

## Research Article



## Geochemical Characteristic 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*

*Correspondence: [ameribrahim565@gmail.com](mailto:ameribrahim565@gmail.com)*

Received: 13 October 2023 / Accepted: 23 May 2024 / Published: 25 May 2024

**Abstract:** The geochemical parameters discussed in this paper are based on the analysis of twelve outcrop carbonaceous samples, mainly black shales, using X-Ray Fluorescence (XRF) and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) techniques. These samples are representative of the Charu, Sagor, and Permian formations. The aim of this study is to define and discuss their characteristics, the distribution abundance of major and minor elements, investigate the dominant mineralogical composition, and reconstruct the depositional environment for these sediments. The bulk chemical results showed that the average values of the major elements are 65.83%, 64.82%, and 71.4% SiO<sub>2</sub>; 18.27%, 22.2%, and 15.66% Al<sub>2</sub>O<sub>3</sub>; 1.53%, 0.99%, and 2.49% Fe<sub>2</sub>O<sub>3</sub>; and 4.06%, 6.25%, and 3.66% K<sub>2</sub>O for the Charu, Sagor, and Permian formations, respectively. The minor elements recorded values of 524.4 ppm, 758.8 ppm, and 446.3 ppm Ba; 366 ppm, 399.3 ppm, and 257.3 ppm Rb; 88 ppm, 67.3 ppm, and 47.3 ppm Sr; and 308 ppm, 288.8 ppm, and 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 a deficiency in carbonates. The high Rb/K ratio suggests a brackish marine environment or rapid deposition that prevented equilibrium between Rb and K in these shales. The high Rb/Sr ratios of 4.16, 5.89, and 5.44 for the Charu, Sagor, and Permian formations, respectively, are possibly attributed to the low Sr content due to reducing conditions prevailing during the deposition of these sediments.

**Keywords:** Geochemical Analysis, Carbonaceous Sediments, Upper Paleozoic, Kuantan Group Malaysia, Depositional Environments

### INTRODUCTION

The Kuantan Group in Malaysia's central belt, characterized by its late Paleozoic carbonaceous sediments, emerges as a focal point for geochemical exploration due to its unique geological attributes and complex depositional environments. This research embarks on an in-depth geochemical analysis of shale and mudstone beds within this group, aiming to unveil the region's paleoenvironmental dynamics. Despite its geological significance, previous studies have predominantly concentrated on macroscopic evaluations with scant attention to detailed chemical compositions. Our study intends to bridge this gap by leveraging advanced analytical techniques, such as XRF (X-ray fluorescence) and ICP-MS (Inductively Coupled Plasma Mass Spectrometry), to furnish a comprehensive elemental analysis. This endeavor not only seeks to enrich our understanding of the mineralogical makeup and weathering history of the source rocks but also aspires to reconstruct the depositional environment of these sediments. The Kuantan Group's geochemical characteristics, particularly the distribution and abundance of major and minor elements, remain underexplored, presenting a significant knowledge gap. This study is poised to address this void, contributing to a more nuanced comprehension of the geochemical processes during the Upper Paleozoic era and its implications for the region's geological and environmental narrative. Through this analytical prism, we aim to enhance existing geological models, potentially unlocking new avenues for mineral exploration and offering insights into past climatic conditions that hold relevance for contemporary environmental assessments and conservation efforts.

This study is predicated on the observation that the geochemical profile of the Kuantan Group's carbonaceous sediments is not comprehensively understood, particularly in the context of trace elements' distribution and implications for environmental reconstructions. Such lacunae in knowledge significantly impede our capacity to infer the geological history and the environmental conditions prevalent during the sediment deposition era. The overarching research problem is the inadequacy of geochemical data,

which hampers a holistic understanding of the Kuantan Group's sedimentary processes and mineralogical constitution.

To address this challenge, our research proposes a twofold solution. Firstly, we aim to conduct an exhaustive elemental analysis using state-of-the-art geochemical analysis techniques, including XRF and ICP-MS. These methods are anticipated to provide a detailed quantification of both major and minor elements, thus filling the existing gaps in geochemical data. Secondly, by integrating these analytical results with geological and mineralogical data, we aspire to reconstruct the depositional environments of the Kuantan Group. This approach will not only elucidate the mineralogical constituents and the geochemical evolution of these sediments but also shed light on the paleoenvironmental conditions during the Upper Paleozoic era.

Recent investigations into the geochemical characteristics of carbonaceous sediments have highlighted the significance of sedimentary geochemical proxies in interpreting paleoenvironmental conditions and providing insights into the depositional history and geochemical processes. For instance, [Zhao et al. \(2017\)](#) presented geochemical data for the Ordovician Wufeng Formation and Silurian Longmaxi Formation black shale deposition in the Sichuan Basin, China. Their study applied geochemical proxies to decipher paleoenvironmental conditions, such as detrital influx, redox conditions, and paleoproductivity, significantly contributing to our understanding of organic carbon accumulation in siliceous shales under dysoxic/anoxic conditions.

[Varaksina et al. \(2017\)](#) conducted lithological and geochemical studies of Paleozoic deposits in the north of the Tunguska syncline, revealing sedimentation within an epicontinental basin and identifying potential oil reservoirs based on the poroperm properties of rocks. Their research into the geochemical study of organic matter showcased several possible sources of hydrocarbons, underlining the complex interactions between sedimentation, geochemistry, and hydrocarbon potential.

Furthermore, [Kovalchuk et al. \(2021\)](#) analyzed Upper Paleozoic carbonaceous shales and siltstones from the area of the Ust'-Kara astrobleme (PayKhoy), focusing on mineralogical and geochemical features altered by post-impact hydrothermal processes. Their findings on anomalous contents of various elements, including Ti, Mn, Cr, and rare earth elements, contribute to the broader understanding of the geochemical features of carbon deposits affected by external events.

These studies illustrate the advanced methodologies and diverse approaches used to interpret the geochemical signatures of carbonaceous sediments and their depositional environments. However, there remains a significant gap in the literature concerning the detailed geochemical characterization of the Kuantan Group in Malaysia. This region, with its unique geological setting and sediment composition, presents an opportunity to expand our knowledge of the Upper Paleozoic era's environmental conditions. Specifically, the absence of comprehensive studies focusing on the integration of geochemical proxies with detailed mineralogical analyses to reconstruct paleoenvironmental conditions in the Kuantan Group underscores a critical research need. Our study aims to address this gap by applying a multidisciplinary approach to elucidate the geochemical behavior, sedimentary processes, and environmental implications associated with the carbonaceous sediments of the Kuantan Group. By doing so, we hope to contribute valuable insights into the paleoenvironmental reconstructions of the Upper Paleozoic era in Southeast Asia.

