

## Investigation of the geochemical signatures and conditions of formation of metacarbonate rocks occurring within the Mamfe embayment of south-eastern Nigeria

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### ABSTRACT

Hitherto unknown metacarbonate deposits constitute parts of the Cretaceous Mamfe embayment which straddles the border between south-eastern Nigeria and western Cameroon. The rock is characterised by a high concentration of LOI, CaO and MgO and depleted content of various insoluble components. Assuming all the CaO and MgO content of the rock were related to calcite and dolomite phases, these two minerals would account for around 22.5 wt% and 76.3 wt% on average, respectively. Among the trace elements investigated, only Ba, Cs, Rb, Sr, Nb, Pb, Zr, Cd, Cu, Ni, U, Y and Zn display concentrations beyond their detection limits. Chondrite normalised rare earth element patterns show that the rock under investigation show moderate to strong fractionation of light rare earth elements (LREE<sub>N</sub>) over heavy rare earth elements (HREE<sub>N</sub>) and distinct negative Eu anomaly. Multivariate statistical treatment and variation plots revealed several geochemical interrelationships, among which are the SiO<sub>2</sub> – Al<sub>2</sub>O<sub>3</sub> – K<sub>2</sub>O – TiO<sub>2</sub> – Fe<sub>2</sub>O<sub>3</sub> – Ba – Nb – Rb – Zr links which is associated with the rock's silicate fraction. The carbonate fraction comprises CaO, MgO, Sr, Pb and Cu. The overall geochemical signatures support development of the metacarbonate deposit from sedimentary carbonate materials that was deposited in a saline, shallow-marine, low-energy seawater environment. The consistency of the rock's chemical properties can be attributed to the relative stability experienced during the parent sedimentary materials' deposition.

*Keywords:* metacarbonate, geochemistry, depositional environment, Mamfe embayment.

### RESUMEN

Depósitos metacarbonatadas desconocidos hasta la fecha, parecen constituir partes de la Bahía de Mamfe, de edad Cretácica, ubicada en la frontera entre el sudeste de Nigeria y Camerún occidental. La roca se caracteriza por una alta concentración de LOI, CaO y MgO, así como el contenido empobrecido de varios componentes insolubles. Suponemos que todo el contenido de CaO y MgO de la roca estaban relacionados con las fases calcita y dolomita, minerales que representan aproximadamente el 22,5% en peso y 76,3% en peso promedio, respectivamente. Entre los elementos traza investigados, sólo las concentraciones de Ba, Cs, Rb, Sr, Nb, Pb, Zr, Cd, Cu, Ni, U, Y y Zn se encuentran por encima de los límites de detección. Elementos de tierras raras normalizados con patrones de Condrita muestran que la roca bajo investigación presenta un moderado a fuerte fraccionamiento de elementos de tierras raras ligeros (LREEN) sobre los elementos de tierras raras pesados (HREEN) y una anomalía negativa distintiva de Eu. El tratamiento estadístico multivariado y las proyecciones variacionales revelaron varias interrelaciones geoquímicas, entre ellos el SiO<sub>2</sub> - Al<sub>2</sub>O<sub>3</sub> - K<sub>2</sub>O - TiO<sub>2</sub> - Fe<sub>2</sub>O<sub>3</sub> - Ba - Nb - Rb - Zr, asociados con la fracción de silicato de la roca. La fracción carbonatada comprende CaO, MgO, Sr, Pb y Cu. Las firmas geoquímicas sugieren el desarrollo del depósito a partir de materiales sedimentarios carbonatados que se depositaron en una solución salina, de poca profundidad marina, y en un medio con agua de mar de baja energía. La consistencia de las propiedades químicas de la roca puede ser atribuida a la estabilidad relativa, experimentado durante la deposición de los materiales sedimentarias parentales.

*Palabras claves:* Geoquímica, ambiente de deposito, Bahía de Mamfe.

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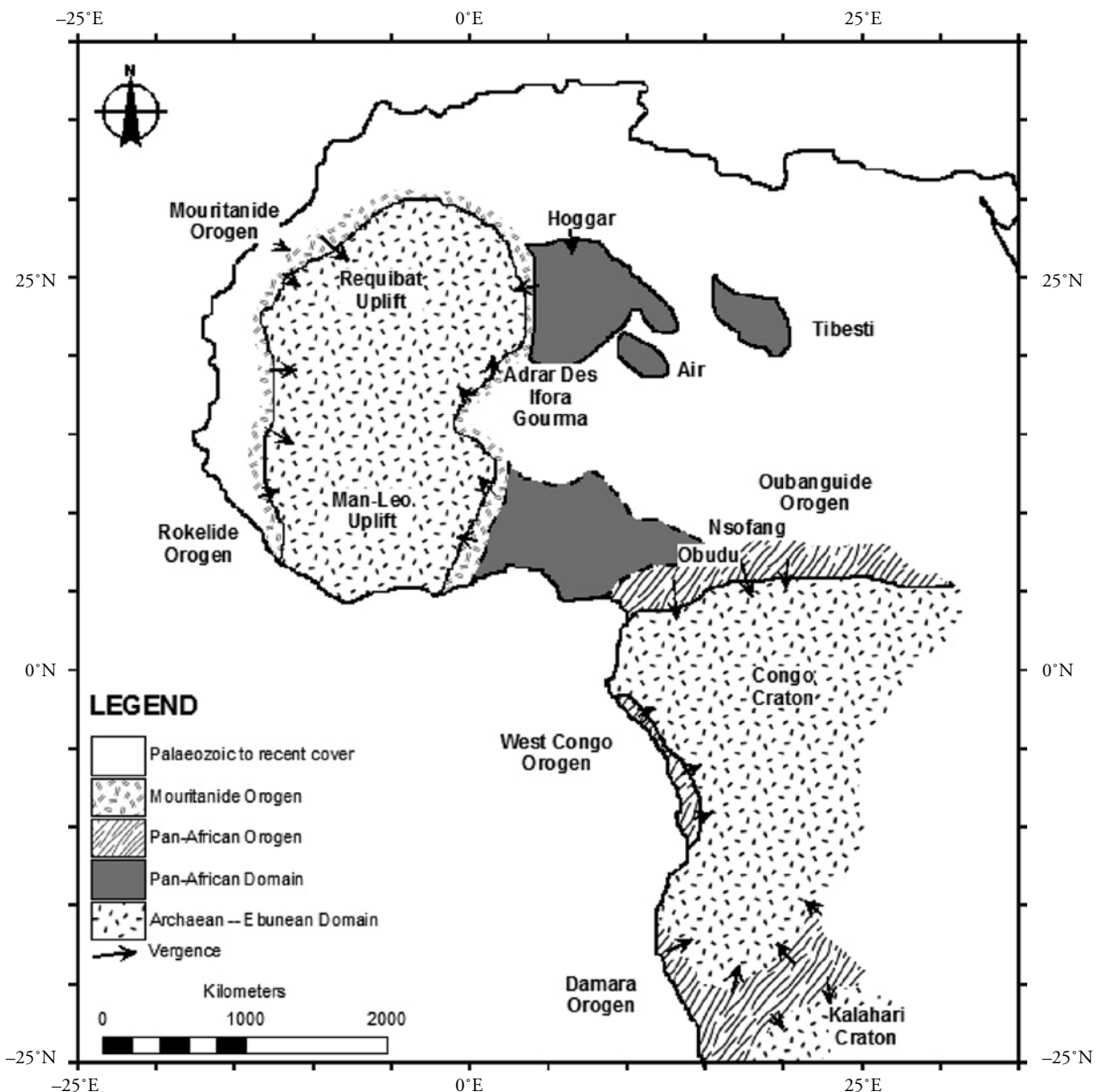


Figure 1. A generalised geotectonic map of Africa, showing the location of Nsofang (modified from Affaton *et al.*, 1991).

## Introduction

Nigeria lies within an area of the ancient African shield, in-between the Archaean to early Proterozoic West African craton and the Congo-Gabon craton (Figure 1). The south-eastern region is characterised by several megastructural features, notably the Calabar flank, the Mamfe embayment, the Anambra basin, the Afikpo syncline, the Abakaliki anticlinorium, the Niger Delta, the Oban massif and the Obudu plateau (Figure 2). Megastructural features, such as the Mamfe embayment, straddle the border between south-eastern Nigeria and western Cameroon (Figure 3). While the Cameroon sector of the basin has benefited from diverse and repetitive studies (for instance, Collignon, 1968; Dumort 1968; Eben, 1984; Eyong, 2003; Hell *et al.*, 2000; Kande, 2000; Kangkolo, 2002; Kangkolo and Ojo, 1995; Ndougsa-Mbarga 2004; Ndougsa-Mbarga *et al.*, 2004, 2007; Ndougsa-Mbarga and Ntep-Gweth, 2005; Ngando *et al.*, 2004; Njjeatih, 1997; Nouayou, 2005; Tabod, 2008; Tokam *et al.*, 2010), the Nigerian segment is yet to be investigated in sufficient detail. The few available works on the Nigerian segment of the Mamfe basin, to the best

of my knowledge, include those of Fairhead and Okereke (1987, 1988), Fairhead (1991), Olade (1975), Petters (1987 and 2004) and Reyment (1965). The paucity of geological information on the Nigerian segment of the embayment has previously led to over-generalisation, some of which may subsequently be proven to be incorrect.

A recent survey by the Nigerian Geological Survey Agency (NGSA) revealed mappable deposits of metacarbonate rock, which had been hitherto unknown in the south-eastern Nigerian sector of the Mamfe embayment. This discovery calls for re-examination of earlier paleo-environmental interpretations of the Mamfe basin. Of particular concern is an earlier viewpoint by Petters *et al.* (1987) that apart from brine seepages which are common, there is no substantial evidence of marine influence during the deposition of the Mamfe Formation's Cretaceous fluvial sequences. The present study which is focused on the investigation of the geochemical features of the newly-revealed metacarbonate deposits is intended to provide invaluable insight into the nature and processes which can be reasonably associated with the conditions of formation of the carbonate deposits. This work represents an effort towards revisiting

ing issues related to paleo-environmental interpretations for the basin. The present study also constitutes an important approach towards the in-depth exploration of the hitherto sparsely-known geology of the Nigerian sector of the Mamfe embayment.

**Geological background**

The Mamfe embayment which is located roughly between latitudes 5° N and 6° N and longitudes 8°45' E and 10° E is a coastal sedimentary basin that straddles the Federal Republic of Nigeria and the Republic of Cameroon (Figure 3). Despite the fact that the sedimentary infill of the Aptian to Albian (Hell *et al.*, 2000; Ndougsa *et al.*, 2004) Mamfe basin is largely covered by dense forestation, the type locality on the bank of the Cross River at Mamfe town in the Republic of Cameroon reveals thickly folded and faulted series of massive arkosic sandstone and grit having intercalations of marl, arenaceous limestone and shale (Reyment, 1965). Metacarbonate deposits, which constitute the focus of the present study, are now revealed to be parts of the Nigerian sector of the Mamfe embayment (Figure 3). Exposure of mostly the clastic infillings in the embayment show fining upward cycles, which is characteristic of fluvial channel fill, with point bar deposits and over bank siltstone/mudrock. A sedimentary deposit comprising sandstone, mudstone, shale, limestone, micro-conglomerates and polygenic conglomerates having about 2,000 m thickness has been reported in the lower Benue trough section (Olade, 1975). These deposits narrow towards the east until it disappear under Tertiary and Recent rocks of the Cameroon volcanic axis. Thus, the Cameroon

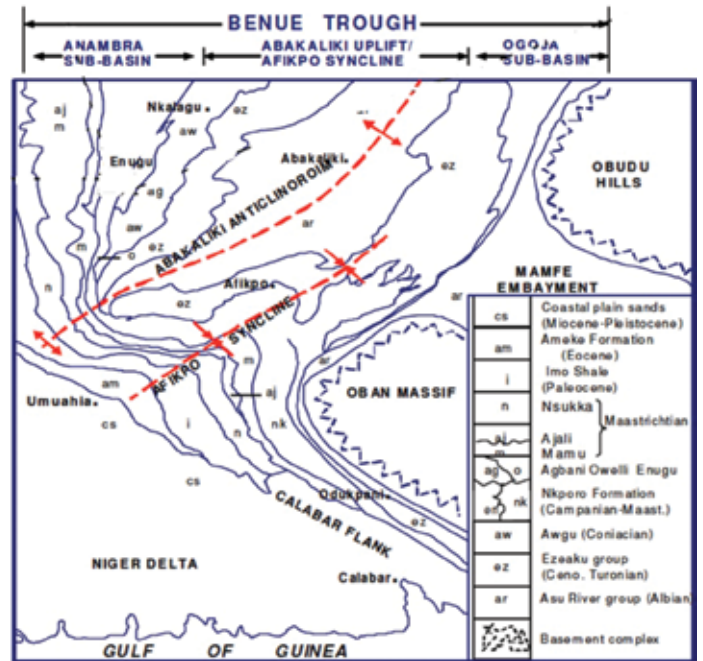


Figure 2. A geological sketch map of south-eastern Nigeria, showing the various megastructural features characterising the region (modified from Ofomata, 1973).

