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RARE EARTH ELEMENTS AND STABLE SULPHUR ($\Delta^{34}S$) ISOTOPE OF BARYTE MINERALIZATION IN LIJI AREA, NORTHERN BENUE TROUGH, NORTHEASTERN NIGERIA

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ABSTRACT

The Liji area lithologically consists of inliers of granite and pegmatite members of the Pan-African granitoids surrounded by Cretaceous sedimentary deposits of Bima, Yolde, Pindiga and Gombe Formations. Epigenetic fracture-filling baryte mineralization hosted by granite, pegmatite and Bima Sandstone were delineated, sampled and analyzed for rare-earth elements (REEs) and stable sulphur isotope geochemistry. The REEs of the distal (unaltered) rocks indicated normal values (26.15-36.81 ppm) before mineralization was marked by enrichment of light rare-earth elements (LREEs) (27.94 ppm) relative to the heavy rare-earth elements (HREEs) (5.34 ppm) and negative Eu anomalies typical of calc-alkaline granites of Pan-African age. The baryte separates were marked by enriched LREEs and depleted HREEs with pronounced positive Eu anomalies indicating the invasion and consequent deposition of baryte-rich hydrothermal fluid under oxidizing conditions in the N-S and E-W striking fractures. Stable sulphur isotope of the baryte gives values that ranged from 18.3 - $19.8^{o}/_{oo}$ CDT indicating that the source of sulphur is from ocean water and not from magmatic, fresh water and connate water sources from the nearby granite, pegmatite and sandstone.

Keywords: *Baryte, Mineralization, Hydrothermal, Liji, REE, Sulphur-Isotope.*

1. INTRODUCTION

The area of study forms part of the Federal survey of Nigeria sheet 152 NW and NE Gombe. The area falls around Liji in Gombe Local Government Area of Gombe state. Geologically the study area conforms with the geology of the Gongola sub-basin of the Northern Benue Trough (Fig. 1). The Benue Trough is a major NE-SW striking rift basin which extends for greater than 1000km, starting from the northern tip of the Niger Delta in the south to the southern tip of the Chad basin in the north. Its width ranges from 50-150 Km containing up to 6000 M of Cretaceous - Tertiary sediments dotted by volcanic plugs [2]. It is geographically sub-divided into three major domains: Southern, Central and Northern [9]. The Trough is believed to have formed from extensional process of Africa and South America which occurred during late Jurassic to early Cretaceous [9]. Sinistral wrenching was believed to be the tectonic process responsible for the evolution of the Trough [4].

The Northern Benue Trough is a Y shaped geological entity made up of three arms namely: the NE-SW striking Muri-Lau basin; the E-W striking Yola arm and the N-S striking Gongola arm [4]. In the Gongola Arm, the Aptian - Albian Bima group, a continental formation represents the basal part of the sedimentary succession. It non-conformably overlies the Precambrian Basement Complex and consists largely of sandstones and clays series deposited in lacustrine-deltaic palaeo environmental setting. The Cenomanian Yolde Formation lies conformably on the Bima group and represents the beginning of marine incursion in

Corresponding author, tel: +234 - 803 - 244 - 1734 the Gongola sub-basin and consists of varieties of sandstones and shales. The Yolde is conformably overlain by marine Pindiga Formation which comprises of Kanawa, Gulani, Deba Fulani, Dumbulwa and Fika members which were deposited during transgression - regression phase that affected the entire Benue Trough. The Lithology of all the marine sediments are characteristically similar consisting of sequences of shales, limetones, mudstones with few horizons of calcareous sandstones, siltstones and sandstones [2, 16, 9].

This paper investigates the origin and some geochemical characteristics of the baryte mineralization of Liji area through the application of rare earth elements and stable sulphur isotopes geochemistry.

2. MATERIALS AND METHODS

A total of ten (10) samples were selected for rare earth element analysis using packages developed by ACMELABS, Vancouver, Canada. The samples were from Liji mineralization area, comprising granite, pegmatite, Bima sandstone, baryte, and hydrothermally altered granite and sandstone. The samples were subjected to total whole rock analysis employing the inductively couple plasma mass spectrometry (ICP/MS). Additionally stable sulphur isotope ($\delta^{34}S$) compositions were dertermined for baryte separates from mineralization areas using the ICP/MS technique of [13].

