

**ON THE GENESIS OF NSOFANG MARBLE OF IKOM AREA OF
SOUTHEASTERN NIGERIA****Ephraim B. E* and Ukwang E. E.**

Department of Geology, University of Calabar, P. M. B. 1115 Calabar – NIGERIA

ABSTRACT: *Physical, petrographical and geochemical data are used to constrain the mode of formation of low grade marble occurring in Nsofang and environs, in Ikom area of southeastern Nigeria. The presence of lamination, vug and cavernous structures as part of the physical features of the marble suggest possible formation at $T < 100$ °C under biological controls, induced during microbial metabolic activity. However, it appears this mode of formation is insignificant as the modal mineralogy of the rock frequently follow the trend: dolomite (90%) + calcite (5%) + quartz (<1%) + talc (<1%) ± phlogopite (<1%) ± Opaque mineral(s) (1%), reflecting impact of low grade metamorphism. The strong linear correlation existing between Mg/Ca and Mn/Sr components supports the participation of metamorphic dolomitization in the formation of the marble. Other elemental geochemical data revealed progressive replacement – type dolomitization as a component applicable mechanism. The intense volcanism associated with the Cameroon Volcanic Line (CVL) most likely drove the hydrothermal system and metamorphism that produced the dolomitization of precursor limestones. It appears the Cenozoic timing of the CVL coincided with the time of dolomitization, while the extrusive activities provided a source of heat and additional ions for the circulating seawater that drove the calcite-dolomite reactions of the replacement-type dolomitization model.*

KEYWORDS: Marble, Dolomite, Dolomitization, Hydrothermal, Mamfe, Nigeria,

INTRODUCTION

In Nigeria, many studies concerning marble and other metasedimentary deposits have been directed at the geochemical characterization and economic perspective (e.g. Abdullateef et al., 2014; Danladi, 1993; Elueze et al., 2015; Elueze and Okunlola, 2001b; Emofurieta and Ekuajemi, 1995; Emofurieta et al., 1995; Ephraim, 2011; Obasi, 2012; Obasi and Isife, 2012; Obasi and Anike, 2012; Ofulume, 1993a; Ofulume, 1993b; Ofulume et al., 2009; Olatunji, 1989), and probably, the geological survey/exploration aspects (e.g. Fatoye and Gideon, 2013; Folami and Ojo, 1991; Moumouni et al., 2016; Odeyemi, et al., 1997; Ojo, et al., 2003; Okunlola, 2001; Tersoo, 2008). On the other hand, studies dedicated to the interpretation of the mode of formation of carbonate-bearing rocks/deposits are sparse. The few available ones include those of Davou and Ashano (2009), Onimisi et al (2013), Obasi and Ogungbuyi (2013), Obasi et al. (2015), and Elueze and Okunlola (2001a). Davou and Ashano (2009) suggested that the dolomitic marble occurring east of the Federal Capital Territory (FCT) of Nigeria formed as a result of microbial activities under anoxic condition. Similarly, Onimisi et al (2013) identified microbial activities under anoxic condition as playing a vital role in the formation of the Itobe marble. According to Onimisi et al (2013), the associated MgO in the Itobe marble were most likely co-precipitated with Ca from hyper-saline waters under anoxic conditions. Obasi and Ogungbuyi (2013) reviewed the geochemical data of trace and rare earth elements in marble from Igarra area of southwestern Nigeria, and concluded that the presence of volatile-

bearing minerals, enriched incompatible elements, coupled with enriched LREE and depleted HREEs are indicative of mantle-derived carbonates. According to Obasi et al. (2015), rare earth elements and parameters such as U, U/Th and Ni/Co ratios indicate that the sediment constituents of the Ikpeshi marble in Igarra area of southwestern Nigeria were deposited under suboxic and anoxic environments. Elueze and Okunlola (2001) employed stable isotope geochemical indices in marble to constrain the geotectonic setting of the Okene – Lokoja area as being rift-like, which amplifies the assertions on the schist belts (Elueze, 1985; Okonkwo and Winchester, 2000).

Vast quantity of low quality dolomitic marble deposits occur in Nsofang and environs in the Ikom area of southeastern Nigeria. This marble deposit constitute the focus of the present research work, which is the third in the series directed towards adequate understanding of the nature, processes and genesis that can be reasonably associated with the marble deposit. The first contribution (Ephraim, 2011) on the compositional appraisal and quality implication of the marble established suitability of the geomaterial for various end-product uses. In the second work (Ephraim, 2012), it was concluded that the overall geochemical signatures displayed by the rock support development of the metacarbonate deposits from precursor sedimentary carbonate materials that was deposited in a saline, shallow-marine, low-energy seawater environment.

In the study by Ephraim (2012), the occurrence of lamination, vug and cavernous structures were considered to reflect the importance of biogenic activity in the development of the rock. The present study seeks to investigate in details if the existing massive dolomite deposits at Nsofang and environs originated solely through organic/biogenic intervention processes. Accordingly, available field, petrologic and geochemical data would be reviewed and interpreted to bear on the genetical model that can reasonably be applied to constrain the formation of the Nsofang marble deposits of southeastern Nigeria. This study is necessitated by the desire for a better understanding of the mode of formation of the Nsofang marble, and to contribute toward studies aimed at deciphering the provenance, genesis and/or geotectonic setting of metacarbonate deposits in Nigeria, since similar studies are currently sparse, and inadequate.

Regional Geological Perspective

Southern Nigeria comprises both basements and sedimentary terranes, and is characterized by tectonic and structural elements such as the Calabar Flank, Obudu Plateau, Oban Massif, Southern Benue Trough, and the Niger Delta (Fig. 1). The Southern Benue Trough further consists of the Abakaliki Anticlinorium, Afikpo Syncline, Ikom – Mamfe Embayment and Ogoja Sub - Basin. These structural elements control and dominate the geologic evolution, and lithostratigraphic succession of the region.

The basement terranes in eastern Nigeria comprise part of an extensive spur or inlier of Precambrian crystalline rocks, overlain and partly surrounded by Cretaceous - Tertiary and younger sediments (Parkinson, 1907).

