
Geochemical characterization of Egbetua stream sediments, southwestern Nigeria: implication for provenance and depositional conditions

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ABSTRACT: *The aim of this work is to determine the provenance, chemical index of alteration, elemental spatial distribution in the stream sediments, stream flow energy and the depositional conditions in the study area. The study area is located in Egbetua area in Akoko Edo Local Government Area of Edo State, Southwestern Nigeria. It is located on latitudes 07° 21' 30'' N and 07° 22' N longitudes 06° 15' 30'' E and 06° 17' E and average elevation of 182 metres. Standard field and laboratory procedures were used in the study. Geochemical analysis was carried out using x-ray fluorescence method. Average concentrations of SiO₂ (78.24 wt. %) and Al₂O₃ (ca. 12.15 wt. %) and the chemical index of alteration (CIA) values of 68.90% indicate felsic granitic source rocks. Ce/Ce*, Eu/Eu* and (La/Yb)_n ratios were used to deduce the prevailing reducing-oxidizing depositional environment of the sediments. Ce/Ce* (0.80) confirmed an oxidizing environment of deposition with low stream flow energy, while Eu/Eu* (0.07) corroborated an oxidizing environment with felsic source rock. (La/Yb)_n (5.95) indicated an oxidizing environment in a low stream energy flow with coarse-grained and clay size sediment input.*

KEYWORDS: Geochemical analysis, major oxide, rare earth element, Egbetua, stream sediments, Nigeria

INTRODUCTION

The major oxides and rare earth elements are useful tools in the study of origins of rocks, ores and waters (Orris and Grauch, 2002). The global campaign for alternative green energy source to reduce carbon emission has spurred interest in rare earth elements (Kingsnorth, 2010). The need to sustain the supply chain of rare earth elements (REE) is of global economic concern; therefore, research into rare earth elements is of environmental friendly relevance to the global energy security and mix.

The aim of this work is to determine the provenance, chemical index of alteration, elemental spatial distribution in the stream sediments, stream flow energy and the depositional conditions in the

study area. The study area is located in Egbetua area in Akoko Edo Local Government Area of Edo State, Southwestern Nigeria. It is located on latitudes 07° 21'30''N and 07° 22'N longitudes 06° 15' 30''E and 06° 17'E and average elevation of 182 metres above mean sea level.

Regional Geology

The study area is classified into the Igarra Schist which lies within the Basement Complex of Southwestern Nigeria in the East of the West African craton of late Precambrian to early Paleozoic Pan-African orogeny (Odeyemi, 1988; Rahaman, 1976). The geology of Southwestern Nigeria comprises of rocks of the Precambrian Basement Complex and the Cretaceous-Paleocene sediments. The Precambrian Basement Complex occupies the greater part of Southwestern Nigeria where it continues in the west with the Dahomey of the West African craton. The Niger-Delta basin lies unconformably on the Basement Complex in the East while it is bounded in the North by the Bida basin at Lokoja and overlain in the South by Cretaceous-Paleocene sediments at Ewekoro, Okitipupa, Abeokuta, Ifon and its environments.

Local Geology of the Study Area

The study area lies within the crystalline Basement Complex rocks of the Southwestern Nigeria. The migmatite-gneiss-quartzite complex is a heterogeneous rock group comprising quartzofeldspathic gneiss and migmatite with grade of basic and calcareous, schist, marbles and quartzite also known as ancient meta-sediments (Oyawoye, 1964, 1976) or older meta-sediments (McCurry, 1976). The main rocks recognized in the study area are grey gneiss, granite gneiss, granite and migmatite.

MATERIALS AND METHODS

The equipment used on the field during the collection of samples includes: field notebook, pen, pencil, GPS, hammer, sampler, masking tape, metre rule, sample bags, set of sieves and funnel. The laboratory materials are pulveriser, pellitizer, oven, desiccators, crucibles and Energy Dispersive X-Ray Fluorescence (EDXRF) spectrometer of model "Minipal 4. Samples of stream sediments were taken from fifteen locations in the study area. Sampling point coordinates taken were recorded in the field notebook. The samples were carefully placed into the sample bags after wet sieving and properly labeled. The samples were pulverized (grind to fine powder) using target pulverizing machine (Planetary Micro Mill Pulverizette 7). 5 grams of each pulverized sample was weighed into a beaker along with 1 grams of binding aid (starch soluble). The mixture was thoroughly mixed to ensure homogeneity and then pressed under high pressure (6 'tonnes') to produced pellets that were then packaged, labeled and used for analysis.

