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Major elements of Bara Formation at Ranikot Fort, Southern Indus Basin, Pakistan

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Abstract: Major elements of fifty one samples of Bara Formation were observed through X-ray fluorescence in order to investigate and determine the geochemical properties of its sediments. The study of major elements (Si, Ti, Al, Na, Ca, K, Mn, Mg, Fe^{+3}, P & S) and their ratios indicate that the Bara Formation is dominantly composed of quartz (low). The silica has originated as either biogenically precipitated or in detrital modes. The studied sediments are less mature and are mostly transported in detrital mode. The study area has faced the changing climatic conditions. The Bara Formation deposited under fluvio-deltaic depositional system with rapid rate of sediment deposition. The fast rate of sediment deposition might have produced the reducing environment, and allowed the mineralization of sulphur, which has been found in the studied rock samples.

Keywords: Geochemistry, XRF, Major elements, Bara Formation and Ranikot Fort.

1. INTRODUCTION

Major elements (Si, Ti, Al, Na, Ca, K, Mn, Mg, Fe^{+3}, S & P) of Bara Formation were studied in order to determine the geochemical properties of its sediments. The study area is located in Fort Ranikot **(Fig. 1)**. The studied area consists of sedimentary and igneous rocks, ranging in age from Paleocene to Recent. The oldest to youngest exposed formations are Khadro, Bara, Laki and Manchhar (Hakro and Baig, 2013). The lower contact of Bara with Khadro is conformable while its upper contact with Laki Formation is unconformable (Shah, 2009). Sandstones, Shales, Siltstones, petrified wood, volcanic fragments, leaf impressions are reported in Bara Formation (Hakro, 2013). The Sandstone is a major constituent which is variable in color, hard, loose, friable, conglomeratic, tabular, cross bedded, and ripple marked. Shale is carbonaceous, fissile, gypsiferous and contains (2–3) inches of coal seam in the upper part of the formation.

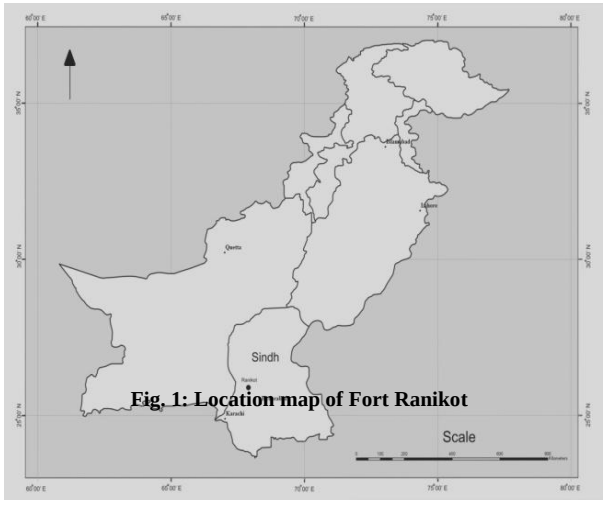

Fig. 1: Location map of Fort Ranikot

Bara Formation is studied by many workers for its coal potential, stratigraphical and sedimentological aspects but little has been done on the geochemical studies of this formation in the past. Previous workers including HSC (1961), Cheema et. al. (1977) and Wnuk, et.al (1993) had described its stratigraphical position, and coal potential. Abdullah et.al (1997) and Baig et.al. (2007) defined its bulk clay mineralogy. Hakro and Baig (2013), Hakro (2013), Khokhar et.al. (2014), and Hakro (2014) described the depositional environment using the grain size data, bulk mineralogy, and the textural maturity of Bara Formation. The current research determines the elemental distribution of Bara Formation for getting information about the geochemical properties of its sediments.

2. MATERIALS AND METHODS

During geological fieldwork, fifty one rock samples of Bara Formation at Ranikot locality were collected **(Fig. 2)**. The geochemical data was acquired by utilizing the X-ray fluorescence method. Hundred gram piece of each sample was washed with distilled water and put in oven for 24 hours at110˚C, sample was crushed and pulverized by grinding mill in order to obtained 200 mesh particle size. Pellets were prepared according to procedures of (Cosgrove, 1973). One gram of each sample free of moisture was weighted in platinum crucible and was placed in Muffle Furnace at 700^{o} C about two hours.

