

Full Length Research Paper

Depositional environment and carbon/oxygen isotopic composition of the Paleocene carbonates exposed around Kalambaina, Sokoto basin, Nigeria

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The limestone-shale sequence exposed at the Kalambaina quarry belongs to the Paleocene marine sediments deposited in the Sokoto Basin during the second phase of sediment deposition when the Tethys Sea moved southwards through the Sahara. The exposed section measured ca.19.5m in thickness. The lower part of the section consists of limestone-shale interbeds while the upper part is phosphatised shale. The limestone is clayey, consisting of marl and shale components. The beds are generally massive to wavy laminated. Petrographic study reveal that the limestones are mud supported and consist of two main carbonate rock types including bioclastic wackestone and bioclastic packstone. Larger foraminifera, corals, bryozoans, echinoderms, algae and gastropods represent the major bioclasts while lithoclasts are the main non-bioclastic grains of the lithofacies. The associated shales consist of many detrital materials, phosphorites, gypsum and carbonaceous organic matter. Carbon/oxygen isotopic composition vary from -5.29‰ to -6.55‰ $\delta^{18}\text{O}$ PDB and -1.24‰ to -3.40‰ $\delta^{13}\text{C}$ PDB in the whole rock compare to the average values of -2.33 $\delta^{18}\text{O}$ and $+0.05$ $\delta^{13}\text{C}$ PDB for Tertiary Sea water. The lighter oxygen and carbon fractions in the samples is a reflection of the depletion of heavier isotope of oxygen and carbon consequent to late stage recrystallisation, influx of fresh water and formation of variable carbonate cements during progressive diagenesis. Estimated formational paleo temperatures for the kalambaina limestone vary from 26.80 to 32.85°C. The study suggests that carbonates of the Kalambaina formation were deposited in shallow marine, shelf lagoonal setting and have undergone several stages of post depositional changes. The late stage cements have reduced the interparticles and moldic porosities of the carbonate.

Key word: Kalambaina, carbonate, sediments.

INTRODUCTION

The type section of the Kalambaina Formation is exposed at the quarry of the Cement Company of Northern Nigeria (CCNN) Kalambaina village in the northwestern Nigeria.

It consists of carbonate rocks including bioclastic wackestone and bioclastic packstone. These carbonate rocks have been diagenetically altered to varying degrees

ranging from early to late diagenesis. Carbon and Oxygen isotopic composition of these carbonate rocks has been carried out for the first time to document the data and to obtain further information on the diagenetic alteration, fractionation trend and paleotemperatures.

Oxygen has three isotopes: ^{16}O (99.765%), ^{17}O (0.0375%) and ^{18}O (0.1995%) (Akande, 1982; Tucker and Wright, 1990). Carbon has two stable isotopes: ^{12}C (98.89%) and ^{13}C (1.11%) (Vogel et al., 1970; Akande, 1982; Tucker and Wright, 1990). Geochemical evidence show that the isotopic compositions of oxygen, carbon, sulphur and strontium in the ocean have undergone large fluctuations or excursions in the geologic past (Boggs, 2001). The ratio of $^{18}\text{O}/^{16}\text{O}$ in the ocean at any given time in the past is built into contemporaneous marine carbonate minerals and the carbon isotopic composition of the ocean at those times. Therefore, a fluctuation in the isotopic ratios of oxygen is reflected in the isotopic ratios of marine carbonates and fossils. $^{18}\text{O}/^{16}\text{O}$ ratios in biogenic marine carbonates reflect both the temperature and $^{18}\text{O}/^{16}\text{O}$ ratio of the water in which these carbonates formed. Commonly, the $^{18}\text{O}/^{16}\text{O}$ ratio are expressed as PDB standard (a Cretaceous belemnite from the Pee Dee Formation) or SMOW – Standard Mean Ocean Water (Gonfiantini, 1986). The carbon isotopic composition is reported as $\delta^{13}\text{C}$ relative to the $^{13}\text{C}/^{12}\text{C}$ ratio with reference to PDB standard (Boggs, 2001).

