GEOCHEMICAL APPLICATION IN UNRAVELING PALEOWEATHERING, PROVENANCE AND ENVIRONMENTAL SETTING OF THE SHALE FROM CHIA GARA FORMATION, KURDISTAN REGION, IRAQ

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ABSTRACT

The geochemical characteristics of the shale of the Chia Gara Formation (Middle Tithonian-Berriasian) from the Imbricated Zone (Barsarin section) and High Folded Zone (Banik section) Kurdistan Region, Iraq, was carried out to constrain their paleoweathering, provenance, and depositional environment. There are no clear differences in the major and trace elements of the Chia Gara Formation between the two studied sections. The chemical index of alteration (CIA) is significantly higher in the Barsarin than the Banik shales, suggesting more intense weathering of the Barsarin than the Banik shales. The samples of the Banik and some of Barsarin are clustered near the A-K line in A-CN-K plot suggests intense chemical weathering (high CIA) without any clear-cut evidence of K-metasomatism. The other samples of Barsarin have a weathering trend parallel to the A-CN line, indicating relatively steady state weathering conditions. The geochemical parameters of the shale (Al_2O_3/TiO_2 , Th/Sc , La/Th , La/Sc , La/Co , Th/Co , Cr/Th , $(La/Lu)_{cn}$ and Eu/Eu^*_{cn}), and the diagrams ($Th/Sc-Zr/Sc$ and $La/Th-Hf$) indicate that they were derived from felsic (from the Rutba Uplift and/or Mosul High) and intermediate (from volcanic material during the spreading of Southern Neo-Tethys Ocean) components. The chondrite-normalized REE patterns are similar to those of Post Archean Australian Shale (PAAS), with the light rare earth element (REE) enrichment, a negative Eu anomaly, and almost flat heavy REE pattern. The geochemical parameters such as authigenic uranium, U/Th , V/Cr , Ni/Co , and V/Sc ratios, and Al_2O_3-V and $Al_2O_3-P_2O_5$ diagrams indicate that these shales were deposited under deep marine suboxic to

anoxic environment and shale of Banik section was deposited slightly under deeper environment than shale of Barsarin section.

Keywords: Chia Gara Formation; Provenance; Paleoweathering; Shale; Geochemistry

INTRODUCTION

The geochemistry of clastic sedimentary rocks is used as an effective tool in the study of source area composition (Cullers, 2000, 2002; Osaie et al., 2006; Armstrong-Altrin, 2009; Saha et al., 2010), intensity of chemical weathering in the source region (Selvaraj and Chen, 2006; Roy et al., 2008; Gallala et al., 2009; Gupta et al., 2012; Raza et al., 2012), paleoclimatic conditions (Nesbitt and Young, 1982; Bhatia, 1983; Taylor and McLennan, 1985; Absar et al., 2009; Raza et al., 2010), provenance (Cullers, 2000, 2002; Armstrong-Altrin, 2009; Bakkiaraj et al., 2010) and tectonic setting of the sedimentary basins (Cullers, 2000; Armstrong-Altrin and Verma, 2005; Joo et al., 2005; Sabaou et al., 2009; Fatima and Khan, 2012). The geochemical composition of clastic sediments is a complex function and depends on other factors such as physical sorting, diagenesis, source material and relief (Nagarajan et al., 2007a, 2007b; Armstrong-Altrin et al., 2004, 2012; Moosavirad et al., 2012). Likewise, geochemical parameters have been used by various authors to understand the paleo-oxygenation conditions of ancient sediments (Calvert and Pedersen, 1993; Jones and Manning, 1994; Nath et al., 1997; Madhavaraju and Ramasamy, 1999; Cullers, 2002; Armstrong-Altrin et al., 2003; Dobrzinski et al., 2004). Determination of the provenance utilizing the elemental geochemistry in identifying source rocks for sedimentary rocks is based on the relative immobility of certain elements like La and Th that have high value in felsic rocks relative to basic rocks and Co, Cr, Sc and Ni have high values in basic rocks relative to felsic rocks within surficial environments in order that the elemental concentration or ratio reflects the composition of source rock much better than weathering and transportation. Therefore, types of rocks and environments are different with the difference in concentration and ratio of these elements (Roaldset, 1973; Cullers et al., 1975, 1979; Bavinton and Taylor, 1980; McLennan et al., 1983; Bhatia, 1985; Bhatia and Crook, 1986; Cullers, 1988; Wronkiewicz and Condie, 1990). The Chia Gara Formation is composed of organic matter-rich limestone and shale, it considered as an important petroleum source rocks (Odisho and Othman, 1992; Al-Beyati, 1998; Al-Ameri and Al-Obaidi, 2004). The Chia Gara Formation was introduced by Wetzel in 1950 (Bellen et al., 1959) in the Chia Gara anticline of the High Folded Zone. The type section of the formation comprises up to 230 m of thin bedded limestone and calcareous shale, with a consistent bullion zone and Phacoid beds at the base. Based on the fossil contents, the Chia Gara Formation

indicates a Mid Tithonian-Berriasian age (Bellen et al., 1959; Jassim and Goff, 2006). The lithofacies of the Chia Gara Formation reflects the marine environment (Buday, 1980; Jassim and Goff, 2006) and Mohialdeen (2008) suggested the deep outer shelf to carbonate slope environments for the depositional setting. The present study examines the geochemistry of the shales of the Chia Gara Formation. The main purpose of this study is to determine the provenance, chemical weathering and the redox conditions for the shale of the Chia Gara Formation.

GEOLOGICAL SETTING

The Chia Gara Formation was studied throughout two sections: Barsarin and Banik (Fig. 1), belongs to the Late Tithonian- Hautrivian sedimentary sequence. It consists entirely of thin beds succession of limestone and shales (Fig. 2a&2b) with rich ammonite faunas and diverse species of foraminifera, radiolarian, ostracodes and tintinnids. The lowermost 21 m is characterized by yellow marly limestones and shales (Bellen et al., 1959). The thickness of the formation ranges 30–300 m, 610 m of monotonous dark colored calcareous mudstones and rare marl bands were described in well Kirkuk-109 by McGinty in 1953 (Bellen et al., 1959) and referred to as the Karimia Mudstone. It conformably is underlain by the Barsarin Formation and conformably overlain by the Lower Sarmord Formation (Fig. 2a&2b). It was deposited during both transgression system tracks (TST) and high system track (HST) stages of the systems tract (Sharland et al., 2001).

Several authors studied the paleontology, stratigraphy and sedimentology of the Chia Gara Formation in Kurdistan Region (Howarth, 1992; Al-Qayim and Saadalla, 1992; Salae, 2001; Jassim and Goff, 2006; Mohialdeen, 2007; Mohialdeen and Al-Beyati, 2007; Mohialdeen, 2008). Sharland et al. (2001) suggest a regional unconformity at Mid Tithonian age on Arabian Plate which refers to the boundary between Megasequences AP7 (Late Toarcian- Early Tithonian) and AP8 (Late Tithonian- Early Turonian).

This may be a breakup unconformity which is a possible phase of ocean floor spreading during the opening of a Southern Neo- Tethys Ocean (Fig. 3). The opening of Southern Neo-Tethys led to the drifting away of a narrow microcontinent; a new passive margin formed along the NE margin of the Arabian Plate. The Rutba Uplift formed the western margin of Mesopotamian Basin. The NE margin was formed by a carbonate ridge along the north facing the passive margin of the Southern Neo-Tethys (Fig. 3).

