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Biogenic and Abiogenic Origins of Authigenic Pyrite of Gombe Inlier, Gongola Arm, Upper Benue Trough N.E Nigeria.

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ABSTRACT

This study constrains the origin of pyrite of the Gombe In-lier to either biogenic or abiogenic using the analytical techniques Scanning Electron Microscopy and Energy Dispersive X-ray Spectroscopy and stable sulfur isotopes studies. The stable isotope compositions are useful indicators of the pathways of both biogenic and abiogenic pyrite formation. Textural and compositional information preserved in sedimentary pyrite from sediment-hosted ore deposits has contributed to elucidate their environment of formation. Backscattered SEM images of pyrite samples of this study were compared with that of the Huitrin Formation, Neuquén Basin in Argentina which is Aptian in age together with that of the offshore core samples of the Captain sands of Western Moray Frith Basin, United Kingdom with an Aptian age, the Valanginian (Lower Cretaceous) Wealden group of the Wessex Basin in Dorset, United Kingdom, the Turonian Afowo Formation in the Dahomey Basin of Nigeria. Result showed that in all SEM images, micrographs indicate either euhedral or framboids pyrites. Their respective isotopes results (mean) were also compared. The isotope result places the samples of the Gombe inlier with strong evidence that they could either have an origin that is biogenic or abiogenic, with a positive $\delta^{34}S$ values signifying a closed system sulfate reduction during the pyrite mineralization of the area and of low temperature mineralization.

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1. INTRODUCTION

The study of authigenic pyrite provides practical as well as purely scientific dimensions in hydrocarbon reservoirs, e.g., for concentrations of dense minerals (such as pyrite grain with density of approximately 5.0 g cm^{-3} compared with silicate mineral density usually of 2.6–2.8 g cm^{-3}) can lead to complications in petrophysical log response interpretation and the assignment of incorrect porosity. Also, pyrite offers a research opportunity because it records the development of the supply of H_2S in a hydrocarbon reservoir, and its sulphur isotopic composition constrains ideas of origin, amongst other uses from its study.

The most commonly encountered authigenic mineral in sediments is of cause pyrite (FeS_2). The Gombe hill forms part of the Gombe inlier of the Gongola Basin, where sediment hosted sulfide mineral occurrence composed primarily of Iron (II) Sulphide (Fe_2S) was reported (Joseph, 2006). The pyrite of the Gombe hill (study area) are massive and occurs as massive concentrations on the Bima or as fracture fillings of both the Bima and the Basement rocks of the area. The pyrite is formed during shallow burial, as a result of the reaction between iron (Fe) released into solution from clay minerals and the H_2S generated from the reduction of interstitial dissolved sulfate by bacteria, using sedimentary organic matter as a reducing agent and energy source (Bata, 2016; Bata *et al*., 2017).Determining the source of sulphide in an ore deposit, however, has proved difficult (Trudinger, 1976), since there are no unequivocal criteria for distinguishing biogenic (organic and biotic) from abiogenic (inorganic and abiotic) sulfide minerals.

The main sulfur pools from which sulfide in sediments can be derived are the mantle and seawater or evaporite sulphate, which are reduced by either chemical or biological mechanisms. In hydrothermal situations, some sulfide may be derived more or less directly from volatile phases in the mantle (Bonatti, 1975), but there is isotopic evidence that, for about the last 2000 m.y., sulfate has been a major source of sulfide in sedimentary deposits (Monster *et al*., 1979; Sangster, 1968, 1976; Schidlowski, 1979).

Sulfur stable isotope fractionation suggests that pyrite framboids from the floating microbial mats have a biogenic origin. Pyrite is also believed to have a biogenic origin attributed to microbial activity since petroleum reservoirs can be attacked by specialized chemoorganotrophic sulfate-reducing bacteria which degrade the oil and precipitate pyrite during the biodegradation process (Bata *et al.,* 2017).

