Scientific Journal for the Faculty of Science-Sirte University Vol. 5, No. 1 (2025) 67-78

Scientific Journal for the Faculty of Science-Sirte University

Journal home page: http://journal.su.edu.ly/index.php/JSFSU/index

DOI: 10.37375/issn.2789-858X

Sulphur, Organic Carbon, Organic Nitrogen, Iron Relationships and Diagenesis of Black Shales in Tenom and Ranau Regions, West Sabah, Malaysia

Amer M. Burgan[1] *, Ramzi Jalgham[1] and Mahfoud Z. Aghanaya[1]

[1]*Department of Petroleum Engineering, Faculty of Engineering, Bani Waleed University, Libya*

DOI: https://doi.org/10.37375/sjfssu.v5i1.3039

ARTICLE INFO:

Received: 26 November 2024.

Accepted: 14 February 2025.

Published: 17 April 2025.

Keywords:

anoxic environment, carbonaceous sediments, Kerogen, pyrite framboids, Sulfur

ABSTRACT

This paper investigates the geochemical relationships and diagenesis of sulphur, organic carbon, nitrogen, and iron in Black Shales outcropping in Tenom and Ranau areas at Western part of Sabah state, Malaysia. The aims of this paper were to assess and investigate the various forms of (organic and inorganic sulphur), organic carbon, organic nitrogen, iron, total Sulphur, and pyrite Sulphur which was determined in two organic fractions (bitumen and kerogen) as well as in the total rock of these carbonaceous sediments, and also to assess the relationships between C, S, and N content in the early stage of microbial diagenesis of the studied black shales. The bulk geochemistry concentration, especially the C-S relationships, showed the important role of reactive iron in controlling the extent of pyrite formation. The degrees of pyritization (DOP) value of HCl–soluble iron is almost uniform in all the analyzed samples and have a value range from (average) 0.99 to 1.0, suggested that iron has been exhausted by pyrite formation. Kerogen appears to be uniform in N and S content, but both components vary in bitumen. N contents in bitumen show no covariance with any other parameters, but bitumen always has a much higher C/N ratio than kerogen. The presence of significant pyrite framboids of the samples studied is another additional evidence for poorly oxygenated (anoxic) bottom waters depositional environment.

1. Introduction

It is well published that there are three basic stages in the process of sedimentary pyrite formation, reaction of H_2S with iron minerals, transformation of black iron monosulphides (FeS type phases) to pyrite (FeS_2), and reduction of sulphate by bacteria. The three-Sulphur source is from seawater sulphate which diffuses into the sediments and is subsequently reduced to H_2S by bacteria. This process only occurs in anoxic conditions, which usually exist in sediments a few centimeters below the sediment-water interface, even when the overlying water is oxygenated.

The quantity of pyrite that can be formed in the sediments by sulphate reduction is determined by factors such as:

1) Redox conditions in the water column. Pyrite can only form in environments where sulphate reduction bacteria may function as obligate an aerobe.

2) Organic matter. Organic matter is required by sulphate-reduction bacteria as an energy source to reduce dissolved sulphate.

3) Diffusion of sulphate. Dissolved sulphate from overlying seawater is the major sulphate source for microbiological reduction.

Corresponding author: E-mail: ameribrahim565@gmail.com

4) Reactive iron. Iron is needed for the reaction of H_2S to form the initial iron sulphide precursor of pyrite. In most sediment, only a small proportion of the H_2S produced by sulphate-reducing bacteria is fixed as iron sulphides (Berner 1982).

The sedimentary pyrite may occur in a variety of textural forms; however, framboidal and euhedral cubic forms are generally the most abundant (Love & Amstutz 1966; Love 1967). Iron monosulphides are thermodynamically unstable and readily oxidize to sulphate when moisture and oxygen are available.

It is well established that an increase of sulphide Sulphur with depth arises as a result of microbiological diagenesis of sedimentary organic matter by sulphate reduction. The reduction of sulphate only occurs in anoxic conditions. By the other meaning, the depletion of dissolved oxygen is common in sediments which contain metabolizable organic matter and anoxic conditions frequently occur in marine sediments below the sediment-water interface.

The H_2S, which is the initial product of sulphate reduction, reacts with iron oxide phases to produce iron monosulphides, which are then transformed to pyrite (Goldhaber & Kaplan 1974).

The aims of this paper are to discuss the use of the various forms of (organic and inorganic Sulphur), organic carbon, organic nitrogen, iron, distributions in assessing the relationships, diagenesis and depositional environment of these black shale sediments.

2. Geological Setting

The Temburong Formation forms the oldest units on Labuan and is considered to be equivalent to the upper part of the Eocene to Oligocene, west Crocker Formation in the Sabah mainland and bult up the core of Labuan Island. (Lee 1977). The formation is flysch sequence predominantly of argillaceous rocks characterized by rhythmic repetition of siltstone and shale. From the nearly Padas River section, the Temburong Formation is known to be argillaceous facies of the sandy West Crocker Formation (Hutchison 2005). The other unit is made up of regular thinly interbedded turbidite sandstone, shale and claystone with laminations of lignite. Both the thin and thick-bedded turbidities contain abundant disseminated organic matter (Levell 1987).

The Trusmadi Formation occupies a broad belt of hilly to mountainous country, approximately 40 km wide, stretching from the southern and of the Trusmadi Mountains N-NE to Sungai Liwagu, they are described in the early memoir of Collenette (1965).

The main body of the Trusmadi Formation is bounded by N-S faults through Tenompok and Kundasan in the Kinabalu area (Hutchison 2005). The outcrop extends 65 km to the Keningau area. (Jacobson 1970), the Formation is well exposed SSW of Ranau, where the road near Kandasan, close to the entrance to the Kinabalu Natonal Park, also offers good exposures.

The Trusmadi Formation also underlies the Klias Peninsula, locally brought to the surface by structural complexity. The Trusmadi Formation is always in fault contact with the Crocker Formation. In general, the Trusmadi Formation lithologicaly resemble the Sapulut Formation, but has been subjected to low green schist facies metamorphism.

3. Materials and Methods

A total of thirty outcrop samples comprising shales, mudstone, siltstone, shaley mudstone and silty shale sediments representative of Temburong and Trusmadi formations, which are commonly carbonaceous and of Tertiary age, were collected from two different localities in West Sabah, Malaysia (Figure 1).

Samples denoted by Tr_1 to Tr_{15} refer to black shales representative of the Trusmadi Formation, collected from a locality approximately km 25 from the Bundu Tuhan junction towards Ranau. Samples denoted by Tm_1 to Tm_1 refer to black shales representative of the Temburong Formation, collected from the Tenom: Pangi-Dame hydroelectricity plant site.

