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Provenance, Tectonic Setting, Source Area Weathering and Paleoenvironment of the Ilaro Formation, Dahomey Basin, Nigeria

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Abstract
The provenance, tectonic setting, source area weathering and paleoenvironment of the Ilaro sandstone of the Dahomey basin have been assessed using geochemical studies. The source area analyses suggest that the sediments were derived from felsic, intermediate and mafic sources with contributions from recycled quartz-rich older sediments. The Chemical Index of Alteration (CIA), Chemical Index of Weathering (CIW), Plagioclase Index of Alteration (PIA), Mineralogical Index of Alteration (MIA), higher Al/K ratio and the A-CN-K ternary plot of the studied samples suggests that the sediments were derived during intense chemical weathering of the source area. The Th/U-Th plot showed a wide trend above the upper crust value; the overall scenario suggests that weathering conditions were high and not constant during sedimentation. Tectonic discrimination diagrams shows the samples plotting mainly in the active continental margin and passive margin zones. The paleoenviromental and paleoclimatic results suggest that the Ilaro sandstone was deposited in mostly oxic humid conditions in a non-marine deltaic environment and the paleosalinity based on low Sr/Ba ratio indicates low saline water during deposition and a continental enviroment of deposition

Keywords: Ilaro Formation, Provenance, tectonic, weathering, paleoenviroment

1. Introduction

Sedimentary rocks can provide vital information for provenance studies, and for reconstructing the tectonic, climate, and geographic setting of sedimentary basins (Basu, 1985). The geochemistry of clastic sediments is the product of interacting factors including provenance, sorting, weathering and tectonism (Johnsson, 1993; McLennan et al., 1993). Major elements and some trace elements like Sc, Zr, Co, Hf, Cr, Y, Th, including rare earth elements (REEs) and their elemental ratios are sensitive indicators of the source rocks, tectonic setting, paleoweathering conditions and paleoclimate of the clastic sedimentary rocks (Bhatia, 1983; Bhatia and Crook, 1986; Roser and Korsch, 1986, 1988; McLennan and Taylor, 1991; Johnsson and Basu, 1993; McLennan et al., 1993; Condie, 1993; Nesbitt et al., 1996; Fedo et al., 1997; Cullers and Podkovyrov, 2000, 2002).

The evolution of the Dahomey Basin (Fig. 1) is generally believed to be due to rifting phenomenon associated with the separation of the mega-continent called Gondwanaland during the early Cretaceous. According to Agagu (1985) the stratigraphy in most parts of the basin is dominated by alternating sands and shales with minor proportion of limestone. Detailed stratigraphy of the Basin has been delineated by several workers (Jones and Hockey, 1964; Adegoke, 1969; Ogbe, 1972; Billman, 1976; Ako et al., 1980; Omatsola and Adegoke, 1981; Okosun, 1990). The Ilaro Formation overlies conformably the Oshosun Formation and consists of massive, yellowish, poorly consolidated, fine to coarse, cross-bedded sandstones, clays and shales with occasional thin bands of phosphate beds being observed at Ilaro. The formation is Eocene in age. The formation are outcropping sandstone deposits that occurs in Ilaro, Ogun-State, South western Nigeria. Generally, Ilaro is on a relief of 200m above sea level and lies between latitude 6°50`N and 6°57`N and Longitude 2°58`E and 3°05`E. The study area is accessible through Papalanto-Ifo road towards Ilaro town. It is also accessible by major road, minor roads and several footpaths. This present research is aimed at interpreting the sediment source-area weathering, provenance, tectonic setting of the Ilaro Formation based on major element, trace and rare earth elements geochemical data.

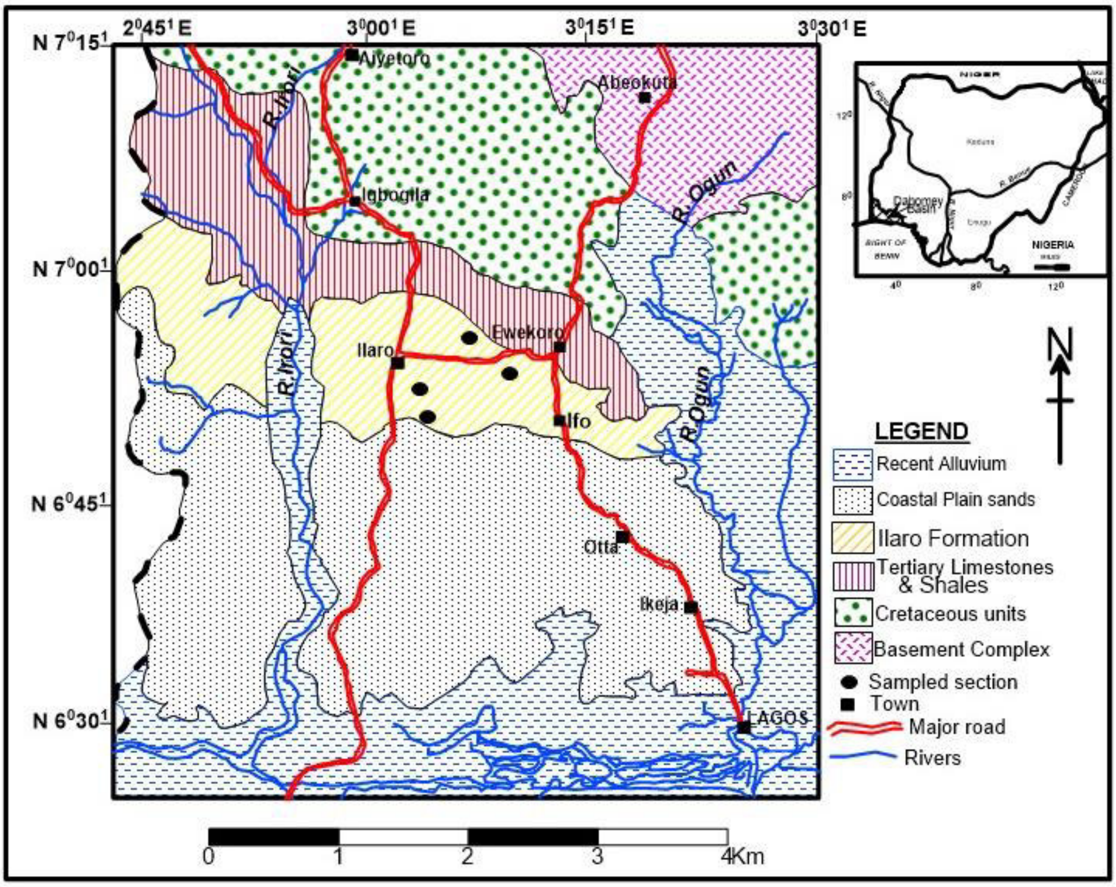


Figure 1. Geological Map of part of the Eastern Dahomey Basin (Modified from Agagu, 1985).

2. Methodology

Ten samples were analyzed for major oxides, trace and rare earth elements using XRay Fluorescence (XRF) and LA-ICP-MS at Stellenbosch University, South Africa. Pulverised sandstone samples were analysed for major element using Axios instrument (PANalytical) with a 2.4 kWatt Rh X-ray Tube. The detailed procedures for sample preparation for the analytical technique are reported below.

Fusion bead method for Major element analysis:

- Weigh 1.0000 g ± 0.0009 g of milled sample
- Place in oven at 110 ºC for 1 hour to determine H2O+
- Place in oven at 1000 ºC for 1 hour to determine LOI
- Add 10.0000 g ± 0.0009 g Claisse flux and fuse in M4 Claisse fluxer for 23 minutes.
- 0.2 g of NaCO3 was added to the mix and the sample+flux+NaCO3 was pre-oxidized at 700 °C before fusion.
- Flux type: Ultrapure Fused Anhydrous Li-Tetraborate-Li-Metaborate flux (66.67 % $Li_2B_4O_7$ + 32.83 % $LiBO_2$) and a releasing agent Li-Iodide (0.5 % LiI).

The result returned eleven major elements, reported as oxide percent by weight (SiO_2, TiO_2, Al_2O_3, Fe2O3, MgO, MnO, CaO, Na_2O, K_2O, SO_3 and P_2O_5). Loss on Ignition (LOI) is a test used in XRF major element analysis which consists of strongly heating a sample of the material at a specified temperature, allowing volatile substances to escape or oxygen is added, until its mass ceases to change. The LOI is made of contributions from the volatile compounds of H_2O+, OH-, CO_2, F-, Cl-, S; in parts also K+ and Na+ (if heated for too long); or alternatively added compounds O2 (oxidation, e.g. FeO to Fe_2O_3), later CO_2 (CaO to $CaCO_3$). In pyro-processing and the mineral industries such as lime, calcined bauxite, refractories or cement manufacturing industry, the loss on ignition of the raw material is roughly equivalent to the loss in mass that it will undergo in a kiln, furnace or smelter. The trace and rare elemental data for this work was acquired using Laser Ablation inductively coupled plasma spectrometry (LA-ICP-MS) analyses. The analytical procedures are as follows: Pulverised sandstone samples were analysed for trace element using LA-ICP-MS instrumental analysis. LA-ICP-MS is a powerful and sensitive analytical technique for multi elemental analysis. The laser was used to vaporize the surface of the solid sample, while the vapour, and any particles, were then transported by the carrier gas flow to the ICP-MS. The detailed procedures for sample preparation for both analytical techniques are reported below.

Pressed pellet method for Trace element analysis:

- Weigh 8 g ± 0.05 g of milled powder
- Mix thoroughly with 3 drops of Mowiol wax binder
- Press pellet with pill press to 15 ton pressure
- Dry in oven at 100 ºC for half an hour before analysing.

The petrography of the sandstone samples was determined by point-counting each thin section.

3. Source area Composition

The geochemical records of clastic sediments have been used to infer their provenance characteristics (Cullers *et al.*, 1988, Taylor and McLennan, 1985; Condie *et al.*, 1992). The rare earth elements (REE), high field strength elements (Zr, Hf, Y and Nb), some transition trace elements (TTE) e.g. Sc, Co, Cr and Ni along with Al, Ti and Th are considered to be relatively immobile during sedimentary processes and thus are useful in discriminating source area composition of clastic sedimentary rocks (Taylor and McLennan, 1985; Wronkiewicz and Condie, 1987; Madhavaraju and Ramasamy, 2002; Armstrong-Altrin *et al.*, 2004). Tables 1 and 2 are major and trace elements concentration and rare earth elements concentrations respectively of the Ilaro Formation samples analysed.

High field strength elements (HFSE) are preferentially partitioned into melts during crystallization and anatexis, and are therefore enriched in felsic rocks than mafic rocks (Feng and Kerrich, 1990). Transition elements, on the other hand, are well-suited in magmatic processes and are highly concentrated in mafic and ultramafic rocks than felsic rocks. The significant enrichment of Zr, Nb, Hf and Ta among the HFSE and depletion of most of the TTE relative to UCC (Fig. 2) can be interpreted as indication of the studied sediments coming from more felsic and fractionated source. The marked enrichments in Zr, Nb, Hf and Co suggest more evolved (felsic) material in the source rocks with minor contribution from basic rocks. Ratios such as Al/Ti, Th/Cr, Th/Co, Th/Sc, and La/Sc in clastic rocks are essentially used to infer the source rock compositions. Aluminum, Th and La are typically enriched in felsic source rocks whereas Ti, Cr, Co and Sc are relatively more concentrated in mafic rocks (Taylor and McLennan, 1985; Cullers *et al.*, 1988, Fralick and Kronberg, 1997; Hayashi *et al.*, 1997). Al/Ti, Th/Cr, Th/Co, Th/Sc and La/Sc ratios of samples from this study compared with those sediments derived from felsic and basic rocks (fine fraction) as well as to UCC values (Table 3), this shows the samples falling within mixed ranges of felsic and mafic rocks. The triangular plot of La-Th-Sc (Fig. 3) and bivariate plot of Th/Co *vs*. La/Sc ratios (Fig. 4) of the analysed samples suggest derivation from felsic rocks of granite and granodiorite composition.

