LOW TEMPERATURE GRAIN-SCALE RETROGRADE ALTERATION OF DETRITAL MINERALS IN AJALI FORMATION FROM BENIN FLANK OF ANAMBRA BASIN, NIGERIA.

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ABSTRACT

Petrographical study of detrital and authigenic minerals from the Ajali Formation in the Benin flank of Anambra Basin was carried out with the aim of interpreting the textural characteristics and alteration patterns. Samples were collected from Ayowgiri sand quarry site and along Fugar-Agenebode road where good exposures of the Ajali Sandstone occurred. Heavy minerals were concentrated using bromoform according to standard procedures. The heavy mineral concentrates were mounted on glass slides with araldite glue. In addition, thin sections of sandstone were prepared. The samples were studied with the aid of polarizing microscopes. The textural features and relationships among the heavy minerals were used in the interpretations. The results indicate that the detrital heavy minerals (Fe-Ti oxides and garnet) have undergone a very low-temperature retrograde changes rather than ordinary *in-situ* dissolution by weathering and burial diagenesis. The alteration of Fe-Ti oxides resulted into the formation of leucoxene and chlorite while that of garnet resulted only into the formation of chlorite. Detrital magnetite was partially dissolved with skeletal remains while the authigenic grains showed well preserved structures. The re-equilibration of these minerals and partial dissolution were probably due to rise in temperature and change in the chemistry of the formation water. Reducing and acidic conditions at elevated temperature probably favoured dissolution and alteration of the detrital Fe-oxides while the formation of authigenic hematite was aided by oxidizing condition. Temperature increase was probably induced by either underneath thin lithospheric plate or igneous activities at the center of the basin. The conversion of the detrital minerals to authigenic chlorite and partial replacement structures represent a typical case of retrograde reaction which could be described as evidence of a very low-temperature anchi-metamorphism at mineral grain level.

Key words: Authigenic, chlorite, Fe-oxides, garnet, retrograde, anchi-metamorphism.

INTRODUCTION

The study of metamorphic alteration in sedimentary environment has posed some challenges because of the nature of gradual transition between diagenesis and metamorphism, and general overlook of such study in sedimentary environment. The critical changes are not visible with the naked eye because they normally occur only on microscopic or submicroscopic scales (Arkai *et al.*, 2003). Because of these, the study of metamorphic changes in sedimentary environment has not been given much attention. Therefore, such alteration in sedimentary environments can, in few cases, only be recognized by means of microscopic investigations and in most cases using other instrumental techniques. These include measurements of the illite Kübler index (formerly called 'crystallinity') and coalified organic matter order-disorder by means of X-ray powder diffraction, measurements of vitrinite reflectance by means of optical microscopy, fluid inclusion thermobarometry, electron probe micro analyzer and scanning electron microscope (e.g Arkai *et al.*, 2003). Akande and Erdtmann (1998) used illite crystallinity (Kübler index) and vitrinite reflectance to infer progressive increase of temperature from the Anambra Basin towards middle Benue Trough. Earlier, Benkhelil (1989) has suggested that low-temperature metamorphism (anchi-metamorphism) affected parts of the lower Benue Trough (Anambra Basin) particularly around the Abakaliki anticlinorium where zeolite and chlorite were identified. These were related to the igneous activities in that area.

The alteration products of some detrital minerals are environmental indicators, and as such have been used for uranium and petroleum exploration (e.g. Yurkova, 1970; Reynolds and Goldhaber, 1978). Furthermore, detrital minerals and their alteration products can be used to deduce the geochemical conditions in depositional and diagenetic environments (Weibel and Friis, 2003). Of the works that have been carried out in the Anambra Basin, none has suggested imprints of

low grade retrograde alteration or metamorphism. Tijani *et al.* (2010) use the textural characteristics of the Ajali Formation to infer fluvial/river system-dominated environment. This study therefore used simple microscopic observation on some detrital minerals and their authigenic products to deduce a very low-temperature retrograde reaction in the Benin flank of the Anambra Basin.