Energy Dispersive X-Ray Fluorescence (EDXRF) spectrometer of model "Minipal 4" was used for the analysis. The pellets were carefully placed in the respective measuring positions on a sample changer of the machine. The selection of filters for the elemental analysis was guided using the periodic table. Time of measurement for each sample was 100 seconds and air was used throughout. The machine was celebrated prior to the analysis of the samples.

Loss on ignition (LOI) was determined gravimetrically by heating 1g of each powdered sample in a cleansed, weighed crucible at 1,000 °C. Thereafter, each crucible and its content were weighed to compute the difference in weight before and after heating as given in formula below:

$LOI = (a-b/1) \times 100 \% = H_2O^+$; where a = weight of crucible + 1g of the sample before heating; b = weight of crucible + 1g of the sample after heating. The major elements analyzed and expressed in oxide weight percentages are Si, Al, Mn, Ti, Mg, Ca, Na, K, P. Initially, the samples were prepared and dried in oven at 110 °C for 24 hours to remove their moisture. 5.0 grams of each dry sample powder was weighed in the silica crucible and then ignited in a furnace at 1,000 °C for 2 to 3 hours to calcinate the impurities in them. Thereafter, the samples were allowed to cool to room temperature in desiccators. Each ignited sample powder was re-weighed to compute the weight of the calcinated impurities such as H₂O, H₂O⁺ and CO₂. 1.0 gram of the stored ignited sample powder was weighed and exactly five times of flux (spectroflux 100B) was added to lower the vitrification temperature. This weighed mixture was mixed properly in a platinum dish and ignited in the pre-set furnace at 1,100 °C for 10 minutes to form a molten mixture. The molten mixture was poured into a mould in the furnace, cooled and removed over a compressed stream of air, tapping the edge with a small iron slab to produce a glass bead. Each glass bead was labeled and slotted into the computerized XRF for major element analysis. Chemical index of alteration (CIA) after Nesbitt and Young (1982) was used to measure the degree of weathering of the source rocks of the stream sediments. The chemical index of alteration was computed using the equation below: $CIA = [((Al_2O_3 / (Al_2O_3 + CaO + Na_2O + K_2O))) \times 100]$

RESULTS AND DISCUSSION

Results

The major oxides composition in wt. % and the chemical index of alteration (CIA) values for sample locations SL1-SL15 in the study area are given in Tables 1 and 2. On the other hand, Table 3 shows the un-normalized rare earth element (REE) composition in parts per million (ppm), while Table 4 shows the ordinary C1-Chondrite composition for rare elements. The chondrite normalized concentration of rare earth elements (in ppm) and some special ratios such as Ce/Ce*, Eu/Eu* (La/Yb)_n for samples from the study area are given in Tables 5 and 6. The plots of spatial distribution of major oxides, rare earth element and REEs ratios in the stream sediments in study area are shown in Figures 1, 2 and 3.

Discussion

SiO₂ is the dominant major element in the stream sediments with range values of 76.1 – 80.1 wt. % and mean value of 78.24 wt. %. Al₂O₃ values range from 11.49 – 13.00 wt. % with a mean concentration of 12.15 wt. %. Fe₂O₃ values range from 1.94 – 3.91 wt. % with a mean values of 2.69 wt. %. Na₂O values range from 1.27-2.10 wt. %. CaO values range from 0.72 – 2.47 wt. % with a mean value of 1.22 wt. %. MnO, MgO, etc. have < 1.0 wt. % average concentration values. The concentration values of SiO₂ and Al₂O₃ are indicative of felsic granitic source rocks for the stream sediments. The CIA values range from 65.51% – 73.68% with mean values of

Tables 1: Major Oxide Analysis of samples SL1-SL15 (in Wt. %)

