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Classification, Maturity, Provenance, Tectonic Setting and Source-Area Weathering of the Ilubirin Stream Sediments, South West, Nigeria

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Abstract: Geochemical study on the Ilubirin stream sediments was carried out to infer their provenance, maturity, classification, enrichment, depletion, tectonic setting and source-area weathering. The sediments can be classified as ferromagnesian potassic, quartz arenites that are non-calcareous. The SiO_2/Al_2O_3 index is high, meaning that the samples are mature, the Index of Compositional Variability also indicate that the sediments are mineralogically mature, while the $Al_2O_3/(CaO+MgO+Na_2O+K_2O)$ ratio indicate that there are stable mobile oxides in the sediments. The plot of SiO_2 versus Al_2O_3+ K_2O+ Na_2O shows that the sediments formed under semi-arid/arid conditions tending towards increasing chemical maturity. Al_2O_3 correlates positively with all the major oxides except SiO_2, suggesting hydraulic fractionation and sorting. The negative linear trend between Al_2O_3 and SiO_2 indicates that the major element composition of the stream sediments is controlled largely by the relative amount of quartz and feldspar versus clay minerals. The depletion of highly mobile Na. K and Ca elements is due to leaching during the formation of clay minerals during increased chemical weathering. The immobile Fe and the less mobile Mg elements were depleted while the immobile Ti was enriched; this suggest that they may are from a felsic source. The high TiO_2/Fe_2O_3 ratios suggests concentration in the sediments of a heavy mineral phase containing Ti minerals such as ilmenite and rutile. The weathering indices (CIA, CIW, PIA and MIA) indicates a high degree of weathering of the source materials. The tectonic setting is the passive continental margin, while the provenance is the quartz-rich sediments of mature continental provenance, associated with a continental passive margin, intracratonic basins, or recycled orogenic provinces.

Keywords: weathering, chemical maturity, provenance, felsic, tectonic setting

1.0 Introduction

The geochemical compositions of stream sediments reflect the average composition of an entire drainage basin (Halamic et al., 2001; Reimann and Melezhik, 2001). According to (Grunsky and Sutphin, 2009), geochemical studies based on the chemical analysis of active stream sediments are an effective tool with several applications. Several authors have used major element discrimination diagrams (Bhatia, 1983) to discriminate the tectonic settings of sedimentary basins and have been applied in topical publications (Kroonenberg, 1994; Zimmermann and Bahlburg, 2003; Armstrong-Altrin et al., 2004). According to (Armstrong-Altrin and Verma, 2005), caution is required in their uncritical use. The most important clues for the tectonic setting of the basin comes from the relative depletion of the most mobile elements like Ca and Na and enrichment of Si and Ti—the most immobile elements, among others. The oxides of these elements are assumed to show enrichment or depletion in quartz, K-feldspar, plagioclase feldspars, and micas. The ratio of the most immobile elements to the most mobile ones increases toward passive margins due to the relative tectonic stability (Bhatia, 1983; Kroonenberg, 1994; Zimmermann and Bahlburg, 2003; Armstrong-Altrin et al., 2004; Roser and Korsch, 1986) and hence prolonged weathering. This can be recorded in sediments as paleoclimate index (Chittleborough, 1991; Harnois, 1988; Nesbitt and Young, 1982) and high degree of sediment recycling.

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Major elements and selected trace and rare earth elements and their elemental ratios are sensitive indicators of the source rocks, tectonic setting, paleoweathering conditions and paleoclimate of the clastic sediments (Bhatia, 1983; Bhatia and Crook, 1986; Roser and Korsch, 1986; Roser and Korsch, 1988; McLennan and Taylor, 1991; McLennan et al., 1993; Johnsson and Basu, 1993; Condie, 1993; Nesbitt, 1996; Fedo, et al., 1997; Cullers and Podkovyrov, 2000; Bhatt and Ghosh, 2001). Ilubinrin stream is located in Ondo State South Western Nigeria.

The study area lies within the latitudes 6^0 28^1N and 6^0 37^1N and longitudes 4^0 32^1E and 4^0 5^1E of the Green wich Meridian (Fig 1). The Elevation rangesbetween 50 and 250 m above the sea level. This area lies between Ekiti State and Edo State respectively. The drainage pattern is mainly Dendritic in which there are many rivers of different sizes. Dendritic system forms in V-shape valleys as a result of the rock types whether porous or non-porous. The drainage in the area is influenced by: lithological variations, structural elements such as faults, joints etc., and geomorphology of the area. The most outstanding characteristics of the drainage systems over the areas of Basement Complex rocks is the proliferation of many small rivers, some of which intersect the minor roads and footpaths in the area. The area has little streams which take their source from hills in the northern part. This present research is aimed at interpreting the sediment source area weathering, provenance, tectonic setting, maturity and classification of the Ilubirin stream sediments based on major oxides geochemical data.

2.0 Materials and Methods

Seven stream sediments were collected at Ilubinrin; the samples were collected using a hand auger and shovel. They were then sieved after drying using $75\mu m$ stainless steel mesh wire. Chemical analysis was carried at Stellenbosch University, South Africa using the Inductively Coupled Plasma–Mass spectrophotometry (ICP-MS) technique to determine the concentration of rare earth and trace elements in the stream sediments.

3.0 Results and Discussion

3.1 Geochemical Composition

Table 1 shows the major oxides component of the Ilubirin stream sediments. The samples are dominated by SiO_2, which ranges from 72.62-94.81% (Average = 91.7%). The wide range of SiO_2 content may be due to effect of hydraulic sorting and slow deposition. Al_2O_3 ranges from 1.52-5.15% (Average = 2.11%), Fe_2O_3 (Average = 1.84%) MgO (Average = 0.08%); K_2O (Average = 0.37%), TiO_2 (Average = 1.66%), Na_2O (Average = 0.06%), MnO (Average = 0.05) and CaO (Average = 0.08%); this low values may be attributed to chemical destruction under oxidizing conditions during weathering or source-area composition. Lack of Na2O in the sediments could be attributed to paucity of plagioclase feldspar in the host rock or their loss during weathering.

