

Geochemical compositions of Neoproterozoic to Lower Palaeozoic (?) shales and siltstones in the Volta Basin (Ghana): Constraints on provenance and tectonic setting

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ABSTRACT

Many researchers have investigated the provenance and tectonic setting of the Voltaian sediments using the geochemistry of sandstones in the basin. The shales and siltstones in the basin have not been used much in the provenance studies. In this paper, the geochemistry of shales and siltstones in the Kwahu Group and Oti Group of the Voltaian Supergroup from Agogo and environs in the southeastern section of the basin has constrained the provenance and tectonic setting. Trace element ratios La/Sc, Th/Sc and Cr/Th and REEs sensitive to average source compositions revealed sediments in the shales and siltstones may mainly be from felsic rocks, though contributions from old recycled sediments and some andesitic rock sediments were identified. The felsic rocks may be granites and/or granodiorites. Some intermediate rocks of andesitic composition are also identified, while the recycled sediments were probably derived from the basement metasedimentary rocks. The enrichment of light REE (LaN/YbN c. 7.47), negative Eu anomalies (Eu/Eu* c. 0.59), and flat heavy REE chondrite-normalized patterns, denote an upper-continental-crustal granitic source materials for the sediments. Trace-element ternary discriminant diagrams reveal passive margin settings for sediments, though some continental island arc settings sediments were also depicted. Mixing calculations based on REE concentrations and modeled chondrite-normalized REE patterns suggest that the Birimian basement complex may be the source of detritus in the Voltaian Basin. REEs are more associated with shales than siltstones. On this basis chondrite-normalized REE patterns show that shale lithostratigraphic units may be distinguished from siltstone lithostratigraphic units. The significant variability in shales elemental ratios can therefore be used to distinguish between shales of the Oti Group from that of the Kwahu Group.

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1. Introduction

Geochemical investigations are widely used to determine the relative abundance of the components of siliciclastic rocks such as major detrital phases, matrix, heavy minerals and metamorphic minerals (Roser, 2000). These investigations highlight the provenance of the sediments, source area weathering, tectonic setting and paleoclimatic environment (Roser and Korsch, 1988; von Eynatten et al., 2008; Gabo et al., 2009). The source(s) of the Voltaian sediments have been investigated by many researchers (Kalsbeek et al., 2008; Carney et al., 2008b, 2010; Kalsbeek and Frei, 2010; Couëffé and Vecoli, 2011) using different approaches including whole-rock geochemistry, regional mapping, detrital zircon dating and petrographic studies. The detrital zircon dating approach, provided a wide range of ages (1000–2200 Ma.) such that the determination of sediments provenance varied. While the age

range 2000–2200 Ma indicates the Birimian Supergroup with inputs from the West African Craton as the sediments provenance, another age range (1000–1200 Ma) suggests the amalgamated West African Craton and Amazonian Craton as sediments' provenance. Considering recycled materials in the sandstones, Anani et al. (2013) have indicated possible sediment contributions from the Pan-African orogenic rocks. The textural and mineralogical alterations of sediments by sedimentary processes have obscured the source characteristics of the sediments, making petrographic interpretations difficult (Weltje and von Eynatten, 2004). Geochemical data of mainly sandstones have been used to deduce the provenance of Voltaian sediments (Anani, 1999, 2000; Kalsbeek et al., 2008; Kalsbeek and Frei, 2010) with little attention to the mudstones.

In other basins, geochemistry of shales and siltstones have commonly been used and found to be better sediments provenance indicators (Ajayi et al., 2006; Abd El-Rahman et al., 2010; Adel et al., 2011). However, in the Volta Basin the shales and siltstones have not been thoroughly investigated for provenance studies. This study used geochemical data, mainly trace elements and rare earth elements

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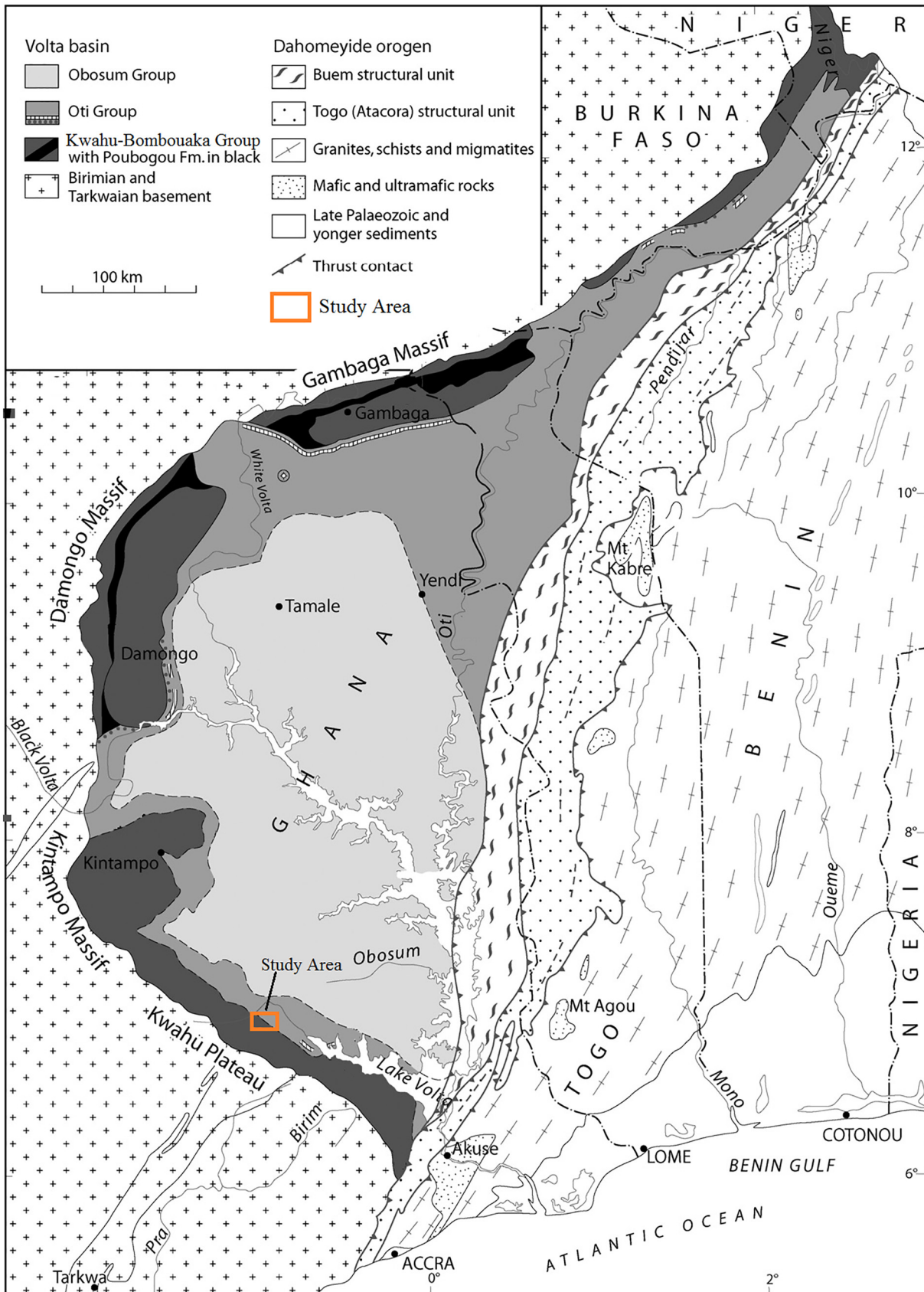


Fig. 1. The Geology of the Volta Basin showing the distribution of its main stratigraphical units after Affaton (1990) and the location of study area in the southeastern section of the Volta Basin.

components of the shales and siltstones in the Kwahu Group and Oti Group of the Voltaian Supergroup from the southeastern part of Ghana to identify the source of the sediments. This is to help resolve controversies of the provenance of the Voltaian sediments.

2. Geological setting

2.1. Voltaian Supergroup

The Voltaian Supergroup in Ghana (Fig. 1) consists of a succession of Neoproterozoic to Lower Palaeozoic (?) sandstones and mudstones with intercalations of limestone deposited on the Birimian Supergroup basement rocks (Kalsbeek et al., 2008).

The Voltaian Supergroup is stratigraphically classified as Kwahu-Bombouaka Group, Oti Group and Obosum-Tamale Group separated from each other by unconformities (Affaton, 1990; Deynoux et al., 2006). The Kwahu Group at the base, is found mainly in the western/south-western portion of the basin. This is followed by the Oti Group in the northern sector with minor occurrences in the southwest. At the top of the sequence is the centrally located Obosum Group. The Kwahu Group comprises Mpraeso Formation, Abetifi Formation and Anyaboni Formation in order of younging. The Oti Group has Afram Formation and Ejura Formation while the Obosum Group is made up of Obosum Formation and Tamale Formation (Carney et al., 2010). The formations consist of cyclic repetition of sandstones, siltstones, shales with minor contents of limestones (Bozhko, 1969; Annan-Yorke, 1971; Affaton et al., 1980; Affaton, 1990; Carney et al., 2010).

The formations in the Volta Basin are generally horizontal with occasional shallow dips (1–2°) to the east or south-east. However, the eastern margins of the basin, has been deformed by Pan-African orogeny (~600 Ma) (Kalsbeek et al., 2008) such that steeper dips in the formations are displayed.

2.2. Study area

The study area is located in the southeastern portion of the Volta Basin in Agogo and its environs (Fig. 1) and bounded by latitudes 6° 42', 57.07" and 7° 1' 19.9" N, and longitudes 1° 16' 23.41" and 0° 54' 42.44" W (Fig. 2). The study area geology comprise of medium grained sandstones, alternating shaly and siltstones beds in the Mpraeso Formation. The Anyaboni Formation which consists of sandstones and shales intercalated with minor siltstones unconformably overlying the Mpraeso Formation. The Afram Formation is made of mainly shales, however, minor siltstones occur.

In the Mpraeso Formation, the alternating shaly and siltstones beds are the lower unit and the medium-grained, moderately sorted and cross-bedded sandstones form the upper unit. Similar textural and structural observations were made by earlier workers around Koforidua, Nkawkaw, Mpraeso, Agogo, etc. (Mason, 1963; Saunders, 1970; Carney et al., 2008a, 2008b, 2010; Couëffé and Vecoli, 2011). Within the Anyaboni Formation, the lower unit consists of multiple coloured shales intercalated with lenticular siltstones. The upper unit is predominantly, medium-grained, feldspathic, ferruginous sandstones. According to Saunders (1970), occasional lenticular conglomeratic intercalations and altered feldspars do occur in the ferruginous sandstones. The Afram shales are flaggy and micaceous with sporadic lenticular siltstones beds.

3. Materials and analytical methods

3.1. Materials

A total of 106 samples comprising shales, siltstones and sandstones were collected from Mpraeso Formation, Anyaboni Formation and Afram Formation in the Kwahu Group and Oti Group respectively;

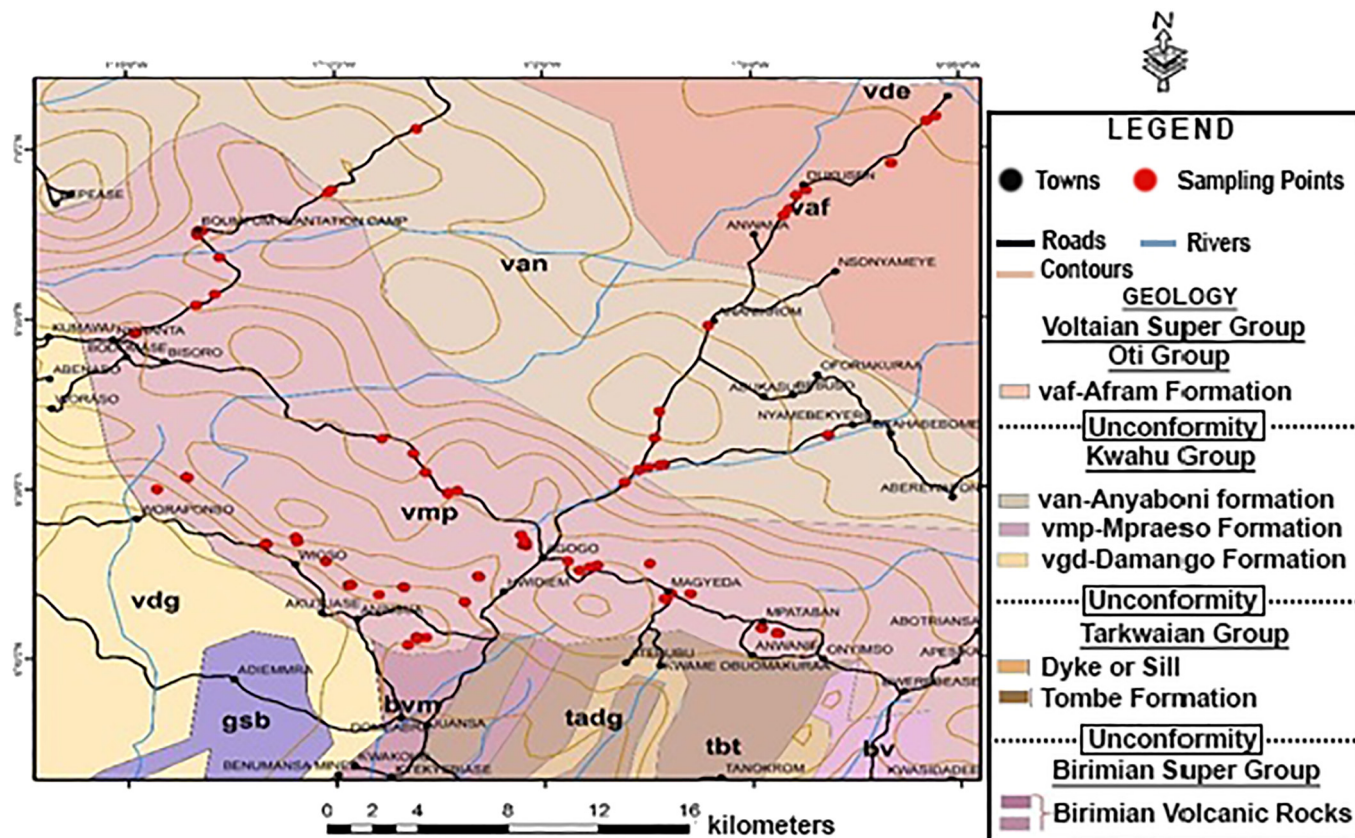


Fig. 2. Geological map of the study area in the south western section of the Voltaian Supergroup unconformably overlying the Birimian Supergroup and showing locations of samples collected from the shales and siltstones composing the Kwahu and Oti Groups.