The REE chondrite-normalized patterns and europium anomaly of clastic sedimentary rocks are also used to provide important clues regarding the source rock composition (Taylor and McLennan, 1985; Wronkiewicz and Condie, 1987). Mafic rocks show less fractionated chondrite-normalized patterns with low LREE/HREE ratios and no or small Eu anomalies, whereas felsic rocks usually show fractionated chondrite-normalized patterns with high LREE/HREE and negative Eu anomalies (Cullers, 1994; Cullers and Graf, 1984; Taylor and McLennan, 1985).

Table 1: Major (wt %) and trace (ppm) elements concentration of the samples of Ilaro Formation

S/N	**IL 1**	**IL 2**	**IL 3**	**IL 4**	**IL 5**	**IL 6**	**IL 7**	**IL 8**	**IL 9**	**IL 10**	**Average**	**UCC**
SiO_2	84.6	84.96	81.21	94.96	94.06	89.17	96.36	87.32	84.26	86.68	88.36	65.89
Al_2O_3	8.9	9.26	10.51	2.27	3.2	6.01	1.14	7.74	7.57	6.16	6.28	15.17
Fe_2O_3	1.95	1.29	3.03	0.28	0.29	0.93	0.7	1.31	4.22	3.75	1.78	5
MnO	0.01	0	0.01	0	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.07
MgO	0.04	0.04	0.06	0.05	0.05	0.08	0.06	0.04	0.05	0.05	0.05	2.2
CaO	0.03	0.03	0.04	0.03	0.03	0.05	0.03	0.03	0.04	0.03	0.03	4.19
Na_2O	0	0	0	0	0	0	0	0	0	0	0	3.90
K_2O	0.03	0.05	0.04	0.02	0.03	0.03	0.02	0.02	0.03	0.03	0.03	3.39
TiO_2	0. 63	0.44	0.6	0.52	0.46	0.73	0.36	0.45	0.36	0.3	0.47	0.5
P_2O_5	0.03	0.02	0.04	0.02	0.02	0.03	0.01	0.02	0.08	0.08	0.04	0.2
LOI	3.54	3.58	4.44	0.86	1.24	2.46	0.51	3.1	3.4	2.88	2.6	-
Sc	8.21	8.08	8.77	8.91	9.07	10.96	7.31	8.8	11.04	10.71	9.19	13.6
V	63.46	40.79	68.89	28.8	26.96	48.46	25.82	39.77	69.11	72.4	48.45	107
Cr	41.35	38.19	61.81	26.68	26.69	47.97	27.27	37.94	47.27	40.36	39.55	85
Co	148.33	177.12	168.44	347.04	272.27	217.27	529.85	227.9	139.67	162.48	239.04	17
Ni	16.42	14.44	19.51	17.82	13.26	22.76	19.61	18.6	16.34	14.71	17.35	20
Cu	12.47	12.82	12.75	20.22	8.46	29.83	15.41	20.66	17.95	16.02	16.66	25
Zn	35.5	28.92	24.28	30.32	25.29	51.54	21.08	39.23	29.17	18.82	30.42	71
Y	9.94	7.09	9	8.77	8.17	11.16	6.99	8.09	8.29	6.41	8.39	22
Zr	308.08	185.76	275.14	419.17	347.97	565.71	491.87	374.24	132.29	122.31	322.25	190
Nb	16.42	11.73	16.99	13.8	12.69	21.66	8.72	11.08	11.99	10.05	13.51	12
Mo	1.31	0.73	1.46	0.86	0.81	1.31	0.58	0.89	2	1.86	1.18	1.5
Hf	8.25	5.44	8.08	10.38	8.81	14.57	12.23	9.12	3.74	2.97	8.36	5.8
Ta	1.55	1.31	1.52	1.65	1.53	2.3	2.01	0.97	1.04	1.02	1.49	1
Rb	2.07	3.8	4.41	2.51	2.97	5.33	2.07	2.7	2.42	1.81	3.01	112.2
Sr	16.17	15.06	22.57	16.46	21.71	22.76	10.18	14.09	57.29	44.78	24.11	350
Cs	0.26	0.46	0.65	0.44	0.56	1.2	0.34	0.36	0.33	0.3	0.49	4.6
Ba	23.59	28.52	33.88	30.25	28.87	29.49	17.75	21.45	59.22	43.8	31.68	550
Pb	22.71	26.32	15.86	12.18	12.89	23.93	6.56	22.29	13	10.44	16.62	17
Th	11.01	7.58	11.11	4.99	5.35	9.18	3.1	10.61	7.39	5.96	7.63	10.7
U	0.98	0.82	1.31	1.37	1	2	1.16	1.3	1.93	1.81	1.37	2.8

UCC: Upper Continental Crust (Taylor and McLennan, 1985; 1995)

The studied samples of Ilaro Formation show fractionated chondrite-normalized REE patterns of enriched LREE and nearly flat REE with pronounced negative Eu anomalies (Fig. 5). These patterns as well as high LREE/HREE ratios (4.38-28.78; avg. = 15.51; n = 10) and negative Eu anomalies (0.54-0.74) values suggest that these rocks were derived from predominantly felsic rocks of the upper continental crust.

Using data from Table 4; in the QFL ternary diagram, the samples plotted in the craton interior field (Fig. 6); according to Dickinson et al (1983) sandstones plotting in the craton field are mature sandstones derived from relatively low-lying granitoid and gneissic sources, supplemented by recycled sands from associated platform or passive margin basins. The major element-based provenance discriminant function diagram of Roser and Korsch (1988) discriminates four major provenance categories of mafic igneous, intermediate igneous, felsic igneous, and quartzose recycled sedimentary. This discriminant function diagram indicates a quartzose recycled sedimentary source for Ilaro sandstone (Figure 7). According to Roser (2000), sediments recycled from felsic sources plot progressively away from the igneous source line into the quartzose field. The concentration of zircon is used to characterize the nature and composition of source rock (Hayashi et al., 1997). Hayashi, et al. (1997) stated that the TiO_2/Zr ratios are so much supportive to distinguish among three different source rock types, i.e., felsic, intermediate and mafic.

Table 2: Rare Earth Element Concentrations (ppm) of the analysed samples of Ilaro Formation

S/N	IL 1	IL 2	IL 3	IL 4	IL 5	IL 6	IL 7	IL 8	IL 9	IL 10	Average	UCC
La	24.69	22.25	28.68	11.21	14.6	20.36	6.6	28.49	28.84	22.07	20.78	30
Ce	43.68	39.03	53.81	20.88	28.5	46.21	14.45	55.02	51.08	38.33	39.1	64
Pr	3.9	3.57	4.97	2.62	3.09	4.19	1.65	5.4	6.06	4.62	4.01	7.1
Nd	12.37	10.48	14.84	8.15	10.5	13.42	6.3	19.04	23.47	17.3	13.59	26
Sm	1.7	1.27	2.13	1.57	1.78	2.3	1.49	2.27	4.1	2.87	2.15	4.5
Eu	0.29	0.29	0.46	0.24	0.31	0.48	0.23	0.37	0.9	0.56	0.41	0.88
Gd	1.32	1.23	1.79	1.18	1.5	2.06	1.55	2.04	3.37	1.87	1.79	3.8
Tb	0.25	0.19	0.33	0.2	0.22	0.27	0.19	0.26	0.4	0.29	0.26	0.64
Dy	1.57	1.28	1.86	1.77	1.57	2.2	1.34	1.28	2.17	1.58	1.66	3.5
Ho	0.29	0.31	0.35	0.32	0.4	0.52	0.3	0.32	0.4	0.29	0.35	0.8
Er	0.8	0.86	1.05	1.15	1.06	1.42	1.02	0.91	0.93	0.66	0.99	2.3
Tm	0.09	0.09	0.18	0.17	0.18	0.23	0.16	0.16	0.12	0.1	0.15	0.33
Yb	1.07	1.03	1.05	1.26	1.17	1.76	1.08	1.03	0.77	0.55	1.08	2.2
Lu	0.16	0.16	0.15	0.13	0.17	0.24	0.19	0.21	0.19	0.08	0.17	0.32
ΣREE	92.18	82.04	111.65	50.85	65.05	95.66	36.55	116.8	122.8	91.17	86.48	183
Eu/Eu*	0.59	0.71	0.72	0.54	0.58	0.67	0.46	0.53	0.74	0.74	0.63	0.66
Ce/Ce*	3.54	3.48	3.59	3.06	3.38	3.98	3.48	3.53	3.07	3.02	3.41	1.02
$(La/Yb)_N$	16.55	15.5	19.59	6.38	8.95	8.3	4.38	19.84	26.87	28.78	15.51	9.69
$(La/Sm)_N$	9.38	11.31	8.69	4.61	5.3	5.71	2.86	8.1	4.54	4.96	6.55	4.27
$(Gd/Yb)_N$	1.02	0.99	1.41	0.77	1.06	0.97	1.19	1.64	3.62	2.81	1.55	1.36

$Eu/Eu^* = Eu_N/(Sm_N \times Gd_N)^{0.5}$ and $Ce/Ce^* = Ce_N/(La_N \times Pr_N)^{0.5}$, where N subscript indicates normalization to chondrite. UCC: Upper Continental Crust (Taylor and McLennan, 1985).

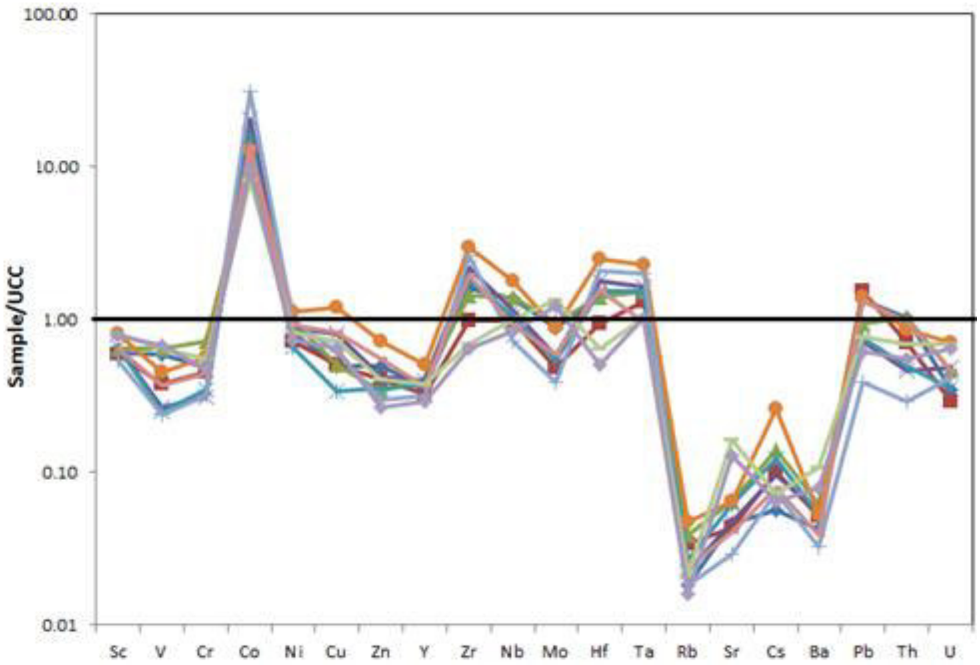


Figure 2: UCC normalized trace elements distribution of sandstone samples of Ilaro Formation. UCC data after Taylor and McLennan (1985; 1995)

The TiO_2 versus Zr plot (Fig. 8) shows the sandstones plotting in both intermediate and felsic zones; this may be due to the sandstones coming from more than one source. The ternary diagram in figure 9 shows all the samples plotting in the SiO_2 end far away from the granite, ultramafic and basalts areas; this suggests derivation from recycled quartz-rich sediments.