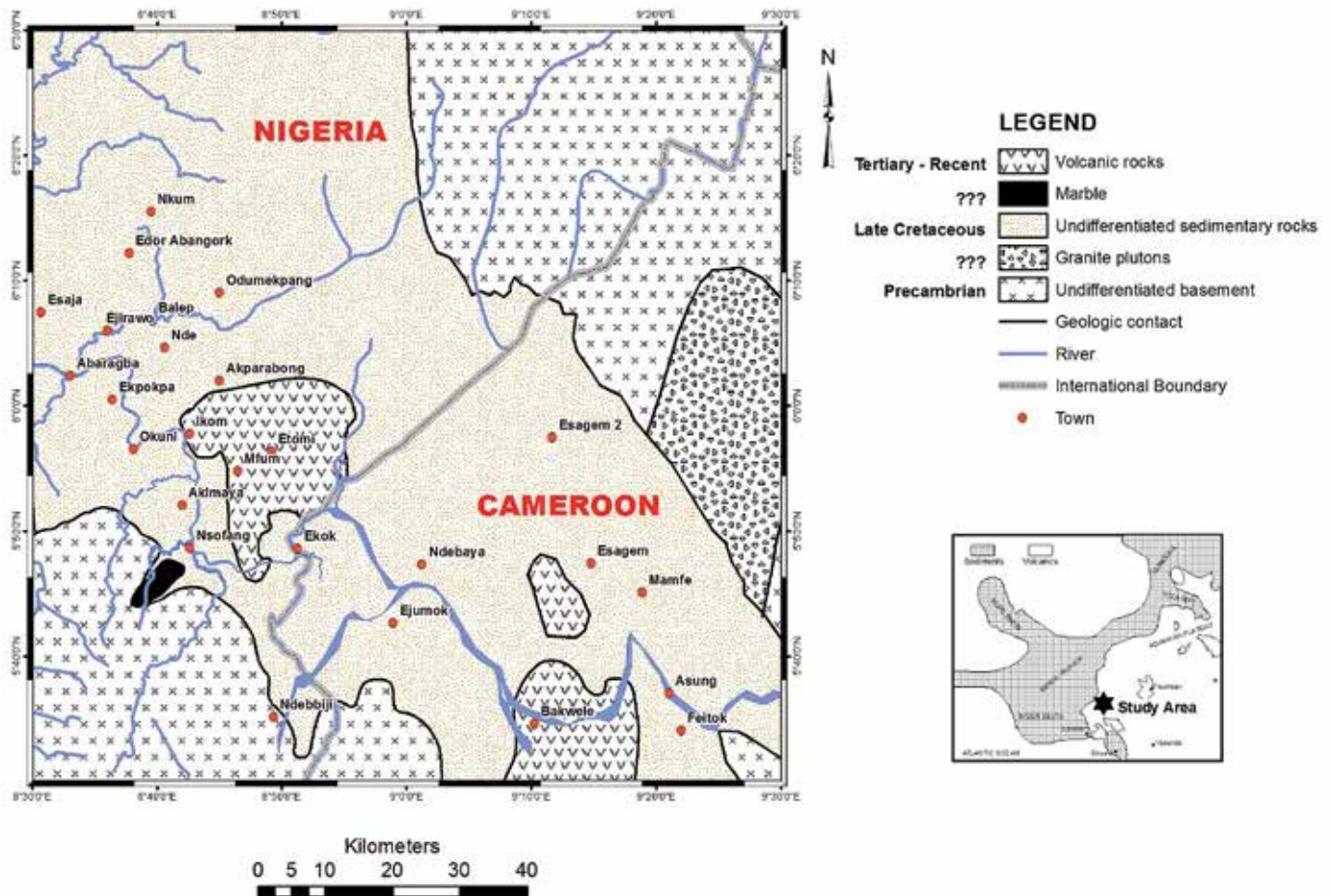
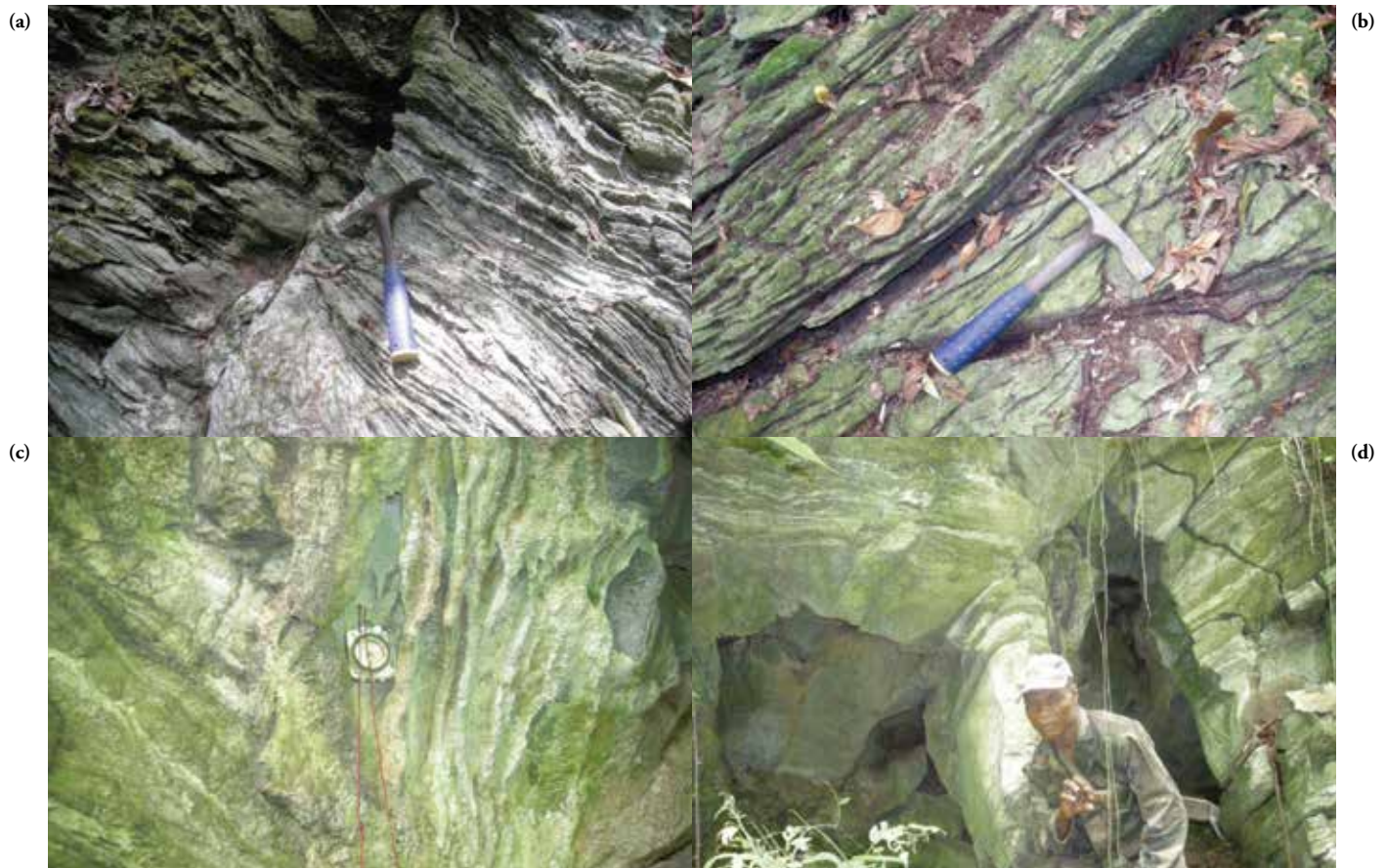


Figure 3. A geological map of south-eastern Nigeria and western Cameroon, showing the location of Nsofang marble within the Mamfe embayment of south-eastern Nigeria



**Figure 4.** Nsofang metacarbonates' outcrop features. (a) Distinct millimeter-scale laminations running parallel to the bedding. Note cavities that are outlined with the laminates. (b) Lamination comparable to algal laminates normally produced on tidal flats by colonies of blue green algae. (c) Small centimeter-sized voids/vugs. (d) Caves developed within the metacarbonates.

volcanic axis, comprising deposits such as basalt, trachyte and rhyolite, unconformably overlies the Mamfe Formation (Fitton, 1980). Metamorphism has so far not been reported in the Nigerian sector of the Mamfe embayment, but the close association of sedimentary deposits with post-dated volcanic rocks appear to provide a good setting for contact metamorphism in the region.

### Field and petrographic aspects

Observation of the metacarbonate deposits (generally consisting of low-lying deposits having several slightly elevated portions) showed that they are distributed within low to very low grade metamorphosed and un-metamorphosed sedimentary sequences in very close association with the basement and volcanic rocks units. Evidence of this association is provided by the close proximity of the units (Figure 3) and the ubiquitous basement and volcanic rock fragments abounding in the vicinity of the deposits. Generally, exposures of the metacarbonate have steep dips of about 26°–40° and consistent NE–SW strike orientation. Joints and fractures having variable orientation are also common features of these outcrops. Millimetre-scale laminations, small centimetre-sized voids/vugs and caves of up to tens of centimetres wide and 1 to 2 metres high are also predominantly conspicuously displayed on the outcrops (Figure 4). The fine laminations ran parallel to sub-parallel to the bedding in most cases (Figure 4a and 4b) and the voids are irregular but occasionally occluded by mostly laminated buff coloured material (Figure 4c). The caves are likewise irregular in shape, usually having solution sculpted walls (Figure 4d). The metacarbonate rocks are dense and somehow uni-

form, having rugged surfaces that possibly indicate the relevance of earlier organic activity and/or weathering in the rocks' evolutionary history. Hand specimen investigation showed that the rocks are characterised by a fairly homogeneous texture, uniform hardness and good resistance to abrasion. Also displayed are whitish or greyish colour, polymodal grain-sized distribution pattern of mostly fine to medium grains with occasional porphyroblasts and distinct linear and planar fabric, highlighted by the laminar structures.

