Factor analysis of the distributions of trace and minor elements, elemental oxides and clay minerals in the Mfamosing Limestone, southeastern Nigeria

N. U. Essien[*1] and A. E. Edet[1]

ABSTRACT

The R-mode factor analysis was carried out using trace and minor elements, elemental oxides and clay minerals as the variables from the Mfamosing Limestone deposits. This was mainly to relate the geochemical/clay mineralogical data to specific geologic processes. Results, based on a 4-mode factor, showed that diagenesis, coprecipitation effects and lithology significantly influenced the distributions of elements, elemental oxides and clay minerals in the deposits.

INTRODUCTION

The Mfamosing Limestone is the northernmost carbonate deposit in the South Atlantic. Its deposition took place during the initial marine transgression into the South Atlantic in Mid-Albian times. Considerable amount of work has been carried out on the Mfamosing Limestone covering aspects of the biostratigraphy (Dessauvagie, 1968; Fayose, 1978, Ramanathan and Kumaran, 1981), depositional environment (Reijer and Petters, 1987, Nair, et al 1992, Akpan, 1990), diagenesis (Oti and Koch, 1990), sequence stratigraphy (Petterfs and Reijer, 1995), chemical composition (Ekweme, 1988) and geotechnics (Edet and Essien, 1994).

Most of these previous investigations were based on the limestone exposure at the type section in Calcemco quarry, located at Mfamosing, Nigeria (Fig 1). In order to address the above deficiency and to further complement on the existing knowledge, a regional field mapping of the deposit was carried out along the depositional strike. During the mapping, samples were collected at Mfamosing (MF), Odukpani (OD), Okoyong Usang Abasi (Ou), Ikot Okpora (OK), and Agoi Ibami (AI) [Fig. 1]

Representative samples from each location were analyzed to determine their major and minor elements, elemental oxide and the clay types. The results were subjected to multivariant and R-mode analyses so as to determine the geological processes responsible for the observed distribution patterns.

REGIONAL GEOLOGY AND STRATIGRAPHY

The Mfamosing Limestone was deposited in the Calabar Flank. Structurally, the Calabar Flank represents that part of the foundered Southern Nigerian Continental margin. It is dominated by a system of NW-SE trending step fault system that resulted in the formation of a horst (Ituk high) and a trough (Ikang trough) structure within the area (Fig 1). The horst became the site for carbonate sedimentation while clastic deposition took place in the graben. The Ikang trough for most part of its depositional history was the site of active clastic sedimentation while the Ituk high was a stable carbonate platform where about 450m of the Mfamosing Limestone accumulated (Reijer and Petters, 1987).

Sedimentation started in the Calabar Flank with deposition of fluvio-deltaic clastics of probably Aptian age on the Precambrian crystalline basement complex, the Oban Massif (Fig. 1). These sediments belong to the Awi Formation (Adeleye and Fayose, 1978). The earliest marine transgression into the Calabar Flank occurred in the Mid-Albian times with the deposition of platform carbonate of the Mfamosing Limestone. This carbonate body was deposited in a variety of depositional environments.

The Mfamosing Limestone is overlain by a thick sequence of black to gray shale unit, the Ekenkpon Formation. This formation is characterized by minor intercalation of marls, calcareous mudstone and oyster beds. This shale unit was deposited during the late Cenomanian-Turonian times.

The Ekenkpon Shales are overlain by a thick marl unit, the New Netim Marl. This unit is nodular and shally at the base and is interbedded with thin layer of Shales in up-section. Foraminiferal (Nyong, 1985) and Coccolith evidence (Perch – Nielson and Petters, 1981) suggest Early Conciacian age for this marl unit.

The New Netim Marl is uncoformably overlain by a carbonaceous dark gray shale, the Nkporo Formation (Reyment, 1965).

