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ORGANIC-GEOCHEMICAL CHARACTERIZATION AND CORRELATION OF CRUDE OILS SAMPLES FROM THE MOST SIGNIFICANT OIL FIELDS IN THE SIRTE BASIN, LIBYA

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ORGANSKO-GEOHEMIJSKA KARAKTERIZACIJA I KORELACIJA UZORAKA SIROVE NAFTE IZ NAJZNAČAJNIJIH NAFTNIH POLJA BASENA SIRTE, LIBIJA

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IZVOD

Organsko-geohemijska karakterizacija i korelacija uzoraka sirove nafte iz najznačajnijih naftnih polja basena Sirte, Libija

Ova doktorska disertacija sastoji se od dve jasno definisane celine.

U prvom delu ove teze vrednosti parametara izračunatih na osnovu raspodela i obilnosti odabranih pentacikličnih terpana u sirovim naftama iz Libije i Srbije, koji su originalno dobijeni iz rezultata gasno hromatografsko – maseno spektrometrijske (GC-MS) analize upoređene su sa kvantifikacionim rezultatima koji su zasnovani na gasno hromatografsko – maseno spektrometrijsko – maseno spektrometrijskoj (GC-MS-MS) analizi. Analizirani parametri su najčešće korišćeni terpanski izvorni i maturacioni parametri, koji su primenjeni na veliku grupu uzoraka od 70 sirovih nafti, koje potiču iz pet naftnih polja. Cilj je bio da se ispita u kojoj meri se merenja odabranih parametara ovim dvema tehnikama slažu i da se odredi uticaj razlika između vrednosti ovih parametara na geohemijsku interpretaciju. U tom cilju, korišćene su dve statističke metode: koeficijent slaganja korelacija i dijagram srednja vrednost-razlika. Dobijeni rezultati pokazuju da izračunavanje C_{27}18α(H)-22,29,30-trisnorneohopan/(C_{27}18α(H)-22,29,30-trisnorneohopan + C_{27}17α(H)-22,29,30- trisnorhopan), C_{29}18α(H)-30-norneohopan/C_{29}17α(H)21β(H)-30-norhopan i C_{29}17α(H)21β(H)-30- norhopan /C_{30}17α(H)21β(H)- hopan odnosa bilo GC-MS ili GC-MS-MS tehnikom ne utiče značajno na interpretaciju. S druge strane, određivanje C_{30}17β(H)21α(H)-moretan/C_{30}17α(H)21β(H)-hopan odnosa, gamaceranskog indeksa i oleananskog indeksa GC-MS ili GC-MS-MS tehnikom može značajno uticati na interpretaciju. Ove razlike se mogu objasniti koeluiranjem i preklapanjem pikova tokom GC-MS analize ali takođe i boljim razdvajanjem, većom preciznošću i boljom selektivnošću GC-MS-MS tehnike. Odstupanje skoro svih parametara od linije jednakosti je slično za nafte iz istog naftnog polja ali su uočene razlike pri analizi nafti iz različitih naftnih polja. Stoga, kada se planira primena GC-MS-MS rezultata u organsko geohemijskim interpretacijama, preporučuje se i regionalna kalibracija odnosa između GC-MS i GC-MS-MS rezultata za svaki naftni sistem.

U drugom delu ove teze četiri uzorka sirovih nafti iz naftnih polja Intisar A, Intisar D and Intisar E (Sirte basen, Libija) ispitivani su sa ciljem da se definiše depoziciona sredina, litologija, termička maturisanost i geološka starost njihovih izvornih stena. Zasićeni biomarkeri (n-alkani, izoprenoidi, sterani i triterpani) analizirani su gasnohromatografsko – maseno spektrometrijskom (GC-MS) i gasnohromatografsko – maseno spektrometrijsko – maseno spektrometrijskom (GC-MS-MS) metodom. Aromatični ugljovodonici (fenantren, metilfenantreni, metil-dibenzotiofeni i trimetilnaftaleni) analizirani su GC-MS metodom. Rezultati pokazuju da su sirove nafte Intisar stvorene iz izvornih stena sa visokim sadržajem glina koje su sadržale smešu marinskog i kopnenog organskog materijala. Maturacioni parametri ukazuju na visok stepen termičke maturisanosti koji odgovara glavnoj fazi stvaranja nafte. Analiza specifičnih biomarkerskih odnosa koji su pokazatelji geološke starosti ukazuje da su nafte Intisar starosti Krede (najverovatnije Donje Krede). Identifikovane su dve grupe izvornih stena nafti Intisar, sliče po tipu prekursorskog organskog metrijala, litologiji, maturisanosti i geološkoj starosti ali različite po redoks uslovima u sredini tokom njihovog taloženja. Nafte koje su stvorene iz ovih izvornih stena verovatno su imale različite migracione puteve.

Ključne reči: sirove nafte, terpani, GC-MS, GC-MS-MS, koeficijent slaganja korelacija, dijagram srednja vrednost-razlika, Sirte Basen, naftno polje Intisar, organskogeohemijska karakterizacija

Naučna oblast: Hemija
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ABSTRACT

Organic-geochemical characterization and correlation of crude oils samples from the most significant oil fields in the Sirte basin, Libya

This thesis consists of two dinstictive parts.

In the first part of this thesis the values of parameters calculated from distributions and abundances of selected pentacyclic terpanes in crude oils from Libya and Serbia, which were originally derived from gas chromatography-mass spectrometry (GC-MS) were compared with quantification results based on gas chromatography-mass spectrometry-mass spectrometry (GC-MS-MS). The parameters analyzed are the most often used terpane source and maturity parameters, which were applied to a large sample set of 70 oils, originating from five oil fields. The aim of the paper was to investigate to which extent the measurements of the selected parameters by these two instrumental techniques agree and to determine influence of differences between parameter values on geochemical interpretation. For that purpose two methods, concordance correlation coefficient and mean-difference plot were used. The obtained results indicate that calculation of C_{27}18α(H)-22,29,30-trisnorneohopane/(C_{27}18α(H)-22,29,30-trisnorneohopane + C_{27}17α(H)-22,29,30-trisnorhopane), C_{29}18α(H)-30-norneohopane/C_{29}17α(H)21β(H)-30-norhopane and C_{29}17α(H)21β(H)-30-norhopane/C_{30}17α(H)21β(H)-hopane ratios either by GC-MS or GC-MS-MS do not significantly influence interpretation. On the other hand, determination of C_{30}17β(H)21α(H)-moretane/C_{30}17α(H)21β(H)- -hopane ratio, gammacerane index and oleanane index by GC-MS vs. GC-MS-MS could notably affect interpretation. These differences can be explained by co-elution and peak overlapping in GC-MS but also by better separation, higher precision and better selectivity of the GC-MS-MS. Deviation of the almost all studied parameters from the line of equality was similar for the oils from the same oil field but some differences were observed for the oils from different oil fields. Therefore, when GC-MS-MS results are to be used in organic geochemical interpretations, a regional calibration of GC-MS vs. GC-MS-MS relationship for each petroleum system is highly recommended.