The works of Berner (1984) and Berner and Westrich (1985) show that the framboidal pyrite is formed in the deposit at the stage of the early diagenesis. Its formation is, however, possible also in the water column, as, for example, in the Black Sea, Framvaren Fjord (Norway) and Pettaquamscutt River estuary. Some authors believe that the formation of framboidal pyrite in the water column is confined to the oxic-anoxic interface, with a high supersaturation with respect to pyrite and a slight undersaturation with respect to the iron monosulfides (Wilkin and Barnes, 1997b). Also, it is interesting that the main factor controlling the pyrite formation in normal marine deposits is the presence of iron and organic substance, whereas in fresh-water deposits, it is the availability of the dissolved sulfate (Berner *et al.,* 1979; Skei, 1988). Cui *et. al.* (2018) based on textures and the new sulfur isotope results, proposed that the Datangpo superheavy pyrite formed via thermochemical sulfate reduction in hydrothermal fluids during late burial diagenesis and, therefore, lacks a biogeochemical connection to the Neoproterozoic sulfur cycle.

In this study, we intend to constrain the origin of pyrite of the Gombe hill to either biogenic or abiogenic using analytical techniques, such as Scanning Electron Microscopy and Energy Dispersive X-Ray Spectroscopy and stable sulfur isotopes studies. The stable isotope compositions are useful indicators of the pathways of both biogenic and abiogenic pyrite formation. Textural and compositional information preserved in sedimentary pyrite from sediment-hosted ore deposits has contributed to elucidate their environment of formation.

2. GEOLOGY OF THE GOMBE HILL

The studied samples were collected/sampled from the Gombe hill. The Gombe hill is an uplifted basement block, over which the Cretaceous sediments have been anticlinally folded with intensely fractured gneisses, biotite granite, and pegmatite at the core of the hill (Benkhelil, 1986). The uplifted block is seen to represent a restraining bond on the Gombe fault. The Cretaceous series of the Gombe hill comprises from the oldest, the Bima Formation, the Yolde Formation, the Pindiga Formation, and the Gombe Formation with a prominent NE-SW trending sinistrial strike slip fault.

The stratigraphic successions in the Gongola Basin which the Gombe hill is a part of have been exhaustively discussed by many authors amongst which are Carter *et al.* (1963); Zaborski *et al.* (1998); and Abubakar (2014).

The Gombe hill and adjacent area comprises rocks of Pan-African (600 ± 150 Ma) crystalline Basement and Cretaceous sediments (Fig. 1). The Bima which is highly variable is the most extensive sedimentary unit in the study area, and together with the Precambrian Basement rocks of the area, they host the pyrite mineralization.