For the ICP/MS analysis, samples were broken to smaller fragments and packaged in a prescription nylon weighing 70 g – 80 g and sent for analysis. Each of the samples were crushed and then pulverized to atleast 85% passing through the 200 mesh size. Five grams (5g) each of the pulverized samples was fused with lithium metaborate/tetraborate which was rapidly digested in a weak nitric acid solution. The resultant solutions were used for the total whole rock analysis using the ICP/MS method. For the determination of stable sulphur isotope ($\delta^{34}S$) in baryte separates, the gas used in mass spectrometric measurements for variety of sulphur compounds was SO_2 [13]. The barytes were attacked at 280°C in a vacuum by dehydrated phosphoric acid containing stannous ions resulting in simultaneous release of SO_2 and H_2S from same specimen. The SO_2 obtained was then used for the determination of stable sulphur isotopes in the samples employing the ICP/MS technique. Abundant isotopic ratio ($^{34}S/^{32}S$) was applied in parts per thousand ($^0/_{00}$) in reference to the standard of troilite (FeS) from the Canon Diablo iron meteorite (CDT). The $\delta^{34}S$ contents of the samples were obtained applying Rollinson [14] formula:

$$\delta^{34}S\,^0/_{oo} = \frac{^{34}S/^{32}S(Sample) - \ ^{34}S/^{32}S(Standard)}{^{34}S/^{32}S(Standard)} \times 1000 \quad (1)$$

3. RESULTS

3.1 Geology and Petrography

The Geology of Liji area comprises of lithologic units that include granites, pegmatites and sedimentary deposits of Bima, Yolde, Pindiga and Gombe Formations (Fig. 2).

The crystalline basement rocks of the area are represented by granite and pegmatite occurring as inliers surrounded by younger rocks. The sedimentary succession consists of Bima sandstone, Yolde Formation, Kanawa member of the Pindiga Formation as well as Gombe sandstone.

The granite occur as massive, leucocratic, medium – very coarse grained texture consisting of quartz, orthoclase, microcline, plagioclase of oligoclase composition (An_{15}), biotite with accessory muscovite, zircon and opaque ores.

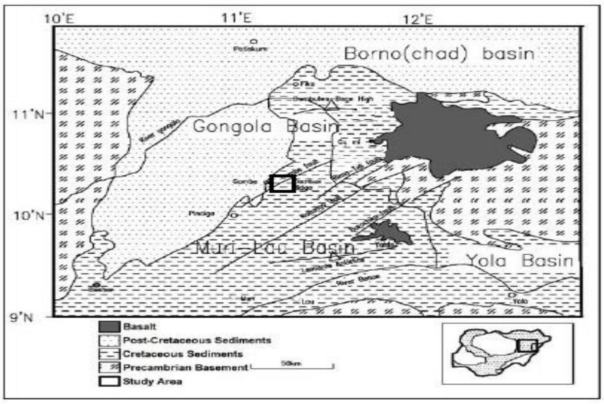

Figure 1: Geological map of the Northern Benue Trough showing the study area (Modified from Zaborski et al., 1997)

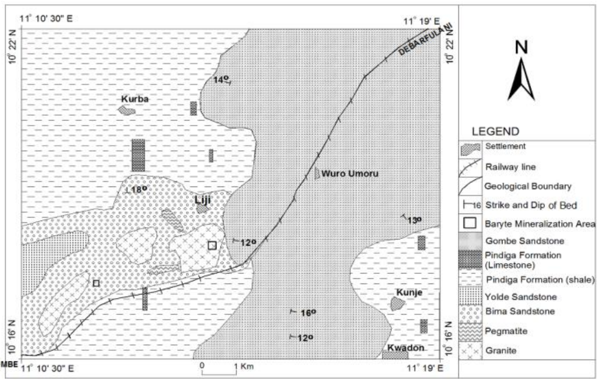

Figure 2: Geological Map of Liji area

The pegmatites are tabular, leucocratic, very coarse grained comprising of quartz, plagioclase of oligoclase composition (An_{11}), orthoclase and muscovite while biotite occur as accessory mineral. The Liji baryte mineralization area is hosted within granite and pegmatite.