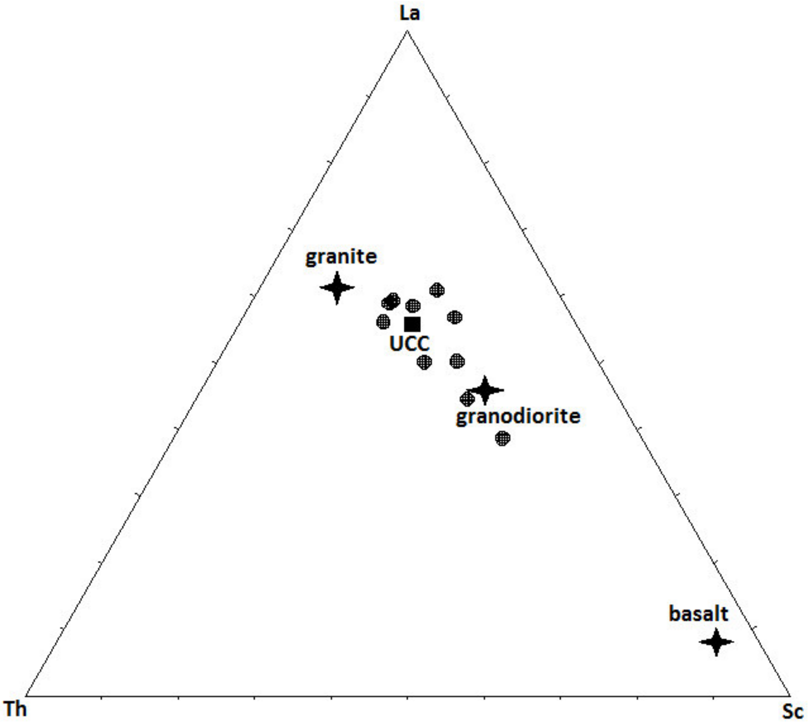


Figure 3. La-Th-Sc ternary plot of the analysed samples of Ilaro Formation (after Jahn and Condie, 1995). Composition of granite, granodiorite, basalt and UCC are also plotted as references

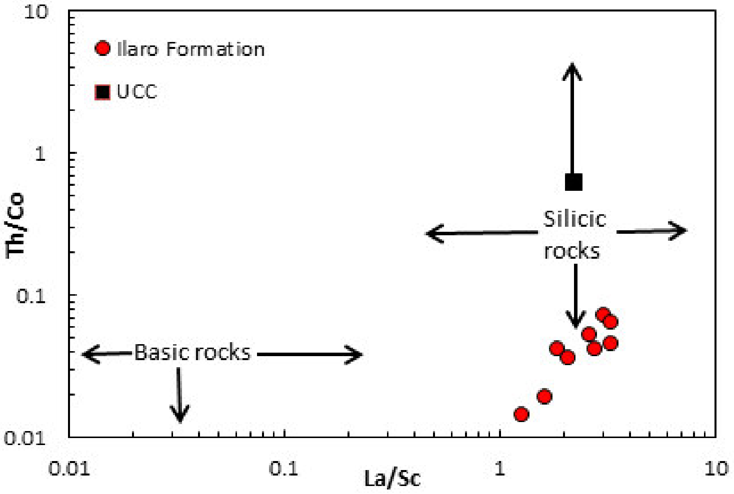


Figure 4. Th/Co versus La/Sc diagram for the samples of Ilaro Formation (Fields after Cullers, 2000)

Table 3: Elemental ratio of the studied samples compared to felsic rocks, mafic rocks and UCC

Ratios	Ilaro Formation	Felsic rocks	Mafic rocks	UCC
Al/Ti	3.17 - 21.05	21 - 70	3.00 - 8.00	30.34
Th/Sc	0.42 - 1.34	0.84 - 20.5	0.05 - 0.22	0.79
Th/Co	0.01 - 0.07	0.67 - 19.4	0.04 - 1.4	0.63
Th/Cr	0.11 - 0.28	0.13 - 2.7	0.018 - 0.046	0.13
La/Sc	0.90 - 3.27	2.5 - 16.3	0.43 - 0.86	2.21

According to Floyd et al. (1989) immobile elements, such as Ti and Ni, can be used to determine the original lithological composition of rocks and to separate immature sediments derived from a magmatic source from normal mature sediments. The Ilaro sandstone plots within the area of an acidic or felsic source (Fig. 10).

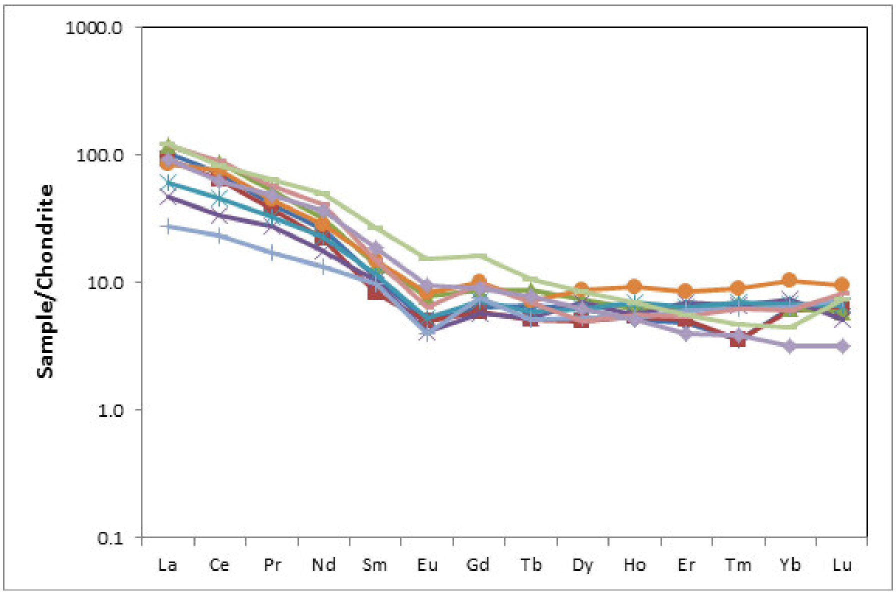


Figure 5: Chondrite-normalized REE pattern for the samples of Ilaro Formation. Chondrite-normalized values are from Sun and McDonough (1989)

The sources of a sedimentary rock suite can be determined using K versus Rb ratios that are generally comparable to standard continental crust values (Floyd et al., 1989). Figure 11 shows the samples plotting in the basic composition zone away from all fields. The Ilaro sandstone sample shows a high Hf component typical of a passive margin source with an increasing old sediment component (Fig. 12). The high Hf value may be due to the concentration of heavy minerals by sorting. One sample plotted in the felsic zone; two plotted in the mixed felsic/basic source but majority plotted in the increasing old sediment component area.

Cr/V–Y/Ni ratios also provide estimates of preferential concentration of chromium over other ferromagnesian elements (Hiscott, 1984; McLennan et al., 1993). The Cr/V ratio measures enrichment of Cr with respect to other ferromagnesian elements, whereas the Y/Ni ratio evaluates the relationship between the ferromagnesian trace elements (represented by Ni) and the HREE, using Y as a proxy (McLennan et al., 1993). Y/Ni ratios generally range across values typical of intermediate to felsic calc-alkaline rocks. Sediments derived from ultrabasic sources usually have high Cr/V ratios much greater than 1 coupled with low Y/Ni less than 1 (Hiscott, 1984). The Cr/V ratio for Ilaro sandstone is between

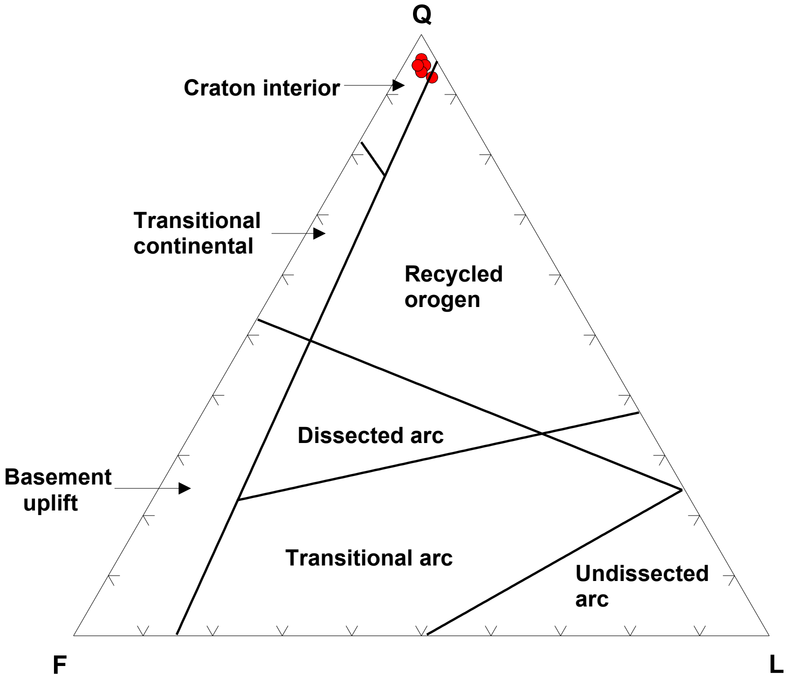


Figure 6. QFL plot showing framework modes for the Ilaro samdstones: Q is total quartz grains, including monocrystalline and polycrystalline types; F is total feldspar grains; L is total unstable lithic fragments. Provenance fields from Dickinson et al (1983).

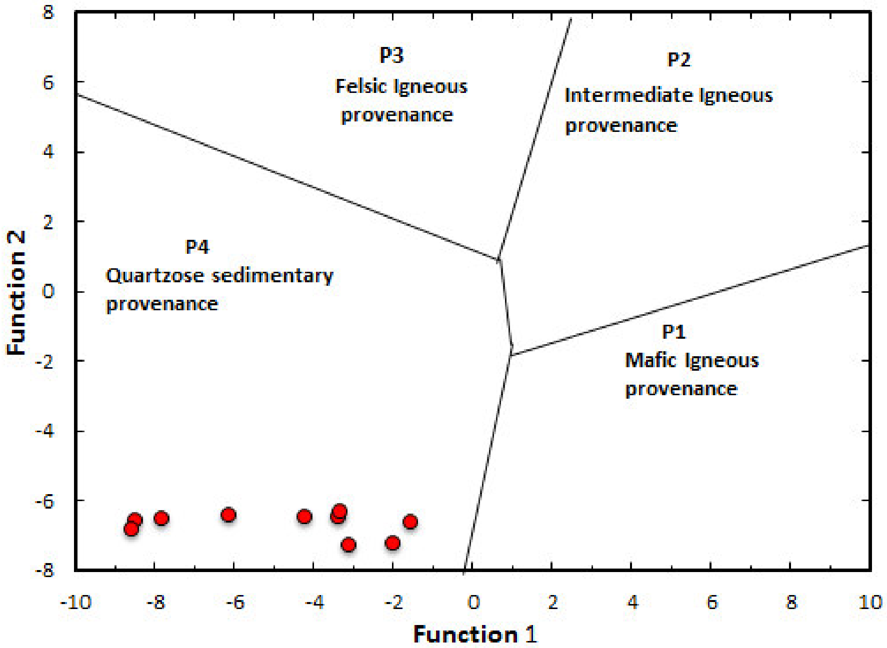


Figure 7. Major element provenance discriminant function diagram for the Ilaro sandstones (Roser and Korsch, 1988).