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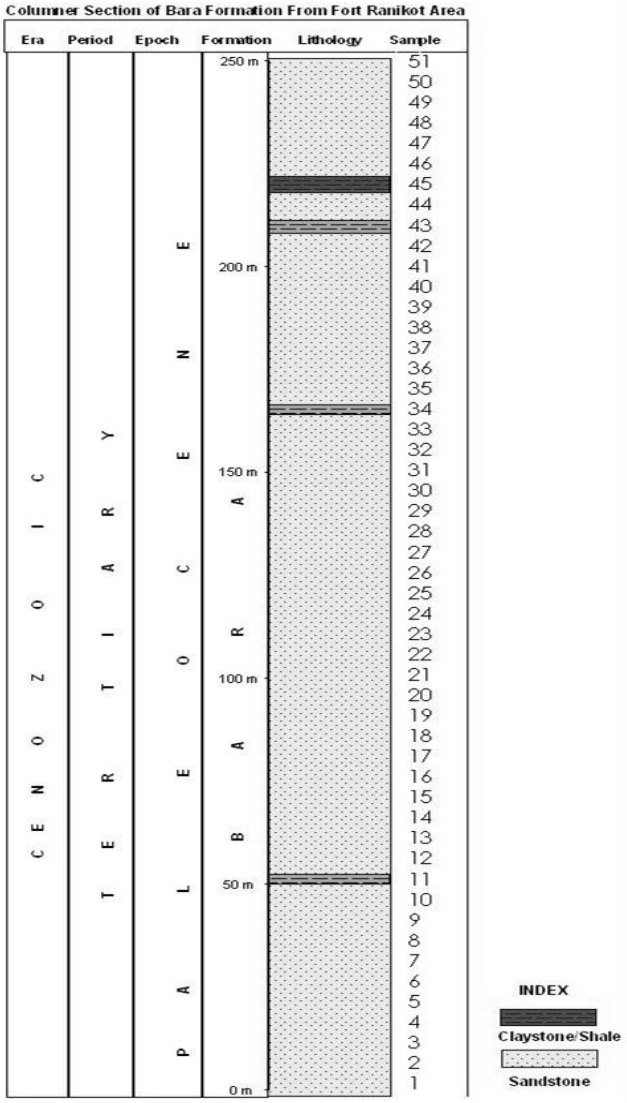

Fig. 2: Columnar Section of Bara Formation at Fort Ranikot

3. RESULTS AND DISCUSSION

Silicon (SiO_2): The content of silicon dioxide of studied sediments varies from (43.79%) to (87.07%) with average (71.94%) of (n=51) samples. Sedimentary Geochemists use Si/Al ratios to identifying the occurrence of different types of silica in sedimentary rocks. Si/Al ratio was used by Couture (1977) for measurement of bigamous silica in sedimentary rocks. He defined that higher value of Si/Al indicate the bigamous silica whereas lower value of Si/Al indicate the presence of terrigenous substance. The Si/Al ratio of studied sediments are (35.51) to (3.03) with (12.1) average, shown in **(Table - 2)**. The highest and lowest values of the studied sediments suggest the presence of some biogenically precipitated silica and detrital silica. Hakro (2013) reported that the sediments of Bara Formation from Ranikot locality are dominantly composed of quartz (low); which is confirmed by the Si/Al ratio in present study. The silica percentage was utilized by Ronov (1965) to measure the comparison between near-shore to basin sediments. Silicon dioxide (SiO_2) is present in highest amount (71.94%) indicating that the studied sediments were deposited under fluvio-deltaic depositional system. **(Fig. 3a)** shows the bivariate diagram of SiO_2 with Al_2O_3, which shows the negative correlation (r2= -0.099) suggesting that the major part of Silica are Quartz (free silica). The petrographic, SEM and XRD results of Hakro (2013) are also in compliance with the presence of silica as Quartz.

Titanium (TiO_2): The content of Titanium dioxide of studied (n=51) samples varies from (0.29%) to (2.28%) with (0.77%) average. Shah (2009), Hakro (2012), Hakro and Baig (2013) and Hakro (2013), reported that Bara Formation at Ranikot area is composed of sandstones and shales. Majority of Ti/Al ratio of studied samples suggest that Bara Formation is composed of sandstone confirming the work of previous authors. Besides, (Ti/Al) ratio is also used by Migdisov (1960) to compute the change in climate during deposition, and the analysis of (Ti/Al) ratio suggest that the study area has faced changing climatic conditions during deposition of sediments. **(Fig. 3b)** shows the bivariate diagram of SiO_2 with TiO_2, which indicates the weak negative correlation (r2= -0.0003) shows that the source of titanium is non-detrital.

