

THE CHEMICAL COMPOSITION AND INDUSTRIAL QUALITY OF BARITE MINERALIZATION IN CALABAR FLANK, OBAN MASSIF, MAMFE EMBAYMENT AND OBUDU PLATEAU, SOUTHEASTERN NIGERIA

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ABSTRACT

Barite occurrences in the Calabar Flank, Oban massif, Mamfe Embayment and Obudu Plateau of Southeastern Nigeria have been sampled and analyzed for the purpose of assessing their chemical composition and industrial quality. Barite occurrences were observed mostly along faults and unconformities marking the boundaries between the Precambrian basement rocks of Oban and Obudu massifs and the Cretaceous sediments of the Calabar Flank and Mamfe embayment. Occurrences were also observed within the sediments. The chemical data show that BaSO_4 , SiO_2 and TiO_2 are the major chemical species of the barite. The Ba and SO_4 content vary between 53.62 – 56.10 wt% and 27.57 – 39.35 wt% respectively across the sampled areas. The specific gravity is 4.45 and this combined with high BaSO_4 (approximately 94 wt%) shows that the mineralization is of high industrial quality and compares favourably with the Azara barite deposits of the Benue Trough. The quality of the barite meets American Petroleum institute (API) requirements for use as drilling mud.

KEYWORDS: Barite, mineralization, quality, chemical composition, southeastern Nigeria.

INTRODUCTION

A typical barite sample is expected to have 65.70% and 34.30% of the element Barium and $(\text{SO}_4)^{2-}$ respectively (Krauskopf and Beiser 1986). Barite has a specific gravity (SG) of 4.5 in pure state and is often referred to as 'heavy spar'. A high density, chemical inertness and widespread occurrence are the properties that are valued for barites application as a weighting agent in drilling fluids. Colour and chemical purity are important properties when considering the suitability of barite for non-drilling applications. Barite has various uses. For instance, high purity grades of barite with fine and well-sorted particles are used as fillers in marine and industrial paints, in brake lining/friction materials and in plastics.

A specialized use of barite based on its high density and ability to absorb radiation is as an aggregate in dense concrete for shielding applications in the nuclear industry and hospital radiation departments. For

barite to be used in the non-petroleum industries, it needs to undergo processing through beneficiation methods such as washing, jigging, heavy metal separation, tabling, floatation and magnetic separation. Most crude barite requires some upgrading to minimum priority of density.

The texture and size distribution of various species of gangue minerals affect the beneficiation of barite. Petrographic examination of barite specimens is very vital in this beneficiation process.

There have been speculations that barites occur in many parts of Cross River State of Nigeria. There have also been attempts to mine barites in some parts of the state using "trial and error" method.

This study was undertaken to geologically map the host rocks and the barite deposits, and determine their relationship with other rocks in the area. It is also the aim of this study to carry out a detailed petrographic and geochemical analysis of these barites to determine their suitability for industrial use.

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GEOLOGICAL SETTING

The geology of southeastern Nigeria consists of two Precambrian basement spurs the Oban massif and the Obudu Plateau. These basement horsts are unconformably overlain by the Cretaceous sedimentary rocks of the Calabar Flank and Ikom-Mamfe embayment (Fig. 1). The barite deposits analyzed in this study occur dominantly along the unconformities and faults at the basement/sedimentary rock boundaries. Some barite deposits also occur within the sedimentary terrains. The two basement horsts are separated by the Mamfe rift. Bassey (1998) had suggested that the Oban massif and the Obudu Plateau could have been a contiguous block prior to the formation of the Mamfe basin. Cretaceous sediments of the Calabar Flank overlie the Oban massif whilst those of the Mamfe basin overlie the Obudu Plateau.

A dolerite dyke intruding the Precambrian rocks in Obudu Plateau yielded an $^{40}\text{Ar}/^{39}\text{Ar}$ plateau age of $140\pm 0.7\text{Ma}$ (Ekwueme 1994a) whilst zircons extracted from the basement rocks (gneisses and schists) of Obudu gave ages of $2062.4\pm 0.4\text{Ma}$ (Palaeoproterozoic) and $2,504.5\pm 0.5\text{Ma}$ (NeoArchaean) (Ekwueme and Kroener 1997, 2006, Kalsbeek et al. 2013). The gneisses in the basement of Oban massif gave Zircon ages of $1931.9\pm 0.8\text{Ma}$ (Palaeoproterozoic) (Ekwueme and Kroener 1998).

The basement rocks have undergone polyphase deformation and polymetamorphism resulting in several generations of folding faulting, shearing and fracturing as reported by Ekwueme (1987, 1994b). The dominant trend of these structures is N-S to NE-SW ($0-30^\circ$) indicative of Pan-African deformation (Onyeagocha and Ekwueme 1982, Ekwueme 1987).

The Calabar Flank is in the southern (Lower) Benue Trough. The oldest sedimentary rock in the Calabar Flank is Awi Formation of Aptian-Albian age (Adeleye and Fayose 1978). It lies unconformably on the Precambrian basement rock of Oban massif. Overlying the Awi Formation is the Mfamosing Limestone Formation of Petters (1982), which is in turn overlain by the Eze-Aku Shale of Reyment (1965), later described by Petters et al. (2010) as Ekenkpon Shales. Associated with these shales are bioturbated marls which are overlain by Nkporo Shale of Campanian-Maastrichtian ages. The youngest formation in the Calabar Flank is the unconsolidated sand belonging to the Benin Formation of Tertiary age.

