Stable Isotope Geochemistry and Ore Genesis of Ishiagu Galena-Sphalerite Mineralization, Southeastern Nigeria

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Authors' contributions

This work was carried out in collaboration between all authors. All authors read and approved the final manuscript.

Article Information

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ABSTRACT

The Ishiagu galena - sphalerite vein mineralization was investigated for its stable isotope composition to determine the characteristics and source of the mineralizing fluid. The $\delta^{34}S$ of galena, sphalerite and chalcopyrite range from $-5.0^0/_{00}$ to $-8.0^0/_{00}$, $-2.0^0/_{00}$ to $-4.9^0/_{00}$ and $-5.5^0/_{00}$ respectively. Siderite samples have $\delta^{18}O_{(SMOW)}$ and $\delta^{13}C_{(PDB)}$ values ranging from $20.59^0/_{00}$ to $23.19^0/_{00}$ and $-1.93^0/_{00}$ to $-1.38^0/_{00}$ respectively. The range of values for the stable isotope compositional ratios suggest that connate brine from the deeply buried , slightly metamorphosed sedimentary Albian Shales of the study area are the sources of sulfur, oxygen and carbon in the ore fluid. Comparing the stable isotope ratios of the study area to other deposits of the Benue Trough revealed that although the source of sulfur and carbon is same for all the deposits of the Benue Trough, the sulfur isotope in the deposits of the Southern Benue contain more of the lighter sulfur isotope (^{32}S) than that of the Central and Northern Benue Trough deposits which is the main reason for absence of barite in the deposit of the study area unlike the Central and Northern Benue deposits. The oxygen isotope compositional ratio of the Southern Benue deposits depicts connate brine while that of the Central Benue deposit is meteoric.

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1. INTRODUCTION

Nigeria is endowed with an extensive galena-sphalerite Metallogenic province. The galena-sphalerite belt of Nigeria is located within the Benue Trough which covers an area of over 4,800sq km with mineralization 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 mineralization districts: the Abakaliki-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 [1,4]. The Ishiagu galena-sphalerite prospect is located at southwest extreme part of the Benue Trough (Fig. 1). Exploitation of galena and sphalerite started as far back as 1925 by the locals who use the mineral as cosmetics and by foreigners who mine it for export [5,1].

Many controversies have been raised on the source of the Ishiagu deposit. The large concentration of intrusive on the area has made some scholars believe that the mineralization took its source from the surrounding intermediate - basic intrusive rocks of the area while another school of thought is of the opinion that the source is from the acidic intrusive that have not been exposed by erosion [6,7,5,1]. Akande et al. [8] suggested connate brine and cretaceous evaporates respectively as the source of the Benue Trough deposits. There is a remarkable difference in the barite content of the Benue Trough deposits from the southwest (Ishiagu district) to northeast (Gabu district) [9]. Establishing the actual source of a deposit is paramount for its characterization and for further exploration of other similar deposits.

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 [10,11,12,13,14]. 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 Cenomenian in environments believed to vary from continental to shallow marine [4]. The presence of deep marine turbidities and mega slumps as well as minor break in sedimentation during the Cenomanian has been identified [15,16,17]. 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 [10]. The overall thickness of the sediment deposited was reported to be over 4000 m [14]. The third sedimentary cycle started after the filling up of the Anambra Basin and subsequent lateral shift of the depocenter southwards into the modern Niger Delta from the late Paleocene to Recent [10].

Sedimentation in the trough started with the deposition of the intracontinental arkosic sandstone of fluviatile 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 3500m [10,18,19,20]. 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 [21,10,12]. 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 [22,23]. Benkhelil [22] proposed transcurrent movement as the basic tectonic mechanism in the formation of the Benue Trough.

Ages of the basin-fills in the Benue Trough generally decreases southwards from pre-Albian to Conacian [24] while sediments thicknesses

increase southwards [23]. Resting uncomfortably on the Basement Complex are the arkosic sandstone and shale of fluvial and lacustrine origin and which was formed at the early Cretaceous rift phase [25,18]. The transgressive depositional phase which occurred from the Middle to Late Albian resulted into the deposition of the Asu River Group sediment on the Southern Benue Trough. Hoque [18] 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 mineralization province [26,27] and [28]. 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 [26]. Three mines were studied, GF4 with the coordinates N5° 56' 22.9" and E 007° 30' 32.5", GF2 of the coordinate N5° 55' 41.5" and E 007° 29' 42.4" and RSP mine

with coordinates N5° 55'40.5" and E 007° 29' 05.3".

This paper is aimed at using the stable isotopes composition of the Ishiagu hydrothermal deposits, Southern Benue Trough to establish the actual source and evolution of the hydrothermal fluid. The stable isotope characteristics of the study area were also compared to that of other deposits of the Benue Trough.