Aluminum (Al_2O_3): The Aluminum trioxide of Bara Formation sediments (n=51) varies from (2.36%) to (16.55%) with an average of (7.74%). Kaolinite and illite holds high concentration of aluminum as compared to Montmorillonite (Weaver and Pollard, 1973). Kolinite, Chlorite, Illite and Montmorillonite clay minerals are present in the Bara Formation at Ranikot (Hakro, 2013). The Al_2O_3/Na_2O ratio was calculated for the maturity index of the studied rock samples, as proposed by Pettijohn (1957). The Al_2O_3/Na_2O ratios (1.76 to 45.87) suggest that the studied sediments are less mature and transported as detrital particles. The ratio of Al_2O_3/SiO_2 of studied rock samples, suggest that sediments of Bara Formation do not contain substantial amount of clay minerals **(Table 2)**. The diagram Al_2O_3/SiO_2 of studied samples is plotted and shown in **(Fig. 3g),** the correlation coefficient (r2=0.0996) shows weak negative correlation with Si, Ti, Fe, Mg, Na, K, Ca, P and S, suggesting that Al_2O_3 is not connected with detrital mineral (quartz), **(Table-3)**. **(Fig. 3g)** exhibits the trend-line which shows negative correlation between Al and Si, only seven samples plotted on it and majority of samples were plotted away from trend-line suggesting that the Aluminums trioxide is not related with quartz.

Table - 1: Major Elements of the Bara Formation at Ranikot Fort.

Sample	SiO2	TiO	Al2O3	Fe2O3	MnO2	MgO	CaO	Na2O	K2O	P2O5	SO3	LOI	Total
1 Ra	72.1	1.67	4.58	13.8	0.19	1.01	1.4	2.6	1.02	0.24	0.23	N.D	98.79
2 Ra	77.1	0.39	8.05	7.04	0.07	2.02	1.4	1.25	1.1	0.06	0.25	N.D	98.69
3 Ra	77.2	0.43	3.15	9.76	0.07	2.02	1.4	1.5	2.18	0.15	1.76	N.D	99.58
4 Ra	71.5	0.41	7.51	8.88	0.05	1.01	2.8	2.57	2.8	0.26	2.05	N.D	99.8
5 Ra	81.3	0.88	5.03	7.1	0.12	1.01	1.4	1.11	0.61	0.34	0.76	N.D	99.69
6 Ra	77.3	0.51	3.58	9.6	0.05	1.01	2.8	1.14	1.3	0.39	1.85	N.D	99.55
7 Ra	74.4	0.49	9.36	7.9	0.04	1.01	2.8	0.41	1.68	0.18	1.42	N.D	99.64
8 Ra	62.2	0.14	8.21	16.05	0.02	1.01	1.4	1.43	1.36	0.21	1.5	5.74	99.26
9 Ra	69.5	1.98	3.81	14.04	0.03	1.01	1.4	0.63	1.58	0.03	0.23	4.32	98.58
10 Ra	80.2	0.29	7.62	5.2	0.03	2.02	1.4	0.51	1.18	0.06	0.24	N.D	98.7
11 Ra	57.4	2.63	8.37	16.02	0.131	2.02	1.4	0.39	1.81	0.13	2.33	6.52	99.421
12 Ra	83.7	0.29	5.71	3.19	0.06	1.01	1.4	0.73	1.3	0.1	1.53	N.D	99
13Ra	74.2	1.43	8.23	9.4	0.609	2.02	1.4	0.63	1.09	0.15	0.51	N.D	99.619
14Ra	78	0.38	5.17	8.81	0.05	1.01	2.8	1.47	0.88	0.11	0.57	N.D	99.27
15Ra	68.1	0.48	10.82	13.1	0.06	1.01	2.8	1.06	1.28	0.18	0.71	N.D	99.56