The Mamfe Embayment is predominantly a fluvial clastic sequence that exhibits point bar fining – upward cycles and over bank mudrocks (Ekwueme *et al.* 1995). This formation has been described as the Asu River Group of Albian age. Associated with the sedimentary rocks of Mamfe rift are basaltic rocks which

exhibit excellent columnar joints (Ekwueme 2012). Type locality of the Mamfe Formation is on the bank of the Cross River at Mamfe in adjoining Cameroon Republic where 800m of massive arkosic sandstones with marl, sandy limestone and shale intercatations are exposed (Reyment 1965). The sequence in the Nigerian part of the Mamfe Basin comprises conglomeritic immature mudstones (Petters et al. 1987). The Mamfe Formation lies unconformably on the Precambrian basement of the Obudu Plateau.

FIELD OCCURRENCE AND DISTRIBUTION OF BARITE

As observed by mining geologist, mainly unconformities and major faults are well exposed during mining operations as features that host barite ore in the study area. The Mamfe rift and the Calabar Flank belong to the lower Benue Trough. The Trough is a geosynclinal structure; and as expected in such regions, accumulation of sediments was followed by uplifting, folding and faulting (Benkheilil 1987). The effects of these stresses created unconformities at the boundary between the basement and the deposited sediments, and faults within the folded sediments. Hence, barite was accumulated in major faults within the carbonaceous shales, limestones, siltstone and calcareous sandstone (of the Cross River and Asu River Groups within the lower Benue Trough) and along the basement-sediments boundary. Hence, these locations were geologically mapped in detail to delineate the ores. This is evident in the location of barite vein within a generalized stratigraphic section at Agoi Ibiami (Fig. 2), within sediments (Fig. 3) and in dolerite dykes along the basement boundary (Fig. 4). It is possible that the mineralization episodes were in pulses in basements, cross-cutting intrusives and in sediments. The reactive calcareous nature of the sandstone helped in the formation of the mineral while the high permeability within the sandstones and shales allowed the localization of the mineralizing fluids in the area. The mineralized veins are generally observed to trend NE-SW (Fig. 5). Oden (2012) recognized barite veins trending N-S and NW-SE in the Benue Trough. He considered these veins older than other veins and more frequent. According to him the vein sets were formed from tension joints reflecting different post-sedimentary deformation phases in the trough. The dips of the veins are near vertical to vertical (80° to 90°). The largest veins are in Gabu-Osina area and these veins are up to 2 km in length. These veins were mapped in this study and the barite ores were characterized using detailed petrographic and geochemical analyses followed by rigorous interpretations.

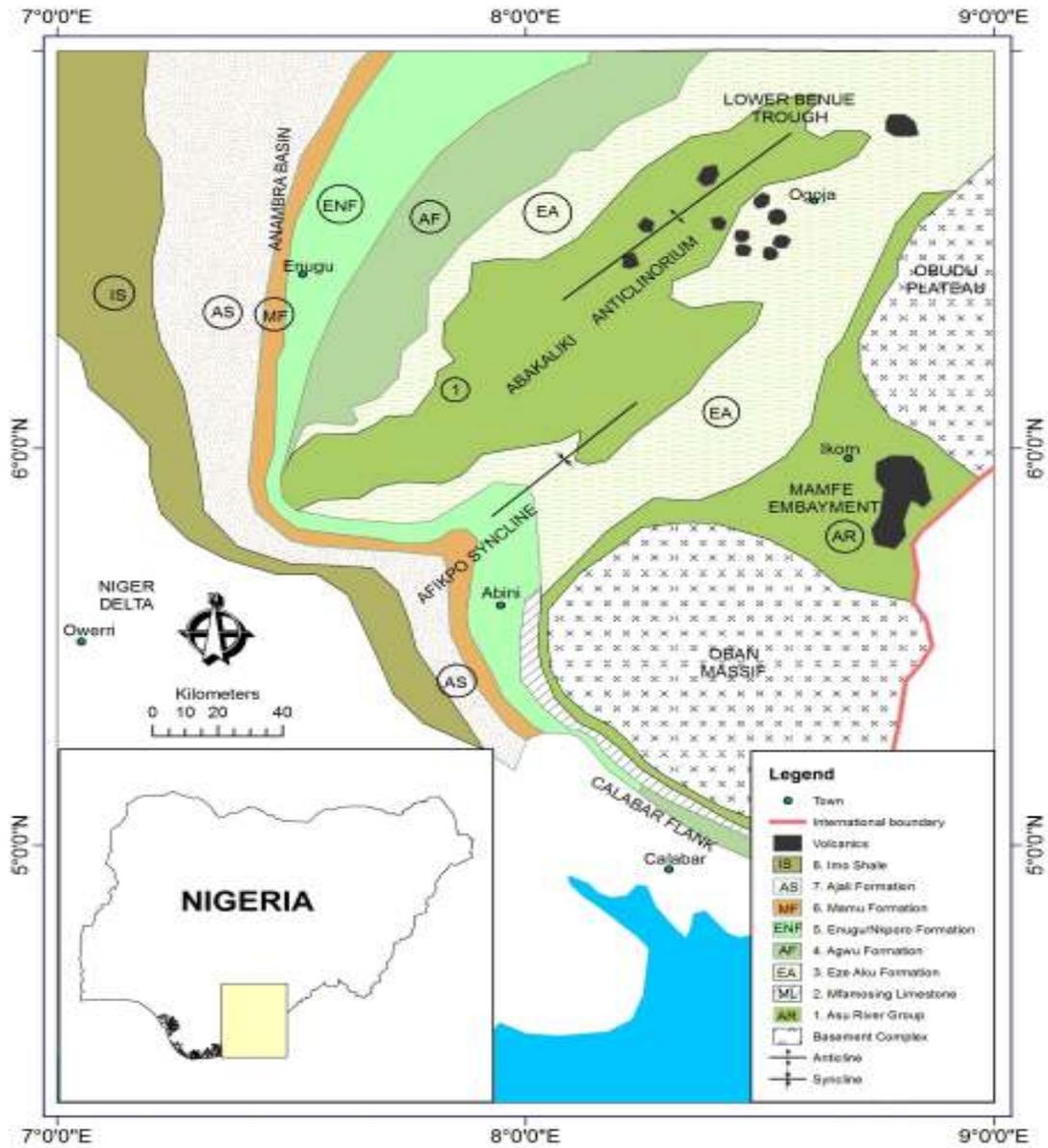


Fig 1: Geologic sketch map of Southeastern Nigeria (After Ekwueme et al. 1995)