1.06 and 0.56 with an average of 0.86 while the Y/Ni ratios is between 0.36 and 0.62 (avg. = 0.49). The observed Cr/V and Y/Ni ratios are low, indicating felsic to intermediate source. Gu et al (2002) also proposed Co/Th versus La/Sc ratios as a provenance indicator; the samples plotted away from the Co/Th ratio of 1.27 and suggesting a mafic to intermediate source (fig. 13).

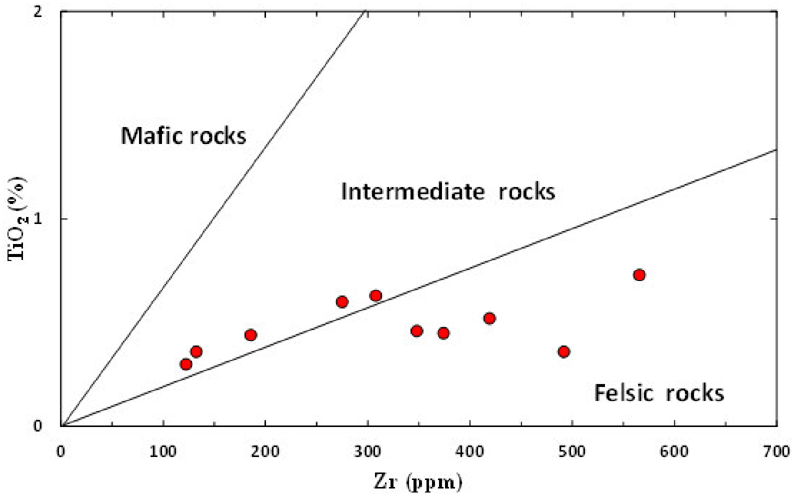


Figure 8. TiO_2-Zr plot for the sediments (Hayashi et al., 1997).

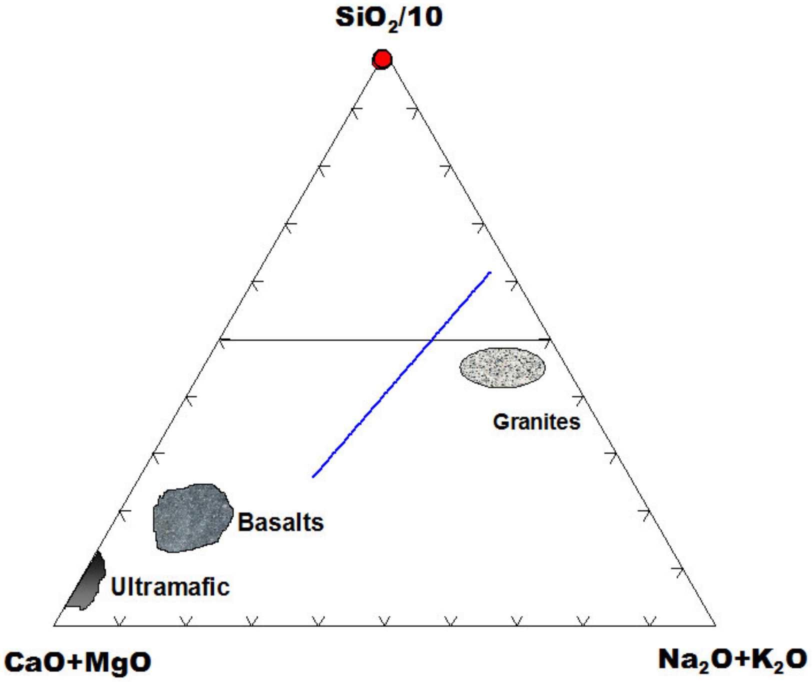


Figure 9. Plot of Na_2O + K_2O, $SiO_2/10$ and CaO + MgO to illustrate possible affinities of the samples to felsic, mafic and ultramafic rocks (after Taylor and McLennan, 1985).

To better constrain the mafic or ultramafic versus felsic character of the Ilaro sandstones, elemental ratios such as Cr/Th and Th/Sc were considered (fig. 14). According to some workers, Hofmann et al (2003) for example, high values of these ratios reflect enrichment in mafic-ultramafic and felsic components respectively. Ilaro sandstones fit a mixing hyperbolic curve between felsic and mafic end members with a major contribution from the felsic end member.

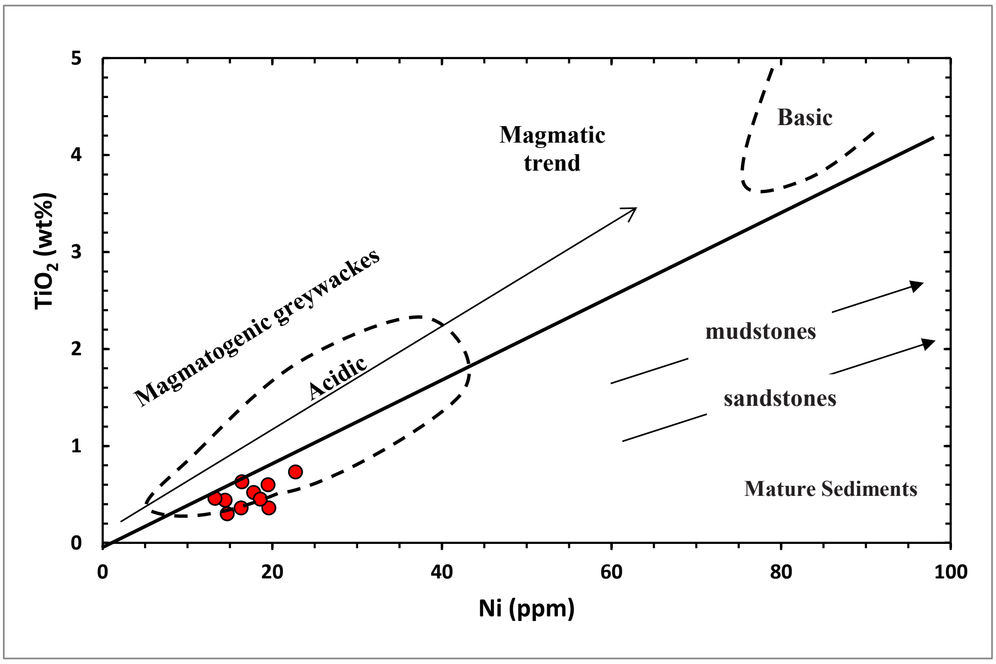


Figure 10. TiO_2 vs. Ni plot. Fields and trends after Gu et al. (2002) and Floyd et al. (1989).

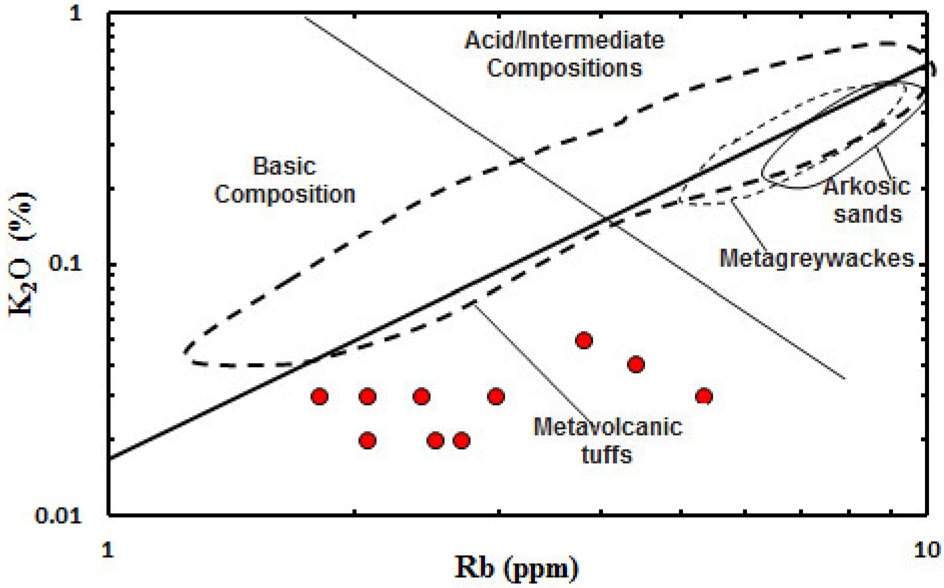


Figure 11. K_2O vs. Rb plot. Fields after Floyd and Leveridge (1987).

In the ternary diagram of V-Ni-Th*10 (fig. 15), fields representative of felsic, mafic and ultramafic rocks plot separately; all the samples plot between the felsic and mafic compositions, but more in the felsic area.

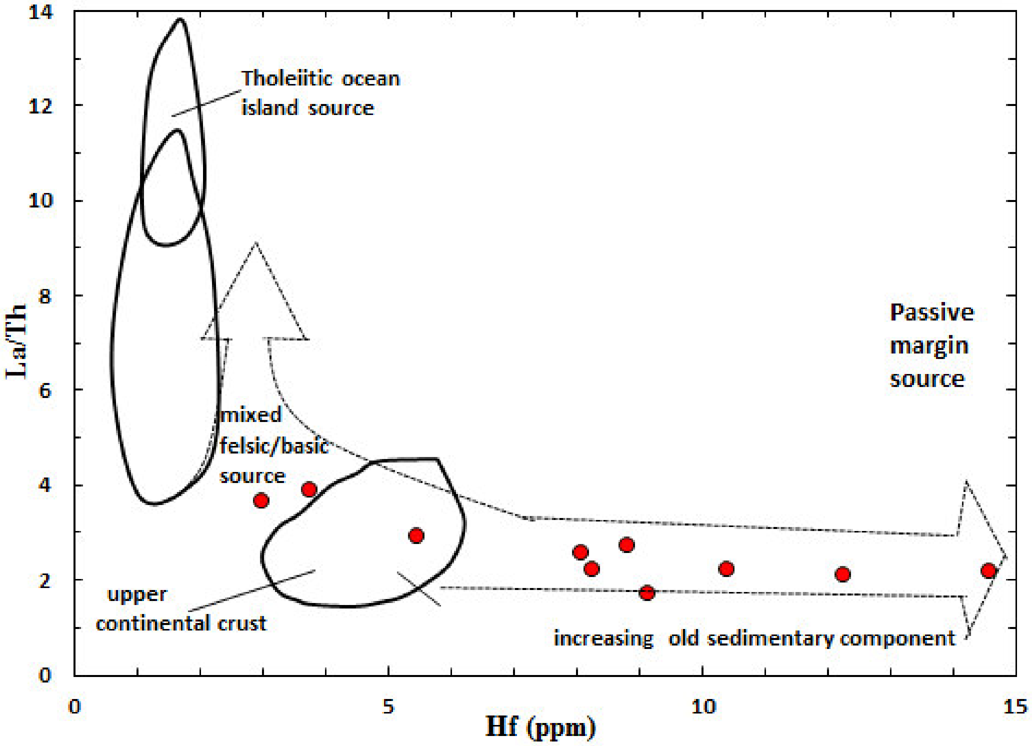


Figure 12: La/Th ratio vs. Hf plot. Fields after Floyd and Leveridge (1987) and Gu et al. (2002)