The overarching aim of this study is to elucidate the geochemical characteristics and depositional environment of the carbonaceous sediments from the Upper Paleozoic Kuantan Group in Malaysia. This investigation is driven by a dual objective: to enhance our understanding of the geochemical processes that influenced these sediments and to reconstruct the paleoenvironmental conditions during their deposition. Specifically, our research endeavors to: (1) characterize the geochemical signatures: we aim to conduct a detailed analysis of major, minor, and trace elements, alongside isotopic studies, to identify the geochemical signatures present in the shale and mudstone beds of the Kuantan Group. This will involve comparing these signatures with those from other regions to understand the local versus global geochemical trends during the Upper Paleozoic era; (2) reconstruct paleoenvironmental conditions: by integrating geochemical data with sedimentological and mineralogical analyses, we intend to reconstruct the depositional environments of the Kuantan Group sediments. This will include assessments of redox conditions, detrital influx, and paleoproductivity, which are crucial for interpreting the climatic and environmental settings of the time; (3) identify the source of organic matter: utilizing organic geochemistry, including biomarker and isotopic analyses, we plan to delineate the sources of organic matter within the carbonaceous sediments. This will help in understanding the contributions of terrestrial versus marine inputs and the conditions that favored organic matter preservation; (4) explore the implications for paleogeography and tectonics: the study will also explore the implications of sediment

geochemistry for the paleogeography of the Malay Peninsula during the Upper Paleozoic, including the influence of tectonic settings on sedimentation patterns.

The novelty of our research lies in its comprehensive approach to studying the Kuantan Group, which has not been extensively explored from a geochemical perspective. By focusing on this group, we aim to fill a significant gap in the literature concerning the geochemical characterization of Upper Paleozoic carbonaceous sediments in Southeast Asia. This study will not only contribute to the global understanding of paleoenvironmental conditions during the late Paleozoic but also enhance our knowledge of the geological history of the Malay Peninsula.

The scope of this research is defined by its focus on the Kuantan Group within the central belt of the Malay Peninsula. Our study will encompass a range of analytical techniques to provide a holistic view of the geochemical, sedimentological, and paleoenvironmental aspects of these sediments. Through this focused approach, we aim to contribute valuable insights to the fields of sedimentary geochemistry, paleoenvironmental reconstruction, and the geological evolution of Southeast Asia.

## METHOD

### Selection of Study Area and Sampling Strategy

To ensure a comprehensive geochemical analysis of the Kuantan Group's Upper Paleozoic carbonaceous sediments, sampling sites were meticulously chosen based on geological significance, accessibility, and representation of diverse depositional environments. The selection process was informed by an extensive review of geological maps and literature to encompass areas rich in carbonaceous sedimentation, indicative of varied paleoenvironmental settings (Figure 1). This strategic approach guarantees that our samples accurately reflect the geochemical diversity and complexity of the Kuantan Group, capturing a broad spectrum of sedimentary processes and environmental conditions prevalent during the Upper Paleozoic era.

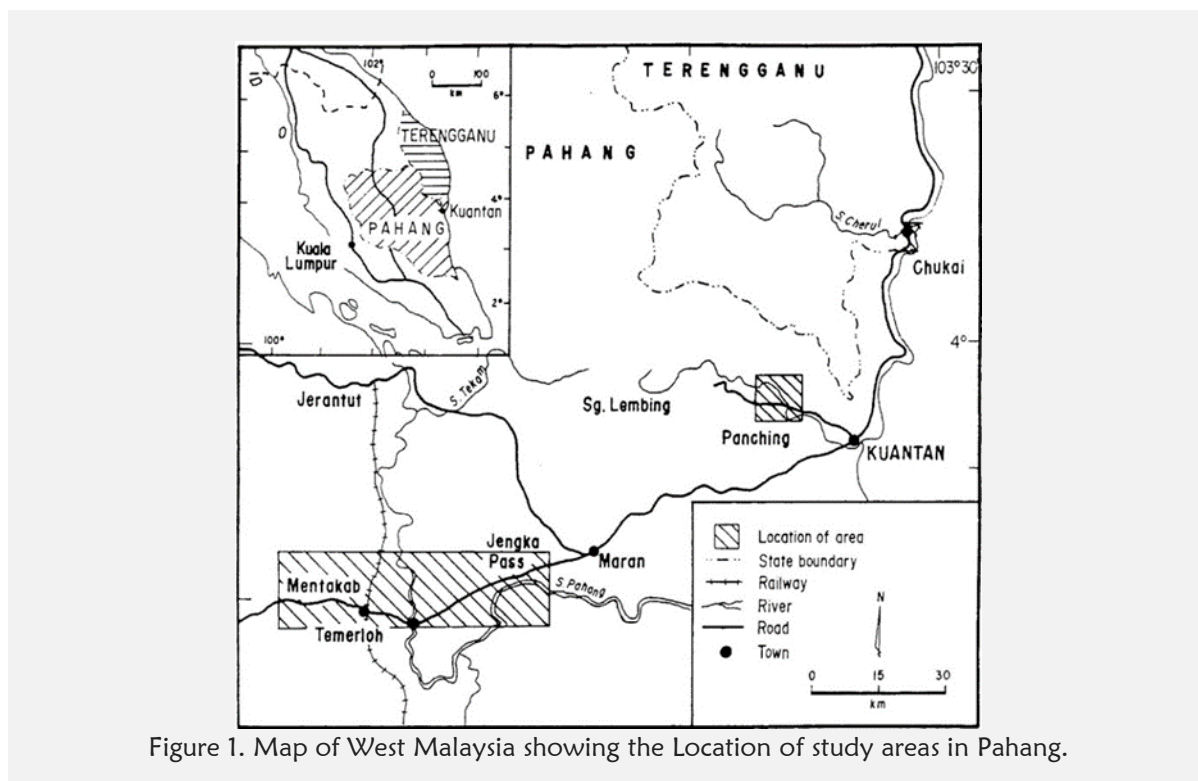


Figure 1. Map of West Malaysia showing the Location of study areas in Pahang.

### Experimental Design and Analytical Techniques

The geochemical characterization of the selected carbonaceous sediment samples was performed using X-ray Fluorescence (XRF) spectrometry and Inductively Coupled Plasma (ICP) spectrometry, leveraging the strengths of each method to achieve a detailed elemental analysis.

**XRF Spectrometry:** This technique was employed for the quantification of major elements (Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K, and P) due to its precision, non-destructive analysis, and capability to provide a comprehensive elemental composition of the sediments. Samples were prepared by crushing to a fine powder, followed by fusion with lithium tetraborate flux to form a homogenous glassy disk suitable for

analysis. The measurement of Loss on Ignition (LOI) was conducted for each sample to account for volatile substances.