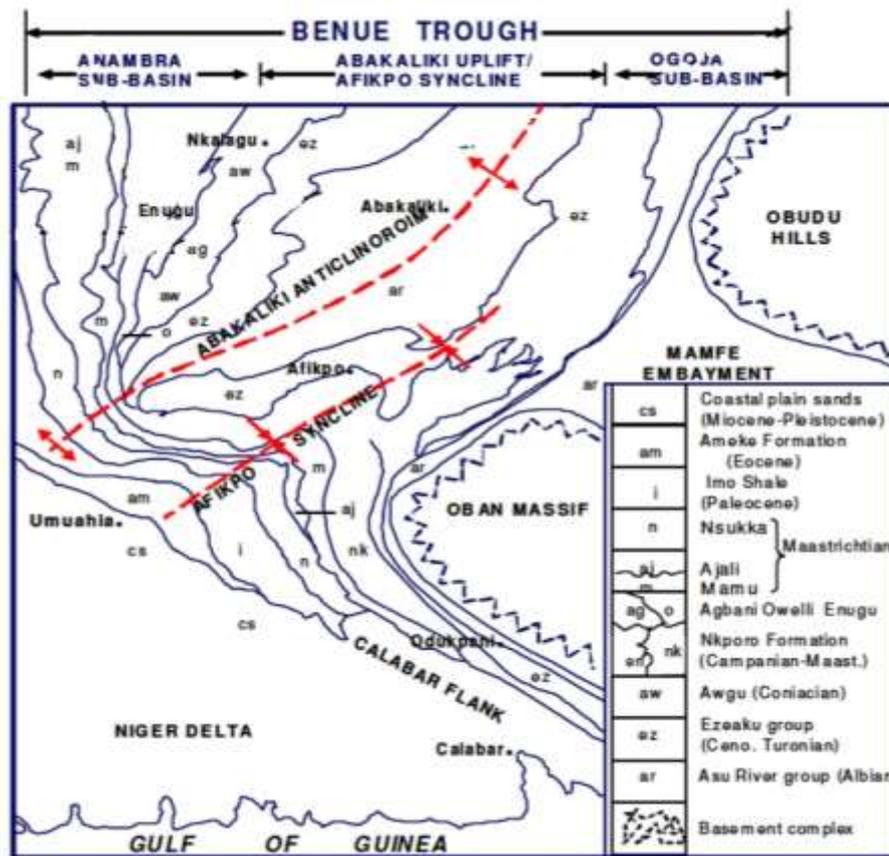


Figure 1. Map of Southeastern Nigeria showing the various tectonic and structural elements occurring within the region

The basement terrane includes Oban Massif, Obudu Plateau and Hawal Massif, with extensions in the neighbouring Cameroun Republic. The sedimentary basins, including the Mamfe basin, comprises Cretaceous – Tertiary sediments, which lie unconformably on rocks of the Precambrian basement Complex. A sedimentary thickness of about 2000m has been reported in the lower Benue Trough (Olade, 1975). The basin narrows towards the east and disappears under Tertiary and Recent rocks. The sedimentary infill largely features siliciclastics, carbonates, evaporites, and volcanoclastics of Aptian (?) to Albian age (Ajonina, 2016). The volcanic and volcanoclastic deposits, including a complex sequence of basalt, trachyte and phonolite lava flows and ignimbrites, are sourced mostly from the Cameroon Volcanic Line (CVL), The CVL represents a 1600 km long chain of Cenozoic volcanic and sub-volcanic complexes that straddles the continent ocean boundary and extends from the Gulf of Guinea to the interior of the African continent (Marzoli et al., 2000).

Local Geology and Mineralization

The Mamfe Embayment, which is located roughly between latitudes 5° N and 6° N and longitudes 8°45' E and 10° E, is the southernmost basin within the West and Central Africa rift system (Fig. 2). It is thought to be a rift splay segment of the southern Benue Trough (Ajonina, 1997; Ajonina et al., 2001, Basse et al., 2013), and one of the three sub basins that constitute the southern (Lower) Benue Trough, the other sub basins are the Abakaliki and Anambra Basins (Reyment, 1965; Whiteman, 1982; Petters et al., 1987; Petters, 1991).

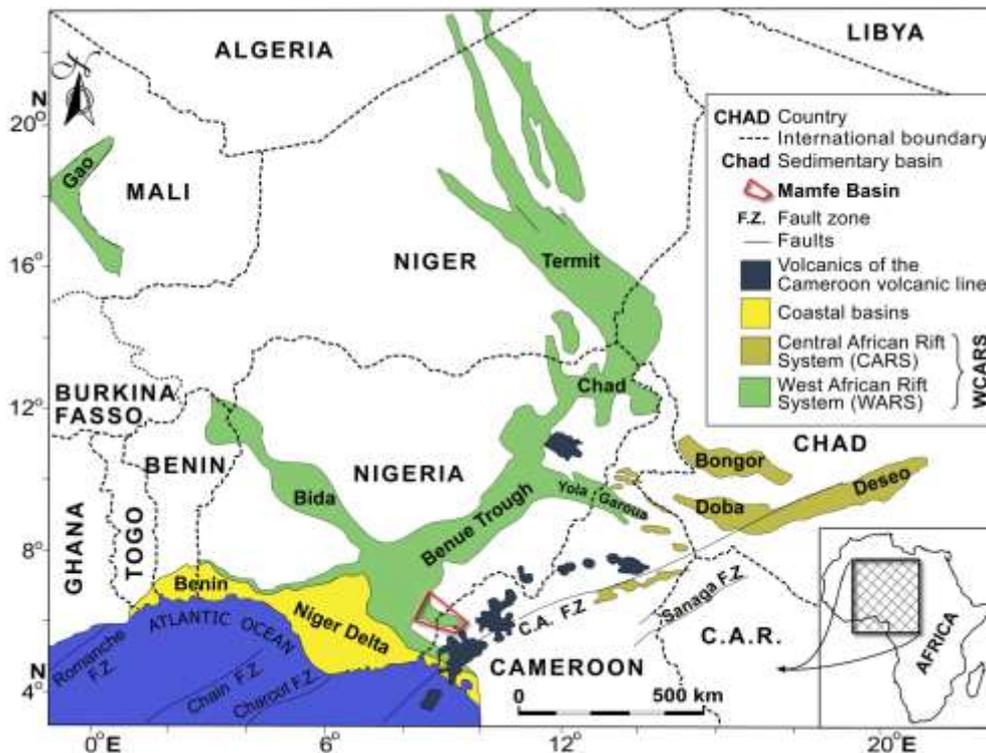


Figure 2. Map of the West and Central African region showing the location of the Mamfe basin, and the various rift systems (Ajonina, 2016; Genik, 1993).

The Mamfe sedimentary basin formed in response to the Gondwana break-up and subsequent separation of the South American and African plates during the Middle to late Jurassic (Fairhead and Green 1989). It possibly resulted from basement rifting associated with the reactivation of an east-west trending mylonite zone along the Mone Faults (Dumort 1968).

The Nsofang marble deposits constitute parts of the carbonate Member of the Cretaceous Mamfe Embayment (Fig. 3). The marble occurs as lensoid bodies distributed within low to very low grade metamorphosed and unmetamorphosed sedimentary sequences (Fig. 3). The outcrops are generally low-lying, although slightly elevated in some locations. Their surfaces are rugged, possibly due to the influence of weathering. Some of the exposure appears to be foliated with steep dips and variable strike orientation. Joints are common and assume cross or east – west orientations. The marble mineralized area is in close association with mostly volcanic rocks, notably basalts and trachytes and other related volcanic rocks of the Cameroon Volcanic Line (CVL) which abound in the vicinity of the deposits.