Figure 2 shows Al_2O_3 correlates positively with all the major oxides except SiO_2, suggesting hydraulic fractionation and sorting. The negative linear trend between Al_2O_3 and SiO_2 indicates that the major element composition of the stream sediments is controlled largely by the relative amount of quartz and feldspar versus clay minerals. The positive correlation between Al_2O_3 with Fe_2O_3, MgO and TiO_2 suggests that they occur in clay minerals formed from weathering of ferromagnesian minerals. The positive linear correlation between Al_2O_3 and K_2O suggests that potassium is associated illitic clays. Also, Al_2O_3 correlates positively with P_2O_5 which may be due to association of phosphorus with clays rather than apatite.

Table 1. Major oxides component (Wt %) of the Ilubirin Stream sediments: some ratios and weathering indices

Oxides (Wt. %)	**ILUB-1**	**ILUB-2**	**ILUB-3**	**ILUB-4**	**ILUB-5**	**ILUB-6**	**ILUB-7**
SiO2	94.06	94.63	93.86	94.7	94.21	94.74	94.81
Al2O3	1.52	1.78	1.81	1.7	1.65	1.57	1.67
Fe2O3	0.87	1.1	0.96	0.83	0.73	0.59	0.94
MnO	0.02	0.02	0.02	0.01	0.01	0.01	0.01
MgO	0.06	0.07	0.06	0.07	0.06	0.06	0.07
K2O	0.03	0.06	0.06	0.06	0.05	0.06	0.05
CaO	0.03	0.04	0.03	0.03	0.03	0.04	0.03
Na2O	0	0	0	0	0	0	0.01
TIO2	0.84	0.79	1.14	0.69	0.71	0.58	0.63
P_2O_5	0.04	0.05	0.05	0.04	0.04	0.04	0.04
SiO2/Al2O3	61.88	53.16	51.86	55.71	57.10	60.34	56.77
K_2O/Al_2O_3	0.02	0.03	0.03	0.04	0.03	0.04	0.03
CaO/MgO	0.50	0.57	0.50	0.43	0.50	0.67	0.43
K_2O/Na_2O	0	0	0	0	0	0	5.00
Na_2O/K_2O	0.00	0.00	0.00	0.00	0.00	0.00	0.20
Log(K2O/Na2O)	0	0	0	0	0	0	0.70
Log ((Fe2O3+MgO)/(Na2O+K2O))	1.49	1.29	1.23	1.18	1.20	1.03	1.23
Fe_2O_3/K_2O	29.00	18.33	16.00	13.83	14.60	9.83	18.80
Log SiO2/Al2O3	1.79	1.73	1.71	1.75	1.76	1.78	1.75
Log(Fe_2O_3/K_2O)	1.46	1.26	1.20	1.14	1.16	0.99	1.27
PIA	98.03	97.73	98.31	98.2	98.16	97.42	97.59
CIA	96.2	94.68	95.26	94.97	95.38	94.01	94.89
CIW	98.06	97.8	98.37	98.27	98.21	97.52	97.66
MIA	92.41	89.36	90.53	89.94	90.75	88.02	89.77

