

# Genesis of the Lead -Zinc Mineralization, Upper Benue Trough, Nigeria, From the Perspective of Fluid Inclusion and Stable Isotopes Study.

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**Abstract:** The lead – zinc ores in the Upper Benue Trough occur as veins within the Albian Bima sandstones. The homogenization and freezing temperatures determined in sphalerites indicate that they were precipitated from a moderately hot mineralizing fluid (176° -254°C) but considerably less saline fluids 16.04 Eq. wt.% NaCl. Sulfur isotopic composition of the sphalerites and galena ranges from + 7.9 to + 14.5 per mil and + 5.3 to +17.5 per mil respectively, suggesting systematic depletion of the sulfides relative to contemporaneous Cretaceous seawater sulfate. The nature of the fluids deduced from the D/H isotopic analyses of fluid inclusions in sphalerite and galena gave  $\delta D$  values of -23 to -28 per mil and -35 per mil respectively. These values are consistent with sedimentary basin formation waters. Deposition of the ores took place when heated formation waters were released probably by aqua-thermal fracturing. Due to loss of pressure and cooling as the fluids rises, metals leached from the sediments combine with reduced sulfur transported probably by the chloride-complexes of the fluids to effect precipitation of the ores along fractures which serve as channel ways for the uprising mineralizing solution.

**Keyword:** Isotopic signatures, Ferruginised, Conglomeratic, Interbedded, Benue Trough, Albian, Turonian.

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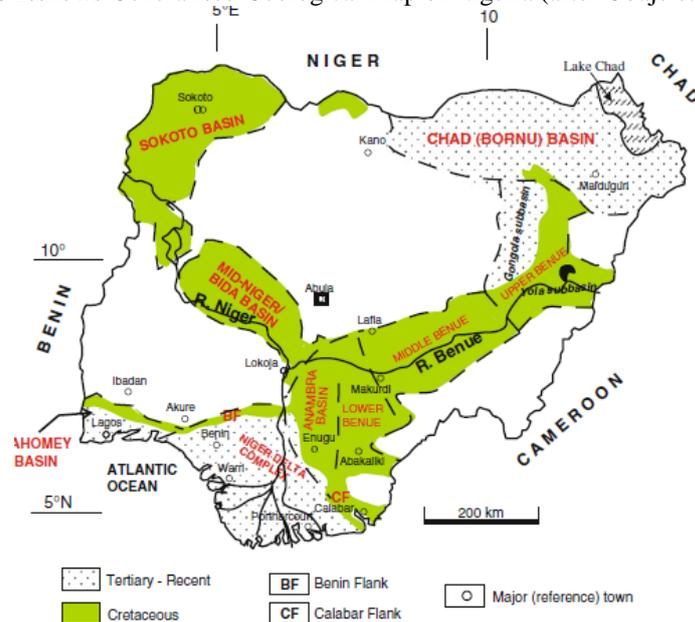
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## I. Introduction

The Benue Trough is an intra-continental rift initiated in the early Cretaceous during the opening up of the South Atlantic, (Grant 1971, Olade 1975)(Fig.1).

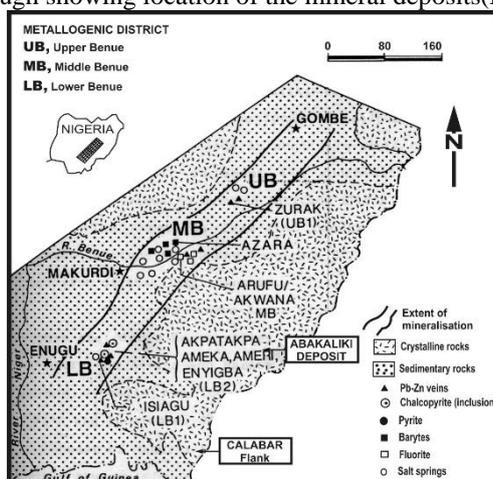
Although the Trough failed to open into a proto-ocean it probably formed a continental extension of an arm of the South Atlantic oceanic transformed fault (Burke, 1974). Within the central axis of the trough are probably a limited number of sub-basins (Benkhelil and Robineau 1983) which were sites of major subsidence during the Aptian and Albian.