16Ra	72.1	0.39	4.05	16.81	0.14	2.02	1.4	1.25	1.19	0.08	0.45	N.D	99.19
17Ra	73.4	0.49	14.57	5.71	0.08	1.01	1.4	1.05	0.85	0.09	0.43	N.D	99.07
18Ra	62.8	0.57	11.06	19	0.18	1.01	1.4	0.54	1.11	0.12	1.87	N.D	99.61
19 Ra	68.1	1.16	2.77	20.26	0.12	1.01	2.8	0.49	1.66	0.21	1.23	N.D	99.83
20 Ra	49	0.39	5.03	39.24	0.12	2.02	1.4	0.43	0.63	0.16	1.56	N.D	99.96
21 Ra	75.4	0.49	16.42	0.17	0.15	1.01	2.8	1.14	1.08	0.12	1.21	N.D	99.95
22 Ra	43.8	0.57	11.85	35.05	0.09	1.01	2.8	0.27	1.53	0.07	2.53	N.D	99.56
23Ra	69.1	0.67	4.05	20.27	0.14	1.01	1.4	1.01	1.05	0.11	0.45	N.D	99.29
24Ra	78	0.76	14.28	0.81	0.09	1.01	1.4	1.1	0.9	0.26	0.66	N.D	99.22
25Ra	67.3	0.74	4.01	22	0.06	1.01	1.4	0.81	1.06	0.19	0.75	N.D	99.3
26Ra	81.4	0.39	9.93	0.5	0.09	1.01	2.8	1.53	0.79	0.06	1.5	N.D	99.97
27Ra	65.7	0.19	16.55	9.65	0.05	1.01	2.8	1.05	0.71	1.12	0.77	N.D	99.62
28Ra	66.5	0.22	5.56	14.04	0.08	1.01	1.4	2.14	0.89	1.16	0.57	5.76	99.29
29Ra	56.4	1.33	6	24.02	0.04	1.01	1.4	0.56	1.19	0.13	0.67	5.74	98.81
30Ra	77.8	0.68	11.71	1.2	0.04	1.01	1.4	2.03	1.5	0.12	2.22	N.D	99.72
31 Ra	87.1	0.32	3.01	3.19	0.04	2.02	1.4	1.02	0.46	0.07	0.81	N.D	99.41
32 Ra	73.1	0.78	10.23	7.01	0.03	1.01	2.8	1.87	0.37	0.34	2.35	N.D	99.84
33Ra	82	0.68	4.23	7.01	0.05	1.01	2.8	0.56	0.61	0.21	0.47	N.D	99.64
34Ra	83.8	0.51	2.36	8.46	0.06	1.01	1.4	0.34	0.43	0.05	0.57	N.D	99
35Ra	65.2	0.56	7.01	18.04	0.07	1.01	1.4	1.28	1.52	0.26	1.38	2.03	99.79
36Ra	78	0.67	11.56	1.28	0.09	1.01	2.8	0.81	0.34	0.27	1.47	N.D	98.34
37Ra	74.5	0.56	6.85	9.02	0.09	1.01	2.8	1.32	1.48	0.19	1.87	N.D	98.99
38Ra	75.6	0.32	8.55	10.4	0.14	1.01	1.4	0.48	0.41	0.08	0.23	N.D	98.63
39Ra	79.8	1.42	7.23	5.42	0.13	1.01	1.4	0.31	1.04	0.5	1.41	N.D	99.68
40Ra	80.5	0.54	8.01	5.51	0.14	1.01	1.4	0.78	0.44	0.16	1.81.-	N.D	98.52
41 Ra	77.2	2.86	8.01	5.67	0.1	1.01	2.8	0.5	0.88	0.05	0.33	N.D	99.39
42 Ra	66.5	0.72	4.05	14.76	0.1	1.02	2.8	0.83	1.52	0.2	0.33	5.52	98.65
43Ra	86.6	0.38	2.53	2.04	0.11	2.02	1.4	1.37	0.61	0.11	1.54	N.D	99
44Ra	45.6	0.31	15.05	26.01	0.12	2.02	1.4	0.36	0.85	0.17	1.72	6.88	99.8
45Ra	47.8	2.28	14.28	23.54	0.15	1.01	1.4	1.14	0.79	0.21	0.22	5.36	98.18
46Ra	72.5	0.64	11.01	8.46	0.22	2.02	1.4	0.24	0.41	0.18	2.01	N.D	99.09
47Ra	81.3	0.58	8.51	3.04	0.174	1.01	1.4	1.46	1.03	0.22	1.32	N.D	100
48Ra	80	0.31	7.61	4.91	0.12	1.01	2.8	1.06	0.28	0.13	0.56	N.D	98.8
49Ra	64.4	0.49	6.81	15.03	0.08	1.01	2.8	2.39	1.32	1.2	1.22	3.82	99.88
50Ra	81.5	0.56	5.01	3.27	0.08	1.01	2.8	2.75	0.25	0.17	2.33	N.D	99.74
51 Ra	74.6	2.69	7.35	8.76	0.254	1.01	1.4	1.1	1.41	0.23	0.56	N.D	99.384

