



**Technical University of Crete**  
**School of Mineral Resources Engineering**  
**MSc Program in Geotechnology & Environment**

# Geochemical evaluation of petroleum source rocks in North Sydney Basin, Australia.



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**School of Mineral Resources Engineering**  
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Basin, Australia.

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## ABSTRACT

The aim of this Master thesis was the study of oil and gas potential of petroleum source rocks in Southeast Australia. More specifically, we analyzed using geochemical methods, rock samples of Upper Permian age, from Northern Sydney Basin, in Australia.

In this thesis work, we used 27 rock samples, taken from three different depths. After we crushed and screened a representative amount of each sample, we analyzed all of them in Rock-Eval Analysis Method. This way we found the organic content of our samples. Subsequently, we chose two samples of each depth, six in total, which went through the complete experimental process.

More specifically, our powdered samples were extracted by Soxhlet method; this way we separated the bitumen from the inorganic components. In the next step the extract was separated in two fractions, asphaltenes and maltenes, by deasphaltation method. Subsequently, the maltene fraction went through the column chromatography method and gave us the saturated, the aromatic and the NSO fraction. Then, the saturated fraction was analyzed in Gas Chromatography-Mass Spectrometry method and the experimental results helped us calculate geochemical indices, in order to define the quality, the quantity and the origin of the organic matter, as well as the depositional environment.

It was found that the formation the samples come from has excellent hydrocarbon potential and it is prone to gas or oil/gas production. The organic matter could be characterized immature or early mature and it is proved to be indigenous; its origin appears to be terrestrial, but there also clues for marine contribution. The results of the biomarkers analysis indicate a peat swamp environment, with anoxic conditions and low salinity.

## ΠΕΡΙΛΗΨΗ

Η παρούσα διπλωματική εργασία είχε ως στόχο τη μελέτη του δυναμικού γένεσης πετρελαίου και φυσικού αερίου στη νοτιο-ανατολική Αυστραλία. Πιο συγκεκριμένα, εξετάσαμε το δυναμικό των σχηματισμών, ηλικίας άνω Περμίου, από την περιοχή της βόρειας λεκάνης του Σίδνεϊ, στην Αυστραλία.

Για την εκπόνηση της εργασίας αυτής, χρησιμοποιήθηκαν 27 δείγματα από τρία διαφορετικά βάθη, από την περιοχή που προαναφέρθηκε. Αρχικά το σύνολο των δειγμάτων, αφού κονιοποιήθηκε και κοσκινίστηκε, υποβλήθηκε στην ανάλυση Rock-Eval, μέσω της οποίας δόθηκαν τα πρώτα στοιχεία σχετικά με το οργανικό περιεχόμενο των δειγμάτων. Έπειτα, επιλέχθηκαν 2 δείγματα από κάθε βάθος, 6 στο σύνολο, τα οποία αναλύθηκαν με τις πρότυπες γεωχημικές μεθόδους για ανάλυση πετρελαίου.

Συγκεκριμένα, τα επιλεγμένα αυτά δείγματα υποβλήθηκαν στη διαδικασία της εκχύλισης με τη μέθοδο soxhlet, μέσω της οποίας διαχωρίστηκαν τα βιτουμένα από τα ανόργανα συστατικά. Στη συνέχεια το εκχύλισμα χωρίστηκε με τη σειρά του στα κλάσματα των ασφαλτένιων και των μαλτενίων, με τη διαδικασία της απασφάλτωσης. Ακολούθησε η διαδικασία της χρωματογραφίας στήλης, στην οποία από το κλάσμα των μαλτενίων συλλέξαμε τρία κλάσματα, τα κορεσμένα, τα αρωματικά και τις ρητίνες. Το κορεσμένο κλάσμα που συλλέξαμε αναλύθηκε με αέρια χρωματογραφία-φασματοσκοπία μάζας, και από τα πειραματικά δεδομένα υπολογίστηκαν γεωχημικοί δείκτες που συντέλεσαν στον προσδιορισμό της ποιότητας, της ποσότητας και της προέλευσης της οργανικής ύλης, καθώς και του περιβάλλοντος απόθεσής της.

Διαπιστώθηκε ότι ο σχηματισμός στον οποίο ανήκουν τα δείγματα που αναλύθηκαν έχει άριστο δυναμικό πετρελαιογένεσης, με οργανική ύλη που χαρακτηρίζεται ανώριμη ή στα πρώτα στάδια ωριμότητας. Ο σχηματισμός προβλέπεται να παράγει φυσικό αέριο ή πετρέλαιο και φυσικό αέριο. Η οργανική ύλη αποδεικνύεται αυθιγενής, ενώ η προέλευσή της εκτιμάται ότι είναι χερσαία με θαλάσσια παρόλα αυτά συνεισφορά. Τα αποτελέσματα της ανάλυσης των βιοδεικτών δείχνουν ένα περιβάλλον βαλτώδες με ανοξικές, κατά κύριο λόγο, συνθήκες και χαμηλή αλμυρότητα.

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## SYMBOLS AND ACRONYMS

SB	Sydney Basin
NSB	Northern Sydney Basin
DOC	Dissolved Organic Carbon
POC	Particulate Organic Carbon
PVT	Pressure-Velocity-Temperature
FID	Flame Ionization Detector
GC/MS	Gas Chromatography/ Mass Spectrometry
TOC	Total Organic Carbon
Tmax	Maximum Temperature
HI	Hydrogen Index
OI	Oxygen Index
PI	Productivity Index
PC	Pyrolyzed Carbon
TAR	Terrigenous to Aquatic Ratio
OEP	Odd to Even Predominance
CPI	Carbon Preference Index
DCM	DiChloroMethane
NSO	Nitrogen-Sulphur-Oxygen
NMR	Nuclear Magnetic Resonance spectroscopy
TIC	Total Ion Current
SIM	Selected Ion Monitoring
Pr	Pristane
Ph	Phytane

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# 1. AUSTRALIA

## 1.1 THE GEOGRAPHICAL POSITION OF AUSTRALIA

The Commonwealth of Australia lies in the Southern Hemisphere, between the South Pacific and Indian oceans, with geographical latitude  $-26^{\circ} 26' 20.73''$  S and longitude  $133^{\circ} 16' 52.76''$  E. It is considered to be the smallest continent and one of the largest countries on Earth. Its total area is 7.692.024 km<sup>2</sup> and its population of 24.992.024 is mainly gathered on the eastern seaboard. Although Australia's capital is Canberra, Sydney and Melbourne are larger and blooming economically and culturally. Australia shares its maritime borders with Indonesia and Timor-Leste in the Northwest, Papua New Guinea and Solomon Islands in the Northeast, Vanuatu and New Caledonia in the East, New Zealand in the Southeast. It is surrounded by the Timor and Arafura Seas to the North, by the Coral Sea to the East and by the Tasman Sea to the Southeast (Ricard et al., 1998).



PICTURE 1.1: The map of Australia with the surrounding islands and seas

## 1.2 THE GEOLOGY OF AUSTRALIA

The surface geology of Australia is mostly consisted of Mesozoic or younger sedimentary rocks, which display the tectonic stability that occurs in the biggest part of the continent. There are data indicating that a Cenozoic cover reaches not only the shoreline, but even further, offshore and forms basins with sediments of great thickness. In the eastern part of Australia as well as in the island of Tasmania, we find different types of rocks, sedimentary, metamorphic and igneous, of Paleozoic age. These areas could be characterized as highlands, because of the uplift that occurred during the formation of Coral and Tasman Seas. Northern Australia is consisted mostly of Proterozo-

ic Metasedimentary rocks that we find particularly in Kimberley, Pine Creek, Macarthur and Mount Isa areas (Blewett, Kennett and Huston, 2012).

As far as the geological regions of Australia are concerned, the rocks of different ages are distributed in the continent as seen in Picture 1.2 below. More specifically, we can see that Archean rocks prevail in the eastern part and have some small appearances in the north and the south. In the center and central west we can see a clear predominance of late Proterozoic to Paleozoic basins that compose the Centralian Basin. Moreover, Proterozoic rocks extend in the northeast, as well as western Tasmania and Broken Hill. Eromanga Basin, which occupies a great part of Australia, consists of Mesozoic rocks, while Cenozoic rocks compose Eucla, Murray and Karumba Basins. As we understand, there is a general trend of younger Orogen rocks in the eastern part of the continent (Blewett, Kennett and Huston, 2012).



PICTURE 1.2: The basic building blocks of Australia, with the major cratons, inliers, orogenic belts and Phanerozoic sedimentary basins shown (Blewett, Kennett and Huston, 2012).

### 1.3 THE SYDNEY BASIN

Sydney Basin is a sedimentary basin, located in the southeast coast of Australia. It is filled with almost horizontal sandstones and mudstone beds of Permian to Triassic age. The basement rocks are composed of units that belong to the Lachlan Fold Belt. Sydney Basin covers a large area of the catchments of the Hawkesbury-Nepean, Hunter and Shoalhaven river systems. The landscape is composed of deep and steep gorges and remnant plateaus, formed by the erosion of coastal streams. Moreover, there is an east-west rainfall gradient which along with the differences in soil, affect the vegetation of eucalypt forests, woodlands and heaths (NSW-Office of Environment and Heritage, no date).

Sydney Basin initiated during the Permian, 299-252 Ma ago, with basin subsidence and evolution of a swamp forest that led gradually to the formation of extensive coal measures (SELS Australia, no date).

### 1.4 THE GEOLOGICAL SETTING OF SYDNEY BASIN

Approximately 298-247 Ma ago, in the Permian- Early Triassic, Australia belonged in Eastern Gondwana, which was the southern hemisphere of the supercontinent Pangea (Breckenridge et al., 2018). The Sydney Basin (SB) is part of the bigger and more complex Bowen- Gunnedah- Sydney Basin that was located in eastern Australia (Breckenridge et al., 2018). Similar formations also occur in Antarctica, South Africa and South America. The SB is underlain by different basement types and exhibits an asymmetric geometry, in which the thickest succession is found in the northeast (Breckenridge et al., 2018). In the southwest, the SB overlies the Early-Middle Paleozoic Lachlan Orogen and to the northeast it is underlain by the Late Paleozoic New England Orogen.

In the Late Carboniferous- Early Permian, the SB was a continental backarc basin, but during the Early Permian it went through a west ward marine transgression over the Lachlan Orogen to the south –west. At the same time the subduction of an east facing convergent margin in the New England Orogen to the north-east was active, as a result of post-rift subsidence and termination of crustal loading (Breckenridge et al., 2018). The Hunter-Bowen Orogeny, which was a compressive tectonic event, took place 265-250 Ma ago and created the Late Permian deformational pattern in the southern New England Orogen. This deformational pattern, which consisted of thrusts and folds and more specifically progressive, west-directed ones, subsequently converted the North Sydney Basin (NSB) to a foreland basin (Breckenridge et al., 2018).

The evolution of the NSB was due to the evolution of the uplifted and over-thrusted New England Orogen that became a major sediment contributor into the NSB. The evolution of the SB into a foreland basin was characterized by sediments with rapid lateral and vertical facies changes that resulted from eustatically and tectonically regressions and transgressions. In the Middle to Late Triassic, the SB was dissected by fold and thrust belts; this deformation turns out to be the reason for the termination of the deposition in the SB during the mid-Triassic time (Breckenridge et al., 2018). There are many similarities in the evolution of the SB and other contemporary basins in southern Gondwana, such as the Karoo Basin in southern Africa. Moreover, the Karoo Basin is similar to the

SB concerning the net progradation of the shoreline, with less evidence for tidal activity (Breckenridge et al., 2018).

## 1.5 OUTCROP ANALYSIS AND FACIES MODEL

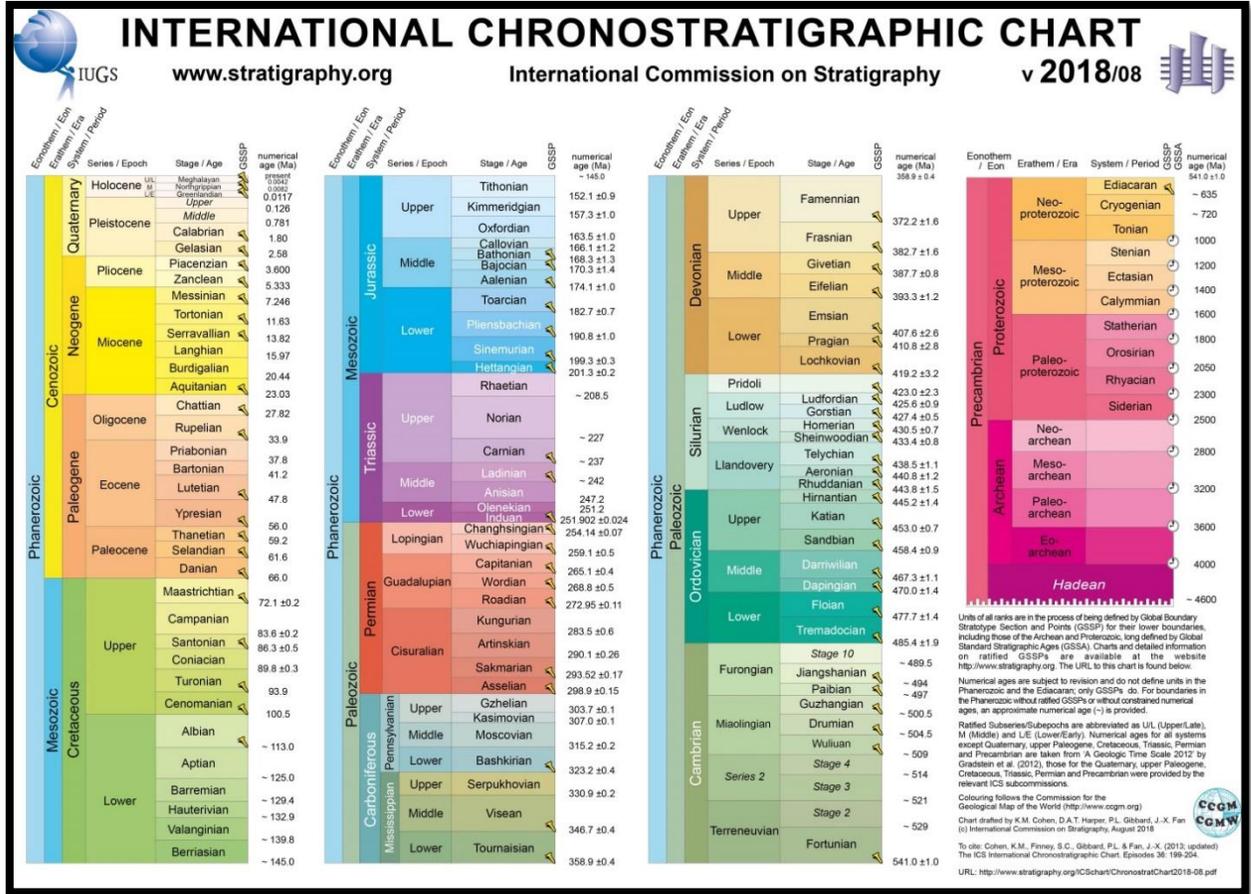
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The studied samples came from a tidally- influenced fluvio-deltaic system, of Upper Permian age, located in Northern Sydney Basin, Southeast Australia. This system went through an outcrop-based integrated study of facies, as well as a sequence stratigraphic and paleoflow analysis that provide information about the spatial and temporal distribution of the depositional environments, the physical processes of deposition that prevail and finally, the evolution of the paleo-environment, based on the stratigraphic and sedimentologic characteristics. First of all, the sedimentary succession is divided in fifteen depositional facies, arranged into three facies associations. Moreover, the first two facies associations are further sub-divided into some more sub-facies associations. This categorization shows us how the dominant physical process can differ, and displays the composition of delta-front, delta plain and fluvial.

The depositional trend in this system is related to an overall shallowing-upward succession that develops from delta-front to delta-plain deposits. Additionally, the coarsening-upward trend sustains progradation and delta plain distributary channel-fill successions dominated by lateral accretion elements are overlain by fluvial-tidal distributary channels, dominated by down current accretion elements (Breckenridge et al., 2018). The data mentioned above, indicate progradation and aggradation of the deltaic system.

The deltaic system contains wave/storm influenced delta-front deposits and tidal influenced delta-plain sediments whose deposition is controlled by fluvial processes. In the delta plain, deposits exhibit an upward increase in the fluvial energy. As far as the frequency and diversity of sedimentary structures are concerned, there is a decrease which suggests tidal influence. The fluvial sediments that overlie are river dominated. Consequently, we can observe an upward decrease of wave and tidal reworking, as well as a predominance of river processes. This trend can be associated with the abrupt topographic gradient and the large availability of coarse-grained sediments, caused by an uplift during active tectonism in the New England Orogen (Breckenridge et al., 2018).

The study of palaeocurrent data indicates that the paleoflow directions exhibit a trend that is parallel to the main structural element, known as the New England Orogen. Moving upwards to the studied succession, the trend changes to being perpendicular to the structural element. The latter show us how this tectonic element affects the sedimentation (Breckenridge et al., 2018).



PICTURE 1.3: International Chronostratigraphic Chart (IUGS).

## 2. OIL FORMATION

### 2.1 THE ORIGIN OF ORGANIC MATTER

---

There are many theories concerning the origin of oil and gas; most of them claim that they come from the organic matter of dead organisms, marine or terrestrial. Terrestrial organic matter includes higher plants and angiosperms. On the other hand, when it comes to marine environment, phytoplankton, zooplankton and bacteria are the three types of organisms that produce the most organic matter and therefore participate in the formation of petroleum and generally fossil fuels. The main contributor, phytoplankton, can be divided into four groups, the diatoms, the blue-green algae, the dinoflagellates and the coccolithophores. Bacteria are too of great importance, because the most crucial of their biogeochemical activities is transforming the bio-polymers of the dead organisms into monomers and thus helping in creating the organic fossil fuels. Overall, although terrestrial organic matter is more abundant than marine, in the latter environment we have more efficient preservation. Every living organism is unique and complex however, they all consist of a limited number of organic component groups; such as lipids, carbohydrates, proteins and lignin.

### 2.2 THE ORGANIC MATTER IN SEDIMENTS

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Organic matter is spread out in the environment, in different forms and concentrations. In order to be transformed into a significant amount of fossil fuels, certain conditions have to occur regarding accumulation, productivity and preservation of organic matter. When we talk about the accumulation of organic matter, we are focusing in marine environments. There, the organic matter is found as Dissolved (DOC), Particulate (POC) or Colloidal matter. Usually we need quiet waters and low-energy, restricted environments for the organic matter to settle down. These environments are usually closed seas, lakes, lagoons and swamps. Organic matter in marine environments is produced through photosynthesis of phytoplankton.

High productivity is connected to bacteria that decompose dead organisms. Large amounts of organic matter may also come from the land, as in shores and deltas. The most important factors that affect productivity are sunlight intensity, availability of nutrients, temperature and oxygen content. The upwelling system is another mechanism that reinforces productivity, when deeper, colder and nutrient-rich water rises up, to replace the warmer surface water. Lastly, in order to achieve high productivity, we need rapid rate of deposition and oxygen-poor water bodies with anoxic bottoms. Areas with this kind of characteristics are continental shelves and large river deltas. However, the productivity of organic matter by itself is not enough to create a good source rock. This potential depends on the occurrence of anoxic conditions and bacterial decay. On one hand, we need absence of oxygen that can oxidize the organic matter. Rapid deposition helps preservation and prevents the destruction of organic matter in the water column. On the other hand, we need anoxic bottoms, which do not allow sea animals interfere with the organic matter. An example of these animals is the marine polychaete worm which eats the sediments to get the organic matter. This process is called bioturbation and creates poor source rocks.