The objective of this paper is to document the carbon/oxygen isotopic composition (for the first time in the study area) for the Paleocene Kalambaina carbonates and to calculate the estimated paleotemperatures during the carbonate build up with regards to the Tertiary Sea water. The Kalambaina Formation falls regionally within the southern extension of the Sokoto Basin in the northwestern Nigeria where Lower Tertiary sediments are exposed. The carbonate beds of the formation are exposed at a quarry around Kalambaina village about 6 km west of Sokoto (Figure 1). The detailed geology and stratigraphy of the Sokoto Basin (Figure 2) are well documented in the works of Kogbe (1972, 1974, 1979); Adeleye (1975); Okosun (1989, 1995); Haynes and Nwabuafo-ene (1998) and Obiosio et al. (1998).

LOCAL STRATIGRAPHIC SETTING

The exposed section at the Kalambaina quarry measured ca. 19.5 m (Figure 3). The section is divisible into two major parts (lower and upper parts). The lower part consists of alternation of limestone-shale interbeds. The base of the quarry at the time of study consists of a white fossiliferous limestone bed of about 1 m thickness. A poorly laminated grey shale (about 2.2 m) overlies the basal limestone bed (Figure 3) with worm burrows. Overlying the shale bed is a clayey fossiliferous, nodular limestone bed about 1.2 m thickness that is in turn

overlain by an approximately 2 m thick fossiliferous, grey shale (with ironstone nodules). Moulds of gastropods and pelecypods were observed in this bed. The last bed in the lower part is a massively bedded, marly, fossiliferous limestone (about 1.3 m) showing significant wavy laminations.

The upper part of the section consists of about 6 m thick shale sediments. These shales are phosphatised and consist of very thin gypsiferous layers and dark carbonaceous materials. High percentages of clastic materials are also observed in these sediments. A 2.5 m thick brownish red oolitic ironstone bed overlies the shale unit. Above the oolitic ironstone is a lateritised topsoil overburden.

MATERIALS AND METHODS OF STUDY

Fieldwork exercise was carried out at Kalambaina quarry and the surrounding areas for a period of one week in December 2010. During this period, lithological sections exposed at the quarry were logged and described by bed from the base to the top as the quarrying activities provided opportunity for obtaining fresh samples. Detailed observations were made to individual bed components, sedimentary structures and lithologic characteristics. Different macrofossils were collected, identified and classified. Oriented limestone samples were collected using chisel and hammer for polished rock slabs and thin sections at the Geological workshop, Department of Geology and Mineral Sciences, University of Ilorin. Since it was difficult to separate the carbonate rocks into different diagenetic stages, bulk samples (whole rock) were powdered using porcelain mortar and pestle at the Department of Geology, Technical University, Berlin, Germany. At least 5 g powdered samples were prepared per sample for isotope study. The measurement of the carbon and oxygen isotopes was carried out at the Christian-Albrechts-University, Kiel, Germany. Powdered samples were reacted with 100% phosphoric acid at 25°C in an off-line vacuum line. The resulting CO_2 was extracted and analyzed for its carbon and oxygen isotopic compositions with a Finnigan MAT 250 Mass Spectrometer. Both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values are reported in per mil notation relative to the PDB (Pee Dee Belemnite) standard. The accuracy of measurement is with $\pm 0.02\text{‰}$ PDB for both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values.

RESULTS AND DISCUSSION

Carbonate petrography

Petrographic characteristics of the carbonate rocks were carried out to discuss the sedimentological properties and classify them into different rock types. Below is the detailed petro-graphic description of the observed

