

ORIGIN OF CARBONATE CEMENTS IN CRETACEOUS SANDSTONES FROM LOWER BENUE TROUGH, NIGERIA: EVIDENCE FROM PETROGRAPHY AND STABLE ISOTOPE COMPOSITION.

MINAPUYE LODIGI AND LEVI C. AMAJOR

Department of Geology, University of Port Harcourt, Port Harcourt, Nigeria

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Abstract

Beds of authigenic carbonates were identified from three Cretaceous lithostratigraphic units of the Lower Benue Trough, Nigeria. Three carbonate lithologies were recognized by petrographic analysis in the study area. Carbonate-cemented sandstones are dominated by ferroan calcite cements with subordinate amount of siderite and dolomite/ankerite cements formed throughout the diagenetic history of the Asu River Group, Eze-Aku Group and Campano-Maastrichtian proto-Niger Delta sequences. $\delta^{18}\text{O}$ for the cements range from -4.22 to -6.91‰(PDB) in Asu River Group; -5.23 to 12.66‰(PDB) in Eze-Aku and -4.45 to 6.89‰(PDB) in Campano-Maastrichtian proto-Niger Delta sandstones. $\delta^{13}\text{C}$ values averaged -5.23‰ PDB for Asu River Group; -11.03‰ PDB and -5.88‰ PDB for Eze-Aku and Campano-Maastrichtian proto-Niger Delta sandstones. Petrography and geochemical data suggest that the mixing of meteoric and marine waters in the sediments caused dolomitization in Asu River group and Eze-Aku Group sediments while deep burial diagenesis under marine depositional environment precipitated calcite cements. Both authigenic and biogenic carbonate cements with low and high $\delta^{13}\text{C}$ values exists in the sandstones analyzed. The low $\delta^{13}\text{C}$ values of Asu River Group, Eze-Aku and Campano-Maastrichtian cements that range from 0 to 2.98 ‰ suggest that they are shallow water carbonates. Biogenic carbonate cements were also identified in some of the sandstones. The carbonate cements were formed under the influence of both meteoric- and marine diagenetic conditions which changed in time and space. The dolomitized rocks occur just below erosion surfaces on the continental sediments and on which shallow marine facies are developed.

Introduction

Most carbonate sediments in deep or shallow marine environment are biogenic deposits or diagenetic products originating from calcareous biogenic debris. Lithification of carbonate deposits in the marine environment may occur in several ways. Upon burial, biogenic calcite or aragonite of foraminiferal and nannofossil may be diagenetically altered to limestone by local dissolution and reprecipitation (Packham and van der Lingen, 1973; Matter, 1974; Schlanger and Douglas, 1974). Limestones and nonskeletal shallow water carbonates (e.g. ooids, grapestones, and

carbonate mud) have $\delta^{13}\text{C}$ compositions that range from 0 to +5‰ (Milliman and Muller, 1977). Lithification can also result from changes in the carbonate equilibria of the interstitial water; for example, changes in the pH, HCO_3^- , or Ca^{2+} of the pore water resulting from diagenesis of volcanic debris may cause dissolution and reprecipitation of biogenic carbonate. Metamorphism of accompanying intrusion of igneous or volcanic rock can lithify carbonate sediments (Engel and Engel, 1970; Thompson, 1972; Garrison, Hein and Anderson, 1973).

In addition to these deep marine biogenic carbonates, there are carbonates of nonbiogenic origin, which have been described in the literature (Lancelot and Ewing, 1972). In contrast to low-magnesium calcite or aragonite typical of deep marine biogenic deposits, inorganic carbonates are commonly siderite, dolomite, rhodochrosite, or high-magnesium calcite. Non-biogenic carbonates are characterized by highly negative $\delta^{13}\text{C}$ values (-15 to -60), suggesting that the carbon was derived from bacterial degradation of organic matter or from oxidation of CH_4 produced by bacterial processes (Russel, *et al.* 1967; Hathaway and Degens, 1969; Lancelot and Ewing, 1972). In contrast, authigenic carbonate formed in a deep marine hypersaline environment have $\delta^{13}\text{C}$ compositions that range from 0 to +5‰ (Milliman and Muller, 1977). Most researchers report that either the calcium or the carbon of deep marine carbonates was derived from biogenically formed calcite or aragonite.

Carbonate cemented sandstones are very common and abundant in clastic sequences and it is desirable to determine the nature and the changes in the carbonate cemented sandstones. Carbonate cements profoundly influence the quality of reservoirs and supply important information on paleoenvironments and the chemical composition and flow patterns of fluid in sedimentary basins (Morad, 2008 a, b, c). This requires the understanding of the origin of the cements and their distribution. This in turn, necessitates understanding the host sediment's depositional, diagenetic histories. This study describes the carbonate cements in the three lithostratigraphic Cretaceous sandstones units, in the intracratonic basin-Lower Benue Trough (Fig.1) & (Fig.2).

The aim is to determine the origin of the carbonate cementation in the three mega

sequences, paleoenvironments and chemical composition of fluids using petrography and isotope composition of the sandstones. The diagenetic evolution of the sandstone deposits will be better constrained on the basis of petrographic and stable isotope geochemical results, which are presented here. This paper therefore presents for the first time petrography, mineralogy and isotopic compositional data from the carbonates in the Cretaceous sandstones from the Lower Benue Trough. The study area is the Afkpo basin, located in the Lower Benue Trough.