The microscopic features (as observed by optical microscopy) show a predominantly carbonate mineralogy and the textural framework could best be described as heteroblastic. Medium grained (~ 1.0–2.0 mm) carbonate minerals are frequently surrounded by finer (<1.0 mm) grain crystals of similar mineral. The boundaries of the medium crystals are often sutured to embayed and the grains are interlocked. Unfortunately, the main carbonate minerals could not be differentiated during optical microscope examinations because the thin sections investigated were not stained with alizarin or any other relevant chemical. Also, much of the silicate mineralogy is so fine-grained that identification by optical means is difficult to impossible, hence the need for using an X-ray diffraction (XRD) technique which is particularly suitable for discerning individual mineral components of the cryptocrystalline phases and for proper differentiation of carbonate minerals into calcite and dolomite. XRD analysis was carried out on powdered samples under the following conditions:  $\text{CuK}_{\alpha 1}$  graphite monochromatic radiation (1.54059 Å) at 30 kV, 30 mA energy. Table 1 gives the results of semi-quantitative XRD studies of representative samples of the metacarbonate rocks. A cursory appraisal of the results (Table 1) indicates that the metacarbonates are

predominantly dolomitic with calcite as subordinate, while quartz, talc, phlogopite and probably muscovite constitute the accessory phases.

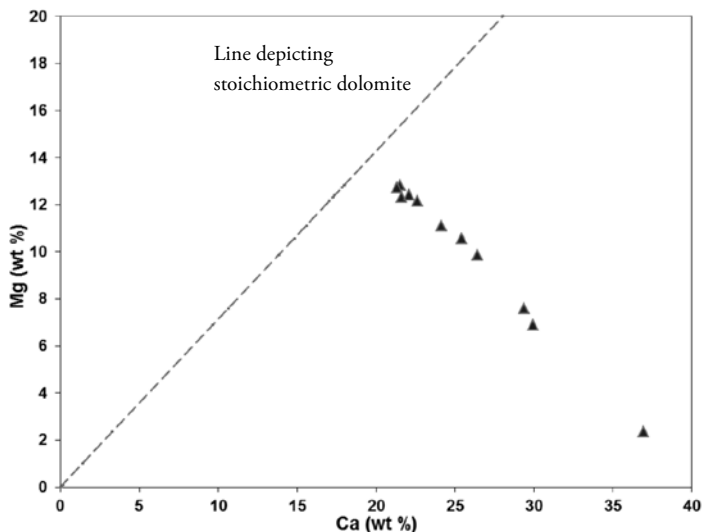
## Geochemistry

### Sampling and analytical procedure

Several unweathered rock samples weighing 1 to 2 kg were collected during fieldwork and traversing of various metacarbonate rock outcrops in Nsofang and its environs in the Ikom area of south-eastern Nigeria. Systematic sampling was hampered by the rocks' irregular exposure and the thick forestation cover. The samples so collected were cleaned to remove evident allogenic material and/or observed weathered phases *in situ* before being transported to the laboratory for further investigation.

Eleven representative metacarbonate rock samples were used for the geochemical analysis which was performed at the Acme Analytical Laboratories in Vancouver BC, Canada. The geochemical analysis involved measuring major, trace and rare earth element abundance as well as determining the total carbon, sulphur and loss on ignition. Prior to the geochemical analysis, about 1 kg of representative rock sample was broken to thumb-nail-sized pieces with a hardened-steel hammer. These pieces were crushed and pulverised to particle size as fine as -60 mesh with the aid of a "jaw-crusher". The samples were powdered in an agate mortar to -200 mesh after coning and quartering and thoroughly homogenised. Every possible precaution was taken to minimise cross-contamination between samples, including cleaning all the crushing, grinding and homogenisation equipment with a brush, compressed-air, distilled water and acetone to remove possible remains from previously crushed samples. Sample preparation and treatment was carried out at the Thin-Section Workshop of Department of Geology, University of Calabar, Calabar, Nigeria.

Loss on ignition (LOI) was determined by igniting 400 mg of each sample split at 1,000°C and then measuring the weight loss. Total carbon and total sulphur concentration was determined with the aid of a LECO carbon-sulphur analyser, after sample ignition at >800°C. Two instrumentation techniques were used for whole-rock geochemical analysis, namely inductively-coupled plasma-emission spectrophotometry (ICP-ES) and inductively-coupled plasma-mass spectrophotometry (ICP-MS). The lithium metaborate-tetraborate fusion digestion technique was found most appropriate for these instrumentation methods. Each sample solution was analysed in duplicate in each analytical run and reproducibility was found to be within  $\pm 2\%$ . The detection limit for all the major and minor element oxides was 0.01%, the only exceptions being  $\text{Fe}_2\text{O}_3$  and  $\text{K}_2\text{O}$  (0.04% detection limits). The trace elements' detection limit came within the 0.01 to 1 ppm range.



**Figure 5.** Comparison of the calcium and magnesium contents of the Nsofang marble with the ratio characteristics of stoichiometric dolomite (modified from Johnson, 2010).

### Geochemical data and interpretation

#### Major element oxides and relevant data

The concentrations of major element oxides and other related chemical data of the metacarbonate rocks are presented in Table 2. A cursory appraisal of the data (Table 2) revealed that LOI, CaO and MgO content frequently constituted more than 95 wt% of the rock composition and this corroborate mineralogical observations (Table 1) that the carbonate phases are the predominating phases in the rock. The high LOI values (Table 2) possibly reflect the low silica composition of the rocks (Table 1). Qadhi (2008) observed that increase of silica and other silicate constituents in marble reduces the LOI value. Apart from LOI, CaO constitute the dominant constituent, with concentrations that ranges from 29.85 to 51.67 wt% (35.79 wt% mean value). This is closely followed by MgO which has concentration varying from 3.88 to 21.25 wt% and 16.70 wt% mean value (Table 2). Assuming that all CaO and MgO content is related to calcite and dolomite phases, these two minerals would account for around 22.5 wt% and 76.3 wt % on average (Table 2). However, the true picture may be slightly different as the non-correspondence of the metacarbonate rocks' sample plots with the line depicting stoichiometric

**Table 1.** Semi-quantitative X-ray diffraction data of representative samples of metacarbonate rocks of Nsofang, Ikom area of southeastern Nigeria.

Sample #	Dolomite	Calcite	Quartz	Talc	Phlogopite	Muscovite
$L_1$	D	SD	Ftr	Tr	Tr	Ftr
$L_2$	CD	CD	Ac	Ftr	Ftr	Ftr
$L_3$	D	SD	Tr	Ftr	Ftr	Ftr

D = Dominant (> 50%)

CD = Codominant (subequal abundance of major components)

SD = Subdominant (20%-50%)

Ac = Accessory (5%-20%)

Tr = Trace  $\ll$  5%)

FTr = Faint trace  $\ll$  1%)

$L_1$  = Outcrop location 1, where  $L_{11'}$ ,  $L_{12'}$ ,  $L_{13}$  geochemical samples were also collected

$L_2$  = Outcrop location 2, where  $L_{21'}$ ,  $L_{22'}$ ,  $L_{23}$  geochemical samples were also collected

$L_3$  = Outcrop location 3, where  $L_{31'}$ ,  $L_{32'}$ ,  $L_{41'}$ ,  $L_{42'}$ ,  $L_{43}$  geochemical samples were also collected

**Table 2.** Concentrations of the major element oxides and related chemical data of metacarbonate rocks of Nsofang, Ikom area of southeastern Nigeria.

	L <sub>11</sub>	L <sub>12</sub>	L <sub>13</sub>	L <sub>21</sub>	L <sub>22</sub>	L <sub>23</sub>	L <sub>31</sub>	L <sub>32</sub>	L <sub>41</sub>	L <sub>42</sub>	L <sub>43</sub>
<b>Major elements oxide, total carbon, total sulphurs and LOI compositions (%)</b>											
SiO <sub>2</sub>	6.21	4.08	3.26	1.08	2.74	0.82	1.6	1.43	1.03	1.37	1.82
TiO <sub>2</sub>	0.06	<0.01	<0.01	0.01	<0.01	0.01	<0.01	0.01	<0.01	<0.01	<0.01
Al <sub>2</sub> O <sub>3</sub>	1.01	0.03	0.03	0.24	0.15	0.15	0.3	0.25	0.14	0.06	0.06
Fe <sub>2</sub> O <sub>3</sub>	0.36	<0.04	<0.04	0.08	0.08	0.08	0.08	<0.04	<0.04	<0.04	<0.04
MnO	0.01	0.01	<0.01	0.01	0.02	0.02	0.02	<0.01	0.01	<0.01	<0.01
MgO	20.42	21.25	20.56	12.6	21.09	20.14	18.43	11.43	3.88	16.35	17.52
CaO	30.26	30.1	30.94	41.09	29.85	31.67	33.78	41.88	51.67	36.94	35.55
Na <sub>2</sub> O	<0.01	<0.01	<0.01	0.01	0.01	0.01	0.04	0.02	<0.01	<0.01	<0.01
K <sub>2</sub> O	0.49	<0.01	<0.01	0.03	0.06	0.06	0.03	0.02	0.02	0.03	0.03
P <sub>2</sub> O <sub>5</sub>	0.05	0.05	0.06	0.02	0.15	0.14	0.14	0.13	0.02	0.04	0.02
LOI	40.8	44.1	44.8	44.6	45.4	46.5	45.2	44.5	43.1	44.9	44.6
TOTAL	99.68	99.69	99.73	99.77	99.56	99.6	99.63	99.72	99.93	99.76	99.67
Total Carbon	11.31	12.16	12.17	12.46	12.18	12.97	12.37	12.61	12.14	12.45	12.21
Total Sulphur	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
<b>Elemental Abundance (ppm)</b>											
Si	29,028	19,072	15,239	5,048	12,808	3,833	7,479	6,684	4,815	6,404	8,507
Ti	360	<60	<60	60	<60	60	<60	60	<60	<60	<60
Al	5,345	159	159	1,270	794	794	1,588	1,323	741	318	318
Fe	2,518	<280	<280	560	560	560	560	<280	<280	<280	<280
Mn	77	77	<77	77	155	155	155	<77	77	<77	<77
Mg	123,153	128,159	123,997	75,991	127,194	121,464	111,151	68,934	23,400	98,607	105,663
Ca	216,268	215,125	221,128	293,670	213,338	226,345	241,426	299,316	369,285	264,010	254,076
Na	<74	<74	<74	74	74	74	297	148	<74	<74	<74
K	4,068	<83	<83	249	498	498	249	166	166	249	249
P	218	218	262	87	655	611	611	567	87	175	87
<b>Computed abundance of carbonate minerals</b>											
Calcite	3	1	4	42	1	7	15	46	83	25	20
Dolomite	93	97	94	58	96	92	84	52	18	75	80

dolomite on the Ca *cf* Mg biplot (Figure 5), similar to that of Johnson *et al.*, (2010), is an indication that dolomite may not be the dominant host mineral for CaO and MgO. It is possible that some MgO are also admixed in the calcite's structural lattices, as observed in the Jabal Farasan marble of central-western Saudi Arabia (Qadhi, 2008). Both CaO and MgO are also possibly bound in the structure of the small and probably insignificant silicate phases, which is represented by quartz, talc, phlogopite and muscovite that constitute parts of the rock's modal mineralogy (Table 1). The insoluble residues, notably, SiO<sub>2</sub> (0.82–6.21 wt%), Al<sub>2</sub>O<sub>3</sub> (0.003–1.01 wt%) and K<sub>2</sub>O (0.01–0.49 wt%) have considerably low abundance. Ignoring sample L<sub>11</sub>, Fe<sub>2</sub>O<sub>3</sub> is frequently less than 0.08 wt% while TiO<sub>2</sub>, MnO and Na<sub>2</sub>O concentration are negligible. Both K<sub>2</sub>O and P<sub>2</sub>O<sub>5</sub> have 0.07 wt% mean concentration (Table 2). The relatively lower abundance of Fe, Mn and P in the samples are probably the reflection of low detrital and organic effects relative to the inorganic chemical carbonate precipitate (Tucker, 1983). The total carbon values are considerably high (11.31–12.97 wt%,

av. 12.28 wt%) as expected for carbonate-bearing rocks, while the same could not be said for total sulphur concentration which are generally below the 0.02 wt% detection limit.

