Contents lists available at Science-Gate



International Journal of Advanced and Applied Sciences

Journal homepage: http://www.science-gate.com/IJAAS.html

# Geological characteristic of the Kroh formation in the upper Perak shales, western Peninsula Malaysia



Monera Adam Shoieb\*, Chow Weng Sum, Mohd Suhaili Ismail, Haylay Tsegab

Department of Geoscience, Universiti Teknologi PETRONAS, Perak Darul Ridzuan, 32610 Seri Iskandar, Tronoh, Malaysia

### ARTICLE INFO

Article history: Received 9 June 2018 Received in revised form 4 January 2019 Accepted 5 January 2019 Keywords: Black shale Organic geochemistry Mineralogy Hydrocarbon generation potential

## ABSTRACT

The unconventional resource has become an interesting field of study and some source rocks have turned to be excellent reservoirs for generation and accumulation. Twenty- five percent of sedimentary rocks from Peninsular Malaysia are Paleozoic shales. The goal of this paper is to evaluate and characterize the shales in the Kroh Formation, which is one of the Western Belt formations in Peninsular Malaysia. Representative shale samples have been taken from different outcrops of the Kroh Formation, were performed to study the mineralogical and geochemical characteristics to determine the quantity of the organic matter and the minerals. The TOC values range from 2.02 to 7.01 wt% and this range indicate that the shales have a very good source generative potential. These values fulfill the basic prerequisites of successful shale gas exploration. Results of X-ray Diffraction (XRD) indicate that the shale samples are mainly comprised of kaolinite as clay minerals and quartz and pyrite as non-clay minerals. In addition to illite, kaolinite, and quartz, Pyrite, calcite, and dolomite were identified within the shales through XRD. FTIR technique confirms the minerals that are present in the XRD. Knowing the clay minerals composition of the shale can be useful in planning for drilling and hydraulic fracturing of the Kroh Formation or similar characteristics.

© 2019 The Authors. Published by IASE. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

# 1. Introduction

Shale is a fine-grained sedimentary rock, containing different types of clay minerals such as illite and kaolinite and quartz and pyrite as nonclay minerals (Peters, 2006). More recently, shale has been recognized as a potential source rock and reservoir for hydrocarbons. It possesses up to 20% of the total organic matter making them potential source rocks for both conventional and unconventional gas.

Black shale is a dark-colored mud rock containing organic matter, silt- and clay-sized mineral grains that accumulated together. A shale gas reservoir is not comprised of a single lithology but a collection of any fine-grained rocks capable of storing significant amounts of gas. Most of the black shales are marine and may have a real extent of thousands of square kilometers. The geochemistry of black shales has played a major role in the characterization of the

\* Corresponding Author.

© Corresponding author's ORCID profile:

https://orcid.org/0000-0003-3373-0707

2313-626X/© 2019 The Authors. Published by IASE. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/) organic material, widening the scope of inferences drawn about the genesis of black shales (Baioumy et al., 2016). Black shales have attracted interest from researchers primarily because of their economic importance in terms of hydrocarbon development potential (Wignall, 1994).

The attention in black shales worldwide within the last decades chiefly stems from the widespread confession that black shales are important to the natural fuel-resource (El-Kammar et al., 1990). Organic geochemistry is the scientist's first choice to obtain information needed to evaluate the richness, type and thermal maturity of a source rock. Different geochemical scales, such as vitrinite reflectance (Ro%), pyrolysis Tmax, and biomarker maturity ratios can be used to indicate the maturity of organic matter (Peters and Casa, 1994). The Western Belt of Peninsular Malaysia comprises a lot of Paleozoic black shales that have the potential to be source rocks. The carbonaceous black shales have a wide distribution on the surface and subsurface.

Twenty- five percent of sedimentary rocks from Peninsular Malaysia are Paleozoic shale. The geology of these shales has been mapped by the Minerals and Geoscience Department and had been studied extensively for their lithologies and stratigraphy (Jones, 1970; Burton, 1986; Cocks et al., 2005;

Email Address: monera\_g03018@ utp.edu.my (M. A. Shoieb) https://doi.org/10.21833/ijaas.2019.02.015

Metcalfe, 2013). However, the mineralogy and geochemistry of those shales have not been studied in detailed. Therefore the major significance of this paper is to determine the quantity of the organic matter and the types of minerals that are present in the shale that will be useful in planning for drilling and hydraulic fracturing.

