

# Geochemical Discriminant for Provenance Characterization and Palaeogeography of Shales from Dahomey Embayment, Southwestern Nigeria

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# Abstract

The geochemical compositions [major, trace and Rare Earth Elements (REE)] of Cretaceous-Tertiary shales from Gbekebo-1 well were used to characterize provenance, paleogeography, source area weathering and tectonic setting of the study area located in the southwestern part of the Dahomey Embayment, Nigeria. Core samples (eight) of shales were obtained and analyzed geochemically using the combined methods of major elements Fusion Inductively Coupled Plasma (FUS-ICP) and trace elements Fusion Inductively Coupled Plasma Emission/Mass Spectrometry (FUS-ICP/MS). An A-CN-K ( $Al_2O_3$ -CaO +  $Na_2O$ -K<sub>2</sub>O) ternary plot, geochemical discriminant function of major elements and chondrite normalized plots of REE suggest an upper continental crust provenance of felsic to intermediate or mixed igneous rocks of tonalite to granodiorite composition. High values of chemical index of alteration (CIA, 82.22 - 96.39) and chemical index of weathering (CIW, 88.10 - 99.17) indicated a palaeogeographic condition marked by wet tropical climate where intense chemical weathering and erosion prevailed. The Cretaceous-Tertiary shales from Gbekebo-1 well are inferred to have been deposited in passive margin setting based on various geochemical tectonic setting discrimination diagrams.

# **Keywords**

Geochemistry, Shale, Provenance, Paleogeography, Dahomey Embayment

# **1. Introduction**

The compositional characteristics of shales are often determined by the effects of surface processes (weathering,

How to cite this paper: Ejeh, O.I. (2016) Geochemical Discriminant for Provenance Characterization and Palaeogeography of Shales from Dahomey Embayment, Southwestern Nigeria. *Journal of Geoscience and Environment Protection*, **4**, 56-68. <u>http://dx.doi.org/10.4236/gep.2016.46005</u> erosion, transportation) on their source rock(s) and subsequent diagenesis [1] [2]. Weathering, erosion, sediment recycling and diagenesis often affect the alkalis (Na<sub>2</sub>O and K<sub>2</sub>O) and the alkali-earth elements (CaO and MgO); whereas  $Al_2O_3$ , TiO<sub>2</sub>, the high field strength elements (HFSE) (Co, Sc, Hf, Ta, Nb, Ti and Y) and some other trace elements are geochemically immobile in nature and are widely known as provenance diagnostic [3]. Very fine grained sediments such as clays or shales are often analyzed for their geochemical attributes with the assumption that they match closely average composition of the upper continental crust [4]. This assumption is based on the fact that thorough mixing occurs in very fine grained sediments, which often host Rare Earth Elements (REE) and Th that are relatively immobile; as such preserve the source rock composition.

In this study, the geochemistry of shale samples from Gbekebo-1 well, southwestern, Nigeria was applied to characterize provenance, paleogeography and source area weathering/tectonic setting of the study area (Figure 1). Geochemical studies aimed at characterizing provenance, inferring sediment source area(s) weathering/tectonic setting and palaeogeography of the Dahomey Embayment that are based on subsurface data sets are rare (e.g. [5]), probably due to inadequate data availability or poor exposures [6]. Since the discovery of oil seeps and tar sands in the Okitipupa area, much effort has been put into exploring the hydrocarbon potentials of the Dahomey embayment [7]-[11]. A number of exploration wells (such as Gbekebo-1, Afowo-1, Araromi-1, Benin west-1, Ife-1, Ore-1, Ise-1, Ojo-1, Lekki-1, etc.) were drilled by Shell d'Arcy (1936-1960), Tennessee Inc (1960-1966) and other firms/agencies. These exploration wells were all dry holes with minor showings of tarry oil and oil sands at varied depths up to the basement [12]. However, large reserves of bitumen have been proven in tar sands deposits of the Abeokuta Group [13]. Furthermore, although no commercial oil discovery was made onshore, the offshore section of the embayment offered a ray of successful discoveries such as the Aje Field.