Geological background

The Afikpo basin is located at the S.W. end of the Benue Trough (Fig.1) and was initiated during the late Cretaceous tectonic movements in the Benue Trough. It contains an estimated 9 km thickness of Cretaceous sediments. Petters and Ekweozor (1982a) reported a stratigraphic nomenclature for the Lower Benue Trough which was restricted to the Anambra basin. For this reason, and for simplicity in this report the older formation and group names are retained. The stratigraphic sequence and the geological map of the study area are presented in Figures 2 and 3 respectively. The basal sediments are the Asu River Group (Albian) consisting of the Awi Formation, Abakaliki Formation and Awe Formation. Unconformably overlying the Asu River Group are the Cenomanian- Early Santonian sediments of the Eze-Aku Group. The Eze-Aku Group includes shales and sandstones with subordinate amount of limestone beds. The Late Turonian-Coniacian calcareous sandstone ridges of storm origin belongs to the Amaseri Sandstones while the Cenomanian-Early Turonian sandstones are non-calcareous sandstones and shales are the Ugep and Abini Sandstones which grades into the shales and limestones of the Adim Member.

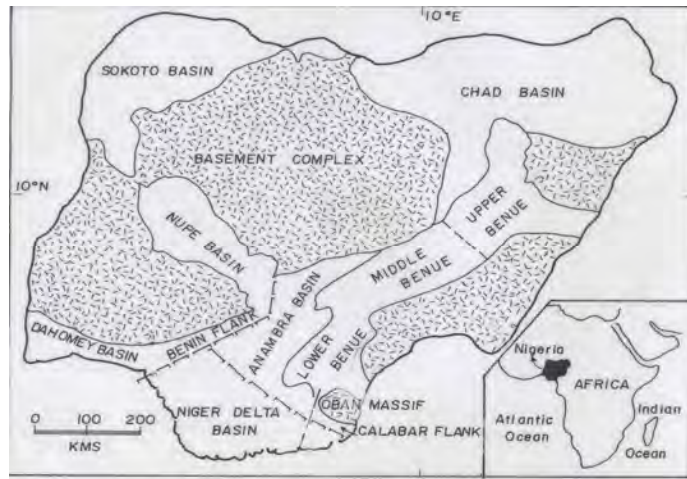


Fig. 1 Geological Map of Nigeria showing the location of Lower Benue Trough (Abakaliki Trough).

The Eze-Aku Group is unconformably overlain by post-Santonian sediments. Following the eastward and westward shifts of the depositional axis in the southern Benue Trough, the paralic Enugu and Nkporo Formations and Mamu and Ajali Formations, and the Ajali Formation were deposited in the subsiding Anambra and Afikpo basins respectively.

The Cretaceous sediments have been extensively studied because of the possible hydrocarbon potential. Sandbodies occur in Asu River Group, Eze-Aku Group and the Cretaceous pro-Niger Delta sediments-Nkporo Shale, Mamu, Ajali and Nsukka Formations; and they are deposited as deltaic complexes during regressive phases. Sandbodies occur in Asu River Group, Eze-Aku Group and the Campano-Maastrichtian pro-Niger Delta sediments (Nkporo Shale, Mamu, Ajali and Nsukka Formations); and they are deposited as deltaic complexes during regressive phases. These stratigraphic sandbodies have been reviewed and discussed in terms of depositional characteristics and geometries (Ladipo, 1988; Ojoh, 1990). Some of the sandstones in the Albian, Turonian-Coniancian and Campano-Maastrichtian

sequences are considered potential reservoir rocks (Whiteman, 1982; Ladipo, 1988). The stratigraphic and sedimentologic history of the Benue Trough is well documented in Petters (1978) and Wright (1981). The occurrence of pyroclastics, volcanism, tectonics, and basic intrusions have been reported in Hoque (1981 and 1984) and Hossain (1981).

The major controls of sedimentation in the trough resulted from worldwide eustatic change in sea level, basin tectonics, and local diastrophism. The earliest sediments in the Benue Trough were Aptian-Albian pyroclastics (Uzuakpunwa, 1974) in the southern Benue Trough. These formed the basal unit of the Albian-Cenomanian depositional sequence (Petters, 1978) and were overlain by 2000-3000 m of sediments of the Asu River Group. Marine sedimentation in the Benue Trough is thought to have begun in Mid-Albian times with deposition of the Asu River Group. Lithologically, the Asu River Group consists of clastic sequences of shales, limestones and sandstones (Fig. 3). These grade northwards into platform carbonates of the Arufu and Gboko members (Reyment, 1965).

STAGES & EPOCHS		LOWER BENUE	MIDDLE BENUE		UPPER BENUE		LOWER BENUE TROUGH	
		ANAMBRA BASIN	LAFIA AREA	BASHAR AREA	GOMBE AREA	LAU AREA	AFIKPO BASIN	
TERTIARY	Eocene	Ameki Fm.					Ameki Fm.	
	Paleocene	Imo Shale	Volcanics	Kerri Kerri Fm	Kerri Kerri Fm	Volcanics	Imo Fm	
MAESTRICHTIAN		Nsukka Fm.	Lafia Formation	Gombe Sandstone	Gombe Sandstone	Lamja Sandstone	Nsukka Fm.	
		Ajali Sandstone					Ajali Fm.	
		Mamu Formation	Mamu Fm.					
CENOZOIC	Campanian	Enugu Shale	Lafia Formation	Unnamed Marine	Pindiga Formation	Numanha Shale	Nkporo Fm	
	Santonian	Awgu Formation					Awgu Formation	Dukul Formation
	Coniacian							
TUROMANIAN	Upper	Eze Aku Shale	Eze Aku Fm.	Zurak Formation	Yolde Formation	Yolde Formation	Eze Aku Group	
	Lower			Muri Sandstone	Bima Sandstone	Bima Sandstone		
CENOMANIAN		Odukpani Fm.	Keana Formation	Keana Fm.				
ALBIAN	Upper	Asu River Group	Asu Awe Formation	Pre-Bima Sediment	Pre-Bima Sediment	Pre-Bima Sediment	Asu River Group	
PRECAMBRIAN				Basement Complex			Basement	
		HOQUE (1977)	OFFODILE (1976)	AYOOLA (1978)	CARTER ET AL (1963) JONES (1963) CRATCHELY & JONES (1965)		ODIGI, 2007	

Fig. 2 Stratigraphic successions in the Benue Trough of Nigeria

The Cenomanian regression restricted marine sedimentation to the southeastern most section of the trough. The Odukpani Formation (a sequence of sandstones, limestones and shales) and calcareous conglomerates were deposited unconformably on the basement rocks in the Calabar Flank and Late Albian and early Cenomanian sediments in the Afikpo basin respectively. The folding and erosion of the Albian-Cenomanian sequence produced the calcareous conglomerates.

