

RARE EARTH ELEMENT GEOCHEMISTRY AND PROTOLITHS OF SCHISTS IN SOUTHEAST, LOKOJA, CENTRAL NIGERIA.

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ABSTRACT

The Nigerian schist belts constitute the most important lithologic units necessary for the unravelling of the geochemical and geodynamic evolution of the basement complex. The schists have however undergone extensive alterations owing to weathering and metamorphism. REE abundance and distribution patterns of Lokoja schists indicate that the schist belts are metamorphosed shale-greywacke sequence. Their provenance possibly contained volcanogenic debris and the passive margin of the West African craton provided most of the materials. The reworking and metamorphism of the sediments took place during the Pan-African Orogeny ca. 687 Ma ago.

KEYWORDS: Schists, Provenance, Reworking, Rare Earth Element, Evolution.

INTRODUCTION

Southeast Lokoja belongs to the Nigerian basement complex and is located around the confluence of Rivers Niger and Benue (Fig. 1). The Nigerian basement is situated in the Pan-African mobile zone lying between the West African craton and the Gabon-Congo craton. Lithologically, the basement is composed of a migmatite-gneiss complex, a metavolcano-sedimentary series or schist belts, which form a supracrustal cover on the former, and intrusive rocks of acidic, intermediate, basic and ultrabasic compositions (Klemm, et al., 1984).

The Nigerian schist belts, whose areal extent is still not well known, have received special attention. Descriptions and reviews of those located in the southwest and northwest of the country have been presented by Fitches et al. (1985), Affaton et al. (1991), and Elueze (1992). Until recently, it was thought that the schist belts occupy a N-S trending trough, which does not extend beyond latitude 8° E. Schist belts have, however, been reported from southeast Nigeria (Ekwueme and Onyeagocha, 1986) and Toteu et al. (1987) believe that these are extension of the Poli schists in Cameroon Republic.

Among the rock units in southeast Lokoja are schists whose field occurrence and petrography have been discussed by Ekwueme and Onyeagocha (1988) and Hockey et al. (1986). The schist belts of Nigeria have been compared to rocks of Archaean greenstone belts (Wright and McCurry, 1970; Hubbard, 1975; Klemm et al 1984; Ige and Asubiojo, 1991; Attoh and Ekwueme, 1997) and the understanding of the composition of these schists is crucial in unravelling the evolution of the basement complex. The discussion of the chemical composition of the schist belts has hitherto been based on major and trace elements (Ekwueme, 2003). Most of these schists are metamorphosed to amphibolite facies grade and have also undergone substantial weathering, rare earth elements are essential in determining their protoliths and petrogenesis since these elements are thought to be rarely affected in their distribution in rocks by those processes.

GEOLOGIC SETTING

Rock types in southeast Lokoja are schists, gneisses, migmatites, granites, and gabbros (Fig. 1). Detailed descriptions of these rocks and their field relationships have been presented in Ekwueme and Onyeagocha (1988). A summary is given here.

The schists include (i) Quartz muscovite schist, (ii) Quartz muscovite biotite garnet schist, (iii) Staurolite garnet schist and, (iv) Cordierite garnet schist. The modal composition of these schists is shown in Table 1. The quartz muscovite schist is fine - medium grained and foliated. Metaquartzitic selvages are present possibly indicating a sandstone sequence of the original pre-metamorphic sedimentary rock. This rock is rich in muscovite and is consequently, light-coloured. The quartz muscovite biotite garnet schist is fine-to-medium grained and has foliation trending NW with dips varying from 15 to 20° NE. It is dark in colour, reflecting the preponderance of biotite in the mode. The staurolite garnet schist is generally medium grained and textures become coarser towards the north (around Emi-Andrew), where crystals of staurolite as long as 5cm occur in the rock. This schist is light coloured and contains flakes of muscovite and garnet porphyroblasts. The rock is associated with metaquartzites, pointing to its possible sedimentary parentage. The cordierite garnet schist occurs as a narrow band running approximately N - S in the middle of the map area (Fig. 1). It is medium to coarse-grained and has been folded parallel to the foliation which trends NE - SW. Geophysical studies have revealed that the schists were emplaced in a NE - SW trending fractures (Madu and Onuoha, 1984). Thin bands of mica and quartz are observed to alternate in outcrops of this schist. Porphyroblasts of garnet are conspicuous in hand specimen and the emplacements of granite in the southern part of the cordierite garnet schist possibly triggered off boron metasomatism which resulted in the extensive tourmalization of the rock. Dips of foliation ranges from 25° to 45° mostly NW and foliations dipping in opposite directions (SE) points to occurrences of a synclinal structure. This has been confirmed by geophysical studies, and the axis lies 5.5km west to Gboloko (Madu and Onuoha, 1984).