The oldest unit of the sedimentary succession is the Bima sandstone. It is massive, thickly bedded, fine – coarse grained, poorly sorted, cross-bedded, indurated and some samples are silicified. Thin section study shows that it comprises of quartz, orthoclase, microcline and biotite with accessory opaque ores. The Gombe baryte mineralization area is hosted within this rock. The Yolde Formation is represented by sandstone unit which appear massive, pink and comprises petrographically of quartz, orthoclase, plagioclase and biotite with few grains of zircon and opaque minerals. The Pindiga Formation is represented by Kanawa member which comprises of dark shale that readily weather to black cotton soil and few limestone beds intercalated within the shale. The limestone consists of crystalline and fossiliferous varities. Petrographic study indicates the presence of calcite, dolomite with minor quartz and microcline. Faunas associated with the fossiliferous limestone are mainly composed of ammonites and gastropods. The Gombe sandstone is characterized by alternating sequences of sandstone, siltstone, mudstone and ironstone. The beds are folded, laminated, biotubated and in some places exhibits liesegang ring structure. Thin section study of the sandstone shows the presence of quartz, feldspar and opaque minerals

3.2 Geology and Perography of the Mineralization Areas

The areas of baryte mineralizations were mapped in greater detail to establish the relationships between host rocks and baryte mineralization. The mineralization areas are outlined as:

i. Liji baryte mineralization Area (LBM)

ii. Gombe baryte mineralization Area (GBM)

The LBM is located within granite and pegmatite. The rocks in the area form a steep sided hill exhibiting numerous exposures of granitic and pegmatitic rocks. Four baryte veins were identified in this area, three are hosted within granite and one hosted by pegmatite (Fig. 3). All the four veins strike E-W direction and individual veins can be recognized from the surface by the prominent hydrothermal alteration zone. The hydrothermally altered granite and pegmatite were the surface expressions of the occurrence of baryte mineralization and serve as prospection guide in the Liji hill. The altered rock is dark brown and fine grained crumpled and baked due to heat of the hydrothermal fluid, micro veins of baryte were noticed to be associated with this zone.

The four (4) baryte veins range in length from 7m to 45m and width varying from 1 to 3.5 M (Fig. 3). The main vein material (baryte) is creamy-white to brownish grey in colour and massive with white streak, hardness is 3 - 4 on Mohr's scale. Cleavage is perfect in two directions at inclined angles. Some samples appear granular having non-metallic lustre. The specific gravity varies from 3.746 - 6.427 g/cm^3 with an average of 4.714 g/cm^3. Petrographic investigation reveals that the hydrothermally altered granite and pegmatite consist essentially of baryte, biotite, quartz and orthoclase with accessory muscovite and opaque ores. The baryte appears to fill micro fractures within grains/crystals with no evidence of replacement of mineral indicating fracture filling type of mineralization.

The GBM occurs within highly indurated clastic sandstone and shaly units of the Bima group. The rocks of the area form a steep sided hill with steeply dipping beds of continental clastic Bima sandstone surrounding the Basement rocks.

There are two baryte veins all of which trend in N-S direction. The first vein which is discontinuous (GB1, GB2, GB3) trends N-S extending for about 500 M within hydrothermally altered Bima sandstone. The first part of the vein (GB1) is 32 M long and 3 - 4.5 M wide (Fig. 4). Wall rock alteration was observed as a marked change in colour and the presence of altered sandstone but largely masked by dust and erosional activity. The main vein material (baryte) is creamy-white in colour with white streak and having hardness of 2 - 3 on Mohr's scale. It has perfect cleavage in two directions at inclined positions and it exhibits non-metallic lustre.

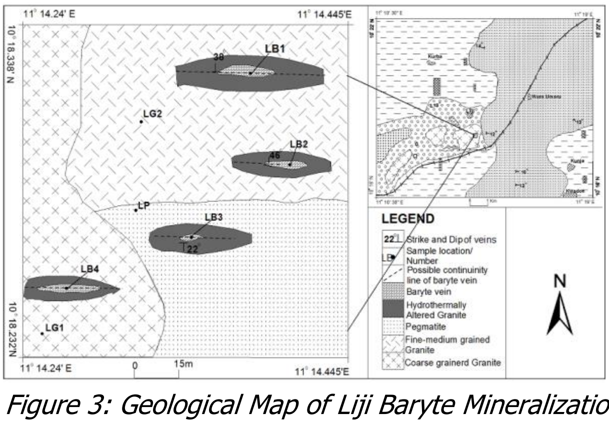

Figure 3: Geological Map of Liji Baryte Mineralization Area

The crystal system is orthorhombic having a specific gravity of 3.938g/cm^3. The physical properties of both GB2 and GB3 are similar to the GB1.