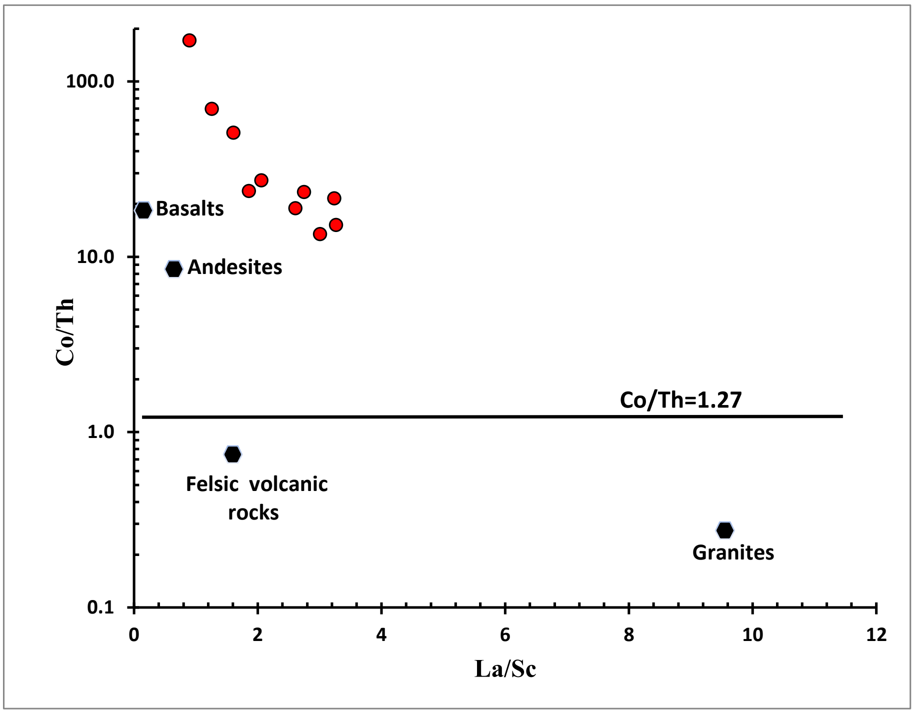


Figure 13: Co/Th ratio vs. La/Sc ratio plot. Average compositions of igneous rocks from Condie (1993) and Gu et al. (2002).

This also suggests a mixed composition of the source area. Average values of La/Co and Th/Co for the studied samples are 0.11 and 0.04 respectively. According to Cullers and Berendsen (1998), sands derived from granitoid sources show higher La/Co and Th/Co values than those derived from basic sources.

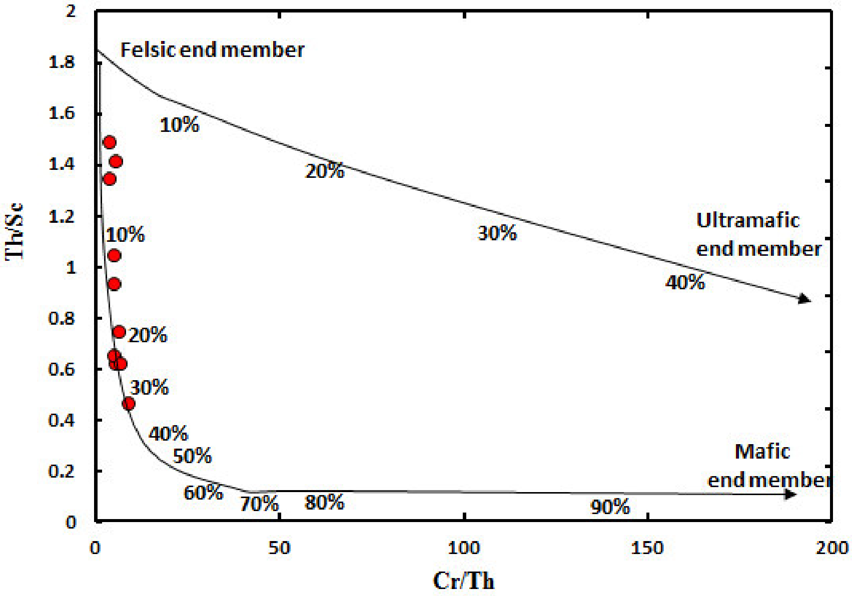


Figure 14. Plot of th/Sc Cr/Th ratio in the sandstone samples (Condie and Wronkiewicz, 1990; Totten et al., 2000). Two mixing curves have been calculated between a felsic and mafic end member, and between a felsic and ultramafic end member. Percentages reported on the mixing curves represent the mafic end-member contribution to the mixing products,

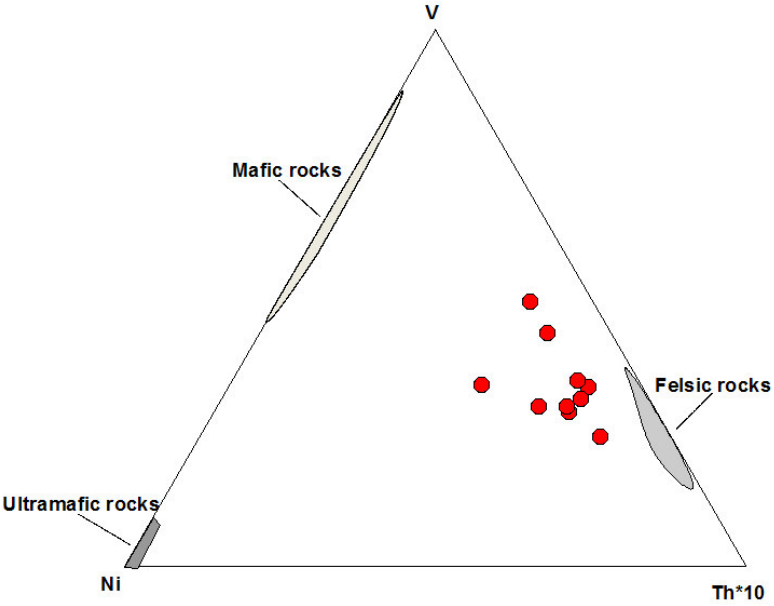


Figure 15: V-Ni-Th*10 plot of the Ilaro sandstone (Bracciali et al., 2007). Shaded areas represent composition of the felsic, mafic and ultramafic rocks.

Figure 16 shows the samples plotting close to the basalts, which suggests an intermediate to mafic source. Totten et al. (2000) showed that Th/Sc ratios near a value of 1.0 are typical of the upper continental crust which tends to be more enriched in the incompatible element Th; whereas, a more mafic component has a ratio near 0.6 and tends to be more enriched in the compatible element Sc (Fig. 17), which shows that the Ilaro sandstones are from more than on lithologic source. Figure 18 is a plot of La/Sc vs. Th/Sc, which according Totten et al. (2000) may be used where there is mixing between a mafic source enriched in the compatible element Sc, and a more continental source enriched in the incompatible elements La and Th. All the samples clustered along the curve close to the NASC and the Island Arc Intermediates suggesting a mixing of a felsic and mafic sources.

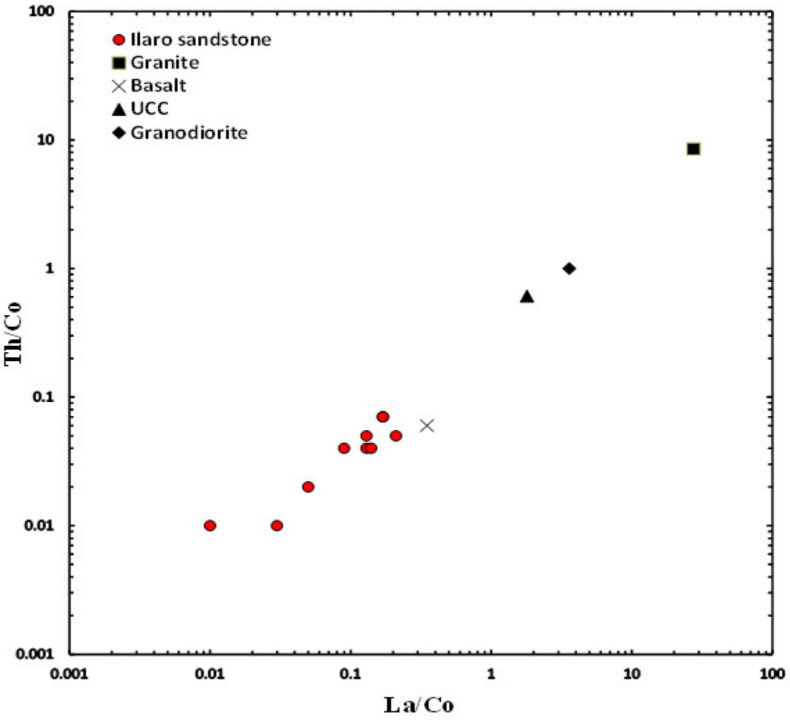


Figure 16. Source rock discrimination diagram for Ilaro sandstone (after Cullers and Berendsen 1998), in relation to average values of granites, basalts, granodiorite (Taylor, 2015) and upper continental crust (Taylor and McLennan, 1985; 1995).

4. Source area weathering

The degree of source area weathering recorded in sediments can be determined by the chemical index of alteration, CIA (Nesbit and Young, 1982). This index can be calculated by: CIA = $\{Al_2O_3/(Al_2O_3+CaO^*+Na_2O+K_2O)\}$ x 100 (molar contents, where CaO* represents the amount of CaO in silicate fraction of the sample). CIA values for the studied samples of Ilaro Formation range from 94 to 99%, with an average value of 98%. The CIA values are higher than average value of UCC (50%) and fresh granite (47%). The higher CIA values suggest intense weathering of the first cycle sediment or recycling in humid and warm paleoclimatic conditions. However, it has been argued that CIA may not directly reflect the paleoweathering conditions especially in sediments with variable provenances. Plotting CIA into A (Al_2O_3) - CN (CaO^*+Na_2O) - K (K_2O) compositional diagram can effectively evaluate chemical weathering, diagenesis-metamorphism and source composition of clastic sediments (Fedo *et al.*, 1995; 1997; Nesbit and Young, 1984; 1989; Nesbit *et al.*, 1997). Weathering effects also can be evaluated in terms of the

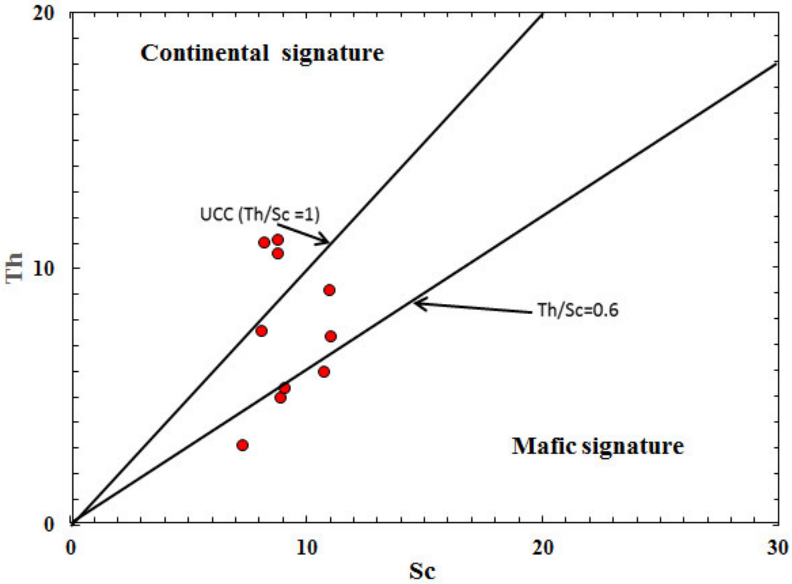


Figure 17. Th vs. Sc plot. Fields and trends from Totten et al. (2000).

