

Geochemical Characteristics of the Carbonaceous Sediments of the Upper Paleozoic Kuantan Group, Malaysia

Amer M. Burgan*

Department of Petroleum Engineering, Faculty of Engineering, Bani Walied University, Libya

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ABSTRACT. This paper discusses the geochemical parameters of carbonaceous samples, mainly black shales, from the Upper Paleozoic Kuantan Group, Malaysia. The reported geochemical parameters are based on average values of twelve outcropped samples, representative of Charu, Sagor, and Permian formations. X-ray fluorescence (XRF) and Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) techniques determined these samples' major and trace elements. This study aims to define and discuss their characteristics and the distribution abundance of major and minor elements, investigate the dominant mineralogical composition, and reconstruct the depositional environment for these sediments. The average values of the major elements are 65.83 %, 64.82 %, 71.4 % SiO₂, 18.27 %, 22.2 %, 15.66 % Al₂O₃, 1.53 %, 0.99 %, 2.49 % Fe₂O₃, 4.06 %, 6.25 %, 3.66 % K₂O and the minor elements read values of 524.4 ppm, 758.8 ppm, 446.3 ppm Ba, 366 ppm, 399.3 ppm, 257.3 ppm Rb, 88 ppm, 67.3 ppm, 47.3 ppm Sr, 308 ppm, 288.8 ppm, 327 ppm Zr for the Charu, Sagor, and Permian formations respectively. The major oxides reflect the dominant mineralogical composition of quartz and other silicate minerals (e.g., illite, kaolinite, smectite) and carbonate deficiency. The high Rb/K ratio suggests a brackish, marine environment or rapid depositions that prevent equilibrium between Rb and K in these studied shales. The elevated Rb/Sr ratios observed in the Charu, Sagor, and Permian formations at 4.16, 5.89, and 5.44, respectively, may be linked to the diminished Sr contents resulting from a prevailing reducing environment during the deposition of these sediments.

Keywords: Brackish environment · Carbonaceous sediments · Geochemical proxies, Malaysia · Palaeozoic · XRF.

1 INTRODUCTION

The sediments of the Panching area, Pahang, consist of Charu, Panching Limestone and Sagor Formation. These three formations comprise the Kuantan group (Metcalf *et al.*, 1980). The samples of the Charu Formation were collected from outcrop (located 28 km from Kuantan town), while the Samples of the Sagor Formation were collected from Bukit Pak Sagor. The Samples of Permian sediments were collected from Jengka Pass (Figure 1).

The Kuantan Group within the Eastern Belt

of Peninsula Malaysia is dominated by Carboniferous, Permian clastic, and carbonate. The stratigraphic sequence of Pahang contains several rock units. Fitch (1951) named them the Arenaceous and Calcareous series. Alexander (1959) replaced the term Calcareous series with 'Kuantan Group'. Metcalf *et al.* (1980) formalized and retained the term Kuntan Group to Charu Formation, Panching Limestone and Sagor Formation.

The present overall structural trend of the country is believed to have been imprinted by

*Corresponding author: A.M. BURGAN, Department of Petroleum Engineering, Faculty of Engi-

neering, Bani Walied University, Libya. E-mail: ameribrahim565@gmail.com

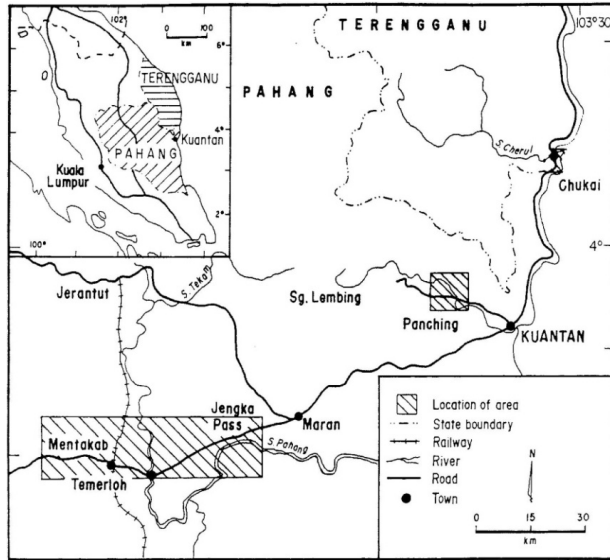


FIGURE 1. Map of West Malaysia showing the Location of study areas in Pahang.

the late Triassic Orogeny (Fateh, 1993). One of the major concepts concerning the geochemistry of trace elements, as demonstrated by Goldschmidt (1954), is that there is a tendency for elements to follow major elements that are similar to them in radius and bond type. Generally, it is well established that certain minor elements can substitute quantitatively for one or more major rock-forming elements in preference to others, e.g., thallium in potassic minerals. Strontium is known to follow this rule and is usually found in calcium-rich minerals (Turekian and Kulp, 1956). Strontium can replace K and Ca and is admitted to Ca minerals or captured by K minerals (Mason, 1966).