Fig. 2 shows the sampling points. Forty samples consisting of six shales and two siltstones from Afram Formation, four shales, five siltstones and six sandstones from Anyaboni Formation and seven shales, six siltstones and four siltstones from Mpraeso Formation were selected for geochemical analysis at Analytical Laboratory System (ALS) Minerals Division in Vancouver, Canada. Another fifteen samples, comprising eleven shales and four siltstones, were selected from the three formations for XRD analysis at the Physics Department Laboratory, University of Ghana, Legon in Accra.

3.2. Geochemical analysis

Major elements oxides and loss on Ignition (LOI) were detected by inductively coupled plasma- atomic emission spectrometry (ICP-AES). Pulverized samples (0.2 g) were decomposed in lithium metaborate/lithium tetraborate and nitric acid digestion, then fused at 1000 °C. LOI was calculated by weight difference after ignition at 1000 °C. The trace elements including rare earth elements (REE) were detected by ICP-mass spectrometry after decomposition and fusion of samples just as for major elements. Corrections for possible isobaric interferences were monitored and corrected on measured masses.

3.3. XRD analysis

The powdered samples were treated with trihexylamine acetate to expand the smectites and then analysed using Empyrean powder X-ray diffractometer (PANalytical), operated at 45 kV, 40 mA. The prepared samples were randomly X-rayed, within the range 2° to 120° 2θ, a step size of 0.1° and scan step time of 2 s.

4. Results

4.1. Mineralogy

The XRD patterns (Fig. 3) indicate quartz as the predominant mineral, with feldspar, sillimanite, illite and/or muscovite occurring as

minor minerals. Other minor minerals identified but not visible in Fig. 3 include montmorillonite and hematite. High quartz contents characterised the siltstones, with feldspar, sillimanite and illite as minors in some of the siltstones. The shales also have high quartz content with minor amounts of illites, muscovites and kaolinite; the montmorillonite occurred mainly in the shales. The presence of some iron base suspected to be hematite and/or chlorite incorporated in the clay minerals were observed in the shale. It is possible that the hematite may be coming from the cementing material in some of the rock samples.

4.2. Geochemistry

The summarized geochemical results for the shales and siltstones in the Anyaboni Formation, Mpraeso Formation and Afram Formation of the Kwahu Group and Oti Group, respectively, are presented in Tables 1, 2 and 3.

4.2.1. Major elements

The SiO₂ content in the siltstones (70–89 wt%) is higher than in the shales (57–69 wt%) for all the formations (Table 1). While the siltstones plot in SiO₂ high concentration regions on the bivariate plot (Fig. 4), the shales plot in high Al₂O₃ concentration regions. This plot, which relates elemental composition to mineralogy, shows clear segregation between quartz dominant siltstones, represented by high SiO₂ content, from the shales, also composed of significant clay/sericite minerals represented by Al₂O₃.

4.2.2. Trace elements

All the samples are characterized by varying trace element concentrations as shown in Table 2. With the high field strength elements (HFSE), Zr recorded high concentrations, Hf and Nb were moderate, and Ta and U showed low to very low concentrations. In the light field strength elements (LFSE), Rb, Sr and Ba have high concentrations, but Cs and Pb were moderate. In the case of the transitional trace elements (TTE), V and Cr recorded high concentrations, Ni and Co were moderate, while Sn was low.

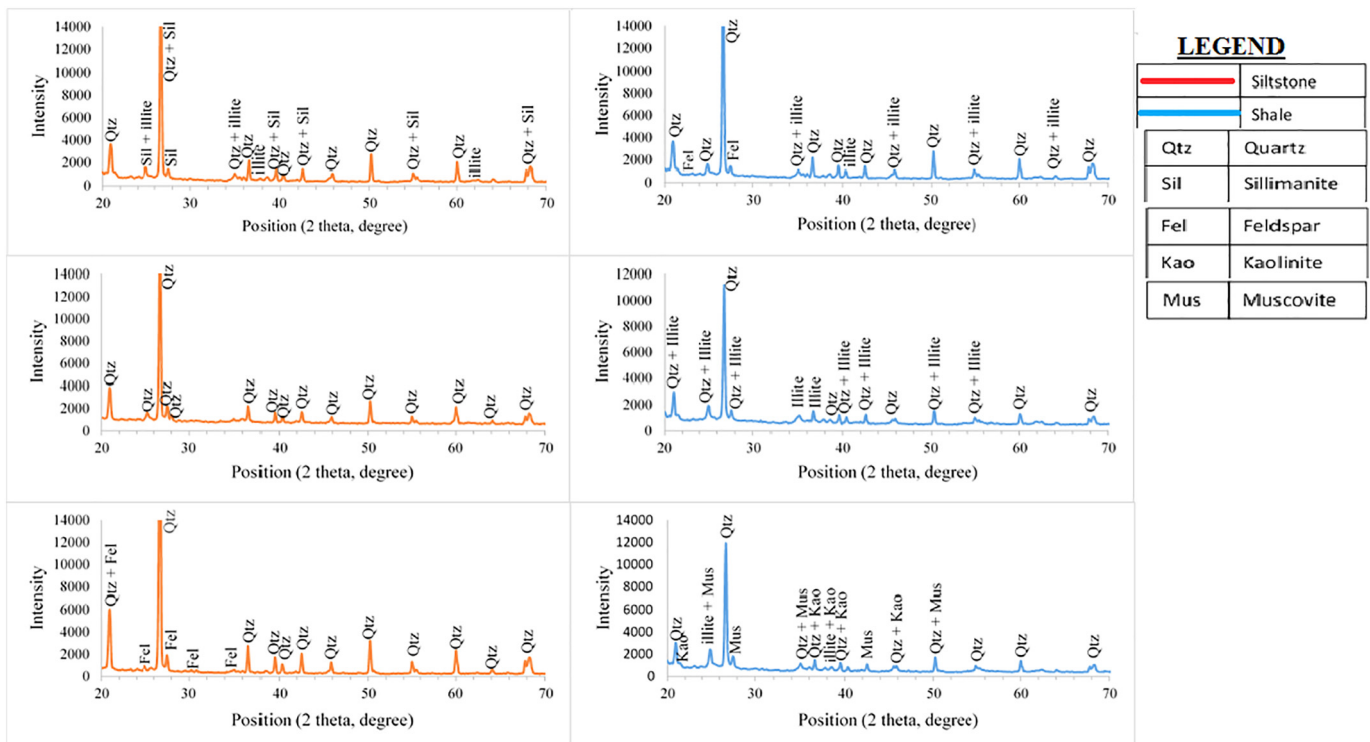


Fig. 3. Representative X-ray diffraction patterns of shales and siltstones in the study area.

Table 1
Major element concentration (wt%) in studied lithologies of Kwahu and Oti Groups.

Sample	Litho	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	MnO	TiO ₂	P ₂ O ₅	LOI	Total
<i>Afram Formation - Oti group</i>													
CAFR 14	Shale	58.70	16.85	7.48	2.01	0.25	0.43	3.48	0.03	0.67	0.03	9.81	99.74
CAFR 15	Shale	61.10	16.15	7.26	2.30	0.25	1.06	3.74	0.05	0.69	0.04	7.80	100.44
CAFR 16	Shale	62.20	16.30	7.12	2.99	0.47	1.61	3.75	0.08	0.70	0.13	6.38	101.73
CAFR 17	Shale	63.10	16.15	6.31	2.80	0.48	1.93	3.27	0.11	0.80	0.16	6.15	101.26
CAFR 18	Shale	63.70	16.70	4.21	2.83	0.36	1.63	3.88	0.06	0.69	0.10	6.58	100.74
CAFR 19	Shale	62.10	16.35	6.57	2.59	0.39	1.74	3.15	0.08	0.80	0.15	7.68	101.60
CAFR 22	Siltstone	83.60	7.88	3.49	0.53	0.04	0.07	3.14	0.02	0.39	0.07	2.17	101.40
CAFR 23	Siltstone	75.60	13.15	4.35	0.37	0.01	0.06	2.24	0.01	0.69	0.02	4.94	101.44
<i>Mpraeso Formation - Kwahu group</i>													
CAMP 25	Shale	62.90	16.25	7.46	1.24	0.16	0.11	4.68	0.02	0.86	0.07	6.61	100.36
CAMP 27	Shale	57.20	17.60	10.45	1.74	0.18	0.13	5.08	0.06	1.05	0.07	6.59	100.15
CAMP 29	Shale	60.30	17.00	10.05	1.31	0.14	0.09	4.78	0.02	0.87	0.09	6.63	101.28
CAMP 30	Shale	64.60	17.45	5.74	0.81	0.01	0.08	3.40	0.01	0.82	0.09	7.51	100.52
CAMP 33	Shale	58.10	18.30	8.95	1.64	0.16	0.10	5.20	0.03	0.87	0.06	7.20	100.61
CAMP 35	Shale	61.20	17.60	7.90	1.40	0.13	0.11	5.03	0.02	0.84	0.07	6.37	100.67
CAMP 40	Shale	62.60	15.60	9.08	1.45	0.20	0.11	5.17	0.03	0.84	0.03	5.58	100.77
CAMP 24	Siltstone	85.00	6.97	3.94	0.64	0.05	0.23	2.40	0.11	0.26	0.01	2.10	101.71
CAMP 26	Siltstone	79.20	8.40	5.36	0.94	0.05	0.25	2.63	0.03	0.49	0.02	2.75	100.12
CAMP 28	Siltstone	85.60	4.52	6.90	0.46	0.04	0.16	2.00	0.04	0.17	0.04	1.25	101.18
CAMP 32	Siltstone	69.00	17.50	3.31	0.65	0.01	0.07	3.37	0.03	0.92	0.03	6.44	101.33
CAMP 36	Siltstone	73.40	11.90	5.98	0.98	0.10	0.08	4.19	0.02	0.65	0.06	3.43	100.79
CAMP 38	Siltstone	78.30	4.94	9.30	0.50	0.14	0.05	1.41	0.36	0.16	0.01	4.82	99.99
<i>Anyaboni Formation - Kwahu group</i>													
CANY 5	Shale	57.50	21.10	7.02	0.90	0.04	0.06	4.58	0.02	1.13	0.06	7.32	99.73
CANY 8	Shale	68.20	17.60	3.66	0.71	0.07	0.09	3.20	0.02	0.92	0.08	6.78	101.33
CANY 10	Shale	64.00	19.95	3.73	0.67	0.02	0.09	3.36	0.01	1.03	0.10	7.91	100.87
CANY 12	Shale	67.80	17.75	2.34	0.45	0.01	0.07	2.91	0.01	0.92	0.02	6.38	98.66
CANY 1	Siltstone	86.70	6.42	2.15	0.46	0.06	0.57	2.41	0.11	0.43	0.02	1.60	100.93
CANY 2	Siltstone	86.90	6.09	2.37	0.43	0.06	0.30	2.04	0.02	0.60	0.01	1.95	100.77
CANY 11	Siltstone	88.30	5.30	3.67	0.15	0.01	0.04	1.53	0.01	0.28	0.01	1.92	101.22
CANY 20	Siltstone	69.40	13.75	3.61	0.98	2.08	3.39	2.78	0.05	0.42	0.11	2.98	99.55
CANY 21	Siltstone	83.20	8.59	3.16	0.18	0.02	0.05	2.82	0.02	0.44	0.04	1.77	100.29