GEOLOGICAL SETTING

The evolution of the Anambra Basin is directly related to the tectonic events that led to the formation of the Benue Trough. The tectonism was initiated by the separation of South American from African plates in the Cretaceous (Murat, 1972; Burke *et al.*, 1972 and Burke, 1996). Rifting occurred via a RRR triple junction located under the present site of Niger Delta and was triggered by block faulting, basement fragmentation and subsidence (Akande and Erdtmann, 1998). According to Reijers (1996), the Benue Trough was made up of several basins which were formed

from differential subsidence of the fault blocks; one of these is the Anambra Basin. The Anambra Basin was formed after the Santonian tectonic pulse ca. 84 Ma (Reijers, 1996). The inversion tectonics of the lower Benue led to its folding and culminated in Abakaliki anticlinorium. The subsidence to the west formed the Anambra Basin and to the east, the Afikpo syncline.

There were three cycles of sedimentation in the Benue Trough. The infilling of the Anambra Basin with sediments commenced during the third cycle of sedimentation in the Campanian-Maastrichtian. The formations resulting from this cycle of sedimentation comprises the Enugu/Nkporo Shale, heterolitic Mamu Formation (with intercalated sub-bituminous coal seams), Ajali Sandstone, Nsukka Formation (with coal seam), Imo Formation, Ameki/Nanka Formation and the Ogwuashi-Asaba Formation (Murat, 1972, Fig. 1). The stratigraphic succession of these formations is as shown in the Table 1.
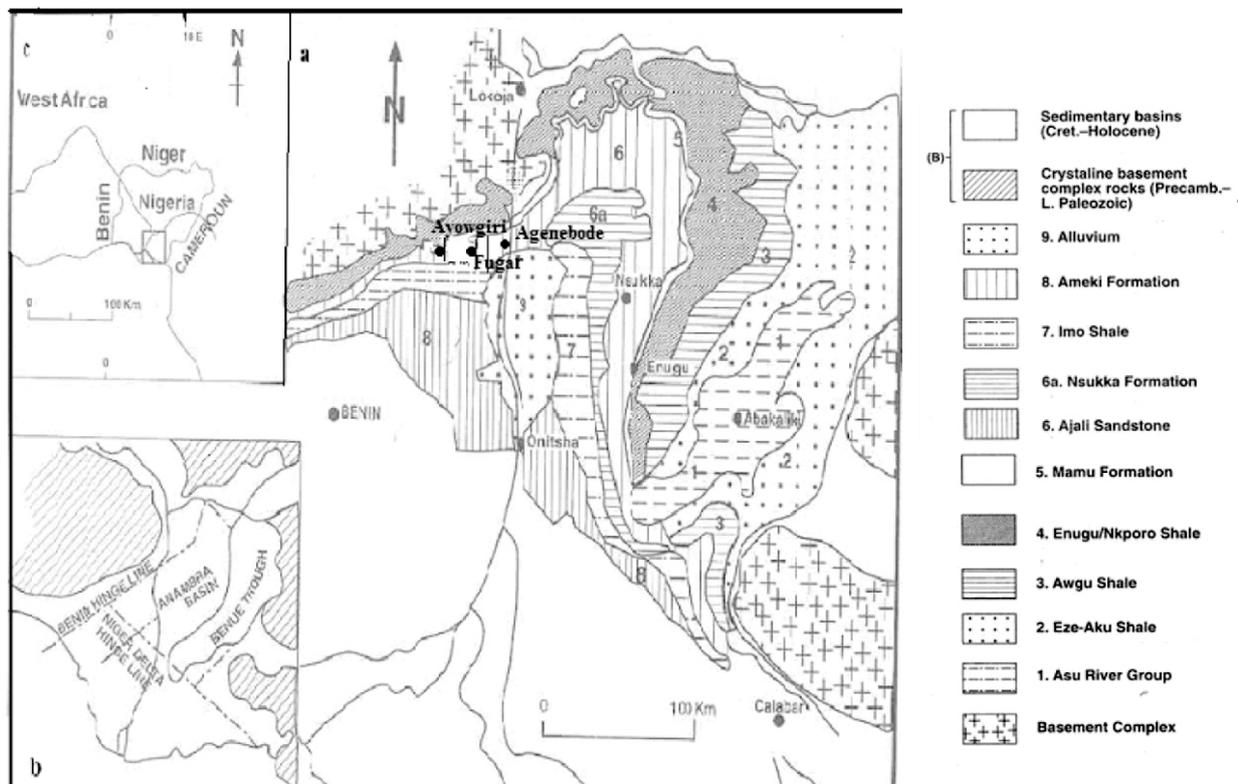
Figure 1. Geological map of the Anambra Basin (a); inset: b (position of Anambra Basin relative to Benue Trough), c (map of Nigeria showing the location of Anambra Basin) (after, Akande and Erdtmann, 1998).