Accessibility to all areas is quite good as most exposures are located at road cuts and quarries. All the study areas are linked by modern highways and branched roads leading to inland towns. Figures 2 and 3 are photographs illustrating the outcrop black shale sections from which the samplings of this study have been done.

Each sample was crushed to rock powder by a crushing machine to reduce the rock aggregate to fine particles by vibrating steel disc mills (Herzog, type: Hsm 100 A).

3.1 Rock-Eval Pyrolysis and Total Organic Carbon (TOC)

Rock–Eval pyrolysis measurement is used to assess the quantity and quality of organic matter of source rock. The analyses were done at Petronas Research Laboratory located in Bangi.

3.2 Scanning Electron Microscopy (SEM)

In this analysis, polished thin sections of black shales coated with an Au-pd conductor (Polaron SEM coating unite E 150) were examined morphologically under LEO 1450 VP (with link EDX, EDS) Scanning Electron Microscopy (SEM) at the Department of Science Biology, Universiti Kebangsaan Malaysia.

Energy-dispersive X-ray spectroscopy (EDX), sometimes called energy-dispersive X-ray analysis (EDXA) or energy-dispersive X-ray microanalysis (EDXMA), is an analytical technique used to determine which chemical elements are present in a sample (qualitative analysis) of a sample.

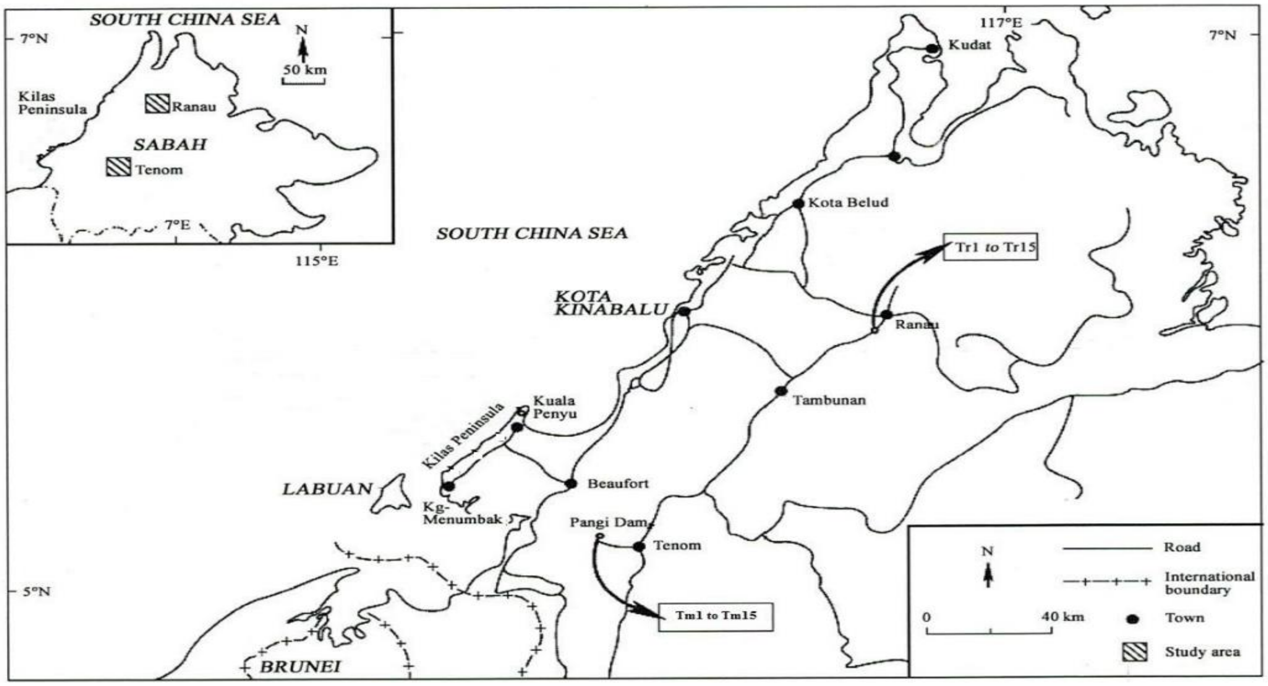

Fig. 1 Map of Sabah showing the location of the study areas in the Ranau and Tenom regions (Source: Leong 1999)

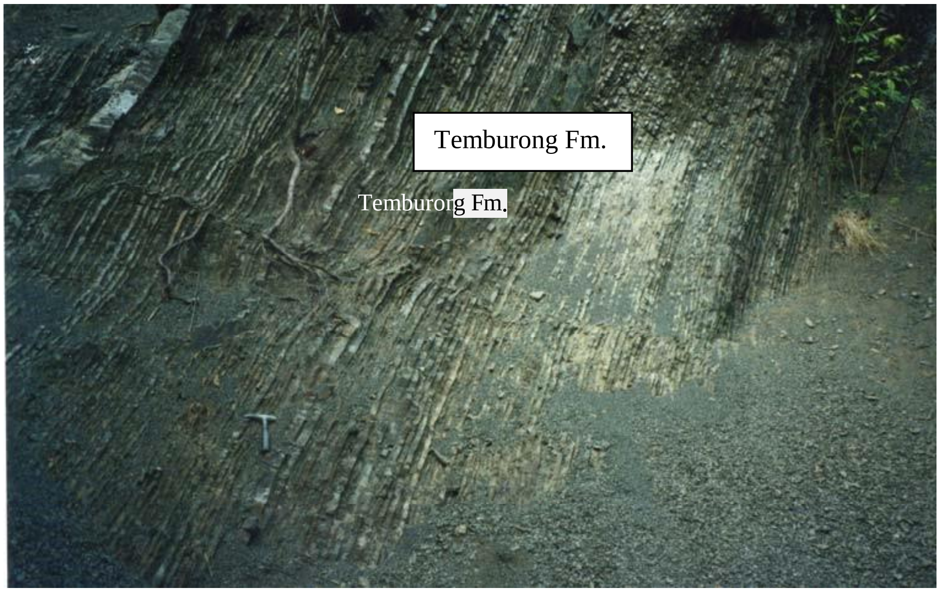

Fig. 2 Close view showing unconsolidated black shales interbedding with turbidite sandstone of Temburong Formation. Location: Pangi-Dame hydroelectricity plant, Tenom, West Sabah

Fig. 3 Photograph of Trusmadi Formation show massive, dark and well consolidated black shales. Location: Km 25 from the Bundu Tuhan junction towards Ranau. West Sabah

3.3 Sulphur Analysis

Sulphur occurs in sediments in several forms such as (FeS_2, FeS, $SO_4^{=}$, S^0 and organic Sulphur). Thus, for this reason quantitative separation of Sulphur is necessary in order to determine the precise amount present in each specie.