In the second part of this thesis four crude oil samples from the oil fields Intisar A, Intisar D and Intisar E (Sirte Basin, Libya) were investigated in order to define depositional

environment, lithology, thermal maturity and geologic age of the corresponding source rocks. Saturated biomarkers (n-alkanes, isoprenoids, steranes and triterpanes) were determined using gaschromatography – mass spectrometry (GC–MS) and gas chromatography – mass spectrometry – mass spectrometry (GC–MS–MS). Aromatic hydrocarbons (phenanthrene, methyl-phenanthrenes, methyl-dibenzothiophenes and trimethyl-naphtalenes) were analyzed by GC–MS. The Intisar crude oils were generated from siliciclastic source rocks containing a mixture of marine and terrestrial organic matter. Maturation parameters indicated high level of thermal maturity corresponding to the main phase of oil generation. The analysis of the age-specific biomarker ratios suggested Cretaceous, most probably Lower Cretaceous age for the Intisar oils. Two source rocks for the Intisar oils were identified, similar in the precursor organic matter type, lithology, maturity and geologic age but different in the redox conditions in the environment during their deposition. The oils generated from these different sources probably migrated over different migration pathways.

Keywords: crude oils, terpanes, GC-MS, GC-MS-MS, concordance correlation coefficient, mean-difference plot, Sirte Basin, Intisar oil field, organic geochemical characterization

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1. Introduction

Organic geochemistry is a multidisciplinary science which connects analytical organic chemistry and chemistry of natural products with geology, petrology, and oceanography. Its main focus is study of Eart's crust organic matter.

The research object of this thesis is crude oils from different parts of the Sirte Basin, Libya. The Sirte (Sirt) basin is a prolific hydrocarbon basin in Libya. It is located on the northern margin of the African plate, covering an area of approximately 600.000 km^2 in northcentral Libya. Over twenty-three large oil fields and sixteen giant oil fields occur in this province. Although this region is one of the largest sources of oil and gas, scientific publications including organicgeochemical interpretation of crude oils from this region are still very scarce.

Crude oil is a complex mixture of a large number of chemical compounds, commonly dominated by hydrocarbons. Due to the complexity of crude oil composition, development of organic geochemistry, from its beginnings until the present day, followed development of instrumental techniques for analysis of organic compounds. From the organic geochemical point of view, the most important compounds in crude oils are sterane and terpane biomarkers, as well as bicyclic and tricyclic aromatic compounds. Sterane and terpane biomarkers are in geological samples (crude oils and extracts of source rocks and coals) usually present at ppm to ppb level. Due to the complex composition of these samples and low abundance of biomarker compounds in them, gas chromatographic – mass spectrometric (GC-MS) analysis was, for many years, the method of choice for identification and quantification of biomarkers in crude oils. Most of the organic geochemical parameters, based on the abundance and distribution of sterane and terpane biomarkers were originally defined on the basis of the results of GC-MS analysis. However, in the GC-MS analyses interferences often occur, due to coelution and peak overlapping, and quite often an additional selectivity is needed to resolve complex biomarker mixtures. With the development of tandem or quadrupole mass spectrometers coupled with GC (GC-MS-MS), many of the shortcomings encountered in analytical separations with GC-MS were overcome. The major advantage of a GC-MS-MS system over GC-MS is a possibility to resolve individual

biomarkers or biomarker groups in complex mixtures and to precisely quantify all resolved isomers. Nowadays, GC-MS-MS and other hyphenated techniques are routinely used in many organic geochemical laboratories. Although the knowledge on the discrepancies between GC-MS and GC-MS-MS results in quantification of sterane and terpane parameters is not a novelty for the organic geochemical scientific community, a detailed comparison of the results of the analysis of the same samples using these two techniques, has not been published so far. In this thesis a comparison of the values of parameters calculated from distributions and abundances of selected pentacyclic terpanes in crude oils from Libya and Serbia, derived from gas chromatography-mass spectrometry (GC-MS) and gas chromatography-mass spectrometry-mass spectrometry (GC-MS-MS) quantification results was performed, using a large sample set of 70 oils. The parameters analyzed are the most often used terpane source and maturity parameters: C_{27}18α(H)-22,29,30-trisnorneohopane/(C_{27}18α(H)-22,29,30-trisnorneohopane + C_{27}17α(H)-22,29,30-trisnorhopane (Ts/(Ts+Tm)), C_{29}18α(H)-30-norneohopane/C_{29}17α(H)21β(H)-30-norhopane (C_{29}Ts/C_{29}H), C_{29}17α(H)21β(H)-30norhopane/C_{30}17α(H)21β(H)-hopane (C_{29}H/C_{30}H), C_{30}17β(H)21α(H)-moretane/C_{30}17α(H)21β(H)-hopane (C_{30}M/C_{30}H), gammacerane index (GI=G×100/C_{30}H) and oleanane index (OI=O×100/C_{30}H). One of the aims of this thesis was to investigate to which extent the measurements of the selected parameters by these two instrumental techniques agree and to understand the nature of their differences.

2. Theoretical part

2.1. Sedimentary organic matter

2.1.1. Origin of sedimentary organic matter

The primary source of the organic substance in sediments is living organisms that contribute to it during their life processes (biosynthesis, excretion, and secretion) and later with their dead bodies (Salomons, Stigliani, 1995; Tissot, Welte, 1984). All types of the organic matter preserved in sediments come predominantly from major domains of life which include prokaryotes (archeobacteria, eubacteria) and eukaryotes (Figure 1).

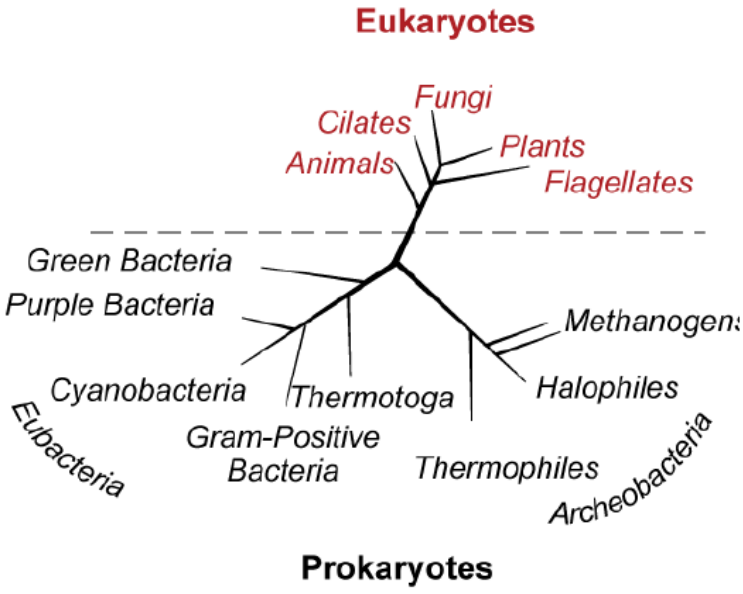

Figure 1. Universal phylogenetic tree showing archeobacteria, eubacteria and eukaryotes as three main domains of life (White et al., 2013).

The fate of organic matter in sediments is determined primarily by its chemical structure determining the rate of degradation, that is, environmental sustainability, but it also depends on the chemical composition and structure of the sediments, as well as on the presence (quality and quantity) of the microbiological population capable of decomposing (Baldock, Skjemstad, 2000; Bossert, Bartha, 1984).

Between the release of biological molecules into the environment and their incorporation into sediments, numerous physical, chemical and biological processes occur that affect the structure, quantity and spatial distribution of organic matter in sediments (Tissot, Welte, 1984) (Figure 2). Possible chemical reactions that transform biomolecules in soil and sediments are often called biogeochemical: they occur in a geologic environment, and many of them occur thanks to microorganisms (NRC, 2000; Mulder, Cresser, 1994).