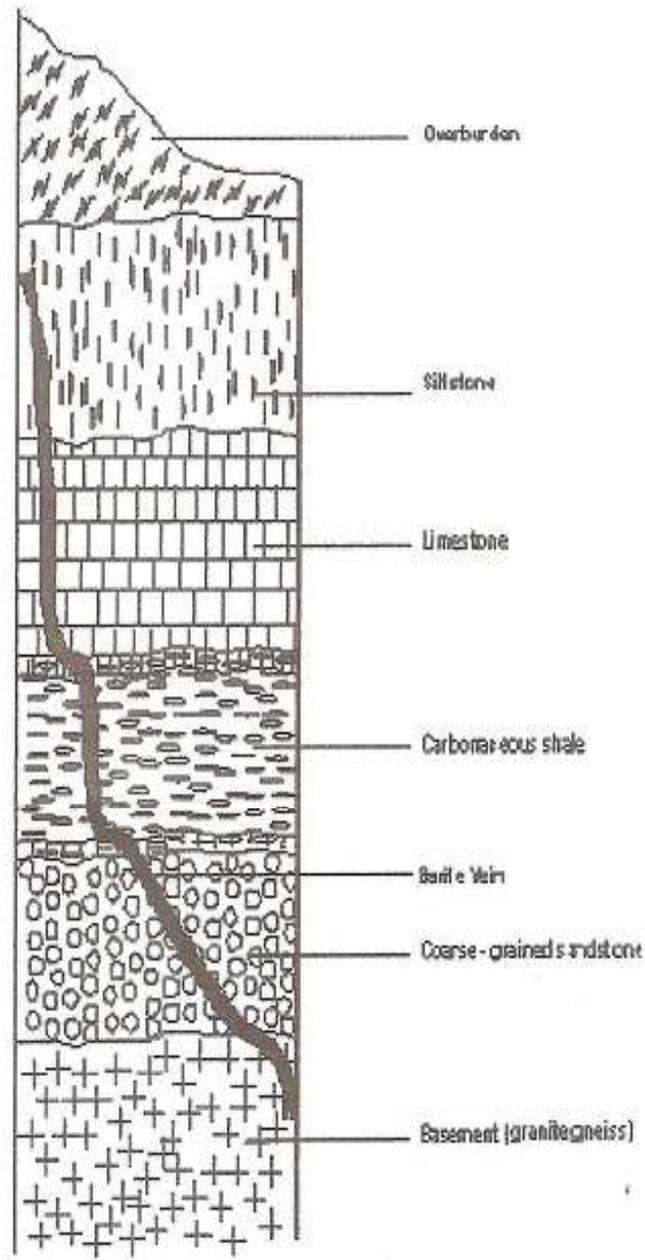


Fig 2: Location of barite vein in a generalized stratigraphic chart at Agoi Ibami (05° 43'27" N, 08° 12' 22"E)

