SOURCE ROCK EVALUATION OF TOTAL ORGANIC CARBON, MINERALOGY, AND ALIPHATIC HYDROCARBON BIOMARKERS (THE ANZA BASIN, KENYA)

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A Thesis Submitted to the Graduate School in Partial Fulfilment of the Requirements for the Master of Science Degree in Chemistry of Egerton University

EGERTON UNIVERSITY

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DECLARATION AND RECOMMENDATION

Declaration

This study is my original work and has not been presented for the award of a degree in any University.

Signature Date 09/07/2024

Chesir Lorna Chemutai

SM11/14394/15

Recommendation

This Thesis has been submitted for examination with our approval as University supervisors.

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DEDICATION

This thesis is dedicated to my husband, Mark Koech, my daughter Emunah Koech, my parents, and my siblings.

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ABSTRACT

One of the essential steps in hydrocarbon exploration and exploitation is to understand the association of organic matter and minerals in petroleum reservoirs which is a vital component of the hydrocarbon-generation process. Understanding how and where hydrocarbons originated, helps to comprehend and predict where they can be discovered, particularly in unconventional reservoirs such as source rocks. The purpose is this study is to characterize the organic matter content of seven source rocks collected from three wells (Chalbi-3, Sirius-1, and Ndovu-1) located in the Anza Basin in the north eastern part of Kenya. These were characterized using: (i) elemental (CHN) analysis for organic matter components; and (ii) X-ray diffraction (XRD), X-ray fluorescence (XRF), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM-EDX), thermogravimetric and differential scanning calorimetry (TG/DSC) for mineralogical characterization, and gas chromatography-mass spectrometry (GC-MS) analysis for saturated aliphatic biomarkers. This evaluation revealed, for all the wells and the depths studied, the source rocks have TOC values of 0.54%, 1.46%, 1.54%, and 1.99 % for Sirius-1, Chalbi-3, and Ndovu-1, respectively. The high quartz content coupled with a fair to good %TOC content, and low H/C values, have demonstrated the potential of the source rocks as being good and capable of oil and/or gas expulsions from the wells. High organic richness has been measured in each source rock sample. The XRF, XRD, and FTIR results revealed that the source rocks were comprised mainly of quartz, followed by silicate-clay minerals and calcite minerals. While Thermogravimetric Analysis (TG/TΔG) and Differential Scanning Calorimetry (DSC)–under a controlled (O_2/air) oxidizing atmosphere and at a heating rate of 10 °C min^{-1}, showed there was a strong correlation between TG and DSC, and that for both processes, the source rocks underwent thermal decomposition in three steps. In addition, solvent-extractable organic matter investigation revealed a unimodal distribution of biomarkers: n-alkanes and isoprenoids (low pristane/ phytane ratios). Thus, the hydrocarbons in the source rocks were derived from algae and bacteria, which had been deposited under weakly anoxic and low oxic environmental conditions with least contributions from terrestrial organic matter sources. Hydrogen Indices are low (HI= H/C: 0.19–0.60 atomic ratios), indicating a predominance of mixed type III/IV (oil/gas-prone). The drilled well depths (1066-3100 m) demonstrated good reservoir rock properties with fair to good hydrocarbon generation potential (TOC values between 0.5–2%) with the existence of commercial hydrocarbon production.

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LIST OF ABBREVIATIONS AND ACRONYMS

AMOCO	American Oil Company
GC	Gas chromatography
GC-MS	Gas-Chromatography Mass-Spectrometry
DSC	Differential Scanning Calorimetry
EOM	Extractable Organic Matter
FTIR	Fourier- Transform Infrared Spectroscopy
ICP-OES	Inductively Coupled Plasma Optical Emission Spectroscopy
IR	Infrared Spectroscopy
MSD	Mass Selective Detector
NIST	National Institute of Standards and Technology
NOCK	National Oil Corporation of Kenya
OM	Organic Matter
SEM-EDX	Scanning Electron Microscopy-Energy-dispersive X-ray
SIM	Selected Ion Monitoring
TCD	Thermal Conductivity Detector
TG	Thermogravimetric
TGA	Thermogravimetric Analyser
TG/DTG/DSC	Thermogravimetric/Derivative Thermogravimetry/Differential Scanning Calorimetry
TOC	Total Organic Carbon
XRF	X-ray Fluorescence
XRD	X-ray Diffraction

CHAPTER ONE

INTRODUCTION

1.1 Background information

The depletion of conventional petroleum sources and the increase in oil prices have led to widespread efforts to search for alternative energy sources (Al-Yasiri, 2021; Kassem *et al*., 2021; Taha *et al*., 2023). Hence, attention is turning to unconventional resources like oil shale and source rocks to satisfy the present and future oil and gas needs. Some source rocks have turned out to be excellent reservoirs for the generation and accumulation of oil and gas. An organic-rich petroleum source rock has a high content of solid insoluble kerogen that can release a petroleum-like liquid under suitable thermal maturation conditions (Curiale & Curtis, 2016), and provide secure access to transportation fuels. The petroleum-generating potential of the source rock is directly related to its volume, organic richness (Total Organic Carbon), and thermal maturity (Ojo *et al*., 2020). Alongside organic richness (kerogen and Bitumen), understanding the mineralogical composition of source rocks is important for optimizing hydrocarbon recovery because the mineral phases present in a rock determine a reservoir's physical and chemical properties. However, mineralogical data is rarely collected during the characterization of conventional reservoirs, which conversely, is one of the most important characteristics of an unconventional reservoir. A careful study of the source rock organic matter also, therefore, requires an investigation into the mineral matrix.

Kenya has a history of oil exploration dating back to the 1950s (Scholvin, 2016). However, most of the wells that were drilled in the past came up with no traces of hydrocarbons (Butare, 2015). After decades of disappointing results, investments in hydrocarbon exploration decreased until 2010 when offshore gas finds in Mozambique and Tanzania and onshore oil finds in Uganda attracted investors back to Kenya (Northrup & Wittemyer, 2013). Kenya is under-explored and has enormous potential, making it attractive for investors (Davies, 2013). In the entire history of Kenya, only 50 wells have been drilled. In Texas (USA), similar in geographical area to Kenya, 500,000 wells have been drilled since 1960 (Macgregor, 2015). This comparison indicates that Kenya may be harbouring large oil deposits which are yet to be trapped. The quantity of the organic matter that is present in the oil shales in Kenya has not been studied in detail. Apart from producing refined fuels, the expected crude oil can also provide petrochemicals for a wide range of uses, both as products themselves and as chemical feedstock used to manufacture other products (Vennestrom *et al*., 2011).

The Anza basin is referred to as the termination of the Central African Rift System in the Chalbi sub-basins in Northern Kenya and an extension of the Melut and Muglad rift basins in South Sudan where working petroleum systems exist (Mohamed *et al*., 2002). After evaluation of organic matter (OM) content as Total Organic Carbon (TOC), Rop (2013) and Gilbert *et al*. (2021) demonstrated that the organic-rich sedimentary rocks of the Anza basin can produce gas and oil. According to Zhang & Hascakir (2020), profitable oil extraction from a source rock can be accomplished if the organic content of the source rock is approximately 2.5% or more. However, there is not a unanimously accepted lower limit of organic matter content for oil shale/ source rock. Above and beyond, the composition and quality of the source rocks may vary within the limits of one deposit. About 90 % of the organic matter preserved in sedimentary rocks is usually in two forms: high molecular weight polymeric material (kerogen, insoluble in usual organic solvents), and the rest is free hydrocarbons (bitumen, soluble in usual organic solvents) (Tissot *et al*., 1984).

The mineral content of the oil shale/source rocks plays a fundamental role in the selective preservation of organic matter (OM) owing to their strong adsorption and catalytic properties during deposition and burial. Alongside kerogen, the inorganic content of the oil shale/source rocks is an important ingredient to generate oil. But to our knowledge, investigations of the various types of minerals in source rocks in the Anza basin are very scarce. Additionally, the quantity of organic matter that is present in the source rocks in Kenya is still limited and needs to be examined in detail.

Numerous thermal and spectral methods have been used to characterize oil shale samples qualitatively and quantitatively. Elemental analysis and thermal gravimetric analysis (TGA), Differential Scanning Calorimetry (DSC) are thermal analysis techniques whereas X-ray diffraction (XRD) and Infra-Red Spectroscopy (IR) are spectral methods have been used as they are more economical and easy to use. A combination of TGA and IR is known to give consistent results for organic matter, as a combination of IR and XRD detects inorganic matter (Biyada *et al*., 2020). In addition, Scanning Electron Microscopy (SEM) provides information on the morphology and the minerals present in the oil shale source rocks (Zhang & Hascakir, 2020).

However, Labus & Matyasik (2019) noted that the main problem encountered during the analysis of organics is that organic matter is dispersed within the rock matrix, which makes it difficult to examine them without taking into consideration the significant influence mineral components of the rock have on kerogen decomposition. Thermogravimetric (TG) and differential scanning calorimetry (DSC) methods are a powerful group of analytical techniques and can provide information on organic matter content and the minerals present in fossil fuels; coal and oil shales (Labus, 2017). The greatest advantage of thermal methods is in allowing not only concentrated organic matter (OM) but also finely dispersed OM, even as low as 0.25%, can be detected and examined (Yusupova *et al*., 1999).

Two factors are essential for a source rock to generate oil: the type of kerogen and the inorganic content of the source rock. Kerogen is the preserved organic matter that is the source of petroleum gases and liquids; whilst the inorganic minerals in the source rock increase the reactivity of organic matter (Guven *et al*., 2015). Hence, thermal and spectral methods have been used to characterize oil shale/source rock samples qualitatively and quantitatively. Thermal gravimetric analysis (TGA) and Differential Scanning Calorimetry (DSC) are thermal analysis techniques that have been used to estimate organic content in the source rock, whereas X-ray diffraction (XRD) and Infra-Red Spectroscopy (IR) are spectral methods that have been used to define minerals in the source rocks. These methods are advantageous since they are economical and easy to use. A combination of TGA/DSC and IR are known to give consistent results for organic matter, especially aliphatic, carboxyl/carbonyl, and aromatic compounds (Guven *et al*., 2015). However, the thermal behaviour of Seyitomer oil shale in Turkey, using TGA/DSC under air injection, showed that organic decomposition occurred at higher temperatures due to oxidation of organic content (Kok *et al*., 2001). A combination of IR and XRD, on the other hand, detects inorganic matter (Biyada *et al*., 2020) as well, while Scanning Electron Microscopy (SEM) provides information on the morphology (structure) and the minerals present in the oil shale/ source rocks (Zhang & Hascakir, 2020).

However**,** no oil of commercial value has been reported from the source rocks of the Anza basin. Also, investigations of various types of minerals and their importance in source rocks of the Anza basin are scarce. Hence, relations between organic matter and mineral matter represent a missing link that highlights the origin and source of the organic matter as well as their environment of deposition. This provided an impetus for the current study, whose emphasis was mainly on investigating the source rock samples of the Anza basin in the North Eastern part of Kenya. In this study, elemental analysis was used to evaluate Total Organic Carbon (TOC) as wt. % C, wt. % H, wt. % N, and wt. % S. Thermal gravimetric analysis/differential scanning calorimetry (TG/DTG/DSC) was used to estimate organic content under oxidative (air/O_2) environment. X-ray diffraction (XRD) and X-ray fluorescence (XRF) were used to detect the minerals in the source rocks. Whilst Fourier Transform Infra-Red (FT-IR) detected organic matter (kerogen) and the minerals in the source rocks. Scanning electron microscopy (SEM) was used to characterise the physical structures and morphology of the source rocks.

1.2 Statement of the problem

The success of Hydrocarbon exploration within the Anza basin hinges on the characteristic organic matter (OM) contents, thermal maturity, generation potentials, and expulsion efficiencies of the source rocks. Preliminary studies conducted by the American Oil Company (AMOCO) within the basin revealed the presence of massive oil reservoirs and source rocks, mainly in the upper cretaceous/Precambrian basement rocks. Also, the Tullow Oil wells in the Turkana region, have higher prospects of oil production. However, until now, little or no substantive data on the association of organic matter and minerals in petroleum source rocks, particularly for the Sirius-1, Ndovu-1, and Chalbi-3 wells of the Anza basin to comprehensively inform of their petroleum potential, has not been reported. The relationship between organic matter and mineral matter represents a missing link that highlights the origin and source of the organic matter as well as their environment of deposition. This has provided an impetus for the current study.

1.3 Objectives

1.3.1 General objective

To characterize the organic matter content, mineral composition, and aliphatic hydrocarbon biomarkers in seven source rocks using a multi-analytical approach.

1.3.2 Specific objectives

i. To measure the total amount of organic carbon (% TOC) and identify the possible petroleum source rocks in the drilled Chalbi-3, Ndovu-1, and Sirius-1 wells in the Anza basin.

ii. To characterise the minerals and surface morphology of source rock samples of the three wells of the Anza basin using FTIR, XRD, XRF, and scanning electron microscopy (SEM).

iii. To characterise thermal behaviour and mass losses of the source rock samples using Thermogravimetric/Derivative thermogravimetric (TG/DTG) and Differential Scanning Calorimeter (DSC).

iv. To determine aliphatic hydrocarbons (biomarkers) in the bitumen (oil) extracts from the source rock samples using GC–MS.

1.4 Research questions

i. What is the total organic content (%) and organic matter quality of the source rock samples from Chalbi-3, Ndovu-1, and Sirius-1 wells?
ii. What are the characteristics of the minerals and surface morphology of source rock samples of the three wells of the Anza basin from FTIR, XRD, XRF, and scanning electron microscopy (SEM) results?
iii. What are the thermal behaviour and mass losses of the source rock samples from Thermogravimetric/Derivative thermogravimetric (TG/DTG) and Differential Scanning Calorimeter (DSC) results?
iv. Which are the normal aliphatic hydrocarbons (biomarkers) in the bitumen (oil) extracts from the source rock samples from GC–MS results?

1.5 Justification

Primary energy demand is increasing fast and it is expected to grow by 41 % from 2012 until 2035, according to BP Outlook 2035 presented in January 2014 (Ramos, 2015). Gilbert *et al*. (2021) demonstrated that the organic-rich sedimentary rocks of the Anza Basin could produce gas and oil. Gilbert *et al*. (2021) and Rop (2013) contributions have focused on the source rock characteristics and their relative importance for hydrocarbon generation. However, investigations into the various types of minerals and their importance in source rocks of the Anza basin are scarce. This provided the stimulus for the present study, to identify the possible presence of source rocks for hydrocarbon generation from the samples and the mineralogy of the source rock samples in the Anza basin.

CHAPTER TWO

LITERATURE REVIEW

2.1 Overview of source rock potential

The National Oil Corporation of Kenya (NOCK) is a government parastatal that is mandated to oversee all exploration and exploitation of crude oil in Kenya. Exploration interest is on the rise following oil discoveries in Tanzania, Mozambique, and Uganda (Pivot, 2019). Porosities, organic matter, and other sedimentological and structural parameters are important features used to understand the essential features of source rocks, reservoir rocks, and cap rocks. Source rock is one of the four petroleum systems that is used as a primary indicator for tracing any possible occurrences of hydrocarbons. It is the fine-grained sedimentary facies rich in organic matter that may generate hydrocarbons (Egbobawaye, 2017).

Successful exploration of oil and gas depends largely upon the quality of the source rock. The source rocks may be directly sampled and analysed to reveal their source potential and thermal maturity. Assessment techniques such as total organic carbon (TOC) analysis provide information that allows the quality of the target rock to be assessed (Aziz *et al.*, 2020). To determine source rock quantity, total organic carbon (TOC) content is determined while the quality is detected by the hydrogen index (HI) property from elemental (CHN/S) analysis. The best samples are then selected for more sophisticated and time-consuming further analysis by techniques such as FTIR, XRD, XRF, SEM, TGA/DSC, and GC-MS. Therefore, to unravel the potentiality of hydrocarbon generation, it is paramount to assess the source rocks via geochemical analyses. This makes it possible to estimate qualitatively and quantitatively their hydrocarbon potentiality.

2.2 Historical exploration of hydrocarbons in Kenya

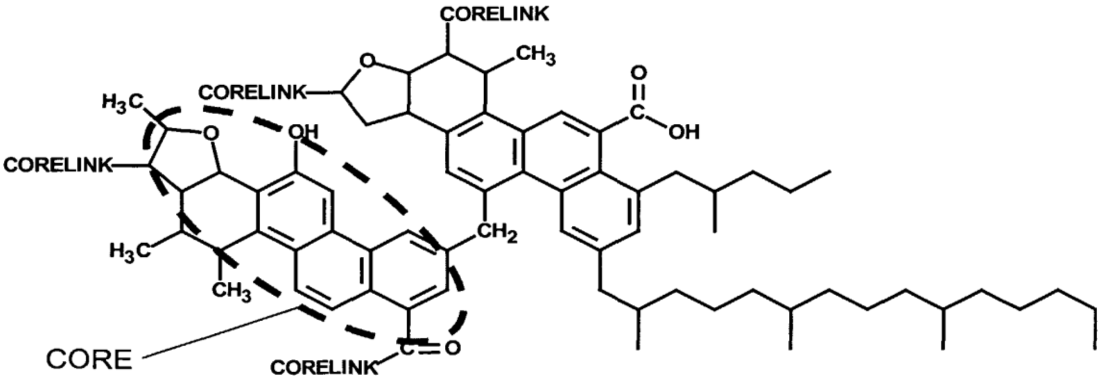
Kenya has a history of oil exploration dating back to the 1950s (Scholvin, 2016) and the first well was drilled in 1960 (Mugendi *et al.*, 2022). Most of the wells that were drilled in the past came up with no traces of hydrocarbons (Butare, 2015). In Texas (USA), which is similar in geographical area to Kenya, 500,000 wells have been drilled since 1960, whereas in the entire history of Kenya, only 50 wells have been drilled (Macgregor, 2015). This comparison, however, points to one fact: Kenya may be harbouring large oil deposits which are yet to be tapped. Driven by the success of offshore gas finds in Mozambique and Tanzania, and onshore oil finds in Uganda, some investors have been attracted back to Kenya for further exploration (Northrup & Wittemeyer, 2013). Although there is an increment in renewable energy consumption in Kenya, oil and gas still have predominance as energy resources.