3.3.1 Total Sulphur (S-total) (adopted from Maxwell, 1968).

In this method about 1.0g of dried sample was digested in a 5ml mixture of bromine and carbon tetrachloride (two parts by volume of Br_2 and three parts CCl_4) for 15 minutes. Next, 10 ml of concentrated HNO_3 was added and left for 15 minutes at room temperature and evaporated to dryness. About 2 ml of 12N HCl and 50ml water were added to the residue, which was left to stand for one minute before being boiled for 5 minutes. After cooling, about 0.5 g of high-grade purity Zn powder was added to reduce ferric iron. After filtration (Whatman No 40), the filtrate was diluted to 250ml with distilled water and a further 2ml of 12N HCl. After boiling the solution, 25ml of hot 5% $BaCl_2$ were added dropwise with thorough stirring. The mixture was heated on a hot plate with occasional stirring for at least one hour and then left overnight. The $BaSO_4$ was collected on a weighted Millipore 0.22-micron filter (dried in an oven at 110^0C for about 4 hours) and weighted again to constant dryness.

3.3.2 Pyrite Sulphur. S - FeS2

In this method the chromous chlorid was utilized as a reducing agent, which is specific for reduced Sulphur (e.g. elemental Sulphur, monosulphides and pyrite Sulphur, but not organic Sulphur or sulphate Sulphur). Pyrite Sulphur was reduced to H_2S by digestion in an atmosphere, absorbed as ZnS in zinc acetate and titrated iodometrically.

3.3.3 Bitumen Extraction and Fractionation

Approximately 60-80g of some selected powdered samples was extracted in Soxhlet apparatus using a dichloromethane/methanol mixture (93:7) for 75 hours.

3.3.4 Organic Sulphur ($S_{org.}$)

The organic Sulphur was determined by using Soxhlet apparatus as a bituminous Sulphur (soluble fraction) and Kerogen Sulphur (insoluble fraction).

3.3.5 Bituminous Sulphur (Soluble Bituminous Fraction) $S_{bit.}$

The bituminous fraction was digested with Br_2 and CCl_4, as described earlier in the total Sulphur section. Due to the low concentration of Sulphur in this fraction, the solution containing oxidized Sulphur ($SO_4^{=}$) was not collected by $BaSO_4$ precipitation; instead, the solution was made to an accurate volume (250ml) and analyzed by ion chromatography available at the Chemistry Department, Universiti Kebangsaan Malaysia.

3.3.6 Elemental Sulphur S^o (In Bituminous Fraction)

In this method, chip of pure copper gauze (0.5g) is placed in the collecting flask of the Sohxlet apparatus in order to react with elemental sulphur during extraction. After filtration, the CuS formed is oxidized by Br_2/CCl_4 (following the procedure described under total sulphur) and analyzed by ion chromatography.

Due to the very low concentrations of elemental sulphur, blank solutions were also run and were found to be free of sulphur. The values presented here are in part per million (ppm).

3.3.7 Insoluble Fraction (Total Sulphur)

The insoluble fraction contains a mixture of Kerogen and Pyrite Sulphur. In this analysis the powder from the Soxhlet extraction was dried in an oven (105^0C) overnight. About 0.2g of dried samples was digested in a 5ml mixture of bromine and carbon tetrachloride (two parts by volume of Br_2 and three parts CCl_4) for 15 minutes. Next, 10ml of concentrated HNO_3 was added and left for 15 minutes at room temperature and was evaporated to dryness.

About 2 ml of 12N HCl and 50ml water were added to the residue, which was left to stand for one minute before being boiled for five minutes. After cooling, about 0.5g of high-grade purity Zn powder was added to reduce ferric iron. After filtration (Whatman No 40), the filtrate was diluted to 250ml with distilled water and a further 2ml of 12N HCl. After boiling the solution, 25ml of hot 5% $BaCl_2$ were added dropwise with thorough stirring.

The mixture was heated on a hot plate with occasional stirring for at least one hour and then left overnight. The $BaSO_4$ was collected on a weighted millipore 0.22-micron filter (dried in an oven at 110^0C for about 4 hours) and weighted again to constant dryness.

3.3.8 Kerogen Sulphur (S_{ken})

The values of kerogen sulphur were obtained by subtracting the total sulphur value (Kerogen + Pyrite sulphur) from the value of Pyrite Sulphur, i.e. Kerogen Sulphur = [(Kerogen + Pyrite sulphur) – Pyrite Sulphur].

3.4 Iron Analysis 3.4.1 Acid Soluble Iron (HCl-Soluble Iron)

In this technique about 0.5g dried black Shales sediments was treated with 15 ml 12N HCl, and boiled in a water bath for about one minute. After cooling, the mixture was filtered using filter paper (Whatman No 42), and then the filtrate diluted with distilled water to 100ml. Finally, the concentration of Iron was determined by using Atomic Absorption Spectrometry (AAS) available at the Geology Department, Universiti Kebangsaan Malaysia.

3.4.2 Free Iron (Sodium Dithionate Soluble Iron)

In this technique the iron was determined by using sodium dithionate extraction and the measurement of the iron present in the studied samples was in the form of iron Sulphide. The samples were treated with 0.1 N HCl for about 30 minutes to remove the carbonate phase.

After filtration, the residue was dried in an oven overnight. About 0.5g residue was accurately weighed and mixed with 2g Sodium dithionate ($Na_2S_2O_4$) in a 250ml conical flask. Then 10ml of citrate buffer solution (10mm citric acid, 0.05% Tween 20, ph 6.0) and 75ml distilled water were added to the mixture, before shaking for about four hours.

The citric buffer solution was made by dissolving 1.92g of citric acid in 1000ml distilled water after adjustment of the pH to 6.0 with 1N NaOH and 0.5ml Tween 20.

After filtration (Whatman No 42) the filtrate was made up to 250ml with distilled water and the concentration of the iron content, also known as free iron or dithionate soluble iron, were analyzed by using atomic absorption spectrometry (AAS).

3.5 Organic Carbon and Organic Nitrogen

The determination of the concentration of organic C and N in the studied samples were carried out using a LECO CHNS-932 instrument available at the Geology Department, University Kebangsaan Malaysia. In this technique the samples were placed inside a silver capsule and completely combusted at a heat temperature of 1000°C.