# 2. Geological Setting

The Dahomey Embayment is part of the Gulf of Guinea province that comprises Benin, Keta, Central, Saltpond,





Tano and Ivory Coast sub-basins [14]. The province is bounded to the east by the Niger Delta province [15] and in the west by the West African Coastal province. The east-west structurally aligned sub-basins in the Gulf of Guinea are divided into three transform fault zones (FZ): St Paul FZ (at northwestern side); Romanche FZ (demarcating Ivory Coast, saltpond and Tano from Keta and Benin sub-basins); and Chain FZ (along the eastern part of the province). The province is a wrench-modified basin, formed at the termination of the tectonic event that lasted from Late Jurassic to Early Cretaceous. This tectonic event marked by transform and block faulting was operational throughout the entire Paleozoic leading to the break-up of the American (north and South) from African palaeo-continents [16]. A three-stage development of the basin has thus been suggested, namely: i) Pre-rift or pre-transform or intra-cratonic stage (Late Proterozoic to Late Jurassic), ii) Syn-rift or syn-transform or rift stage (Late Jurassic to Early Cretaceous) and iii) Post-rift or post-transform or drift stage (Late Cretaceous to Holocene) [17]-[20].

The stratigraphy of the Dahomey embayment has been discussed by a number of workers such as [21]-[25], amongst others. The sedimentary successions of this basin ranged from Cretaceous to Recent. The stratigraphic package is broadly divided into the Cretaceous Abeokuta Group (Ise, Afowo, and Araromi Formations) and Cenozoic units (Ewekoro, Akinbo, Oshosun, Ilaro, Ogwashi-Asaba and Benin Formations) [23] [26]. Rocks of the pre-transform stage in the Benin and Dahomey Embayment constitute the lower part of Ise Formation (Figure 2) composed of conglomerates, sandstones, shales of fluvio-deltaic environment [14] [17] [23]. The Afowo Formation at its type section (Afowo-1 well, Figure 2) comprised medium to coarse sandstones with thick to thin intercalations of siltstones and claystones; while the Araromi Formation (Maastrichtian to Paleocene) (type section Araromi-1 well, Figure 1) is marked by shale units similar to Awgu and Nkporo shales. At the base, this formation exhibited shale thickening seaward with siltstone, limestones and marl. Overlying the Araromi Formation is the Ewekoro which consist of limestone, shales and mudstone/claystone. Akinbo Formation is shaly with some clay interbeds, nodules of calcareous and phosphatic materials, impure limestone and glauconite [27]. The Oshosun Formation is made up of greenish clays and glauconitic shales intercalated with sandstones and limestones [5]. The Oshosun Formation is overlain by Ilaro, Ogwashi-Asaba and Benin Formations all of which consist of medium to coarse sands, alternating sands and clays, coastal plain sands respectively. A NNW-SSE correlation sketch involving Ise-1, Gbekebo-1, and Benin West-1 (Figure 2) indicated that these wells penetrated Araromi, Ewekoro, Oshosun and Ogwashi-Asaba/Benin Formations.



Figure 2. A NNW-SSE correlation of wells drilled in the Dahomey Embayment (modified after [23]).

# **3. Samples and Analytical Methods**

Eight core samples of shale obtained at different depths from Gbekebor-1 well (Figure 1) were analyzed for fifty-five elemental components (10 major and 45 trace/REE) using the combined methods of Fusion Inductively Coupled Plasma (FUS-ICP) and Fusion Inductively Coupled Plasma emission/Mass Spectrometry (FUS-ICP/ MS). Pre-analytical sample preparation that included crushing with agate mortar and pestle were undertaken at the Geology laboratory, Delta State University, Abraka; following which the samples were packaged and sent to the Activation laboratories, Ontario, Canada for the FUS-ICP and FUS-ICP/MS analyses. Details of FUS-ICP and FUS-ICP/MS are as reported by [28] and [29] respectively. Prior to the laboratory analyses (ICP-MS) more than 95% of each sample was ground so as to pass through a 200 mesh for a complete fusion of even the resistant minerals that may be present. Next, the main analyses involved the use of lithium metaborate/tetraborate fusion, followed by ICP and ICP/MS. Quality control technique was ensured through mass balance and elemental totals of oxides is usually between 98% to 101%.

