

THE PALEOENVIRONMENTAL SIGNIFICANCE OF PYRITIC NODULES FROM LOKPANTA OIL SHALE INTERVAL IN THE PETROLEUM SYSTEM OF LOWER BENUE TROUGH, NIGERIA

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Abstract

Petrographic, Scan Electron Microscopy (SEM), X-Ray Diffraction (XRD), rare earth element (REE) and sulphur isotope ($\delta^{34}\text{S}$) studies were carried out on the pyritic nodules collected from the Lokpanta oil shale interval of the Lower Benue Trough, Nigeria. This is to ascertain the origin of the nodules and their implications in the hydrocarbon generation and accumulation in the region.

The mineralogical composition (from SEM and XRD) of the nodules indicates calcite, pyrite, barite and anhydrite as common minerals. The petrographic studies show that the pyrite is subhedral to euhedral in texture. Barite and anhydrites occur as pores, veins and cavity fillings and together with pyrite constituted the only sulphate minerals. Calcite is the only carbonate mineral and occurred as the matrix. The sulphur $\delta^{34}\text{S}$ values range from +0.9 to +1.6‰ with an average of +1.6‰ which correspond to authigenic pyrite. The REEs result show high enrichment of LREEs relative to HREEs suggesting seawater source while the positive europium (>1) anomaly values indicate anoxic event, and reducing diagenetic conditions in a significantly high temperature.

Although, the Lokpanta oil shale interval is deposited under an Oceanic Anoxic Event (OAE) and is capable of generating hydrocarbon in the study area, the authigenic nature and euhedral texture of the pyrite grains suggest metamorphic or thermal alteration for the formation of the nodules. Moreover, the volcanic intrusions and hydrothermal activities within the study area could also enhance the formation of the pyritic nodules. The generation and accumulation of hydrocarbon in the Lower Benue Trough could further be investigated using heat flow model.

Keywords: Oil shale; anoxic event; calcite; pyritic nodules; palaeoenvironment.

1. Introduction

Pyrite concretions are one of the two significant sulphide in iron-rich sedimentary rocks, the other been marcasite which is associated with coal while pyrites are associated with black shale. Pyrite concretions occur as minor constituent of most rocks [4] and are typically abundant in rocks that are rich in organic matter such as black shale, oil shale and coals [35]. The chemical action subsequent to sedimentation is responsible for various sedimentary structures. Pyrite concretions are believed to have been formed by precipitation or segregation of mineral matter [5].

England et al. [17] studied the petrographic and sulphur isotopes signatures in the rounded pyrite nodules from the siliciclastics sequence of Witerwatersand Basin in South Africa. The large range in textures and the source-rock Lithology gave rise to the sedimentary-hosted diagenetic pyrite, volcanic-hosted massive sulphide and hydrothermal pyrite. The euhedral pyrite and pyrite overgrowth were undoubtedly authigenic and had restricted $\delta^{34}\text{S}$ value (-0.5 to +2.5 ‰), which are chemically different from rounded pyrite and probably the products of metamorphism or hydrothermal alteration. However, the rounded grains of detrital pyrite

were concluded to show a strong indicator of an oxygen poor atmosphere and hydrothermal mineralization.

Keith and Degens [21] studied the contents of Ni, Co, As, Ag, Pb, Mn, Cu and Ti in pyrite from marine and freshwater shales. Variability in both environments was shown to be high and the only clear distinction between the two types was the relatively large concentration of As, Ag and Cu in the freshwater pyrites. Mitchell [25] differentiated magmatic/hydrothermal pyrite on the basis of the high levels of Ag, Sn and Te and the low levels of T, V and Mo in the former. Similarly the marine samples contained more Ti, Cr, Co, Ni, Cu, Zn, and Se than the freshwater samples [45]. The concentration of Y, Ba, La and Ce determined in the samples indicated that contamination remained in spite of extensive purification. The impurities were a feature of the marine pyrite and were attributed to sediment incorporated during growth of the pyrite.

Element ratios such as Co/Ni and Se/S have been used for distinguishing several ore forming environments instead of abundances [9,16,23]. However, both criteria appear to have limitations in characterizing syngenetic sedimentary pyrites. Co/Ni ratio of less than unity are believed to indicate a sedimentary origin, i.e. Co of $<10\text{‰}$ and Ni of $<50\text{‰}$ [23]. The characterization of sedimentary pyrite by Se/S ratio $<10^{-6}$ may also be of limited application since pyrite in black shales may contain 100‰ or even 1000‰ Se, giving Se/S $>10^{-5}$, which indicates that the ratios may be affected by gross variation in host rock composition.

Raiswell and Plant [36] investigated trace element incorporation into pyrite during diagenesis of black shales of Yorkshire, England, and deduced that trace element content of marine biogenic Jet Rock pyrite is extremely low. Only a few of the elements such as Cu, As, Mo, Ni, Zn, and Co had been shown to occur in the sulfide phase of concentrations in excess of ‰ . Mo and As are few, and Cu appeared to be the only element enriched in the pyrite relative to the host sediment while two textural forms were identified as the early framboidal form which grew uniformly throughout the sediments and acted as nuclei for euhedral at the site of concretionary growth.

Previous studies in the Lower Benue Trough had not specifically focused on the pyrite concretionary bodies found in several localities. This study therefore is focused on the palaeo-environmental significance of the pyrite concretion in the petroleum system of the Lower Benue Trough, using petrography, inorganic geochemical technique and sulphur isotopic signature. The aim of this paper is to determine whether the concretions were formed under an anoxic oxygen event (AOE) or hydrothermal alteration due to volcanic activities. This is to ascertain the origin of the nodules and their implications in the hydrocarbon generation and accumulation in the lower Benue Trough.