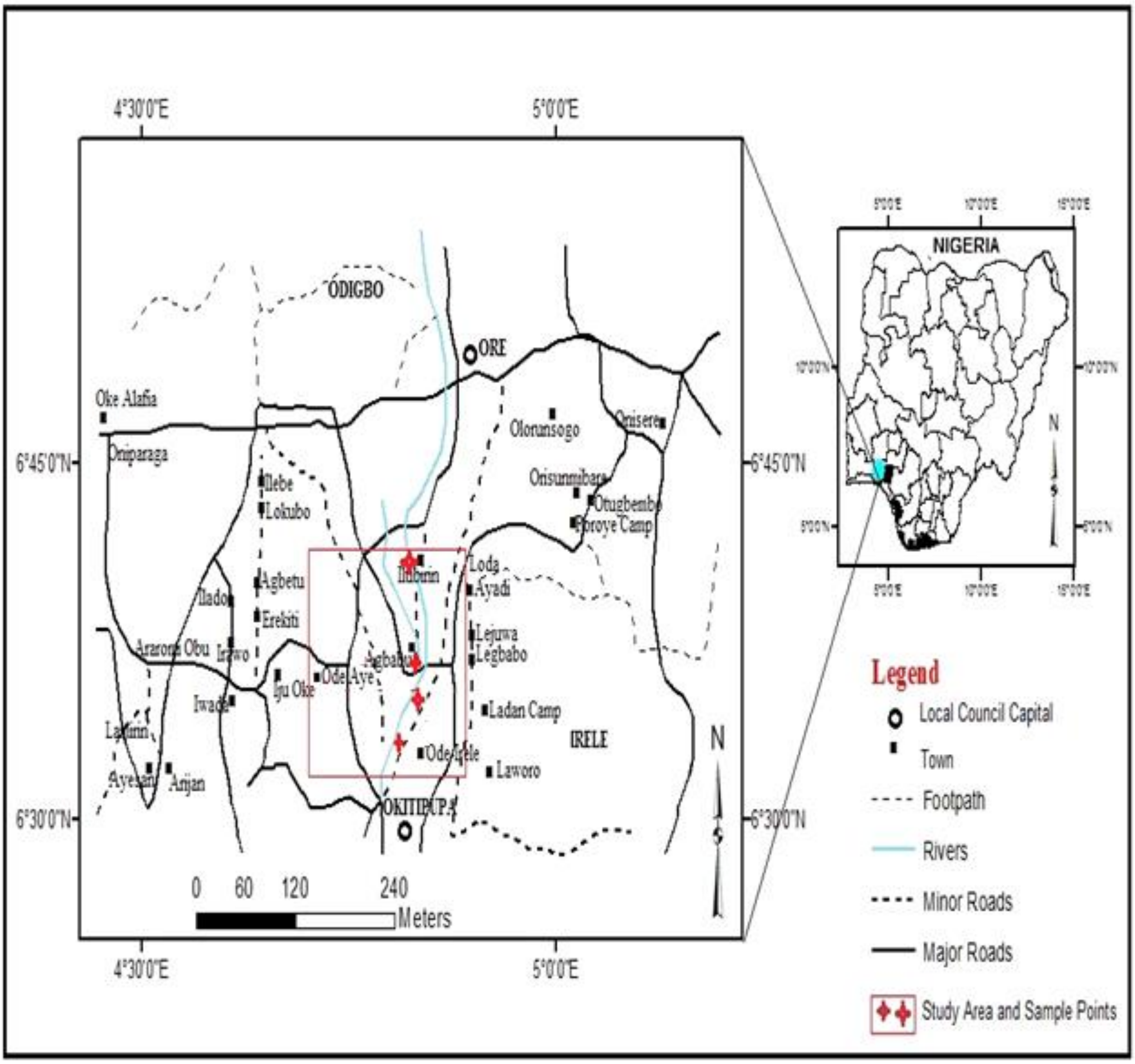

Fig 1. The study area and sample points

3.2 Geochemical classification

The classification schemes used in this study was adopted from the geochemical classification diagrams of several authors (Pettijohn et al., 1972; Blatt et al., 1972; Herron, 1988; Lindsey, 1999). The ternary diagram proposed by Blatt et al. (1972) shows the stream sediments are ferromagnesian potassic sandstones (Fig. 3). This ternary diagram omitted sandstones with less than 5% of Al_2O_3, consequently, quartz arenites is missing.

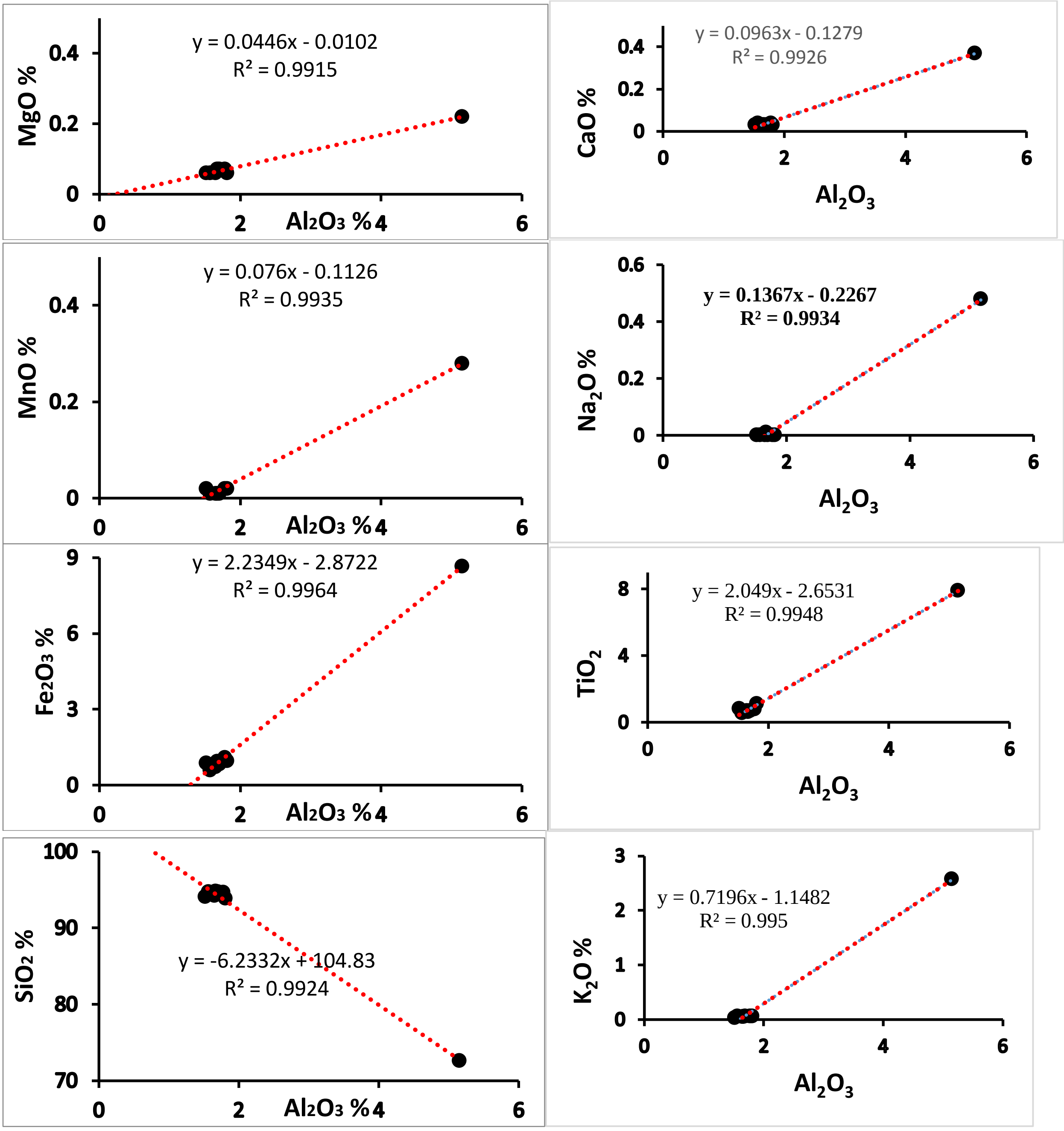

Fig. 2. Cross-plots of major oxides against Al_2O_3 showing the correlations.

Based on the work by Lindsey (1999) using data from Pettijohn (1963 and 1975), the average lithic arenites plotted in the ferromagnesian potassic sandstones field, but the average greywacke plotted in the sodic sandstone field and average arkoses appeared in the potassic sandstones field. Figure 4 shows a plot in the quartzarenite zone, lack of more plots is due to paucity of Na_2O in the samples.

According to Pettijohn (1963), the lithic arenites are a diverse and poorly defined class. In addition to abundant rock fragments of widely varying composition, many lithic arenites contain clay matrix with different compositions which can contain higher levels of Fe and Mg. Also, many rock fragments of lithic sandstones are composed of materials that vary greatly in composition. Based on compositional fields for major classes of sandstones (Lindsey, 1999), the studied sediments plotted in the lithic arenite field (Fig. 5).