[*]Corresponding author. Email: nseessien@yahoo.com
Manuscript received by the Editor February 15, 2007; revised manuscript accepted October. 17, 2007.
[1]Department of Geology University of Calabar , Calabar, Nigeria

This shale unit was deposited during the late Campanian – Maastrichtian times and caps the Cretaceous sequence in the Calabar Flank. It is overlain by a pebbly sandstone unit of the Tertiary Benin Formation.

MATERIALS AND METHODS

The samples obtained during this study were then subjected to various chemical analyses. These include trace and minor elemental determination (AAS) and clay mineralogy (XRD). The elemental oxides were calculated from results obtained. To differentiate all the clay mineral phases present, x-ray analyses were carried on:

(a) untreated samples

(b) after glycolation for 5 days

(c) after heating to temperature of 550^{0}C

The trace and minor elements analyzed for include Be, Cr, Nb, Ni, Rb, Sr, V, Y, Zn, and Zr. The elemental oxides calculated were CaO, Na_2O, K_2O, P_2O_5, FeO, CO_2, and H_2O. others include SiO_2, TiO_2, Al_2O_3, MnO.

RESULTS AND DISCUSSION

Results obtained from the determinations of trace and minor elements of the Mfamosing Limestone are shown in Table 1 while the calculated values of elemental oxides are shown in Table 2.

X-ray diffractogram of clay minerals from the different locations are as shown in Fig 2. The correlation coefficient between variables and R-mode results are presented in table 4 and 5.

When compared with the average trace and minor elemental abundance in carbonate rocks, the trace and minor element present in Mfamosing Limestone depicted lesser values (Mason, 1966). However, Ba, Nb and Rb indicated higher values.

Also, the general abundance of major elemental oxides in the Mfamosing Limestone is below average values obtained in carbonate rocks.

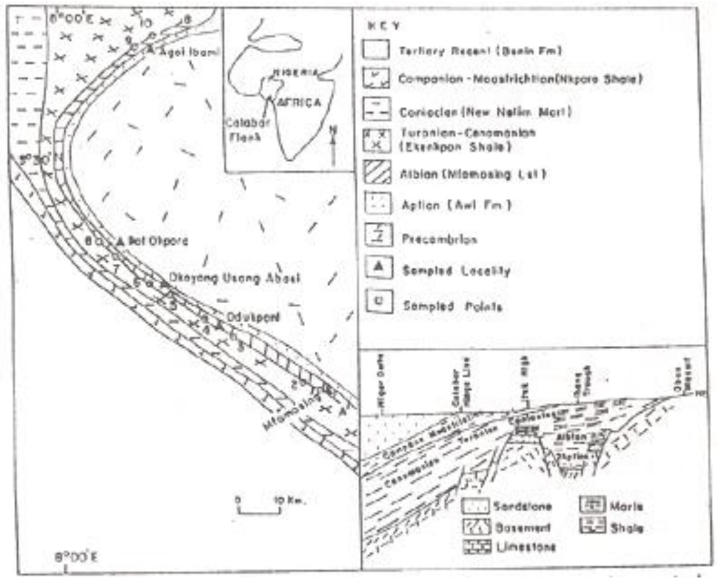

Fig 1. Sample location map and Structural elements and conceptual subsurface distribution of Cretaceous sediments in the Calabar Flank

