

GEOCHEMICAL ASSESSMENT OF THE PETROLEUM SOURCE ROCK POTENTIAL IN LOWER SHIRE BASIN (MALAWI)

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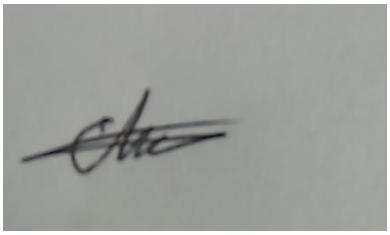
THYOLO, MALAWI

DISSERTATION SUBMITTED TO NDATA SCHOOL OF CLIMATE AND EARTH SCIENCES OF THE MALAWI UNIVERSITY OF SCIENCE AND TECHNOLOGY IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE BACHELOR OF SCIENCE DEGREE IN PETROLEUM GEO-SCIENCE

28 April 2023.

DECLARATION

I Christopher Longwe declare that this research project is my original work and has not been presented elsewhere for examination for award of degree or publication. Where other (researchers')work has been used, this has been a knowledge and cited in accordance with the Malawi university of science and technology.



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Date: 28th April 2023.

DISSERTATION APPROVED BY:

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ABSTRACT

One of the essential steps in hydrocarbon exploration and exploitation is to understand the source rock evolution and the related petroleum system. Understanding how and where hydrocarbons were originated, help to comprehend, and predict where they can be discovered. Geochemical source rock evaluation provides valuable information ready to be used for upgrading areas under investigation, concentrating exploration activities in particular places and reducing risks .

This study involved use of geochemical parameter (TOC, HI, OI, PP, GP, S2, S1 etc.) which was delivered from rock eval pyrolysis process to classify organic matter richness, kerogen types and their thermal maturity of hydrocarbons present in the collected rock samples. Geochemical analysis of the surface cretaceous sedimentary rocks was undertaken to understand oil and gas potentially of the petroleum source rocks in the lower shire river, based on the case study on the two basins namely, Lengwe and Mwabvi.

Shire basin is located within middle east Africa, and it is made up of perma-Triassic and cretaceous sedimentary rocks and intruded by a variety of alkaline rocks of Jurassic to cretaceous age. It is located within eastern Africa rifting valley that was developed and is associated with the rifting process.

Geochemical methodology approach has been used in assessment of petroleum source rocks whereby data collected from eval rock pyrolysis process has been used. Excellent organic matter richness has been measured in each rock sample as indicated by high TOC values which is of greater than 2wt%.Very poor and fair petroleum potential has measured for the samples indicated by very low S1 and S2. Many samples have shown to be in post-maturity window , two samples are in mature and one in immature window hence giving hope and encourage for some more exploration to be conducted in the area. Thus, a considerably amount of petroleum that has already been generated from them, type 1v kerogen have been reported for all samples, indicating inactive source rocks.

Keywords: geochemical evaluation, organic matter, kerogen, maturity, petroleum potential, predictive model.

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My thanks go to all the people who have supported me to complete the research work directly or indirectly. Above all, The Almighty God, through His love and grace, predestined my academic journey which today I cherish. Thanks.

DEDICATION

This research I dedicate to God, my family and department of earth sciences, Malawi university of science and technology for their unrelenting support and confidence in my ability to distinctively demonstrate scientific knowledge in the fields of oil and gas,

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List of Abbreviation

HI – Hydrogen Index

OI – Oxygen Index

PP – Petroleum Potential

TOC – Total Organic Carbon

TOM – Total Organic Matter

CHAPTER 1

1.0 INTRODUCTION

1.1 Background

Exploration of hydrocarbon is essential for a country's prosperity and economy. The unconventional hydrocarbon resources had been explored at a large scale due to the depletion of conventional hydrocarbon resources. The source rock potential, depositional environment, thermal maturation, and biodegradation of ejected hydrocarbons can all be determined *vial* organic geochemistry (Tissot, B.P.,& Welte, D.H, 1984)pyrolysis is a more comprehensive method that can measure useful geochemical parameters in the process of source rock geochemical assessment (i.e., determination of kerogen type and maturity). Geochemical source rock evaluation provides valuable information ready to be used for upgrading areas under investigation, concentrating exploration activities in particular places and reducing risks. Hence the purpose of this study is to determine the hydrocarbons potentiality of the Lengwe in the NW-SE trending cretaceous tertiary with the help of geochemical analysis of rock samples sediments. Shire river basin evolved through extension tectonics due to the active continental rifting currently taking place in the east Africa rift(EAR) in the late Paleozoic time and continued in the Mesozoic and tertiary (Dulanya, 2017)). The study involved the determination of the quantity, quality and thermal maturity of the rock sediments in order to evaluate hydrocarbons occurrence , their commercial viability and further predictive model for the shire river basin. The great east Africa rift system (EARS) is the part of the greater rift valley that runs from red sea through Ethiopia and Kenya up to the Tanzanian carton. The EARS is an active extensive fault dominated rift with the chain of marginally down-warped depression associated with the active volcanism evidenced by early basalts and phonolite flood lava (Kolawole, 217)). EARS range from geological periods mid-Miocene to early Pliocene (Chikondi chisenga, 2018)), , followed by the subsequent faulting that resulted in symmetrical grabens and basins.

The EAR region is geologically and structurally diverse and has significance for scientific studies and natural resources exploration. The recent findings of hydrocarbons in Uganda and Kenya, among other recent discoveries attest to the untapped potential that exists in the region (Focus, 2015) Therefore, EARS Region has witnessed and attracted intensive oil and gas exploration activities that are at different stages. Lower shire basin is located at the southern end of the Malawi rift within the Mozambique belt in the southern part of Africa. The large parts of the basin are overlaid by superficial cover from the fluvial deposits of the shire river and other drainage system in the area. The Lower shire basin has recently been a major target of oil and gas for many exploration companies (Enns, 2018) the shire river is within east Africa system where most of the other countries such as South Sudan, Angola, Kenya etc. Petroleum working system has been proved and oil discovered (Rop, 2018).

Hydrocarbons are organic compounds that are primarily composed of hydrogen and carbon elements, which may be monomeric or polymeric forms, for example, alkanes and naphthalene among another minor constituent. They are formed from organics matter accumulated in a suitable depositional environment and underwent burial and subsequent sedimentation, digenesis and mid metamorphisms as the overlying loose sediment continued being deposited. Overlying weight exert heat and pressure upon the buried organic matter. However, hydrocarbons do not occur anywhere but only in the mature source rocks such as laminated carbonates and shale. These sources rocks possess definite characteristics that qualify them to become favorable for oil and gas accumulation, given the presence of good structural and properties.

Petroleum process of formation, generation and migration are guided by four main petroleum system namely source rocks, reservoir rock, trap, and seal. These petroleum systems are independent (Magon, 2009) for formation of oil and gas. All system must exist simultaneously from organic matter to kerogen and then oil or gas accumulation to generate economically extractable hydrocarbons. The mechanisms of oil and gas generation vary from basin to basin depending on sedimentary facies, burial history, tectonic and other geological factors.

Petroleum geochemistry helps fundamentally to understand the properties of the source rocks, producible and non-producible zones and source of organic matter based on the depositional history. The term source rocks refer to an organic-rich fined grained sedimentary rock which can produce hydrocarbons due to the thermal maturation (Rezaee, 2002). Hydrocarbons generation potential of the source rock is a calculated volume that utilizes multiple rock properties such as source rock volume, total organic carbon, kerogen types and pyrolysis (Espitallie, 1974). More information on the rock eval pyrolysis has been discussed in the appendix section

1.2 Problem statement

Primary energy demand is increasing fast and it is expected to grow by 41% from 2012 until 2035 according to BP outlook 2035 presented on January 2014. In addition, the increment in the industrialization and electrification of non-OECD countries as well as the fast population growth is causing an increase in the energy consumption(BP,2014).The increase in demand increases the price of crude oil which leaves the importing countries such as Malawi at a disadvantage in such that their economy becomes unstable and loses power in economic sectors. In-order to boost our country, it is by stopping being overdependent on importing some of these natural resources. This starts by making use of locally found natural resources that country is blessed with. Hence searching for reservoirs in our country is preliminary survey which can attract investor to come and do some seismic survey and facilitate the exploitation of this crude oil. This will help both to reach the global oil demand for the future and to boost the economy of our country Malawi. So far, many explorations of oil have started taking place in most parts of Malawi and Lower shire valley basin is not an exception. Airborne geophysical survey was conducted in this area by Ghana based oil and gas pacific. Their results were impressive whereby they found thick sediments greater than 2.0 kilometers around Nchalo, Chapananga, to the west of Mwanza fault and makhango to west of Thyolo escarpment. But no geochemical survey has been carried out to identify and deduce information on their geochemical properties that may have enabled storage and expulsion of organic matter and their maturity since

characterization of the rock sediments in terms of its carbon content quantity, quality and its maturation stage provide basic information of the petroleum source rocks potential. Therefore, this study will give further details of the study area in terms of its paleo-environment and give insight of whether the area has potential of the source rocks, types of kerogens and whether it is gas or oil prone.

1.3 Main Objective

The main objective of this research was to evaluate petroleum source rock potential of Lengwe and Mwabvi domain in shire basin using geochemical data obtained from programmed pyrolysis of the rock samples. It involved determining the source, the quantity, the quality and thermal maturity of the organic matter of the rock sediments to assess hydrocarbons occurrence, their commercial viability and develop a predictive model for lower shire basin.

2.3.1 Specific Objectives

To characterize the evolution level of the organic matter of rock samples.

To determine kerogen types of each rock sample.

To define the rocks samples maturation.

To build predictive basin model to guide future exploration of hydrocarbons in lower shire valley.

2.4 Research questions

What are the characteristics and level of the organics matter content of rock sediments found at Lengwe and Mwabvi basin?

What is the kerogen type of rock samples?

What is the description of rock samples and their maturation?

What is the relationship between geochemical properties of rock sample and depth where it was collected?

Does the lower shire basin have probability or chance of containing source rocks potential?