Major Oxides	SL1	SL2	SL3	SL4	SL5	SL6	SL7	SL8	SL9	SL10	SL11	SL12	SL13	SL14	SL15
SiO ₂	79.43	77.49	78.38	79.02	78.54	77.75	77.41	80.1	78.82	79.26	77.42	76.1	76.1	78.43	79.31
TiO ₂	0.83	0.84	0.82	0.93	1.12	0.93	1.24	0.82	0.96	0.66	0.96	1.06	1.06	0.53	0.67
Al ₂ O ₃	12.46	12.6	12.02	11.96	11.82	13	12.21	11.49	12.02	12.56	11.93	12.08	12.08	11.91	12.05
Fe ₂ O ₃	2.41	3.02	2.65	2.01	2.33	2.58	3.12	1.94	2.04	2.23	3.14	3.91	3.91	2.72	2.31
MnO	0.03	0.03	0.54	0.03	0.03	0.06	0.03	0.02	0.03	0.05	0.72	0.11	0.11	0.07	0.05
MgO	0.03	0.05	0.04	0.08	0.07	0.05	0.03	0.09	0.07	0.06	0.03	0.02	0.02	0.06	0.06
CaO	0.82	0.72	0.93	1.02	1.01	0.84	0.86	1.02	0.94	2.47	1.32	1.71	1.71	1.65	1.34
Na ₂ O	1.27	2.06	1.76	2.00	1.77	1.87	2.10	2.05	2.02	1.95	1.93	2.02	2.02	1.99	1.90
K ₂ O	2.36	2.92	2.53	2.59	2.93	2.51	2.72	2.04	2.63	0.42	2.18	2.63	2.63	2.20	2.01
P ₂ O ₅	0.005	0.01	0.02	0.005	0.02	0.01	0.01	0.005	0.11	0.01	0.005	0.02	0.02	0.03	0.01
LOI	0.36	0.26	0.31	0.36	0.36	0.4	0.27	0.42	0.36	0.33	0.37	0.34	0.34	0.41	0.29
*CIA	73.68	68.85	69.72	68.07	67.43	71.35	68.25	69.22	68.26	72.18	68.72	65.51	65.51	67.10	69.65

*Chemical Index of Alteration

Table 2: Major oxide and CIA values for Samples in wt. % (n = 15)

Major Oxides	MIN.	MAX.	MEAN
SiO ₂	76.10	80.1	78.24
TiO ₂	0.53	1.24	0.90
Al ₂ O ₃	11.49	13	12.15
Fe ₂ O ₃	1.94	3.91	2.69
MnO	0.02	0.72	0.13
MgO	0.02	0.09	0.05
CaO	0.72	2.47	1.22
Na ₂ O	1.27	2.1	1.91
K ₂ O	0.42	2.93	2.35
P ₂ O ₅	0.005	0.11	0.02
CIA	65.51	73.68	68.90

Table 3: Un-normalized Rare Elements Analysis of Samples SL1-SL15 (in ppm)

REE	SL1	SL2	SL3	SL4	SL5	SL6	SL7	SL8	SL9	SL10	SL11	SL12	SL13	SL14	SL15
Sc	4	9	4	6	4	3	2	9	6	7	7	8	2	2	7
Y	342	122	464	186	159	706	192	103	820	30	356	247	132	726	63
La	133	152	91	134	126	127	118	121	133	40	146	78	64	113	140
Ce	148	121	122	168	184	199	156	189	164	55	159	110	124	246	132
Pr	4	9	11	2	4	6	4	5	4	9	5	9	4	9	6
Nd	48	52	56	62	41	82	38	50	67	71	64	41	42	47	62
Pm	7	5	9	3	3	4	13	4	3	5	5	7	11	6	3
Eu	4	2	4	7	4	6	5	3	5	11	3	5	1	3	2
Gd	9	3	3	3	2	7	4	4	3	14	12	2	5	7	16
Tb	2	<1	3	10	16	5	1	12	9	7	4	1	1	5	4
Ho	2	3	5	7	1	3	8	2	4	2	5	12	1	9	7
Er	3	2	2	4	6	7	4	6	5	3	4	<1	3	9	6
Tm	9	4	5	4	9	5	2	6	5	13	8	4	1	3	8
Yb	26	10	12	6	17	14	19	7	8	14	33	8	13	18	38
Lu	8	4	5	4	5	11	4	6	4	7	6	3	1	8	4

Table 3: Rare Earth Elements and their Chondrite Concentration (after McLennan 1989; Barat *et al.* 2012; Obaje *et al.* 2015)