Fig. 1: Location map and tectonic zones of the Unstable Shelf, Iraq (modified from Buday and Jassim, 1984)

Fig. 2: Columnar sections for Chia Gara Formation, (a) Barsarin area (b) Banik area

Fig. 3: Late Tithonian-Cenomanian geodynamic development of the Arabian Plate (Sharland et al., 2001)

SAMPLING AND METHODS

The samples were collected from two sections: the first section was near the Barsarin village at longitude 44°39'13" N and latitude 36°37'48" E in the Imbricated Zone, and the second section was near Banik village at longitude 42°58'3.8" E and latitude 37°13'31.4" N in the High Folded Zone (Fig. 1). Thirty five fresh samples were collected along these two sections; 21 samples from Barsarin and 14 samples from Banik (Fig. 2). The 35 samples were crushed, and then powdered to 200 mesh with an agate pulverizer. These samples were analyzed for major oxides (SiO_2 , Al_2O_3 , Fe_2O_3 , TiO_2 , CaO , MgO , MnO , Na_2O , K_2O and P_2O_5) by inductively coupled plasma-atomic emission spectrometry (ICP-AES) after fused bead and acid digestion, under the analysis code ME-ICP06; trace elements (Rb, Sr, Ba, Th, U, Y, Zr, Nb, Hf, Sc, V, Cr, Co, Ni, Cu, Zn and Mo) and rare earth elements (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Er, Ho, Tm, Yb, and Lu) were analyzed by inductively coupled plasma-mass spectrometry (ICP-MS) under the analysis code ME-MS81 at the ALS international laboratory in Spain. Loss on ignition (LOI) data was determined after drying the samples in oven 100 °C for 24 h, to remove moisture content, next ignition the samples at 1000 °C for 2 h. Chemical analysis of the major elements has precisions up to 5 %; whereas it varies between 0 and 9 % for the trace and REEs. Internationally

recognized standard materials OREAS-121 and AMIS0304 were used as references. Based on these standards, the accuracy and precision of the analysis were within $\pm 2\%$ for elements Nb, Ni, Zn, Mo, Ce, Pr, Sm, Eu, Tb and Lu; $\pm 5\%$ for Sr, Ba, Th, Y, Zr, Co, Dy, Ho, Tm and Yb; and $\pm 10\%$ for Rb, U, Hf, Sc, V, Cr, La, Nd, Gd and Er. Comparison of data between the present study and the published data of Post Archean Australian Shale (PAAS) and Upper Continental Crust (UCC) was done whenever possible. The REE data were normalized to the chondrite values of Taylor and McLennan (1985).

RESULTS

Major Element Geochemistry

The content of major oxides of the Chia Gara Formation is reported in Table 1. The results show few differences in composition among the two sections. In general, the shales of the Chia Gara Formation in Barsarin and Banik sections have high CaO content (11.55- 33.8, 22.28% and 0.84- 45.7, 25.4%, respectively). Such content has a great dilution effect on the other oxides, such as SiO₂ content (23.2-46.5, 32.67% and 9.01- 45.3, 27.66%), Al₂O₃ (5.05- 17.1, 10.36% and 4.6- 23.6, 11.19%), Fe₂O₃ (1.8- 7.12, 4.04% and 1.5- 8.65, 3.88%), MgO (0.27-1.84, 0.65% and 0.51- 1.48, 0.75%), Na₂O (0.02- 0.58, 0.16% and 0.01- 0.52, 0.10%), K₂O (0.5- 1.65, 0.90% and 0.45- 4.13, 2.53%), MnO (0.01- 0.02, 0.011% and 0.01- 0.03, 0.012%), TiO₂ (0.33- 1.05, 0.64% and 0.31- 1.2, 0.59%). Except for CaO, the studied shale shows depletion in all elements relative to those of the PAAS (Fig. 4). The CaO enrichment in these samples, as well as the significant correlation between CaO and LOI ($r = 0.903$; $n = 35$), suggest that LOI and CaO are incorporated into calcite rather than other minerals. On the other hand, Al₂O₃ shows positive correlations with SiO₂, Fe₂O₃, and TiO₂ ($r = 0.643$, 0.905 , and 0.947 , respectively; $n = 35$).

Fig. 4: UCC normalized spider diagrams for major oxides of the shale from Chia Gara Formation (PAAS values after Taylor and McLennan, 1985)

Table 1: Major oxides contents (wt%) for shale of the Chia Gara Formation; compared with PAAS (Taylor and McLennan, 1985) and UCC (Wedepohl, 1995)

Sample no.	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	MnO	TiO ₂	P ₂ O ₅	LOI	Total
Barsarin section												
CBN 1	25.4	12.25	6.48	24.2	0.81	0.04	1.65	0.02	0.66	0.54	26.3	98.35
CBN 2	27.1	9.79	3.23	27	0.72	0.11	1.1	0.01	0.57	0.24	28.9	98.77
CBN 3	23.9	7.06	2.55	33.6	0.67	0.23	1.05	0.01	0.4	0.13	30.0	99.60
CBN 4	25.6	5.05	1.8	33.8	0.78	0.38	0.7	0.01	0.33	0.09	29.5	98.04
CBN 5	36.0	6.47	2.9	25.4	0.49	0.58	0.82	0.01	0.4	0.03	25.0	98.10
CBN 6	27.6	7.62	3.61	27	0.7	0.5	0.9	0.01	0.47	0.05	24.3	92.76
CBN 7	32.1	6.64	3.58	19.15	0.29	0.51	0.77	0.01	0.43	0.06	19.4	82.94
CBN 8	46.5	13.4	6.39	12.8	0.72	0.35	1.51	0.02	0.85	0.08	17.75	100.37
CBN 9	42.1	12.4	3.86	15.05	0.83	0.15	1.35	0.01	0.89	0.09	18.4	95.13
CBN 10	23.2	5.78	2.2	31.9	1.84	0.02	0.52	0.01	0.36	0.01	30.0	95.84
CBN 11	32.3	8.68	3.23	23.9	0.94	0.02	0.86	0.01	0.59	0.07	23.1	93.70
CBN 12	33.4	9.26	3.52	23.6	0.66	0.05	0.98	0.01	0.59	0.1	22.4	94.57
CBN 13	44.7	11.1	4.07	14.3	0.73	0.03	1.08	0.01	0.73	0.09	17.75	94.59
CBN 14	33.9	8.15	2.94	26.5	0.41	0.04	0.81	0.01	0.56	0.05	22.9	96.27
CBN 15	33.8	10.65	4.37	20.7	0.37	0.04	0.66	0.01	0.67	0.09	21.2	92.56
CBN 16	34.9	16.55	6.54	11.55	0.53	0.08	1.06	0.01	1.05	0.14	20.1	92.51
CBN 17	33.6	14.35	4.63	15.55	0.77	0.07	0.7	0.01	0.84	0.08	19.3	89.90
CBN 18	33.7	11.6	3.88	20.5	0.3	0.04	0.57	0.01	0.69	0.09	21.2	92.58
CBN 19	38.4	12.25	4.03	17.75	0.27	0.02	0.55	0.01	0.71	0.13	19.7	93.82
CBN 20	26.1	11.35	3.83	24.7	0.29	0.02	0.5	0.01	0.7	0.08	23.9	91.48
CBN 21	31.7	17.1	7.12	18.85	0.44	0.1	0.86	0.01	0.92	0.21	22.8	100.11
Average	32.67	10.36	4.04	22.28	0.65	0.16	0.90	0.011	0.64	0.12	23.04	94.87
Banik section												
CBK 1	45.3	23.3	8.65	0.84	1.48	0.05	3.5	0.03	1.13	0.2	16.95	101.43
CBK 2	9.01	4.6	1.5	45.7	0.62	0.01	0.62	0.01	0.24	0.06	38.8	101.17
CBK 3	42.9	23.6	7.64	1.81	1.06	0.05	2.67	0.02	1.2	0.24	18.85	100.04
CBK 4	27.8	10.85	3.45	23.3	0.89	0.05	2.95	0.01	0.48	0.28	28.6	98.66
CBK 5	24.2	8.26	2.45	31.2	0.73	0.08	2.42	0.01	0.41	0.25	30.9	100.91
CBK 6	32.9	11.1	2.85	21.1	0.77	0.14	4.13	0.01	0.47	0.23	25.6	99.30
CBK 7	30.6	8.09	2.95	27.1	0.62	0.24	3.87	0.01	0.38	0.11	26.3	100.27
CBK 8	32.6	9.29	3.72	22.1	0.65	0.52	3.97	0.01	0.51	0.22	25.5	99.09
CBK 9	20.7	6.51	2.71	34.3	0.71	0.04	2.48	0.01	0.37	0.12	31.1	99.05
CBK 10	26.9	9.28	2.94	28.1	0.62	0.05	3.01	0.01	0.54	0.17	28.3	99.92
CBK 11	27.8	9.69	4.51	27.2	0.61	0.04	2.86	0.01	0.57	0.11	26.9	100.3
CBK 12	35.3	15.35	6.66	14.75	0.65	0.01	1.71	0.01	0.93	0.4	22.6	98.37
CBK 13	10.4	4.82	1.63	45.7	0.51	0.02	0.45	0.01	0.31	0.28	37.3	101.43
CBK 14	20.8	11.9	2.69	32.4	0.58	0.03	0.75	0.01	0.76	0.08	30.7	100.70
Average	27.66	11.19	3.889	25.4	0.75	0.10	2.53	0.012	0.59	0.20	27.74	100.06
Total avg.	30.17	10.78	3.96	23.84	0.70	0.13	1.72	0.01	0.62	0.16	25.39	97.48
PAAS	62.40	18.78	7.18	1.29	2.19	1.19	3.68	0.11	0.99	0.16	6.00	
UCC	66.00	15.20	5.00	4.20	2.20	3.90	3.40	0.08	0.50	-	-	