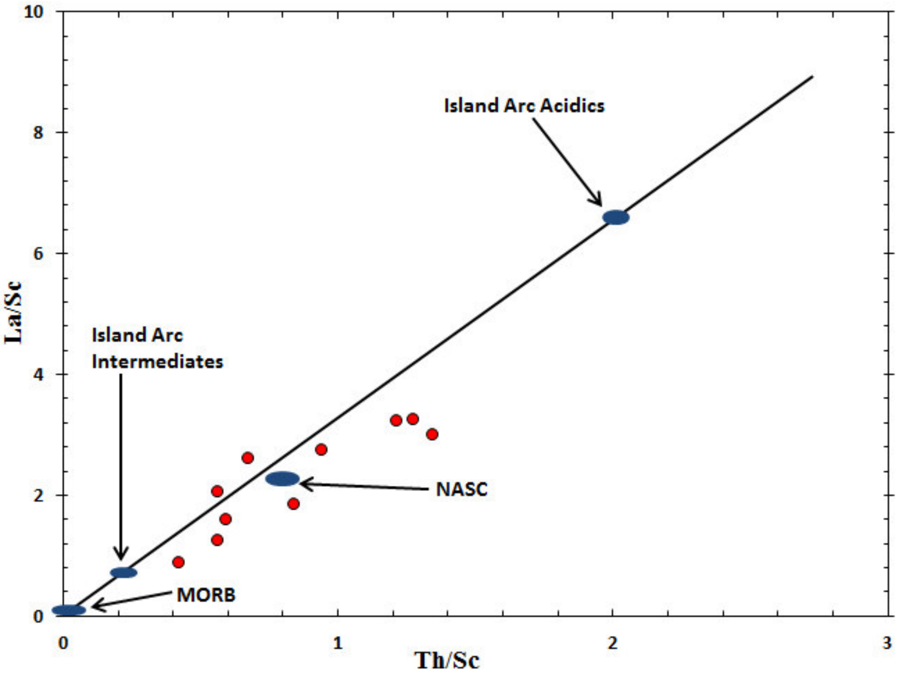


Figure 18. La/Sc vs. Th/Sc ratio plot. Fields from Totten et al. (2000). Values of different igneous rock types and the North American shale composite (NASC) are included for reference (Taylor and McLennan,1985; Sun and McDonough,1989; Gromet and Silver,1983).

molecular percentage of the oxide components, using the formulae: chemical index of weathering (CIW) = $Al_2O_3/(Al_2O_3 + CaO^* + Na_2O)$ based on Harnois (1988). The CIA and CIW are interpreted in similar way with values 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 CIW values range between 96 and 99%, indicating high degree of weathering of the source materials. The intensity of the chemical weathering can also be estimated using the Plagioclase Index of Alteration (Fedo et al., 1995); in molecular proportions: PIA = $[(Al_2O_3-K_2O)/ (Al_2O_3 + CaO^* + Na_2O-K_2O)] \times 100$ where CaO* is the CaO residing only in the silicate fraction. Unweathered plagioclase has PIA value of 50. The PIA values for the Ilaro sandstones ranged from 96-99%, also indicating high degree of weathering. The Mineralogical Index of Alteration (MIA) proposed by Voicu et al. (1997) is another 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. MIA value is between 88 and 98% (Average = 96%), which indicates intense weathering condition.

The A-CN-K diagram (fig. 19) for the samples of Ilaro Formation shows a tight cluster of data-point at the A apex indicating substantial loss of Ca, Na and K, and abundance of kaolinite and/or chlorite in the samples. The position of the samples on the A-CN-K diagram, as well as their corresponding CIA values indicate that these sediments were generated from a source area strongly affected by intense chemical weathering which results in the depletion of selectively leached elements (e.g. Ca, Na, K) from the weathering profiles (Nesbitt *et al.*, 1980; Wronkiewicz and Condie, 1987).

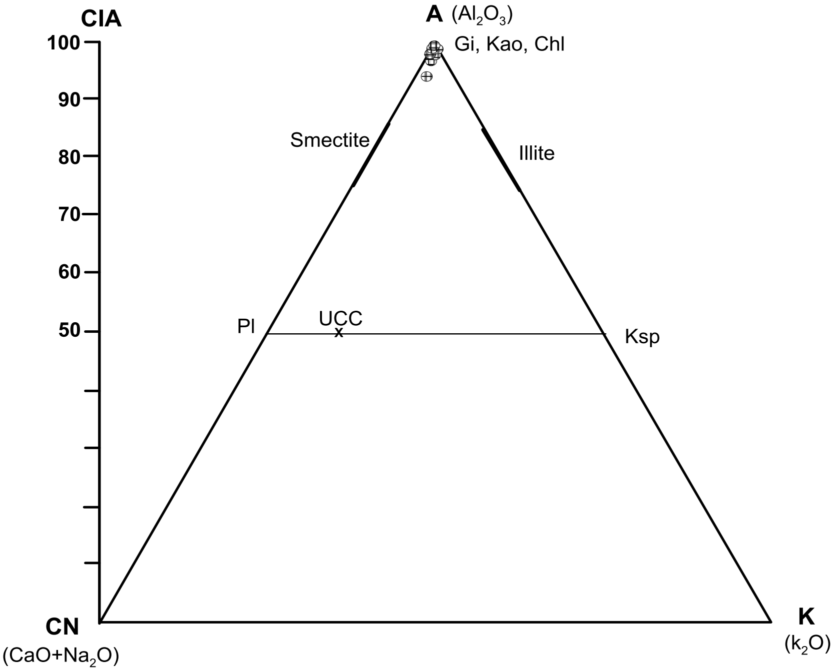


Figure 19: A-CN-K ternary plot for the analysed samples of Ilaro Formation (after Fedo *et al.*, 1995). UCC: upper continental crust (Taylor and McLennan, 1985); Ksp: K-feldspar; Pl: plagioclase; Gi: gibbsite; Chl: chlorite; Kao: kaolinite.

Some elemental ratios, K/Na, Al/K, Ti/Na, Rb/K, Rb/Sr and Sr/Ba have also been widely used as proxy to examine the degree of weathering based on the fact that these elements commonly display remarkably different mobility are fractionated to different degrees during weathering (Sawyer, 1986; Ding *et al.*, 2001; Yang *et al.*, 2004; Roy *et al.*, 2008). Yang *et al.*, (2004) suggested that high ratios of K/Na, Rb/Sr, Al/K, Rb/K and Ti/Na and low Sr/Ba ratio indicate strong chemical weathering. Na and Sr are more mobile than K, Al, Rb and Ba and consequently easily removed from parent rock during weathering. Both K and Rb are integrated into clay minerals by adsorption and cation exchange during initial weathering of fresh rocks. But with increasing weathering intensity, K is preferentially leashed compared to Rb (Wronkiewicz and Condie, 1989). In the present study, Rb/K, Rb/Sr and Sr/Ba do not show any significant correlation with CIA values whereas Al/K shows strong positive correlation with CIA. These suggest that ratios of Rb/K, Rb/Sr and Sr/Ba are not controlled by the degree of weathering of the studied samples. Higher Al/K ratio (52.67-357.58; molar content) of the studied samples than UCC suggests that the sediments were derived during intense chemical weathering of the source area. Several authors (Taylor and McLennan, 1985; McLennan et al., 1990, 1995; Gu et al., 2002) have used the Th/U ratio to decipher the weathering history due to the oxidation and loss of uranium during the weathering process. Most of the Ilaro samples showed a wide trend above the upper crust value (fig. 20), while four samples plotted slightly below the upper crust mean value. The overall scenario suggests that weathering conditions were high and not constant during sedimentation. McLennan et al. (1995) suggested that a ratio near 3.8 indicates a relatively unweathered source, but according to Pe-Piper et al. (2008), the precise value will vary according to local hinterland geology.

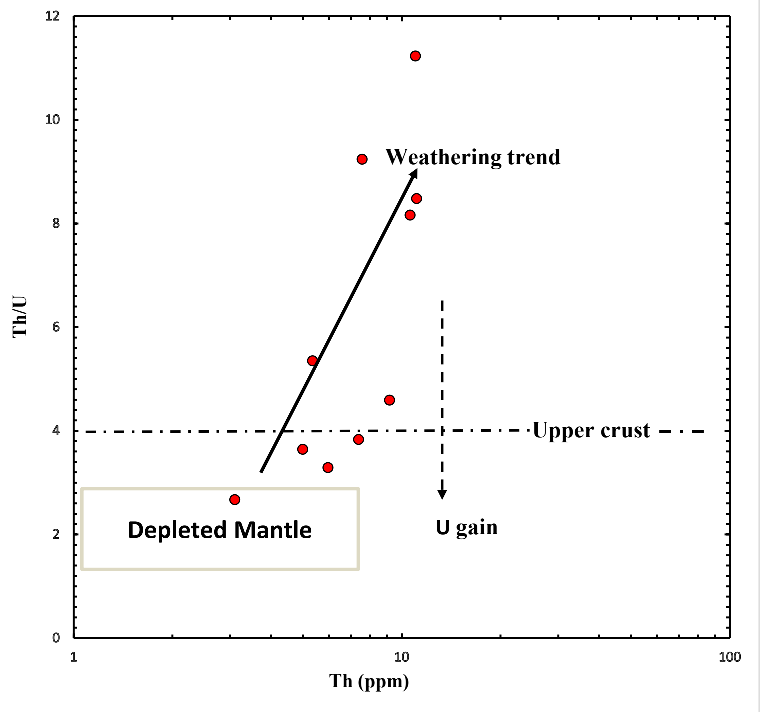


Figure 20: Th/U vs. Th plot for Ilaro sandstone. Fields and trends from Gu et al. (2002).

5. Tectonic setting

Several authors (Maynard et al., 1982; Bhatia, 1983; Bhatia and Crook 1986; Roser and Korsch, 1986; Kroonenberg 1994) have related sandstone geochemistry to specific tectonic environment. Inert trace elements in clastic sediments have also been used successfully in discrimination diagrams of plate tectonic settings (Varga and Szakmany, 2004; Elzien et al., 2014), these elements are probably transferred quantitatively into detrital sediments during weathering and transportation, reflecting the signature of the parent material (Armstrong-Altrin et al., 2004). Figures 21 (a) and (b) are tectonic classification diagrams based on Bhatia (1983), the Ilaro sandstones plotted mainly in the passive margin zone. Roser and Korsch (1986), consider passive margin sediments are largely quartz-rich sediments derived from plate interiors or stable continental areas and deposited in stable intracratonic basins or on passive continental margins. Figures 22 (a), (b) and (c) are tectonic discrimination diagrams based on trace and rare earth elements of the Ilaro sandstones, it shows the plots in non-specific zones which might be due to secondary enrichment of certain elements.