2.5 Significance of study

Geochemical assessment of petroleum source rocks potential helps in deducing chemical properties of the rock sediments. Previously, the properties of thick sedimentary rocks of 2km exposed at Lengwe and Mwabvi basin had been poorly understood. This research project aims at unraveling the mysteries of occurrence of oil and gas in this part of lower shire river basin by deducing the chemical properties of the sedimentary rock hence providing tangible knowledge for policy-decision making on the target field as Petroleum exploration and exploitation is a capital-intensive venture that demand a more sensitive and cautionary evaluation of every stage of exploratory and appraisal drilling and development. The discovering of petroleum will increase socio-economic activities and development of the local community, government, and the country at large

CHAPTER 2

2.0 LITERATURE REVIEW

This section contains the sources that I have used in this research, in details it covers research methodology, theoretical flamework that I have established, and it will also explain how my finding are connected to the existing body of the research of my topic, providing some descriptions and explanations such as the oil and gas formation, the petroleum system concept and the source rock fundamentals, among others. Thus, it might help to understand in a better manner the contents of this research

2.1 Formation of OIL and GAS Overview

Petroleum formation might be understood as a relatively simple process. Basically, the organic matter contained within the source rock is “cooked” due to an increase of temperature during sediment burial, subjecting it to the thermal cracking and eventually

leading to the release of hydrocarbons (Bordenave, 1997). It should be noticed that different types of organic matter generate different quantities and types of hydrocarbons (Tissot, B.P.,& Welte, D.H, 1984). Several millions of years ago, plants, plankton species and microorganisms lived and died in the oceans. As a result, they were decomposed and settled on the sea bottom, becoming accumulated organic matter, and forming organic rich layers of sediments over geological time. As more sediments layers were accumulated, burial depth, pressure and temperature increased, inducing slow thermal cracking reactions that occurred long periods of time and thus forming hydrocarbons (A.Legauit, 2008). Finally, this petroleum migrated into the reservoir rocks by a porous and permeable carrier bed. Oil and gas formations differ from basin to basin and depend on several factors such as burial history, tectonic movements, sedimentary facies, and other geological processes. Living or dead organic matter, as well as dissolved organic matter can be supplied into the sediments. When organic-rich sediments are deposited at the bottom of the oceans, seas or lakes, biogenic methane gas is generated from the organic matter by microbial anaerobic processes. Heat increases with burial depth, causing the organic matter to transform progressively into insoluble organic matter called kerogen. As heat increases, kerogen undergoes further transformation into hydrocarbons (Tissot, B.P.,& Welte, D.H, 1984). To continue with a proper explanation, it is necessary to introduce a fundamental concept within the oil and gas exploration point of view, the petroleum system.

2.2 Petroleum systems

The definition of petroleum system is extremely important since it involves the elements and processes needed so that hydrocarbons can be generated and accumulated. Thus, a clear definition of it is fundamental to comprehend, locate and analyze a source rock. A petroleum system is composed basically of a source rock, where hydrocarbons are generated and eventually are expelled and migrate to a reservoir rock, where oil and gas are accumulated, a seal rock, an impermeable rock which does not allow oil and gas to go up to the surface, and an overburden rock. The term petroleum includes hydrocarbons in the form of liquid or gas, whereas the term system involves the elements mentioned above, as well as the processes which are needed so that petroleum can be accumulated, such as

generation, migration, trap formation and accumulation. Petroleum system formation takes long periods of time. The age of a petroleum system can be reported using geochemical studies and tracking the burial history. On the other hand, after generation, migration and accumulation of hydrocarbons occur, preservation time starts, leading to the preservation itself, modification, or destruction of petroleum. Thus, time and entrapment are two key factors for a petroleum system to exist (Magon, 2009). Petroleum systems are in sedimentary basins, but it is important to mention that not all sedimentary basins contain it (Peter, k.,Schenk, O., & Wygraa, B., 2009). Figure 1 represents a typical petroleum system where the different elements and processes can be distinguished.

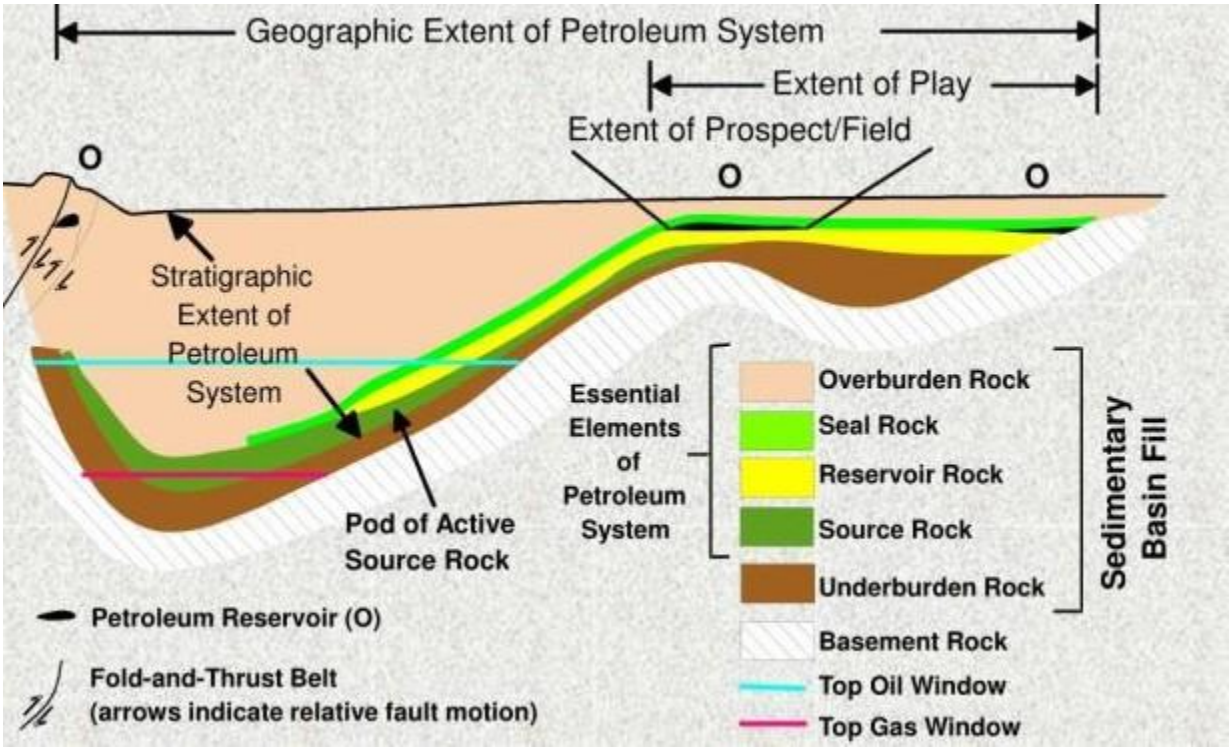


Figure 1 petroleum stream *(Magon, 2009)*

One of the aims of petroleum geochemistry is to evaluate and characterize the source rocks, thereby a few fundamentals about its formation and development should be introduced.

2.3 Source rocks fundamentals

A fine-grained rock rich in organic matter capable of generating petroleum in commercial quantities given the proper temperature and pressure is called source rock (Katz, 1995). Source rocks can be originated in different paleo-environments such as deep marine, lacustrine and deltaic (sua'rez-Ruiz, 2012). Among others, shales and carbonates rocks are the sedimentary rocks which can become good petroleum source rocks (Zimmerle, 1995). Shales rocks may contain less than 5% TOC, whereas carbonates source rocks may contain as much as 10% to 30 % TOC (palacas, 1988). Three main aspects are to be considered when characterizing a source rock: the amount and type of organic matter present at any given time, and the thermal maturity (Carvajal-0rtiz, H., & Gentzis, I, 2015). A proper evaluation of the source rocks is crucial to reach the hydrocarbons reservoirs. Four types of source rocks can be found in terms of petroleum generation potentiality. Effective, active, inactive, and spent source rocks. Firstly, a potential source rock can be any rock that contains sufficient organic matter to generate petroleum (sua'rez-Ruiz, 2012). An effective source rock is a potential source rock which has reached an adequate thermal maturity to generate petroleum. When a source rock is generating and expelling hydrocarbons either biological or by temperature at the critical moment, it is called active. An inactive source rock might show petroleum potential, but it stopped generating oil and gas. Finally, a spent source rock reached post maturity stage and might generate wet or dry gas, but it cannot generate any oil (Magon, 2009) .

Physical, biochemical, and geological processes are behind the creation of a source rock, resulting in the formation of a fine-grained sedimentary rock rich in organic matter, manly carbon and hydrogen elements (martinelli, 2009). A few phases need to be considered when a source rock is formed such as production, accumulation, and preservation of the organic matter (Mackenzie, 2005). Thus, the amount and type of organic matter found in a source rock are subjected to environmental and depositional conditions. Biological activities take part in the production and transformation of organic matter. On the other

hand, depositional Conditions develop the concentration of the organic matter and finally the post-depositional conditions preserve it (Jacobson, 1991).

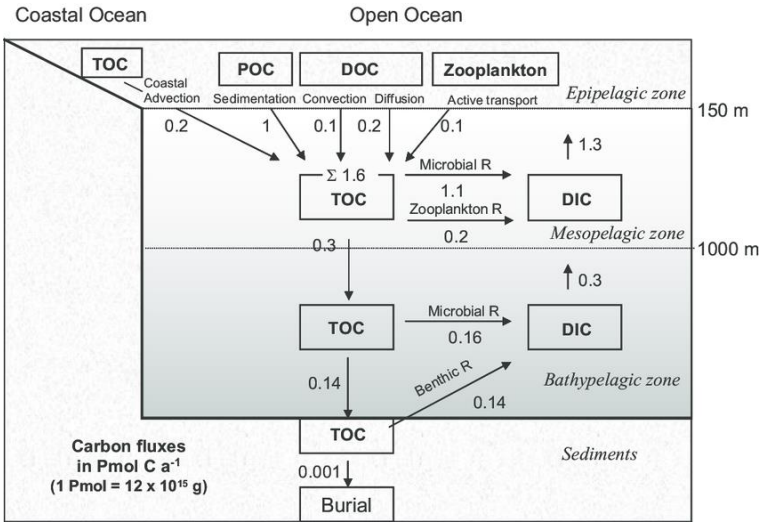


Figure 1.the organic matter in the water column. (Mackenzie, 2005)

Biologic productivity, sediment mineralogy and oxidation of the water column play a key role in controlling the organic matter content. Highest concentrations of organic matter can be found near the water surface, both in colloidal and particulate form (Barker, 1979). From the water surface to the water sediment interface, the organic matter pass through chemical and biological processes. The role of oxygen in the water column is significantly important. On the one hand, it permits the biological productivity of organic matter. On the other hand, it supports biodegradation and oxidation. In addition, physical abrasion or chemical changes led by water EH and pH can alter the organic matter (Jacobson, 1991). Once in the bottom of the sea, some of the matter is converted into simple molecules due to the action of bacteria, worms, and bottom feeders. A reduction of organic richness is produced because of biodegradation and oxidation, separating only resistant organic material. This remaining matter is incorporated into the sediments (Tissot, B.P.,& Welte, D.H, 1984). Concentration and preservation of organic matter in the sediments are controlled mainly by oxygen and energy levels. Low oxygen or anoxic environment improves the preservation of organic matter, creating reducing environments which protect organic materials from oxidation and the action of bottom feeders, which implies the absence of bioturbation (Bjørlykke, 2010). Low water circulation affects positively to

create anoxic conditions, as it reduces the exchange of oxygen and organic matter. Furthermore, this low-energy environments allow a better deposition of sediments. Thus, source rocks are formed in low-energy environments (Jacobson, 1991). Equally important is the mineralogy role in the source rock development. Minerals, which are transported and precipitated in the sediments, might react with organic compounds, and dilute a portion of organic matter, affecting the source rock ability to generate and expel hydrocarbons (McCarthy et al., 2011)