*ICP Spectrometry:* Trace elements (Ba, Cr, Ga, Rb, Sr, and Zr) were analyzed using ICP spectrometry for its sensitivity and accuracy in detecting low-concentration elements. This technique complements XRF by providing detailed insights into the trace elemental composition critical for understanding geochemical processes. Standard Curves based on International Rock Standards were utilized to ensure accuracy and reliability of the measurements.

### Rationale for Analytical Choices

The integration of XRF and ICP spectrometry offers a robust framework for geochemical analysis, combining the comprehensive elemental coverage of XRF with the trace element sensitivity of ICP. This dual approach is pivotal for reconstructing the Kuantan Group's depositional environments and for identifying specific geochemical signatures that shed light on sedimentary processes and paleoenvironmental conditions. By addressing the limitations of each method through this combined approach, we optimize the geochemical profiling of the carbonaceous sediments, facilitating a nuanced understanding of the Kuantan Group's geological history and environmental dynamics during the Upper Paleozoic.

## RESULTS & DISCUSSION

### Major Elements

The results of the chemical analysis for the carbonaceous sediments in this study are given in [Table 1](#) and the average for the various formations are given in [Table 2](#). Generally, the established data show high concentrations of the SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>O and Fe<sub>2</sub>O<sub>3</sub> and low value of the CaO, and MgO content, reflects mainly the presence of quartz and other silicate minerals (e.g. kaolinite, smectite, chlorite, illite) and deficiency in carbonates (Calcite and dolomite minerals).

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<sup>6</sup>)

Oxides	Permian Fm.		Sagor Fm.				Charu Fm.					
	Per3	Per2	Per1	Sa4	Sa3	Sa2	Sa1	Ch5	Ch4	Ch3	Ch2	Ch1
SiO <sub>2</sub>	74.6	68.55	69.97	66.48	62.72	67.58	62.49	72.61	56.89	69.02	62.25	68.39
TiO <sub>2</sub>	0.6	0.71	0.64	0.86	0.89	0.83	0.89	0.72	0.76	0.75	0.72	0.77
Al <sub>2</sub> O <sub>3</sub>	12.82	18.83	15.34	22.03	23.9	20.79	23.28	17.26	19.9	18.16	17.69	18.35
Fe <sub>2</sub> O <sub>3</sub>	0.48	1.99	5	1.06	1.01	0.76	0.78	0.5	1.56	1.19	3.38	1.02
MnO	0	0.01	0.03	0	0	0	0	0	0	0	0	0
MgO	0.24	0.33	0.15	0.66	0.66	0.63	0.84	0.16	0.55	0.56	0.55	0.65
CaO	0.99	0.4	0.05	0.03	0.03	0.03	0.03	0.03	0.02	0.03	0.03	0.03
Na <sub>2</sub> O	0.14	0.21	0.24	0.33	0.23	0.14	0.28	0.2	0.21	0.31	0.18	0.19
K <sub>2</sub> O	3.39	4.71	2.87	5.88	6.34	6.04	6.72	3.34	4.71	3.75	4.15	4.33
P <sub>2</sub> O <sub>5</sub>	0.02	0.02	0.08	0.02	0.02	0.01	0.01	0.03	0.04	0.03	0.05	0.05
LOI*	6.616	4.61	4.98	3.42	4.29	3.23	4.17	4.73	15.28	5.25	10.89	6.35
Total	99.44	100	99.35	100.73	100	100.04	99.4	99.58	99.09	99.05	99.89	100.13
Ba	426	517	396	689	786	718	842	522	622	468	470	540
Cr	18	28	55	25	23	18	14	26	26	30	28	25
Ga	25	29	20	29	34	34	31	28	25	30	24	32
Rb	283	334	155	366	362	415	454	349	447	320	334	380
Sr	60	49	33	96	26	64	74	109	78	97	67	80
Zr	418	285	278	309	308	271	267	389	196	283	370	302

\*LOI: Loss on Ignition

### SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> 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 silica (Opal or radiolarians diatoms and spicules) (Pettijohn, 1957).

The results obtained by XRF showed that the silica contents in the Permian samples is slightly higher than that in the Charu and Sagor samples. The presence of SiO<sub>2</sub> content in these analyzed samples could be related to the detrital material input being rich in silica materials derived from some periodic volcanic activity during deposition of these sediments (Sidibe, 1993). The grain size of all samples are silty mudstone, which contain abundant silt-size quartz grains. Hence, they are rich in silica.

Highly distinctive variations is observed for the Al<sub>2</sub>O<sub>3</sub> content among the samples studied, however, the Al<sub>2</sub>O<sub>3</sub> content of the carbonaceous sediments in the Permian samples is lower than that in the Charu and Sagor samples. The source of alumina contents in the study samples is believed to be



related to the abundance of clay minerals and feldspars present in shales and mudstones of these rock units. This trend could be also be related to the detrital materials being rich in alumina.

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

Oxides	Permian Fm.	Sagor Fm.	Charu Fm.
	n=3	n=4	n=5
SiO <sub>2</sub>	71.4	64.82	65.83
TiO <sub>2</sub>	0.67	0.86	0.72
Al <sub>2</sub> O <sub>3</sub>	15.66	22.5	18.27
Fe <sub>2</sub> O <sub>3</sub>	2.49	0.9	1.53
MnO	0.01	0	0
MgO	0.24	0.7	0.49
CaO	0.36	0.03	0.03
Na <sub>2</sub> O	0.2	0.25	0.22
K <sub>2</sub> O	3.66	6.25	4.06
P <sub>2</sub> O <sub>5</sub>	0.03	0.02	0.4
LOI	5.25	3.78	8.5
Ba	446.3	758.8	524.4
Cr	33.7	20	27
Ga	24.7	32	29.8
Rb	257.3	399.3	366
Sr	47.3	67.3	88
Zr	327	288.8	308

#### *Fe<sub>2</sub>O<sub>3</sub> Total Iron Content*

Highly distinctive variation is observed for the Fe<sub>2</sub>O<sub>3</sub> content among the analysed samples (Table 2). However, the amount of iron concentration in the Sagor samples appear to be relatively lower than those in the Permian and Charu shales. The highest value of the Fe<sub>2</sub>O<sub>3</sub> in the Permian Formation shales is 2.49 wt.%, which can be attributed to the presence of Fe-rich chlorite, biotite and/or to the formation of Fe – hydroxide in sufficiently high quantities. The high concentration of Fe<sub>2</sub>O<sub>3</sub> are indicative of oxidation, hydration and leaching processes during weathering (Schau & Henderson, 1983).