**Figure 1:** shows Generalised Geological Map of Nigeria (after Obaje et al., 2009)



Lead- zinc-barite-fluorite mineralization of these sub-basins coincide approximately with the lower Benue , Abakaliki-Isiagu Pb-Zn mineral district; middle Benue, Arufu-Akwana Ba-F mineral district; and upper Benue Zurak-Wase Pb-Zn mineral district (Figure 2).

**Figure 2:** shows the Benue Trough showing location of the mineral deposits (Modified after Ogundipe, 2017).



Although mining of the lead-zinc ores commenced in all districts as early as 1925, the upper Benue deposits have been relatively less studied. Most of the studies were centered on the geology and origin of the lower Benue lead-zinc-copper deposits but which was always projected to the upper Benue Trough Zurak-Wase lead-zinc deposits. The magmatic-hydrothermal model (Farrington 1952, Orajaka 1965 and Nwachukwu 1975) was based on the morphology and epigenetic characteristics of the veins. The Juvenal and connate brines model proposed by Offodile (1976), suggests interaction between juvenile solutions and connate brines. The circulating connate brines model (Grant, 1971; Olade, 1976; Olade and Morton, 1985) relies mostly on fluid inclusion data, mode of occurrence and geological settings of the lead-zinc ores.

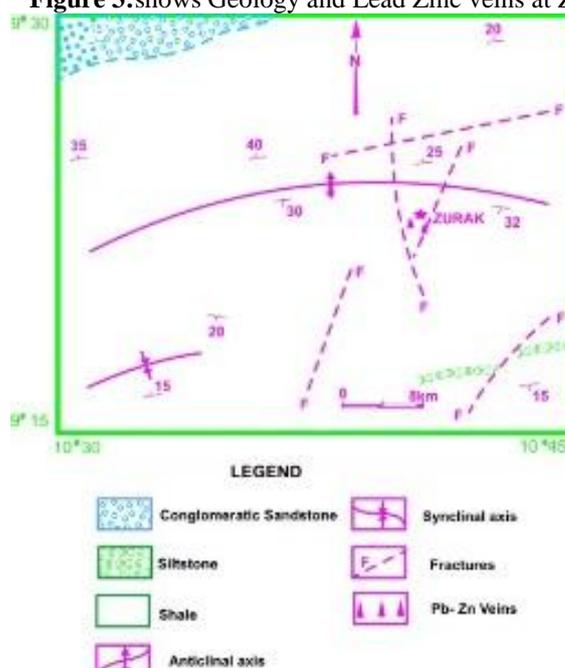
The controversy on the genesis of the Benue Trough lead-zinc ores may be resolved if geochemical H-C-O-S and Pb isotopic studies in addition to fluid inclusion analyses are used as bases for postulating a genetic model for each of the unique geotectonic lower, middle, and upper Benue Trough. Akande et al. (1988) carried out a fluid inclusion and stable isotope studies on the Pb – Zn – b – f deposits in the lower and middle Benue which did not extend to the upper Benue. The Benue Trough is not a single homogenous geotectonic unit in view of the individual prevailing tectonic, lithologic, paragenetic and thermometric characteristics of the three mineral districts. Ozasuwa et al. (1981) have shown that the rate of subsidence in the Benue Trough varies from lower Benue (deeper) to Middle Benue (shallow) to upper Benue (deep). Similarly distinctive lithologic successions and paragenetic sequences have been mapped in the mineralogical districts (Farrington 1952). Finally, Ogundipe (1987) has shown that each of the designated mineral district has its own characteristic temperature of formation, lead and sulfur isotopic signatures.

As part of a serialized contributions towards solving the controversy on the genesis of the Benue Trough lead-zinc-barite-fluorite deposits, this study presents new data and interpretation on filling temperatures, salinities and stable isotopic data on the nature and gross composition of the mineralizing fluids related to ore minerals in an attempt to formulate a genetic model for the upper Benue lead-zinc deposits.