2.4 Kerogen and its thermal transformation

The portion of sedimentary organic matter which survived the initial decomposition process and can generate petroleum is called kerogen (Vandenbroucke, 2003). It is insoluble in organic solvents and represents "the major organic carbon reservoir in the Earth´s crust" (Engel, 1993). On the other hand, bitumen is the organic matter that is soluble in organic solvents. The elemental analysis of kerogen encompasses the following elements: C, H, N, O, S, and probable Fe from pyrite (Vandenbroucke, M., & Largeau, C, 2007).Figure 6 represents a schematic illustration of the organic matter classification within a source rock. Biological activity at the early stage, following by temperature and pressure are responsible for the physiochemical transformation of organic matter in a sedimentary basin (Tissot, B.P.,& Welte, D.H, 1984). Higher temperatures and long period of geological time are involved in the transformation of kerogen into oil and gas (Bjørlykke, 2010). Thus, increments in burial depth increase temperature and pressure, which along with geological time play an important role in the organic matter transformation (McCarthy et al., 2011). It should be mentioned that the number of hydrocarbons that might be generated in a source rock is exposed to kerogen composition and concentration, as well as the geothermal gradient evolution during burial history (Engel, 1993).

The thermal maturation process, by which organic matter is altered changing its chemical composition and creating hydrocarbons, can be divided into three consecutively stages, diagenesis, catagenesis and metagenesis.

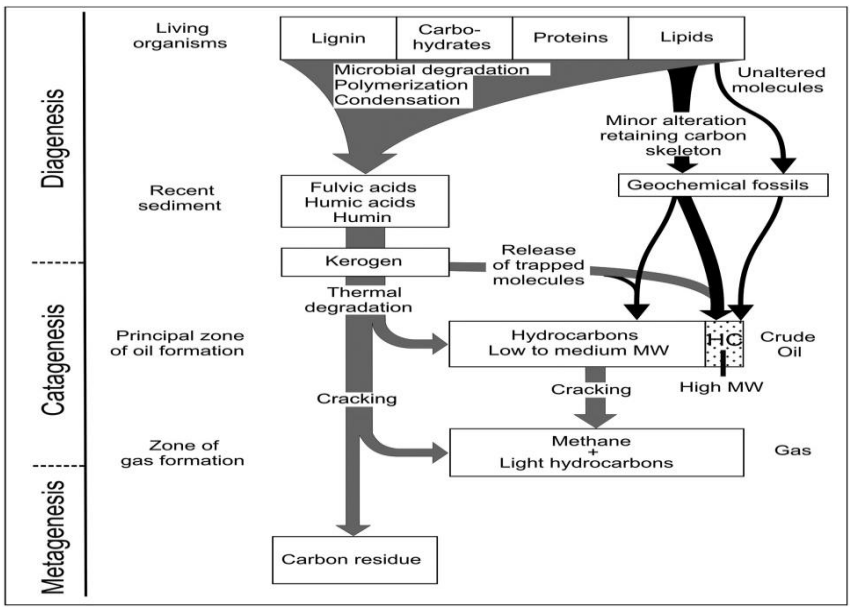


Figure 2, sedimentary organic matter composition in a source rock (Mackenzie, 2005)

Digenesis is the first stage of thermal maturation process of organic matter. It comprises the natural changes occurring from the moment of sediment depositions until the first signal of thermal alteration process (Ali, S. a, Clark, W. J., Moore, W. R., & Dribus, J. R, 2010). Thus, this alteration starts in the water column (Magon, 2009), being microbial activity, the first process taking place (Tissot, B.P.,& Welte, D.H, 1984). The temperature, at which the alteration of organic matter in source rocks takes place, is ranged below 50 °C (Magon, 2009). With reference to the depth interval, this phase is extended from one hundred to one thousand meters (Tissot, B.P.,& Welte, D.H, 1984). In this stage, oxidation along with other chemical process decompose the material. On the one hand, anoxic deposition conditions might convert the material from biogenic gas into dry gas. The term biogenic gas is referred to the gas generated during the degradation of organic matter in anaerobic conditions by bacterial microorganisms (Rice & Claypool, 1981). On the other hand, the increase of temperature and pH promote the transformation of organic matter into kerogen and bitumen. Figure illustrates a general scheme of the evolution of the organic matter during its thermal maturation process. Increasing burial depth due to successive sediment depositions, causes increment in pressure and temperature and the source rock undergoes catagenesis. During this phase, hydrocarbons are generated at temperatures

range from 50 °C to 150 °C and at several kilometers beneath the surface (Tissot, B.P.,& Welte, D.H, 1984). Therefore, a thermal decomposition causes chemical bonds of kerogen brakes down, creating mostly oil but also gas (K. E. Peters, Walters, & Moldowan, 2007). A secondary cracking of oil molecules takes place during this phase due to the increment in temperature, generating wet gas such as methane, ethane, propane, and heavier hydrocarbons (McCarthy et al., 2011).

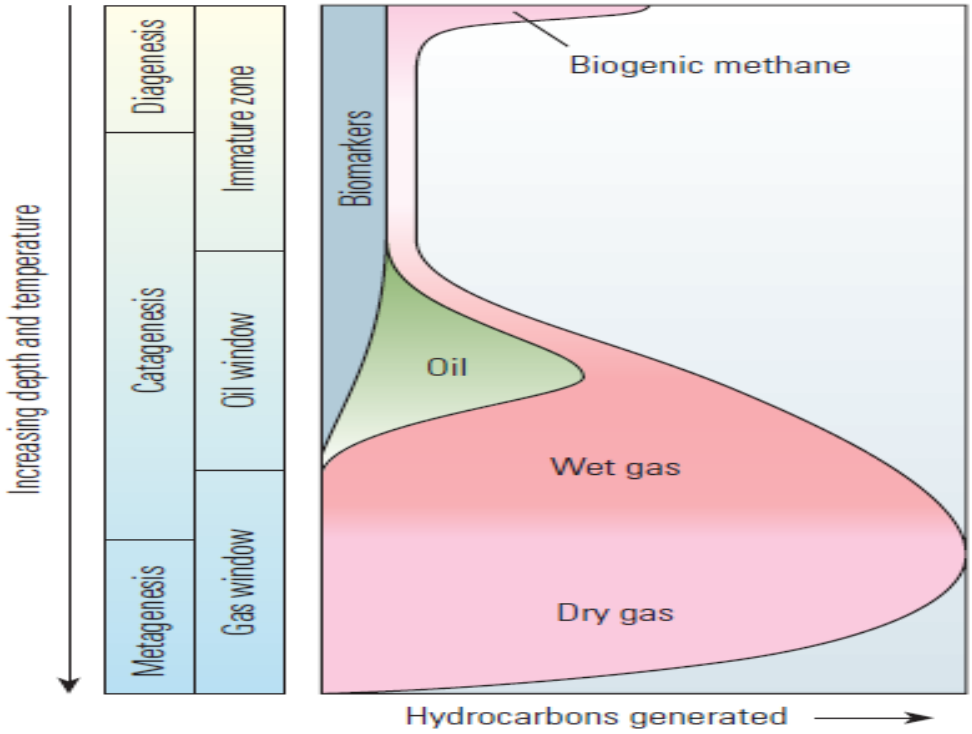


Figure 3.Thermal transformation of kerogen (McCarthy et al.2011)

The last step in the thermal transformation of kerogen is called metagenesis. Temperature ranges from 150 °C to 200 °C. In addition, higher burial depth might cause source rock to be influenced by magma and hydrothermal effects (B. P. Tissot & Welte, 1984). Thus, at this stage, the increment in heat causes chemical changes within the kerogen, transforming it into methane and a carbon residue. Furthermore, late methane, or dry gas along with non-hydrocarbons gases such as carbon dioxide (CO2), nitrogen (N2) and hydrogen sulfide (H2S) might be generated as the source rock moves further down (McCarthy et al., 2011). Source rocks are said to be thermally immature, or potential source rocks, as the rocks must be exposed to more heat to generate petroleum. Source rocks, which are found at the oil

window, are said to be thermally mature, or effective source rocks, as the rocks have been generating petroleum, or are actively generating it. The last but not the least, source rocks are said to be thermally postmature, or spent source rocks, as the rocks have entered at the gas window and have already generated petroleum. Thus, they have consumed all the hydrogen necessary for further oil and gas generation (McCarthy et al., 2011). On the other hand, it should be mentioned that maturation process can be also altered due to the influence of heat arising from the crustal tectonics or igneous bodies.

Vitrinite reflectance is good source rock evaluation tool used to assess the thermal maturation (Senate & Landis, 1991). Vitrinite is a maceral found in coals and kerogens which is formed due to the thermal alteration of lignin and cellulose in plant cell walls. Vitrinite undergoes complex chemical reactions when temperature is increased, increasing its reflectance. Thus, reflectivity is measured under a microscope, using an oil-immersion objective lens and one photometer. This measurement is represented in percentage of light reflected in oil, named as Ro (McCarthy et al., 2011). The use of this technique in each source rock sample would provide a definitive and reliable measurement of the thermal maturation. Hence, it is highly recommended its usage.

Another method of assessing thermal maturation is by drawing the graph of T_{MAX} against carbon content. This will be explained in detail in methodology section.

2.5Kerogen classification

To evaluate a source rock properly, a differentiation between kerogen types must be performed. As different types of organic matter have different chemical structures, the hydrocarbon potential varies (B. P. Tissot & Welte, 1984). Thus, four types of kerogens are distinguished based on its origin. Furthermore, the hydrogen, carbon and oxygen content can be used for such classification. Each type of kerogen can produce or generate different types of petroleum (B. Tissot, Durand, Spiralia, & Combat, 1974). Figure 8 shows the van Krevelen diagram used to classify kerogen types and its level of thermal maturation. In earlier times, kerogen classification used to be made based on its elemental composition,

as shown in Figure 8. As soon as Rock-Eval Pyrolysis was developed, it was found that HI and OI parameters are directly proportional to H/C and O/C ratios, thus HI and OI replaced them on the Van Krevelen diagram, respectively (Mackenzie, 2005).