3.6 Determination of the Concentration of C and N in Kerogen Fraction

The Kerogen fraction was only analyzed for C and N by a LECO CHNS-932 analyzer at 1100ºC after the sample have been dried in an oven at 110ºC.

3.7 Determination of the Concentration of C, N and H in Bituminous Fraction

The bitumen fraction was evaporated to dryness at room temperature and a small portion was removed to determine the concentration of C, N, and H by a LECO CHNS-932 analyzer at 1100ºC.

3.8 Separations of Organic Carbon from in Organic Carbon

Since the sediments contain Carbon present at the inorganic and organic phases, some type of separation is necessary. In this study the determination of the Organic C content was performed using the Krom and Berner (1983) technique.

The separation is done by combustion of the sample to (1350ºC) in a stream of oxygen for a first total carbon determination. Then the organic Carbon is removed from a separate subsample by ashing (450ºC) and the second combustion (at 1350ºC) determines the Carbonate (inorganic) Carbon. The difference between the two values is equivalent to the organic Carbon content.

4. Results and Discussions

The Tertiary black shales of West Sabah were analyzed to determine various forms of (organic and inorganic Sulphur), organic carbon, organic nitrogen, iron, total Sulphur, and pyrite Sulphur which was determined in two organic fractions (bitumen and kerogen) as well as in the total rock.

The whole rock composition of the Trusmadi and Temburong samples is shown in Table 1 and the composition of the soluble organic phase (bitumen) and insoluble organic phase (kerogen) in Table 2.

4.1 Framboidal and euhedral pyrite

The sedimentary pyrite may occur in a variety of textural forms; however, framboidal and euhedral cubic forms are generally the most abundant (Love & Amstutz 1966; Love 1967). In This task the analysed samples of the Trasmadi and Tembourng formation by SEM display significant amounts of Framboidal and euhedral pyrite (Figures 4A & 5A).

The EDX spectrum (Figures 4B & 5B) display peaks of elements S & Fe atoms which confirmed elemental composition of pyrite minerals in the study samples.

Goldhaber & Kaplan (1974) suggest separate pathways of framboidal and euhedral pyrite formation, depending on metastable iron sulphide intermediates. Any pathways forming euhedral and framboidal pyrite require elemental Sulphur if intermediate iron monosulphides are involved. Berner (1970) and Sweeney & Kaplan (1973) conclude that the formation of pyrite occurs by addition of Sulphur to the FeS precursor rather than loss of Fe.

Thus reaction (2) above can provide both Fe^{2+} and S^0 for the formation of pyrite. This is consistent with the report by Berner (1964) which states that elemental Sulphur accounts for an appreciable fraction of the total Sulphur in the near surface sediments and decreases rapidly with depth. Goldhaber et al. (1977) state that elemental Sulphur can also be formed by the oxidation of FeS.

The FeS in sediments may be easily oxidized during bioturbation and is transformed to iron oxide and elemental Sulphur in a matter of minutes to hours.

4.2. Total Sulphur (S-total)

The distribution of total Sulphur in the black shales of this study (Table 1) reveals gradual increases in the concentration of this Sulphur form with depth and time (i.e. from younger to older sequences) implying that the diagenetic addition of reduced Sulphur is taking place in the sediment column.

The measured total Sulphur (average) of the Trusmadi and Temburong formations is 3.88 and 1.44 respectively and could also include sulphate Sulphur. The high sulphate Sulphur values must be due to the oxidation of iron sulphides, especially iron monosulphides (FeS).

The reduced Sulphur in the study samples increases with burial depth and time, from low values in the samples of the Temburong Formation, and reaches a maximum at the samples of the Trusmadi Formation. This pattern suggests the continuous diagenetic addition of reduced Sulphur under conditions where the time and depth of burial are related (Berner 1980).

Such depth and time parameters of increasing sulphur content have also been described in many different marine depositional environments, e.g. shelf environment (Filipek & Owen, 1980), marine basins (Goldhaber & Kaplan 1980) and brackish water (Jorgensen 1978).

All these environments show increases in sulphide with depth in sediments which have no evidence of reworking apart from bioturbation. It is concluded that the diagenetic gradient of increasing sulphide in the

Tertiary black shales sediment of West Sabah from younger to older sequences is most reasonably explained as a result of diagenesis in a burial depth/time sequence.

4.3 Carbon Sulphur Relationships (C/S ratio)

Under steady-state conditions of diagenesis, pyrite gradually increases with depth to reach a maximum concentration, below which it is uniformly abundant (Mohamed Md. Tan 1985). Since organic matter must be consumed to form pyrite, it is expected that organic concentration, below which it is uniformly abundant (Mohamed Md. Tan 1985). Since organic matter must be consumed to form pyrite, it is expected that organic carbon will decrease with depth and become uniform roughly at the same point as pyrite.

The C/S ratio of the analysed samples (Table 1) show that the C/S ratio (average) of the Trusmadi and Temburong formations is of 0.26 and 0.46 respectively.

The decrease of C/S ratio in these sediments implies that there are variations in the amount of organic carbon being deposited at different horizons, thus involving the ratio of C/S changes continuously with sulphate reduction.

Pore water sulphate in the sediments is reduced to H_2S and HS- by bacteria using metabolisable organic matter, as in the following reaction:

$$2CH_2O + SO_4^{=} \longrightarrow H_2S + 2HCO_3^{-}$$

The dissolved sulphide then reacts with iron minerals to form iron monosulphides and subsequently pyrite. The equation suggests that reduced sulphur organic carbon should be inversely correlated. However, modern sediments show a good positive correlation between sulphide sulphur and organic carbon (Goldhaber & Kaplan 1974) with a mean of approximately 2.8.

In modern marine environments the metabolisable organic matter undergoes oxic degradation in the water column, and so the remaining organic matter is more refractory to sulphate reduction.

Thus, the proportion of readily metabolisable organic matter is the main factor limiting pyrite formation and the existence of reasonably good correlation between organic carbon and sulphur in marine sediments suggests that the proportion of readily metabolized materials remains roughly constant.

Hence, even where there are variations in the amount of organic carbon being deposited at different horizons, the ratio of C/S changes continuously with sulphate reduction. Therefore, consumption of organic carbon and accumulation of sulphide sulphur will cause decreasing C/S ratios with depth. Such variations have been observed in a variety of different depositional environments (Filipek & Owen, 1980, Goldhaber & Kaplan, 1974). It can be concluded that the existence of a decreasing C/S profile indicates that the Trusmadi and Temburong samples have been reworked at their site of deposition, and they may not represent a continuous depth/time sequence.