Trace Element Geochemistry

The trace element content of the Chia Gara Formation is given in (Table 2). The studied shale shows enrichment of Sr, U, V, Ni and depletion in Rb, Ba, Th, Y, Zr, Nb, Hf, Sc, and Co relative to PAAS (Fig. 5). The enrichment of the shale with Sr at Barsarin section (112- 877, 769 ppm) indicates the association with the carbonate phase, especially calcite mineral, which is higher than that of the Banik section (132- 403, 260 ppm). On the other hand, the Al_2O_3 content was significantly correlated with Rb, Th, Y, Zr, Nb, Hf, Sc, and REE, indicate their association with the detrital phase.

Fig. 5: PAAS normalized spider diagrams for trace elements of the shale from Chia Gara Formation (PAAS values after Taylor and McLennan, 1985)

Rare Earth Element Geochemistry

The content of total rare earth elements (ΣREE) in the Chia Gara shale varies from 39.78 ppm to 196.41 ppm with an average of 123.25 ppm, significantly lower than for upper continental crust (UCC; 146.37 ppm) and PAAS (184.77 ppm; Table 3). It is suggested that the effect of dilution by carbonate materials, is the major control on the REE contents (significant correlation between ΣREE and CaO is -0.854). ΣREE have a significant correlation with SiO_2 , Al_2O_3 , Fe_2O_3 , and TiO_2 (0.751, 0.869, 0.858, and 0.937, respectively) suggest the typical role of clay minerals on the distribution of REEs (McLennan, 1989; Condie, 1991).

Table 2: Trace element concentrations (ppm) for shale of the Chia Gara Formation; compared with PAAS (Taylor and McLennan, 1985) and UCC (Wedepohl, 1995)

Large ion lithophile elements				High field strength elements						Transition elements							
	Rb	Sr	Ba	Th	U	Y	Zr	Nb	Hf	Sc	V	Cr	Co	Ni	Cu	Zn	Mo
Barsarin section																	
CBN 1	57.5	1085	91.9	8.86	51.4	15.7	132	18	3	11	619	90	65	283	141	184	502
CBN 2	31.7	1505	367	7.31	22.8	20.9	110	15.4	2.8	7	684	90	15	212	51	117	351
CBN 3	25.5	1120	72.9	5.04	18.7	21.8	86	10.7	2	6	908	100	7	234	55	156	288
CBN 4	14.9	1420	50	3.94	17.25	18.6	70	9	1.6	5	600	110	5	217	34	131	171
CBN 5	16.4	747	54.9	5.36	15	18.2	81	10.6	1.8	6	287	70	16	166	41	116	155
CBN 6	18	877	41.4	6.69	16.35	19	100	13.6	2.3	8	295	80	9	140	26	111	104
CBN 7	14.5	531	50.7	6.43	9.59	14.2	91	12.6	2	6	462	80	8	241	34	162	114
CBN 8	34.2	817	94.1	12.1	10.85	32.1	169	23.4	4.6	13	564	150	15	224	40	177	128
CBN 9	31.2	785	70.1	10.6	9.93	25.8	203	25.5	5.2	11	725	140	9	180	41	201	96
CBN 10	13.2	1165	36	5.26	11.3	16.4	92	11.6	2	5	287	60	6	81	17	63	63
CBN 11	21	831	45.2	7.7	13	22.0	131	17.9	3.3	8	482	80	6	163	30	110	146
CBN 12	26.4	725	63.8	7.54	14.4	18.8	139	17.9	3.6	8	440	90	8	157	30	99	120
CBN 13	28.3	573	54.6	9.8	11.65	21.8	163	21.9	3.7	10	639	110	8	226	41	154	157
CBN 14	20.8	868	47	7.39	7.23	17.6	125	16.4	3	7	482	80	7	100	30	122	56
CBN 15	21.7	706	65.6	9.96	14.55	22.4	153	20.2	3.7	10	572	90	9	210	40	114	208
CBN 16	34.4	465	73.3	15.25	7.76	23.9	235	31.8	5.6	12	677	140	14	189	40	168	111
CBN 17	24.9	379	75.9	13.4	7.44	18	183	26	4.9	10	500	100	10	116	31	112	91
CBN 18	21.4	412	65.3	11.8	10.8	18.6	166	23.8	4.3	9	447	90	7	138	40	107	126
CBN 19	20.7	378	69	11.4	10.3	18.5	161	22.6	4.4	9	368	100	8	139	36	100	172
CBN 20	19.2	402	63.5	9.5	6.36	16.9	133	19.6	3.4	9	377	80	9	105	24	98	68
CBN 21	36.3	363	91.1	14.15	7.98	23.5	195	27.6	5	10	604	190	10	108	43	160	58
Average	25.3	769	78.3	9.0	14.0	20.2	139	18.9	3.4	8.6	525	101	12.0	173	41.2	132	156.4
Banik section																	
CBK 1	105.5	132	198	16.3	20.5	21.4	200	27	5.2	18	686	150	46	197	95	144	206
CBK 2	18	138	44.1	2.86	7.99	5.5	45	5.8	1	4	124	30	8	47	15	24	37
CBK 3	82	156	169	16.3	20.7	24.2	214	29.2	5.4	18	442	150	33	189	75	131	220
CBK 4	58.4	232	126	7.04	31.9	16.3	91	9.8	2	10	697	90	15	212	102	135	333
CBK 5	45.7	403	121	5.24	29.6	12.9	97	8.1	2.1	7	651	100	10	168	58	84	314
CBK 6	63.2	189	150.5	7.06	25.3	18	89	9.6	2.1	9	726	110	14	233	99	140	242
CBK 7	38.1	270	73.8	5.89	14.75	15.4	71	9.2	1.6	6	428	110	10	243	72	120	134
CBK 8	44.1	268	127.5	6.97	22.2	26	117	13	2.7	8	1020	170	13	400	124	147	266
CBK 9	34.5	306	61.2	4.88	14.9	15.8	74	9	1.7	6	521	100	5	199	69	104	132
CBK 10	40.6	268	88.7	6.79	17.8	22.2	114	12.3	2.7	8	522	120	11	269	71	126	121
CBK 11	38.7	272	85.5	7.64	20.4	24.5	117	13.8	2.8	8	652	140	24	384	115	191	154
CBK 12	47.2	227	121	11.95	17.05	32.6	177	20.7	4.1	13	1100	210	19	393	84	150	278
CBK 13	16.4	392	34.5	3.77	8.69	17.5	70	7.4	1.4	5	430	80	6	129	41	199	47
CBK 14	30.4	392	79.9	8.4	10.45	23.5	162	18.5	4	10	381	280	7	118	31	68	23
Average	47.3	260	105.7643	7.9	18.7	19.7	117	13.8	2.8	9.3	599	131	15.8	227	75.1	126	179
Total av	36.3	514	92.0	8.45	16.35	20.0	128	16.35	3.1	8.95	562	116	13.9	200	58.2	129	168
PAAS	160	200	650	14.6	3.1	27	210	19	5	16	150	110	23	55	50	85	-
UCC	112	350	550	10.7	2.8	22	190	25	5.8	11	60	35	10	20	25	71	1.5