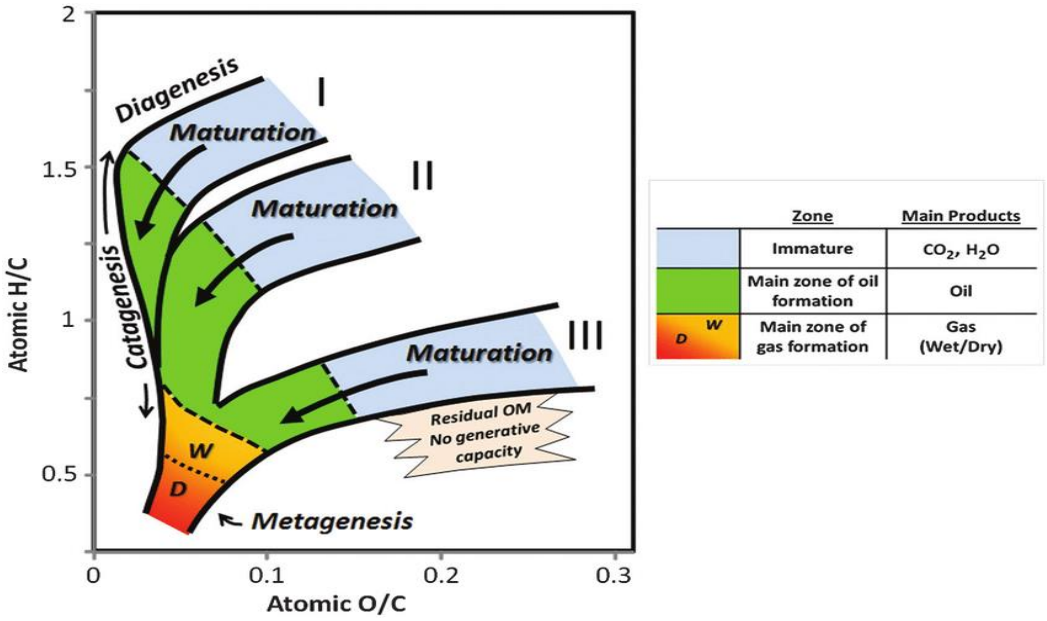


Figure 4, Van krevelen diagram (B.P. Tissot &Welte,1984)

Type I kerogen originates mainly from lacustrine environments, although it can also be originated from marine environments. It is composed of algae, plankton and other matter which were reworked by bacteria and microorganisms. It shows high H/C atomic ratio and low O/C atomic ratio (B. P. Tissot & Welte, 1984). It is oil-prone, but depending on the thermal maturation phase can also generate gas. Type I kerogen is not usual and represents less than 3 % of oil and gas reserves in the world (Baskin, 1997), although it presents high hydrocarbon potential (Tissot, B.P.,& Welte, D.H, 1984). Type II kerogen originates in reducing environments from deep marine settings. Remains of plankton, among others, reworked by bacteria compose this kind of kerogen. It shows high H/C and low O/C ratios (Tissot, B.P.,& Welte, D.H, 1984). Type II kerogen can generate mainly oil, but also gas, providing enough heating and maturation (Vandenbroucke, 2003). Type III kerogen derives from continental plants and contains vegetal debris. It has been deposited in shallow to deep marine or non-marine environments. It shows low initial H/C ratio and high initial O/C ratio (Tissot, B.P.,& Welte, D.H, 1984) . This sort of kerogen usually

generates dry gas (McCarthy et al., 2011). Type IV kerogen derives from residual organic matter which might have been altered by weathering, combustion or biologic oxidation in swamps or soils (McCarthy et al., 2011). It shows very low H/C ratio and a relatively high O/C ratio. This kind of kerogen is referred as a "dead carbon", having no potential for petroleum generation (Tissot, B.P.,& Welte, D.H, 1984). It should be noted that this type of kerogen is not represented in Figure 8, as it does not present any information regarding petroleum potentiality. Equally important is the degree of hydrogen content in kerogens. Hydrogen-rich kerogens generate both oil and gas, nevertheless, hydrogen-poor kerogens generate mainly gas. Additionally, when hydrogen is depleted from kerogen, petroleum generation ceases, despite the amount of available carbon (Baskin, 1997).

TOC content is a strong indicator of the organic richness, as well as the ability of a source rock to generate hydrocarbons (Jarvis, 1991). Thus, a proper determination of this parameter is key in any geochemical source rock evaluation. In addition, other geochemical parameters can be calculated from it. TOC measurement is performed by combustion under air or oxygen atmosphere at temperatures range up 49 to 1500oC, depending on the method used. Furthermore, an acid treatment might be needed to reach a correct TOC measurement (Bordenave, 1993). For more on TOC measurements: Bordenave, M. L. (1993). Applied Petroleum Geochemistry. (Technip, Ed.). Paris. It should be noted that TOC content can be measured using TG/DSC analysis, but then, several geochemical parameters must be assumed due to the apparatus limitations. Thus, it is highly recommended to perform an individual TOC analysis for each source rock sample.

2.6 Geochemistry of Formation Water and Its Implications for Petroleum Source

Geochemical properties of formation water reflect the sedimentary environments and the sealing conditions of the formation, which are of great significance for oil and gas exploration. Formation water is a geological fluid that exchanges material and energy with

surrounding rocks and preserves much information about original sedimentary water. In petroleum reservoirs, formation water coexists with oil and gas in different phases. Formation water consequently can record the processes of formation, migration, accumulation, preservation, and alteration of petroleum. In fact, the type, salinity, and ionic composition of formation water have been widely used to elucidate the source of formation water, the dynamic environment of water, the strength of water-rock interaction, and in the exploration of oil and gas reservoirs (Garven, 1989; Zhang et al., 2021). In essence, the composition of formation water is the result of the alteration and mixing effect of flow processes as well as water-rock interactions that occur during sedimentation and burial (Jinn et al., 2006).this has been applied in this research .

2.7 Petroleum geochemistry and source rocks potential

Petroleum geochemistry is vital device for lowering uncertainty in exploration and production of hydrocarbons viable basins (Allan, 990).it is used as the imperative science for understanding the properties of the source rock indexed as volume and maturity of organic matter, producible and non-producible, oil or gas migration pathways and suggestive sustainable production of resultant hydrocarbons (Hunt, 1979). Over time, the reliance on petroleum geochemistry has been steadily and has resulted in improved confidence on areas mapped for further exploration. The mechanisms were used to explain how oil and gas generated from organics remains portrayed certain paleo-parameters of a particular basin (Tissot, B.P.,& Welte, D.H, 1984) as result of sediment provenance burial history, tectonics and other geologic processes that occurred in the basin.

CHAPTER 3.

3.0 METHOLOGY

3.1 Introduction

This chapter presents the methods materials and technical approach that were used to attain the objectives of this study. Discussed in more detail are the descriptions of the research strategy, research methods, data collection and management methods and the type of data analysis.

3.2 Study Area

3.2.1 Location & Geological setting

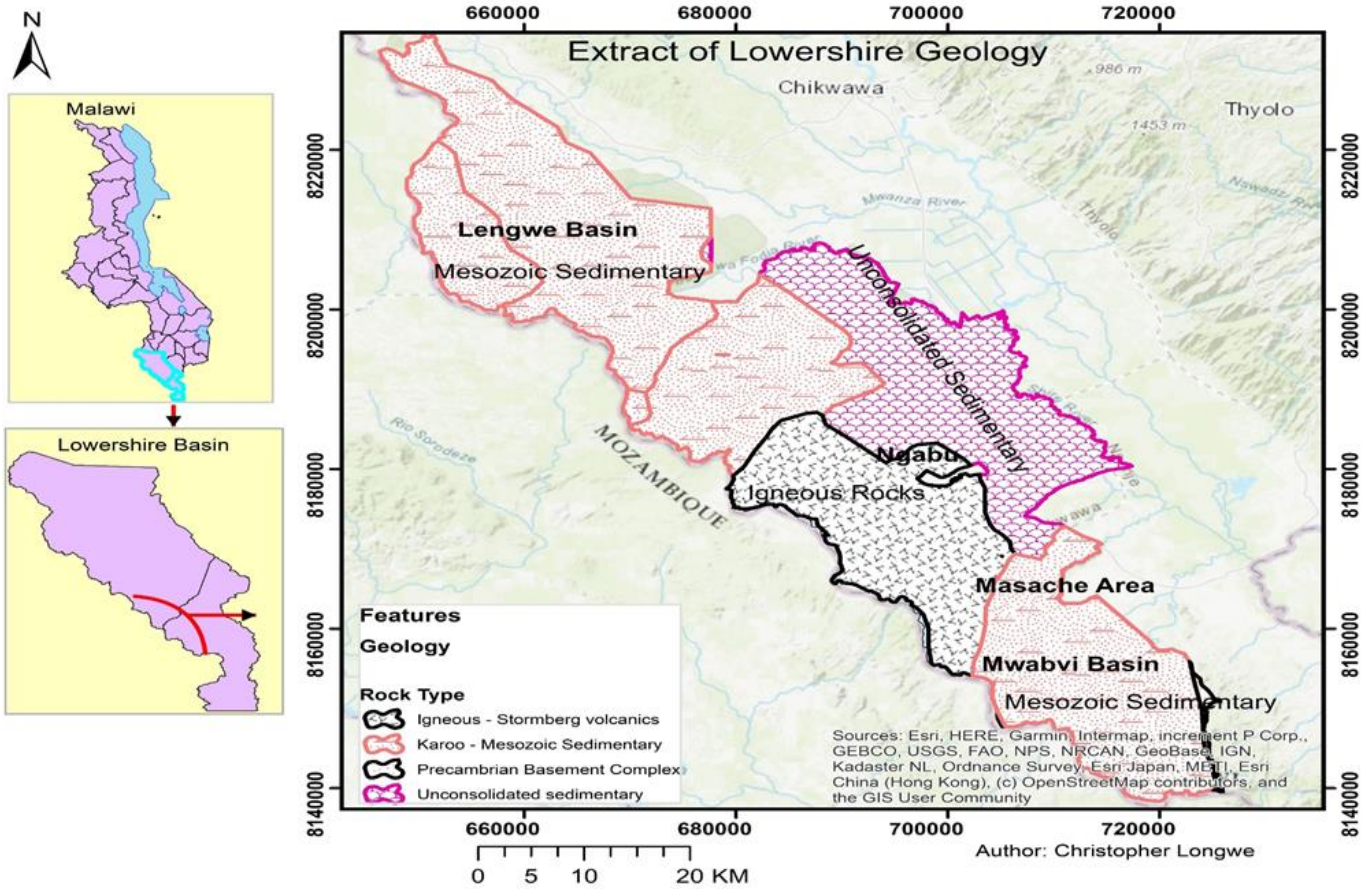


Figure 5 Geological location

The Lower Shire Basin occupies the southern end of the Malawi Rift. The basin developed during the Karoo times and re-activated during the Cenozoic time due to the rifting

associated with the EARS (casting., 1990). It is situated near the southern end of Malawi between latitudes 15030'S and 16045'S and longitudes 34015'E and 35015'E and bordered by the Malawi-Mozambique boundary on its southern edge. This area has been chosen because the previous researchers on the composition of water in lower shire basin recommended that it is associated with high level of organic matter since it has highly deep depth enabling water to flow at very slow rate which allows the accumulation of the organic matter. It all must also be noted that this area is also associated with coal which also formed from organic remains under enormous pressure in sedimentary sequence. This makes this area to have high probability of the petroleum source rocks

