Geochemical characterization of Lokoja-Basange Sandstone at Imiegba and Okpekpe areas, Benin flank of Anambra basin, Nigeria: implications for provenance, tectonic setting and source-rock weathering

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Abstract

This study investigates the geochemical attributes of the Lokoja-Basange Sandstone situated in Okpekpe and Imiegba areas of the Benin Flank of Anambra Basin, Nigeria. The aim of this study is to unveil its provenance, tectonic setting, and source rock weathering extent. Using energy dispersive x-ray fluorescence (EDXRF) "Minipal 4" spectrometer analysis, nine outcrop samples were examined for major oxide concentrations. The results show significant average SiO_2 (77.09 wt. %), Al_2O_3 (12.10 wt. %), Fe_2O_3 (2.72 wt. %), Na_2O (1.64 wt. %), K_2O (2.41 wt. %), while TiO_2, MnO, MgO, CaO, P_2O_5, LOI had average concentrations of less than 1.00 wt. %. Bivariate plots of log $[Fe_2O_3/K_2O]$ versus log $[SiO_2/Al_2O_3]$ indicate 77.80% litharenites and 22.20% arkose sediments. The $[Al_2O_3]$-$[CaO+Na_2O]$-$[K_2O]$ ternary plot, the tectonic discriminant diagrams of $[SiO_2/20]$-$[K_2O+Na_2O]$-$[TiO_2+Fe_2O_3+MgO]$, log $[K_2O/Na_2O]$ versus SiO_2, $[SiO_2/Al_2O_3]$ versus log $[K_2O/Na_2O]$ and bivariate discriminant functions plot indicate that the sediments have felsic igneous provenance and quartzose sedimentary origin, within a passive margin tectonic setting and the source-area underwent moderate to near complete chemical weathering in semi-arid to humid climatic conditions with increasing chemical maturity. Conclusively, the chemical alteration index (CIA) ranges from 65.4% to 74.2%, averaging 70.70%; the chemical index of weathering (CIW) averages 82.37%; the plagioclase index of alteration (PIA) averages 78.88%; and the mineralogical index of alteration (MIA) averages 41.43%. These data signify extensive weathering of felsic igneous source rocks, highlighting mineralogical maturity of Lokoja-Basange Sandstone. In essence, this study enriches insights into the sandstone's origins, sedimentary context, and weathering history.

Keywords: Geochemical Characterization; Lokoja-Basange Sandstone; Anambra Basin; Provenance; Tectonic Setting; Source-Rock Weathering.

1. Introduction

The study area is located at Imiegba and Okpekpe in Etsako East Local Government Area of Edo State, Nigeria. It is located on the latitudes 071127'N - 071200"N and longitudes 062400"E – 0628 00"E and average elevation of about 182 metres (Figs. 1 and 2). The study area is accessible via trunk A and minor roads.

The aim of this study is to determine the provenance, tectonic setting and source-rock weathering level of the Lokoja-Basange Sandstone in the study area using geochemical proxies. Lokoja-Basange Sandstone is also called Lokoja-Basange Formation. The study area belongs to the tropical rain forest region of Nigeria. Rainy season occurs between March and October while the dry season lasts from November to February of every year. The mean annual rainfall is approximately 2,000 mm and the temperature in the area varies between 28^0C and 38^0C with high temperature between February and April (Duze and Ojo [1]).

Several researchers have worked on the stratigraphy, sedimentology, palynology, etc. of the study area; however, there is gross scarcity of publications on the major oxide geochemistry of Lokoja-Basange Sandstone. This present study seeks to address this research gap.
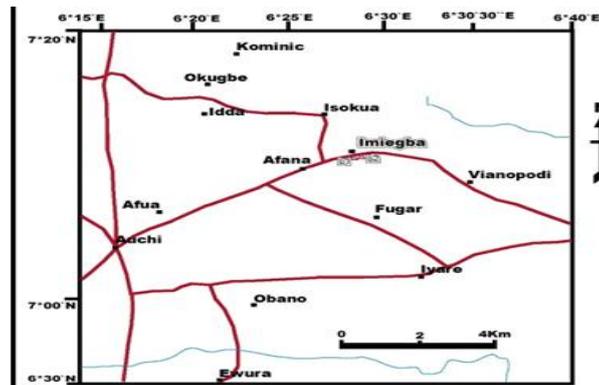
Fig. 1: Accessibility Map of the Study Area (Modified after Nwajide ang Rejers [10]).