0 50m
 ┌───┐ Barite Length

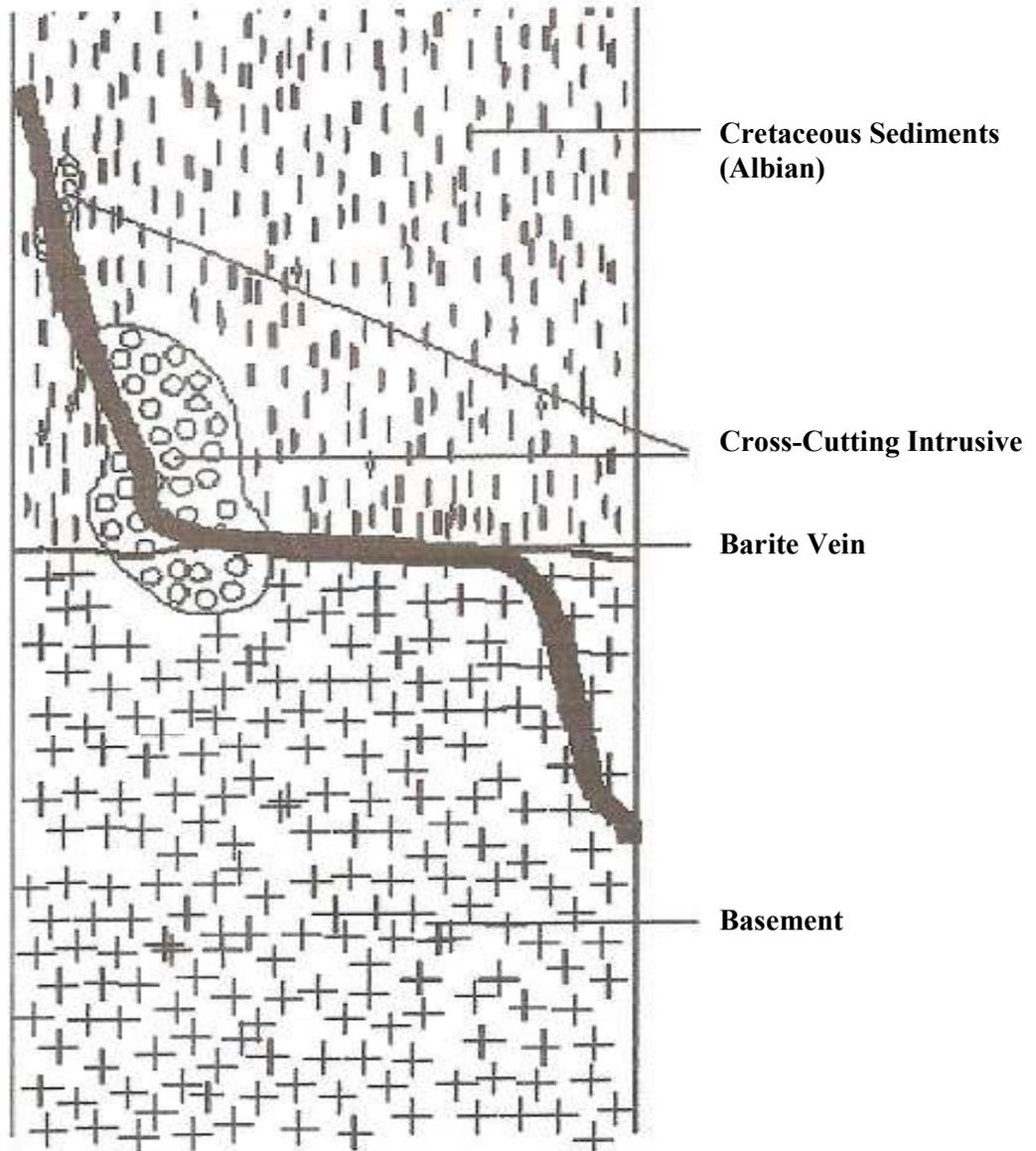


Fig 3: Generalized model of Barite Mineralization in Cross River State

0 50m

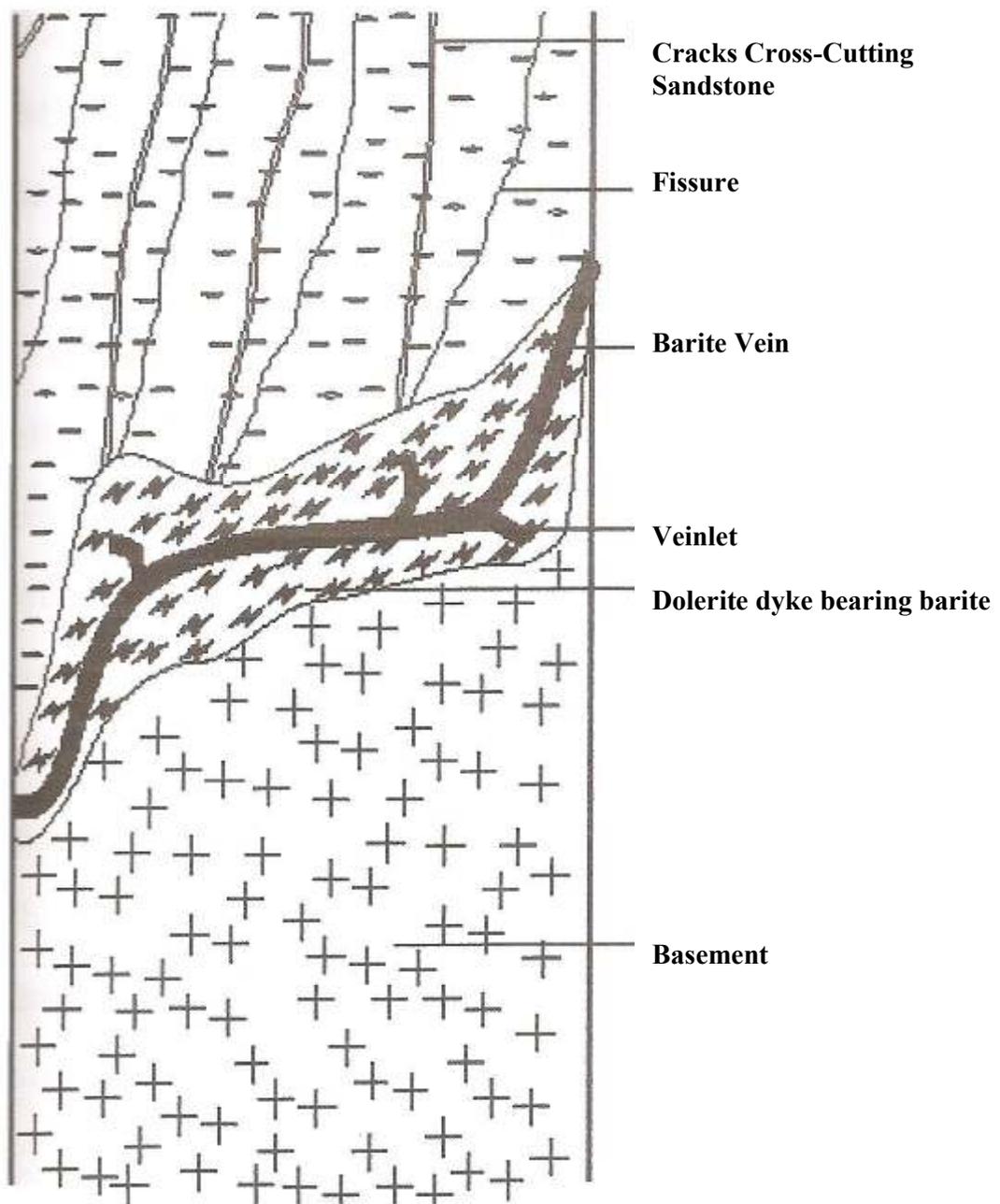


Fig 4: Sketch of barite bearing dolerite dyke occupying the boundary between sandstone and basement at Okurike ($05^{\circ} 37' 07''\text{N}$, $08^{\circ} 31' 25''\text{E}$)