This study aims to discuss how to use the distribution abundance of major and minor elements within the carbonaceous sediments to investigate the dominant mineralogical composition, the weathering history of the source rocks, and the depositional environment for the studied sediments.

2 METHODOLOGY

The inorganic geochemical characteristics discussed here are based on a total of twelve samples comprising carbonaceous shale and mudstone beds, which are commonly carbonaceous and of late Paleozoic age, were collected from two different localities (Central and Panching) in the central belt of the Malay Peninsula, along

road cuts to Kuantan districts (State of Pahang). The central Pahang area covered exposures along Mentakab – Temerloh and Jengka Pass Road, whereas the Panching area covered rock exposures between the West of Kuantan town and east Sungai Lembing.

All the selected samples were crushed to rock powder by a crushing machine to reduce the grain size by vibrating a steel disk mill (Herzog, type: Hsm 100A). The major element compositions (Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K, and P) were determined by X-ray fluorescence (XRF) spectrometry at the Geology Department, University Kebangsaan Malaysia. One gram of carbonaceous sample was dried at 110°C for 4 hours and then powdered with lithium tetraborate ($\text{Li}_2\text{B}_4\text{O}_7$) flux of 5 grams.

The powdered samples were placed in a platinum crucible and then heated in an induction furnace at 1100°C for one hour. During heating, the molten specimens were stirred to remove bubbles and to get homogeneous glass beads used for XRF analysis. Loss on ignition (LOI) was measured on every rock sample provided for XRF analysis. The trace elements (Ba, Cr, Ga, Rb, Sr, and Zr) were determined by inductively coupled plasma (ICP) spectrometry PERKIN ELMER OPTIMA 43000 DV with standard curved based on international rock standards at the Chemistry Department, University Kebangsaan Malaysia.

3 RESULTS AND DISCUSSION

3.1 Major elements

Major and trace elements of the analyzed samples are given in (Table 1). The calculated average values for the various formations are given in Table 2). Generally, the data shows high concentrations of SiO_2 , Al_2O_3 , K_2O , and Fe_2O_3 and low values of CaO and MgO content. This composition mainly reflects the presence of quartz and other silicate minerals (e.g., kaolinite, smectite, chlorite, illite) and carbonate deficiency (calcite and dolomite minerals).

3.1.1 SiO_2 and Al_2O_3 Contents

Silica is the dominant constituent of all clays and shales. It is present as part of the clay minerals complex, as unrecompensed detritus silicates, and as free silica in the form of detrital quartz and biochemically precipitated sil-

TABLE 1. Major, minor, and trace chemical analysis of the black shales in the studied areas, major elements in wt.%, and minor elements in ppm (10^6).

Oxides	Charu Fm.					Sagor Fm.				Permian Fm.		
	Ch1	Ch2	Ch3	Ch4	Ch5	Sa1	Sa2	Sa3	Sa4	Per1	Per2	Per3
SiO ₂	68.39	62.25	69.02	56.89	72.61	62.49	67.58	62.72	66.48	69.97	68.55	74.60
TiO ₂	0.77	0.72	0.75	0.76	0.72	0.89	0.83	0.89	0.86	0.64	0.71	0.60
Al ₂ O ₃	18.35	17.69	18.16	19.90	17.26	23.28	20.79	23.90	22.03	15.34	18.83	12.82
Fe ₂ O ₃	1.02	3.38	1.19	1.56	0.50	0.78	0.76	1.01	1.06	5.00	1.99	0.48
MnO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.01	0.00
MgO	0.65	0.55	0.56	0.55	0.16	0.84	0.63	0.66	0.66	0.15	0.33	0.24
CaO	0.03	0.03	0.03	0.02	0.03	0.03	0.03	0.03	0.03	0.05	0.40	0.99
Na ₂ O	0.19	0.18	0.31	0.21	0.20	0.28	0.14	0.23	0.33	0.24	0.21	0.14
K ₂ O	4.33	4.15	3.75	4.71	3.34	6.72	6.04	6.34	5.88	2.87	4.71	3.39
P ₂ O ₅	0.05	0.05	0.03	0.04	0.03	0.01	0.01	0.02	0.02	0.08	0.02	0.02
LOI	6.35	10.89	5.25	15.28	4.73	4.17	3.23	4.29	3.42	4.98	4.61	6.62
Total	100.13	99.89	99.05	99.09	99.58	99.4	100.04	100	100.73	99.35	100	99.44
Ba	540	470	468	622	522	842	718	786	689	396	517	426
Cr	25	28	30	26	26	14	18	23	25	55	28	18
Ga	32	24	30	25	28	31	34	34	29	20	29	25
Rb	380	334	320	447	349	454	415	362	366	155	334	283
Sr	80	67	97	78	109	74	64	26	96	33	49	60
Zr	302	370	283	196	389	267	271	308	309	278	285	418

TABLE 2. Chemical composition (on average) of major elements in wt.% and minor elements in ppm.