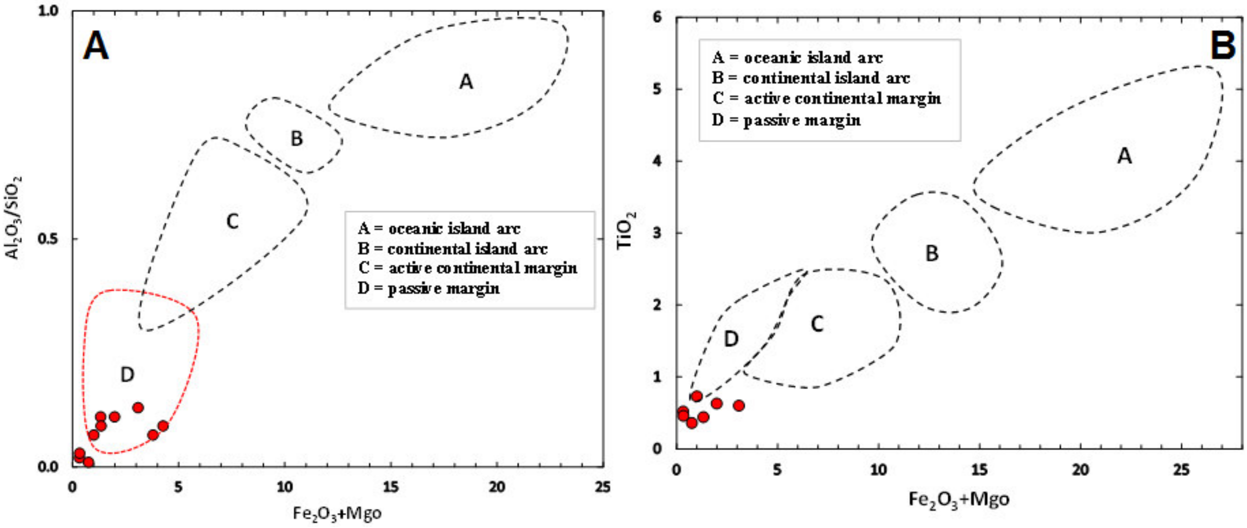


Figure 21: (a) Tectonic setting discrimination plot of TiO_2 versus Fe_2O_3 + MgO of the studied samples. Dashed lines denote the major fields representing various tectonic settings (after Bhatia 1983). (b): Tectonic setting discrimination plot of Al_2O_3/SiO_2 versus Fe_2O_3 + MgO, after Bhatia (1983).

Figure 23 is another tectonic discrimination diagram; this shows the samples plotting mainly in the active continental margin zone while few fall in the continental island arc field. High La/Sc ratios are characteristic of active continental margin and passive margin greywackes respectively. Passive margin settings also show low Ti/Zr ratios (Bhatia and Crook, 1986).

6. Paleoenviroment and Paleoclimate

Redox condition is important for recognizing the sediment deposition in marine or non-marine environments. According to McKay et al (2007), the accrual of certain trace metals in sediments is directly or indirectly controlled by redox conditions through either a change in redox state and/or speciation. Element ratios such as U/Th, Ni/Co, Cu/Zn, (Cu+Mo)/Zn and V/Cr, have been used to evaluate paleoredox conditions. The U/Th ratio is higher in organic rich mudstones compared to sandstones (Jones and Manning, 1994). U/Th ratios below 1.25 suggest oxic conditions of deposition; values above 1.25 indicate suboxic and anoxic conditions ((Jones and Manning, 1994; Hallberg, 1976).

The Ilaro sandstone displays very low U/Th ratio (0.09 – 0.37), which indicate that the Ilaro sandstones were deposited in an oxic environment. A number of authors have used the Ni/Co ratios as a redox indicator (Bjorlykke, 1974; Dypvik, 1984; Dill, 1986; Brumsack, 2006; Nagarajan, 2007). The Ni/Co ratios below 5 indicate oxic environments, while ratios above 5 indicate suboxic and anoxic environments (Jones and Manning, 1994). For the studied samples, the Ni/Co ratios vary between 0.04 and 0.12, which is very low signifying that Ilaro sandstone was deposited in a well oxygenated environment. According to Hallberg (1976), Cu/Zn and (Cu+Mo)/Zn ratios can be used as redox parameters, high Cu/Zn ratios indicate reducing depositional conditions, while low Cu/Zn ratios suggest oxidising conditions. For this present investigation the Cu/Zn ratios range from 0.33-0.85, indicating more oxidising conditions. The ratio (Cu+Mo)/Zn is shown to be a relevant paleoredox indicator for bottom water and sediment surface. For the present study the (Cu+Mo)/Zn ratios is between 0.37 and 0.95, which suggests oxic paleoenvironment.

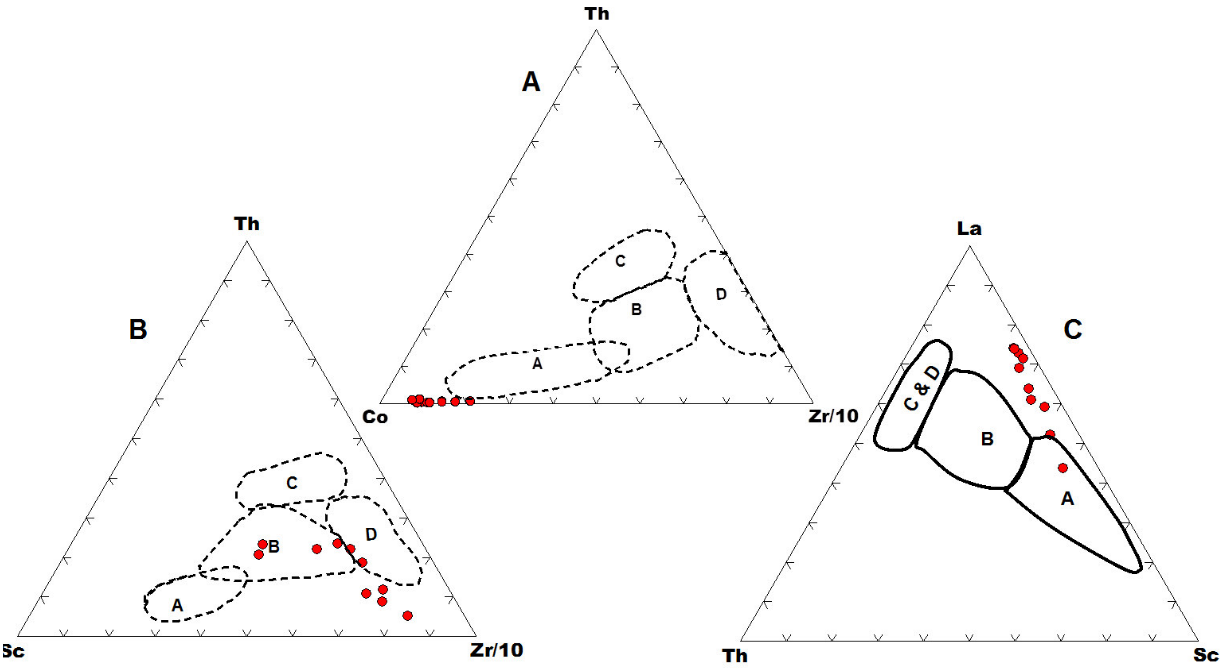


Figure 22 **(a):** Th - Co - Zr/10 plot; **(b):** Th - Sc - Zr/10 plot and La – Th – Sc plot of the Ilaro sandstone. All fields from Bhatia and Cook (1986): A = oceanic island arc; B = continental island arc; C = active continental margin; D = passive margin

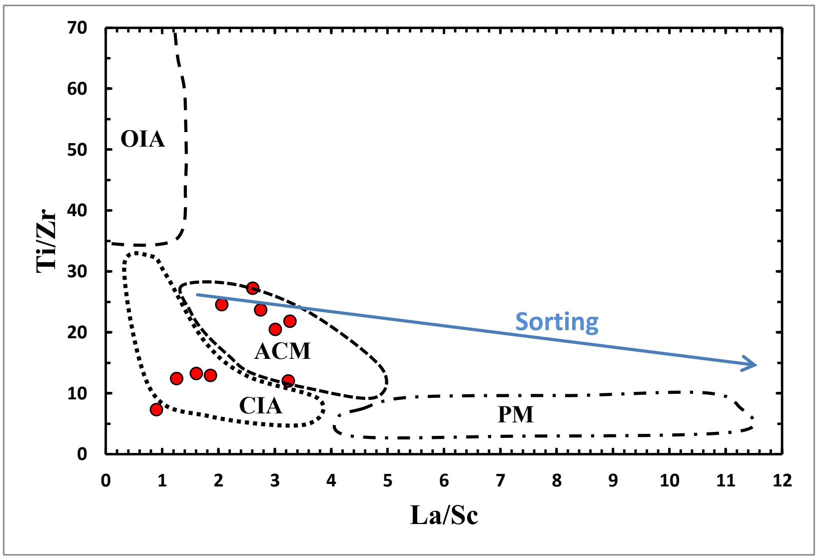


Figure 23: Ti/Zr ratio versus La/Sc ratio plot. Fields after Bhatia and Crook (1986):oceanic island arc = OIA, continental island arc = CIA, active continental margin = ACM and passive margin = PM. The sorting trend after Gu et al. (2002).

V/Cr ratio has been utilized as an index of paleooxygenation (Bjorlykke, 1974; Shaw et al,. 1990; Nagarajan, 2007) due to the incorporation of Cr in the detrital fraction of sediments and its possible substitution for Al in the clay structure (Kimura and Watanabe, 2001). Bellanca et al (1996) stated that vanadium solubility in natural waters, its extraction from seawater and absorption onto sediments are mainly influenced by redox conditions. Vanadium may be bound to organic matter by the incorporation of V^{4+} into porphyrins, and is generally found in sediments deposited in reducing environments (Kimura and Watanabe, 2001). The V/Cr ratios above 2 indicate anoxic conditions, whereas values below 2 suggest more oxidizing conditions (Jones and Manning, 1994). The V/Cr ratios of Ilaro sandstone range between 0.95 and 1.79 which indicates that they were deposited in an oxic environment. According to Hetzel et al. (2009), the V/Sc ratios below 9.1 indicate oxic depositional environment. V/Sc ratio for the Ilaro samples is between 2.97 and 7.86, which indicates oxic depositional environment. Ni is mainly enriched in organic-rich sediments where these metals are trapped with organic matter (Leventhal and Hosterman, 1982; Gilkson et al., 1985). V accumulates relative to Ni in reducing environments, where sulphate reduction is more efficient. The proportionality of these two elements V/(V+Ni) is very significant to delineate information on Eh, pH and sulphide activity in the depositional environment (eg. Madhavaraju and Lee, 2009). The V/(Ni+V) ratios below 0.46 indicate oxic environments, but ratios above 0.54 to 0.82 suggest suboxic and anoxic environments (Hatch and Leventhal, 1992). The V/(Ni + V) ratios for the Eocene Ilaro sandstone range from 0.57 to 0.83 (Avg. = 0.72), which indicate suboxic to anoxic environment of deposition.

The degree of chemical weathering is a function of climate and rates of tectonic uplift (Wronkiewicz and Condie, 1987). The rising chemical weathering intensity suggests the decrease in tectonic activity and/or the change of climate towards warm and humid conditions which are more favourable for chemical weathering in the source region (Jacobson et al., 2003). The applicability of the ratios of $SiO_2/(Al_2O_3+K_2O+Na_2O)$ for paleoclimatic condition (Suttner and Dutta, 1986) during deposition of sediments in the basin is well recognized by many workers. Figure 24 shows the samples plotting in humid to semi-humid climatic conditions, which reflects paleoclimatic condition during the deposition of Ilaro sandstone. Figure 25 is another paleoclimatic bivariate log plot by Suttner and Dutta (1986) showing the samples plotting in the humid zone, this paleoclimatic condition will influence increase mineral instability.