Fig. 2: Map of Nigeria Stratigraphy of Anambra Basin, Study Area and Samples Locations (Modified after Nwajide and Rejers [10] in Obaje and Alli [14]).

2. Regional geological setting

The study is in the Anambra Basin. Anambra Basin is one of seven sedimentary basins in Nigeria. Anambra Basin is stratigraphically divided into two main components, namely: eastern and western parts.

In the eastern portion of the Anambra Basin, Nkporo Formation and Enugu Formation are the oldest formations and they are made up of brackish water and prodelta facies. They are Campanian to Early Maastrichtian in age and they constitute the first phase of marine regressive phase in the basin. Mamu Formation lies conformably on the Nkporo Formation. Mamu Formation is Maastrichtian in age, and it represents regressive (continental influence) and transgressive (marine incursive) phase leading to marginal marine facies deposition (Obaje and Alli [14]; Obaje and Ahmed [12]; Obaje et al. [13]). Another marine regressive cycle led to the deposition of continental Ajali Formation conformably on the Mamu Formation. Ajali Formation is Upper Maastrichtian age. During Paleocene, another marine transgressive cycle led to the deposition of Nsukka and Imo Formation, respectively on the Ajali Formation. In the Eocene, another marine regressive cycle led to the deposition of Bende Formation and Nanka Sandstone, which are made up of continental facies. During Oligocene, another marine transgressive cycle caused the deposition of Ogwashi-Asaba Formation conformably on the Bende Formation and Nanaka Sandstone. Ogwashi-Asaba Formation is the organic rich carbonaceous shales and coal seams (Nwajide [11]).

Conversely, the western Anambra Basin is also popularly called Benin Flank of Anambra Basin. In the western part of Anambra Basin, the stratigraphy is slightly different. The oldest formation is Lokoja-Basange Formation, and it is Campanian in age, and it is made up of continental facies. Lokoja-Basange Formation is a lateral equivalent of Nkporo Formation and Enugu Formation (Obaje and Alli [14]; Obaje and Ahmed [12]; Obaje et al. [13]). Lokoja-Basange Formation lies unconformably on the Neoproterozoic basement rocks in the study area. Overlying Lokoja-Basange Formation is Mamu Formation. The continental Ajali Formation conformably overlie the Mamu Formation. The Paleocene to Oligocene formations which are conspicuously present in the eastern portion of Anambra Basin are absent in the western part of Anambra Basin.

3. Materials and methods

Nine outcrop samples were collected from the study area for major oxide geochemical analysis. Energy Dispersive x-ray fluorescence (EDXRF) spectrometer model "Minipal 4" was used for the analysis. The samples were milled, sieved to 63μm (230 mesh) and divided into four portions. A portion was used for the analysis, while the remaining portions were archived. 5g of each sample was used to make a glass bead, which was fed to the EDXRF machine for major oxide analysis. Duplicate samples and international standard reference samples were used to ascertain the authenticity of the results and the accuracy of the machine. The equipment indicated instrumental error of <2.5%, which was noted to be within acceptable international standard. The machine has 100% detection limit for major elements and 0.1 ppm for trace and rare earth elements with elemental range of Be to Am.

4. Result and discussion

4.1. Result

The bulk major oxides geochemical result of the samples from the study area given in their weight percentages is presented in Table 1. The result indicates major oxide concentrations as follows: SiO_2 (73.50 wt. % - 80.50 wt. %; average 77.09 wt. %), Al_2O_3 (11.00 wt. % - 13.20 wt. %; average 12.10 wt. %), Fe_2O_3 (1.74 wt. % - 3.41 wt. %; average 2.72 wt. %), Na_2O (1.06 wt. % - 2.10 wt. %; average 1.64 wt. %), K_2O (2.07 wt. % - 2.70 wt. %; average 2.41 wt. %), TiO_2 (0.04 wt. % - 1.15 wt. %; average 0.83 wt. %), MnO (0.02 wt. % - 0.59 wt. %,

average 0.10 wt.%), MgO (0.03 wt. % - 0.09 wt. %; average 0.06 wt. %), CaO (0.76 wt. % - 1.22 wt.%, average 0.96 wt. %), P_2O_5 (0.01 wt. % - 0.02 wt.%, average 0.00 wt. %), LOI (0.24 wt. % - 0.42 wt. %; average 0.34 wt. %).