1.2 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 intrusives are post Cretaceous and was formed during the Santonian tectonic episode. CI intrusive is located at the northeastern part of the study area while the GI is at the northwestern (Fig. 2). 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
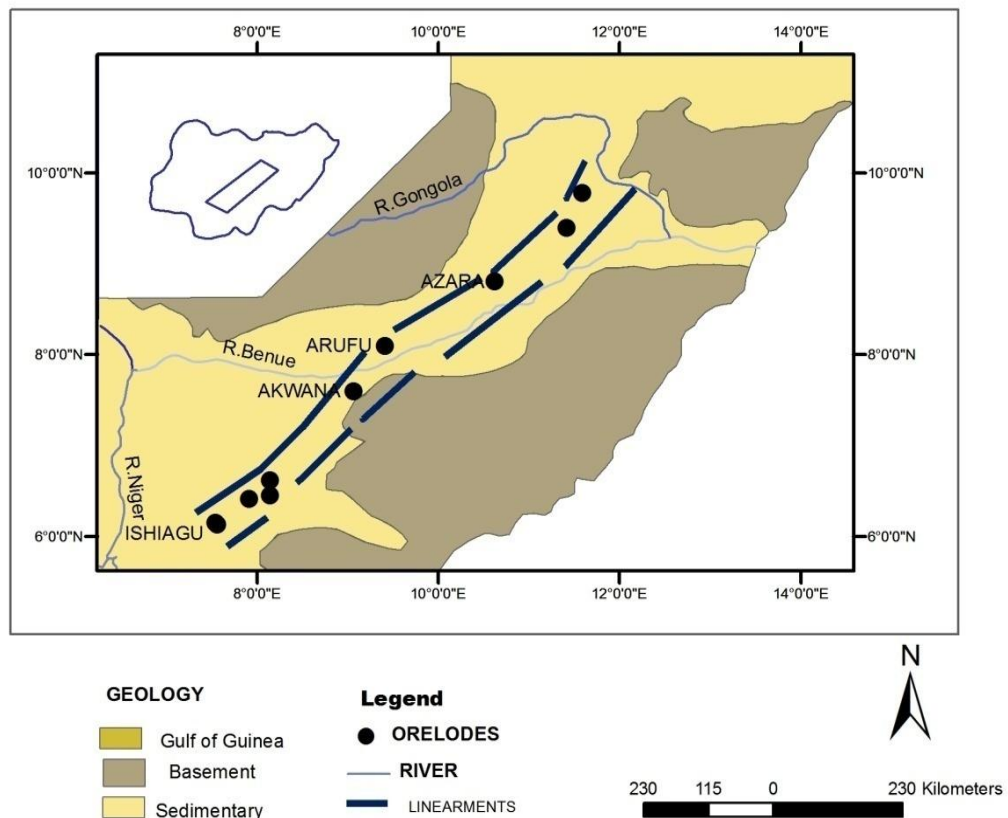

Fig. 1. Location map of the study area within the Benue Trough

rocks comprising essentially of plagioclase feldspars of labradorite composition, olivine, augite and opaque minerals (Plates 1 and 2). There are little variations in textural characteristics within each intrusive. The shale is 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 carbonaceous Albain shale of Ishiagu area. GF2 Mine comprises of two subparallels, approximately NNW-SSE striking veins. The mineralogy of GF4 and RSP deposits consist of sphalerite, galena, chalcopyrite, marcasite, siderite, calcite and quartz in decreasing 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 12m to 120m while their widths vary from 2.5m to 4m.The deposits within the study area are similar in both mineral assemblage and structural orientations except the absence of sphalerite in GF2 deposit.