Oxides	Charu Fm. n=5	Sagor Fm. n=4	Permian Fm. n=3
SiO ₂	65.83	64.82	71.40
TiO ₂	0.72	0.86	0.67
Al ₂ O ₃	18.27	22.5	15.66
Fe ₂ O ₃	1.53	0.90	2.49
MnO	0.00	0.00	0.01
MgO	0.49	0.70	0.24
CaO	0.03	0.03	0.36
Na ₂ O	0.22	0.25	0.20
K ₂ O	4.06	6.25	3.66
P ₂ O ₅	0.4	0.02	0.03
LOI	8.5	3.78	5.25
Ba	524.4	758.8	446.3
Cr	27	20	33.7
Ga	29.8	32	24.7
Rb	366	399.3	257.3
Sr	88	67.3	47.3
Zr	308	288.8	327

ica (opal or radiolarians diatoms and spicules) (Pettijohn, 1957).

The results obtained by XRF showed that the silica contents in the Permian samples are slightly higher than that in the Charu and Sagor samples. The presence of SiO₂ content in these analyzed samples could be related to the de-

trital material input being rich in silica materials derived from some periodic volcanic activity during the deposition of these sediments (Sidibe, 1993). The grain size of all samples is silty mudstone, which contains abundant silt-size quartz grains. Hence, they are rich in silica.

Al₂O₃ distinctly varies in all samples; however, they are specifically lower than the carbonaceous sediments of Permian samples compared to others. The source of alumina contents in the study samples is believed to be related to the abundance of clay minerals and feldspars in the shales and mudstones of these rock units. This trend could also be related to the alumina-rich detrital materials.

3.1.2 Fe₂O₃ Total Iron Content

Highly distinctive variation is observed for the Fe₂O₃ content among the analyzed samples Table 2. However, the iron concentration in the Sagor samples appears to be relatively lower than those in the Permian and Charu shales. The highest value of the Fe₂O₃ in the Permian Formation shales is 2.49 wt.%, which can be attributed to Fe-rich chlorite, biotite, and Fe-hydroxide formation in sufficiently high quantities. The high concentration of Fe₂O₃ indicates oxidation, hydration, and leaching pro-

cesses during weathering (Mikkil and Henderson, 1983).

Generally, the relatively higher iron content in the Permian, Charu, and Sagor samples could be related to the presence of hematite, pyrite, and other iron oxide minerals occurring together with minor amounts of carbonaceous organic matter. Hematite and magnetite are abundant in the black shales of Sg. Charu area and hematite are present in the shales of Sagor Formation (Sidibe, 1993).

Laminated shales are richer in Fe_2O_3 concentration than mudstones because of interlaminar ferrous-rich clay (e.g., chlorite) and are more reduced than mudstone, as Mason and Moor (1982) suggested. Such a case could explain the Permian, Charu, and Sagor shales and mudstones. The chemical trend could also be due to the Eh-pH controls on the minerals and weathering.

3.1.3 CaO and MgO Contents

The CaO content in the analyzed samples is generally low and observed only in trace amounts. Exceptions are with the Permian samples, which showed relatively higher CaO. In general, Ca content is due to calcite (CaCO_3) cement and calcareous organic fragments associated with sediments. CaO in the study samples here is perhaps related to calcite cement or skeletal fragments in the fossiliferous shales and mudstones. Generally, the results obtained by XRF showed that the Mg content in the Sagor and Charo samples appears to be relatively higher than that of the Permian samples. The relatively high content of Mg in the Charu and Sagor samples could be related to the abundance of volcanic materials due to volcanic activity during the deposition of these formations and the presence of dolomite fragments in the form of detrital sediments. On the other hand, the low MgO content in the Charo and Permian samples is possibly related to the lesser content of Mg in the source materials.

3.1.4 Na_2O , K_2O and TiO_2 Contents

No distinctive variation is observed for the Na_2O content among the analyzed samples [Table 2](#). However, Samples of the Charu, Sagor, and Permian formations show Na_2O content within an average value of 0.22 %, 0.25 % and

0.20 %, respectively. Wedepohl (1970) suggested that major parts of the Na in argillaceous rocks occur in detrital phases such as clay minerals and feldspars. Some sodium occurs as adsorbed elements on mineral phase and iron exchange sites in clay minerals or as dissolved Na^+ in interstitial fluid.

The source of Na ions in the analyzed samples could be related to the Na-feldspar or clay mineral present in the carbonaceous sediments of these formations. Na_2O content could also be related to the influence of prevailing fluids from granitoid intrusion into sedimentary rocks of those areas, as suggested by workers such as Sidibe (1993).

K_2O content in the sedimentary rocks is a function of their K-feldspar, K-mica, and glauconitic minerals. The results obtained by XRF showed that the K_2O contents in the Charu, Sagor, and Permian are sufficiently high to suggest that illite is probably the main clay mineral available in these shales. The high K contents are almost certainly due to the original presence of illite in large quantities (McLennan *et al.*, 1983). The high K_2O content indicates that these sediments did not leach strongly during erosion (Campbell & Williams, 1965).