# 4. Results and Interpretations

# 4.1. Major Elements

Results of major elements (oxides in wt %) are listed in **Table 1** alongside average values of North American Shale Composite (NASC) [30] and Post-Archean Australian Shale (PAAS) [4] for comparison. The major elements compositions of the shales vary widely. The range and average values of major elemental oxides are as follows: SiO<sub>2</sub> (40.96 - 54.18, average 46.61), Al<sub>2</sub>O<sub>3</sub> (12.9 - 24.51, average 18.89), Fe<sub>2</sub>O<sub>3</sub><sup>T</sup> (5.41 - 7.37, average 6.15), MgO (0.13-5.94, average 2.25), TiO<sub>2</sub> (0.69 - 1.42, average 0.96), MnO (0.009 - 0.106, average 0.045), CaO (0.08 - 5.24, average 1.92), Na<sub>2</sub>O (0.06 - 0.60, average 0.28), K<sub>2</sub>O (0.64 - 1.45, average 1.07), and P<sub>2</sub>O<sub>5</sub> (0.07 - 0.44, average 0.15). Loss on ignition (LOI) values ranged from 13.98 - 25.92 wt%. The major oxides showed enrichment (>1 wt%) in SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and Fe<sub>2</sub>O<sub>3</sub><sup>T</sup>; whereas the alkalis (Na<sub>2</sub>O and K<sub>2</sub>O) and alkali-earth elements (MgO and CaO) and other elements indicated slight enrichment to depletion. A plot of log (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>) versus log (Fe<sub>2</sub>O<sub>3</sub>/K<sub>2</sub>O) proposed by [31] for chemical classification of sedimentary rocks reveals that the shale samples from Gbekebo-1 well plotted within the shale and Fe-shale fields (**Figure 3**).



Figure 3. Chemical classification of shales from Gbekebo-1 well (classes of fields after [31]).

| Table 1. Major elements compositions (in wt%) of shale samples from Gbekebo-1 well. |             |               |               |             |           |             |               |               |       |       |
|---|-------------|---------------|---------------|-------------|-----------|-------------|---------------|---------------|-------|-------|
| Sample code   | Gbk_1       | Gbk_2         | Gbk_3         | Gbk_4       | Gbk_5     | Gbk_6       | Gbk_7         | Gbk_8         | NASC  | PAAS  |
| Depth (m)<br>range  | 34.7 - 35.7 | 243.5 - 244.8 | 341.7 - 342.6 | 573 - 573.8 | 590 - 591 | 779 - 780.6 | 955.5 - 956.5 | 997.9 - 998.8 |       |       |
| Formation   | Benin       | Ogwashi-Asaba | Oshosun       | Ewekoro     | Ewekoro   | Ewekoro     | Araromi       | Araromi       |       |       |
| Lithology   | Shale       | Shale         | Shale         | Shale       | Shale     | Shale       | Shale         | Shale         |       |       |
| $SiO_2$   | 48.09       | 54.18         | 40.96         | 51.18       | 47.98     | 44.15       | 44.70         | 41.65         | 64.80 | 62.80 |
| $TiO_2$   | 0.942       | 1.357         | 1.420         | 0.691       | 0.783     | 0.727       | 0.857         | 0.933         | 00.70 | 01.00 |
| $Al_2O_3$   | 17.03       | 22.97         | 24.51         | 12.90       | 15.57     | 15.07       | 21.14         | 21.91         | 16.90 | 18.90 |
| $\mathrm{Fe_2O_3}^\mathrm{T}$   | 06.01       | 5.750         | 6.330         | 5.410       | 6.090     | 5.850       | 6.410         | 7.370         | 05.65 | 07.22 |
| MnO   | 0.024       | 0.106         | 0.032         | 0.051       | 0.072     | 0.053       | 0.012         | 0.009         | 00.06 | 00.11 |
| MgO   | 0.130       | 0.650         | 0.300         | 5.900       | 4.450     | 4.860       | 1.120         | 0.590         | 02.86 | 02.20 |
| CaO   | 0.080       | 0.200         | 0.140         | 0.420       | 2.890     | 5.740       | 1.220         | 4.670         | 03.63 | 01.30 |
| Na <sub>2</sub> O   | 0.080       | 0.070         | 0.060         | 0.370       | 0.370     | 0.600       | 0.460         | 0.250         | 01.14 | 01.20 |
| $K_2O$  | 1.240       | 1.350         | 0.640         | 0.820       | 1.030     | 1.090       | 1.450         | 0.960         | 03.97 | 03.70 |
| $P_2O_5$  | 0.080       | 0.080         | 0.070         | 0.070       | 0.110     | 0.250       | 0.100         | 0.440         | 00.13 | 00.16 |
| LOI   | 25.35       | 13.99         | 25.92         | 21.44       | 19.90     | 21.19       | 21.05         | 19.71         | -     | -     |
| Total   | 99.07       | 100.7         | 100.4         | 99.26       | 99.24     | 99.58       | 98.52         | 98.48         |       |       |
| $MgO + Fe_2O_3^T$   | 6.140       | 1.300         | 6.630         | 11.31       | 10.54     | 10.71       | 7.530         | 7.960         |       |       |
| $Fe_2O_3^T/K_2O$  | 4.847       | 0.481         | 9.891         | 6.598       | 5.913     | 5.367       | 4.421         | 7.677         |       |       |
| Al <sub>2</sub> O <sub>3</sub> /TiO <sub>2</sub>                                    | 18.08       | 16.93         | 17.26         | 18.67       | 19.89     | 20.73       | 24.67         | 23.48         |       |       |
| K <sub>2</sub> O/Na <sub>2</sub> O  | 15.50       | 19.29         | 10.67         | 2.216       | 2.784     | 1.817       | 3.152         | 3.840         |       |       |
| $SiO_2/Al_2O_3$   | 2.824       | 2.359         | 1.671         | 3.967       | 3.082     | 2.930       | 2.114         | 1.901         |       |       |
| Moles   |             |               |               |             |           |             |               |               |       |       |
| SiO <sub>2</sub>  | 0.800       | 0.902         | 0.682         | 0.852       | 0.798`    | 0.735       | 0.744         | 0.693         |       |       |
| $Al_2O_3$   | 0.167       | 0.225         | 0.240         | 0.127       | 0.153     | 0.148       | 0.207         | 0.215         |       |       |
| $\mathrm{CaO}^*$  | 0.001       | 0.001         | 0.001         | 0.006       | 0.006     | 0.010       | 0.007         | 0.004         |       |       |
| Na <sub>2</sub> O   | 0.001       | 0.001         | 0.001         | 0.006       | 0.006     | 0.010       | 0.007         | 0.004         |       |       |
| MgO   | 0.003       | 0.016         | 0.007         | 0.146       | 0.110     | 0.121       | 0.028         | 0.015         |       |       |
| Fe <sub>2</sub> O <sub>3</sub>  | 0.038       | 0.036         | 0.040         | 0.034       | 0.038     | 0.037       | 0.040         | 0.046         |       |       |
| K <sub>2</sub> O  | 0.013       | 0.014         | 0.007         | 0.009       | 0.011     | 0.012       | 0.015         | 0.010         |       |       |
| $\mathrm{CaO}^* + \mathrm{Na_2O}$   | 0.002       | 0.006         | 0.003         | 0.004       | 0.004     | 0.020       | 0.021         | 0.002         |       |       |
| $Fe_2O_3 + MgO$   | 0.041       | 0.052         | 0.047         | 0.180       | 0.148     | 0.158       | 0.068         | 0.061         |       |       |
| $\begin{array}{c} CaO^{*} + \\ Na_{2}O + K_{2}O \end{array}$                        | 0.015       | 0.020         | 0.010         | 0.013       | 0.015     | 0.032       | 0.036         | 0.012         |       |       |
| CIA   | 91.76       | 93.36         | 96.39         | 85.81       | 86.93     | 82.22       | 87.71         | 92.27         |       |       |
| CIW   | 98.82       | 99.12         | 99.17         | 91.36       | 92.73     | 88.10       | 93.67         | 96.41         |       |       |