Table 1. Stratigraphy of Lower Benue/Anambra Basin (after Akande and Ertdmann, 1998).

Era	System	Series	Stages	Formation
Cenozoic	Tertiary	Miocene	Stages not defined	Ogwashi-Asaba
		Oligocene		Ameki/Nanka
		Eocene		Imo shale
		Plaeocene		Nsukka
				Ajali Ss.
Mesozoic	Cretaceous	Upper	Maastrichtian	Mamu
				Enugu/Nkporo shale
			Campanian	
			Santonian	
			Coniacian	Awgu Shale
			Turonian	Eze-Aku Shale
			Cenomanian	Odukpani Fm
		Lower	Albian	Asu River Gp.
			Aptian	
PreCambrian	Basement Complex			

The total thickness of these units is estimated to be about 2000 m (Petters, 1977). Different aspects of these formations have been described by Reyment (1965), Murat (1972), Nwajide (1979), Arua (1986), Anyanwu and Arua (1990), Obi *et al.* (2001), Umeji and Nwajide (2007) and Adekoya *et al.* (2011) among others. The Ajali Sandstone has been variously referred to as false bedded, white sandstone (Reyment, 1965). The formation is poorly sorted, and cross bedded.

Based on the lithology, paleocurrent directions and absence of marine fossils, Hoque and Ezepue (1977) suggested fluvial and fluvio-deltaic depositional environment for the Ajali Sandstone. Whiteman (1982) considered it as continental facies of regressive deltaic complex. Worm tracks and fragments of plants are the only preserved fossils in the sandstone. On the other hand, the Ajali Sandstone is considered to be deposited in tidal and inter tidal environments (Amajor, 1984; Ladipo, 1986). They argued that the presence of planar and trough cross sets which show herringbone stratification, reactivation surface sets, the presence of scolithus and ophiomorpha borings; and bundle structures are reasons for tidally influenced regime.

METHODS
Samples were collected from Ayowgiri sand quarry and along Fugar-Agenebode road (Figure 1) where good exposures of the Ajali Sandstone occurred. Heavy minerals were concentrated using bromoform according to standard procedures (Morton and Hallsworth, 1999). The heavy mineral concentrates were mounted on glass slides with araldite glue. In addition, thin sections of sandstone were prepared. The samples were studied with the aid of polarizing microscopes. The textural features and relationships among the heavy minerals were used in the interpretations.

RESULTS
The Ayowgiri-Fugar section of the Ajali Sandstone is fine- to coarse-grained, poorly sorted, friable quartz arenite. Individual mineral grains are mostly angular. The formation is cross-bedded and red-brownish stained in places probably due to the effect of weathering. The horizontal beds dip at about 15^0 E while the cross beds dip at about 28^0 E in Fugar. Microscopic examination revealed limited number of light minerals and diverse heavy species. The light minerals are quartz and microcline while the

detrital heavy minerals are altered pyroxene, tourmaline, zircon, rutile, Fe-Ti oxides, biotite, garnet, staurolite and kyanite. The authigenic ones are rutile, leucoxene, Fe-chlorite (chamosite) and hematite.

Quartz dominantly occurs as detrital grains and in some cases with sutured margins probably due to intrastratal pressure dissolution (Figure 2a). Quartz overgrowth (authigenic quartz) occurs on few grains with both the overgrowth and detrital quartz showing different interference colours under crossed polars. Microcline shows characteristic iron-grid twinning with perthitic intergrowth (Figure 2b). Grains of altered pyroxene show traces of green colouration with prominent two cleavage directions intersecting at almost 90^0 (Figure 2c). Zircon is present as zoned euhedral grains with doubly terminations (Figure 2d). It occurs either as elongated, prismatic or fragmental grains. The fragments have v-shaped edges (Figure 2e). Tourmaline occurs as euhedral crystals with two varieties recognized (blue-indicollite: bto and green-elbaite: gto). The mineral contains some unidentified inclusions and is probably zoned (Figure 2f).