#### Trace element composition

The trace elements geochemical data of the metacarbonate rocks are presented in Table 3. As shown in Table 3, only Ba, Cs, Rb, Sr, Nb, Pb, Zr, Cd, Cu, Ni, U, Y and Zn have concentrations beyond their detection limits since many trace elements concentrations were below the relevant detection limits (Table 4). The rock's trace element concentrations are not as low as expected and Sr and Ba values are highly variable (Table 3), possibly suggesting a complex distribution of the element (Georgieva, 2009). Light ion lithophile element (LILE) concentration, notably Ba (55 ppm average), Sr (145.1 ppm average) and probably Rb (2.7 ppm average) are considered moderate. Sr concentration particularly appears to be appro-

**Table 3.** Trace element composition and relevant ratios of metacarbonate rocks of Nsofang, Ikom area of southeastern Nigeria.

	L <sub>11</sub>	L <sub>12</sub>	L <sub>13</sub>	L <sub>21</sub>	L <sub>22</sub>	L <sub>23</sub>	L <sub>31</sub>	L <sub>32</sub>	L <sub>41</sub>	L <sub>42</sub>	L <sub>43</sub>
<b>Ba</b>	190	22	6	33	78	70	37	37	19	57	52
<b>Cs</b>	3.9	0.2	<0.1	0.2	0.4	0.3	0.2	0.2	0.1	0.3	0.4
<b>Rb</b>	17.8	0.5	0.3	0.8	2.7	2.2	0.9	0.7	0.6	1.2	1.5
<b>Sr</b>	59.1	53.8	60.1	167.7	97.4	95.6	100.1	181.4	552.3	115.8	112.6
<b>Nb</b>	1.5	0.2	0.1	0.3	0.2	0.3	0.2	0.2	0.1	<0.1	<0.1
<b>Pb</b>	0.9	0.4	0.5	0.7	0.6	0.5	0.7	0.8	1.1	0.3	0.5
<b>Zr</b>	35.7	4.1	6.7	7.7	14.9	15.1	7.8	12.4	3.8	5.4	12.8
<b>Cd</b>	0.2	0.2	0.7	0.3	0.2	0.1	0.3	0.3	0.1	0.3	0.3
<b>Cu</b>	0.9	0.7	1.6	0.6	1	0.6	2.7	1.5	12.1	0.2	0.2
<b>Ni</b>	0.3	<0.1	0.8	3.9	1.2	1.7	1.3	3.5	1.6	1.1	1
<b>U</b>	0.5	1.3	3	0.8	0.3	0.3	0.6	0.6	2.3	2.3	1.8
<b>Y</b>	5.7	2.7	2	1.8	0.6	0.7	1.4	2	1	0.7	0.6
<b>Zn</b>	9	5	6	8	4	5	7	6	3	5	4
<b>Mn/Sr</b>	1.30	1.43	1.28	0.46	1.59	1.62	1.55	0.42	0.14	0.66	0.68
<b>Mg/Ca</b>	0.57	0.60	0.56	0.26	0.60	0.54	0.46	0.23	0.06	0.37	0.42

priate, given the fact that Sr content of recent carbonates are expected to range from 30 ppm to 200 ppm (Shearman and Shirmohammadi, 1969). Among the high-charged cations, Zr has concentration ranging from 4.1 to 35.7 ppm (11.5 ppm mean value), Nb concentration ranging from 0.1 to 1.5 ppm (0.3 ppm mean value) and U content varying from 0.3 and 3.0 ppm. Y concentration ranged from 0.6 to 5.7 ppm; Zn (5.6 ppm average), Cu (2.0 average) and Ni (1.6 ppm average) display moderate concentration, while Cd (0.3 ppm average), Pb (0.6 ppm average) and Cs concentration (0.6 ppm average) appear low. Figure 6 illustrates the composition of the trace elements of the metacarbonate rock normalised to the average upper continental crust of Taylor and McLennan (1981).

#### Rare earth element geochemistry

Table 5 gives the rare earth elements (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) abundance in the rock, together with other relevant data.

The REE values shown in Table 5 are quite low ( $\Sigma\text{REE} = 1.33\text{--}6.12$  ppm, excluding sample L<sub>11</sub> having an abnormal 15.41 ppm concentration) and the concentration of most components from locations L<sub>22</sub>, L<sub>23</sub>, L<sub>42</sub> and L<sub>43</sub> are below detection limits (Table 5). The tabulated data (Table 5) clearly show that LREE components dominate over HREE, and that total LREE and HREE concentrations decrease from 12.53 to 1.1 ppm and from 2.88 to 0.27 ppm, respectively (Table 5). Identification of REE fractionation in the metacarbonate rocks was carried out by normalising (Haskin *et al.*, 1968) the concentration of the rare earth elements to average chondritic meteorites, and the result for samples having concentrations beyond detection limits is presented as REE pattern (Figure 7). A cursory appraisal of the chondrite-normalised rare earth element (REE<sub>N</sub>) plot show that all samples exhibit similar REE<sub>N</sub> patterns, moderate to strong fractionation of light rare earth elements (LREE) over heavy REE (HREE) ( $\text{La}_N/\text{Yb}_N = 0.98\text{--}9.35$ ) and distinct negative Eu anomaly,  $\text{Eu}/\text{Eu}^*$  ranging from 0.48 to 0.60. It is also obvious that La – Nd – Sm – Eu appear to define an inclined straight line and the heavy rare earth elements (HREE) exhibit uncoordinated zig-zags patterns in the Gd – Dy – Ho – Er – Yb – Lu spans (Figure 7).

**Table 4.** Measured trace elements occurring below detection limits in metacarbonate rocks of Nsofang, Ikom area of Southeastern Nigeria

	Detection Limits (in ppm except otherwise stated)	Comments
<b>Ag</b>	<0.1	No sample revealed measureable amounts
<b>Be</b>	<1	No sample revealed measureable amounts
<b>Bi</b>	<0.1	No sample revealed measureable amounts
<b>Co</b>	<0.2	2 samples showed traces of 0.3 – 0.4 ppm
<b>Ga</b>	<0.5	1 sample showed traces of 1.4 ppm
<b>Hf</b>	<0.1	2 sample showed traces of 0.2 – 0.8 ppm
<b>Mo</b>	<0.1	3 samples showed traces of 1 – 2 ppm
<b>Sb</b>	<0.1	No sample revealed measureable amounts
<b>Sc</b>	<1	1 sample showed traces of 1ppm
<b>Se</b>	<0.5	1 sample showed traces of 0.6 ppm
<b>Sn</b>	<1	No sample revealed measureable amounts
<b>Ta</b>	<0.1	1 sample showed traces of 0.1ppm
<b>Th</b>	<0.2	4 samples showed traces of 0.2 – 0.6 ppm
<b>Tl</b>	<0.1	No sample revealed measureable amounts
<b>V</b>	<8	5 samples showed traces of 9 - 22 ppm
<b>W</b>	<0.5	1 sample showed traces of 1.6ppm
<b>Hg</b>	<0.01 (ppb)	No sample revealed measureable amounts
<b>Au</b>	<0.5 (ppb)	No sample revealed measureable amounts

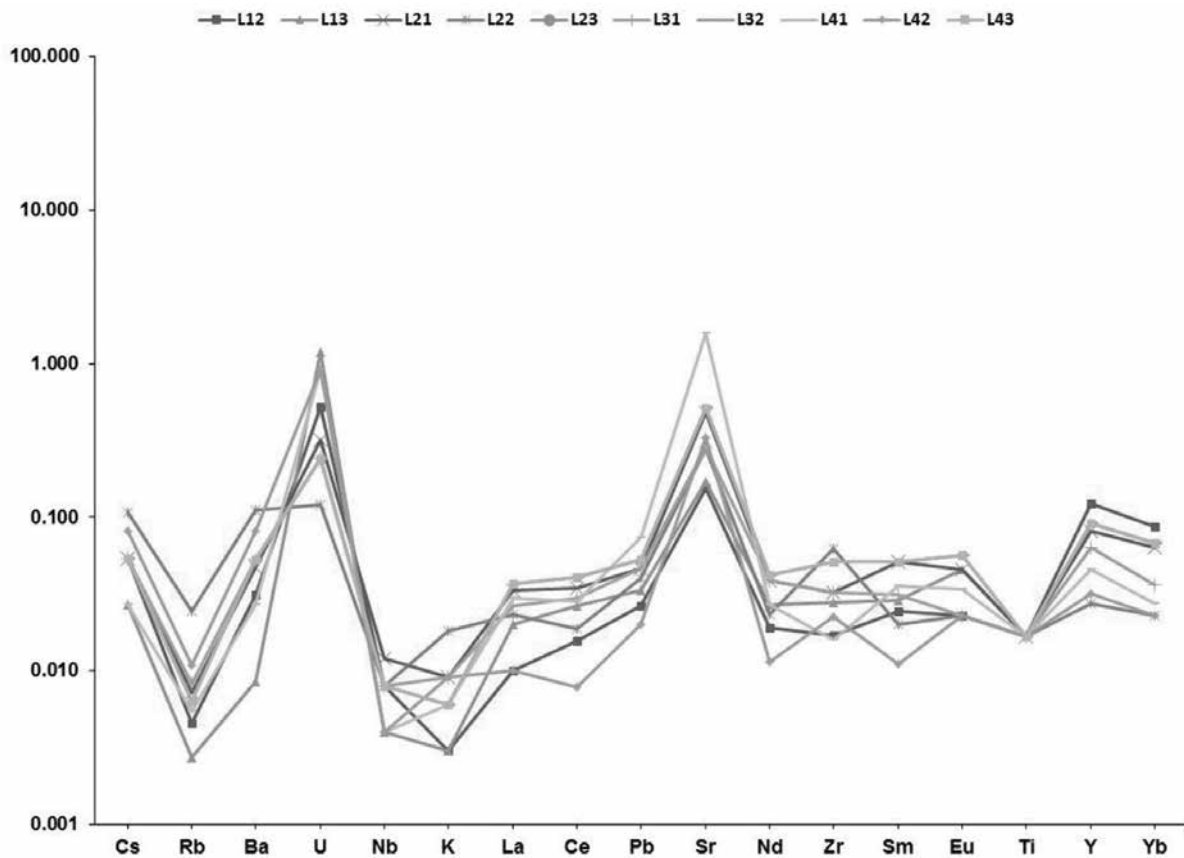


Figure 6. Selected trace element concentrations of Nsofang metacarbonate rock normalized to the composition of average upper continental crust of Taylor and McLennan (1981).

Table 5. Rare earth element composition of metacarbonate rocks of Nsofang, Ikom area of southeastern Nigeria.