Malawi Rift lies within the Mozambique belt (ca 700-400 my BP) in the southern part of Africa. It is underlain by para- and orthogneiss crystalline rocks (carter,G.S.,Bennet, J.D, 1973). These metamorphic rocks are overlain by Permo-Triassic and Cretaceous sedimentary rocks and intruded by a variety of alkaline rocks of Jurassic to Cretaceous age. The topmost units are younger sediments that are found in the major drainage basins of the country associated with Cenozoic to recent deposition and rifting processes. Detailed geological accounts of the study area are documented in various publications of the Geological Survey of Malawi covering the study area (Habgood, 1965) The study area comprises Proterozoic metamorphic rocks of both igneous and sedimentary parentage and assigned to the Basement Complex. These are uncomfortably overlain by Karoo volcano-sedimentary rocks and later by Cretaceous and Quaternary sequences. The Lengwe and mwabvi domain are one of the most well-known Karoo domains within the study area (Fig 6).

3.3.0 Sample size and technique

This research involved sampling technique such as random sampling where the samples within selected areas around Lengwe and mwabvi basin that where highly concentrated of complex sedimentary rocks were collected to reflect the true reflection of area. This also enabled the comparison of the estimated parameters. 8 samples were collected, 4 at Lengwe and other 4 at Mwabvi basin.

3.3.1 Data collection

Data used in this study is geochemical data from programmed pyrolysis of the rock samples which includes TOC, S1 S_2, S_3, HI, OI, and Tmax, which were collected at Malawi geology survey in Zomba. Mr. Brave Manda and his colleague, who is also respected staff member of Malawi geology survey in Zomba, in geochemical department collected the samples from the stated site and sent it to the Netherland where Rock-Eval pyrolysis was conducted. The results have not been released to the world as there are still some tests being done. Other data included in this study are HI, OI, PP, and PI which were delivered from the measured parameters by using simple mathematics formulas as shown in the appendix.

3.4 material and methods

Study will employ both qualitative and quantitative evaluation of the petroleum source rocks in the basin.

3.4.1 Averaging and references for the result evaluation

The data obtained during the rock eval pyrolysis process has been averaged according to the good standard of geochemical parameters to evaluate the organic matter characterization, maturation stage and petroleum potential for each rock sample. The regions have been demarcated by following the references standard as shown in flow diagram below.

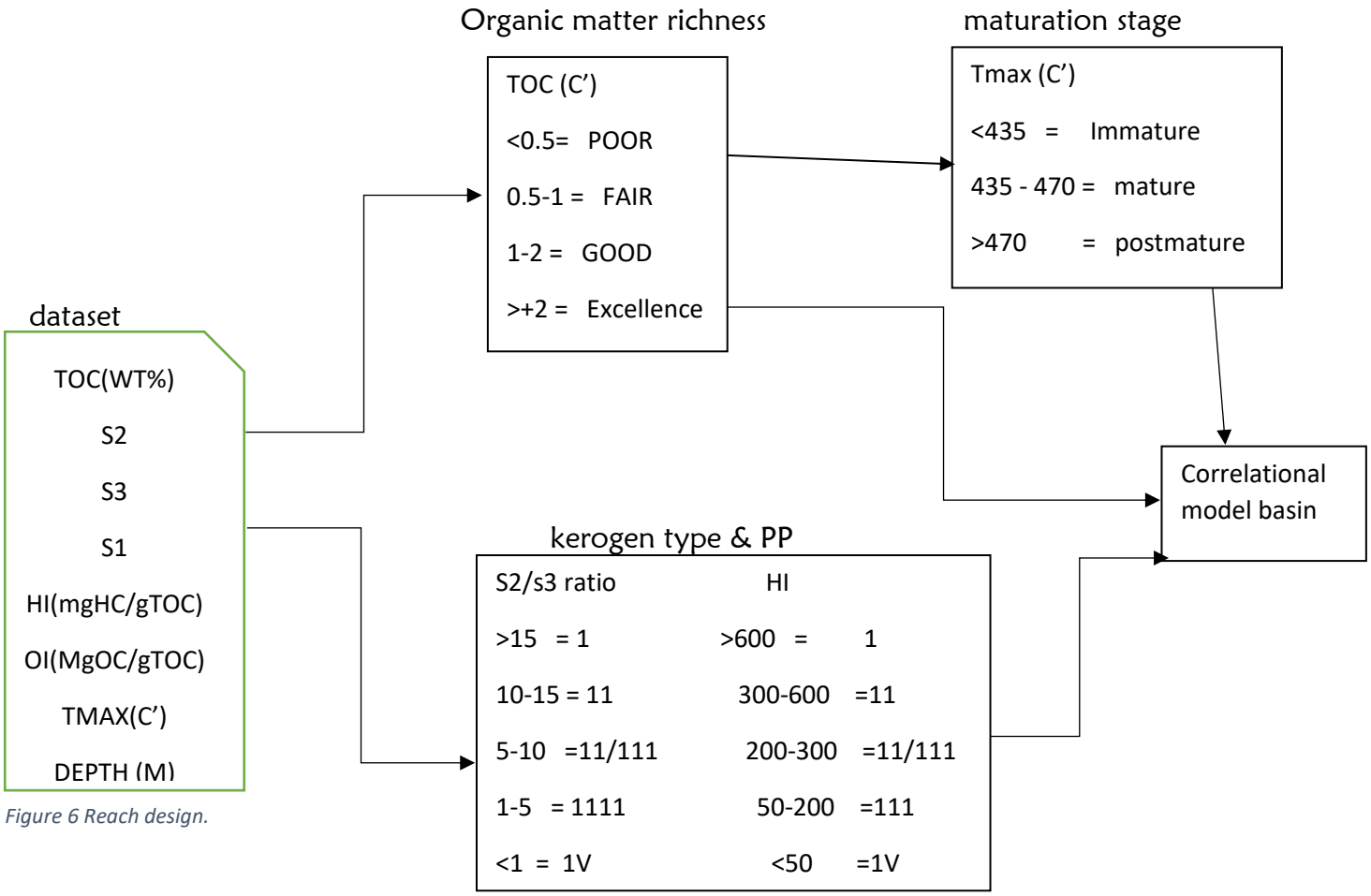


Figure 6 Reach design.

Form the flow diagram above, to determine organic matter richness as explained in the chapter 2, the Total carbon content, S1 and S2 will be averaged and compared with values from references shown in the figure 7. Then scatter plot will be plotted for carbon content against S2 and region was demarcated within the graph according to the reference's standard. The results will be based on the region where data for rock samples has fallen.

To classify the kerogen types of the sample as explained in the literature review on kerogen classification, the HI and OI values obtained was averaged and compared with the values of standard for classifying kerogen and its main products expelled at the peak maturity was determined. The results were based on the region where data for each sample was fallen when scatter plot of the hydrogen index against S2/S3 ratio was plotted and region within the scatter plot was demarcated according to the reference table below.

Table 1.standard references table for classifying kerogen type.

Kerogen type	HI (mgHC/g TOC)	S2/S3 Ratio	Main products expelled at peak maturity
1	>600	<15	Oil
11	300-600	10-15	Oil
11/111	200-300	5-10	Missed oil and gas
111	50-200	1-5	Gas
1v	<50	<1	Non

To determine the maturation stage of the rock samples as explained in the literature review on the kerogen and its thermal transformation, the Tmax and Production index values obtained was averaged and compared with the standard references for classifying the maturation stage of the rock samples. The results were based on the region where data for each rock sample was fallen when scatter plot of the Tmax against production index was plotted and region within the scatter plot was demarcated according to reference table below.

Table 2 reference table for maturation stage

Stage of the thermal maturation	Tmax(C')
Immature	<435
Mature	435-470
Post mature	>470

3.3.2 correlation comparison

To build model of the lower shire valley, a proper evaluation of the results obtained from the measurements and calculations will be considered in this section. To perform such appraisal, line graph is used. Whereby, the carbon content, hydrogen index and generative potential of each sample will be plotted against the depth where the sample were

collected, hence relationship among the parameters will be used to build predictive petroleum potential model of lower shire valley.

3.4 Software used.

In this research, GIS software such as QGIS was used to create map and excel was used to create graphs for the analysis of results and Microsoft word has been used for the success of this dissertation.

3.5 Limitations of the project

Every research has its ups and downs as there is always room for error and uncertainty especially when it comes to data collection.in this research availability of the data to use was very limited in such that some data were not found as we have not embarked much in geochemical evaluation of the source rocks here in Malawi. For examples the Mr. Brave Manda and his colleagues from zomba geological department of survey only did Rock-eval pyrolysis without doing vitrinite reflectance and now they are doing bio-maker processing which takes months to be conducted hence I have used the only data from rock-eval pyrolysis which are available at this time.

CHAPTER 4

4.0 Results and Discussions

In this chapter the samples definition and location and the results obtained from the source rock evaluation using Rock-Eval pyrolysis are presented. Following the temperature program and considering all measurements and assumptions, S1, S2, S3, TOM, TOC, HI, OI, PP and Tmax have been calculated. Hence, the characterization of the organic matter content, the rock sediment maturation definition and the source rock generation potential determination have been performed for each sample.

4.1 Sample definition, Results and Evaluations

Eight rock sediment samples collected from the outcrops of the Lengwe and mwabvi are investigated in this work. A general description of the source rocks is presented, and source

rock geochemical parameters determined during the completed experiment from Rock-eval pyrolysis analysis for each sample above has been discussed in terms of its organic matter quantity, kerogen and maturation stage using graph.