2. Geological Setting

The Benue trough has been described as a rift bounded tension structure produced as the south America and Africa drifted apart (triple rift system known as an aulacogen) and have been documented by some workers [3,19,20,26,29,31,42]. The Benue Trough was subjected to four main depositional cycles, each of which was associated with transgression and regression of the sea [37].

The stratigraphic succession of the lower Benue Trough comprises of the Asu River group representing the first and the oldest cycles of the shallow marine to brackish water sediment, which were deposited in Albian and end around the Cenomanian (Fig. 1). These sediments were deposited on the Basement Complex and consist of roughly 2000m of poorly bedded shales (Abakaliki Shales), siltstone and limestone, and mudstone [1]. The presence of Cenomanian sediments and Santonian intrusions of dykes and sill extrusions that possess important mineralization zones along the gently folded axis of the Abakaliki anticline had been reported [7,3,30,46].

The Eze-Aku Formation overlies the Asu River group and consists of black calcareous shales, shelly limestone, siltstone and sandstone, which were deposited as a result of renewed transgression in the depositional cycle of the Benue Trough [34,39]. This formation attained a thickness of 1000m in some places, representing shallow water deposit [39]. The Awgu Formation consists mainly of shale and limestone indicating a marine influence [30]. Further lithostratigraphic synthesis has shown a lower shale unit of Awgu shale and an upper sandstone unit of Agbani sandstone [1]. The rapid sandstones were interpreted as being the first indication

of the onset of active tectonic phase of faulting, folding and uplift of the Abakaliki anticlinorium which later led to the termination of this depositional cycle.

This study centers on the Cenomanian to Turonian interval corresponding to the Eze-Aku Formation, which host the concretionary bodies. The detailed geology and information on the raw oil shale are already published [10,11,12,13,14,].

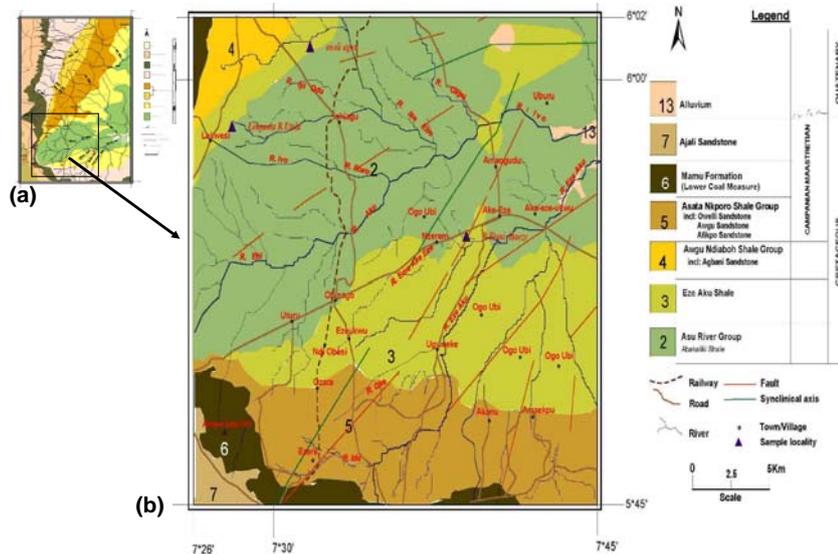


Fig.1: Geological map of the Lower Benue Trough (a) and the sampling locality of nodules (b)

3. Sample Material and Methods

The methods employed in this study are divided into two parts; fieldwork and laboratory analyses. The fieldwork involved the determination and location of samples. The materials employed for the field work include Global positioning system (GPS), compass clinometer, measuring tapes, chisel, sledge hammer, sample bags, field notebook, digital Sony cyber-shot camera, pens, pencil, topographic and geological maps.

The lithologic sections of each location were drawn to scale. The samples were photographed, collected and stored in labeled sample bags. A total of 24 samples were collected from three different stations namely: Aka-Eze, Onoli-Awgu and Lokpanta towns. The pyrite concretions were embedded along the bedding plane and are found within fissile black shales (Fig. 2a-b). Some appear to have displaced the host shale and no fossil imprint and striation were observed on the nodules.

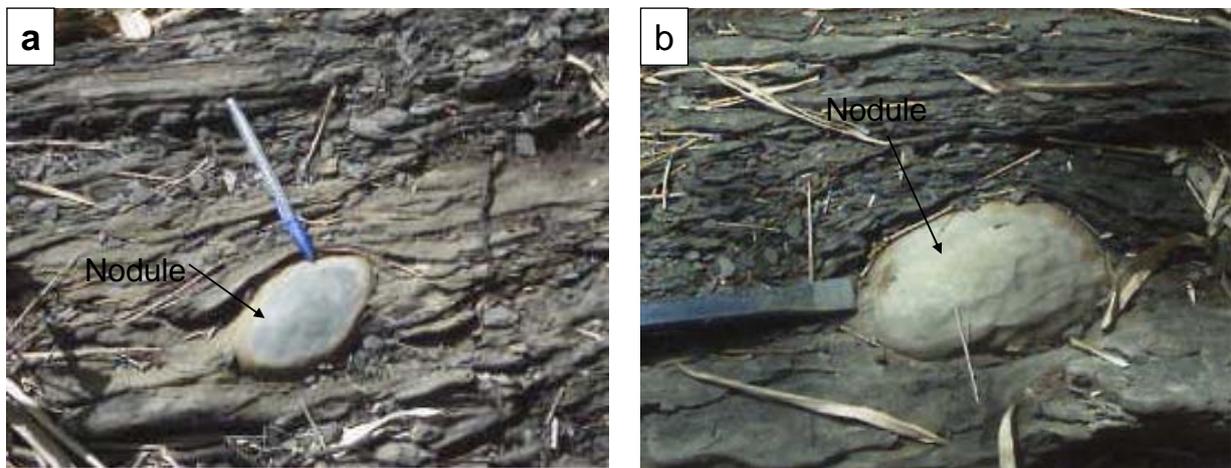


Fig. 2: Pyritic nodules associated with highly laminated dark grey shale (a) and mode of emplacement of nodule (b)