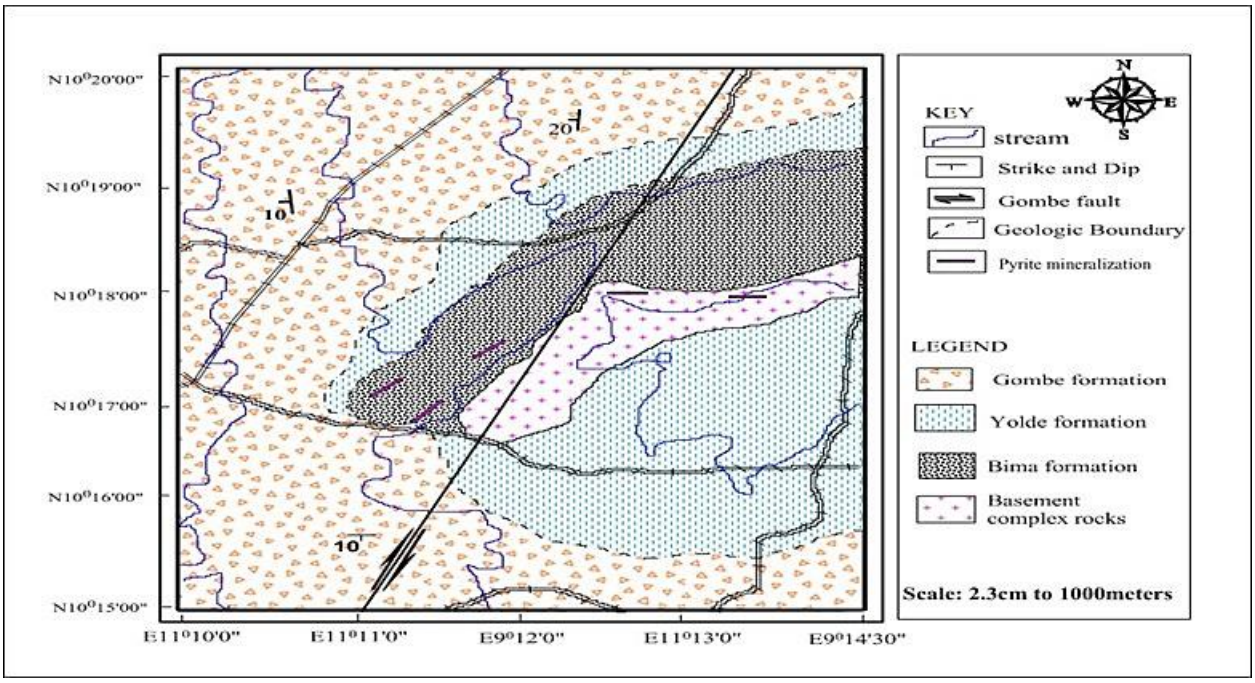

Figure 1: Geologic Map of the Study Area

3. METHOD OF STUDY

A combined Scanning Electron Microscopy and Energy Dispersive X-Ray Spectroscopy with stable sulfur isotope analysis were employed in this study. Results were compared with the work of Bata *et.al.* (2017).

3.1. Scanning Electron Microscopy and Energy Dispersive X-Ray Spectroscopy

Mineral textures, crystal habit, and morphology of the studied samples were examined using Philips XL30 Series Scanning Electron Microscope (SEM) with EDAX (EDS detector) at the Microscopy Laboratory, Department of Earth and Fundamental Geology, University of Silesia, Katowice, Poland. The samples were made into polished sections and later coated with carbon for the combined SEM-EDS analyses. The SEM-EDS equipment was set at 15.00 kV and 0.01–0.1 Na for image acquisition, and ~0.3Na for chemical analysis. The working distance is between 1 and 15 mm for optimal image quality and chemical analysis. SEM micrographs were

recorded digitally in both back-scattered electron and in secondary electron modes with their corresponding EDS spectral images.

3.2. Analytical methodology for isotopic analysis of sulfur using mass spectrometer

Sulfur isotopic analysis was conducted on five (5) samples of pyrite (sulphide) at the Queen's Facility for Isotope Research, Department of Geological Sciences, Miller Hall, Queen's University Kingston, Ontario, Canada. All results were calibrated to certified reference materials, reported in standard permil notation (‰) and relative to the following international standards of Vienna Canyon Diablo Troilite (VCDT) for $\delta^{34}S$. Precision, in permil notation (‰) is based upon duplicate sample analyses. Accuracy (std.dev.), reported in permil notation (‰), is based upon primary or secondary standard analyses 0.2‰ for $\delta^{34}S$.

Samples were weighed into tin capsules and the sulfur isotopic composition measured using a MAT 253 Stable Isotope Ratio Mass Spectrometer coupled to a Costech ECS 4010 Elemental Analyzer. $\delta^{34}S$ values were calculated by normalizing the $^{34}S/^{32}S$ ratios in the sample to that in the VCDT international standard, values are reported using the delta (δ) notation in units of permil (‰) and are reproducible to 0.2 permil.

4. RESULTS

The locations and geologic ages of the studied samples are presented in Table 1 and Figure 2. Backscattered SEM images of pyrite samples from the Huitrin Formation, Neuquen Basin in Argentina which is Aptian in age together with that of the offshore core samples of the Captain sands of Western Moray Frith Basin, United Kingdom with an Aptian age, the Valanginian (Lower Cretaceous) Wealden group of the Wessex Basin in Dorset, United Kingdom, the Turonian Afowo Formation in the Dahomey Basin of Nigeria, the Aptian Bima Formation of the Gongola Basin in northeast Nigeria and the Precambrian Basement rocks of the Gombe hill, Gongola Basin northeast Nigeria were all compared and studied. The result showed that in all SEM images (Figures 3 and 4), micrographs indicate either euhedral or framboids pyrites.