Table 1: Bulk Chemical Composition and Ratios of Major Oxides of Samples from the Study Area

OXIDE	SL1	SL2	SL3	SL4	SL5	SL6	SL7	SL8	SL9	MIN.	MAX	MEAN	STD. DEV.
SiO_2	75.4	73.5	77.8	79.2	78.4	77.6	77.1	80.5	74.3	73.5	80.51	77.09	2.29
TiO_2	0.81	0.82	0.82	0.95	1.15	0.91	1.14	0.04	0.84	0.04	1.15	0.83	0.32
Al_2O_3	11.5	12.5	12.1	11	12.8	13.2	12.3	11.9	11.6	11	13.2	12.1	0.69
Fe_2O_3	3.41	3.22	2.56	2.51	2.23	2.8	3.32	1.74	2.65	1.74	3.41	2.72	0.54
MnO	0.02	0.03	0.59	0.04	0.03	0.05	0.07	0.06	0.05	0.02	0.59	0.1	0.18
MgO	0.05	0.03	0.04	0.09	0.06	0.05	0.04	0.09	0.07	0.03	0.09	0.06	0.02
CaO	0.85	0.76	0.91	1.22	1.11	0.8	0.86	1.04	1.12	0.76	1.22	0.96	0.16
Na_2O	1.29	1.06	1.67	2	1.71	1.7	2.1	2.08	1.11	1.06	2.1	1.64	0.4
K_2O	2.16	2.52	2.53	2.59	2.19	2.5	2.7	2.07	2.46	2.07	2.7	2.41	0.22
P_2O_5	0.01	0.01	0.02	0.01	0.02	0.01	0.01	0.01	0.01	0.005	0.02	0.01	0.00
LOI	0.37	0.24	0.31	0.37	0.3	0.41	0.28	0.42	0.35	0.24	0.42	0.34	0.06
CIA	72.7	74.2	70.3	65.4	71.9	72.5	68.5	69.7	71.1	65.44	74.2	70.70	2.63
CIW	84.3	87.3	82.5	77.4	82.0	84.1	80.6	79.3	83.8	77.4	87.3	82.37	2.97
PIA	81.3	84.6	78.8	72.3	79.0	81.1	76.5	76.0	80.3	72.3	84.6	78.88	3.58
MIA	45.4	48.5	40.7	30.9	43.7	45.1	37	39.4	42.2	30.9	48.5	41.43	5.25
SiO_2/Al_2O_3	6.58	5.88	6.42	7.20	6.13	5.88	6.27	6.74	6.44	5.88	7.20	6.39	0.42
TiO_2/Al_2O_3	0.07	0.07	0.07	0.09	0.09	0.07	0.09	0.00	0.07	0.00	0.09	0.07	0.03
K_2O/Na_2O	1.67	2.38	1.51	1.30	1.28	1.47	1.29	1.00	2.22	1.00	2.38	1.57	0.46
Fe_2O_3+MgO/K_2O+Na_2O	1.00	0.91	0.62	0.57	0.59	0.68	0.70	0.44	0.76	0.44	1.00	0.70	0.17
$Al_2O_3+CaO+Na_2O$	13.6	14.3	14.7	14.2	15.6	15.7	15.3	15.1	13.8	13.6	15.7	14.70	0.77
$Al_2O_3 - K_2O$	9.3	9.98	9.59	8.41	10.6	10.7	9.61	9.87	9.09	8.41	10.7	9.68	0.72
$Al_2O_3+CaO+Na_2O+ K_2O$	15.8	16.8	17.2	16.8	17.8	18.2	18.0	17.1	16.2	15.8	18.20	17.10	0.81
$SiO_2/20$	3.77	3.67	3.89	3.96	3.92	3.88	3.86	4.03	3.72	3.67	4.03	3.86	0.12
$K_2O + Na_2O$	3.45	3.58	4.2	4.59	3.9	4.2	4.8	4.15	3.57	3.45	4.80	4.05	0.47
$TiO_2+Fe_2O_3+MgO$	4.27	4.07	3.42	3.55	3.44	3.76	4.5	1.87	3.56	1.87	4.50	3.60	0.76
$CaO+Na_2O$	2.14	1.82	2.58	3.22	2.82	2.5	2.96	3.12	2.23	1.82	3.22	2.60	0.47
SiO_2/Al_2O_3	6.58	5.88	6.42	7.20	6.13	5.88	6.27	6.74	6.44	5.88	7.20	6.39	0.42
Log (FeO_3/ K_2O)	0.20	0.11	0.01	0.01	0.01	0.05	0.09	0.08	0.03	0.01	0.20	0.07	0.06
Log (SiO_2/Al_2O_3)	0.82	0.77	0.81	0.86	0.79	0.77	0.80	0.83	0.81	0.77	0.86	0.81	0.03
Function 1	2.48	2.60	2.95	3.69	2.83	-2.30	-2.84	1.56	-3.38	-3.38	-1.56	0.84	2.83
Function 2	1.22	0.97	0.49	0.84	0.09	0.13	0.92	0.03	-0.76	-0.76	0.92	0.44	0.62