Table - 2: Ratios of Elements of Samples from Ranikot Fort.

Sample	Al_2O_3/ SiO_2	Al_2O_3/ Na_2O	Fe_2O_3/Al_2O_3	MnO_2/ Fe_2O_3	K_2O/Al_2O_3	MgO/ Al_2O_3	SiO_2/ Al_2O_3	Na_2O/ K_2O	TiO_2/ Al_2O_3	Fe_2O_3/FeO (ppm)
1 Ra	0.06	1.76	3.01	0.01	0.22	0.22	15.7	2.54	0.36	1.58
2 Ra	0.1	6.44	0.87	0.009	0.13	0.25	9.57	1.13	0.04	1.57
3 Ra	0.04	2.1	3.09	0.007	0.69	0.64	24.5	0.68	0.13	1.84
4 Ra	0.1	2.92	1.18	0.005	0.37	0.13	9.51	0.91	0.05	1.34
5 Ra	0.06	4.53	1.41	0.01	0.12	0.2	16.9	1.81	0.17	1.56
6 Ra	0.04	3.14	2.68	0.005	0.36	0.28	21.6	0.87	0.14	1.84
7 Ra	0.12	22.82	0.84	0.005	0.17	0.1	7.94	0.24	0.05	1.94
8 Ra	0.13	5.74	1.95	0.001	0.16	0.12	7.57	1.05	0.01	17.44
9 Ra	0.05	6.04	3.68	0.002	0.41	0.26	18.2	0.39	0.51	1.68
10 Ra	0.09	14.94	0.68	0.005	0.15	0.26	10.5	0.43	0.03	1.58
11 Ra	0.14	21.46	1.91	0.008	0.21	0.24	6.55	0.21	0.31	1.67
12 Ra	0.06	7.82	0.55	0.01	0.22	0.17	14.7	0.56	0.05	7.91
13Ra	0.11	13.06	1.14	0.06	0.13	0.24	9	0.57	0.17	16.48
14Ra	0.06	3.51	1.7	0.005	0.17	0.19	15.1	1.67	0.07	17.62
15Ra	0.15	10.2	1.21	0.004	0.11	0.09	6.29	0.82	0.04	40.93
16Ra	0.05	3.24	3.97	0.008	0.29	0.49	17.8	1.05	0.09	146.45
17Ra	0.19	13.87	0.39	0.01	0.05	0.06	5.03	1.23	0.03	67.17
18Ra	0.17	20.48	1.71	0.009	0.1	0.09	5.67	0.48	0.05	57.57
19 Ra	0.04	5.65	7.31	0.005	0.59	0.36	24.6	0.29	0.41	24.11
20 Ra	0.1	11.69	7.8	0.003	0.12	0.4	9.73	0.68	0.07	66.5
21 Ra	0.21	14.4	0.01	0.88	0.06	0.06	4.58	1.05	0.02	0.22
22 Ra	0.27	43.88	2.95	0.002	0.12	0.08	3.69	0.17	0.04	64.54
23Ra	0.05	4.009	5.004	0.006	0.25	0.24	17.1	0.96	0.16	23.29
24Ra	0.18	12.98	0.05	0.11	0.06	0.07	5.45	1.22	0.05	1.22
25Ra	0.05	4.95	5.48	0.002	0.26	0.25	16.5	0.76	0.18	51.16
26Ra	0.12	6.49	0.05	0.18	0.07	0.1	8.19	1.93	0.03	1.56
27Ra	0.25	15.76	0.58	0.005	0.04	0.06	3.97	1.47	0.01	1.4
28Ra	0.08	2.59	2.52	0.005	0.16	0.18	12	2.4	0.03	1.66
29Ra	0.1	10.71	4.003	0.001	0.19	0.16	9.45	0.47	0.22	1.43
30Ra	0.15	5.76	0.1	0.03	0.12	0.08	6.64	1.35	0.05	17.14
31 Ra	0.03	2.95	1.05	0.01	0.15	0.67	28.9	2.21	0.1	5.38
32 Ra	0.14	5.47	0.68	0.004	0.03	0.09	7.14	5.05	0.07	1.47
33Ra	0.05	7.55	1.65	0.007	0.14	0.23	19.4	0.91	0.16	1.47
34Ra	0.02	6.64	3.58	0.007	0.18	0.42	35.5	0.79	0.21	1.62
35Ra	0.1	5.47	2.57	0.003	0.21	0.14	9.3	0.84	0.07	1.67
36Ra	0.14	14.27	0.11	0.07	0.02	0.08	6.45	2.38	0.05	5.84
37Ra	0.08	4.65	1.46	0.009	0.24	0.16	12.1	0.89	0.09	1.46
38Ra	0.11	17.81	1.21	0.01	0.04	0.11	8.84	1.17	0.03	1.61
39Ra	0.09	23.32	0.74	0.02	0.14	0.13	11	0.29	0.19	1.47
40Ra	0.09	10.26	0.68	0.02	0.05	0.12	10.1	1.77	0.06	1.48
41 Ra	0.1	16.02	0.7	0.01	0.1	0.12	9.63	0.56	0.35	1.43
42 Ra	0.06	4.87	3.64	0.006	0.37	0.25	16.5	0.54	0.17	1.81
43Ra	0.02	1.84	0.8	0.05	0.24	0.79	34.3	2.24	0.15	1.47
44Ra	0.32	41.8	1.72	0.004	0.05	0.13	3.03	0.42	0.02	1.61
45Ra	0.29	12.52	1.64	0.006	0.05	0.07	3.34	1.44	0.15	1.3
46Ra	0.15	45.88	0.76	0.02	0.03	0.18	6.58	0.58	0.05	1.45
47Ra	0.1	5.82	0.35	0.05	0.12	0.11	9.54	1.41	0.06	1.03
48Ra	0.09	7.17	0.64	0.02	0.03	0.13	10.5	3.78	0.04	1.31
49Ra	0.09	2.55	2.45	0.005	0.21	0.16	10.5	1.81	0.08	1.66
50Ra	0.06	1.82	0.65	0.02	0.04	0.2	16.3	11	0.11	1.29
51 Ra	0.09	6.68	1.19	0.02	0.19	0.13	10.2	0.78	0.36	1.33