The most extensive marine transgression in the trough occurred during Turonian times. Next to be deposited in the southern Benue Trough during the major transgression was the Eze-Aku Group, which comprises of Turonian and Coniacian strata which unconformably

overlie the Albian -Cenomanian Asu River Group. The Turonian-Coniacian sediments are predominantly shales which grade into bioclastic limestones and sandstones.

During the major Santonian tectonics, older strata were folded, faulted, intruded and uplifted. Overlying the pre-Santonian strata, are the Campano-Maastrichtian proto-Niger Delta sediments which were deposited in the Anambra and Afikpo basins. The Campano-Maastrichtian beds comprise of sandstones, siltstones and shales deposited in variety of environments. Maximum burial of the Cretaceous sediments probably occurred in the Late Paleocene or Early Eocene during which the Campano-Maastrichtian beds were deformed by terminal Cretaceous tectonism (Odigi, 2007).

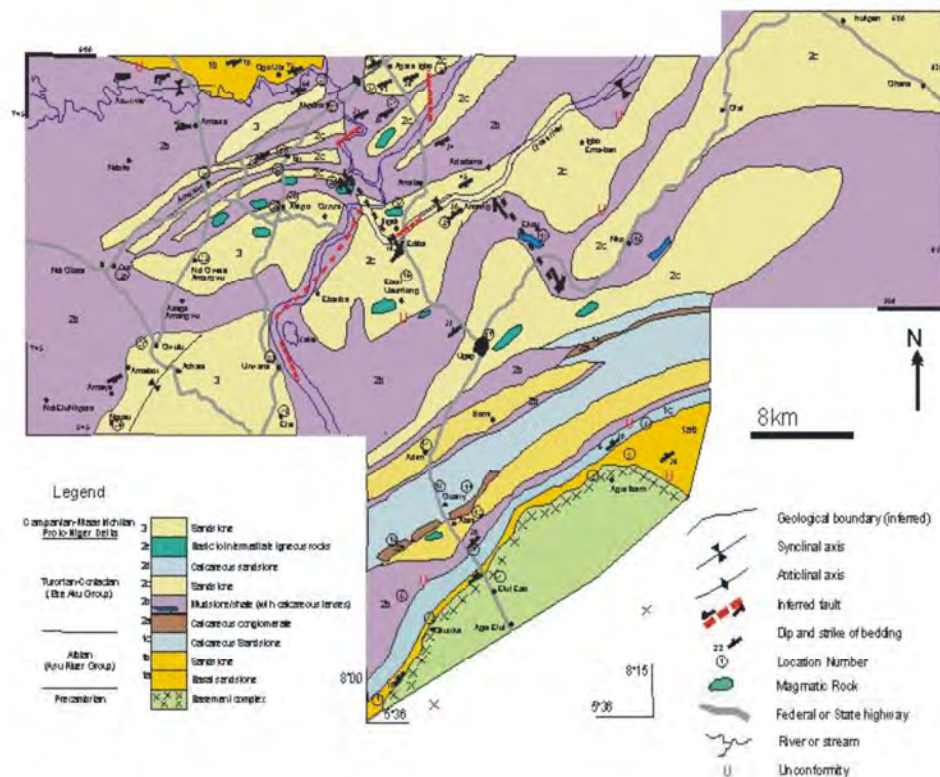


Fig. 3 Geological map of the study area.

Materials and methods

20 polished, blue-epoxy-impregnated thin sections of porous and calcite-cemented sandstones were selected from fresh outcrop samples. Stained acetate peels were also prepared for all calcite-cemented samples. Thirteen sandstone samples were analyzed for general and carbonate mineralogy. Three (3) outcrop representative samples were analyzed from Asu River Group, eight (8) from Eze-Aku and three (3) from Campano-Maastrichtian proto-Niger Delta post-Santonian sandstones.

Carbonate cement mineralogy was determined by staining thin-sections using the method of Dickson (1966). Thin sections were examined in transmitted light and selected non-carbonate thin-section samples were studied using blue-light epifluorescence (with incident light of $\lambda = 560$ nm), and in backscatter mode in an scanning electron microscope (BSEM) equipped with an energy-dispersive X-ray analyzer (EDXA).

Twelve polished thin sections were prepared and examined by optical petrographic methods to study textures. Texture, mineralogy and chemical composition of samples were also studied using techniques of backscatter scanning electron microscopy (BSEM) and energy-dispersive analysis by X-rays (EDXA). Details of the SEM and EDXA techniques have been given by Hein and Scholl (1978). The samples were examined in backscatter mode, which can provide textural information given sufficient chemical differences between phases present (Pye and Krinsley, 1988).