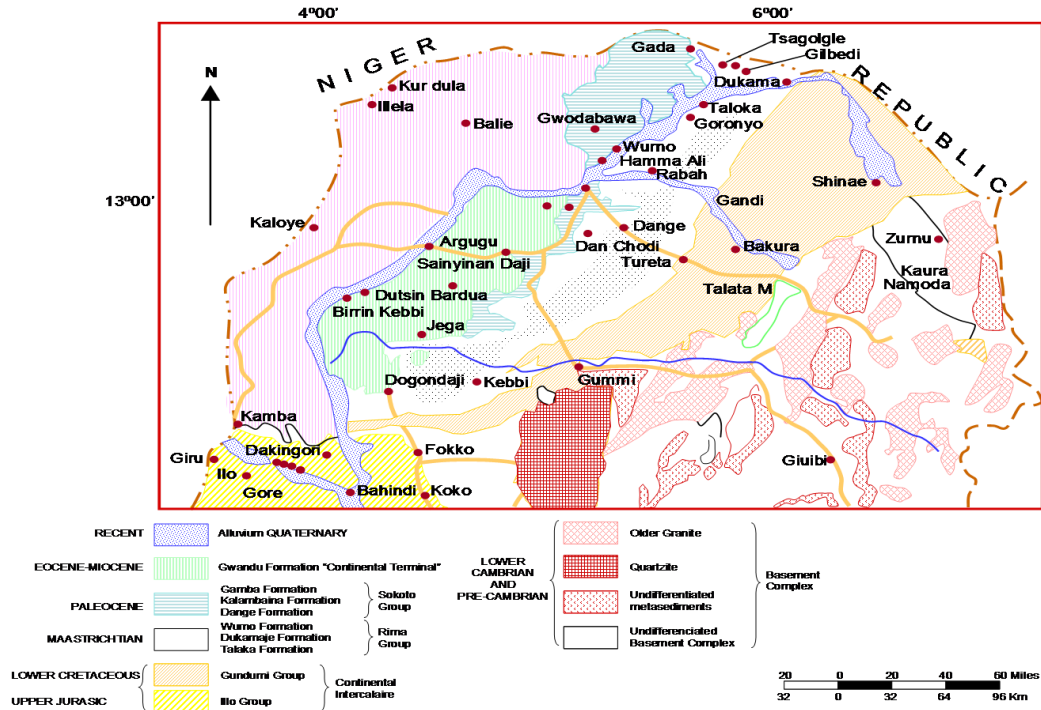


Figure 1. Geological sketch map of northwestern Nigeria showing Kalambaina Formation type locality (modified from Obiosio et al., 1998).

AGE	FORMATION	GROUP	ENVIRONMENT
QUATERNARY	Sandy drifts, laterites		Continental
EOCENE - MIOCENE	Gwanda Formation	"Continental Terminal"	Continental
UPPER PALEOCENE	Unconformity	Sokoto Group	Marine
	Gamba Formation		
	Kalambaina Formation		
	Dange Formation		
MAASTRICHTIAN	Unconformity	Rima Group	Brackish water with Brief dukamaje Formation Marine intercalation
	Dukamaje Formation		
	Wurno Formation		
	Taloka Formation		
LOWERMOST CRETACEOUS OR OLDER	Unconformity	"Continental Intercalaire"	Continental
	Illo and Gundumi Formation		
PRECAMBRIAN	Major Unconformity		
BASEMENT COMPLEX			

Figure 2. Generalised stratigraphic setting of the Sokoto Basin (modified from Obiosio et al., 1998).

microfacies.

Bioclastic wackestone

The lithosome consists of bioclastic grains including

larger foraminifera, smaller foraminifera, corals, echinoderms, fragments of mollusk grains and many broken fragments of unidentifiable bioclasts (Figure 4). Non-bioclastic grains are not significant except the few lithoclasts that were observed. The larger foraminifera are partly recrystallised to sparry calcite in the internal

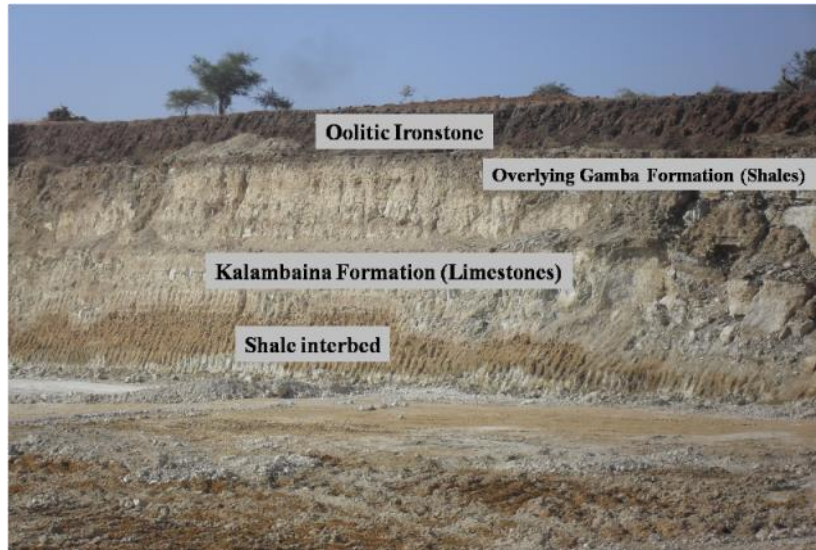


Figure 3. Lithostratigraphic section exposed at Kalambaina quarry. Notice the lower part of the section consisting of limestone-shale interbeds and the upper part mainly shale and oolitic ironstone.