0 50m

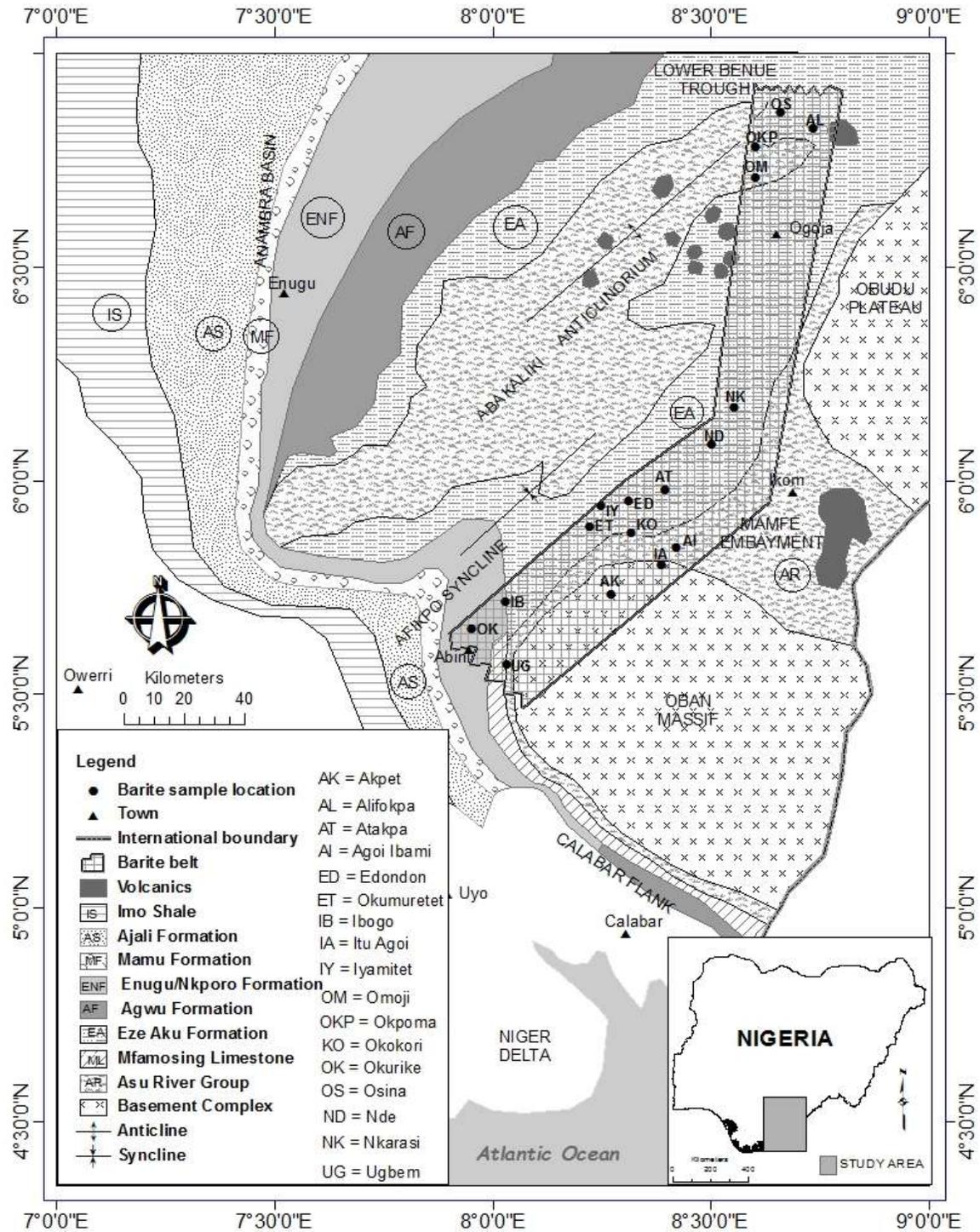


Fig 5: Map of barite mineralization zone in Cross River State (Modified after Ekwueme, 2003)