2.1.2. Transformation of organic matter in sedimentary rocks

Once it enters the sediment, organic matter is further buried by the effect of continuous sedimentation. Within the sediment, the physico-chemical and biological properties change gradually with increasing depth (compaction, reduction in water content, disappearance of bacterial activity, qualitative transformation of the mineral phase) and the organic substance passes through the diagenesis phase. Diagenesis begins in recently deposited sediments and comprises microbial and chemical transformations of sedimentary organic matter at low temperatures (Tissot, Welte, 1984).

During early diagenesis, one of the major transformation agents is microbiological activity. Aerobic microorganisms living in the upper layers of sediment consume molecular oxygen, and energy is obtained by degradation of organic matter, which is converted to CO_2, NH_3 and H_2O in this process. The efficacy of microbiological degradation depends on the granulometric composition of the sediments, and is usually complete in sand and partially complete in sludge (Tissot, Welte, 1984).

However, even in highly oxic sediments, in which the environmental factors favor rapid degradation of organic matter and its recycling through microbiologic biomass, certain molecules "persist" during diagenesis, unchanged or with minor structural changes and as such are

incorporated into sediments. That part is small and is only 0.01 - 0.1 % of total production of organic matter (Sacket, 1964). The most abundant compounds in this fraction are free hydrocarbons and their related compounds (Tissot, Welte, 1984).

n-Alkanes

Among biogenic hydrocarbons, n-alkanes are the dominant group and have been identified in many plant and animal species.

In recent detrital sediments with a significant amount of continental flushing, which includes minerals of clay, sludge and organic material of plants, there are often *n*-alkanes with an odd number of C atoms and high molecular weight (from *n*-C_{25} to *n*-C_{33}). These hydrocarbons originate from the cuticular waxes of continental higher plants (Tissot, Welte, 1984) and can be either directly synthesized by plants or obtained during early diagenesis (defunctionalization) of acids, alcohols or esters with a even number of C-atoms (Singer, Finnerty, 1984).

Long-chain n-alkanes, without any domination of even or odd homologs, are probably derived from bacterial waxes, and are usually followed by an *iso*- and *anteiso*-alkane series that are typical of bacterial origin (Tissot, Welte, 1984).

iso- and *anteiso*-Alkanes

These hydrocarbons in recent sediments might origin from plant or bacterial waxes. The characteristic of *n*-alkanes from vegetable waxes is of C_{25} to C_{31} range and domination of odd-type homologues, while those that originate from bacterial waxes include a wider range of C atoms, most often without any domination of even or odd homologs (Tissot, Welte, 1984).

Acyclic isoprenoids

Fitol (an ester-bound side chain of chlorophyll), which is probably the most abundant isoprenoid compound in the biosphere, is generally considered the main source of isoprenoids with 20 or less C atoms in sediments (Tissot, Welte, 1984). However, numerous studies have

shown that acyclic isoprenoids in sediments may also be stimulated by many other biomolecules other than phytoles (Rontani, Volkman, 2003).

Steroids

Steroids represent a group of compounds widely distributed in living organisms. Steroid derivatives in recent sediments exist as sterols, stanols (reduced form without any double bonds) and as corresponding hydrocarbons, steranes (Tissot, Welte, 1984).

Steranes can originate partly from animals, and partly from plants. Since the contribution of terrestrial animals to the biomass sediments is insignificant, C_{27} and C_{28} steranes found in sediments are most likely derived from zoo and phytoplankton, while C_{29} steroids can originate either from continental plants, or from brown algae and phytoplankton. Steroids-rich sediments are characteristic of the marine and lake environment where steroids mostly originate from autochthonous organic matter (Tissot, Welte, 1984).

Pentacyclic triterpenoids

Pentacyclic triterpenoids contain either only six-membered rings or four six-membered rings and one five-membered ring. They most often contain 30 carbon atoms and often occur in plants but also in prokaryotic organisms. It is believed that pentacyclic triterpanes in sediments can be partly originated from plants. However, their main sources are prokaryotic organisms. The microbiological population in the upper layers of sediments is considered to be the dominant source of prevalent hopanes. Corresponding molecules occur in young immature sediments as alcohols, ketones and petroleum aromatic hydrocarbons but very rarely as saturated hydrocarbons (Tissot, Welte, 1984).

2.2. Formation of oil and gas

2.2.1. Kerogen

The main and the most important product of diagenetic changes is kerogen - an insoluble part of the sedimentary organic substance.

During diagenesis, preserved geomonomers are subjected to random polymerization and polycondensation, with the formation of geopolymers: fulvo acids, humic acids and humin. By further processes of insolubilization from the humic substances with the release of CO_2, H_2, CH_4 and NH_3, the degree of polymerization increases and at the depth of several hundreds to one thousand meters kerogen is formed (Figure 2). Kerogen is an organic substance with a crosslinked macromolecular structure, insoluble in organic solvents and aqueous alkaline solutions.

Except from kerogen, in the sedimentary organic substance, in a significantly less represented part, there are also free hydrocarbons and some other compounds, mostly of lipid origin. During sedimentation and diagenesis, these molecules can retain the chemical structure of the compounds from the living world. Therefore, in organic-geochemical literature they are called "molecular fossils" or "biological markers".

Kerogens are characterised into four types based on the composition of the organic matter and the depositional environments of the sediments. The four types are I, II, III and IV, whereas II-S is part of II type (Killops and Killops, 2005; Aboglila et al., 2010). Different types of kerogens also have different atomic ratios (i.e. oxygen to carbon: O/C and hydrogen to carbon: H/C. Different types of kerogens and their corresponding atomic rations are usually represented in the Van Krevelen diagram (Fig 3; Tissot and Welte, 1984).

Type I kerogen is quite rare because it is derived from lacustrine algae and planktons. It is limited to anoxic lakes and a few unusual marine environments. Type I kerogen has H/C ratio greater than 1.25 and low O/C ratio (less than about 0.15; Fig 3), and accordingly, high generative capacities for liquid hydrocarbons (Waples, Dougle, 1985; Robinson, 1969; Engel, Macko et al., 1993).

Type II kerogen is derived from different sources, including marine algae, pollen and spores, leaf wax, and fossil resin found in marine sediments under anoxic conditions. This type has contributions from bacterial-cell lipids. Type II kerogen has great capacities to generate liquid hydrocarbons and can also generate gas (Waples, Dougle, 1985; Nasir, 2013). Immature type II kerogen has lower H/C ratios (less than about 1.3) and equivalent or higher O/C ratios (in the range of about 0.03-0.18; Engel, Macko et al., 1993).

Type III kerogen is mainly derived from terrestrial organic matter, which is lacking fatty or waxy components and major contributors are lignin and cellulose. It is deposited under oxic conditions or in non-marine environment. This type III kerogen has relatively low H/C ratios (generally less than 1) and higher O/C ratios (in the range of about 0.3 to 0.03; Fig 3; Tissot and Welte, 1984; Engel, Macko et al., 1993). Type III kerogen has much lower hydrocarbon-generative capacities than Type I and type II kerogens (Killops and Killops, 2005; Waples, Dougle, 1985).

Type IV kerogen contains reworked orgain debris various in origin and deposited in highly oxidized environment (Smyth et al., 1983). It has H/C ratio always less than 0.5 and has no ability to produce oil or gas.