4.4 Carbon Nitrogen Relationship (Molar C/N ratio)

The C/N ratios of the study samples (Table 1) show that the average C/N ratios of the Trusmadi and Temburong formations are 8.23 and 4.6 respectively, suggesting that these sediments have undergone a continuous diagenetic modification and so represent a depth/time sequence.

Sediments with significant contributions of inorganic nitrogen may also show decreasing C/N trends with depth (Muller 1977) as organic C and organic N are removed but inorganic ammonia remains unaffected.

The relatively low C/N ratios of the Temburong and Trusmadi samples are probably due to the contributions of nitrogen from inorganic ammonium (fixed in the clay minerals) and the preservation of organic N compounds absorbed by clay minerals (especially montmorillonites) which are protected against microbiological attack.

The presence of these resistant forms of N is one of the main reasons why the C/N ratios are low in these sediments. The Temburong Formation sediments are found to be in the range of diatoms (4.7-6.4) and average plankton (approximately 6), as reported by Muller (1977). This indicates that the ultimate source of organic matter buried in the sediment is probably from the water column flora and fauna; these organisms might have originated from in situ biomass or might be brought in by the circulation from other sites.

4.5 Iron and Degree of Pyritization (DOP)

Iron plays a major rule in the formation of pyrite in black shale marine sediments. In certain circumstances, the concentration and reactivity of iron compounds can be one of the principle limiting factors on pyrite formation. Natural surface water contains negligible amounts of dissolved iron (3.4 ppm of iron at 35/mil salinity; Wedepohl et al. (1969).

Furthermore, the concentration of iron in most organic material is also low. Detrital and skeletal carbonates also contain, and are associated with, only small proportions of iron (Berner, 1972 and 1984). Thus, most previous workers have concluded that clay minerals are the main source of iron for pyritization (Goldhaber & Kaplan, 1975).

In most sediments, iron is present in a variety of forms; as a water solution species, an exchangeable cation, a non-exchangeable organic complex, as hydrated oxides and as a lattice constituent in different minerals (Mohamad Md Tan 1985).

The fine-grained reagents hematite, limonite, goethite and chlorite were completely dissolved in hot 12N HCl, which did not attack pyrite. Thus, it is possible to define a degree of pyritization (DOP) (Berner 1970).

$$\text{DOP} = \text{Fe-FeS} + \text{Fe-pyrite} / \text{Fe-pyrite} + \text{Fe-HCl}$$

Sediments which are iron limited may be expected to have DOP values close to 1.0 provided HCl and H_2S reactivities are indeed similar.

In this study, two types of iron determination were carried out. Firstly, iron was determined by solution in hot concentration HCl using the technique of Berner (1970).

The values of iron (Table 1) so obtained probably include all the iron in the detrital phases, plus iron originally and present as FeS, but are unlikely to include iron from pyrite. Thus, this treatment removes essentially all acid-extractable iron.

The DOP of this type of iron determination was calculated according to the above relation. Secondly, iron was also extracted using sodium dithionate and this is considered to be iron present only as oxide. This technique is commonly used to measure the free iron oxide content of soil (Bromfield & William 1963).

The calculation of DOP (dithionate soluble iron) is according to the following equation:

$$\text{DOP} = \text{Fe-FeS} + \text{Fe-pyrite} / \text{Fe-FeS} + \text{Fe-pyrite} + \text{Fe-Dithionate}.$$

There is a slight difference in the calculation of the DOP values for the two forms of iron. For HCl-soluble iron, the equation does not contain monosulphide iron which is present in dithionate-soluble iron. Monosolfides is easily dissolved in hot concentrated HCl but is likely to be dissolved in the dithionate extraction.

Table 1 clearly shows the HCl-soluble iron is relatively constant with depth/time for all the study rock units.

The degrees of pyritization (DOP) value of HCl–soluble iron is almost uniform in all the analyzed samples and appear to have a value range from (average) 0.99 to 1.0 (Table 1), suggesting that iron is the limiting factor for pyrite formation.

4.6 Sulphur Relationship in Kerogen and Bitumen Fractions

Kerogen in the Trusmadi and Temburong samples (Table 2) appear to vary in the C/N and C/S ratios. The links between bitumen and kerogen is approximately 10 times more abundant than bitumen and its composition is less precisely known. The observed changes in bitumen composition may be accompanied by corresponding changes in kerogen composition which are too small to be detected. Links between bitumen and rock composition will therefore be mainly considered, initially in respect of Sulphur speciation. Two types of Sulphur (H_2S and S^0) are available to be picked up by sedimentary organic matter.

Considering kerogen, it is possible that H_2S reacted with the Trusmadi and Temburong kerogen after reactive iron became exhausted (at threshold DOP of about 0.99). Thus, although there is no linear correlation between kerogen sulphur and the elemental sulphur in the sediments of Temburong Formation (Figure 6) this is not considered to be a causal link arising from the reaction of elemental sulphur with kerogen.

The changes in S^0 are too small to be responsible for the changes in kerogen sulphur, even if it could be demonstrated that the latter was not assimilated. It is concluded that, for the reasons given above, the present data can give no unequivocal evidence for the origin of kerogen Sulphur.

The composition of kerogen and bitumen are given separately in Tables 2 and 3. It should be noted that the value of kerogen sulphur is obtained by the difference between total sulfur and pyrite Sulphur ($S\text{-}_{kerogen} = S\text{-}_{total} - S\text{-}_{pyrite}$).

The whole rock content of organic carbon and organic nitrogen in the Trusmadi and Temburong samples are plotted in separate graphs (Figure 8) and can also be seen to be weakly-correlated in the case of Trusmadi samples ($r = 0.34$), and there is no linear correlation in the case of samples from Temburong formations.

The same samples after Soxhlet extraction - that is, in the kerogen fraction (Figures 7 & 8) - are also weakly correlated in organic carbon and organic nitrogen in the case of the Trusmadi samples ($r = -0.81$), and do not show linear correlation in the cases of the Temburong samples. This is to imply that the bitumen fraction does not contain any significant amount of nitrogen in these study samples.

5. Conclusion

The measured total Sulphur (average) of the Trusmadi and Temburong formations, illustrate gradual increases in the concentration of this Sulphur form Temburong to Trusmadi Formation.

The pattern suggests also the continuous diagenetic addition of reduced Sulphur is taking place in the sediment column, under conditions where the time and depth of burial are related, and could also include sulphate Sulphur.