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## 2.3 THE TRANSFORMATION OF ORGANIC MATTER

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After the organic matter is deposited, it begins to transform, under the influence of several physicochemical procedures. There are four stages of transformation of the organic matter, diagenesis, catagenesis and metagenesis.

Diagenesis is the first stage and it starts right after the death of the organisms and the deposition of the organic matter in sediments. In the beginning, organic matter is deposited as an unconsolidated mud, that contains up to 80% water and afterwards it is transformed into mudstones and shales. During diagenesis, organic matter goes under some serious changes; biopolymers are transformed into geomonomers through hydrolysis. Later on, geomonomers are combined randomly and form geopolymers. When geopolymers form blocks, we have the formation of kerogen. Aside from kerogen, bitumens and biogenic methane constitute the products of diagenesis. We may also find structured and amorphous material. In this stage, the temperature is about 50° to 60°C.

Catagenesis is the second stage of the transformation of organic matter. Here we have the breakage of the heteroatoms' bonds and the formation of heterocompounds. As a result, kerogen appears with lower H/C ratio and it forms bulk oil and gas. The temperature during catagenesis ranges between 60° and 150°C.

In the next stage called Metagenesis, we have thermal cracking of the C-C bonds in hydrocarbons, something that leads to the formation of dry gas (methane). At the same time, in the residual kerogen, we have the formation of pyrobitumens, solid structures, rich in carbon, formed from the aromatic rings of kerogen. Moreover, in this stage, thermochemical sulfate reduction (TSR) may occur, and produce sour gas. During metagenesis, the temperature can reach up to 300°C.

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## 2.4 KEROGEN

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Kerogen is a complex, disseminated organic matter, insoluble in non-polar solvents and non-oxidizing mineral acids. It is formed during diagenesis, as mentioned above, but it is partially preserved in the following stages of transformation, until metamorphism. The graphical plot of Van Krevelen, that uses the Oxygen to Carbon (O/C) and Hydrogen to Carbon (H/C) ratios, helps us divide kerogen into four categories.

Type I kerogen has the highest concentration in Hydrogen and low concentration of oxygen; hence it has the highest potential of generating oil and gas. It is formed mostly from lipids, coming from algae and bacteria. It consists mainly of alginite, liptinite and aliphatic chains and it is found in lacustrine and generally shallow marine environments.

Type II kerogen comes from mixed marine sources as well as some higher organisms, such as algae, pollen, seeds and waxes. It is found mostly in marine reducing environments. The main macerals contained in this type of kerogen are exinite, liptinite, cutinite and rezinite. This type is considered to be the main for forming source rocks.

Type III kerogen has low concentration of hydrogen and higher concentration of oxygen, therefore it has quite low potential for generating hydrocarbons; it can produce mostly gas, when in high temperatures. It comes from the cellulose and lignin of terrestrial organic matter. In this type of kerogen, the macerals we can find are vitrinite and inertinite. It can be found in coals and debris of continental vegetation.

Type IV kerogen has extremely low concentration of hydrogen and high concentration of oxygen. It characterizes carbonates with low potential of producing gas. It comes from oxidized material of continental vegetation or oxidized kerogen and it consists mostly of inertinite.

## 2.5 OIL-FORMATION FACTORS

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In order to have oil formation, certain conditions must be met. Firstly, we need a source rock that permits the oil formation. Some faults, joints or primary porosity are essential to make routes for the oil migration. Then a reservoir rock is required in order for the oil to be accumulated, as well as a seal rock, to prevent the oil from migrating through the rock. Finally, we need a trap, where hydrocarbons stay barred from further movement.

In more detail, source rocks are sedimentary formations, usually made of fine-grained sediments, rich in organic matter, such that they can produce a significant amount of oil or gas when buried and heated. Anoxic conditions are crucial for the preservation of organic matter, while lakes, deltas and lagoons are the most appropriate depositional environments for petroleum source rocks.

Oil migration is about the transport of the oil components from the source rock to the reservoir rock, where they can accumulate and produce the hydrocarbons. This process includes two stages, the primary and the secondary migration. In primary migration, we are talking about the transport of the petroleum from the source rock, to other formations with higher permeability. Secondary migration is the movement of the oil, from any porous and permeable layer to its final accumulation. The last one can go through great distance, even hundreds of kilometers (Pasadakis, 2015; Pasadakis, 2017). The timing of oil migration is of great importance; if it occurs before a suitable combination of reservoir and seal rocks establishes, then the oil will not be trapped.

Reservoir rocks are sedimentary rocks in which oil could accumulate. A petroleum reservoir should be porous and permeable. Porosity is the void space in a rock and it expresses the capability of the rock to keep petroleum in it. Permeability is the property that defines how easily a fluid can pass through the rock. These two properties are affected from the grain packing geometries of the reservoir rock, as well as the diagenetic changes that occur after the deposition.

As mentioned previously, the presence of a seal rock (cap rock, top seal) is critical for an oil field, as it can isolate the petroleum and confine it in the reservoir rock. A suitable seal rock is usually consisted of a fine-grained formation with small pore size, high ductility, thickness and most importantly wide lateral extend. The most appropriate seals are considered to be shales and evapo-

rites, such as halite, anhydrite and dolomite. Faults can act as seals as well; it depends on the hydraulic conditions and the type of the rocks juxtaposed across the fault.

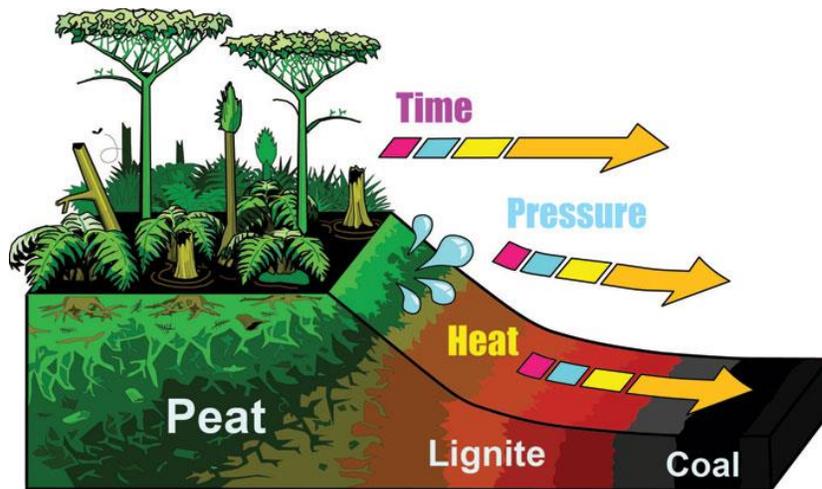
The last requirement in order to have an oil formation system is the presence of a trap. It reflects a barrier to oil migration towards the earth surface, so that an oil accumulation is created. A trap may contain both oil and gas. Traps are divided to structural, stratigraphic and hydrodynamic. Some examples to structural traps could be the tectonic structures, diapiric structures such as salt domes, as well as folds and anticlines. Some examples to stratigraphic traps could be pinchouts and unconformities (depositional traps) or mineral precipitation and mineral dissolution (diagenetic traps). Hydraulic traps can form when moving water controls the distribution of oil and gas traps. Although they are quite uncommon, their impact in some foreland basins is significant.

### 3. COAL GEOLOGY

#### 3.1 DEFINITION-FORMATION-CLASSIFICATION

Coal is an organic sedimentary rock that contains more than 50% by weight of carbonaceous material. Except for carbon, it contains also other elements in various quantities; the most important of them are hydrogen, oxygen, sulfur and nitrogen. Along with oil and natural gas, they constitute the three most important fossil fuels. Coal is a combustible rock and one of its main uses is generating electricity.

Coal forms from the accumulation and preservation of plant material, usually in a swamp environment. More specifically, when a plant dies and falls into a swamp, the standing water, which is oxygen-deficient, protects the plant debris from decay. Under the water the plant debris is also protected from the insects and from other organisms that would consume it in the land. In order to form a thick layer, the rate of plant debris accumulation should be greater than the rate of decay. If so, a coal seam is produced. Next it should be buried under sediments such as sand or mud, the weight of which contributes in the compaction and later on, in the transformation into coal. The accumulation of plant debris takes a very long time, in fact thousands of years. During these years, the conditions of water depth should be ideal, in order to form a coal seam. Moreover, the coal seam formation requires one of the following conditions: either a rising water level that follows the rate of plant debris accumulation, or a subsiding landscape that follows the rate of plant debris accumulation. We understand that the formation of coal requires a perfect balance between the conditions mentioned above, and for such a long period of time. This is why these conditions rarely occurred in the history of Earth.



PICTURE 3.1: The formation of Coal

When the plant debris is subjected to higher pressure and temperature during its burial, there are changes in composition and properties. These changes are also called 'organic metamorphism'

and define the rank of the coal. The ranks are cited below, along with their properties, from the lowest to the highest.

1. Peat: An organic sediment, with a carbon content less than 60% on a dry, ash-free basis. Peat is freshly accumulated plant debris that could be partially carbonized. In time, as the peat is buried deeper, the increasing temperature and pressure contribute to its transformation into a rock called coal.



PICTURE 3.2: Peat (geology.com)

2. Lignite: It is the lowest rank of coal. Lignite is formed when peat is compressed, dewatered and lithified (King, no date). Lignite is a rock of brown to black color that contains 60 to 70% of carbon on a dry, ash-free basis. Sometimes we can recognize in lignite plant structure. It has less than 8300 British Thermal Units per pound in a mineral-matter-free basis.

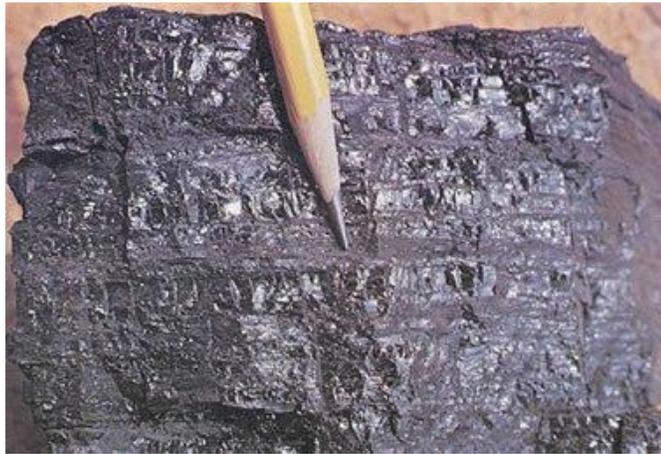


PICTURE 3.3: Lignite (geology.com)

3. Sub bituminous: A lignite with higher level of organic metamorphism. Sub bituminous coal has 71-77% carbon content on a dry, ash-free basis and a heating value of 8300 to 13000

British Thermal Units per pound in a mineral-matter-free basis. It is categorized in sub bituminous A, B and C ranks, based on its thermal value.

4. Bituminous: A sub bituminous coal with higher level of organic metamorphism. Bituminous coal has 77 to 87% carbon content on a dry, ash-free basis and heating value, much higher than lignite or sub bituminous coal. Bituminous is the most abundant rank of coal and it is categorized in low-volatile, medium-volatile and high-volatile bituminous, based on its volatile content. Bituminous coal is usually a banded sedimentary rock, and as we can see in picture 3.4 below, it may have bright and dull bands, with horizontal orientation across the specimen (King, no date).



PICTURE 3.4: Bituminous Coal (*geology.com*)

5. Anthracite: The highest rank of coal, with a carbon content more than 87% on a dry free-ash basis. It has a bright luster and breaks with a semi-conchoidal fracture (King, no date). Anthracite has the highest heating value per ton on a mineral-matter-free basis and it can be subdivided into semi-anthracite, anthracite and meta-anthracite, based on its carbon content.

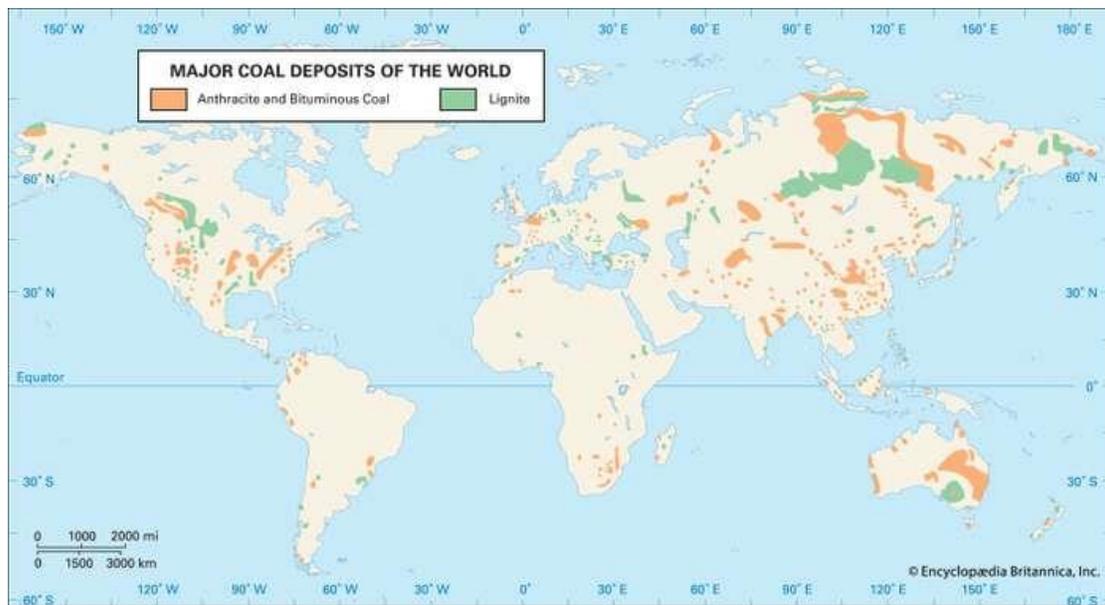


PICTURE 3.5: Anthracite (*geology.com*)

### 3.2 WORLD DISTRIBUTION OF COAL

World coal reserves and resources are difficult to evaluate, mostly because of two basic problems. First of all, there is the problem of the differences in some terms, such as proven reserves and geological resources. Proven reserves refer to the part of the reserves that are recoverable, while geological resources refer to the total amount of the coal, whether it is recoverable at present or not. In order for a coal reserve to be economically mineable, it has to be of a minimum thickness and in a maximum depth. These parameters do change, and they depend on the quality of the coal, the demand, the mining techniques used at the time and many other factors. Secondly there is a problem about the rate at which the commodity is consumed. When we talk about worldwide reserves of coal, we should also take into consideration the years in which coal will be mineable, and not only the quantity of the coal (Kopp, 1998).

Under these circumstances, almost 80% of the world's total coal reserves are distributed in just 10 countries. United States of America are in the first place, with the world's biggest coal reserves (approximately 13%). The reserves are highly dispersed across the country, with Wyoming, Illinois, Montana, Ohio, Pennsylvania and Texas being some of the States with most of them. The US is the world's second largest producer and consumer of coal and nearly 43% of their electricity is generated by coal. Russia holds the second place with 18% of the world's total coal reserves. In the third place we find China, with 13% of the world's total reserves that are concentrated in the north and north-west part of the country. China is the world's biggest producer and consumer of coal and as of December 2012, the world's biggest coal importer. Moreover, more than 80% of China's electricity is generated by coal. Australia holds the fourth place, with 9% of the world's coal reserves. This country is the world's fifth producer and the second exporter of coal, after Indonesia. In the next places we find India, Germany, Ukraine, Kazakhstan, Colombia and finally Canada (Mining Technology, 2013).



PICTURE 3.6: Coal Deposits of the world (Encyclopædia Britannica, Inc).

### 3.3 COAL DEPOSITS IN AUSTRALIA

As it was mentioned above, Australia belongs in the 10 countries with the words biggest coal reserves. This country is the fifth larger producer and the second larger exporter in the world. It becomes clear that coal is the most important energy resource for Australia; in fact, nearly 60% of the country's electricity is produced from coal.

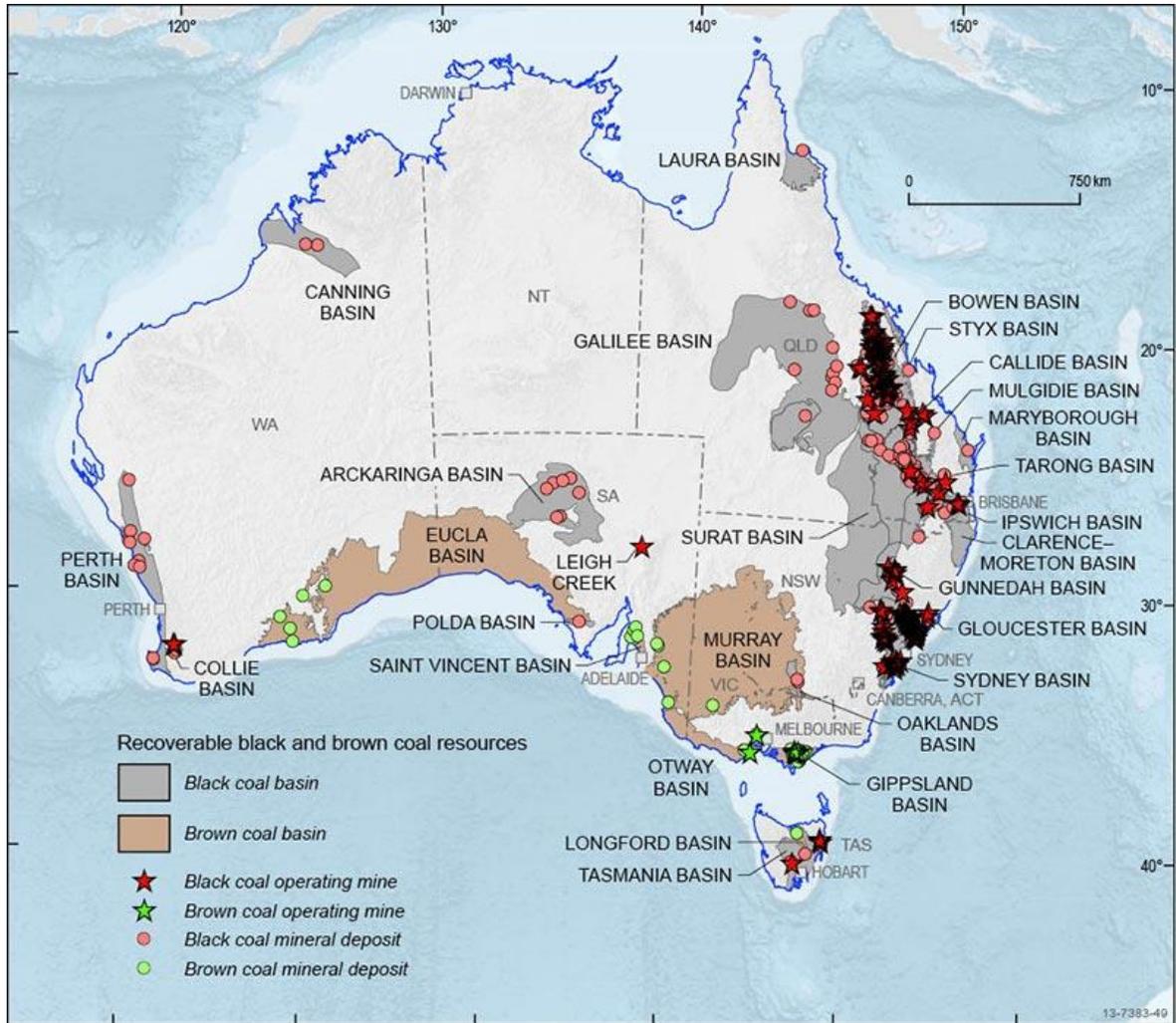
Australia has its own terminology when it comes to Coal classification, as we see in Table 1 below. The term 'brown coal' used in Australia, refers to lignite, the lowest-in-energy coal that is mainly used for electricity generation. The term 'black coal' in Australia is used to describe sub-bituminous, bituminous coal and anthracite. Black coal has higher energy than the brown one and it is used in coke production, as well as in, alumina refineries, cement and paper manufacturing and many other industrial applications. Coal can be used right after it is extracted from the ground; the only essential processing needed is crushing and screening. Nevertheless, black coal can usually get washed in order to remove other material, something that improves its quality and limits ash content.