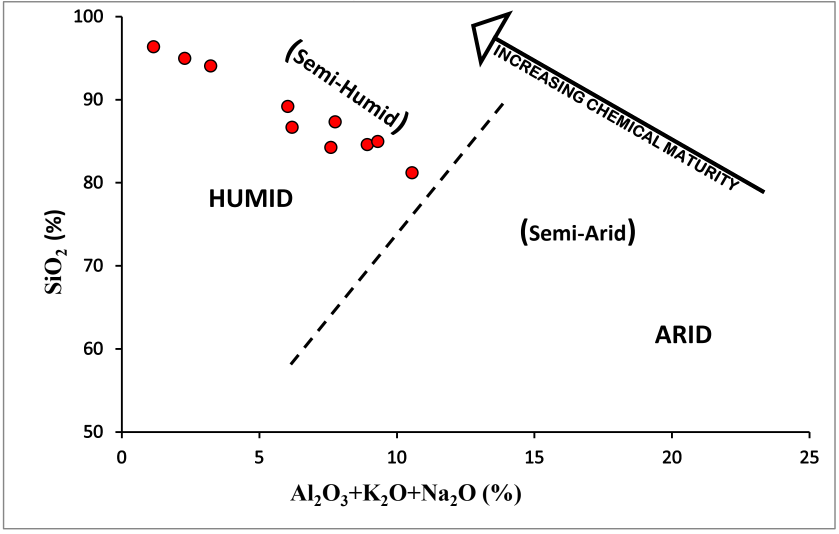


Figure 24: Bivariate plot of SiO2 vs. (Al_2O_3 + K_2O + Na2O) to discriminate paleoclimatic condition during the deposition of the Eocene sediments (after Suttner and Dutta, 1986).

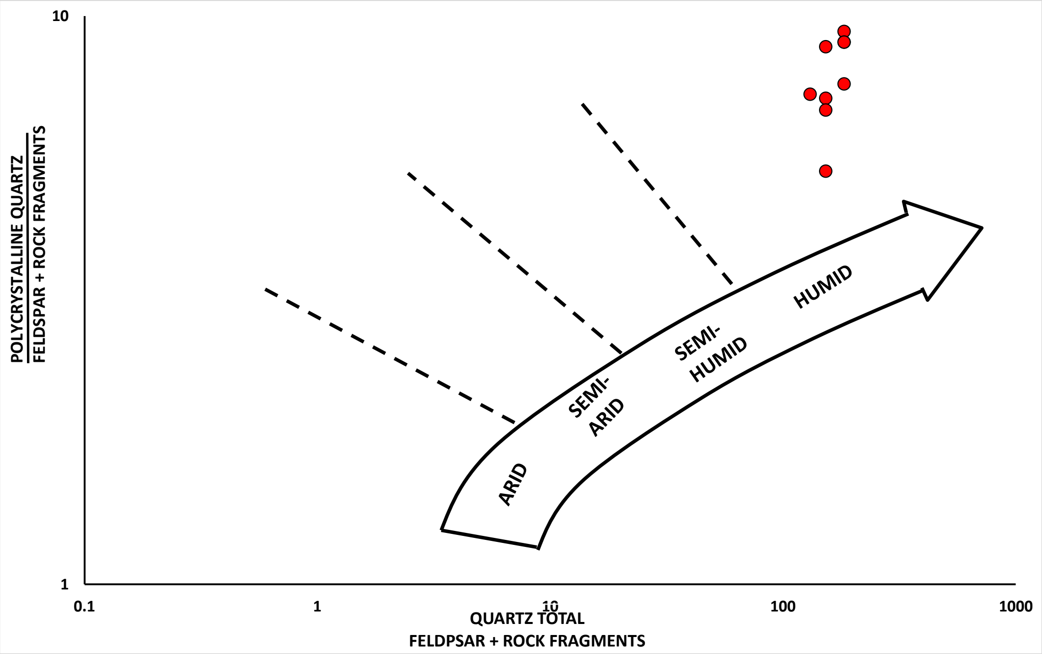


Figure 25: Bivariate log/log plot of the ratio of polycrystalline to feldspar plus rock fragments against the ratio of total quartz to feldspar plus rock fragments (after Suttner and Dutta, 1986).

The Mn* value is a significant paleochemical indicator of the redox conditions of the depositional environment (Bellanca et al., 1996; Cullers, 2002; Machhour et al., 1994). The expression for calculating Mn* value is $Mn^*=\log[(Mn_{sample}/Mn_{shales})/(Fe_{sample}/Fe_{shales})]$, where the values used for the Mn_{shales} and Fe_{shales} are 600×10^{-6} and 46150×10^{-6}, respectively (Wedepohl, 1978). The reduced iron and manganese form different solubilities of compounds across a redox boundary, while manganese tends to accumulate in more oxygenated conditions above the redox boundary (Bellanca et al., 1996). The Ilaro sanstones have mainly negative Mn* values (except one sample with value of 0.2) ranging from -3.78 to 0.20 with an average of -1.03. This suggests that the sandstones may have been deposited in suboxic and anoxic conditions.

According to Liu et al. (1984); Deng and Qian (1993) and Wang (1996), Sr and Ba are regarded as indicators of paleosalinity. A high Sr/Ba ratio reflects high salinity, and a low Sr/Ba ratio indicates low salinity (Deng and Qian 1993). The Ilaro sandstones have a Sr/Ba ratio between 0.53 and 1.02 (average 0.72), indicating low saline water during deposition and a strong continental rather than marine influence.

Figure 26 indicate a metamorphic source rock in a humid climate. This particular diagram can discriminate only sources of metamorphic and plutonic rocks (humid or arid conditions) and does not discriminate between different tectonic settings. Based on Weltje et al. (1998) diagram (fig. 27), the Ilaro samples plotted in number 2 fields, which point to the sedimentation on either a low-relief with a temperate and sub-humid climate or on tropical, humid conditions within an area with a moderate relief. From figure 28, the Ilaro sandstones are classified as non-marine and deltaic sandstones. The aforementioned paleoenviromental and paleoclimatic results suggest that the Ilaro sandstone was deposited in mostly oxic deltaic conditions.

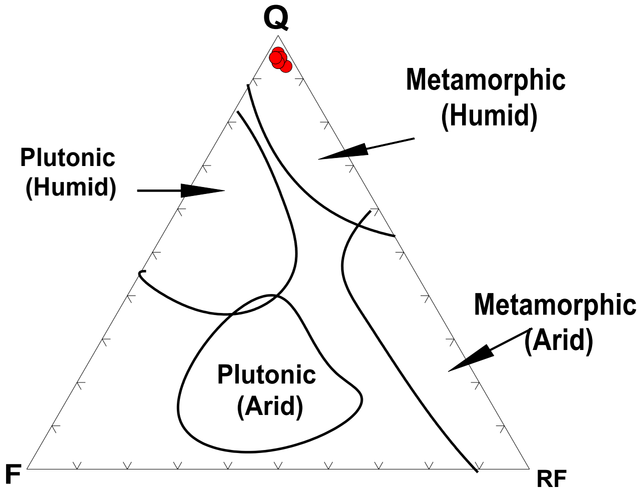
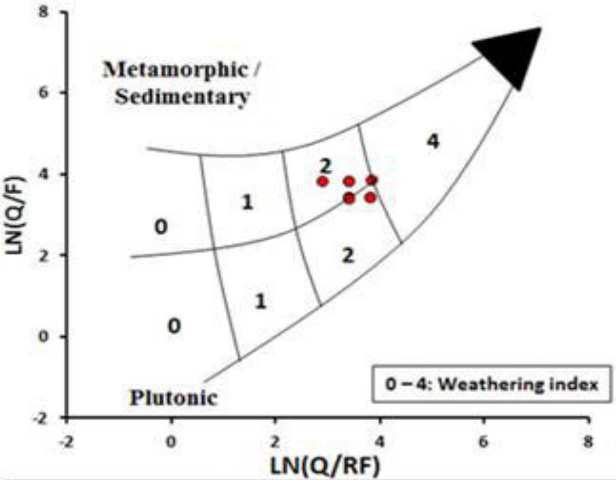


Figure 26: Q-F-R plot of the Ilaro sandstone indicating paleoclimate of the source (after Suttner et al., 1981).



Semi-quantitative weathering index		Physiography (relief)		
		High (mountains) 0	Moderate (hills) 1	Low (plains) 2
Climate (precipitation)	(Semi) Arid and mediterranean 0	0	0	0
	Temperate subhumid 1	0	1	2
	Tropical humid 2	0	2	4

Figure 27. Log-ratio plot after Weltje et al. (1998). Q: quartz, F: feldspar, RF: rock fragments. Fields 1-4 refer to the semi-quantitative weathering indices defined on the basis of relief and climate as indicated in the table.

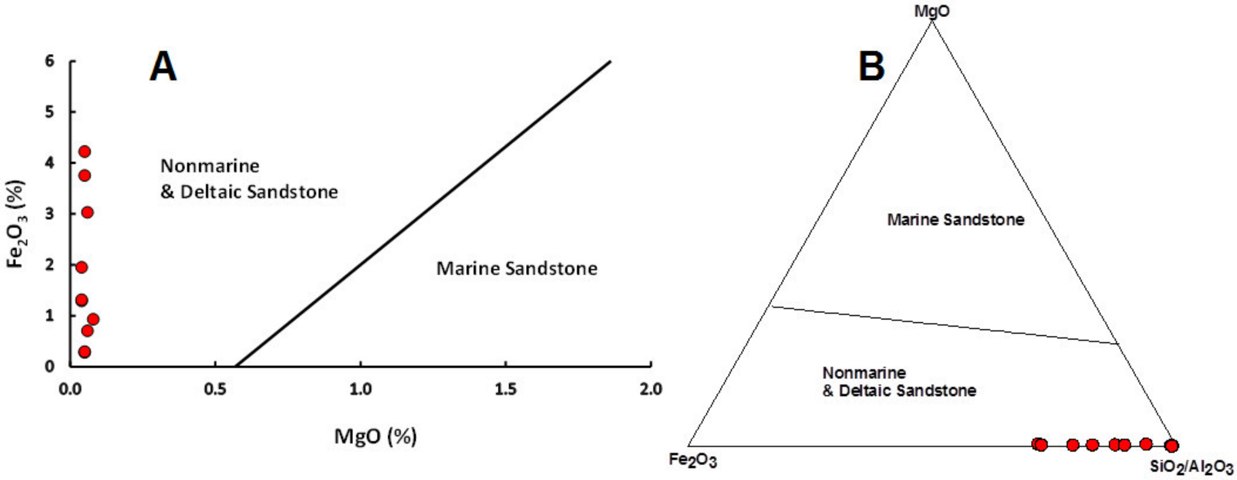


Figure 28: Binary (A) and ternary (B) diagrams showing characterization and differentiation of marine from nonmarine sandstones. The Ilaro sandstones plotted in the nonmarine and deltaic field (after Ratcliffe et al., 2007).

7. Conclusions

The source area analyses of the Ilaro sandstone suggest that the sediments were derived from multiple sources. All the weathering indices indicate that the sediments were derived during intense chemical weathering of the source area. The Th/U-Th plot also showed that weathering conditions were high and not constant during sedimentation. The tectonic setting is of the active continental margin and passive margin types. The paleoenviromental and paleoclimatic studies suggest that the Ilaro sandstone was deposited in mostly oxic humid deltaic conditions. The Ilaro sandstones have a low Sr/Ba ratio indicating low saline water during deposition and a strong continental rather than marine influence.

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