Major elemental ratios in studied lithologies of Kwahu and Oti groups

Sample	Litho	CIA	K ₂ O/Na ₂ O	Na ₂ O/K ₂ O	SiO ₂ /Al ₂ O ₃	SiO ₂ /TiO ₂	K ₂ O/Al ₂ O ₃	Al ₂ O ₃ /TiO ₂	Al ₂ O ₃ /K ₂ O	Fe ₂ O ₃ /Al ₂ O ₃	Fe ₂ O ₃ /K ₂ O
<i>Afram Formation - Oti group</i>											
CAFR 14	Shale	77.45	8.09	0.12	3.48	87.61	0.21	25.15	4.84	2.15	2.15
CAFR 15	Shale	72.20	3.53	0.28	3.78	88.55	0.23	23.41	4.32	1.94	1.94
CAFR 16	Shale	68.58	2.33	0.43	3.82	88.86	0.23	23.29	4.35	1.90	1.90
CAFR 17	Shale	68.37	1.69	0.59	3.91	78.88	0.20	20.19	4.94	1.93	1.93
CAFR 18	Shale	69.11	2.38	0.42	3.81	92.32	0.23	24.20	4.30	1.09	1.09
CAFR 19	Shale	70.40	1.81	0.55	3.80	77.63	0.19	20.44	5.19	2.09	2.09
CAFR 22	Siltstone	69.02	44.86	0.02	10.61	214.36	0.40	20.21	2.51	1.11	1.11
CAFR 23	Siltstone	83.93	37.33	0.03	5.75	109.57	0.17	19.06	5.87	1.94	1.94
<i>Mpraeso Formation - Kwahu group</i>											
CAMP 25	Shale	74.76	42.55	0.02	3.87	73.14	0.29	18.90	3.47	1.59	1.59
CAMP 27	Shale	74.61	39.08	0.03	3.25	54.48	0.29	16.76	3.46	2.06	2.06
CAMP 29	Shale	75.52	53.11	0.02	3.55	69.31	0.28	19.54	3.56	2.10	2.10
CAMP 30	Shale	82.25	42.50	0.02	3.70	78.78	0.19	21.28	5.13	1.69	1.69
CAMP 33	Shale	75.18	52.00	0.02	3.17	66.78	0.28	21.03	3.52	1.72	1.72
CAMP 35	Shale	75.18	45.73	0.02	3.48	72.86	0.29	20.95	3.50	1.57	1.57
CAMP 40	Shale	72.02	47.00	0.02	4.01	74.52	0.33	18.57	3.02	1.76	1.76
CAMP 24	Siltstone	69.47	10.43	0.10	12.20	326.92	0.34	26.81	2.90	1.64	1.64
CAMP 26	Siltstone	71.58	10.52	0.10	9.43	161.63	0.31	17.14	3.19	2.04	2.04
CAMP 28	Siltstone	64.65	12.50	0.08	18.94	503.53	0.44	26.59	2.26	3.45	3.45
CAMP 32	Siltstone	82.35	48.14	0.02	3.94	75.00	0.19	19.02	5.19	0.98	0.98
CAMP 36	Siltstone	71.23	52.38	0.02	6.17	112.92	0.35	18.31	2.84	1.43	1.43
CAMP 38	Siltstone	72.69	28.20	0.04	15.85	489.38	0.29	30.88	3.50	6.60	6.60
<i>Anyaboni Formation - Kwahu group</i>											
CANY 5	Shale	81.03	76.33	0.01	2.73	50.88	0.22	18.67	4.61	1.53	1.53
CANY 8	Shale	83.55	35.56	0.03	3.88	74.13	0.18	19.13	5.50	1.14	1.14
CANY 10	Shale	85.16	37.33	0.03	3.21	62.14	0.17	19.37	5.94	1.11	1.11
CANY 12	Shale	84.90	41.57	0.02	3.82	73.70	0.16	19.29	6.10	0.80	0.80
CANY 1	Siltstone	64.17	4.23	0.24	13.50	201.63	0.38	14.93	2.66	0.89	0.89
CANY 2	Siltstone	68.78	6.80	0.15	14.27	144.83	0.33	10.15	2.99	1.16	1.16
CANY 11	Siltstone	76.02	38.25	0.03	16.66	315.36	0.29	18.93	3.46	2.40	2.40
CANY 20	Siltstone	53.23	0.82	1.22	5.05	165.24	0.20	32.74	4.95	1.30	1.30
CANY 21	Siltstone	73.71	56.40	0.02	9.69	189.09	0.33	19.52	3.05	1.12	1.12

Table 2

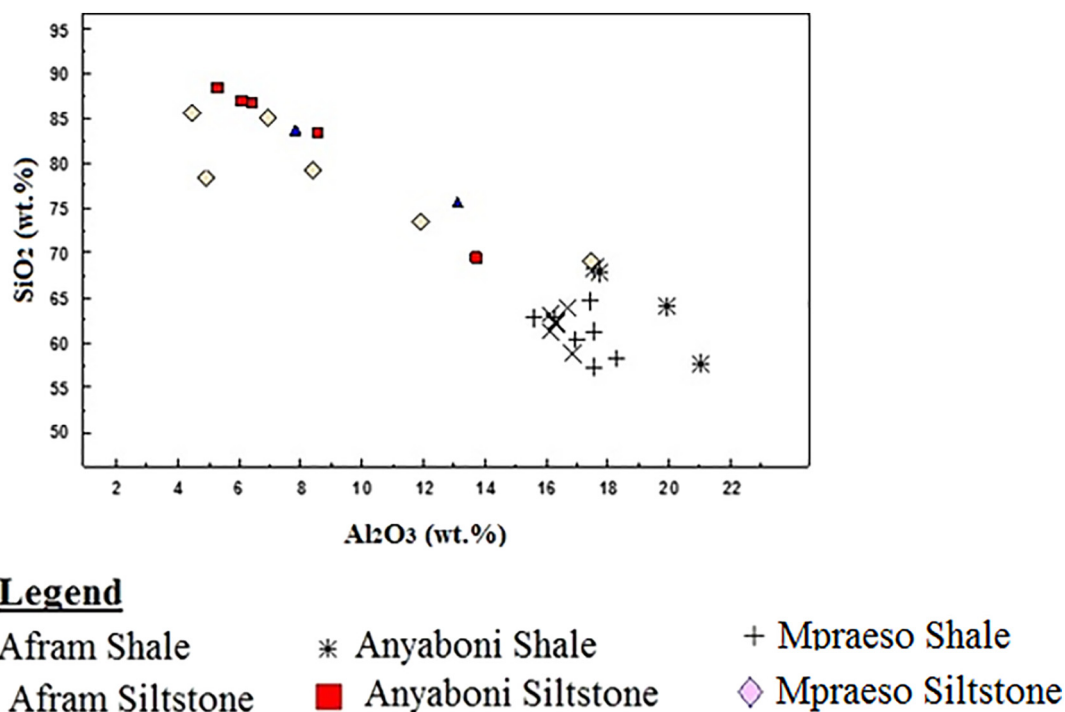
Trace element concentrations (ppm) in studied lithologies of Kwahu and Oti Groups.