#### 1.1. Geological setting

Paleozoic rocks are marine and account for about 25% by area of Peninsular Malaysia. The Paleozoic formations of Peninsular Malaysia are distributed in three northwesterly to northerly trending zones parallel to the general elongation trend of the Peninsula. They are the Western Belt, Central Belt and Eastern Belt (Fig. 1). Each of these zones is characterized by distinctive structure, stratigraphy, tectonic and sedimentary history.

The Western Belt forms part of the Sibumasu Terrane, derived from the NW Australian Gondwana margin within the late Cambrian- Early Permian. The Central and Eastern Belts represent the Sukhothai Arc constructed in the Late Carboniferous-Early Permian on the margin of the Indochina Block (derived from the Gondwana margin in Early Devonian). This arc was then separated from Indochina by back-arc spreading in the Permian. The Bentong-Raub suture zone forms the boundary between the Sibumasu Terrane (Western Belt) and Sukhothai Arc (Central and Eastern Belts) (Metcalfe, 2013).

Kroh Formation which is part of the Baling Group in the Western Belt is Upper Ordovician to Lower Devonian in age. It consists of black, very thin- to thinbedded, mudstone, carbonaceous shale, often siliceous; calcareous rocks and chert with lenses of arenaceous (Fig. 2) (Burton, 1970).

# 2. Materials and methods

#### 2.1. Materials

Six representative samples were taken from six locations in the Gerik area, upper Perak (Fig. 1). They are carbonaceous shale and have been dated and assigned the Upper Ordovician to Lower Devonian age (Burton, 1970). The outcrop samples were collected and to avoid oxidized and weathered materials, fresh samples were selected by removing the surface materials of the outcrop. All of the shale samples were selected for Total Organic Carbon (TOC), X-ray Diffraction (XRD) and Fourier Transmittance Infrared (FTIR) tests.



Fig. 1: Geological map of the Malay Peninsula showing the study area, After (Tate et al., 2008)

PERIOD/EPOCH		FORMATION/UNIT	STRATIGRAPHIC COLUMN	DESCRIPTION
NERY	HOLOCENE	Alluvium (Qa)		Surficial deposits - unconsolidated gravel, sand, silt and clay of fluviatile and colluvial origin.
QUATER	PLEISTOCENE	Nenering beds (Qnn)	000000	Semi-consolidated deposits consist of gravelly, sandy and silty beds, chanelling is common.
	TERTIARY			Unconformity
CRETACEOUS		Berapit formation (Kbr)	a.o.o.o.o	Conglomerate, grey to reddish, very poorly sorted, subangular to rounded clast of up to 40cm in diameter.
	JURASSIC			
TRIASSIC				
PERMIAN		Gerik formation (Pgk)	v v v v v v v v v v v v v v v v v v v	Mainly tuffs of rhyolitic and rhyodacitic composition, occasionally metamorphosed; limestone and calcareous shale lenses occur sporadically; interbeds of tuff, limestone and calcareous shale also occur.
CARBONIFEROUS		Kubang Pasu (Ckp)		Well-bedded areno-argillaceous rocks with subordinate ribbon chert. The rocks had been invariably metamorphosed especially the one closer to the granite body.
DEVONIAN			b d	Argiliaceous facies: Mainly shale and phyllite; commonly carbonaceous, with subordinate chert. Calc.silicate facies: Grey calc.silicate homfels.
	SILURIAN	Kroh formation (SDk)	d b a	Calcareous facies: Grey to dark grey impure limestone. Arenaceous facies: Grey to dark grey impure limestone. Arenaceous facies: Mainly metasandstone, occur sporadically within the argillaceous facies. (It is difficult to establish the order of the rock succession owing to folding, faulting, and the lenticular shape of the rock units as well as a repetitious character of its components)

Fig. 2: Schematic stratigraphic column of the Betong-Pengkalan Hulu Transect area, Malaysia showing the Kroh Formation