The laboratory analyzes involved petrographic analyses which were complimented with Scanning electron microscope analysis and X-ray diffraction analysis. The geochemical analysis involved rare earth element determination using Inductively Couple Plasma-Mass Spectrometer (ICP-MS) and the sulphur isotopes composition. The pyrite concretion samples were mechanically separated into 3 parts, which include the central (nucleus) where the pyrite was suited, the body matrix which seem to be part of the host shale sediments and the rim of the concretions (Fig.3a-c). The sulphur isotope analysis was conducted on the central (nucleus) while the ICP-MS was conducted on both the nucleus and the body matrix.

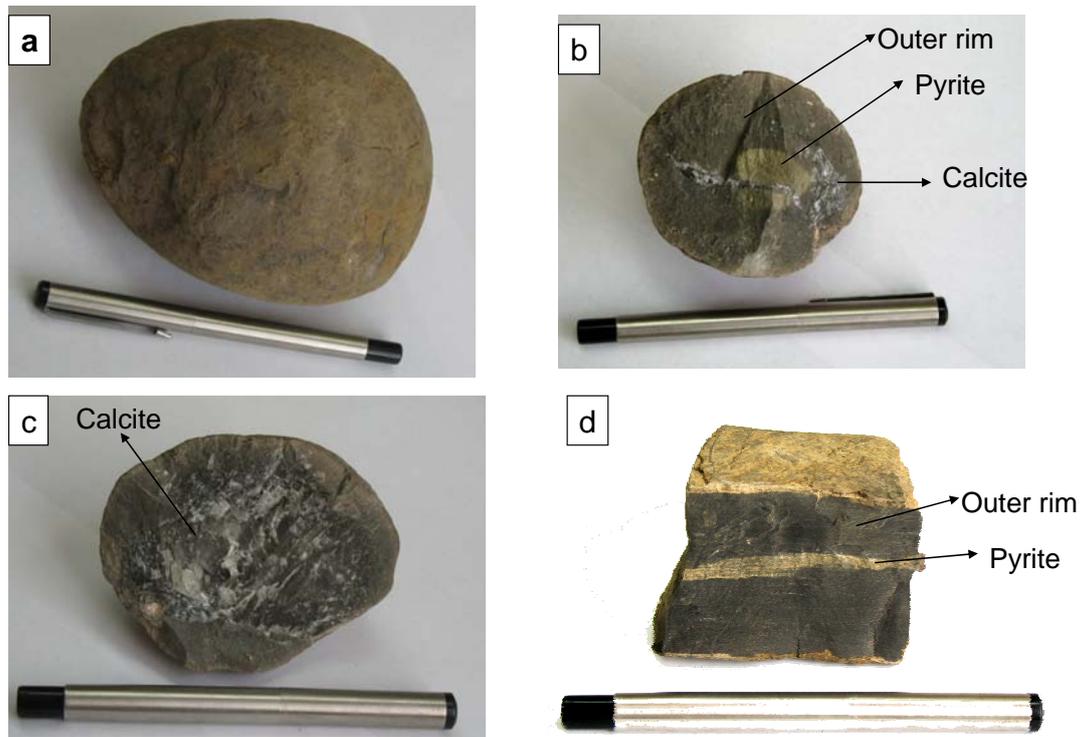


Fig. 3: Morphology of the Pyritic nodule (a), and Illustration of the internal structure of the pyritic nodule (b, c and d) The pen is 10.5 cm long

3.1 Scan electron microscope (SEM) analysis

The scan electron microscope (SEM) analysis on the samples was carried out using VEGA TESCAN Digital Microscopy with INCA Analyzer (Emission Scanning Microscope). The coated sample is placed in the sample chamber in the electron optics column and evacuated to high vacuum approximately 2×10^{-6} (torr). Instead of using light, as in the petrographic microscope, the SEM image is formed by an internally generated electron beam. The beam is produced by heating a "hairpin" tungsten filament in the electron gun until the filament emits electrons. The electrons are accelerated through the column by a 5-to30-KV accelerating voltage, demagnified and focused through a series of lenses into a finely focused beam, which bombards the sample. The beam used a diameter of 100 angstroms. The interaction of the primary electrons beams with the sample produces a radiation such as secondary electrons, characteristic x-rays, auger electrons, backscatter electrons and "bremsstrahlung" (continuous or background) X-rays. The SEM analysis was carried out at the Research Institute of Petroleum and Development, (RIPED), Beijing China.

3.2 X-ray diffraction analysis

X-ray powder diffraction was used to establish the mineralogy of the samples, both the pyrite nucleus and the matrix of the nodules. The XRD analysis was conducted on crystalline component of each material using automated X'Pert Pro Panalytical X-ray diffraction (XRD) model. Each sample was placed into the sample holder, with two slits of $1/2^\circ$ and 1° selected for the incident beam path and 5.0 mm slit for the diffractive path. The random powder

mounts are analyzed over an angular range of 5 to 90° 2 theta at a rate of 1° per minute using a sample spinner to reduce the effect of preferred orientation.

3.3 Inductively coupled plasma-mass spectrometer (ICP-MS) analysis

The inductively coupled plasma-mass spectrometer analytical technique was used to determine the elemental composition of the pyritic concretions especially the Rare Earth Elements (REEs). The REEs are uniquely suited to study a variety of geological processes. The distinctive chemistry of the REEs across the series from La to Lu has been applied to sediment provenance [24,43]. The REEs concentrations were normalized with normalization values of shale from the Upper continental crust (UCC). The ICP-MS analysis was carried out at the Actlabs Laboratory, Canada.