2.3 The state of petroleum exploration in Kenya

The National Oil Corporation of Kenya (NOCK) is a government parastatal that is mandated to oversee all exploration and exploitation of crude oil in Kenya. Currently, Kenya has four (4) petroleum exploration basins: Lamu Basin, Anza Basin, Mandera Basin, and Tertiary Rift Basin. The breakthrough of petroleum exploration came in March 2012, with the discovery of an oil well dubbed Ngamia-1 Well, in the Lokichar Basin in Turkana County. As of December 2015, seventy-four (74) wells had been drilled. To-date, twelve (12) hydrocarbon discoveries have been found, nine (9) of which are in Turkana County. The other three are in the Anza Basin and Offshore Lamu.

2.4 The chemistry of organic matter

Organic matter is present in rocks in both low molecular weight or ‘‘free’’ and high molecular weight or ‘‘kerogen’’ forms. The most important property of a source rock is its kerogen content, which determines its potential to produce oil and gas. About 90 % of the organic matter preserved in sediments is a high molecular weight, insoluble, polymeric material called kerogen, and the rest is solvent-soluble and is called bitumen (Tissot *et al*., 1984). The structure of kerogen (**1**) is complex and consists of various aromatic groups and some oxygenated functional groups.



1

The term "CORE" means a contiguous ring system, and the term "CORELINK," simply means a link to a ring system, as illustrated above in structure **1**. Bitumen, on the other hand, is a native substance of variable colour, hardness, and volatility, composed principally of the elements carbon and hydrogen and sometimes associated with mineral matter such as quartz (silica) and clay minerals. The bitumen is also called "lipids' or simply "extractables" and is soluble in organic solvents such as benzene, methanol, and carbon disulphide (Hinkle & Batzle, 2006). Bitumen includes compounds such as n-paraffins derived from fatty acids, waxes, hydrocarbons (saturated, unsaturated, cyclic, or aromatic), and also fats, alcohols, and pigments.

Two factors that are therefore essential for a source rock to generate oil are the type of kerogen and the inorganic content of the source rock. Kerogen is the preserved organic matter that is the source of petroleum gases and liquids, whilst the inorganic minerals in the source rock increase the reactivity of organic matter (Guven *et al*., 2015). Hence, various spectral and thermal methods have been used to characterize oil shale/source rock samples qualitatively and quantitatively.

2.5 Biomarkers

Biological markers (Biomarkers) are complex molecular fossils/compounds that were once-living organisms that are ubiquitous in sediments, rocks, and crude oils and are nonbiodegradable (Hakimi *et al*., 2019). The biomarkers of interest are aliphatic hydrocarbons found in the form of *n*-alkanes, acyclic isoprenoids, bicyclic sesquiterpene, and polycyclic terpenoids. The distribution of *n*-alkanes biomarkers compounds in petroleum samples can convey information about the types of sources and the maturity level of petroleum (Hakimi *et al*., 2019). Specific isoprenoid compounds are pristane (Pr) and phytane (Ph), and their (Pr/Ph) ratio can be used to determine the environmental conditions which are oxidative or reductive environments during the deposition process of organic material. The type of oil that originated from the marine environment is indicated by the unimodal distribution of n-alkane compounds (*n*-C16-*n*-C23).

2.6 Geo-analytical Techniques

Several methods have been developed for the extraction of petroleum hydrocarbons and analysis of mineral matter in the source rock matrix which are highlighted.

2.6.1 Total Organic Carbon (TOC)

In the combustion (elemental analysis) method, the value of TOCs can be obtained from the amount of CO_2 that is produced by the oxidation of all types of organic carbons in samples with excess O_2. This elemental analysis method has been used to determine the TOC contents of various geologic materials, including soil, sediments, and sedimentary rocks. First, carbonate minerals have to be removed by acid treatment before combustion to determine TOC contents (Liu *et al*., 2019). In the final analysis, Total Organic Carbon (TOC) measurements provide evidence of the organic richness and spatial distribution of organic components in the source rocks that are vital for evaluating the hydrocarbon-generating potential of petroleum source rocks (Rop, 2013).

2.6.2 Fourier Transform Infrared (FTIR)

Infrared spectroscopy (IR) is a widely used analytical technique in geoscience studies and is used as a screening tool to recognize samples containing clays and organic compounds (Stanienda, 2016). FTIR is a spectrometer that determines the material structure by applying an Infrared beam on the sample and the ratio between the incidents to transmittance wave is measured. The wave range used is between 400-4000 cm^{-1}. The technique has some advantages over XRD including, (i) faster generation of spectrum (≤ 1–2 min), (ii) small amount of samples required (about 0.3g) required, (iii) does not require additional treatments of samples, and (iv) it is cheaper compared to XRD method.

2.6.3 X-ray Diffraction (XRD)

In XRD, the atoms in the crystals are responsible for the X-rays’ scattered behaviour. As the X-rays follow the atom’s regular patterns, the observed pattern will be similar. The diffractograms follow Bragg’s law for calculating the resulting angle, which is phase-dependent (Als-Nielsen & McMorrow, 2011) and is illustrated in Figure 2.1.

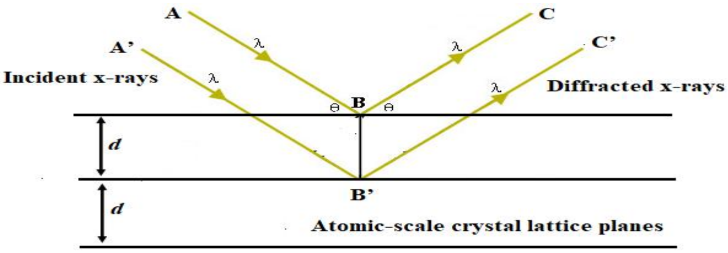


Figure 2.1: Schematic diagram for X-ray diffraction

Bragg equation

$$\lambda = 2d\,Sin\theta \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

where, λ = X-ray wavelength (nm)

d = spacing between diffracting planes

θ = angle between the incident rays and diffracting planes

In XRD (X-ray diffraction) the inter-planar spacing or d-spacing of a crystal is used for characterization and identification purposes.

X-ray diffraction is not only routinely used for the qualitative identification of minerals in geological samples, by fingerprinting approach (Al-jaroudi *et al*., 2007), but it has also been proven to be effective in the quantification of mineralogical data (Ruan & Ward, 2002). Quantification is based on the fact that the peak intensities from an individual mineral are proportional to the latter's content in the sample. Measurement of peak intensities should, therefore, provide information regarding the relative amount of the corresponding mineral phase.

2.6.4 X-ray Fluorescence Analysis (XRF)

X-ray fluorescence (XRF) technique is one of the major instruments in diagnostics; due to its ability to analyse the sample (Sabri, 2020). The analysis of major and trace elements in geological materials by x-ray fluorescence is made possible due to the behavior of atoms when they interact with radiation. In XRF analysis, a sample is irradiated by high-energy photons emitted by the XRF analyser, displacing electrons in the inner orbital shell of an atom, normally the “K-shell” (Kodom *et al*., 2012). This displacement only takes place if the photons emitted into the sample have a higher energy than the energy holding the electron in the K-shell. Once the electron is ejected from the K-shell, the atom becomes unstable, and an electron from a higher orbital shell, normally the “L-shell” or “M-shell” moves down to the newly created vacancy (Figure 2.2). The incident X-ray beam originates from a Rh target (in the X-ray tube), though W, Mo, Cr, and others can also be used. For an electron to move to a lower energy state or lower orbital shell, energy must be released. This release of energy is known as fluorescence. This energy is then captured by the X-ray detector and because the released energy is unique to each element, such elements can be differentiated, and their concentrations quantified.

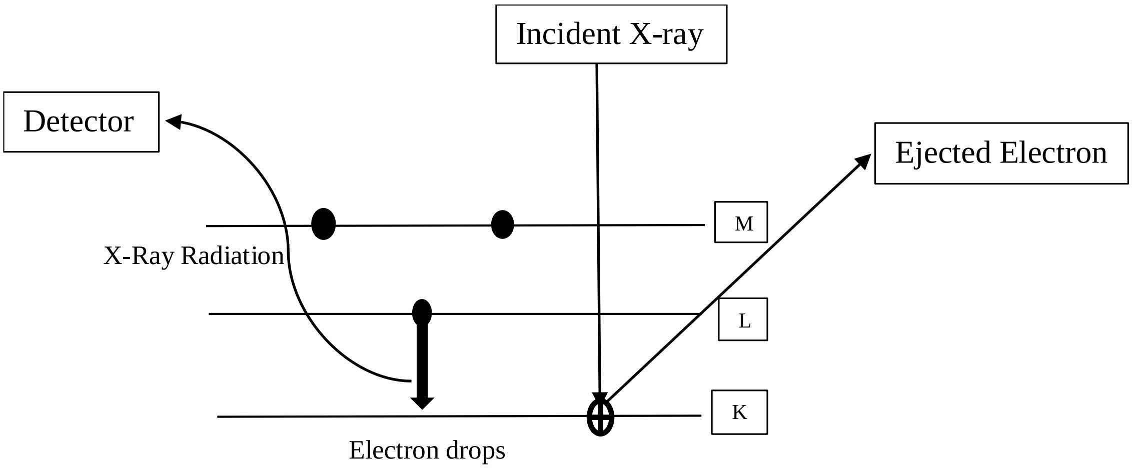


Figure 2.2: A schematic of a typical energy dispersive X-ray fluorescence spectrum

The Energy Dispersive X-ray Fluorescence detector captures and sorts the energy of released photons and collects the entire spectrum of elements within seconds of irradiating the sample. If a sample has many elements present, as is typical for most minerals and rocks, the use of a wavelength dispersive spectrometer allows the separation of the emitted X-ray spectrum into characteristic wavelengths for each element present. Various types of detectors (gas flow proportional and scintillation) are used to measure the intensity of the emitted beam. The intensity of the energy measured by these detectors is proportional to the abundance of the element in the sample.

2.6.5 Scanning Electron Microscopy (SEM)

The SEM gives the magnified images of the size, shape, composition, crystallography, and other physical and chemical properties of a specimen. It offers the opportunity to analyze the material to be examined with an electron beam (Figure 2.3) generated in a vacuum environment and thinned with electromagnetic lenses in the same situation to create a high-resolution image (Ural, 2021). The images found in the microscope are created by counting the reflections or electrons reflected from the interaction of the electron beam with the material. The character of the soil/rock microstructure can be seen over a wide range of magnification by SEM. Generally, SEM analysis is employed to facilitate the microstructural comparison and explanation. In the SEM images, a microscope is used to qualitatively identify the microstructural developments in the matrix of the stabilized soil/rock specimens.

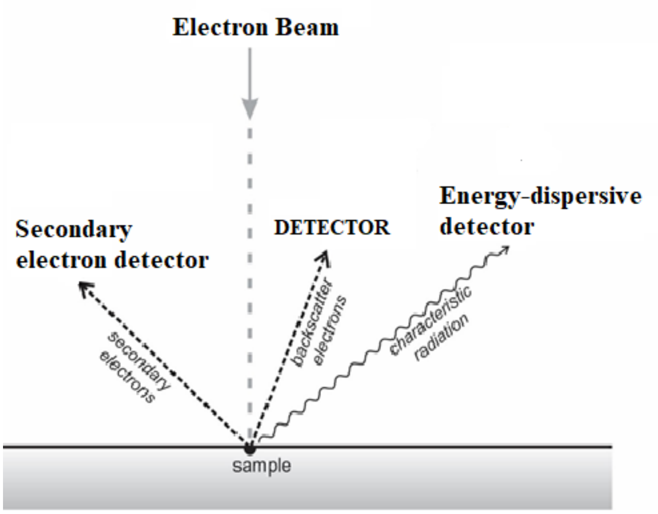


Figure 2.3: Inside a Scanning electron microscope

2.7 Thermal analysis

Thermal analysis is defined as a group of techniques in which a physical property of a substance is measured as a function of temperature, while the substance is subjected to a controlled temperature program. Thermal analytical instruments monitor the changes in physico-chemical properties caused by different processes. Two thermal analysis methods which are commonly used to evaluate oil shale/source rock samples, under controlled heating are: thermogravimetry (TG/DTG) and differential scanning calorimetry (DSC). A combination of TGA-DSC is illustrated in Figure 2.4, which simultaneously measures both weight loss percentages (orange curve) and heat flow (green curve) during sample material analysis, as a function of temperature or time under a controlled atmosphere. In Figure 2.4, the y-axis on the left-hand side (inner) represents weight loss percentages (TG–red line), and the y-axis on the left-hand (outside) gives derivative weight loss percentages (DTG–blue line) and on right-hand heat flow behaviour of sample material (DSC–green line). Most of the reactions are connected to the mass loss which is determined on TG curves as a function of temperature.

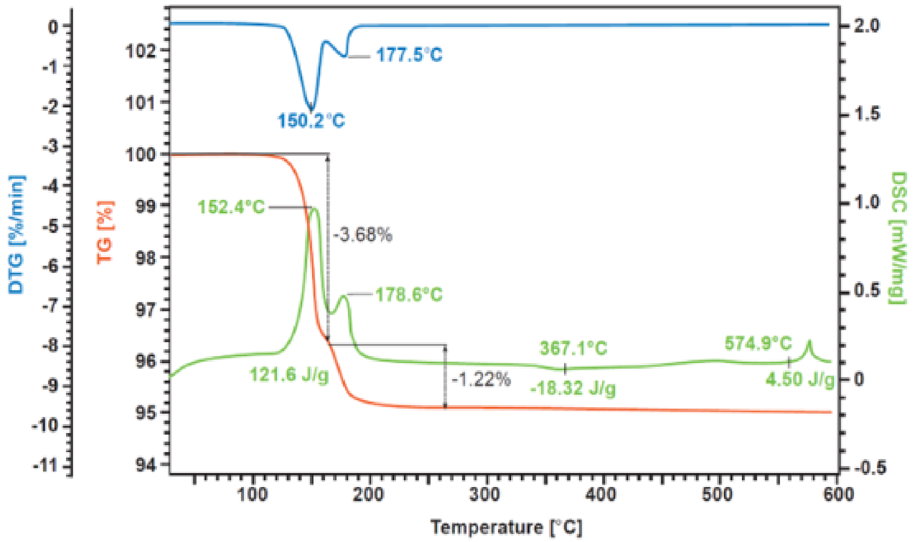


Figure 2.4: Typical TGA/DSC outcome (Pope *et al*., 2020)

This combination has the advantage that it does not only improve productivity but also simplifies the interpretation of the results therein. Additionally, a Thermogravimetric/Differential Scanning Calorimetry (TG/DSC) analysis device can also be used for onsite analysis, due to the portability of the instrumentation (Sanders & Gallagher, 2002).

2.7.1 Thermogravimetric Analysis (TGA)

Thermogravimetry (TG/DTG) is a technique that measures the mass loss of a sample as a function of temperature or time, and can be used to measure any reaction involving mass change (Mureddu *et al*., 2018). Thermogravimetric analysis (TGA) is conducted on an instrument referred to as a thermogravimetric analyser (Figure 2.5). A thermogravimetric analyser continuously measures mass while the temperature of a sample is changed over time (Saadatkhah *et al*., 2020). A typical thermogravimetric analyser consists of a precision balance with a sample pan located inside a furnace with a programmable control temperature (Rostek & Biernat, 2011). The temperature is generally increased at a constant rate (or for some applications the temperature is controlled for a constant mass loss) to incur a thermal reaction. The thermal reaction may occur under a variety of atmospheres including ambient air, vacuum, inert gas, oxidizing/reducing gases, corrosive gases, carburizing gases, vapours of liquids, or "self-generated atmosphere"; as well as a variety of pressures including a high vacuum, high pressure, constant pressure, or a controlled pressure.

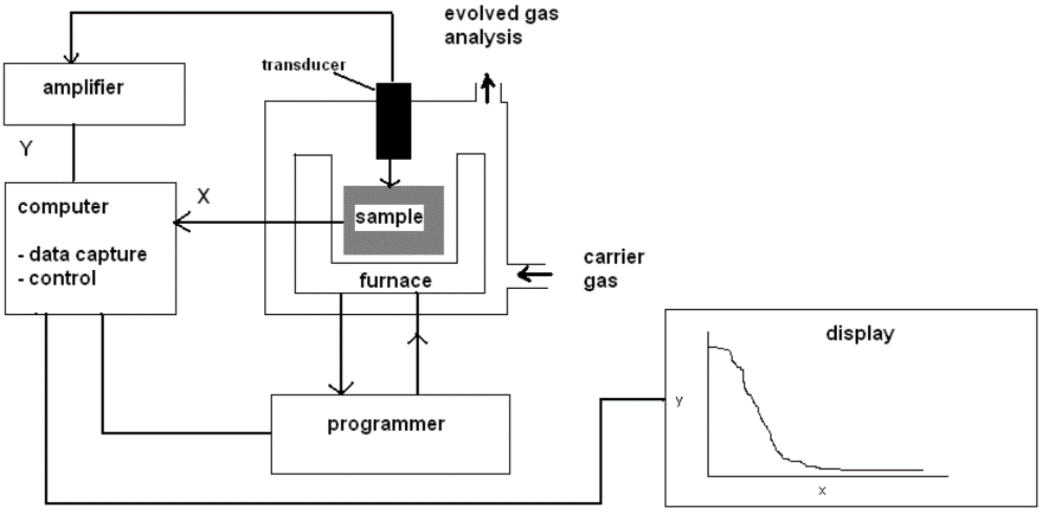


Figure 2.5: Typical sketch diagram of a thermogravimetric analyser

TG provides information about physical phenomena, such as phase transitions, absorption, and desorption; as well as chemical phenomena including chemisorption, thermal decomposition, and solid-gas reactions (e.g., oxidation or reduction). Derivative thermogravimetry (DTG) gives the rate of mass change as a function of temperature or time. It is quite beneficial for overlapping processes and now and again in kinetic studies. A thermogravimetric analyser continuously measures mass while the temperature of a sample is changed over time (Saadatkhah *et al*., 2020). Thus, mass, temperature, and time are the base measurements in thermogravimetric analysis. Resolution of individual stages of more complex TG curves can be achieved from the DTG curve as illustrated by the blue line in Figure 2.4.

Accordingly, the main assumptions in TG/DTG are that the total loss of mass of the sample during the heating process corresponds to (i) release of volatile compounds such as moisture or hydrocarbon gases, (ii) the molecular decomposition of organic matter such as kerogen, which is closely related to the presence of hydrocarbons in the source rock, and (iii) combustion of carbon black and mineral matter residues; but the value of the maximum temperature of decomposition depends on the maturity of organic matter. The technique can, therefore, analyse mass loss or gain of samples due to decomposition, oxidation, or loss of volatiles such as moisture.