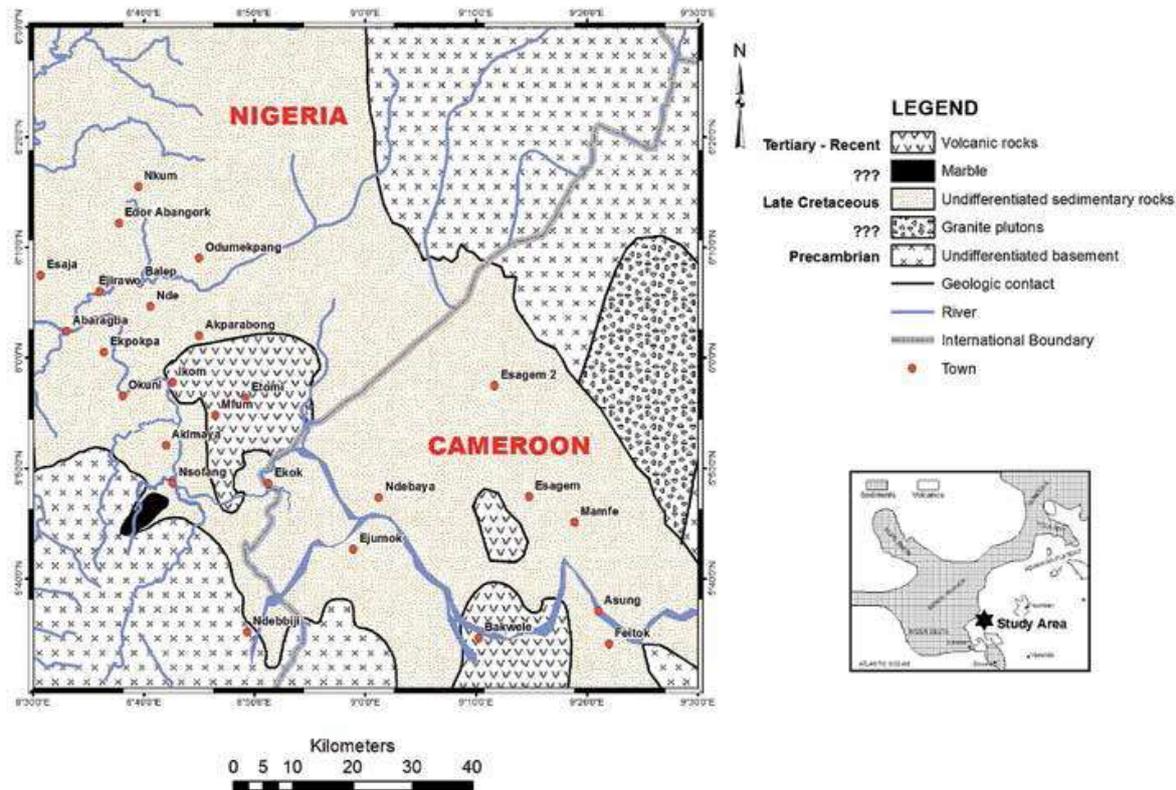


Figure 3. Geologic map of south-eastern Nigeria and western Cameroon, showing the location of Nsofang marble within the Mamfe embayment of south-eastern Nigeria

CHARACTERIZATION OF THE MARBLE

Petrographic and Mineralogical Characteristics

In hand specimen, the rocks are characterized 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. These distinct linear and planar fabric are highlighted by the laminar structures, which is produced by variation in coloration. The grain sizes are mostly medium to coarse.

Both thin section microscopy and X-ray diffraction (XRD) studies were employed to shed more light on the petrographic features and mineralogical compositions of the rock. Optical examination of thin sections shows that the marble is frequently heteroblastic with the various grains sizes forming mortar fabric. The revealed mineralogy showed that the carbonate fraction constitute the dominating phases in the marble, almost to the complete exclusion of the silicate fraction, as it frequently follow the trend: Dolomite (90%) + Calcite (5%) + [Clay + Carbonaceous Matter] (4%) + Opaques (probably pyrite) (1%) + Quartz (<1%). Indication is that dolomite constitutes the most abundant mineral, while calcite, quartz and iron minerals are subordinate. In addition, clay and carbonaceous matter constitute the matrix, and the binding cement. The dolomite, in thin sections, frequently consists of euhedral rhombic dolomite,

having a mean size of 130 μm and tangential to straight contacts. The quartz grains occur as detrital quartz grains, with little or no polycrystalline quartz grains observed. Similarly, no pellets, fossils, oolites, intraclasts or other organic/biogenic grains were observed in any of the thin sections examined.

Results of XRD analysis carried out on the marbles are displayed in Figures 4. In agreement with the microscopic studies, the XRD diffractograms (Fig. 4) confirmed that the carbonate phases are predominantly dolomitic with calcite as subordinate in most cases, while quartz, talc and phlogopite constitute the accessory phases which in most cases are not beyond 1% (Table 1). Thus, the primary assemblage of these marble is dolomite (calcite) \pm quartz \pm talc \pm phlogopite \pm Opaque mineral(s) (probably pyrite), reflecting impact of low grade metamorphism.

