

MARINE ORIGIN OF NIGERIAN BRINES - A CONTRIBUTION FROM RECENT TRACE ELEMENT STUDY

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(Received 29 September 2000; Revision accepted 22 June, 2004)

ABSTRACT

Trace element analyses which employ the X – ray fluorescence (XRF) and pelletisation have been carried out on 17 salt samples extracted from Nigerian brines. Results of the analyses reveal that these samples, from the Albian – Turonian formations in the middle Benue and Anambra basins, have Sr values of between 148ppm and Ba values of between 105 ppm and 135 ppm. Enhanced values of Ni (9ppm), Co (4ppm), and Cu (35ppm), indicate close association with carbonate rocks from the area. Such carbonates were deposited during marine maxima. Co, Ni and Cu enrichment in the brines possibly resulted from marine scavenging at the ocean floor occasioned by Albian – Turonian marine effects. These marine effects on the middle Benue and Anambra basins and the tectonic activities of the area provided optimum marine conditions for Co, Cu and Ni enrichment. Similarity in geology and structures in the brine fields correlate well with similar NaCl contents in the salts extracted from the brines. Absence of rock salt in these fields, similar geology and chemistry of the salt samples from the brines point to a common marine source.

KEYWORDS: Marine, Scavengers, Glauconite, Albian, Turonian.

INTRODUCTION.

The origin of the Nigerian brine fields has generated interesting discussions among scientists in general and Nigerian scientists in particular. Among the various models, which are not what this paper aims at documenting, is the marine source. This is because the Benue valley and the associated sub-basins made up of Albian – Maastrichtian sediments, harbours over 90% of the brine fields recorded in Nigeria. Results of rock salt drilling in one of the southeastern Nigerian brine fields did not indicate any evidence to show that the brines do originate from any primary sources. Despite the 2-D and 3-D gravity models proposed for most of the structures in the Benue and Anambra valleys (Adighije, 1979) and Ajakaiye (1981), actual drilling for rock salt has generated negative results. It is important to note that the Nigerian brine fields have pronounced genetical and structural relationships that are amenable to a combination of geological, gravity and geochemical interpretations which may offer acceptable palaeoenvironmental model of the Nigerian brine fields.

The brine fields and their geological associations are given by Offodile (1976 and 1984) are summarized in Figure 2 as follows:

- (a) Lamurde anticlinorium -Middle Albian
- (b) Keana anticlinorium -Turonian
- (c) Abakaliki anticlinorium -Mid. Santonian to Maastrichtia

Each of these anticlinoria is associated with sub-basins that formed receptacles for marine and continental sedimentation in the Benue and Anambra valleys. These three structurally-related anticlinoria have associated brine fields as given in Figure 2. These are:

- (a) Ayaba and Todi field-Dadiya sub-basin.
- (b) Awe, Azara and Ribi fields - Awe and Wukari sub-basins.
- (c) Abakaliki, Ogoja, Uburu, Okposi,

Enyigba fields - Afikpo sub-basins.

This study aims at the examination of the trace element content of the salt samples recovered from 17 brine ponds and lakes in Benue and Anambra basins (Fig. 1). It is also intended to relate their enrichment or depletion in these elements to any particular palaeoenvironment and to their possible source. It is worthy of mention that there has not been any record of rock salt anywhere in Nigeria for now. Nor are there any salt mines. What we record are brine ponds and lakes from where, for over 1000 years, salt has been extracted traditionally for domestic consumption. Such traditionally extracted salt samples have serious contamination due to the ash used as filters.

METHOD OF STUDY

Samples were collected in 50 litre plastic containers and emptied into stainless steel cylinders measuring 0.5 m in diameter by 1 m in height. Period of collection was December to March, during cessation of the rains. These cylinders were allowed to stand for 48 hours to allow decantation of clear brine. Clear brine samples from the cylinders were decanted into stainless steel vats measuring 1.5 m in diameter by 0.5 m in height and left in the open, clean and airy hall for 7 days. As soon as salt crystals were observed, they were removed with long stainless steel spoons to avoid bodily contact with the samples. The scooped samples were dried in the sun until moisture tests gave negative results. The samples were stored in 250 ml flasks for analysis. 250 gm of samples from each location were ground into fine powder in agate mortar. 10 to 15 gm of such samples were bound with polyvinyl alcohol (OVA). The semi-paste samples were subjected to 10 tons/inch² load using 40 mm diameter and 5 mm thick pellets holders. Melinex films were used to cover the pellets before they were dried in an oven at 150C for 2 hours. The pellets were labelled and stored in sealable plastic bags for