2.7.2 Differential Scanning Calorimetry (DSC)

DSC is an analytical method that measures the difference in heat flow rate to the sample and a reference sample while they are subjected to a pre-controlled temperature program. It is a method widely used to characterise source rocks or oil shales that are undergoing combustion or pyrolysis. A DSC curve shows the heat exchange (endothermic or exothermic) effects; which allows the DSC to provide information on heat absorption, the heat released from the sample, or the heat involved in molecular decomposition. In this work, however, the DSC curves were used to provide qualitative information only, and no calculations are expected from them.

2.8 The Anza basin

In this study, the area investigated was the Anza basin (Figure 3.1). It lies between longitudes 37°05’E and 37°47’E and latitudes 2°22’N and 3°20’N and is situated within the offshore depobelts of the Chalbi desert. On the eastern and western sides, the Anza basin is bordered by the volcanic mountains Kulal and Huri-Marsabit respectively which erupted during the quaternary era (Hendrie *et al.*, 1994). The Anza region is generally a product of rifting facies (Cheruiyot, 2012) of basin development owing to it being an extension arm of the notable East African Rift System and the series of lakes in the EARS containing mineable salt deposits (Rop, 2013). Most of the probable reserves of recoverable hydrocarbons manifest in rifts with post-rift (Dindi, 1994) in the kaisut and Ndovu sag sub-basins. These sub-basins bear marine sediment assemblages (Chand *et al.*, 2012). The geological set up of the Anza basin includes Precambrian basement rocks with tertiary volcanics that have sedimentary sub-basins regarded as possible basins for exploration of oil and gas (Rop, 2013).

2.9 The Status of oil exploration in the study area

Anza basin has deep sediment deposition sequences (2000–11,000 m) which deepen towards the South Anza sub-basin. It shares similar tectonic and lithological compositions with South Sudan’s Muglad basin which is oil-producing (Gilbert *et al.*, 2021). Geochemical evaluation of rock samples was evaluated by Gilbert *et al.* (2021) and Rop (2013) from drilled wells; Chalbi-3, Ndovu-1, and Sirius-1 wells, using Rock-Eval and TOC analysis. The Sirius-1 well exhibited a high TOC in the range of 1.77%–5.945%, displayed from a 1106 to 1725 m depth section. This indicates very good source rocks that had potential for oil and gas (Madec & Espitalie, 1985; Peters, 1986). Also, the Sirius-1 samples were evaluated for saturated fractions of the rock extracts for n-alkanes, steranes, diasteranes, and hopanes. They displayed unimodal distributions in the range of n-C27–n-C30. This suggested that they were derived from terrestrial OM and were mature source rocks due to the abundance of heavy carbon numbers, and were therefore, capable of generating gas-oil condensates to oil (Affouri *et al.*, 2013). The data also showed that the section lying between 1495–1625 m, for the same well (Sirius-

1), had higher values of TOC (3.2–5.94 wt.% TOC). Ndovu-1 well, on the other hand, is from the Palaeocene-Cretaceous age, with sandstone-mudstone bearing shale deposited sediments. Its source rocks had very poor wt.% TOC, below the 0.5% TOC threshold. Finally, Chalbi-3 well bumped into predominantly Palaeocene Cretaceous sandstones interbedded with thin intervals of siltstone, claystone, and shale. The Chalbi-3 displayed kerogen type III and had mature source rocks, but with very low HI compared to OI. A petro physical study of the wells has revealed the need for further investigations to map out the source rocks' enrichment potential.

Therefore, to unravel the potentiality of hydrocarbon in this area, it was paramount to assess the source rocks using various geochemical analysis techniques. The methods used for the assessment of the source rocks are elemental analysis, Fourier transform infrared (FTIR) spectroscopy, Scanning Electron Microscopy (SEM), X-ray fluorescence (XRF), X-ray diffraction (XRD) techniques, thermogravimetric and differential scanning calorimetry (TG/DSC), and gas chromatography-mass spectrometry (GC-MS). Assessment of total organic carbon (TOC), provides information that allows the quality of the target rock to be assessed (Wright *et al*., 2015).

CHAPTER THREE

MATERIALS AND METHODS

3.1 Sampling Site

The source rock samples were collected from—Chalbi-3, Sirius-1, and Ndovu-1 wells—all located in the Anza basin, and are marked in Figure 3.1.

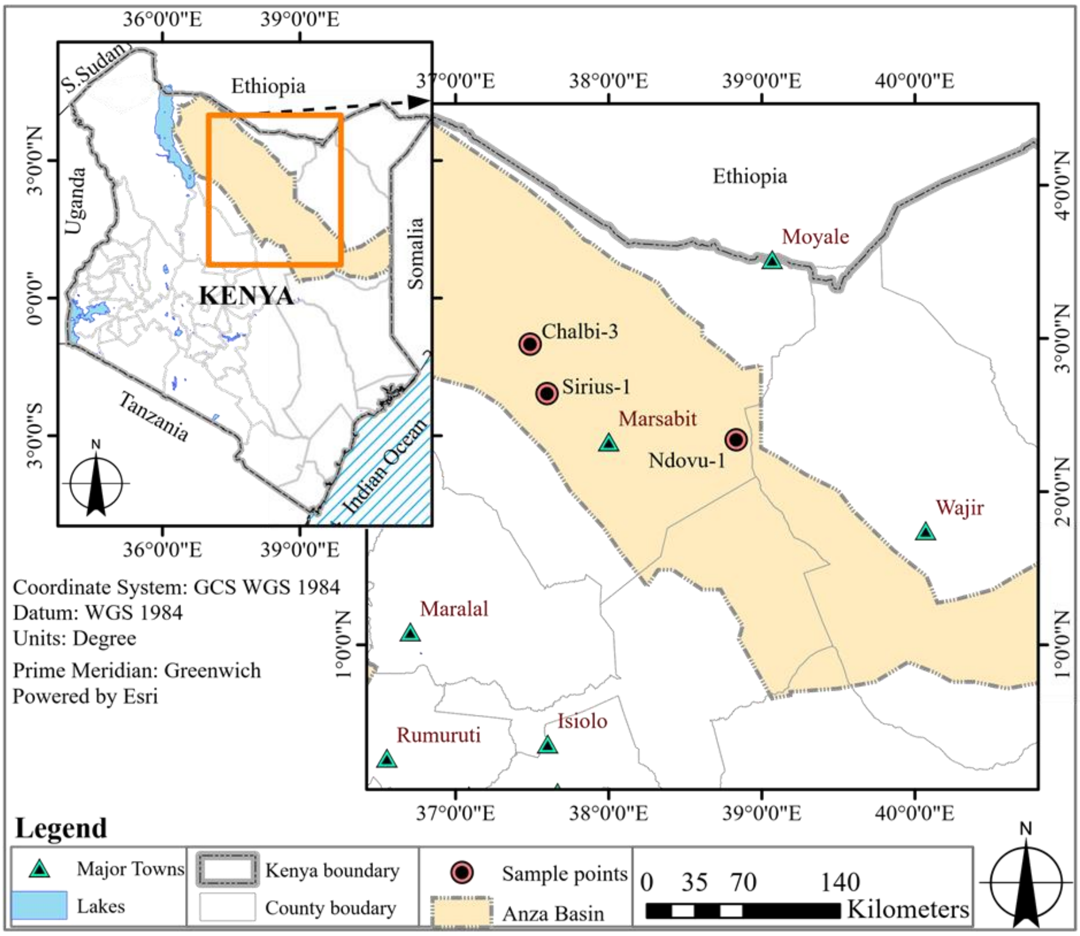


Figure 3.1: Geological map of Kenya, showing the AnzaBasin including the location of the studied exploratory wells Chalbi-3, Sirius-1, and Ndovu-1 (Modified and adapted from Gilbert *et al*. (2021))

3.2 Source rock samples

A total of seven potential source rock samples were collected from three wells namely, Chalbi-3, Sirius-1, and Ndovu-1, located in different parts of the north-eastern part of the Anza basin. A map of sample locations and geographic coordinates is depicted in Figure 3.1. The source rocks had been previously collected by the National Oil Corporation of Kenya (NOCK) and kept in their laboratories in Nairobi. The samples used in this study were collected at depths ranging from 1063 to 3100 metres provided in Table 3.1. This section, between 1063 m and 3100 m depth, was selected because of the reported potential for the production of hydrocarbons for dark grey coloured source rocks. Also, the study hypothesized that at lower depths there was greater potential for hydrocarbon production compared to an intermediate depth of 1,041 metres that was drilled to yield oil at the Tullow well, Block 10BB (Ngamia-1), located in the Turkana County, Kenya.

Table 3.1: General information about the studied samples

Well/Sample	Depth Interval of well (m)	No. of samples per depth
Chalbi-3		
A	2630	1
B	3100-2819	1
C	2652-2710	1
Sirius-1		
D	2316	1
E	2344-1186	1
F	2082-2231	1
Ndovu-1		
H	1067	1
Total number of source rock samples		7

The source rock samples were crushed (Plate 1) and sieved to a particle size less than 0.2 mm and were then stored in air-tight brown paper bags at room temperature conditions until use.

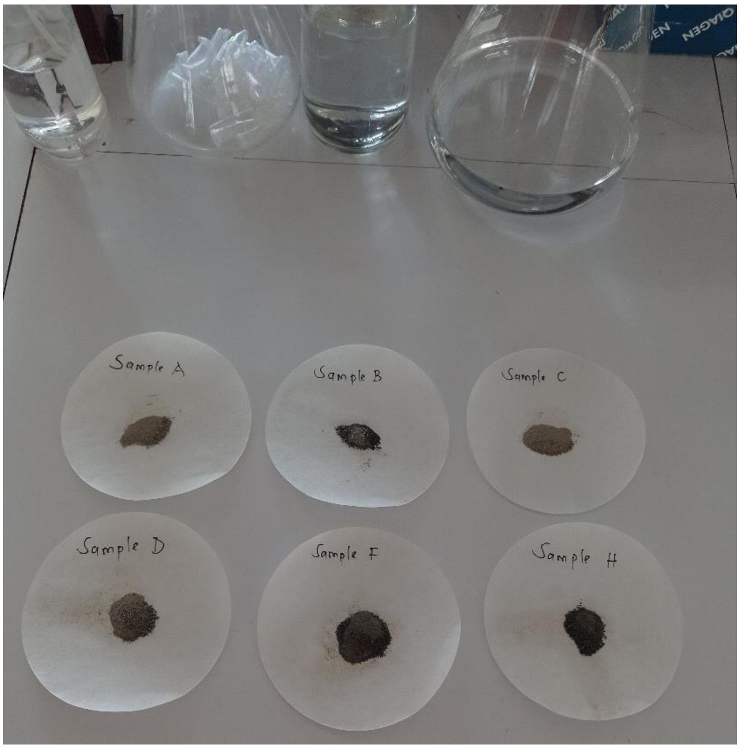


Plate 1: Crushed source rock samples

3.3 Characterisation of source rocks

Several methods have been developed for the extraction and analytical determination of petroleum hydrocarbons in shale samples.

3.3.1 C/H/N/S Elemental Analysis

Total organic carbon content in the samples (TOC), which is generally regarded as an indicator of kerogen and bitumen amounts in source rocks was determined after the removal of carbonate–oxidized inorganic carbon with 2M HC1. Approximately 3.0 g of sample was treated with excess 2M HCl acid and was left to digest for 12 hours in the fume chamber and then rinsed with distilled water on a Whatman filter paper to neutral pH and dried for 24 hours in the oven at 110 °C. Subsequently, after cooling to room temperature, 3–10 mg of each sample powder was placed into a tin capsule and placed into the analytical cycle of the system and heated between 1700–1800 degrees Celsius. The gases (N_2, CO_2, H_2O, and SO_2) liberated from the sample were successively separated on a gas chromatograph separation column and detected by a highly sensitive thermal conductivity detector (TCD) which generated a signal proportional to the amount of the specific element in the sample. The chemical composition of organic matter contained in the inorganic carbon-free samples was expressed as weight percentage (wt.%) of C/H/N/S elements.

Note: The effect of the carbonate on the resultant %TOC content was corrected by calculating the %TOC content in the carbonate-free fraction. Likewise, most of the sulphate was eliminated in the acid medium.

The CHN analysis was conducted on a Thermo Scientific Flash 2000 CHNS/O Analyser, at the University of KwaZulu-Natal (UKZN) in South Africa.

3.3.2 Fourier Transform Infrared (FTIR)

Fourier transform infrared (FTIR) spectroscopy was chosen as one method of analysis because it is non-destructive, uses a small sample size, quick with easy sample preparation, and fast analysis (Painter *et al*., 1981). In FTIR the interaction of infrared radiation with vibrating polar sample molecules leads to a change in dipole moment. Thus, FTIR analysis was conducted to identify organic matter and the minerals present in the source rocks. A mixture of 1.0 mg of each of the powdered samples (A, B, C, D, E, and F) and 150.0 mg of KBr (pre-heated KBr to 110 °C to remove any absorbed water and other potential volatile impurities) was ground with a pestle and mortar to a consistent homogeneity of less than 2 µm and placed on a crystal-sample holder on the FTIR spectrophotometer. The FTIR spectra were recorded at room temperature and were obtained in transmission mode, in the mid-infrared range (400 to 4000 cm^{-1}), using a Jasco-4700 ATR spectrophotometer and Spectra manager software. The analysis was carried out at the United States International University–Africa (USIU, Nairobi).

3.3.3 X-ray Diffraction (XRD) analysis

An X-Ray diffractometer (XRD) was used for minerals identification using a Bruker D8 Advanced XRD instrument with Cu $K\alpha$ radiation source; at the University of KwaZulu-Natal, South Africa. The powdered source rock samples were placed in a two-circle goniometer sample holder maintained at 45 kV and 40 mA, respectively. The X-ray source was a 2.2 kW Cu X-ray tube (that is Cu $K\alpha$ radiation of wavelength (λ) of approximately 0.15406 nm). The diffractograms were obtained by continuous scan from 8° to 90° at low 2θ angles at 0.02° intervals for good accuracy and precision. The measured data are compared with the theoretical single-phase diffractogram to identify the minerals present.

3.3.4 X-ray Fluorescence Technique (XRF)

A Bruker (energy dispersive XRF) X-ray Fluorescence (XRF) spectrometer was employed to measure the amount of significant element oxides and some trace elements. The elemental concentration and their emitted energies in *keV* for all collected rocks were determined.

All measurements were carried out under vacuum using a Bruker spectrometer with Mo, Cu, and Al as sources of incident X-ray radiation. When the source rock samples were irradiated with X-rays, the intensity as a function of energy was calculated over the energy range of 1–20 *keV* under the same computing conditions. The analysis was carried out at the University of KwaZulu-Natal in South Africa.

3.3.5 Morphology study of source rock by Scanning Electron Microscopy (SEM)

Scanning Electron microscopy (SEM) analysis of the source rocks of the oil shale samples was performed at the University of KwaZulu-Natal, South Africa. A high magnification Field Emission Scanning Electron Microscope (Model: JOEL/JSM-7500F) was used to scan the surface morphology of the original samples. A thermal source was used for the electron mission. A beam of electrons was applied in the range between 100- 30,000 electron volts. The electrons collected from the final lens interacted with the specimen and penetrated to a depth of 1𝓜m to generate signals used to produce an image.

3.3.6 Thermogravimetric Analysis (TGA/DTG/DSC)

TG, DSC, and DTG analysis with the control experiments conducted at 25 °C. During these experiments, the mass of each powdered sample was 20 mg, the heating rate was 5 °C/min, and the final temperature was 1000 °C. The experiment was carried out in an air atmosphere.

TG, DSC, and DTG analysis experiments were conducted on the samples to identify the changes in their composition with temperature. The essential part of the study was the analysis of mineral composition and organic matter content in the examined rocks which was performed using thermal methods (TG/DTG/DSC). TG analysis was used to measure the changes in rock mass with temperature. DSC analysis determined the heat flow difference between a heated sample and the control reference material. DTG analysis was conducted to measure the rate of change of mass to temperature. All the analyses were performed using the equipment model TGA/DSC1 with a microbalance model MX5 of measuring range 5 g and resolution 1 µg and Stare software from Mettler Toledo. These samples were analysed at the University of KwaZulu-Natal and Durban University of Technology in South Africa. The samples were powdered and put into the alumina (Al_2O_3) crucible in an amount of about 30–45 mg; with a similar amount of pure Al_2O_3 in the reference container, which acted as standard or control. each sample was heated under dry purified air/oxygen at a controlled flow rate of 50ml/min (in the oxidising atmosphere) in the temperature range of 30 °C to 1000 °C, at a heating rate of 10 °C min^{-1} for TGA and DSC, respectively. After 15 minutes, the TGA/DTG/DSC curves were generated.

3.4. Molecular compounds

3.4.1 GC reagent

Gas chromatograph grade organic solvents: dichloromethane, methanol, hexane, and toluene. Activated silica gel was previously activated overnight at 100 ℃ in an oven and suspended in solvent (n-hexane) before use.

3.4.2. Extraction

The bitumen was obtained by extraction for 7 h in a Soxhlet extractor (Plate 2) using an azeotropic mixture of dichloromethane and methanol (CH_2Cl_2/MeOH, 93:7 v/v). Approximately 10–15 g of the crushed and dried source rock samples from the Chalbi-3, Sirius-1, and Ndovu-1 wells, were used. The solvent was removed by evaporation on a rotary evaporator and the extractable organic matter (EOM) was kept in small glass vials.

Plate 2: Soxhlet extractor

3.4.3. Liquid Chromatography (LC)

A 25 mm i.d. column was packed with pre-activated silica gel (28–200 mesh) (Plate 38). The EOM was poured on the column (Plate 3) and fractionated using different elution solvents in increasing order of polarity. The solvents employed were respectively in the order: n-hexane, toluene, and a mixture of methanol/dichloromethane (2:1) for:

i. The saturated (aliphatic) hydrocarbons were eluted with n-hexane.
ii. Aromatic hydrocarbons were eluted with toluene.
iii. And the polar compounds containing nitrogen, sulphur, and oxygen (NSO) were eluted with dichloromethane: methanol (1:2 v/v).

Plate 3: Column packed with pre-activated silica gel

The successive solvents were removed on a rotary evaporator (Plate 4). The oil extracts were dried with nitrogen gas and stored in dry vials under nitrogen.