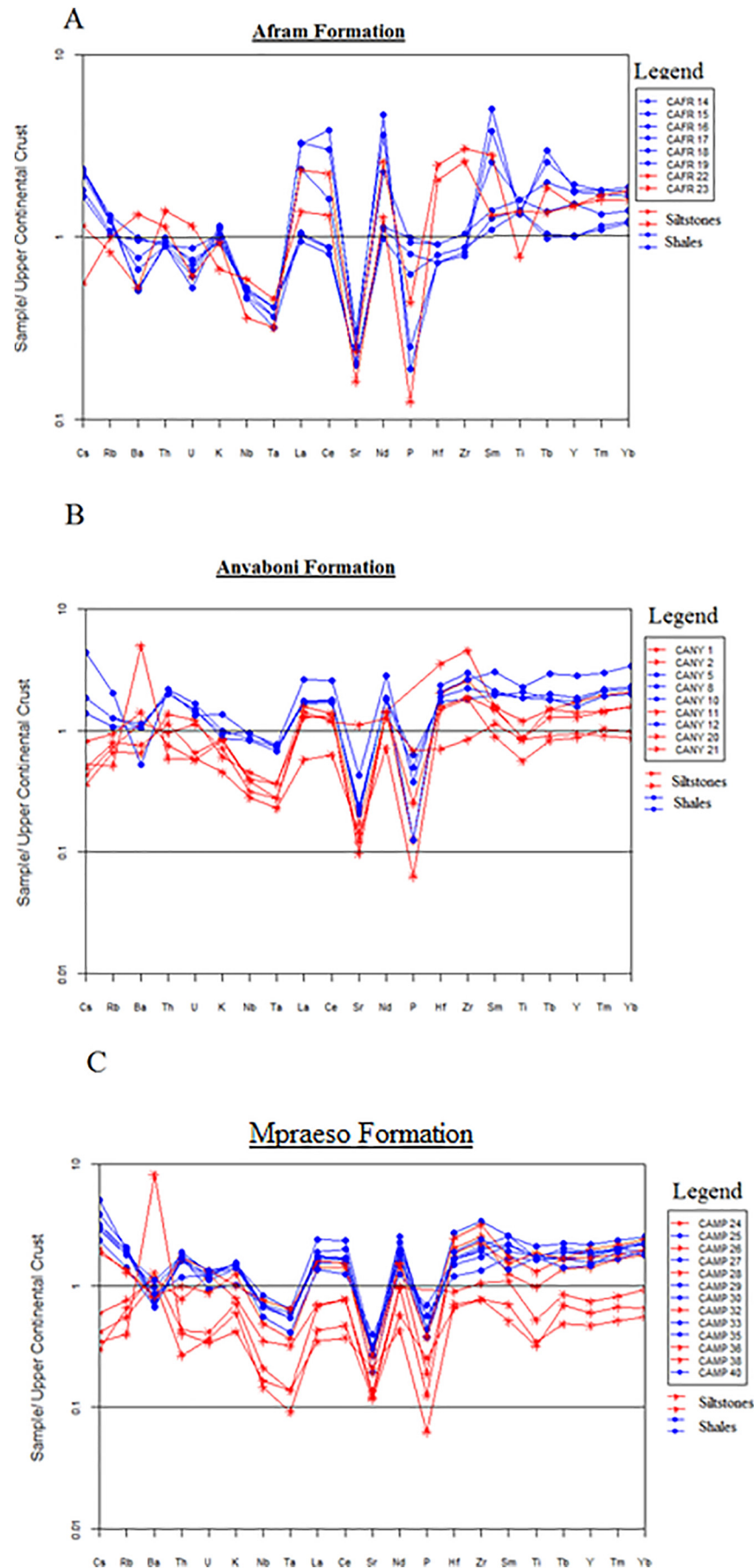
Sample	Litho	LFSE					HFSE							TTE							
		Rb	Sr	Ba	Cs	Pb	Zr	Nb	Hf	Ta	Th	U	Y	Sc	V	Cr	Co	Ni	Cu	Ga	
Afram Formation - Oti group																					
CAFR 14	Shale	137.00	87.90	363.00	8.04	12.00	157.00	11.80	4.20	0.80	9.62	2.44	39.70	16.00	125.00	80.00	14.00	32.00	29.00	23.70	
CAFR 15	Shale	147.50	106.50	547.00	8.78	10.00	150.00	11.70	4.20	0.80	9.51	1.70	42.80	16.00	115.00	80.00	22.00	53.00	21.00	22.40	
CAFR 16	Shale	139.00	68.90	289.00	8.62	12.00	157.00	11.50	4.20	0.70	9.48	1.48	22.20	16.00	104.00	70.00	17.00	41.00	15.00	21.10	
CAFR 17	Shale	120.50	70.70	423.00	6.72	11.00	197.00	13.10	5.30	0.90	10.65	1.97	33.40	15.00	111.00	80.00	18.00	87.00	36.00	20.10	
CAFR 18	Shale	147.50	71.60	279.00	8.46	3.00	166.00	12.60	4.60	0.90	9.90	1.84	22.30	16.00	115.00	80.00	17.00	41.00	29.00	23.70	
CAFR 19	Shale	116.00	84.00	528.00	6.16	8.00	197.00	12.70	5.30	0.80	9.94	2.10	38.60	15.00	118.00	80.00	16.00	54.00	36.00	20.80	
CAFR 22	Siltstone	111.00	81.60	729.00	2.05	34.00	581.00	9.00	14.40	0.70	12.15	1.71	32.90	4.00	16.00	40.00	4.00	10.00	8.00	10.50	
CAFR 23	Siltstone	92.20	56.20	290.00	4.25	12.00	493.00	14.60	11.90	1.00	14.90	3.23	32.70	10.00	71.00	50.00	3.00	9.00	14.00	16.00	
Mpraeso Formation - Kwahu group																					
CAMP 25	Shale	211.00	92.90	373.00	11.75	12.00	381.00	16.70	9.50	1.20	17.15	3.08	41.50	15.00	87.00	60.00	12.00	19.00	19.00	21.50	
CAMP 27	Shale	234.00	110.00	424.00	14.25	17.00	398.00	20.60	9.90	1.40	20.10	3.61	47.80	18.00	113.00	80.00	55.00	24.00	54.00	26.10	
CAMP 29	Shale	219.00	103.00	405.00	11.70	12.00	326.00	17.10	8.70	1.20	17.20	3.49	39.40	16.00	94.00	70.00	9.00	18.00	13.00	23.60	
CAMP 30	Shale	158.50	68.10	368.00	8.65	16.00	255.00	17.50	6.90	1.30	17.95	2.64	37.30	16.00	93.00	60.00	9.00	15.00	31.00	23.70	
CAMP 33	Shale	202.00	93.90	539.00	11.10	26.00	457.00	17.20	11.00	1.20	18.10	3.30	34.10	12.00	89.00	70.00	19.00	34.00	17.00	23.00	
CAMP 35	Shale	198.50	95.30	609.00	10.75	24.00	645.00	17.30	15.90	1.20	18.65	3.71	41.60	12.00	86.00	60.00	19.00	34.00	21.00	21.10	
CAMP 40	Shale	218.00	138.00	476.00	18.70	36.00	365.00	13.80	9.50	0.90	12.65	3.39	32.30	16.00	91.00	70.00	22.00	25.00	13.00	20.50	
CAMP 24	Siltstone	72.50	42.50	693.00	1.09	43.00	199.00	5.20	5.20	0.30	4.55	1.16	16.20	6.00	25.00	30.00	14.00	17.00	15.00	8.50	
CAMP 26	Siltstone	85.20	47.10	631.00	2.18	12.00	486.00	8.80	11.80	0.70	8.30	3.42	31.20	6.00	33.00	30.00	34.00	34.00	12.00	11.70	
CAMP 28	Siltstone	61.90	40.80	588.00	1.53	4.00	145.00	3.60	3.80	0.20	2.86	1.02	10.30	3.00	20.00	40.00	6.00	8.00	8.00	6.80	
CAMP 32	Siltstone	144.50	66.30	450.00	7.39	13.00	432.00	18.70	10.70	1.40	18.10	3.70	44.30	15.00	100.00	60.00	5.00	8.00	16.00	22.60	
CAMP 36	Siltstone	151.00	91.60	458.00	6.84	22.00	598.00	12.10	14.30	0.80	10.60	2.43	37.10	10.00	58.00	60.00	24.00	43.00	12.00	15.00	
CAMP 38	Siltstone	44.40	72.60	4510.00	1.28	8.00	147.00	4.10	4.10	0.30	4.29	0.95	13.20	6.00	19.00	50.00	9.00	12.00	8.00	5.50	
Anyaboni Formation - Kwahu group																					
CANY 5	Shale	226.00	149.50	285.00	16.20	20.00	496.00	23.60	12.10	1.70	23.30	3.71	62.70	18.00	122.00	80.00	8.00	10.00	11.00	28.40	
CANY 8	Shale	142.00	83.00	618.00	6.90	14.00	424.00	23.90	11.00	1.60	21.30	4.06	38.50	13.00	97.00	70.00	10.00	19.00	24.00	22.90	
CANY 10	Shale	141.50	75.40	573.00	6.84	26.00	349.00	21.30	10.00	1.60	23.30	4.66	43.30	15.00	111.00	70.00	5.00	8.00	15.00	25.20	
CANY 12	Shale	119.50	72.30	580.00	5.10	16.00	566.00	20.80	13.70	1.50	21.40	4.14	40.50	15.00	102.00	70.00	3.00	15.00	13.00	22.30	
CANY 1	Siltstone	82.00	42.40	629.00	1.57	18.00	495.00	7.80	11.90	0.60	10.20	3.16	28.30	4.00	27.00	30.00	7.00	12.00	17.00	7.60	
CANY 2	Siltstone	73.80	33.70	357.00	1.32	10.00	864.00	11.20	20.60	0.80	14.65	3.40	38.20	4.00	26.00	40.00	5.00	12.00	9.00	7.10	
CANY 11	Siltstone	57.70	50.00	2730.00	1.93	13.00	344.00	7.00	8.60	0.50	6.30	1.63	19.30	4.00	24.00	30.00	3.00	6.00	11.00	7.40	
CANY 20	Siltstone	105.50	388.00	777.00	3.01	13.00	161.00	9.50	4.10	0.60	8.07	1.60	20.70	7.00	50.00	40.00	8.00	18.00	11.00	17.20	
CANY 21	Siltstone	88.60	58.90	417.00	1.80	21.00	357.00	10.00	9.10	0.80	12.10	1.81	30.80	4.00	26.00	20.00	5.00	9.00	5.00	9.40	
Trace elements and elemental ratios in studied lithologies of Kwahu and Oti groups																					
Sample	Litho	Zn	Li	Sn	Th/U	Sc/Th	Cr/Th	Cr/Ni	Zr/Th	Rb/Sr	Zr/Hf	Co/Th	Th/Sc	Zr/10	Zr/Sc						
Afram Formation - Oti Group																					
CAFR 14	Shale	94.00	10.00	3.00	3.94	1.66	8.32	2.50	16.32	1.56	37.38	1.46	0.60	15.70	9.81						
CAFR 15	Shale	132.00	30.00	3.00	5.59	1.68	8.41	1.51	15.77	1.38	35.71	2.31	0.59	15.00	9.38						
CAFR 16	Shale	113.00	40.00	2.00	6.41	1.69	7.38	1.71	16.56	2.02	37.38	1.79	0.59	15.70	9.81						
CAFR 17	Shale	103.00	40.00	3.00	5.41	1.41	7.51	0.92	18.50	1.70	37.17	1.69	0.71	19.70	13.13						
CAFR 18	Shale	117.00	40.00	3.00	5.38	1.62	8.08	1.95	16.77	2.06	36.09	1.72	0.62	16.60	10.38						
CAFR 19	Shale	110.00	30.00	3.00	4.73	1.51	8.05	1.48	19.82	1.38	37.17	1.61	0.66	19.70	13.13						
CAFR 22	Siltstone	30.00	10.00	2.00	7.11	0.33	3.29	4.00	47.82	1.36	40.35	0.33	3.04	58.10	145.25						
CAFR 23	Siltstone	27.00	20.00	3.00	4.61	0.67	3.36	5.56	33.09	1.64	41.43	0.20	1.49	49.30	49.30						
Mpraeso Formation - Kwahu group																					
CAMP 25	Shale	73.00	30.00	4.00	5.57	0.87	3.50	3.16	22.22	2.27	40.11	0.70	1.14	38.10	25.40						
CAMP 27	Shale	71.00	30.00	5.00	5.57	0.90	3.98	3.33	19.80	2.13	40.20	2.74	1.12	39.80	22.11						
CAMP 29	Shale	68.00	30.00	4.00	4.93	0.93	4.07	3.89	18.95	2.13	37.47	0.52	1.08	32.60	20.38						
CAMP 30	Shale	78.00	40.00	4.00	6.80	0.89	3.34	4.00	14.21	2.33	36.96	0.50	1.12	25.50	15.94						
CAMP 33	Shale	67.00	30.00	3.00	5.48	0.66	3.87	2.06	25.25	2.15	41.55	1.05	1.51	45.70	38.08						
CAMP 35	Shale	63.00	30.00	3.00	5.03	0.64	3.22	1.76	34.58	2.08	40.57	1.02	1.55	64.50	53.75						
CAMP 40	Shale	88.00	20.00	3.00	3.73	1.26	5.53	2.80	28.85	1.58	38.42	1.74	0.79	36.50	22.81						
CAMP 24	Siltstone	83.00	30.00	1.00	3.92	1.32	6.59	1.76	43.74	1.71	38.27	3.08	0.76	19.90	33.17						
CAMP 26	Siltstone	81.00	50.00	2.00	2.43	0.72	3.61	0.88	58.55	1.81	41.19	4.10	1.38	48.60	81.00						
CAMP 28	Siltstone	38.00	40.00	1.00	2.80	1.05	13.99	5.00	50.70	1.52	38.16	2.10	0.95	14.50	48.33						
CAMP 32	Siltstone	41.00	40.00	4.00	4.89	0.83	3.31	7.50	23.87	2.18	40.37	0.28	1.21	43.20	28.80						
CAMP 36	Siltstone	67.00	10.00	2.00	4.36	0.94	5.66	1.40	56.42	1.65	41.82	2.26	1.06	59.80	59.80						
CAMP 38	Siltstone	370.00	40.00	1.00	4.52	1.40	11.66	4.17	34.27	0.61	35.85	2.10	0.72	14.70	24.50						
Anyaboni Formation - Kwahu group																					
CANY 5	Shale	44.00	10.00	5.00	6.28	0.77	3.43	8.00	21.29	1.51	40.99	0.34	1.29	49.60	27.56						
CANY 8	Shale	70.00	70.00	4.00	5.25	0.61	3.29	3.68	19.91	1.71	38.55	0.47	1.64	42.40	32.62						
CANY 10	Shale	41.00	50.00	4.00	5.00	0.64	3.00	8.75	14.98	1.88	34.90	0.21	1.55	34.90	23.27						
CANY 12	Shale	23.00	50.00	4.00	5.17	0.70	3.27	4.67	26.45	1.65	41.31	0.14	1.43	56.60	37.73						
CANY 1	Siltstone	25.00	10.00	2.00	3.23	0.39	2.94	2.50	48.53	1.93	41.60	0.69	2.55	49.50	123.75						
CANY 2	Siltstone	21.00	10.00	2.00	4.31	0.27	2.73	3.33	58.98	2.19	41.94	0.34	3.66	86.40	216.00						
CANY 11	Siltstone	44.00	30.00	1.00	3.87	0.63	4.76	5.00	54.60	1.15	40.00	0.48	1.58	34.40	86.00						
CANY 20	Siltstone	43.00	20.00	2.00	5.04	0.87	4.96	2.22	19.95	0.27	39.27	0.99	1.15	16.10	23.00						
CANY 21	Siltstone	17.00	5.00	2.																	

Table 3

Rare earth elements (ppm) and elemental ratios in studied lithologies of Kwahu and Oti Groups.

Sample	Litho	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	La/Yb	Eu/Eu*	La/Sc	La/Th	ΣREE
<i>Afram Formation - Oti group</i>																				
CAFR 14	Shale	97.80	246.00	31.00	122.50	22.70	4.03	14.40	1.92	10.05	1.71	4.84	0.60	4.12	0.57	23.74	0.68	6.11	10.17	617.94
CAFR 15	Shale	98.40	194.50	24.70	94.20	17.10	3.29	12.35	1.65	9.10	1.62	4.46	0.60	3.87	0.58	25.43	0.69	6.15	10.35	525.22
CAFR 16	Shale	31.80	56.40	7.21	28.70	5.72	1.13	4.40	0.67	4.22	0.88	2.82	0.38	2.68	0.36	11.87	0.69	1.99	3.35	185.57
CAFR 17	Shale	30.70	55.30	7.41	29.50	6.28	1.33	5.51	0.88	5.38	1.08	3.35	0.44	3.09	0.42	9.94	0.69	2.05	2.88	199.07
CAFR 18	Shale	28.20	51.70	6.50	25.40	4.95	1.01	4.05	0.63	4.07	0.83	2.53	0.36	2.61	0.37	10.80	0.6	1.76	2.85	171.51
CAFR 19	Shale	70.70	104.00	15.30	59.10	11.60	2.31	8.94	1.28	7.62	1.43	4.11	0.57	3.68	0.52	19.21	0.69	4.71	7.11	344.76
CAFR 22	Siltstone	69.90	142.50	17.30	67.20	12.65	2.12	8.84	1.20	6.31	1.22	3.98	0.53	3.50	0.59	19.97	0.61	17.48	5.75	374.74
CAFR 23	Siltstone	41.30	83.80	9.22	33.20	5.94	3.91	5.01	0.87	5.76	1.17	3.91	0.56	3.93	0.61	19.97	0.59	4.13	2.77	241.89
<i>Mpraeso Formation - Kwahu group</i>																				
CAMP 25	Shale	50.10	105.00	12.30	48.10	9.81	1.66	8.14	1.21	8.17	1.63	5.16	0.63	4.98	0.72	10.06	0.57	3.34	2.92	313.66
CAMP 27	Shale	72.00	150.00	16.80	65.30	11.35	1.88	9.24	1.43	8.77	1.79	5.70	0.78	5.55	0.88	12.97	0.56	4.00	3.58	417.02
CAMP 29	Shale	53.00	109.00	13.10	51.30	9.74	1.60	7.48	1.21	7.53	1.49	5.12	0.68	4.98	0.75	10.64	0.57	3.31	3.08	321.81
CAMP 30	Shale	46.70	98.80	11.10	42.00	7.62	1.29	6.23	1.08	6.64	1.37	4.37	0.66	4.26	0.62	10.96	0.57	2.92	2.60	286.19
CAMP 33	Shale	51.90	106.50	11.80	45.40	8.71	1.64	6.68	1.07	6.32	1.29	4.02	0.55	4.20	0.64	12.36	0.66	4.33	2.87	296.77
CAMP 35	Shale	56.30	127.00	14.85	59.30	11.70	2.17	8.94	1.30	7.47	1.58	4.77	0.66	4.80	0.73	11.73	0.65	4.69	3.02	354.66
CAMP 40	Shale	40.70	79.90	8.61	32.10	6.10	1.07	5.08	0.90	5.75	1.16	3.93	0.62	3.91	0.59	10.41	0.59	2.54	3.22	238.75
CAMP 24	Siltstone	20.10	49.10	5.97	25.10	4.92	0.87	3.29	0.54	3.35	0.65	1.96	0.27	2.03	0.27	9.90	0.66	3.35	4.42	140.62
CAMP 26	Siltstone	20.90	49.50	6.14	25.60	5.60	0.94	5.05	0.88	5.59	1.13	3.48	0.55	3.97	0.63	5.26	0.54	3.48	2.52	167.16
CAMP 28	Siltstone	12.90	30.00	3.56	15.00	3.15	0.48	2.19		1.98	0.37	1.11	0.17	1.21	0.18	10.66	0.56	4.30	4.51	87.60
CAMP 32	Siltstone	48.50	97.60	10.50	38.50	6.83	1.14	6.16	1.07	7.20	1.50	4.98	0.71	5.24	0.77	9.26	0.54	3.23	2.68	290.00
CAMP 36	Siltstone	41.90	90.00	10.30	39.10	7.75	1.33	6.32	1.07	6.70	1.42	4.20	0.59	4.31	0.59	9.72	0.58	4.19	3.95	262.68
CAMP 38	Siltstone	10.40	23.80	2.74	11.10	2.29	0.39	2.35	0.44	2.43	0.54	1.42	0.22	1.43	0.22	7.27	0.51	1.73	2.42	78.97
<i>Anyaboni Formation - Kwahu group</i>																				
CANY 5	Shale	78.20	164.50	18.65	73.80	13.80	2.41	11.00	1.88	11.30	2.34	7.15	0.99	7.42	1.13	10.54	0.6	4.34	3.36	475.27
CANY 8	Shale	50.20	108.00	12.15	46.50	8.98	1.42	7.14	1.15	7.03	1.49	4.64	0.69	4.79	0.69	10.48	0.54	3.86	2.36	306.37
CANY 10	Shale	52.50	115.50	12.75	47.80	8.76	1.56	7.52	1.17	6.90	1.43	4.20	0.63	4.41	0.69	11.90	0.59	3.50	2.25	324.12
CANY 12	Shale	52.10	112.00	12.55	47.90	9.51	1.58	7.79	1.27	7.79	1.60	4.80	0.72	5.13	0.75	10.16	0.56	3.47	2.43	320.99
CANY 1	Siltstone	39.60	81.20	9.67	37.00	6.96	1.16	5.44	0.83	5.20	0.99	3.26	0.47	3.48	0.48	11.38	0.58	9.90	3.88	227.36
CANY 2	Siltstone	38.30	83.10	9.61	37.00	7.11	1.12	5.65	0.95	5.74	1.30	4.22	0.65	4.59	0.71	8.34	0.54	9.58	2.61	241.84
CANY 11	Siltstone	17.30	40.30	4.60	18.60	4.03	0.67	3.01	0.53	3.40	0.70	2.09	0.34	2.13	0.33	8.12	0.59	4.33	2.75	120.99
CANY 20	Siltstone	42.90	75.60	8.70	32.70	5.13	1.13	4.31	0.58	3.54	0.69	2.14	0.30	1.88	0.27	22.82	0.73	6.13	5.32	206.71
CANY 21	Siltstone	47.00	88.70	9.66	36.80	6.72	1.26	6.00	0.96	5.60	1.14	3.45	0.48	3.47	0.50	13.54	0.61	11.75	3.88	245.78