Kerogen fraction appears to be uniform in N & S content, but both components vary in bitumen, however, N contents in bitumen fraction show no covariance with any other parameters, but bitumen always has a much higher C/N ratio than kerogen.The presence of a diagenetic gradient in these study sediments is indicated by the low C/N & C/S ratios and increasing sulphide from younger to older sequences.

The average C/N ratios of the Trusmadi and Temburong formations are 8.23 and 4.06 respectively, suggesting that these sediments have undergone a continuous diagenetic modification and so represent a depth/time sequence.

The low C/N ratios of the Temburong and Trusmadi formations are probably due to the contributions of nitrogen from inorganic ammonium (fixed in the clay minerals) and the preservation of organic N compounds absorbed by clay minerals (especially montmorillonites) which are protected against microbiological attack.

The presence of these resistant forms of N is one of the main reasons why the C/N ratios are low in these sediments.

The decrease in the C/S ratio of these sediment implies that there are variations in the amount of continuously with sulphate reduction organic carbon being deposited at different horizons, thus involving the ratio of C/S changes.

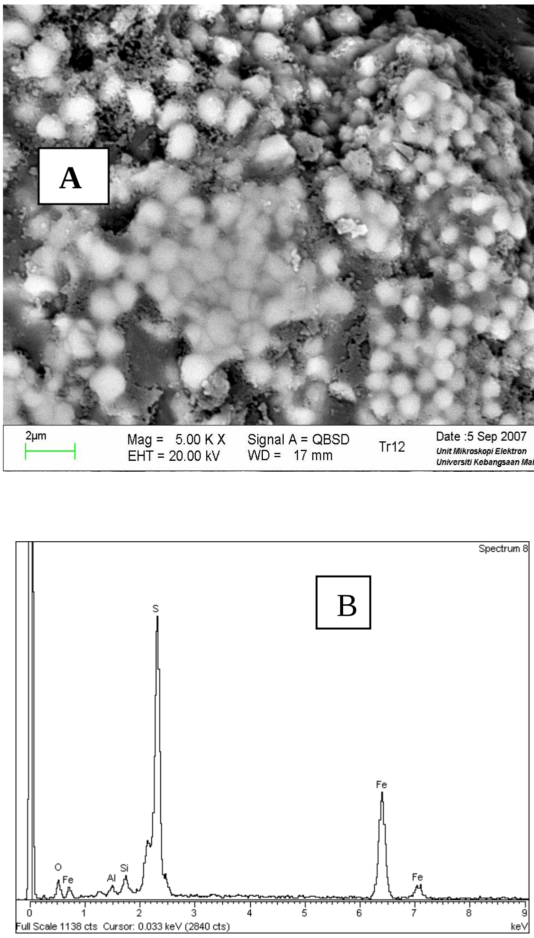

Fig. 4. A) SEM of sample Tr12 showing framboids pyrite. B) Energy dispersive X-ray spectrum (EDX) of pyrite

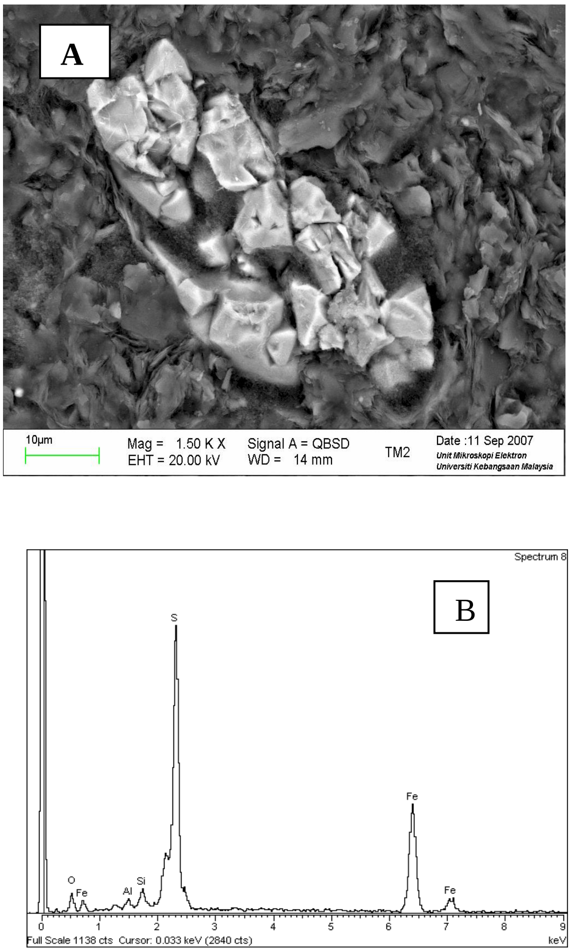

Fig.5. A) SEM of sample Tr12 showing euhedral pyrite. B) Energy dispersive X-ray spectrum (EDX) of pyrite

Table 1. chemical composition of Tertiary black shale in West Sabah

A) Trusmadi Formation

Sam. No.	%Org. C	%Org. N	% HCl-Sol. Iron	%Free Iron	DOP HCl-Sol.Iron	%Tot. S	% Pyrite	S^0 ppm	% S bit.	% S keg.	C/N	C/S
Tr$_1$	0.78	0.084	0.011	0.003	0.99	1.78	1.3	0.37	0.02	0.48	9.26	0.44
Tr$_5$	0.89	0.100	0.008	0.002	1.00	3.36	3.2	0.63	0.03	0.13	8.90	0.26
Tr$_7$	0.55	0.061	0.008	0.001	1.00	3.37	3.1	0.58	0.02	0.25	9.02	0.18
Tr$_8$	0.72	0.084	0.009	0.001	0.99	3.13	3.0	0.43	0.02	0.12	8.57	0.24
Tr$_9$	0.57	0.073	0.010	0.001	1.00	3.23	3.0	0.42	0.02	0.11	7.81	0.19
Tr$_{13}$	0.67	0.114	0.007	0.002	1.00	3.25	3.1	0.73	0.02	0.13	5.80	0.22
Average	**0.70**	**0.086**	**0.011**	**0.002**	**1.00**	**3.58**	**2.8**	**0.53**	**0.02**	**0.20**	**8.23**	**0.26**