Samples for stable carbon and oxygen isotopic analysis of carbonates were selected from outcrops for which detail petrographic and mineralogical information was available (Odigi, 2007). The preparation of samples for stable isotope analysis follows that described by McCrea (1950). Small amount of whole-

rock samples were ground for 15 minutes in a ball mill, and 10-100 mg subsamples, depending on the estimated carbonate content, were taken for $^{13}\text{C}/^{12}\text{C}$ and $^{18}\text{O}/^{16}\text{O}$ analysis. Carbon dioxide was extracted from samples by reacting with excess 100% orthophosphate acid *in vacuo* at a constant temperature of 25.2 ± 0.05 °C. $\delta^{18}\text{O}$ was calculated using the constants $\alpha^{18}\text{CO}_2$ calcite=1.01025 (Friedman and O'Neil, 1977) and $\alpha^{18}\text{CO}_2$ dolomite=1.011 (Sharma and Clayton, 1965).

Isotopic analysis was performed on a VG-903 triple collector mass spectrometer. Results are quoted on the conventional δ (‰) scale in per mil (‰) deviation from the PDB standard. The normal analytical precision of duplicate analysis is better than $\pm 0.1\%$ for both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$.

RESULTS

Carbonate layers range in thickness from 10 to 30 cm, and they are commonly seen around Ugep, Idomi, Adim, Annong and Nko of the study area (Fig. 3). Stratigraphically, they are Albian, Turonian-Coniacian and Campanian-Maastrichtian carbonates which occur in the Asu River Group, Eze-Aku Group and proto-Niger Delta succession. The limestone beds were deposited by sedimentation during the Albian Turonian and Maastrichtian transgressions. In the Asu River Group, Eze-Aku Group and proto-Niger Delta successions, carbonate is cement for the sandstones. These deposits might, therefore, be called replacement zones and beds. The carbonate beds run W-E between Ugep and Nko, and can be correlated between outcrops. Some of the limestone layers occur as concretions in the Turonian sandstones.

Petrography

Three carbonate lithologies are apparent: (1) foraminifera, bivalve and crinoids limestone, (2) carbonate-cemented and

replacement feldspar, and clastic beds, and (3) micritic limestone.

Fossiliferous Limestone

Sandstones from the three lithostratigraphic units are rich in foraminifera, fragmented bivalve shells and crinoid spines (Fig 4a-c). Recrystallized foraminiferal and bivalve tests and crinoid spines commonly replaced by sparry calcite, occur in the deposits. Pyrite is common and clay minerals in the limestone are variable, but consist of smectite. Much of the fish remains are burrowed and are marked by calcite and trains of detrital grains (Fig.4d).

Coarse-grained sandstone

Calcite, dolomite and replaced feldspar are the common authigenic carbonate lithology. Feldspars are partly to completely replaced by carbonate (Fig. 5a). Plagioclase grains were also partly replaced. Relict grains are seen in the cement. Framework grains are cement supported; clasts float in cement. Foraminiferal tests in the sandstones are recrystallized (Fig.4a). Sparry calcite makes up 25-60% of some of the sandstones. Calcite grains are as large as 2 mm, their boundaries can be either sharp or indistinct.

Micritic limestone.

4a

4b

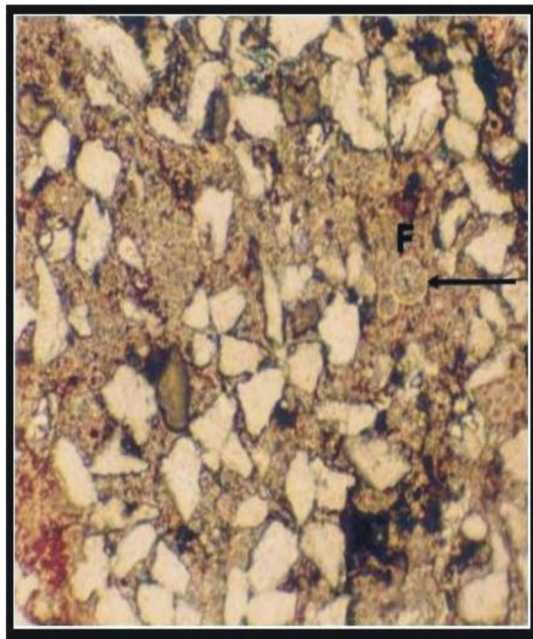
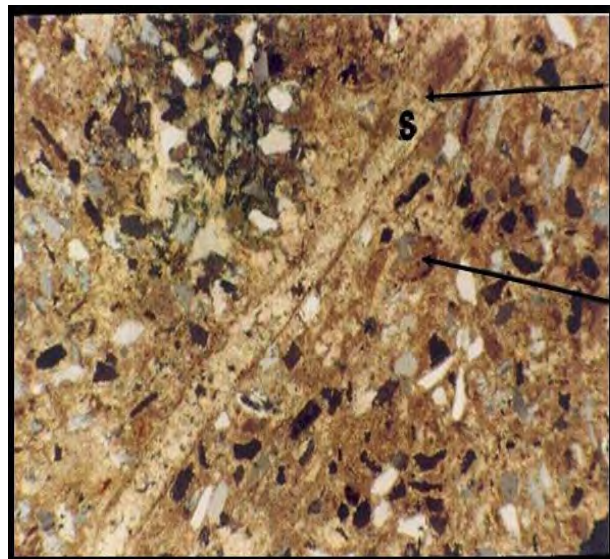