The chondrite normalized REE patterns (Taylor and McLennan, 1985) of the studied shales are given in Figure (6). The moderate negative Eu anomalies ($\text{Eu}/\text{Eu}^*_{\text{cn}}$ is between 0.59 and 0.75 with an average of 0.67) which are attributed to the Eu-depletion in the source area. The Chia Gara samples have highly enriched light rare earth element (LREE) patterns where $(\text{La}/\text{Sm})_{\text{cn}} = 4.02$; moreover, these are slightly lower than UCC (4.20) and PAAS (4.33; Taylor and McLennan, 1985). The slightly higher $(\text{La}/\text{Yb})_{\text{cn}}$ ratios (7.94- 12.07, 9.79; Table 4) than UCC (9.21) and PAAS (9.15), indicate the LREE enrichment. The patterns show enrichment in light REE (LREE) and depletion in heavy REE (HREE) in addition to the flat HREE pattern. The Chia Gara shale has flat to moderately fractionated HREE patterns which $(\text{Gd}/\text{Yb})_{\text{cn}} = 1.47$ (Table 4).

Fig. 6: Chondrite normalized rare earth elements, the plot for shale samples from Chia Gara (Taylor and McLennan, 1985)

Table 3: Rare earth element concentrations (ppm) for shale of the Chia Gara Formation

Sample no.	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	ΣREE
CBN 1	24.8	52.1	5.22	20.4	4.32	0.85	3.24	0.52	2.98	0.63	1.63	0.21	1.59	0.24	118.73
CBN 2	28.5	48.4	5.47	21.7	4.26	0.84	3.38	0.51	3.16	0.7	1.78	0.27	1.71	0.27	120.95
CBN 3	21.7	34.6	4.28	17.2	3.73	0.69	3.12	0.48	3.03	0.62	1.75	0.26	1.84	0.22	93.52
CBN 4	19.1	29.1	3.68	14.5	2.97	0.61	2.67	0.41	2.57	0.57	1.55	0.22	1.44	0.19	79.58
CBN 5	21.6	41.2	4.67	19	3.8	0.83	3.07	0.51	3.02	0.65	1.49	0.24	1.61	0.23	101.92
CBN 6	23.9	49.6	5.56	21.4	4.74	0.84	3.7	0.58	3.28	0.7	1.91	0.27	1.71	0.23	118.42
CBN 7	21	39.9	4.35	17.5	3.4	0.66	2.69	0.39	2.45	0.51	1.48	0.2	1.5	0.2	96.23
CBN 8	41	81.2	8.65	33.9	7.58	1.48	6.25	0.98	5.49	1.14	2.98	0.45	2.91	0.42	194.43
CBN 9	33	61.1	6.62	26	5.12	0.98	4.01	0.73	4.5	0.92	2.5	0.39	2.64	0.4	148.91
CBN 10	18.8	37.9	4.14	16.9	3.41	0.78	3.21	0.47	2.68	0.57	1.63	0.2	1.6	0.23	92.52
CBN 11	25.6	47.3	5.02	19.9	4.53	0.91	3.56	0.58	3.62	0.72	2.09	0.3	2.05	0.32	116.5
CBN 12	25.7	46.5	5.09	19.6	3.81	0.69	3.37	0.55	3.02	0.67	1.89	0.28	1.83	0.28	113.28
CBN 13	30.1	55.2	6.02	24	4.85	0.96	3.54	0.61	3.73	0.78	2.12	0.34	2.18	0.32	134.75
CBN 14	25.6	47.8	5.23	20.3	4.08	0.87	3.56	0.54	3.1	0.66	1.89	0.25	1.9	0.24	116.02
CBN 15	31.3	60.1	6.72	25.5	5.2	1.04	4.03	0.7	4.03	0.84	2.23	0.35	2.17	0.3	144.51
CBN 16	42.1	76.2	7.91	29.8	5.76	1.07	4.29	0.73	4.3	0.89	2.57	0.38	2.75	0.41	179.16
CBN 17	39.1	70.9	7.26	26.7	4.98	0.91	3.6	0.57	3.38	0.76	2.05	0.32	2.31	0.3	163.14
CBN 18	35	66.3	6.78	25.6	5.14	0.87	3.84	0.6	3.68	0.72	2.05	0.31	1.96	0.32	153.17
CBN 19	35.5	67.3	7.18	27	5.54	0.99	4.05	0.59	3.73	0.74	1.96	0.3	2.04	0.32	157.24
CBN 20	29.9	55.5	6.07	23.4	4.66	0.87	3.67	0.61	3.45	0.71	1.84	0.24	1.85	0.27	133.04
CBN 21	42.8	79.4	8.36	31.3	5.87	1.16	4.58	0.74	4.38	0.91	2.45	0.4	2.58	0.35	185.28
Average	29.34	54.652	5.92	22.93	4.65	0.9	3.69	0.59	3.5	0.73	1.99	0.29	2.01	0.29	131.482
CBK 1	40	77.5	7.82	29.6	6.04	1.04	4.11	0.64	4.18	0.78	2.22	0.36	2.41	0.36	177.06
CBK 2	9	17.4	1.69	6.7	1.18	0.24	1.02	0.14	0.89	0.19	0.6	0.07	0.6	0.06	39.78
CBK 3	43.7	84.5	8.88	33.4	6.93	1.25	5.22	0.77	4.68	0.95	2.43	0.41	2.85	0.44	196.41
CBK 4	22.9	42.7	4.78	18.4	3.54	0.79	3.13	0.47	2.79	0.55	1.58	0.21	1.57	0.22	103.63
CBK 5	18.9	31.8	3.72	14	2.55	0.58	2.15	0.32	1.97	0.39	1.09	0.15	1.14	0.17	78.93
CBK 6	25.7	45	5.18	20.4	3.77	0.83	3.25	0.51	2.68	0.57	1.57	0.23	1.61	0.2	111.5
CBK 7	20.3	34.5	3.88	15.1	3.24	0.69	2.47	0.37	2.1	0.47	1.23	0.16	1.3	0.17	85.98
CBK 8	25.1	41.7	5.01	19.9	4.24	0.8	3.53	0.53	3.19	0.77	2.29	0.31	1.96	0.32	109.65
CBK 9	18.2	29.2	3.45	13.7	2.6	0.46	2.12	0.35	2.05	0.43	1.27	0.18	1.28	0.19	75.48
CBK 10	26.2	45	5.35	21.2	3.93	0.8	3.33	0.53	3.13	0.67	1.98	0.27	1.93	0.24	114.56
CBK 11	30.1	50.9	5.96	24	4.33	0.88	3.93	0.58	3.62	0.78	2.12	0.32	2.08	0.32	129.92
CBK 12	40	75.2	8.32	31.8	6.62	1.3	5.69	0.84	4.85	1.06	2.93	0.4	3.04	0.43	182.48
CBK 13	17.1	28.9	3.61	14.3	2.95	0.61	2.41	0.37	2.23	0.49	1.38	0.15	1.33	0.19	76.02
CBK 14	30.6	48.9	5.94	22.8	4.73	0.94	3.58	0.59	3.43	0.76	2.33	0.33	2.41	0.34	127.68
Average	26.27	46.66	5.26	20.38	4.05	0.80	3.28	0.50	2.99	0.63	1.79	0.25	1.82	0.26	114.94
Total av	27.81	50.66	5.59	21.66	4.35	0.85	3.49	0.55	3.25	0.68	1.89	0.27	1.92	0.28	123.25
PAAS	38.2	79.6	8.83	33.9	5.55	1.08	4.66	0.77	4.68	0.99	2.85	0.41	2.82	0.43	184.77
UCC	30	64	7.10	26	4.5	0.88	3.8	0.64	3.50	0.80	2.30	0.33	2.20	0.32	146.37