The ICP-MS analysis was conducted on 15 samples. The pyrite concretion samples were mechanically separated into 3 parts, which include the central (nucleus) where the pyrite was suited, the body which seem to be part of the host shale sediments and the rim of the nodules. However, only the body and the rim were analyzed with this technique.

3.4 Sulphur isotope analysis

The determination of sulphur isotope was carried out using elemental analysis isotope ratio mass spectrometry (EA-IRMS). The technique involves initially converting the bulk pyrite portion to pure SO₂. The samples are placed in clean tin capsules and loaded into an automatic sampler. The tin capsules are flash-combusted raising their temperature in the region of the sample to approximately 1700°C. The combustion gases are then swept in a helium stream over combustion catalyst (Tungsten Oxide/Zirconium Oxide). Water is removed by a Nafion membrane, and sulphur dioxide is separated by packed column gas chromatograph held at an isothermal temperature. The resultant chromatograph peak enters the ion source of the IRMS where it is ionized and accelerated. Gas species of different mass are separated in the magnetic field and then simultaneously measured on a Faraday cup universal collector array.

4. Results and Interpretation

4.1 Mineralogy and petrography

The major authigenic minerals in the concretions are pyrite and calcite which constitute more than 70% by weight, accompanied by anhydrite and barite of approximately 21% (Table1). The x-ray diffractogram showing the peaks of identified minerals from the Aka-Eze, Onoli Awgu and Lokpanta towns is shown in Figure 4.

Table 1: Average mineral composition of the nodules collected from study locations

Composition	Calcite	Pyrite	Barite	Anhydrite	Total
Nodule 1					
Aka-Eze Town	24.61	53.20	17.76	4.49	100.0
Nodule 2					
Onoli Awgu Town	60.63	39.37	-	-	100.0
Nodule 3					
Lokpanta Town	44.58	39.79	8.74	6.89	100.0

The polished thin sections showed that pyrite, barite and anhydrite were the sulphate minerals while calcite was the carbonate mineral. The pyrite concretions showed abundant cluster aggregate of pyrite (Fig 5a – black in colour). The calcite mineral formed the matrix of the pyrite nodule and it was observed as light brown to dark brown patches (Figs. 5a and 5b). The anhydrite is seen as a group of microgranular and prismatic-aligned fiber with thick tubular habit (Fig. 5b). The pink coloration is characteristic of anhydrite. Barite which is typically known to occur in veins and cavity filling are also observed as been precipitating in microveins (Figs. 5c and 5d).

The SEM result indicates euhedral to subhedral granular texture (Figs. 6a, b, c and d). The euhedral texture mostly show sections of cubes pyrite grains which appears as framboid

texture (Figs. 6a and 6b). The pyrite grains were either sandwiched with, occurring as pores or having contact with calcite (Fig. 6c). Barite was observed as vein filling (Fig. 6d).

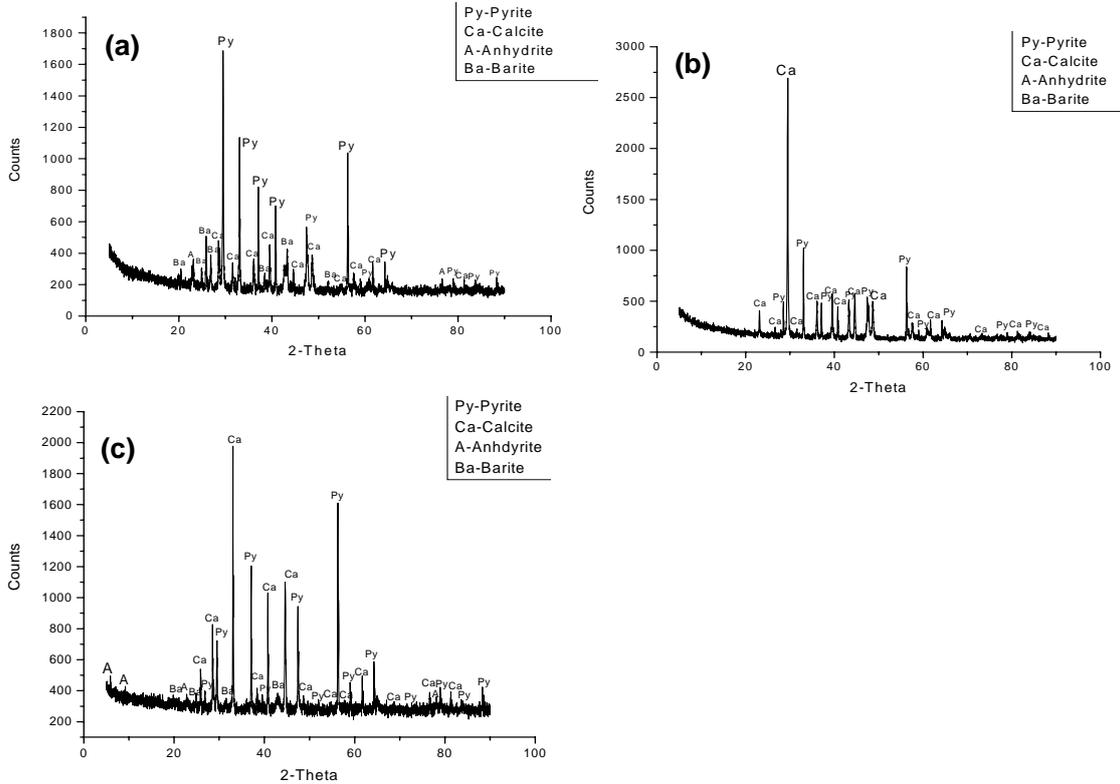


Fig. 4: X-ray diffractogram of nodule sample from Aka-Eze (a), Onoli Awgu (b) and Lokpanta (c) towns.