The distribution of TiO_2 in the study samples shows that the concentration of the elements in the Permian shales is less than that of the Sagor and Charu samples. However, the three study formations have an average TiO_2 content value of 0.67 %, 0.86 %, and 0.72 %, respectively. TiO_2 in the carbonaceous samples in this study is probably related to some ilmenite or rutile-bearing materials from volcanic sources and clay minerals present in the carbonaceous sediments of these formations. Weaver and Pollard (1973) suggest TiO_2 may be a minor constituent in the octahedral site in illite and kaolinite.

3.1.5 Loss on Ignition (LOI)

The elements present in the ignition content loss comprise volatile elements, including H_2O and CO_2 . The loss on ignition (LOI) data ([Table 2](#)) shows a distinct variation in the abundance of organic matter in the shales.

The Charu samples possess the highest (LOI) compared to the Sagor and Permian samples. Among the samples studied, the values of the

(LOI) of the Charu samples had an average value of 8.5 %. The Sagor and Permian shales recorded an average of 3.78 % and 5.25 %, respectively. The decrease in (LOI) values of the Sagor shales could be related to the unit having less organic matter than the Charu and Permian samples.

3.2 Minor Constituents

3.2.1 Barium (Ba) and Chromium (Cr) Content

The Ba content in the Panching area increases from the Charuto Sagor Formation; the average values recorded for both formations are 524.4 ppm and 758.8 ppm, respectively. Since shallow marine conditions prevailed in the Panching area during the deposition of the Charu and Sagor formations (Metcalf *et al.*, 1980), it can be inferred that the increase in barium content in the Charu Formation may be due to a change in the depositional system (Sidibe, 1993). In the Permian samples, the Ba content has an average value of 446.3 ppm. The Ba content is known to be captured by potassium-bearing minerals; since the carbonaceous shales and mudstones of the Sagor and Charu are richer in K₂O than that of the Permian shales, it can also be inferred that the barium content is related to the abundance of K-bearing minerals. Barium is too large to replace Ca or Na; potassium is the only major element of comparable ionic size (Mason, 1966).

According to Li Shengrong and Zhenmin (1996), Ba minerals, such as barite, are easier to dissolve in water under the action of the electrolytes KCl and MgCl₂. For this, the Ba element may be transformed from the continent to the ocean in the cyclic processes of epigenetic water. Ba can be easily absorbed on offshore hydrolytic sediments; therefore, Ba's content is low in seawater, especially in pelagic water. This caused the Ba element to prefer hot-brine sediments over normal ones (Li Shengrong and Zhenmin, 1996).

The chromium content in this study shows that the average values in the Charu, Sagor, and Permian samples are 27 ppm, 20 ppm, and 33.7 ppm, respectively. This trend suggests that these rock units contain nearly similar source materials. The shale's relatively high Cr contents are expected, owing to the substitution of Cr for Mg in chlorite and its adsorption on il-

lite (Kelepertsis and Kontis, 1997). They further suggest that some of the Cr amounts in the shales are contributed by organic material, which could be the case in the studied samples.

3.2.2 Gallium (Ga) and Rubidium (Rb) Content

It is well established that the Ga element is usually camouflaged in aluminium-bearing minerals and enriched in pegmatite feldspars and micas. The chemical analysis of the studied samples in the Panching area shows that the Ga content slightly increased from the Charu to Sagor Formation. The average values are 29.8 ppm and 32 ppm, respectively. The Ga content of these rocks positively correlates with Al₂O₃ content. In the central Pahang, the Ga average value in the Permian samples is 24.7 ppm. This trend could be related to the rock units in this area having relatively the same source materials as in the Panching area.

Rubidium is found camouflaged in the aluminous materials. Its average values in the Panching area are higher than in the central Pahang area. However, the Rb content is relatively high in the Charu and Sagor samples, with an average value of 368 ppm and 399.3 ppm, respectively. In the central Pahang area, the XRF analysis showed that the Rb content in the Permian samples is 156.5 ppm.

The Charu, Sagor, and Permian carbonaceous sediments displayed high Al₂O₃ content, so the Rb trend is perhaps related to the aluminous minerals present in these carbonaceous samples since the Rb element was found camouflaged in the aluminous materials.

3.2.3 Strontium (Sr) and Zirconium (Zr) Content

The geochemical analysis shows that the Sr content of the studied samples is moderately high in the Charu and Sagor samples and relatively low in the Permian samples. The average values are 88 ppm in the Charu samples and 67.3 ppm in the Sagor sample. The average Sr content in the Permian is 47.3 ppm. These values are considerably lower than those given by Show (1954), who reported a value of 700 ppm, and those given by Turekian and Kulp (1956), who reported a value of 300 ppm. On the other hand, Hevesy and Wüerstlin (1934) reported a value of 20 ppm for shales and phyllites, which is too low. Sr can replace Ca or K, admitted to

Ca minerals or captured by K minerals (Mason, 1966).

Generally, the Sr element is higher in the basalts and gabbro than in granite rocks. The detected values of Sr content in the Charo and Sagor samples could be related to the presence of mafic and ultra-mafic rock fragments in the carbonaceous sediments occurring as detrital minerals.