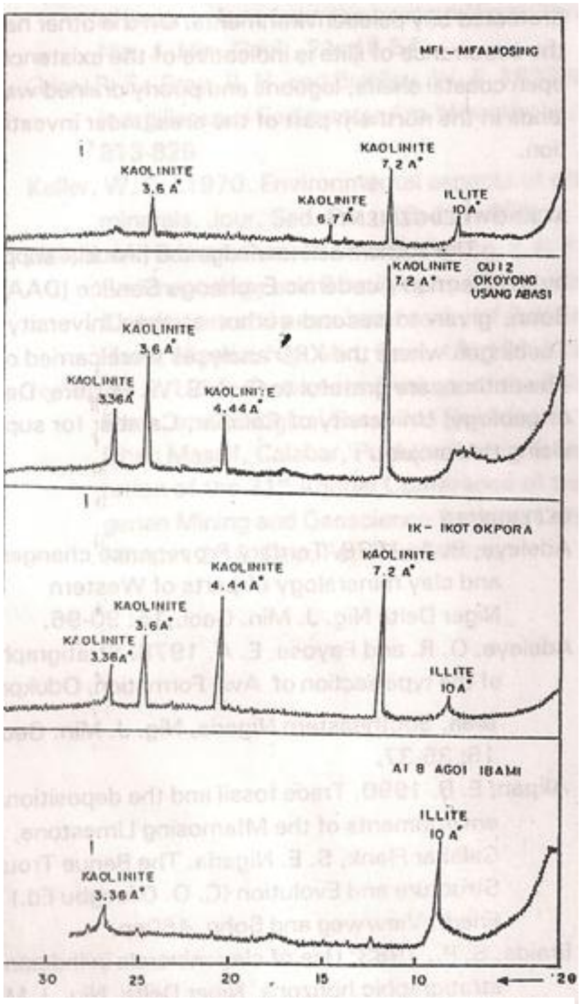

Fig. 2. X-ray diffractogram of clay minerals from the different locations

Table 1 .Abundance of trace and minor elements in the Mfamosing Limestone

Sample point	Sample Code	Location	Ba ppm	Cr ppm	Nb ppm	Ni ppm	Rb ppm	Sr ppm	V ppm	Y ppm	Zn ppm	Zr ppm
1.	MF1	Mfamosing	9	0	4	0	8	375	6	4	0	18
2.	MF2	-	0	0	2	0	6	256	9	2	6	1
3.	OD1	Odukpani	191	0	6	2	27	340	14	7	12	93
4.	OD2	-	0	0	2	0	9	286	6	2	0	2
5.	OU1	Okoyong Usang Abasi	3	0	3	0	6	330	7	3	4	4
6.	OU2	-	0	0	2	0	16	402	10	9	20	9
7.	OK1.	Ikot Okpora	118	0	4	1	36	467	24	11	3	40
8.	OK2	-	9	0	2	0	10	428	6	4	4	6
9.	AI 1	Agoi Ibami	226	0	4	0	56	225	8	15	1	36
10.	AI 2	-	72	0	2	0	26	240	6	13	0	14
Average abundance of trace and minor elements in the Mfamosing Limestone =			62.8	0	3.1	0.3	15	344.9	9.8	7.0	5.0	22.3
*Average abundance of trace and minor elements in Carbonate rocks =			20	11	0.3	20	20	610	20	30	20	19

*Mason (1966)

Table 2. Elemental oxides of the Mfamosing Limestone.