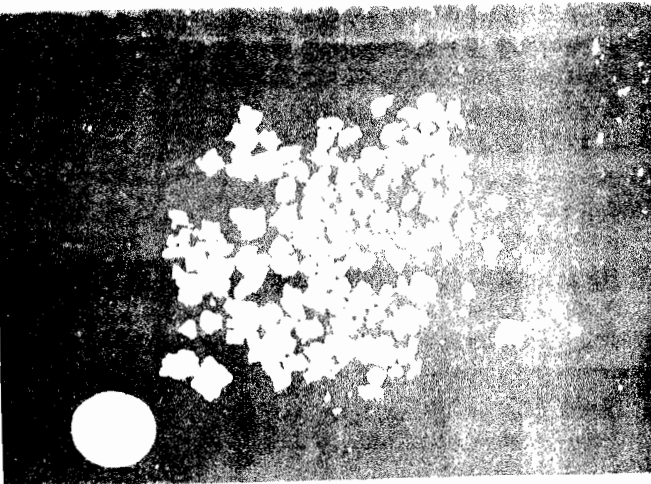


Plate 1 - Crystals of Salt from Uburu Brine

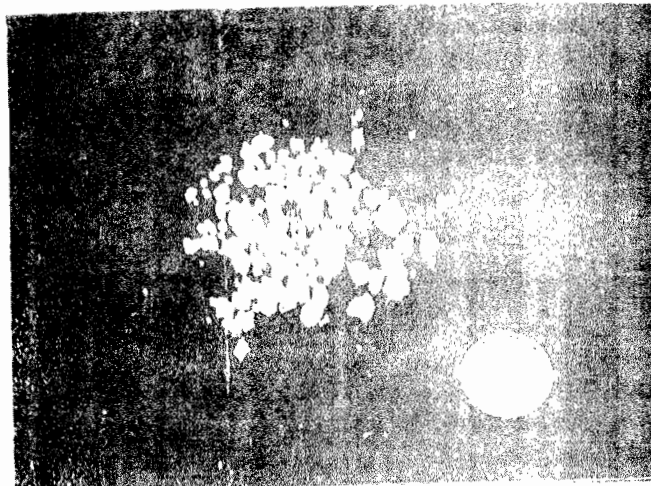


Plate 2 - Crystals of Salt from Akiri Brine

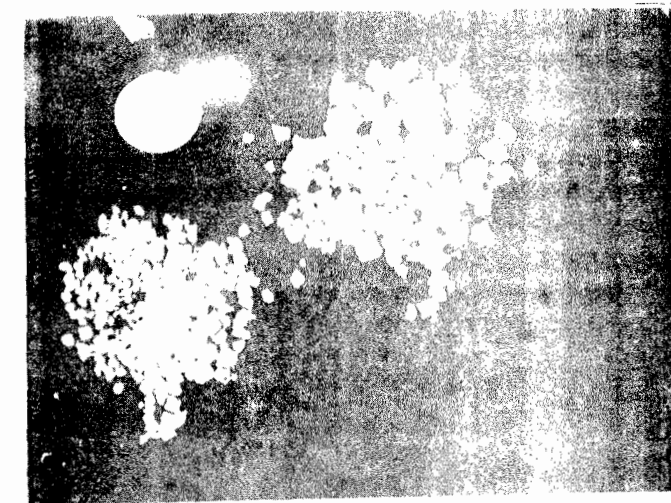


Plate 3 - Crystals of Salt from Ayaba Brine

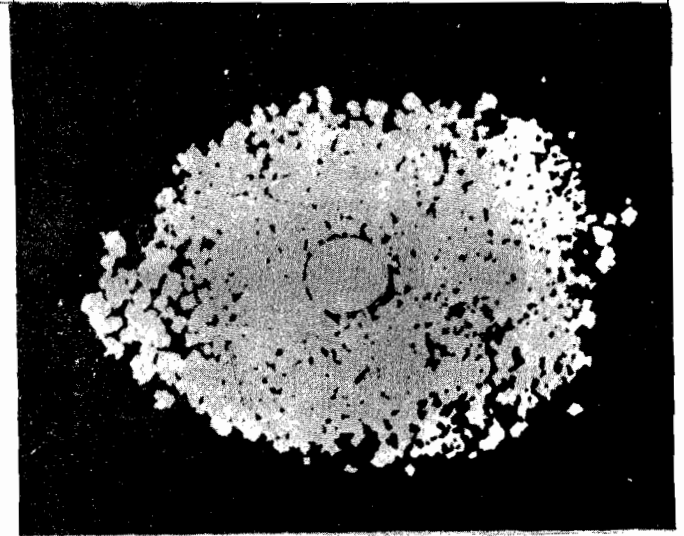


Plate 4 - Crystals of Salt from Keana Brine

University of Leeds. Standard monitors of similar compositions were test-run from time to time in the course of the analysis in order to ensure that the equipment was operating within the manufacturer's specified error limits. Values of trace elements were read off from an Elonex computer machine connected to the X-ray equipment. In all, 16 trace elements and total % NaCl contents were analyzed for in each sample.