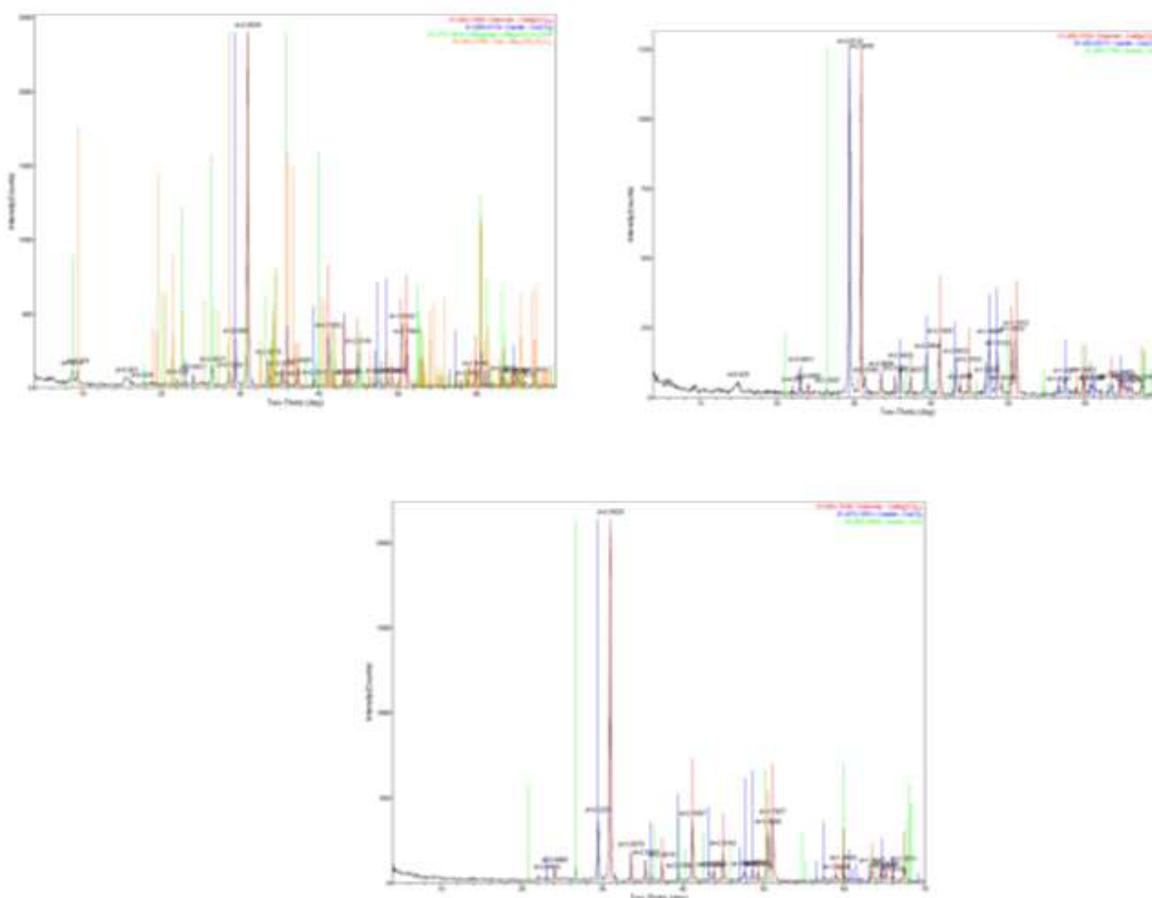


Figure 4. X-Ray Diffraction (XRD) diffractograms with mineral match colours superimposed on traces of the respective mineral (red colour is used to denote dolomite, blue is used for calcite, green is used for phlogopite and orange for talc)

Geochemical Characteristics

Detailed geochemical study undertaken by Ephraim (2012) resulted in the scheme detailing the abundance of the chemical components and related parameters of the marble (Table 1). As shown, the major and trace-element compositions reflect the mineral assemblage of the rock and offer significant clues regarding earlier diagenetic history.

Table 1. Geochemical data of Nsofang marble, Ikom area of Southeastern Nigeria

	L11	L12	L13	L21	L22	L23	L31	L32	L41	L42	L43	Mean	St. Dev
SiO ₂	6.21	4.08	3.26	1.08	2.74	0.82	1.6	1.43	1.03	1.37	1.82	2.31	1.649
TiO ₂	0.06	<0.01	<0.01	0.01	<0.01	0.01	<0.01	0.01	<0.01	<0.01	<0.01	0.01	0.015
Al ₂ O ₃	1.01	0.03	0.03	0.24	0.15	0.15	0.3	0.25	0.14	0.06	0.06	0.22	0.278
Fe ₂ O ₃	0.36	<0.04	<0.04	0.08	0.08	0.08	0.08	<0.04	<0.04	<0.04	<0.04	0.08	0.094
MnO	0.01	0.01	<0.01	0.01	0.02	0.02	0.02	<0.01	0.01	<0.01	<0.01	0.01	0.005
MgO	20.42	21.25	20.56	12.6	21.09	20.14	18.43	11.43	3.88	16.35	17.52	16.7	5.415
CaO	30.26	30.1	30.94	41.09	29.85	31.67	33.78	41.88	51.67	36.94	35.55	35.79	6.793
Na ₂ O	<0.01	<0.01	<0.01	0.01	0.01	0.01	0.04	0.02	<0.01	<0.01	<0.01	0.01	0.009
K ₂ O	0.49	<0.01	<0.01	0.03	0.06	0.06	0.03	0.02	0.02	0.03	0.03	0.07	0.14
P ₂ O ₅	0.05	0.05	0.06	0.02	0.15	0.14	0.14	0.13	0.02	0.04	0.02	0.07	0.054
LOI	40.8	44.1	44.8	44.6	45.4	46.5	45.2	44.5	43.1	44.9	44.6	44.41	1.459
TOTAL	99.68	99.69	99.73	99.77	99.56	99.6	99.63	99.72	99.93	99.76	99.67	-	-
Total C	11.31	12.16	12.17	12.46	12.18	12.97	12.37	12.61	12.14	12.45	12.21	12.28	0.407
Total S	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	0
Calcite	3	1	4	42	1	7	15	46	83	25	20	22.5	-
Dolomite	93	97	94	58	96	92	84	52	18	75	80	76.3	-
Ba	190	22	6	33	78	70	37	37	19	57	52	55	49.91
Cs	3.9	0.2	<0.1	0.2	0.4	0.3	0.2	0.2	0.1	0.3	0.4	0.6	1.11
Rb	17.8	0.5	0.3	0.8	2.7	2.2	0.9	0.7	0.6	1.2	1.5	2.7	5.08
Sr	59.1	53.8	60.1	167.7	97.4	95.6	100.1	181.4	552.3	115.8	112.6	145.1	141.16
Nb	1.5	0.2	0.1	0.3	0.2	0.3	0.2	0.2	0.1	<0.1	<0.1	0.3	0.4
Pb	0.9	0.4	0.5	0.7	0.6	0.5	0.7	0.8	1.1	0.3	0.5	0.6	0.23
Zr	35.7	4.1	6.7	7.7	14.9	15.1	7.8	12.4	3.8	5.4	12.8	11.5	9.03
Cd	0.2	0.2	0.7	0.3	0.2	0.1	0.3	0.3	0.1	0.3	0.3	0.3	0.16
Cu	0.9	0.7	1.6	0.6	1	0.6	2.7	1.5	12.1	0.2	0.2	2	3.42
Ni	0.3	<0.1	0.8	3.9	1.2	1.7	1.3	3.5	1.6	1.1	1	1.6	1.19
U	0.5	1.3	3	0.8	0.3	0.3	0.6	0.6	2.3	2.3	1.8	1.3	0.95
Y	5.7	2.7	2	1.8	0.6	0.7	1.4	2	1	0.7	0.6	1.8	1.49
Zn	9	5	6	8	4	5	7	6	3	5	4	5.6	1.8
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	-	-
∑LREE	12.53	2.01	3.29	4.68	2.71	2.74	4.03	5.29	3.74	1.2	1.1	-	-
∑REE	15.41	2.93	4.04	5.51	3.07	3.07	4.52	6.12	4.27	1.47	1.37	-	-

The concentrations of CaO (29.85 to 51.67 wt. %, av. 35.79 wt. %), MgO (3.88 to 21.25 wt. %, av. 16.70 wt. %) and LOI (40.8 and 46.50 wt. %, av. 44.41 wt. %) are expectedly high. Very high also is the total carbon concentration (11.31 – 12.97 wt. %, av. 12.28 wt. %) while the total sulphur concentrations are generally below detection limit of 0.02 wt. %. The SiO₂ contents range from 0.82 to 6.21 wt. %, Al₂O₃ contents from 0.03 to 1.01 wt. %, and Fe₂O₃ and P₂O₅ contents vary between <0.04 and 0.36 wt. % and between 0.02 and 0.15 wt. % respectively. The contents of TiO₂, MnO, Na₂O and probably K₂O are very low.