The second vein (GB4) is located about 1.3Km SW of the GB3. It occurs within indurated shaly unit of the Bima Formation. It strikes N016E and dips 36° E. The length is about 16 M and the width ranges from 1.2 M to 2.6 M. The vein is surrounded by alteration zones which show veinlets of baryte randomly injected into the host rock. These altered sandstones are also marked by change in colour and composition. The main vein material is white in colour, massive and dense. It has hardness of 2 - 3 on Mohs scale with perfect cleavages in two directions and the specific gravity is 3.941 g/cm^3. Petrographic investigation of hydrothermally altered Bima sandstone reveals the presence of quartz, microcline, orthoclase, baryte, biotite, muscovite and opaque minerals. The baryte appears to fill pore spaces between grains without any evidence of replacing the pre-existing minerals indicating that the style of the mineralization is a pore space filling type.

3.3 Rare Earth Elements Distribution Patterns in LBM and GBM

The chondrite-normalized REE diagram of the distal samples of the LBM and GBM (Fig. 5) indicate no clear separation between the distal granite and pegmatites but a slight separation of the distal sandstone at the HREE side. The plot depicts a generally high LREE values of the samples and lower values of the HREE but show slightly zigzag trend in the sandstone. The plot also show prominent negative europium anomaly in all the samples except sandstone which is devoid of Eu anomaly. The significant negative Eu anomaly in the granite and pegmatites which is common in Pan-African granitoids revealed the presence of plagioclase and K-feldspars which were concentrated in these rocks. However, the sandstone which failed to show Eu anomaly might have been due to variation of sources of its original materials.

The chondrite-normalized REE plot of the proximal samples consisting of hydrothermally altered granites and sandstones is presented in Fig. 6. In the plot, the samples were observed to show marked enrichment of LREE relative to HREE. The plot show similar trend in the HREE which is nearly flat except for one sandstone sample which depicts slightly zigzag pattern and much lower HREE.

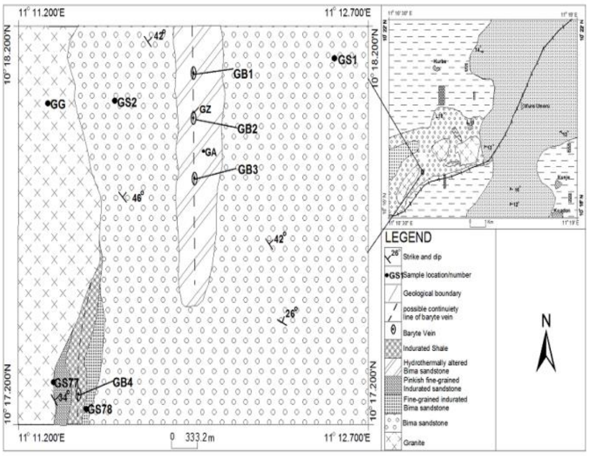

Figure 4: Geological Map of Gombe Baryte Mineralization Area.

Table I: Rare Earth Elements Composition of LBM and GBM (ppm)