2. MATERIALS AND METHODS

Eight ore samples were analyzed for their sulfur, oxygen and carbon isotopes compositions. Five out of the ten 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 ($\delta^{34}S$) were obtained from the galena, sphalerite and the chalcopyrite while oxygen and carbon isotope compositional ratios ($\delta^{13}C$ and $\delta^{18}O$) were obtained from two of the samples that contain siderite intergrowth. Sample preparations and analysis was done by the Environmental Isotope Laboratory, Department of Geosciences, University of Arizona. For the determination of sulfur, oxygen and carbon isotope compositional ratios, the procedure of [29] was adopted for the sample preparation. Sulfide separates were combusted at 1030ºC with oxygen and venadium-V-oxide as the oxidizing agents. This was done using an elemental analyzer (COSTECH) coupled to the mass spectrometer. The sulfur isotope compositional ratio of the sulfur in SO_2 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 70ºC to convert the siderite to CO_2 for mass difference measurement
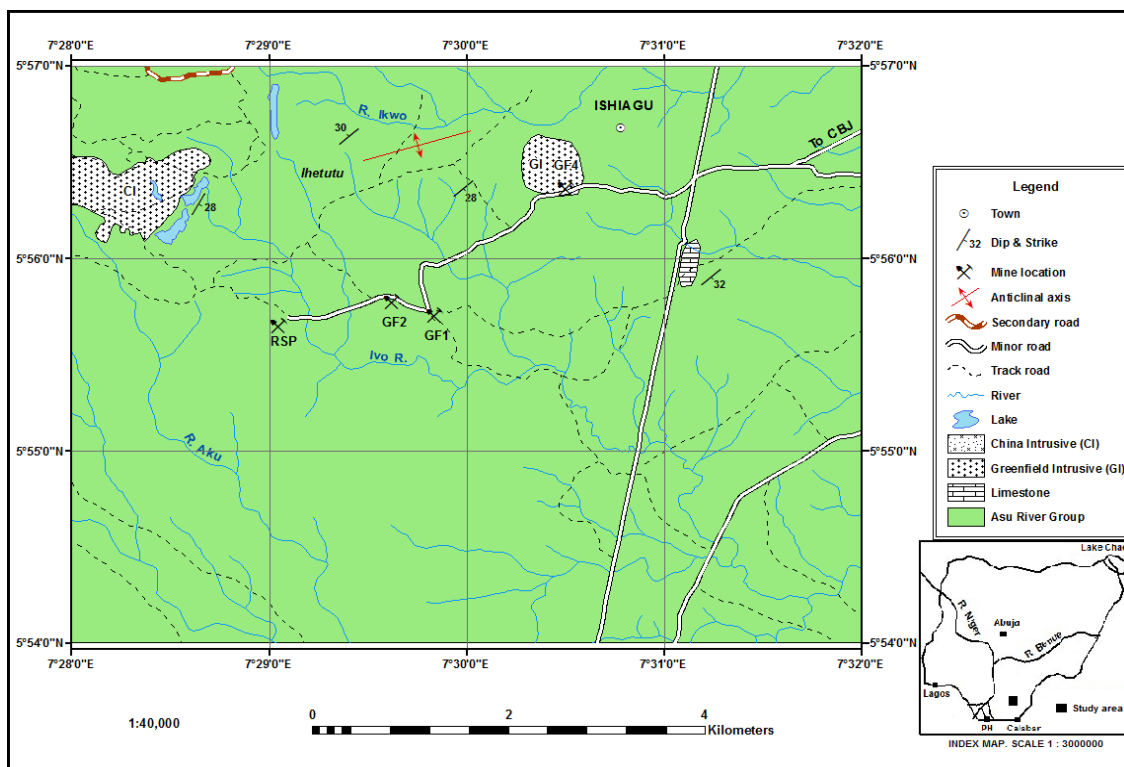

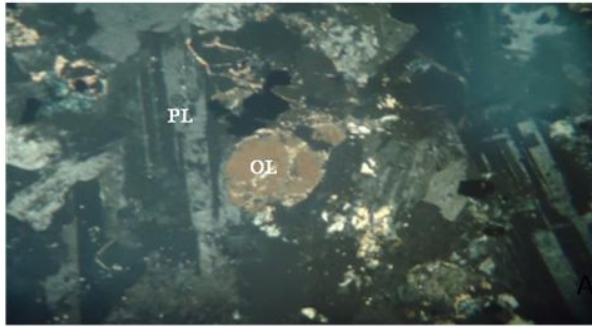**Fig. 2. Geologic map of the study area**

169

Plate 1 Photomicrograph of Ultrabasic Intrusive (S14z) showing Olivine(OL) and Plagioclase (X40)
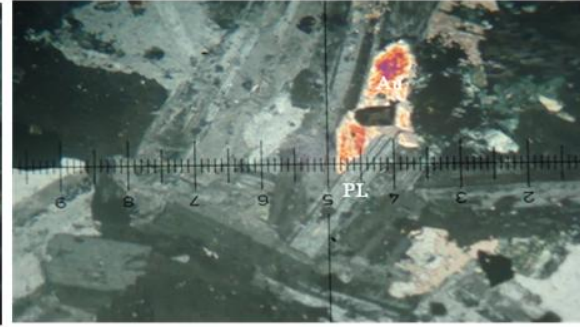

Plate 2 Photomicrograph of Gabbro showing Plagioclase (PL), Augite(Au) and some Iron Minerals (IM) (X 40)

of the carbon and oxygen isotope compositional ratios. 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 $\delta^{34}S$ were reported relative to Troilite of the Canyon Diablo Meteorite (CDT) while the $\delta^{13}C$ and $\delta^{18}O$ were reported relative to Pee Dee Belemnite (PDB) and Standard Mid Oceanic waters (SMOW) respectively. All the stable isotope compositional ratios are presented in their per mil values ($^0/_{00}$). The sulfur, oxygen and carbon isotope compositional ratios was plotted on a Natural Sulfur, Oxygen and Carbon Isotope Reservoir diagram by Hoefs [29] respectively to establish the source of the sulfur, oxygen and carbon in the hydrothermal fluid that formed the deposit of the study area. Carbon isotope compositional ratios of the siderite were also plotted against the oxygen counterpart to establish the evolutionary pathway of the ore fluid.