MINERAL COMPOSITION

The schists contain index minerals garnet, staurolite and cordierite (Table 1). Ekwueme (1983) and Onyeagocha and Ekwueme (1990) used these index minerals to place metamorphic isograds in Lokoja area. The mineral assemblages occurring in these schists (Table 1) indicate that the metamorphism was regional medium-pressure type and increased in grade from east to west. The schists were metamorphosed to grades ranging from upper greenschists to medium amphibolite.

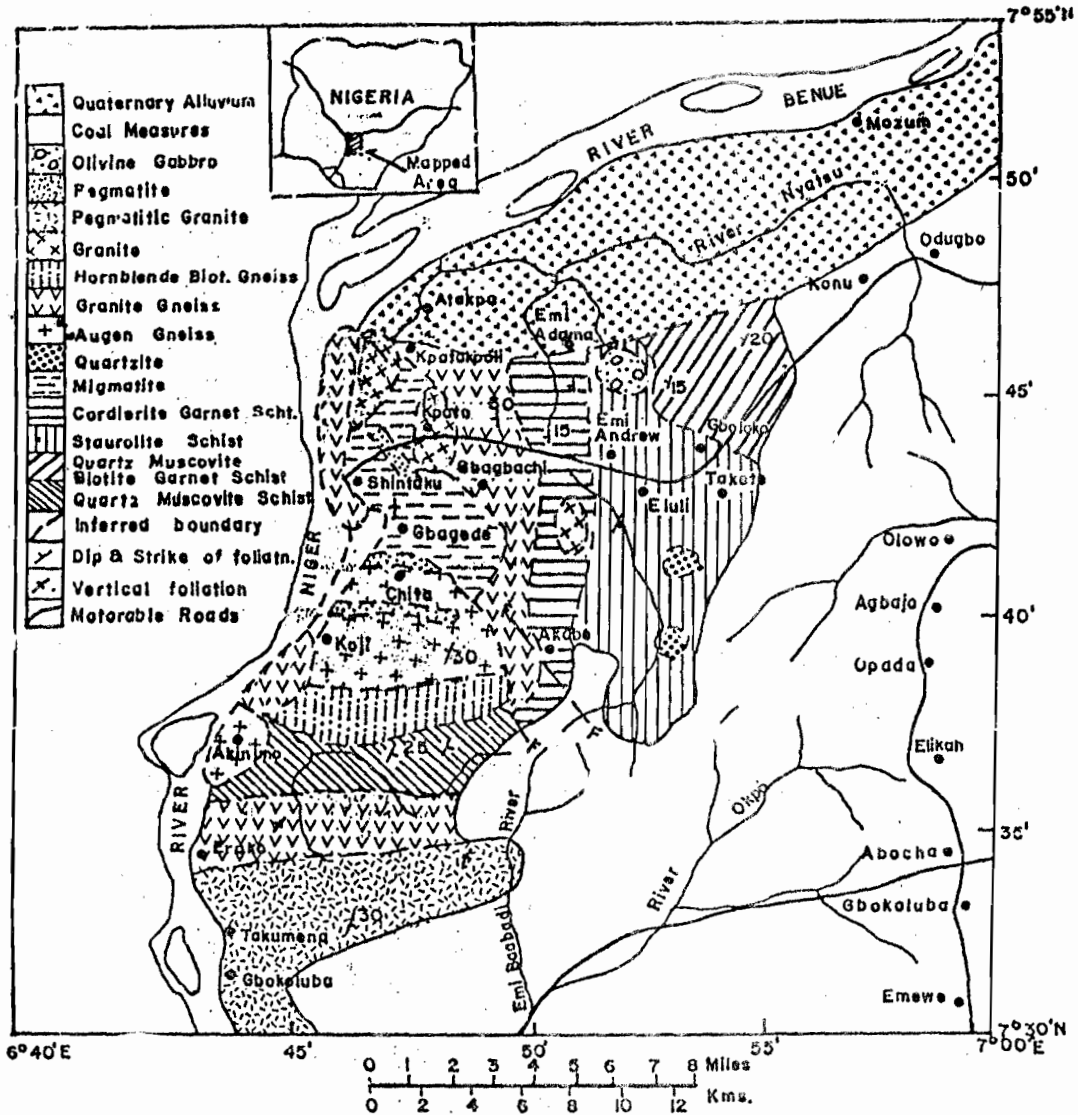


Fig 1: Geological Map of Southeast Lokoja, Nigeria (after Ekwueme, 1983).

TABLE 1: Average Modal composition of Schists in Southeast Lokoja.

| | *QMS (n=12) | QMBGS (n=15) | SGS (n=25) | CGS (n=20) |
|--------------|----------------|-----------------|---------------|---------------|
| Quartz | 30 | 30 | 20 | 20 |
| Plagioclase | 15 | 10 | 5 | 5 |
| K-feldspar | 20 | - | - | 12 |
| Biotite | 2 | 35 | 20 | 25 |
| Muscovite | 31 | 6 | 9 | 10 |
| Chlorite | - | 15 | 10 | 5 |
| Staurolite | - | - | 30 | - |
| Cordierite | - | - | - | 10 |
| Garnet | - | 2 | 2 | 5 |
| Tourmaline | 1 | 2 | 4 | 6 |
| Clinozoisite | 1 | - | - | 2 |

*QMS= Quartz muscovite schist; QMBGS= Quartz muscovite biotite garnet schist; SGS= Staurolite garnet schist; CGS= Cordierite garnet schist.

CHEMICAL COMPOSITION