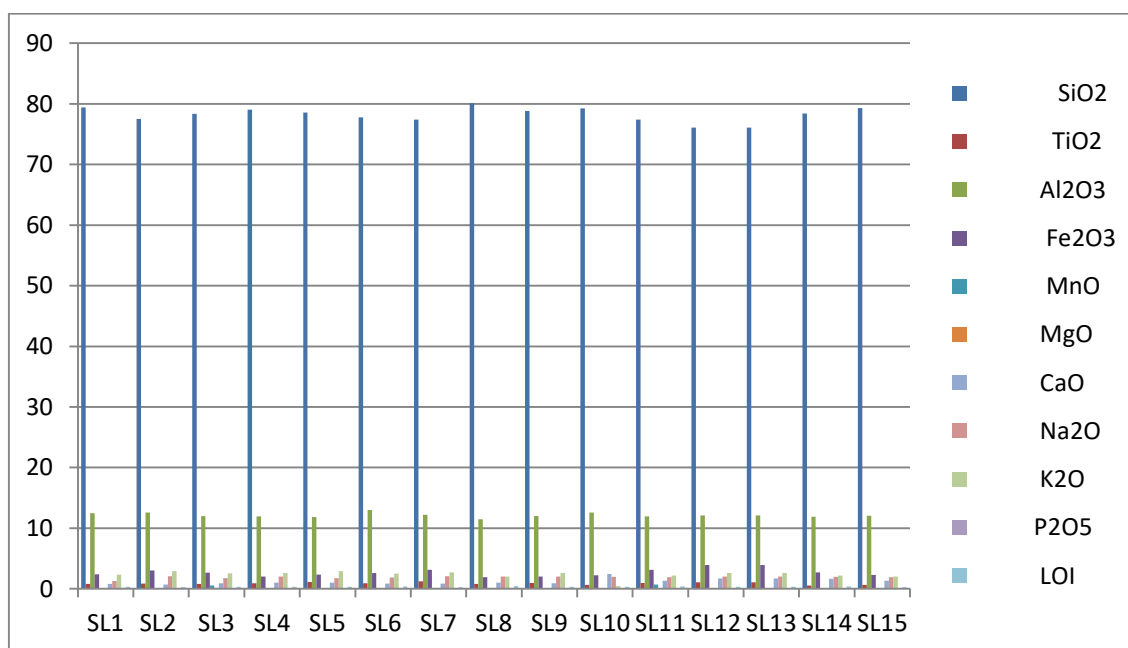
S/NO	Rare Earth Element (REE)	Ordinary and CI-Chondrite (ppm)
1	Sc	5.58
2	Y	1.56
3	La	0.325
4	Ce	0.798
5	Pr	0.122
6	Nd	0.567
7	Pm	-
8	Sm	0.186
9	Eu	0.0692
10	Gd	0.255
11	Tb	0.047
12	Dy	0.305
13	Ho	0.070
14	Er	0.029
15	Tm	0.03
16	Yb	0.209
17	Lu	0.0349

Table 4: Chondrite Normalized Rare Earth Elements Concentrations of SL1-SL15 (in ppm)

Loc.	(Sc) _n	(Y) _n	(La) _n	(Ce) _n	(Pr) _n	(Nd) _n	(Eu) _n	(Gd) _n	(Tb) _n	(Ho) _n	(Er) _n	(Tm) _n	(Yb) _n	(Lu) _n
SL1	0.71	219.3	409.23	185.46	32.78	84.65	57.8	35.29	42.55	28.57	14.35	300	124.4	229.22
SL2	1.61	78.205	467.69	151.62	73.77	91.71	28.9	11.76	21.27	42.86	9.57	133.33	47.84	114.61
SL3	0.71	297.43	280	152.88	90.16	98.76	57.8	11.76	63.82	71.43	9.57	166.66	57.42	143.27
SL4	1.07	119.23	412.3	210.52	16.46	109.34	101.16	11.76	212.77	100	19.34	133.33	28.71	114.61
SL5	0.71	101.92	387.69	230.57	32.78	72.31	57.8	7.84	340.43	14.3	28.71	300	81.33	143.27
SL6	0.53	452.56	390.76	249.37	49.18	144.62	86.71	27.45	106.38	42.56	33.49	166.66	66.99	315.19
SL7	0.36	123.07	363.07	195.48	32.78	67.01	72.25	15.67	21.27	114.3	19.14	66.66	90.91	114.61
SL8	1.61	66.03	372.3	236.84	40.98	88.18	43.35	15.67	255.32	28.57	28.71	200	33.49	171.92
SL9	1.07	525.64	409.23	205.51	32.78	118.16	72.25	11.76	191.49	57.14	23.92	166.66	38.27	114.61
SL10	1.25	19.23	123.07	68.92	73.77	125.22	158.96	54.9	85.11	28.57	14.35	433.33	66.99	200.57
SL11	1.25	228.2	449.23	199.25	40.98	112.87	43.35	47.05	21.27	71.43	19.14	266.66	157.89	171.92
SL12	1.43	158.33	240	137.87	73.77	72.31	72.25	7.84	21.27	171.43	4.78	133.33	38.28	85.96
SL13	0.36	84.61	196.92	155.4	32.78	74.07	14.45	19.61	106.38	14.3	14.35	33.33	62.2	28.65
SL14	0.36	465.38	347.69	308.27	73.77	82.89	43.35	27.45	85.11	128.57	43.06	100	86.12	229.22
SL15	1.25	40.38	430.76	165.41	49.18	109.34	28.9	62.74	21.27	100	28.71	266.66	181.82	114.61