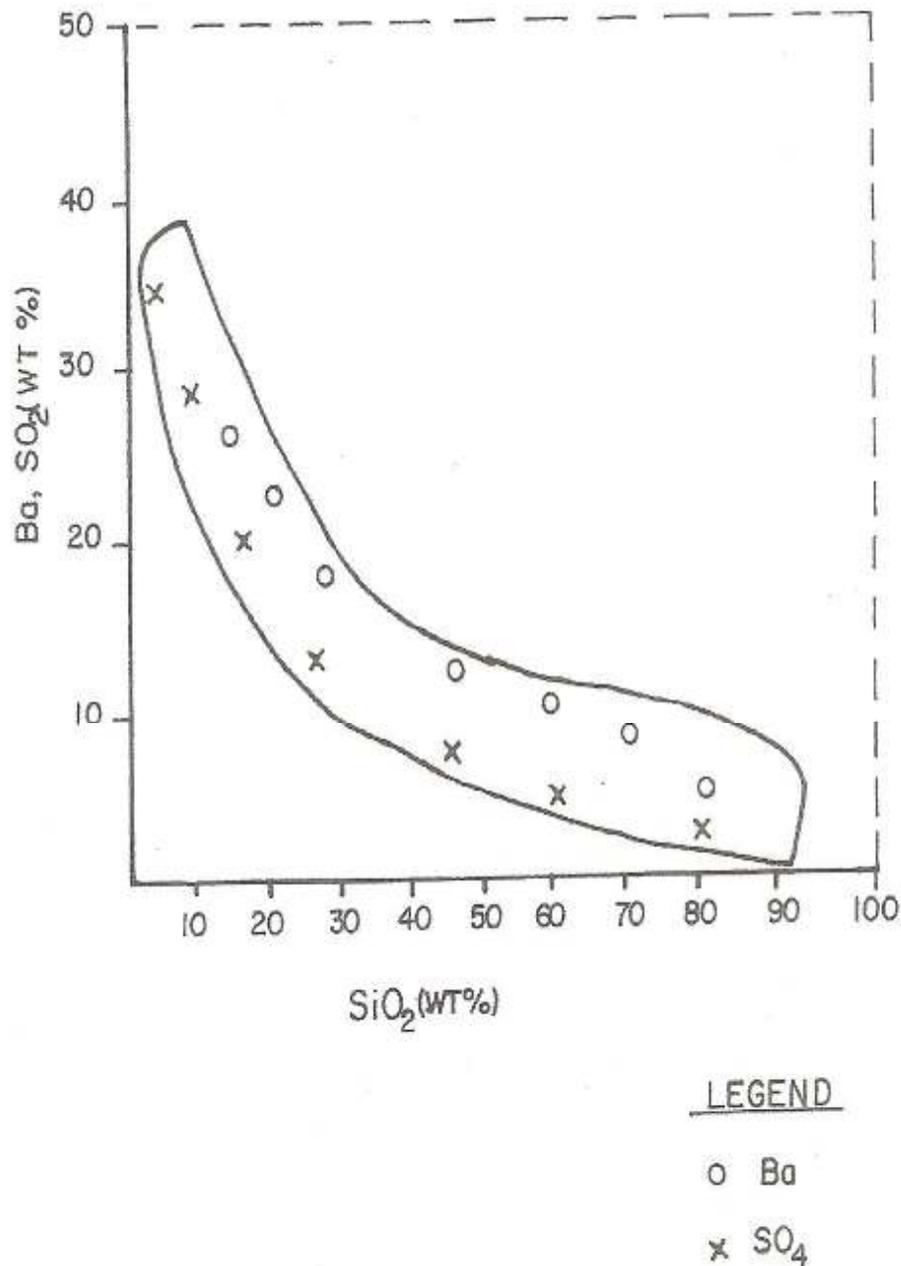


Fig 6: Plot of Ba and SO_4 versus SiO_2 for Rocks of Calabar Flank, Oban Massif, Mamfe Embayment and Obudu Plateau Southeastern Nigeria

PETROGRAPHY

Barite is a colourless mineral with one directional cleavage, moderate relief, high birefringence grey colour, and extinction angle of approximately 35° . It is often associated with gangue minerals such as quartz, calcite, biotite, chlorite and sulphides. The barite content in Itu Agoi samples is 92%, while that of Okokori, Gabu and Agoi Ibiami samples are 87%, 94% and 86% respectively (Table 1). Associated gangue minerals in Itu Agoi samples include quartz, biotite and calcite.

Okokori samples have quartz and muscovite, while Gabu-Osina samples contain chlorite and biotite and needles of pyrite and chalcopryrite.

CHEMICAL COMPOSITION AND INDUSTRIAL QUALITY

In areas where barite mineralization was observed during geological mapping and sampling, a pair of samples of host rocks was collected at each site for possible variation in chemical contents. To ensure

the evaluation of the industrial quality of barite occurrences in the study area, Cross River State has been divided into three geological zones.

Zone 1: Constitutes the southern part and places with economic barite occurrences are Akpet and Agoi areas. Here mineralization occurred within the sediments but dominantly at the boundary between basement and sediments. Typical host rocks here are phyllite, schist, gneiss, sandstone and siltstone (Table 2). This part belongs to the Calabar Flank/ Oban basement massif.

Zone 2: This is the central part of Cross River State. It falls within the Mamfe Embayment which is composed of Cretaceous sediments with basaltic flows in Ikom (Ekwueme 2012). The dominant rocks are sandstone and places with significant occurrences of barite include Okokori, Nsakwon, Atakpa, Nkarasi (Table 3).

Zone 3: This is the northern part of Cross River State. It is situated at Ogoja / Obudu Plateau and consists geologically of basement rocks overlain by the Asu River Group of Cretaceous age. Barite occurs dominantly in the Cretaceous sedimentary rocks but there are also occurrences at the boundary of the basement and sedimentary rocks. There are salt ponds in Okpoma. Rocks constituting the Obudu Plateau basement include, high-grade schists, gneisses, amphibolites, dolerite, pegmatites and granulites.

Table 2 shows the chemical composition of some host rocks. In zone 1 where barite occurs mainly at the basement/sediment boundary the typical basement rocks are phyllite, schist and gneiss. The chemical data show that barite content of the host rocks decreases with increasing SiO_2 content (Fig. 6). For instance, in Akpet the Ba plus SO_4 content is 8.6% whilst the SiO_2 content is 85%; in schist from Agoi Ibiami the Ba plus SO_4 content is 20% whilst the SiO_2 content is 46% and in the gneiss at Ibogo Ba plus SO_4 is 15% whilst the SiO_2 content is about 70%. The schist in Itu Agoi is barren of barite and the SiO_2 content is 64%. A close examination of Table 3 which shows the chemical composition of barite samples indicates that the barite