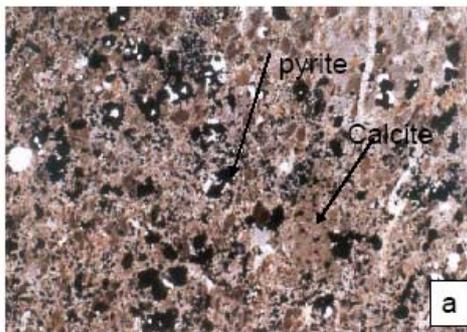


Fig: 5a. Polished thin section photomicrograph showing scattered aggregates of pyrite (black.), calcite (brown), anhydrite (white/pink), barite (white in veins). (x 40)



Fig: 5b. Polished thin section showing anhydrite as microgranular and prismatic-aligned fibre (x 40)

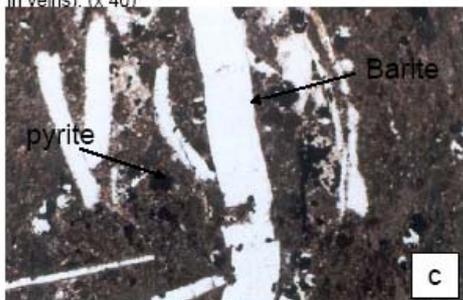


Fig: 5c. Polished thin section photomicrograph of barite in veins and cavity filling are observed precipitating in microveins (x 40)

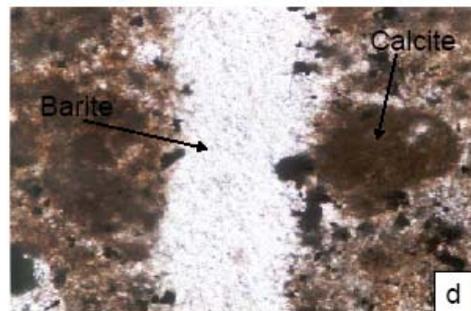


Fig.5d: Polished section showing barite vein (x 40)

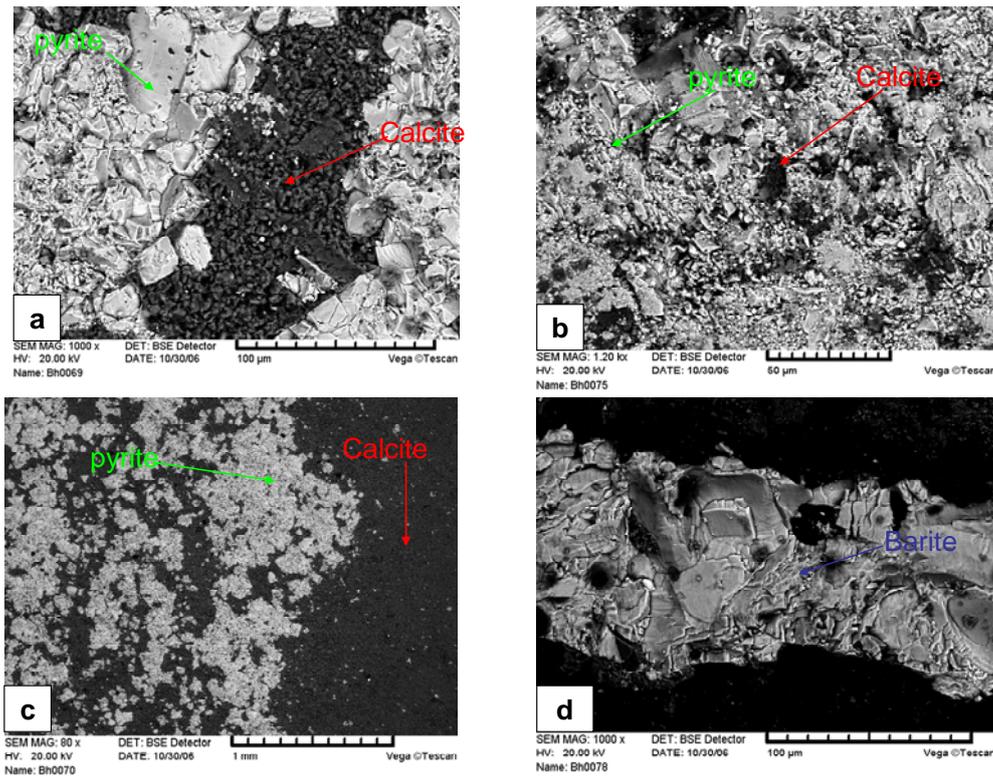


Fig. 6: SEM showing Pyrite grains (a), calcite (b), anhydrite (c) and barite vein (d)

4.2 Sulphur Isotope Geochemistry

The results show a relatively narrow range of $\delta^{34}\text{S}$ values between +0.9‰ and +1.6‰ (average of +1.6‰) and a sulphur percentage range of between 33 and 46% (Table 2). These data reflects a homogeneous sulphur isotope composition and this value corresponds to sulphur derived from metamorphic rocks [22,32,33,40].

Raiswell [36] stated that subhedral to euhedral texture is often associated with heavy $\delta^{34}\text{S}$ isotope value while framboid texture is associated with light $\delta^{34}\text{S}$ isotope value. Similarly, euhedral texture occurs with pyrite formed in a closed system while framboid occurs with pyrite formed in an open system. However, the $\delta^{34}\text{S}$ isotope values are positive indicating a relatively high value, thus suggesting a closed system.