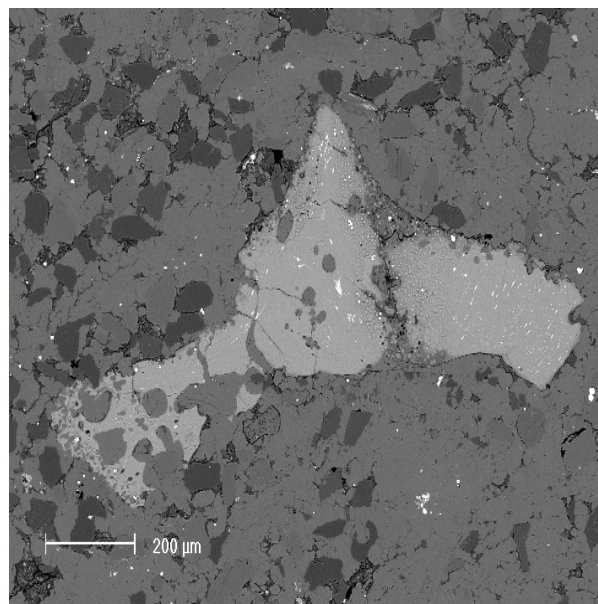
Fig. 4 Photomicrograph of polished thin sections

(a) arkose sandstone from Awe Formation showing calcite spar containing benthic foraminifera chamber (plane polarized light) (b) subarkose sandstone from Campanian-Maastrichtian Proto-Niger Delta sequence showing a broken bivalve shell fragment with micritic envelope enclosing calcite spar

(c)



(d)



(c) arkose sandstone from Awe Formation showing calcite spar growing around a crinoid spine
(d) BSEM showing fish tooth remnant with microboring.

Micritic limestone occurs in Campanian-Maastrichtian where calcareous sandstones outcrop. It consists of intraclasts of pelmicrite, oomicrite and borrowed biomicrite made up of pure carbonates, 70 to 85% calcite (Fig. 4b). Some fossil ghosts or layers of microspar and sparry calcite occur in the micrite.

Figure 6 shows a paragenetic sequence derived from detailed petrography. The relative timing of diagenetic events in the cements of the sandstones analyzed is based on petrographic relationships. The diagenetic events that affected the carbonate cementation in the sandstones are summarized in Figure 6.

Carbonate mineralogy

The dominant carbonate mineral in the study area is ferroan calcite with MgCO_3 content that ranges from 1 to 20.5 mol%. Of

secondary importance is dolomite, and siderite (Table 1). Authigenic carbonates are composed of high- and low magnesium calcite, dolomite and iron carbonates. Few of the limestone beds are monomineralic, but those that contain shale contain two carbonate minerals.

Isotope composition

Carbon and oxygen isotopes

Oxygen and carbon isotopic compositions were determined for fourteen fresh outcrop samples (Table 1). $\delta^{13}\text{C}$ is variable, ranging from +3.00 to -4.68‰. The $\delta^{13}\text{C}$ values of calcite cement for Albian, Turonian and Campano-Maastrichtian sandstones range from 0.0 to 2.98 ‰ PDB, whereas $\delta^{18}\text{O}$ values range from -3.98 to -16.03 ‰ PDB (Table 1). For Fe-rich calcites, $\delta^{18}\text{O}$ ranges from -6.91 to

+4.22‰ relative to PDB whereas Mg-rich calcites range from -16.03 to -5.23‰.

The calcite cements of the Cretaceous sandstones fall into two data group A, B & C according to isotopic compositions (in Fig 7, the arrow shows the isotopic composition changes during the Cretaceous times). Point A represents an ideal Cretaceous seawater composition. A distinctive group B (samples 2, 5c-Asu River Group, 15, 76a of Eze-Aku Group and 20a, 20b, 20c-post-Santonian) has a more positive $\delta^{13}\text{C}$ (4.66 to 2.96 ‰ PDB). Values for five of the samples in group B are close to zero, which is typical for biogenic carbonates. The isotopic compositions of samples 2, 5c, 15, 20a, 20c and 76a reflect primary marine signature (Marshall, pers. Com. 2006, Odigi, 2007). Isolated sample 5b has lowest $\delta^{13}\text{C}$ value, indicative of bacterial sources of bicarbonate (Hudson, 1977; Irwin *et al*; 1977). The group C samples 34, 36, 76b, 81, 93e from Eze-Aku Group (as shown in Fig. 7), are characterized by lighter $\delta^{18}\text{O}$ and negative $\delta^{13}\text{C}$ values (-4.68 to -0.75‰ PDB $\delta^{13}\text{C}$, -16.03 to -11.67‰ $\delta^{18}\text{O}$ PDB), which resulted from precipitation in meteoric condition during the uplifting of the pre-Santonian proto-Niger Delta, deformed sediments. The samples in group C are close to the region marked D (Fig 7) represents precipitation at more elevated temperatures resulting from burial and thermotectonics of the Benue Trough. The heavy oxygen isotopic composition, however, is indicative early cements (within the encircled region marked B, as shown in Fig 7). The $\delta^{18}\text{O}$ ‰ values are heavy and compatible with early marine

cementation ($\delta^{18}\text{O}$ -4.57 to -6.26‰). But they show a trend towards even lighter values downward to the region of D (Fig 7), reflecting diminishing early cement values and increasing proportions of later cement. Progressive decrease in oxygen isotope composition primarily reflects increasing temperature or fractionation of the precipitating waters (Land *et al*; 1975; Anderson and Arthur, 1983; Anketell and Mriheel, 2000).

The Eze-Aku samples have similar $\delta^{18}\text{O}$ values when compared to those studied by Irwin and Hurst(1983) and Lonoy *et al*; 1985. The Jurassic sandstones from the North Sea (Irwin and Hurst,1983) and Hild field Vilking Graben (Lonoy *et al*; 1986) were found to have been buried relatively deep between 4-5 km at about 56-68°C. Therefore, the inferred burial depth and temperature of the Eze-Aku and post-Santonian sandstones is 4-5 km at 60°C.