**Fig. 4.** Bivariate plot of SiO₂ against Al₂O₃ showing separation between shales and siltstones.**Fig. 5.** Spider-diagrams of trace element compositions in the shales and siltstones in the Afram Formation, Anyaboni Formation and Mpraeso Formation normalized against UCC values after Taylor and McLennan (1985).



The abundance of the trace elements were normalized to average upper continental crust (UCC) values, and displayed in spider diagrams (Fig. 5). These diagrams show that while K and Th abundance are close to that of the UCC in some rock samples, La, Nb, Ce, are moderately high, but Sr, Nb, Ta and P appear to be depleted. The patterns appear to show enrichment of Cs, Rb, La, Ce and Nd in all the shales, and some siltstone. However, the Ba results show some level of inconsistency; whereas they show depletion in the shales, the two siltstone samples fall on opposite sides of the UCC (Fig. 5). The elements Zr, Hf, Nb, U and Th show varying concentrations, which may be due to the carbonate content in the samples.

4.2.3. Rare earth elements

The rare earth elements (REE) recorded variable concentrations as shown in Table 3. The total REE content is higher in the shales (171.51–617.94 ppm) than in the siltstones (78.97–290.00 ppm), and the range of variation is also wider in the shales than in the siltstone. The chondrite-normalized REE patterns of the shales and siltstones (Fig. 6) appear similar to the distribution patterns of UCC as presented by Taylor and McLennan (1985). However, the shales appear clearly separated from the siltstones, with the shales showing more abundance REE than the siltstones. These patterns signify that the REEs concentrations are a result of higher clays and zircon content in the shales than in the siltstones. The patterns show distinctly enriched LREE (La, Ce, Pr, Nd, Sm) with variable negative Eu anomalies averaging 0.62 in the shales and 0.59 in the siltstones, and almost flat HREEs (Gd, Tb, Dy, Ho, Er, Tm, Yb). Negative Eu anomalies range between 0.51 and 0.72 (Table 3) in all the shales and siltstones samples. The Afram shales of the Oti Group have moderate Eu anomalies (0.64–0.68), while the shales of the Anyaboni Formation and Mpraeso Formation of the Kwahu Group, showed relatively strong to moderate Eu anomalies (0.52–0.63).

5. Discussions

5.1. Geochemistry

The chemical compositions of clastic rocks are principally controlled by source area rocks, erosion, sorting, redox environment and diagenesis (Johnsson, 1993). However, these compositions could be altered by the extent of metamorphic mineral reactions (Johnsson, 1993). With little modification by secondary processes, clastic sediments whole-rock geochemistry is useful in fingerprinting provenance and depositional setting of sedimentary rocks.

5.1.1. Major elements

The generally higher content of K_2O , Fe_2O_3 and TiO_2 in the shales than in the siltstones when compared with Al_2O_3 , show that K_2O , Fe_2O_3 and TiO_2 are associated with clay-size phases (Madhavaraju and Lee, 2010). Positive correlations between Al_2O_3 and K_2O , TiO_2 and Fe_2O_3 indicate that K, Ti, Fe and Al are associated entirely with detrital phases as Al concentration in sediments is considered a reasonable good measure of detrital flux (Peinerud, 2000; Nagarajan, et al., 2007). However, the SiO_2 correlating negatively with Al_2O_3 in all the siltstones (Mpraeso siltstones $r = -0.88$ and Anyaboni siltstones $r = -0.99$) signifies detrital quartz influence on sediments. It further suggests the presence of biogenic siliceous components of aluminosilicates that are not associated with detrital quartz (Robertson, 2007). The elements K and Rb are likely to have been obtained from phyllosilicates in the source rocks due to the positive correlation between Al_2O_3 and K_2O .

5.1.2. Trace elements

The shales and some siltstones are enriched in Cs and Rb, but have varied Ba concentrations because they may have been preferentially exchanged and adsorbed onto clays in these rocks due to their large ionic sizes (Nesbitt et al., 1980; Wronkiewicz and Condie, 1987). The high Rb concentrations found in the shales and siltstones may be due to its lower mobility during weathering processes than K. The Rb may therefore have been preferentially retained in weathered illite (Taylor and Eggleton, 2001; Li et al., 2005). The high abundance of Ba in some shales and siltstones may be an indication of detrital flux (Temraz, 2005; Aly, 2015). The high Ba content in siltstones may also be an indication of original syn-sedimentary barite crystals in composite sediments (Aly, 2015). The strong positive correlation between Al_2O_3 and the trace elements Cr, Sc and V in the Anyaboni shales ($r = 0.79, 0.85, 0.98$), siltstones ($r = 0.28, 0.93, 0.95$), Mpraeso siltstones ($r = 0.63, 0.97, 0.99$) suggests bonding of the Cr, Sc and V with clay minerals as noted by Fedo et al. (1996). It is possible that weathering of some silicate minerals released these TTEs that were later concentrated in the sediments (Fedo et al., 1996; Bauluz et al., 2000).

5.1.3. Rare earth elements

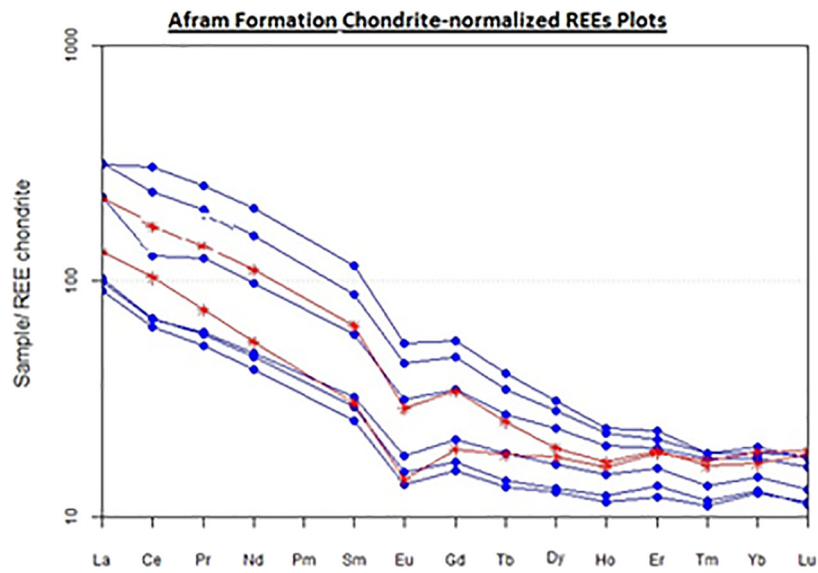
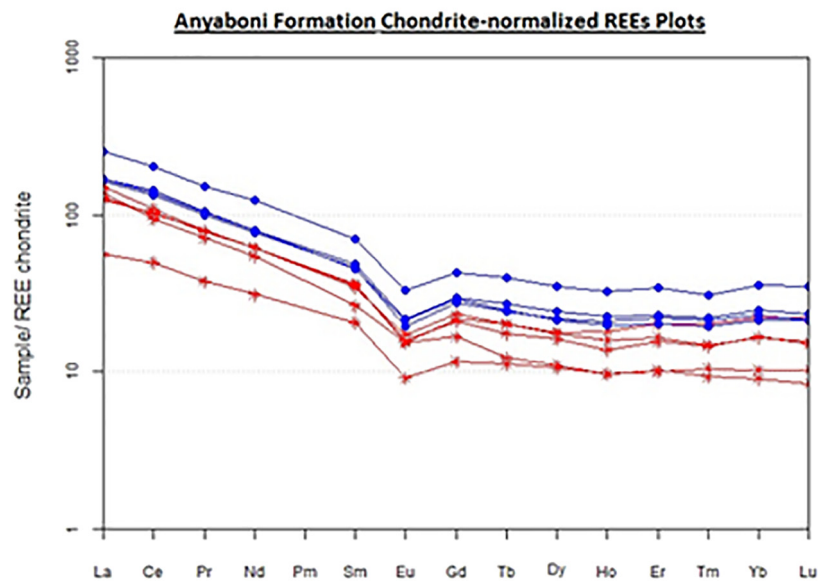
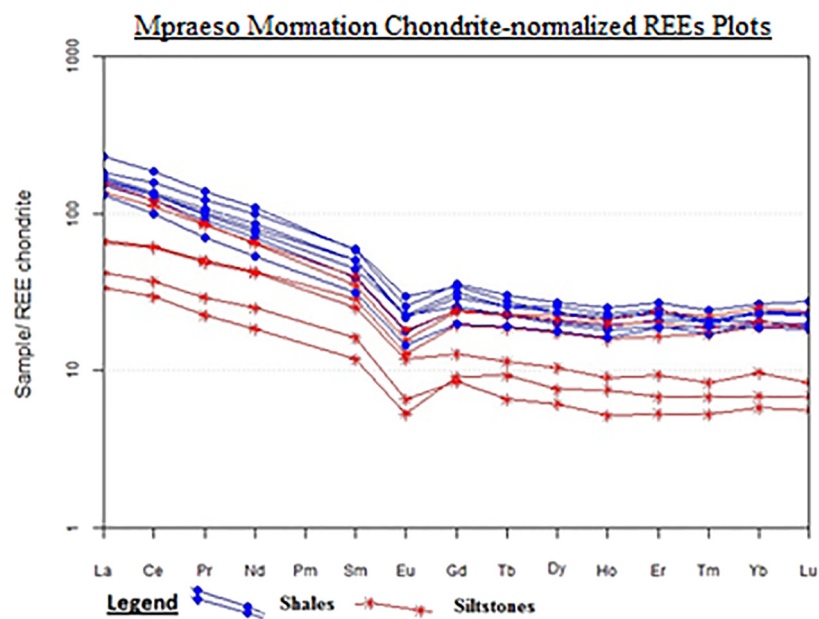
Weathering of silicate minerals, probably the phyllosilicates, may have introduced some REEs into sediments composing the shales and siltstones (Liaghati, 2004; Sanz-Montero et al., 2009). Similarly, weathering may have produced K-bearing clay minerals such as illite (Dudek, 2012) that primarily controlled the abundance and distribution of LFSE in the sediments (Feng and Kerrich, 1990; McLennan et al., 1993).

Shales are generally known to have higher total REE content than siltstones even though both silts and clay sediments host the bulk of REEs (Cullers et al., 1987, 1988). The higher total REE content in the shales (Table 3) suggests that the clay minerals in the shales, especially those rich in alumina and Fe^{3+} are hosting the REEs (Cullers et al., 1987, 1988; Condie, 1991) and are not affected by post-depositional diagenetic activities and redistribution (Pettijohn, 1975; Condie, 1991). Comparably, quartz dilution ($SiO_2 > 70\%$) may have lowered composite total REE content in the siltstones (Taylor and McLennan, 1985).