Plate 4: Rotary evaporator

3.4.4 Gas Chromatography coupled to Mass Spectrometry (GC–MS)

The saturated and aromatic fractions were separately analysed in the gas chromatography-mass spectrometer (GC–MS model; HP5975B MSD) at the Government Chemist laboratories in Nairobi. The spectrometer was attached directly to the ion source (operated in the electron impact mode at 70 eV ionisation voltage, 100 mA filament emission current, and 230 °C interface temperature). Separation was achieved on a fused silica capillary column coated with DB5 (30 mm × 0.25 mm i.d., 0.25 µm film thickness). The carrier gas was helium (He) at 1.2 ml/min, in constant flow mode. The GC operating conditions were programmed as follows: initial temperature held at 50 °C (5 min), increased from 40 to 300 °C at a rate of 10 °C $\text{min}^{-1,}$ and held for 40 minutes. The gas chromatograph was coupled with a 5975C mass selective detector (MSD). Selected individual compounds were identified by either marching retention times to well-characterized materials that served as reference samples, or by interpretation of mass spectrometric fragmentation patterns along with literature data (Nirmala *et al.,* 2019).

Note: the ions m/z 85 and m/z 191 for the analysis of n-alkanes and terpanes (respectively) and the m/z 217 and m/z 218 for steranes, were not monitored due to the unavailability of the selected ion mode (SIM): *NIST5a* program in the GC-MS spectrometer.

Precautions:

- A blank sample was prepared consisting of silica gel that had no biomarkers that acted as a guard column, and to retain any contaminants in the samples before the GC–MS analysis. Thence, any contaminants present in the blank sample would be subtracted when analysing the GC-MS results.

- For compatibility with GC-MS conditions, the final sample solutions were prepared in the following solvents:
  i. hexane: dichloromethane (1:4) for saturated (aliphatic) hydrocarbons,
  ii. hexane: dichloromethane (1:9) for aromatic hydrocarbons, and
  iii. methanol: ethyl acetate (1:4) for polar compounds (NSO) before analysis:

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Characterisation of source rock samples

The physicochemical characteristics of the source rocks were assessed by Carbon-hydrogen-nitrogen (CHN) analysis, Fourier transform infrared spectroscopy (FTIR), Scanning electron microscopy(SEM), X-ray fluorescence (XRF), X-ray diffraction (XRD), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and Gas chromatography-mass spectroscopy (GC-MS).

4.1.1 Elemental (CHN) analysis

The data for carbon-hydrogen-nitrogen elemental analysis; and the atomic H/C and N/C ratios are provided in Table 4.1 and Appendix A. Sulphur (S) was not detected in the samples. TOC (wt. %) indicates the quantity of OM, including bitumen and kerogen of a rock sample (Akrout *et al.*, 2011). The TOC values of the source rock samples were respectively: Ndovu-1 (H) sample contained the highest TOC content of 1.99 ± 0.1502%; while Chalbi-3 (B) had 1.54 ± 0.0530%; Sirius-1 samples (D and F) had 1.45 ± 0.1051% and 0.54 ± 0.0559%, respectively. All the analysed source rock samples had a present-day TOC above 0.5 wt. %, revealing that all the studied depth intervals have the potential to act as efficient petroleum source rocks (Peters & Cassa, 1994).

Table 4.1: Data set of % Elemental composition (Mean ± SE for n = 3) for selected samples from Anza Basin wells.

Sample	Depth, m	C (TOC)	H	N	H/C ratio	N/C ratio
Ndovu-1 (H)	1066	1.992 ± 0.150	0.743 ± 0.030	0.189 ± 0.004	0.373	0.095
Chalbi-3 (B)	3100	1.541 ± 0.053	0.377 ± 0.023	0.062 ± 0.004	0.245	0.402
Sirius-1 (D)	2316	1.455 ± 0.105	0.270 ± 0.044	0.045 ± 0.007	0.186	0.084
Sirius-1 (F)	2082	0.538 ± 0.056	0.322 ± 0.040	0.042 ± 0.006	0.599	0.078

The spread of TOC values ranged from fair to good generative potential (Zetra *et al*., 2021), in agreement with the Peters scale presented in Table 4.7.

Table 4.2: Geochemical parameters describing source rock richness from Total Organic Carbon (TOC) weight percentage (Peters, 1986)

Richness	TOC (wt. %)
Poor	0.0-0.5
Fair	0.5-1.0
Good	1.0-2.0
Very good	>2.0

From Table 4.1, the results of the elements H and N were respectively: %H— Ndovu-1 (H; 0.74 ± 0.0295%), Chalbi-3 (B; 0.37 ± 0.0233%), and Sirius-1 (D; 0.27 ± 0.0442%; F; 0.32 ± 0.0402%); while for %N—Ndovu-1 is 0.18 ± 0.0039%, Chalbi-3 is 0.06 ± 0.0035%, and for Sirius-1 (D; 0.045 ± 0.0065%) and (F; 0.042 ± 0.058%). This shows that the Anza Basin source rock samples are high in hydrogen and very low in nitrogen percentages; which are the principal characteristics of an oil-rich source rock. Compared to the samples of oil shale of Indian origin which had 6.1% Carbon, 0.08% Nitrogen, and 1.2% Hydrogen (Nassef *et al.*, 2015), the studied source rocks from the Anza Basin contained only moderate amounts of carbon and hydrogen; but had comparably low amounts of nitrogen. The low content of nitrogen plays an important role. It improves the quality and stability of extracted oil, particularly, during refining and storage of the oil (Niu *et al*., 2013).

4.1.2 Fourier transform infrared spectra analysis

The spectra of the studied source rock samples are provided in Figure 4.1 and Appendix B. The peaks seen in Figure 4.1 indicate the presence of both organic compounds and the mineral matrices present in the source rock samples. Despite the source rock samples containing medium values of %TOC, aliphatic and aromatic absorption bands at 3000–2800 cm^{-1} for organic matter (C-H groups) are absent. They were probably overlapped by strong absorption bands of inorganic minerals (Guven *et al*., 2015). The mineral matter contents were qualitatively determined from XRF and XRD laboratory analyses of the source rock samples.

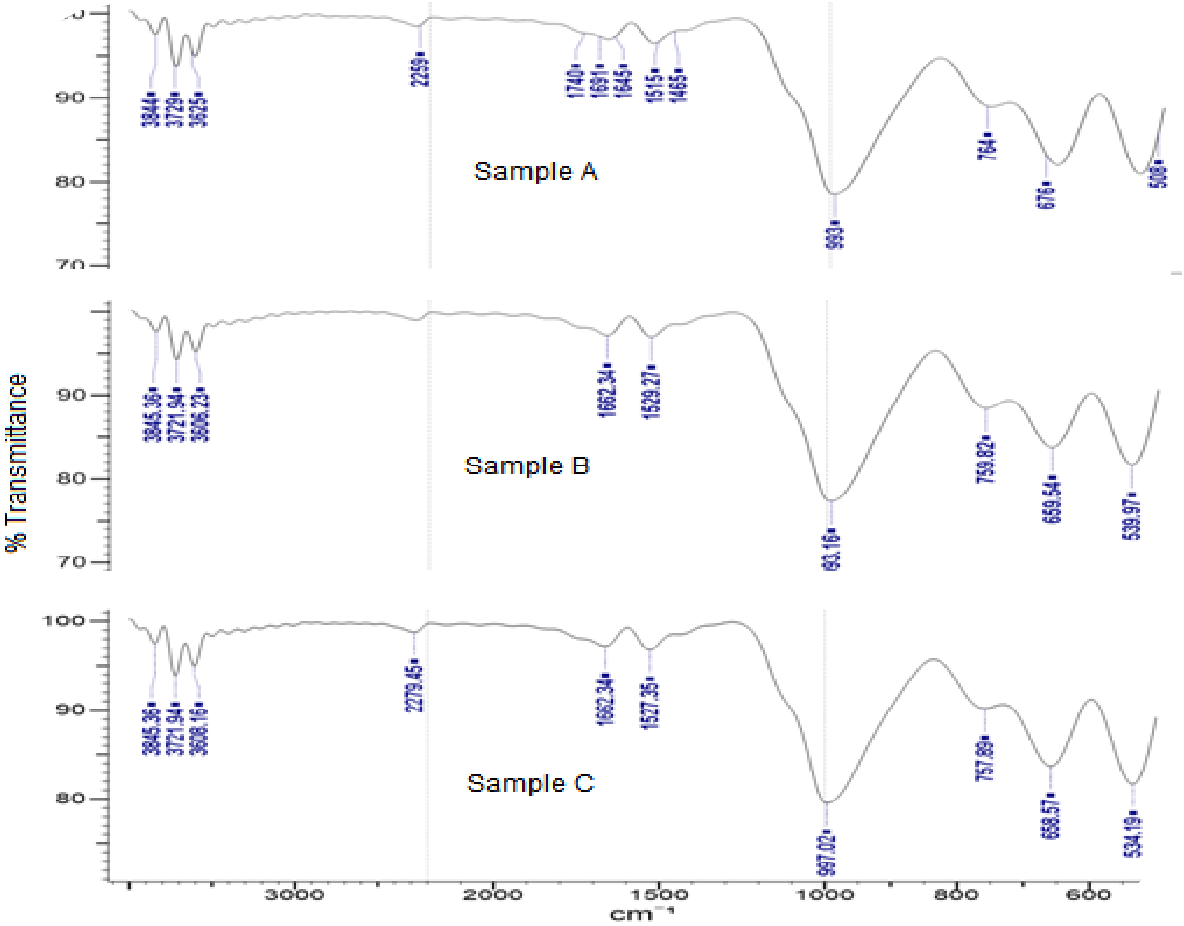


Figure 4.1: FTIR spectra of acid-treated source rocks samples A, B, and C

The aromatic zone (1679–1533 cm$^{–1}$) is observed in all samples, which mainly signifies the presence of C=C aromatic groups as well as C–C– skeletal vibration of polynuclear aromatic hydrocarbons. Additionally, the peaks lying in the range 1645–1428.99 cm$^{–1}$ constitute alkenes and N-H groups. The wavelengths appearing in all the samples lying between 784.89 and 757.8 cm$^{–1}$ indicate aromatic compounds, in particular mono- and poly-nuclear aromatics. The contributions seen at 689.43 to 658.57 cm$^{–1}$ are ascribed to the vibrations of a linear skeletal chain of CH_2 groups comprising more than four CH_2 groups (Bouamoud *et al*., 2018). Other peaks are seen at 2259 cm$^{–1}$ for Chalbi-3 (A) and at 2279.45 cm^{-1} for Chalbi-3 (C)) sample representing (C≡C) bonds. The characteristic band for OH- stretching and NH-stretching appeared at 3424.96 cm$^{–1}$ for aliphatic hydrocarbons in Chalbi-3 (D and E) samples. This may also be attributable to moisture (H-O-H), alcohols, and/or carboxylic acids (Razvigorova *et al*., 2008); besides owing to organic OH in organic matter (Bouamoud *et al*., 2018). In the Chalbi-3 (A) sample, a shoulder appears at 1740-1691 cm$^{–1}$, which arises from the carbonyl stretching mode of ketones, aldehydes, and carboxylic present. The FTIR spectra of samples (B and C) for Chalbi-3 well exhibited characteristic peaks at wavelengths 539.7 and 534.19 cm$^{–1}$ signifying C-X bonds which could be chloroalkanes, bromoalkanes, or iodoalkanes. The appearance of CH groups in the current study points to the presence of organic matter (OM) in the source rocks of the Anza Basin and is supported by the determined > 0.5 %TOC values of the examined source rocks. Organic matter is one of the components of sedimentary rocks (Bouamoud *et al*., 2018) that is only detectable by FTIR and non-detectable in XRD analysis, thanks to the amorphous nature of the complex structure of organic carbon.

In the FTIR spectra (Figure 4.1), all the samples exhibited peaks in the region 3900 to 3600 cm^{-1}. These bands were attributed to the –OH group associated with Si and Al belonging to clay minerals (Bouamoud *et al*., 2018). These were, however, found in the Chalbi-3 (A, B, and C), and Sirius-1 (F) samples that consist of clay minerals (Gilbert *et al*., 2021). The broad sharp peak appears at 993 (7) cm^{-1}; with small peaks around 759.82 (757.89 and 764.0) cm^{-1}; 659.54 (658.57 and 676) cm^{-1} and 539.97 (534.19 and 508.0) cm^{-1} represents Si-O stretches, Si–O–Al Stretching, and (Al, Mg) ≡ O– H. Si–O– (Mg, Al) stretches derived from quartz and silica (Bouamoud *et al*., 2018; Guven *et al*., 2015). The band at approximately 993 ≤ 1000 cm^{-1} for Si-OH stretch and Si–O–Si, Si–O stretching vibrations supports the presence of quartz in all the samples. After elimination of the carbonate ion using 2M HCl, the peak due to the carbonate ($CO_3^{2–}$) at 1431 cm$^{–1}$ and asymmetric stretching at 871 cm$^{–1}$ are missing in all the samples, except the Sirius-1 (D and E) samples (Appendix B), where the FTIR peaks due to CO_3^{2-} are observed. The Sirius-1 (D and E) samples probably contain acid-resistant carbonate rock such as calcite and dolomite whose origin is the Precambrian basement rocks overlain by Upper Jurassic rock with minor outcrops of Limestone with the Anza rift system Gilbert *et al*. (2021). The wavelengths at 511.04 cm^{-1} for the Sirius (E and F) and Chalbi-3 (A and D) along with the peak observed at 508 cm^{-1} in the Chalbi-3 (A) sample; all indicate the presence of clay and minerals (Nassef *et al*., 2015).

Based on FTIR results, therefore, the studied source rocks contain organic matter (OM), along with sandy-clay minerals and limited carbonate minerals.

4.1.3 X-ray Diffraction (XRD) analysis

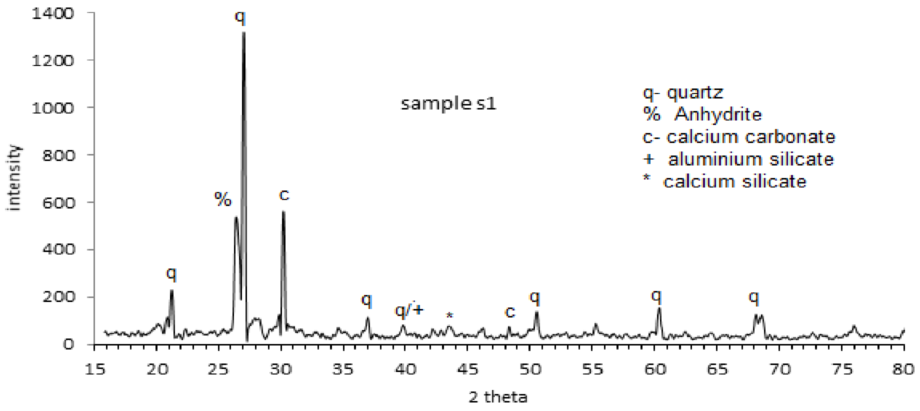
Representative XRD diffractograms for the studied source rocks are shown in Figure 4.2 and Appendix C. The identification of different minerals was facilitated by comparing their corresponding 2-theta (2θ) values with those reported previously (Labus, 2017; Niu *et al*., 2013) each mineral has unique fingerprints. From the XRD spectra, the dominant mineral in all the source rock samples is quartz. Calcite (calcium carbonate), calcium silicate, aluminium silicate, albite, hematite, and anhydrite are also identified as the main components in the source rocks. The key minerals are summarized in Appendix D. The presence of these minerals was further confirmed by FTIR analysis.

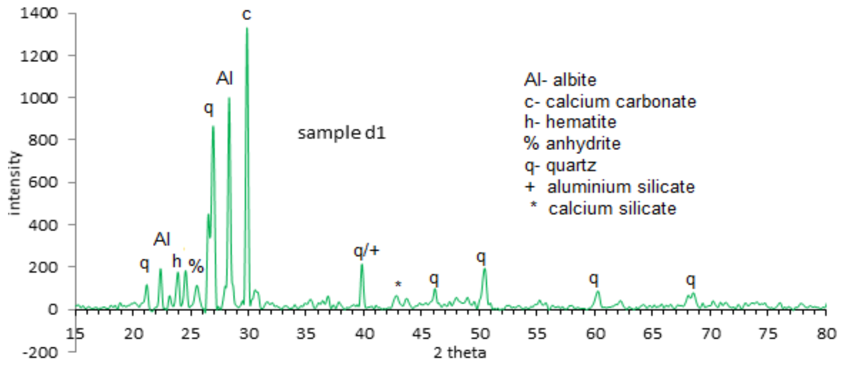
Quartz has been identified in XRD analysis by the strong peak at 20.8° and a stronger peak at 26.6°. Calcite ($CaCO_3$), on the other hand, has a strong peak at 29.4°, while the anhydrite peak appeared between 24-25° and hematite at 33.2°. This was supported by the calculated *d*-spacing values provided in Table 4.3. Furthermore, the Si–O stretching vibrations observed in the FTIR results (Figure 4.1) at around 785 cm^{-1}, 689 cm$^{-1,}$ and 507 cm^{-1} confirmed the presence of quartz (Nayak & Singh, 2007). The appearance of ν (Si–O–Si) and δ (Si–O) bands also supports the presence of quartz (Nayak & Singh, 2007); whereas the vibrations observed at about 993 cm^{-1} indicate the possibility of the presence of hematite, as 689 cm^{-1} stretch shows the likelihood presence of calcite (Nayak & Singh, 2007). Hence, a combination of XRD and FTIR results helped identify various forms of minerals in the source rocks summarised in Appendix D.