Table 2: Sulphur isotope analysis results of the nodule samples, ISO method

Analyte symbol	Approximate% sulphur	$\delta^{34}\text{S}$ (CDT) ‰
Location 1 Aka-Eze		
NPS1	44	1.3
NPS2	43	1.4
NPS3	42	0.9
NPS4	45	1.4
NPS5	46	1.1
Location 2 Onoli Awgu		
NPS6	35	1.4
NPS7	34	1.5
NPS8	33	1.6
NPS9	36	1.3
NPS10	36	1.2
Location 3 Lokpanta		
NPS11	39	1.2
NPS12	38	1.3
NPS13	37	1.4
NPS14	40	1.1
NPS15	41	1.0

4.3 Inductively coupled plasma-mass spectrometer (ICP-MS)

The REE concentration values are presented in Table 3. From the ICP-MS data, the REEs concentration values were normalized with Upper Continental Crust values and plotted against atomic number REEs on a bivariate plot (Figs. 7a, b, c, d, e, f, g, h, and i). The bivariate plots revealed patterns that indicated enrichment in light REEs (LREEs) relative to the heavy REEs (HREEs) which is an inverse of pattern associated with seawater and typical with iron-rich nodules deposited from seawater [15]. The cerium and europium anomalies are basically used to determine the paleo-diagenetic or post deposition events. Here, positive europium anomaly (>1) is common with virtually all the nodules sampled which suggest anoxic event, reducing condition in a significantly high temperature.

Table 3 REE concentration values

Sample	Li ppm	Be ppm	B ppm	Na ppm	Mg ppm	Al ppm	P ppm
Detection Limit (DL)	0.3	0.1	2	0.5	2	0.2	5
LOC-12	17.0	3.2	4	1465	5542	6096	566
LOC-13	14.5	1.5	<DL	15136	2904	32967	1494
LOC-22	64.0	2.3	13	783	992	70855	420
LOC-23	4.7	0.3	4	201	2219	2021	325
LOC-32	69.1	2.4	13	928	1116	78538	439
LOC-33	10.4	1.4	10	14238	2087	29654	1441

K ppm	Ca ppm	Ti ppm	V ppm	Cr ppm	Mn ppm	Fe ppm	Co ppm	Ni ppm
6	31	0.09	0.05	0.05	0.03	3.7	0.03	0.06
1196	165780	561	179	28.5	348	73105	13.2	39.5
13646	16616	8031	164	81.3	739	46356	22.8	36.0
8332	2592	7865	101	83.1	163	23313	12.5	21.7
990	77060	463	161	14.4	183	16557	5.78	30.4
9073	2802	8276	106	88.9	179	25037	13.3	23.3
13393	15765	7704	157	81.0	820	45325	21.4	34.1

Cu ppm	Zn ppm	Ga ppm	Ge ppm	As ppm	Se ppm	Rb ppm	Sr ppm	Y ppm
0.03	0.08	0.01	0.02	0.06	0.2	0.04	0.03	0.02
19.7	409	3.24	0.52	24.7	15.9	17.1	195	0.45
26.2	69.4	19.4	1.20	0.65	0.3	7.84	323	4.07
67.0	88.3	22.6	1.51	3.48	1.9	43.9	77.1	23.2
12.9	23.2	1.49	0.22	11.8	4.8	9.39	214	0.05
37.0	89.0	23.9	1.57	3.54	1.9	44.2	84.6	24.3

Zr ppm	Nb ppm	Mo ppm	Ru ppm	Pd ppm	Ag ppm	Cd ppm	Sn ppm	Sb ppm
0.09	0.04	0.08	0.01	0.01	0.01	0.06	0.06	0.1
1.45	2.68	24.5	0.07	0.05	0.08	7.93	15.6	34.9
11.3	14.2	1.44	<DL	0.32	0.24	0.08	7.76	0.1
170	38.9	2.45	<DL	4.17	0.70	0.22	20.1	0.4
0.23	1.90	25.8	0.09	<DL	0.05	0.16	11.8	4.6
174	40.6	2.66	<DL	4.17	0.73	0.21	20.4	0.5
11.1	13.4	1.30	0.02	0.30	0.23	0.06	9.78	0.1

Cs ppm	Ba ppm	La ppm	Ce ppm	Pr ppm	Nd ppm	Sm ppm	Eu ppm	Gd ppm
0.02	0.03	0.03	0.03	0.004	0.03	0.04	0.03	0.03
1.86	102	2.15	3.65	0.466	1.85	0.31	0.08	0.26
0.06	285	9.32	23.4	2.91	11.7	2.24	0.64	1.68
2.46	380	76.8	164	18.5	67.0	10.8	1.93	7.11
0.52	25.0	0.44	0.69	0.095	0.37	0.05	<DL	0.04
2.48	447	78.0	171	19.4	70.8	11.5	2.10	7.72
0.05	316	8.43	22.8	2.72	10.9	2.10	0.63	1.59
Tb ppm	Dy ppm	Ho ppm	Er ppm	Tm ppm	Yb ppm	Lu ppm	Hf ppm	Ta ppm
0.03	0.04	0.02	0.04	0.006	0.05	0.04	0.05	0.02
0.03	0.28	0.06	0.18	0.023	0.13	<DL	0.09	5.10
0.20	1.45	0.26	0.69	0.094	0.55	0.07	0.78	1.07
0.81	6.14	1.07	2.82	0.405	2.56	0.36	6.21	3.27
<DL	0.36							
0.88	6.65	1.16	3.03	0.436	2.76	0.39	6.43	3.74
W ppm	Re ppm	Os ppm	Pt ppm	Au ppm	Tl ppm	Pb ppm	Th ppm	U ppm
0.08	0.01	0.08	0.01	0.01	0.05	0.03	0.01	0.03
0.76	<DL	<DL	<DL	0.25	0.52	24.4	<DL	1.25
0.66	<DL	<DL	0.02	0.06	0.42	14.6	0.84	1.57
3.92	<DL	<DL	0.06	0.14	1.65	57.1	28.7	7.88
0.57	<DL	<DL	0.01	0.03	0.81	4.45	<DL	1.38
4.07	<DL	<DL	0.07	0.15	1.84	68.0	28.9	8.22