Whole-rock chemical analysis of representative samples of schists from southeast Lokoja was done by X-ray fluorescence following the method of Norrish and Hutton (1969). The rare earth element analysis was performed by optical emission spectroscopy (ICP-OES; ARL 3520) and the determination of REE contents was carried out after separation by ion exchange resins. Samples SS2 and SS3 were analyzed by Instrumental Neutron Activation (INAA) at the U. S. Geological Survey Laboratory in Reston. Other samples were analysed at the Geochemical Laboratory, Institut für Geologie, Technical University of Braunschweig, Germany. The results of the analysis are shown in Table 2, 3 and 4.

Major and Trace Elements

The schists are characterized by high SiO_2 (up to 75%) and Al_2O_3 (up to 20%) (Table 2). The $\text{Al}_2\text{O}_3 / (\text{Na}_2\text{O} + \text{K}_2\text{O} + \text{CaO})$ is greater than one, and the Niggli al is also greater than Niggli (alk + c). These parameters reflect the aluminium-rich nature of the parent rocks, resulting in the formation of staurolite and cordierite during the metamorphism. The TiO_2 content is, however, high when compared to values expected in clay-rich sediments, and only quartz muscovite schist and staurolite garnet schist (SS3) have $\text{TiO}_2 / \text{Al}_2\text{O}_3$