4.2. Discussion

4.2.1. Chemical composition

The major oxide geochemical result shows average concentrations of SiO_2 (77.09 wt. %), Al_2O_3 (12.10 wt. %), Fe_2O_3 (2.72 wt. %), Na_2O (1.64 wt. %), K_2O (2.41 wt. %), while TiO_2, MnO, MgO, CaO, P_2O_5, LOI have average concentrations of less than 1.00 wt. %. The concentration of SiO_2 in the samples corroborated with the observed very coarse-grained texture of the sandstone outcrops in the study area. In addition, the high concentration values of Fe_2O_3 in the samples are predicated by the high content of iron in the outcrops, which were observed in the field to have very pronounced ferruginous reddish-brown coloration. The very low values of CaO, MgO and LOI are indicative of absence of carbonate and organic source parent rocks.

The bivariate plot of log [Fe_2O_3/K_2O] versus log [SiO_2/Al_2O_3] indicated that the sediments are 77.80% litharenites and 22.20% arkose in composition (Fig. 3).
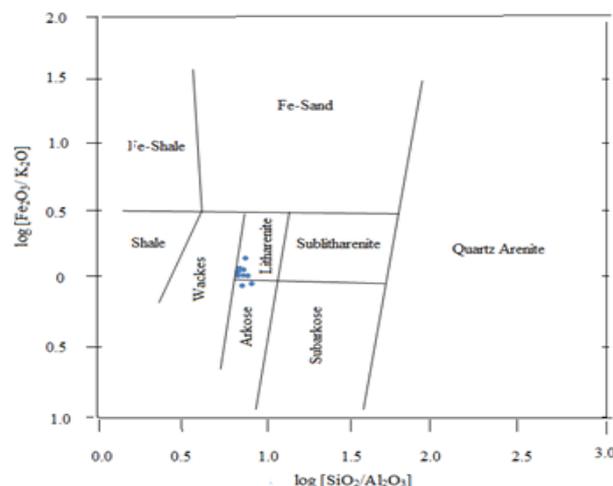
Fig. 3: Bivariate Plot of Log [Fe_2O_3/K_2O] Versus Log [Sio_2/Al_2O_3] (After Herron [6]).