B) Temburong Formation

Sam. No.	%Org. C	%Org. N	%HCl-Sol. Iron	%Free Iron	DOP HCl-Sol.Iron	%Tot. S	%Pyrite S	S^0 ppm	% S bit.	% S keg.	C/N	C/S
Tm$_1$	0.41	0.076	0.009	0.003	0.99	2.31	1.2	0.56	0.01	1.10	5.39	0.18
Tm$_3$	1.32	0.091	0.028	0.001	0.97	1.39	1.0	1.40	0.01	0.38	13.5	0.95
Tm $_4$	0.35	0.100	0.009	0.003	0.99	1.26	0.9	1.60	0.02	0.34	3,50	0.28
Tm$_{10}$	0.45	0.187	0.013	0.002	0.99	1.18	1.0	0.56	0.01	0.17	2.14	0.38
Tm$_{11}$	0.44	0.118	0.012	0.001	0.98	0.80	0.7	0.58	0.04	0.06	3.37	0.55
Tm$_{12}$	0.40	0.068	0.011	0.002	0.99	0.90	0.8	0.53	0.01	0.09	5.88	0.40
Average	**0.56**	**0.110**	**0.013**	**0.002**	**0.99**	**1.44**	**0.9**	**0.87**	**0.02**	**0.17**	**4.06**	**0.46**

Table 2 Composition of the kerogen fraction

Sample No.	%C	%H	%N	%S	C/N	C/S
Trusmadi Fm.						
Tr1	0.77	0.555	0.173	0.106	4.46	7.28
Tr5	0.99	0.484	0.092	0.159	10.74	6.21
Tr6	1.18	0.545	0.060	0.149	19.72	7.94
Tr7	0.73	0.615	0.142	0.151	5.12	4.81
Tr13	0.97	0.601	0.133	0.190	7.27	5.09
Average	0.92	0.560	0.120	0.151	9.462	6240
Temburong Fm.						
Tm1	0.45	0.604	0.048	0.091	9.29	4.90
Tm3	1.16	0.545	0.092	0.081	12.55	14.26
Tm4	039	0.572	0.049	0.098	7.96	3.98
Tm10	0.41	0.538	0.146	0.020	2.86	20.70
Tm11	0.39	0.559	0.082	0.020	4.78	19.60
Tm12	0.40	0.560	0.053	0.035	7.45	11.29
Average	**0.53**	**0.568**	**0.098**	**0.054**	**8.27**	**12.45**

n.d; not determind

Sample No.	%C	%H	%N	%S	%O	C/N	C/S
Trusmadi Fm.							
Tr$_1$	n.d	n.d	n.d	n.d	n.d	n.d	n.d
Tr$_5$	-	-	-	-	-	-	-
Tr$_6$	-	-	-	-	-	-	-
Tr$_7$	-	-	-	-	-	-	-
Tr$_{13}$	-	-	-	-	-	-	-
Temburong Fm.							
Tm$_1$	73.86	8.74	1.24	0.41	15.72	60	180
Tm$_3$	85.85	9.15	1.68	0.50	02.82	51	172
Tm$_4$	75.08	8.16	1.17	0.44	15.15	64	171
Tm$_{10}$	66.88	6.98	1.68	0.61	23.85	40	110
Tm$_{11}$	77.78	7.34	1.87	0.41	12.63	42	190
Tm$_{12}$	n.d	n.d	n.d	n.d	n.d	n.d	n.d
Average	**75.89**	**8.07**	**1.53**	**0.47**	**14.03**	**51**	**165**

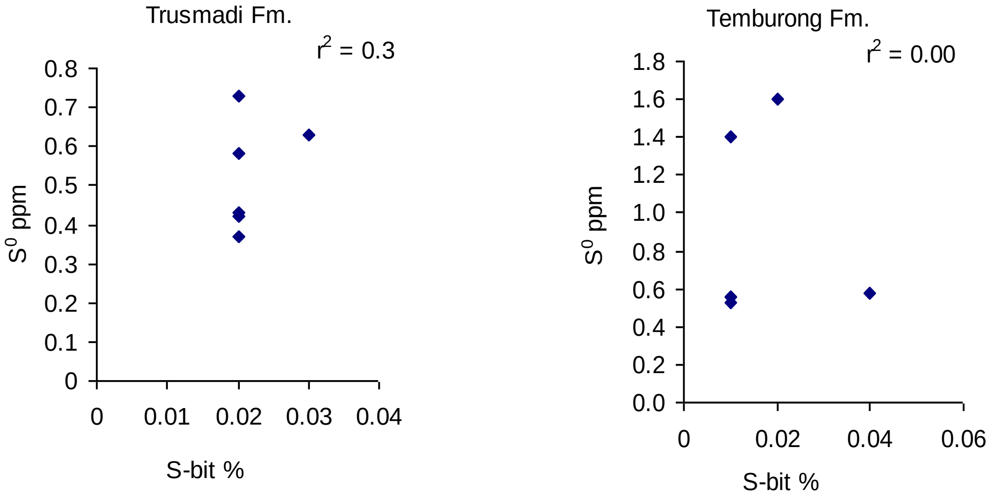

Fig. 6. Relationship between the Sulphur content of bitumen and elemental Sulphur (S^0)

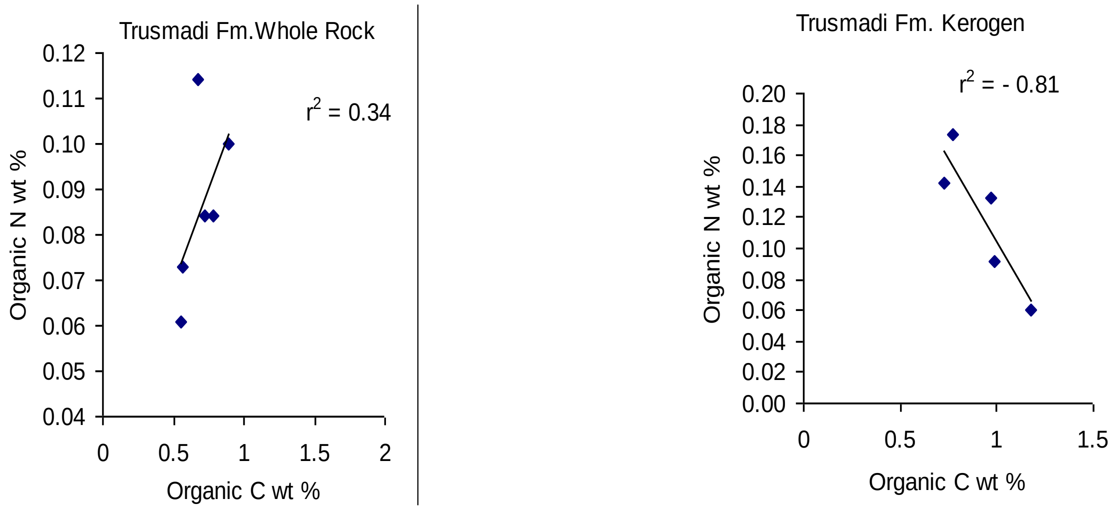

Fig. 7. Relationship between organic carbon and organic nitrogen of Trasmadi Formation