2.2.2. Bitumen

By settling of the original sedimentary layers and their burial by accumulation of new sedimentary layers in the phase of the diagenesis, the organic substance reaches greater depths where it is exposed to higher temperatures, pressures and the effect of mineral catalysts. Its further change at depths of more than 1000 m, temperatures of 50 – 150 °C and pressures of 300 – 1.700 bar, represents the phase of transformation of the organic substance of the geosphere, which is called catagenesis. Under these conditions, macromolecular kerogen degrades into products that are composed of smaller molecules, soluble in organic solvents, and have the general name bitumen (Figure 2).

Sedimentary rocks, in which bitumen was once created, is being currently created or will be created, are called source rocks.

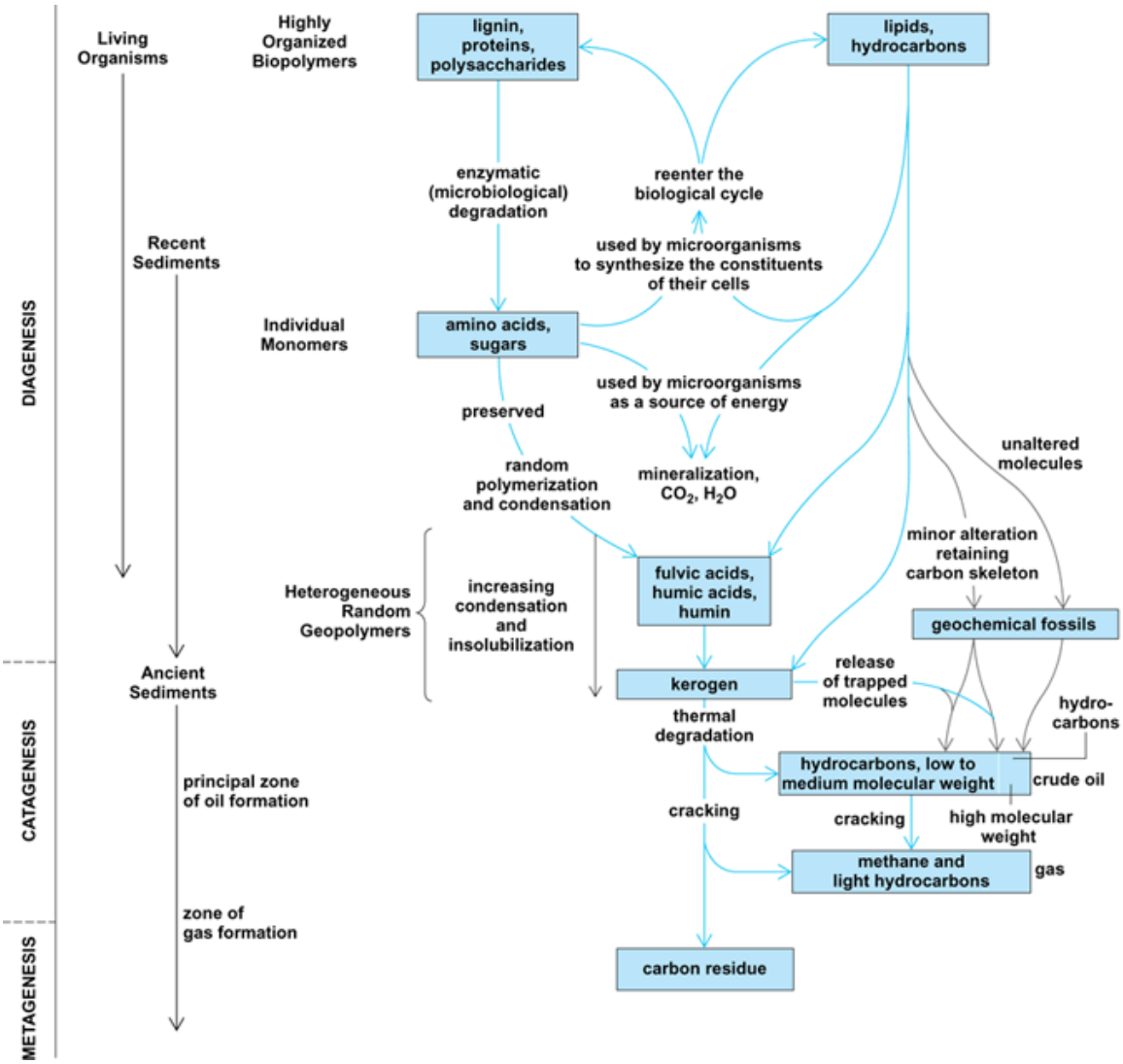

Figure 2. Transformation of organic matter during sedimentation and maturation (Tissot, Welte, 1984).

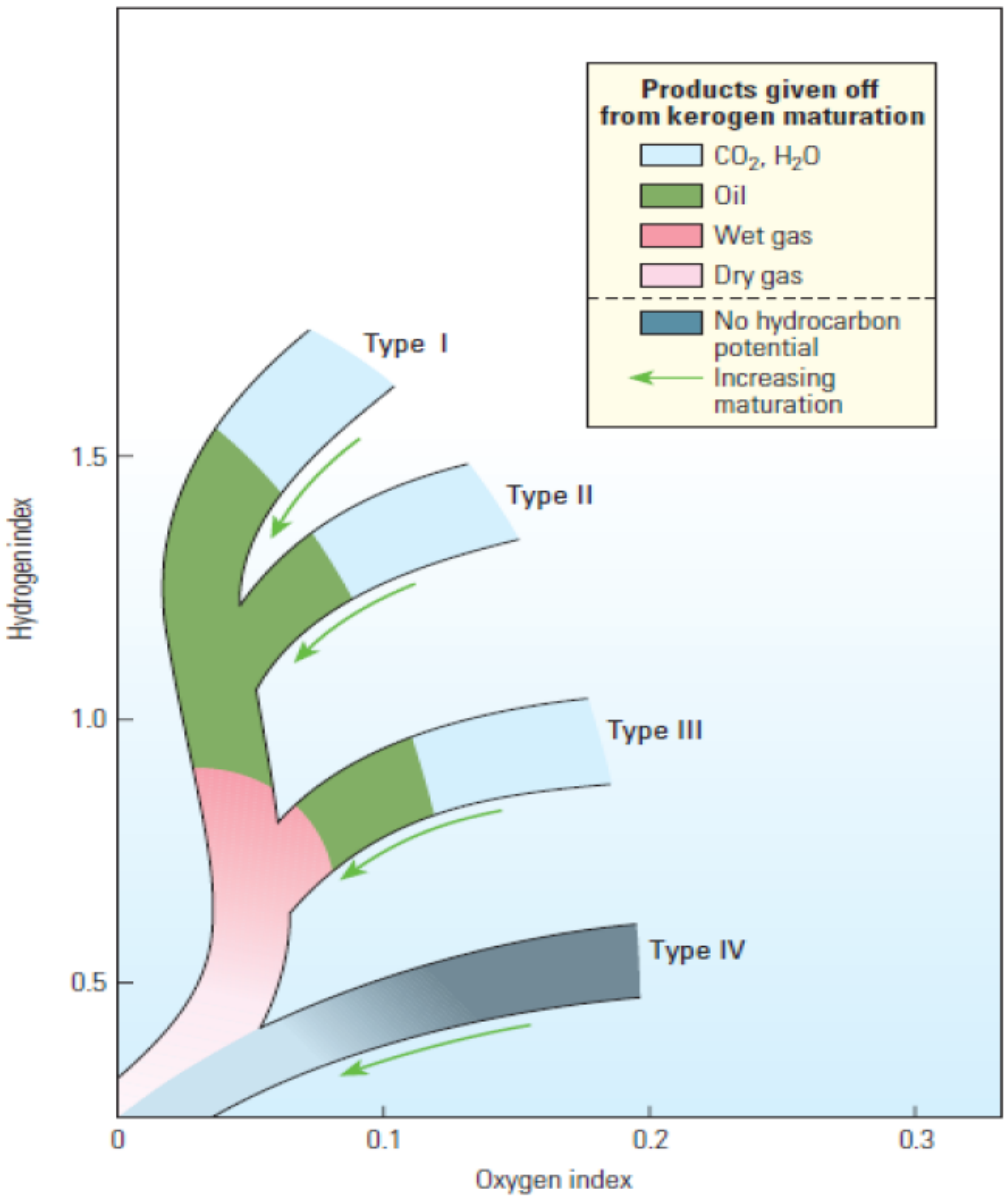

Figure 3. Van Krevelen diagram showing maturation pathways for different types of kerogen under the influence of increased heat and pressure during burial which generates non-hydrocarbon gases at the beginning stages then oil, wet gas and finally dry gas (Tissot, Welte, 1984; Nasir, 2013).