3. RESULTS AND DISCUSSION

3.1 Sulfur Stable Isotope Studies

The $\delta^{34}S$ from galena ranges from -5.0 $^0/_{00}$ to -8.0$^0/_{00}$(average: -6.7$^0/_{00}$, n:8) while $\delta^{34}S$ of sphalerite ranges from -2.0$^0/_{00}$ to -4.9 $^0/_{00}$

(average: -3.6, n:7) (Table 1). The $\delta^{34}S$ of chalcopyrite has the value of -5.5$^0/_{00}$. The overall range of the sulfur isotope compositional ratio for all the sulfides (galena, chalcopyrite and sphalerite) is from -8.0$^0/_{00}$ to -2.0$^0/_{00}$. The average $\delta^{34}S$ value of galena from GF2, GF4 and RSP mines are -5.4$^0/_{00}$, -7.9$^0/_{00}$ and -5.6$^0/_{00}$ respectively while the $\delta^{34}S$ value of sphalerite GF4 and RSP are -4.7$^0/_{00}$ and -2.0$^0/_{00}$.

3.2 Oxygen and Carbon Stable Isotope Studies

The $\delta^{18}O$ value obtained from GF2 and GF4 mines range from 20.59 $^0/_{00}$ to 23.19$^0/_{00}$ (mean 21.9$^0/_{00}\pm$ 0.3). The $\delta^{13}C$ value for the siderite range from -1.93$^0/_{00}$ to -1.38$^0/_{00}$ (Mean =-1.66) Table 2.

The average results of the $\delta^{34}S$, $\delta^{18}O$ and $\delta^{13}C$ values from the study area compared with some other deposits of the Benue Trough is shown in Table 3.

3.3 Source of the Hydrothermal Fluid

The wider range of $\delta^{34}S$ for the sulfur species (galena, sphalerite and chalcopyrite) in the deposit implies that sulfur in the hydrothermal fluid that formed the deposit is of a sedimentary

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

Samp. Nos	Host rock	Ore type	$\delta^{34}S_{sph}$	$\delta^{34}S_{chal}$	$\delta^{34}S_{gal}$
GF2A	Shale	gal			-5.0
GF2B	Shale	gal			-5.7
GF4A	Intrusive	sph/gal	-4.5		-8.0
GF4B	Intrusive	sph-gal-chal	-4.9	-5.5	-8.0
GF4C	Intrusive	sph-gal	-4.9		-7.8
RSP$_1$	shale	sph-gal	-2.0		-5.1
RSP$_2$	shale	sph-gal	-2.0		-6.1
RSP$_3$	shale	sph-gal	-2.0		-5.5

Table 2. Results of oxygen and carbon stable isotope studies

Sample ID	Host rock	$\delta^{13}C_{(PDB)}$	$\delta^{18}O_{(SMOW)}$
Analytical precision		±0.08	±0.10
GF2B	Shale	-1.38 ⎱ Ave -1.43	23.19
GF2B	Shale	-1.47 ⎰	23.04
GF4C	Intrusive	-1.93 ⎱ Ave -1.79	20.80
GF4C	Intrusive	-1.65 ⎰	20.59

Table 3. Results of the sulfur, oxygen, and carbon isotope compositional ratios of the deposits of the Benue trough as compared to that of the study area (in $^0/_{00}$) ([37,39])