### **Geological Setting and Mineralization**

The Benue Trough set within a riftogenic geotectonic environment is in-filled by about 5000m of sedimentary and volcanoclastic sediments (Nwachukwu 1972). The sedimentary successions were deposited by a repetitive transgressive and regressive phases commencing from the Albian to Cenomanian. Three distinctive lithologic units comprising mostly carbonaceous shale in the lower Benue, platform carbonates in the middle Benue and arenaceous sediments in the upper Benue were deposited by these polycyclic marine movements. In the upper Benue, the Bima sandstone was deposited in a fluvial-deltaic environment as an entirely continental sediment consisting of poorly sorted medium-coarse grained arkosic sandstone and greywackes interbedded by very thin bands of siltstones and mudstones. (Figure 3)

**Figure 3:** shows Geology and Lead Zinc veins at Zurak



In places, the formation could be differentiated into two end members- a basal weakly indurated conglomeratic ferruginised feldspathic unit overlain by a fine to medium argillaceous silty thin bands of siltstones and mudstones. After the Albian transgression and during subsequent interplay of marine and transitional marine conditions that heralded the Turonian transgression, the paralic sediments of the Yolde and Pindiga Formations were deposited (Carter et. al, 1963). The Yolde Formation is an entirely yellowish argillaceous fine-grained sandstone interbedded with alternating yellow to greenish mudstone. This is overlain conformably by the Pindiga Formation which consists of dark to black clayey shales, mudstones and fossiliferous limestone. The Sekule and Numanha Formations which overlies the Pindiga Formation as shales and limestones with occurrences of sandstones were deposited in a marine environment prevalent during the upper Senonian transgression. Structural deformation of the Cretaceous sediments in the upper Benue are expressed in form of folds, faults and fractures produced essentially by the non-coeval Cenomanian and pervasive Santonian deformations. The most compelling structural elements are the Lamurde and Jarawa anticlines (Carter et. al, 1963; Cratchley and Jones, 1965). Benkhelil (1980) has described the Jawara anticlinorium as a complex structure encompassing several small anticlines disposed en-echelon along a N50E direction for more than 60km. Pre and post mineralization magmatism in form of andesite, basalts, lava flows and agglomerates have been mapped within the basement complex as well as the sedimentary successions. The precise role of magmatism in the mineralization of the upper Benue Trough has not been well understood. Nevertheless, it is not unlikely that the pervasive volcanic activity may have increased the geothermal gradient in the basin from which high homogenization temperatures measured in the fluid inclusions emanated.

Lead-zinc mineralization in the upper Benue Trough is confined to well-defined steeply dipping fractures and faults striking in an N-S direction. A close examination of the mineralized structures of abandoned mine workings revealed that the strike length of the veins varies from a few meters with thickness ranging from a few centimeters to two meters. The most abundant sulfide mineral is sphalerite which occurs in two forms,- a massive reddish-brown type and a dark brownish-black variety. Galena which is generally subordinate to sphalerite in relative abundance occurs either as perfect cubes or as inter-granular crystals within the late dark brownish black sphalerite. Chalcopyrite occurs as a minor sulfide. The commonest hydrothermal gangue minerals are quartz and siderite. Most of the siderite has been dissolved and re-crystallized as hematite (Ogundipe 1987).

## II. Materials And Methods.

### Fluid Inclusion Study.

Micro thermometric measurement were carried out on sphalerites from upper Benue Trough in order to determine the probable temperatures of deposition of the ore minerals. The sphalerites exhibit different shades of color banding ranging from golden yellow to reddish brown which makes colorific classification of inclusions fairly simple. In this study, primary inclusions are assigned to those inclusions that are isolated and large in size relative to adjacent ones. In the same way, all those inclusions aligned parallel to the color bands are assigned

primary origin. Most inclusions worked upon are primary in origin while those occurring on obvious planes or trails suggesting pseudo-secondary or secondary inclusion were avoided. Homogenization temperatures were obtained from an average of five reproducible measurements on each sample in most cases. The degree of reproducibility was always within 0.2°C at about 200°C for large optically clear inclusions.