XRF results showed that the Zr element is high in the Charu and the Sagor samples. The Charu samples recorded an average concentration of 308 ppm, and the Sagor samples recorded 288.8 ppm. In the central Pahang, the Permian samples recorded an average Zr content of 372 ppm. The high Zr content in these rock units could be related to the abundance of felsic rock fragments that are probably rich in Zircon and that occur as detrital heavy minerals or to the detrital Zircon present in the carbonaceous sediments within the study areas.

4 SOURCE MATERIALS AND DEPOSITIONAL ENVIRONMENTS

Geochemical distribution has been used in constructing ancient sedimentary environments, as demonstrated by many workers, such as Mason and Moore (1982). The silica content SiO_2 in the studied samples seems to be decreasing with increasing Al_2O_3 for the Charo and Sagor formations and increasing with decreasing Al_2O_3 for the Permian Formation. As large amounts of quartz mineral are found in the residual material, it is reasonable to assume that the desilicification occurred mainly due to the destruction of aluminosilicates. Table 2 shows that the SiO_2 , TiO_2 , Al_2O_3 , Fe_2O_3 , MgO , and K_2O oxides give rise to similar trends. Except for samples from the Permian Formation, the trends are different. The trends in CaO , Na_2O , and MnO are different. The results illustrate a similar element composition for the Charu and Sagor samples, reflecting the homogeneity of the sediment suite.

The enrichment of MgO in the studied carbonaceous sediments is related to the decrease of CaO due to the weathering effect on parent materials. The high MgO content is often correlated with low-temperature oxidative diagenesis. Andrews (1980) suggested that a drop in CaO accompanies the increase of MgO contents in the rock.

The decrease of CaO and MnO with increasing Na_2O , MgO , and K_2O shows variation in chemical composition, which also reflects changes in the mineralogical composition of the sediments due to weathering effects and early diagenetic processes that take place in these sediments (Shaw and Weaver, 1965; Dreyer, 1971; Nesbitt and Young, 1984, 1989).

Compared with the Charu, Permian, and Sagor shales, the samples from the Sagor Formation contain high SiO_2 and less MgO and K_2O contents. The Sagor Formation shales have an average, higher Al_2O_3 , and lower CaO than shales of the other formations. The Permian Formation samples show a marked enrichment of SiO_2 and Fe_2O_3 , which suggests a changing environment of deposition or changes in the source materials. The abundance of Si, Ti, Al, and K in shales may be perturbed from parent materials by weathering, transport, and depositional processes; the decrease in calcium contents of these shales can be attributed to the terrigenous influx, the low abundances of fossils and shell fragments, which could contribute a major amount of calcium to them (Nesbitt and Markovics, 1996).

The average values from this study show differences and similarities when compared with the average values of shales and glacial clays from other places (Table 4). SiO_2 content of the shales of this study is higher than the other averages presented, except for the average data presented by Campbell and Williams (1965), which exhibit slightly higher SiO_2 content when compared with other averages.

The high SiO_2 content in these shales suggests that SiO_2 is mainly associated with silicate minerals (clay minerals). The shales have a low average CaO and MgO compared with the other average data presented and show higher K_2O , except for those presented by Campbell and Williams (1965), which show higher values.

A plot of Al_2O_3 vs. K_2O and TiO_2 (Figure 2) illustrates a strong positive correlation. In contrast, in the case of Al_2O_3 vs. MgO , the plot shows a weak correlation coefficient indicating that these elements are of detrital origin, which occurs as in the detrital clay minerals (illite or smectite).

The positive correlation of Al_2O_3 vs. MgO and TiO_2 indicates that the elements Mg and