Their respective isotopes results (mean) in the order presented above are: −2.9‰ for Neuquen Basin, Argentina; 27.6‰ for the Captain sands of Western Moray Frith Basin, United Kingdom; −14.4‰ for the Wessex Basin in Dorset, United Kingdom; −9.6‰ for the Turonian Afowo Formation in the Dahomey Basin of Nigeria; 9.9‰ for the Aptian Bima Formation of the Gongola Basin in northeast Nigeria, and 17.5‰ for the Precambrian Basement rocks of the Gombe Inlier, Gongola Basin northeast Nigeria (Table 1).

Table 1. Details of locations, geologic ages and sulfur data of studied pyrite samples. (1,2,3, &4 After Bata 2016, Bata et al., 2017)

S. No	Country	Locality	Stratigraphic Name	Geologic age	Mean $\delta^{34}S$ (‰)
1.	Argentina	Neuquén Basin	Huitrin Formation	Aptian	−2.9‰
2.	United Kingdom (UK) Western Moray Frith Basin		Valhall Formation (Captain Sand)	Aptian	27.6‰
3.	United Kingdom (UK) Dorset UK, Wessex Basin		Wealden Group	Valanginian (Lower Cretaceous)	−14.4‰
4.	Nigeria	Dahomey Basin	Afowo Formation	Turonian	−9.6‰
5.	Nigeria	Gongola Basin	Bima Formation	Aptian	9.9‰
6.	Nigeria	Gongola Basin	Basement	Precambrian	17.5‰

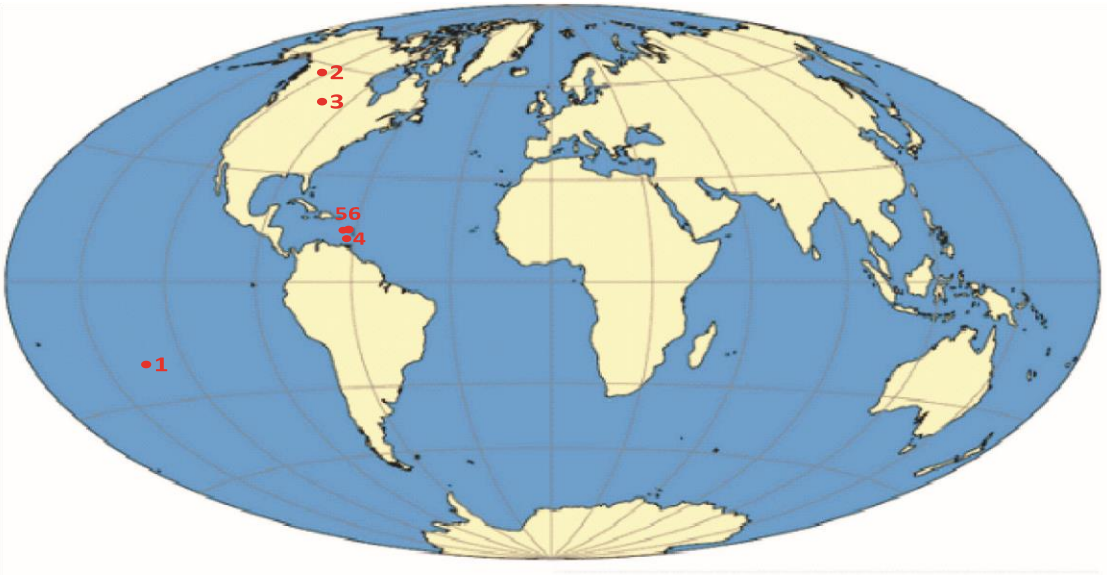

Figure 2. Present day paleogeographic map of the world showing approximate locations of the studied samples. Details of studied localities are presented in Table 1.