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

Laminated shales are richer in Fe<sub>2</sub>O<sub>3</sub> concentration than mudstones, because of interlamina ferrous - rich clay (e.g. chlorite) and they are more reduced than mudstone as suggested by Mason & Moor (1982). Such case could be happened in the Permian, Charu and Sagor shales and mudstones. The chemical trend could be also due to the Eh - pH controls on the minerals and weathering.

#### *CaO and MgO<sub>3</sub> Contents*

The CaO content in the analysed samples is generally low and observed only in a small and trace amounts. Exceptions are with the Permian samples, which showed relatively higher CaO. In general, Ca content is due to calcite (CaCO<sub>3</sub>) cement and calcareous organic fragments associated with sediments. The presence of CaO in the study samples here is perhaps related to calcite cement or to skeletal fragments present in the fossiliferous shales and mudstones.

Generally, the results obtained by XRD showed that the Mg content in the Sagor and Charo samples appear to be relatively higher when compared to the Permian samples. The relatively high content of Mg in the Charu and Sagor samples could be related to the abundance of volcanic materials as a result of volcanic activity during deposition of these formations and/or related to the presence of dolomite fragments in the form of detrital sediments. On the other hand, the decrease in MgO content in the Charo and Permian samples possibly related to the lesser content of Mg in the bearing materials.

#### *Na<sub>2</sub>O, K<sub>2</sub>O and TiO<sub>2</sub> Contents*

No distinctive variation is observed for the Na<sub>2</sub>O content among the analysed samples (Table 2). However, Samples of the Charu, Sagor and Permian formations show Na content within an average value of 0.22 %, 0.25% and 0.20 % respectively. According to Wedepohl (1970), major parts of the Na present in the argillaceous rocks occurs 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  $\text{Na}^+$  in interstitial fluid.

The source of Na ions in the analysed samples could be related to the Na - feldspar or clay mineral present in the carbonaceous sediments of these formations.  $\text{Na}_2\text{O}$  content could be also related to the influence of prevailing fluids from granitoid intrusion into sedimentary rocks of those areas as suggested by workers such as [Sidibe \(1993\)](#).

$\text{K}_2\text{O}$  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  $\text{K}_2\text{O}$  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  $\text{K}_2\text{O}$  content indicates that these sediments was not strongly leached during erosion period ([Campbell & Williams, 1965](#)).

The distribution of  $\text{TiO}_2$  in the study samples show that the concentration of the elements in the Permian shales is less than its concentration in the Sagor and Charu samples. However, the three study formations having an average Ti content value of 0.67 %, 0.86 % and 0.72 % respectively. The presence of  $\text{TiO}_2$  in the carbonaceous samples in this study is probably related to some ilmenite or rutile - bearing materials brought in from volcanic sources, and/or clay mineral present in the carbonaceous sediments of these formations. According to [Weaver & Pollard \(1973\)](#), Ti is a minor constituent in the octahedral site in many illite and kaolinite.

#### *Loss on Ignition (LOI)*

The elements present in the loss on ignition (LOI) content comprise volatile elements, including  $\text{H}_2\text{O}$  and  $\text{CO}_2$ . The LOI data ([Table 2](#)) show a distinct variation in the abundance of organic matter present in the shales.

The Charu samples have the highest LOI compared to the Sagor and Permian samples. Among the samples studied, the Charu samples have an average LOI value of 8.5%, while the Sagor and Permian shales recorded average values of 3.78% and 5.25%, respectively. The decrease in LOI values of the Sagor shales is believed to be related to these units being poor in organic matter compared to the Charu and Permian samples.

#### **Minor Constituents**

##### *Barium(Ba) and Chromium(Cr) Content*

The Ba content in the Panching area increases from the Charu to the Sagor Formation, with average values of 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 the influence of granitoid intrusion and changes in the depositional system ([Sidibe, 1993](#)).

In the Permian samples, the Ba content has an average value of 446.3 ppm. Ba is known to be captured by potassium-bearing minerals. Since the carbonaceous shales and mudstones of the Sagor and Charu formations are richer in  $\text{K}_2\text{O}$  than the Permian shales, it can also be inferred that the barium content is related to the abundance of potassium-bearing minerals. Barium is too large to replace Ca or Na; the only major element of comparable ionic size is potassium ([Mason, 1966](#)).

According to [Shengrong & Zhenmin \(1996\)](#), Ba minerals such as barite are easier to dissolve in water under the action of electrolytes like KCl and  $\text{MgCl}_2$ . Therefore, 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, resulting in low Ba content in seawater, especially in pelagic water. This explains why Ba prefers hot-brine sediments over normal sediments.

The chromium content in this study shows average values of 27 ppm, 20 ppm, and 33.7 ppm in the Charu, Sagor, and Permian samples, respectively. This trend suggests that the rock units of these formations contain nearly similar amounts of source materials. The relatively high Cr content in the shales is expected due to the substitution of Cr for Mg in chlorite and its adsorption on illite ([Kelepertsis & Kontis, 1997](#)). According to the same authors, some of the Cr content in the shales is contributed by organic material. Among the samples studied here, a similar situation could occur in these rock units.

##### *Gallium(Ga) and Rubidium (Rb) Content*

It is well established that gallium (Ga) is typically found camouflaged in aluminium-bearing minerals and is enriched in pegmatite feldspars and micas. The chemical analysis of the studied samples

from the Panching area shows a slight increase in Ga content from the Charu to Sagor Formation. The average values are 29.8 ppm and 32 ppm, respectively.

The increase in Ga content may be due to the rise in  $\text{Al}_2\text{O}_3$  content in these rock units. In central Pahang, the average Ga value in the Permian samples is 24.7 ppm. This trend could be related to the rock units in this area having similar amounts of source materials as in the Panching area. Overall, it can be said that the relatively high Ga content in these rock units is related to the increase in  $\text{Al}_2\text{O}_3$  content, as Ga is typically camouflaged in aluminium-bearing minerals, as mentioned above.

Rubidium (Rb) is found camouflaged in aluminous materials. Its average value in the Panching area is higher than in the central Pahang area. However, the Rb content is relatively high in the Charu and Sagor samples, with average values of 368 ppm and 399.3 ppm, respectively. In the central Pahang area, XRF analysis showed that the Rb content in the Permian samples is 156.5 ppm. The Charu, Sagor, and Permian carbonaceous sediments displayed high  $\text{Al}_2\text{O}_3$  content, so the Rb trend is perhaps related to the aluminous minerals present in these carbonaceous samples, as Rb is typically found camouflaged in aluminous materials.