Table 5: Ratios of Ce/Ce*, Eu/Eu* and (La/Yb)_n for Samples SL1-SL15

S/No	Ce/Ce*	Eu/Eu*	(La/Yb) _n
SL1	0.8	0.07	3.3
SL2	0.8	0.07	9.78
SL3	0.8	0.07	4.88
SL4	0.8	0.07	14.36
SL5	0.8	0.07	4.77
SL6	0.8	0.07	5.82
SL7	0.8	0.07	3.99
SL8	0.8	0.07	11.12
SL9	0.8	0.07	10.69
SL10	0.8	0.07	1.8
SL11	0.8	0.07	2.85
SL12	0.8	0.07	6.27
SL13	0.8	0.07	3.17
SL14	0.8	0.07	4.04
SL15	0.8	0.07	2.37
Average	0.8	0.07	5.95

**Figure 1: Spatial distribution of major oxides in Stream Sediments from the Study Area**

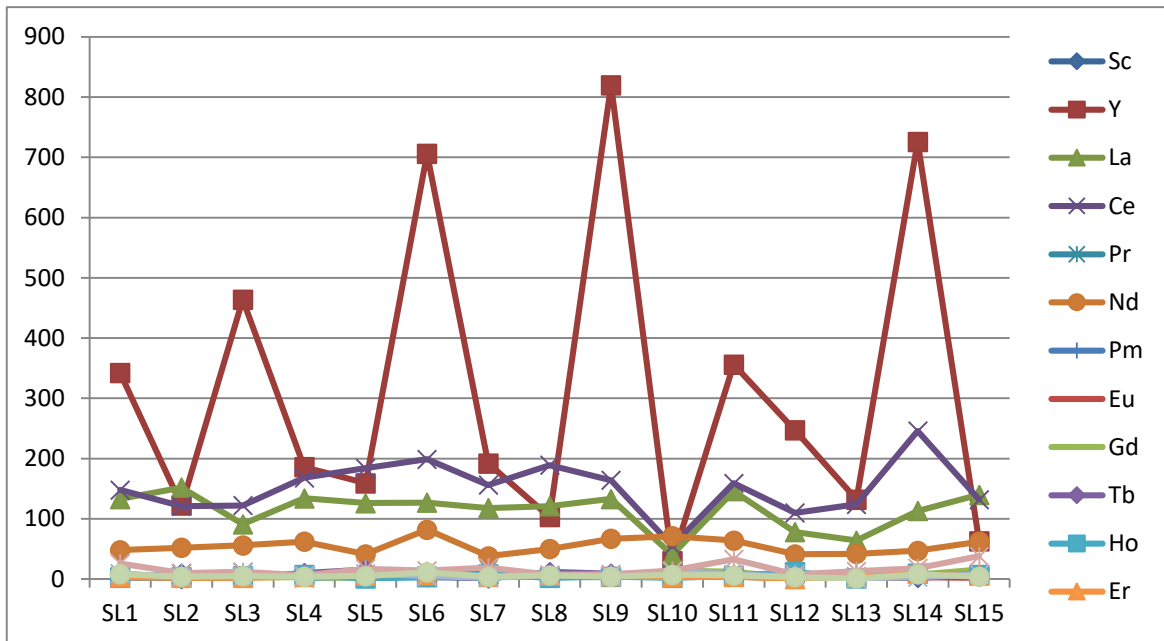


Figure 2: Plot of spatial distribution of REE in the Study Area

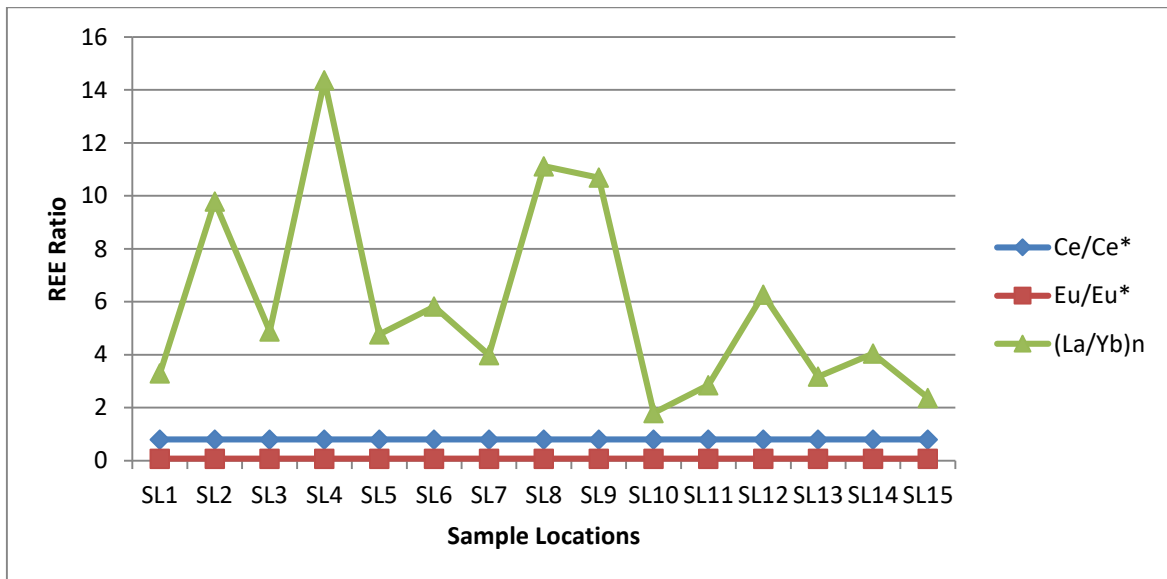


Figure 3: Plot of some REE ratios in stream sediments from the Study Area

68.90%. The CIA values further confirmed that the stream sediments have felsic granitic source rocks.

The rare earth elements analyzed are Sc, Y, La, Ce, Pr, Nd, Pm, Eu, Gd, Tb, Ho, Er, Tm, Yb and Lu. Using highest to lowest mean concentration values, Y has mean values of 309.87 ppm with range of 30.00-820.00 ppm. Ce has mean values of 151.80 ppm with range of 55.00-246.00 ppm. La has mean values of 114.40 ppm with range of 40.00-152.00 ppm. Nd

has mean values of 54.87 ppm with range of 38.00-82.00 ppm and Yb has mean values of 16.20 ppm with range of 6.00-38.00 ppm. Conversely, Sc, Pr, Pm, Eu, Gd, Tb, Ho, Er, Tm and Lu have < 15.00 ppm average concentration values in the study