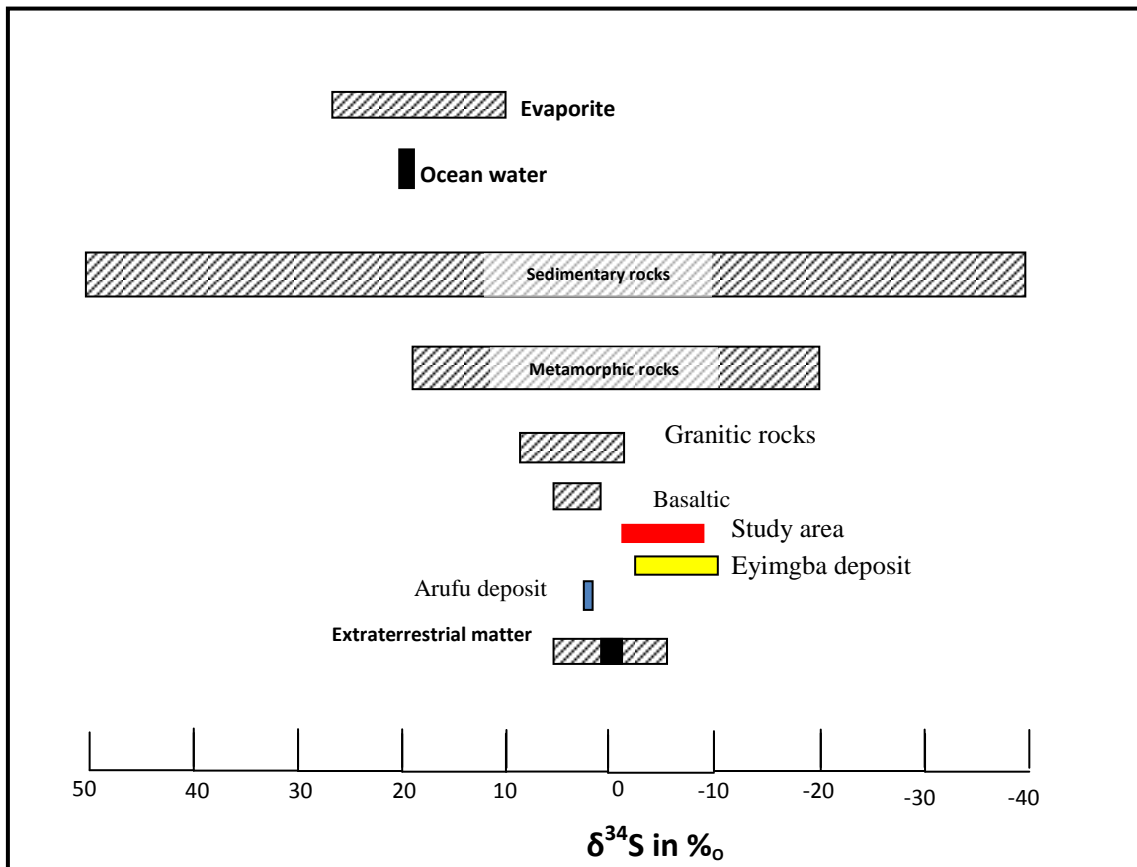| Location		$\delta^{34}S_{gal}$	$\delta^{34}S_{sph}$	$\delta^{34}S_{Bar}$ (Ave.)	$\delta^{18}O_{(SMOW)}$ (Ave.)	$\delta^{13}C_{(PDB)}$ (Ave.)
Northern Benue Deposits	Gulani			+12.8		
Central Benue Deposits	Arufu	+2.3				
	Ariki				- 15.8	-1.4
Southern Benue Deposit	Enyingba/ Ameri	-7.1 to - 10.4	-3.7 to -7.8		+20.25	-2.6 to 2.3
	Ishiagu*	-5.1 to -8.0	-2.0 to -4.9		+21.9	-1.7

Fig. 3. Natural sulfur isotope reservoir modified from Hoefs (1973)

source. Sedimentary sulfides have a wide range of $\delta^{34}S$ and are typically depleted in the heavy isotope [30]. The hydrothermal fluid is depleted of heavy sulfur isotope (^{34}S) hence it contains more of the lighter sulfur isotope (^{32}S) and invariably high reduced sulfur specie (H_2S) [30,31]] (Table 1). Lighter stable isotopes (^{32}S and ^{12}C) are highly embedded on reduced sulfur and carbon species while heavier isotopes (^{34}S and ^{13}C) are highly embedded on the oxidized sulfur and carbon species (Bachinski, 1968). ^{34}S and ^{13}C denotes the presence of SO_4^{2-} and CO_3^{2-} respectively while ^{32}S and ^{12}C denotes the presence of H_2S and CH_4 respectively. The negative value of the isotope compositional ratio in the study area suggests the abundance of the lighter sulfur isotope and invariably high concentration of H_2S in the hydrothermal fluid that formed the deposit. The variation in the $\delta^{34}S$ values between the three deposits studied (RSP, GF2 and GF4) is a function of their host geology since the average $\delta^{34}S_{gal}$ value from GF2 and RSP deposits which are hosted by the Albian Shale is lower than that of the GF4 deposit which is hosted by the intrusive (Table 1). The GF4 deposit is 0.6 percent depleted in heavy isotope