Detrital biotite, garnet, staurolite and authigenic chlorite are index metamorphic minerals recovered from the Ajali Sandstone. Biotite occurs as tabular, brownish mineral with strong pleochroism and a prominent cleavage that is parallel to its longer axis (Figure 2g). Staurolite occurs as yellow, worn crystals. The surface of staurolite is characterized by sub-parallel ridges and grooves (Figure 2h) that may suggest high-energy environment during or prior to its final deposition. Rutile occurs as both detrital and authigenic varieties. Some of the detrital grains are slightly reddish-brown, smooth and well-rounded with prominent cleavages in two directions (Figure 2i). The authigenic grains are white to colourless, structureless and opaque. Leucoxene, a hydrous titanium oxide, occurs as white opaque minerals (Figure 3a). It normally forms from alteration of titanium-iron oxides. The detrital Fe-oxides recovered from the Ajali Sandstone are ilmenite, magnetite and titano-magnetite. The grains of these minerals show high degree of alteration. Apart from leucoxene and rutile, other alteration product of ilmenite and titanomagnetite is chlorite (Figures 3a to c). Magnetite mainly occurs as skeletal grains due to partial dissolution (Figure 3c). Garnet occurs as euhedral isotropic mineral and is spatially associated with authigenic chlorite. In some cases, it has been altered leaving behind chlorite pseudomorphs (Figures 3d and e).
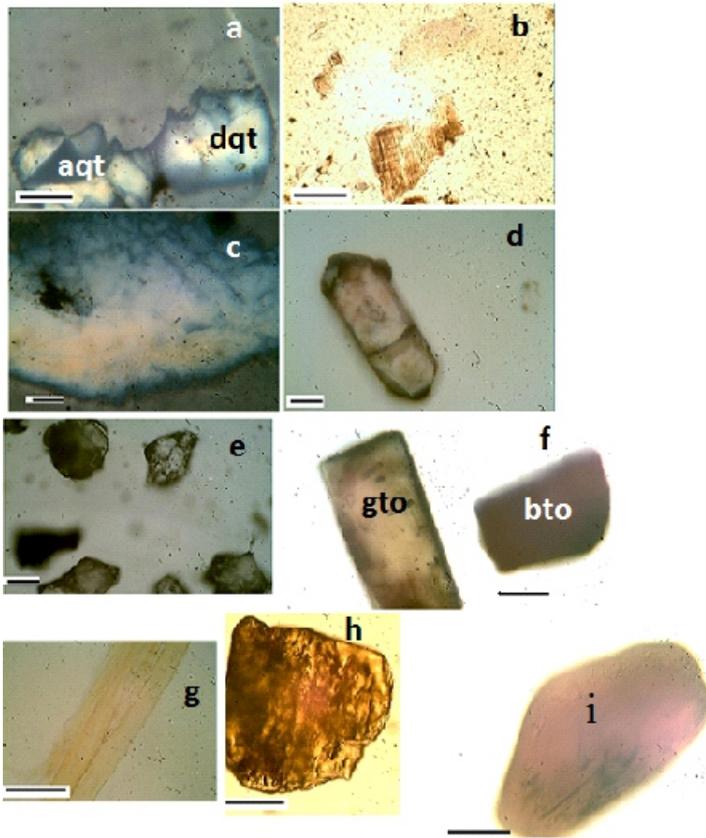
Figure 2: Photomicrograph of light and heavy detrital minerals from Ajali sands. a:- quartz, aqt:- authigenic quartz, dqt:- detrital quartz; b:- microcline; c:- pyroxene; d:- zircon; e:- zircon; f:- tourmaline; bto:- blue tourmaline, gto:- green tourmaline; g:- biotite; h:- staurolite and i:- rutile. Bar scale: 4 um.