TABLE 1 : Coal classification terminology in Australia and Europe (Geoscience Australia).

Coal Rank	Australian Terminology	European Terminology
<b>Lignite</b>	Brown Coal	Brown Coal
<b>Sub-Bituminous Coal</b>	Black Coal	Brown Coal
<b>Bituminous Coal</b>	Black Coal	Black Coal
<b>Anthracite</b>	Black Coal	Black Coal

Black coal reserves can be found in New South Wales, South Australia, Western Australia, Queensland and Tasmania. New South Wales and Queensland have the biggest amount of Australia's total identified in situ resources, 23 and 63 percent respectively. These two states are also the largest coal producers. More specifically, the basins in which we find the greatest quantities of black coal are the Bowen Basin in Queensland and the Sydney Basin in New South Wales. The age of black coal resources in Australia ranges from Permian to Jurassic; however, the majority of them have their origins in Permian.

Brown coal resources can be found in South Australia, Victoria, Western Australia, Tasmania and Queensland. More specifically, brown coal occurs in the Otway Basin in Victoria, the Murray Basin in Victoria and South Australia, the North St Vincent's Basin in South Australia and finally the Eucla Basin in Western Australia. It is worth mentioning that in Gippsland in Victoria, we can find a coal deposit that reaches 330 m of thickness.



PICTURE 3.7: Brown and Black coal resources, coal basins and operating mines in Australia, as in December 2012 (Geoscience Australia).

## 4. ORGANIC GEOCHEMICAL ANALYSIS

Our samples come from Northern Sydney Basin, Southeast Australia, as it was mentioned before. They were sent from Dr. Maravelis Angelos and they were analyzed in the Laboratory of PVT and Core Analysis, located in the School of Mineral Resources, in the Technical University of Crete. The samples analysis was based on a standard analytical protocol for geochemical characterization of source rocks and oil reservoirs. The experimental procedure included Rock-Eval Analysis, Extraction by Soxhlet method, Asphaltene Removal, Column Chromatography method, as well as Gas Chromatography- Mass Spectroscopy method (GCMS).

### 4.1 SAMPLES PREPARATION

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The first step is to take a look at the samples and try to figure out their macroscopic features. Next, we can count them, record them and take some pictures. In order for our samples to follow the experimental procedure, a representative part of each sample is selected to be crushed and screened. The quantity we need is 50-100 gr and the final grain size is up to 250  $\mu\text{m}$ . Then, the samples stay in an oven at around 70°C and for about 24 hours, so as to remove any moisture present in the sample. Lastly, the samples are kept in airtight containers, in a dry environment until they are analyzed.

### 4.2 ROCK-EVAL ANALYSIS

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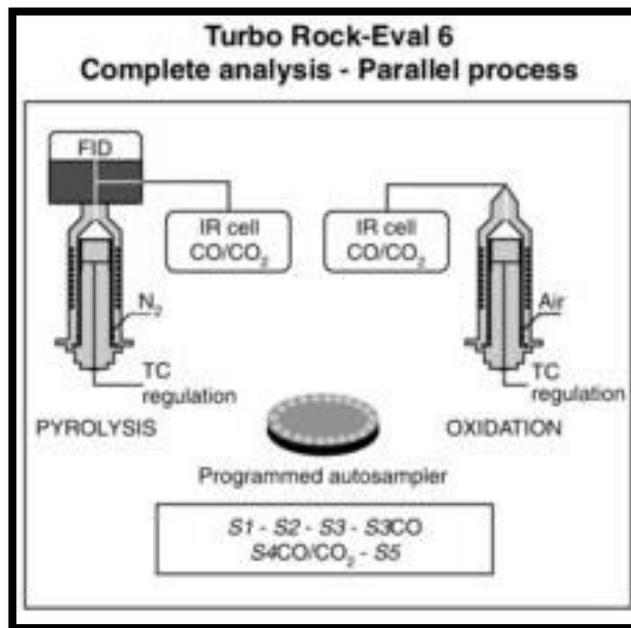
The Rock-Eval pyrolysis method is used in geochemical studies to detect oil shows that may occur, evaluate the petroleum potential, define the kerogen type and lastly characterize the maturity level of the organic matter. This technique was introduced by the French Institute of Petroleum (IFP) in the 70's and the Rock-Eval 6 apparatus is the latest version of the homonymous product line, commercialized since 1996 by Vinci Technologies.



PICTURE 4.1: Rock-Eval Analysis apparatus (Laboratory of PVT and Core Analysis, Technical University of Crete).

This method uses temperature programmed pyrolysis of organic matter, in an inert atmosphere (usually helium). We use about 100 mg ground rock sample and in the end we manage to determine the quantity of free hydrocarbons present in the sample and the hydrocarbons that could be potentially released after maturation, as well as the total organic carbon (TOC).

The experimental procedure is briefly described below: The released hydrocarbons are monitored by a flame ionization detector, called FID. As a result, we have the formation of S1 peak, which represents the thermovaporized free hydrocarbons, and S2 peak that displays the pyrolysis products from cracking of organic matter. Subsequently, we have the combustion (oxidation) of the residual rock recovered after pyrolysis up to 850°C, under artificial air. The CO and CO<sub>2</sub> that are released during pyrolysis and combustion are monitored by means of an infra-red cell. This complementary data acquisition allows the determination of the organic carbon content (TOC) and the mineral carbon content (MinC) (Behar et al., 2001).



PICTURE 4.2: Presentation of Rock-Eval 6 apparatus (Behar et al., 2001).

The parameters measured from Rock-Eval Analysis are the following:

- **S1:** It is the amount of free hydrocarbons in gas and oil, volatile in 300°C. It is calculated from the area of S1 peak.
- **S2:** It is the amount of hydrocarbons released during thermal cracking of the nonvolatile organic matter, in about 600°C. S2 parameter is calculated from the area of S2 peak and it gives us information about the quantity of hydrocarbons that the source rock could potentially produce.

- **S3**: It is the amount of the organic CO<sub>2</sub> released during the pyrolysis of kerogen. S3 is calculated from the area of S3 peak and it provides us with information about the oxygen content of our sample.
- **Tmax**: It is the temperature at which we have the maximum release of hydrocarbons from the thermal cracking of kerogen, during pyrolysis. Tmax corresponds to the highest point of S2 peak and it is an indication for the thermal maturation of the organic matter of our sample.
- **TOC**: It is the total organic carbon (wt%-weight percent) and it can be defined as the sum of the residual organic carbon and the pyrolyzed organic carbon. TOC can be determined by oxidizing the organic matter left in the sample after pyrolysis. It is calculated by the following equation:

$$\text{TOC: } 0.82 * (\text{S1} + \text{S2})/10 + \text{S4}/10.$$

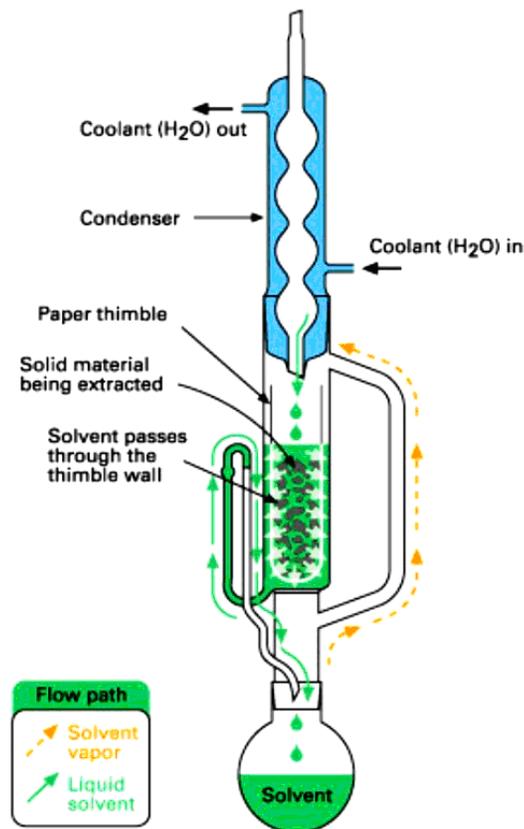
Based on the parameters measured from Rock-Eval Analysis, a series of geochemical indices can be calculated. They are presented below:

- **Production or Productivity Index (PI)**: It is defined by the ratio of S1 parameter to the sum of S1 and S2 parameters  $[S1 / (S1+S2)]$ . PI expresses the evolution level of the organic matter and it characterizes the amount of hydrocarbons, already produced in the analyzed sample, compared with the maximum amount that could be produced. Lastly, PI characterizes the maturity level of our samples.
- **Petroleum Potential or Pyrolyzed Carbon (PC)**: It expresses the total amount of hydrocarbons that a specific source rock could produce, under the appropriate temperature and for enough time. It is defined as  $[0.82*(S1+S2)/10]$  and it is an indication of the type of organic matter.
- **Hydrogen Index (HI)**: It is defined as  $[(100*S2)/\text{TOC}]$  and it is used to typify the origin of the organic matter. HI varies in geological samples, with values from about 100-600. Moreover, we have noticed that marine organisms and algae exhibit higher H/C ratios than land plants.
- **Oxygen Index (OI)**: It is defined as  $[(100*S3)/\text{TOC}]$  and it is related to the O/C ratio. OI values range from about 0 to 150.
- **S2/S3**: It expresses the quantity of hydrocarbons that can be produced from the organic matter the sample contains, to the quantity of the CO<sub>2</sub> produced. This index is used to define the kerogen type; values of this ratio ranging between 0 and 2.5 display type III kerogen and gas production,  $2.5 < S2/S3 < 5$  values exhibit type III kerogen and oil and gas pro-

duction, while  $5 < S_2/S_3 < 10$  show type I and II kerogen, and oil production. However, this index should be used with caution, because it can be affected by the inorganic content of the sample and increase significantly the  $S_3$  values (Pasadakis, 2015).

#### 4.3 EXTRACTION BY SOXHLET METHOD

In this method, rock samples are extracted in a Soxhlet apparatus, with the help of solvents, in order to separate bitumen from the inorganic components. This technique is based on the separation of bitumen, through the sample's rinsing by a pure and heated solvent that keeps making circles in the soxhlet. The solvent stays in motion by successive evaporations and condensations.



PICTURE 4.3: Schematic representation of the Extraction by Soxhlet method.

The procedure of the Extraction is described below: in the beginning we weight out powdered rock sample, 20-100 gr, according to its TOC value, and we place it in a thimble, along with some baked glass wool on top of the sample. Then, we place the thimble in the soxhlet, using long tweezers. After that, we put copper strip and some boiling balls (usually 6) in a spherical flask of 500ml size. The copper strip is used to bind the elemental Sulphur present in the sample and the boiling balls are used in order to succeed an even boiling. In the flask, we add the solvents too; in this case we use a mixture of Dichloromethane (DCM-  $\text{CH}_2\text{Cl}_2$ ) and Methanol ( $\text{CH}_3\text{OH}$ ), in a volume ratio of 9:1. Afterwards we connect the Soxhlet apparatus, we turn on the heating element located below the flask and lastly we start the water circulation for the condensers, which is above the soxhlet

tube. We run this procedure for about 24 hours; before we stop it, we need to make sure that the solvent in the tube is clear. Next, we evaporate the solvents of our extract, using a rotary evaporator, we transfer it in a smaller volumetric flask and leave it in the desiccator for about 24 hours. In this way we can calculate the concentration of bitumen (in ppm) (selected methods of the organic geochemistry laboratory).

#### 4.4 ASPHALTENE REMOVAL METHOD

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Asphaltene removal or deasphaltation is the procedure of abstraction of the asphaltenes from the bitumen. Asphaltenes are the heaviest and most polar fraction of petroleum, insoluble in light normal alkanes, but soluble in light aromatic hydrocarbons. Asphaltenes are consisted of aromatic rings, cyclic naphthenes and they contain nitrogen and Sulphur compounds. The asphaltene fraction removal is accomplished with dissolution of the extract in pentane. After this procedure we end up with two fractions, maltenes which are soluble in pentane and asphaltenes.

The experimental procedure goes as follows: We place our extract in a vial of known weight and we add 0.5 ml of pentane. Next, we mix these components with a vortex mixer for about 1-2 minutes. When the sample is homogeneous, we push it through a 0.45 micron Teflon filter cartridge, which is attached to a 10 ml Luer-lock glass syringe. In this way, we collect the maltene filtrate in a clean vial that we have previously weighted. We perform up to 3 rinses with 1 ml of pentane each, to transfer any sample left through the filter system. The asphaltenes, which are left in the filter, can be removed by rinsing the cartridge with chloroform (CHCl<sub>3</sub>) and subsequently collect them in a new vial. Lastly, we can remove the solvents of the asphaltene and the maltene vial, by nitrogen stream.

#### 4.5 COLUMN CHROMATOGRAPHY METHOD

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In this method, the maltene fraction we collected after the deasphaltation, is separated again in three fractions; the saturate fraction, the aromatic hydrocarbon fraction and the fraction of hetero-compounds (resins- NSO). This technique is based on elution solvents of increasing polarity that constitute the mobile phase and a silica/alumina column that constitute the stationary phase. The classification of petroleum samples comes from their ability to be dissolved by certain solvents. This method is also known as SARA, from the first letters of Saturates, Aromatics, Resins and Asphaltenes.



PICTURE 4.4: Column Chromatography method (Laboratory of PVT and Core Analysis).

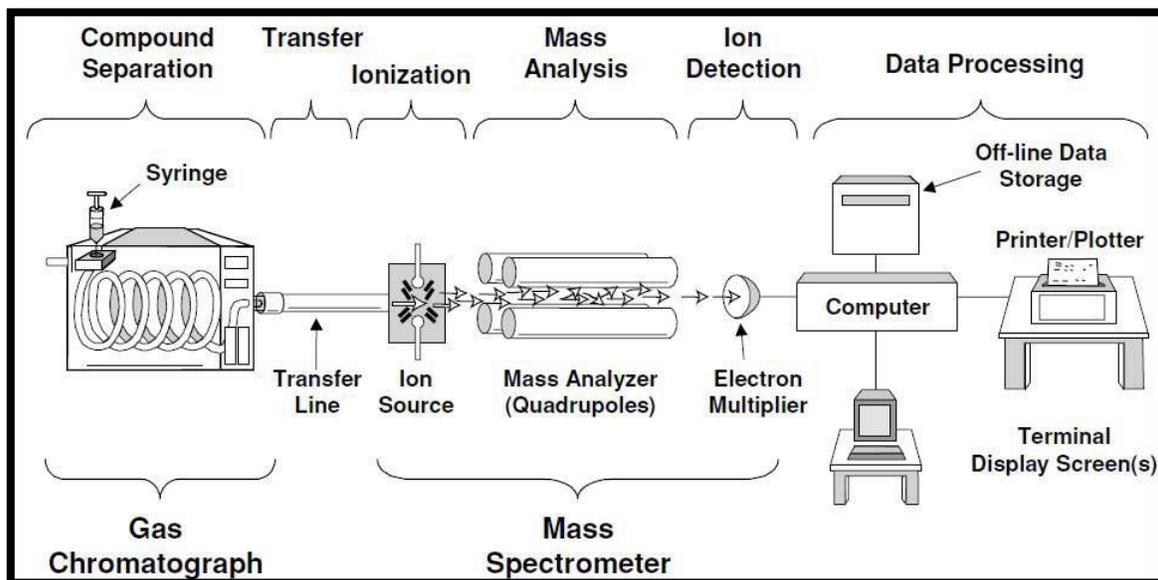
The experimental procedure is the following: We place a small quantity of glass wool and a small cut piece of a GF/A filter paper into the tip of a 5 ml column and then we pack it with silica gel and alumina slurry in a volume ratio 5:1. At that point, our sample of maltenes is dissolved in 0.5 ml pentane and loaded onto the column. When the sample reaches down the column, we elute with 7 ml pentane and we collect the saturate fraction. Subsequently, we gradually elute with 7 ml of aromatic hydrocarbon, usually toluene, while we continue collecting saturates. As soon as the aromatic front is almost at the bottom of the column, we change the vial and we start collecting the aromatic fraction. Afterwards, we elute with the last solvent, the most polar one, which is a mixture of toluene and methanol in 60:40 ratio. When the heterocompound front is reaching the bottom of the column, we change again vial and start collecting the NSO fraction. The three fractions we have collected are drained in nitrogen stream and then we leave them in the desiccator.

#### 4.6 GAS CHROMATOGRAPHY-MASS SPECTROMETRY

GC/MS is the primary method used for biomarkers evaluation, as well as quantitative and qualitative identification of the components in an oil sample. A typical GCMS system can perform the following functions:

- Compound separation by gas chromatography
- Transfer of the separated compounds to the ionizing chamber of mass spectrometer
- Ionization

- Mass analysis
- Detection of the ions by the electron multiplier
- Acquisition, processing and display of the data by computer (Peters et al., 2005).



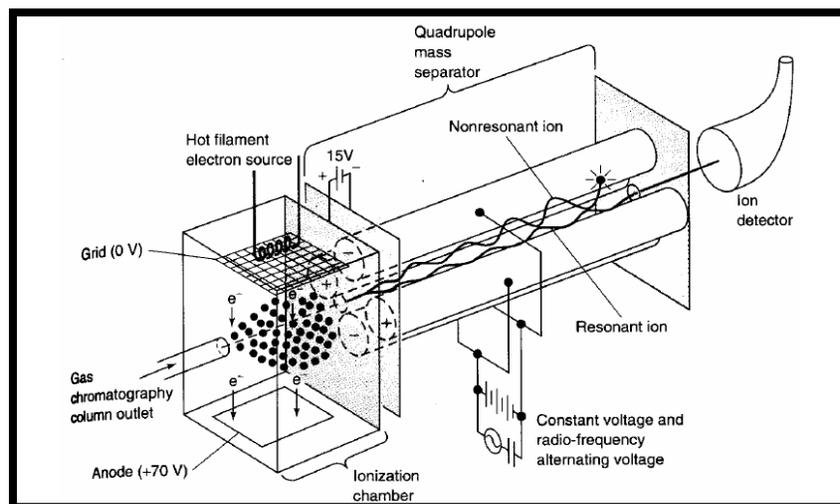
PICTURE 4.5: Schematic representation of GC/MS (Peters et al., 2005).