than the standard while RSP deposit is 0.4 percent. The more negative $\delta^{34}S$ values of GF4 deposit can be attributed to the basic intrusive host. The intrusive provided the ore fluid with Fe^{2+} which helped to further reduce the sulfur that formed the GF4 deposit. The intrusive plus thermal gradient provided heat to the surrounding carbonaceous shale for the inorganic reduction of the sedimentary sulfates to sulfides. Dewatering and thermal degradation of carbonaceous shale can be an effective process for the massive release of methane and subsequent thermo chemical sulfate-hydrocarbon reduction in high temperature >140ºC or hydrothermal environment [32]. The plot of $\delta^{34}S$ values on the Natural Sulfur Isotope Reservoir by Hoefs (1973) indicated that connate brine from the deeply buried, slightly metamorphosed sedimentary rocks are the source of the sulfur in the hydrothermal fluid (Fig. 3). The shales of the Southern Benue especially in areas adjacent to intrusive bodies are slightly metamorphosed having been heated to an estimated temperature of about 240ºC before the Santonian peak of tectonism [33].
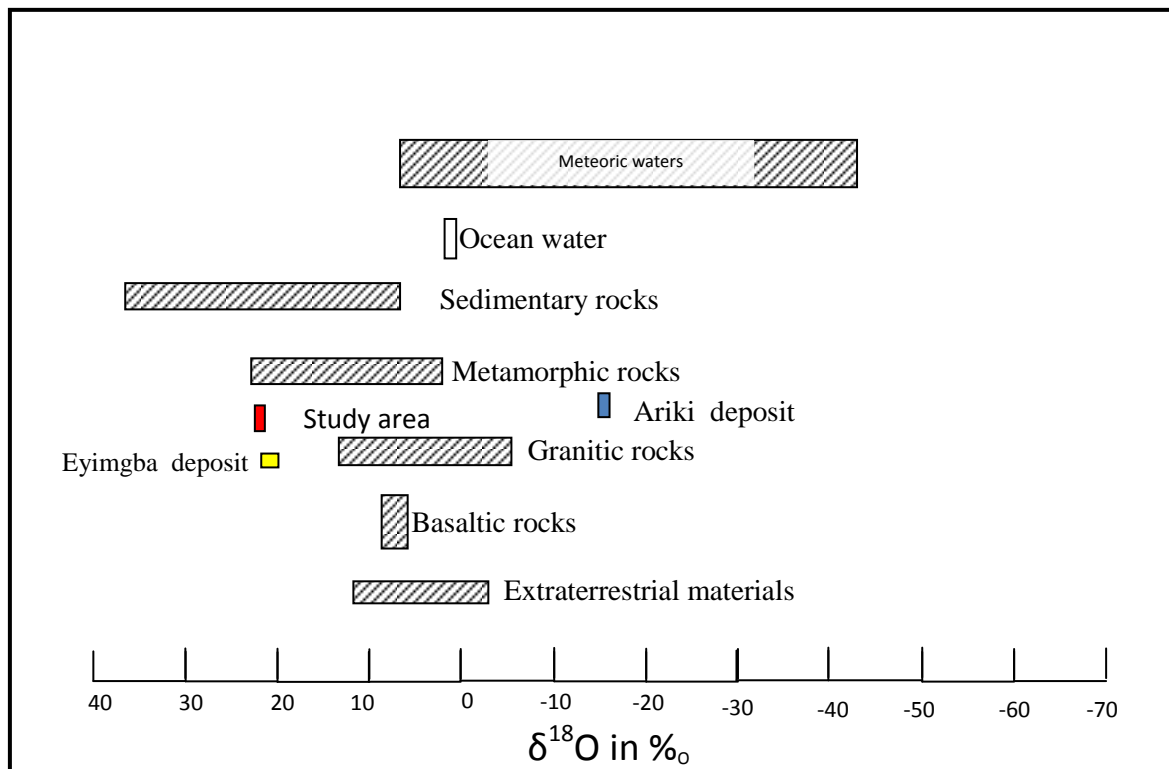