Geochemical stable isotopic analyses revealed differences between the Asu River Group, Eze-Aku and post-Santonian sandstones (Fig 7 and Table 1). The differences suggest that the following processes operated: dissolution and reprecipitation, and recrystallization during burial (increase in temperature due to subsidence, burial and thermotectonism), which led to further negative shift in $\delta^{18}\text{O}$ values. These stable isotopic signatures display trends from Asu River Group to Eze-Aku to Campano-Maastrichtian post-Santonian sandstones.

Table 1: Characteristic of Cretaceous carbonates, from Southern Benue trough, Nigeria

	Sample	Lithology	Petrology	X-ray Mineralogy	MgCO ₃ mol %	δ ¹⁸ O	δ ¹³ C
Asu River Group	2	Calcareous sandstone	Calcite cemented and sparry cemented Arkose/subarkose	100% calcite	2.0	-4.22	2.99
	5b	Calcareous sandstone	Cemented sandstone Arkose/subarkose	FeCO ₃ 20% calcite	5.0	-6.91	-4.66
	5c	Calcareous sandstone	Cemented sandstone Arkose/subarkose	100%Mg-calcite	1.5	-4.57	0.82
Eze-Aku Group	8	Limestone	Calcite cemented	100%Mg-calcite	20.5	n.d.	n.d.
	15	Limestone	Calcite cemented and replaced foraminefera	100%Fe-calcite	7.0	-6.26	0.91
	36	Calcareous sandstone	Calcite cemented and replaced feldspar	100%Fe-calcite	1.5	-10.75	-0.18
	48	Calcareous sandstone	Calcite cemented	95%Fe-calcite 50% siderite	3.0	-16.09	3.34
	76	Calcareous sandstone and shale	Calcite cemented and replaced carbonaceous shall and sparry calcite sandstone	87% dolomite 13% Fe-calcite	1.5	-5.23	0.46
	93	Calcareous sandstone	Calcite cemented arksoe sandstone	100%Fe-calcite	7.5	-12.88	-1.5
Proto-Niger Delta	20a	Siliceous limestone	Micritic Cemented carbonate mud	100%Fe-calcite	2.5	-4.45	3.01
	20b	Limestone	Micritic calcite cemented	100%Fe-calcite	5.0	-6.89	2.98
	20c	limestone	Calcite cemented	95%Fe-calcite 50%Mg-calcite	1.0	-6.30	2.50

Considering the isotopic data for all the samples, δ¹³C values decreases with age, with depth of burial, and with increasing molar percentage of MgCO₃ in the calcites. These correlation are not well developed but are best defined if the biogenic values are omitted. A better developed relation is a decrease in δ¹⁸O with depth of burial and increasing age. There is an overall poorly defined decrease in δ¹⁸O with decreasing mole percentage of MgCO₃ in the calcites.

Table 2: $\delta^{13}\text{C}$ (PDB) of various carbonate gases and organic compound

	Average	$\delta^{13}\text{C}^*$ (‰)	Range
Authigenic carbonates (this study)	-17.20		-7.16 to -21.09
Biogenic carbonates(this study)	+1.29		-0.70 to +2.64
Recent biogenic sediments and marine biogenic calcite	n.d.		-2.0 to -30
Organic matter			
Terrestrial	n.d.		(~) -23 to -28
Marine plankton	n.d.		(~) -18 to -23
Crude oil	n.d.		(~) -26 to -30
DSDP gases			
CO ₂ Biogenic	-18.8		-7.5 to -32.0
CH ₄	-72.3		-47 to -90.0
Gases experimenta			
CO ₂ Biogenic	-14.0		-9.2 to -18.5
CH ₄	-83.9		-70.6 to -94.3

* Data from Cheney & Jesen (1965), Degens (1969), Letolle & Martin (1970); Clapool, Presley & Kaplan (1973). n.d. – not determined.