GC is composed of a light carrier gas that constitutes the mobile phase, and a liquid of high boiling point, in the form of a thin membrane, which constitutes the stationary phase and it is located on the internal surface of the column. We can use porous solid materials as stationary phase, while as a mobile phase we usually use helium (He). The oil sample is either inserted as a liquid, evaporates instantly and mixes with inert carrier gas the in the injector, or it is inserted directly on the column (on-column-injection). The amount of the sample injected should be quite small (some  $\mu\text{g}$ ) in order to avoid overloading of the column. As such, we usually insert our sample with split-splitless injection, where the sample is mixed with the carrier gas and only a small part of it enters the column. Then, it moves through the column, which can be capillary, or packed.

The components of the vaporized sample are separated as a result of the partitioning between the two phases mentioned above. The separation is based on the volatility of compound, which means that the lowest boiling point the compound has, the fastest it will travel through the column. In addition, the separation is based on partition and surface adsorption type interactions. The chromatographic column is placed in a temperature-programmed oven that controls the temperature and increases it gradually. Heavy compounds are analyzed in high temperatures, while light compounds with high volatility are analyzed in low temperatures. Thus, the column preserves the capability of high separation for all the compounds present in the sample. At the end of the chromatographic column we find a Flame Ionization Detector (FID), which detects the compounds coming out of the column, and records a signal, based on the compounds' concentration. Each peak

represents a specific compound and the sum of the peaks displays the gas chromatogram of the sample. The quantitative determination of the compounds of each sample is accomplished by calculating the area of each peak. In this way we can calculate the geochemical biomarkers (Pasadakis, 2004; Pasadakis, 2015; Peters et al., 2005).

After the separated compounds exit the chromatographic column, they are analyzed by the Mass Spectrometer. In fact, they pass directly to the ionization chamber (source) of the mass spectrometer, where they are ionized by an electron beam. More specifically, every molecule that elutes from the gas chromatograph can form molecular ions. Each molecular ion, when hit with electrons in the ionizing chamber, it can go through fragmentation or rearrangement. These fragment ions are accelerated by a high differential voltage in vacuum conditions. Subsequently these ions get analyzed according to their mass/charge ratio, by means of a magnetic or quadrupole mass spectrometer. Then, an electron multiplier spots the positive ions and as a result, we have the formation of a fragmentation pattern, which is called mass spectrum and it is characteristic for every molecule (Peters et al., 2005).



PICTURE 4.6: Schematic representation of Mass Spectrometer.

In order to analyze the Geochemical Biomarkers of the saturate fraction, we use both the Gas Chromatography and the Mass Spectrometry. In this way we achieve a quantitative and a qualitative determination of our sample. The chromatography helps us separate the compounds of the sample and the spectrometry identifies each component.

Data acquisition in GC/MS analysis can be accomplished by Total Ion Current method (TIC) or by Selected Ion Monitoring method (SIM). The mass spectrum for each compound is characteristic for its identification. SIM method provides better analytical signal, due to more time given for the calculation of each ion. So, when we are interested in specific compound groups in Biomarker Analysis, we mostly use SIM method.

## 5. BIOMARKERS

According to Pasadakis (2015) biomarkers or fossil biomarkers are complex organic compounds detected in sediments, which have properties that can lead directly to a known biological precursor. The notion of biomarkers was used for the first time by Eglinton and Calvin, in 1967. Biomarkers consist mostly of carbon and hydrogen, but nitrogen and oxygen can also be found in these molecules. Their structure gives us information about the conditions of the deposition, alteration and preservation of the organic matter (Pasadakis, 2007).

Biomarkers can last till the beginning of metagenesis, as the high temperatures that occur during catagenesis are responsible for the pyrolysis of these molecules.

In Petroleum Geochemistry, Biomarkers help us identify the type of organic matter, characterize the depositional environment, define the maturity and the biodegradation level of organic matter and find possible paths of oil migration as well as other secondary processes. Moreover, the study of biomarkers gives us information about the correlation between different oils, as well as correlation between oils and their source rocks. In all cases it must be combined with the geological information about the specific area we are studying.

Nowadays, the analysis of Biomarkers has become essential in the exploration and exploitation of hydrocarbons. This analysis takes place in geochemical laboratories, with the use of Gas Chromatography- Mass Spectroscopy Analysis (GC-MS), or other techniques such as GC-MS/MS, Nuclear Magnetic Resonance spectroscopy (NMR), X-ray diffraction, etc. So far, we have studied almost all the compound groups in hydrocarbons in order to detect biomarkers. However, the ones with a special role are alkanes, acyclic isoprenoids, diterpanes, triterpanes and steranes (Pasadakis, 2015).

### 5.1 NORMAL ALKANES

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Normal Alkanes were the first compounds used as biomarkers, due to their analytical easiness with Gas Chromatography. If we take a closer look at the definition of biomarkers, we realize that Normal Alkanes should not be considered as one them. The reason is that they come from many different sources and they are created by many different processes. However, the information they can provide us about the origin of the organic matter, especially in the C15 – C35 range, is crucial, although it can be affected by thermal maturation and biodegradation processes. Thus, normal alkanes can be considered biomarkers. They are characterized by high concentrations in bitoumens and oil, because they came from lipids of terrestrial or marine organisms. These organisms built different molecules, composed of various carbon chains and number of unsaturated bonds, depending on the environment they live in. Hence, terrestrial plants need coating waxes, which are lipids in the form of solid waxes, in order to protect themselves against water evaporation, attacks from other organisms and mechanical stability. The lipids these organisms produce have carbon chains with range C25- C35. On the other hand, marine plants need lipids for thermal isolation, support in the water and nutrient storage. The lipids mentioned above have carbon chains up to C25. Therefore, a high concentration of n-alkanes in either of these two ranges, gives us some information about the type of the organic matter. Algae and bacteria produce lipids with long carbon chains, bigger than C25. The difference between them and higher plants is that bacteria display

smooth distribution of n- alkanes concentration of carbon atoms, while higher plants display high concentrations of odd-numbered carbon chains (mostly C27, C29, C31).

## 5.2 ISOPRENOIDS

Isoprenoids or terpenoids are chemical compounds formed by the oligomerization or polymerization of isoprene. Isoprenoids are created by many isoprene units, linked together, forming cyclic or acyclic structures. Isoprene or 2-methyl-1, 3-butadiene, is a very important compound group of biomarkers and it can be found in hydrocarbon molecules, alcohols and esters. Isoprenoids are composed and used by any living organism; they are very stable compounds due to the covalent bonds and thus, they can survive the processes of diagenesis.

### 5.2.1 Acyclic isoprenoids

Regular acyclic isoprenoids are acyclic hydrocarbon molecules, with branches of methyl in the fourth carbon atom. These compounds are formed when a head-to-tail connection takes place. Typical examples of this group are Farnesane (C15), Pristane (C19) and Phytane (C20). When there is a tail-to-tail or head-to-head connection, we have the formation of irregular isoprenoids, such as squalane (C30) and Lykopane (C40) or Diphytane respectively.

The most known acyclic isoprenoids are pristane and phytane. They come from the breakage of chlorophyll's molecules. Therefore, when phytol, which is a side chain of chlorophyll, is released from the molecule of chlorophyll via hydrolysis, it can either go under oxidation and produce pristane C19 or go under reduction and produce phytane C20. Consequently, the pristane/phytane (Pr/Ph) ratio provides us with information about the depositional environment. However, it is now considered a low specificity index, because the thermal maturity seems to affect this ratio.

## 5.3 HOPANES

Terpanes or cyclic terpenoids are saturated hydrocarbons which are formed during the chemical transformation of organic matter. Hopanes are a group of pentacyclic compounds that belong in the group of terpanes. More specifically, they are hydrocarbons with 27- 35 carbon atoms with a naphthenic structure, which consists of an hexacyclic and a pentacyclic ring. Hopanes can be found both in recent and older sediments, as well as in petroleum. The most common hopane series are 17 $\beta$  (H),21 $\beta$  (H)-hopane, 17 $\beta$  (H),21 $\alpha$  (H)-moretane and 17 $\alpha$  (H),21 $\beta$  (H)-hopane. The most known ones are norhopane (C29) and hopane (C30) (Pasadakis, 2015).

Hopanes are used as indices for the depositional environment, maturation and also in studies about oil and source rock correlations. This is due to the isomerization of hopanes in sediments. More specifically, with increasing temperature  $\beta\beta$  hopanes are turning into  $\alpha\beta$  and  $\beta\alpha$  configurations. Later on, when the temperature gets even higher,  $\beta\alpha$  hopanes (moretananes) are turning into  $\alpha\beta$  hopanes, which are more stable.

## 5.4 STERANES

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Steranes are hydrocarbons, coming from the reduction of sterols. These compounds cannot be detected in living organisms. Sterols can be found in all eukaryotic organisms, as well as in some prokaryotic ones. Sterols are part of the cellular membranes and are responsible for the mechanical properties of the cell and the control of their metabolism. During diagenesis sterols are turning into steranes, through some chemical or microbiotic procedures. Animals produce mainly cholesterol, higher plants produce sitosterol and fungi produce ergosterol. These characteristic sterols create steranes that can be detected in petroleum. Steranes have 26- 30 carbon atoms in sediments, but the most common ones are C27, C29 and C30; they appear in regular steranes structure or in diasteranes structure. Steranes are used as indices for the origin of organic matter, the thermal maturation, as well as in oil and source rock correlations.

## 5.5 GEOCHEMICAL EVALUATION OF OIL USING SATURATED BIOMARKERS

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### 5.5.1 n-Alkanes

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- Terrigenous to aquatic ratio (TAR)

It is used to confirm the origin of the organic matter, marine or terrestrial. TAR is calculated by the height or area of the chromatographic peaks, during Gas Chromatography.

$$\text{TAR: } (nC27 + nC29 + nC31) / (nC15 + nC17 + nC19)$$

High values of this ratio point at greater quantity of terrestrial organic matter. However, we should take into consideration, that TAR index is sensitive to thermal maturity and biodegradation processes.

- Carbon Preference Index (CPI, CPI (1))

It is the ratio of the concentration of odd- numbered n-alkanes to even-numbered n-alkanes. It was created by Bray and Evans in 1961, for the area C24- C34 of n-alkanes, but it can be used in other areas as well. The concentrations can be replaced with heights or areas of chromatographic peaks, coming from Gas Chromatography.

$$\text{CPI}_{C24-C34} : \left[ \frac{(C25+C27+C29+C31+C33)}{(C24+C26+C28+C30+C32)} + \frac{(C25+C27+C29+C31+C33)}{(C26+C28+C30+C32+C34)} \right] \times \frac{1}{2}$$

CPI is mainly used for maturity characterization. Values greater or less than unity display low maturity, while values approaching unity, show us increasing maturity (Hunt, 1995; Marzi et al, 1993). This ratio can also provide information about the depositional environment; high values of CPI display low maturity and land- plant input, while oils and source rocks with CPI close to unity may indicate a predominance of marine input and/or thermal maturation.

CPI (1) index gives us the same information as CPI index.

$$\text{CPI (1)} : \frac{(C_{23} + C_{25} + C_{27} + C_{29})}{[C_{22} + 2(C_{24} + C_{26} + C_{28}) + C_{30}]} \times 2$$

- Odd-to-Even Predominance (OEP)

This index was introduced by Scalan and Smith in 1970 and it is defined by the ratio of odd-numbered n-alkanes to even-numbered n-alkanes.

$$\text{OEP} : \left[ \frac{C_i + 6C_{i+2} + C_{i+4}}{4C_{i+1} + 4C_{i+3}} \right]^{(-1)^{i+1}}$$

where  $C_i$  is the concentration of the n-alkane with  $i$  carbon atoms.

In oxidizing environments, we often observe a carbon chain with even number of carbon atoms, and thus OEP ratio has values lower than 1. In reducing environments there is a predominance of odd carbon atoms; therefore, we find OEP values greater than unity.

Even-predominance carbon chains, with CPI or OEP values below 1.0, display sometimes low-maturity oils or bitumens from carbonate or hypersaline environments

OEP ratio provides similar information as CPI index. As a result, values significantly above (odd preference) or below (even preference) unity, show us low thermal maturity, while values close to unity suggest, thermal maturity (Pasadakis, 2015).

We should not forget that CPI and OEP indices can be highly influenced by biodegradation and thermal maturity processes. Therefore, we should use them with caution and take into consideration the environment as well as other factors.

### 5.5.2 Isoprenoids

- Pristane/Phytane ratio (Pr/Ph)

The pristane/phytane (Pr/Ph) ratio is one of the most commonly used correlation parameters which have been used as an indicator of depositional environment (Peters et al., 2005). It is believed to be sensitive to diagenetic conditions; Pr/Ph ratios substantially below unity could be taken as an indicator of petroleum origin and/or highly reducing depositional environments. Very high Pr/Ph ratios (more than 3) are associated with terrestrial sediments. Pr/Ph ratios ranging between 1 and 3 reflect oxidizing depositional environments (Hunt, 1996). According to Lijmbach (1975) low Pr/Ph values (<2) indicate aquatic depositional environments including marine, fresh and brackish water (reducing conditions), intermediate values (2–4) indicate fluviomarine and coastal swamp environments, whereas high values (up to 10) are related to peat swamp depositional environments (oxidizing conditions). The pristane/phytane (Pr/Ph) ratio is now accepted as a low specificity index for redox conditions in the source rock and an indicator of source organic matter.

- Pr/n-C17 and Ph/nC18 ratio

Waples (1985) stated that by increasing maturity, n-alkanes are generated faster than isoprenoids in contrast to biodegradation. Accordingly, isoprenoids/n-alkanes (Pr/n-C17 and Ph/n-C18) ratios provide valuable information on biodegradation, maturation and diagenetic conditions. The early effect of microbial degradation can be monitored by the ratios of biodegradable to the less degradable compounds. Isoprenoid hydrocarbons are generally more resistant to biodegradation than normal alkanes. Thus, the ratio of the pristane to its neighboring n-alkane C17 is provided as a rough indication to the relative state of biodegradation. This ratio decreases as weathering proceeds and maturity increases.

The Pr/n-C17 ratio is used as an indicator of thermal maturity and depositional environment. Values from 0.3-0.6 show us marine environment, while values greater than unity stand for terrestrial environment.

The Ph/nC18 ratio is used in the same way, as Pr/C17 ratio.

- C<sub>19</sub>/C<sub>31</sub> index

This index represents the ratio of light to heavier hydrocarbons and it is used to characterize the depositional environment. High values of C19/C31 ratio display marine environment, while low values come from waxy oils. Waxy oils are usually formed from terrestrial organic matter, related to lacustrine source rocks and coals (Peters, 2005).

- nC<sub>24</sub><sup>+</sup>/nC<sub>24</sub><sup>-</sup> index

It is the ratio of the heavy to light hydrocarbons, and the definition is as presented below:

$$\frac{nC_{24}^{+}}{nC_{24}^{-}} = \frac{C_{25} + C_{26} + C_{27} + C_{28} + C_{29} + C_{30} + C_{31} + C_{32} + C_{33} + C_{34}}{C_{17} + C_{18} + C_{19} + C_{20} + C_{21} + C_{22} + C_{23} + C_{24}}$$

This index is combined with the C19/C31 ratio to provide us information about the origin of organic matter (Moldowan, 2004).

- R<sub>22</sub> index (Hyper Salinity Environment)

This index shows us the predominance of the C22 compound.

$$R_{22} = \frac{2C_{22}}{C_{21} + C_{23}}$$

It is more suitable as an index, than the C21 and C23 odd-numbered n-alkanes, because the odd-numbered alkanes are fewer in number than the alkanes that come from terrestrial environments. According to Ten Haven (1985), values of R22 index, when greater than 1.5 suggest high salinity environments.

### 5.5.3 Hopanes

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- C29-norhopane/C30-hopane Index

This index gives us information about the type of source rock and the depositional environment. Values lower than unity suggest silicate source rocks, while greater values display carbonate rocks, rich in organic matter. When we are dealing with samples from similar depositional environments, this index increases with increasing maturity, as norhopane is more stable than hopane. Moreover, high values of this ratio could point to reducing depositional environment, as well as biodegradation processes (Pasadakis, 2015).

- Tricyclic/ Tetracyclic Terpanes Index

These indices provide us with information about the source rock, as well as the depositional environment of the organic matter.

### 5.5.4 Steranes

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- Diasteranes/Steranes Index

This ratio is used as an index to thermal maturity. However, it can be affected by the lithology and the reducing or oxidizing conditions (Pasadakis, 2015).

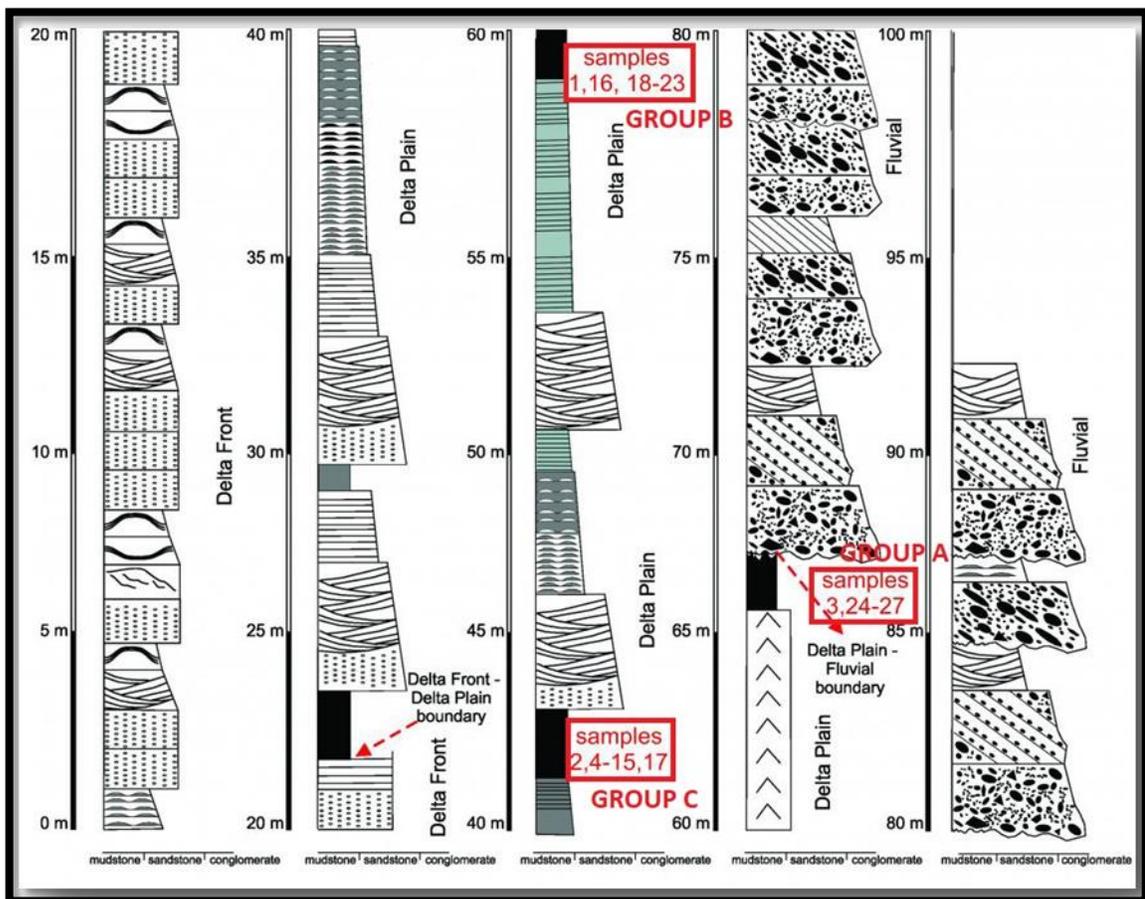
Diasteranes are found in small concentrations in oils and oil extracts of carbonate source rocks, while diasteranes in high concentrations suggest oils that come from clastic formations. Low values of diasteranes/steranes ratio indicate anoxic environment (Moldowan, 2004).