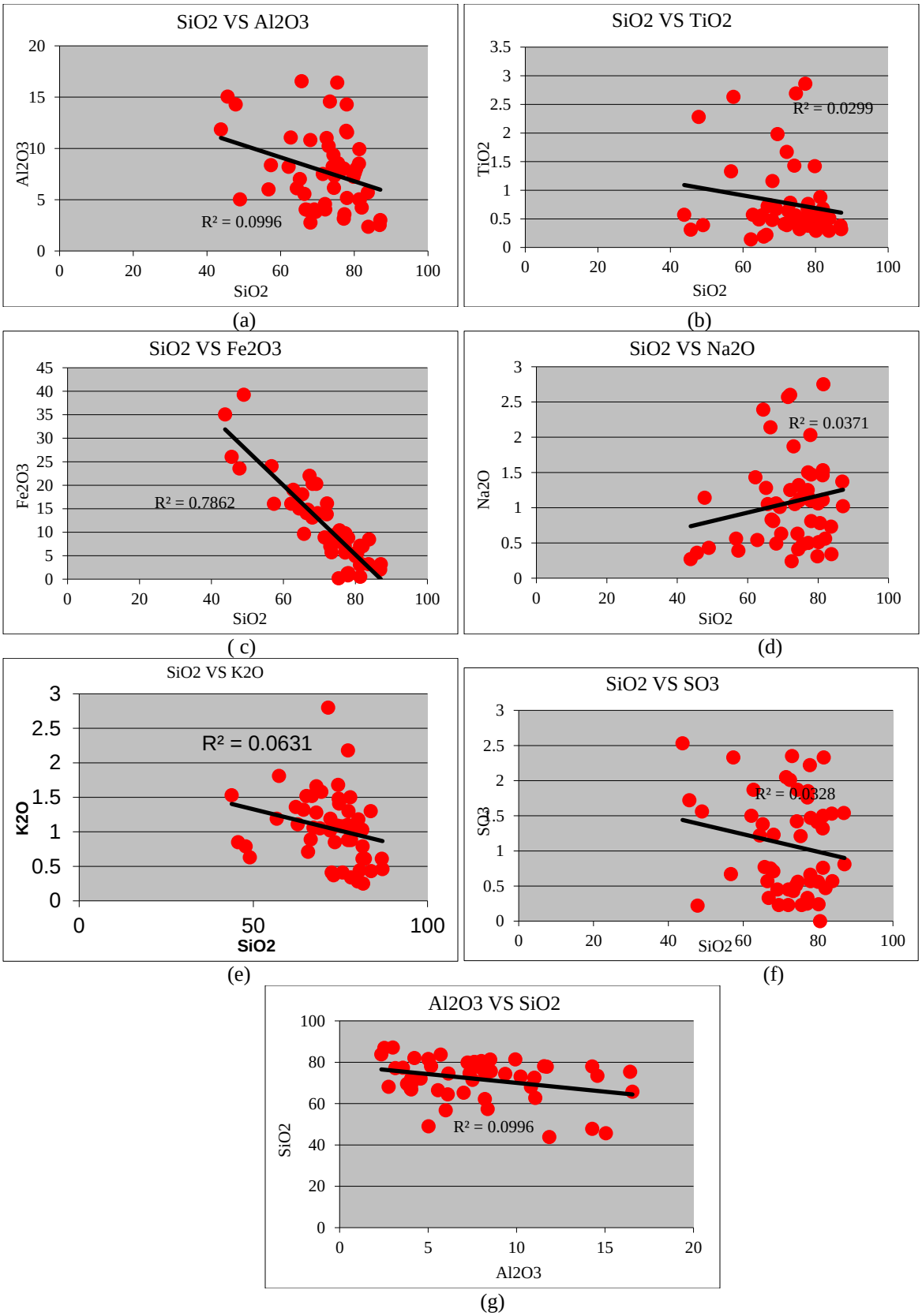

Fig. 3: The Bivariate Diagrams of Major Elements from Ranikot Fort.