Table 4: Weathering parameters, major oxides and rare earth element ratios for the shale of Chia Gara Formation

Sample no.	CIA	PIA	CIW	Al ₂ O ₃ /TiO ₂	LREE/HREE	ΣREE	Ce/ Ce*	Eu/ Eu*	(La/Yb) _n	(La/Sm) _n	(Gd/Yb) _n	(La/Lu) _n
Barsarin section												
CBN 1	86.44	98.76	98.94	18.56	9.75	118.73	1.07	0.69	10.54	3.61	1.65	10.73
CBN 2	86.29	95.96	96.43	17.18	9.27	120.95	0.91	0.68	11.26	4.21	1.60	10.96
CBN 3	78.83	88.67	90.32	17.65	7.26	93.52	0.84	0.62	7.97	3.66	1.37	10.24
CBN 4	71.53	77.43	80.15	15.30	7.27	79.58	0.81	0.66	8.96	4.05	1.50	10.44
CBN 5	69.81	74.52	77.22	16.18	8.42	101.92	0.96	0.74	9.07	3.58	1.55	9.75
CBN 6	74.40	80.15	82.24	16.21	8.57	118.42	1.01	0.61	9.44	3.17	1.75	10.79
CBN 7	72.54	77.57	79.83	15.44	9.22	96.23	0.98	0.67	9.46	3.89	1.45	10.90
CBN 8	82.77	91.08	92.09	15.77	8.43	194.43	1.01	0.66	9.52	3.40	1.74	10.13
CBN 9	86.36	95.68	96.17	13.93	8.25	148.91	0.97	0.66	8.45	4.06	1.23	8.56
CBN 10	90.17	98.75	98.87	16.06	7.74	92.52	1.01	0.72	7.94	3.47	1.63	8.49
CBN 11	89.68	99.16	99.25	14.71	7.80	116.5	0.98	0.69	8.44	3.56	1.41	8.31
CBN 12	88.29	98.03	98.25	15.70	8.53	113.28	0.95	0.59	9.49	4.25	1.49	9.53
CBN 13	89.73	99.02	99.12	15.21	8.89	134.75	0.96	0.71	9.33	3.91	1.32	9.77
CBN 14	88.97	98.22	98.41	14.56	8.56	116.02	0.97	0.70	9.10	3.95	1.52	11.07
CBN 15	92.63	98.69	98.78	15.90	8.86	144.51	0.97	0.69	9.75	3.79	1.51	10.83
CBN 16	92.13	98.32	98.43	15.77	9.98	179.16	0.98	0.66	10.35	4.60	1.26	10.66
CBN 17	93.55	98.33	98.42	17.08	11.28	163.14	0.99	0.66	11.44	4.94	1.26	13.53
CBN 18	93.93	98.82	98.88	16.81	10.36	153.17	1.01	0.60	12.07	4.29	1.59	11.35
CBN 19	94.87	99.44	99.47	17.25	10.45	157.24	0.99	0.64	11.76	4.03	1.61	11.52
CBN 20	94.91	99.39	99.42	16.21	9.53	133.04	0.97	0.64	10.92	4.04	1.61	11.50
CBN 21	93.13	98.01	98.11	18.59	10.30	185.28	0.98	0.68	11.21	4.59	1.44	12.70
Average	86.24	93.52	94.23	16.19	9.04	131.48	0.97	0.66	9.86	3.97	1.49	10.50
Banik section												
CBK 1	85.47	99.16	99.30	20.62	10.76	177.06	1.03	0.64	11.22	4.17	1.38	11.53
CBK 2	86.70	99.17	99.29	19.17	10.14	39.78	1.05	0.67	10.14	4.80	1.38	15.57
CBK 3	88.52	99.21	99.31	19.67	10.07	196.41	1.01	0.64	10.36	3.97	1.48	10.31
CBK 4	76.32	97.89	98.51	22.60	8.85	103.63	0.96	0.73	9.86	4.07	1.62	10.81
CBK 5	74.09	95.54	96.91	20.15	9.70	78.93	0.89	0.76	11.20	4.67	1.53	11.54
CBK 6	69.19	93.49	96.02	23.62	9.50	111.5	0.91	0.72	10.79	4.29	1.64	13.34
CBK 7	61.85	83.13	91.11	21.29	9.40	85.98	0.91	0.75	10.55	3.94	1.54	12.40
CBK 8	60.68	74.44	84.45	18.22	7.50	109.65	0.87	0.63	8.65	3.73	1.46	8.14
CBK 9	69.75	96.67	98.02	17.60	8.59	75.48	0.86	0.60	9.61	4.41	1.34	9.94
CBK 10	73.01	97.34	98.26	17.19	8.48	114.56	0.89	0.68	9.17	4.20	1.40	11.33
CBK 11	74.97	98.04	98.66	17.00	8.45	129.92	0.89	0.65	9.78	4.38	1.53	9.77
CBK 12	89.05	99.76	99.79	16.51	8.48	182.48	0.97	0.65	8.89	3.80	1.52	9.66
CBK 13	89.69	98.50	98.65	15.55	7.89	76.02	0.86	0.70	8.69	3.65	1.47	9.34
CBK 14	92.88	99.12	99.18	15.66	8.27	127.68	0.85	0.70	8.58	4.07	1.20	9.34
Average	78.01	95.10	96.96	18.91	8.98	114.94	0.93	0.67	9.75	4.08	1.46	10.49
Total avg.	82.98	94.16	95.32	17.28	9.00	123.25	0.95	0.67	9.79	4.02	1.47	10.49
PAAS					9.49	184.77	1.02	0.65	9.15	4.33	1.34	9.22
UCC					9.54	146.37	1.03	0.65	9.21	4.20	1.40	9.73

DISCUSSION

Paleo-Weathering of the Source Area

The intensity and degree of chemical weathering in clastic rocks can be evaluated by using the relationship between alkali and alkaline earth elements (Nesbitt and Young, 1982). In weathering section, the insoluble elements (Al, Ba, Rb) are resistant, and labile elements (Na, Ca, and Sr) are mainly leached from the profile (Nesbitt et al., 1980). These chemical changes are reflected in the sedimentary record (Wronkiewicz and Condie, 1987) supplying a useful tool for estimating source area weathering conditions. The degree of weathering can be quantified by calculating the chemical index of alteration (CIA), (Nesbitt and Young, 1982), plagioclase index of alteration (PIA; Fedo et al., 1995) and chemical index of weathering (CIW; Harnois, 1988). Nesbitt and Young (1984) used the ternary diagram (A-CN-K) considering Al_2O_3 -(CaO + Na_2O)- K_2O to deduce weathering trends. The chemical index of alteration (CIA) was calculated with the formula:

$$\text{CIA} = [\text{Al}_2\text{O}_3 / (\text{Al}_2\text{O}_3 + \text{CaO}^* + \text{Na}_2\text{O} + \text{K}_2\text{O})] \times 100 \text{ (Nesbitt and Young, 1982)}$$

Where CaO^* is the CaO content incorporated in the silicate fraction of the studied samples (Fedo et al., 1995).