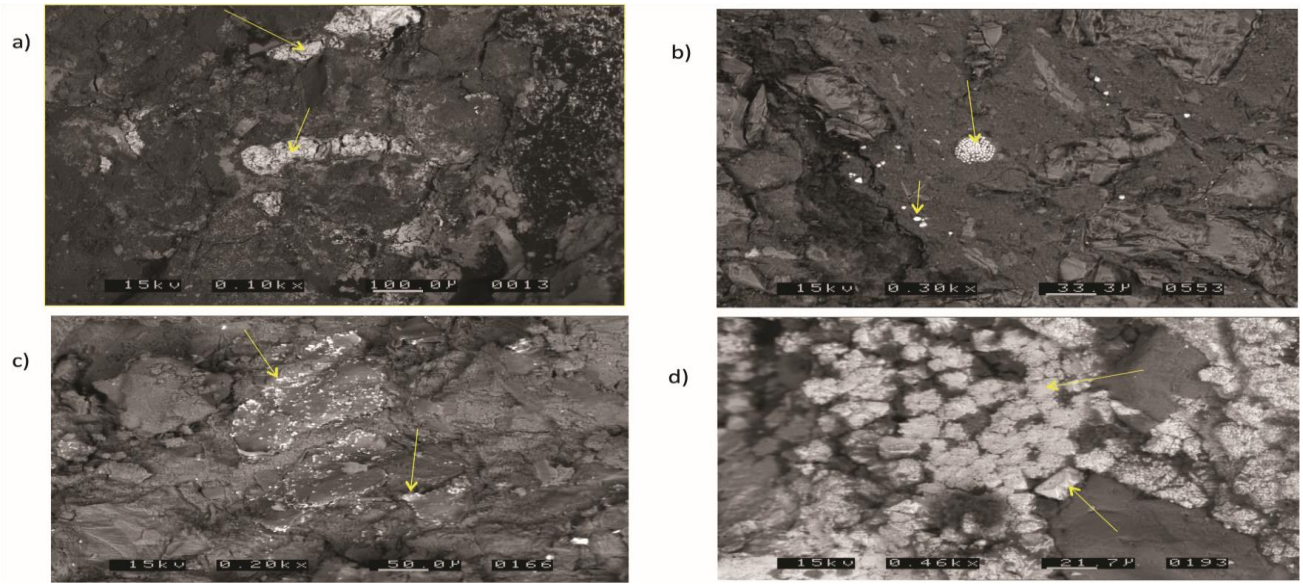

Figure 3. Backscattered SEM Images of (a) Euhedral pyrite (yellow arrow) from the Huitrin Formation Neuquén Basin, Argentina, (b) Framboidal pyrite (yellow arrow) from Dahomey Basin, Nigeria, (c) Euhedral pyrite (yellow arrow) from Valhall Formation (Captain Sand) Western Moray Frith Basin, UK, and (d) Euhedral pyrite (yellow arrow) from Wealden Group Wessex Basin, UK.