4.1.1Sample NA20799-1, NA20799-2 and 20799-3







These rock Sediments were collected in mwabvi basin at the same area but at the different depth and all was carbonite rock sediments of the black and grey in color. It must be noted that the rock samples which was black in the color obtained high values of the TOC and hydrogen index compared with two rocks samples which was in grey in color and that HI, PP, TOC and S2 values increases with the depth while OI and S1 values decreases with the depth. The geochemical parameters determined during pyrolysis phase and depth at which the Samples were collected are shown in the table below.

Table 3 Geochemical parameters determined during pyrolysis and its depth.

Sample name	S1 (mg/g)	S2 (mg/g)	pp (mg/g)	Tmax (C')	TOC (WT%)	HI (mg/g)	0I (mg/	Depth (m)
Na2099-3	0.4	0,17	0.45	521	9	0.2	0.68	1.5
Na20799-1	O.59	O,05	0.64	457	5	9	410	0.5
Na20799-2	O.45	0.49	O,94	450	5	016.2	247.8	1

4.1.2 Sample NA20817-1, NA20817-2, AND NA NA20817-3







These rock sediments were collected in Lengwe basin and at the same area but at the different depth. All was brown rock sediment formed in Jurassic to cretaceous period.it should be noted that for this samples also the estimate of PP, TOC and HI values increases with the depth while OI decreases with the depth. The geochemical parameters delivered from pyrolysis process and depth at which the Samples were collected are shown below.

Table 4 Geochemical parameters determined during pyrolysis process and its depth.

Sample name	S1 (mg/g)	S2 (mg/g)	pp (mg/g)	Tmax (mg/g)	TOC (mg/g)	HI (mg/g)	OI (mg/g)	Depth (m)
NA20812-1	O. O5	0.04	0.09	521	6	O.44	0.33	1.5
NA20812-2	0.13	0.05	0.18	546	9	o.32	0.14	3.5
NA20812-3	0.21	O. 12	0.33	536	20	1,27	97.5	5

4.1.3.1 Sample NA20812-1 and Sample NA20812-2





These rock sediments were also collected in Lengwe basin and at the same area but at the different depth and all was carbonaceous shale, dark in color. rock sediment was formed in the Jurassic period within the Mesozoic time. It should be noted that values of PP and HI of the rock samples delivered from rock eval pyrolysis process increases with the ;depth(m) while the OI values decrease with increases in the depth. Its geochemical parameters determined during pyrolysis phase and depth at which the Samples were collected are shown below.

Table 5 geochemical parameters determined during pyrolysis process & its depth.

Sample name	S1 (mg/g)	S2 (mg/g)	PP (mg/g)	Tmax (C')	TOC (WT%)	HI (mg/g)	OI (mg/g)	Depth (m)
NA20817-1	0.43	0.14	0.57	274	11	2	17.3	1.4
NA20817.2	0.39	0.9	1.29	521	28	0.71	0.45	1.8

4.1.2 Interpretation of the results

4,1,2.1 Organic Richness and Petroleum Potential

Figure- below shows organic matter richness and petroleum potential of all samples a after plotting scatter plot to show relationship between Carbon content(w%) against PP(mgCH/gTOC).

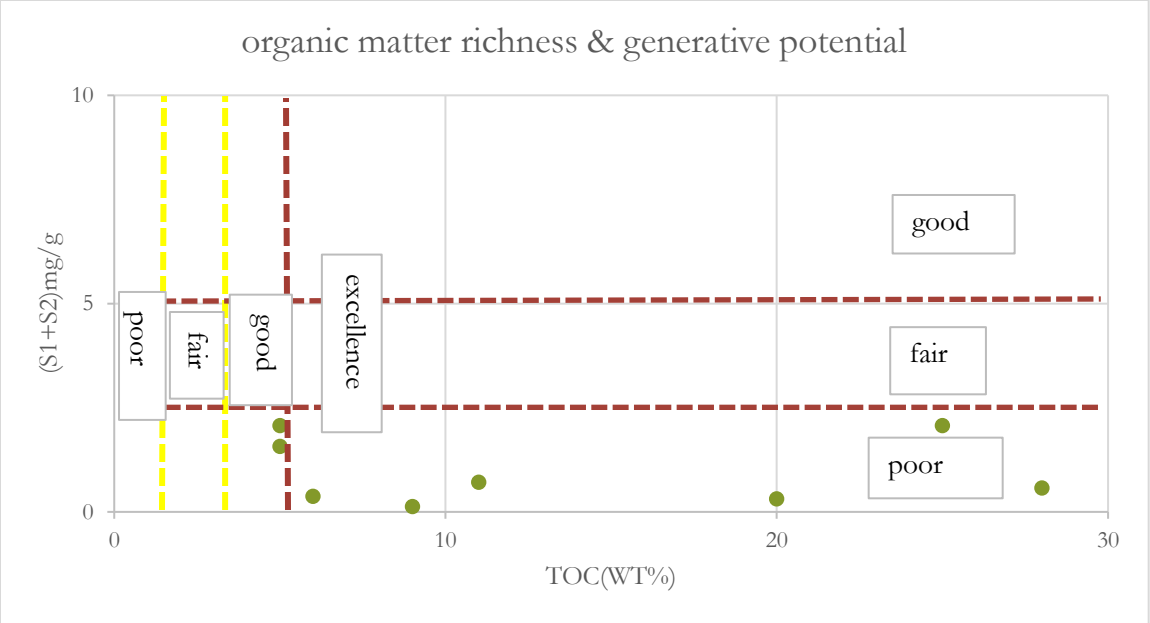


Figure 8 Organic matter richness & generative potential

From the graph it shows that all the Samples have obtained an excellent organic matter richness as all the samples has TOC(WT%) values greater than 2. Based on TOC (wt.%) results, it seems that no petroleum has been generated from the source rocks due to their relatively high TOC values, or they had higher TOC values and some of it has already been converted to hydrocarbons. Thus, it might indicate immature or early mature source rocks. Hence, if thermal maturation undergoes, and considering the positive results in terms of petroleum potential, more hydrocarbons generation might be expected for each sample. In any case, these results should be compared with others geochemical parameters already calculated such as S1, S2, and Tmax. Thus, based on TOC results, a further geochemical investigation is strongly suggested for each sample.

Despite samples showing highly rich in organic matter, the petroleum potential which is the sum of number of free hydrocarbons (gas& oil) in the sample and number of hydrocarbons generated through thermal cracking on nonvolatile organic matter. Indicate that all rock samples have poor capabilities to generate petroleum if thermal maturation continues, this can be because the rock sediments were outcrops that means it was exposed to oxygens and heat. Hence allowing more hydrocarbons to escape from the sediments.

From the graph only one rock samples (Na20799-1), which has fallen in the region of the fair, demonstrating its fair petroleum potential. This rock samples were collected at high deeper depth compared to the other samples. this means that at high deeper there is high probability that rocks samples can generate many hydrocarbons Therefore, considering pp results obtained, further investigation should be performed for each sample.

Relationship between organic matter richness and its petroleum potential is really confusing as shown in figure 9 above. Whereby rock samples have high quantities of organic matter but have poor capabilities to produce hydrocarbons this may be because of its exposure to sun and air hence allowing hydrocarbons to escape. This can also be because of the good geologic controlling factors of the organic matters accumulation which including primary productivity, Pele-o-redox conditions, and sedimentation rate. This is so because according to the previous study by DR mamaliga he concluded that shire valley has good geologic controls which can helps in preserving of organic matter and looking at the results of organic matter ,it really supports the point.

4.1.2.1 Thermal maturation

Figure- below shows thermal maturation level of all samples a after plotting scatter plot to show relationship between hydrogen index(mgCH/gTOC) and tmax(˚C)

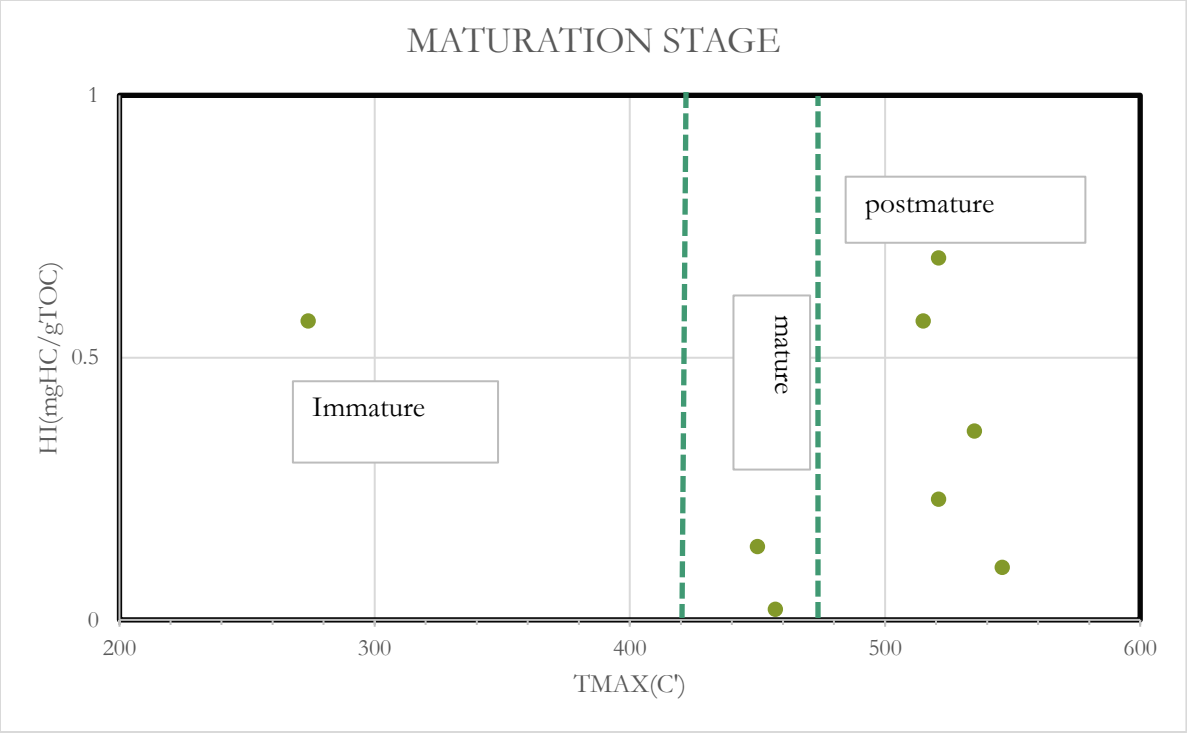


Figure 9 maturation stage

with the results from figure above it shows five samples have fallen in the post-mature region showing that it already surpasses oil window, and it can only generate wet and dry gas as it is only gas that can be generated at temperature above 470°C. this also indicates that rock sample are spent source rocks. this can be because of the geologic control such as climate, sedimentation rate and surface paleo productivity. Taking in consideration the facts that these samples are just an outcrop hence there are exposed to bad geologic controls such as high temperature that can make it to start generating hydrocarbons at an early stage end up in disturbing the normal maturation level of the organic matters.