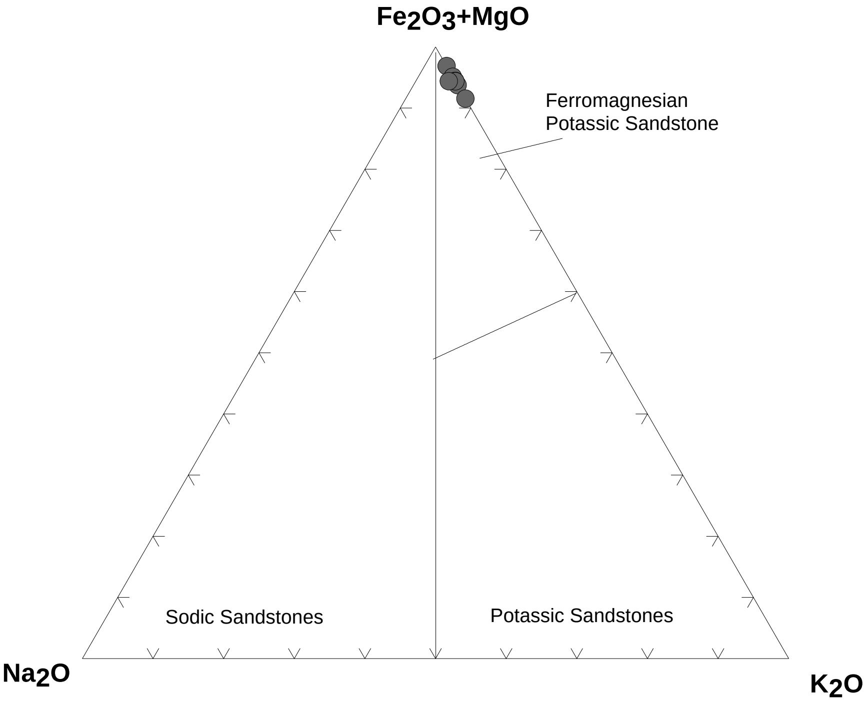

Figure 3. Ternary diagram of Na_2O-K_2O-(Fe_2O_3+MgO) of the stream sediments, from Blatt et al., 1972.

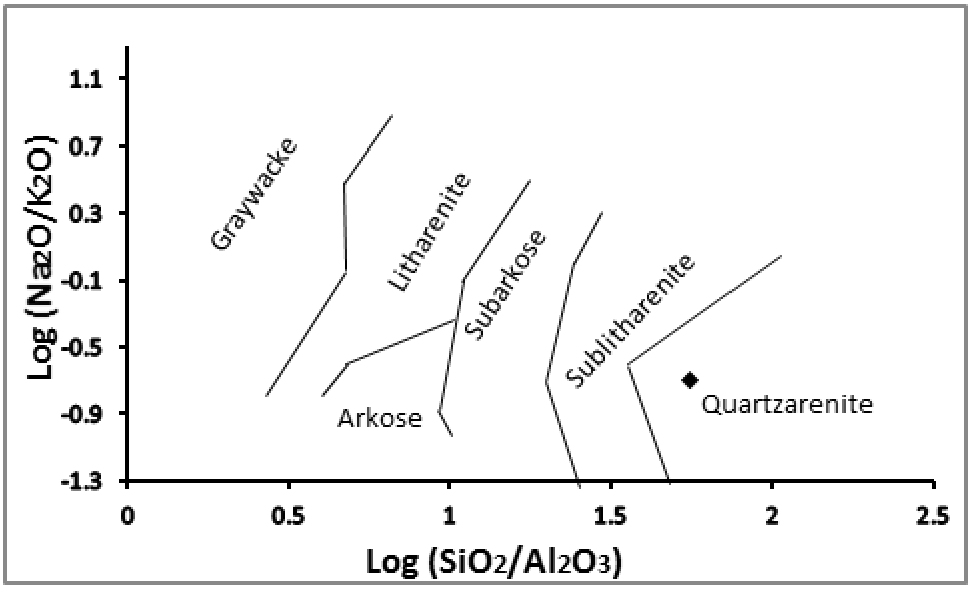

Figure 4. Chemical classification of the stream sediments based on Pettijohn scheme (1972).

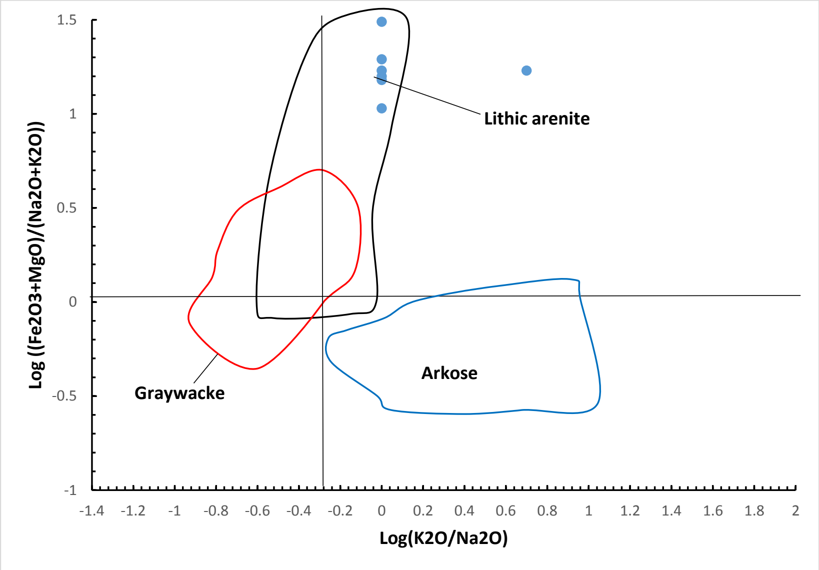

Figure 5. Compositional fields for major classes of sandstones (data from Pettijohn, 1963; 1975): Log (Fe2O3+MgO)/(Na2O+K2O) versus log (K_2O/Na_2O), adapted from Lindsey, 1999).