Figure 3:
Photomicrograph of authigenic and detrital heavy minerals from Ajali sands. a:- ilm, altered ilmenite; chl, chlorite (diffuse); le, leucoxene; b:- chl, chlorite; ttm, titanomagnetite; c:- partially dissolved magnetite; d:- chl, pisolithic chlorite; e:- chl, pseudomorph of chlorite after garnet (grt); f:- pseudo-hexagonal crystal of chlorite; g:- reniform hematite.
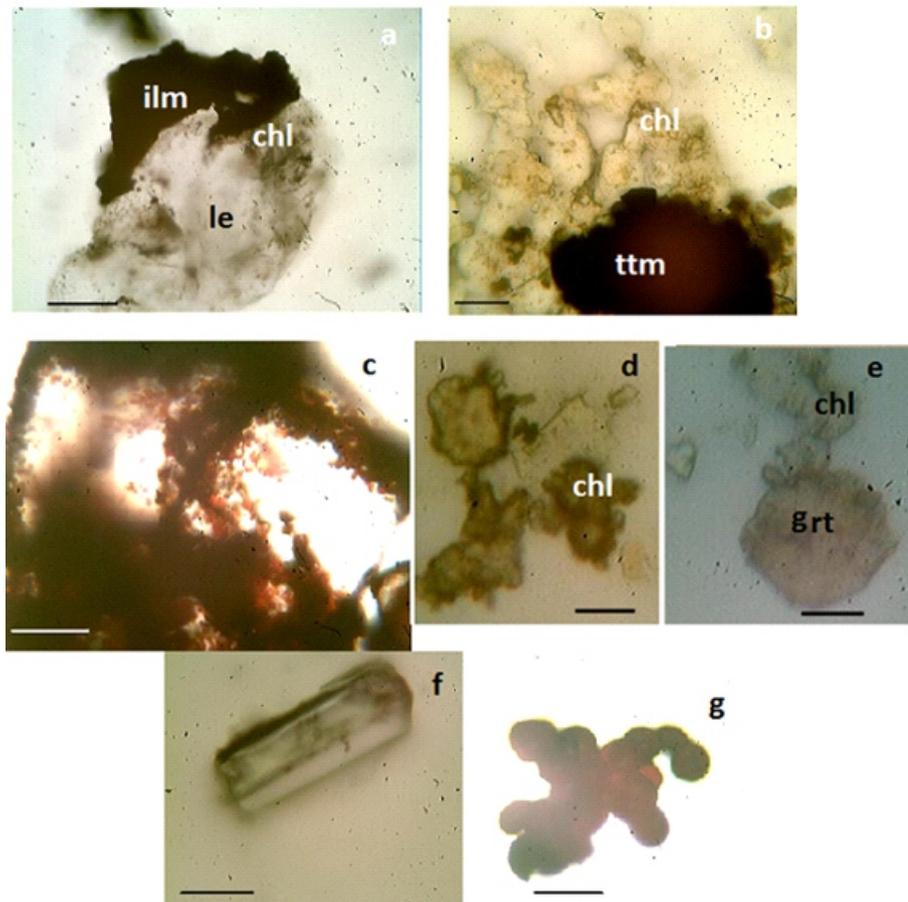
Chlorite occurs as green (chamosite) to colourless crystals in four different forms, namely: diffuse matrix, pisolithic to rounded form and pseudomorphs after garnet, and pseudo-hexagonal crystals (Figures 3a, b, d and f). The mineral is intimately associated with detrital garnet and Fe-oxides (ilmenite and titano-magnetite). In some cases, it occurs as a major component of corona in the Fe-oxides (Figure 3a and b). Hematite occurs as authigenic mineral. Some grains are sub-angular while others have reniform habit (Figure 3g).

DISCUSSION

The alteration of detrital mineral is generally believed to be due to weathering, hydrothermal influence and diagenesis. However, the conversion of garnet and iron oxides to chlorite in the Ajali Sandstone represents typical retrograde alteration.

Garnet
The conversion of garnet in weathered saprolite to gibbsite and goethite has long been discussed by Velbel (1984). Such alteration normally begins at the grain boundaries and along fractures. However, the smooth, lustrous nature of the angular surfaces indicates that the garnet grains from Ajali Sandstone have not been affected by weathering. Many of the garnet grains are represented by chlorite pseudomorphs and mostly have been converted to chlorite. These indicate fluid-induced compositional changes promoted by elevated temperature. The elevated temperature and fluid aided retrogression of garnet from state of metastability to a more stable mineral (chlorite). This very low-temperature anchi-metamorphism took place with increasing temperature and was made possible by vast volume of formation water. The chemical reaction may be complex, however, the essential components could be represented by the following reaction sequence where garnet is converted to iron rich chlorite (chamosite) and authigenic quartz:

$$2Fe_3Al_2Si_3O_{12} (garnet) + 6H_2O \longrightarrow$$
$$2Fe_3Al_2Si_2O_{10}3H_2O (chlorite) + 2SiO_2$$
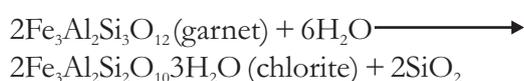
The association of these minerals indicates low temperature retrograde conversion of the oxides and garnet to iron rich chlorite (chamosite).