RESULTS AND DISCUSSION.

Results of the chemical analysis of the salt samples in parts per million (ppm), are given in Table 1. Results of the analyses reveal that these samples, from the Albian-Turonian formations in the middle Benue and Anambra basins, have Sr values of between 148 ppm and 170 ppm and Ba values of between 105 ppm and 135 ppm. Enhanced values of Ni (9ppm), Co (4ppm), and Cu (35ppm), indicate close association with carbonate rocks from the area. Such carbonates were deposited during marine maxima. Plots of values for Co, Ni and Cu against Sr and Ba are shown in Figures 3,4, and 5.

A look at the plots of Co against Sr and Ba shows similar trends (Figs 3 & 4). Co concentrations tend to increase with Sr and Ba values hence fields as shown in Figure 3 & 4. Similarly plots of Ni against Ba and Sr have positive correlation as shown in Figs. 5 & 6. The similar results of the sample from Akiri brine (11) in the middle Benue valley to that of Okposi brine (3) in the Anambra basin (Fig 2), indicate possible genetic and palaeoenvironmental relationships. These locations are well over 400 km apart (Fig. 1), separated by different geological formations

On the other hand, Cu-Ba and Cu-Sr plots show negative correlation (Figs 7,8). The trends are paralleled and do indicate similar concentration/depletion processes for Cu and Sr. Uranium (U) was not recorded in any of the samples. However thorium (Th) values of between 3 and 5 ppm for all the samples indicate similar processes of The enrichment in the Benue Trough.

Carbonate rocks, with their attendant high Ba and Sr concentration, are formed during transgressive maxima

chemical analysis.

Four pellets were loaded at the same time into a Phillips PW 1400 model of an X-ray fluorescence machine at the laboratory of the Department of Earth Sciences,

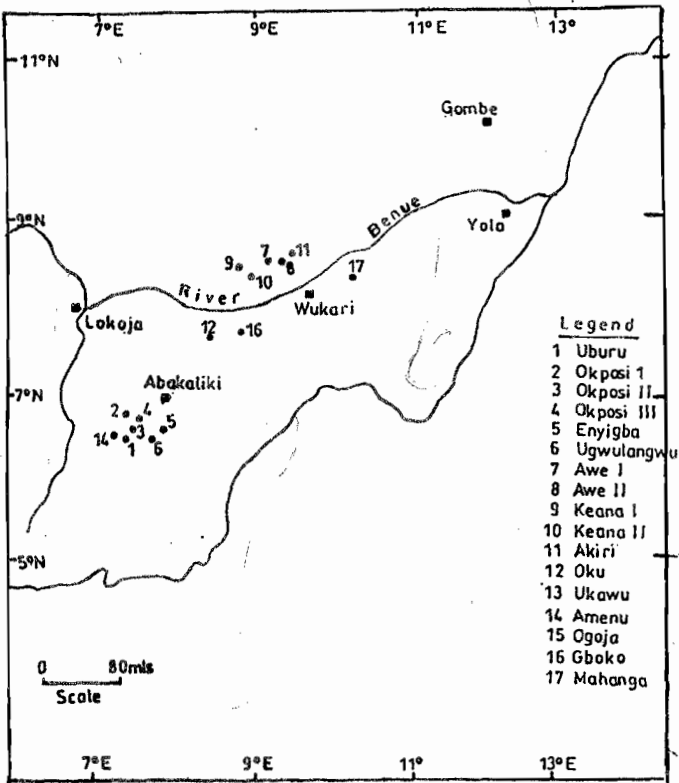


Figure 1 - Sample Locations Map

(Wray and Daniels, 1957). During such maxima shells and tests of marine organisms with aragonitic structure favour the inclusion of Sr, Ba and Pb than does calcitic shells. However when stabilization to calcite takes place, some of the Sr and Ba are retained while the rest are recycled into the sea water. Such losses contribute to relatively high Sr and Ba values in sea water already rich in NaCl. Thus the relatively high Sr and Ba values recorded from the salt samples from the brines in the Benue valley indicate possible marine palaeoenvironment. [average concentration of Sr and Ba in sea water. Sr 7.70 ppm (Culkin, F and Cox, R.A 1966); Ba 0.015 ppm (Hanor, J.S and Cham, L.H 1977)]. Odum (1957) maintains that saline sea water rich in Sr

and Ba leads to the precipitation of SrSO₄ and BaSO₄. Odum, (1957) also is of the opinion that SrSO₄ and BaSO₄ are later on replaced by SrCO₃, such replacements being greater in SrSO₄ than in BaSO₄. It is likely that the presence of barytes in the Benue valley has a lot to do with such precipitation in a marine setting.