#### **4.2. Trace Elements**

**Table 2** shows the trace elements concentration of the selected shale samples from Gbekebo-1 well compared with NASC and PAAS alongside their elemental ratios. The trace elements showed wide variability when compared to NASC and PAAS. High enrichment concentration values are recorded by Ba, Sr, Zr, and Cr. The enrichment to slight enrichment exhibited by Y, Zr, Hf, Ta, Th, and U are indications of the presence of heavy minerals (e.g. zircon) that are resistant to weathering, erosion and diagenesis.

#### 4.3. Rare Earth Elements

The results of rare earth element (REE) concentration of the shales from Gbekebo-1 well are shown in **Table 3**. The REE concentration values are comparable to that of PAAS and NASC (**Table 3**). The REE patterns of the chondrite normalized values are marked by Light Rare Earth Elements (LREE) enrichment, negative Eu anomalies, and a rather flat Heavy Rare Earth Elements (HREE) pattern (**Figure 4**).

## 5. Discussion and Inferences

#### 5.1. Geochemistry and Provenance Discrimination

Using major elemental compositions, provenance can be discriminated into mafic, intermediate, felsic igneous rocks and Quartzose sedimentary rocks fields as reported by [32]. Following this approach by [32] shale samples of the Gbekebo-1 well plot in the mafic and Quartzose sedimentary fields, implying a mixed source area (**Figure 5(a)**). The ratio of  $Al_2O_3/TiO_2$  in shales has been suggested to be similar to that of the source rock [33] as such it is used as an index of provenance. Hayashi *et al.* [33] stated that ratios that exhibited values greater than twenty-one implied that the sediments are of felsic origin. The average values of  $Al_2O_3/TiO_2$  for this study is 19.96 wt% (range from 16.93 to 24.67 wt%) indicating felsic to intermediate or mixed sources.