Table 4.3: *d*-values (d (Å) of single peaks) of selected minerals in samples

Possible Minerals	**Current work**	*****
Quartz	4.23, 3.36, 1.81, 1.53, 1.37	4.26, 3.34, 1.82, 1.54, 1.38
Calcite	3.12, 1.95,	3.04, 1.91
Anhydrite	3.40, 2.01	3.50, 2.09
Albite	3.96, 3.16	4.02, 3.19
Calcium Silicate	2.09, 2.11, 2.98	2.7 – 3.8
Hematite		2.6990, 1.6957, 2.2001

*Represents Å values of different elements in referenced text (Nayak & Singh, 2007)





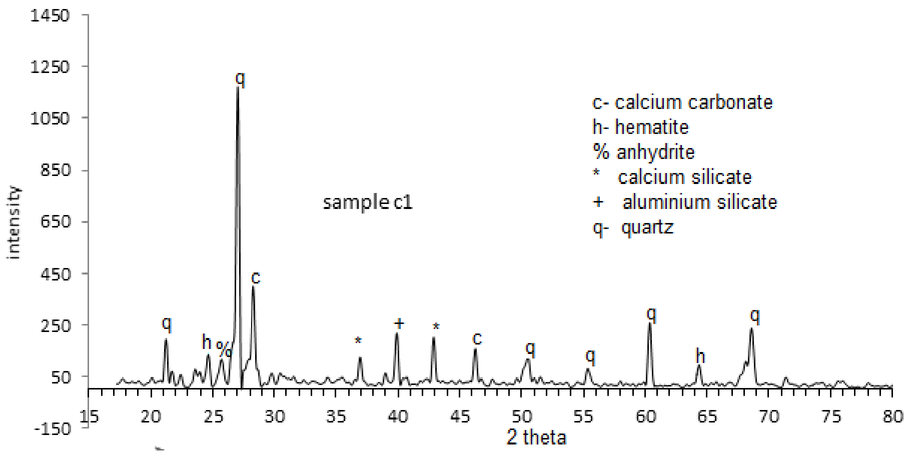


Figure 4.2: XRD patterns of source rock samples of Anza Basin at 30 °C

4.1.4 X-ray Florescence (XRF) analysis

The results related to the XRF analysis of the source rocks from the three wells are given in Table 4.4. The oxides identified through X-ray fluorescence (XRF) analysis are SiO_2, Al_2O_3, Fe_2O_3, K_2O, CaO, MgO, TiO_2 Na_2O MnO; BaO, CuO, C, and SO_3. SiO_2 was observed to be the most abundant with its content varying between 12.06 and 36.53 wt. %, followed by Al_2O_3 with its content ranging within the limits of 4.36–8.06 wt. %. Fe_2O_3 was the third most abundant oxide. The higher concentrations of SiO_2 and Al_2O_3 in the studied samples are consistent with the occurrence of quartz and clay minerals. In addition, the slightly high concentrations of SiO_2 and Al_2O_3 elements also could be due to the input of detrital matter during the deposition of the sediments and is supported by the presence of TiO_2 (0.15–3.31 %). On the whole, the results show that silicate minerals (quartz and aluminium silicate), carbonate minerals (calcite and/or dolomite), alumina, iron oxide, and calcium oxide are the dominant minerals. Other minerals such as Mn, Ti, Cu, and Ba, are present in small or trace quantities.

Table 4.4: Chemical composition (% wt) of source rock samples of Anza basin (XRF analysis)

Sample	Depth	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	Na_2O	K_2O	MnO	TiO_2	Cu	Ba	C	S
C1	3099.8	17.64	3.59	7.10	6.27	1.71	3.31	0.91	*	0.42	0.12	0.5	2.66	4.33
C2	2819.4	36.53	2.26	4.91	0.74	1.11	2.19	0.28	*	*	*	*	2.98	*
S2	2316.5	12.06	3.10	4.37	11.68	1.33	0.85	*	0.39	0.15	*	*	12.44	*
D1	1297.8	24.04	20.31	8.06	1.19	0.85	1.29	2.34	*	3.13	*	*	*	*

*-not detected, C1C2 (Chalbi-3 well), S2 (Sirius- 1 well), D1 (Ndovu-1 well)

4.1.5 Morphology study of source rock of oil shale (SEM analysis)

Figure 4.3 shows the SEM of selected source rock samples. The major phases in all source rocks are intergranular pores or white flakes that developed between quartz (silica), calcite, or other brittle minerals as seen in the XRF and XRD results provided in sections 4.1.3 and 4.1.4. Generally, this study shows the distribution of minerals in source rocks and gives an understanding of the microstructure relationships among the main constituent and the matrix of the source rock.

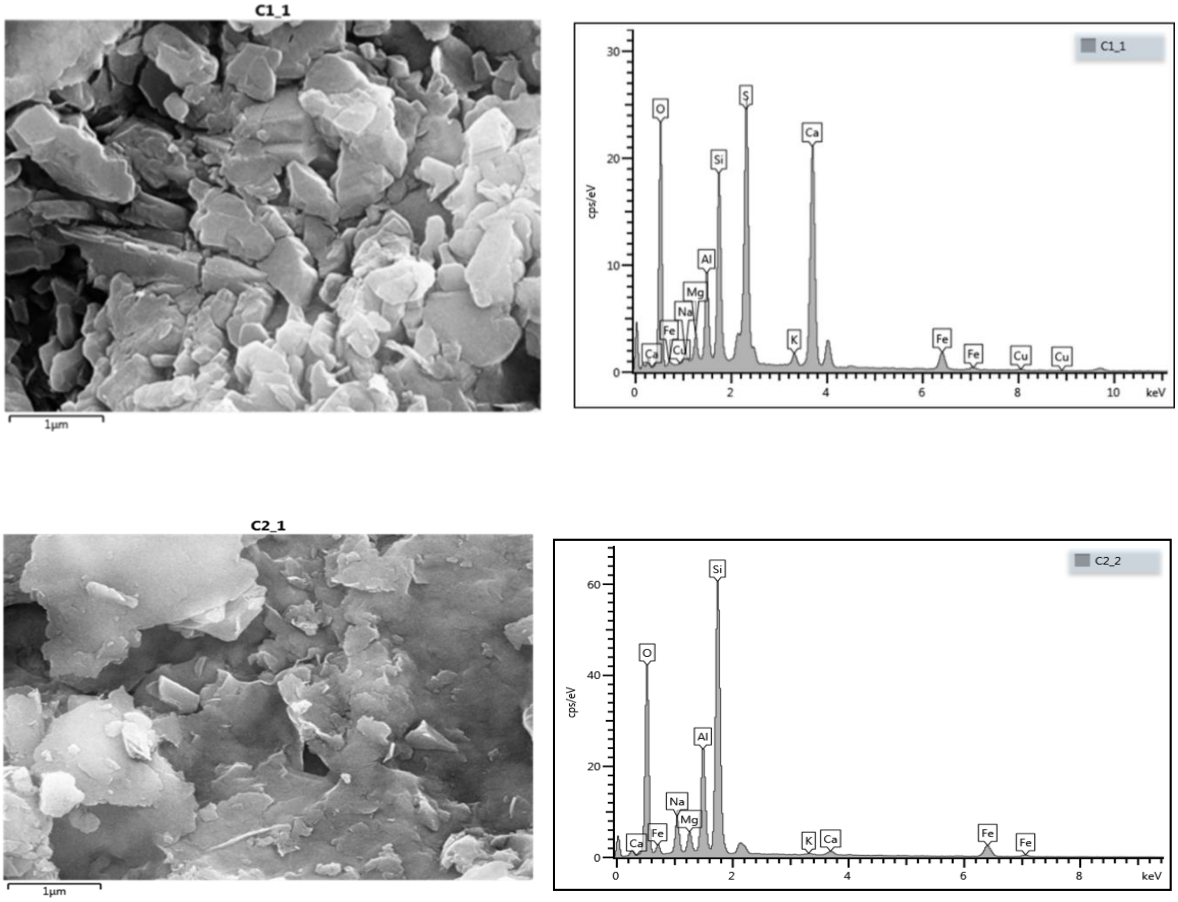


Figure 4.3: Scanning Electron Microscopy for selected source rock samples

4.1.6 Thermogravimetric (TG) analysis and Differential Scanning Calorimetry (DSC).

The results of the TG, DTG, and DSC experiments under oxidative (air/O_2) atmospheres are shown in Figure 4.4 for the source rock samples B, D, and H (Appendix F for samples A, C, E, and F). The TG curves indicate weight loss percentages and the DSC curves represent the heat flow behaviour of source rock samples during the analysis.

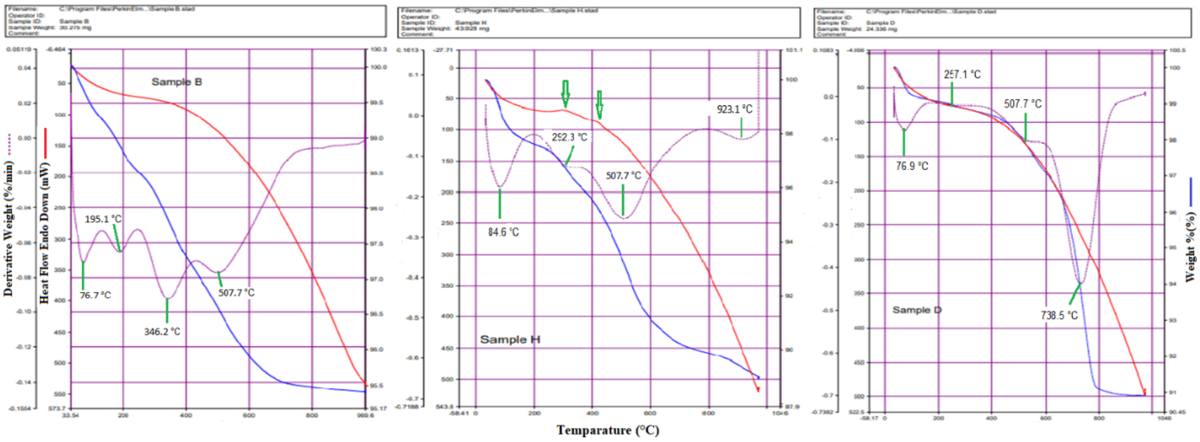


Figure 4.4: TG (blue line), DTG (purple line), and DSC (red line) curves under oxidative (air/O_2) atmospheres

The main reactions occurred in three or four stages, namely: 30–250 °C; 300–600 °C; and 600–1050 °C provided in Table 4.5. At each stage, weight loss took place from the evolution of gas/moisture from the samples during heating and was determined from the TG/ΔTG curve(s) seen in Figure 4.4.

The first stage: The first reaction occurred when the source rock samples were subjected to a heating rate of 10.0 °C/min under air/O_2 atmosphere, and was observed at temperatures less than 250 °C for all the samples. A small mass loss is observed, due primarily to the evaporation of water, including adsorbed and interlayer water from clay minerals and/or CO_2 emissions. In this region, total mass loss as in the range 0.7–19.8% (Table 4.6). The mass loss is attributed to evaporation of moisture and release of interlayer water (free and bound water) associated with quartz and clay minerals that are dispersed in the rock; and light fractions of organic matter (Matyasik *et al*., 2021). Thus, the H_2O components in the crystalline structure and light organic matter are decomposed using DSC (Bouamoud *et al*., 2018; Labus, 2017). Dehydration of clay minerals has been demonstrated to exhibit visible maxima between 70 and 250 °C on the ΔTG curves (Labus, 2017). The first segment, up to about 300 °C on the DSC curves, in all the samples (Figure 4.4), shows a small endothermic peak further revealing the dehydration of clay minerals.

The second stage— clearly, two independent reactions were seen, under an oxidising environment (air/O_2), and were attributed to oxidation (combustion) and decomposition of organic matter. The two reaction steps are low-temperature (first peak) and high-temperature (second peak) intervals which involve episodes of gas evolutions during oxidation and/or decomposition of the source rock samples. The first peak, referred to as the low-temperature oxidation peak, is observed between 257 to 360 °C and is due to the oxidation reaction of light hydrocarbons (bitumen). The second peak, referred to as the high-temperature oxidation peak, appears at 438 to 550 °C and originates from the oxidation of heavy hydrocarbons (kerogen), fixed carbon, and possibly other components. Kerogen is a macro-molecular material (usually insoluble in common organic solvents) that is the main source of TOC in source rocks. The maximum thermo-oxidation reaction was precisely detected in the temperature range of 450 to 580 °C on the TG/DTG curves (Figure 4.4). A major mass loss is observed at this stage (temperature interval of 250 to 600 °C, and is attributed primarily to the combustion and decomposition of bitumen and kerogen into volatiles. Under an air atmosphere, the reaction is more rapid, and two peaks are observed in both the DTG (all samples) and DSC curves (observed only in E (one peak); and H (two peaks). The combustion of the source rock sample E was, however, more exothermic (more energetic) than that of sample H (Figure 4.4 and Appendix G). This was semi-quantitatively verified based on the peak heat flow values of 60 *m*W/*m*g for sample E and approximately 2 *m*W/*m*g for sample H, observed on the respective DSC curves. Therefore, the introduction of a reasonable amount of air/oxygen to oxidise the source rock during combustion coupled with the released heat energy can facilitate the production of petroleum hydrocarbons from source rocks.

The final region—lies between 600 and 1050 °C, most of the weight loss was caused by the decomposition of clay minerals and/or carbonates and was accompanied by 0.2–5.0 wt.% loss (mean = 1.6 wt.%) (Table 4.6), for respective samples A, D, E, F and H. Samples C, D and F gave a reaction in the temperature range 723.1-746.7 °C, which was attributed decomposition of calcite ($CaCO_3$) and or dolomite ($CaMg\ (CO_3)_2$; in agreement with the work of (Labus & Matyasik, 2019) where calcite decomposition occurred in the region lying between 541 and 845 °C.

The main temperature range between 300 and 650°C is where most of the weight loss occurred. And This was a result of the oxidation of organic matter, in particular, thermo-oxidation of the heavier fraction of kerogen and fixed carbon in the source rocks to CO_2 and H_2O (Labus, 2017). The entire reaction processes were dependent on the maturity of the organic matter; the main source of hydrocarbons in source rocks (Labus & Matyasik, 2019; Matyasik *et al.*, 2021).

Table 4.5: Reaction regions °C of source rock samples (at a heating rate of 10 °C/min)

Heating Rate	Source Rock Sample	Vaporization of moisture and devolatilization of volatile matter	Combustion of light compounds	Combustion of heavy compound	Decomposition of minerals/ residues
	Chalbi-3				
	A	30-200	300-400	400-600	600-950
	B	30–250	250–410	410–600	
10 °C/min	C	30-220	300-420	450-550	600-800
	Sirius-1				
	D	30-200	200-400	400–600	600–850
	F	30–296		296–600	600–800
	E	30–200	200–380	380–600	600–970
	Ndovu-1				
	H	30–250	250–400	400–600	800–990

Table 4.6: Representative % weight loss of source rock samples from the Anza basin, at 10 °C min^{-1} heating rate under air/O_2 atmosphere

Sample	**Depth, m**	**1**	**2**	**3**	**4**	**5**
Chalbi-3						
A	2630	1.1	0.5	1.8	0.2	2.5
B	2819–3100	0.8	1.0	0.6	nd	1.6
C	2710-2652	0.8	1.3	0.6	0.1	2.0
Sirius-1						
D	2317	0.7	≈ 0.1	≈ 0.5	5.0	5.6
E	1186–2344	19.8	20.0	10.8	0.2	31.0
F	2082–2231	2.3	Nd	2.0	2.2	4.2
Ndovu-1						
H	1067	0.7	Nd	3.7	0.4	4.1

† **1**—weight loss during TG analysis from 30 to 250 °C (%); **2**—weight loss during TG analysis from 300 to 450 °C (%), **3**—weight loss during TG analysis from 450 to 650 °C (%), **4**—weight loss during TG analysis from 650 to 1000 °C (%); **5**—total weight loss during TG analysis from 300 to 1050 °C (%). nd = not detected.

4.2 Organic matter and minerals

4.2.1 n-Alkanes and isoprenoids (nonpolar hydrocarbons)

Gas chromatographic analysis of extracted n-alkanes (C14+) revealed that the studied samples contained a substantial amount of saturated hydrocarbons in the range of C17 to C23 (Figure 4.5 Appendix H). The n-alkanes exhibited unimodal profile hydrocarbons consisting of nC_{14}–nC_{23}, with a predominance of short (n-C14–n-C20) to middle (n-C21–n-C25) chain n-alkanes, suggesting that the organic matter was contributed from both microbial, algal and with a small contribution of terrestrial materials (Shanmugam, 1985). The presence of long-chain hydrocarbons (> C_{20}) in the examined source rocks reflects the continental contribution of the organic matter from higher terrestrial plants (Zetra *et al*., 2018).

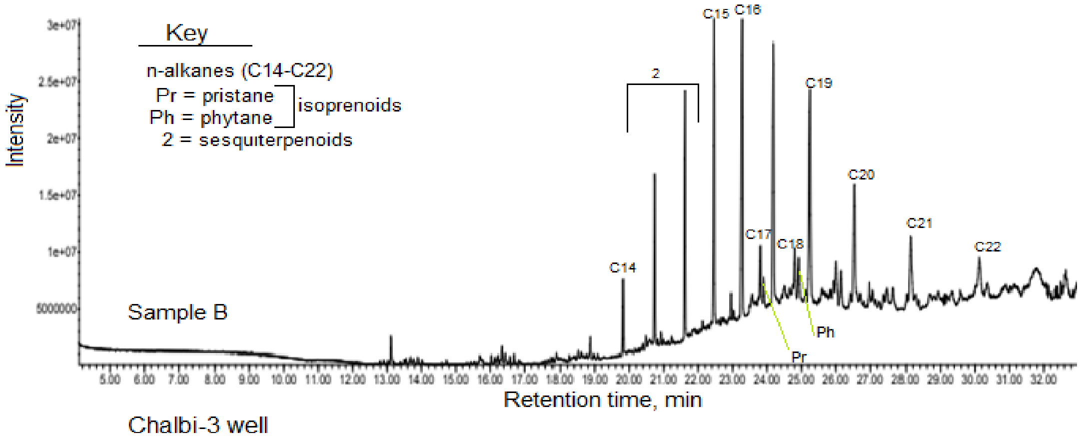


Figure 4.5: Representative n-alkanes and isoprenoid hydrocarbons in the selected source rock samples (with TOC >1.5%)

The saturated hydrocarbons were identified by comparing the retention times on the chromatograms and m/e fragments on the GC-MS spectra (Zetra *et al*., 2018), shown in Figure 4.6.