Sample point	Sample code	Locality	SiO_2 %	TiO_2 %	Al_2O_3 %	Fe_2O_3 %	MnO %	MgO %	CaO %	Na_2O %	K_2O %	P_2O_5 %	FeO %	CO_2 %	H_2O %
1	MF1	Mfamosing	4.101	0.026	0.573	0.226	0.052	0.380	52.286	0.000	0.093	0.069	0.000	0.000	41.360
2	MF2	Mfamosing	0.000	0.011	0.222	0.137	0.074	0.257	55.326	0.000	0.014	0.051	0.000	0.000	42.100
3	OD1	Odukpan	13.226	0.106	2.841	3.332	0.115	2.477	39.915	0.034	0.653	0.199	0.000	0.000	36.080
4	OD2	Odukpan	0.856	0.019	0.412	0.217	0.033	0.331	54.421	0.000	0.045	0.094	0.000	0.000	42.870
5	OU1	Okoyong Usang Abasi	3.130	0.021	0.488	0.383	0.035	0.295	52.995	0.000	0.041	0.069	0.000	0.000	41.460
6	OU2	Okoyong Usang Abasi	4.008	0.055	1.149	1.210	0.048	0.449	50.508	0.000	0.226	0.276	0.000	0.000	40.850
7	OK1	Ikot Okpora	25.508	0.084	5.071	0.623	0.018	0.278	36.253	0.000	1.029	0.066	0.000	0.000	30.240
8	OK2	Ikot Okpora	4.244	0.o18	0.546	0.257	0.013	0.138	52.228	0.000	0.144	0.071	0.000	0.000	41.400
9	Al1	Agoi Ibami	17.323	0.072	2.786	0.615	0.103	0.319	42.448	0.000	1.387	0.183	0.000	0.000	34.140
10	Al2	Agoi Ibami	6.093	0.032	1.381	0.261	0.070	0.420	50.147	0.000	0.577	0.107	0.000	0.000	40.040
	Average abundance of elemental oxides in the Mfamosing Limestone		7.849	0.044	1.547	0.726	0.056	0.552	48.656	0.0034	0.4209	0.1824	0.000	0.000	39.054
	*Average abundance of elemental oxides in carbonate rocks		5.19	0.06	0.81	0.54	-	7.89	42.57	0.05	0.33	0.04	-	41.54	0.77

*From Mason, 1966.

Table 3. Abundance of clay minerals in the Mfamosing Limestone.

Sample points	Sample Code	Locality	Kaolinite	lllite	Smectite	Mixed Layer
1	MF1	Mfanosing	60	5	30	5
2	MF2*	Mfanosing	50	30	-	20
3	OD1	Odukpan	60	30	5	5
4	OD2	Odukpan	85	5	5	5
5	OU1	Okoyong Usang Abasi	50	40	-	10
6	OU2*	Okoyong Usang Abasi	60	20	-	20
7	OK1	Ikot Okpora	80	10	-	10
8	OK2*	Ikot Okpora	80	10	-	10
9	Al1	Agoi Ibami	-	90	-	10
10	Al2*	Agoi Ibami	5	90	-	5
Average abundance of clay minerals in Mfamosing Limestone			53	33	4	10

*Samples in clay mineral diffractogram (Fig. 2)

Table 4 . Correlation matrix of trace and minor elements, elemental oxides and clay minerals in the Mfamosing Limestone.