Floyd and Leveridge [34] proposed a plot of La/Th against Hf to discriminate provenance; and in this study the samples plotted in felsic to mixed felsic/basic sources (**Figure 5(b**)). They are of upper continental crust deposited in passive margin source. McLennan *et al.* [3] plotted Th versus Sc to infer provenance and when applied in this study the Gbekebo-1 well samples fell mostly in intermediate source with some continental component input (**Figure 5(c**)). Gu *et al.* [35] used Co/Th versus La/Sc diagram for provenance discrimination and its application to this study revealed samples plotting close to or above the line at Co/Th = 1.27, an indication of



Figure 4. Chondrite-normalized REE patterns of shales from the Gbekebo-1 well.

| Table 2. Trace elements concentration (in ppm) of shale samples from Gbekebo-1 well. |             |               |               |             |           |             |               |               |      |      |
|--|-------------|---------------|---------------|-------------|-----------|-------------|---------------|---------------|------|------|
| Sample code  | Gbk_1       | Gbk_2         | Gbk_3         | Gbk_4       | Gbk_5     | Gbk_6       | Gbk_7         | Gbk_8         | NASC | PAAS |
| Depth (m)<br>range   | 34.7 - 35.7 | 243.5 - 244.8 | 341.7 - 342.6 | 573 - 573.8 | 590 - 591 | 779 - 780.6 | 955.5 - 956.5 | 997.9 - 998.8 |      |      |
| Formation  | Benin       | Ogwashi-Asaba | Oshosun       | Ewekoro     | Ewekoro   | Ewekoro     | Araromi       | Araromi       |      |      |
| Lithology  | Shale       | Shale         | Shale         | Shale       | Shale     | Shale       | Shale         | Shale         |      |      |
| Sc   | 11.00       | 18.00         | 18.00         | 11.00       | 13.00     | 12.00       | 18.00         | 17.00         | 15   | 16   |
| Ni   | 30.00       | 50.00         | 40.00         | 30.00       | 50.00     | 50.00       | 50.00         | 70.00         | 58   | 55   |
| Be   | 3.000       | 4.000         | 4.000         | 3.000       | 3.000     | 3.000       | 3.000         | 3.000         |      |      |
| Ga   | 23.00       | 31.00         | 32.00         | 18.00       | 21.00     | 19.00       | 27.00         | 27.00         | -    | -    |
| Nb   | 23.00       | 31.00         | 34.00         | 17.00       | 21.00     | 17.00       | 16.00         | 22.00         | 13   | 1.9  |
| Ba   | 526.0       | 421.0         | 402.0         | 1720        | 125.0     | 1343        | 140.0         | 160.0         | 636  | 650  |
| Та   | 1.800       | 2.500         | 2.700         | 1.400       | 1.700     | 1.300       | 1.300         | 1.500         | 1.1  | -    |
| Co   | 11.00       | 19.00         | 14.00         | 14.00       | 15.00     | 12.00       | 16.00         | 14.00         | 26   | 23   |
| Cu   | 20.00       | 20.00         | 20.00         | <10.0       | <10.0     | <10.0       | 20.00         | 20.00         | -    | -    |
| Sr   | 122.0       | 116.0         | 114.0         | 180.0       | 184.0     | 184.0       | 338.0         | 202.0         | 142  | 200  |
| V  | 77.00       | 128.0         | 108.0         | 117.0       | 183.0     | 157.0       | 194.0         | 172.0         | 130  | 96   |
| Ge   | <1.00       | 1.000         | 1.000         | <1.00       | 1.000     | <1.00       | 1.000         | 1.000         |      |      |
| Mo   | <2.00       | 3.000         | 4.000         | <2.00       | 3.000     | 2.000       | 5.000         | 13.00         |      |      |
| As   | < 5.00      | 7.000         | < 5.00        | < 5.00      | < 5.00    | < 5.00      | 5.00          | 12.00         |      |      |
| Ag   | 1.700       | 1.400         | 1.300         | 0.600       | 0.700     | 0.600       | 0.600         | 0.800         |      |      |
| In   | < 0.20      | < 0.20        | < 0.20        | < 0.20      | < 0.20    | < 0.20      | < 0.20        | < 0.20        |      |      |
| Bi   | < 0.40      | < 0.40        | < 0.40        | < 0.40      | < 0.40    | < 0.40      | < 0.40        | < 0.40        |      |      |
| Sn   | 3.000       | 4.000         | 4.000         | 2.000       | 3.000     | 2.000       | 3.000         | 4.000         |      |      |
| Sb   | < 0.50      | 0.600         | < 0.50        | 0.500       | 0.600     | < 0.50      | 0.600         | 0.600         |      |      |
| Cs   | 2.800       | 8.100         | 5.500         | 3.500       | 4.200     | 3.900       | 7.000         | 4.600         |      |      |
| Zn   | 140.0       | 100.0         | 90.00         | 80.00       | 80.00     | 130.0       | 140.0         | 110.0         | -    | -    |
| Th   | 13.20       | 18.00         | 18.70         | 8.600       | 11.10     | 9.000       | 11.80         | 16.10         | -    | -    |
| U  | 4.400       | 3.700         | 5.800         | 1.700       | 2.400     | 2.700       | 3.100         | 13.30         | -    | -    |
| Cr   | 100.0       | 140.0         | 130.0         | 90.00       | 170.0     | 160.0       | 190.0         | 250.0         | 125  | 110  |
| Rb   | 46.00       | 85.00         | 49.00         | 42.00       | 51.00     | 46.00       | 66.00         | 61.00         | 125  | 160  |
| Zr   | 367.0       | 297.0         | 273.0         | 127.0       | 157.0     | 143.0       | 124.0         | 219.0         | 200  | 210  |
| Hf   | 9.000       | 7.500         | 7.000         | 3.000       | 3.800     | 3.500       | 3.100         | 5.500         | 6.3  | 5.0  |
| Pb   | 15.00       | 22.00         | 19.00         | 15.00       | 14.00     | 12.00       | 13.00         | 11.00         |      |      |
| TI   | 0.300       | 0.400         | 0.500         | 0.100       | 0.100     | < 0.10      | 0.200         | 0.400         |      |      |
| W  | 1.000       | 2.000         | 2.000         | 1.000       | 1.000     | 1.000       | 1.000         | 11.00         |      |      |
| <br>Th/I⊺  | 3 000       | 4 865         | 3 224         | 5 059       | 4 625     | 3 333       | 3 806         | 1 211         |      |      |
| Dh/Cr  | 0 277       | 0.722         | 0.420         | 0.222       | 0.277     | 0.250       | 0.105         | 0.202         |      |      |
|  | 0.577       | 0.733         | 0.450         | 10.47       | 15.22     | 17.79       | 16 10         | 15 50         |      |      |
| Cr/Th  | 1.5/6       | 1.//8         | 6.952         | 10.47       | 15.32     | 17.78       | 16.10         | 15.53         |      |      |
| Cr/Zr  | 0.272       | 0.471         | 0.476         | 0.709       | 1.083     | 1.119       | 1.532         | 1.142         | 0.63 | 0.52 |