Figure 4. Photomicrograph of bioclastic wackestone. Notice the big grain of larger foraminifera (LF) at the center of photo. Notice also the transverse section of echinoderm (E) at the top left of photo.

parts. The shell wall exhibits radial fibrous pattern in larger rotalid foraminifera. The groundmass is of micritic mud.

Bioclastic packstone

The rock type consists of abundant larger foraminifera

(Fusulinid, transverse section) showing septa and initial chamber of shell (Figure 5). They are partly perforated. Many of the foraminifera are elongated in shape. Corals are also well observed. Many fragments showing arched rows of cells are articulating coralline algae (Figure 5). Original shell microstructure is poorly exhibited and partly destroyed probably by leaching and subsequent infilling of calcite cement. Transverse sections of cup corals

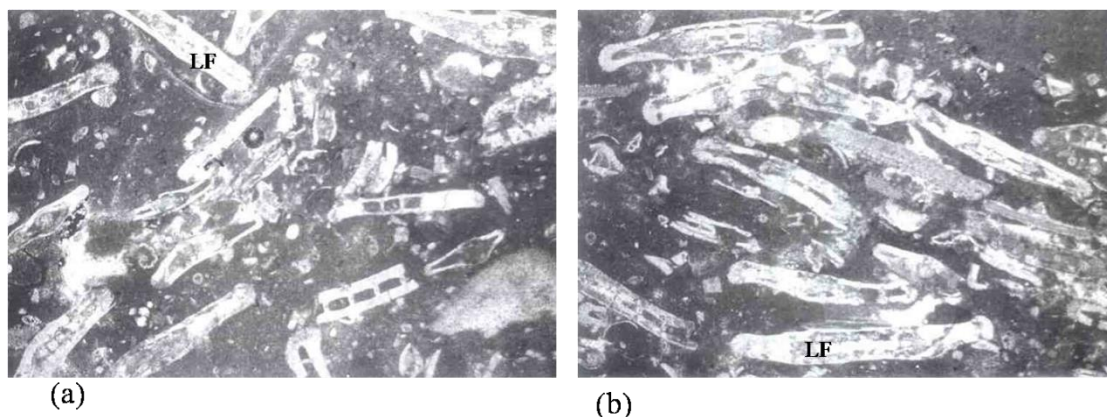


Figure 5. Photomicrograph of bioclastic packstone. Notice the several grains of larger foraminifera (LF). See also the transverse section of echinoderm (E), lower centre of photo and coral (C) with complete recrystallization upper center of photo.

showing solid radial septa and recrystallised wall structure are observed. Bryozoans are also present. They occur in small size and not so much abundant. Many small molluscan fragments were observed. Generally, the matrix is of calcareous mud.

Depositional environment

The bioclastic wackestone and bioclastic packstone microfacies consist of larger foraminifera, corals, echinoderms, bryozoans and fragments of gastropods and pelecypods. The presence of larger foraminifera indicates shallow marine environment (ranging from 1-100 m water depth) on the continental shelf where water is clear enough for light to penetration (Selley, 1980; Boardman, 1987). The presence of coral suggests restricted shallow tropical waters with temperature ranging from 25 – 29°C and in water depth up to 90 m (Boardman, 1987). The presence of gastropod bioclast suggests shallow water, lagoonal environment (probably not >200 m) on the edge of the continental shelf (Wilson and Jordan, 1982; Adekeye and Akande, 2002, 2006). The presence of echinoderms suggests shelf lagoonal environment or shallow to moderate water depths with normal marine salinity. The broken fragments of these bioclasts represent a textural inversion suggesting that particles from high energy environments have moved across the shoal down to low energy setting in the shelf area (Wilson, 1975; Flugel, 1982; Tucker and Wright, 1990).

In general, the presence of wavy lamination, abundance of lime mud supported carbonate faunas, presence of larger foraminifera and corals indicate shallow marine (shelf) lagoonal environment of deposition (Figure 6).

Carbon/oxygen isotopic composition of the carbonates

Twelve bulk samples (whole rock) from the Kalambaina carbonates were analyzed for their carbon and oxygen isotopic composition. Table 1 shows the result of the analysis. The plot of the carbon/oxygen isotopic composition of the limestone is shown in Figure 7.