#### *Strontium (Sr) and Zirconium (Zr) Content*

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, 67.3 ppm in the Sagor samples, and 47.3 ppm in the Permian samples. These values are considerably lower than those reported by [Shaw \(1954\)](#) at 700 ppm and by [Turekian & Kulp \(1956\)](#) at 300 ppm. On the other hand, [von Hevesy & Würstlin \(1934\)](#) reported a value of 20 ppm for shales and phyllites, which is obviously too low. Sr can replace Ca or K, being incorporated into Ca minerals or captured by K minerals ([Mason, 1966](#)).

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

XRF results showed that the Zr content is high in the Charu and Sagor samples. The Charu samples recorded an average concentration of 308 ppm, while the Sagor samples recorded 288.8 ppm. In 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 probably rich in zircon occurring as detrital heavy minerals or to the detrital zircon present in the carbonaceous sediments within the study areas.

#### **Interpretation of Chemical Distributions and Significant Ratios**

Geochemical distribution has been used in constructing ancient sedimentary environments, as demonstrated by many researchers, including [Mason & Moore \(1982\)](#). Previous studies have addressed the main factors influencing the distribution of chemical elements and clay minerals in ancient marine environments.

The silica content ( $\text{SiO}_2$ ) in the studied samples appears to decrease with increasing  $\text{Al}_2\text{O}_3$  for the Charu and Sagor formations and to increase with decreasing  $\text{Al}_2\text{O}_3$  for the Permian Formation. As large amounts of quartz are found in the residual material, it is reasonable to assume that desilication occurred mainly due to the destruction of aluminosilicates.

Results tabulated in [Table 2](#) show that the oxides  $\text{SiO}_2$ ,  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{MgO}$ , and  $\text{K}_2\text{O}$  exhibit similar trends, except for samples from the Permian Formation, where the trends are obviously different. In the case of  $\text{CaO}$ ,  $\text{Na}_2\text{O}$ , and  $\text{MnO}$ , the trends are also different. The results illustrate a similar elemental composition for the Charu and Sagor samples, reflecting the homogeneity of the sediment suite.

The enrichment of  $\text{MgO}$  in the studied carbonaceous sediments is related to the decrease of  $\text{CaO}$ , which is due to the weathering effect on parent materials. High  $\text{MgO}$  content often correlates with low-temperature oxidative diagenesis. According to [Andrews \(1980\)](#), a drop in  $\text{CaO}$  accompanies the increase of  $\text{MgO}$  contents in the rock. The decrease of  $\text{CaO}$  and  $\text{MnO}$  with increasing  $\text{Na}_2\text{O}$ ,  $\text{MgO}$ , and  $\text{K}_2\text{O}$  indicates variation in chemical composition, reflecting changes in the mineralogical composition of the sediments due to weathering and early diagenetic processes ([Shaw & Weaver, 1965](#); [Drever, 1971](#); [Nesbitt & Young, 1984, 1989](#)).

Compared to the Charu and Permian shales, the Sagor Formation samples contain high  $\text{SiO}_2$  and less  $\text{MgO}$  and  $\text{K}_2\text{O}$ . The Sagor Formation shales have, on average, higher  $\text{Al}_2\text{O}_3$  and lower  $\text{CaO}$  than shales of the other formations. The Permian Formation shows a marked enrichment of  $\text{SiO}_2$  and  $\text{Fe}_2\text{O}_3$ , suggesting changes in the environment of deposition or in the source materials.

The abundance of Si, Ti, Al, and K in shales may be influenced by weathering, transport, and depositional processes. The decrease in calcium content in these shales can be attributed to terrigenous influx and the low abundance of fossils and shell fragments, which could otherwise contribute significant amounts of calcium (Nesbitt & Markovics, 1996).

The average values from this study show some differences and similarities when compared with the average values of shales and glacial clays from other locations (Table 4).  $\text{SiO}_2$  content in the shales of this study is higher than other averages presented, with the exception of the data presented by Campbell & Williams (1965), which exhibit slightly higher  $\text{SiO}_2$  content. The high  $\text{SiO}_2$  content in these shales suggests that  $\text{SiO}_2$  is mainly associated with silicate minerals (clay minerals).

The shales have lower average CaO and MgO compared to other average data presented and show higher  $\text{K}_2\text{O}$ , except for the data presented by Campbell & Williams (1965), which show higher values.

A plot of  $\text{Al}_2\text{O}_3$  vs.  $\text{K}_2\text{O}$  and  $\text{TiO}_2$  (Figure 2) illustrates a strong positive correlation. In contrast, the plot of  $\text{Al}_2\text{O}_3$  vs. MgO shows a weak correlation coefficient, indicating that these elements are of detrital origin, occurring in detrital clay minerals (illite or smectite).