Figure 6 shows the samples plotting in the Fe-sand zone. According to Farquhar et al. (2014), the third axis from the Herron (1988) scheme (not shown in Fig. 6), classifies samples by Ca content by dividing samples into non-calcareous (Ca < 4 %), calcareous (4 % < Ca < 15 %), and carbonate (Ca > 15 %) samples. The stream sediments classified as non-calcareous.

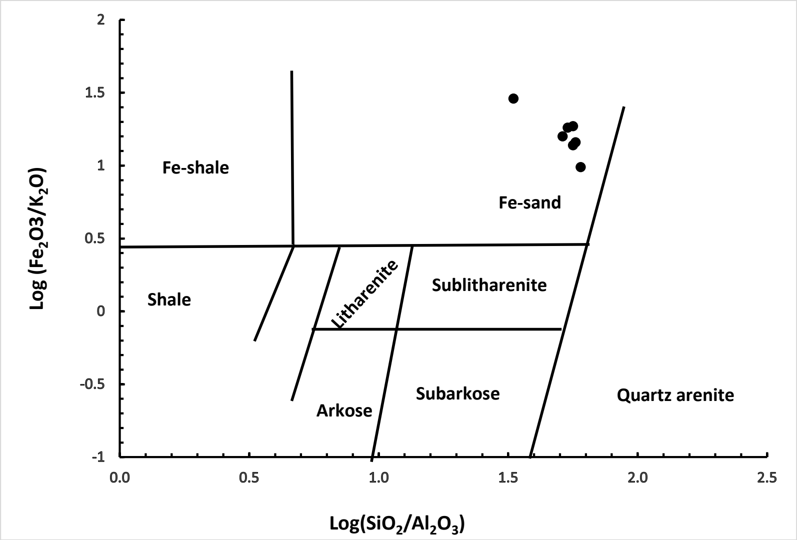

Figure 6. Chemical classification of the stream sediments based on log (SiO_2/Al_2O_3) *vs.* log (Fe_2O_3/K_2O) diagram of Herron (1988).

Based on the study of a reference set, Lindsey (1999) proposed the following guidelines for chemical classification of sandstones:

1) quartz arenite: log (SiO_2/Al_2O_3) □□1.5

2) graywacke: log (SiO_2/Al2O_3) < 1 and log (K_2O/Na_2O) < 0

3) arkose (includes subarkose): log (SiO_2/Al2O_3) < 1.5 and log (K_2O/Na_2O) □□0 and log ((Fe_2O_3+MgO)/(K_2O+Na_2O)) < 0

4) lithic arenite (subgraywacke, includes protoquartzite): log (SiO_2/Al2O_3) < 1.5 and either log (K_2O/Na_20) < 0 or log ((Fe_2O_3+MgO)/(K_2O+Na_2O)) □□0. If log (K_2O/Na_2O) < 0, lithic arenite can be confused with graywacke.

The stream sediments falls within the requirements of the first condition and thus classifies as a quartz arenite.

3.3 Maturity

Figure 7 indicates that the stream sediments formed under semi-arid/arid conditions tending towards increasing chemically maturity. The high values given from the ratio of SiO_2/Al_2O_3 indicate that all the samples have low degree of clayness. The higher the SiO_2 content the lower the degree of clayness. Potter (1978) stated that maturity of sandstones is reflected by the SiO_2/Al_2O_3 index. High ratios indicate mineralogically mature (quartzose, rounded) samples, while low ratios represents chemically immature samples. The SiO_2/Al_2O_3 ratio for the Ilubirin stream sediments range between 51.86 and 61.88, which is high; this shows that the samples are mature. The Na_2O/K_2O and Fe_2O_3/K_2O ratios can also be used in determining chemical maturity and mineral stability, respectively (Pettijohn et al., 1987; Herron, 1988). The paucity of Na_2O in the samples disallowed the use of the Na_2O/K_2O ratio. By extrapolation, samples with a low SiO_2/Al_2O_3 ratio and a higher Fe_2O_3/K_2O ratio should be mineralogically less stable and more prone to reactivity during supercritical CO_2 exposure (Farquhar et al., 2014). The samples studied have a much higher SiO_2/Al_2O_3 ratio and low Fe_2O_3/K_2O ratio, thus, they are mineralogically more stable and less prone to reactivity during supercritical CO_2 exposure. The $Al_2O_3/(CaO+MgO+Na_2O+K_2O)$ ratio can be used in determining the stability of mobile oxides as proposed by Gill and Yemane (1996). From the positive values obtained (9.8 to 12.7), it shows that there are stable mobile oxides in the stream sediments.

An approach towards assessing detrital mineralogy is to use the Index of Compositional Variability (Cox *et al.*, 1995). The Index of Compositional Variability (ICV) is defined as: $(Fe_2O_3+Na_2O+CaO+MgO+TiO_2)/Al_2O_3$. More matured sandstone with mostly clay minerals displays lower ICV values that are less than 1.0 and such sandstones are derived from cratonic environment (Cox et al., 1995). The results of the Index of Compositional Variability range between 0.81 and 1.21 with an average of 1.03, this indicate that the sands are mineralogically mature.

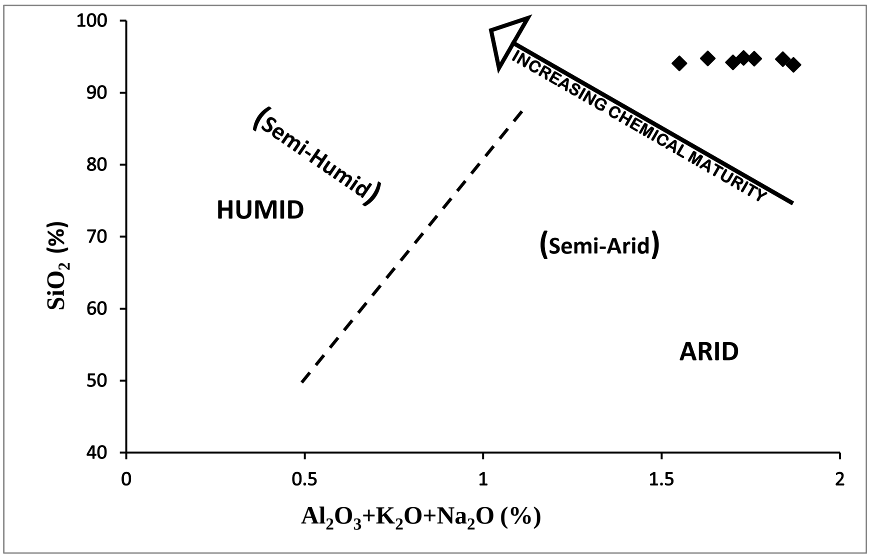

Figure 7. Chemical maturity of the Ilubirin stream sediment expressed by bivariate plot of SiO_2 versus Al_2O_3+ K_2O+ Na_2O (After Suttner & Dutta, 1986).