2.2.3. Formation of oil and gas

As a result of increased sedimentation and burial, the amount of bitumen in sedimentary rock increases, and at one point the pressure becomes high enough. As a result, bitumen begins to move through fractures and cavities and tries to leave the original source rock. This moment represents the beginning of migration of bitumen.

There are two forms of migration. Primary migration occurs through the original source rock in which bitumen wass created. This migration is slow and it is measured in meters. At the moment when the bitumen leaves the original source rock secondary migration begins. It continues until the bitumen reaches the rock with accumulation properties in which it gradually accumulates. Accumulation of migrated bitumen creates oil, and these rocks are designated as reservoirs or reservoir rocks. The depth of the reservoir rock is always lower than the depth of the source rock because bitumen always migrates towards the area of lower pressures (Waples, 1985).

Chemical composition of the bitumen in source rocks is different from the chemical composition of the oil. These differences are concequence of changes in source rocks, changes during migration, and changes in reservoir rocks. These transformations of organic matter are usually maturation processes of izomerization, cracking, deasphalting and biodegradation.

In the final phase of the transformation of the organic matter in the subsurface, at the depths of approximately 10000 m and under maximum pressures and temperatures, the rest of kerogen is decomposing and gives the main product methane, i.e., natural gas (Figure 4). Because of that, this final phase of the transformation of the organic matter in the subsurface is called methanogenesis.

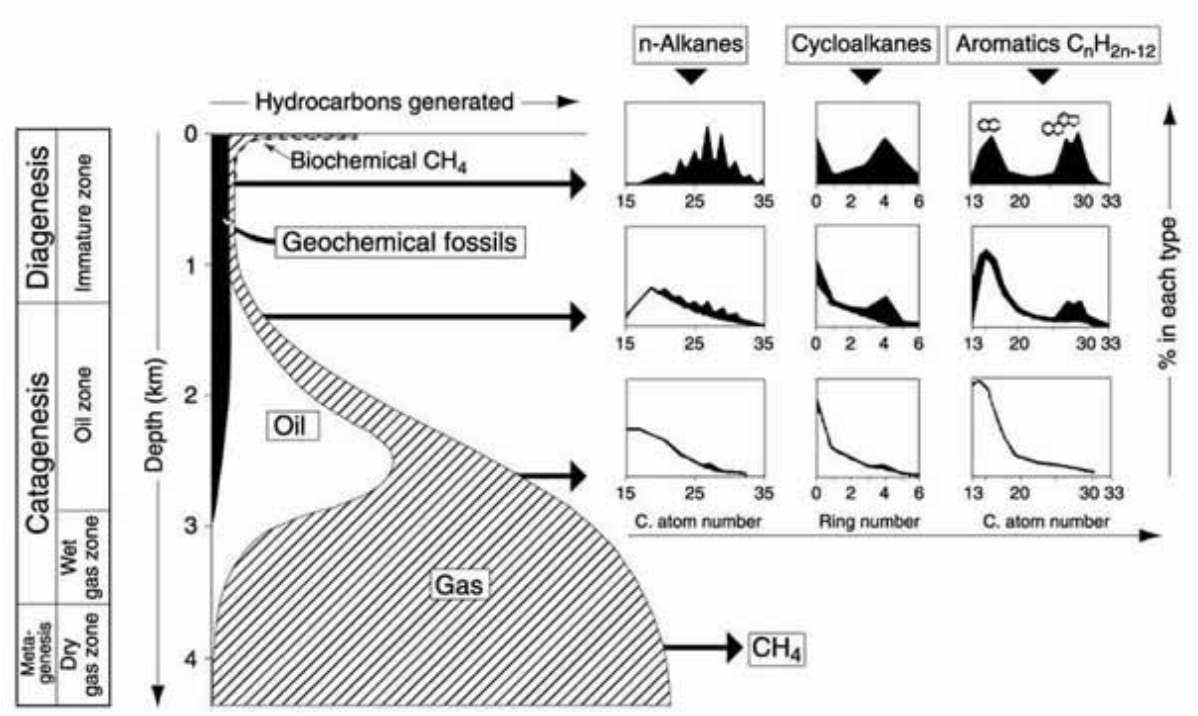

Figure 4. Evolution of the organic fraction in the subsurface and the hydrocarbons produced (Tissot, Welte, 1984).

2.3. Transformations of crude oil in reservoirs

2.3.1. Cracking and deasphalting processes

Oil cracking is an important process which occurs in sours rocks. As a result of this process large molecules are broken into smaller molecules, which leads to the increased amounts of low molecular weight compounds, but also thermodynamically more stable structural and stereochemical isomers of certain compounds.

As the oil becomes lighter asphaltene molecules become less soluble and gradually precipitate. This process is called *deasphalting*. Precipitation of asphaltenes in reservoir rocks leads to decrease in sulfur content and increase in content of saturated and aromatic hydrocarbons (Vitorović, Jovančićević, 2005; Waples, Dougle, 1985).

2.3.2. Biodegradation and water washing

Biodegradation (microbiological degradation) is an in-reservoir transformation process of crude oil. During this process microorganisms consume petroleum hydrocarbons for which they have the strongest preferences. Compounds that are crude oil constituents vary greatly in their susceptibility to degradation by microorganisms. Some compounds are readily biodegradable, while others are persistent during biodegradation. The most biodegradable compounds have simple molecular structures (often similar to those of organic compounds occurring in nature), are water soluble, non-toxic, and can be transformed by aerobic metabolism (Atlas, 1995). In contrast, compounds that are persistent during biodegradation often have a complex molecular structure (especially structures that are usually not found in nature) and low water solubility.

Biodegradation of hydrocarbons is described as quasi-sequential which means that the more resistant classes of compounds can be attacked before the total consumption of less resistant classes (Peters, Moldowan, 1993).

The sequence of biodegradability of the compound classes in crude oils is usually described as: n-alkanes (the most biodegradable) > acyclic isoprenoids > hopanes (25-norhopanes present) ≥ steranes > hopanes (no 25-norhopanes) ≈ diasteranes > aromatic steroids > porphyrins (the least biodegradable; Peters, Moldowan, 1993; Wenger et al., 2002; Figures 5 and 6).