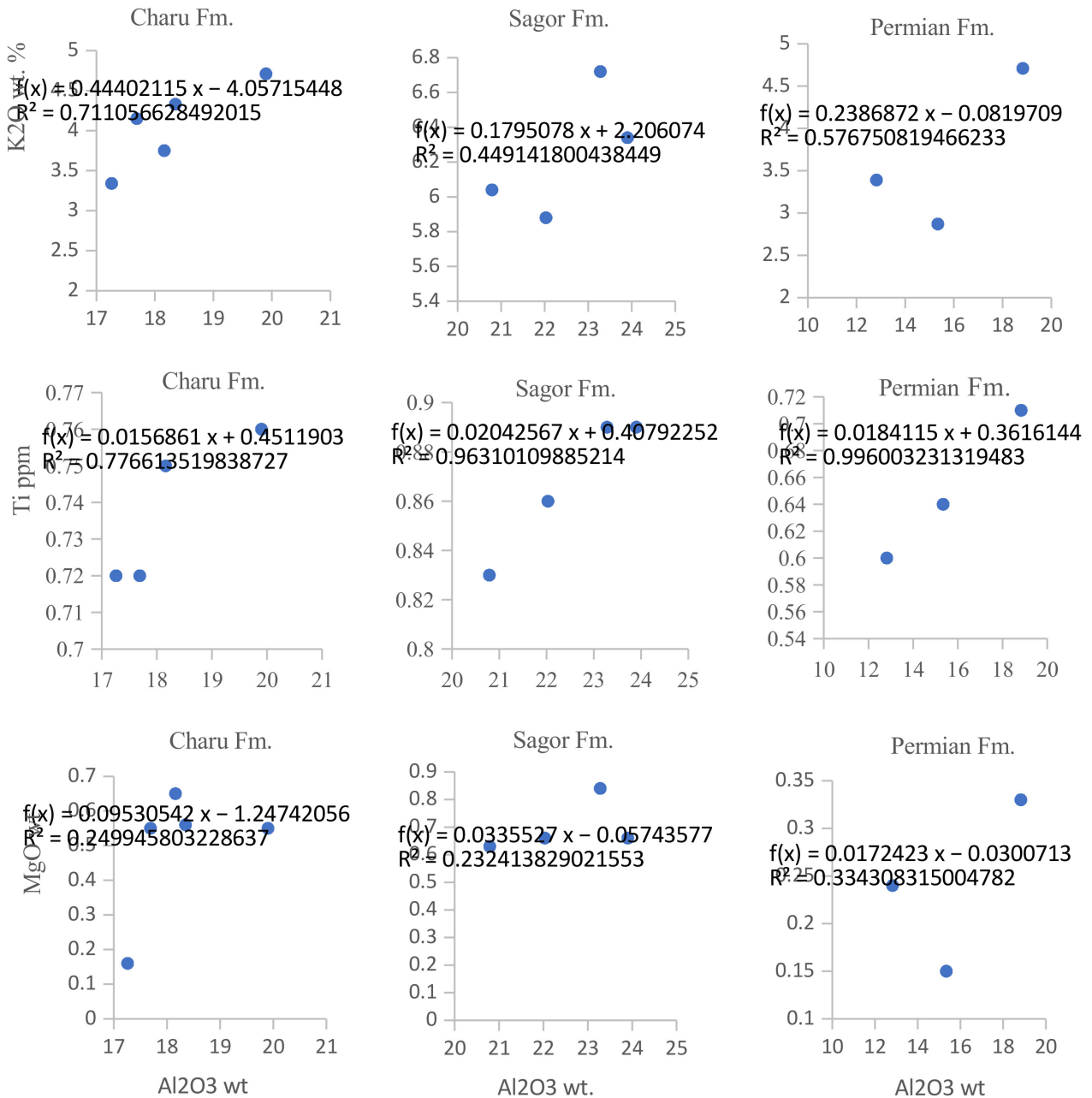


FIGURE 2. Bivariate plots of the samples from Charu, Sagor, and Permian Formations: (a) Al₂O₃ vs. K₂O, (b) Al₂O₃ vs. TiO₂ and MgO, and (c) Al₂O₃ vs. MgO. Al₂O₃ shows a strong positive correlation with K₂O & TiO₂ but is a slightly weaker positive correlation with MgO.

Ti are originally associated with aluminosilicate phases, assuming a minor of Mg with carbonates (Dolomite) during diagenesis (Bellanca *et al.*, 1999). It is also indicated that the effect of weathering conditions was a very important factor in the provenance area, where K and Mg are fixed in clay minerals, and Ca is preferentially leached (Nesbitt *et al.*, 1980). A plot of Al_2O_2 vs. SiO_2/Al_2O_2 ratio (Figure 3) shows a strong negative correlation and varies when plotting against the Fe_2O_3/Al_2O_3 , Na_2O/Al_2O_3 and K_2O/Al_2O_3 . These results reflect the presence of clay minerals in these sediments.

The values of the Sr/Ca and Rb/K ratios in this study show some similarities and differences between the Sr/CA and Rb/K values. However, the Charu Sagor and Permian samples exhibit Sr/Ca values ranging from 0.001 to 0.009 and Rb/K values varying from 0.006 to 0.009. The Sr/Ca ratio shows an increase with decreasing Ca.

Each sample's Sr and Rb contents were determined and correlated with Ca and K, respectively. The results are given in (Table 3) and the composition of the average value for each formation with other published results is described in Table 4. The average Sr/Ca ratios in the Charu and Sagor formations tend to have higher values than those in the Permian samples (Table 4). The average Sr/Ca ratios are 0.29 and 0.27, respectively, whereas the Sr/Ca ratio is 0.01 in the Permian samples. The Sr content is correlated with Ca, and none of these formations shows a strong correlation coefficient. However, the plots of Sr vs. Ca (Figure 4) show a weak correlation coefficient among the black shale samples, suggesting that in these sediments, the Sr contents are not associated with gypsum ($CaSO_4 \cdot 2H_2O$) or celestite ($SrSO_4$) and the deficiency of CaO in the shales prevent substitution of Sr for Ca in Ca-rich minerals. The Sr element increases as the Ca content increases in granite and granodiorite rocks Turekian and Kulp (1956).