In addition to that, age of the rock samples, Since the age of rock samples are not well known as the area lacks specific data of the ages of the rocks. The age of the rock samples influence maturation in such that oldest rocks cannot generate oil and can generate only gas or nothing at all despite being exposed to good geological process.

Also, from the graph it shows that two samples have fallen in mature region. This indicate that it is still in oil window such that it can generates oil. This also indicate that rock samples

are active source rocks type. This may be so because the rocks are exposed to good geological controls, and it must be noted that these two samples were collected at the deeper depth compared to the other samples. This gives us the hope for the area to contains oil. Despite lack of good specific data for the age of the rocks of the area we can also conclude that the area is composed of the young rocks as it is only young rock samples which can generate oil when exposed to the good geological process,

On the other hand, one sample was fallen in the immature region. This shows that rock sample is yet to produce hydrocarbons which might be oil or gas. Depending on the depth where this rock was collected 'in between those falls in mature and post-mature rock' we can conclude that upon its maturation it can generate both oil and gas and this also gives us the hope that area contains petroleum sources rocks given that rock samples have good description which were black in colour but not as those in mature region. This also shows that rocks samples are young as it is a capable of producing hydrocarbons in time to come if it will continue to be exposed to the good preservation conditions.

4.1.2.2 Kerogen types

Figure- below shows kerogen types of all samples a after plotting scatter plot to show relationship between hydrogen index (mgH. /gtoc) and oxygen index (mgCo2. /gtoc)

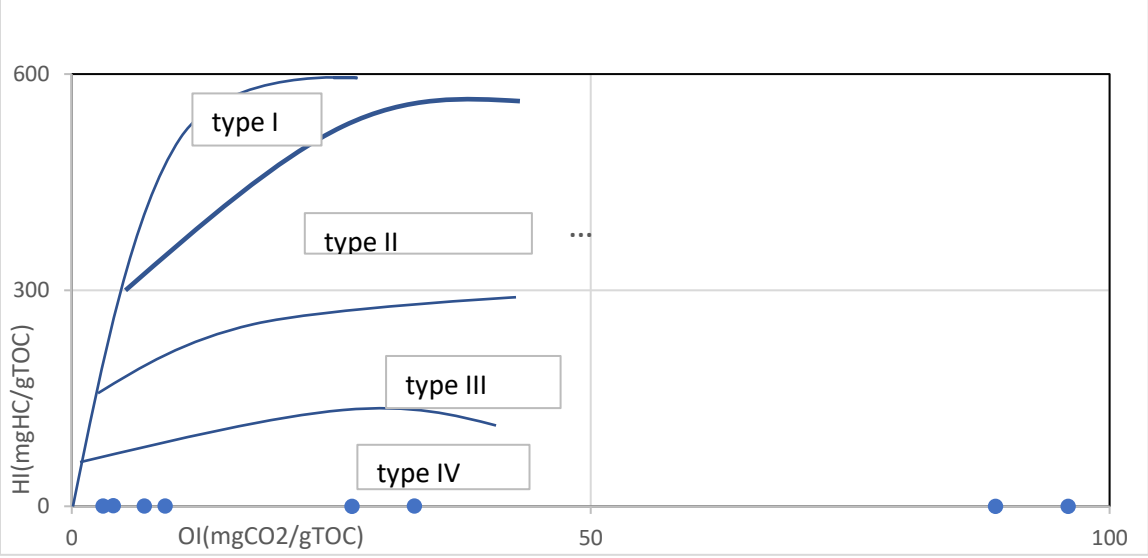


Figure 10 kerogen type

The graph above shows that all samples has fallen in the type IV region. This means it has low ratio of hydrogen to carbon and high ratio of the oxygen to carbon such that it cannot produce any hydrocarbons but capable of producing only water and carbon dioxide. Despite that samples showed to be highly rich in organic matters it turns out that the rock samples cannot produce any hydrocarbons except hydrocarbons and water, this shows that the organic matter was delivered from lacustrine or marine environment which is compose of the algae and planktons which are capable of producing hydrocarbons particularly oil just end up producing carbon-dioxide and water as if it was made up of residual organic which have altered by weathering, combustion or biogenic oxidation in swamps or soils.

This may due to different factors which include but not limited to, firstly as already highlighted that these are just an outcrop samples hence it is not exposed to good geological controls that can preserve the hydrocarbon e.g., these rocks are exposed to high temperature which can make these samples to start generating hydrocarbons at early stage hence it can be that all hydrocarbons has been generated, this also support the results of maturation level of the organic matter that shows that majority of the rock samples has fallen in post-mature stage that also shows that samples has already surpasses oil window that means it has already generated oil.

Another reason may be lack of seals hence hydrocarbon is able to move from one rock to another. It should be noted that lower shire valley is made up of many faults and folds thus the petrophysical data of area such as porosity and permeability is not yet known but it, but it must be the cause of samples failing to produce hydrocarbons.

4.1.2.1 Correlational relationship to build predictive model.

The figure below shows the relationship between the different composition of the rocks which include carbon contents, ratio of hydrogen to carbon and its generative potential with the depth at which the rock samples were collected.

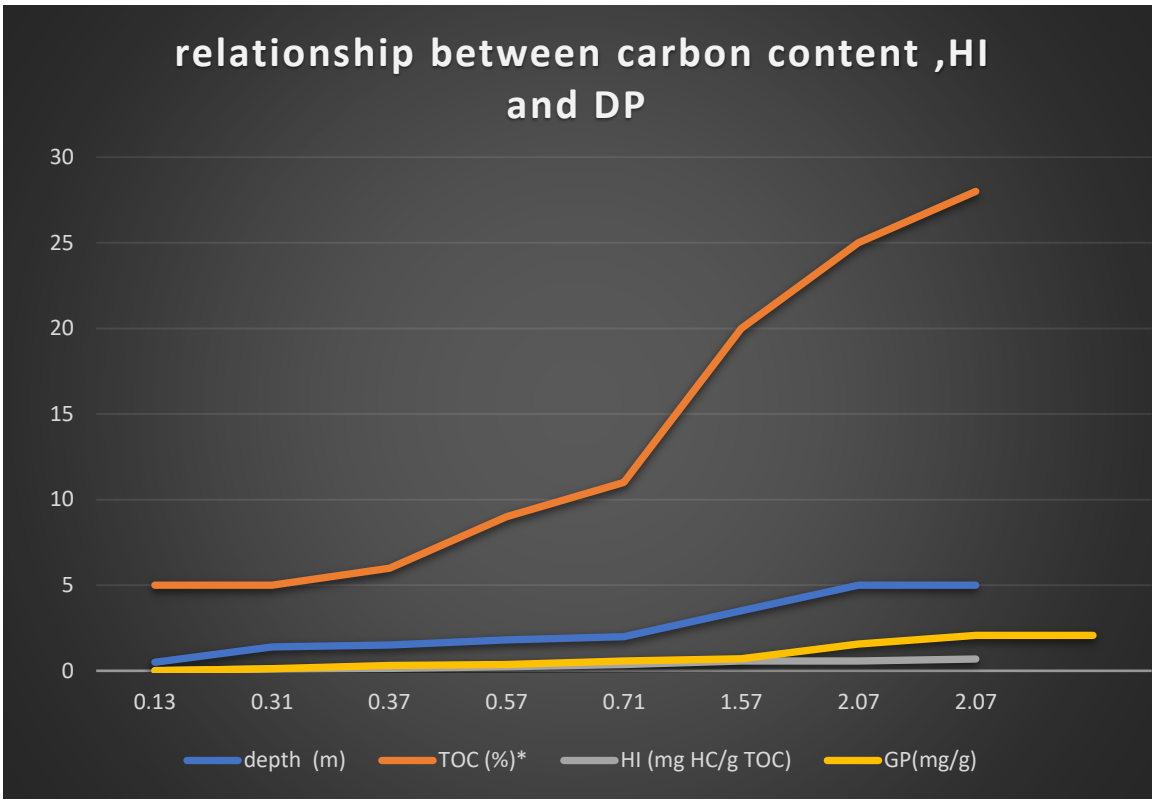


Figure 11 research model

From the graph above it shows that there is direct relationship between the carbon content, hydrogen index and generative potential (S1 +S2) with the depth. This means as the depth increases the generative potential of the rock samples which is ability of samples to produce hydrocarbon increases, this is shown by increasing in organic matter richness and amount of the hydrogen released as the depth increases.

On the other hand, it also shows that the quality of kerogen also changes as depth increases this is shown by increase in ratio of hydrogen to oxygen as depth increase. This gives hope that despite these samples showing that it can not generate any hydrocarbons there is probability that drilling down core samples it can generate hydrocarbons.

With these results keeping in mind that all factors that controls petroleum generation characteristics of the lower shire valley are good according to the previously researchers we can assume that lower shire basin has high probability of having stacked petroleum system at deeper depth hence core samples should be drilled for the further investigation in the area.

6.0 Recommendation

Further investigations are required to be applied to this research work, to compare and correlate results, as well as it would provide clues about the reliability of pyrolysis technique itself within geochemical source rocks evaluation field. Furthermore, those new studies would add value to the presents work. Thus, an improvement in the evaluation and interpretation of the results would be expected, several methods described below can be conducted for such purpose.

Since Pyrolysis analysis cannot measure the volatile products evolved from the sample because of the physical and chemical changes due to the increment in temperature during experiment. Thus, it is highly recommended to couple a Mass Spectrometer method to measure these volatile products and it can also measure two important geochemical parameters such as S1 and S2 hence it can be correlated and compared to one obtained from rock eval pyrolysis technique.

Vitrinite reflectance is good source rock evaluation tool used to assess the thermal maturation (Senate & Landis, 1991). Vitrinite is a maceral found in coals and kerogens which is formed due to the thermal alteration of lignin and cellulose in plant cell walls. Vitrinite undergoes complex chemical reactions when temperature is increased, increasing its reflectance. Thus, reflectivity is measured under a microscope, using an oil-immersion objective lens and one photometer. This measurement is represented in percentage of light reflected in oil, named as Ro (McCarthy et al., 2011). The use of this technique in each source rock sample would provide a definitive and reliable measurement of the thermal maturation. Hence, it is highly recommended its usage.

Deep core samples should be drilled and well logging technique should be conducted to obtain the petrophysical data such as porosity, water saturation, permeability, resistivity etc. deep core samples will help to improve the results in such that it will remove negative impact , the sun has on the outcrops rocks hence giving the accurate results without errors.