### 2.2. Methods

# 2.2.1. Total organic carbon (TOC)

Total organic carbon (TOC) content is the amount of organic matter in a rock, and it determines how much hydrocarbon could be generated from a source rock, which ultimately affects the production potential of hydrocarbon reservoirs in a petroleum system. TOC was measured on powdered samples using a TOC analyser. TOC values are measured in terms of weight percentage of organic carbon. About 3g of a sample was treated with 10% hydrochloric acid of 37% concentration in order to remove the inorganic carbon from the samples. They were then left for 12 hours in the fume chamber before being rinsed with reverse osmosis water 3 times and dried in the oven at 60°C for 24 hours. After drying, 60mg of each sample were being weighted and placed on ceramic boats. Percentage of organic carbon was measured using multi n/c 3100 (Ibad and Padmanabhan, 2018).

## 2.2.2. X- ray diffraction (XRD)

XRD analysis is a beneficial method for identifying minerals that are present in the shales. Shale samples were first ground into powder, and the XRD analysis was performed with a Rigaku D/max-2500P °C. The samples were prepared according to the (Hardy, 1988). Samples of shales were pulverized mechanically using a grinder mortar for Riveted-based quantitative XRD analyses to identify the various mineral phases. Then the powdered samples were sieved before being used in the X-ray diffractometer in the laboratory. Diffractograms were recorded by stepscanning through 2-theta (2 $\theta$ ) in the range of 2°-80° with a scan speed of 1°20/mm, step interval of 0.02° and a dwell time of 0.5 seconds using a Bruker D8 Advance X-ray diffractometer.

### 2.3. Fourier transmittance infrared (FTIR)

Fourier Transmittance Infrared (FTIR) is one of the methods of infrared spectroscopy used to identify and analyze the chemical compounds of materials. An Agilent Technologies Cary 660 Series FTIR Spectrometer was used to run FTIR model- spectrum 100. FTIR is a spectrometer that determines the material structure by applying Infrared beam on the sample and the ratio between the incidents to transmittance wave is measured. The wave range used is between 400-4000 cm<sup>-1</sup>. Data collection was done using the Resolutions Pro software package which was also used for background and automatic baseline correction of all spectra (Washburn and Birdwell, 2013).

### 3. Results and discussion

#### 3.1. Quantity of the organic matter

The total organic carbon (TOC wt.%) content is an important parameter that has been used to determine the quantity of the organic matter and hydrocarbon generative potential of the source rock (Peters and Cassa, 1994). Six hand specimens from the Kroh Formation were studied for their total organic carbon. The technique by Dow and Pearson (1975), was applied to determine the quantity of the organic matter. The values of TOC for the shale samples vary from sample to sample depending on the type of shales and their characteristic properties (Fig. 3). The shale samples have TOC values ranging from 2.02 to 7.01 wt. % and the average is 4.09 wt. %. This means the TOC is reflective of a very good source potential generative (Peters et al., 1993). This average fulfills the basic prerequisites of successful shale gas exploration (Nunez-Betelu and Baceta, 1994).

The different values for the total organic carbon may cause due to changes in the deposition rates, the

degree of oxygenation of the bottom water and terrestrial organic matter supply rate from the continents (Tissot and Welte, 1984; Heydari et al., 1997).



Fig. 3: TOC% results from the Kroh formation

## 3.2. Bulk mineralogy

mineral contents of a rock in The an unconventional reservoir are important when the operators want to perform hydraulic fracture successfully. operations The mineralogical characterization of shale rocks is important, particularly for drilling and production processes. Six shale samples from the Kroh Formation were analyzed in detail using the X-Ray Diffraction (XRD) and Fourier Transform Infrared (FTIR) to identify the minerals present in the shale samples. XRD is the most current tool for characterizing the clay minerals and different minerals that are present within the shale rock sample (Butt, 2012).

The XRD shows that the Kroh Formation has various minerals from clay minerals such as illite and kaolinite, nonclay minerals like pyrite and quartz (Fig. 4). All of these minerals were identified by the fact that each mineral has unique fingerprints. Although shale can contain large amounts of various minerals depending on its burial history and sedimentation, only these minerals were found in these samples by XRD. Fourier transform infrared (FTIR) spectroscopy is a nondestructive, alternative vibrational technique to obtain information of shale with certain advantages over other techniques, such as small sample size requirement, quick and easy sample preparation, and fast analysis (Painter et al., 1981). The FTIR analysis was conducted to identify the minerals that present in the black shale. Table 1 present a summary of important infrared bands and their possible bond assignments (Nayak and Singh, 2007).