TABLE 2: Average Major Element Composition (in %) of schists in Southeast Lokoja

| | *QMS | QMBGS | SGS1 | SGS2 | SGS3 | CGS |
|----------------------------------|--------|-------|--------|--------|-------|-------|
| SiO ₂ | 75.04 | 62.26 | 62.89 | 69.57 | 56.80 | 63.13 |
| TiO ₂ | 0.47 | 0.95 | 1.05 | 0.96 | 0.99 | 0.91 |
| Al ₂ O ₃ | 13.47 | 16.13 | 17.02 | 14.23 | 20.44 | 17.19 |
| Fe ₂ O ₃ * | 3.01 | 7.57 | 7.54 | 5.71 | 9.31 | 7.06 |
| MnO | 0.01 | 0.17 | 0.15 | 0.12 | 0.11 | 0.16 |
| MgO | 0.57 | 3.61 | 4.06 | 2.55 | 3.74 | 3.23 |
| CaO | 0.17 | 1.77 | 1.44 | 1.72 | 1.32 | 1.80 |
| Na ₂ O | 0.34 | 3.45 | 2.86 | 2.87 | 1.57 | 2.46 |
| K ₂ O | 5.59 | 2.79 | 2.49 | 2.03 | 3.30 | 2.66 |
| P ₂ O ₅ | 0.10 | 0.24 | 0.04 | 0.16 | 0.23 | 0.27 |
| H ₂ O | 0.10 | 0.13 | 0.18 | 0.13 | 0.21 | 0.11 |
| **LOI | 1.62 | 0.91 | 1.45 | 1.01 | 1.15 | 0.83 |
| Total | 100.49 | 99.98 | 101.17 | 101.06 | 99.17 | 99.81 |
| <u>Niggli Values</u> | | | | | | |
| al | 56 | 38 | 40 | 41 | 45 | 42 |
| fm | 14 | 33 | 36 | 30 | 35 | 32 |
| c | 2 | 8 | 6 | 9 | 6 | 8 |
| alk | 28 | 21 | 17 | 20 | 14 | 17 |
| si | 535 | 249 | 252 | 339 | 215 | 264 |
| k | 0.92 | 0.35 | 0.36 | 0.32 | 0.58 | 0.41 |
| mg | 0.42 | 0.65 | 0.68 | 0.63 | 0.61 | 0.64 |
| q | 323 | 65 | 84 | 159 | 59 | 96 |

*See explanation for Table 1; * Total Fe as Fe₂O₃; **LOI = loss on ignition.

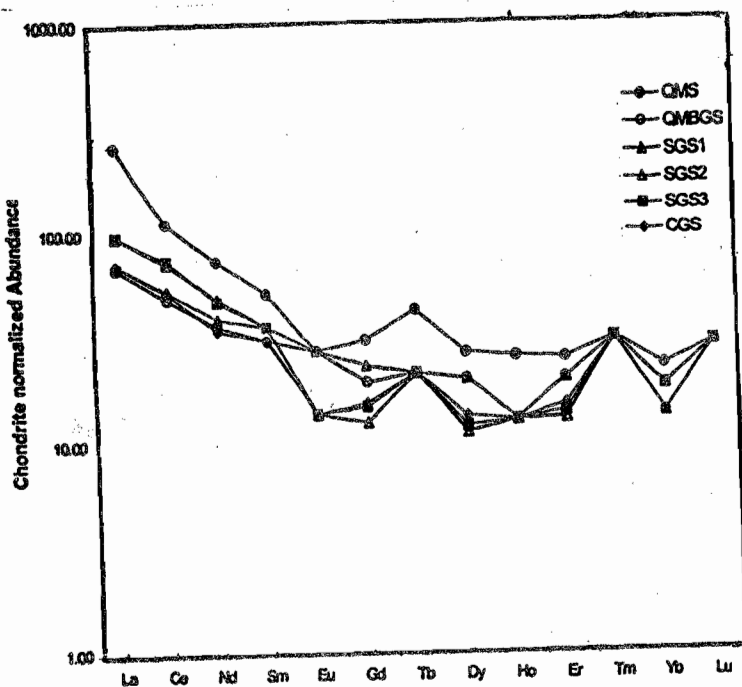


Fig. 2: Rare earth elements (Rock/ chondrites) plot for schists in Southeast Lokoja

ratios approximately equal to 0.040 expected in clays. Other schists in the area have higher TiO₂ / Al₂O₃ ratios, and this is indicative of sediments contaminated by basic to intermediate volcanic components (Spears and Kanaris-Sotiriou, 1976). K₂O / Na₂O is variable in the schists (Table 2). Some samples have K₂O greater than Na₂O, which is characteristics of pelites and semi-pelites, whereas others have Na₂O greater than K₂O

which characterizes greywackes (Pettijohn, 1975). Taylor and McLennan (1985) noted that K₂O / Na₂O ratio less than one is also characteristic of volcanogenic greywackes. The variation of K₂O / Na₂O ratio in metasediments has been attributed to: (i) the mixed nature or association of two compositionally different lithologic units e.g. shale-greywacke sequence as parent rock, (ii) facies changes and (iii) addition of materials through metasomatism. The first case is most likely for the Lokoja schists.