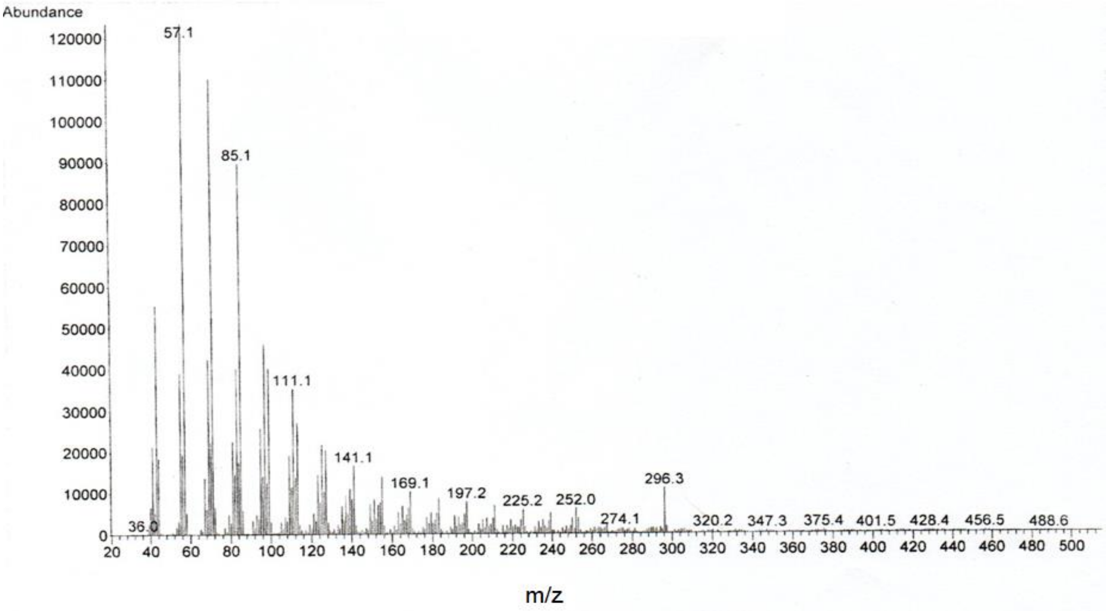


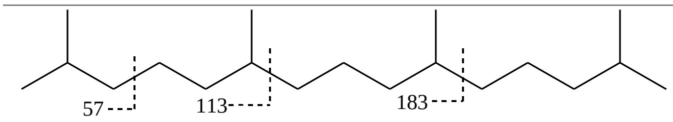
Figure 4.6: Mass spectra of n-alkane fragments

Some compounds were identified by comparing m/z fragmentation patterns with those from previous research reports (Zetra *et al*., 2021). The saturated hydrocarbon fraction gave mass fragments at m/z: 57, 71, 85, 99, and others, which followed a linear pattern up to m/z 252(3) molecular ion(s) observed in Figure 4.6. The base peak at m/z 57 is due to the release of the butyl group ($-C_4H_9$) (Nirmala *et al*., 2019), followed by successive increments of 14 units due to the extension of ethylene group (–CH_2–) in n-alkanes. The fragment appearing at m/z 252 belongs to n-cosane ($C_{20}H_{42}$) which is commonly found in source rocks (Zetra *et al.*, 2018).

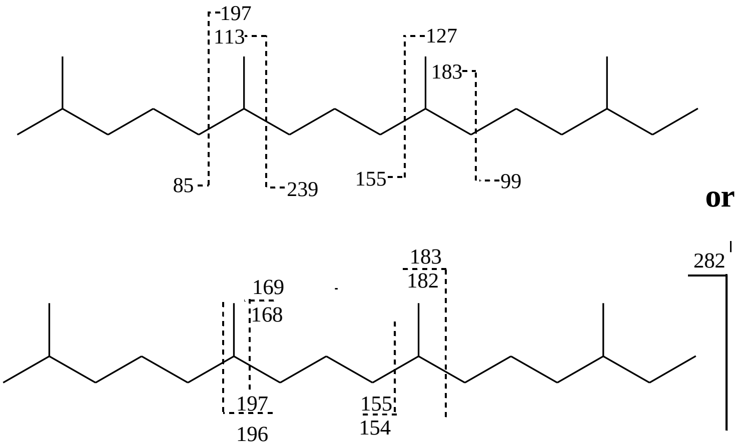
The Isoprenoid biomarkers were also identified by the fragmentogram at m/z 57. Isoprenoid hydrocarbons were abundant in all of the source rock samples and are represented by pristane (Pr) and phytane (Ph) indicated in Figure 4.5 and Appendix H. Pristane ($C_{19}H_{40}$) and phytane ($C_{20}H_{42}$) have the characteristic i-C_{19} peak and i-C_{20} peak at m/z 183 and at m/z 197 molecular ions, respectively (Figure 4.6). These peaks, due to branching, are also characteristic of the mass spectra of isoprenoids (Zetra *et al.*, 2018). Pristane (2,6,10,14-tetramethylpentadecane, $C_{19}H_{40}$) is a C_{19} -isoalkane with a boiling point near that of n-heptadecane ($C_{17}H_{36}$), whereas phytane (2,6,10,14-tetramethylhexadecane, ($C_{20}H_{42}$) is a C_{20} -isoalkane with a boiling point near that of n-octadecane ($C_{18}H_{38}$) and were identified because they are found always as doublets (Figure 4.5). It follows that the biomarker groups present in the saturated hydrocarbon fraction include: n-alkanes, and acyclic isoprenoids, examples of which are reported in Table 4.7.

Table 4.7: Selected isoprenoids in the source rock samples based on mass spectra fragmentation

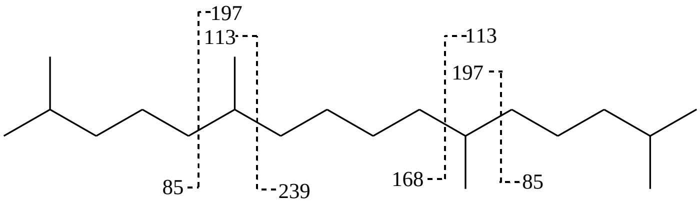
Selected Isoprenoids



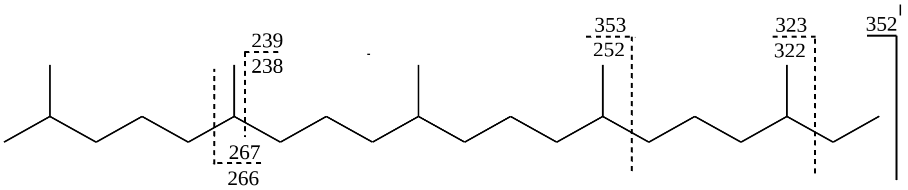
Pristane



Phytane



Croctane



2,6,10,14,18-pentamethyl licosane

4.2.2 Source Rock Richness, Kerogen Type, and Generation Potential

For Prospective source-rock samples to be called active or effective, the source rocks must meet certain requirements for quantity, quality, and thermal maturity of the organic matter. For source rocks characterization, the generally accepted criteria described by Peters (1986) displayed in Table 4.2 were used. According to Peters (1986), values between 0.5 and 1.0% indicate a fair source generative potential, TOC values from 1.0 to 2.0% reflect a good generative potential, TOC values between 2.0 and 4.0% refer to a very good generative potential, and rocks with TOC greater than 4.0% are considered to have excellent generative potential. By and large, therefore, the higher the TOC the better the chance and potential for hydrocarbon generation (Peters & Cassa, 1994).

4.2.3 Quantity of Organic Matter

Ndovu-1 stands out alone as it was from the South of the Anza sub-basin and drilled at a depth of 1066 m (Figure 3.1), and also exhibited the highest value of 1.99% %TOC. Wells Chalbi-3 and Sirius-1 are both located in the North Anza Sub-basin and demonstrated fair to good quantity of OM, respectively, and had TOC values in the range of 0.5 to 1.5% (Table 4.1). Based on The TOC data, Ndovu-1 samples have very good generation potential. The results exhibited by well Ndovu-1 contrast all the values cited by Gilbert *et al*. (2021), which were lower than the 0.50 wt. % TOC threshold, in the depth interval of 880 to 1350 m. The only explanation for the difference could be that evaluation of sedimentary source rocks based on their TOC wt. % content alone might not be sufficient to satisfy all the requirements of an effective source rock. Also, the value %TOC possibly included inert carbon that has little or no generating potential (Peters & Cassa, 1994).

The well Sirius-1, in the current study, registered %TOC values of 0.538 and 1.455, at a depth of 2082 and 2316 m, respectively (Table 4.1) which is in agreement with the hypothesis that %TOC content tends to increase with depth. This follows the pattern in a report ‘Petroleum Potential of the Anza Basin’ by Rop (2013), which showed that the TOC contents of the Sirius-1 well increased with increasing depth as follows: TOC 0.54–1.68% (1228.0–1244.7 m); TOC 0.54–0.9% (1250.7–1316.5 m); TOC 0.53–2.7% (1483.2–11530.8 m); and TOC up to 4.8% (1656.0–2326.8 m), respectively. Other studies for the Sirius-1 well, reported that the source rocks belong to both the Lower Cretaceous and Upper Cretaceous formations, and have good to excellent source rock potential with TOC values ranging between 1.0 and 4.6 wt.% (Awo, 2018) as well as a range of 1.77 to 5.945 wt.% at a depth of 1106–1929 m (Gilbert *et al*., 2021).

The well Chalbi-3, on the other hand, contained a mean value of 1.541 wt. % TOC at 3100 m depth. The well is as a composite of sandstones, with different shale proportions and tends to release better %TOC quantities (Gilbert *et al*., 2021). This value is similar to the value of 1.544 wt. %TOC at 2316 m depth for well Sirius-1, and less than that of Ndovu-1 (1.99% TOC) at 1066 m depth. Similarly, TOC wt. % values (0.538% – 1.541%) appear to increase within the same deeper part of these depths (2082–3100 m) and intermittently towards 1066 m depth as seen in Table 4.1. This indicates that there is no uniform variation in maturity of the organic matter with depth as well as variations in H/C ratios. The differential values of total organic carbon (%TOC) observed in the present study may be due to changes in the deposition rates, organic matter maturity, and supply rate (Shoieb *et al*., 2022) in the different regions of the Anza basin. As a whole, this data agrees with the proposed hypothesis that the quantity of the organic matter (%TOC) varies with depth.

4.2.4 Source Rock Quality (Hydrogen and Nitrogen Indices)

The most important factors controlling the quality of organic matter are the relations of elemental composition expressed as the atomic hydrogen-to-carbon along with oxygen-to-carbon ratios. These factors have a significant influence on the hydrocarbon potential of possible source rocks since their ratios are used to classify the insoluble portion of organic matter because C, H, and O make up most of the kerogen structures (Monin *et al*., 1980).

The Hydrogen index (HI = H/C ratio) represents the amount of hydrogen relative to the amount of organic carbon (OM) present in the rock at the formation depth. The Hydrogen Index also corresponds to the amount of hydrogen contained within the kerogen, and high Hydrogen Index values indicate greater potential to generate oil. Table 4.1 provides the results of the Hydrogen Indices (H/C ratios) for source rocks samples B (Chalbi-3 well), D and F (Sirius-1 well), and H (Ndovu-1 well).

Samples B (Chalbi-3), D and F (Sirius-1), and H (Ndovu-1) have Hydrogen indices ranging from 0.19 to 0.60 (with a mean value of 0.35). Because all the studied samples have H/C < 0.6, the kerogens present are termed Type III/or IV (Tissot *et al*., 1984). Because the samples were collected from the Anza basin, with a semi-desert environment, the Type III and Type IV Kerogens are derived from terrestrial plants (Hakimi *et al*., 2016), and have a higher probability of gas generation compared to oil generation in Type III kerogens (Ombati *et al*., 2023). Moreover, their hydrogen content is lower, which indicates a higher relative abundance of condensed aromatic and oxygen-containing structures in the kerogen structures as was confirmed by the FTIR spectra (Figure 4.1).

The source rocks from the Chalbi-3 well exhibited a low Hydrogen Index value, suggesting that the organic matter in these source rocks was oxidized and/or highly mature containing mainly Type III (Gas prone) kerogen. Gilbert *et al.* (2021) also found that the Chalbi-3 well contained type III kerogen, an indication that well Chalbi-3 had mature source rocks with little amount of extractable hydrocarbons. Only sample F from the Sirius-1 well had the highest H/C ratio of 0.60 at a depth of 2082 m, indicating its source rock is carbon-rich. This was in agreement with the results reported by Gilbert *et al*. (2021). It is also worth noting that the generation of petroleum, besides being controlled by the type and richness of the organic matter present, is also dependent on temperature and time with temperature being the more significant (Moumouni *et al*., 2007).

From the current study, the N/C ranges from 0.078 to 0.402 (average 0.165) for the source rocks, which are low and suggest that the preserved organic matter of the source rocks had undergone extensive degradation during the early stages of diagenesis and thermal alteration; and could cause loss of heteroatoms from the kerogens (Vandenbroucke & Largeau, 2007). Moreover, low N/C values are a good indicator showing that the quality of petroleum products to be generated from these source rocks will have higher environmental safety. Usually, the presence of nitrogen and sulphur elements in petroleum oil has a negative effect on the refining and stability of petroleum oil as well as environmental instability through pollution.

4.2.5 XRD and XRF

Both XRF and XRD results showed that CaO content is relatively high in comparison to the low MgO amount. This indicates the amount of calcite present in these source rock samples is moderate. What is more, the low percentage of Mg is proof that dolomite is found in these samples, even if, in negligible quantities. Secondly, the mineral content also varied in different wells and with different depths (Table 4.4). In particular, the silicate mineral (Al + Si) and carbonate mineral (Ca + Mg) content were quite different at different depths.

The SiO_2/Al_2O_3 (values of ratios are in parentheses) obtained from the present samples are Chalbi-3: C1 (2.48); C2 (7.44); Sirius-1: S2 (2.76); and Ndovu-1: H (2.98). Sandstones which are high in quartz content as well as high SiO_2:Al_2O_3 ratios, have greater potential reservoir quality of petroleum (Ratcliffe *et al*., 2007). Clay minerals play an important role in fundamental geological research and the oil industry and, their association with organic matter in sedimentary rocks can predict the quality of organic-rich source rock, hydrocarbon generation, and expulsion processes (Bouamoud *et al*., 2018). Consequently, the resultant (SiO_2/Al_2O_3) values indicate that all sampled source rocks of the Anza Basin have exhibited good potential reservoir quality for hydrocarbons, which is in agreement with the conclusions reached under %TOC and H/C discussed earlier.

4.2.6 Thermal analysis

From the XRD and XRF results (Tables 4.3 and 4.4), the dominant component is quartz, followed by iron oxide and alumina. The aluminium and iron minerals indicated the presence of clay minerals in the source rocks. Also, low amounts of sodium and potassium in the samples exposed the presence of clay minerals in the studied samples. It follows, therefore that due to the sorptive properties of clay, organic matter (molecules) were attracted to the clay surface making their surfaces hydrophobic. This enabled the observed characteristic peak maxima to shift to lower temperatures on the TG/ΔTG thermograms (Figure 4.4). Also, the observed endothermic DSC peaks, at the onset of each peak, were much smaller than expected because the organic matter in the source rock(s) had been replaced by the adsorbed water on the clay minerals (Labus, 2017).

The first observed single-step decomposition process at higher temperatures occurred in samples D (at 507.7 °C), E (at 438.5 °C), F (at 538.5 °C), and H (at 507.7 °C). In this instance, medium and high-temperature oxidation reactions merged into a single peak in the temperature range of 400 to 600 °C. This is an effect due to the minerals in the source rocks. Minerals such as calcite and dolomite tend to merge combustion-oxidation reactions into a single-step process (Ariskina *et al*., 2021). The plausible reason is that the inorganic minerals act as catalysts, which lower the activation energies and accelerate both medium and high-temperature oxidation, leading to a single–step to generate coke, CO, and CO_2 simultaneously.

Looking at sample E (Appendix F), a more intense exothermic peak was observed at 438.5 °C on the DSC curve and is characterised by the largest mass loss of 10.8% (Table 4.6). This probably indicates the combustion of aliphatic carbons that are characterised by long chains. This is supported by Labus (2017), who stated that mass loss during the combustion of organic matter (under an oxidative atmosphere) is observed up to the temperature of 500 °C, and is related to the presence of light hydrocarbons in bitumen. As a result, the major species of organic matter present in the examined sedimentary source rock (sample E) are light hydrocarbons. What is more, a large mass loss in the temperature range of 350 to 450 ° C may indicate the presence of kerogen that is rich in oxygen. Therefore, sample E possibly contains kerogen type III.

The remaining samples D, F, and H, clearly demonstrated one peak on their respective DTG curves at higher temperatures 507.7 or 538.5 °C. However, Thermo-oxidative destruction of organic matter starts in the temperature region of 130-300 °C and ends at 600–700 °C (Yusupova *et al*., 1999). A rock is a porous medium where oxidation reactions occur and as such has a significant influence on the chemical reactions taking place in in-situ combustion (Ariskina *et al*., 2021) due to mineral matter catalysis. It is sensible, therefore, to suggest the overall reaction taking place in the studied samples is straightforward single-stage thermo-oxidation of the heavier (high) molecular-weight kerogen and fixed carbons in the OM. This applies to samples D (at 507.7 °C), E (at 438.5 °C), F (at 538.5 °C and H (at 507.7 °C), where a single peak was observed.

To the contrary, a two–stage decomposition/oxidation process was observed in samples A (at 338.5 and 507.7 °C); B (at 346.2 and 507.7 °C); and C (at 396.2 and 492.3 °C)—showing that the decomposition occurs in two separate reaction steps—low-temperature (first peak) and high-temperature (second peak) reaction intervals (maximal temperatures are shown in brackets). The first reaction interval (between 338.5 and 400 ° C) corresponds to the thermo-oxidation of volatile organic compounds (bitumen). The second reaction interval (492.3–507.7 °C) shows thermo-oxidation of the heavier macro–molecules of kerogen and fixed carbon in the source rocks (Shekarifard *et al*., 2021). The temperature differences observed resulted from variations in the complex structures of macro-molecules of kerogen and activation energies of the reactions involved, which are brought about by mineral matter (inorganic minerals) catalysis. This can accelerate or retard the changes observed therein. Additionally, in the range 492.3 to 507.7 °C for samples A, B, and C oxidation of pyrite, FeS, has accompanied the decomposition of organic matter. Even though sulphur was detected only in sample C by XRF analysis.

However, the ‘quartz peak’ signifying the presence of quartz in the source rocks at 573 °C on the DSC curves was absent. This may be because the small quartz particle size enabled it (quartz) to be strongly dispersed in the rock, and in turn, yielded no thermal inversion. It can, therefore, be concluded that investigated rocks had very fine-grained structures with low detectable quartz (Labus, 2017). It is worth noting that in all the analysed samples, the highest weight losses were recorded between 300 and 650 °C in TG/DTG analyses, an indication that lower temperature values were sufficient for the complete decomposition of organic matter in the source rocks of the Anza basin.