## 6. EXPERIMENTAL PROCEDURES

At first we received our samples, sent from the Petroleum Geologist Dr. Maravellis Angelos. The sampling, as it was said before, took place in Northern Sydney Basin, Southeast Australia, in the context of a research concerning the "Outcrop analysis and facies model of an Upper Permian tidally-influenced, fluvio-deltaic system". This research was carried out by Jake Breckenridge, Erin Holmes, Angelos G. Maravelis, William J. Collins, Octavian Catuneanu and Kevin Ruming.

### 6.1 SAMPLE PREPARATION

We had 27 samples, divided in three groups, depending on the depth they were taken from. Therefore, we set group A, which included samples 3, 24, 25, 26 and 27, from 32.5 m depth approximately. Group B consisted of samples 1, 16 and 18 to 23, from 40 m depth. Lastly group C contained samples 2, 4 to 15 and 17 and was taken from 57.5 m depth approximately.



PICTURE 6.1: Stratigraphic column with the samples position (Breckenridge et al., 2018).

All our 27 samples went through Rock- Eval Analysis. However, it could not be possible for the total of the samples to run the complete experimental procedure; the time and the cost would be more than we could afford. Thus, we chose 2 samples from each group, 6 samples in total. They

were the ones with the greater organic carbon amount. So, the samples that went through the whole process were NSB4, 8, 19, 20, 25 and 27. All of the experimental procedures are described below.

## 6.2 ROCK-EVAL ANALYSIS

Rock-Eval Analysis is the first stage to geochemical evaluation of our samples. As we said, this technique was applied to all our samples (27). Below we can see the results of Rock-Eval Analysis (Table 2) and the experimentally calculated value of Total Organic Carbon (TOC), as well as the indices that are calculated based on these results (Table 4). The evaluation of our results is based on Table 3 which provides us with information about the quality, quantity and thermal maturity of organic matter and rock samples.

TABLE 2: Classification of organic matter based on Quality, Quantity and Thermal Maturity (Peters & Cassa, 1994).

Potential (quantity)	TOC (wt.%)	Rock-Eval (mg/g rock)		Bitumen (ppm)	Hydrocarbons (ppm)
		S1	S2		
Poor	<0.5	<0.5	<2.5	<500	<300
Fair	0.5–1	0.5–1	2.5–5	500–1000	300–600
Good	1–2	1–2	5–10	1000–2000	600–1200
Very good	2–4	2–4	10–20	2000–4000	1200–2400
Excellent	>4	>4	>20	>4000	>2400

(a)

Kerogen (quality)	Hydrogen index (mg hydrocarbon/g TOC)	S2/S3	Atomic H/C	Main product at peak maturity
II	300–600	10–15	1.2–1.5	Oil
II/III	200–300	5–10	1.0–1.2	Oil/gas
III	50–200	1–5	0.7–1.0	Gas
IV	<50	<1	<0.7	None

(b)

Maturity	Maturation			Generation		
	R <sub>o</sub> (%)	T <sub>max</sub> (°C)	TAI	Bitumen/TOC*	Bitumen (mg/g rock)	Production index (S1/(S1+S2))
Immature	0.20–0.60	<435	1.5–2.6	<0.05	<50	<0.10
Mature						
Early	0.60–0.65	435–445	2.6–2.7	0.05–0.10	50–100	0.10–0.15
Peak	0.65–0.90	445–450	2.6–2.7	0.15–0.25	150–250	0.25–0.40
Late	0.90–1.35	450–470	2.9–3.3	–	–	>0.40
Postmature	>1.35	>470	>3.3	–	–	–

(c)

TABLE 3: Experimental results of Rock-Eval Analysis.

Sample	Tmax	S1	S2	S3	TOC
NSB 1	605,00	0,02	0,34	8,32	9,14
NSB 2	443,00	1,00	65,27	18,68	59,69
NSB 3	606,00	0,05	0,63	22,20	17,58
NSB 4	430,00	0,65	96,41	1,52	37,72
NSB 5	430,00	0,50	40,53	24,73	48,79
NSB 6	442,00	0,06	1,41	0,26	1,35
NSB 7	442,00	0,34	49,67	14,24	53,18
NSB 8	433,00	0,17	48,32	1,86	25,53
NSB 9	440,00	0,68	97,74	10,59	62,73
NSB 10	436,00	0,44	63,22	11,36	42,14
NSB 11	446,00	0,02	6,05	1,30	5,60
NSB 12	436,00	0,76	153,78	2,56	65,90
NSB 13	429,00	0,28	69,32	4,80	37,25
NSB 14	432,00	1,55	192,89	2,14	68,18
NSB 15	437,00	0,43	65,33	10,79	52,45
NSB 16	442,00	0,27	48,33	8,88	40,59
NSB 17	438,00	0,01	0,38	0,41	0,81
NSB 18	441,00	0,17	43,68	4,76	38,55
NSB 19	435,00	0,70	128,41	6,72	64,88
NSB 20	440,00	0,45	83,15	7,58	57,76
NSB 21	431,00	0,52	56,09	1,74	30,16
NSB 22	431,00	1,05	101,21	1,98	49,05
NSB 23	433,00	0,38	34,86	3,55	20,39
NSB 24	438,00	0,03	2,59	1,58	3,65
NSB 25	434,00	0,66	94,87	8,05	64,35
NSB 26	440,00	0,01	0,65	1,86	2,27
NSB 27	436,00	0,31	75,80	6,58	53,70

**S1 parameter:** It is the amount of free hydrocarbons (in gas and oil). If  $S1 > 1$  mg/g, it may be indicative of an oil show. S1 can be contaminated by drilling fluids and mud.

Looking at the values of our samples, there are two (2) of them (NSB14 and 22) with  $1 < S1 < 2$  mg/g so they have good potential of hydrocarbon production. Seven of our samples have  $0.5 < S1 < 1$  mg/g and as such they have fair potential of producing hydrocarbons and finally, the rest 18 samples have values from 0.01-0.50 mg/g, revealing poor hydrocarbon potential.

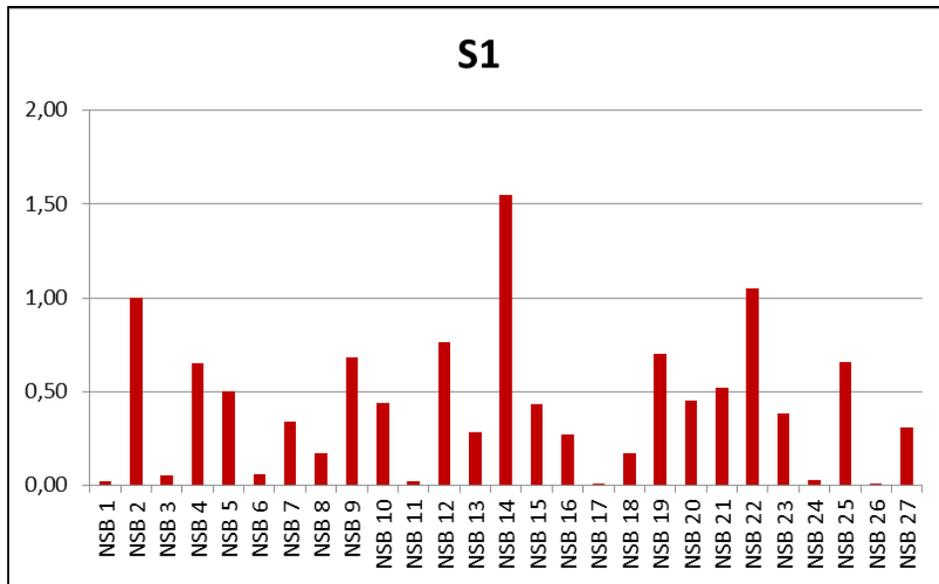


FIGURE 6.1: S1 values of our samples.

**S2 parameter:** It is an indication of the quantity of hydrocarbons the sediments could potentially produce should burial and maturation continue.

As we observe our samples, there are 5 of them with  $S2 < 2.5 \text{ mg/g}$ , representing poor hydrocarbon potential. We can find a sample with S2 value ranging from 2.5-5 mg/g and another one with value ranging from 5-10 mg/g, meaning fair and good hydrocarbon potential, respectively. The rest of our samples have S2 values greater than 20 mg/g, showing excellent potential of producing hydrocarbons.

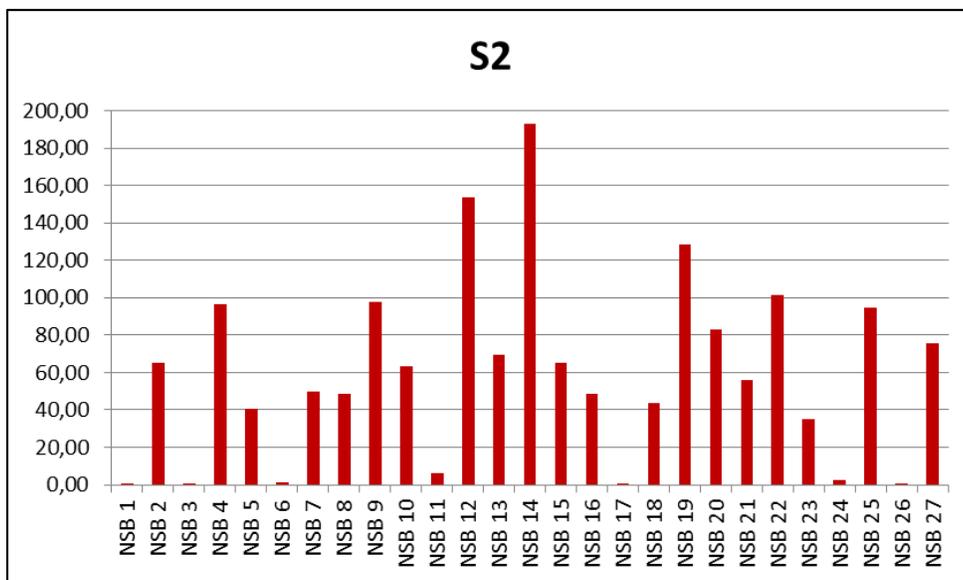


FIGURE 6.2: S2 values of our samples.

**S3 parameter:** It is the amount of CO<sub>2</sub> produced during pyrolysis of kerogen till 390 degrees Celsius. This temperature is of great importance, because above 390°C CO<sub>2</sub> is produced, coming from the breakdown of inorganic carbonate compounds. S3 is an indication of the amount of oxygen in the kerogen.

Here the S3 values of our samples range from 0.26 to 24.73 mg CO<sub>2</sub>/g rock.

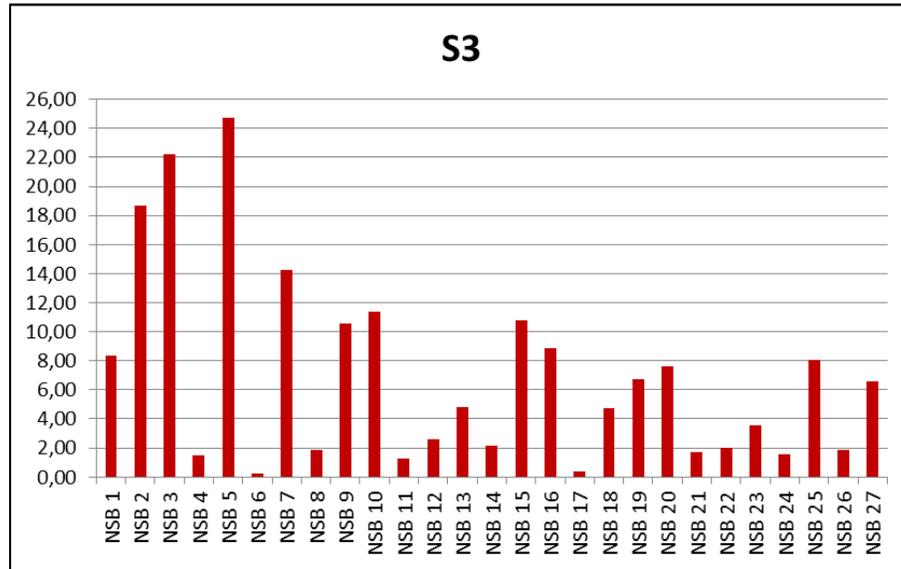


FIGURE 6.3: S3 values of our samples.

**Tmax parameter:** It is the temperature at which the maximum release of hydrocarbons from cracking of kerogen occurs during pyrolysis. Tmax is an indication of the stage of maturation of the organic matter.

Nine of our samples appear with Tmax < 435°C, therefore, they are characterized as thermally immature. Most of our samples, more specifically 16 of them, have Tmax values ranging from 435°-445°C, proving thermal maturity (early mature). Only two samples (NSB 1 and 3) appear to have Tmax > 470°C and that is the reason they are characterized as postmature.

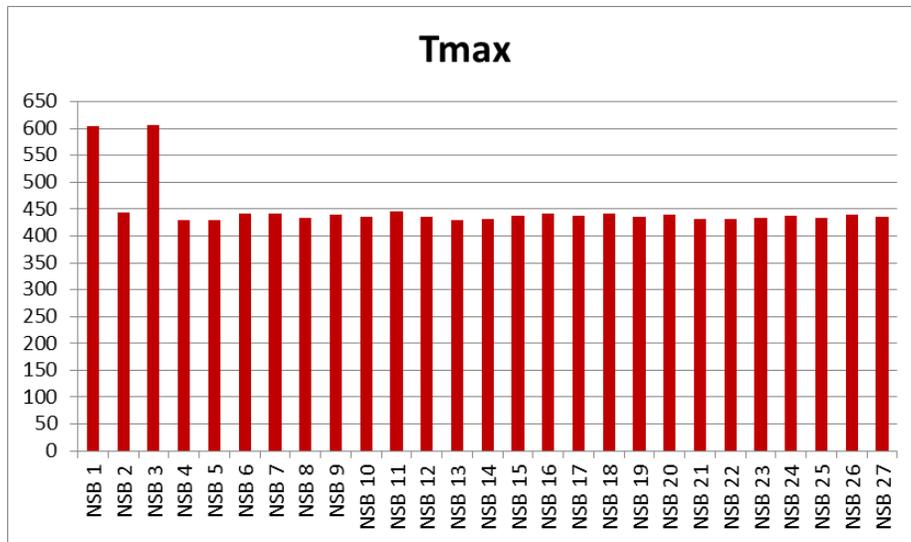


FIGURE 6.4: Tmax values of our samples.

**TOC parameter:** Looking at our samples, there is one with TOC value between 0.5 and 1% wt, showing fair hydrocarbon potential. There is another one with  $1 < TOC < 2$ , showing good hydrocarbon potential and two samples with very good potential, as they have TOC values between 2 and 4% wt. the rest of our samples have TOC values greater than 4% wt and therefore they can be characterized with excellent potential of producing hydrocarbons.

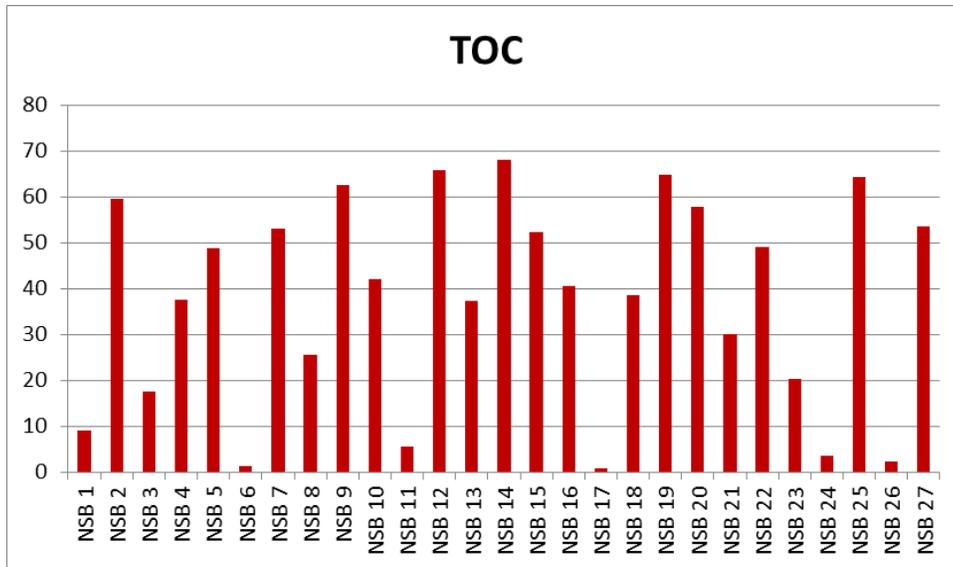


FIGURE 6.5: TOC values of our samples.

TABLE 4: Indices calculated from Rock-Eval Analysis.

Sample	HI	OI	PI	S1+S2	S2/S3
NSB 1	4	91	0,06	0,36	0,04
NSB 2	109	31	0,02	66,27	3,49
NSB 3	4	126	0,07	0,68	0,03
NSB 4	256	4	0,01	97,06	63,43
NSB 5	83	51	0,01	41,03	1,64
NSB 6	104	19	0,04	1,47	5,42
NSB 7	93	27	0,01	50,01	3,49
NSB 8	189	7	0	48,49	25,98
NSB 9	156	17	0,01	98,42	9,23
NSB 10	150	27	0,01	63,66	5,57
NSB 11	108	23	0	6,07	4,65
NSB 12	233	4	0	154,54	60,07
NSB 13	186	13	0	69,6	14,44
NSB 14	283	3	0,01	194,44	90,14
NSB 15	125	21	0,01	65,76	6,05
NSB 16	119	22	0,01	48,6	5,44
NSB 17	47	51	0,03	0,39	0,93
NSB 18	113	12	0	43,85	9,18
NSB 19	198	10	0,01	129,11	19,11
NSB 20	144	13	0,01	83,6	10,97
NSB 21	186	6	0,01	56,61	32,24
NSB 22	206	4	0,01	102,26	51,12
NSB 23	171	17	0,01	35,24	9,82
NSB 24	71	43	0,01	2,62	1,64
NSB 25	147	13	0,01	95,53	11,79
NSB 26	29	82	0,01	0,66	0,35
NSB 27	141	12	0	76,11	11,52

**Oxygen Index (OI):** Oxygen Index is related to the oxygen to carbon ratio (O/C). High values of this index represent very immature sediments and may be due to high concentration of humic acids. In mature sediments, high values are due to carbonate minerals (Katz, 1983).

