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

Abstract

The Ishiagu galena–sphalerite deposit occurs in the Cretaceous (Albian) carbonaceous shale intruded by basic to ultrabasic igneous rocks. It is located at the south western part of the Benue Trough. Tectonic events of the Santonian Era led to the folding, fracturing and faulting of the rocks of the Ishiagu area. Epigenetic galena–sphalerite vein occur as fissure filling in the NW-SE trending fractures both in the shale and the intrusive. Apart from galena and sphalerite, the ore consist of chalcopyrite with siderite, quartz and calcite as gangue minerals. Stable isotopes of three ore bodies were studied in the area. The δ34S of galena, sphalerite and chalcopyrite range from -5.0‰ to -8.0‰, -2.0‰ to -4.9‰ and -5.5‰ respectively. Siderite samples have δ18O (SMOW) and δ13C (PDB) values ranging from 20.59‰ to 23.19‰ and -1.93‰ to -1.38‰ respectively. The range of values for the stable isotope compositional ratios suggest that connate brine from the deeply buried, anchimetamorphsed 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 (32S) than that of the Central and Northern Benue Trough deposits which is the main reason for absence of barite in the deposits of the study area unlike the Central and Northern Benue deposits. The oxygen isotope compositional ratio of the Southern Benue deposits depicts connate brine from the deeply buried, anchimetamorphic sedimentary rocks as its source while that of the Central Benue deposit is meteoric.

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 4,800sq km with mineralization at many centers (Farrington, 1952). 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 (Burke et al., 1970). It extends from the northern limit of...
the Niger Delta to the southern margin of the Chad Basin (Benkhelil, 1982). 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 (Farrington, 1952; Nwajide, 2013). The Ishiagu galena-sphalerite prospect is located at southwest extreme part of the Benue Trough. 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 (Bogue, 1952; Farrington, 1952).

Many controversies have been raised on the source of the Ishiagu deposit. The large concentration of intrusives 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 (Tattam, 1944; Mc Conel, 1949; Bogue, 1952; Farrington 1952). Olade (1985) and Akande (1987) 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) (Oha, 2017). 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 (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 Cenomenian 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 (Ojoh, 1990; Nwachukwu, 1972; Okoro and Igwe, 2014). 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 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 (Murat, 1972).

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 3500m (Murat, 1972; Hoque, 1977, 1984; Olade, 1975, 1978). These sediments belong to the Albian Asu River Group, Cenomanian Odakpani 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 (Grant, 1971; Murat, 1972; Whiteman, 1982). 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 (Benkhelil, 1987; Reijers, 1996). Benkhelil (1989) 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 Coniacian (Amajor, 1987) while sediments thickness increases southwards (Reijers, 1996). 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 (Uzuakpunwa, 1974; Hoque, 1984). 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 (1984) 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 (Ezepeue,
The mineralization occurs in a series of successive and symmetrical closely spaced, steeply dipping subparallel fractures which trend NW-SE / N-S and dip SW (Olade and Morto, 1980; Ezepue, 1984).

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.

**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 intrusive is located at the northeastern part of the study area while the GI is at the northwestern part. The names of these intrusives 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 feldspars of labradorite composition, augite and opaque minerals. 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. Figure 1 shows the positions of the three mines within the study area. GF4 Mine 4 (GF4) with the coordinates N5°056'12.9011 and E007°030'13.2511 is 6.20km southwest of the Ishiagu Community Bank Junction which is on the Ishiagu-Afikpo major road. The GF2 Mine 2 (GF2) of the coordinate; N5°55'14.1511 and E007°029142.4111 is 2.0km southwest of GF4 mine while RSP mine (RSP) is 1.3km west of GF2. RSP mine is of the coordinates; N5°55'14.0511 and E007°029'05.3111. GF2 Mine 2 (GF2) 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 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 12m to 120m while their widths vary from 2.5m to 4m. The mine deposits within the study area are similar in both mineral assemblage and structural orientations except the absence of sphalerite in GF2 deposit.

Fig. 1 Geologic Map of the study area (After?)