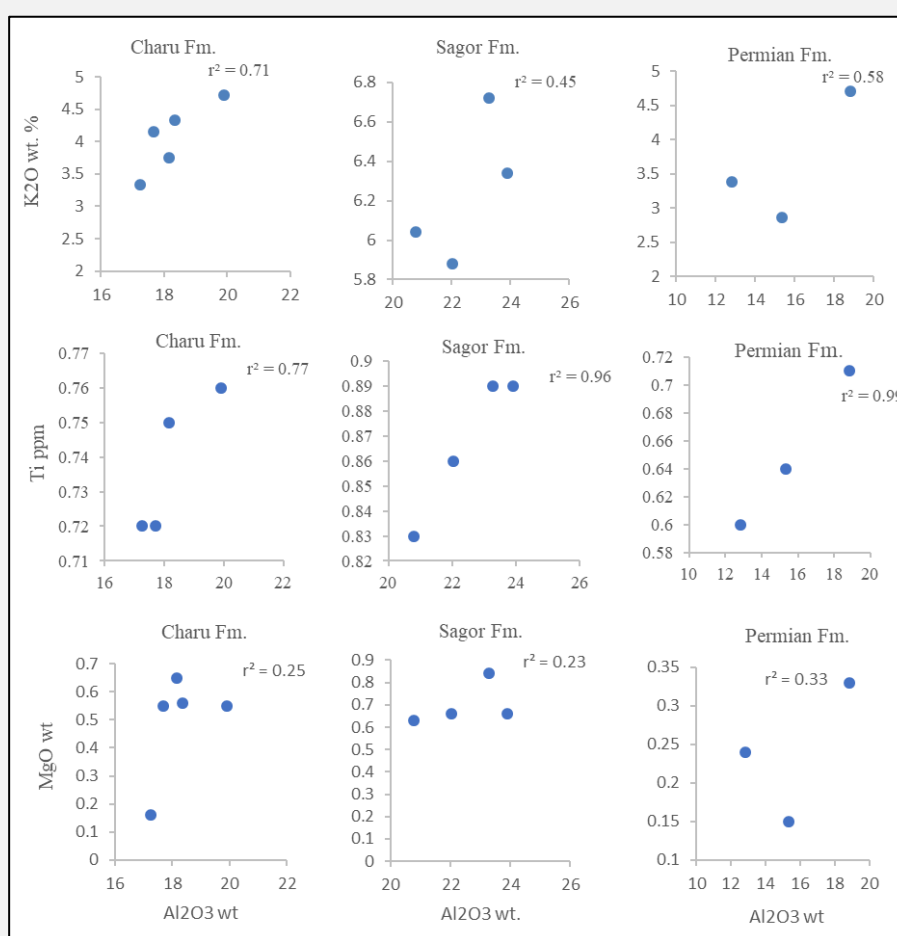
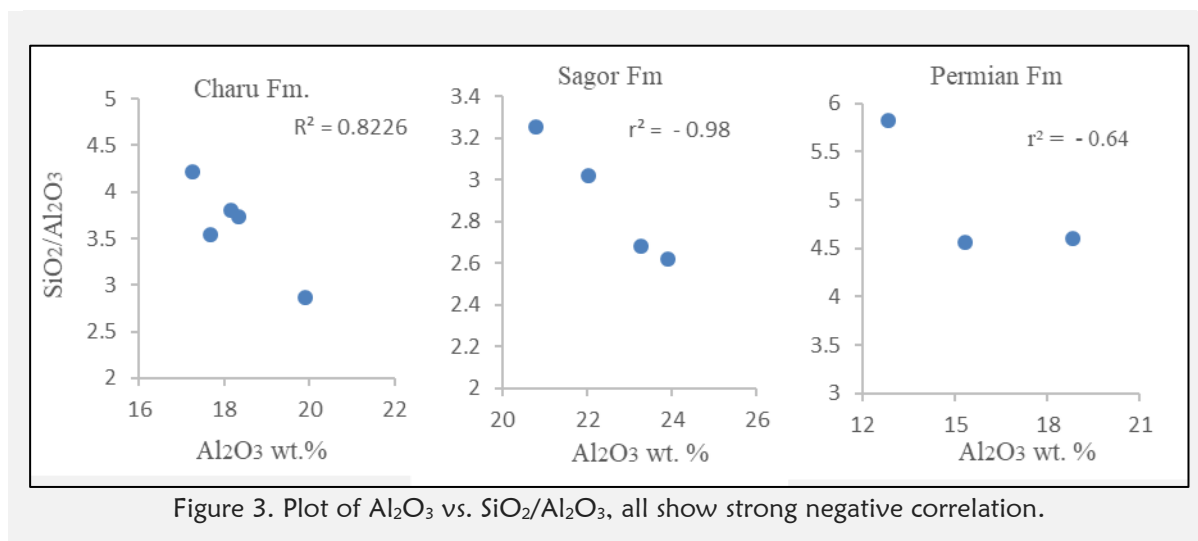


Figure 2. a Cross-plot of  $\text{Al}_2\text{O}_3$  vs.  $\text{K}_2\text{O}$ ,  $\text{TiO}_2$  and MgO of the Charu, Sagor and Permian formations. Except for  $\text{Al}_2\text{O}_3$  vs. MgO (weak positive correlation coefficient), all the others illustrate a strong positive correlation.

The positive correlation of  $\text{Al}_2\text{O}_3$  vs. MgO and  $\text{TiO}_2$  indicates that Mg and Ti are originally associated with aluminosilicate phases, assuming minor association of Mg with carbonates (dolomite) during diagenesis (Bellanca et al., 1999). It also suggests that weathering conditions were a significant 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  $\text{Al}_2\text{O}_3$  vs. the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio (Figure 3) shows a strong negative correlation. When plotting  $\text{Al}_2\text{O}_3$  against the  $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ ,  $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ , and  $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$  ratios, the results vary, reflecting the presence of clay minerals in these sediments.



The Sr/Ca and Rb/K ratios in this study show both similarities and differences when compared with each other. 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 increases as Ca decreases.

The Sr and Rb contents of each sample were determined and correlated with Ca and K, respectively. The results are given in Table 3, and the average composition values for each formation, along with other published results, are described in Table 4.

The average Sr/Ca ratios in the Charu and Sagor formations tend to be higher than those in the Permian samples (Table 4). The average Sr/Ca ratios are 0.29 and 0.27, respectively, whereas in the Permian samples, the Sr/Ca ratio is 0.01.

Table 3. Comparison of the Composition of Major and Minor Elements in This Study with Average Shales by Previous Workers

Oxides/Elements	Glacial Shale (5)	Av. Shale (4)	Av. Shale (3)	Av. Shale (2)	Permian Fm. (1)	Sagor Fm. (1)	Charu Fm. (1)
$\text{SiO}_2$	59.12	58.50	64.83	58.10	71.4	64.82	65.83
MgO	3.30	2.50	2.66	2.44	0.24	0.70	0.49
$\text{Al}_2\text{O}_3$	15.82	15.0	15.72	15.44	15.66	22.5	18.27
$\text{K}_2\text{O}$	3.93	3.20	2.50	3.24	3.66	6.25	4.06
CaO	3.07	3.10	2.42	3.11	0.36	0.03	0.03
$\text{Fe}_2\text{O}_3$	6.99	4.72	5.08	6.47	2.49	0.90	1.53
Rb (ppm)	153	140	97	126	257.3	399.3	366
Sr (ppm)	267	300	210	270	47.3	67.8	88
Rb/Sr	0.57	0.47	0.46	0.47	5.44	5.89	4.16

Note: Major elements are in wt. %, minor elements are in ppm. Average of 12 samples: 5 Charu Fm., 4 Sagor Fm., 3 Permian Fm. in the current study; Clarke, 1924 (average of 72 samples: 51 Paleozoic, 21 Mesozoic and Cenozoic); Campbell & Williams, 1965 (average of 113 samples); Turekian & Wedepohl, 1961; Goldschmidt, 1954; Mason, 1966.

Table 4. Major and Minor Constituents and Significant Ratios

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

The Sr content is correlated with Ca, but none of these formations show 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 ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) or celestite ( $\text{SrSO}_4$ ). The deficiency of CaO in the shales prevents significant substitution of Sr for Ca in Ca-rich minerals. According to Turekian & Kulp (1956), the Sr element increases as the Ca content increases in granite and granodiorite rocks.