The Rb/K ratio shows more marked differences than the Sr/Ca ratio. The average Rb/K ratios are 0.009, 0.006, and 0.007 for the Charu, Sagor, and Permian formations. They suggested that these rock units' shales were deposited in a normal environment. The Rb/K ratios vary from about 0.004 for shales formed

in brackish water environments to 0.006 for normal marine shales (Campbell and Williams, 1965).

The high Rb/K ratios suggest a marine environment (Campbell and Lerbekmo, 1963). The high Rb/K ratio in this study suggests either a brackish sequence or rapid deposition that prevented equilibrium between Rb and K in the shale and marine water. The Charu Formation shales show an increase in Sr/Ca and Rb/K ratios largely due to an increase in Sr and a decrease in K.

The Permian Formation shales show some trends that are not very significant. The average Sr/Ca ratio is 0.01, and the average Rb/K ratio is 0.007. These values are not too different from those in the other shales of the other formations. However, there is a strong suggestion that the shales in this formation are chemically different from the other shales and can be used to differentiate them from those of the other formations. The high Rb/Sr ratios of 4.16, 5.89, and 5.44 for the shales from Charu, Sagor, and Permian formations are attributed to the lowest contents of Sr due to reducing conditions. The Rb/Sr ratio values are considerably higher than the other ratios in Table 3. Variations in Sr/Ca and Rb/K ratios among the study units can be interpreted as the result of fluctuation between normal marine and brackish conditions.

5 CONCLUSION

This research investigates the geochemical characteristics of the carbonaceous sediments of the Upper Paleozoic Kuantan Group, Malaysia, using ICP and XRF techniques. The obtained and discussed results show that the Charu, Sagor, and Permian formations' shales have high SiO_2 , Al_2O_3 , Fe_2O_3 , and K_2O concentrations and low CaO and MgO contents. This finding may reflect the presence of quartz and other silicate minerals and lack of carbonates. The K_2O contents are sufficiently high in all the shales, suggesting that illite is probably the main clay mineral in these carbonaceous sedimentary units.

Highly distinctive variation is observed for the Fe_2O_3 content among the analyzed samples; the iron concentration in the Sagor samples appears to be relatively lower than those in the Permian and Charu shales. The highest value of the Fe_2O_3 in the Permian Formation shales

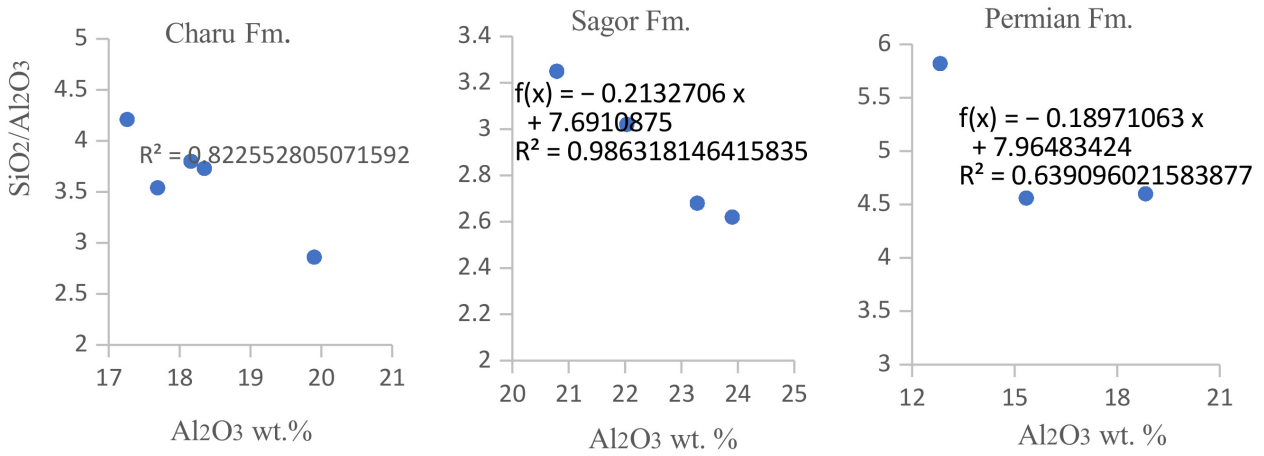


FIGURE 3. Crossplots of the samples from Charu, Sagor, and Permian Formations: Al_2O_3 vs. SiO_2/Al_2O_3 shows a strong negative correlation for the Charu and Sagor samples but is in slightly weaker negative correlation for the Permian samples.