Composition of the trace elements of the marble, given in Table 1, have been normalized to the average crust of Taylor and McLennan (1981) and the spider-plot presented as Figure 5a. Generally, the trace elements are not as low as expected, and values for Sr and Ba are highly variable (Table 1), possibly suggesting a complex distribution of the elements (Georgieva, 2009). The light ion lithophile elements (LILE), notably Ba (av. 55 ppm), Sr (av. 145.1 ppm) and probably Rb (av. 2.7 ppm) display relatively elevated contents, while Zr has a concentration that ranges from 4.1 to 35.7 ppm with a mean value of 11.5 ppm, Nb has a concentration that ranges from 0.1 to 1.5 ppm with a mean value of 0.3, and U contents vary between 0.3 and 3.0 ppm. Concentration of Y changes from 0.6 to 5.7 ppm. Also, Zn (av. 5.6 ppm), Cu (av. 2.0), and Ni (av. 1.6 ppm) display moderate concentrations, while concentrations of Cd (av. 0.3 ppm), Pb (av. 0.6 ppm) and Cs (av. 0.6 ppm) appear low.

The Rare earth elements (La, Ce, Nd, Sm, Eu, Tb, Yb, Lu) abundance in the marble are quite low ($\Sigma\text{REE} = 0.1 - 0.002$) and concentration of most of the components (eg. in locations L23, L42 and L 43) are below detection limit (Table 1). The tabulated data (Table 1) show that LREE components dominate over the HREE, and the total concentration of LREE and HREE decreases from 320 to 130 ppm and from 22 to 11 ppm, respectively (Table 1). The chondrite – normalized (Nakamura, 1988) REE (REE_N) pattern (Fig. 5b) show all the investigated samples displaying similar REE_N patterns, moderate to strong fractionation of light REE (LREE) over heavy REE (HREE) ($\text{La}_N/\text{Yb}_N = 112 - 123$) and distinct negative Eu anomaly (mean $\text{Eu}/\text{Eu}^* = 112 - 223$, where Eu^* is the value obtained by interpolating between Sm_N and Gd_N). Also, La – Nd – Sm – Eu appears to demonstrate an inclined straight line. Additionally, the heavy REE (HREE) are unfractionated ($\text{Gd}_N/\text{Yb}_N = 223 - 443$) but display indistinct zigzags patterns in the Gd – Dy – Ho and Er – Yb – Lu spans (Fig. 5b).

Interrelationships existing between various geochemical parameters of the Nsofang marble have been investigated, and the results presented as cross-plots, in Figure 6. As shown (Fig. 6 a-f), non-linear, vague and inconsistent inter-relationships are displayed by Ca versus Fe, Mn, and between Mg versus Fe, Mn, as well as by Sr versus Al₂O₃ and Sr versus Na. Similarly, Na/Ca versus Mg/Ca and Na/Ca versus Sr/Ca ratios cross-plots (Figs. 6 g-h) show lack of strong relationship between the various components unlike the Mg/Ca versus Mn/Sr variation diagram (Figs. 6i) which display strong positive linear relationship. In addition, Strontium composition display enrichment trends with increasing CaO (Fig. 6j), and depletion trends with increasing MgO (Fig. 6k).