Iron (Fe_2O_3): The iron content of studied (n=51) samples of Bara Formation varies from (0.17%) to (39.24%) with an average value of (11.15%). The Fe_2O_3/Al_2O_3 ratio is utilized to find the relationship of iron with clay minerals by Hirst (1962), Spears (1964), Calvert (1978), Baig (1982) and Hakro (2012). The Fe_2O_3/Al_2O_3 ratios of studied samples indicates weak relationship with clay minerals **(**Table - 2). Mn/Fe ration is used by Goldschmith (1937), Nicholls & Loring (1962), Sulaiman (1972), Baig (1984) and Hakro (2012) for the identification of depositional environment of sedimentary rocks. The Mn/Fe ratios of studied samples suggest the near shore to off shore depositional environment of Bara Formation. The leaching process is liable for low Mn/Fe ratio, (Cosgrove et. al., 1973). High concentration of Fe_2O_3 can be formed due to strong chemical weathering (Baig, 1984). Hematite is present in Bara Formation at Ranikot area, as investigated by Hakro (2012), in the shape of hematite (amorphous) coated on surface of grains of sandstone and clay minerals. The correlation coefficient (r2) shows strong negative correlation with SiO_2 **(Table - 3)**; suggests that iron is not connected with detrital and clay minerals. Fe_2O_3 showed positive correlation with Ti, Mg, K, P and S **(Table -3)** indicates its poor relationship with aluminosilicate minerals.

Magnesium (MgO): The MgO distribution in studied (n=51) samples range from (1.01 %) to (2.02 %), with mean values of (1.22%). The Mg/Al_2O_3 ratio calculated according to Spears (1964) for the presence of montmorillonite and clay minerals, (Table - 2). The weak positive correlation of MgO with iron suggests its presence in the lattices of montmorillonite. The negative correlation MgO is observed with Si, Ti, Al, Ca, Na, K and P suggest that it is not connected with detrital mineral i.e. quartz. Magnesium shows positive correlation with iron indicating its possible substitution in the clay minerals lattices probably in smectite and chlorite. Due to the close ionic radii of Mg (0.80) and Fe^{+2} (0.86) which might have substituted in the clay minerals. Present study confirms the finding of Hakro (2012) for the presence of Montmorillonite in Bara Formation.

Calcium (CaO): The CaO distribution in (n=51) studied samples ranges from (1.4%) to (2.8%), with mean value of (1.92%). CaO content in hydrolysate sediments is not more than (1%), separated from calcium carbonate and dolomite (Goldschmidt, 1954). A small quantity of Ca^{+2} is situated in transferable site of clay minerals, feldspars and pyroxene minerals, as mentioned by Goldberg and Arrhenius (1958). Quartz (low), Feldspar, Kaolinite and other clay minerals are reported in the sediments of Bara Formation at Ranikot locality (Hakro, 2013). The correlation coefficient of CaO is positive with Si, Al, Na, K, P and S, indicating its relationship with clay minerals and feldspars. A weak correlation coefficient of Calcium with Al_2O_3 (r2=0.011) confirms its connection with feldspar and clay minerals.

Sodium (Na_2O): The (Na_2O) concentration in Bara Formation varies from (0.24 %) to (2.75 %), with mean value of (1.07%) of (n=51) samples. The montmorillonite (smectite) contains smaller amounts of Na^+ in the inter-layered position in comparison with other cations such as Ca^{+2} and Mg^{+2} (Weaver and Pollard, 1973). Na/K ratio is utilized by Nicholls and Loring (1960) to determine the rate of deposition of sediments. These Na/K ratios of studied samples indicates medium to high rate of deposition of sediments. Hakro (2013) reported the presence of plagioclase and orthoclase feldspars in Bara Formation at Ranikot locality. The sodium (Na_2O) in studied samples is making connection with aluminosilicates, corresponding to weak positive correlation coefficient with Si, Ca, P and S, suggesting the connection of Na_2O with lattices of clay minerals and plagioclase feldspar.

Potassium (K_2O): The (K_2O) concentration in Bara Formation sediments varies from (0.25 %) to (2.18%), with mean value of (1.05%). The montmorillonite frequently holds minor amount of potassium and sodium oxides in their lattices as compared to other cations (calcium and magnesium) (Weaver and Pollard, 1973). Na/K ratio is utilized by Bloxam and Thomas (1969) in order to determine the rate of deposition of sediments and Illite crystallinity. The Na/K ratios of studied samples indicate medium to high rate of deposition of sediments, and presence of degraded illite. The K_2O/Al_2O_3 ratio is utilized to measure sand proportion in sediment by Calvert (1976); The K_2O/Al_2O_3 ratio of studied samples suggests the abundance of sand in sediments and rapid rate of deposition of sediments. The correlation coefficient shows a very weak positive correlation of K_2O with Ti, Fe, Ca, Na, and S, this correlation suggested that K_2O is associated feldspar and clay minerals. Chester and Hughes (1967), Chester and Aston (1976) suggested that some amount of K_2O in sediments is associated with sodic feldspar. The studied samples showed positive correlation significant at a (0.01%) level of K_2O with Na, Ca, and Fe; all elements of Lithophile group of elements, suggesting that detrital minerals e.g. feldspars are present in these sediments.

Table -3: Correlation Coefficient Values of Oxides from Fort Ranikot.