The relatively high positive correlation between Ca and Sr in limestones in the Anambra Basin (Ibe, 1998), points to a possible transgressive maxima in the Benue Trough from where the samples were collected. It is worthy of note that limestones occur in all the locations where the brines were sampled.

Offodile (1976) has pointed out the marine characteristics of the brine fields based on sea water and brine sample analyses.

Offodile (1976) also noted similar regional

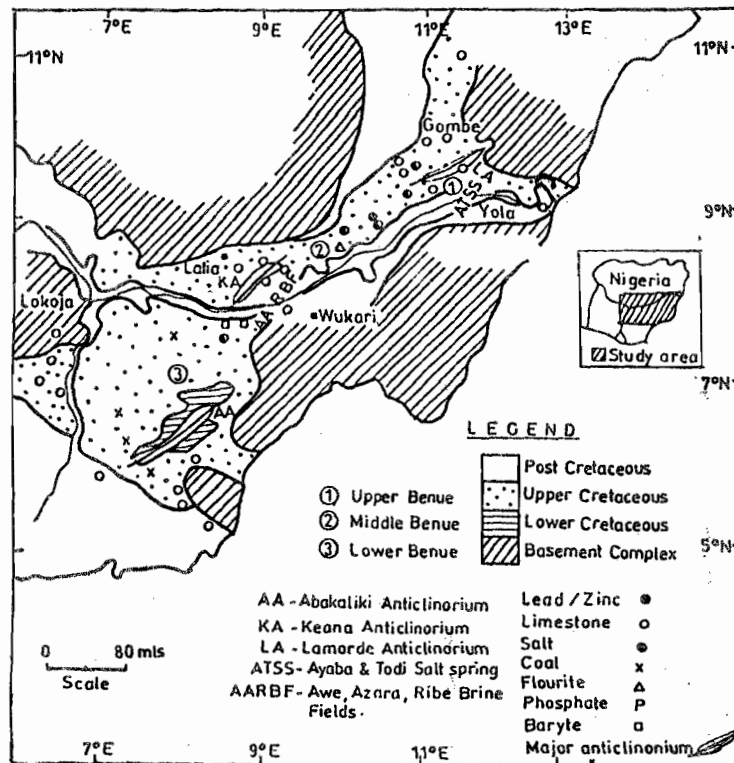


Figure 2 - The Benue Valley Brine Fields

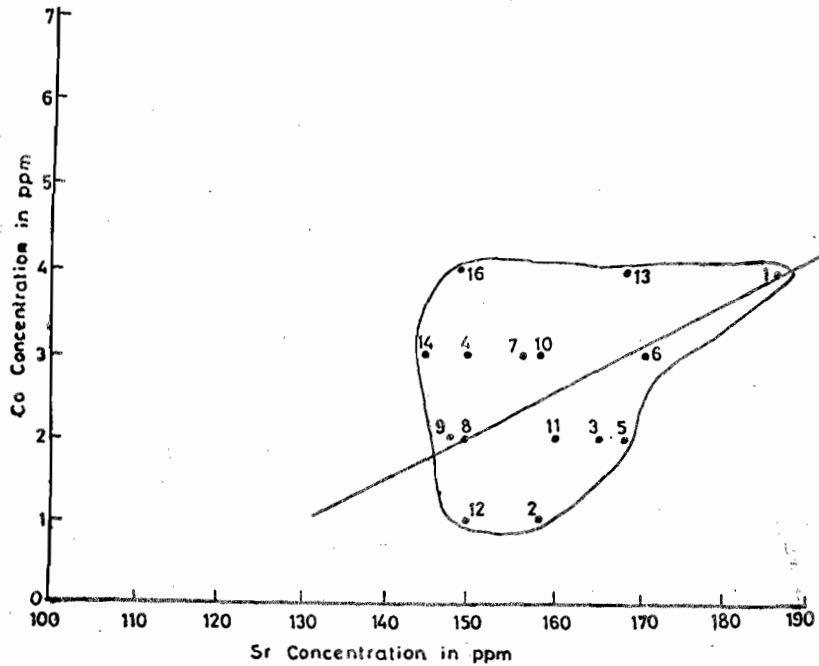


Figure 3 - Co-Sr Trend of Salts from Nigerian Brines

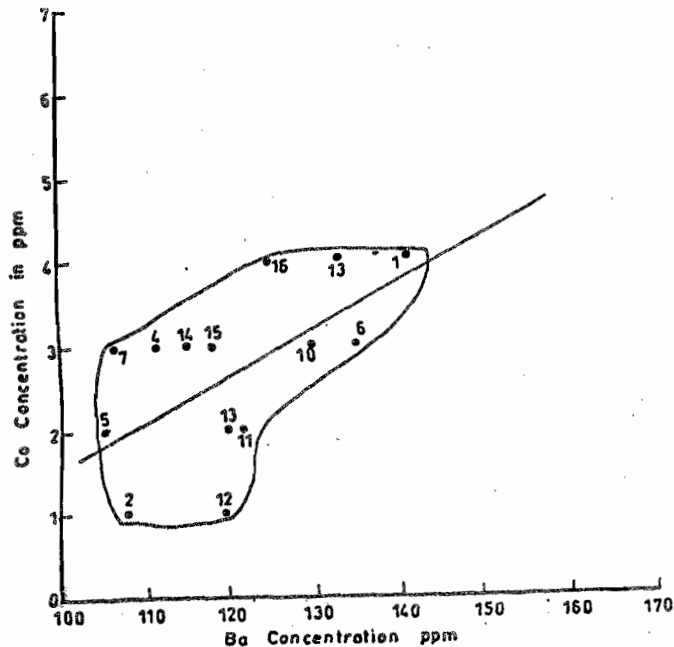


Figure 4 - Co-Ba Trend of Salts from Nigerian Brines

Gboko and Keana areas, Okposi, and Pindiga areas (middle Benue, southeastern Nigeria and upper Benue valleys respectively), the brines occur in transitional sandy to silty beds that are mappable.

Such relatively arenaceous beds resulted during the regressive phases of the late Albian to Turonian age. Bodies of sea water were trapped in sub-basins that are characteristic of the transitional beds of the late Albian to Turonian.

Furthermore electrochemical processes at the sea floor give either positive or negative charge to the floor. According to Goldberge (1954), when the floor is positively charged, then negatively-charged manganese micells are attracted. If however the