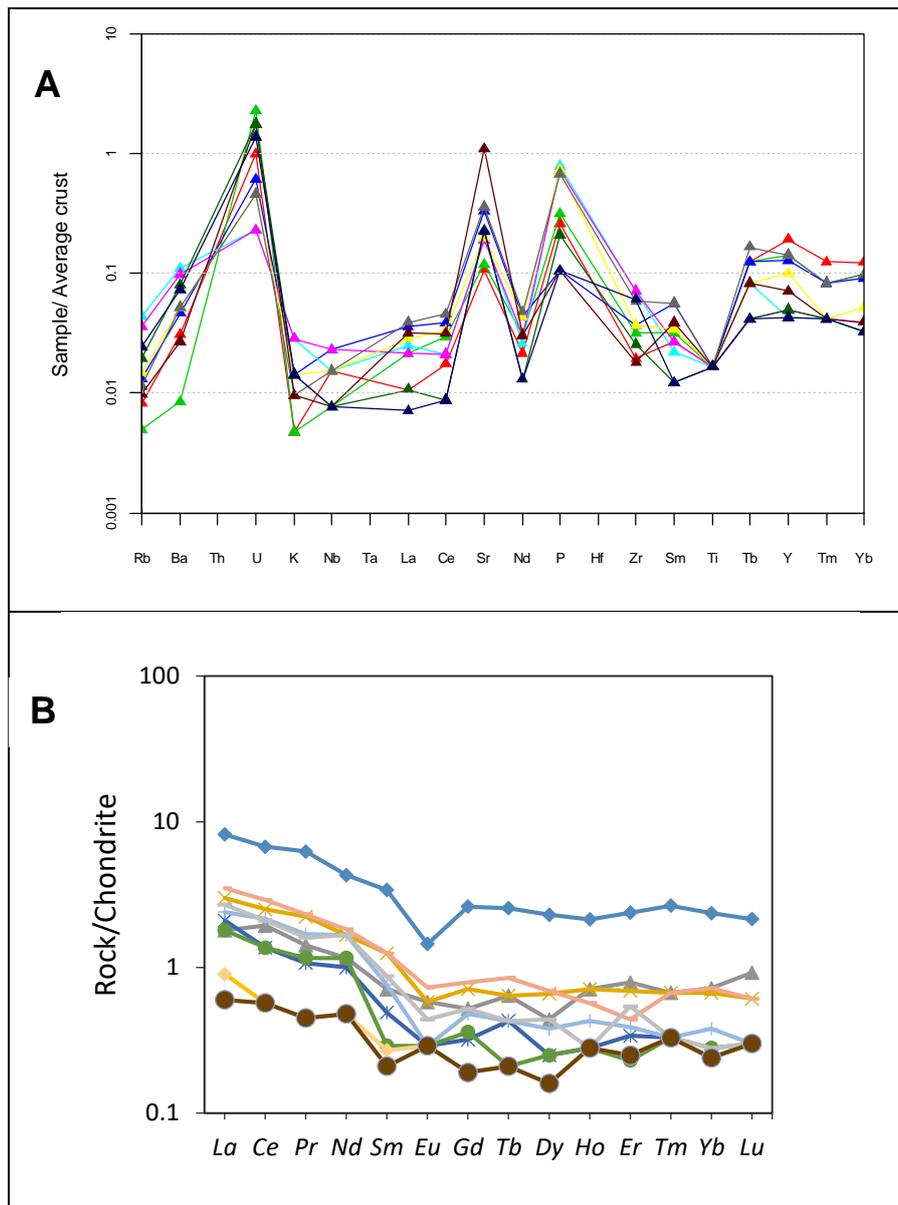


Figure 5. Spidergram plots illustrating: (A) Composition of trace elements of the marble normalized to the average crust of Taylor and McLennan (1981); (B) Composition of rare earth elements (REE) of the Nsofang marble normalized to the composition of chondrite after McDonough and Sun (1995)

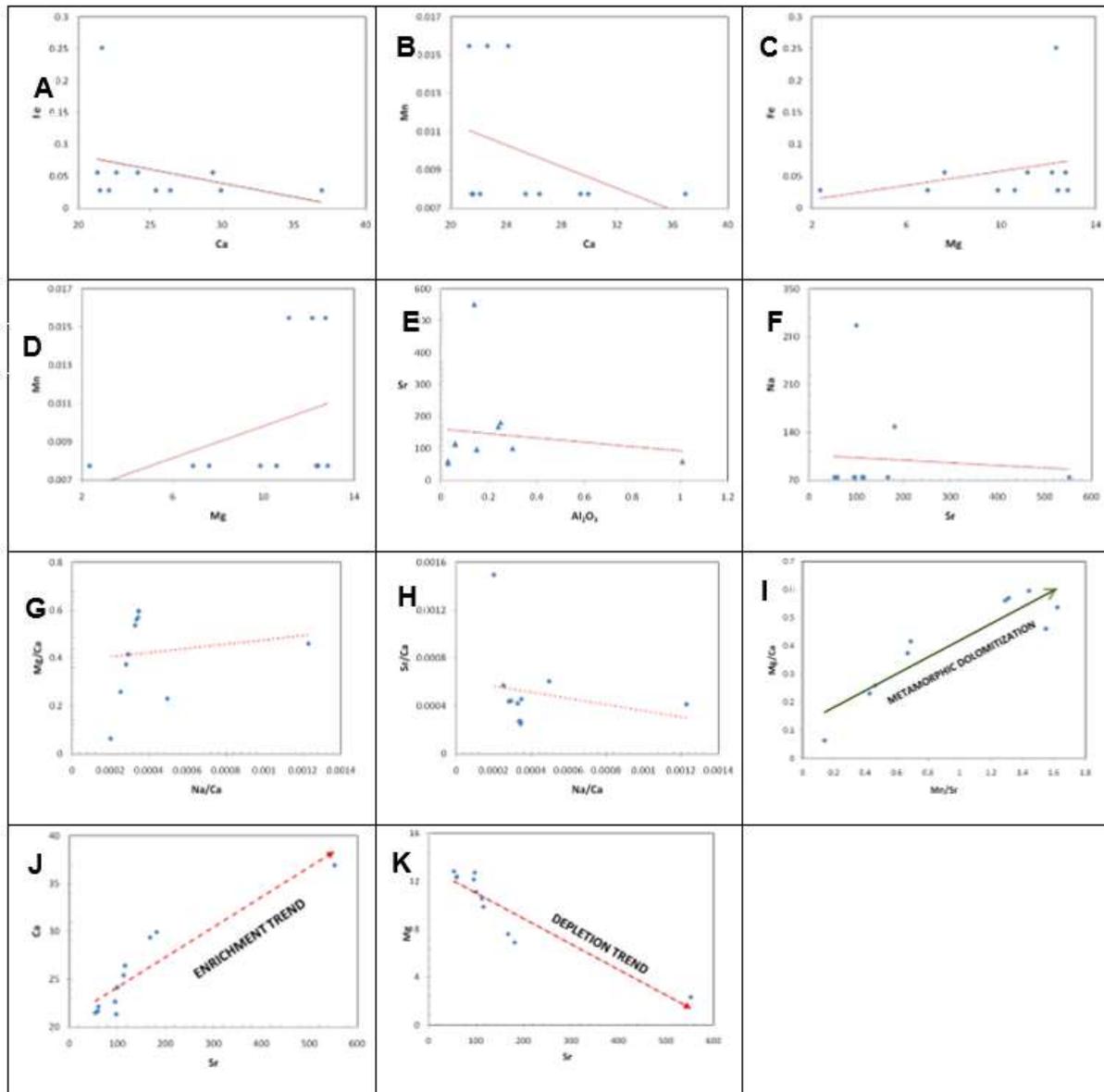


Figure 6. Geochemical interrelationship cross-plots showing: (A) weak correlation between Ca and Fe, (B) weak correlation between Ca and Mn, (C) weak correlation between Mg and Fe, (D) weak correlation between Mg and Mn, (E) non-linear relationship between Sr and Al_2O_3 , (F) lack of strong relationship between Sr and Na, (G) absence of significant positive correlation between Na/Ca versus Mg/Ca (H) absence of significant positive correlation between Na/Ca versus Sr/Ca, (I) strong linear relationship between Mg/Ca versus Mn/Sr, (J) enrichment trend displayed on the Sr versus Ca plot, (K) depletion trend displayed on the Sr versus Mg plot

DISCUSSIONS AND CONCLUSIONS

The sedimentary antecedent of Nsofang marble had earlier been established from both field and chemical evidences (Ephraim, 2012). The chemical signature of the investigated rock (Table 1) reflect the paragenesis determined by X-ray powder diffraction (XRD) (Fig. 4), and observed by optical microscopy on thin sections. Both petrographic and chemical data agree that dolomite constitute the dominant phase in the rock mode. Accordingly, any reasonable and acceptable genetic model for the marble must consider the conditions under which the mineral, dolomite, formed and the rate of precipitation under these conditions. The formation of dolomite [$\text{CaMg}(\text{CO}_3)_2$] within Earth surface conditions is still considered an enigmatic process, giving rise to the widely held “dolomite problem” concept (Arvidson and Mackenzie, 1999; Davou and Ashano, 2009; Deelman, 2011; Yoo and Shelton, 2000). For brevity, the core of the “dolomite problem” is the apparent paradox posed by the meager distribution of dolomite in modern marine depositional environments versus its relative abundance in the ancient sedimentary rocks of marine origin.