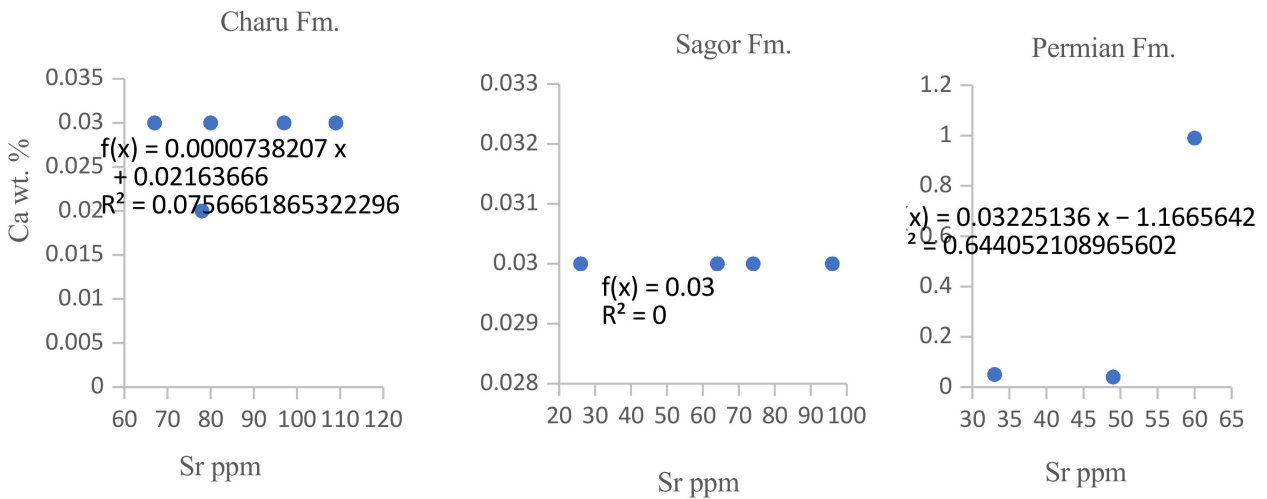


FIGURE 4. Cross plots of the samples from Charu, Sagor, and Permian Formations: Sr vs. Ca. None displays a correlation coefficient.

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TABLE 3. Comparison of the composition of the major and minor elements in this study with those of average shales by previous workers.

Oxides	Charu Fm. ¹	Sagor Fm. ¹	Permian Fm. ¹	Av. Shale ²	Av. Shale ³	Av. Shale ⁴	Glacial Shale ⁵
SiO ₂	65.83	64.82	71.4	58.1	64.83	58.5	59.12
MgO	0.49	0.7	0.24	2.44	2.66	2.5	3.3
Al ₂ O ₃	18.27	22.5	15.66	15.44	15.72	15	15.82
K ₂ O	4.06	6.25	3.66	3.24	2.5	3.2	3.93
CaO	0.03	0.03	0.36	3.11	2.42	3.1	3.07
Fe ₂ O ₃	1.53	0.9	2.49	6.47	5.08	4.72	6.99
Rb	366	399.3	257.3	126	97	140	153
Sr	88	67.8	47.3	270	210	300	267
Rb/Sr	4.16	5.89	5.44	0.47	0.46	0.47	0.57

Note: major elements in wt.%, minor elements in ppm. 1. (average of 12 samples: 5 Charu Fm., 4 Sagor Fm., 3 Permian Fm. in the current study); 2. Clark, 1924, p. 34 (average of 72 samples: 51 Paleozoic, 21 Mesozoic and Cenozoic); 3. Campbell and Williams, 1965 (average of 113 samples); 4. Turkian and Wedepohl, 1961; 5. Goldschmidt, from Mason (1966), p.43.

TABLE 4. Major, minor constituents, and significant ratios.

Formation	Av. Sr ppm	Av. Ca %	Sr/Ca ratio	Av. Rb ppm	Av. K %	Rb/K ratio
Charu	88	0.03	0.29	366	4.06	0.009
Sagor	67.8	0.03	0.27	399.3	6.25	0.006
Permian	47.3	0.36	0.01	257.3	3.66	0.007

can be attributed to the presence of Fe-rich chlorite and/or related to Fe-hydroxide formation. Shales from the Permian Formation display an increase in Fe₂O₃ contents and a decrease in SiO₂, which suggests a change in the environment of deposition or a change in source materials.

The high Rb/Sr ratios for the shales of the Charu, Sagor, and Permian formations are attributed to the low Sr content as a response to reducing environmental conditions. The high Rb/K ratios indicate either brackish marine or rapid deposition that prevented equilibrium between K and Rb in shale and marine waters.

Sr/Ca and Rb/K ratio variations can be interpreted as fluctuations between normal marine and brackish conditions. The plot of Al₂O₃ vs. K₂O and TiO₂ illustrates a strong positive correlation. In contrast, in the case of Al₂O₃ vs. MgO, the plot shows a weak correlation coefficient, indicating that these elements are of detrital origin, which occurs as in the detrital clay minerals.

The plot of the Al₂O₃ vs. SiO₂/Al₂O₃ ratio shows a strong negative correlation and varies to some extent when plotting against the Fe₂O₃/Al₂O₃, Na₂O/Al₂O₃ and K₂O/Al₂O₃.

These results probably reflect the presence of clay minerals in these sediments.

The plots of Sr vs. Ca show a weak correlation coefficient among the black shale samples, suggesting that in these sediments, the Sr contents are not associated with gypsum (CaSO₄·2H₂O) or celestite (SrSO₄) and the deficiency of CaO in the shales prevent extensive substitution of Sr for Ca in Ca-rich minerals.

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