Illite is a secondary mineral precipitate phyllosilicate or layered alumino-silicate.

Kaolinite is identified by its characteristic 7.0 and 7.3  $A^{\circ}$  basal spacing (Fig. 4). The kaolinite peak is crystalline clear and it was common in all the six samples. The XRD peak intensities suggest kaolinite is the dominant clay mineral in the Kroh Formation. The presence of 3623 cm<sup>-1</sup> in the samples confirmed the

presence of kaolinite (Tuddenham and Lyon, 1960) (Fig. 5 and Table 1).



Fig. 4: The XRD peak of a shale from the Kroh formation in the KR-3 samples



Fig. 5: General FIIR spectral features of shale sample from Kroh formation

 
 Table 1: Important infrared bands of clay minerals with their possible assignments

	1 0
Wavelengths (cm <sup>-1</sup> )	Assignment
3696	Al≡O–H Stretching
3622	Al≡0–H (inter-octahedral)
3450	H-O-H Stretching
1633	H-O-H Stretching
1033	Si–O–Si,Si–O Stretching
914	Al≡O–H Stretching
790	Si–O Stretching, Si–O–Al Stretching (Al, Mg) $\equiv$ O– H. Si–O– (Mg, Al) Stretching
693	Si–O , Si–O–Al Stretching

The strong diffraction at 4.2A°, 3.3A°, 2.4A° and 1.8A° suggested the presence of quartz in the samples (Fig. 4). Quartz is present in all shale samples analyzed from the Kroh Formations. Presence of quartz will be good in the hydraulic fracture because fractures are more prevalent and created more easily in silica-rich and carbonate-rich shales than in clay minerals. The appearance of Si–O stretching vibrations were observed at 797 and 530 cm<sup>-1</sup> from FTIR analysis (Van der Marel and Beutelspacher, 1976). The appearance of Si-O-Si also supported the presence of quartz in all the samples (Fig. 5). Pyrite is present in most of the samples, especially those high in organic matter. It is identified by its characteristic of 2.2A° basal spacing. Other minerals identified from XRD analysis that have

low peak intensities are calcite with 2.0 A° basal spacing and dolomite at 1.3 A° basal spacing (Fig. 4).

## 4. Conclusion

Carbonaceous shale samples of the Kroh Formation exposed in the Gerik area (upper Perak) were investigated using organic geochemical and mineralogical methods. The results of the analysis were used to determine the organic richness and the minerals present in the shale. TOC results show that the shale samples have a very good source generative potential based on the TOC values (2.02-7.1%). Shale is the most abundant sedimentary rock and is a combination of a wide variety of minerals, but the minerals found in these samples are illite, kaolinite, and silica (quartz). Other minerals present such as pyrite, calcite, and dolomite. Clay minerals dominate the mineralogy, followed by quartz.

# Acknowledgment

The authors would like to acknowledge the support providing by the PRF project "Advanced Shale Gas Extraction Technology Using Electrochemical Methods".

# **Compliance with ethical standards**

# **Conflict of interest**

The authors declare that they have no conflict of interest.

# References

Baioumy H, Ulfa Y, Nawawi M, Padmanabhan E, and Anuar MNA (2016). Mineralogy and geochemistry of Palaeozoic black shales from Peninsular Malaysia: Implications for their origin and maturation. International Journal of Coal Geology, 165: 90-105.

https://doi.org/10.1016/j.coal.2016.08.007

- Burton CK (1970). The geology and mineral resources of the Baling area, Kedah and Perak. Memoir/Geological Survey Malaysia, 12: 1-150.
- Burton CK (1986). The Baling group/Bannang Sata group of the Malay/Thai Peninsula. Journal of Southeast Asian Earth Sciences, 1(2): 93-106. https://doi.org/10.1016/0743-9547(86)90024-3
- Butt AS (2012). Shale characterization using x-ray diffraction. Ph.D. Dissertation, Dalhousie University, Halifax, Nova Scotia, Canada.
- Cocks LRM, Fortey RA, and Lee CP (2005). A review of Lower and middle Palaeozoic biostratigraphy in west peninsular Malaysia and southern Thailand in its context within the Sibumasu Terrane. Journal of Asian Earth Sciences, 24(6): 703-717. https://doi.org/10.1016/j.jseaes.2004.05.001
- Dow WG and Pearson DB (1975). Organic matter in Gulf Coast sediments. In the Offshore Technology Conference, Houston, Texas, USA: 1-10. https://doi.org/10.4043/2343-MS
- El-Kammar AM, Darwish M, Philip G, and El-Kammar MM (1990). Composition and origin of black shales from Quseir area, Red