4.2.2. Provenance

The provenance of sedimentary rocks refers to source rock(s) from which the sediments that formed the sedimentary rocks originated from. The study of provenance has economic importance because it could be used as a tool for mineral exploration. According to Kroonenberg

[7], geochemistry and petrography of sands and sandstones reflect the following three basic factors, namely: (i) provenance, (ii) transport and deposition, and (iii) post depositional processes. Kroonenberg [7] established that provenance outweighed the other two processes.
The ternary plot of A-CN-K also written as [Al$_2$O$_3$]-[CaO+Na$_2$O]-[K$_2$O] after Nesbitt and Young [9] and Gu et al. [4] indicates that the sandstone samples from the study area have felsic igneous rock provenance (Fig. 4). Also, the plot on the bivariate discriminant functions diagram of Roser and Korsch [15] indicates that the sediments have felsic igneous provenance and quartzose sedimentary origin (Fig. 5). The quartzose sedimentary provenance is indicative that the sediments from the study area had undergone recycling and reworking from pre-existing sedimentary rocks. In line with Roser and Korsch [15], the discriminant functions 1 and 2 are computed using the formula below:

Discriminant Function 1 = (−1.773 × TiO$_2$ %) + (0.607 × Al$_2$O$_3$ %) + (0.76 × Fe$_2$O$_3$T %) + (−1.5 × MgO %) + (0.616 × CaO %) + (0.509 × Na$_2$O %) + (−1.22 × K$_2$O %) + (−9.09).

Discriminant Function 2 = (0.445 × TiO$_2$ %) + (0.07 × Al$_2$O$_3$ %) + (−0.25 × Fe$_2$O$_3$T %) + (−1.142 × MgO %) + (0.432 × Na$_2$O %) + (1.426 × K$_2$O %) + (−6.861).
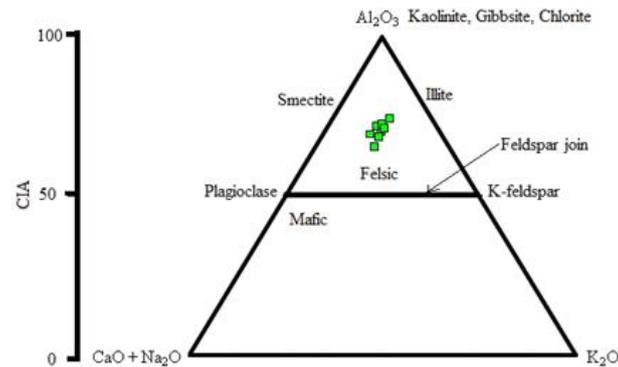
Fig. 4: [Al$_2$O$_3$]-[Cao+Na$_2$O]-[K$_2$O] Ternary Diagram Showing Weathering Trend of Lokoja-Basange Sandstone Samples from the Study Area (After Nesbitt and Young [9]; Gu Et Al. [4]).
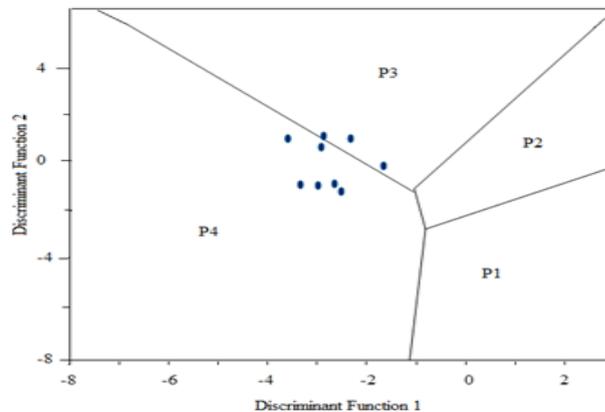
Fig. 5: Tectonic Discriminant Function 1 Against Function 2 Diagram (After Roser and Korsch [15]). P1: Mafic Provenance, P2: Intermediate Igneous Provenance, P3: Felsic Igneous Provenance, and P4: Quartzose Sedimentary Provenance.