Both Eu (europium) and Ce (cerium) exhibit redox behaviour dependent on the oxidation and reduction state of the fluid medium. Unlike the other REEs, Ce and Eu may exist in valence state other than +3, and the presence of reduced or oxidized forms of these two elements can be used to describe paleo-depositional and diagenetic conditions. Cerium (Ce) is used to describe low temperature system while europium (Eu) is used to describe oxygen depletion conditions in high temperature, high pressure system [27]. Evidence has indicated that the REEs occur in trivalent state in low temperature aqueous systems with the exception of Ce, which may be oxidized to Ce⁺⁴ and be subsequently removed by co-precipitation with Fe/Mn oxyhydroxide or by precipitation of CeO₂. Thus, if Ce⁺³ predominate, there should be no Ce anomaly observed in the REE plot. Therefore, according to the REE plot, Ce⁺⁴ must have dominated at Onoli Awgu (Fig. 7d, e, and f) town because Ce showed slightly negative anomalies (slightly oxidizing). A positive anomaly does not necessarily indicate a reducing system but may suggest reductive dissolution of mineral containing relatively more Ce than would be expected compared to La and Pr (Murthy et al., 2004). The enrichment or depletion in Ce is relative to La and Pr. This is expressed as the Ce anomaly and is quantified as

$$Ce/Ce^* = Ce / [(La_N) * (Pr_N)]^{0.5} \quad (1)$$

where N represents the normalized values, while Ce and Ce* represent Ce⁺³ and Ce⁺⁴ respectively.

Samples with Ce/Ce* values greater than 1 are considered to have positive cerium anomaly and suggest deposition under low oxygen conditions or the reduction dissolution of Ce-bearing phases and samples with less than 1 are said to have a negative cerium anomaly (deposition under oxidizing conditions). Likewise, Eu europium exhibits redox behaviour where the soluble Eu⁺³ can be reduced to soluble Eu⁺² under extremely reducing conditions. The Eu anomaly is calculated as

$$Eu/Eu^* = Eu_N / [(Sm_N) * (Gd_N)]^{0.5} \quad (2)$$

Eu/Eu* values that are greater than 1 are indicative of reducing conditions (Eu⁺² is more abundant than Eu⁺³). This positive anomaly is generally associated with the presence of calcium bearing minerals where Eu⁺² are substituted for Ca⁺² in the mineral matrix under low oxygen depletion conditions. Eu⁺² are not known to occur in low temperature environment which is probably why most of the values in Table 3 are > 1 (Fig. 7). Thus, suggesting a reducing system with slightly elevated temperature and an anoxic event [41]. A negative Eu/Eu* value of less than 1 may indicate the preferential loss of calcium bearing minerals during weathering and deposition of the provenance of sediments under investigation.

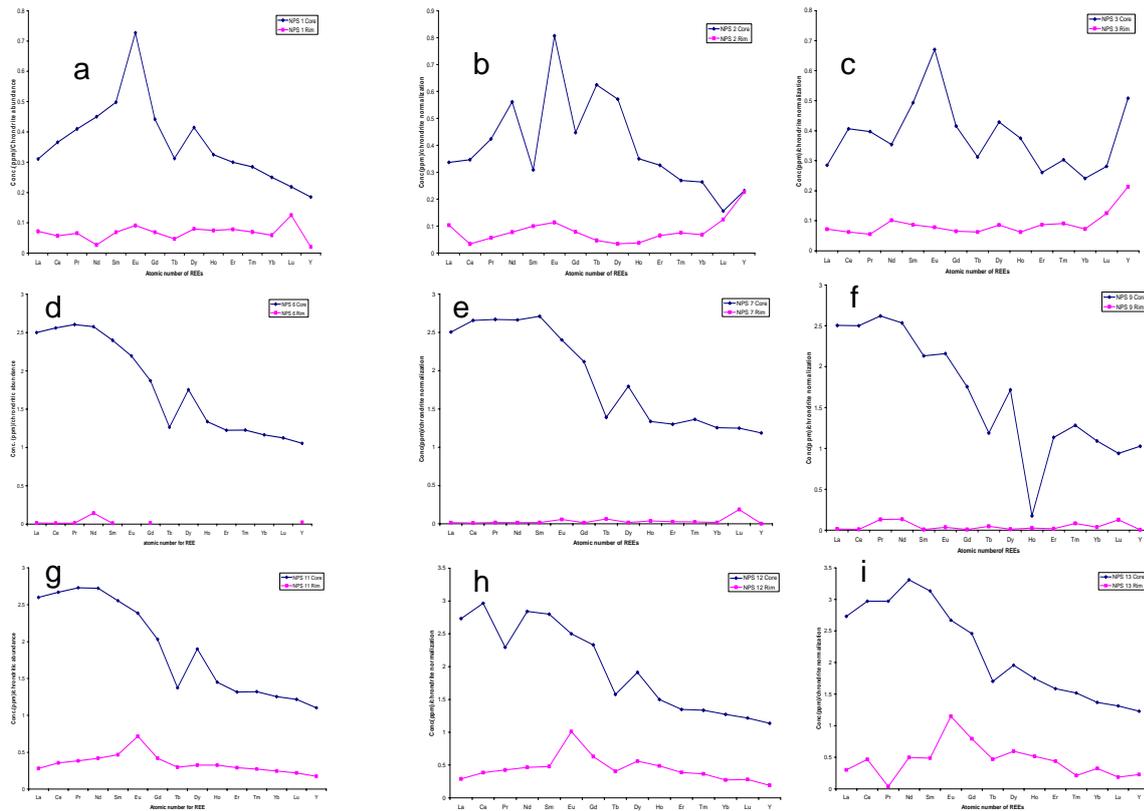


Fig. 7: Plots of upper continental crust-normalized pattern for the pyritic nodules from Aka-Eze (a-c), Onoli-Awgu (d-f) and Lokpanta (g-i)