Sea, Egypt. Journal of the University of Kuwait-Science, 17(1): 177-189.

- Hardy R (1988). X-ray powder diffraction of sediments. In: Tucker ME (Ed.), Techniques in sedimentology: 191-228. Blackwells, Oxford, UK.
- Heydari E, Wade WJ, and Anderson LC (1997). Depositional environments, organic carbon accumulation, and solar-forcing cyclicity in Smackover Formation lime mudstones, northern Gulf Coast. AAPG Bulletin, 81(5): 760-774.
- Ibad SM and Padmanabhan E (2018). Spectroscopic and petrographic characterization of shale from kubang pasu formation, Malaysia. Petroleum and Coal, 60(2): 321-329.
- Jones CR (1970). The geology and mineral resources of the Grik area, Upper Perak. Geological Survey Headquarters, Virginia, USA.
- Metcalfe I (2013). Tectonic evolution of the Malay Peninsula. Journal of Asian Earth Sciences, 76: 195-213. https://doi.org/10.1016/j.jseaes.2012.12.011
- Nayak PS and Singh BK (2007). Instrumental characterization of clay by XRF, XRD and FTIR. Bulletin of Materials Science, 30(3): 235-238. https://doi.org/10.1007/s12034-007-0042-5
- Nunez-Betelu L and Baceta JI (1994). Basics and application of rock-eval/toc pyrolysis and 58; An example from the uppermost Paleocene/lowermost Eocene in the Basque Basin, Western Pyrenees. Munibe Ciencias Naturales, 46(1): 43-62.
- Painter PC, Rimmer SM, Snyder RW, and Davis A (1981). A fourier transform infrared study of mineral matter in coal: The application of a least squares curve-fitting program. Applied Spectroscopy, 35(1): 102-106. https://doi.org/10.1366/0003702814731932
- Peters EJ (2006). Petrophysics. University of Texas at Austin, Austin, Texas, USA.
- Peters KE and Cassa MR (1994). Applied source rock geochemistry. In: Magoon LB and Dow WG (Eds.), The petroleum system—From source to trap: 93-120. American Association of Petroleum Geologists, USA.
- Peters KE, Kontorovich AE, Moldowan JM, Andrusevich VE, Huizinga BJ, Demaison GJ, and Stasova OF (1993). Geochemistry of selected oils and rocks from the central portion of the West Siberian Basin, Russia. AAPG Bulletin, 77(5): 863-887.
- Tate RB, Tan DNK, and Ng TF (2008). Geological map of peninsular Malaysia. Scale 1:1000000, Geological Society of Malaysia & University, Kuala Lumpur, Malaysia.
- Tissot BP and Welte DH (1984). Diagenesis, catagenesis and metagenesis of organic matter. In: Tissot BP and Welte DH (Eds.), Petroleum formation and occurrence: 69-73. Springer, Berlin, Germany. https://doi.org/10.1007/978-3-642-87813-8\_6
- Tuddenham WM and Lyon RJP (1960). Infrared techniques in the identification and measurement of minerals. Analytical Chemistry, 32(12): 1630-1634. https://doi.org/10.1021/ac60168a026
- Van der Marel HW and Beutelspacher H (1976). Atlas of infrared spectroscopy of clay minerals and their admixtures. Elsevier Publishing Company, Amsterdam, Netherlands.
- Washburn KE and Birdwell JE (2013). Multivariate analysis of ATR-FTIR spectra for assessment of oil shale organic geochemical properties. Organic Geochemistry, 63: 1-7. https://doi.org/10.1016/j.orggeochem.2013.07.007
- Wignall PB (1994). Black shales. No. 30, Oxford University Press, Oxford, UK.