Materials and methods

Eight ore samples from three different mines 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
For the determination of sulfur, oxygen and carbon isotope compositional ratios, the procedure of Hoefs (1973) was adopted for the sample preparation. Sulfide 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. The sulfur isotope compositional ratio of the sulfur in SO₂ 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 CO₂ for mass difference measurement of the carbon and oxygen isotope compositional ratios. The oxygen and carbon isotope mass differences were measured on the CO₂ gas using an automated carbonate preparation device (KIEL–III), coupled to a Gas-Ratio Mass Spectrometer, Fannigan MAT 252. The δ³⁴S were reported relative to Troilite of the Canyon Diablo Meteorite (CDT) while the δ¹³C and δ¹⁸O were reported relative to Pee Dee Belemnite (PDB) and Standard Mid Oceanic (SMOW) waters (SMOW) respectively. All the stable isotope compositional ratios are presented in their per mil values (‰). The sulfur, oxygen and carbon isotope compositional ratios was plotted on a Natural Sulfur, Oxygen and Carbon Isotope Reservoir diagram by Hoefs, (1973) 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.

RESULTS AND DISCUSSION

Stable Isotope Studies

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Sulfur Stable Isotope Studies

The $\delta^{34}$S from galena ranges from $-5.0^{\circ/00}$ to $-8.0^{\circ/00}$ (average: $-6.7^{\circ/00}$, n:8) while $\delta^{34}$S of sphalerite ranges from $-2.0^{\circ/00}$ to $-4.9^{\circ/00}$ (average: $-3.6^{\circ/00}$, n:7) (Table 1). The $\delta^{34}$S of chalcopyrite has the value of $-5.5^{\circ/00}$. The overall range of the sulfur isotope compositional ratio for all the sulfides (galena, chalcopyrite and sphalerite) is from $-8.0^{\circ/00}$ to $-2.0^{\circ/00}$. The average $\delta^{34}$S value of galena from GF2, GF4 and RSP mines are $-5.4^{\circ/00}$, $-7.9^{\circ/00}$ and $-5.6^{\circ/00}$ respectively while the $\delta^{34}$S value of sphalerite GF4 and RSP are $-4.7^{\circ/00}$ and $-2.0^{\circ/00}$.

Table 1 Sulfur Isotope Partition Function and Compositional Ratios of the Samples

<table>
<thead>
<tr>
<th>Samp. Nos</th>
<th>Host rock</th>
<th>GPS Location</th>
<th>Ore type</th>
<th>$\delta^{34}$S sph</th>
<th>$\delta^{34}$S chal</th>
<th>$\delta^{34}$S gal</th>
</tr>
</thead>
<tbody>
<tr>
<td>GF2A</td>
<td>Shale</td>
<td>05$^\circ/{55}'41.5'' 007^\circ/29'42.4''</td>
<td>gal</td>
<td>-5.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>GF2B</td>
<td>Shale</td>
<td>05$^\circ/{55}'41.5'' 007^\circ/29'42.4''</td>
<td>gal</td>
<td>-5.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>GF4A</td>
<td>Intrusive</td>
<td>05$^\circ/{56}'22.9'' 007^\circ/30'32.5''</td>
<td>sph/gal</td>
<td>-4.5</td>
<td>-8.0</td>
<td></td>
</tr>
<tr>
<td>GF4B</td>
<td>Intrusive</td>
<td>05$^\circ/{56}'22.9'' 007^\circ/30'32.5''</td>
<td>sph-gal-chal</td>
<td>-4.9</td>
<td>-5.5</td>
<td>-8.0</td>
</tr>
<tr>
<td>GF4C</td>
<td>Intrusive</td>
<td>05$^\circ/{56}'22.9'' 007^\circ/30'32.5''</td>
<td>sph-gal</td>
<td>-4.9</td>
<td></td>
<td>-7.8</td>
</tr>
<tr>
<td>RSP$_1$</td>
<td>shale</td>
<td>05$^\circ/{55}'40.5'' 07^\circ/29'05.3''</td>
<td>sph-gal</td>
<td>-2.0</td>
<td>-5.1</td>
<td></td>
</tr>
<tr>
<td>RSP$_2$</td>
<td>shale</td>
<td>05$^\circ/{55}'40.5'' 07^\circ/29'05.3''</td>
<td>sph-gal</td>
<td>-2.0</td>
<td>-6.1</td>
<td></td>
</tr>
<tr>
<td>RSP$_3$</td>
<td>shale</td>
<td>05$^\circ/{55}'40.5''</td>
<td>sph-gal</td>
<td>-2.0</td>
<td>-5.5</td>
<td></td>
</tr>
</tbody>
</table>