area. The rare earth elements were normalized using Ordinary and C1-Chondrites, respectively. The result of the rare earth elements ratios, e.g., Ce/Ce*, Eu/Eu* and (La/Yb)_n were calculated. Ce/Ce*(0.80) indicated an oxidizing environment of sediments deposition at low fluvial flow energy. Eu/Eu* (0.07) also indicated an oxidizing environment and felsic granitic source rock. (La/Yb)_n (5.95) also indicated oxidizing environment in a low fluvial flow energy with coarse and clay size sediments input.

CONCLUSION

The average concentrations of SiO₂ (78.24 wt. %) and Al₂O₃ (12.15 wt. %) and the chemical index of alteration (CIA) values of 68.90% indicate felsic granitic source rocks. The average ratio of Ce/Ce* (0.80) indicates that the source stream from which the sediments were collected flew with low flow energy in an oxidizing environment. Similarly, the average ratio of Eu/Eu* (0.07) points to an oxidizing environment with felsic granitic source rock. On the other hand, the average ratio of (La/Yb)_n (5.95) is indicative of an oxidizing environment in a low stream flow energy with coarse-grained and clay size sediments input. The ascending order of the spatial concentrations/distribution of the rare earth elements in the study area is Y>Ce> La> Yb >Nd, while the descending order of concentrations is Sc< Pr< Pm< Eu< Gd< Tb< Ho< Er< Tm<Lu.

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