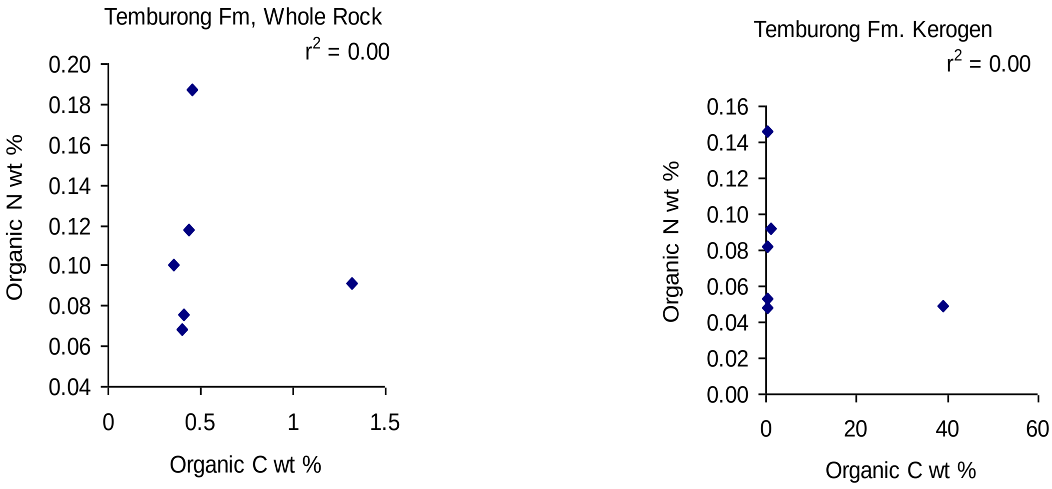

Fig. 8. Relationship between organic carbon and organic nitrogen of Temburong Formation

Conflict of interest:

The authors declare that there are no conflicts of interest

References

Berner, R. A. (1964). Distribution and diagenesis of sulfur in some sediments from the Gulf of California. *Marine Geology*, *1*(2), 117–140. https://doi.org/10.1016/0025-3227(64)90011-8

Berner, R. A. (1970). Sedimentary pyrite formation. *American Journal of Science*, *268*(1), 1–23. https://doi.org/10.2475/ajs.268.1.1

Berner, R. A. (1972). Sulfate reduction pyrite formation and the oceanic budget. In Dyrssen, D. & Janger, D. (ed.) *Nobel Symposium 20, the changing Chemistry of the Ocea*n. Almquist and Wiksell, Socholm. 437-361.

Berner, R. A. (1980). *Early Diagenesis and Theoretical Approach*. Princeton Univ. Press.

Berner, R. A. (1984). Sedimentary pyrite formation: An update. *Geochimica Et Cosmochimica Acta*, *48*(4), 605–615. https://doi.org/10.1016/0016-7037(84)90089-9

Bromfield, S. M., & Williams, E. G. (1963). An examination of the biological reduction method for estimating active iron in soils. *Journal of Soil Science*, *14*(2), 346–359. https://doi.org/10.1111/j.1365-2389.1963.tb00958.x

Collenette, P., (1965). The geology and mineral resources of the Pensiabgan and Upper Kinabatangan area, Sabah, Malaysia. *Geological Survey Borneo Region, Malaysia*, *Memoir* 12.

Filipek, L. H. & Owen, R. M. (1980). Early diagenesis of organic carbon and sulphur in the outer shelf sediments from the Gulf of Mexico. *American Journal of Science* 280:1097-1112.

Goldhaber, M. B. & Kaplan, I. R. (1975). Controls and consequences of sulfate reduction rates in recent marine sediments. *Soil Science* 119:42-55.

Goldhaber, M. B.& Kaplan, I. R. (1980). Mechanism of sulphur incorporation and isotope fractionation during early diagenesis in sediments of the Golf of California. *Marine chemistry* 9: 95-143.

Goldhaber, M. B., Aller, R. G., Cochran, J. K., Rosenfeld, J. K., Martens, C. S. & Berner, R. A. (1977). Sulphate reduction, diffusion and bioturbation in Long Island Sound sediments. Report of the Foam group. *American Journal of Science* 277: 193-237.

Goldhaber, M. B., and Kaplan, I. R. (1974). The sulphur cycle. In Goldberg, E. D. (ed.). *The Sea* 5, Willey, New Yourk 569-655.

Hutchison, C.S. (2005). *Geology of North-West Borneo: Sarawak, Brunei and Sabah.*Hydrocarbons of biological origin from one- billion-year sediments.

Jacobson, G. (1970). Gunong Kinabalu area, Sabah, Malaysia. *Geological Survey of Malaysia Report*, *8.*

Jorgensen, B. B. (1978). A comparison of methods for the quantification of bacterial sulfate reduction in coastal marine sediments. *Geomicrobiology Journal*, *1*(1), 11-27.

Lee, C. P. (1977). The geology of Labuan Island, Sabah, East Malysia. BSc. *Thesis*. University of Malaya, Malaysia.

Leong, K. M. 1999. Geological setting of Sabah, In Petronas (ed.). *The Petroleum Geology and Resources of Malaysia*. pp.675–497.

Levell, B. (1987). The nature and significance of regional unconformities in the hydrocarbon-bearing Neogene sequence offshore West Sabah. *Bulletin of the Geological Society of Malaysia*, *21*, 55–90. https://doi.org/10.7186/bgsm21198704

Love, L. G. (1967). Early diagenetic iron sulphide in recent sediments of the Wash (England). *Sedimentology*, *9*(4), 327-352.

Love, L. G. & Amstutz, G. C. (1966). Review of microscopic pyrite. *Fortschritte der Mineralogie*, *43*, 273-309.

Mohamed MD Tan, 1985. *Aspects of carbon, Nitrogen and Sulphur Diagenesis in sediments*. PhD thesis. University of East Anglia.

Müller, P. J. (1977). CN ratios in Pacific deep-sea sediments: Effect of inorganic ammonium and organic nitrogen compounds sorbed by clays. *Geochimica et Cosmochimica Acta*, *41*(6), 765-776.

Sweeney, R. E. & Kaplan, I. R. (1973). Pyrite framboid formation: Laboratory synthesis and marine sediments. *Economic Geology* 68: 618-634.

Wedepohl, K. H. (1969). *Handbook of Geochemistry*. Vol 1 SpringerVerlag, Berlin, p 4