The Al₂O₃ / Na₂O ratio is a maturity index for sediments. Mature sediments have values of 10 or more. For mature greywackes, the value is 4.8. Most samples of Lokoja schists have values greater than 4.8 but less than 10 (Table 2), indicating that they were mostly immature sediments. Some samples (SS1 and CGS) have values between 5 and 6, which indicate igneous provenance. The fact that some samples of quartz muscovite schist and staurolite garnet schist have values greater than 10 suggest that sections of the sedimentary sequence did attain maturity.

The mixed nature of the pre-metamorphic lithology of the Lokoja schists is also reflected in the trace element contents (Table 3), which is variable in the same rock unit. Cr is rather high in all samples except quartz muscovite schist. This is indicative of the metasedimentary nature of the schists (Condie, 1967; Argast and Donnelly, 1986). The Rb content is higher than the value of 60 and 30 ppm quoted for shales and greywackes respectively (Taylor, 1965). They are closer to the values of 100 ppm given for high-Ca granites (Turekian and Wedepohl, 1961). The Sr content is also similar to that of high-Ca granites (El Bouseily and El Sakkary, 1975).

REE Composition and Discussion

Girty et al. (1993) agree with McLennan et al (1990), Taylor and McLennan (1985), Condie (1991) and McLennan and Taylor (1991) that the REEs, Th and Sc are carried in the solid load during transportation from source rocks to final site of deposition and that because of their low solubility in most natural waters, these elements are relatively immobile during weathering, transportation and diagenesis and are therefore, transferred from source areas to sites of deposition in

TABLE 3: Average Trace Element Composition (ppm) of Schists in Southeast Lokoja

| | *QMS | QMBG | SGS1 | SGS2 | SGS3 | CGS |
|----------------------------|------|------|------|------|------|-----|
| As | 7 | 1 | - | 4 | 4 | 15 |
| Ba | 729 | 404 | 665 | 311 | 477 | 587 |
| Co | 88 | 67 | 90 | 51 | 58 | 87 |
| Cr | 1 | 106 | 105 | 127 | 84 | 103 |
| Cu | 13 | 25 | 27 | 81 | 81 | 19 |
| Ga | 13 | 12 | 20 | 11 | 10 | 14 |
| Mo | 6 | 7 | 10 | 5 | 3 | 5 |
| Nb | 19 | 9 | 9 | 7 | 9 | 7 |
| Ni | 4 | 64 | 75 | 29 | 71 | 53 |
| Pb | 8 | 23 | 10 | 15 | 20 | 15 |
| Rb | 229 | 96 | 80 | 71 | 77 | 86 |
| Sc | 4 | 16 | 19 | 27 | 27 | 17 |
| Sr | 49 | 207 | 197 | 175 | 95 | 204 |
| Th | 35 | 3 | 1 | 5 | 5 | 1 |
| U | 4 | 2 | 3 | 4 | 3 | 3 |
| V | 10 | 119 | 153 | 88 | 88 | 143 |
| Y | 50 | 30 | 32 | | | |
| Zn | 15 | 46 | 112 | 71 | 81 | 133 |
| Rare Earth Elements | | | | | | |
| La | 92 | 23 | 24 | 33 | 33 | 24 |
| Ce | 103 | 44 | 48 | 65 | 67 | 47 |
| Nd | 47 | 23 | 25 | 31 | 30 | 22 |
| Sm | 10 | 6 | 7 | 7 | 7 | 6 |
| Eu | 2 | 2 | 2 | 1 | 1 | 1 |
| Gd | 8 | 5 | 6 | 3 | 4 | 4 |
| Tb | 2 | 1 | 1 | 1 | 1 | 1 |
| Dy | 8 | 6 | 6 | 3 | 4 | 4 |
| Ho | 2 | 1 | 1 | 1 | 1 | 1 |
| Er | 5 | 4 | 4 | 3 | 3 | 1 |
| Tm | 1 | 1 | 1 | 1 | 1 | 1 |
| Yb | 5 | 3 | 3 | 4 | 4 | 3 |
| Lu | 1 | 1 | 1 | 1 | 1 | 1 |