7.0 Conclusion

Rock eval pyrolysis analysis has shown to be a valuable technique within the geochemical source rock evaluation field, providing information regarding hydrocarbon generation potential, organic matter characteristics, maturation level of the rock samples and quality of the organic matter. Several conclusions can be drawn based on the detailed analysis of the rock samples collected as follows.

High organic richness in general has been described in each sample, indicating high TOC values thus, a high petroleum potential. All samples show excellent petroleum potential Nevertheless, it should be noted that TOC contains residual carbon or as it is called "dead carbon", which has not capacity to generate petroleum. Thus, S2 is a better petroleum potential indicator.

S1 values vary between poor and good petroleum potential as these are the hydrocarbons that have already been generated in the source rock. Sample NA20799_1 has shown the fair petroleum potential, indicating a fair petroleum generation ready to be expelled to the carrier system into the reservoir rock. On the contrary, sample NA20808_1 have shown the poorest petroleum potential, which can be underestimated, as it is classifies as poor.

Based on S2 values, poor potential has been shown for all rock samples. S2 represents the number of hydrocarbons that can still be generated if thermal maturation undergoes. Again, sample NA20799_1 have shown fair petroleum potential, adding an enormous value to this sample. Overall S2 results indicate that these rock samples have shown poor capabilities to generate petroleum if thermal maturation continues. Equally important to mention is the hydrocarbons migration interpretation. S2 (the number of hydrocarbons which might be generated if thermal maturation continues) decreases when thermal transformation of kerogen increases. Prior to any hydrocarbon expulsion, the petroleum potential, quantified by S2, is transformed by natural cracking into thermo-vaporizable hydrocarbons, quantified by S1 (the number of hydrocarbons which have already been generated in the subsurface). It should be noted that the hydrocarbons represented by S1

will eventually migrate out of the source rock throughout the carrier system into the reservoir rock. Thus, prior to any petroleum expulsion, S1 increases as S2 decreases. In this research work, the geochemical results have shown that S1 values are lower than S2 values in each source rock sample, which might be interpreted as hydrocarbons migrated out of the investigated source rocks into the carrier system.

DSC signal has been used for tracking Tmax values, thus, indicating the thermal maturation of each source rock sample. Maturity indicates the source rock ability to generate petroleum. DSC signal has shown Tmax values for samples NA20799_3,NA20799_3, NA20812_3, NA20817_1 and NA20817_2 is higher than 470°c, indicating post maturity in each sample. Source rocks are said to be thermally postmature, or spent source rocks, when they have entered at the gas window and have already generated petroleum. Another interpretation can be drawn. Good and very good petroleum potential may be reported in the samples, as indicated by TOC. Thus, these high Tmax values might suggest that theses source rock samples have a considerable amount of organic matter that is hard to decompose. Furthermore, they have already generated a large amount of petroleum and there is a window for more petroleum generation, samples NA20799_2and NA20799_1 it Tmax value show that it is in the mature whereby can produce hydrocarbons while sample NA20812_1 it Tmax show that it is the immature stage where it cannot generate hydrocarbon currently .

With reference to the source rock type, all samples are poor potential source rock as they have shown poor petroleum potential. Due to their advance thermal maturation, we can think that they are spent source rocks or inactive rocks. The difference between both is that inactive source rocks show petroleum potential, but it stops generating petroleum whereas spent source rock are said to be in postmature stage and can still generate wet or dry gas.

Kerogen types are described by HI parameter. All samples contain type 4, These source rocks are classified as no hydrocarbons prone.

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9.0 Appendix A

9.1 Rock EVAL PYROLYSIS

Eval pyrolysis is a method used to rapidly evaluate the petroleum-generative potential and thermal maturity of rocks developed by Espitalie et al..The technique involves heating pulverized rock under an inert atmosphere and analyzing the evolved gases. Quantitative and reproducible parameters from this process allow comparison of samples rapidly and inexpensively and the data obtained can be readily compared to other methods, such as elemental analysis for source rock potential and vitrinite reflection for maturity (Espitallie, 1974). The technique involves passing a stream of helium through 100 mg of pulverised rock heated initially at 300°C. The temperature is then programmed to increase at about 25°C/min up to 550°C. The vapours are analysed with a flame ionisation detector (FID), resulting in peaks as shown in Figure A.1. The first peak represents any free hydrocarbons in the rock that were either present at the time of deposition or were generated from the kerogen since deposition and these are reported as S1. Heating at 300°C simply distils the free hydrocarbons out of the rock (Hunt, 1995) .

The carboxyl groups in the kerogen break off between 300°C and 350°C, yielding CO2, which is trapped and analysed later during the cooling cycle using a thermal conductivity detector (TCD) and reported as S3. Between about 350°C and 550°C, hydrocarbons are generated by cracking the kerogen until only residual nongenerating carbon remains and reported as S2. In addition, high molecular-weight bitumen that was not distilled out and reported in S1 is cracked into smaller molecules and included in S2.

The areas under the curves are labelled S1, S2 and S3 respectively with S1 and S2 being proportional to the flame ionisation detector (FID) carbon in the vaporized products. Results are reported as milligrams of hydrocarbon based on calibrating the detector with standards. The TOC value is calculated separately.

The ratio of mg HC in S2/g TOC is called the Hydrogen Index (HI). The ratio of mg CO2 in S3/g TOC is called the Oxygen Index (OI). Hydrogen Index can be roughly. correlated

with atomic H/C ratio and Oxygen index (OI) with the atomic O/C ratio of the van Krevelen diagram.

As kerogen breaks down and loses hydrocarbons with greater burial, peak two gets smaller and peak one, which represents the released hydrocarbons, gets larger. Dividing the area (S1) by the combined areas S1 and S2 yields the Production Index (PI). This value increases steadily during hydrocarbon generation and the beginning of significant oil generation is around a PI of 0.1 and the end of oil generation around 0.4

As generation proceeds, higher temperatures are required to crack the remaining kerogen but the temperature at which maximum hydrocarbon generation occurs is recorded as Tmax. The beginning of oil generation starts at around Tmax 430°C and ends at around Tmax 460°C. Rock-Eval pyrolysis Tmax is frequently used as a maturity indicator, because as the maturity of the kerogen increases the temperature at which maximum pyrolysis occurs also increases. Actual Tmax temperatures are dependent upon kerogen type so when comparing maturity values with other maturity measurements the type of kerogen must be considered. Tmax values for small S2 peaks (0.2 MG/HC/GTOC) are unreliable.

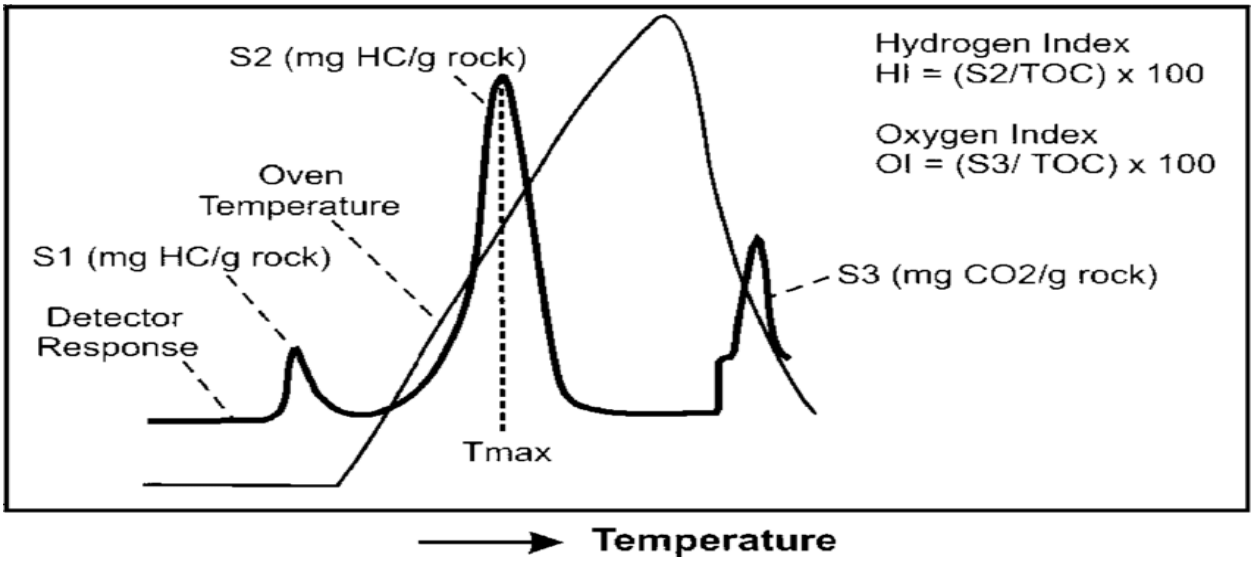


figure A1 Schematic of pyrogram delivered from Rock-Eval

Figure A.1. Schematic representation of the program derived from Rock-Eval pyrolysis. Peak S1 indicates the hydrocarbons distilled from the sample at 300°C. Peak S2 are the hydrocarbons generated during pyrolysis and the temperature at which 4 the maximum hydrocarbons are generated is termed Tmax. The total of S1 and S2 give an estimate of the generative potential of the sample. S3 is a measure of the organic CO2 generated by the sample up to 390°C. The flat-topped curve illustrates the oven temperature during pyrolysis. TOC is determined separately so that HI and OI can be calculated. (Hunt, 1995).

10 APPENDIX B

10.1Rock-eval pyrolysis data

Sample name	S1 (mg/g0	S2 (mg/g)	S3 (mg/g)	PP (mg/g)	TMAX (C')	PI (wt. ratio)	HI (mg HC/g TOC)	OI (mg CO2/g TOC)	TOC (%)*
NA20799_1	0.59	0.49	20.5	1.08	457	0.56	9	410	5
NA20799_2	0.45	0.81	4.95	1.26	450	o.38	16.2	247.5	5
NA20799_3	0.4	0.05	0.17	0.45	521	0.89	0.2	0.68	25
NA20812_1	0.05	0.04	0.03	0.09	515	0.56	0.44	0.33	9
NA20812_2	0.43	0.14	10.73	0.57	274	0.75	1.27	97.5	11
NA20812_3	0.39	0.09	0.04	0.48	521	0.81	O.32	0.14	28
NA20817_1	0.13	0.12	1.04	0.25	546	0.52	2	17.3	6
NA20817_2	0.21	0.05	0.09	0.26	535	o.81	0.71	0.45	20

Table B1, Geochemical Data obtained from rock-Eval pyrolysis.