Ta

| Continued |       |       |       |        |       |       |       |       |  |
|-----------|-------|-------|-------|--------|-------|-------|-------|-------|--|
| Th/Sc     | 1.200 | 1.000 | 1.039 | 0.782  | 0.854 | 0.750 | 0.656 | 0.947 |  |
| Th/Zr     | 0.036 | 0.061 | 0.068 | 0.068  | 0.071 | 0.063 | 0.095 | 0.074 |  |
| La/Th     | 2.932 | 3.589 | 3.465 | 3.233  | 3.577 | 3.656 | 3.246 | 3.385 |  |
| Co/Th     | 0.833 | 1.056 | 0.749 | 1.628  | 1.351 | 1.333 | 1.356 | 0.870 |  |
| La/Sc     | 3.518 | 3.589 | 3.600 | 2.527  | 3.054 | 2.742 | 2.128 | 3.206 |  |
| La/Co     | 3.518 | 3.400 | 4.629 | 1.986  | 2.647 | 2.742 | 2.394 | 3.893 |  |
| Th/Co     | 1.200 | 0.947 | 1.336 | 0.6143 | 0.740 | 0.750 | 0.738 | 1.150 |  |
| Th/Cr     | 0.132 | 0.129 | 0.143 | 0.096  | 0.065 | 0.056 | 0.062 | 0.064 |  |
| Ba/La     | 13.59 | 6.517 | 6.204 | 61.87  | 3.149 | 40.82 | 3.655 | 2.936 |  |

Table 3. Rare earth elements concentration (in ppm) of shale samples from Gbekebo-1 well.