Since there is no direct method to quantify the contents of CaO belonging to silicate and non-silicate fractions, here we used the method suggested by McLennan et al. (1993) to calculate the CaO in silicate fraction; the molar proportion of Na_2O is regarded as the molar proportion of CaO of the silicate fraction, when the CaO content was high. The CIA, PIA, and CIW values of ~ 60 indicates low weathering, ~ 60-80 moderate weathering, and more than 80 indicate intensive weathering (Fedo et al., 1995). The calculated CIA values of the shale from Chia Gara for two sections vary between 60.68 to 94.91% (average= 82.98%; Table 4). The result of PIA shows no significant difference between Barsarin (93.52) and Banik (95.10; Table 4) shales. This average is higher than the PAAS values (70-75; Taylor and McLennan, 1985), suggesting an intensive degree of chemical weathering in the source area (Fig. 7). The CIA values were plotted on A-CN-K diagram (Fig. 7), to evaluate the mobility of the elements during the advance of chemical weathering. All the shale samples fall above the plagioclase-feldspar line and exhibit a definite trend. The samples of Banik section and some of Barsarin are clustered near the A-K line, towards the illite composition (Barsarin section) and the muscovite composition (Banik section), and do not indicate any clear-cut evidence of K-metasomatism or direct weathering back to the source (Fig. 7). The other samples of Barsarin section do not incline to K_2O -apex, the linear

weathering trend of these shales intersects the plagioclase-K-feldspar joint and is sub parallel to the A-CN joint, indicating of relatively steady state weathering conditions and predicts a source rock with a plagioclase/K-feldspar ratio of about 5:1 (Fig. 7).

Fig. 7: A-CN-K ternary diagram in molecular proportions for the Chia Gara shales (after Nesbitt and Young, 1984). Also plotted is the average Upper Continental Crust (UCC) and Post Archean Australian Shale (PAAS) (Taylor and McLennan, 1985)

The A-CN-K diagram indicates that the samples were derived from the upper continental crust (UCC) influenced by intense chemical weathering (Madhavaraju et al. 2016). The samples that are concentrated nearly parallel to A-K line close to muscovite and illite composition, suggests the advance in weathering; the K- feldspar was destroyed by K leaching out and the residues were enriched with Al and therefore trend towards the A apex (Wouatong et al., 2013).

The quantitative measure of plagioclase weathering is estimated by calculating the PIA:

$$PIA = [(Al_2O_3 - K_2O) / (Al_2O_3 + CaO^* + Na_2O - K_2O)] \times 100 \text{ (Fedo et al., 1995)}$$

The PIA values range from 74.44 to 99.76% (average= 94.16%) indicating a high degree of alteration at the source area.

The chemical index of weathering was calculated with the formula:

$CIW = [Al_2O_3 / (Al_2O_3 + CaO + Na_2O)] \times 100$ (Harnois, 1988)

The CIW values vary from 77.22 to 99.47% (average= 95.32%; Table 4). The PIA values of the studied shale are comparable to the calculated CIW values (Harnois, 1988) this does not include K_2O . Based on CIA, PIA, and CIW values (> 80%), it can be concluded that the litho-components in the shale were subjected to intense chemical weathering and these results support the humid paleoclimate conditions in the source area during Late Jurassic-Early Cretaceous.

Provenance

The chemical analyses of the major, trace and rare earth elements of the clastic sediments were widely used to distinguish the source rock identity (Armstrong-Altrin et al., 2015; Tobia and Shangola, 2016; Tobia and Mustafa, 2016; Zaid, 2017). In order to deduce the provenance of the rocks, several discrimination diagrams were proposed based on major and trace elements (Roser and Korsch, 1988; Floyd et al., 1989; McLennan et al., 1993; Verma and Armstrong-Altrin, 2013, 2016; Verma et al., 2016).

The ratios of Al_2O_3/TiO_2 in clastic sedimentary rocks are regarded as a powerful tool to distinguish the types of source rocks (Garcia et al., 1994; Andersson et al., 2004), since the ratio < 14 in sediments is indicative of mafic source rocks, whereas ratios ranging from 19 to 28 reveal felsic source rocks. Al_2O_3/TiO_2 ratios in the shale of the Chia Gara Formation, which range from 13.93 to 23.62 (Table 4), suggest that these sediments are derived from felsic source rocks.

The ratio of Th/Sc is a dependable tool for source composition and the discrimination between felsic and mafic source components (McLennan et al., 1990; McLennan and Taylor, 1991). Thorium is highly incompatible and common in crustal sources. Thus, the Th/Sc ratio will be high in the rocks derived from the earth's crust and low in that derived from the mantle. The Chia Gara samples show Th/Sc ratios between 0.79 and 1.42 (average= 1.04) for Barsaren section and between 0.72 and 0.98 (average= 0.84) for Banik section. For Chia Gara (0.96) as a whole, the Th/Sc ratio is nearly similar to PAAS (0.91; Taylor and McLennan, 1985) and higher than of UCC (0.79; McLennan, 2001).

La/Th ratios are useful indicators for providing source area composition, while Hf reveals the degree of recycling. The average La/Th values of the shale from Barsarin and Banik sections are 3.39 and 3.49, respectively (Table 5). The samples show higher values relative to PAAS and UCC (2.61 and 2.80, respectively). On a La/Th vs. Hf plot (Floyd and Leveridge, 1987; Spalletti et al. 2012), the Chia Gara shale samples are scattered in the felsic and toward the andesitic fields (Fig. 8).

Fig. 8: La/Th vs Hf diagram for the shale of Chia Gara Formation (fields after Floyd and Leveridge, 1987)

The REEs, Sc, Co, Th, and Cr are employed to predict the composition of the source area (Taylor and McLennan, 1985; McLennan and Taylor, 1991). These elements have very short residence times in seawater and are transferred into the sedimentary record. This represents compatible (Sc and Co) and incompatible elements (REEs and Th), and ratios that are useful in discriminating between mafic and felsic source rocks. However, the ratios La/Sc, La/Co, Th/Sc, Th/Co, Cr/Th, $(La/Lu)_{cn}$ and Eu/Eu^*_{cn} , are significantly different in mafic and felsic rocks and may constraints on the provenance composition (Wronkiewicz and Condie, 1990; Cox et al., 1995; Cullers, 1995; Asiedu et al., 2004; Dai et al., 2016). The ratios of the Chia Gara shales are compared with those of sediments derived from felsic and mafic rocks as well as with UCC and PAAS values (Table 6). These ratios for Barsarin are higher than that for Banik shale (except Cr/Th), and the comparison suggests these ratios are within the range of felsic rocks.