4.4 Implications on the Petroleum system of Lower Benue Trough

The Benue Trough is characterized by extensive magmatic activities as evidence by the widespread occurrence of intrusive and extrusive rocks [29]. These rocks influence several events in the trough. Basaltic occurrences have been mapped in some areas within the trough such as Awe, Arufu and south of Markurdi [29]. The areas of occurrence of these basaltic rocks are known to coincide with zones of mineralization which characterize the trough. These include: Lead-Zinc, barite, salt and fluorite mineralization [18]. Mineralization in the trough is associated with steeply dipping faults and fracture systems in the basin. The basaltic rocks are believed to be the source of sulphur [8].

The igneous and volcanic activities in the trough provided the heat source for transportation of hydrothermal solution (seawater) that leached basaltic rocks [29]. Here, the leachate composed of minerals such as the calcite, barite, anhydrite and pyrite in elemental form led to the formation of the pyritic nodules. It is believed that the calcite was derived from the leaching of limestone present in the Eze-Aku Formation [28]. The barite was derived from the mineralization as a result of tectonic event in the basin. The presence of calcium and

sulphate at high temperature led to the precipitation of anhydrite [6]. The occurrence of pyrite under this circumstance is due to inorganic reduction of sulphate to sulphide at temperature of 75-175°C and this would have implications on hydrocarbon accumulation [44].

Previous studies of the Lower Benue Trough, together with the present study, show that the depositional model postulated by Khunt et al [47], Akande and Erdtmann, [2] and Ojoh [30] can be maintained and enlarged (Fig. 8). From the data now available, it seems reasonable to assume that the nodules are formed by hydrothermal alteration and oxygen deficiency. The oil shale interval must have experience enormous heat and would have contributed to generation of gaseous hydrocarbon noted in the area.

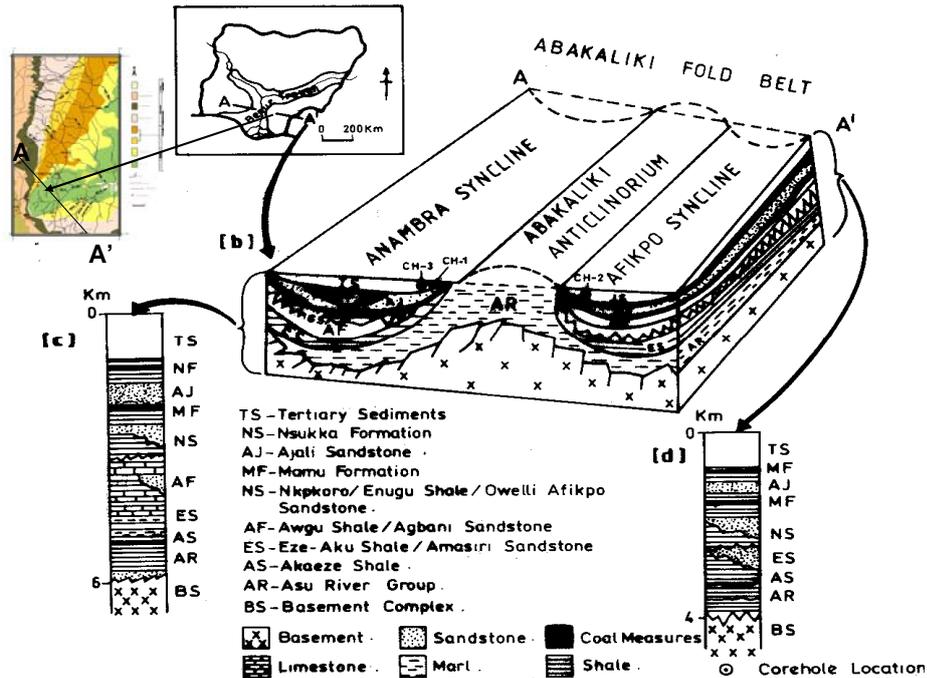


Fig. 8 Depositional model of Abakaliki fold belt (Modified from [2,30,47])

5. Conclusion

The pyritic concretions from Eze-Aku shale Formation have revealed four types of authigenic minerals from the petrography and XRD studies which include; pyrite (sulphide), barite and anhydrite (sulphates) and calcite (carbonate). The sulphur isotope ($d^{34}\text{S}$) average value of +1.6‰ have shown to be from basaltic rocks associated with mid oceanic ridge sediments, thus a marine source. Basalts are known to have narrow $d^{34}\text{S}$ average value of +1.0‰. The REES patterns indicated the source fluid as seawater with enrichment of LREEs relative to the HREEs, which is typical of ferromanganese nodules derived from sediments deposited by seawater. The positive europium anomalies suggest a reducing condition and hydrothermal activities and the slightly negative cerium anomalies suggest a possible oxidizing condition. However, the overall values suggest an anoxic event. Palaeoenvironmentally, about 95 to 90 millions years ago, there was an "Oceanic Anoxic Event" (OAE) that was experienced in the Atlantic and around the world particularly during the Cenomanian-Turonian age. This event must have played an important role in the formation of the pyritic concretion. The seawater must have carried basaltic sediments rich in organic matter from the Atlantic and deposited it in the basin. Subsequent mineral segregation could also led to the formation of the pyrite nodules.

A comprehensive microprobe analysis should be carried out on the nodules to find out the mineral(s) that can caused the various enrichment and depletion observed with some particular rare earth elements in the normalization patterns and the textural attributes. Likewise the temperature of the system should be determined.

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