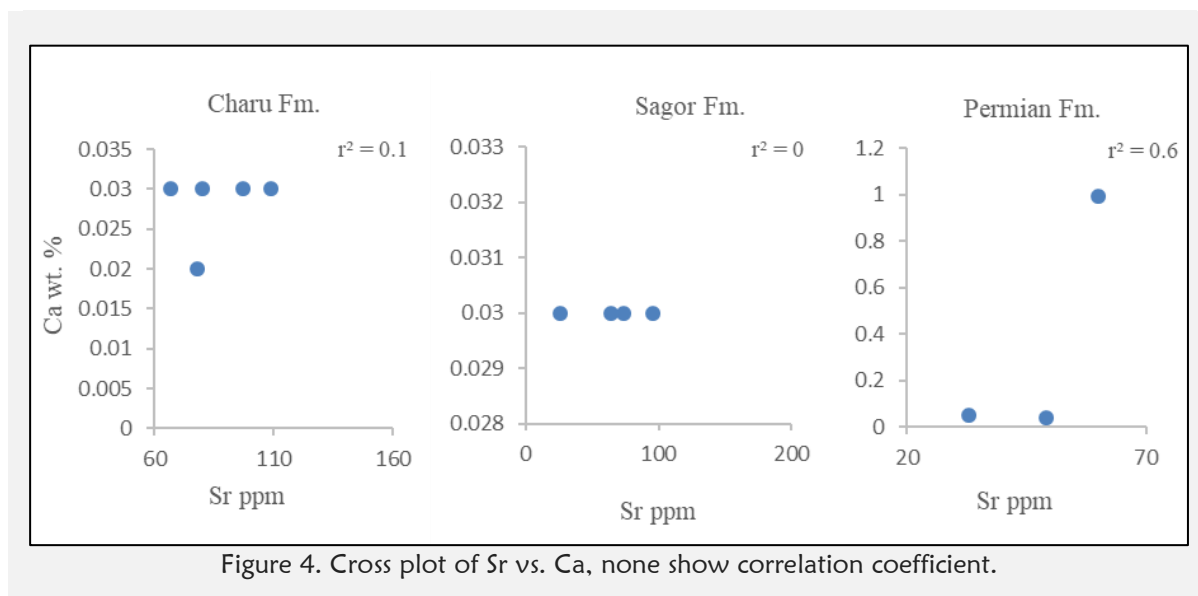


Figure 4. Cross plot of Sr vs. Ca, none show correlation coefficient.

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, respectively. This suggests that the shales of these rock units were deposited in a normal marine 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 & Williams, 1965). High Rb/K ratios suggest a marine environment (Campbell & Lerbekmo, 1963).

The author believes that the high Rb/K ratios in this study suggest either a brackish sequence or rapid deposition that prevented equilibrium between Rb and K in the shales 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 themselves 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 the Charu, Sagor, and Permian formations, respectively, are attributed to the lowest contents of Sr due to reducing conditions. The Rb/Sr ratio values are considerably higher than the other ratios presented in Table 3. Variations in Sr/Ca and Rb/K ratios among the study units can be interpreted as being due to fluctuations between normal marine and brackish conditions.

## CONCLUSION

The investigation of the geochemical characteristics of the carbonaceous sediments of the Upper Paleozoic Kuantan Group, Malaysia, using ICP and XRF techniques, shows that the shales of the Charu, Sagor, and Permian formations have high concentrations of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ , and  $\text{K}_2\text{O}$ , and low CaO and MgO contents. This reflects the presence of quartz and other silicate minerals and the lack of carbonates.

The  $\text{K}_2\text{O}$  contents are sufficiently high in all the shales to suggest that illite is probably the main clay mineral present in these carbonaceous sedimentary units. Highly distinctive variation is observed for the  $\text{Fe}_2\text{O}_3$  content among the analyzed samples. The amount of iron concentration in the Sagor samples appears to be relatively lower than in the Permian and Charu shales. The highest value of  $\text{Fe}_2\text{O}_3$  in the Permian Formation shales can be attributed to the presence of Fe-rich chlorite and/or related to the formation of Fe-hydroxide.

Shales from the Permian Formation display an increase in  $\text{Fe}_2\text{O}_3$  content and a decrease in  $\text{SiO}_2$ , 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 due to reducing environmental conditions. The high Rb/K ratios indicate either brackish marine conditions or rapid deposition that prevented equilibrium between K and Rb in the shales and marine waters. Variations in Sr/Ca and Rb/K ratios can be interpreted as fluctuations between normal marine and brackish conditions.

The plot of  $\text{Al}_2\text{O}_3$  vs.  $\text{K}_2\text{O}$  and  $\text{TiO}_2$  illustrates a strong positive correlation, whereas in the case of  $\text{Al}_2\text{O}_3$  vs.  $\text{MgO}$ , the plot shows a weak correlation coefficient, indicating that these elements are of detrital origin occurring in detrital clay minerals. The plot of  $\text{Al}_2\text{O}_3$  vs. the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio shows a strong negative correlation. Variations are observed when plotting against the  $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ ,  $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ , and  $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$  ratios, reflecting 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 content is not associated with gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) or celestite ( $\text{SrSO}_4$ ). The deficiency of CaO in the shales prevents significant substitution of Sr for Ca in Ca-rich minerals.

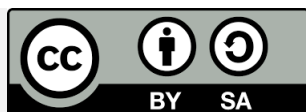
### Acknowledgment

Thanks are due to The University Kebangsaan Malaysia and the Geology Department, University of Malaya, for providing research facilities. Appreciation is also extended to the Libyan Ministry of Higher Education for providing the research grant and to Assistant Lecturer Moamer Mosbah from Bani Walid University for his help during the preparation of this work.