Table 5: Trace element ratios for the shale of Chia Gara Formation

Sample no.	La/Sc	La/Th	La/Co	Zr/Sc	Th/Sc	Zr/Hf	Th/U	Cr/Th	Ti/Zr	U/Th	V/Cr	V/Sc	Ni/Co	U-Th/3
Barsarin section														
CBN 1	2.25	2.80	0.38	12.00	0.81	44.00	0.17	10.16	29.97	5.80	6.88	56.27	4.35	48.45
CBN 2	4.07	3.90	1.90	15.71	1.04	39.29	0.32	12.31	31.06	3.12	7.60	97.71	14.13	20.36
CBN 3	3.62	4.31	3.10	14.33	0.84	43.00	0.27	19.84	27.88	3.71	9.08	151.33	33.43	17.02
CBN 4	3.82	4.85	3.82	14.00	0.79	43.75	0.23	27.92	28.26	4.38	5.45	120.00	43.40	15.94
CBN 5	3.60	4.03	1.35	13.50	0.89	45.00	0.36	13.06	29.60	2.80	4.10	47.83	10.38	13.21
CBN 6	2.99	3.57	2.66	12.50	0.84	43.48	0.41	11.96	28.17	2.44	3.69	36.88	15.56	14.12
CBN 7	3.50	3.27	2.63	15.17	1.07	45.50	0.67	12.44	28.32	1.49	5.78	77.00	30.13	7.45
CBN 8	3.15	3.39	2.73	13.00	0.93	36.74	1.12	12.40	30.15	0.90	3.76	43.38	14.93	6.82
CBN 9	3.00	3.11	3.67	18.45	0.96	39.04	1.07	13.21	26.28	0.94	5.18	65.91	20.00	6.40
CBN 10	3.76	3.57	3.13	18.40	1.05	46.00	0.47	11.41	23.45	2.15	4.78	57.40	13.50	9.55
CBN 11	3.20	3.32	4.27	16.38	0.96	39.70	0.59	10.39	27.00	1.69	6.03	60.25	27.17	10.43
CBN 12	3.21	3.41	3.21	17.38	0.94	38.61	0.52	11.94	25.44	1.91	4.89	55.00	19.63	11.89
CBN 13	3.01	3.07	3.76	16.30	0.98	44.05	0.84	11.22	26.84	1.19	5.81	63.90	28.25	8.38
CBN 14	3.66	3.46	3.66	17.86	1.06	41.67	1.02	10.83	26.85	0.98	6.03	68.86	14.29	4.77
CBN 15	3.13	3.14	3.48	15.30	1.00	41.35	0.68	9.04	26.25	1.46	6.36	57.20	23.33	11.23
CBN 16	3.51	2.76	3.01	19.58	1.27	41.96	1.97	9.18	26.78	0.51	4.84	56.42	13.50	2.68
CBN 17	3.91	2.92	3.91	18.30	1.34	37.35	1.80	7.46	27.51	0.56	5.00	50.00	11.60	2.97
CBN 18	3.89	2.97	5.00	18.44	1.31	38.60	1.09	7.63	24.91	0.92	4.97	49.67	19.71	6.87
CBN 19	3.94	3.11	4.44	17.89	1.27	36.59	1.11	8.77	26.43	0.90	3.68	40.89	17.38	6.50
CBN 20	3.32	3.15	3.32	14.78	1.06	39.12	1.49	8.42	31.55	0.67	4.71	41.89	11.67	3.19
CBN 21	4.28	3.02	4.28	19.50	1.42	39.00	1.77	13.43	28.28	0.56	3.18	60.40	10.80	3.26
Average	3.47	3.39	3.22	16.13	1.04	41.13	0.86	12.05	27.60	1.56	5.20	61.05	14.42	11.02
Banik section														
CBK 1	2.22	2.45	0.87	11.11	0.91	38.46	0.80	9.20	33.87	1.26	4.57	38.11	4.28	15.07
CBK 2	2.25	3.15	1.13	11.25	0.72	45.00	0.36	10.49	31.97	2.79	4.13	31.00	5.88	7.04
CBK 3	2.43	2.68	1.32	11.89	0.91	39.63	0.79	9.20	33.61	1.27	2.95	24.56	5.73	15.27
CBK 4	2.29	3.25	1.53	9.10	0.70	45.50	0.22	12.78	31.62	4.53	7.74	69.70	14.13	29.55
CBK 5	2.70	3.61	1.89	13.86	0.75	46.19	0.18	19.08	25.34	5.65	6.51	93.00	16.80	27.85
CBK 6	2.86	3.64	1.84	9.89	0.78	42.38	0.28	15.58	31.65	3.58	6.60	80.67	16.64	22.95
CBK 7	3.38	3.45	2.03	11.83	0.98	44.38	0.40	18.68	32.08	2.50	3.89	71.33	24.30	12.79
CBK 8	3.14	3.60	1.93	14.63	0.87	43.33	0.31	24.39	26.13	3.19	6.00	127.50	30.77	19.88
CBK 9	3.03	3.73	3.64	12.33	0.81	43.53	0.33	20.49	29.97	3.05	5.21	86.83	39.80	13.27
CBK 10	3.28	3.86	2.38	14.25	0.85	42.22	0.38	17.67	28.39	2.62	4.35	65.25	24.45	15.54
CBK 11	3.76	3.94	1.25	14.63	0.96	41.79	0.37	18.32	29.20	2.67	4.66	81.50	16.00	17.85
CBK 12	3.08	3.35	2.11	13.62	0.92	43.17	0.70	17.57	31.49	1.43	5.24	84.62	20.68	13.07
CBK 13	3.42	4.54	2.85	14.00	0.75	50.00	0.43	21.22	26.54	2.31	5.38	86.00	21.50	7.43
CBK 14	3.06	3.64	4.37	16.20	0.84	40.50	0.80	33.33	28.12	1.24	1.36	38.10	16.86	7.65
Average	2.92	3.49	2.08	12.76	0.84	43.29	0.45	17.71	30.23	2.37	4.57	64.41	14.37	16.09
Total avg.	3.25	3.43	2.77	14.78	0.96	42.00	0.70	14.32	29.03	1.93	4.84	62.79	14.39	13.05
PAAS		2.61			0.91				28.26	0.21	1.36	9.38	2.39	
UCC		2.80			0.79				15.77	0.26	1.71	5.45	2.00	

Table 6: Elemental ratios for the shale from Chia Gara Formation compared with those of fine-fractions derived from felsic and mafic source rocks

Elemental ratio	Range of sediments		UCC ²	PAAS ²	Average of studied shale		
	Felsic rocks ¹	Mafic rocks ¹			Barsarin ³	Banik ³	Chia Gara ³
La/Sc	2.5- 16.3	0.43- 0.86	2.21	2.4	3.47	2.92	3.25
La/Co	1.8- 13.8	0.14- 0.38	1.76	1.66	3.22	2.08	2.77
Th/Sc	0.84- 20.5	0.05- 0.22	0.79	0.90	1.04	0.84	0.96
Th/Co	0.67- 19.4	0.04- 1.4	0.63	0.63	0.98	0.59	0.82
Cr/Th	4.0- 15.0	25- 50	7.76	7.53	12.05	17.7	14.32
(La/Lu) _n	3.0- 27	1.10- 7	9.73		10.93	10.56	10.71
Eu/Eu*	0.4- 0.94	0.71- 0.95	0.63	0.63	0.67	0.68	0.67

(¹) Cullers (1994, 2000), Cullers and Podkovyrov (2000); (²) Taylor and McLennan (1985); (³) This study

According to the Th/Sc–Zr/Sc diagram (Fig. 9), Chia Gara samples are clustered between granite and andesite rocks along with the magmatic compositional variation trend of rocks, which indicates the mixed source rocks between felsic and intermediate.

Fig. 9: Th/Sc vs. Zr/Sc provenance and recycling discrimination plot (after McLennan et al., 1993) for the shale of Chia Gara Formation. Average source rock compositions are of Proterozoic age (after Condie, 1993)

Rare earth elements of sedimentary rocks can provide an important clue to unravel the source rock signatures (Bhatia and Crook, 1986; Gu et al., 2002; Armstrong-Altrin et al., 2013), as these elements have weak activity and are difficult to dissolve in water. Therefore, they can reflect source-area information. Mafic rocks commonly have low $(La/Yb)_{cn}$ ratio and do not have Eu anomaly, while silicic rocks commonly have higher $(La/Yb)_{cn}$ ratio and Eu anomaly (Cullers et al., 1997). The Chia Gara shales show LREE enrichment $((La/Yb)_{cn} = 7.94-11.76, \text{average} = 9.79)$ and relatively flat HREE pattern $((Gd/Yb)_{cn} = 1.20-1.75, \text{average} = 1.47)$, and clear negative $((Eu/Eu^* = 0.59-0.76, \text{average} = 0.67; \text{Table 4})$. Based on the aforementioned analysis, it can be summarized that REE characteristics indicate a mixture of felsic and intermediate source rocks.