Conditions required for biodegradation of crude oil include presence of an oil-water interface, because microorganisms live in the water phase and relatively shallow reservoirs, e.g., 2000 m or less. At higher temperatures, biodegradation can proceed, but its speed is significantly reduced. Aerobic bacteria can grow in relatively cool reservoirs, i.e., below 80 °C, which are invaded by oxygen-charged waters. In addition to dissolved oxygen, nutrients such as nitrate and phosphate must be present and the salinity of the water must be less than 100 to 150 ‰. The presence of

H_2S is unfavorable for aerobic microorganisms and it should not exceed 5 % (Engel, Macko et al., 1993; Ramadan, 2013).

It has been considered for a long time that aerobic biodegradation is a dominant process in reservoir rocks although anaerobic processes may be even more important (Milner et al., 1977; Blanc, Connan, 1994; Zengler et al., 1999; Ramadan, 2013).

Water washing usually accompanies biodegradation. It involves selective dissolution of the most soluble components of crude oils in waters. Water washing and biodegradation often occur together, with more effects of biodegradation than water washing (Waples, Dougle, 1985).

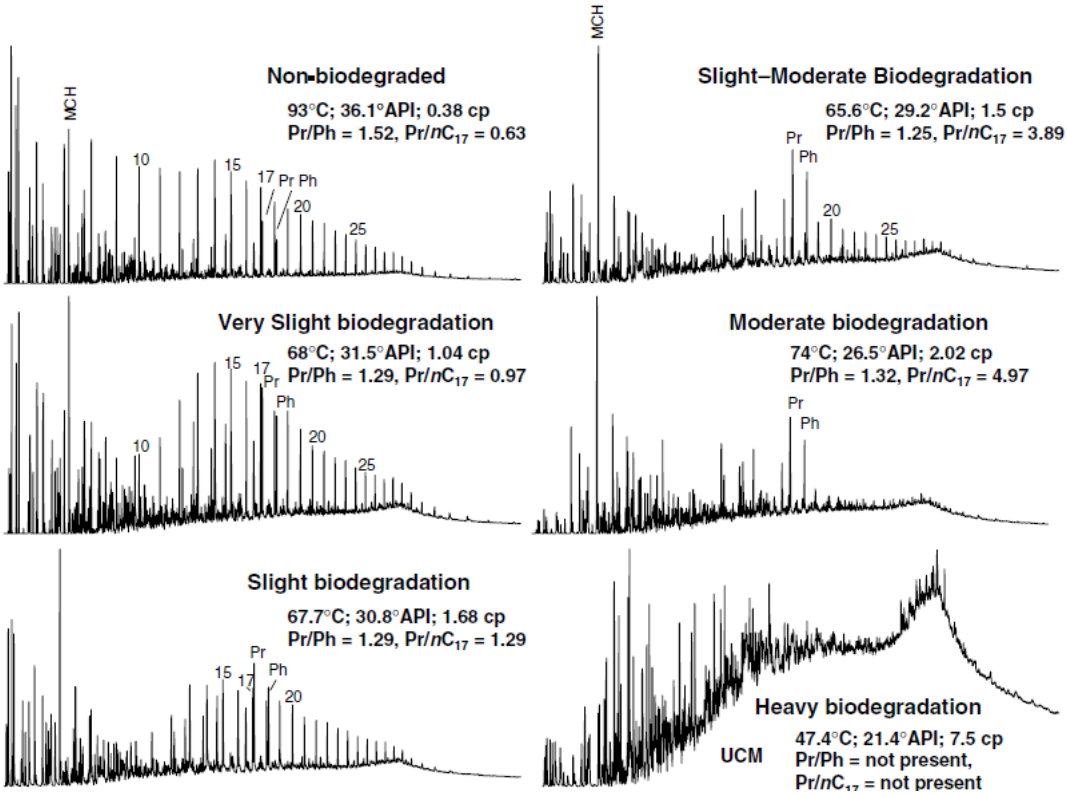

Figure 5. Changes in the distribution n-alkanes and isoprenoids (Pristane and Phytane) from Africa crude oils at different degrees of biodegradation. Shown are reservoir temperature, API gravity, viscosity, and pristane/phytane (Pr/Ph) and pristane/nC_{17} (Pr/nC_{17}) ratios (Wenger, 2002; Peters et al., 2005).

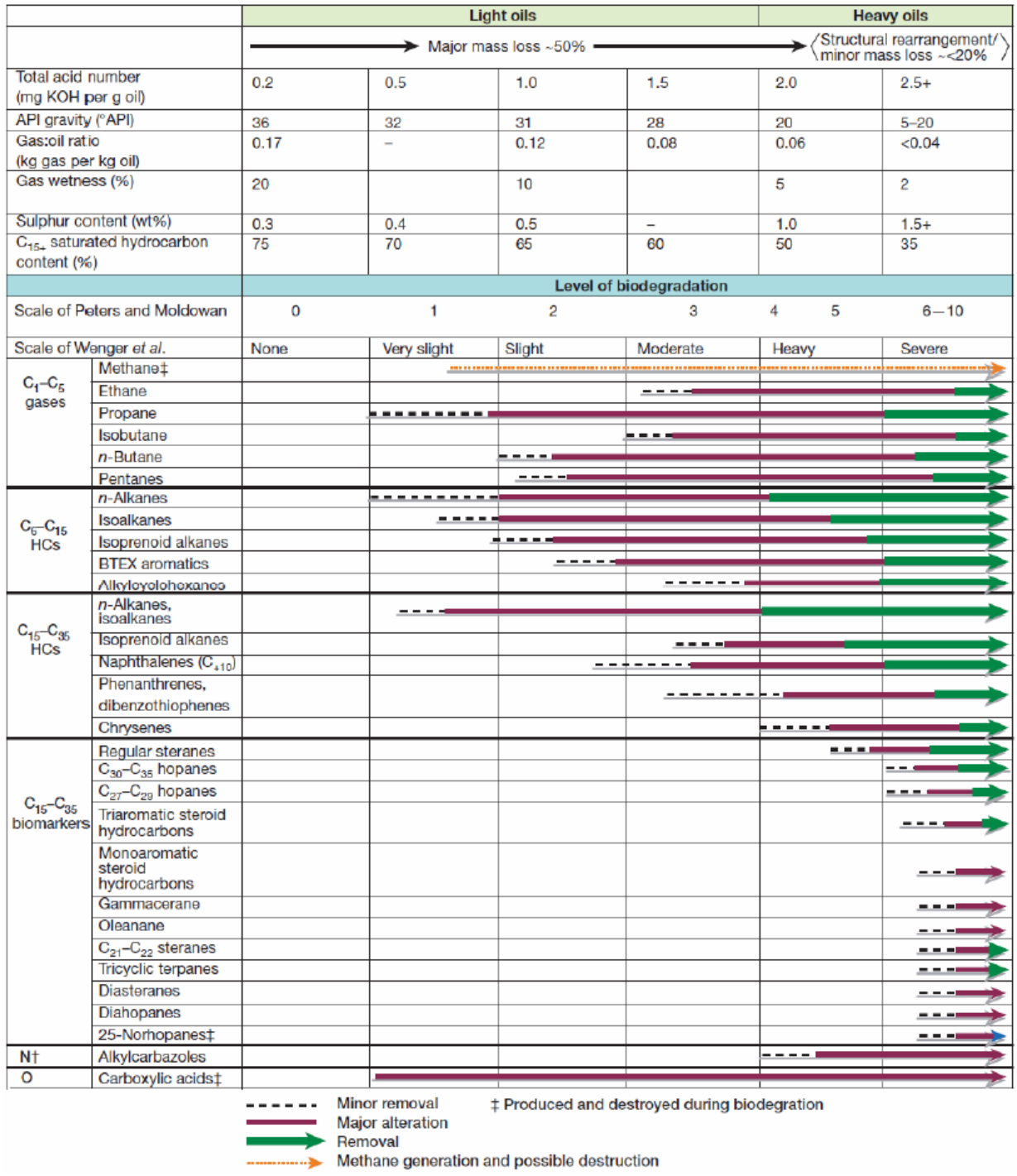

Figure 6. Biodegradation scale (Wenger et al., 2002).

