMPETING INTERESTS

Authors have declared that no competing interests exist.

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