The enriched REE in chondrite-normalized plot (Fig. 6) suggest felsic sources for sediments in the shales and siltstones (Taylor and McLennan, 1985; Wronkiewicz and Condie, 1989). Also the negative Eu anomalies (Fig. 6) and high LREE/HREE values (between 5 and 11, average 6.7) further suggest felsic rocks for composite sediments (Cullers and Graf, 1984; Taylor and McLennan, 1985). However, the lower LREE/HREE values (4.2 and 4.5) with little Eu anomalies at some locations indicate the presence of some mafic derived sediments in some of the shales and siltstones (Cullers and Graf, 1983, 1984; Cullers, 1994). The negative Eu anomalies (0.60 to 0.68) suggest felsic source as argued by some researchers (Cullers, 1994; Cullers et al., 1988; and Cullers and Podkovyrov, 2000), who place the range for felsic sources as 0.40 to 0.94. The depletion of Eu in the shales and siltstones may be due to the absence of plagioclases (Bhatia, 1985); in fact, Eu anomaly is used to evaluate plagioclase in sediments (McLennan et al., 1990). Sediments re-working or intracrustal differentiation of upper continental crust at shallow depth could also account for the absence of plagioclase (McLennan, 1989). Perhaps, source rocks fractionations were limited and therefore sediments/seawater inherited this Eu anomaly from their source igneous rocks in the upper crust (Taylor and McLennan, 1985; McLennan and Taylor, 1991; Awwiller, 1994).

Zircon presence or the co-occurrence of zircon and other heavy minerals in the shales and siltstones is shown by the Zr and Th correlations, (Afram shales $r = 0.84$; Anyaboni siltstones $r = 0.78$; Mpraeso shales $r = 0.69$). The increase abundance of Zr in shales suggest that zircon minerals were selectively concentrated by grain size

Fig. 6. Chondrite-normalized REE patterns of shales and siltstones in Afram Formation, Anyaboni Formation and Mpraeso Formation (after Taylor and McLennan, 1985). The patterns are similar to upper continental crust.



fractionation of the sediments. Thus the high Zr/Hf values (34.90–41.94) signify the control of zircon abundance in all the shales and siltstones. According to Bauluz et al. (2000), felsic rocks are enriched in HFSE than mafic rocks, implying that the enrichment of HFSE in the shales and siltstones, denotes mainly felsic source for composite sediments.

5.2. Provenance and compositional variation

The REE, Th and Sc in sedimentary rocks are considered reliable indicators of provenance and tectonic setting (Taylor and McLennan, 1985; McLennan, 1989). This is because their distributions are not seriously affected by secondary processes –diagenesis and metamorphism (McLennan and Taylor, 1991; Condie, 1993). This means the degree of sediment reworking and compositional variation could be evaluated with the Th/Sc against Zr/Sc diagram (McLennan et al., 1993). The bivariate plot of Th/Sc versus Zr/Sc (Fig. 7) shows felsic provenance, and recycled materials for many of the shales and siltstones (Fedó et al., 1997; Taylor and McLennan, 1985). The enrichment of Zr and Th (HFSE) in the sediments is more indicative of felsic provenance than mafic source areas (Bauluz et al., 2000); however, minor andesitic properties were revealed in some of the shales. A similar range of Th/Sc values were recorded in both the shales and siltstones – i.e. Afram 0.59–3.04 and Anyaboni 1.15–3.66 and Mpraeso 0.76–1.55 in the Oti Group and Kwahu Group respectively. This is an indication that, sorting may not have had any serious effect on concentrating Th and Sc (Mongelli et al., 2006) as it did on Zr that resulted in a wide range of Zr/Sc values (9.38 to 216.00). Therefore, the elements Th and Sc are not derived from easily depleted minerals during weathering. On the strength of this, Th and Sc were considered to be potential source fingerprints (Nyakairu and Koeberl, 2001), and were used to infer the felsic sources of the sediments. The positive linear correlation trend between Th/Sc and Zr/Sc ($R^2 = 0.81$), indicates chemical differentiation of igneous rocks for the elements (Meinhold et al., 2007), and the recorded narrow low range of values for Th/Sc (0.59–3.66), is characteristic of sediments from felsic source materials.

Many heavy minerals in sedimentary rocks are dominated by trace elements (Zr in zircon, REE in monazite and allanite) (Johnsson and Basu, 1993), hence the Zr abundance in sediments signifies zircon enrichment (Garzanti et al., 2011). Though Zr is heavily enriched in zircon, it is also easily recycled with the zircon in sediments (Johnsson and Basu, 1993). However, Sc is present in sediments in labile phases (McLennan, 1993). It implies that, Zr/Sc values are capable of being used to analyse heavy minerals concentrations in sediments during sorting. The Zr/Sc ratio is also one of the useful proxies in evaluating the presence or absence of recycling in sediments (Cole et al., 2009). The Zr/Sc values recorded in the shales and siltstones, spanned over a wide range (9.38–216.00) to signify significant zircon enrichment consistent with reworking during transport (McLennan et al., 1993). The observed wide range of Zr/Sc values, demonstrates that the entire sediments did not originate from the source regions but consists of appreciable recycled materials. Comparatively, the Zr/Sc values in the shales are lower (Afram 9.81–13.13; Anyaboni 23.27–37.73; Mpraeso 15.94–53.75) than the Zr/Sc values in the siltstones (Afram 49.30–145.25; Anyaboni 86.00–216.00; Mpraeso 24.50–81.00). The above range of Zr/Sc values demonstrates that heavy minerals were concentrated in the sediments mainly by recycling. The Th/Sc versus Zr/Sc plot further suggests that typical upper continental crust is the source for sediments rather than lower continental crust. The trend of Rb/Sr values (0.27 to 2.27) in the shales and siltstones affirm the upper continental crustal origin of the sediments.

The chondrite-normalized REE diagram (Fig. 6) shows LREE enrichment and an almost flat HREE patterns in the shales and siltstones that denote felsic sources for the sediments (Wang et al., 2016). The negative Eu anomalies in this diagram signify source rocks differentiation that is similar to granite (Rudnick, 1992). The observed LREE enrichment and

HREE depletion may be due to low heavy minerals (zircon) concentrations in the sediments (Nyakairu and Koeberl, 2001). It can also be argued that, the shales and siltstones had blend of various source sediments through a number of sedimentary cycles. It is on basis of enriched LREE and depleted HREEs that detrital (siliciclastic) origin for the trace elements was inferred instead of seawater fractionation (Ali et al., 2014). According to Taylor and McLennan (1985), Eu anomalies better fingerprint source-rock characteristics, such that the range of negative Eu anomalies 0.51 to 0.66 (Table 3) in the shales and the siltstones, affirm the inferred felsic source(s) for the sediments (Cullers and Graf, 1984). It further suggests that the sediments were eroded from magmatic arcs (Taylor and McLennan, 1985). The negative Eu anomalies in the range 0.67 to 0.73 could still be considered as indicating felsic source(s) as noted by Cullers, 1994, Cullers et al., 1988, and Cullers and Podkovyrov, 2000.

The REE ratios differentiate felsic source components from that of mafic and avoid quartz dilution effects (Taylor and McLennan, 1985; Bhatia and Crook, 1986; Girty et al., 1996). The established La/Sc, Th/Sc, Cr/Th, Eu/Eu*, La/Th, Th/Co, Th/Cr, Zr/Y, and Nb/Y values which differ significantly in mafic and felsic source rocks (Taylor and McLennan, 1985; Cullers et al., 1987, 1988; Cullers, 1994, 2000; Cullers and Podkovyrov, 2000, 2002; Armstrong-Altrin et al., 2004), have been compared with the same elemental ratio values obtained in this study (Table 4), to provide further information on the sediments felsic provenance in the shales and siltstones.

The Afram shales have strong to moderate Eu anomalies than the Anyaboni shales and Mpraeso shales (Table 4). The siltstones in the Anyaboni Formation and Mpraeso Formation have low Th/Sc ratio values than Afram Formation siltstones. With the exception of the Afram shales having average Th/Sc value of 0.63 ($n = 6$), the rest of lithologies recorded higher average Th/Sc values of 2.26 for the Afram siltstones ($n = 2$), 1.48 for the Anyaboni shales ($n = 4$) and 2.39 for siltstones is, ($n = 5$), 1.19 for the Mpraeso shales ($n = 7$) and 1.01 for Mpraeso siltstones ($n = 6$) than the value of 0.9 for UCC (Taylor and McLennan, 1985). These average values suggest relatively felsic source-rock composition for the sediments. According to Cullers (1994), clastic rocks with Cr/Th values in the range 2.5 to 17.5 and Eu/Eu* values between 0.48 and 0.78, originate mostly from felsic sources rather than from mafic sources. In Table 4, Cr/Th and Eu/Eu* values for the studied shales and siltstones also fall in felsic provenance range.

In the La/Th vs. Hf discrimination diagram (Fig. 8), for differentiating various arc components and source rocks by Floyd and Leveridge (1987), three Afram shales depicted slightly high La/Th values (10.17, 10.35 and 7.11) while the rest of the shales and siltstones have uniformly low La/Th values (2.25–5.75). The Hf concentrations in some shales and siltstones were low (3.80–5.30) ppm, while in others, slightly Hf high concentrations (8.70–20.60) ppm were recorded. Perhaps the low Hf concentrations may be attributed to low zircon contents in sediments. The Afram shales and Mpraeso siltstones with La/Th values (<5) and Hf contents (2–6) ppm are felsic in composition. This is because Floyd and Leveridge (1987) established that, arcs of felsic compositions have both low or uniform La/Th values (<5) and Hf concentrations between 3 and 7 ppm. The obtained La/Th values in the shales and siltstones are similar to those in granites and granodiorites (McLennan, 2001). In shales and siltstones with Hf contents above 10 ppm, much higher than what felsic rocks are known to contain, may be originating from metasedimentary sources (Taylor and McLennan, 1985) and suggest passive margin tectonic setting. However shales and siltstones with low La/Th values and increasing Hf concentrations (the Anyaboni shales and siltstones, Mpraeso shales) indicate sediments derived from felsic source rocks with some input from recycled old sediment. Probably the progressive unroofing of arc rocks and/or incorporation of sedimentary basement rocks increased the Hf content through the release of zircon (Floyd et al., 1989). Some Afram shales and an Anyaboni siltstone consist of low Hf concentrations and slightly high La/Th values

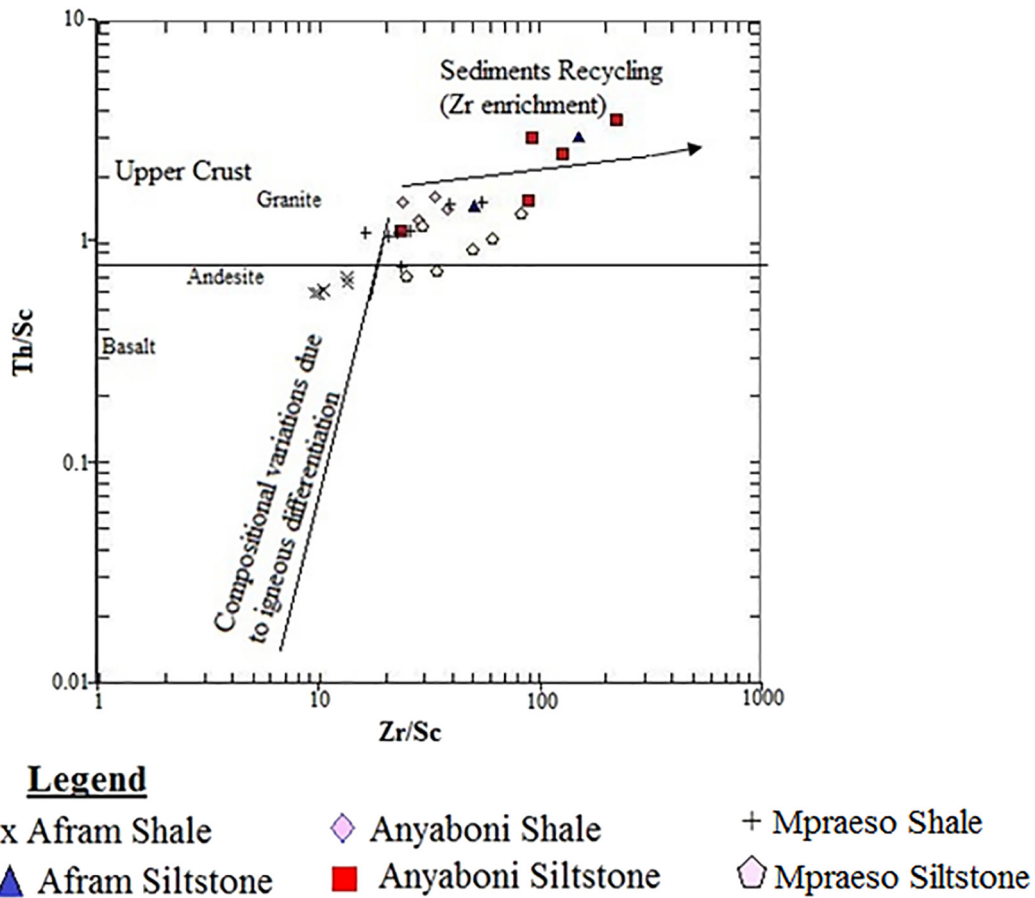


Fig. 7. Th/Sc v. Zr/Sc discrimination diagram (after McLennan et al., 1993) illustrating compositional variations and sediment recycling of sediments in the shales and siltstones.

to suggest a mixture of felsic and mafic source region (Fig. 8) that most likely involve oceanic crust obducted onto continental margin (Floyd et al., 1989). The general depletion of Nb and Ta, Cs enrichment (Fig. 5) and anomalous REE patterns in especially the shales affirm mafic source materials input (Floyd et al., 1989).