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Oxygen and Carbon Stable Isotope Studies

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

Table 2 Results of Oxygen and Carbon Stable Isotope Studies

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Host rock</th>
<th>$\delta^{13}$C (PDB)</th>
<th>$\delta^{18}$O (SMOW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Analytical precision</td>
<td>±0.08</td>
<td>±0.10</td>
<td></td>
</tr>
<tr>
<td>GF2B Shale</td>
<td>-1.38</td>
<td>Ave -1.43</td>
<td>23.19</td>
</tr>
<tr>
<td>GF2B Shale</td>
<td>-1.47</td>
<td>23.04</td>
<td></td>
</tr>
<tr>
<td>GF4C Intrusive</td>
<td>-1.93</td>
<td>Ave -1.79</td>
<td>20.80</td>
</tr>
<tr>
<td>GF4C Intrusive</td>
<td>-1.65</td>
<td>20.59</td>
<td></td>
</tr>
</tbody>
</table>
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 below.

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 $\%_\text{oo}$) (Foloruso, 2015; Akande, 1989)

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

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Discussion

Source of the Hydrothermal Fluid

The wider range of $\delta^{34}\text{S}$ 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 source. The hydrothermal fluid is depleted of heavy sulfur isotope ($^{34}\text{S}$) hence it contains more of the lighter sulfur isotope ($^{32}\text{S}$) and invariably high reduced sulfur specie ($\text{H}_2\text{S}$) (Barnes, 1967; Kendall, 1998) (Table. 1). The variation in $\delta^{34}\text{S}$ between the three deposits studied (RSP, GF2 and GF4) is a function of their host geology. The more negative $\delta^{34}\text{S}$ of GF4 mine can be attributed to the basic intrusive host. The intrusive may have provided iron in the ore fluid which helped to further reduce the ore fluid that formed the GF4 deposit. The intrusive also provided heat to the surrounding carbonaceous shale for the inorganic reduction of the sedimentary sulphates to sulfides. The plot of $\delta^{34}\text{S}$ values on the Natural Sulfur Isotope Reservoir by Hoefs (1973) indicated that connate brine from the deeply buried, anchimetamorphosed sedimentary rocks is the source of the sulfur in the hydrothermal fluid (Fig. 2).
The $\delta^{18}$O values (Table 2) implies that the hydrothermal fluid that formed the siderite is enriched with $^{18}$O than the Standard Mean Ocean Water (SMOW) (Craig, 1961) 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 anchimetamorphosed sedimentary rock of the study area (Fig. 3).

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 3). The ore fluid is enriched in lighter and reduced carbon isotopes. The reduced carbon isotope occurred in the form of CH$_4$ (Barnes, 1967; Kendall, 1998). Fig. 4 shows that marine and fresh water carbonates are the possible sources of the carbon though the small range of value initially observed indicated only one source. 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 tend to be negative with the $\delta^{13}$C values ranging from -2 to -10 (Barnes, 1967). 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 ancinhemorphosed 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 is the same (Akande, 1989; Folorunso, 2015; Muhammad, 2015). 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. 5). This kind of calcite is formed by water-rock interaction and show mixing between mantle derived carbon and sea water carbon (Rollinson, 1993).

Fig. 4 Natural carbon isotope reservoir modified from Hoefs (1973)
Fig. 5  The $\delta^{18}$O $\text{Vs} \delta^{13}$C Diagram showing the evolution of the ore fluid. Modified from Rollinson (1993)
The deposit of Ishiagu area was formed by connate brine from the anchi–metamorphosed sedimentary rocks of the area. Sedimentary sulfides and methane were leached out from the sedimentary rock during its transit of the ore fluid. The intrusive host of the GF4 deposit has slight effect on the isotope compositional ratios of the ore fluid. The source of sulfur 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 ore fluid that formed the Ishiagu deposit is similar in evolution to that of the mid ocean ridge hydrothermal calcite.

REFERENCES