The paragenesis of the inclusions are simple. They are mostly two-phase, liquid + vapor inclusions with the degree of filling varying between 0.8 to 0.90. All inclusions used did not give any evidence of decrepitation even when heated about 20° above the homogenization temperatures. Similarly during the heating runs no leakage, necking down or changes in volume or shape due to recrystallization of the inclusions were observed which suggests that the wide range in the homogenization temperatures was not due to these phenomena. The trapping temperature is estimated to about 210° C after the necessary pressure correction has been done. This is based on depth of burial of not more than 400 meters calculated from depth of boiling/temperature of boiling of homogenization temperatures curve (Hass 1970). Since no evidence of boiling was found in the fluid inclusions, a minimum pressure of 40 bars would be required to prevent boiling at 254° C. Fluid inclusion measurements were carried out at the Centre de Recherche Petrographiques et Geochimique, (C.R.P.G). Nancy, France. The system used is the Chaixmeca heating and freezing stage developed at the C.R.P.G (Poty et. al 1976).

Sulfur isotopic analysis was carried out on sphalerite and galena from the upper Benue after the technique used by Robinson and Kusakabe (1975). The results of ten measurements obtained from the two types of sphalerite (red-brownish sphalerite and dark brownish-black sphalerite) as well as galena is shown in Table 1.

**Table 1: shows Sulfur Isotopic data for the Zurak Upper Benue deposits**

Sample No.	Localit y	Sample Description	$\delta^{34}\text{S}_{\text{sph}}$	$\delta^{34}\text{S}_{\text{gal}}$	$\delta^{34}\text{S}_{\text{sph-gal}}$	Isotopic Temp.
ZUR 2	Zurak	Reddish-brown sphalerite	+7.9			
ZUR 13	“	As above	+8.0			
	“	Cubic galena coexisting with sphalerite		+5.3	+2.7	177°C <sup>1</sup>
ZUR 16	“	Reddish-brown sphalerite	+8.08			
ZUR 19	“	Cubic galena		+5.9		153°C <sup>1</sup>
ZUR 1	“	Dark brownish-black sphalerite	+13.4			
ZUR 4	“	As above	+14.5			
ZUR 6	“	Cubic galena		+17.5		
ZUR 7	“	As above		+17.4		
ZUR 14	“	Cubic galena		+13.9		

### III. Result

The result of homogenization temperatures obtained in sphalerites from Zurak area ranges from 176° to 254° C (mean 206° C ± 20° C). Table 2

**Table 2: shows the Freezing and homogenization temperatures for fluid inclusions in sphalerite from Zurak deposit**

Locality	Sample No	Description of Sample	Homogenization Temperature(°c)	Mean (°c)	Freezing Temperature (°c)	Mean (°c)
Zurak	Zur 16	Massive reddish brown sphalerite	191,217,231,206, 212,193,226,216 198,228,207,205	211	-11,-11,-11 -11,-11,-11 -11,-12,-12 -11,-12	-11
	Zur 5	Dark brownish black sphalerite	191	191	-	-
	Zur 10	Massive sphalerite	182	182	-10	-10
	Zur 20	Massive sphalerite	185,213,196,242 187,180,253,179 221,220	208	-11,-11,-11	-11
	Zur 21	Massive sphalerite	207,187,202,236 248,212,250,198 234,188	216	-11,-11,-12 -11,-11	-11

The result of the freezing measurements gave values ranging from -11°C to -12°C (mean -12°C ± 0.5°C) which corresponds to 16.04 equivalent weight percent NaCl. In contrast to the homogenization temperatures, the freezing temperatures exhibit a very narrow range of variation. This implies that the mineralizing fluids are less saline with an identical chemical characteristics which kept the salinity essentially constant even though the temperature fluctuates between 176°C and 254°C. It should be noted that

homogenization temperatures measured in similar ore minerals from the lower Benue Trough ranges from 121°C to 160°C (Ogundipe 1987). It is reasonable therefore to suggest that the upper Benue sulfide minerals were deposited from the hottest mineralizing solutions in the entire Benue Trough. The high temperature at Zurak may have some bearing on the reported volcanic activity and emplacement of mantle-derived magma within the lower crust of the upper Benue (1963; Cratchley and Jones 1965). The magma may have increased the geothermal gradient in this mineralogical belt although the precise relationship between magmatism and mineralization still remain enigmatic.