In samples A, E, and H, the reaction in the temperature range 907.7 and 923.1 °C could be explained by the decomposition/dehydroxylation of clay minerals present in the source rocks. These may include clay minerals such as chlorites ($(Mg, Fe, Al)_3(Si, Al)_4O_{10}(OH)_2$), muscovite ($(KF)_2(Al_2O_3)_3(SiO_2)_6(H_2O)$), carbonates (calcite) and residual organic matter (Labus & Matyasik, 2019) and residual organic matter burnt up to a temperature of almost 956 °C (Matyasik *et al.*, 2021).

Some of the problems encountered with the interpretation of experimental curves include: though little or no sulphur (S) was detected in the XRF results, separation of the combustion of organic matter from the decomposition of pyrite (FeS) in the organic-rich rocks; especially in the temperature range 300–600 °C was quite difficult. Secondly, some reactions represent not only the oxidation of organic matter but also mineral matter catalysis that could assist thermo-oxidation of kerogen (hydrocarbons). These problems could have shed more light if the TG/DTG/DSC experiments had been conducted under an inert (N_2) atmosphere as well as under air/O_2, or simply by selectively extracting kerogen from the source rocks before the analysis was done.

4.2.7 Maturity

The dominancy of n-C14–n-C24 (seen in Figure 4.5) shows that the organic compounds in the studied source rocks were derived from the contributions of microorganisms and terrestrial materials during the formation process of petroleum organic compounds. The presence of isoprenoid biomarkers also confirmed that the organic matter in the source rocks was derived from phototropic organisms (Nirmala *et al.*, 2019). The isoprenoids/n-alkanes ratios for (Pr/n-C17 and Ph/n-C18) ranged from 0.4–0.6 and 0.63–0.86, respectively, while the Pr/Ph ratios ranged from 0.40 to 1.20. All these values indicate that the organic matter was deposited under sub-oxic to anoxic (reducing) conditions during the deposition of the sediments. However, the higher abundance of nC17 and nC18 relative to isoprenoids was proof of the high maturity of the source rocks in the Anza basin, which was in agreement with the results reported by Gilbert *et al*. (2021) and Tissot *et al*. (1984). Further discussion was not carried out due to the absence of a single ion chromatogram (SIM) for (m/z) monitoring programs.

Despite the absence of commercial oil and gas discoveries in the Anza Rift, the obtained results provide positive indications for future exploration and finding of hydrocarbon gas and light oil deposits in the North Eastern part of the sedimentary basin.

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The association of organic matter and mineralogy of the sedimentary source rocks in the Anza basin of the north eastern part of Kenya was investigated using multi–analytical techniques.

i. The results of elemental organic (CHN) analysis indicate that all the source rocks drilled from the three wells- Chalbi-3, Sirius-1, and Ndovu-1 were rich in hydrocarbon content (TOC > 0.50%) and had a good potential to generate hydrocarbons upon heating. The low H/C and low N/C ratios imply that the source rocks contained type III/IV kerogens, and the source rocks are most likely oxidized and/or highly mature.
ii. The mineral part of the source rock samples is mainly constituted of Quartz and clay minerals. The FTIR observations confirmed the XRD, XRF, and SEM analysis results.
iii. Thermo-oxidative decomposition of the source rocks by TG/TDG/DSC analyses occurred in three or four steps: (1) evaporation of moisture, release of interlayer water associated with quartz and clay minerals and CO_2 emission in the temperature range of 30 to 250 °C, (2) the thermo-oxidation of bitumen (according to the heating rate ranging from 260 °C to 401 °C), (3) the thermo-oxidation of the kerogen (between 365 and 560 °C), and (4) finally, the decomposition of calcite mineral (between 541 °C and 815 °C). Accordingly, it can be concluded that thermo-oxidative destruction of organic matter starts in the temperature region of 250-300 °C and ends at 400–600 °C.
iv. The saturated fractions of all the samples are characterised by a unimodal distribution of short (n-C14–n-C20) to middle (n-C21–n-C23) chain n-alkanes. The dominancy of short-chain (< n-C20) alkanes is characteristic of marine OM originating from algae and microorganisms, while the long-chain hydrocarbons (>C20) reflect continental contribution of the organic matter from higher terrestrial plants. Therefore, the organic matter had dual contributions from algae and terrestrial higher plant sources and was in an advanced stage of maturity.

5.2 Recommendations

i. The total organic carbon (TOC) ranges for all four source rock samples match the generally accepted criteria for fair to good potential for petroleum generation. The three wells have potentially extractable oil/gas generation from 1066 - 3100 m. This makes them effective source rock candidates for generating commercial amounts of oil/gas in the Anza Basin.

ii. The TG/DSC should be carried out under an inert (Ar/N_2) atmosphere to trace endothermic and exothermic reaction processes. The results obtained would be comparable to those of the Rock-Eval analysis.

iii. Should incorporate a single ion monitoring program in GC-MS as well as the data ibrary to assist in the identification process of biomarkers in extracted fractions.

iv. To measure and identify volatile products generated during thermal analysis, an integrated Fourier Transform Infrared Spectrometer (TG/DSC-FTIS), a Gas Chromatograph (TG/DSC-GC), or a Mass Spectrometer (TG/DSC-MS) needs to be coupled to the TG/DSC device.

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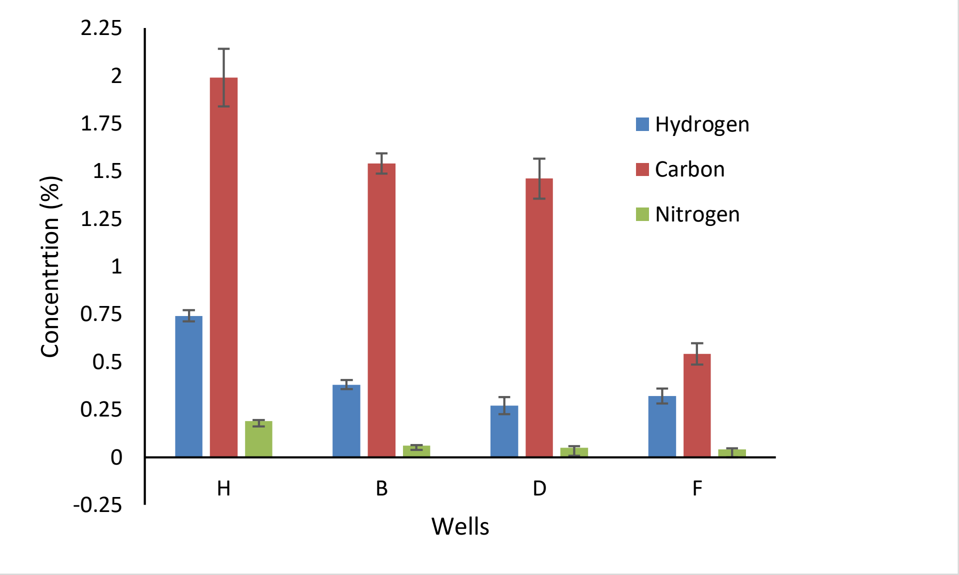
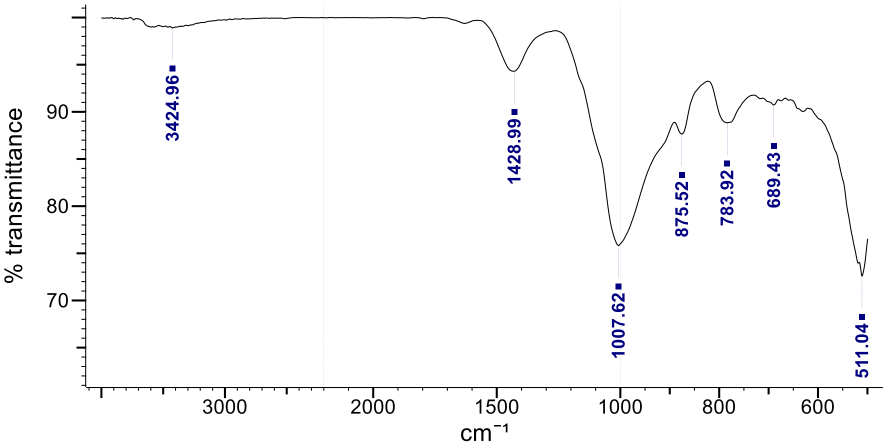
APPENDICES

Appendix A: Concentrations of Hydrogen, Carbon, and Nitrogen in the studied source rock samples of different wells

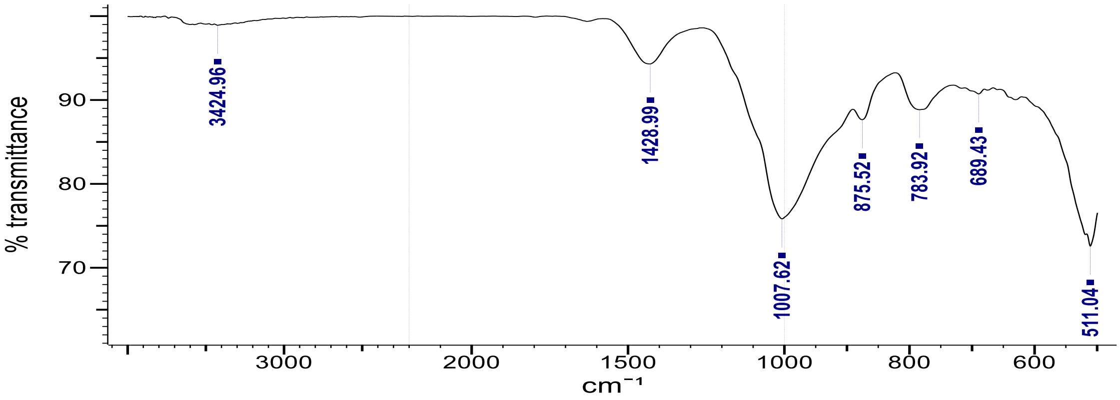


Appendix B: FTIR spectra of acid-treated source rocks samples D, E, and F

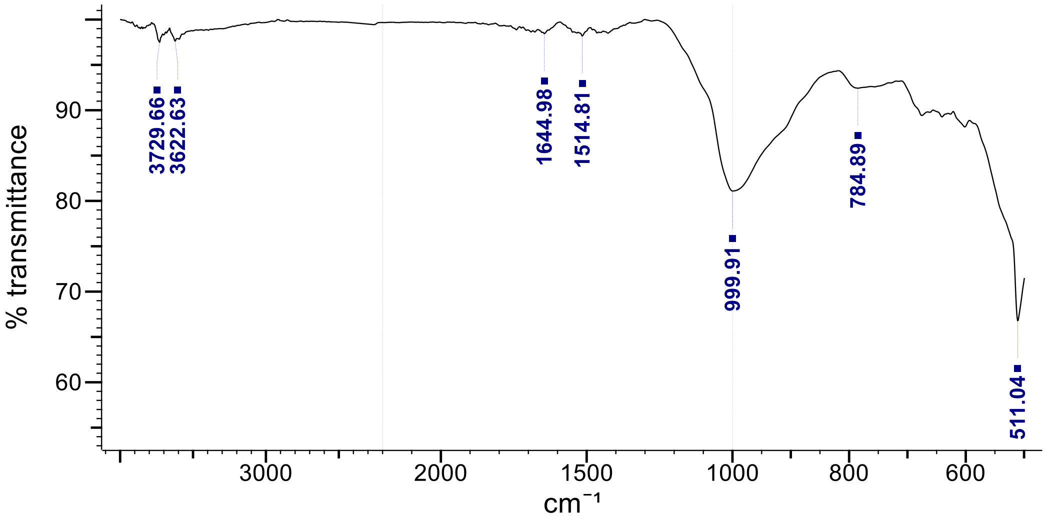
SAMPLE D



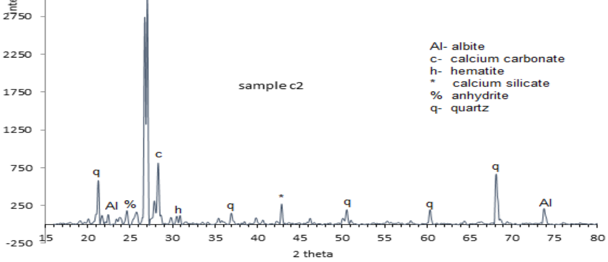
SAMPLE E

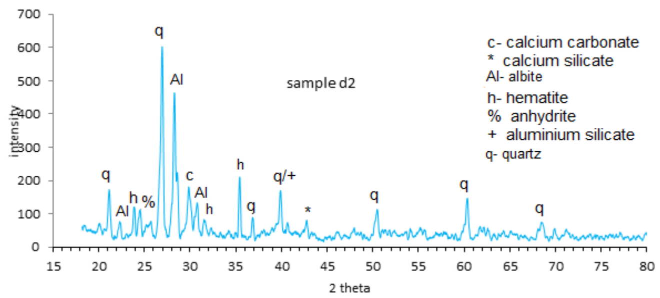


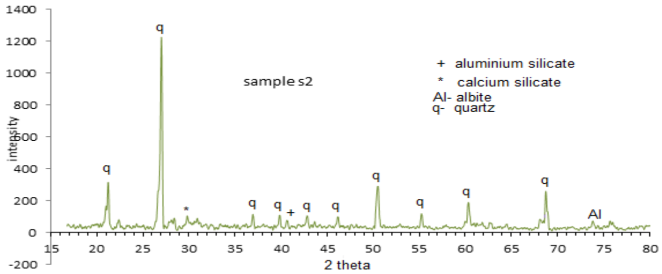
SAMPLE F



Appendix C: XRD patterns of source rock samples of Anza Basin at 30 °C





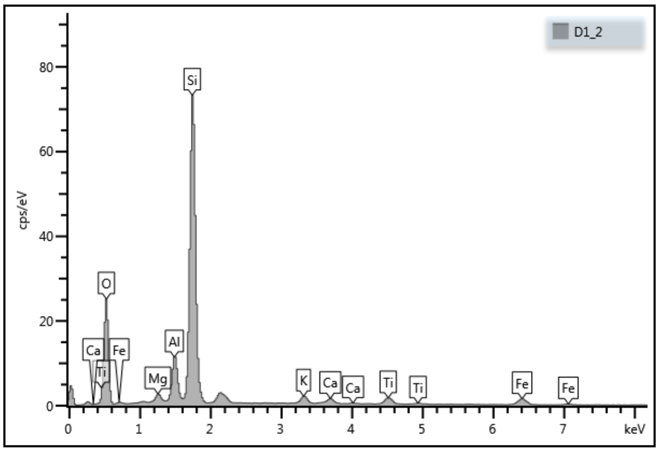


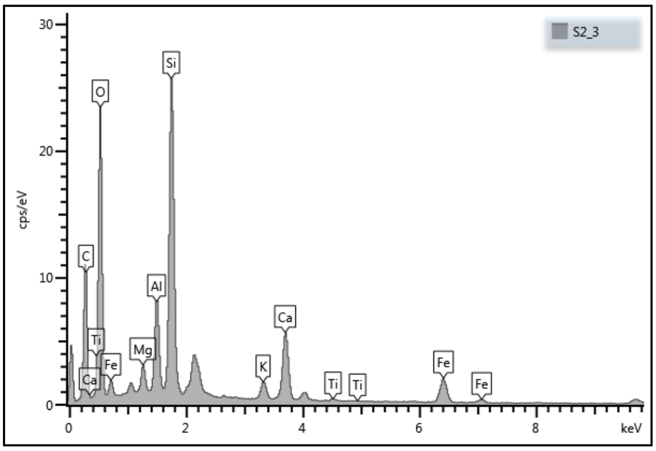
Appendix D: Composition of Minerals in Anza Basin

Sample	Depth, m	Minerals
Chalbi-3 (C1)	3099.8	Quartz Calcium carbonate Aluminium silicate Calcium silicate Hematite Anhydrite
Chalbi-3 (C2)	2819.4	Albite Calcium carbonate Calcium silicate Anhydrite Hematite Quartz
	2231.1	Quartz

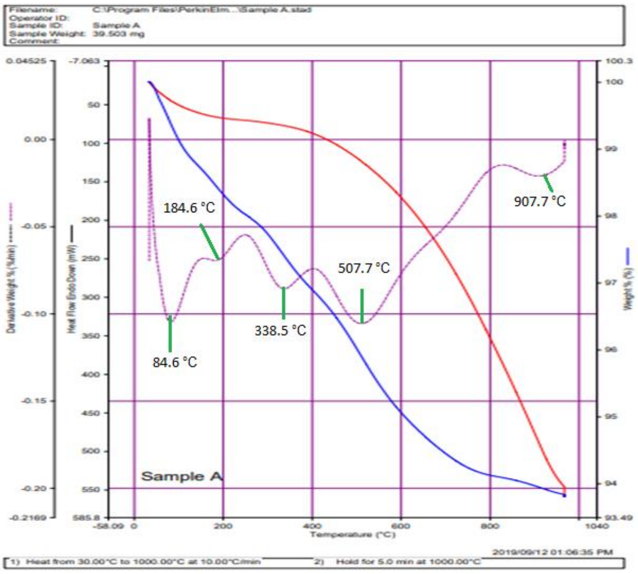
Sirius-1 (S1)		Anhydrite
		Calcium carbonate
		Calcium silicate
		Aluminium silicate
	2316.5	Albite
Sirius-1 (S2)		Calcium silicate
		Aluminium silicate
		Quartz
	1297.8	Albite
Ndovu-1 (D1)		Calcium carbonate
		Hematite
		Anhydrite
		Quartz
		Aluminium silicate
		Calcium silicate
	1011.6	Calcium carbonate
		Calcium silicate
Ndovu-1 (D2)		Albite
		Anhydrite
		Aluminium silicate
		Quartz

Appendix E: XRF spectra of source rock samples D1_2 and S2_3.