| Sample code        | Gbk_1       | Gbk_2         | Gbk_3         | Gbk_4       | Gbk_5     | Gbk_6       | Gbk_7         | Gbk_8         | NASC | PAAS |
|--------------------|-------------|---------------|---------------|-------------|-----------|-------------|---------------|---------------|------|------|
| Depth (m)<br>range | 34.7 - 35.7 | 243.5 - 244.8 | 341.7 - 342.6 | 573 - 573.8 | 590 - 591 | 779 - 780.6 | 955.5 - 956.5 | 997.9 - 998.8 |      |      |
| Formation          | Benin       | Ogwashi-Asaba | Oshosun       | Ewekoro     | Ewekoro   | Ewekoro     | Araromi       | Araromi       |      |      |
| Lithology          | Shale       | Shale         | Shale         | Shale       | Shale     | Shale       | Shale         | Shale         |      |      |
| La                 | 38.70       | 64.60         | 64.80         | 27.80       | 39.70     | 32.90       | 38.30         | 54.50         | 32   | 38   |
| Ce                 | 72.90       | 125.0         | 123.0         | 49.00       | 72.20     | 65.10       | 74.30         | 114.0         | 73   | 80   |
| Pr                 | 8.590       | 14.30         | 13.90         | 5.460       | 8.290     | 7.340       | 8.780         | 13.60         | 7.9  | 8.83 |
| Nd                 | 31.30       | 52.90         | 50.70         | 19.50       | 30.10     | 27.40       | 32.20         | 52.00         | 33   | 33.9 |
| Sm                 | 6.100       | 10.10         | 9.400         | 3.200       | 5.800     | 5.200       | 6.000         | 9.800         | 5.7  | 5.55 |
| Eu                 | 1.300       | 2.260         | 2.200         | 0.830       | 1.320     | 1.200       | 1.370         | 2.190         | 1.24 | 1.08 |
| Gd                 | 4.600       | 7.400         | 7.400         | 2.300       | 4.200     | 4.000       | 4.300         | 7.600         | 5.2  | 4.66 |
| Tb                 | 0.700       | 1.200         | 1.200         | 0.400       | 0.700     | 0.600       | 0.700         | 1.100         | 0.85 | 0.77 |
| Dy                 | 4.300       | 6.600         | 6.200         | 1.900       | 3.500     | 3.300       | 3.600         | 6.100         | 6.2  | 4.68 |
| Но                 | 0.800       | 1.300         | 1.200         | 0.400       | 0.700     | 0.600       | 0.700         | 1.200         | 1.04 | 0.99 |
| Er                 | 2.400       | 3.700         | 3.300         | 1.000       | 2.000     | 1.700       | 1.900         | 3.300         | 3.4  | 2.85 |
| Tm                 | 0.380       | 0.550         | 0.490         | 0.160       | 0.280     | 0.250       | 0.300         | 0.480         | 0.5  | 0.4  |
| Yb                 | 2.400       | 3.600         | 3.000         | 1.00        | 1.700     | 1.500       | 1.900         | 3.100         | 3.1  | 2.82 |
| Lu                 | 0.350       | 0.500         | 0.450         | 0.150       | 0.240     | 0.230       | 0.270         | 0.440         | 0.48 | 0.43 |
| Y                  | 24.00       | 38.00         | 37.00         | 11.00       | 20.00     | 18.00       | 18.00         | 37.00         | 27   | -    |
| Eu/Eu*             | 0.720       | 0.764         | 0.778         | 0.891       | 0.780     | 0.774       | 0.786         | 0.747         |      |      |
| $\mathrm{Eu}^*$    | 1.805       | 2.959         | 2.826         | 0.931       | 1.692     | 1.550       | 1.744         | 2.930         |      |      |
| ΣLREE              | 157.6       | 266.9         | 261.8         | 105.0       | 156.1     | 137.9       | 159.6         | 243.9         |      |      |
| ΣHREE              | 15.93       | 24.85         | 23.24         | 07.31       | 13.32     | 12.18       | 13.67         | 23.32         |      |      |
| ΣREE               | 173.5       | 291.8         | 285.0         | 112.3       | 169.4     | 150.1       | 173.3         | 267.2         |      |      |
| LREE/HREE          | 9.893       | 10.74         | 11.27         | 14.36       | 11.72     | 11.32       | 11.68         | 10.46         |      |      |
| La/Sm              | 6.344       | 6.396         | 6.894         | 8.688       | 6.845     | 6.327       | 6.383         | 5.561         |      |      |



**Figure 5.** Discriminant diagrams for provenance of shales from Gbekebo-1 well. (a) Discriminant function diagram after [32]; (b) La/Th-Hf diagram after [34]; (c) Th versus Sc diagram after [3]; (d) Co/Th-La/Sc diagram after [35].

felsic to intermediate igneous source (**Figure 5(d**)). The chondrite normalization patterns of the REE (**Figure 4**) marked by a rather flat HREE, LREE enrichment, and a negative Eu anomaly suggestive of a felsic provenance. Negative Eu anomaly represents a differentiated source, related to granite [4].