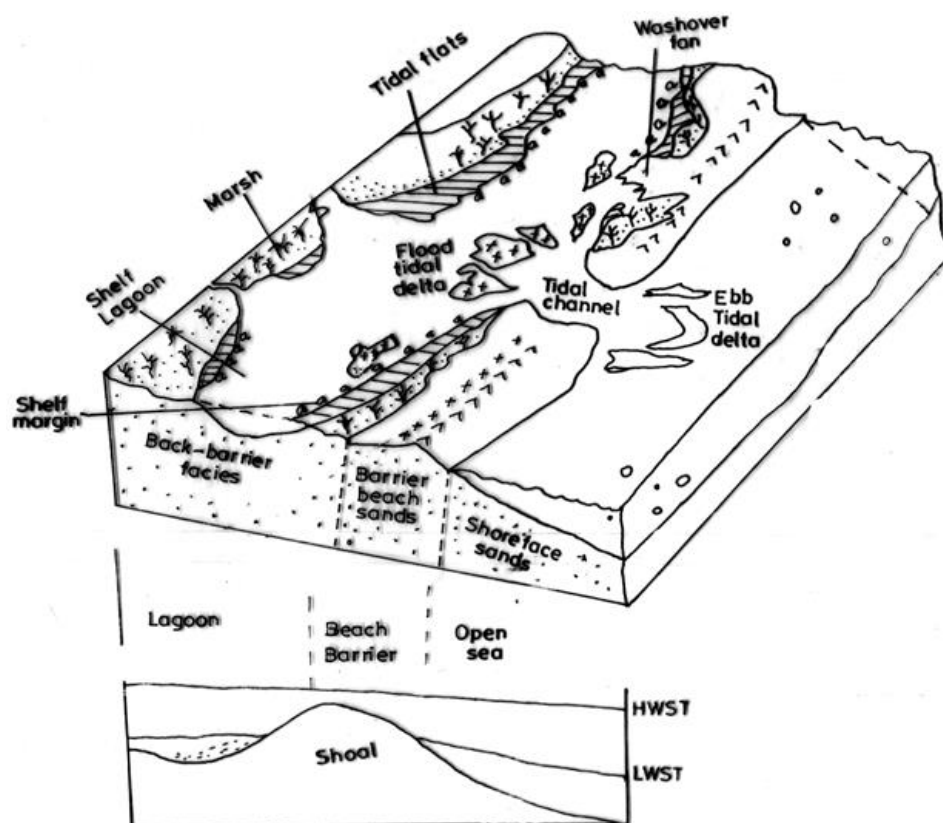
Keith and Weber (1964) suggested that the carbon content of the ocean has been fairly constant throughout the geologic time although small variations exist from one basin to the other. The average values of the carbon/oxygen isotopic composition for the Tertiary Sea water is $+0.05 \delta^{13}\text{C}$ and $-2.33 \delta^{18}\text{O}$ PDB (Keith and Weber, 1964).

The $\delta^{18}\text{O}$ values of the twelve samples from the Paleocene limestone in the Kalambaina quarry range from -5.29 to -6.58‰ PDB (mean of -6.03 ± 0.02). $\delta^{13}\text{C}$ values of the same samples range from -1.24 to -3.40‰ PDB (mean of -2.06 ± 0.02) (Table 1). The range of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ mean values in the carbonate samples under study deviated greatly from the predicted range of mean values for the unaltered marine carbonates (Boggs, 2001) of the Tertiary Sea water as mentioned above. The differences between these published values and the data presented in this work can be attributed to some factors including the following:

- (1) Diagenetic alteration. According to Scholle and Arthur (1980) and Marshall (1992), $\delta^{13}\text{C}$ values of sedimentary carbonates change during diagenesis towards lighter fraction because of the low carbon content of diagenetic fluids compared to that of the rock.
- (2) Relatively high influx of continental (terrestrial) organic carbon incorporated into the limestone during build up (due to shallow burial depth). Water runoff from the continents (where terrestrial organic matter is abundant)

Table 1. Carbon/Oxygen isotopic composition of the selected Kalambaina carbonates in the Kalambaina quarry.