	Ba	Cr	Nb	Ni	Rb	Sr	V	Y	Zn	Zr	SiO_2	TiO2	AI2O3	Fe2O2
Ba	1.00000													
Cr	.53274	1.00000												
Nb	-29398	-51153	1.00000											
Ni	.11567	.32692	.43825	1.00000										
Rb	.61348	.59694	-02232	.42347	1.00000									
Sr	.57451	.70369	-64615	.02504	.42919	1.00000								
V	.19413	-05286	.43087	.63210	.30665	.00319	1.00000							
Y	.21264	24292	.20904	.64544	.74691	.09077	.49062	1.00000						
Zn	-02358	.21926	.23737	.85941	.27660	-08236	.49542	.69477	1.00000					
Zr	.61203	66176	-01150	.70697	.70721	.62.687	.45348	.59930	.53972	1.00000				
SiO_2	.57674	49883	.12094	.58325	.87091	.45755	.67729	.71115	.38606	.78459	1.00000			
TiO_2	43715	46121	.21144	.86122	.71413	.33004	.66166	.80135	.75163	.90231	.82316	1.00000		
AI_2O_3	.54427	.55840	.08450	.68456	.84132	.46704	.70514	.73798	.49573	.83814	.97972	.88805	1.00000	
FeO	.14661	-03163	.58358	.55199	.21519	-03570	.37859	.23812	.21299	.48927	.29357	.53713	.33435	1.00000
MnO	-08182	-27170	.51988	.22729	.23923	-36165	.00573	.31671	.09027	.10586	.02055	.21243	.02750	.58698
MgO	.18801	-03922	.45402	.28897	.08791	.05207	.12402	-05329	-11435	.37052	.12055	.26689	.13532	.90568
CaO	-58086	-49289	-18961	-65271	-85245	-45182	-68039	-70039	-39905	-84656	-97819	-87252	-97546	-47637
Na_2O	.62464	.87825	-65251	.01089	.51887	.92605	-14488	.05162	-11062	.61647	.43348	.29990	.45155	-03721
K_2O	.67864	.67480	-10750	.42603	.98367	.55987	.34040	.69785	.26759	.77680	.90634	.73354	.88313	.19273
P2O6	.41644	.45890	-36204	-08079	48379	.68680	-14216	18711	-18876	.47250	.37644	.31085	31108	.35882
H2O	-57829	-53158	-08641	-57952	-88187	-49428	-65771	-70616	-38016	-80660	-99500	-82981	-98171	-30351
Kaolinit	-39633	-16498	.30494	.34548	-44798	-39428	.33770	-25995	.28895	-17377	-15395	-00840	-08277	.10215
Lllit	.18960	.06265	-09851	-25306	.45889	.11473	-36392	.34519	-23800	.04381	.11826	-02334	.04745	-05864
Smectie	.21121	.17192	.12073	.03390	.02817	.45332	-03842	-16556	-16842	.41427	.10729	.12912	.08731	.38407
Maxlayer	.21956	.03262	-01669	.09487	.06746	.34145	.21256	-20866	-04971	.38254	.12782	.28953	.16214	.60288
Calcite	-18245	-33102	-25754	-53444	-58350	-36427	-30562	-43052	-29600	-69345	-62676	-66903	-63228	-56091
Quartz	-11137	-06443	.07643	.06572	.04912	.03603	.58315	.05591	-03170	-05589	.36423	.04253	.34321	-20622
LOI	-60332	-61738	-02597	-56665	-89711	-53256	-59822	-67152	-35302	-81318	-98548	-81954	-97686	-27841

	Mno	MgO	CaO	NaO	KO	PO	HO	Kaolinite	lllite	Smectite	Mixlayer	Calcite	Quartz	LOI
Mno	1.00000													
MgO	.55448	1.00000												
CaO	-13713	-30722	1.00000											
Na2O	-28062	.07521	-43456	1.00000										
K2O	.12718	.08849	-88547	.62745	1.00000									
P2O5	17040	.36385	-38495	.67813	.50428	1.00000								
H2O	-06532	-13698	.97856	-47750	-9203	-35271	1.00000							
Kaolinit	-36136	-02716	13619	-39849	-43552	-51673	.19516	1.00000						
lllte	.53212	.04492	-10384	.18280	.39605	.34802	-14999	-91682	1.00000					
Smectite	-00007	.54690	-19425	.38908	.10167	.39260	-11877	-16041	-04361	1.00000				
Mixlayer	-39348	.58950	-25375	.26821	.11311	.58929	-19143	-19438	.00976	.33105	1.00000			
Calcite	.32601	.48161	.69455	-35052	-59100	-44859	.64391	.09973	-09973	-34490	-31359	1.00000		
Quartz	-24314	-26155	-27155	-06008	.10810	-31748	-36528	-14049	-14049	-29316	-03398	-00911	1.00000	
LOI	-02925	-12820	.96888	-54928	.93978	-38124	.99330	.19652	-15043	-12366	-16959	.63312	-34073	1.00000

Table 5. Four factors for trace and minor elements, elemental oxides and clay minerals in the Mfamosing Limestone.