The major elements suggested mafic igneous to quartzose sedimentary sources, while the trace/REE revealed felsic to mixed sources. This disparity may be attributed to La and Th used in the provenance discrimination exercise, and their abundance in the felsic igneous rocks. However, the source of the Gbekebo-1 well shales are of old upper continental crust of felsic to intermediate igneous rocks of tonalite to granodiorite compositions with some mafic and Quartzose detrital contributions.

### 5.2. Geochemistry and Palaeogeography

The intensity of weathering and thus the palaeoclimatic condition(s) or the paleogeography of the source area can be inferred from chemical index of alteration (CIA) and chemical index of weathering (CIW). Nesbitt and Young [36] attributed CIA values of about 70 - 75 for shales, while [37] reported CIW values of about 90 - 98 for intensely weathered Archean shales. In this study CIA and CIW values ranged from 82.22 - 96.39 and 88.10 - 99.17 respectively (**Table 1**). These very high values CIA and CIW are product of CaO and Na<sub>2</sub>O depletion, a clear indication of intense or prolonged source area weathering probably under tropical conditions. Concentra-

tions of  $Al_2O_3$ ,  $CaO + Na_2O$  and  $K_2O$  in moles of the shale samples from the Gbekebo-1 well plotted in a ternary diagram (**Figure 6**) after [1] [38] to estimate the trend of decomposition (chemical weathering), the composition of source rock and the likely effects of metasomatism. The weathering trend paralleled the  $Al_2O_3$ -CaO + Na<sub>2</sub>O line for the fact that Na and Ca are leached out by chemical weathering of plagioclase feldspar followed by K-feldspar, liberating K and tending toward  $Al_2O_3$  peak. The weathering trend progressed close to the composition of illite. However, the parallel and non-divergent nature of the trend revealed a possible lack of potassium metasomatism as part of the sedimentary process. The  $Al_2O_3$ -CaO +  $Na_2O$ -K<sub>2</sub>O ternary plot also enabled estimation source rock compositions through a backward projection of weathering trend line to the feldspar line. The point of intersection implies an approximate ratio of plagioclase to k-feldspar in the source rock(s). In this study a tonalite to granodiorite has been suggested, which is related to the composition of the southwestern Nigeria crystalline Basement Complex rocks that comprised gray gneisses of granodioritic to tonalitic composition [39] [40].

# 5.3. Geochemistry and Tectonic Setting

Major elements were applied for provenance discrimination based on plots proposed by [42] and [43]. A plot of SiO<sub>2</sub> versus log K<sub>2</sub>O/Na<sub>2</sub>O (**Figure 7(a**)) revealed most of the shale samples plotted in the passive margin setting, although one sample plotted in the active continental margin. Furthermore, in the discriminant plot of Bhatia (1983), the shale sample plotted solely in the passive margin setting (**Figure 7(b**)).

## 6. Conclusion

The provenance characteristics and palaeogeography of the shales from Gbekebo-1 well, southwestern Nigeria have been investigated with geochemical methods. The study revealed that the shales from the Dahomey Embayment were derived mostly from felsic continental sources with some mafic to Quartzose sedimentary input. The provenance characteristics indicated that the Gbekebo-1 shales were deposited on a passive margin setting that received most of its detritus from the nearby southwestern Nigeria Basement Complex rocks. Inferred protoliths (source rocks) from this study consist of tonalite to granodiorite composition subjected to prolong intense chemical weathering likely under a tropical palaeo-climatic condition.



Figure 6. A-CN-K ternary diagram of molar compositions of  $Al_2O_3$ -(CaO + Na<sub>2</sub>O)-K<sub>2</sub>O for shales from Gbekebo-1 well, after [38]. CIA scale shown on the left side of the figure for comparison.



Figure 7. Major element tectonic setting discrimination diagrams for shales from Gbekebo-1 well. (a) Log ( $K_2O/Na_2O$ ) versus SiO<sub>2</sub> after [42]; (b) Discriminant function diagram, after [43].

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