	L11	L12	L13	L21	L22	L23	L31	L32	L41	L42	L43
La	2.7	0.3	0.6	1	0.7	0.6	0.8	1.1	0.9	0.3	0.2
Ce	5.9	1	1.7	2.2	1.2	1.2	1.9	2.6	1.8	0.5	0.5
Pr	0.7	0.1	0.16	0.25	0.12	0.13	0.19	0.26	0.18	0.05	0.05
Nd	2.6	0.5	0.7	1	0.6	0.7	1	1.1	0.7	<0.3	<0.3
Sm	0.63	0.11	0.13	0.23	0.09	0.11	0.14	0.23	0.16	0.05	<0.05
Eu	0.1	0.02	0.04	0.04	<0.02	<0.02	0.02	0.05	0.03	<0.02	<0.02
Gd	0.66	0.15	0.13	0.18	0.08	0.09	0.12	0.2	0.13	<0.05	<0.05
Tb	0.12	0.03	0.03	0.03	0.02	0.01	0.02	0.04	0.02	<0.01	<0.01
Dy	0.73	0.21	0.14	0.21	0.08	0.08	0.12	0.22	0.14	0.05	<0.05
Ho	0.15	0.05	0.05	0.05	<0.02	<0.02	0.03	0.04	0.02	<0.02	<0.02
Er	0.48	0.21	0.16	0.14	0.07	<0.03	0.08	0.09	0.11	0.05	0.05
Tm	0.08	0.03	0.02	0.02	0.01	<0.01	0.01	0.02	0.01	<0.01	<0.01
Yb	0.49	0.19	0.15	0.14	<0.05	0.06	0.08	0.15	0.06	<0.05	<0.05
Lu	0.07	0.03	0.03	0.02	<0.01	<0.01	0.01	0.02	<0.01	<0.01	<0.01
$\Sigma$ REE	15.41	2.93	4.04	5.51	3.07	3.07	4.52	6.12	4.27	1.47	1.37
$\Sigma$ LREE	12.53	2.01	3.29	4.68	2.71	2.74	4.03	5.29	3.74	1.2	1.1
$\Sigma$ HREE	2.88	0.92	0.75	0.83	0.36	0.33	0.49	0.83	0.53	0.27	0.27



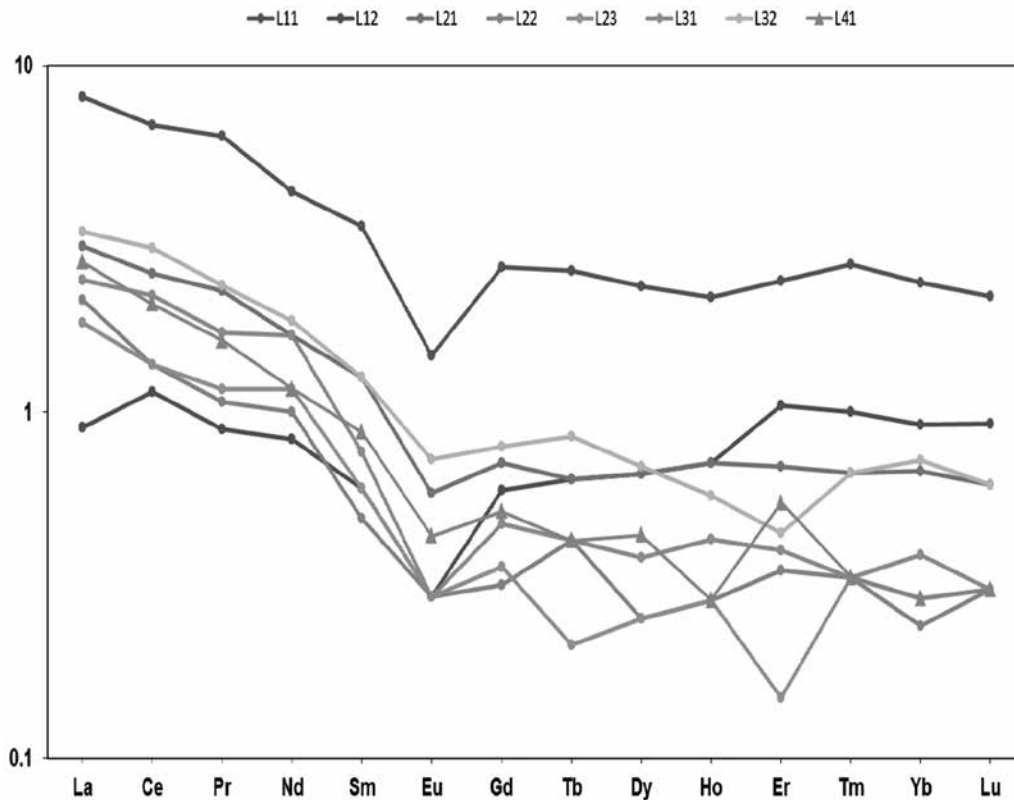


Figure 7. Chondrite normalised (Haskin, 1968, 71) rare earth element patterns of the Nsofang metacarbonate rock.

Table 6. Correlation coefficients of major element components and selected trace elements of metacarbonate rocks of Nsofang, Ikom area of Southeastern Nigeria.

	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MnO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	LOI	Total C	Ba	Nb	Ni	Pb	Rb	Sr	Zr
SiO <sub>2</sub>	1																		
TiO <sub>2</sub>	0.78	1																	
Al <sub>2</sub> O <sub>3</sub>	0.62	0.94	1																
Fe <sub>2</sub> O <sub>3</sub>	0.73	0.98	0.96	1															
MnO	-0.23	-0.19	-0.05	-0.02	1														
MgO	0.53	0.23	0.11	0.28	0.38	1													
CaO	-0.57	-0.27	-0.16	-0.32	-0.38	-1.00	1												
Na <sub>2</sub> O	-0.20	-0.13	0.11	-0.06	0.44	0.00	0.00	1											
K <sub>2</sub> O	0.75	0.99	0.95	0.99	-0.10	0.26	-0.30	-0.14	1										
P <sub>2</sub> O <sub>5</sub>	-0.13	-0.15	0.02	-0.04	0.82	0.35	-0.37	0.51	-0.08	1									
LOI	-0.69	-0.82	-0.74	-0.73	0.57	0.19	-0.15	0.18	-0.76	0.50	1								
Total C	-0.85	-0.79	-0.66	-0.72	0.36	-0.15	0.18	0.16	-0.75	0.39	0.88	1							
Ba	0.62	0.90	0.87	0.93	0.09	0.34	-0.38	-0.15	0.94	0.07	-0.57	-0.59	1						
Nb	0.74	0.98	0.96	0.99	-0.11	0.26	-0.30	-0.11	0.99	-0.07	-0.75	-0.70	0.91	1					
Ni	-0.63	-0.33	-0.09	-0.27	-0.05	-0.56	0.56	0.13	-0.32	0.10	0.27	0.54	-0.29	-0.24	1				
Pb	0.05	0.37	0.53	0.38	-0.10	-0.65	0.60	0.16	0.36	-0.05	-0.58	-0.36	0.21	0.37	0.29	1			
Rb	0.76	0.99	0.94	0.98	-0.09	0.28	-0.32	-0.15	1.00	-0.08	-0.76	-0.75	0.95	0.98	-0.34	0.34	1		
Sr	-0.44	-0.20	-0.13	-0.24	-0.22	-0.92	0.91	-0.08	-0.22	-0.30	-0.21	0.05	-0.30	-0.25	0.30	0.69	-0.23	1	
Zr	0.63	0.89	0.88	0.91	0.08	0.35	-0.39	-0.12	0.92	0.15	-0.55	-0.56	0.95	0.91	-0.20	0.29	0.93	-0.33	1

### Geochemical interrelationships

The interrelationships between the major element oxides and trace elements of the metacarbonate rock have been investigated and the results presented as correlation coefficients (Table 6) and co-variation plots (Figures 8–11). Also, following the procedure adopted by Veizer *et al* (1992), R-mode factor analysis have also been employed to reveal any communality of chemical elements and, indeed, the most likely identity of the host minerals. The rotated factor matrix is presented in Table 7, together with eigenvalues, total variance percentage and cumulative percentage.

Examination of changes of the major elements oxides with respect to CaO concentration reveal that SiO<sub>2</sub> and MgO are significantly decreased with increasing CaO content in the rock (Table 6, Figure 8). CaO composition also display an expected weak negative correlation with most of the insoluble residues, notably TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, MnO, K<sub>2</sub>O and P<sub>2</sub>O<sub>5</sub> (Table 6, Figure 8), and both SiO<sub>2</sub> *cf* MgO and SiO<sub>2</sub> *cf* Al<sub>2</sub>O<sub>3</sub> cross-plots (Figure 8) show significant positive correlation between the involved com-

ponents. The TiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub> and K<sub>2</sub>O concentration appear consistent with those of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> (Table 5). Furthermore, there appear to be no correlation between CaO and Na<sub>2</sub>O (Table 6, Figure 8).

Examination of variations of trace element in the rock reveals Pb, Ni, Sr and Cu enrichment with increasing CaO values while Ba, Nb, Rb and Zr display weak negative correlation with CaO (Table 6, Figure 9). It is also interesting to observe that most trace elements display positive interrelationships with the major insoluble residue components of the rock (Table 6) and prominent among these are the SiO<sub>2</sub> – Al<sub>2</sub>O<sub>3</sub> – K<sub>2</sub>O – TiO<sub>2</sub> – Fe<sub>2</sub>O<sub>3</sub> – Ba – Nb – Rb – Zr links (Table 6, Figure 10).

In the rotated factor matrix (Table 7), loading greater than ± 0.55 are highlighted and considered significant members of each of the 3 factor score groupings. As shown in Table 7, Factor 1 (comprising significant loadings of Si, Ti, Al, Fe, K, Ba, Cs, Rb, Nb, Zr, Y and Zn) account for 38.59% of total data variance while Factor 2 (high loadings of Ca, Sr, Pb and Cu) account for 17.15% of total data variance. Factor 3 (with high loadings of Mn, Ba, U and Y) account for 12.68% of total data variance.

**Table 7.** Varimax rotated R – mode factor analysis of bulk rock composition of metacarbonate rocks of Nsofang, Ikom area of southeastern Nigeria. The highlighted loadings are greater than ±5.5

	Factor 1	Factor 2	Factor 3
LOG Si	0.58	-0.34	-0.53
LOG Ti	0.94	0.01	-0.18
LOG Al	0.75	0.51	0.36
LOG Fe	0.95	0.08	0.17
LOG Mn	0.03	0.01	0.78
LOG Mg	-0.09	0.00	0.00
LOG Ca	0.00	0.71	-0.06
LOG Na	0.00	0.41	0.18
LOG K	0.88	-0.04	0.36
LOG P	0.15	0.03	0.48
LOG Ba	0.69	-0.21	0.57
LOG Cs	0.91	-0.30	0.14
LOG Rb	0.86	-0.20	0.38
LOG Sr	-0.42	0.67	0.22
LOG Nb	0.95	0.11	0.08
LOG Pb	0.36	0.82	0.05
LOG Zr	0.79	-0.18	0.39
LOG Cd	-0.10	-0.25	-0.53
LOG Cu	-0.09	0.86	-0.10
LOG Ni	-0.31	0.47	0.48
LOG U	-0.52	-0.10	-0.70
LOG Y	0.64	0.27	-0.65
LOG Zn	0.65	0.08	-0.25
Eigenvalue	8.88	3.95	2.92
Percent of total variance	38.59	17.15	12.68
Cumulative percentage	38.59	55.75	68.43

### Interpretation and Discussion

#### Evaluation of consistency of primary chemical signatures

A number of geochemical parameters have been proposed for testing the degree of preservation of primary chemical signatures in carbonate-bearing rocks (Kaufman *et al.*, 1993; Narbonne *et al.*, 1994; Pandit *et al.*, 2003; Veizer, 1983). In particular, the Mn/Sr ratio has been accepted as a definitive indicator for the degree of preservation and/or post-depositional alteration (Brand and Veizer, 1980; Derry *et al.*, 1992; Veizer *et al.*, 1989, 1992). The Mn/Sr ratio of the Nsofang marble varies between 0.14 and 1.62 with an average of 1.01 ppm. These values are considered to fall within acceptable limits for carbonate rocks that are well-preserved and unaffected by post-depositional alteration (Derry *et al.*, 1992; Kaufman *et al.*, 1992, 1993; Kaufman and Knoll, 1995). Moreover, Brand (1983) has suggested that trace element signatures can aid in interpretation of depositional environment conditions despite post-digenetic alteration. The chemical signatures of the marble can therefore be taken as representative of the precursor rock.