floor is negatively charged, iron accumulates. Manganese dioxide then scavenges Ni and Cu while hydroxides of iron scavenge Co. Thus chemical scavenging at the sea floor in a purely saline marine setting leads to the concentration of Co, Ni and Cu.

The Asu River Formation (late Albian) in the Benue basin is rich in brines. Despite the occurrence of lead and zinc mineralisations in the areas rich in brines, the result of the study does not show any lead or zinc enrichment. Thus the meteoric origin of the brines and the resultant salt may not be acceptable. Pb values of between 1 and 5 ppm in all the analysed samples confirms this proposition. It is worthy of note that there is no way that the dynamics of sub-surface fluids would not influence the chemistry of brines. Thus minor traces of meteoric elements may be found in analysis of this type, hence the 1 ppm to 5 ppm Pb values recorded.

Albian to Turonian marine transgressions and regressions in the study area not only provided saline water but also made terrigenous sediments available

trends to the brine fields. For instance the Awe Formation of Albian age in the middle Benue valley has been correlated with Abakaliki shales and Odukpani Formations of southeastern Nigeria (Fig 9). Furthermore the same Awe Formation has been correlated with the Yolde Formation of the Upper Benue valley (Fig.9) in the northeastern Nigeria (Offodile, 1976). From drill data in