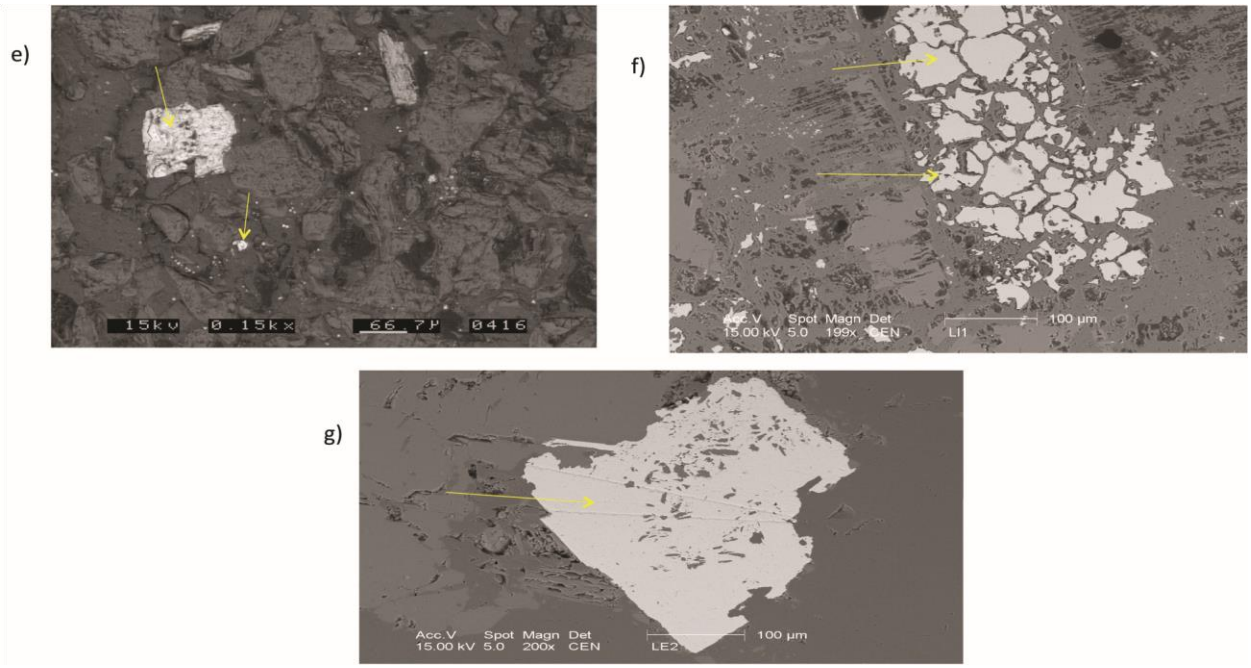

Figure 4: Backscattered SEM Images of (e) Framboidal Pyrite (yellow arrow), from Dahomey Basin, Nigeria, (f) Euhedral Pyrite from Bima Formation, Gongola Basin, Nigeria and (g) Euhedral Pyrite from Basement rocks Of Gongola Basin, Nigeria.

5. DISCUSSION

The massive concentrations and fracture fillings of samples of pyrite studied from the Gombe hill represents authigenic pyrites containing sulphur and iron (II) from both seawater sulphate and clay minerals. The isotopic compositions of sulphur measured ($\delta^{34}S$) gives an indication to its source (Spirakis and Heyl, 1995). Whether euhedral or framboidal, there is evidence that the samples studied could either have an origin that is biogenic or abiogenic from the plots (shaded portion) of compositions of values of $\delta^{34}S$ measured (Figure. 5). Figure 5 also depicts compositional value from other studies that plots exclusively on the biogenic and abiogenic origin. Joseph *et al.* (2007), gave values of sulfur compositions with an average of +10‰ of samples of same area (Gombe area), which also plots on the shaded (grey) portion of Figure 5, in the same manner as this study.

Open (sedimentary) system conditions are represented by negative $\delta^{34}S$ values with respect to sulphate reduction which takes place in low temperature shallow environment, while positive values may also imply a large extent of closed system (sedimentary) sulphate reduction (Spirakis and Heyl, 1995). The positive $\delta^{34}S$ values calculated in this study portrays a closed system sulphate reduction during the pyrite mineralization of the area. It has been noted that a wider $\delta^{34}S$ variation is akin to low temperature mineralization as compared to high temperature mineralization which has a narrower range of $\delta^{34}S$ (Hoefs, 1973). The wide variation in the $\delta^{34}S$ data (+9.9‰ to +17.5‰) obtained from this study might likely be suggesting that the mineralizing fluids were of relatively low temperature (60˚C–80˚C) at the time of precipitation. This temperature favors the survival of bacteria necessary for the reduction of sulphates (Rollinson, 1993) and by inference a biogenic origin for the pyrites studied.