Sample number	Location	Age	Sample description	$\delta^{13}\text{C}$ (‰ PDB)	$\delta^{18}\text{O}$ (‰ PDB)
ADE-1	Kalambaina quarry	Paleocene	Fossiliferous limestone	-1.73	-5.65
ADE-2	Kalambaina quarry	Paleocene	Fossiliferous limestone	-1.36	-6.53
ADE-3	Kalambaina quarry	Paleocene	Fossiliferous limestone	-1.31	-6.37
ADE-4	Kalambaina quarry	Paleocene	Fossiliferous limestone	-3.40	-5.98
ADE-5	Kalambaina quarry	Paleocene	Fossiliferous limestone	-2.36	-6.10
ADE-6	Kalambaina quarry	Paleocene	Fossiliferous limestone	-1.51	-5.75
ADE-7	Kalambaina quarry	Paleocene	Fossiliferous limestone	-1.45	-6.58
ADE-8	Kalambaina quarry	Paleocene	Fossiliferous limestone	-2.86	-5.60
ADE-9	Kalambaina quarry	Paleocene	Fossiliferous limestone	-2.43	-6.03
ADE-10	Kalambaina quarry	Paleocene	Fossiliferous limestone	-1.24	-5.29
ADE-11	Kalambaina quarry	Paleocene	Fossiliferous limestone	-2.52	-6.26
ADE-12	Kalambaina quarry	Paleocene	Fossiliferous limestone	-2.53	-6.18

**Figure 6.** Schematic diagram representation of the carbonate depositional environment of the study area.

brings organic rich water with low $^{13}\text{C}/^{12}\text{C}$ ratio ($\delta^{13}\text{C}$) into the shallow marine water environments of the primary carbonate build up (Marshall, 1992).

(3) Increased rate of erosion of organic rich sediments, such as dark shale and limestones, on land could also produce the same effect of increasing runoff of low $\delta^{13}\text{C}$