#### Distribution of chemical species

The reduction in SiO<sub>2</sub> content compared to increasing CaO concentration (Figure 8) agree with the fact that the rock comprises distinct silicate and carbonate fractions, having contrasting variations. The carbonate fraction increases at the expense of the silicate fraction and vice versa. The positive relationship between SiO<sub>2</sub> and MgO (Table 6, Figure 8) most likely confirm earlier observations that MgO constitutes parts of the silicate fraction. The positive relationship existing between SiO<sub>2</sub> and MgO (Table 6, Fig. 8) most likely confirm earlier observations that MgO also constitute parts of the silicate fraction. The positive relationship displayed between SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> (Fig. 8), together with the consistency observed in the variation of TiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub> and K<sub>2</sub>O with those of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>, (Table 6) and the weak negative correlation existing between CaO and the various insoluble residues (Fig. 8) suggests that the non-carbonate or silicate fractions are mainly aluminosilicates. However, where Al<sub>2</sub>O<sub>3</sub> is extremely low (as in sample L<sub>12</sub>, L<sub>13</sub>, L<sub>42</sub> and L<sub>43</sub>), clearly the SiO<sub>2</sub> cannot have been introduced into the original sediment in aluminosilicate phases and was probably therefore either in traces of detrital quartz or in siliceous organisms.

Among the trace elements investigated, Sr, Pb and Ni appear to be enriched in the carbonate fractions as implied by the consistency that these components display with CaO, which is an important member of the carbonate fraction. The enrichment of Sr in carbonates is often accounted for by the fact that Sr<sup>2+</sup> readily substitutes for Ca<sup>2+</sup> in calcium – bearing struc-

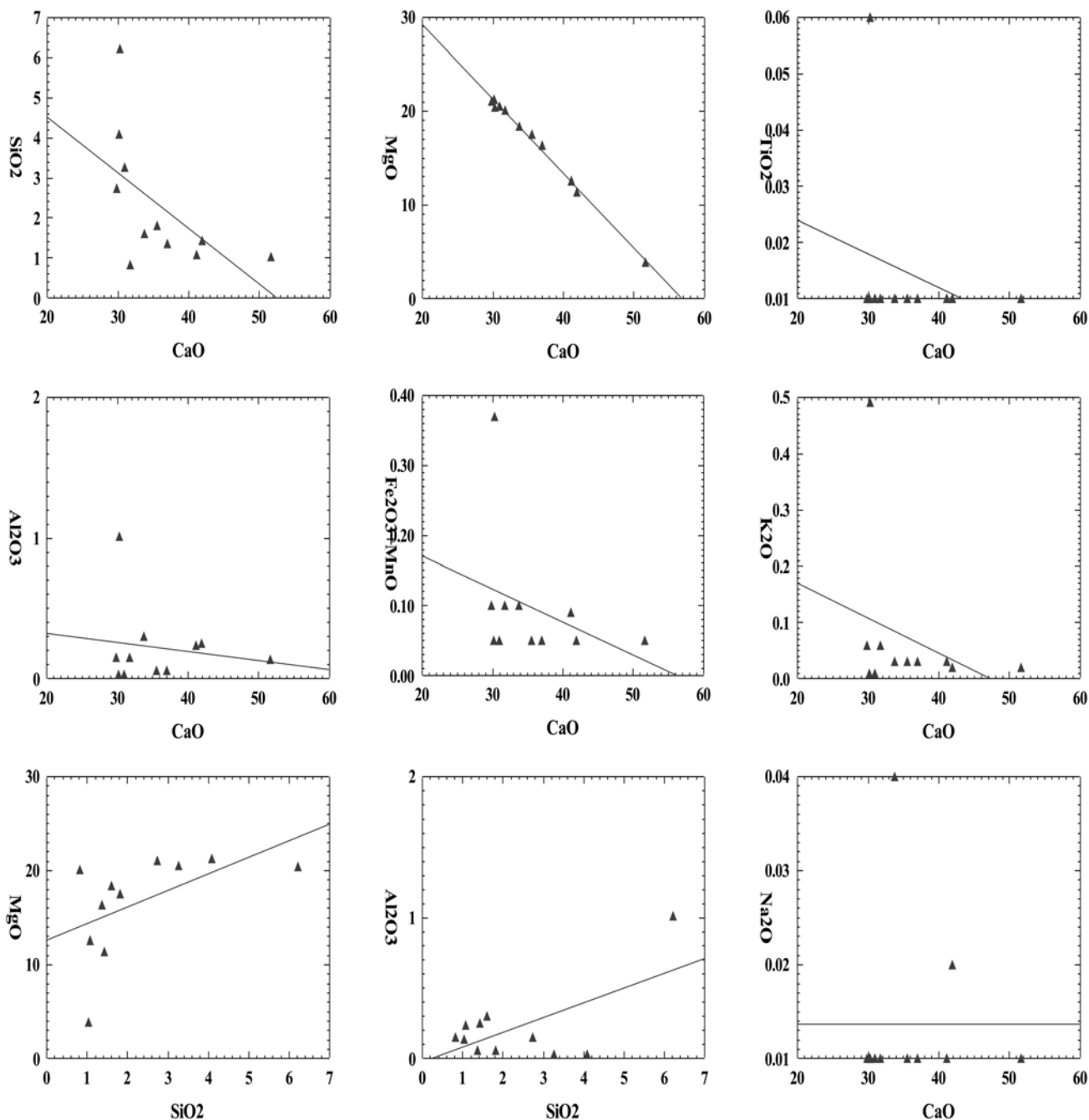


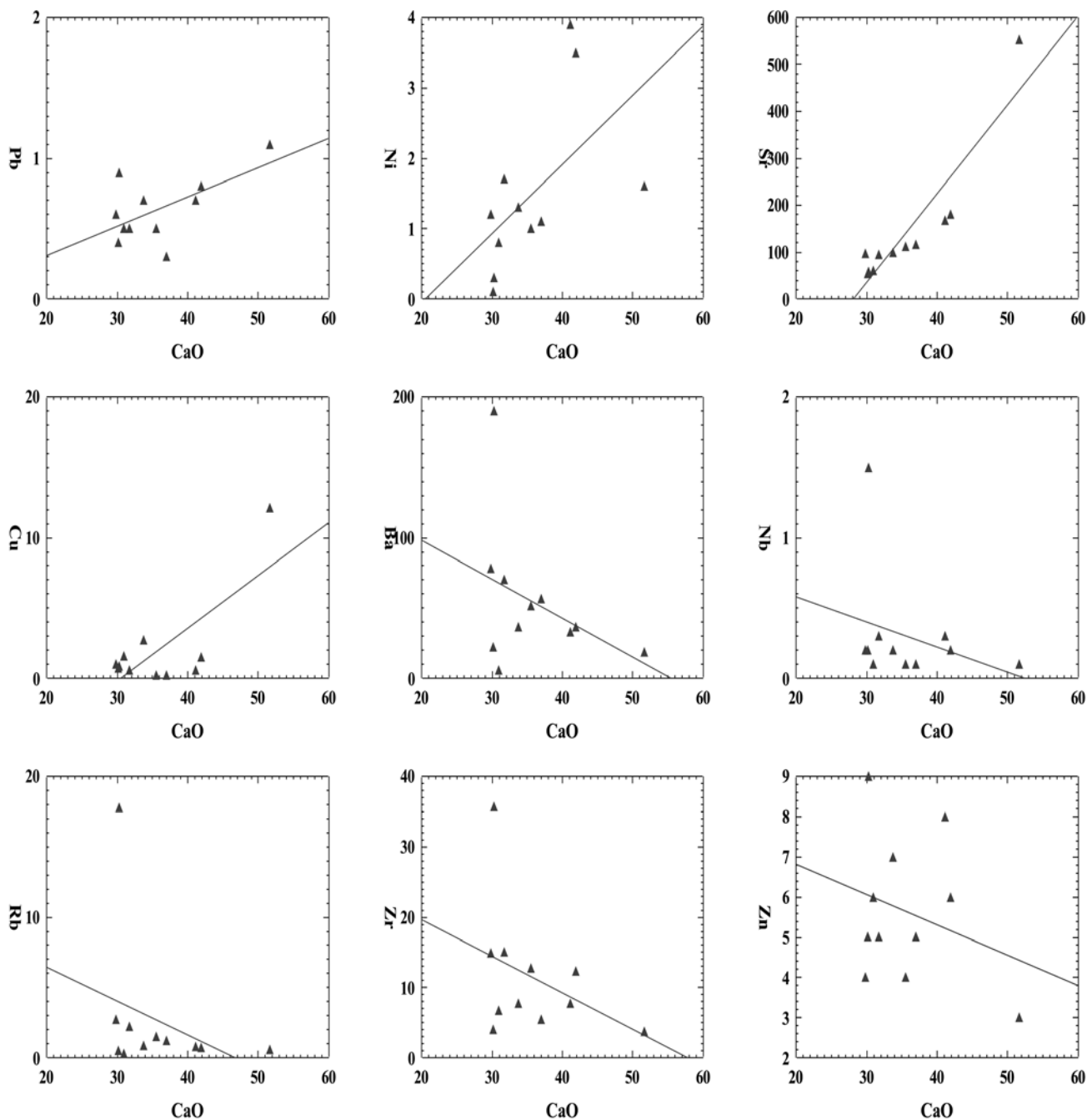
Figure 8. The degree of correspondence amongst the major element oxides.

ture. However, in the Nsofang metacarbonates, both Ca and Sr display very strong positive correlation (Figure 9) which rather suggests that both components are probably bound together in the same calcium – bearing lattice structures. This is consistent with the position of Dissanayake (1981) that Sr being the main trace elements in limestone and dolomites is often presume to be located in the lattices of carbonate minerals. The observed lack of significant positive correlation between Sr and Na (Table 6; Figure 11) is an indication that  $\text{Na}_2\text{O}$  is not controlled by the carbonate phases, and consequently does not form parts of the lattices of the Ca – Mg carbonates nor occur as inclusions in the carbonate phases (Fritz and Katz, 1972; Land and Hoops, 1973). The lack of strong relationship between Sr and Na, together with the absence of significant positive correlation between  $\text{Na}/\text{Ca}$  versus  $\text{Mg}/\text{Ca}$  or  $\text{Sr}/\text{Ca}$  (Figure 11), also

precludes the consideration of an evaporitic hypersaline (Sass and Katz, 1982) conditions as existing during developments of the protoliths of the metacarbonate.

Other trace elements, notably Ba, Nb and Rb, tend to concentrate in the silicate fractions as inferred from the weak negative correlation they displays with CaO (Figure 9) and the positive interrelationships they exude with major insoluble residue components of the rock (Figure 10). Arising from the marked correlation exhibited between Zr and  $\text{Al}_2\text{O}_3$  (Figure 10), it thus seems reasonable to suggest that much of the rock's Zr composition was probably not introduced as detrital zircon but also formed parts of the rock's silicate fraction.

The strong positive interrelationships amongst the various trace elements and major insoluble residues (Figure 10) underline the relevance



**Figure 9.** The degree of correspondence of selected trace elements with CaO composition of the Nsofang metacarbonate rock.