occurrences in Akpet, Agoi Ibiami, Ibogo and Itu Agoi are all of high quality with Ba plus SO_4 content of 90% and above. There is no indication that the composition of the host rocks has effect on the quality of the barite. A close study of Table 3 shows that barite occurrences in the other two zones which are mostly within the sediments are also of high quality with Ba plus SO_4 content of 90% and above, the only exception is the barite occurrence in Okurike in Zone 1 which is composed of sandstone. Barite occurrence in Okurike has very high SiO_2 content of 73% compared with other occurrences in which SiO_2 content is low (see Table 3). The barite in Okurike is of low quality having Ba plus SO_4 content of only 18%. It is most likely that the mineralization in the study area is independent of the host rock composition. The chemical composition of the barite is consistent with the modal composition (Table 2). It is possible that the mineralizing fluid of the barite is from other sources rather than from the host rocks. Previous studies of barite occurrences in the Benue Trough had pointed to evaporates as the source of the mineralizing fluids (Akande and Mucke 1989; Akande et al. 1989, 1992; Nwachukwu 1972). This is most likely the case for barites in the geological regions of Cross River State studied. An evidence of evaporates as the source is the rich salt ponds in Okpoma an area whose barite deposit has been sampled in this study. Mbipom et al. (1990) used the results of their resistivity survey in Okpoma area to suggest that even though the brine occurs at a depth of 20m, the source of the brine is deep-seated and possibly from compacted Shale or basement. The barite in Okpoma has Ba plus SO_4 content of 86.6% (Table 3). The industrial quality of barite occurrences in the geological zones of Cross River State analyzed in this study is higher than that of the famous and well-known Azara barite deposits studied by Ajile (1989) and Bassey (1998) (Table 3). Oden (2012) noted that in the Benue Trough the quality of barite increases with depth of the veins. He observed that in most occurrences, the quality of the material from top part of a vein (0-5m depth) is always lower than that from the deeper parts of the same vein. Hence, it is most likely that as mining gets deeper better quality barite can be obtained in this area.

Table 1: Modal Composition of Associated Minerals of Barite-Bearing Samples in Calabar Flank, Oban massif, Mamfe Embayment and Obudu Plateau, Southeastern Nigeria

MINERAL	OS	OM	GA	AT	NS	EK	AG	IA	AK	OK
Barite	96	86	94	95	93	87	86	92	90	20
Quartz	Tr	8	-	-	2	9	10	2	4	71
Biotite	2	1	2	1	1	1	4	3	-	-
Muscovite	<1	1	1	<1	<1	2	-	-	6	4
Calcite	1	Tr	<1	<1	<1	1	Tr	3	-	5
Chlorite	<1	-	2	2	3	<1	-	-	-	-
Plagioclase	-	4	<1	1	-	-	-	-	-	-
Total	100	100	100	100	100	100	100	100	100	100

OS B: Barite-bearing sample from Osina
 Om B: Barite-bearing sample from Omoji
 Ga B: Barite-bearing sample from Gabu
 At B: Barite-bearing sample from Atakpa
 Ns B: Barite-bearing sample from Nsakwon
 Ek B: Barite-bearing sample from Okokori
 AG B: Barite-bearing sample from Agoi Ibami
 IA B: Barite-bearing sample from Itu Agoi
 AK B: Barite-bearing sample from Akpet 1
 OK B: Barite-bearing sample from Okurike

Table 2: Major Elements Composition of Host Rocks in Calabar Flank, Oban Massif, Mamfe Embayment and Obudu Plateau Southeastern Nigeria

Wt%	NG D	BC	AM A	OKP	BA S	AK		OK		AG		IB		IA		UG	
						1	2	1	2	1	2	1	2	1	2		
SiO ₂	47.10	68.10	47.28	71.00	63.10	85.60	85.80	87.78	87.89	46.20	46.40	69.59	70.00	63.20	64.79	87.74	87.80
Al ₂ O ₃	13.41	15.00	16.13	10.11	15.67	1.02	103	2.30	2.10	26.58	26.52	6.62	5.98	17.45	15.76	2.34	2.19
Fe ₂ O ₃	10.32	4.11	8.50	3.80	6.11	0.64	0.60	0.16	0.24	1.56	1.60	3.23	3.21	7.63	6.39	0.16	0.24
TiO ₂	3.10	0.46	3.14	0.55	0.86	0.43	0.42	0.12	0.14	0.33	0.35	0.46	0.45	0.96	0.90	0.11	0.13
MnO	0.16	0.07	0.14	0.05	0.12	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.13	<0.01	<0.01
Na ₂ O	2.31	3.18	1.45	1.60	3.01	0.10	0.08	0.10	0.09	0.08	0.08	0.11	0.09	1.93	3.55	0.11	0.10
K ₂ O	1.06	5.55	0.78	4.29	2.71	0.86	0.84	0.83	0.85	0.14	0.43	0.71	0.69	3.79	2.21	0.83	0.85
CaO	5.99	2.09	9.40	2.39	2.95	0.04	0.04	0.05	0.04	0.04	0.05	0.04	0.05	0.82	2.14	0.05	0.06
MgO	8.84	0.27	5.67	1.01	3.44	0.16	0.14	0.07	0.09	0.11	0.14	0.19	0.17	3.45	3.07	0.07	0.08
P ₂ O ₅	0.12	0.18	0.28	0.16	0.20	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.17	0.17	<0.01	<0.01
Ba	1.50	0.6	4.00	1.60	1.01	5.12	5.02	4.15	4.15	12.20	11.80	9.44	9.00	0.00	0.00	4.13	4.16
SO ₄	0.80	0.32	2.53	0.83	0.06	3.52	3.56	3.10	2.90	8.43	8.45	6.52	6.46	0.00	0.00	3.10	2.91
LOI	0.47	0.12	0.70	0.46	0.54	2.30	2.40	1.20	1.21	3.54	3.56	3.31	2.90	2.15	0.72	1.22	1.20
TOTAL	95.18	100.05	100	97.86	99.78	98.81	99.95	99.88	99.72	99.23	99.40	100.20	99.05	101.46	99.67	91.88	99.74
K ₂ O/Al ₂ O ₃						0.83	0.38	0.01	0.11	0.01	0.01	0.01	0.01	0.22	0.14	0.38	0.05
Na ₂ O/Al ₂ O ₃						0.08	0.04	0.0	0.01	0.0	0.0	0.01	0.01	0.14	0.05	0.05	0.05