Fe- oxides
The different Fe-Ti oxides gave different alteration products as revealed from the microscopic studies. Iron-titanium oxide could be subjected to alteration at the source area (Riezebos, 1979). The fragile textures which could have been destroyed mechanically during transportation are still preserved. Hence, the alterations in these detrital minerals were *in-situ*. Similarly, high weathering rate generally could result in the relative enrichment of opaque minerals (predominantly leucoxene, ilmenite and virtually opaque rutile) (Van Loon and Mange, 2007). Detrital magnetite appears to have suffered both dissolution and alteration. The effect of this dissolution is the skeletal remains of magnetite. Alteration related to diagenetic changes may be largely due to both oxidizing and reducing conditions (Weibel, 2003). Iron oxides (ilmenite, titanomagnetite, magnetite and hematite) are generally unstable under reducing and neutral-acidic conditions (Weibel, 2003) with the formation of coarse leucoxene at the advanced stage of alteration. Ilmenite and titano-magnetite are assumed to have multiple stage alteration processes: ilmenite to pseudo-rutile to leucoxene + chlorite. The proportion of chlorite is more with titano-magnetite. This may be related to higher concentration of Fe. Hence, the formation of leucoxene and chlorite from Fe-Ti may be due to change in environmental temperature and redox environmental conditions at that time. Hematite in Ajali Sandstone is predominantly authigenic. Hematite did not show any sign of alteration (Figure 3g), thus, it probably formed in an oxidizing environment. However, the reddish stains observed in the formation probably represent the effect of weathering. Any detrital hematite would have been completely dissolved at the initial stage of alteration of the detrital minerals. The authigenic hematite probably formed after the cessation of alteration processes and reversal of the reducing environment to oxidizing condition at or near the surface. The corona and replacement textures (Figure 3a, b and d) are indicative of metamorphic reactions promoted by a change in temperature. The formation of these authigenic heavy minerals: Fe-chlorite and leucoxene indicates retrograde

reactions. Chlorite usually forms from clay when there is progressive increase in temperature. The authigenic chlorite identified in this study was not formed from this prograde conversion of clay minerals but rather from retrograde conversion of Fe-Ti oxides and garnet.

CONCLUSIONS.

The corona structures and partial replacement textures are indicative of low temperature retrograde anchi-metamorphic reactions promoted by rise and fall in temperature and redox state of the formation. This retrogression noticeable at grain-scale affected only detrital garnet and Fe-Ti oxides and caused the formation of chlorite and leucoxene. The dissolution and alteration of the heavy resistant minerals could not have been accomplished by ordinary burial and diagenetic processes. The alteration was aided by reducing nature and elevated temperature of formation water. The cessation of the alteration was likely aided by decrease in temperature and reversal to oxidizing state of the reaction environment which enhanced the formation of hematite.

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REFERENCES

Adekoya, J.A., Aluko, A.F. and Opeloye, S.A. 2011. Sedimentological characteristics of Ajali Sandstone in the Benin flank of Anambra Basin. *Ife Journal of Science* 13 (2), 327-337.

Akande, S.O. and Erdtmann, B.D. 1998. Burial metamorphism (thermal maturation) in Cretaceous sediments of southern Benue Trough and Anambra Basin, Nigeria. *American Association of Petroleum Geologist Bulletin* 82 (6), 1191-1206.

Amajor, L.C. 1984. Paleocurrent, petrography and provenance analyses of the Ajali Sandstone (Upper Cretaceous), Southeastern Benue Trough, Nigeria. *Sedimentary Geology* 54, 47-60.

Anyanwu, N.P.C. and Arua, I. 1990. Ichnofossils from the Imo Formation and their palaeo-environmental significance. *Journal of Mining and Geology* 26, 1-4.

Árkai, P., Sassi, F.P. and Desmons, J. 2003. Very low- and low-grade metamorphic rocks. Recommendations by the IUGS Sub commission on the Systematics of Metamorphic Rocks. Web version. www.bgs.ac.uk/scmr/home.html. 12 pp.

Arua, I. 1986. Paleo-environment of Eocene deposits in the Afikpo syncline, southern Nigeria. *Journal of African Earth Sciences* 5, 279-284.

Benkhelil, J. 1989. The origin and evolution of the Cretaceous Benue Trough, Nigeria. *Journal of African Earth Sciences* 8, 251-282.