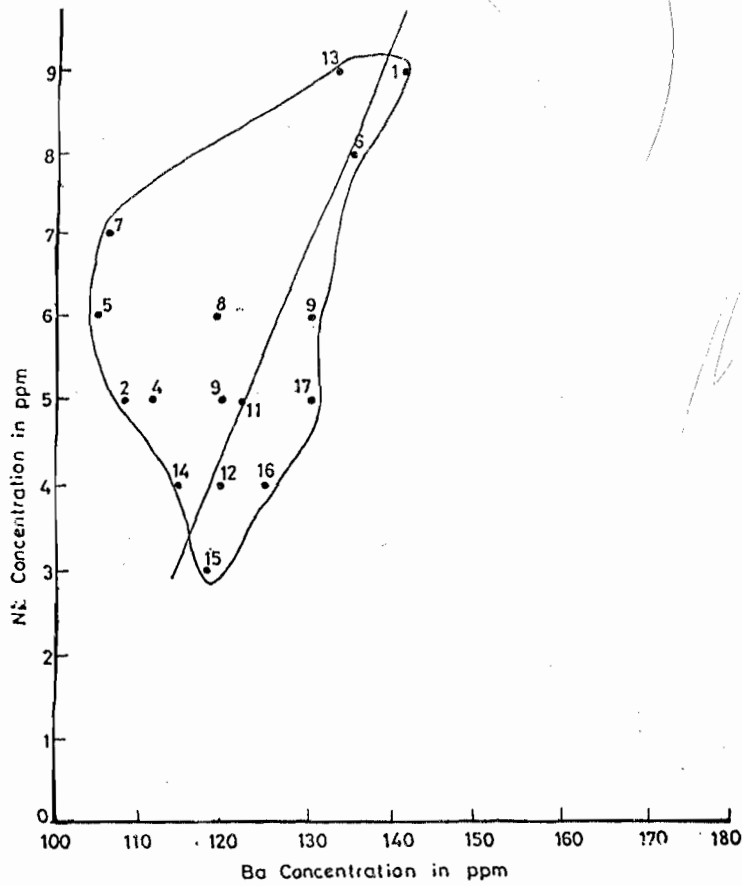


Figure 5 - Ni-Ba Trend of Salts from Nigerian Brines

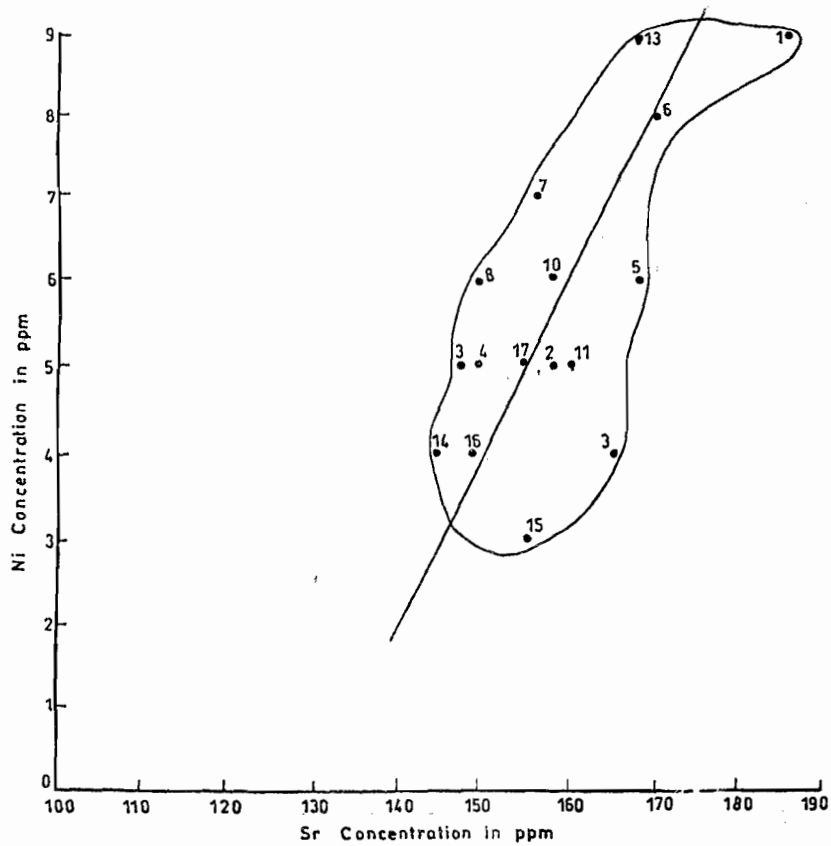


Figure 6 - Ni-Sr Trend of Salts from Nigerian Brines

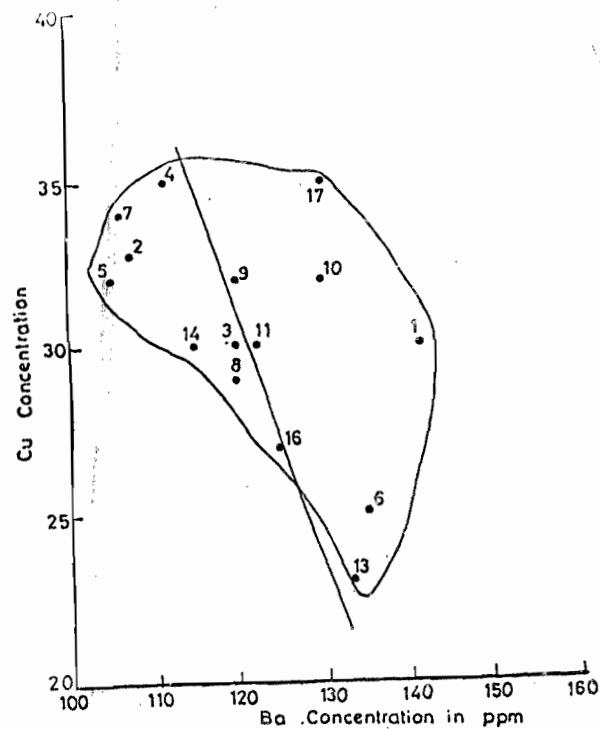


Figure 7 - Cu-Ba Trend of Salts from Nigerian Brines

for the storage of the brines during the folding episodes in the valley. Such folding led to the migration of the brines into the porous sands formed during regressive phases. The issuing of the brines from the flanks of the anticlinal structures in the Benue valley has been documented by Offodile (1976 and 1984). Uburu and

Okposi brines are some of the cases of warm brine springs that issue from such flanks. It is evident that the over-pressured brines flow out through fault planes that characterized the Benue valley.

In addition the presence of migrating brines into sandstones cause low gravity effect. Where such sand bodies have symmetrical shapes, they result into 3-D gravity residuals. Hence rock salt models and interpretations, pose serious conclusions if geologic, chemical and palaeoenvironmental analyses are not carried out before applying the models. In the valley, most of the gravity anomalies are of the 2-D type as pointed out by Adighije (1979). Kogbe (1981) has attempted to correlate the stratigraphic sequence of the various provinces in the Benue Trough and has confirmed their genetic relationships in terms of biostratigraphy.