Section 1

Row	1	2	3	4
Ba	0.3935	-0.5845	-0.1397	-0.2106
Cr	0.4063	-0.7943	-0.0096	-0.0179
Nb	0.2837	0.3253	0.3253	0.-897
Ni	0.8081	0.2246	0.2161	0.2898
Rb	0.7889	-0.3072	0.0124	-0.4761
Sr	0.2194	-0.9183	0.1756	-0.0199
V	0.7578	0.2087	0.0318	0.3929
Y	0.8342	0.1456	-0.1086	-0.3131
Zn	0664	0.2539	-0.07997	0.2520
Zr	0.7716	-0.4052	0.3951	0.0012
SiO^2	0.9284	-0.2673	0.0243	-0.0856
TiO_2	0.9206	-0.0766	0.2603	0.0307
AL_2O_3	0.9545	-0.2661	0.0493	-0.0073
Fe_2O_3	0.3518	0.2747	0.8646	0.0388
MnO	0.1648	0.5401	0.5046	-0.5847
MgO	0.1033	0.1176	0.9266	-0.0102
CaO	-0.9246	0.2323	-0.2121	0.0752
Na_2O	0.2089	-0.9350	0.1583	-0.1327
K2O	0.7961	-0.4324	0.0242	-0.1327
P_2O5	0.1216	-.05827	0.5145	-0.3998
H_2O	-0.9221	0.2964	0.0560	0.1142
Kaolinite	0.0123	0.3115	-0.0565	0.8911
Lllite	0.0293	-0.0348	-0.0229	-0.9709
Smectite	-0.0425	-0.3445	0.6709	0.0905
Mixed layer	0.0759	-0.1689	0.7306	-0.029
Calcite	-06116	0.1124	-0.4883	0.0890
Quartz	0.3244	0.0360	-0.4023	0.2628
LOI	-0.9004	0.3651	-0.0467	0.1136

Percent of Variation for Rotated Factors

Factor 1 37.54234

Factor 2 16.87846

Factor 3 14.42293

Factor 4 11.65426

SiO_2, Al_2O_3, Fe_3O_2, K_2O and P_2O_2 values obtained from the analyses are above average value in carbonate rocks. The below average abundance of most of the trace and minor elements and elemental oxides in the Mfamosing Limestone is as a result of losses during intense diagenesis. The Mfamosing Limestone is characterized by overprinting of diagenetic events (Essien, 1996). CaO values (52.286-55.326%) is highest at Mfamosing area, the type locality of the Mfamosing Limestone. This high state of purity indicates its suitability in various industrial applications such as the manufacture of paint, Portland cement and fertilizer. The R-mode factor analysis was first carried out by determining the relationships between possible variables (trace, minor elements, clay minerals and elemental oxides) by grouping them into association. These possible variables are then grouped into associations based on correlation coefficient (Tables 4 and 5). In order to minimize variance, factor loading were rotated according to varimax variation (Kaiser, 1958). In this study, a 4-factor model was chosen since the variables with loading exceeding 0.5 are considered significant of a particular factor. The associations for the model for the orthogonal varimax solution include:

Factor 1. Ni, Rb, V, Y, SiO_2, TiO_2, Al_2O_3

Factor 2. Nb, MnO

Factor 3. Fe_2O_3, MgO, Smectite, mixed layer, P_2O_3

Factor 4. Kaolinite

Factor 1.This accounted for 37% of variance in the data for the model. The association of components in this factor represents trace and minor elements such as Y, V, Zr, Ni, Rb, and T , which could substitute aragonite and calcite during diagenesis.

Factor 2. This factor explained 18% of data variability and, presumably, the associations Nb-Mn indicate co-precipitation of the elements

Factor 3. This accounted for 14% of variance in the data for the model. It is interpreted to represent lithology factor of mainly clay component.

CONCLUSION

This preliminary study has demonstrated the usefulness of factor analysis in determining variables that influence the distribution of trace and minor elements, elemental oxides and clay minerals in the Mfamosing Limestone. The study has identified diagenesis, mainly through substitution, co-precipitation and lithology as factors influencing elemental and clay mineral distributions in the rock formation.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the DAAD Research fellowship extended to the second author in Germany.