* See explanation for Table 1

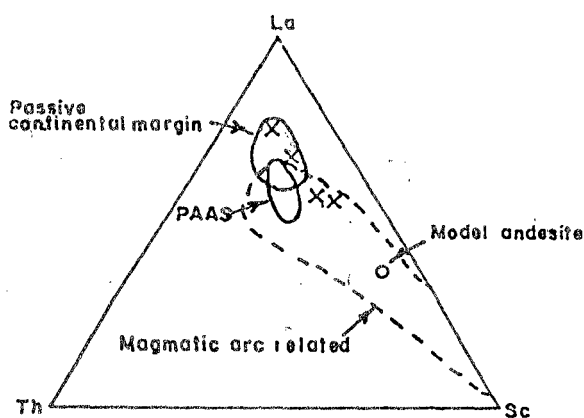


Fig. 3: La - Th - Sc ternary plot of schists of Southeast Lokoja (after McLennan and Taylor, 1985 and McLennan et al., 1990)

unchanging proportions. The rare earths, Sc and Th are not affected greatly by metamorphism (McLennan, 1989; Taylor and McLennan, 1985), thus their composition in a metamorphosed clastic rock should be representative of the average composition of their source rocks. This is in contrast to other elements such as K, Na, Ca, U, Fe, Mn, Rb, Pb and Sr which are fractionated to varying degrees during weathering, transport, diagenesis and metamorphism (McLennan, 1989). Murray et al. (1990) have also shown that REE abundance and relative fractionation are indicators of depositional environment.

Schists in southeast Lokoja are enriched in both LREE and HREE (Tables 3 and 4) when compared to the average values given by Condie (1991) for Archaean and Early Proterozoic continental crust. This may reflect the younger age of the Lokoja schists since the REE abundance appears to increase with decreasing age. The REE distribution patterns of all the schists (Fig. 2) are characterized by variable LREE_N values ($La_N = 71 - 270$; $Ce_N = 48 - 113$), a well-developed Eu anomaly ($Eu/Eu_N = 0.55 - 0.98$) and a fairly uniform range of HREE contents ($Yb = 14 - 23$) (Table 4). The REE patterns (Fig. 2) are similar to those reported for shales and greywackes (McLennan and Taylor, 1991; Yaowanoyothin and Barr, 1991; Girty et al., 1993). The patterns are also similar to those shown by North American metamorphosed shale components (Gromet et al., 1984) and average shales (Condie, 1991). The fan-shaped arrangement of the single REE spectra as shown by the Lokoja schists (Fig. 2) has been interpreted as an indication of systematic and progressive depletion of the REE (La_N/Yb_N ranges from 4.96 to 11.91) (Stähle, et al., 1987). The increase in La_N/Yb_N ratios, i.e. depletion of HREE, is connected, according to Stähle, et al. (1987), with an increase of SiO_2 and a decrease of Zr. This is true for the Lokoja schists. The depletion in HREE may be due to dissolution of zircon during metamorphism since zircon is the most important phase for concentrating the HREE (Henderson, 1984). The decrease of apatite as indicated by P_2O_5 contents (Table 2) may contribute to the general depletion in the REE.

The chondrite-normalized REE distribution patterns for the Lokoja schists (Fig. 2) display no systematic change as a result of varying metamorphic grade. They show light-REE enrichments trends and negative Eu anomalies. McLennan et al. (1990) and Girty et al. (1993) have reported similar REE distribution patterns including Eu anomalies that vary from 0.58 to 1.08 and 0.46 to 0.93 respectively for sediments from passive continental margins. These range values compare favourably with 0.55 and 0.98 obtained for the Lokoja schists.

Samples of the Lokoja schists were plotted on a La-Th-Sc ternary diagram (Fig. 3) of McLennan and Taylor (1985)

and McLennan et al. (1990). The quartz mica schist and staurolite garnet schists plot in the field of passive continental margin, whilst the quartz muscovite biotite garnet schist and cordierite garnet schist plot in the magmatic arc related field. The latter field overlaps a part of post Archaean Australian shale field. It is therefore evident that the protoliths of the schists came from a provenance composed of sediments containing some igneous rocks debris. A mixture of shale and greywacke is the most likely pre-metamorphic rock. The REE pattern is very similar to those of greywacke-shale turbidites of Proterozoic age (McLennan and Taylor, 1991). Since the patterns for shales are similar to those of their sources, it is concluded that the protoliths were derived from continental sources, most likely the West African craton and Congo craton.