The absence of proven salt domes in Nigeria despite the preponderance of such 3-D gravity anomalies implies that the salt dome models should be

Table 1: Result of Trace Element Analysis of Salts from Nigerian Brines

No.	Field	Sc	V	Cr	Co	Ni	Cu	Zn	Rb	Sr	Ba	Pb	Th	U	%NaCl
1	Uburu	0	1	0	4	9	30	6	4	186	141	0	5	0	99.87
2	Okposi 1	0	2	0	1	5	33	4	2	158	108	1	4	0	99.85
3	Okposi 2	0	1	0	2	4	30	5	3	165	120	1	5	0	99.93
4	Okposi 3	0	1	0	3	5	35	4	3	150	111	1	5	0	99.88
5	Enyigba	0	1	0	2	6	32	5	3	168	105	5	4	0	99.80
6	Ugwulangu	0	1	0	3	8	25	6	4	170	135	2	4	0	99.91
7	Awe I	0	1	0	3	7	34	5	3	156	106	1	4	0	99.75
8	Awe II	0	2	0	2	6	29	5	4	150	119	1	3	0	99.75
9	Keana I	0	1	0	2	5	32	6	3	148	120	1	4	0	99.88
10	Keana II	0	1	0	3	6	32	5	4	158	130	2	4	0	99.87
11	Akiri	0	1	0	2	5	30	5	3	160	122	1	5	0	99.91
12	Oku	0	1	0	1	4	29	4	4	150	120	1	3	0	99.88
13	Ukawu	0	1	0	4	9	23	5	4	168	133	2	4	0	99.92
14	Amenu	0	2	0	3	4	30	4	4	145	115	2	5	0	99.91
15	Ogaja	0	1	0	3	3	30	3	4	155	118	1	4	0	99.72
16	Gboko	0	2	0	4	4	27	4	4	149	125	2	3	0	99.78
17	Mahanga	0	2	0	3	5	35	5	5	150	130	1	4	0	99.73

NOTE: All values except %NaCl are in Parts Per Million (PPM)