4.2.3. Tectonic setting

The plots of the major oxide ratios of [SiO$_2$/20]-[K$_2$O+Na$_2$O]-[TiO$_2$+Fe$_2$O$_3$+MgO] of the sediments on the tectonic discriminant charts of Kroonenberg [7] and Roser and Korsch [15] indicate that the sediments from the study area were deposited in passive margin tectonic setting (Figs. 6-8).
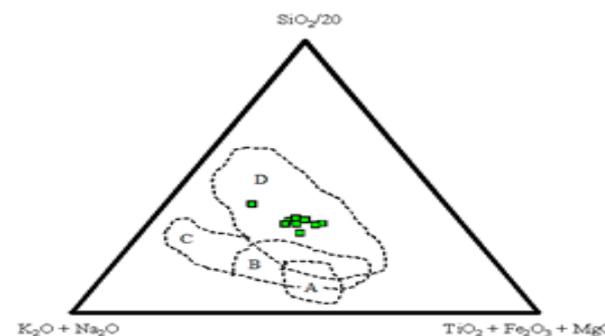
Fig. 6: Plot of Major Oxide Ratios on the Tectonic Discrimination Chart (After Kroonenberg [7]). A: Oceanic Island Arc; B: Continental Island Arc; C: Active Continental Margin; D: Passive Margin.
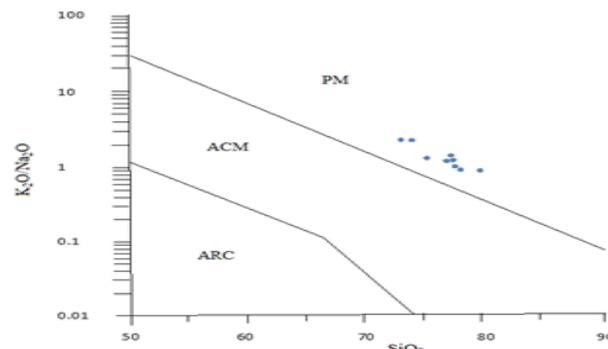
Fig. 7: Plot of K_2O/Na_2O versus SiO_2 Tectonic Discriminant Diagram for Lokoja-Basange Sandstone (after Roser and Korsch [15]).
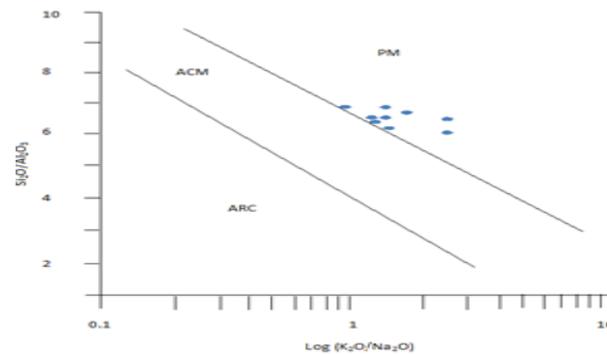
Fig. 8: Tectonic Discriminant Plot of $[SiO_2/Al_2O_3]$ Versus Log (K_2O/Na_2O) (After Roser and Korsch [15]; Maynard et al. [8]. ARC: Oceanic Island Arc, ACM: Active Continental Margin, PM: Passive Margin.

4.2.4. Weathering of source-rock

The interpretation of the degree of chemical weathering of the source-rock area was achieved through the use of the following: chemical alteration index (CIA) proposed by Nesbitt and Young [9], chemical index of weathering (CIW) by Harnois [5], plagioclase index of alteration (PIA) by Fedo et al. [2], [3] and mineralogical index of alteration (MIA) by Voicu et al. [17]. The computation of CIA, CIW, PIA and MIA are conveyed as follows in molecular magnitude:

$$CIA = [Al_2O_3/(Al_2O_3 + CaO* + Na_2O + K_2O)] \times 100$$

$$CIW = [Al_2O_3/(Al_2O_3 + CaO* + Na_2O)] \times 100$$

$$PIA = [(Al_2O_3 - K_2O)/(Al_2O_3 + CaO* + Na_2O - K_2O] \times 100$$

$$MIA = 2 \times (CIA - 50)$$

The chemical alteration index (CIA) of the samples from the study area has range of 65.4% – 74.2% with average of 70.70%, the chemical index of weathering (CIW) values are 77.4% – 87.3% with average values of 82.37%, the plagioclase index of alteration (PIA) values are 72.3% – 84.6% with average values of 78.88% and the mineralogical index of alteration (MIA) values are 30.9% - 48.5% with average values of 41.43% (Table 1). The values of CIA, CIW, PIA and MIA are indicative of moderate to near complete weathering of felsic igneous source rocks and suggest that the samples from the study area are mineralogically matured sandstones. The high values of the plagioclase index of alteration are indicative of near complete chemical weathering of plagioclase in the source rocks, which in turn led to the depletion in the concentrations of CaO, K_2O and Na_2O and the increase in the concentration of Al_2O_3 as clay weathering end-product.