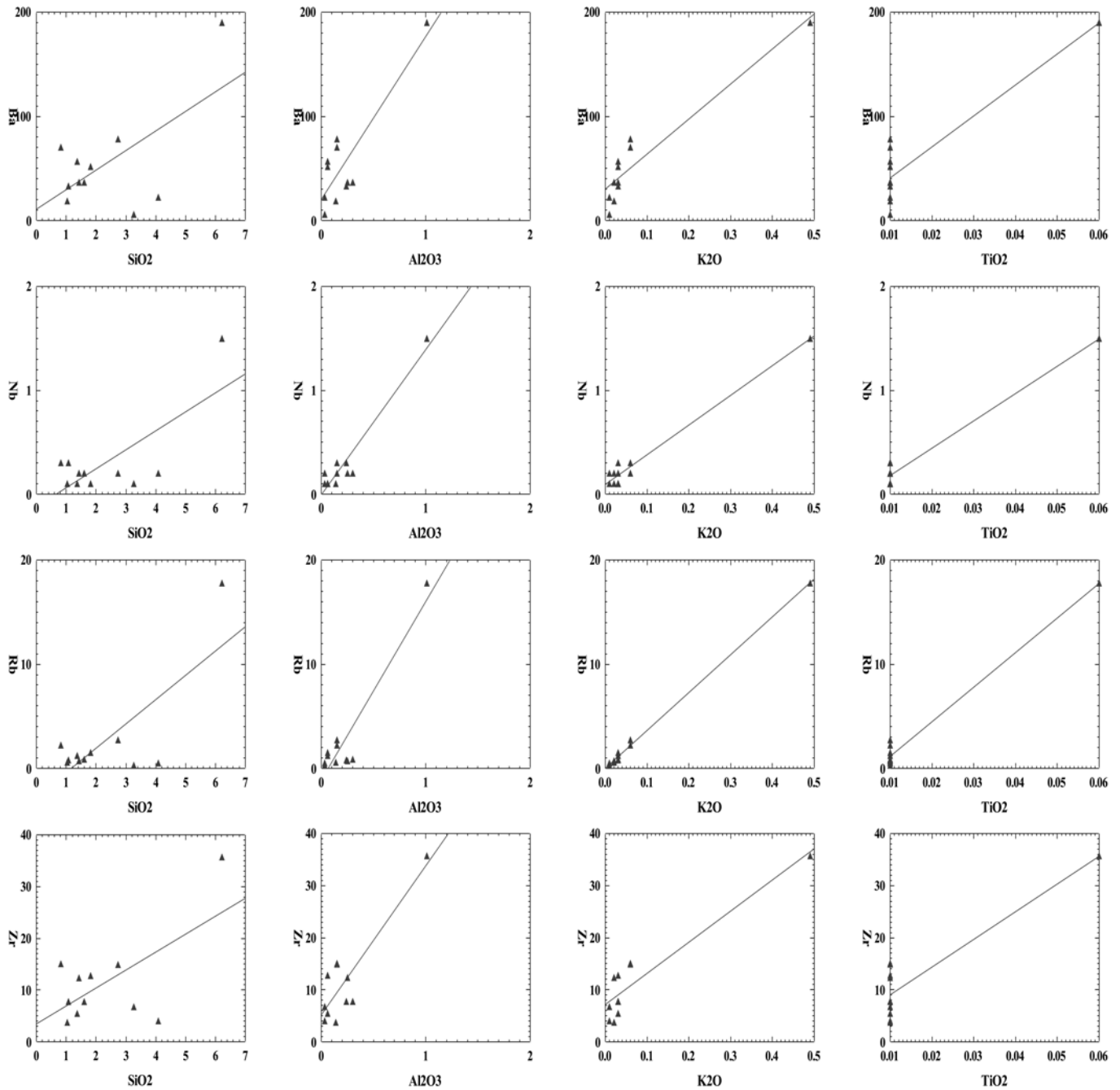
of the minor aluminosilicate phase in controlling the distribution of both insoluble components and most trace elements. Accordingly, the positive correlation among  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{K}_2\text{O}$ , Ba, Nb, Rb and Zr (Figure 10) is taken to imply that all these components are contained in different proportions of aluminosilicate phases, as appropriately reflected in the Factor 1 loadings (Table 7). The strong positive interrelationship amongst Ba, Rb and  $\text{K}_2\text{O}$  (Table 6, Figure 10) underline the relevance of K-bearing minerals in the aluminosilicate phases. It has long been known that Ba and Rb are especially retained in K-bearing minerals, and common K-bearing minerals are mostly the feldspars. However, the non-linear interrelationships involving Na, Pb, Sr and  $\text{Al}_2\text{O}_3$  (Table 6, Figure 11) and  $\text{Na}_2\text{O}$  and CaO (Figure 8) corroborate petrographic observations (Table 1) that feldspar does not constitute a significant phase in the modal mineralogy

of the rock, rather quartz, talc, and phlogopite or muscovite are the main aluminosilicate phases in the rock.

The high loadings of Ca, Sr, Pb and Cu of Factor 2 (Table 7) most likely reflect the composition of the carbonate fraction, while the high loadings of Mn, Ba, U and Y recorded for Factor 3 could not be readily interpreted. The exclusion of MgO as a significant component in all three Factor score groupings could be explained by considering diverse sourcing of the MgO.

#### *Conditions of formation of metacarbonate deposit*

In an effort to gain insight into the pre-metamorphic conditions of the parent materials of the metacarbonate deposits, the chemical data of the rock were plotted on discrimination diagrams like Garrels & McK-

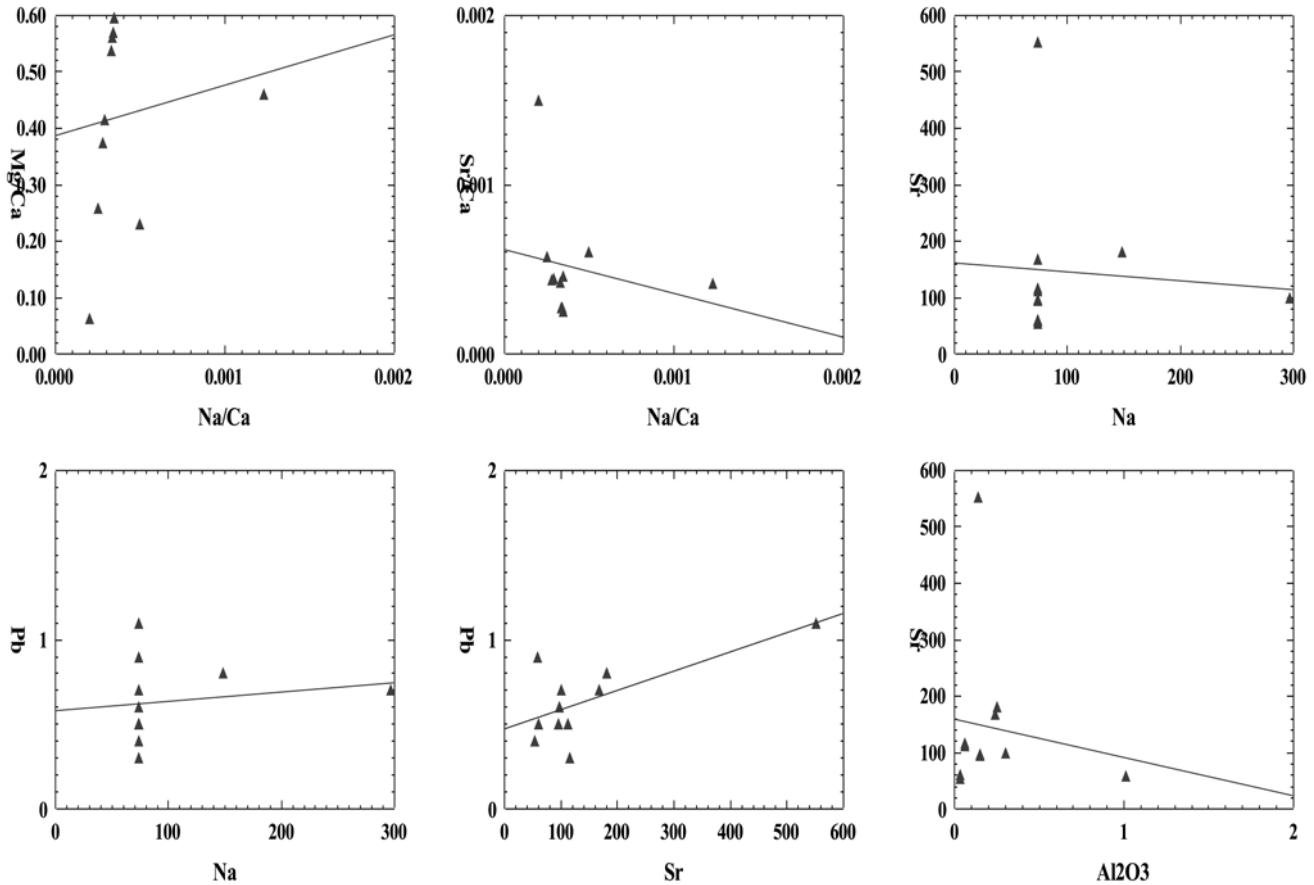


**Figure 10.** Cross-plots showing the varying degrees of positive inter-relationships displayed between various trace elements and the insoluble components of the Nsofang metacarbonate rock

enzie's  $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$  cf  $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$  diagram (1971) and Leyreloup *et al.*'s  $\text{MgO}-\text{CaO}-\text{Al}_2\text{O}_3$  discrimination diagram (1977). The samples dominantly plotted in the sedimentary field on the  $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$  cf  $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$  diagram (Figure 12), thereby confirming that the rock is largely of sedimentary origin. On the  $\text{MgO}-\text{CaO}-\text{Al}_2\text{O}_3$  discrimination diagram (following Leyreloup *et al.*, 1977) (Figure 13), the metacarbonate rock samples plotted outside the magmatic funnel, thereby supporting the sedimentary antecedents of the rock. The sedimentary origin of the precursor rocks is also clearly observed in the bedded nature of the metacarbonate rocks (Figure 4) and the fact that Sr and total REE abundance of the rock rarely exceed 200 ppm and 25 ppm, respectively, thereby agreeing with observations that sedimentary carbonates are usually characterised by low Sr and total REE content (Nothdurft *et al.*, 2004; Veizer *et al.*, 1992).

Additionally, interrelationships observed earlier between major insoluble residue components and selected trace elements (notably the  $\text{SiO}_2-\text{Al}_2\text{O}_3-\text{K}_2\text{O}-\text{TiO}_2-\text{Fe}_2\text{O}_3-\text{Ba}-\text{Nb}-\text{Rb}-\text{Zr}$  links) (Figure 10) points to the close association of the parent carbonate rocks with aluminosilicate phases, which is a diagnostic sedimentary feature.

Having confirmed the sedimentary nature of the protoliths, it became necessary to investigate the nature and characteristics of the depositional environment of the parent sedimentary carbonate, and for this, the trace element composition of the rock, especially the rare earth elements are involved. According to Tanaka and Kawabe (2006), unaltered marine sedimentary carbonates are expected to preserve the chemical characteristics (i.e. REE features) of the medium in which the carbonates precipitated. However, care must be taken when making such an interpretation



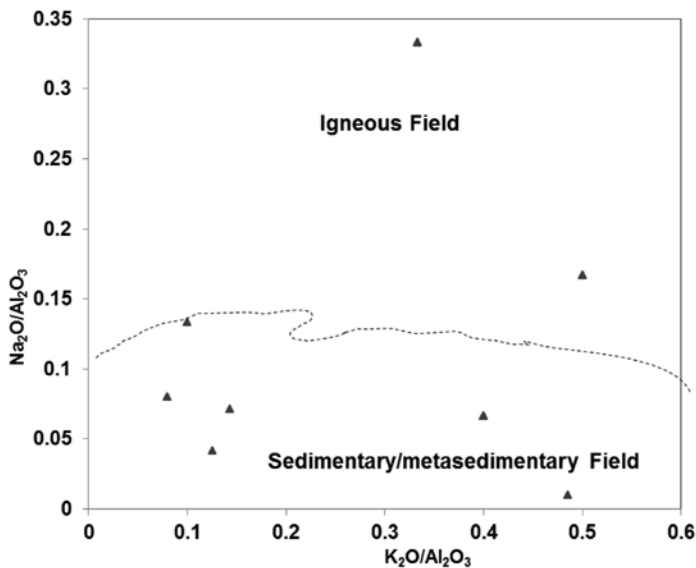
**Figure 11.** Cross-plots showing vague and inconsistent inter-relationships displayed among various chemical components of Nsofang metacarbonate rock

because carbonate REE content could also be influenced by non-carbonate materials, such as fine-grained siliciclastic material in excess of 5% (Banner *et al.*, 1988). Fortunately, in the case of the Nsofang metacarbonate rocks, petrographic and geochemical observations have shown that non-carbonate phases are negligible, and this precludes the consideration of an additional influence on the REE chemistry of the rock by non-carbonates.