3.4 Source-area weathering

According to Nesbitt and Young (1982), the evaluation of the degree of chemical weathering of the sediments' source rocks can be determined by calculating the Chemical Index of Alteration (CIA), where CIA = molar $(Al_2O_3/[Al_2O_3+CaO+Na_2O+K_2O])$.This index works correctly when Ca, Na, and K decrease as the intensity of weathering increases (Duzgoren-Aydin *et al.*, 2002). The Chemical Index of Weathering (CIW) proposed by Harnois, (1988) is similar to the CIA except for the exclusion of K_2O in the equation: CIW = molar $(Al_2O_3/(Al_2O_3+ CaO + Na_2O))$. The CIA and CIW are interpreted in similar way with value of 50 for unweathered upper continental crust and roughly 100 for highly weathered materials, with complete removal of alkali and alkaline-earth elements (McLennan *et al.*, 1983; McLennan, 1993; Mongelli *et al.*, 1996). Low CIA values (i.e. 50 or less) also might reflect cool and / or arid conditions (Fedo et al., 1995). The intensity of the chemical weathering can also be estimated using the Plagioclase Index of Alteration

(Fedo et al., 1995); in molecular proportions: PIA = $[(Al_2O_3\text{-}K_2O)/(Al_2O_3 + CaO^* + Na_2O\text{-}K_2O)] \times 100$ where CaO* is the CaO residing only in the silicate fraction. Unweathered plagioclase has PIA value of 50 while Phanerozoic shales have PIA value of 79.

The CIA values for the samples ranged between 94 and 96%, while CIW ranged from 97-98% indicating a high degree of weathering of the source materials. The PIA values ranged from 97-98%, this also indicates high degree of weathering.

Voicu et al. (1997) also proposed the Mineralogical Index of Alteration (MIA) as a weathering parameter calculated as: MIA = 2*(CIA-50). MIA values between 0 and 20% are designated as incipient, i.e. just starting; 20-40% (weak); 40-60% (moderate) and 60-100% as intense to extreme degree of weathering. The extreme value of 100% indicates complete weathering of a primary material into its equivalent weathered product (Voicu and Bardoux, 2002). MIA values for the samples ranged between 88 and 92%, which intense weathering of the source material, this is in agreement with the CIA, CIW PIA.

Figure 8 shows that all the samples plotted at the A end member, which suggests intense chemical weathering and transportation of the sediments. The chemical composition of weathering products in a river basin is expected to exhibit entrenched concepts on mobility of various elements during weathering (Nesbitt et al., 1980; Singh et al., 2005), and therefore to assess the state of chemical and physical weathering (Vital and Stattegger, 2000; Singh et al., 2005; Liu et al., 2007). Elemental ratios calculated with respect to Al are used to identify and evaluate the major element mobility. According to Singh et al. (2005), the ratio of the content of element X and Al_2O_3 in rivers divided by the ratio of the same element content of upper continental crust (UCC) gives the elemental ratio.

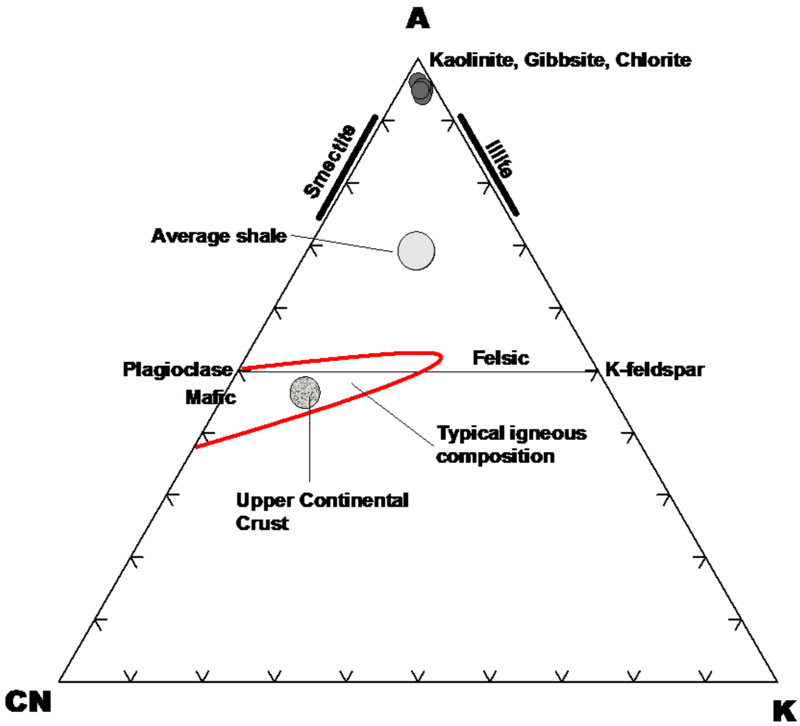

Fig. 8. Ternary diagram showing the weathering trend of the stream sediments (all in molar proportions); Al_2O_3–CaO +Na_2O−K_2O (A–CN–K). Fields from Gu et al. (2002).

The elemental ratio refers to the relative enrichment or depletion of the element, i.e., >1 indicates enrichment, <1 indicates depletion, and =1 indicates no change in the relative abundance of the element. The stream sediments have, CaO, K_2O, Na_2O, Fe_2O_3, MgO values less than 1, while SiO_2, and TiO_2 have values greater than 1. The depletion of highly mobile Na. K and Ca elements is due to leaching during the formation of clay minerals during increased chemical weathering. The immobile Fe and the less mobile Mg elements were depleted while the immobile Ti was enriched; this suggest that they may are from a felsic source.