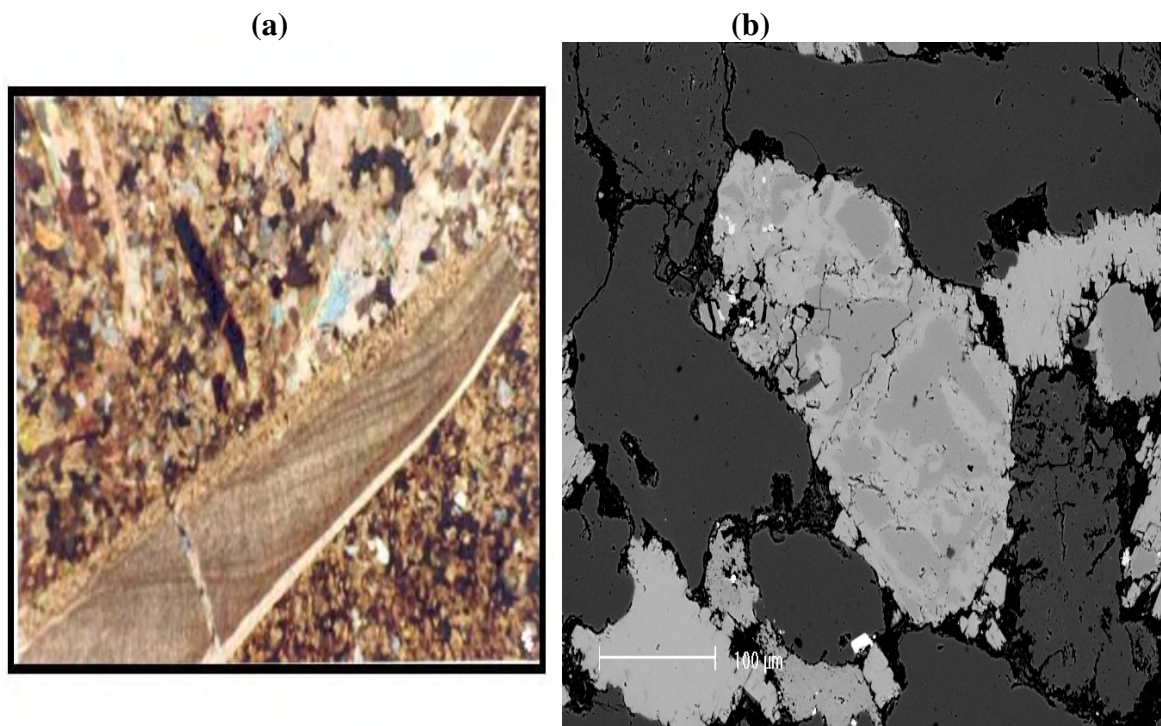


Fig. 5. SEM showing (a) K-feldspar broken down to be replaced with calcite, (b) photomicrograph of polished thin section of fish fin.

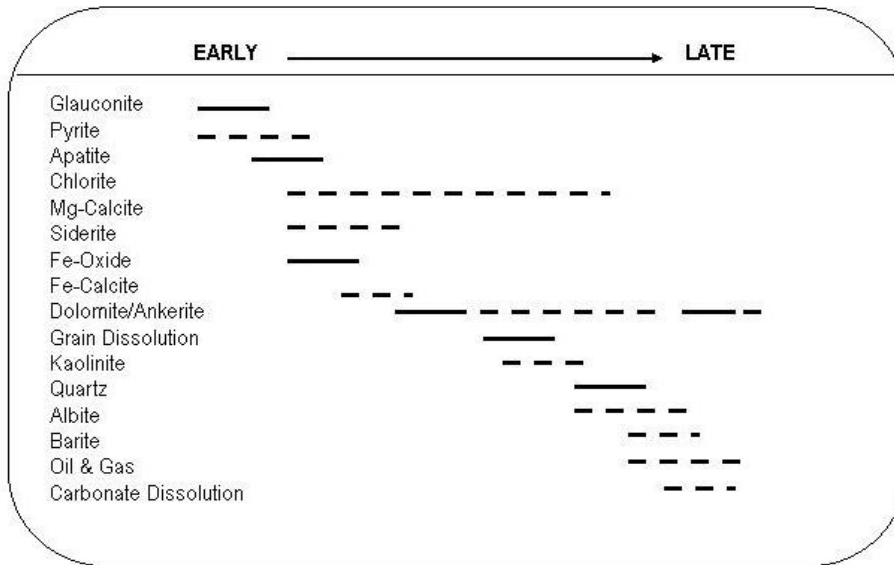


Fig. 6. Paragenetic sequence of sandstones from the study area

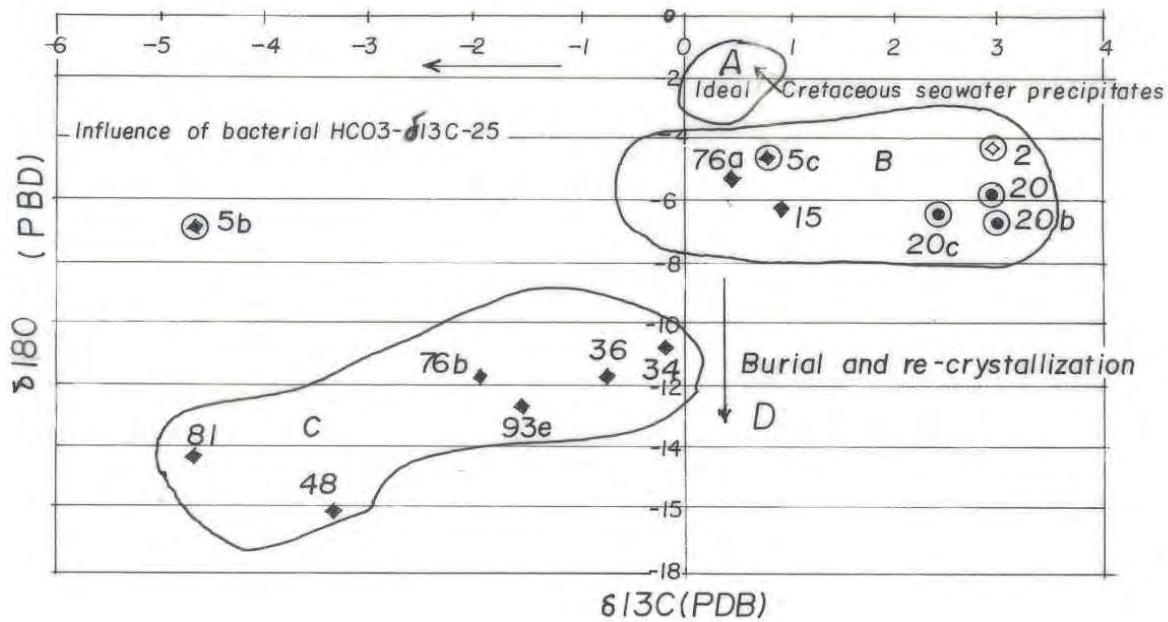


Fig 7. Plot of $\delta^{13}C$ vs $\delta^{18}O$ for Cretaceous sandstones. Samples 2, 5b, 5c Asu River Group; 15, 36, 48, 76a, 76b, 81, 93e Eze-Aku Group; 20a, 20b, 20c proto-Niger Delta (Campano-Maastrichtain)

Discussion

Authigenic carbonates in deep- and shallow marine include isolated dolomite rhombs, carbonate nodules, and pyroclastic rocks (Peterson et al. 1970); Lancelot and Ewing, 1972; Irwin, et al; 1977). Sedimentary sections from the southeastern Benue Trough contain authigenic carbonates beds that are of different thickness.