In our samples, OI values range from 4 to 127 mg CO<sub>2</sub>/g TOC.

**Hydrogen Index (HI):** Hydrogen Index is associated to the hydrogen to carbon ratio and it is used to define the origin of the organic matter. In our samples, HI values range between 4 and 283. The

samples with HI values <50 mg HC/g TOC are NSB1, 2, 17 and 26 and exhibit kerogen type IV. The majority of the samples with values that range from 50 to 200 mg HC/g TOC (NSB2, 5, 6, 7, 8, 9, 10, 11, 13, 15, 16, 18, 19, 20, 21, 23, 24, 25 and 27) display kerogen type III. The remaining samples (NSB4, 12, 14 and 22) have HI values >200 mg HC/g TOC.

**S1-TOC plot:** It is used to distinguish the indigenous from the non-indigenous hydrocarbons, in order to find out whether our samples have been ‘contaminated’ or not, by migrated hydrocarbons (Hunt, 1996). Oil migration can be shown by high S1 values and low TOC values.

As we see in the S1-TOC plot below (Figure 6.6), all of our samples are within the borders of “Indigenous Hydrocarbons”. Therefore, the formation studied, from Northern Sydney Basin seems to produce hydrocarbons, without the contribution of oil that has migrated from other formations.

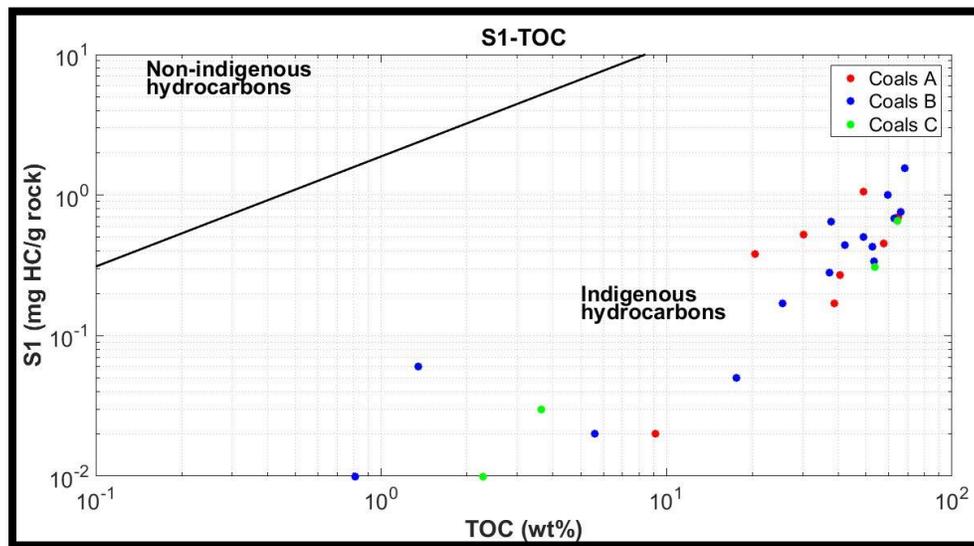


FIGURE 6.6: S1- TOC plot.

**S2-TOC plot:** It is widely used to characterize the type of source rock. Looking at our S2-TOC plot (Figure 6.7), the majority of NSB samples reveal a Gas Prone source rock, of type III kerogen. There are some samples showing a type II/III, Oil/Gas Prone source rock, while just a few samples display type IV, Dry Gas Prone source rock.

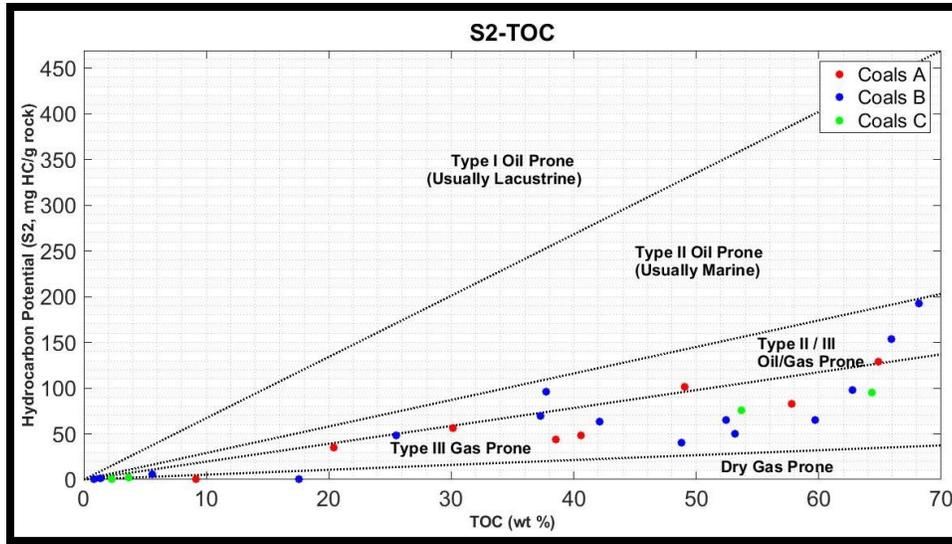


FIGURE 6.7: S2-TOC plot.

**(S1+S2)-TOC:** The S1+S2 sum is defined as the sum of free hydrocarbons, capable of pyrolysis and it expresses the total potential of hydrocarbons production (SP). Values  $SP < 2$  kg/t exhibit poor potential for oil production and gas production. SP values between 2 and 6 kg/t display fair source rocks and fair potential for oil production. Source rocks with good to excellent petroleum potential have SP values greater than 6kg/t (Tissot and Welte, 1984; Dymann et al., 1996).

In the S1+S2-TOC plot below (Figure 6.8), we can see that the majority of our samples have high values of both TOC and S1+S2. A few samples seem to have lower TOC and S1+S2 values and they characterize fair, good and excellent potential of hydrocarbon production.

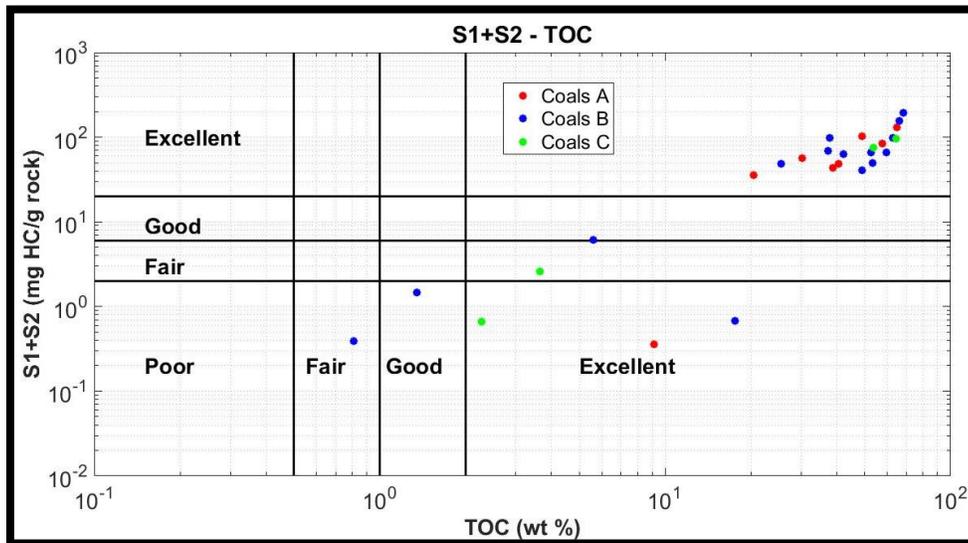


FIGURE 6.8: S1+S2-TOC plot.

**HI-TOC plot:** The HI-TOC plot (Figure 6.9) gives us additional information about the source rock type. In this plot below, the majority of our samples show that the formation they come from, is a gas source. Two of our samples show the probability of some oil production as well and finally one of the samples indicates a source that could produce adequate gas.

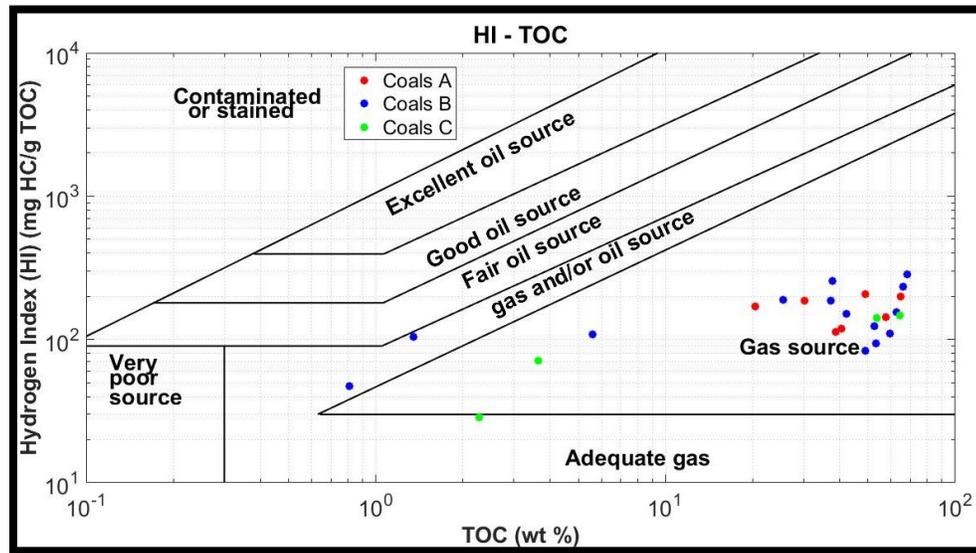


FIGURE 6.9: HI-TOC plot.

**HI-Tmax plot:** This plot helps us define the type of kerogen and the thermal maturity. In this specific plot we combine information given from Hydrogen Index (HI), the Tmax Temperature and the Vitrinite Reflectance (Ro). Tmax values indicate the level of organic matter's thermal maturity and thus, create in the plot below (Figure 6.10) three areas that divide the organic matter (OM) to immature, mature (Oil Window) and postmature (Condensate- Wet Gas Window). Our samples are gathered around the line that separates immature and mature OM, with Tmax values around 435°C (429-442°C) and HI values that range from 4 to 283 mg. The last index gives us information about the origin of OM; hydrogen to carbon ratio (H/C) appears to be higher in marine organisms and algae, than it is in land plants.

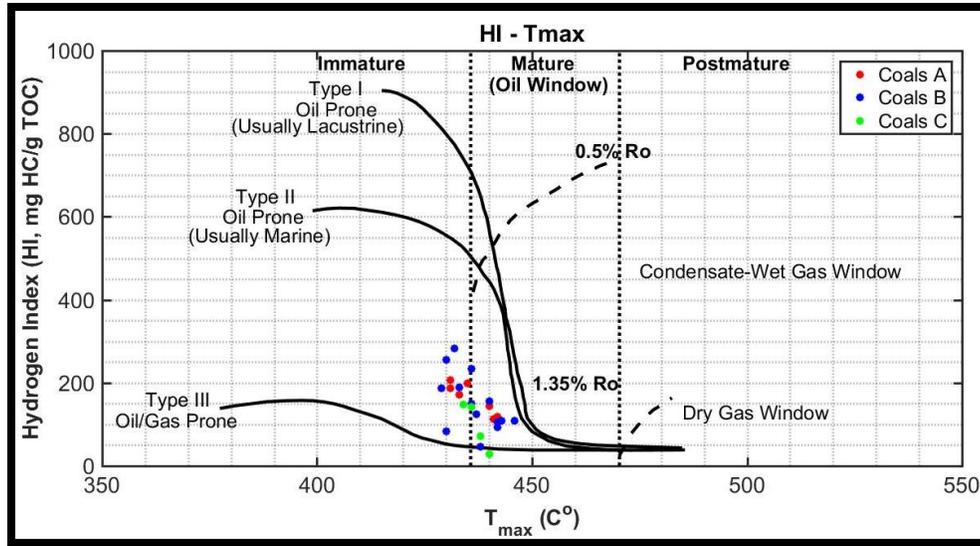


FIGURE 6.10: HI-Tmax plot.

**PI-Tmax plot:** Looking at the PI-Tmax plot below (Figure 6.11), we observe that all of our samples have quite low PI values, lower than 0.8.

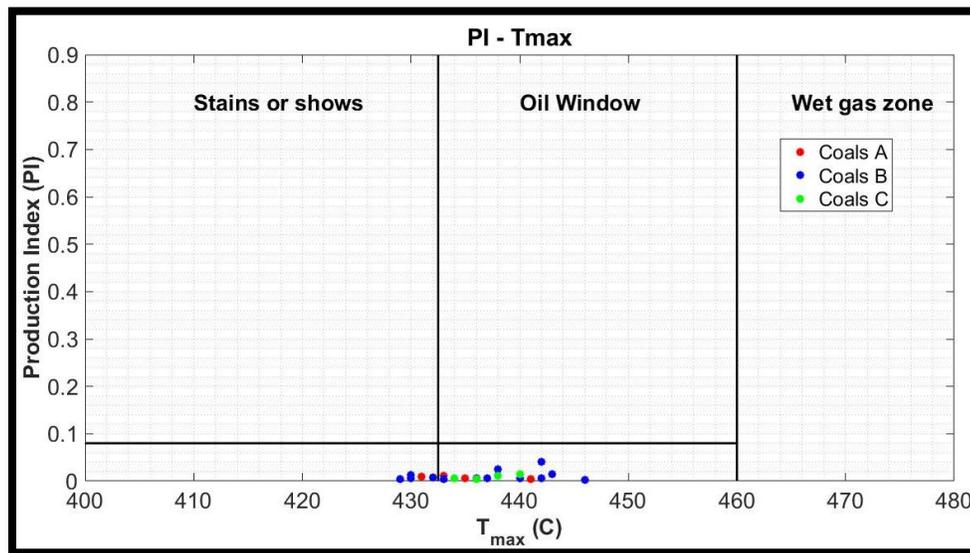


FIGURE 6.11: PI-Tmax plot.

**HI-OI (Van Krevelen) plot:** This plot uses the Oxygen and the Hydrogen Index, in order to help us categorize the organic matter into four types. From our plot in Figure 6.12, we find out that our samples are very dispersed, with HI values ranging from 4 to 283 and OI values ranging from 3 to 126.

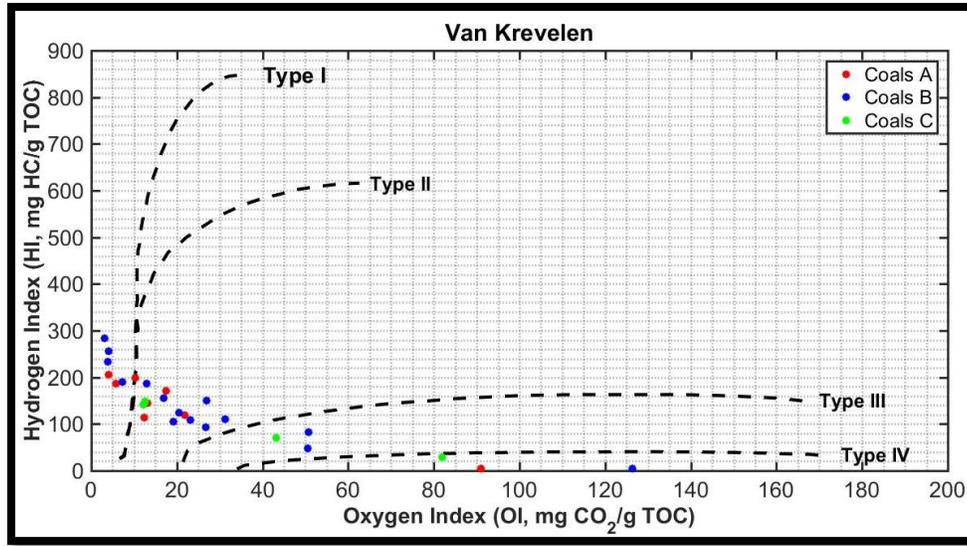


FIGURE 6.12: HI-OI (Van Krevelen) plot.

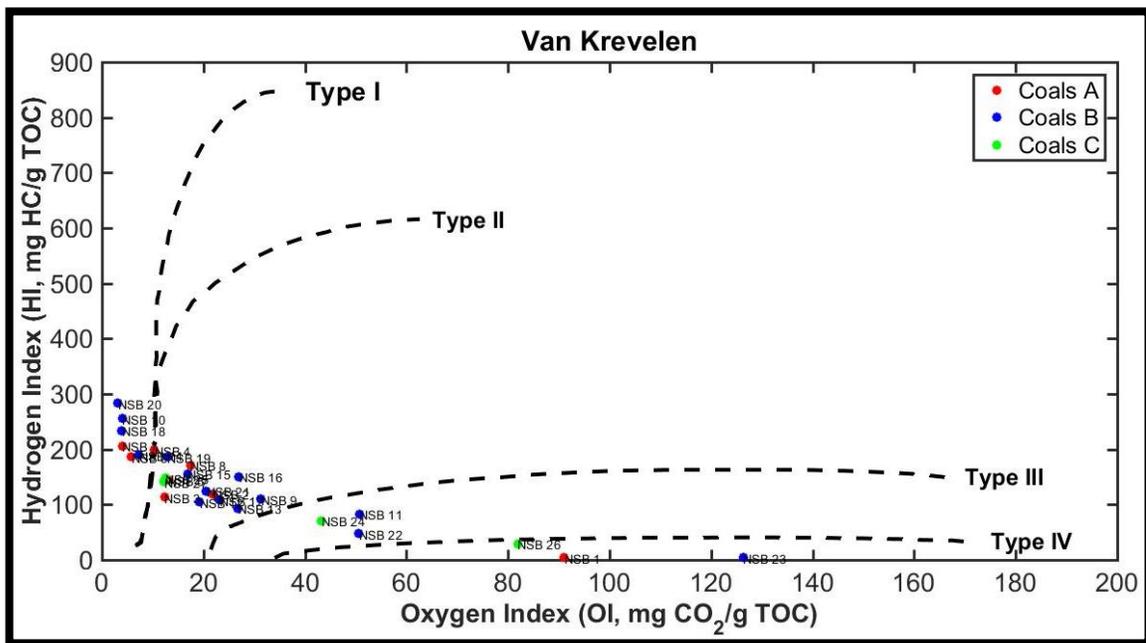


FIGURE 6.13: HI-OI (Van Krevelen) plot, showing the numbers of each sample.

### 6.3 EXTRACTION BY SOXHLET

In this stage, rock samples are extracted in a soxhlet apparatus, using a solvent mixture, in order to remove bitumens. As it has been mentioned before, the samples chosen to be extracted and run through all the experimental process were NSB4, 8, 19, 20, 25 and 27. Below we can see the table displaying the sediment’s mass, the extract’s mass and the extract in ppm (Table 5). We can also see in Figure 6.14 a chart with the extract of each sample in ppm.