Often, carbonate precipitation is prevented by several kinetic limitations in salt water. Lippmann (1973) identified hydration of Mg as the kinetic barrier preventing the precipitation of dolomite and, possibly, magnesite from sea water, and Althoff (1977) concluded that the process of ordering Mg and Ca in the dolomite structure constitute another crucial factor that is often overlooked in the formation of dolomite. Furthermore, laboratory conditions of over 100°C temperatures and about 20atm pressures accomplished for synthesis of ordered dolomite is frequently at variance with conditions of formation of dolomite in the natural environment (Welch, 2001). It therefore appears that the primary requirement for dolomitization is sufficient supply of Mg-bearing dolomitizing fluid and temperatures elevated above surface conditions.

With dolomite constituting the predominant composition of the Nsofang marble, and the controversial outlook associated with dolomite formations, there is no doubt that probing the processes of formation of the dolomite composition of the Nsofang marble constitute a key factor in understanding the genesis of the marble deposits.

In an earlier study (Ephraim, 2012), field and petrographic features, notably the occurrence of lamination, vug and cavernous structures were considered to reflect the possible relevance of biogenic activity at some point in the evolutionary history of the rock, and hence the genesis of the Nsofang marble. Although this model is consistent with the current acceptance of microbial mediation as a demonstrated mechanism to precipitate dolomite under Earth surface conditions (Bontognali et al, 2010), It appear questionable whether the existing massive dolomite deposits at Nsofang and environs originated solely this way. Some of the strands of evidence that work against the acceptance of this microbial mediation model as the main dolomitization process of the Nsofang marble include: 1) the fact that, massive dolomitization, such as the type considered, typically forms at depth and elevated temperature through replacement of precursor limestone by reaction with flowing dolomitizing fluids large enough to transport the required amounts of Mg^{2+} (Carmichael, 2006; Qing and Mountjoye, 1994), 2) recorded paucity of biogenic grains in most of the thin sections examined (Ephraim, 2011; 2012) and, 3) low abundance of organic chemical species index, notably Fe, Mn and P in the rock (Table 1) often reflect low detrital and organic effects relative to inorganic chemical carbonate precipitate (Tucker, 1983). It therefore becomes necessary to investigate the relevance of inorganic processes in the formation of the Nsofang marble.

Inorganic mode of formation of dolomites to consider in this regards includes: 1) replacement of pre-existing calcite under conditions of high salinity, pH, Mg/Ca ratio, and elevated temperature suggested by Krauskopf and Bird (1995) and, 2) formation via primary precipitation from aqueous solution, especially for dolomites that are associated with saline evaporate deposits (Sass and Katz, 1982; Vasconcelos and McKenzie, 1997; Wright, 1999; Wright and Oren, 2005; Wright and Wacey, 2005). The lack of strong relationship between Sr and Na (Fig. 6f), together with the absence of significant positive correlation between Na/Ca versus Mg/Ca or Sr/Ca (Figure 6 g-h), precludes the consideration of the later model, ie formation via primary precipitation from aqueous solution for dolomites that are associated with saline evaporate deposits.

A projection of the chemical data of the Nsofang rock on the schematic classification diagram after Fairbridge (1970), meant for Ca – Mg carbonate rock system (Fig 7), accentuate the relevance of the process of dolomitization in the evolutionary history of the marble. Also, when the chemical data of the Nsofang marble are plotted on the Ca vs Mg diagram of Johnstone et al (2010) (Fig. 8), there is non-correspondence of the plotted points with the line depicting stoichiometric dolomite, pointing to the fact that the dolomitic components of the marble are not primary in origin, thereby supporting the exclusion of the primary precipitation model as a possible genetical model.

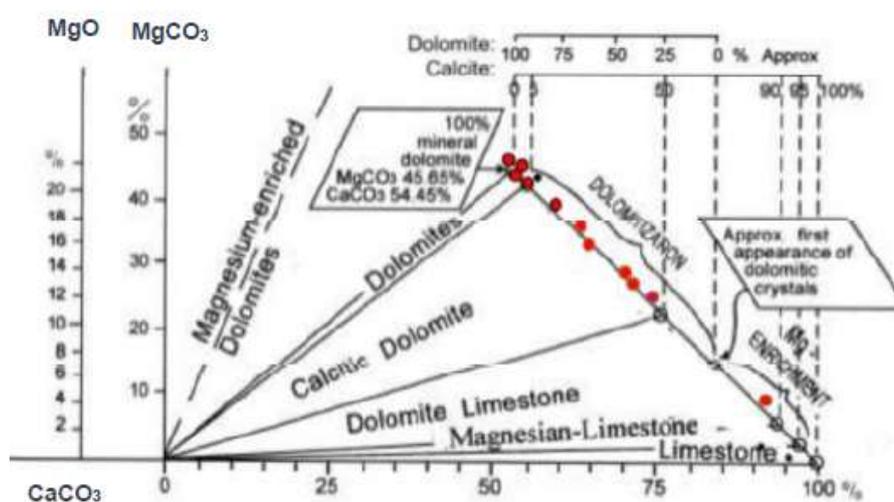


Figure 7. Projection of the chemical data of Nsofang marble on the schematic classification meant for Ca – Mg carbonate rock system (after Fairbridge, 1970)

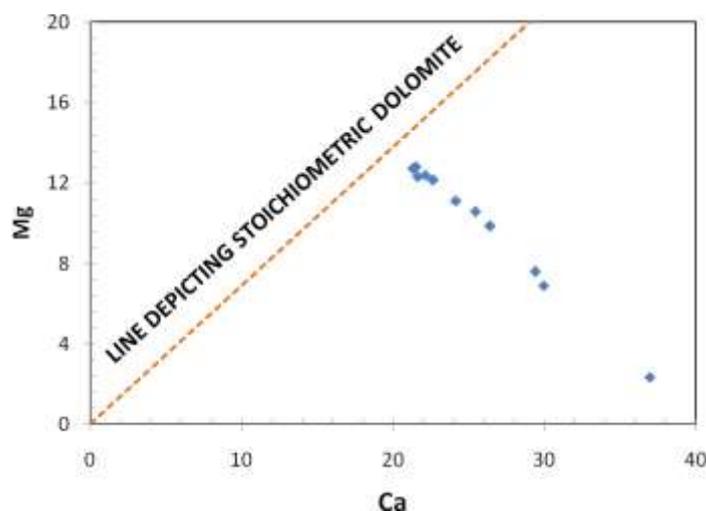


Figure 8. Comparison of the calcium and magnesium contents of the Nsofang marble with the ratio characteristics of stoichiometric dolomite (modified from Johnson, 2010).