	SiO_2	TiO_2	Al_2O_3	Fe_2O3	MgO	CaO	Na_2O	K_2O	P_2O_5	SO_3
SiO_2	-	0.029	0.099	0.78	0.003	0.0032	0.037	0.063	0.019	0.032
TiO_2	0.029	-	0.0003	0.01	0.004	0.016	0.029	0.023	0.018	0.029
$Al2O3$	0.099	0.0003	-	0.005	0.013	0.011	0.010	0.012	0.009	0.02
$Fe2O5$	0.78	0.01	0.005	-	0.012	0.020	0.070	0.043	0.0008	0.005
MgO	0.003	0.0048	0.013	0.012	-	0.16	0.047	-0.05	0.050	0.006
CaO	0.0032	0.016	0.011	0.02	0.16	-	0.03	0.0035	0.03	0.05
Na_2O	0.037	0.029	0.010	0.070	0.04	0.032	-	0.015	0.126	0.023
K_2O	0.063	0.023	0.012	0.04	-0.05	0.003	0.015	-	0.0003	0.062
P_2O_5	0.019	0.018	0.009	0.0008	0.05	0.034	0.126	0.0003	-	0.0002
SO_3	0.0004	0.010	0.014	0.0001	0.023	0.009	0.0005	0.23	0.02	-

Phosphorous (P_2O_5): The phosphorous in (n=51) studied samples ranges from (0.03 %) to (1.16%) with mean value of (0.22%). The higher content of (P_2O_5) exists in the lattice of mineral like sedimentary phosphate (Baig, 1984). The very weak positive correlation of P_2O_5 with Al, Fe, Ca, Na, and S, **(Table - 3)**; supports the above statement regarding the occurrence of P_2O_5 in the studied sediments. It seems that the Eh – pH conditions of the environments of deposition of these sediments were frequently changing at the time of sedimentation, and the principal phosphate ions H_2PO4^- in acidic solutions and $(HPO_2)^{-2}$ in alkaline solutions, probably both were available from time to time as mentioned by Krauskopf (1979). The correlation coefficient (**Table - 3)** shows a very weak positive correlation of P_2O_5, with Al, Fe, Ca, Na, and S. These associations suggested a weak relationship of P_2O_5 with aluminosilicates minerals.

Sulphur (S): The concentrations of sulphur ranges from (0.22%) to (2.53%), with average value of (1.08%). The average sulphur in shales is (0.25%) (Krauskopf, 1979), average concentration of European Paleozoic shales is (0.32%) (Minami, 1935a). In the studied samples the amount of sulphur is high; indicates the substantial availability of metabolizable organic matter, sulphate reducing bacteria and dissolved sulphide in the depositional environments. Shishkina (1964) believes that the high content of the organic matter and high accumulation rate of the sediments is the main reason for the existence of sulphides in certain Pacific Ocean trenches. The fast deposition rate of the Bara Formation sediments might have produced the reducing environments during the deposition of the sediments and may be the reason of the presence of sulphur in the studied samples. The correlation coefficient **(Table - 3)** shows very weak positive correlation of sulphur with Si, Ti, Al, Ca and P, indicates that in the studied samples the sulphur is not associated with the aluminosilicate minerals. The association of sulphur with metals like Ni, Cu, Zn, Pb and Mo, suggested that either the sulphide of these metals were present in these sediments in minor amounts as mentioned by Degens (1965), or this association is based on the pronounced affinity of these metals for sulphur, being the metals of the Chalcophile group as mentioned by Goldschmidt (1954) and Brownlow (1979).The correlation shown by sulphur with P_2O_5 (r2 = +0.02) may be either, due to the presence of" organism "biophile" group mentioned by Goldschmidt (1937), as both may be derived from organic organisms, or this relationship may be due to similar ionic potential of sulphur (0.20) and P_2O_5 (0.25) reported by Mason (1952);being the soluble complex-anions and explained by Rosler & Lange (1972). The silicon and sulphur correlation is negative and very weak. This relationship indicated that there exists no relationship between sulphur and SiO_2, may be that sulphur is not detrital and SiO_2 is detrital. Minerals of sulfide group e.g. Pyrite, which need the presence of sulphur, are not present in the investigated sediments.

4. CONCLUSIONS

- Bara Formation is dominantly composed of quartz (low), and the origin of silica is either biogenically precipitated or detrital silica.
- The Ti/Al ratio suggests that the study area has faced the changing climatic condition during the deposition of Bara Formation sediments.
- The studied sediments are less mature and transported as detrital particle.
- The studied sediments indicate the presence of montmorillonite and clay minerals.
- The studied samples show medium to high rate of deposition and presence of degraded illite. The abundance of sand in sediments suggests rapid rate of deposition.

- The presence of sulphur indicates sufficient availability of metabolizable organic matter, and reducing depositional environment.
- On the basis of its dominant quartz mineral composition, ratios of various elements, and less maturity, it is suggested that Bara Formation was deposited under fluvio-deltaic depositional system.

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