Constraining felsic or mafic provenance of the sediments, a mixing model using Th/Sc vs Cr/Th ratios (Condie and Wronkiewicz, 1990) was generated (Fig. 9). Some siltstones in the Afram Formation and Anyaboni Formation characterized as average Archean crustal granite (3.75–10) with Th/Sc values from 2.5 to 4.5 and Cr/Th values <3.5.

Probably these siltstones received sediments from mainly granitic rocks (felsic sources). Sediment sources with mixed materials (felsic and mafic), the Th/Sc values range between 0.5 and 2.0 with corresponding Cr/Th values between 3.0 and 8.0 (Cullers, 1994; Lahtinen, 2000). The values for both Th/Sc and Cr/Th in some of the studied shales and siltstones are within the above stated ranges, hence characterizing them as mixed felsic and mafic materials. However, two Mpraeso siltstones and some Afram shales recorded Cr/Th values >8 and low Th/Sc values (<1.5) to suggest the presence of localized strong mafic source sediments in them. In general, sediments composing the studied shales

Table 4

Range of elemental ratios values in studied shales and siltstones compared to similar ratios values in fractions derived from felsic and mafic rocks (after Cullers, 1994, 2000; Cullers et al., 1988; Cullers and Podkovyrov, 2000).

Elemental ratio	Range of values in shales and siltstones in Formations in Kwahu and Oti						Range of values in sediments in felsic and mafic rocks	
	Afram		Anyaboni		Mpraeso		Felsic	Mafic
	Shale	Siltstone	Shale	Siltstone	Shale	Siltstone		
Eu/Eu*	0.64–0.68	0.57–0.58	0.53–0.58	0.52–0.72	0.55–0.63	0.51–0.62	0.40–0.94	0.71–0.95
La/Sc	1.76–6.11	4.13–17.48	3.47–4.34	4.33–11.75	2.54–4.69	1.73–4.30	2.50–16.30	0.43–0.86
Th/Sc	0.59–0.71	1.49–3.04	1.29–1.64	1.15–3.66	0.79–1.55	0.72–1.38	0.84–20.50	0.05–0.22
Cr/Th	8.05–8.41	3.29–3.36	3.00–3.43	1.65–4.96	3.34–5.53	3.31–13.99	4.00–15.00	25.0–500
La/Th	2.85–10.35	2.77–5.75	2.25–3.36	2.61–5.32	2.60–3.58	2.42–4.42	16.30–25.0	0.43–0.86
Th/Co	0.56–0.69	3.04–4.97	2.13–7.13	1.01–2.93	0.37–1.99	0.24–0.48	0.67–19.40	0.04–1.40
Th/Cr	0.12–0.14	0.30–0.30	0.29–0.33	0.20–0.61	0.18–0.31	0.09–0.30	0.13–2.70	0.018–0.046
Zr/Y	3.50–7.44	15.08–17.49	7.91–13.98	7.78–22.62	8.27–5.50	9.75–16.12	–	–
Nb/Y	0.27–0.57	0.27–0.45	0.38–0.62	0.28–0.46	0.40–0.50	0.28–0.42	–	–
(La/Yb) _N	6.02–15.14	6.37–12.10	6.39–7.22	4.92–13.83	6.10–7.86	3.19–6.00	–	–

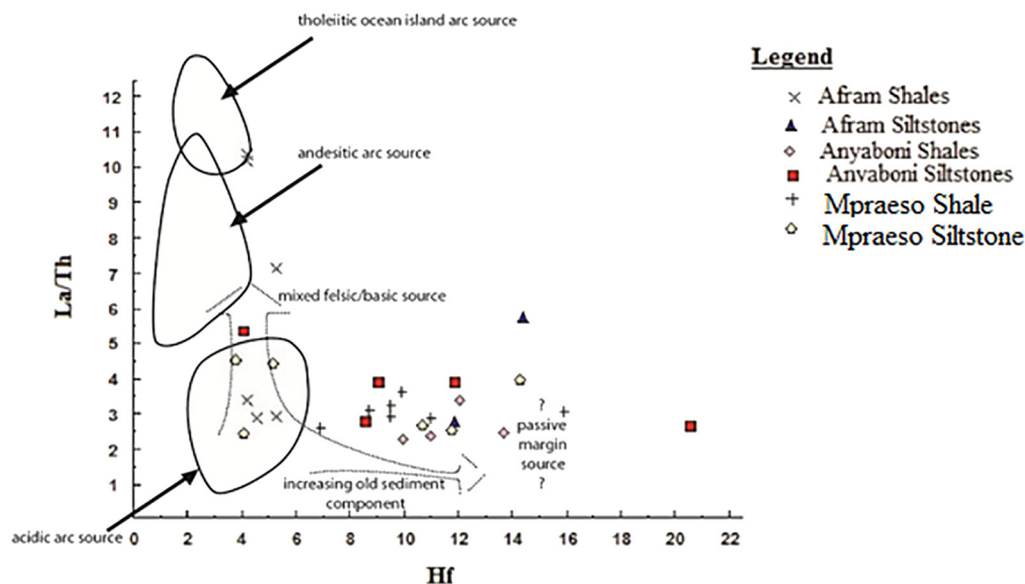


Fig. 8. Source rock La/Th-Hf discrimination diagram to constrain provenance compositions of the clastic sediments in the shales and siltstones.

and siltstones were sourced from mainly felsic materials with inputs from mixed felsic and mafic areas alongside old recycled materials.

The abundance of least fractionated trace elements (REE Th, and Sc) in sediments are related to that of their provenance (McLennan et al., 1980). Implying that the REE, Th, and Sc in the sediments composing

the studied shales and siltstones must be related to their source rocks by these trace elements. To investigate this relationship, a mixing calculations was performed to model REE data of the studied shales, siltstones and selected end members REE data of Birimian basement complex, obtained from Block et al. (2016) and UCC data from Condie

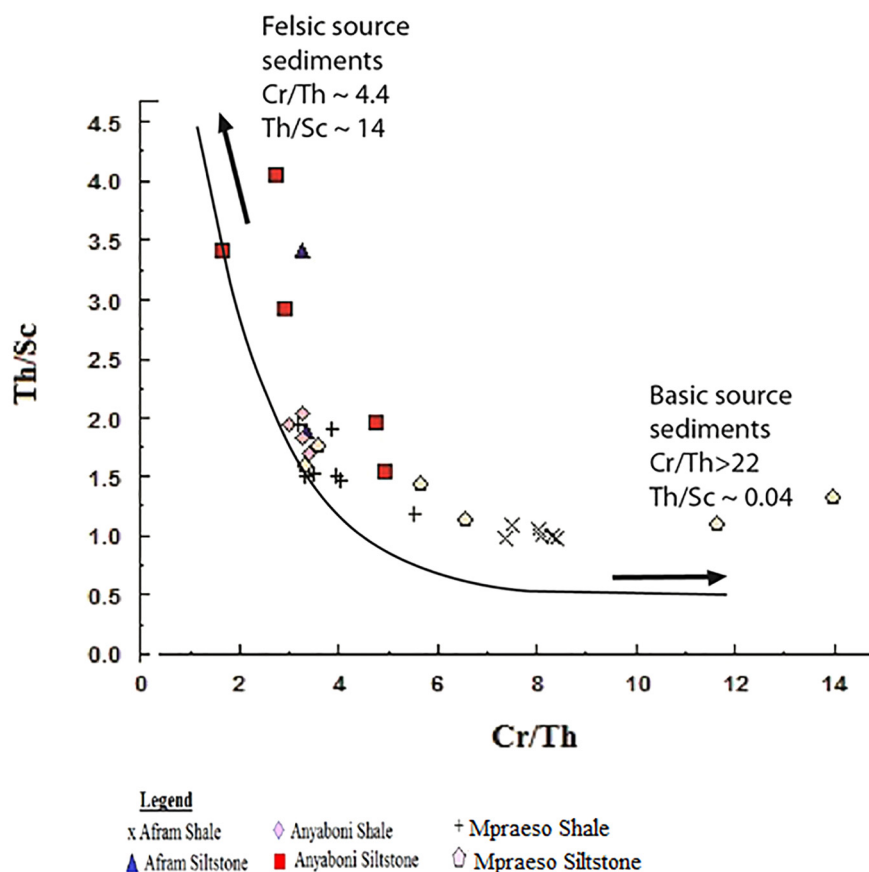


Fig. 9. Th/Sc versus Cr/Th diagram (after Totten et al., 2000) to further constrain provenance characteristics of shales and siltstones.

(1993) to determine if the Birimian basement complex contributed materials into the Volta Basin. The mixing calculations followed the matrix procedure put forward by Kasanzu et al. (2008):

$$\begin{bmatrix} E_u \\ E_u^* \\ La \\ Yb \\ Gd \\ Yb \end{bmatrix} = \begin{bmatrix} 0.90 & 0.87 & 1.04 \\ 11.00 & 45.23 & 6.00 \\ 2.20 & 3.62 & 1.40 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} 0.66 \\ 12.07 \\ 2.07 \end{bmatrix} \text{ shale matrix}$$

$$\begin{bmatrix} E_u \\ E_u^* \\ La \\ Yb \\ Gd \\ Yb \end{bmatrix} = \begin{bmatrix} 0.90 & 0.87 & 1.04 \\ 11.00 & 45.23 & 6.00 \\ 2.20 & 3.62 & 1.40 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} 0.56 \\ 10.93 \\ 1.82 \end{bmatrix} \text{ siltstone matrix}$$

where x = TTG (tonalite-trondhjemite-granodiorite), y = granite and z = basalt. The mixing calculations results (Table 5), modeled with chondrite-normalized REE patterns (Fig. 10) show reasonable well matching between sediments composing the shales and siltstones and sediments derived from Birimian basement complex. Thus it is inferred that the Birimian basement complex is the source terrain that mainly supplied sediments into the Volta Basin.

5.3. Tectonic setting

The trace elements La, Th, Zr and Sc are quantitatively transferred into clastic sediments during primary weathering and transportation, due to their relatively low mobility and residence time in ocean water, therefore are used to fingerprint tectonic settings (Bhatia and Crook, 1986). The low mobility of La, Zr, Sc and Th informed the choice of Bhatia and Crook (1986) ternary diagrams which is based on Th, Zr, and Sc to determine the depositional tectonic setting in the study area. In these diagrams (Figs. 11 and 12), the shales and the siltstones in the Afram Formation, Anyaboni Formation and Mpraeso Formation plotted mainly in the Passive Margin, with a few in the Continental Island Arc fields. It is possible that the shales and siltstones that plotted in Continental Island Arc field, formed on either 'well-developed continental crust or on thin continental margin' with a provenance of a "dissected magmatic arc-recycled orogen" (Bhatia, 1983; Bhatia and Crook, 1986).

It was realized that Th/Sc values greater than three (>3) and La/Sc values greater than six (La/Sc > 6) in some of the shales and siltstones are not characteristic of passive-margin setting (Bhatia and Crook, 1986). These values rather suggest controls by certain localized source factors that enriched sediments with Th (Descourvieres et al., 2011), accounting for the plotting of some shales and siltstones outside defined tectonic settings boundaries (Figs. 11 and 12). Probably, hydraulic

Table 5

Results from mixing calculations of Birimian basement complex end members compared with average shales and siltstones in Kwahu and Oti groups.

Elements/elemental ratios	Kwahu and Oti groups												Birimian basement complex					
	Afram Formation				Anyaboni Formation				Mpraeso Formation				Mixing end members					
	Ave. Shale (n = 6)		Ave. siltstone (n = 2)		Ave. shale (n = 4)		Ave. siltstone (n = 5)		Ave. shale (n = 7)		Ave. siltstone (n = 6)		TTG		GR (n = 19)		BA (n = 5)	
	ppm	N	ppm	N	ppm	N	ppm	N	ppm	N	ppm	N	ppm	N	ppm	N	ppm	N
La	59.6	251.48	55.60	234.60	58.25	245.78	37.02	156.20	52.96	223.45	25.78	108.79	26	70	48	130	11	30
Ce	117.98	192.78	113.15	184.89	125.00	204.25	73.78	120.56	110.89	181.19	56.67	92.59	45	47	115	120	27	28
Nd	59.90	128.27	50.20	107.49	54.00	115.63	32.42	69.42	49.07	105.08	25.73	55.10	20	28	54	76	15	21
Sm	11.39	74.46	9.30	60.75	10.26	67.07	5.99	39.15	9.29	60.72	5.09	33.27	4.5	19	8.7	38	3.8	16
Eu	2.18	37.64	1.59	27.33	1.74	30.04	1.07	18.41	1.62	27.86	0.86	14.78	1.3	15	1.0	11.0	1.3	15
Gd	8.78	42.70	8.03	39.05	9.54	46.44	5.78	28.14	8.80	42.82	4.23	20.57	4.1	13	8.2	27	4.2	14
Tb	1.17	31.32	1.04	27.67	1.34	36.56	0.77	20.59	1.17	31.32	0.72	19.21	0.6	11	1.3	22	0.7	12
Yb	3.34	19.66	2.95	21.85	4.00	31.99	2.11	18.29	2.10	27.46	2.00	17.83	1.5	6.1	3.5	14	2.7	11
Lu	0.47	18.50	0.45	23.62	0.58	32.09	0.3	18.03	0.33	27.73	0.26	17.45	0.2	6.0	0.6	15	0.5	12
Eu/Eu*		0.66		0.56		0.53		0.56		0.54		0.57		0.93		0.36		0.99
La _N /Yb _N		12.07		10.93		7.73		9.21		8.11		6.23		11.62		9.19		2.73
La _N /Sm _N		3.48		4.03		3.67		3.97		3.73		3.12		3.60		3.4		1.80
Gd _N /Yb _N		2.07		1.82		1.47		1.63		1.55		1.24		2.21		1.89		1.27

Note: TTG, Granite and Basalt values were from Condie (1993) as sourced from Asiedu et al., 2017; N represents chondrite normalized values; Eu/Eu* = $Eu_N / \sqrt{Sm_N \cdot Gd_N}$; REE normalization standards were from Sun and McDonough (1989) standard values. GR = Granite TTG = Tonalite-Trondhjemite-Granodiorite and BA = Basalt.