TABLE 5: Results of Soxhlet Extraction.

Sample	Sediment (g)	Extract (g)	Extract (ppm)
NSB 19	39,9805	0,7084	17719
NSB 20	20,5437	0,4861	23662
NSB 4	41,0960	0,8659	21070
NSB 8	43,0657	0,3845	8928
NSB 25	20,0659	0,3371	16800
NSB 27	12,4858	0,2083	16683

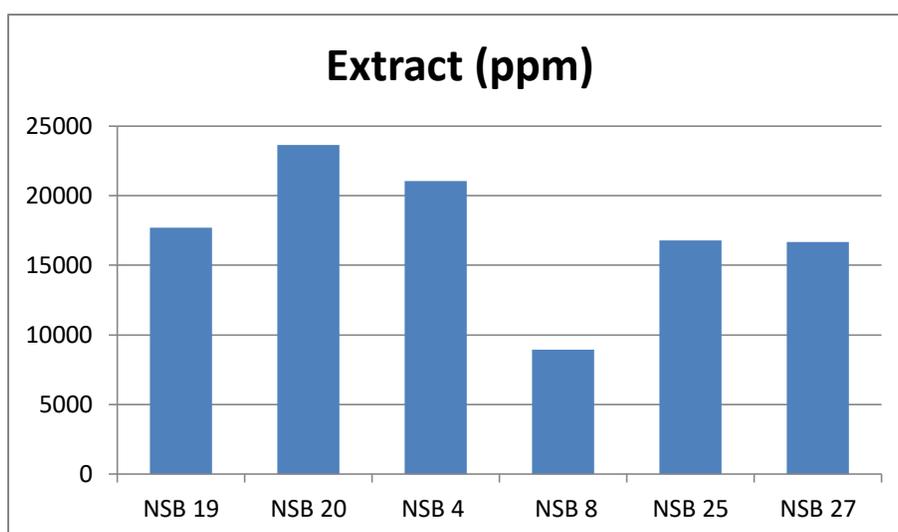


FIGURE 6.14: Chart of the extract concentration in ppm.

#### 6.4 ASPHALTENE REMOVAL FROM BITUMEN AND PETROLEUM

In this stage, the asphaltene fraction of an oil or bitumen is removed by precipitation, in a light hydrocarbon solvent such as pentane, followed by filtration. The results of deasphaltation are presented below, in Table 6 and Figure 6.15. The latter exhibits the percentages of asphaltenes and maltenes in each sample.

TABLE 6: Results of the Asphaltene Removal.

Sample	Sample (g)	maltenes (%)	asphaltenes (%)
NSB 19	0,0563	37,48	64,48
NSB 20	0,0528	12,69	88,26
NSB 4	0,0412	12,38	88,11
NSB 8	0,0446	30,94	66,37
NSB 25	0,0582	37,97	61,34
NSB 27	0,0545	19,82	83,30

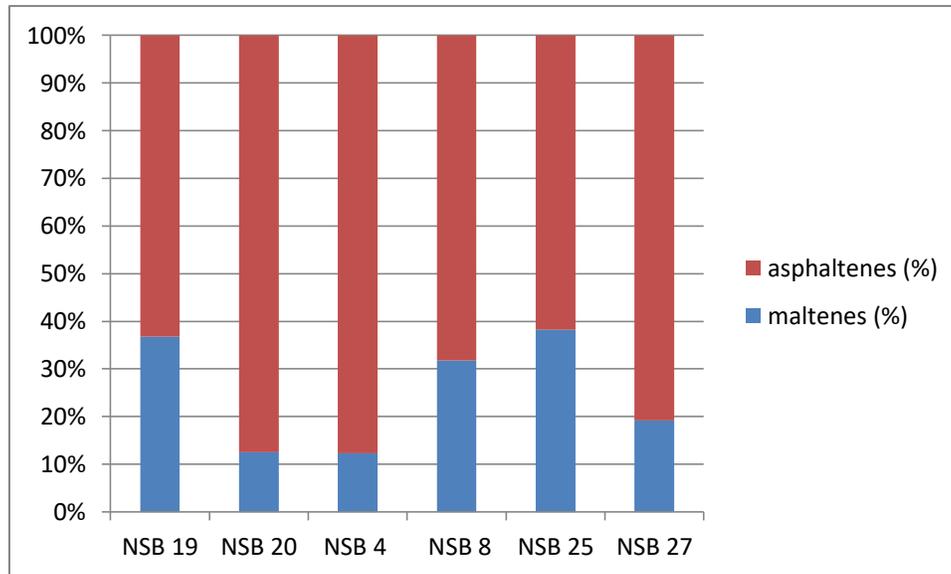


FIGURE 6.15: Chart of the asphaltenes and maltenes, after the deasphaltation.

## 6.5 COLUMN CHROMATOGRAPHY METHOD

In this experimental procedure, the deasphalted bitumens or oils are separated into saturate, aromatic and NSO fractions. For that purpose, we use a constructed alumina/silica column, as well as elution solvents of increasing polarity. The results are presented in the Table 7 and Figure 6.16 below.

TABLE 7: Results of Column Chromatography.

Sample	Sample (g)	Sat (g)	Arom (g)	NSO (g)	Sat (%)	Arom (%)	NSO (%)
NSB 19	0,0211	0,0031	0,0108	0,0072	14,69	51,18	34,12
NSB 20	0,0067	0,0008	0,0031	0,0026	12,31	47,69	40,00
NSB 4	0,0051	0,0006	0,0024	0,0016	13,04	52,17	34,78
NSB 8	0,0138	0,0021	0,0071	0,0051	14,69	49,65	35,66
NSB 25	0,0221	0,0030	0,0102	0,0069	14,93	50,75	34,33
NSB 27	0,0108	0,0005	0,0046	0,0037	5,68	52,27	42,05

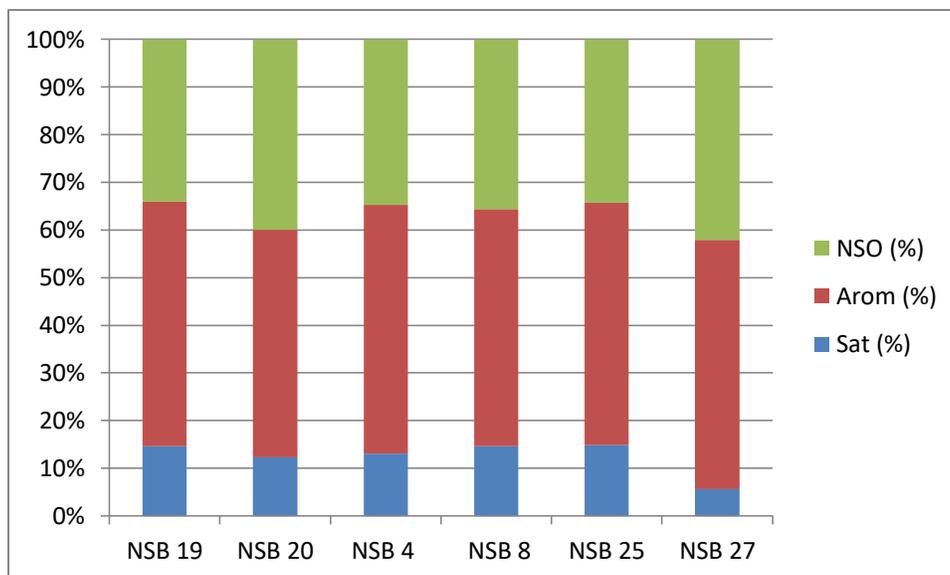


FIGURE 6.16: Chart of the fractions after Column Chromatography.

## 6.6 GAS CHROMATOGRAPHY- MASS SPECTROMETRY METHOD (GC-MS)

After Column Chromatography, the saturate and the aromatic fraction can be inserted in GC/MS, to be analyzed for biomarkers. In our case the saturate fraction was analyzed for alkanes, hopanes and steranes.

### 6.6.1 n-Alkanes

TABLE 8: Concentration (ppm) of n-alkanes of our samples.

Compounds	NSB4	NSB8	NSB19	NSB20	NSB25	NSB27
C10	0	0	0	0	0	0
C11	0	0	0	0	0	0
C12	0	0	0	0	0	0
C13	0	0	1	0	0	0
C14	0	5	11	0	0	1
C15	11	14	25	2	8	18
C16	39	23	40	31	37	56
C17	77	33	59	87	71	106
Pr	100	96	137	118	106	148
C18	105	40	71	139	92	142
Ph	16	17	20	26	18	26
C19	140	50	90	194	111	191
C20	172	51	107	235	128	233
C21	230	66	135	300	155	297
C22	234	72	141	292	166	312

C23	326	100	211	402	204	440
C24	164	75	112	195	158	222
C25	214	102	159	237	187	296
C26	73	50	58	88	84	117
C27	88	72	77	108	94	149
C28	42	31	42	43	61	80
C29	45	45	50	49	55	99
C30	16	13	15	15	22	28
C31	17	13	16	20	21	30
C32	9	6	7	7	11	12
C33	11	7	11	29	18	13
C34	9	5	9	14	11	8
C35	6	4	5	10	7	8

TABLE 9: Saturates Indices of n-alkanes of our samples.

Saturates indices	NSB4	NSB8	NSB19	NSB20	NSB25	NSB27
Pr/Ph	6,10	5,65	6,91	4,45	5,85	5,61
Pr/nC17	1,31	2,92	2,34	1,35	1,51	1,40
Ph/nC18	0,16	0,43	0,28	0,19	0,20	0,19
CPI	1,87	1,80	1,86	1,96	1,55	1,84
CPI (1)	1,67	1,60	1,71	1,66	1,36	1,67
OEP (1)	1,51	1,31	1,54	1,51	1,21	1,51
OEP (2)	0,75	0,67	0,72	0,75	0,58	0,69
OEP 27-31	1,62	1,99	1,71	1,81	1,33	1,79
nC24+/nC24-	0,36	0,71	0,48	0,33	0,52	0,43
TAR	0,66	1,35	0,83	0,62	0,89	0,88
nC19/nC31	8,07	3,71	5,45	9,87	5,26	6,39
R22	0,84	0,87	0,81	0,83	0,93	0,85

**Pristane/Phytane (Pr/Ph) ratio:** The ratios of our samples range from 4.45 to 6.91 (>3), which means we are dealing with terrestrial sediments. According to Lijmbach (1975) our samples are related to peat swamp depositional environments (oxidizing conditions). As far as the source rock, the high values of this ratio indicate coal-sourced oils; (3.0-10.0) (Hunt, 1995).

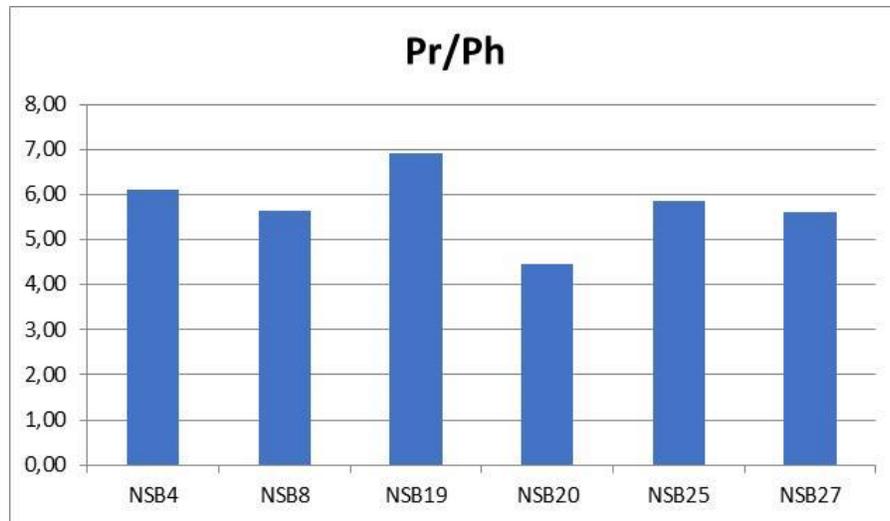


FIGURE 6.17: Pr/Ph plot of our samples.

**Pr/n-C17 and Ph/n-C18 ratios:** The Pr/n-C17 ratio is used as an indicator of thermal maturity and depositional environment. Values from 0.3-0.6 show us marine environment, while values greater than unity stand for terrestrial environment. In our samples this ratio ranges between 1.31 and 2.92 and that show us immature organic matter of terrestrial origin.

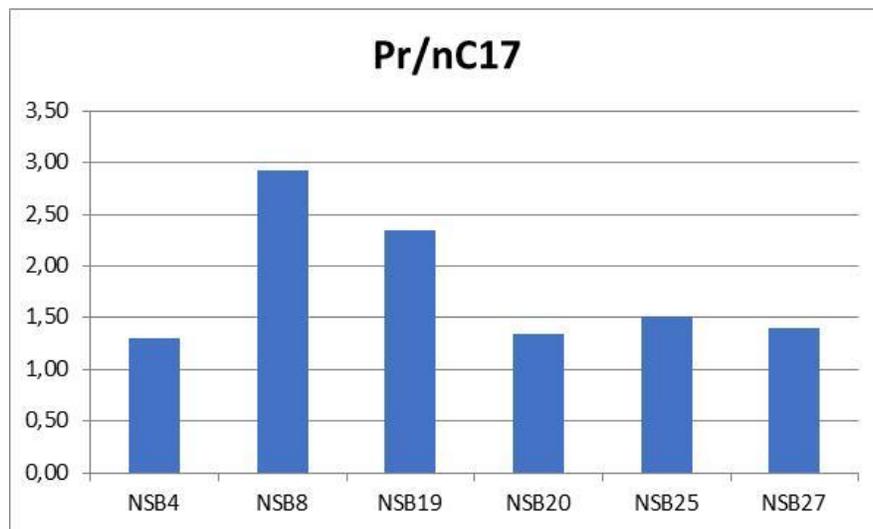


FIGURE 6.18: Pr/nC17 plot of our samples.

The Ph/nC18 ratio is used in the same way, as Pr/C17 ratio. Both ratios are used in the determination of depositional environment and thermal maturity.

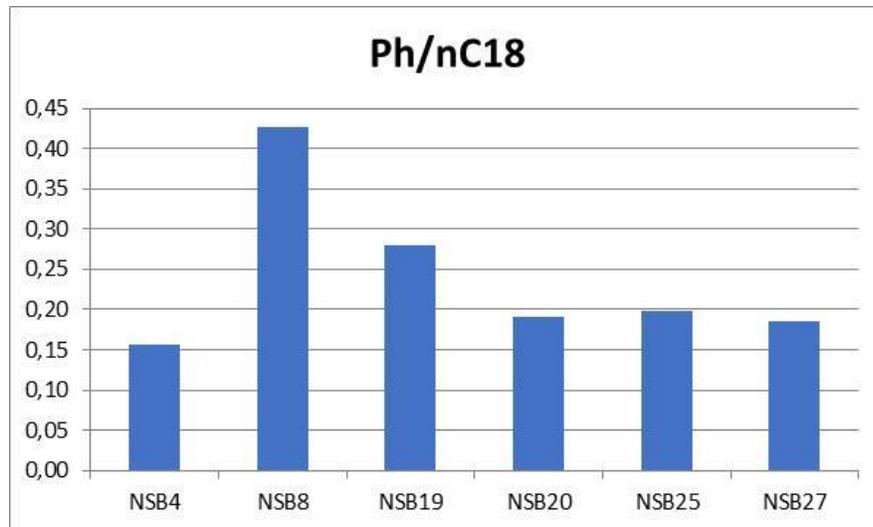


FIGURE 6.19: Ph/nC18 plot of our samples.

**R22 Index:** It is used to characterize the environment, based on the salinity levels. Values of this index, greater than 1.5 suggest hyper salinity environment. Here, all our samples have values lower than unity, ranging from 0.81 to 0.93. This tells us that we are dealing with a low salinity environment.

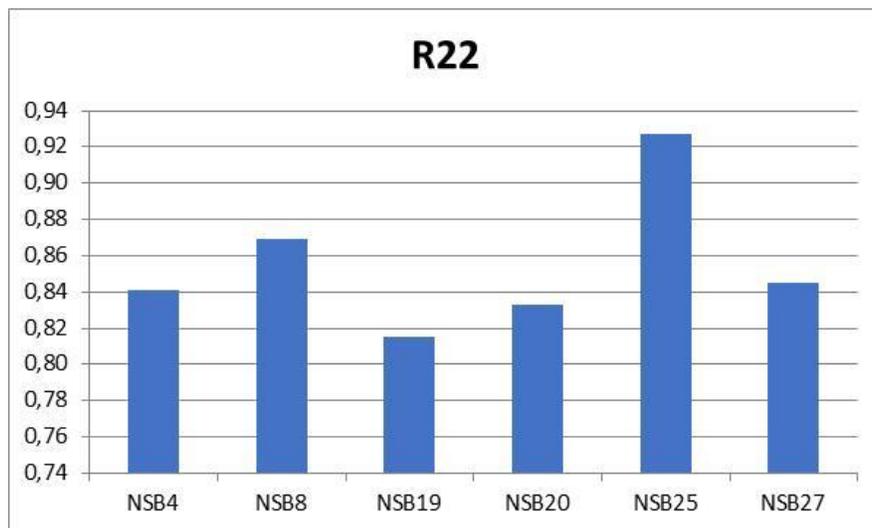


FIGURE 6.20: R22 plot of our samples.

**Carbon Preference Index [CPI, CPI (1)]:** In almost all our samples CPI and CPI (1) indices range between 1.5 and 2.0; only one sample (NSB 25) has CPI (1) value lower than 1.5 (1.36). This shows us origin from coastal sediments. Moreover, we observe that the values of the samples are greater than unity; something that displays low maturity sediments and maybe land plant input (Hunt, 1995; Marzi et al., 1993).

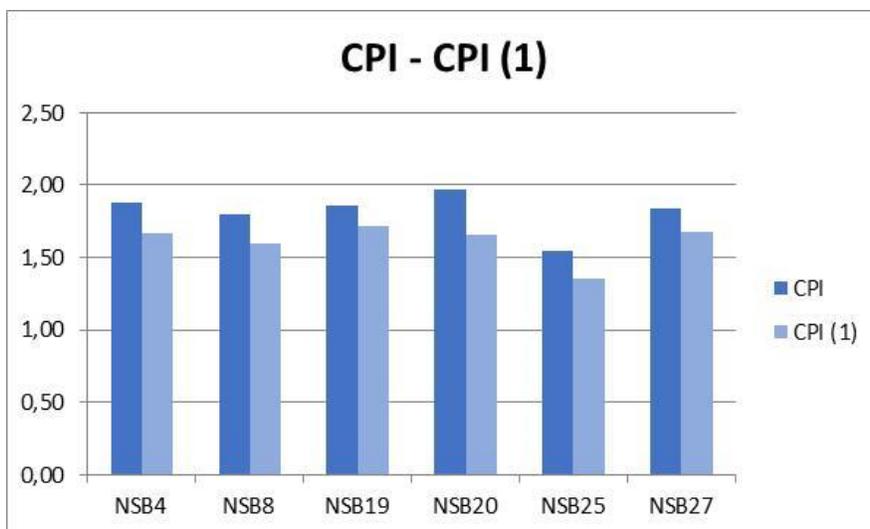


FIGURE 6.21: CPI-CPI (1) plot of our samples.