Geochemical Parameters Indicative of Redox Conditions

The redox-sensitive elements are considered as a useful tool for recognizing the deposition of the sediments in non-marine and marine environments. These multi valence elements such as V, U, Ni, Cr, and Mo, their mobilization, precipitation, and concentration are mainly controlled by redox conditions and are enriched in anoxic sediments (Dypvik, 1984; Yarincik et al., 2000; Yang et al., 2004; Guo et al., 2007). Also, the ratios of these elements (U/Th, V/Cr, Ni/Co, and V/Sc) have been used to estimate the paleoredox conditions (Hatch and Leventhal, 1992; Jones and Manning, 1994; Pattan et al., 2005; Deepulal et al., 2012; Akinyemi et al. 2013; Armstrong-Altrin et al. 2015; Tobia and Shangola, 2016; Ramos-Vazquez et al., 2017; Anaya-Gregorio et al., 2018). The combined use of trace elements and their ratios may allow distinguishing the various depositional environments (oxic, suboxic, and anoxic).

The authigenic U was used as procurator of redox conditions in marine sediments because it preserved in the oxygenated water. Meanwhile, becomes enriched in anoxic environment (Ramos-Vazquez et al., 2017; Anaya-Gregorio et al., 2018). Authigenic U was intended from the formula $= U_{total} - (Th/3)$. The sediments of high authigenic U contents incline to be formed under anoxic conditions which allow great amounts of organic matter to accumulate and fixed (Wignall and Myers, 1988; Deepulal et al., 2012). Jones and Manning (1994) suggest less than 5ppm of authigenic U to be indicative of oxic conditions. The shales of Chia Gara Formation are enriched in authigenic U (13.05 ppm) (Table 5 and Fig. 10), which reflect anoxic environment for the studied shales.

U/Th is considered as a reliable tool to infer the oxygenation condition in the basin of deposition (Dypvik, 1984; Madhavaraju and Ramasamy, 1999; Jones and Manning, 1994; Rimmer, 2004; Nagarajan et al., 2007a; Madhavaraju and Gonzalez- Leon, 2012;

Fig. 10: Chemostratigraphic profiles of redox-sensitive trace element ratios for the shales of Chia Gara Formation (after McKirdy and Hall, 2011)

Madhavaraju et al., 2016). The U/Th ratio can be regarded as a redox index, with high values (>1.25) associated anoxic environment and low values (< 0.75) associated oxidic environment (Jones and Manning, 1994; McKirdy et al., 2011). The high U/Th value of the Chia

Gara shales (1.56 for Barsarin section and 2.37 for Banik section; Table 5) is indicative of the anoxic environment (except the upper part of the formation have more oxygenation conditions).

The V/Cr values of the sediment can be also considered as a bottom water oxygenation index (Dill, 1986; Nagarajan et al., 2007a; Akinyemi et al., 2013). Bjorlykke (1974) reported the incorporation of Cr in the detrital fraction of sediments and its possible substitution for Al in the clay structure. 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 (Shaw et al., 1990). The V/Cr ratios more than 2 suggest anoxic conditions, whereas values less than 2 indicate more oxidizing conditions (Jones and Manning, 1994). The V/Cr ratios for the Chia Gara shales are more than 2 (5.20 for Barsarin, 4.57 for Banik, and 4.84 for average Chia Gara shale; Table 5). Accordingly, the Chia Gara shales are accumulated under anoxic conditions.

Kimura and Watanabe (2001) proposed V/Sc as a proxy indicator, and they suggested that V/Sc ratios below 9 indicate oxidizing conditions and more than 9 is suboxic. The shales are characterized by the elevated values of V/Sc (61.05 for Barsarin, 64.41 for Banik, 62.79 for the average of Chia Gara); and are higher than PAAS (9.38) and UCC (5.45) as shown in Table 5. Therefore, the shales of Chia Gara Formation are accumulated in suboxic conditions (Fig. 10).

The Ni/Co ratios are a powerful tool for paleoredox conditions (Dypvik, 1984; Dill, 1986; Jones and Manning, 1994; Nagarajan et al., 2007a; Deepulal et al., 2012). The values of Ni/Co ratios less than 5 suggest oxic environments, whereas the values more than 5 indicate suboxic and anoxic environment of deposition (Jones and Manning, 1994). The Chia Gara shales have high Ni/Co values (14.42 for Barsarin, 14.37 for Banik, 14.39 for the average of Chia Gara shales; Table 5). These elevated values suggest that the deposition of the shales was established under anoxic conditions.

The studied parameters (authigenic U, U/Th, V/Cr, V/Sc, and Ni/Co) strongly imply that the shales of Chia Gara Formation were accumulated under anoxic environment; with slightly more oxygenated at the upper part of the formation.

The Al_2O_3 , P_2O_5 , and V contents can be employed in the discrimination of the depositional environments for the mudstones. The V concentration is somewhat lower in freshwaters than marine deposits. The P_2O_5 contents considerably vary in seawater and controlled by many factors such as depth and temperature of the water (Dhannoun and Al-Dlemi, 2013). Figure (11a) shows V vs. Al_2O_3 plots of the Chia Gara shale, and the shallow marine and freshwater shales are distinguished from the deep marine one. The deep marine environment for the studied shale is

consistent with the above paleoredox conditions (suboxic to anoxic). Figure (11b) shows P_2O_5 vs. Al_2O_3 plot of the Chia Gara samples. In this diagram, most of the samples fall in the deep depositional environments and the shale of Banik section is deeper than that of Barsarin. This interpretation has confirmed the results of V vs. Al_2O_3 . These sediments were deposited in the deep marine environment, where the P content was high as a result of high biologic products.

Fig. 11: Plots of (a) Al_2O_3 vs. V and (b) Al_2O_3 vs. P_2O_5 for the shale from Chia Gara Formation for paleoenvironmental reconstruction (after Mortazavi et al., 2013)

CONCLUSIONS

The shale of Chia Gara Formation shows high CaO content that causes a high dilution effect on the other major, trace, and rare earth elements; and is enriched in Sr, U, V, Ni and depleted in Rb, Ba, Th, Y, Zr, Nb, Hf, Sc, and Co. Chondrite normalized REE patterns show enrichment in LREE and depletion HREE in addition to the nearly flat HREE pattern, with negative Eu anomalies and moderate fractionation between LREE and HREE. Geochemical parameters (CIA, CIW, and PIA) and A-CN-K diagram, reveal intense chemical weathering in the source area. The shale of Barsarin area was subject to more intense chemical weathering than at Banik. The ratios (Al_2O_3/TiO_2 , Th/Sc, La/Th, La/Sc, La/Co, Th/Co, Cr/Th, $(La/Lu)_{cn}$ and Eu/Eu^*_{cn}), and the diagrams (Th/Sc-Zr/Sc and La/Th-Hf) suggest a mixing source of felsic and intermediate rocks. The felsic rocks are derived from the Rutba Uplift or/and Mosul High which were a positive area at the time of deposition; and the intermediate rocks may derive from the volcanic material during the spreading of Southern Neo-Tethys Ocean. The authigenic uranium and U/Th, V/Cr,

Ni/Co, and V/Sc ratios refer suboxic to anoxic deep marine environment of deposition for the shale of Chia Gara Formation.

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