Titanium is relatively immobile compared to other elements during sedimentary processes, and hence is a good indicator of source rock composition (McLennan et al., 1993). There is a positive correlation between Ti and Fe (fig. 9); according to Singh, (2009), Fe_2O_3 and

TiO_2 in stream sediments can be expected to be correlate positively due to sorting effects. Linear arrays of data points along lines extending toward the origin in binary Fe_2O_3–TiO_2 plots demonstrate that the elements were immobile, and that they were also hydraulically fractionated in a similar manner (Young, et al., 2013). The Ilubirin stream sediments have TiO_2/Fe_2O_3 ratio between 0.67 and 1.19, which suggests concentration in the sediments of a heavy mineral phase containing Ti minerals such as, ilmenite and rutile.

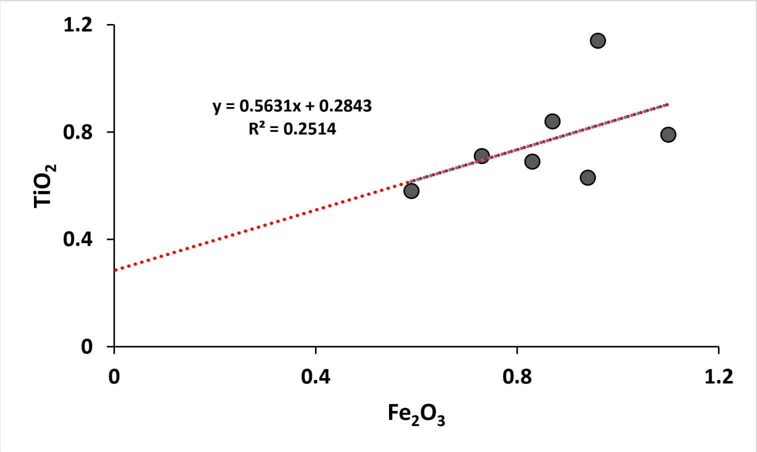

Fig. 9. Positive correlation of Fe_2O_3–TiO_2 plots for the stream sediments

3.5 Provenance and tectonic settings

Several authors (Blatt et al., 1980; Bhatia, 1983; Bhatia and Crook, 1986; Roser and Korsch, 1986 & 1988) have related sandstone geochemistry to specific tectonic environment. The discriminant function plot of Roser and Korsch (1988) defined four (4) main provenances: mafic igneous provenance; intermediate igneous provenance; felsic igneous provenance; and quartzose sedimentary provenance (Fig. 10). The stream sediments samples plot in the field P4, quartz-rich sediments of mature continental provenance, associated with a continental passive margin, intracratonic basins, or recycled orogenic provinces. Roser and Korsch (1986) created a tectonic discrimination diagram using K_2O/Na_2O ratio versus SiO_2 (Fig.11) to determine the tectonic setting of clastic terrigenous sedimentary rocks. The cross plot is used to discriminate between sediments deposited in the Passive Continental Margin (PM), Active Continental Margin (ACM) and the Oceanic Island Arc (OIA). A sample plot in the Passive Margin, lack of more plots is due to the paucity of Na_2O. Figure 12 is another tectonic diagram by Maynard et al., (1982), which also shows the plots in the Passive Margin field, though also affected by the paucity of Na_2O. Figures 13 and 14 are also tectonic discrimination diagrams of the Ilubirin stream sediments indicating the Passive Margin zone.

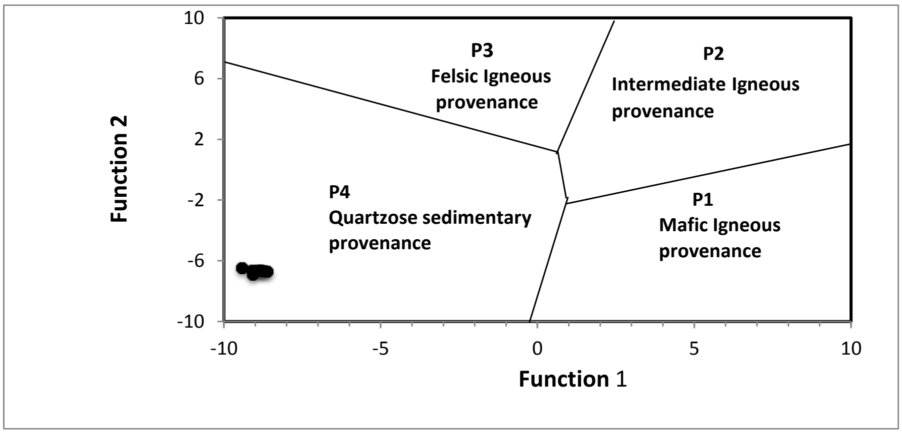

Fig. 10. Discriminant function diagram using major elements for the provenance signatures of the stream sediments (After Roser & Korsch, 1988).

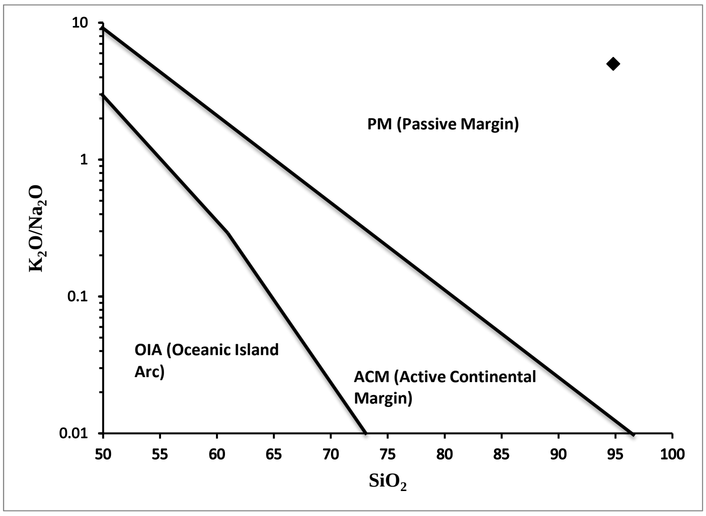

Fig. 11. Tectonic discrimination plot for the stream sediments (After Roser and Korsch, 1986).