Elements/elemental ratios	Mixing results													
	Afram Formation						Anyaboni Formation				Mpraeso Formation			
	Shales		Siltstones		Shales		Siltstones		Shales		Siltstones			
	88%TTG:12%GR:0%BA		90%TTG:10%GR0%BA		78%TTG22%GR0%BA		88%TTG12%GR0%BA		70%TTG30%GR0%BA		87%TTG0%GR13%BA			
	ppm	N	ppm	N	ppm	N	ppm	N	ppm	N	ppm	N		
La	28.58	120.59	28.05	118.73	30.92	130.47	28.63	120.81	32.55	137.34	24.10	101.70		
Ce	53.21	86.94	51.54	84.21	60.66	99.12	53.38	87.22	65.84	107.58	42.72	69.81		
Nd	23.99	51.36	23.17	49.62	27.61	59.12	24.07	51.54	30.12	64.50	19.37	41.47		
Sm	4.99	32.63	4.89	31.97	5.44	35.55	5.00	32.70	5.75	37.58	4.41	28.83		
Eu	1.26	21.81	1.27	21.93	1.23	21.26	1.26	21.79	1.21	20.27	1.30	22.41		
Gd	4.58	22.29	4.48	21.81	5.02	24.42	4.59	22.34	5.32	25.89	4.11	20.01		
Tb	0.68	18.24	0.67	17.79	0.76	20.23	0.68	18.28	0.81	21.61	0.61	16.38		
Yb	1.73	10.20	1.69	9.92	1.95	11.46	1.74	10.23	2.10	12.32	1.65	9.72		
Lu	0.25	9.72	0.24	9.34	0.29	11.40	0.25	9.76	0.32	12.56	0.24	9.37		
Eu/Eu*		0.81		0.83		0.72		0.81		0.67		0.93		
La _N /Yb _N		11.82		11.83		11.39		11.81		11.14		10.47		
La _N /Sm _N		3.70		3.70		3.67		3.69		3.65		3.53		
Gd _N /Yb _N		2.18		2.19		2.13		2.18		2.10		2.06		

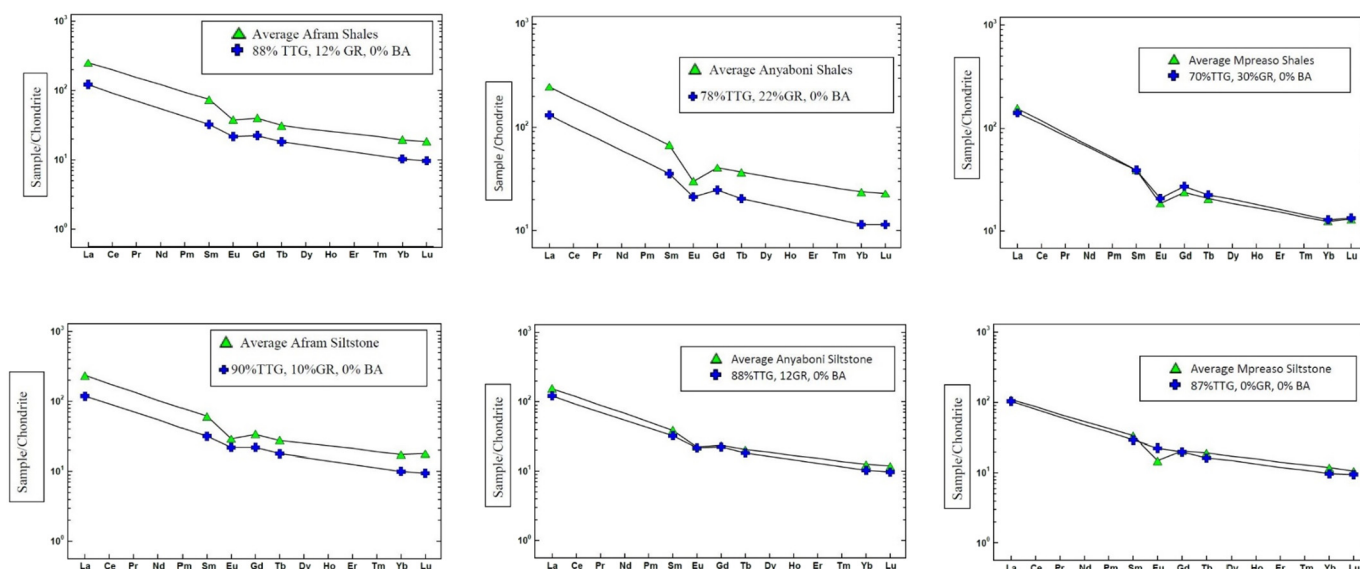


Fig. 10. Results of the mixing calculations for the REEs plotted with average shales and siltstones in Afraim Formation, Anyaboni Formation and Mpraeso Formation in Kwahu Group and Oti Group.

sorting may have had significant influence on the chemical composition of the clastic sediments composing the shales and siltstones and therefore controlled some trace elements (Th, U, Zr, Hf and Nb) distribution (Garcia et al., 2004; Armstrong-Altrin, 2009). The clear distinction between the siltstones enriched with Zr from recycled older sediments and other shales and siltstones compose of source Zr is shown in Fig. 7. The high Zr/Sc values (14.21–89.25) in the siltstones, signify heavy mineral accumulation through sediments recycling and sorting, resulting in Zr enrichment (McLennan et al., 1993), with far less Th/Sc

values (Bhatia and Crook, 1986). The low Th/Sc values (0.59–3.04) suggest the depletion of plagioclase and unstable mineral in the Passive Margin setting.

Some previous researchers in the Volta Basin have also interpreted the tectonic settings of the Kwahu-Bombouaka Group as a continental succession and the Oti Group interpreted as passive margin deposits (Affaton et al., 1980; Trompette, 1994). Though sediment geochemistry does not provide age constraints of Continental Island Arc materials, it is likely that, older Continental Island Arc basement relics from exposed

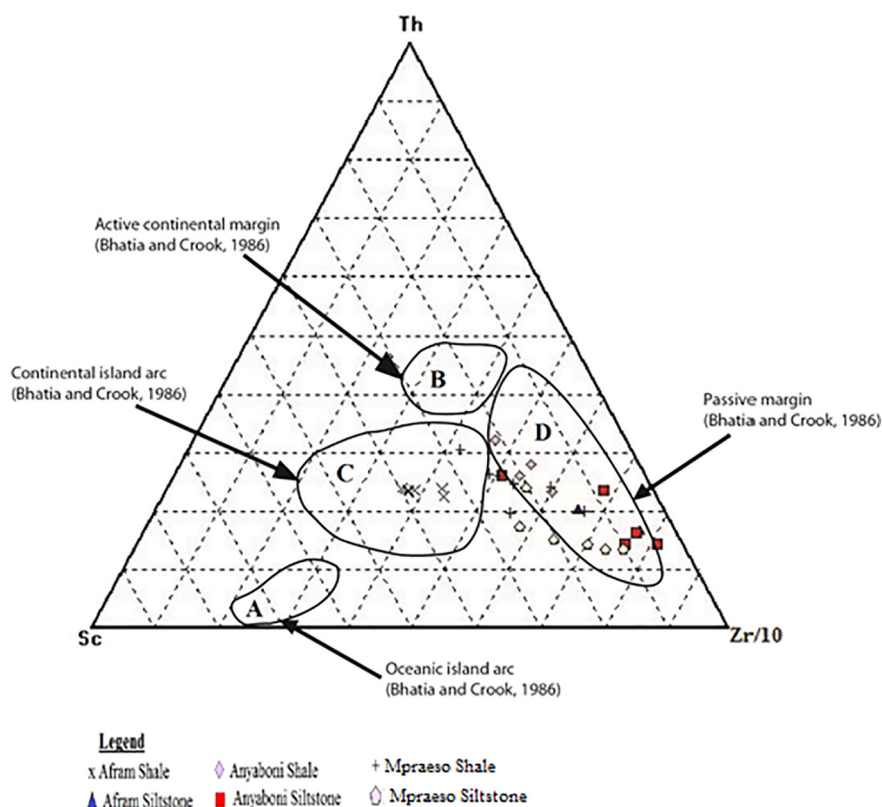


Fig. 11. Ternary Th-Sc-Zr/10 discrimination plot after Bhatia and Crook (1986). A) Oceanic island arc; B) Active continental margin; C) Continental island arc; D) Passive margin.

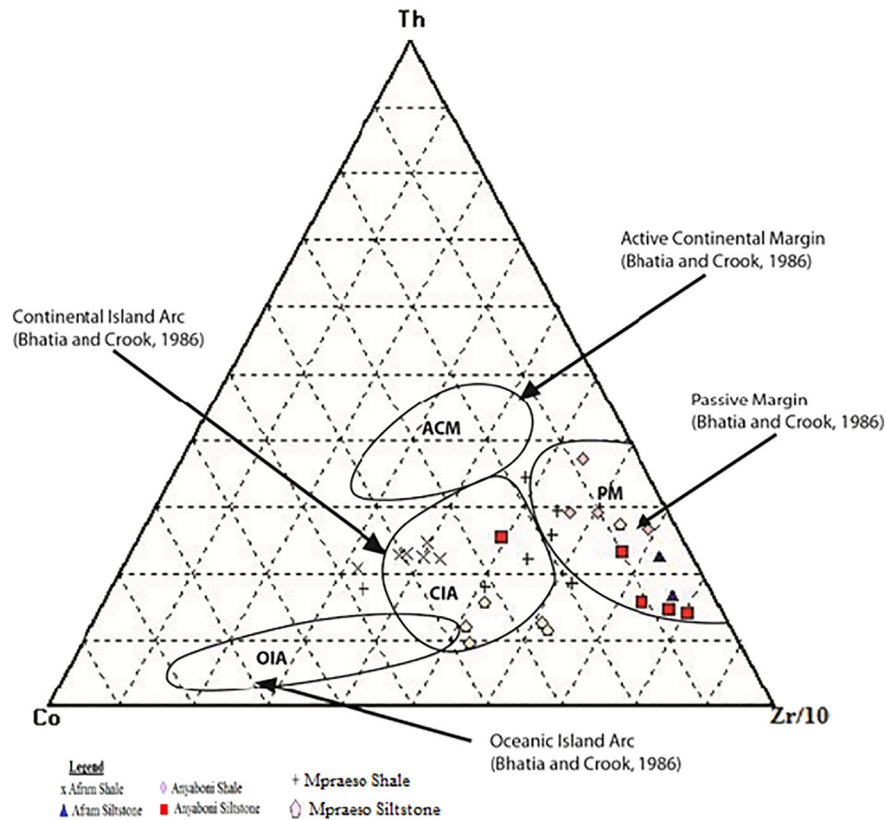


Fig. 12. Ternary Th–Co–Zr/10 discrimination plot (after Bhatia and Crook, 1986). ACM Active continental margin, CIA Continental island arc, OIA Oceanic island arc and PM Passive margin.

rocks at the Passive Margin environment may have imparted its signature on the whole-rock chemistry of the sediments.

6. Conclusion

Comprehensive composition and provenance analysis of the shales and siltstones in the Kwahu Group and Oti Group of the Voltaian Supergroup from Agogo and its environs have been undertaken using trace element geochemistry and mineralogy. The conclusions drawn concerning the provenance and tectonic setting of the shales and siltstones are:

- Trace element geochemistry in the siltstones were controlled by quartz dilution resulting in low composition. Relative abundance of quartz and K-feldspar concentrations in siltstones were due to selective depletion of plagioclase and micas principally, biotite. The shales are clay dominated and have higher trace element concentrations resulting from incorporated aluminosilicates and sulphide minerals than the siltstones.
- The provenance of sediments composing the shales and siltstones are from mainly felsic areas and recycled materials with minor mafic inputs as revealed from chondrite-normalized REE patterns and geochemical ratios (Th/Sc, Zr/Sc, La/Sc, Th/Co and Cr/Th). Though the chondrite-normalized REE patterns and Eu anomalies demonstrate that the sediments are Upper Continental Crustal materials, Th/Sc and Cr/Th values indicate the presence of some Archean cratonic basement granitic materials in the siltstones.
- Mixing calculations based on REE concentrations show that the shales are modeled as: Afram – 88%TTG, 12%GR, 0%BA, Anyaboni – 78%TTG, 22%GR, 0%BA while Mpraeso – 70%TTG, 30%GR, 0%BA, and the siltstones are modeled as: Afram – 90%TTG, 10%GR, 0%BA, Anyaboni – 88%TTG, 12%GR, 0%BA and Mpraeso – 87%TTG, 0%GR and 13%BA.
- The shales and siltstones were deposited mainly in Passive Margin

tectonic setting that overlaps into Continental Island Arc setting. The detritus supplied mainly by the Birimian basement complex underlying the Voltaian Basin.

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