The composition of schists in southeast Lokoja have also been plotted on various discriminatory/classification diagrams (Ekwueme, 2003). All the schists cluster around average Proterozoic shales in the SiO_2 / Al_2O_3 versus K_2O / Na_2O diagram of Cameron and Garrels (1980). They however plot in the field of shale and greywacke in the ACF diagram.

TABLE 4: REE Abundances expressed as rock/chondrite ratios for Schists of Southeast Lokoja

| | QMS | QMBGS | SGS1 | SGS2 | SGS3 | CGS |
|--------|--------|-------|-------|-------|-------|-------|
| La | 270.59 | 67.65 | 70.59 | 97.06 | 97.06 | 70.59 |
| Ce | 113.19 | 48.35 | 52.75 | 71.43 | 73.63 | 51.65 |
| Nd | 73.44 | 35.94 | 39.06 | 48.44 | 46.88 | 34.38 |
| Sm | 51.28 | 30.77 | 35.90 | 35.90 | 35.90 | 30.77 |
| Eu | 27.40 | 27.40 | 27.40 | 13.70 | 13.70 | 13.70 |
| Gd | 30.77 | 19.23 | 23.08 | 12.58 | 14.77 | 15.38 |
| Tb | 42.55 | 21.28 | 21.28 | 21.28 | 21.28 | 21.28 |
| Dy | 26.67 | 20.00 | 20.00 | 11.20 | 12.03 | 13.33 |
| Ho | 25.64 | 12.82 | 12.82 | 12.82 | 12.82 | 12.82 |
| Er | 25.00 | 20.00 | 20.00 | 13.00 | 14.00 | 15.00 |
| Tm | 31.25 | 31.25 | 31.25 | 31.25 | 31.25 | 31.25 |
| Yb | 22.73 | 13.64 | 13.64 | 18.18 | 18.18 | 13.64 |
| Lu | 29.41 | 29.41 | 29.41 | 29.41 | 29.41 | 29.41 |
| La/Lu | 9.20 | 2.30 | 2.40 | 3.30 | 3.30 | 2.40 |
| La/Sm | 5.28 | 2.20 | 1.97 | 2.70 | 2.70 | 2.29 |
| La/Yb | 11.91 | 4.96 | 5.18 | 5.34 | 5.34 | 5.18 |
| Ce/Sm | 2.21 | 1.57 | 1.47 | 1.99 | 2.05 | 1.68 |
| Eu/Eu* | 0.78 | 0.98 | 0.98 | 0.68 | 0.55 | 0.55 |

Metagreywacke are derived from igneous rocks of basic to intermediate composition (Argast and Donnelly, 1986). A plot of the composition of the metagreywackes of Lokoja schists on CaO - K₂O - Na₂O diagram show that they were possibly derived from granodiorite protoliths. The major, trace and rare earth elements of the quartz muscovite biotite garnet schist and cordierite garnet schists compare favourably with that of granodiorite reported in Cox et al. (1979), which is the same rock as the high-Ca granite of Turekian and Wedepohl (1961).

Rb-Sr whole rock isochron age of 687 ± 13 Ma was obtained on the schist of Lokoja area (Caen-Vachette and Ekwueme, 1988). This indicates that the rocks were metamorphosed during the Pan-African Orogeny. Schists of similar age and composition occur in northwestern Nigeria, which is not far from the Lokoja area (Fitches et al., 1985). It is possible that the Lokoja schists are southward extension of the schist belts in northwestern Nigeria.

CONCLUSIONS

Shale-greywacke sequence is the most probable protoliths of the Lokoja schists. This is also the inferred protoliths of schists in other parts of Nigeria (Rahaman, 1976; Ekwueme and Onyeagocha, 1986; Imeokparia and Emofurieta, 1991). The REE abundance and patterns indicate that the shale-greywacke sequence was derived from continental provenance containing basic-intermediate igneous rocks. The West African and Congo cratons could have provided the pre-metamorphic rocks.

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