NG D: Ngakpu Dolerite
 BC: Busi Charnockites
 Am A: Amunga Amphibolites
 OK P: Okordem Pegmatite
 BAS: Bagga Schist
 IA: Garnet-mica-schist from Itu Agoi (After Ekuweme 2003b)

AK: Phyllite from Akpet 1
 UG: Siltstone from Ugbem
 OK: Sandstone from Okurike
 AG: Schist from Agoi Ibami
 IB: Gneiss from Ibogo

Table 3: Chemical Composition of Barite Samples from Calabar Flank, Oban Massif, Mamfe Embayment and Obudu Plateau Southeastern Nigeria

Wt%	AK		OK		AG		IB		IA		ET	ED	KO	NS	AT	ND	NK	EK	Ga	OS	AL	OKP	AZ ₁	AZ ₂
	1	2	1	2	1	2	1	2	1	2														
SiO ₂	5.55	5.54	73.70	72.89	6.58	6.62	3.61	3.62	2.19	2.21	11.00	14.00	9.30	1.80	<0.01	<0.01	8.60	11.65	<0.01	<0.01	1.20	9.40	5.70	3.29
Al ₂ O ₃	0.34	0.33	3.33	3.30	0.91	0.94	0.44	0.46	0.96	0.87	0.01	5.68	1.58	2.65	1.19	1.94	0.13	3.60	<0.01	1.36	1.25	1.84	9.06	10.62
Fe ₂ O ₃	0.04	0.05	1.07	1.09	0.09	0.07	0.14	0.13	0.15	0.13	0.49	5.82	0.41	0.35	0.31	0.56	0.37	3.11	0.23	0.24	0.25	0.99	9.14	9.67
TiO ₂	0.003	0.004	0.09	0.08	0.004	0.004	0.40	0.44	0.004	0.005	0.13	0.18	0.14	0.14	0.15	0.15	0.15	0.16	0.15	0.14	0.14	0.11	0.13	4.70
Na ₂ O	0.05	0.06	0.09	0.08	0.06	0.05	0.07	0.05	0.06	0.05	0.04	0.32	0.03	0.02	0.03	0.10	0.05	0.17	0.02	0.02	0.02	0.01	0.02	1.18
K ₂ O	0.002	0.001	0.79	0.78	0.02	0.03	0.004	0.004	0.04	0.03	1.39	1.11	0.63	0.36	1.39	0.83	0.83	0.87	1.01	0.83	1.11	0.22	1.40	0.25
CaO	0.09	0.09	0.05	0.05	0.05	0.05	0.08	0.07	0.07	0.06	0.80	1.20	0.60	1.40	0.80	1.40	1.40	0.90	<0.01	1.10	0.40	0.16	1.01	1.24
MgO	0.07	0.08	0.09	0.10	0.08	0.07	0.06	0.05	0.08	0.08	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.67	0.05	8.49
Ba	54.80	54.78	10.80	10.75	53.64	53.62	55.62	55.71	56.10	56.00	50.51	39.41	51.12	54.26	56.26	55.41	52.32	45.26	55.60	56.55	55.86	56.21	47.01	46.60
SO ₄	38.52	38.50	7.54	7.50	37.50	37.52	39.00	38.71	39.20	39.16	35.35	27.57	35.77	38.25	39.35	38.76	36.50	31.67	38.90	39.56	39.07	30.47	31.28	16.90
LOI	0.30	0.32	2.13	2.15	0.84	0.86	0.16	0.15	0.85	0.85	0.15	4.45	0.31	0.05	0.40	0.65	0.04	2.38	0.20	0.07	0.25	0.15	0.50	0.06
Total	99.76	99.73	99.68	98.75	98.77	98.83	99.58	99.43	99.64	99.49	99.89	99.75	99.90	98.29	99.90	99.82	100.40	99.78	96.14	99.88	99.56	100.23	100.10	94.30

AK: Barite vein in Akpet 1

OK: Barite vein in Okurike

AG: Barite vein in Agoi Ibami

IB: Barite vein in Ibogo

IA: Barite vein in Itu Agoi

ET: Barite vein in Okukuretet

ED: Barite vein in Edondon

KO: Barite vein in Okokori

NS: Barite vein in Nsakwon

AT: Barite vein in Atakpa

ND: Barite vein in Nde

NK: Barite Vein in Nkarasi

EK: Barite vein in Ekukunela

Ga: Gabu Barite sample

OS: Osina Barite sample

AL: Alifokpa barite sample

OKP: Okpoma barite sample

AZ₁: Azara barite sample (After Ajile, 1989AZ₂: Azara barite sample (After Bassey 1998)

CONCLUSION

Barite occurs in basement/sediment boundaries marked by unconformities and faults in the Calabar Flank/Oban massif and Mamfe Embayment/Obudu Plateau as well as within sedimentary rocks of Cretaceous age in Cross River State of southeastern Nigeria. The chemical composition of the barite ores shows that they are of high industrial quality and suitable for use as weighting agent in drilling mud. The chemical compositions of the host rocks suggest that the source of the mineralizing fluids which facilitated the formation of the barite are evaporates as indicated by the occurrence of large salt ponds at Okpoma in the study area. This paper has therefore, established the geological and structural features that facilitated the emplacement of barite ores in Cross River State. It has also used geochemistry to characterize and determine the genesis of barite ores and their industrial quality.

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