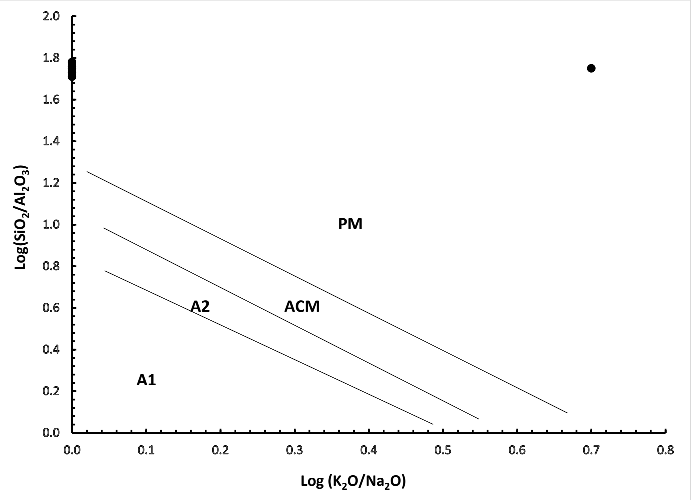

Figure 12. K_2O/Na_2O versus SiO_2/Al_2O_3 ratio – ratio diagram of the stream sediments, after Maynard et al; (1982). A1= arc setting and andesitic detritus; A2= evolved arc setting, felsic pluton detritus ACM= Active Continental Margin; PM= Passive Margin.

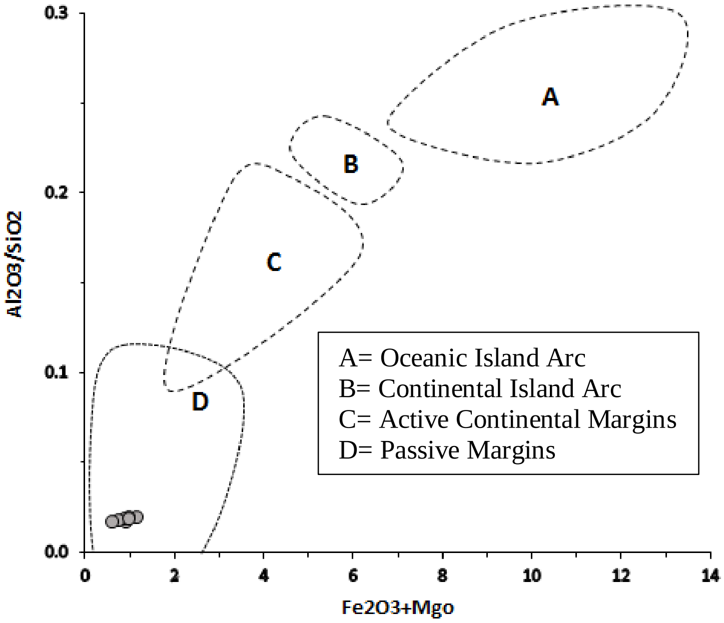

Fig. 13. Tectonic setting discrimination Plot of Al_2O_3/SiO_2 versus Fe_2O_3 + MgO of the stream sediments. Dashed lines denote the major fields representing various tectonic settings (after Bhatia 1983).

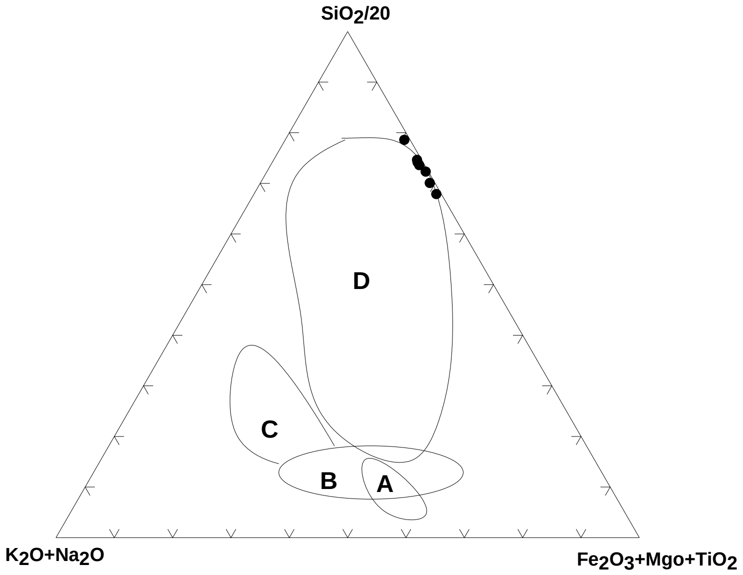

Figure 14. Plot of the major element composition of the stream sediments on the tectonic setting discrimination diagram of Kroonenberg (1994). A: Oceanic island Arc, B: continental island Arc, C: active continental margin, D: passive margin.

4. Conclusions

The sediments can be classified as ferromagnesian potassic, quartz arenites that are non-calcareous. The sediments formed under semi-arid/arid conditions tending towards increasing chemical maturity. The SiO_2/Al_2O_3 index is high, meaning that the samples are mature and there are stable mobile oxides in the sediments. The Index of Compositional Variability values indicate that the sediments are mineralogically mature. The weathering indices indicates a high degree of weathering of the source materials. The depletion of highly mobile Na. K and Ca elements is due to leaching during the formation of clay minerals during increased chemical weathering. The immobile Fe and the less mobile Mg elements were depleted while the immobile Ti was enriched; this suggest that they may are from a felsic source. The Ilubirin stream sediments TiO_2/Fe_2O_3 ratios suggests concentration in the sediments of a heavy mineral phase containing Ti minerals such as, ilmenite and rutile. There is a positive correlation between Ti and Fe due to sorting effects and hydraulic fractionation. The tectonic setting is the passive continental margin, while the provenance is the quartz-rich sediments of mature continental provenance, associated with a continental passive margin, intracratonic basins, or recycled orogenic provinces.

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