	LBM					GBM			
	LG	LP	LZ	LA	LB1	GP	GS	GZ	GA	GB1
La	9.6	4.7	6.5	55.2	3.0	6.5	7.5	12.9	17.5	2.7
Ce	15.5	6.3	12.9	116.1	2.6	12.9	15.3	24.7	29.6	2.0
Pr	1.99	0.78	0.91	14.58	0.41	1.51	1.51	2.80	2.94	0.21
Nd	7.7	3.2	3.2	56.8	1.7	5.8	5.7	11.1	9.4	0.9
Sm	1.70	0.95	0.94	11.32	0.58	1.80	0.92	2.66	1.38	0.46
Eu	0.32	0.22	0.81	1.39	n.d	0.16	0.32	0.43	n.d	n.d
Gd	1.76	1.27	1.89	8.22	3.14	1.74	0.69	3.26	2.24	3.30
Tb	0.29	0.25	0.37	1.01	0.13	0.34	0.10	0.43	0.12	0.10
Ho	0.30	0.27	0.60	0.66	0.09	0.38	0.09	0.41	0.08	0.04
Er	0.81	0.75	2.02	1.71	0.19	1.09	0.29	1.10	0.23	0.10
Tm	0.10	0.14	0.33	0.24	0.03	0.16	0.04	0.16	0.03	0.03
Yb	0.63	1.06	2.28	1.34	0.24	1.03	0.33	0.97	0.27	0.24
Lu	0.08	0.16	0.33	0.18	0.03	0.14	0.05	0.14	0.04	0.02

Note: LG= Distal Granite; LP= Distal Pegmatite; LZ= Proximal Granite; LA= Proximal Granite; LB1= Baryte Separate; GP= Distal Pegmatite; GS= Distal Sandstone; GZ= Proximal Sandstone; GA= Proximal Sandstone; GB1= Baryte Separate; n.d = not detected

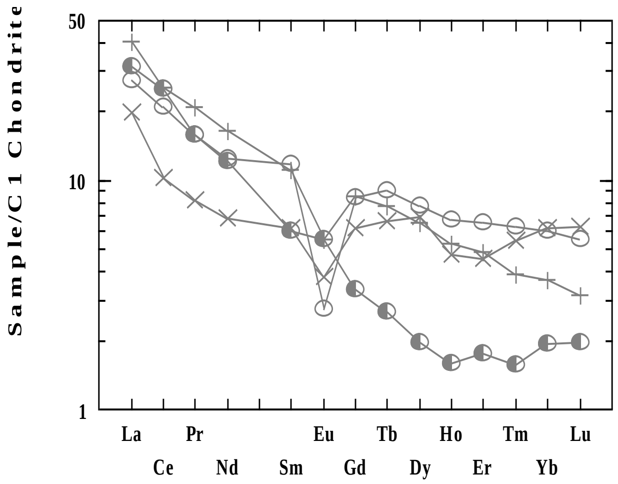

Figure 5: Chondrite-normalized REE patterns of distal samples of LBM and GBM. [Normalizing values were those of Taylor and McLennan, [15]].

+ - LBM-Distal granite, **X** - LBM-Distal pegmatite.
○ - GBM-Distal Pegmatite, ◑ - GBM-Distal Sandstone

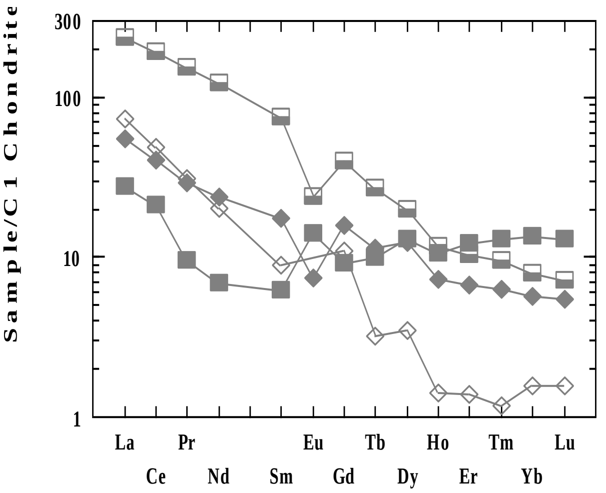

Figure 6: Chondrite-normalized REE pattern of proximal samples. [Normalizing values were those of Taylor and McLennan, [15].