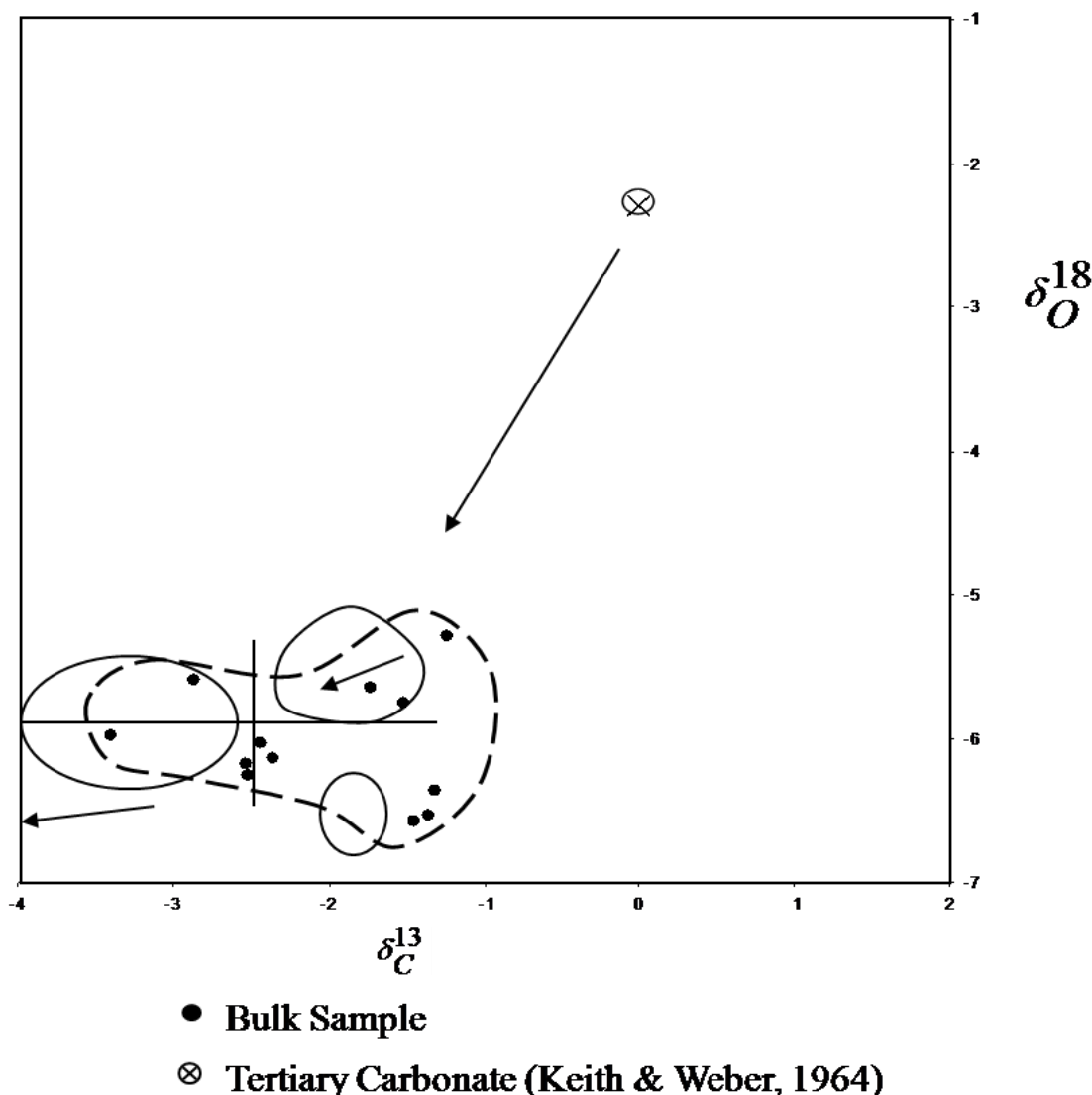


Figure 7. Carbon and oxygen isotope composition plot for the Kalambaina carbonates. Trend shown by arrow illustrates the pathway of changes in the isotope composition of the carbonates during progressive diagenesis and recrystallisation. The symbol $\otimes$ is the average value for the Tertiary limestone (Keith and Weber, 1964).

to the ocean. Terrestrial plant biomass has $\delta^{13}\text{C}$ values of about -25‰ PDB (Shackleton, 1967).

(4) The oxidation of organic matter could have caused a shift towards lighter $\delta^{13}\text{C}$ value hence depletion in the ^{13}C values of the resulting carbonates.

The rock-water ratio in connection with cementation process and recrystallisation of micritic matrix in burial should result in significantly more negative (lighter) $\delta^{18}\text{O}$ values (Kenneth, 1982; Huber et al., 1995; Williams et al., 1988). This is controlled by porosity and permeability of the rocks (Corfield, 1995). Fresh water inflow (percolation) may also contribute lighter $\delta^{18}\text{O}$ in the same set of samples mentioned above. This could explain the

enrichment of lighter ^{18}O in the recrystallized sparry calcite formed during the late stage fresh water diagenesis.

Estimated stable oxygen isotope paleotemperatures were calculated using the equation from Erez and Luz, (1983) given below:

$$T(^{\circ}\text{C}) = 16.998 - 4.52 \times (\delta^{18}\text{O}_{\text{cal.}} - \delta^{18}\text{O}_{\text{w}}) + 0.28 \times (\delta^{18}\text{O}_{\text{cal.}} - \delta^{18}\text{O}_{\text{w}})^2$$

Where: $\delta^{18}\text{O}_{\text{cal.}}$ = the equilibrium oxygen isotope composition of calcite. $\delta^{18}\text{O}_{\text{w}}$ = the oxygen isotopic composition of the water from which the calcite was precipitated.

The estimated formational paleotemperatures for the Kalambaina carbonates range between 26.80 and 32.85°C.

Conclusion

This study of the carbonates of the Paleocene Kalambaina Formation at the CCNN quarry near Kalambaina village reveals at least two carbonate rock types: bioclastic wackestone and bioclastic packstone. These rock types have been diagenetically altered. The presence of sparry calcite in the rock indicates late diagenetic stage. Carbon/Oxygen isotopic composition of the rocks vary from -5.29‰ to -6.58‰ $\delta^{18}\text{O}$ PDB and -1.24‰ to -3.40‰ $\delta^{13}\text{C}$ PDB in the whole rock compared to the average values of -2.33 $\delta^{18}\text{O}$ and +0.05 $\delta^{13}\text{C}$ PDB for Tertiary Sea water. The lighter oxygen and carbon fractions in the samples is a reflection of the depletion of heavier isotope of oxygen and carbon as a result of late stage recrystallization, influx of fresh water and formation of variable carbonate cements during progressive diagenesis.

The study suggests that carbonates of the Kalambaina Formation were deposited in shallow marine environment during the Paleocene marine transgression into the Sokoto basin. No evidence of hydrothermal alteration was observed in the carbonates.

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