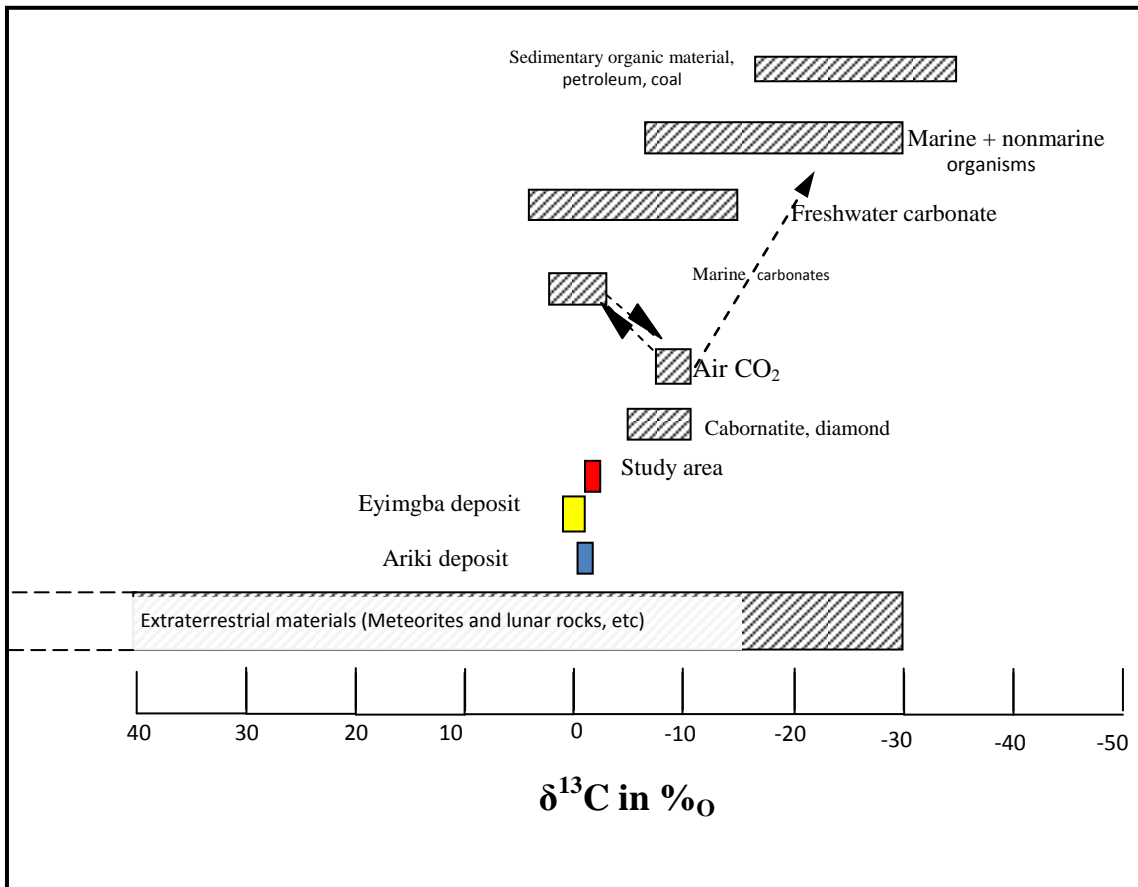**Fig. 4. Natural oxygen isotope reservoir adapted from Hoefs (1973)**

Fig. 5. Natural carbon isotope reservoir modified from Hoefs, 1973

The $\delta^{18}O$ values (Table 2) implies that the hydrothermal fluid that formed the siderite is 2.1% enriched with ^{18}O than the Standard Mean Ocean Water (SMOW) [34] while the small range of value observed (2.6) implies a single source of oxygen for all the deposits. The source of oxygen is within the range found in the deeply buried, slightly metamorphosed sedimentary rock of the study area (Fig. 4).

The range of values of the $\delta^{13}C$ from the two mines (R = 0.55) implies a single source for the carbon that formed the deposits (Table 2). The ore fluid is 1.61% richer in lighter or reduced carbon isotopes more than the Pee Dee Belemnite. The reduced carbon isotope occurred in the form of CH_4 (Barnes, 1967; Kendall, 1998). Fig. 5 shows that marine and fresh water carbonates are the possible sources of the carbon. Most marine carbonates regardless of the age of formation have constant $\delta^{13}C$ value of 0 ± 4 $^0/_{00}$ while carbonate species in fresh water environment tend to be negative with the $\delta^{13}C$ values ranging from -2 to -10 [30,35]. This implies that the source of the carbon in the siderite is marine carbonates.