REFERENCES

Adeleye, D. R. and. Fayoso E. A (1978). Stratigraphy of the type section of Awi Formation, Odukpani Area, South-Eastern Nigeria, *Nigeria Journal, Min, Geol*.15:35-37

.Akpan, E. B. (1990).Trace fossil and depositional environments of the Mfamosing Limestone, Calabar Flank, SE Nigeria. In: The Benue Trough Structure Evolution,(Ofoegbu, C. O. ed.) Friedr. Vieweg and Sohn.

Dessauvagie, T. F. J. (1968). Cenomanian Trocholinas from Nigeria. *Micro-paleont*; 14 (19): 64-72.

Edet, A. E. and Essien N. U. (1994). Geotechnical characteristics of some carbonate rocks from the Calabar Flank, Southeastern Nigeria: Implications for the construction materials.In: Proceedings 7th International Congress IAEG(Oliveira, R. Rodrigues, L. F. Coelho A. G. and Pounha A. eds.) Balkema Rotterdam : 3365-3368.

Ekwueme, B. N. (1985). The chemical composition and industrial quality of limestones and marls on the Calabar Flank, south-eastern Nigeria. *Nig. Jour Min. Geol*. 22:51 – 56.

Essien, N. U.(1996). Mfamosing Limestone: a Mid-Albian carbonate platform in south – eastern Nigeria. Ph.D. Thesis, University of Calabar, Calabar, Nigeria.

Fayose, E. A. (1978) .Depositional environments of carbonates, Calabar Flank, Nigeria. *Nig. Jour. Min. Geoi*. 15:1-13.

Kaiser. H. F. (1958). The Varimax criteria for analytical relation in factor analysis, *Psychology* 23:187-200.

Mason, B. (1966). P*rinciples of Geochemistry*. John Wiley & Sons Inc., New York. 328pp.

Nair, K. M, Ramanathan, R. M. and Ukpong, E. E. (1982). Sedimentology and stratigraphy of cretaceous carbonates and associated rocks of Calabar Flank, Nigeria. Nig. *Jour.Min. Geol*. 18:120-129.

Nichol, I. (1973). The role of computerized data system in geochemical patterns in stream sediment related coprecipitation of managese oxide. *Trans. Inst. Min. Metall. Sect. B. App. Earth Sci.* 77 :113-115

Nyong, E. E. (1995). Cretaceous sediments in the Calabar Flank, In: Geological Excursion Guidebook on Oban Massif, Calabar, published in Commemoration of the 31st Annual Conference of the Nigeria Mining & Geosciences Society, Calabar, March 12-16.

Olade, M. A. (1978). Early Cretaceous basalt volcanism and initial continental rifting in Benue Traigh, Nigeria. *Nature*, 273:458-459.

Oti, M. N. and Koch, R. (1990). Mid-Cretaceous shelf carbonates: the Mfamosing limestone, lower Beneue Trough, Nigeria. *Arch. Sc. Geneva,* 34 Fasc 2:211-218

Perch – Nielson, K. and Petters, S. W. (1981). Cretaceous and Eocene microfossil ages from the southern Benue Trough, Nigeria, *Arch. Sc. Geneva, 34 Fasc* 2:211-218

Ramanathan, R. M. and Kumaran, K. P. N. (1981). Age and palececology of M-I well in Calabar Flank, South-Eastern *Nigeria. Jour. Nig. Min. Geol.* 28:163-171

Reijers, T. J. A. and Petters, S. W. (1987). Depositional environments and diagenesis of Albian carboante on the Calabar Flank, S. E. *Nigeria. Jour. of Petroleum Geology*, 10(3):283-294.

Reyment, R. A. (1965). Aspects of the Geology of Nigeria; University . Press, Ibadan, Nigeria, 145pp

Saefar, R. and Sinclair, A. J. (1975). Factor analysis of stream sedimient geochemical data, Mount Nansa Area, Yukon. *Mineral Deposita*, 9:241-252.