2.4. Composition of crude oil

Crude oil is a naturally occurring complex mixture made up predominantly of carbon and hydrogen compounds, but also containing nitrogen, sulfur, and oxygen together with smaller amounts of nickel, vanadium, and other elements (Palanna et al., 2009).

The most abundant compound classes in crude oils are:

- Saturated hydrocarbons – this class consists mainly from normal alkanes, isoprenoids, and other branched compound, alicyclic hydrocarbons, including steranes, diterpanes and triterpanes. Usually, saturated fraction is most abundant in petroleum, acounting from 60 to 75 % of the total content of petroleum.

- Aromatic hydrocarbons - this class consists from alkylaromatic hydrocarbons or simple aromatics, naphtheno-aromatic hydrocarbons, and smaler aromatic compounds containing sulphur (thiophenes). Their content in crude oil is usually from 20 to 45 %.

- NSO compounds or resins – these compounds are different molecules with one or more heteroatoms, fatty acids and porphyrins

- Asphaltenes - asphaltenes are very large, highly aromatic molecules, rich in heteroatomes.Their content in petroleum can be from 0 to 20 %. Asphaltenes are insoluble in light solvents, and can be extracted from bitumen by addition of light hydrocarbons such as pentane or heptane

Review of petroleum fractions and their most important constituents is given in Table 1.

Table 1. Petroleum fractions and their most important constituents (Waples, Dougle, 1985; Vitorović, Jovančićević, 2005).

Fraction	Components
Saturated fraction	n-alkanes Isoprenoids and other branched compounds Alicyclics, including steranes, diterpanes and triterpanes
Aromatic fraction	Alkylaromatic hydrocarbons Naphthenic-aromatic hydrocarbons Lighter aromatic compounds containing sulphur (thiophenes)
Resins (NSO-compounds)	Higher fatty acids and alcohols Aliphatic and cyclic ketones Porphyrins
Asphaltenes	Asphaltenes

2.5 Biomarkers in crude oil

"Molecular fossils" or "biological markers" or "biomarkers" are compounds of lipid type, found in crude oils, which are in structure identical or very similar to the compounds found in biosphere (Eglinton, Calvin, 1967).

Review of the most significant biomarkers in organic geochemistry and their precusors is given in Table 2.

Table 2. The most important biological markers and their biological precursors (Vitorović, Jovančićević, 2005).

Biological markers	**Precursors**
n-Alkanes (> C_{22})	Waxes of terrestrial plants
n-Alkanes (C_{17}, C_{22})	Lipids of algae
Isoprenoids (< C_{20})	Chlorophyll
Isoprenoids (> C_{20})	Lipids or chlorophyll of hypersaline algae
Porphyrins	Chlorophyll
Steranes	Steroids
Triterpanes	Bacterial triterpenoids
Diterpanes	Constituents of plant resins
Naphthenoaromatic compounds	Steroids, triterpenoids

2.5.1. n-Alkanes

n-Alkanes occur in petroleum as homologous series in range from n-C_6 to n-C_{40}, but very often they can be found with more than 40 and even up to 110 carbon atoms (Killops et al., 2000). Potential biological precursors of n-alkanes can be found in virtually all extant organisms. Distribution and relative contents of normal alkanes in crude oil depends on the precursor organisms, thermal maturity and biodegradation.

n-Alkanes can be analysed by gas chromatography and by gas chromatography – mass spectrometry (SIM method; fragmentogram of ions m/z = 71; Figure 7). Using these results, different specific correlation parameters can be calculated and used to estimate origin, degree of thermal maturity and biodegradation level of crude oil.

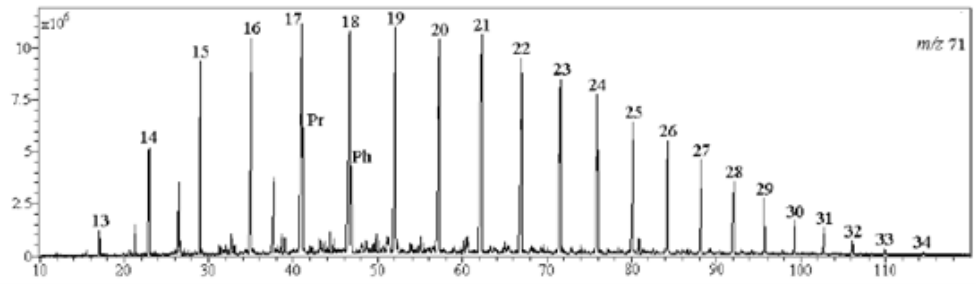

Figure 7. Gas chromatogram of alkane fraction of bitumen from the Valjevo-Mionica Basin, Serbia (Šajnović et al., 2012).

Using the distribution of odd and even n-alkane homologues of nonbiodegraded crude oils, a Carbon Preference Index (CPI) can be calculated. CPI is used as a measure of the strength of the odd-carbon predominance in n-alkane group. CPI is usually calculated using n-alkane range of C_{24}-C_{34} (Bray and Evans, 1961).

$$CPI = 1/2 \left(\frac{C_{25}+C_{27}+C_{29}+C_{31}+C_{33}}{C_{24}+C_{26}+C_{28}+C_{30}+C_{32}} + \frac{C_{25}+C_{27}+C_{29}+C_{31}+C_{33}}{C_{26}+C_{28}+C_{30}+C_{32}+C_{34}}\right)$$

A review of the most common applications of the CPI index and n-alkane maximum in organic geochemical interpretations is given in Table 3.

Table 3. CPI and *n*-alkane maximum of biolipid main fractions (a) geolipid fractions of recent sediments (b) and geolipid fractions of the ancient sediments (c)

		CPI	**Maximum**
a	High terrestrial plants	> 10	C_{25}-C_{29}
	Some marine algae	~ 1	C_{17}, C_{22}
	Many marine organisms	~ 1	C_{17}
	Planktons, bacteria	~ 1	C_{17}

b	Terrestrial recent sediments	1.5-2	C_{25}
	Marine recent sediments	~ 1	C_{17}, C_{22}
c	Terrestrial ancient sediments	1-1.5	C_{17}-C_{22}
	Marine ancient sediments	1	C_{17}

2.5.2. Isoprenoid alkanes

The second most abundant class of hydrocarbons in crude oils is group of regular acyclic isoprenoids (i.e. C_{10}, C_{11}, C_{13-16}, C_{18-21}). Among them, the most common and dominant are C_{19} (pristane) and C_{20} (phytane; Figure 8). Both of them originate from phytyl side chain of cholorophyll.

Reducing or anoxic conditions in sediments promote cleavage of the phytyl side chain to yield phytol, which undergoes reduction to dihydrophytol and then phytane. Oxic conditions promote competing conversion of phytol to pristane by oxidation of phytol to phytenic acid, decarboxylation to pristene and then reduction to pristane (Figure 8; Peters et al., 2005).