**nC24<sup>+</sup>/nC24<sup>-</sup> and nC19/nC31 Indices:** nC24<sup>+</sup>/nC24<sup>-</sup> index is the ratio of heavy to light hydrocarbons, while nC19/nC31 is the reverse one. If we take a closer look at the figures 6.22 and 6.23 below, we observe that the nC24<sup>+</sup>/nC24<sup>-</sup> values of all our samples are lower than unity, while the nC19/nC31 values are greater than unity in all the samples. As a result, the combination of these two indices, show clearly the predominance of the light hydrocarbons in our samples.

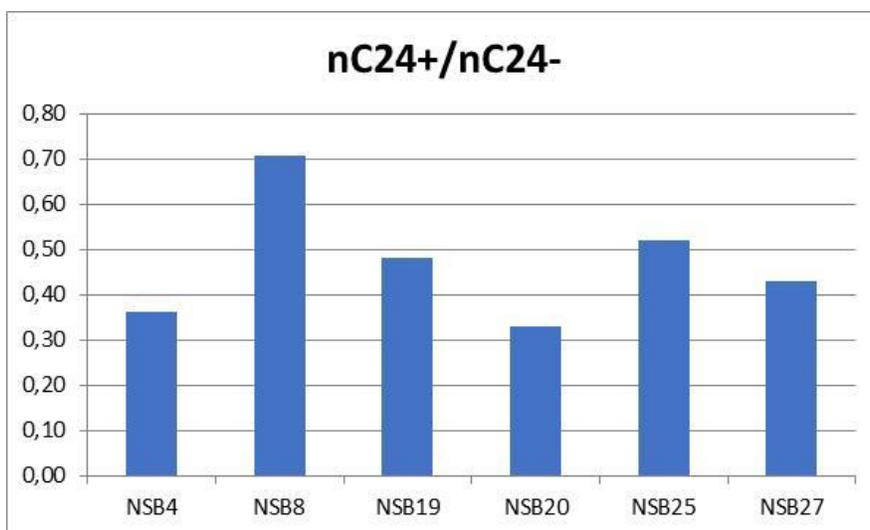


FIGURE 6.22: nC24<sup>+</sup>/nC24<sup>-</sup> plot of our samples.

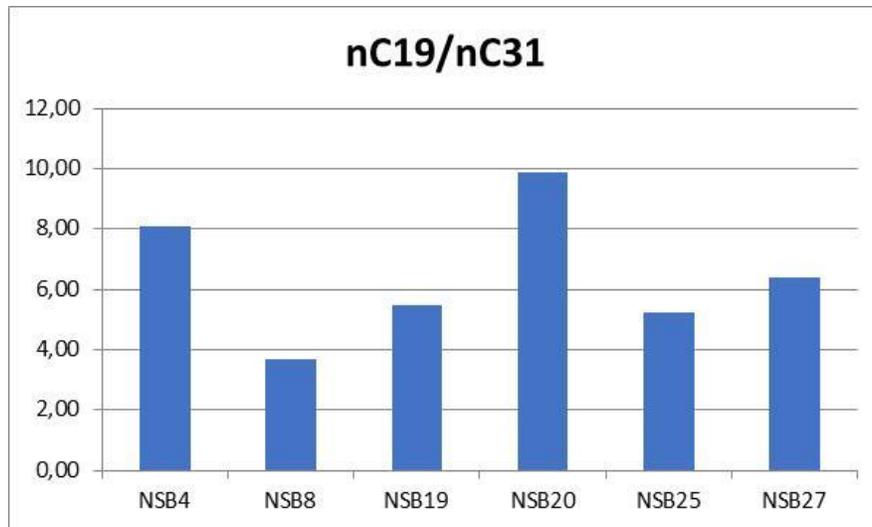


FIGURE 6.23: nC19/nC31 plot of our samples.

**TAR Index (Terrigenous to Aquatic Ratio):** This ratio is used to define whether the origin of the organic matter is terrestrial or marine. Here, as we see in Figure 6.24, all our samples except for one (NSB8) have TAR values below unity. Therefore, the organic matter of our samples has mostly aquatic origin.

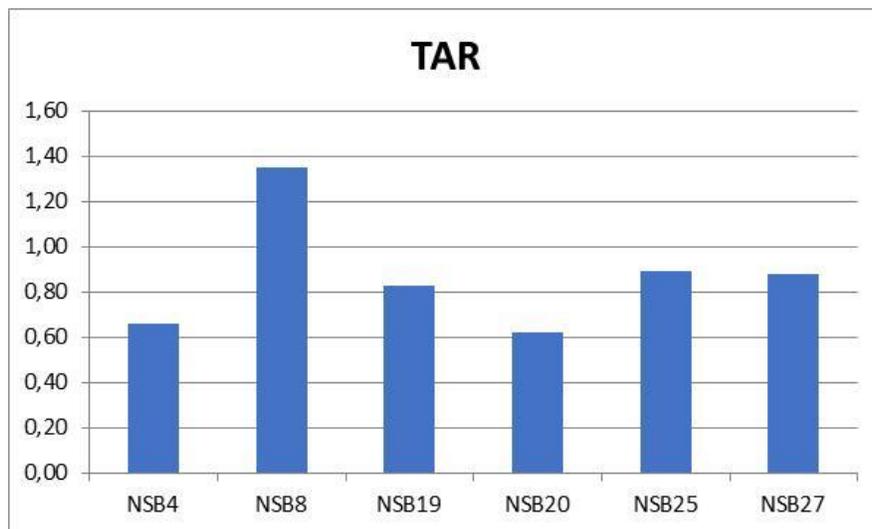


FIGURE 6.24: TAR plot of our samples.

**OEP (1)- OEP (2)- OEP (27-31) Indices (Odd-to-Even-Predominance):** These indices, along with CPI indices, designate low thermal maturity, when they appear with values significantly above or below the unity. Values that approach unity show a thermally mature sample. OEP (1) index has values in our samples that range from 1.21 to 1.54, OEP (2) has the lowest values, ranging between 0.58 and 0.75, while OEP (27-31) has values very similar to CPI(1) index and range between 1.33 and 1.99.

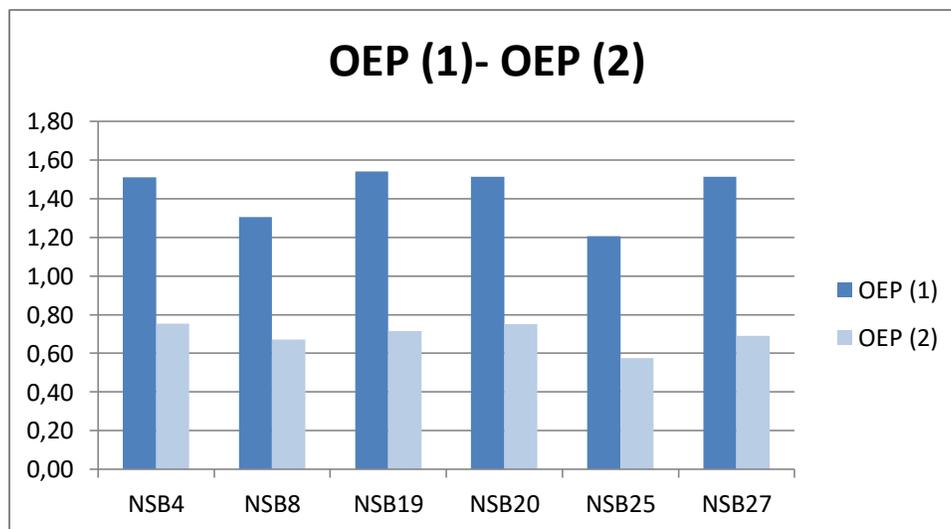


FIGURE 6.25: OEP (1) and OEP(2) plot of our samples.

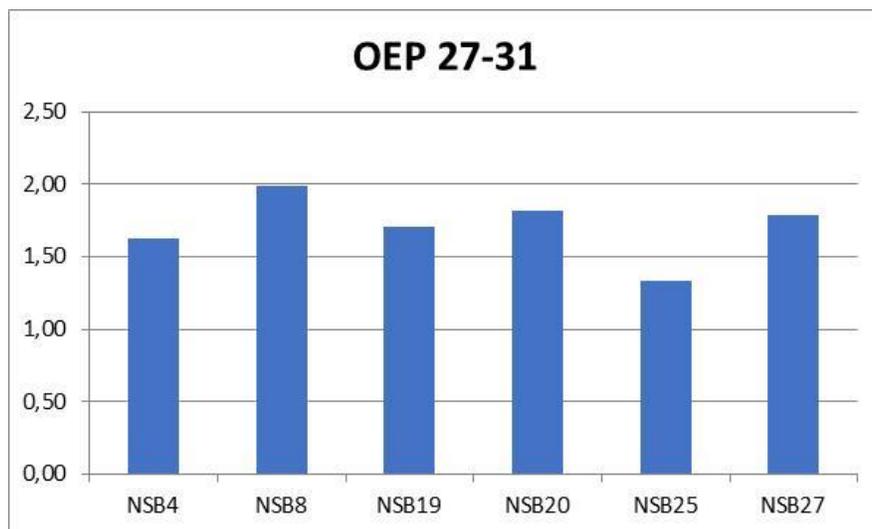


FIGURE 6.26: OEP (27-31) plot of our samples.

### 6.6.2 Hopanes

**C24 Tetracyclic Terpane/C30  $\alpha\beta$  Hopane:** It is used as a source rock indicator. C24 is a ring opened hopane (also called Des-E-Hopane) that is often prominent in carbon samples. This ratio measures the conversion of hopane into des-E-hopane as a result of bacterial activity (Peters and Moldowan, 1993). As we see in our plot, all our samples have values that range from 0.012 to 0.033, something that indicates thermal immaturity and anoxic conditions during the deposition of our sediments.

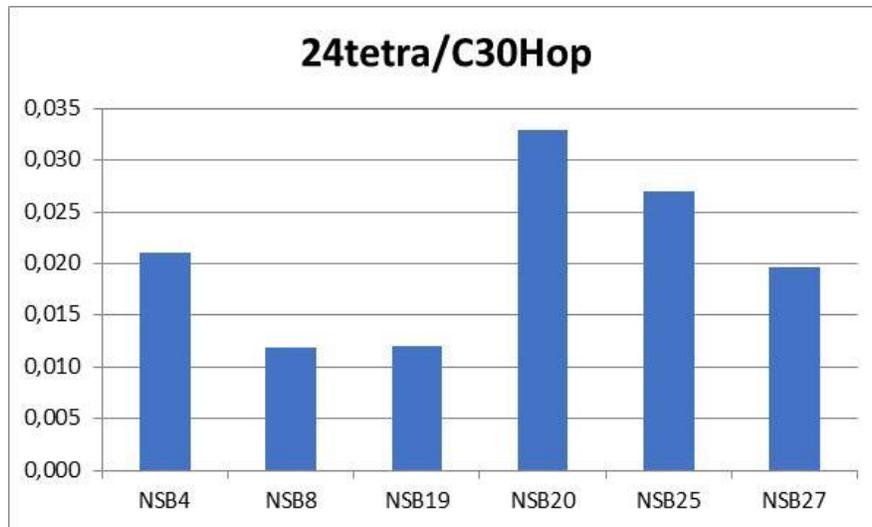


FIGURE 6.27: C24tetra/C30Hop plot of our samples.

**C24 Tetracyclic Terpene/C26 Tricyclic Terpene:** Also, a source rock indicator. C24 is a ring opened hopane (also called Des-E-Hopane) that is often prominent in carbon samples (Peters and Moldowan, 1993). When this ratio has values greater than unity, designates carbonate organic matter. In Figure 6.28, four out of six samples have values greater than unity.

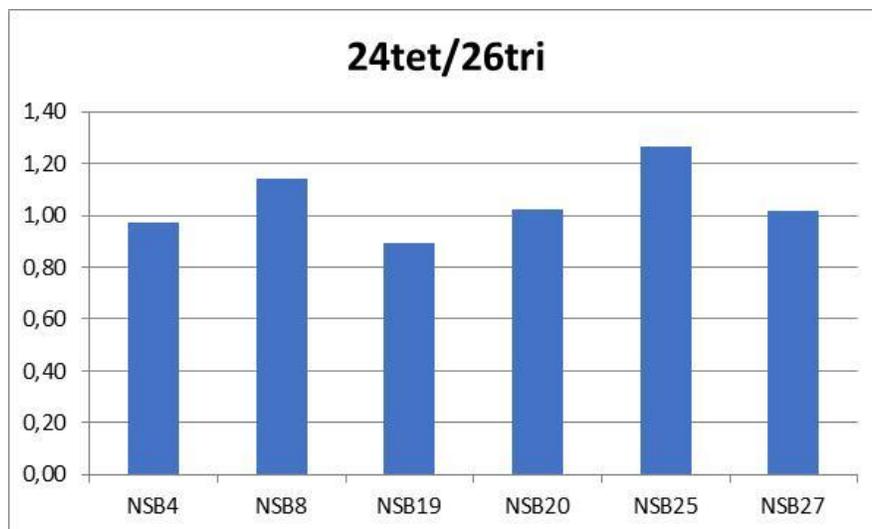


FIGURE 6.28: C24tetra/C26tri plot of our samples.

**C29 norHopane/C30 Hopane:** According to Waples and Machihara (1991), high values of this index could be related to oils that come from carbonate source rocks, while values below unity can be associated to silicate source rocks. Moreover, C29nor/C30Hop index is increasing with the increase of thermal maturity in anoxic environments (Moldowan, 2004).

In Figure 6.29 below, we can see that NSB4 and 19 have C29nor/C30Hop values below 1, while NSB8 has a value that equals 1. NSB 20 and 27 on the other hand, exceed 1, having values of 1.53 and 1.02 respectively.

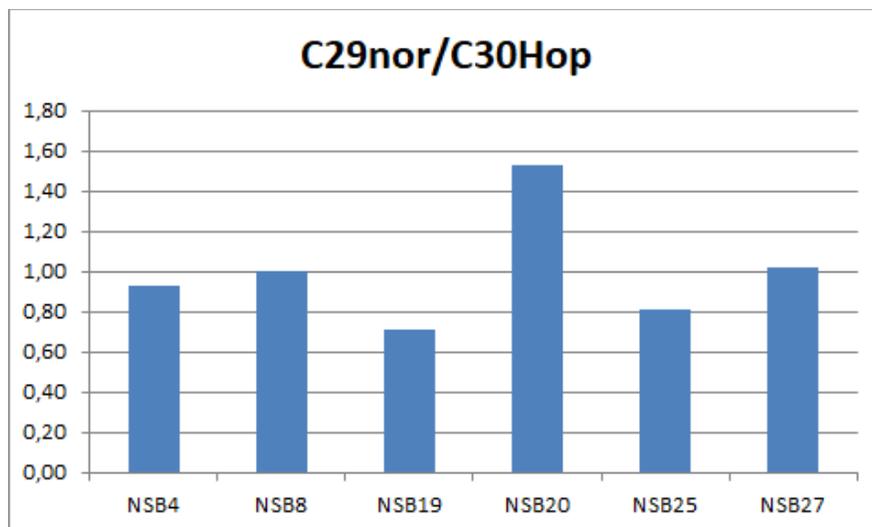


FIGURE 6.29: C29nor/C30Hop plot of our samples.

## 7. CONCLUSIONS

During this thesis work, the object was to define the petroleum potential of a formation in Southeast Australia, by taking 27 rock samples, from three different depths, from Northern Sydney Basin. Then, we applied the standard geochemical methods in the Laboratory of PVT and Core Analysis, in the Technical University of Crete, in Greece. All the samples were prepared and went through the Rock-Eval Pyrolysis method. However, only 6 samples went through the complete geochemical process and were analyzed in Gas chromatography for the evaluation of the biomarkers.

After taking into consideration the data we have gathered, and the results from the experimental procedures, we came to the following conclusions. The pivot tables that follow (TABLES 9&10) were made in order to demonstrate the results gathered.

TABLE 10: Characterization of the samples, based on some experimental results.

Samples	Hydrocarbon Potential				Kerogen Type		Maturation
	TOC	S1	S2	Bitoumens (ppm)	HI	S2/S3	Tmax
NSB4	excellent	fair	excellent	excellent	II/III	I	Immature
NSB8	excellent	Poor	excellent	excellent	III	I	Immature
NSB19	excellent	Fair	excellent	excellent	III	I	Early mature
NSB20	excellent	Poor	excellent	excellent	III	II	Early mature
NSB25	excellent	Fair	excellent	excellent	III	II	Immature
NSB27	excellent	poor	excellent	excellent	III	II	Early mature

TABLE 11: Pivot table with the interpretation of the biomarkers results.

Samples	Carbonate origin	Silicate origin	Oxidizing conditions	Anoxic conditions	Marine origin	Terrestrial origin	Low salinity	High salinity
NSB4								
NSB8								
NSB19								
NSB20								
NSB25								
NSB27								

The samples analyzed display excellent hydrocarbon potential and the organic matter could be characterized as immature to early mature. The kerogen is type II/III, oil and gas prone and type III, gas prone, something that is confirmed by HI index, as well as by quite a few Rock-Eval plots (S2-TOC, HI-TOC, HI-Tmax). In addition, it is clear that our samples are indigenous (S1-TOC plot).

All the samples analyzed exhibit terrestrial origin with possible plant input, something that agrees with the information about a low salinity environment. However, there are results indicating marine origin (TAR index). Additionally, there are indications about organic matter of carbonate origin, but there is also evidence for silicate origin of the organic matter. The information obtained about the depositional environment reveals the presence of a peat swamp environment with anoxic conditions. The latter hypothesis is in agreement with the process of coal formation that was analyzed in this thesis.

It is obvious that there are many contradictions deriving from processing the experimental results. Looking at Rock-Eval plots, there were not any common features discernible between the samples of each group, nor could the samples of these groups be categorized. In fact, Van Krevelen plot shows that the samples are completely scattered and the only thing each group has in common is the depth they were taken from. This could be attributed to the fact that all our samples belong to the same formation, so it is self-evident that they would have common features.

However, during the experimental procedures there were some restrictions. First of all, the number of the samples we could analyze in GC/MS was limited, due to the time needed in order to complete all the stages of the experimental procedure and more importantly, the cost of consumables that would exceed the permitted limits that concern a Master thesis work. Moreover, there were some issues that came up during the analysis of the samples, due to the high TOC values they exhibited. More specifically the extraction of samples NSB 25 and 27 had to be cancelled and run the procedure from the beginning.

In conclusion, the picture we have shaped about the studied formation is that it constitutes a very promising gas source. However, to obtain more data about the formation's properties and potential, we could do a more extensive research, with the geochemical analysis of more samples of the studied formation. Additionally, a more thorough study of the area could be commissioned, in order to acknowledge the properties of the adjacent formations and the existence of any exclusion zones around the coal resources, such as the study concerning the Sydney Basin bioregion, carried out by Herron et al. (2018). We could also examine the composition of the gas, as well as the relation of the gas sources to the total gas content (Scott and Hamilton, 2006; Faiz et al., 2007; Pinetown, 2013; Ward and Kelly, 2013).

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