4.2.5. Paleoclimate and chemical maturity

The plot of the major oxide ratios of SiO_2 versus $[Al_2O_3+K_2O+Na_2O]$ in the paleoclimate and chemical maturity discriminant chart of Sutter and Dutta [16] indicates that the sediments from the study area were deposited in slightly semi-arid to dominantly semi-humid paleoclimatic conditions with increasing chemical maturity of the sandstones due to moderate to near complete chemical weathering of the source-rocks (Fig. 9).
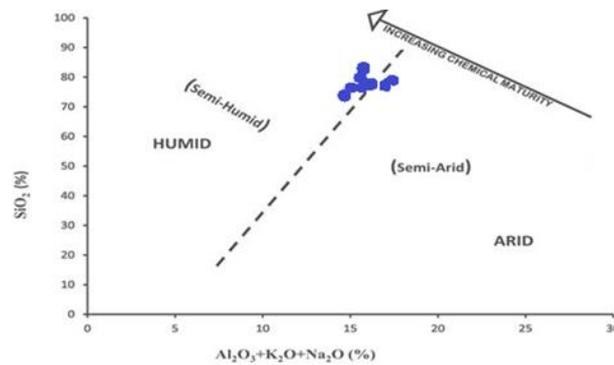
Fig. 9: Paleoclimate and Chemical Maturity Discriminant Plot of [Sio$_2$) Versus [Al$_2$O$_3$+K$_2$O+Na$_2$O] (After Sutter and Dutta [16]).

5. Conclusion

The samples from the study area have average concentrations of the major oxides to be as follows: SiO$_2$ (77.09 wt. %), Al$_2$O$_3$ (12.10 wt. %), Fe$_2$O$_3$ (2.72 wt. %), Na$_2$O (1.64 wt. %), K$_2$O (2.41 wt. %), while TiO$_2$, MnO, MgO, CaO, P$_2$O$_5$, LOI have average concentrations of less than 1.00 wt. %.

The bivariate plot of log [Fe$_2$O$_3$/ K$_2$O] versus log [SiO$_2$/Al$_2$O$_3$] indicated that the sediments from the study area are 77.80% litharenites and 22.20% arkose in composition. The bivariate plot of log [K$_2$O/Na$_2$O] versus SiO$_2$ and plot of [SiO$_2$/Al$_2$O$_3$] versus log [K$_2$O/Na$_2$O] established that the sediments were deposited in passive margin tectonic setting. The plot on the ternary diagram of [SiO$_2$/20]-[K$_2$O+Na$_2$O]-[TiO$_2$+Fe$_2$O$_3$+MgO] also established that the sediments were deposited in passive margin tectonic setting.

Moreover, the bivariate plot of SiO$_2$ versus [Al$_2$O$_3$+ K$_2$O +Na$_2$O] indicated that the sediments from the study area were deposited in slightly semi-arid to dominantly semi-humid paleoenvironment with the sediments having high chemical maturity inferred to have been predicated by the moderate to near complete weathering of the source-rock area.

Additionally, the bivariate plot on the discriminant functions diagram of Roser and Korsch [15] confirmed that the sediments from the study area have felsic igneous provenance and quartzose sedimentary source which agreed with findings from the ternary plot of [Al$_2$O$_3$]-[CaO+Na$_2$O]-[K$_2$O]. The quartzose sedimentary provenance of the sediments from the study area confirmed that they were reworked and recycled from pre-existing sedimentary source.

Conclusively, the average values of the chemical alteration index (CIA) of 70.72%, the chemical index of weathering (CIW) of 82.34%, the plagioclase index of alteration (PIA) of 78.86% and the mineralogical index of alteration (MIA) of 41.43% confirmed that moderate to near complete weathering occurred on the felsic igneous source rocks; therefore, Lokoja-Basange Sandstone is mineralogically matured.

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