Burke, K.C. 1996. The African Plate. *South African Journal of Geology* 99, 341-409.

Burke, K.C., Dessauvagie, T.F.J. and Whiteman, A.J. 1972. Geological history of the Benue valley and adjacent areas. In: Dessauvagie, T.F.J. and Whiteman, A.J. (Editors) African Geology. University of Ibadan Press, Nigeria, pp. 187-218.

Dill, H.G. 1998. A review of heavy minerals in clastic sediments with case studies from the alluvial fan through near shore marine environments. *Earth Science Review* 45, 103-135.

Hoque M. and Ezepue, M.C. 1977. Petrology and palaeogeography of the Ajali Sandstone. *Journal of Mining and Geology* 14(1), 6-22.

Ladipo, K.O. 1986. Tidal shelf depositional model for the Ajali Sandstone, Anambra Basin, Southern Nigeria. *Journal of African Earth Sciences* 5(2), 177-185.

Murat, R.C. 1972. Stratigraphy and paleogeography of the Cretaceous and Lower Tertiary in southern Nigeria. In: Dessauvagie, T.F.J. and Whiteman, A.J. (Editors), African Geology. University of Ibadan Press, Nigeria, pp. 251-266.

Morton, A.C. and Hallsworth, C. 1999. Processes controlling the composition of heavy mineral assemblages in sandstones. *Sedimentary Geology* 124, 3-29.

Nwajide, C.S. 1979. A lithostratigraphic analysis of the Nanka Sands, southeastern Nigeria. *Journal of Mining and Geology* 16, 103-109.

Obi, G.C., Okogbue, C.O. and Nwajide, C.S. 2001. Evolution of the Enugu Cuesta, A tectonically driven erosional process. *Global Journal of Pure and Applied Sciences* 7,

321-330.

Petters, S.W. 1977. Mid Cretaceous paleo-environments and biostratigraphy of Benue Trough. *Geological Society of America Bulletin* 89, 151-154.

Reijers, T.J.A. 1996. Selected chapters on geology: Sedimentary geology and sequence stratigraphy in Nigeria and three case studies and a field guide. Shell Petroleum Development of Nigeria, 197 pp.

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

Reynolds, R.L. and Goldhaber, M.B. 1978. Origin of south Texas roll-type uranium deposit: 1. alteration of iron-titanium oxide minerals. *Economic Geology* 73, 1677-1689.

Riezebos, P.A. 1979. Compositional downstream of opaque and translucent heavy residues in some modern Rio Magdelena sand (Colombia). *Sedimentary Geology* 23, 179-225.

Tijani, M.N., Nton, M.E. and Kitagawa, R. 2010. Textural and geochemical characteristics of the Ajali Sandstone, Anambra Basin, SE Nigeria: Implication for its provenance. *Comptes Rendus Geoscience* 342, 136-150.

Umeji, O.P. and Nwajide, C.S. 2007. Age control and designation of the standard stratotype of Nsukka of Anambra Basin, southwestern Nigeria. *Journal of Mining and Geology* 43(2), 147-166.

Van Loon, A.J. and Mange, A.M. 2007. In situ' dissolution of heavy minerals through extreme weathering, and the application of the surviving assemblages and their dissolution characteristics to correlation of Dutch and German silver sands. In: Mange, M.A. and Wright, T.D. (Editors), *Developments in Sedimentology* (Heavy Minerals in use) 58, Elsevier, pp. 189-213.

Velbel, M. A. 1984. Natural weathering mechanisms of almandine garnet. *Geology* 12, 631-634.

Whiteman, A., 1982. Nigeria: It's petroleum geology resource and potentials I & II, Graham and Trotman ltd.

Wiebel, R. 2003. Alteration of detrital Fe-Ti oxides in Miocene fluvial deposits, central Jutland, Denmark. *Bulletin of the Geological Society of Denmark* 50, 171-183.

Weibel, R. and Friis, H., 2003. Alteration of opaque heavy minerals as a reflection of the geochemical conditions in depositional and diagenetic environments. In: Mange, M.A. and Wright, T.D. (Editors), *Developments in Sedimentology* (Heavy Minerals in use) 58, Elsevier, pp. 277-303.

Yurkova, R.M. 1970. Comparison of post sedimentary alteration of oil-, gas- and water-bearing rocks. *Sedimentology* 15, 41-52.