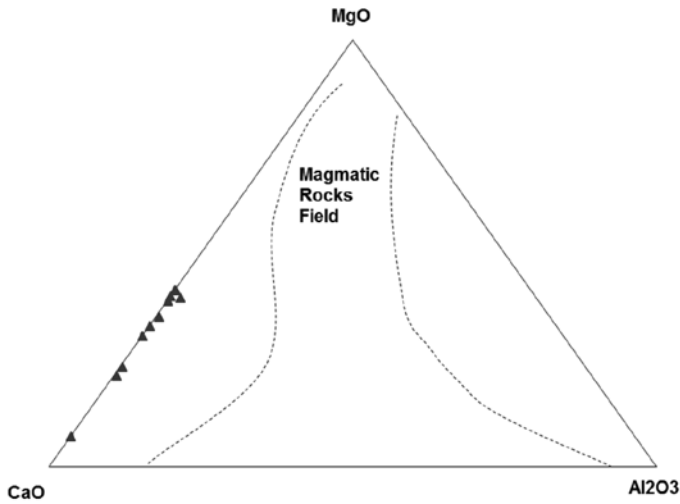
In outlining the REE pattern differences between shallow coastal waters and deep waters, Tanaka *et al.*, (1990) observed that data points for La, Nd, Sm, and Eu for coastal waters fall on a nearly straight line, and their REE patterns are characterised by marked discontinuity between Eu and Gd. Similar observations have been made on the REE patterns of the Nsofang metacarbonate rock (Figure 7), and the indication is that the protoliths of the rock was deposited in a shallow, near-shore marine environment.

Besides, the observed uncoordinated zigzag patterns in the Gd – Dy – Ho – Er – Yb – Lu spans of the heavy rare earth elements (HREE) of the Nsofang metacarbonate (Figure 7) require further investigation, as such features can also be associated with a surface or shallow water environment (Masuda and Ikeuche, 1979; Tanaka *et al.*, 1990). Interpretation of a surface or shallow marine depositional environment for the parent carbonate material of the Nsofang rocks is in agreement with the reported negligible  $\text{Na}_2\text{O}$ ,  $\text{Fe}_2\text{O}_3$ , MnO (Table 3) and Sr concentration (Table 4) (Clarke, 1911; Frank 1975; Turekiah and Wedepohl, 1961).

Davou and Ashano (2009) considered low concentration of  $\text{Na}_2\text{O}$  to imply a shallow, near-shore, low energy “clean water” marine environment of deposition for the parent carbonate materials of the marble deposit occurring east of the Federal Capital Territory (FCT) of Nigeria. Moreover, most sedimentary carbonates in Nigeria’s Cretaceous basins have been interpreted as product of shallow marine environment of deposition. Enu and Adegoke (1988) used microfacies and microfaunal evidence to interpret the Ewekoro limestone occurring within the eastern Dahomey basin of south-western Nigeria as products of deposition in shallow marine environment. Adekeye and Akande (2002) integrated lithological, paleontological and sedimentary data to reveal that the sedimentary sequence of the Yandev area in the Benue trough (consisting of a limestone–shale sequence) were deposited in a shallow marine shelf lagoonal environment.



**Figure 12.** Composition of the Nsofang metacarbonate rock on the  $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$  of  $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$  discrimination diagram of Garrels and Mackenzie (1971).



**Figure 13.** Composition of the Nsofang metacarbonate rock on the MgO – CaO – Al<sub>2</sub>O<sub>3</sub> diagram by Leyreloup *et al.*, (1977).

Among the sedimentary cycles delineated for the Mfamosong limestone of the Calabar flank, is an initial transgressive cycle that occurred and resulted in a normal shallow marine environment (Fayose, 1978). Akande *et al.*, (1988) concluded that shallow water epicontinental seas, flanked by fault-bounded basement uplands seems to have been the primary environments of deposition of carbonate materials in Nigeria. Following Ikhane *et al.*, (2009) the low Al<sub>2</sub>O<sub>3</sub> concentration measured in Nsofang rock is interpreted as being indicative of a low energy environment.

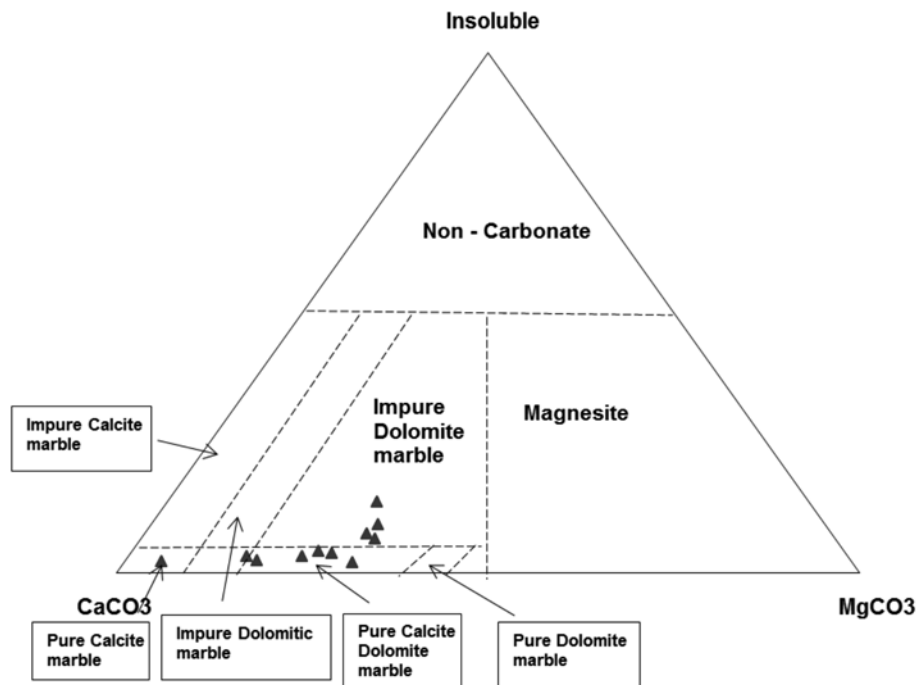
When the relevant chemical data of the Nsofang metacarbonate deposit are projected on the CaCO<sub>3</sub> – MgCO<sub>3</sub> – others (insoluble component) diagram (Figure 14) adapted from Harker (1939), Carr and Rooney (1985) and Davou and Ashano (2009), indication is that the metacarbonate rock is dolomitic. The occurrence of lamination, vug and cavern-

ous structures as part of the structural features (Figure 4) of the Nsofang metacarbonates possibly reflects the relevance of biogenic activity at some point in the evolutionary history of the rock. The lamination probably represents relic organic imprints similar to the type produced on tidal flat environments by colonies of blue green algae, while the irregular shape of the caves and small cavities with their sculptured walls suggest formation through dissolution of lithified carbonate material. There is therefore every indication that the metacarbonate rocks most likely began as calcitic material before conversion to dolomitic prior to metamorphism.

Dolomitisation of sedimentary carbonate material is a widely-reported process for many Nigerian carbonates and metacarbonates (e.g. Davou and Ashano, 2009; Odigi and Amajor, 2008; Oti, 1983; Petters, 1978). The prior demonstrated existence of precursor carbonate sedimentary material most likely provided the required setting for extensive dolomitisation of the precursor rock of the Nsofang metacarbonate. However, as already known (e.g. Deelman, 2008; Purser *et al.*, 1994; Welch, 2001), the condition of formation of dolomite in the natural environment is frequently different from synthesis of ordered dolomite, accomplished at temperature of over 100°C and 20 atm pressure in the laboratory. The source of high MgO is of considerable importance in the conversion of the sedimentary carbonate to dolomitic rock.

According to Akcay *et al.*, (2003), possible MgO sources for dolomitic carbonate-bearing rocks include pore-water, seawater and clay minerals. Pore-water trapped in limestone may promote dolomitisation (Kupecz and Land, 1991) because these waters are typically Ca-enriched and their molar Ca/Mg ratio increases with increasing temperature (Kupecz and Land, 1991). However, a pore-water MgO source for the Nsofang metacarbonates is not likely because pore-water is usually characterised by moderate to high salinity (10–25 wt% NaCl equiv.; Gomez-Fernandez *et al.*, 2000; Yao and Domicco, 1997) and Na<sub>2</sub>O and K<sub>2</sub>O concentration in carbonate tends to decrease with increasing salinity but appears to increase with depth (Clarke, 1911).

The metacarbonate rocks of Nsofang are characterised by low Na<sub>2</sub>O values and shallow depth of deposition, which is at variance with consid-



**Figure 14.** Composition of the Nsofang metacarbonate rock on the CaCO<sub>3</sub> – MgCO<sub>3</sub> – others (insoluble components) classification diagram, adapted from Harker (1939), Carr and Rooney (1985) and Davou and Ashano (2009).

eration of the pore-water source. Seawater, another major source of MgO for sedimentary dolomitic rocks, contains significant Mg concentration (-3.7%) (Taylor and Sibley, 1986; Tucker and Wright, 1992). Land (1985) concluded that seawater is the only widely-available fluid having sufficient magnesium to cause massive dolomitisation, and diagenetic dolomitisation of calcite-rich carbonates requires large volumes of water to supply the required Mg (Land, 1992). The low Na<sub>2</sub>O and K<sub>2</sub>O concentration in the metacarbonate, combined with the moderate Sr content, support the seawater source of MgO and, with seawater as the major source of MgO, the low Pb concentration in the rock (Table 6) can be readily explained. Wedepohl *et al.*, (1974) advanced the view that calcite and dolomite cannot incorporate appreciable concentrations of Pb since sea and interstitial water usually contains very little Pb.

Clay minerals represent another important major source of MgO, which is frequently regarded as a source of MgO for dolomitisation, especially for late-stage dolomite formations (Morteani *et al.*, 1982; Kupecz and Land, 1991; Warren, 2000). Given that Nsofang metacarbonate contains a quantity of quartz, talc, phlogopite and probably muscovite (Table 1), it is highly probable that transformation of these materials may release additional (though negligible) MgO for the carbonates.

Detailed analysis of the textural and structural features preserved in the Nsofang metacarbonate rocks reveal that the precursor sedimentary materials were affected by several widespread, laminae-parallel, diagenetic processes, most likely controlled by fine-scale layer-parallel differences in initial porosity and permeability. Xu (2011) observed that fenestral fabrics such as lamination and open space structures like vug and cavernous structures are usually formed in shallow, near-coast supratidal and upper intertidal carbonate environments (Flügel, 2004). The fenestral fabrics, formed in tidal flats, are generally attributable to diagenetic processes, associated with the degradation of microbial mats (Hofmann *et al.*, 1980).

## Summary and Conclusions

The hitherto unknown metacarbonate deposits of the Cretaceous Mamfe embayment comprised distinct carbonate and minor silicate fractions. While the carbonate fraction include Ca, Mg, Sr, Pb and Cu, the silicate fraction are associated with Si, Ti, Al, Fe, K, Ba Cs, Rb, Nb, Zr, Y and Zn. Geochemical data, integrated with field information, have been used to infer a metasedimentary petrogenetic affiliation for the rock. Indication is that the metacarbonate deposits were formed from sedimentary carbonate materials that were deposited in a saline, shallow-marine environment, possibly in a supratidal and/or upper intertidal environments. Seawater seemingly constituted a major source of MgO. Generally, the consistency in the chemical properties of the rock most likely reflects relative stability during deposition of the initial sediments.

Future studies, possibly including isotopic and geochronological data, would shed more light on the evolutionary history of the metacarbonate deposit. However, the present study provides a basis for revisiting earlier paleo-environmental interpretations and intense exploration of the geology of the Nigerian sector of the Mamfe embayment as this could be very rewarding for the country.

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