Of considerable importance is the inverse relationship displayed on both the Fairbridge (1970) CaCO_3 vs MgCO_3 schematic classification diagram (Fig. 7) and the Ca vs Mg diagram of Johnstone et al (2010) (Fig. 8). Naseem (2004) interpreted a similar inverse relationship between CaO and MgO components of the jhimpir dolomite of Sindh in Pakistan as indicating progressive dolomitization. This may also be applicable to the Nsofang marble. However, the very strong negative correlation ($r = -1.00$) displayed between Mg^{2+} and Ca^{2+} components on these diagrams (Figs. 7 & 8) appear to go beyond indicating progressive dolomitization processes to confirming replacement type dolomitization model as the most applicable genetic trend. Akcay et al (2003) remarked that dolomites formed by substitution of Ca^{2+} in calcite crystals by Mg^{2+} often display negative correlations between Ca and Mg contents, and this is what is clearly observed in Fig. 8. The idea of substitution of Ca^{2+} in calcite crystals is consistent with already known fact that Mg^{2+} , Fe^{2+} and Mn^{2+} can substitute Ca^{2+} to form dolomite, ankerite and kutnohorite respectively, at different physicochemical conditions. However, within the context of structural modification in the Nsofang marble, only replacement of Ca^{2+} in the calcite crystals of the parent carbonate rocks are favored; replacements by both Fe^{2+} and Mn^{2+} components of the rock are not consistent with the weak correlations existing between these components and both Ca and Mg (Fig. 6a-d). Several workers (e.g. Graf and Goldsmith, 1955; Harker and Tuttle, 1955) promotes the views that it is only at high temperature that Mg^{2+} can substitute for Ca^{2+} to an appreciable percent in the calcite structures. Bearing this in mind, the chemical data of the Nsofang marble were projected on the Mg/Ca vs Mn/Sr variation diagram (Fig. 6i), regarded as an important scheme in investigating alterations in carbonate systems (Kaufmann and Knoll, 1995; Pandit et al., 2003, 2009). Indication from the strong linear relationship displayed on this diagram (Fig. 6i) is that the progressive replacement – type dolomitization that affected the protoliths of the Nsofang marble was most likely associated with metamorphic (closed-system metamorphic devolatilization) overprinting. Melezhik et al., (2001) acknowledged that a linear correlation between Mg/Ca and Mn/Sr often signal the participation of metamorphic dolomitization (closed-system metamorphic devolatilization) in the formation of the rock considered. This interpretation agrees with the complete absence of Ce anomaly on the chondrite – normalized rare earth elements pattern of the marble samples (Fig. 5). Marine water commonly possesses

a negative Ce anomaly (Hu et al., 1988) which is then inherited by carbonates formed in equilibrium with seawater in marine environment. Deep seawaters are usually associated with large negative Ce anomaly while coastal seawaters do not normally possess large negative Ce anomaly (Tanaka et al., 1990). Cebbar et al. (1985) explained further that Ce fraction in well oxygenated waters, such as near-shore water, would yield a positive Ce anomaly or less of the Ce depletion. Absence of Ce anomaly, as in the case with the Nsofang marble, is often taken to denote diagenetic and/or metamorphic overprinting (Koszela, 2003). Koszela (2003) have enumerated the possible causes of Eu anomaly in sedimentary rocks to include, enrichment of plagioclase contents, sedimentation in alkaline pore water of anoxic marine conditions and interaction of the rocks with magmatic or metamorphic fluids (McLennan, 1989). The non-linear relationship existing between Sr and Al_2O_3 (Fig. 6e) together with the observed paucity of feldspar phases in the modal mineralogy of the rock (Ephraim, 2011) show that plagioclase is not an important phase in the rock, and hence, preclude the consideration of enrichment of plagioclase contents as the likely cause of the negative Eu anomaly exhibited by the Nsofang marble. Similarly, sedimentation in alkaline pore water of anoxic marine conditions is ruled out because the protoliths of the marble appear to have been deposited under normal redox conditions in shallow marine oxygenated waters. The distinct negative Eu anomaly exhibited by the Nsofang marble is therefore probably connected to interaction of the precursor rock with magmatic/ metamorphic fluids, which also support the observations that the marble has been subjected to metamorphic overprinting. Ephraim et al (2011) used paragenetic mineral assemblage of the rock to propose an attainment of at least the greenschist facies metamorphism.

Of considerable importance at this point is the fact that the Nsofang marble is closely associated with volcanic components of the Cameroon Volcanic Line (Ajonina, 2016; Ephraim 2011, 2012). Also, sedimentary infillings of the Mamfe embayment, of which the precursor carbonate rock probably constitute a part have consistently been dated Cretaceous (Ajonina, 2016; Le Fur, 1965; Reymont, 1965), while the region was subjected to intense volcanism and associated basic magmatism during the Cenozoic Era (Le Fur, 1965; Youmen, 1994). From the foregoing, it becomes reasonable to suggest that the intense volcanism and magmatism associated with the Cameroon Volcanic Line likely drove the hydrothermal system that produced the dolomitization of the precursor rocks. Until geochronological and isotopic data are available to suggest otherwise, the Cenozoic timing of the volcanism and associated basic magmatic are considered, to coincide with the time of dolomitization, and the associated extrusive/intrusive activities of the volcanism provided a source of heat and additional ions that were added to the circulating seawater. This interpretation agree with the works by Carmichael (2006), Fanning et al. (1981), Saller (1984), Aharon et al. (1987), and Flood et al. (1996), which showed that normal seawater at elevated temperatures is capable of driving the calcite to dolomite reactions of replacement-type dolomitization models. Moreover, in higher-energy environment, Ca and Mg are ordered in the dolomite structure, because this is the best possible arrangement to attain as the elevated temperature allows the two ions to reach their proper sites rapidly. Examination of the interrelationships of strontium with CaO and MgO reveals strong Sr enrichment with increasing CaO (Fig. 6j) and, depletion with increasing MgO (Fig. 6k), suggesting that strontium was lost from calcite during the calcite-dolomite conversion. Loss of Sr during calcite-dolomite reaction is possible considering the fact that Strontium's ionic radius (1.16\AA) is similar to that of Ca (1.00\AA) but much larger than that of Mg (0.72\AA) (Shannon and Prewitt, 1969).

It is therefore obvious that the Cenozoic volcanism most likely aided the calcite-dolomite replacements, and indeed the formation of the Nsofang marble, by providing the desired elevated temperature, and by providing relevant ions that were added to the circulating seawater which interacted with the precursor rock to cause dolomitization, and hence marble formation. This model appears to adequately constrain the evolutionary history of the Nsofang marble of Ikom area of southeastern Nigeria.

Future studies, possibly including fluid inclusion, isotopic and geochronological data, would constrain the source and nature of the dolomitizing fluids applicable, and also shed more light on the temperature regime, as well as the actual timing of the various events within the deposits.

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