Appendix F: TG, DTG, and DSC curves for samples A, C, E, and F



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Operator ID:
Sample ID: Sample A
Sample Weight: 39.503 mg
Comment:

2019/09/12 01:06:35 PM

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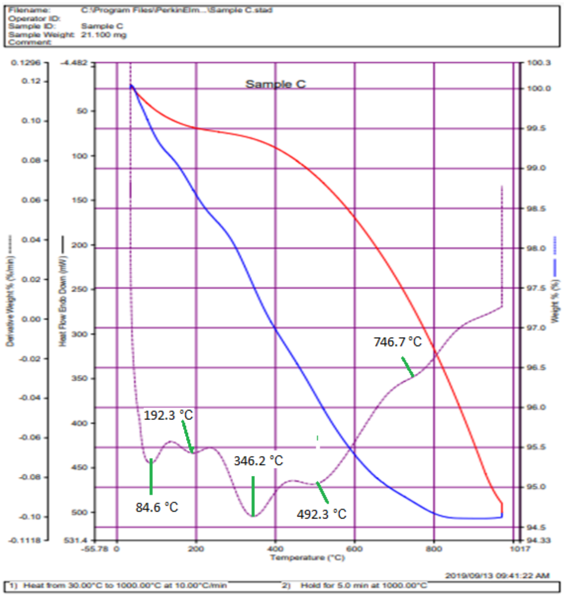
2) Hold for 5.0 min at 1000.00°C



Filename: C:\Program Files\PerkinElm...\Sample C.stad
Operator ID:
Sample ID: Sample C
Sample Weight: 21.100 mg
Comment:

2019/09/13 09:41:22 AM

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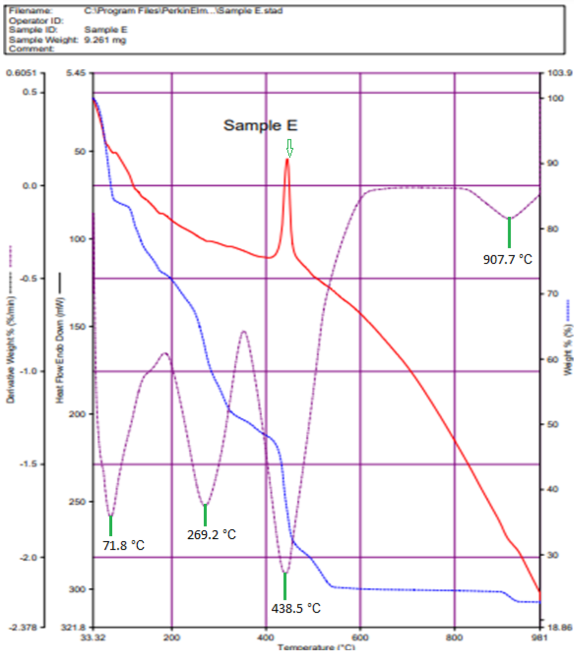
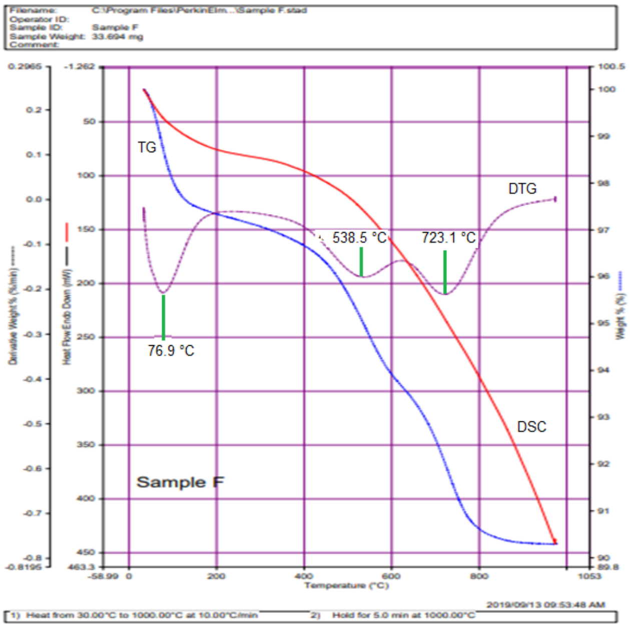
2) Hold for 5.0 min at 1000.00°C



Filename: C:\Program Files\PerkinElm...\Sample E.stad
Operator ID:
Sample ID: Sample E
Sample Weight: 9.261 mg
Comment:

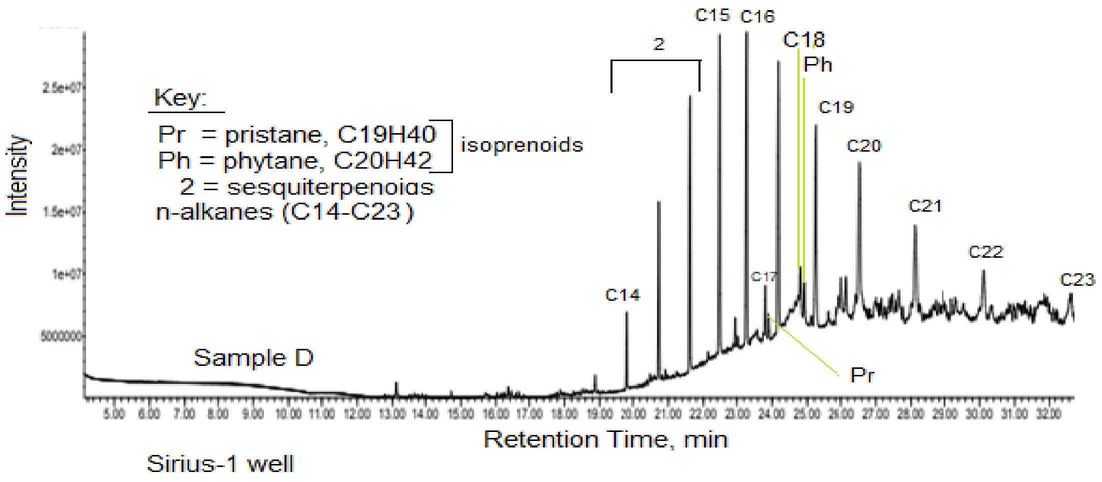


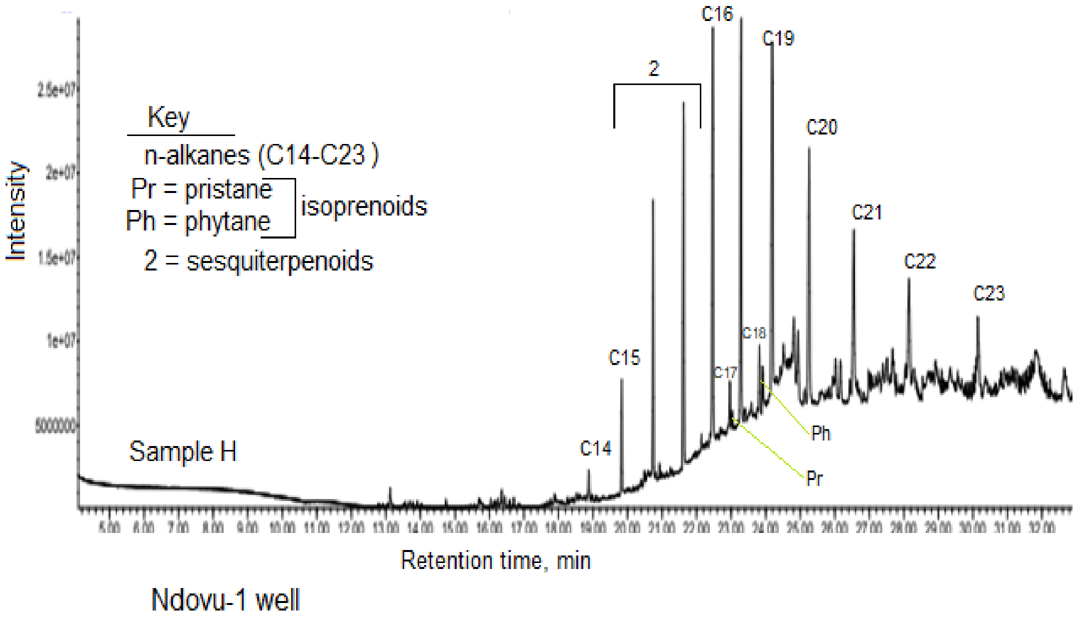
Filename: C:\Program Files\PerkinElm...\Sample F.stad
Operator ID:
Sample ID: Sample F
Sample Weight: 33.694 mg
Comment:

2019/09/13 09:53:48 AM

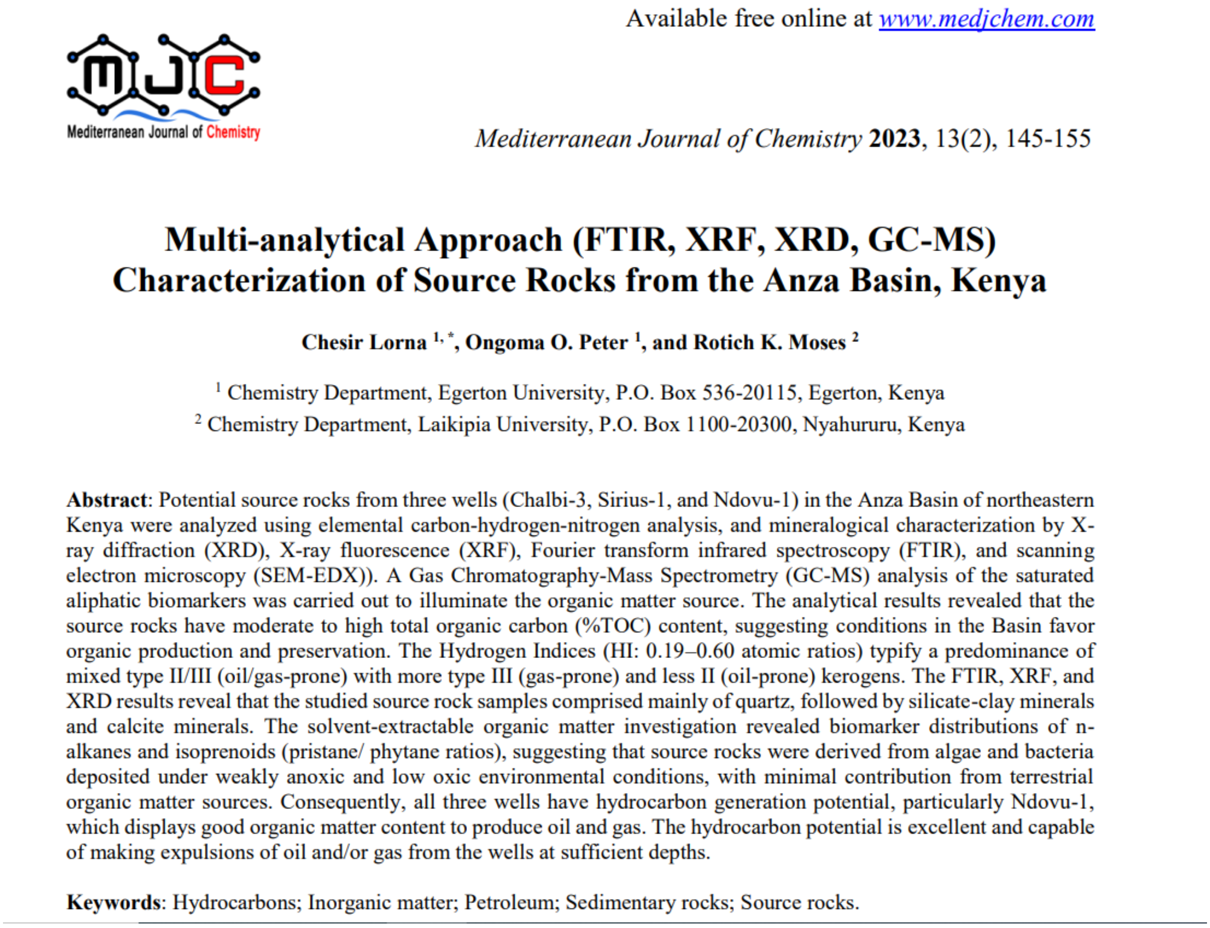
1) Heat from 30.00°C to 1000.00°C at 10.00°C/min
2) Hold for 5.0 min at 1000.00°C

Appendix G: n-alkanes and isoprenoid hydrocarbons distribution in the source rock.





Appendix H: Abstract page of publications



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Mediterranean Journal of Chemistry

Mediterranean Journal of Chemistry **2023**, 13(2), 145-155

Multi-analytical Approach (FTIR, XRF, XRD, GC-MS) Characterization of Source Rocks from the Anza Basin, Kenya

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Abstract: Potential source rocks from three wells (Chalbi-3, Sirius-1, and Ndovu-1) in the Anza Basin of northeastern Kenya were analyzed using elemental carbon-hydrogen-nitrogen analysis, and mineralogical characterization by X-ray diffraction (XRD), X-ray fluorescence (XRF), Fourier transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM-EDX)). A Gas Chromatography-Mass Spectrometry (GC-MS) analysis of the saturated aliphatic biomarkers was carried out to illuminate the organic matter source. The analytical results revealed that the source rocks have moderate to high total organic carbon (%TOC) content, suggesting conditions in the Basin favor organic production and preservation. The Hydrogen Indices (HI: 0.19–0.60 atomic ratios) typify a predominance of mixed type II/III (oil/gas-prone) with more type III (gas-prone) and less II (oil-prone) kerogens. The FTIR, XRF, and XRD results reveal that the studied source rock samples comprised mainly of quartz, followed by silicate-clay minerals and calcite minerals. The solvent-extractable organic matter investigation revealed biomarker distributions of n-alkanes and isoprenoids (pristane/ phytane ratios), suggesting that source rocks were derived from algae and bacteria deposited under weakly anoxic and low oxic environmental conditions, with minimal contribution from terrestrial organic matter sources. Consequently, all three wells have hydrocarbon generation potential, particularly Ndovu-1, which displays good organic matter content to produce oil and gas. The hydrocarbon potential is excellent and capable of making expulsions of oil and/or gas from the wells at sufficient depths.

Keywords: Hydrocarbons; Inorganic matter; Petroleum; Sedimentary rocks; Source rocks.

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Evaluation of hydrocarbon generation potential of source rocks by Thermogravimetric and Differential Scanning Calorimetry

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Department of Chemistry, Egerton University, P.O. Box 536-20115, Egerton, Kenya

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Abstract

Understanding the association of organic matter and minerals in petroleum source rocks is a vital component of the hydrocarbon-generation process, especially in unconventional reservoirs, which are the targets of hydrocarbon exploration today. In this study, five source rock samples selected from three wells namely, Chalbi-3, Sirius-1, and Ndovu-1wells from the Anza basin, were investigated to characterise the thermal decomposition process using differential scanning calorimetry (DSC) and thermogravimetry (TG/DTG) with a heating rate of 10 °C min^{-1} in an oxidizing atmosphere. The Anza basin is a sedimentary basin located in the north-eastern part of Kenya. The source rocks displayed variable degrees of organic richness, with TOC contents ranging from 0.54 to 1.99 wt. %, at subsurface depths ranging from 1067–3100 m. The Ndovu-1 (H) sample had the highest TOC value, while Sirius-1 (F) had the lowest. In all the analyses, the TG/DSC curves allowed three distinct decomposition regions of organic matter and inorganic matter decomposition identified as i) low-temperature oxidation of bitumen (temperature ranging from 257 °C to 350 ° C), ii) thermo-oxidation of the kerogen (between 430 and 560 °C), and iii) high-temperature decomposition of calcite mineral (between 723 and 747 °C), and clay minerals in the temperature range 907 and 923 °C. There was also a strong correlation between the mass loss and combustion of organic matter in the source rocks.

Keywords: source rocks, TG/DTG/DSC analysis, Thermo-oxidative decomposition, Anza basin

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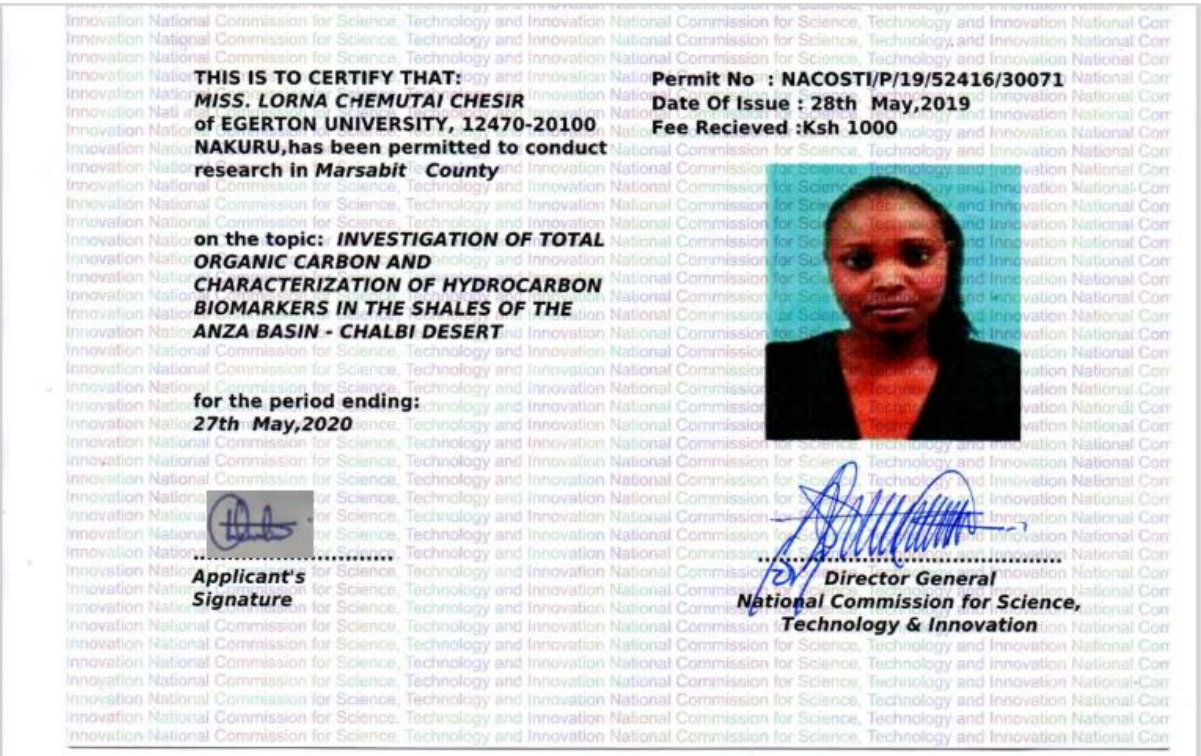
Appendix I: Research Permit



THIS IS TO CERTIFY THAT:
MISS. LORNA CHEMUTAI CHESIR
of EGERTON UNIVERSITY, 12470-20100
NAKURU,has been permitted to conduct
research in *Marsabit County*

on the topic: *INVESTIGATION OF TOTAL ORGANIC CARBON AND CHARACTERIZATION OF HYDROCARBON BIOMARKERS IN THE SHALES OF THE ANZA BASIN - CHALBI DESERT*

for the period ending:
27th May,2020

Permit No : NACOSTI/P/19/52416/30071
Date Of Issue : 28th May,2019
Fee Recieved :Ksh 1000

Applicant's Signature

Director General
National Commission for Science, Technology & Innovation