The occurrence of authigenic carbonate implies major redistribution and reorganization of elements within the sedimentary sections and coexisting pore waters. To understand the magnitude and significance of this chemical mobility, some questions need to be addressed: (1) what is the origin of the carbon and oxygen? (2) what are the chemical and physical conditions in which carbonates precipitated? In general, conditions most conducive to carbonate precipitation are high p^H and carbonate species in the pore water.

We suggested that the alteration of pyroclastics and basic volcanic rocks in the Benue Trough provided the bulk cations required to form authigenic carbonate cements. The Asu River Group and Eze-Aku Group are associated with pyroclastics and basic rocks in the southeastern Benue Trough. Odigi (2007) found that some of sandstones in the three lithostratigraphic sections contain abundant authigenic smectite. He also found out that pyroxene, plagioclase, and other reactive minerals from the basic rocks were replaced by smectite.

Dolomitization is a widely reported process (Land, 1980 and Land et al, 1975; Machel and Mountjoy (1986). One of the frequently suggested mechanisms is for dolomitization in zones of mixed marine and meteoric waters. Based on the petrologic and diagenetic features observed in the sediments,

the following features were recognized from continental to marine:

- (1) The dolomitized sediments are laterally and vertically restricted to sediments representing the continental to marine boundary.
- (2) The dolomitized zone coincides with the decoloured zone at the top of the alluvial fan sediments. This zone is likely to have been decoloured through the influence of a reducing environment.
- (3) Evidence of cementation in a marine diagenetic environment in the overlying sediments (beach, tidal channel, distributary mouthbar, tidal sandstone ridges) implies that there may have been a transition zone with mixed marine and continental influences in the upper part of the continental succession.
- (4) Dolomite developed during early diagenetic stages before compaction. Dolomite crystals show interpenetration contacts with silici-clastic grains, and are affected by pressure-solution surfaces (Odigi, 2007).

The source of Mg for the dolomite and magnesium calcite can be attributed to the alteration of the pyroclastics and basic rocks, which released Mg into the pore waters. Possibly the alteration of these rocks was sufficiently abundant to provide Mg for both smectite and carbonate.

Alternatively, the dolomite may have been formed from a calcite precursor; as calcite replaced silicates containing Mg, the freed Mg would have been available to substitute for Ca in the carbonates. On the basis of textural evidence, we would favour primary precipitation of dolomite. The evidence is not clear, and dolomitization of

limestone or Mg incorporation during recrystallization may have played a role in Mg enrichment. It is suggested that dolomitization is a more likely process that contributed to the Mg enrichment. Few carbonates of this study that are dolomitic have higher $\delta^{18}\text{O}$ content and therefore favour dolomitization by solution-redeposition mechanism.

The possible source(s) of carbon and their corresponding $\delta^{13}\text{C}$ values are: (1) sea-water bicarbonate (including that in pore-waters), $\delta^{13}\text{C}$ close to zero (Table 4, Fig 7), (2) sea water influenced by volcanogenic CO_2 , $\delta^{13}\text{C}$ -7.0‰ (Pineau et al.1976); calcites closely associated with volcanic rocks have $\delta^{13}\text{C}$ values that range from about +1 to +5‰ (Milliman and Muller, 1977), (biogenic calcite and aragonite, $\delta^{13}\text{C}$ close to zero, (4) CO_2 derived from metabolic oxidation of organic matter, $\delta^{13}\text{C}$ -18 to -23‰, or about the same as the $\delta^{13}\text{C}$ of the organic matter used as a food by the bacteria (Presley and Kaplan, 1968; Degene, 1969; Table 4, (5) CO_2 derived from oxidation of CH_2 , $\delta^{13}\text{C}$ about -18 to -23‰; bacteriogenic CH_4 *per se* has values of -50 to -90‰ (Claypool et al.1973). From the above, it is also suggest that the some of the carbon for the carbonates was produced by oxidation of organic matter under anaerobic conditions, an origin supported by low $\delta^{13}\text{C}$ values that range from -4.68 to -0.75‰. The occurrence of pyrite and ferrous carbonate is in favor of an anaerobic environment.

Biogenic calcite is a possible precursor for the authigenic carbonates because foraminiferas occur in abundance; foraminiferal were observed in thin sections and with the SEM in the sandstones. The relative heavy $\delta^{13}\text{C}$ composition of some biogenic calcites suggests that carbon source for the sandstones with carbonate cement.

CONCLUSIONS

From our analysis of carbonate material taken from outcrop samples, the following conclusions were reached: (1) Authigenic carbonates, high- and low magnesium calcite, dolomite and siderite formed at depth in the sediment of the Cretaceous sea. (2) Carbon for the carbonates was produced by oxidation of organic matter under anaerobic conditions, an origin supported by low $\delta^{13}\text{C}$ values that ranges from -0 to 4.66‰ for Asu River Group, and -0.18 to -1.56‰ for Eze-Aku Group. Low $\delta^{18}\text{O}$ values for calcite cements suggest that an incursion of meteoric water affected these rocks in the Eze-Aku sediments. However, because the region may have been affected by a high rift-related geothermal gradient at this time, the low values could also result from abnormally high temperatures of precipitation. The alteration of these rocks provided the high pH and abundant carbonate species in pore waters necessary for the carbonate precipitation. (3) Carbonate cementation from the study supply information on paleoenvironment and chemical composition of the fluids in the sedimentary basin. (4)The stable isotopic composition of elements have been modified from sea water (Cretaceous) by dissolution, precipitation and re-crystallization during burial. This had led to a more negative shift in $\delta^{18}\text{O}$ values.

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