■ - LBM-Proximal granite, ⊟ - LBM-Proximal granite
◆ - GBM-Proximal sandstone, ◇ - GBM-Proximal sandstone

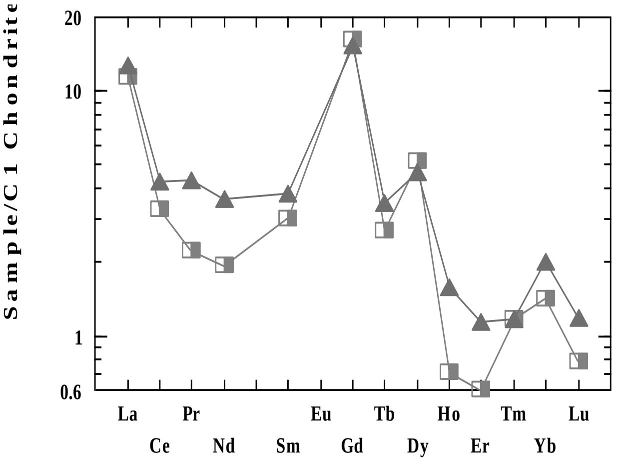

Figure 7: Chondrite-normalized REE pattern of Baryte separates. [Normalizing values were those of Taylor and Mclennan, [15].

▲ - LBM-Baryte separate, ◧ - GBM-Baryte separate

However, negative Eu anomally was observed in one altered sample each of granite and sandstone, reflecting depletion of feldspars in the crystal/melt fractionation as a result of hydrothermal effect. One sample of granite show positive Eu anomaly while the sandstone show no Eu anomaly.

3.4 Stable Sulphur Isotope Study

Stable sulphur (δ^{34}S) isotope study is the most widely used tool in determining the origin of hydrothermal fluids and provides the best geochemical information. Hydrothermal fluids may be derived from five major sources which include magmatic water, metamorphic water, connate water, sea water or meteoric water as well as mixture of two or more waters [10, 12].

The stable sulphur (δ^{34}S) isotope study was conducted on one baryte separate each from LBM and GBM. This study was aimed at deciphering the origin of the mineralizing fluids responsible for the deposition of the baryte. The result of the Sulphur (δ^{34}S) isotope analysis of the two baryte separates is given in Table 2.

Baryte separates of LBM and GBM yielded δ^{34}S values of 18.3‰ and 19.8‰ (CDT) which averages 19.05‰ CDT. These compositions reflect ocean water influences indicating that the source of sulphur is of ocean water origin (Fig. 8). These rules out the magmatic source of the sulphur from the granitic (Pan-African) host rock, which implies that the baryte mineralization was of younger age related to the Cretaceous sediments of the area.

The above values are much higher than those of Joseph et al. [7] who reported stable sulphur isotope values that ranged from +5‰ - 19‰ CDT for pyrite of Gombe hill, pointing to fresh water sulphate as the source of sulphur. The values reported in this work are somehow higher than those obtained on the Gulani baryte separates which range from 12.3‰ to 13.1‰ which attributed the source of the sulphur to formational waters [5].

Table 2: Sulphur (δ^{34}S) isotope values relative to Canon Diablo Troilite (CDT) of baryte (sulphate) [expressed per mil ($^{o}/_{oo}$)].

S/N	Mineralization Area	Sample No.	Material Analyzed	δ^{34} S Values ($^{o}/_{oo}$)
1.	Liji Baryte Mineralization Area (LBM)	LB1	Baryte Separate	18.3
2.	Gombe Baryte Mineralization Area (GBM)	GB1	Baryte Separate	19.8

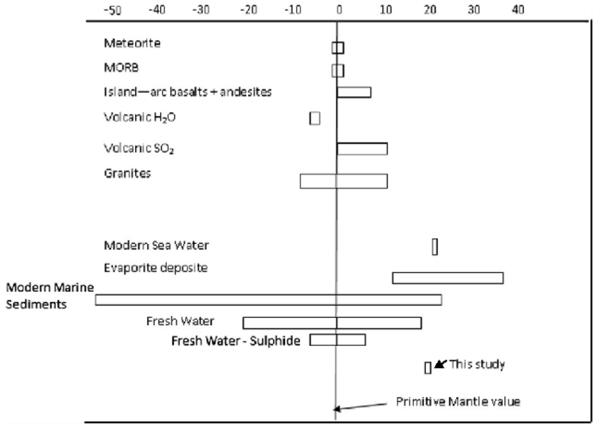

Figure 8: Baryte sulphur isotope values plotted in the natural sulphur isotope reservoir diagram (Modified from Rollinson [14]).