### REFERENCES

- Andrews, A. J. (1980). Saponite and celadonite in layer 2 basalts, DSDP Leg 37. *Contributions to Mineralogy and Petrology*, 73(4), 323-340. <https://doi.org/10.1007/BF00376627>
- Bellanca, A., Masetti, D., Neri, R., & Venezia, F. (1999). Geochemical and sedimentological evidence of productivity cycles recorded in Toarcian black shales from the Belluno Basin, Southern Alps, northern Italy. *Journal of Sedimentary Research*, 69(2), 466-476. <https://doi.org/10.2110/jsr.69.466>
- Campbell, F. A., & Lerbekmo, J. F. (1963). Mineralogic and chemical variations between Upper Cretaceous continental Belly River shales and marine Wapiabi shales in western Alberta, Canada. *Sedimentology*, 2(3), 215-226. <https://doi.org/10.1111/j.1365-3091.1963.tb01215.x>
- Campbell, F. A., & Williams, G. D. (1965). Chemical composition of shales of Mannville group (lower Cretaceous) of central Alberta, Canada. *AAPG Bulletin*, 49(1), 81-87.
- Clarke, F. W. (1924). *The Data of Geochemistry (fifth edition)*. US Government Printing Office. <https://doi.org/10.3133/b770>
- Drever, J. I. (1971). Early diagenesis of clay minerals, Rio Ameca basin, Mexico. *Journal of Sedimentary Research*, 41(4), 982-994.
- Goldschmidt, V.M. (1954). *Geochemistry*. Oxford University Press.
- Kelepertsis, A. E., & Kontis, E. (1997). Geochemical and mineralogical characteristics of Pleistocene lignites and associated sediments of Marathousa coal field, Central Peloponnese, Greece. *Chinese Journal of Geochemistry*, 16, 8-19. <https://doi.org/10.1007/BF02843368>
- Kovalchuk, N. S., Makeev, B., & Svetov, S. A. (2021). Mineralogical and geochemical specificity of carbonaceous rocks from the area of Ust'-Kara astrobleme (Pay-Khoy). *Vestnik of Geosciences*, 11, 3-15. <http://dx.doi.org/10.19110/geov.2021.11.1>
- Mason, B. (1966). *Principles of Geochemistry*. John Wiley & Sons, Inc.
- Mason, B., & Moore, C.B. (1982). *Principles of Geochemistry* (4th ed.). New York: John Wiley & Sons, Inc.
- McLennan, S. M., Taylor, S. R., & Eriksson, K. A. (1983). Geochemistry of Archean shales from the Pilbara Supergroup, western Australia. *Geochimica et Cosmochimica Acta*, 47(7), 1211-1222. [https://doi.org/10.1016/0016-7037\(83\)90063-7](https://doi.org/10.1016/0016-7037(83)90063-7)
- Metcalf, I., Idris, M., & Tan, J. T. (1980). Stratigraphy and palaeontology of the Carboniferous sediments in the Panching area, Pahang, West Malaysia. *Geological Society of Malaysia (GSM)*, 13, 1-26.
- Nesbitt, H. W., & Markovics, G. (1980). Chemical processes affecting alkalis and alkaline earths during continental weathering. *Geochimica et Cosmochimica Acta*, 44(11), 1659-1666. [https://doi.org/10.1016/0016-7037\(80\)90218-5](https://doi.org/10.1016/0016-7037(80)90218-5)
- Nesbitt, H. W., & Markovics, G. (1997). Weathering of granodioritic crust, long-term storage of elements in weathering profiles, and petrogenesis of siliciclastic sediments. *Geochimica et Cosmochimica Acta*, 61(8), 1653-1670. [https://doi.org/10.1016/S0016-7037\(97\)00031-8](https://doi.org/10.1016/S0016-7037(97)00031-8)
- Nesbitt, H. W., & Young, G. M. (1984). Prediction of some weathering trends of plutonic and volcanic rocks based on thermodynamic and kinetic considerations. *Geochimica et Cosmochimica Acta*, 48(7), 1523-1534. [https://doi.org/10.1016/0016-7037\(84\)90408-3](https://doi.org/10.1016/0016-7037(84)90408-3)
- Nesbitt, H. W., & Young, G. M. (1989). Formation and diagenesis of weathering profiles. *The Journal of Geology*, 97(2), 129-147. <https://doi.org/10.1086/629290>

- Pettijohn, F.J. (1957). *Sedimentary Rocks* (3rd ed.). New York: Harper Bros.
- Schau, M., & Henderson, J. B. (1983). Archean chemical weathering at three localities on the Canadian Shield. *Precambrian Research*, 20(2-4), 189-224. [https://doi.org/10.1016/0301-9268\(83\)90073-6](https://doi.org/10.1016/0301-9268(83)90073-6)
- Shaw, D. B., & Weaver, C. E. (1965). The mineralogical composition of shales. *Journal of Sedimentary Research*, 35(1), 213-222. <https://doi.org/10.1306/74D71221-2B21-11D7-8648000102C1865D>
- Shaw, D. M. (1954). Trace Elements in Pelitic Rocks: Part I: Variation During Metamorphism. *Geological Society of America Bulletin*, 65(12), 1151-1166. [https://doi.org/10.1130/0016-7606\(1954\)65\[1151:TEIPR\]2.0.CO;2](https://doi.org/10.1130/0016-7606(1954)65[1151:TEIPR]2.0.CO;2)
- Shengrong, L., & Zhenmin, G. (1996). Silicalites of hydrothermal origin in the Lower Cambrian black rock series of South China. *Chinese Journal of Geochemistry*, 15(2), 113-120. <https://doi.org/10.1007/BF02843348>
- Sidibe, Y. T. (1993). *Lithostratigraphy, sedimentology and geochemistry of upper paleozoic Kuantan group rocks in northeast Pahang and South Terengganu, Malaysia* (Doctoral dissertation, UKM, Bangi).
- Turekian, K. K., & Kulp, J. L. (1956). The geochemistry of strontium. *Geochimica et Cosmochimica Acta*, 10(5-6), 245-296. [https://doi.org/10.1016/0016-7037\(56\)90015-1](https://doi.org/10.1016/0016-7037(56)90015-1)
- Turekian, K. K., & Wedepohl, K. H. (1961). Distribution of the elements in some major units of the earth's crust. *Geological Society of America Bulletin*, 72(2), 175-192. [https://doi.org/10.1130/0016-7606\(1961\)72\[175:DOTAIS\]2.0.CO;2](https://doi.org/10.1130/0016-7606(1961)72[175:DOTAIS]2.0.CO;2)
- Varaksina, I. V., Timoshina, I. D., Kontorovich, A. E., & Tumashov, I. V. (2017). Lithology, organic geochemistry, and petroleum potential of the northern areas of the Kureika syncline. *Russian Geology and Geophysics*, 58(3-4), 467-478. <https://doi.org/10.1016/j.rgg.2016.09.023>
- von Hevesy, G., & Würstlin, K. (1934). Über die Häufigkeit des Strontiums [About the abundance of strontium]. *Journal of Inorganic and General Chemistry*, 216(3), 312-314. <https://doi.org/10.1002/zaac.19342160312>
- Weaver, C. E., & Pollard, I. D. (1973). *The Chemistry of Clay Minerals*. New York: American Elsevier.
- Wedepohl, K. H. (1970). *Handbook of Geochemistry* (Vol. I and II). Berlin: Springer-Verlag.
- Zhao, J., Jin, Z., Jin, Z., Hu, Q., Hu, Z., Du, W., Yan, C., & Geng, Y. (2017). Mineral types and organic matters of the Ordovician-Silurian Wufeng and Longmaxi Shale in the Sichuan Basin, China: Implications for pore systems, diagenetic pathways, and reservoir quality in fine-grained sedimentary rocks. *Marine and Petroleum Geology*, 86, 655-674. <https://doi.org/10.1016/j.marpetgeo.2017.06.031>



Copyright (c) 2024 by the authors. This work is licensed under a [Creative Commons Attribution-ShareAlike 4.0 International License](https://creativecommons.org/licenses/by-sa/4.0/).