The oxygen of the hydrothermal fluid that formed the deposits of the Southern Benue Trough is associated with the slightly metamorphosed sedimentary rocks while that of the Central Benue deposits is from the meteoric waters from the carbonate evaporates (Table 3). The sources of carbon and sulfur for the whole Benue Trough deposit are the same [36,37,38]. A combined study of carbon and oxygen isotope compositional ratios of the siderite revealed that the evolutionary pathway of the siderite of the study area is similar to that of the mid-ocean ridge hydrothermal calcite (Fig. 6). This kind of calcite are formed by water-rock interaction and show mixing between mantle derived carbon and sea water carbon [35].
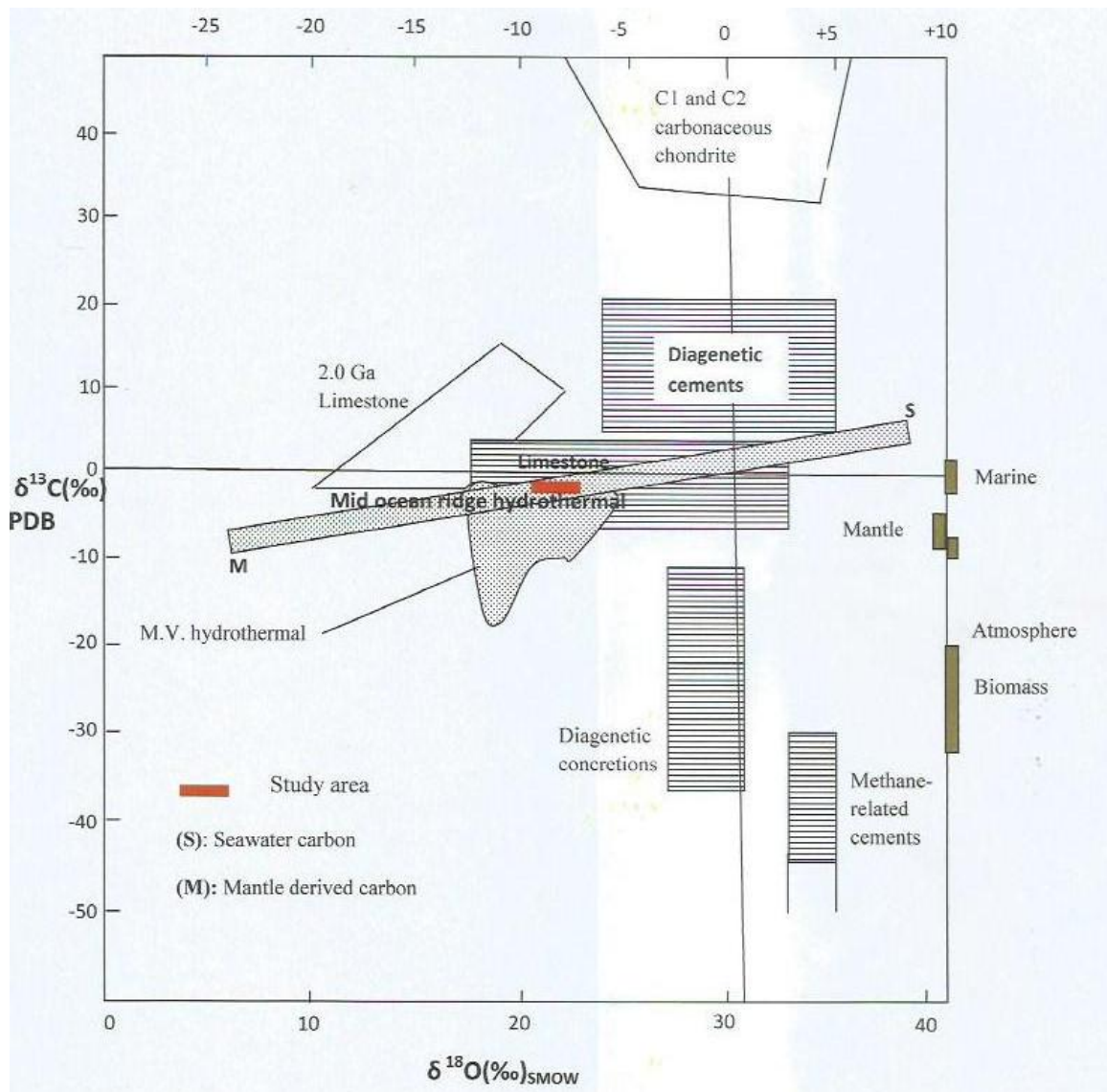
Fig. 6. The δ¹³C Vs δ¹⁸O diagram showing the evolution of the ore fluid. Modified from Rollinson (1993)

4. CONCLUSION

The deposit of Ishiagu area was formed by connate brine from the deeply buried slightly metamorphosed sedimentary rocks of the area. The ore fluid is enriched with the lighter sulfur and carbon isotopes. Sedimentary sulfides and methane were leached out from the sedimentary rock during the transit of the ore fluid. The intrusive host of the GF4 deposit has slight effects on the isotope compositional ratios of the ore fluid due to its basic nature. The source of sulfur and carbon in the Ishiagu deposit is the same with that of the other parts of the Benue Trough but their source of oxygen is different. The central Benue deposit contain heavier sulfur isotope than the southern Benue deposits. The ore fluid that formed the Ishiagu deposit is similar in evolution to that of the mid oceanic ridge hydrothermal calcite.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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