The hydrothermal mineralizing fluid most likely derived its barium from the host rock (Bima Sandstone) with possible contribution from the basement rocks while the sulphur might have been sourced from ocean water that deposited the shaly unit of the Bima sandstone as well as the nearby marine Pindiga Formation. This is in line with the view of [1] on account of metal contribution from host basement in the Middle Benue Trough. Moreover the barytes of Liji study area are best described as epigenetic fissure filling deposit type where hydrothermal mineralizing fluid precipitated the baryte minerals in the fissures that runs sub-parallel to the Gombe fault system. The tectonic event responsible for creation of Gombe fault running NE-SW might have resulted in creation of subsidiary fissures sub-parallel to the Gombe fault system [17]. Such fissures trending N-S and E-W later became conduit through which the hydrothermal fluid exploited during migration and subsequent deposition of the baryte.

4. DISCUSSION

The REE diagram of the distal samples show no significant separation of samples which reflect the normal background nature of the samples before the mineralizing hydrothermal fluid invasion despite varying host rocks (granite, pegmatite and sandstone) of the samples. The pattern also show enrichment of LREE and depleted HREE with significant negative Eu anomalies characteristics of calc-alkaline granitoids of Pan-African age. The sandstone was devoid of Eu anomalies indicating that their original material is from different sources. El-Nafaty [5] studied the REE of baryte mineralization of Gulani area and observed that distal samples were characterized by high LREE and lower values of HREE similar to those of this study.

The REE pattern of the proximal samples samples (hydrothermally altered granite, pegmatite and sandstone) show enriched LREE and depleted HREE for the granites, but erratic pattern in the sandstones with significant negative Eu anomalies which reflects depletion of feldspars during crystal-melt segregation due to the effect of hyrothermal fluid intrusion into the host lithologies. The above strongly agree with the view of El-Nafaty [5] who stated that the REE pattern of the baryte mineral separates show enriched LREE relative to HREE with erratic trend and pronounced positive Eu anomalies. The positive Eu anomalies were believed to be due to intrusion of mineralizing hydrothermal fluid which leached baryte from the host lithologies and consequently deposited them within fractures and pore spaces in the host rocks under oxidizing environmental conditions which enhanced the formation of trivalent Eu^{3+} and hence the positive anomalies. This conclusion was similarly drawn on the baryte separates of the Gulani area by El-Nafaty [5].

The stable sulphur isotope of the baryte gave average value of 19.05$^{o}/_{oo}$ CDT indicating that the source of the sulphur is from ocean water. This result discount the magmatic sulphur source of the host granite and pegmatite as well as connate water sulphur from the host sandstone conforming with the view of Ohmoto and Rye [10] where they indicated that deposits with sulphur-isotope values near 20 $^{o}/_{oo}$ should derive their sulphur from ocean water.

Joseph *et al.* [8] reported stable sulphur isotope values that ranged from 5$^{o}/_{oo}$ – 19$^{o}/_{oo}$ CDT for pyrite deposits of the Gombe hill pointing to fresh water as the source of sulphur ruling out the magmatic and metamorphic source of sulphur despite the proximity with the basement rocks. The values reported in this work are somehow higher than those obtained on the Gulani baryte separates which ranged from 12.3$^{o}/_{oo}$-13.1$^{o}/_{oo}$CDT [5]. He interpreted these values to formational waters as the source of sulphur discounting the magmatic and ocean water sources of sulphur from the nearby volcanic rocks and marine sediments.

Akande and Abimbola [1] reported a stable sulphur isotope value ranging from -10 - 21°/$_{oo}$ CDT for sulphide minerals from Pb-Zn-F-Ba mineralization of the Benue Trough and observed that the ore solution evolved in probable evaporitic environment and that metals, sulphur and fluorine were likely of basinal source with probable contribution from basement.

5. CONCLUSION

Epigenetic fracture and pore space filling baryte mineralization of the Liji area has been investigated through the application of rare earth elements and stable sulphur isotope studies. The study indicates that baryte originated from hydrothermal fluid which leached barium from pre-existing granite, pegmatite and sandstone while the sulphur was sourced from ocean water. The barium and the sulphur were concentrated in the pre-existing N-S and E-W fracture system of the Liji area to form the baryte under oxidizing conditions.

6. ACKNWLEDGEMENT

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