#### **IV. Discussion.**

One of the primary objectives of the study of mineral deposits is to identify the source(s) of the different constituents of the ore-forming solutions from which the ore and gangue minerals were deposited. Sulfur isotopic data would be helpful in establishing the source of sulfur while hydrogen isotopes would also provide an answer to the type of water that transported the metals to the site of deposition.

The  $\delta^{34}\text{S}$  values in both the sphalerites and galena are isotopically heavy. The data also show very narrow isotopic variation (1 per mil) for each paragenetic mineral which suggest isotopic homogeneity of the hydrothermal solutions. The  $\delta^{34}\text{S}$  of the coexisting but not necessarily cogenetic sphalerite and galena show a depletion of about 9 per mil and 12 per mil respectively with respect to contemporaneous seawater sulfate. On the contrary the late dark-brownish black sphalerites was depleted by only about 4 per mil while the late non-coexisting galena was enriched by about 1 per mil relative to contemporaneous seawater sulfate which suggest isotopic disequilibrium during the deposition of the late galena.

For the source of sulfur with this type of enrichment generally in the heavy isotope of sulfur, a sedimentary reduced sulfur derived directly or indirectly from seawater sulfate is the most probable source, (Goldhaber and Kaplan, 1975). Sedimentary reduced sulfur can be generated through syn-sedimentary bacteria reduction of seawater sulfate during early diagenesis. Alternatively sulfide sulfur can be produced by thermochemical reduction of seawater sulfate in the presence of either organic matter, petroleum or ferrous -rich sediment. Bacterial reduction of seawater sulfate can be achieved under a steady supply of organic matter, seawater and near-surface temperature conditions which occur in the first few meters of sediment beneath the seawater-sediment interface (Bernier 1985). In view of the peculiar geotectonic setting of the upper Benue deposits such as location in arkosic sandstone with probably little or no organic matter including high homogenization temperatures in excess of 200°C and high positive  $\delta^{34}\text{S}$  values, synsedimentary bacteria reduction of seawater sulfate may not have been responsible for the source of the reduced sulfur. However, non-bacterial reduction of seawater sulfate involving a thermal reduction of seawater sulfides in  $^{34}\text{S}$  may be due to inadequate supply of sulfate arising from marine condition in the lower and middle Benue to continental conditions in the upper Benue which probably affected the amount of sulfate available in the pores of the sediments or available for reduction. During the reduction process, the amount of sulfate available was so limited such that a major part of the total available sulfate was reduced sulfide. This system therefore may be a sulfur poor system and the limited amount of metals precipitated may have been determined by the shortage of sulfide sulfur. This may probably be the reason why the upper Benue sulfides occur as small deposits.

The application of Hydrogen Isotope is based on the premise that the deuterium content of water in fluid inclusions can be used to characterize the water that formed the aqueous components of mineralizing solutions from which the ore minerals were deposited. This is because waters of diverse origin (meteoric, magmatic, formation, seawater, connate etc.) show systematic variations in their deuterium isotopic composition. The  $\delta\text{D}$  measurements carried out on the fluids extracted from fluid inclusions in sphalerite and galena gave values ranging from -23 per mil and -28 per mil for red-brownish and dark- brownish black sphalerites respectively while the only galena gave -35 per mil. These isotopic values indicate that they are neither seawater nor simply unmodified meteoric water with added salts. The data is consistent with sedimentary basin formation fluids (Clayton et al 1966, Highton and Friedman 1969, Sheppard 1984, Charef and Sheppard 1987). But because the  $\delta\text{D}$  values are depleted in deuterium relative to seawater, these formation waters cannot be simply of connate seawater origin in which a dominant component of the water may have been meteoric in origin.

#### **V. Conclusion**

The data and interpretation of fluid inclusions and stable isotopes of sulfur and hydrogen have shown that the upper Benue lead-zinc deposits are deposited from circulating warm hydrothermal fluids in fractured sediment-in- fills of the sub-basins that occur along the central axis of the Benue Trough.

Metals leached from the sediments combine with reduced sulfur transported probably by the chloride-complexes of the ore fluids to effect precipitation of the ores along fractures which serve as channel ways for the mineralizing solution.

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