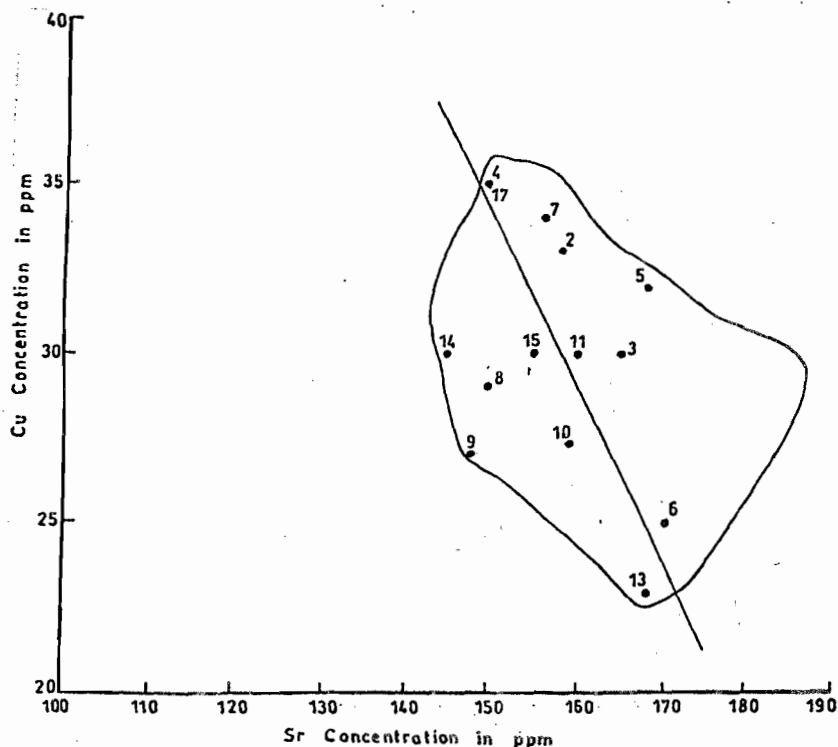


Figure 8 - Cu-Sr Trend of Salts from Nigerian Brines

CHRONO STRATIGRAPHY	LITHO- STRATIGRAPHY				
	BENIN FLANK	ANAMBRA BASIN	CALABAR FLANK	LOWER-MIDDLE BENUE	UPPER BENUE
MAESTRICHIAN	Araromi Shale	Nsukka Fm. Ajoji Sandstone Maru Formation Enugu & Nkporo Sh.	Nkporo Shale		Fika Shale
CAMPANIAN					
SANTONIAN					
CONIACIAN		Awgu Formation		Awgu Formation	Sekule Fm. Numanba Sh.
TURONIAN		Eze Aku Formation	Eze Aku Formation	Eze Formation Makurdi Fm. Keana Fm. Awe Fm.	Pindiga Fm. Yalde Fm.
CENOMANIAN			Odukpai Fm.		
ALBIAN		Asu River Group	Asu River Group Mfamosing Lst. Awi Fm.	Asu River Group	Bima Sst.
APTIAN		Salt ?			

Figure 9- Lithostratigraphic Correlation of some of the Sedimentary Sub-basins of Nigeria.

(Adapted from Reyment, 1980 ; Kogbe, 1981 a and b ; Petter, 1982)

applied with utmost caution in relation to the Nigerian brine fields. The low values obtained for Pb in the samples suggest that the galena occurrences in the Benue trough are possibly of different palaeoenvironments.

Similar genetical models for the brine and lead occurrences may mean contamination of the salts derived from the brines. The perfect cubic crystals obtained for all the salt samples (Plates 1 to 4) and the over 99.80% NaCl content for all the samples, show that salt from Nigerian brines, when processed, are likely to have high purity required of industrial salts. Results of

this study have confirmed the submissions of Offodile (1976), Uzuakpunwa (1981) and Kogbe (1981) on the marine origin of the Nigerian brines and their biostratigraphic relationships respectively.

CONCLUSION

Trace element analysis of salt samples extracted from the Nigerian brines in the Benue valley reveals over 99.80% NaCl content, zero U, Cr, Y, Zr, Nb, Sc and very low values in U and Pb. However the presence of glauconite (a mineral that forms exclusively

under marine conditions), in calcereous rocks associated with the brines, indicate transitions from marines palaeoenvironment (Goldberge, C.D. (1954). Also chemical scavenging actions of manganese oxide and iron hydroxide in a purely marine setting possibly led to the concentrations of Cu, Co and Ni in the salt samples analysed. It is possible that these elements were concentrated by marine organisms during the transitional stages and later associated with the bodies of sea water when the sea receded.

Association of the salts with Sr and Ba also point to marine source for brines. This is because of the ease with which aragonitic limestones stabilize to calcitic limestones in a marine setting. The failure of gravity dome models proposed for the brine fields in Benue valley and southeastern Nigerian brine fields means that alternative models for the existence of salt in the Nigerian brine fields be designed. Sticking to domal models may mean primary salt deposits. Such salt deposits have not been confirmed by any drilling done in the study area. Geochemical models may have convincing data as past and present studies, biostratigraphy, regional setting and structure have shown.

ACKNOWLEDGEMENT

The authors are grateful for the funds made available by the World Bank, through the National Universities Commission of Nigeria.

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