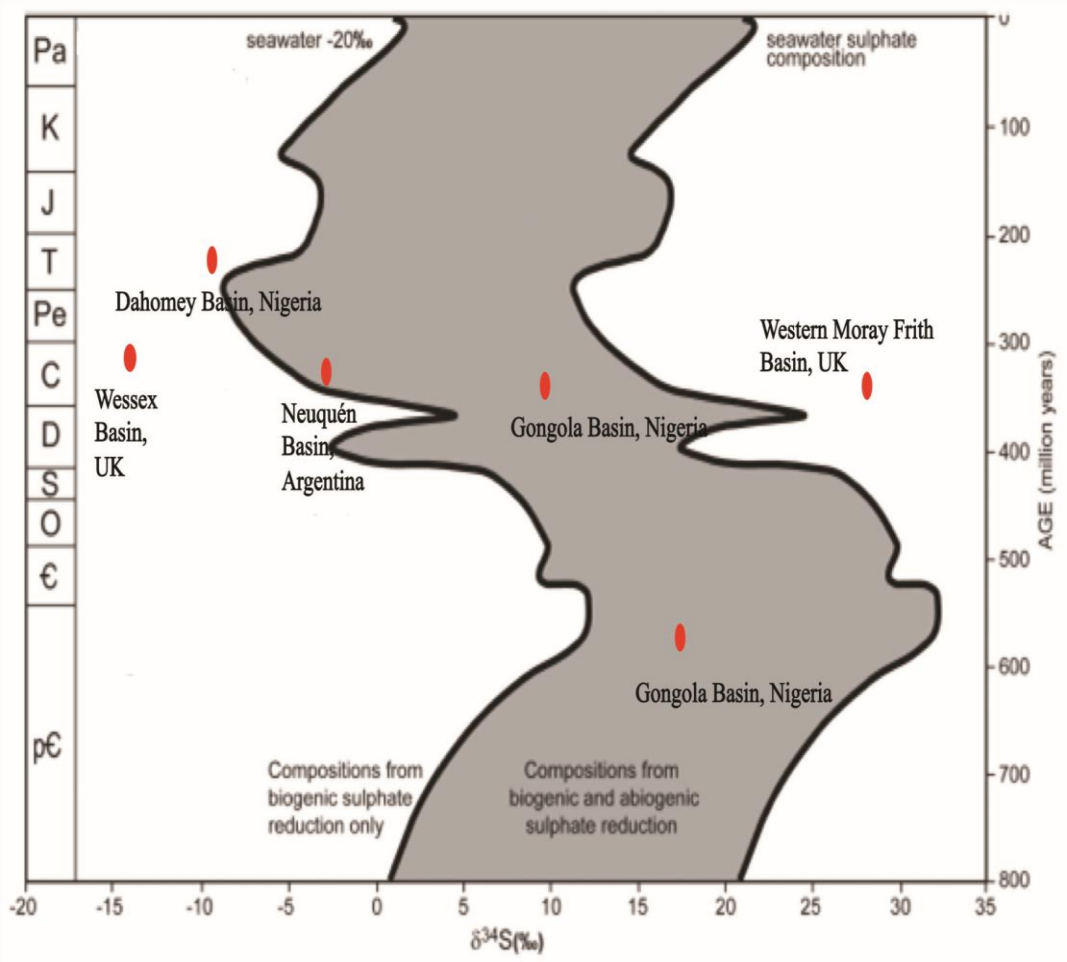

Figure 5. Mean Isotopic Compositions of Pyrite Sulphur in some parts of the Argentina, United Kingdom (UK) and Nigeria. Data is compared with seawater sulphate over last 800 million years, in some cases indicating microbially-induced isotopic fractionation and in others, possibly non-microbial isotopic fractionation. Shaded region indicates compositional field which could be explained by both biogenic and abiogenic sulphate reduction. Seawater composition from Claypool et al. (1980). (Modified from Bata, 2016).

Ohmoto and Rye (1979) identified three important sources of sulphur in mineral deposits as follows:

1.Deep seated sources (mantle and homogenized crust)

2. Local country rocks

3. Sea water or marine evaporites

They also pointed out that $\delta^{34}S$ values near 0‰ are considered to signatures of an igneous sulfur source whereas more positive values are likely to represent a sedimentary sulfur source. The positive $\delta^{34}S$ values of +9.9‰ to +17.5‰ obtained in this study makes a sedimentary sulphur source more likely, precluding the proximal Basement complex rocks (Pan-African) as possible sulfur sources. For the fact that there is paucity of marine sediments within the Bima Formations (but which was deposited under a fresh water condition) and for the range of $\delta^{34}S$ values obtained, the use of marine evaporites as possible sulphur source make it untenable for the Gombe hill mineralization and therefore, a fresh water continental source is hereby proposed (e.g., Rollinson, 1993).

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