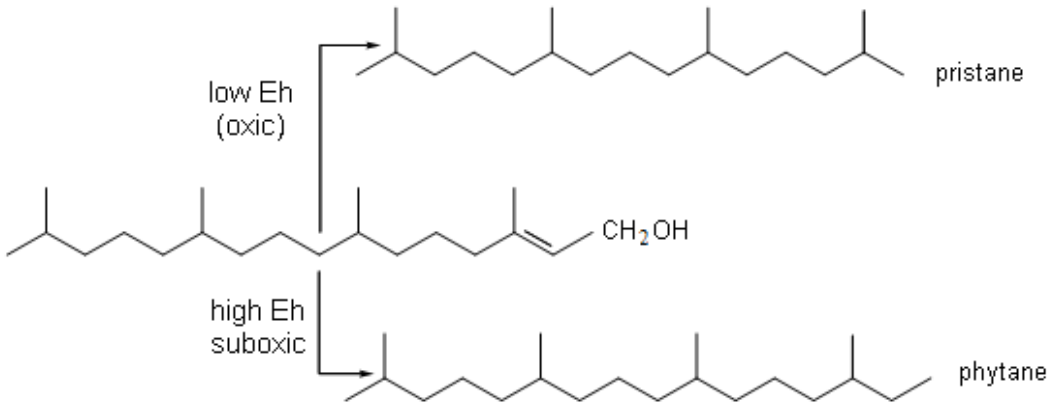

Figure 8. Diagenetic origin of pristane and phytane from phytyl side chain of cholorophyll (Peters et al., 2005).

Pristane and phytane are usually identified by GC or GC-MS analysis using ion fragmentograms m/z = 183, or using ion fragmentograms m/z = 71 with alkane fractions. Using these results a pristane/phytane (Pr/Phyt) ratio, a specific correlation parameters can be calculated. Pr/Phyt < 1 in crude oils indicates anoxic source-rock deposition, while Pr/Phyt > 1 indicates oxic deposition.

2.5.3. Polycyclic alkanes of terpane type

A wide range of triterpanes from C_{19} tricyclic to C_{30} pentacyclic homohopanes have been identified in crude oils. They are present in oils in trace amounts, and their concentration is expressed in ppm. Many terpanes in petroleum originate from bacterial (prokaryotic) membrane lipids (Ourisson, Albrecht, and Rohmer, 1982). These bacterial terpanes include several homologues series including acyclic, bicyclic (its origin is microbial), tricyclic, tetracyclic and pentacyclic compounds (Peters et al., 2005). Summary of most significant triterpanes identified in oil with their biological precursors, and characteristics of their depositional environments is given in Table 4.

Tri-, tetra- and pentacyclic triterpanes are usually identified by GC-MS or GC-MS-MS analysis using ion fragmentograms m/z = 191 (Figures 9 and 10). Based on the distribution and abundances of some of these compounds or their stereoisomers, numerous source and maturity parameters can be calculated. The highest significance in the organic geochemical interpretations have pentacyclic triterpanes.

Presence of oleanane, ursane and lupane is considered indicator of terrestrial origin. Presence of gammacerane is usualy interpreted as indicator of depositional environmnent related to the stratified water. Ratios of moretane/hopane, Ts/Tm and ratios of C_{31}- C_{35} 22R and 22S epimers are in organic geochemical interpretations considered reliable maturity indicators (Peters et al., 2005).

Table 4. Summary of crude oil triterpanes with biological precursors, and characteristics of their depositional environments (Peters, Moldowan, 1993).

Compound	**Biologic precursor**	**Environments of deposition**	**Literature**
C_{35}-hopane	bacteria	Marine, reductive conditions	Peters i Moldowan, 1991; Moldowan *et al.*, 1992
C_{29}-hopane	prokaryotes	Carbonate, salt	Clark and Philp, 1989
Gammaceran	Protozoa, bacteria	Marine, evaporite	Fu *et al.*, 1986; Venkatesan, 1989
C_{30}*17α(H)-diahopane	unknown	Continental, Oxic or oxidative	Peters and Moldowan, 1991
Oleanane	vascular plants, angiosperms	Continental Cretaceous age and younger	Ekweozor and Udo, 1988; Riva *et al.*, 1988
C_{24}-Tatracyclic terpane	unknown	different	Connan *et al.*, 1986; Philp i Gilbert, 1986
Tricyclic terpane	Bacteria, algae Tasmanites	Marine or lake	Albrecht, 1986; Simoneit *et al.*, 1993; Revill *et al.*, 1994

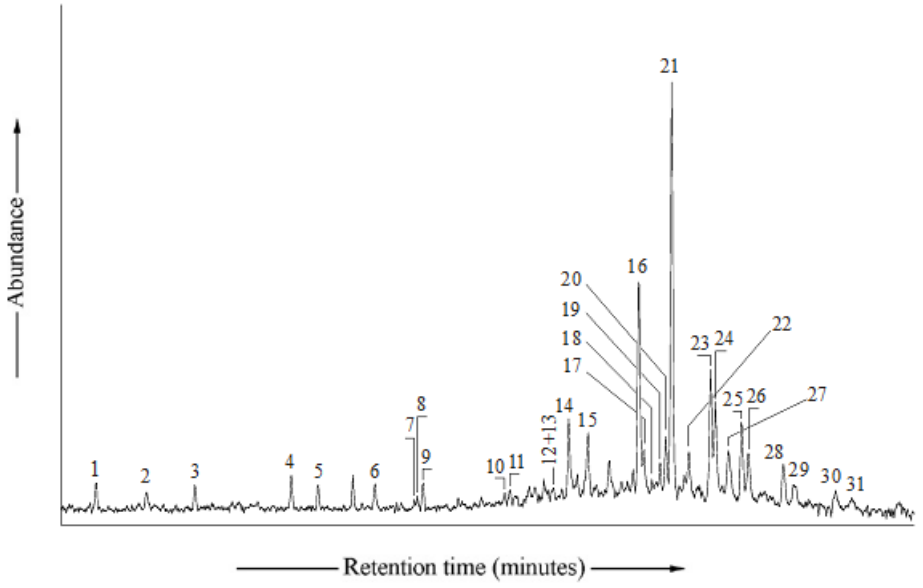

Figure 9. GC-MS fragmentograms of triterpanes *m/z* 191, from the Kikinda crude oil, Serbia (Šolević et al., 2008).

Table 5. Identification of the peaks in the chromatogram shown in Figure 9 (terpane fragmentogram *m/z* 191; Šolević et al., 2008).

Peak	**Compounds**
1	C_{19}-tricyclic terpane
2	C_{20}- tricyclic terpane
3	C_{21}- tricyclic terpane
4	C_{23}- tricyclic terpane
5	C_{24}- tricyclic terpane
6	C_{25}- tricyclic terpane
7	C_{24}-tetracyclic terpane
8	C_{26}22(S)- tricyclic terpane
9	C_{26}22(R)- tricyclic terpane
10	C_{28}22(S)- tricyclic terpane
11	C_{28}22(R)- tricyclic terpane
12	C_{29}22(S)- tricyclic terpane
13	C_{29}22(R)- tricyclic terpane
14	C_{27} 18α(H),22,29,30-trisnorneohopane, Ts
15	C_{27} 17α(H),22,29,30-trisnorhopane, Tm
16	C_{29} 17α(H)21β(H)-hopane
17	C_{29} 18α(H),30-norneohopane
18	C_{30} 17α(H)-diahopane
19	C_{29} 17β(H)21α(H)-moretane
20	Oleanane
21	C_{30} 17α(H)21β(H)-hopane
22	C_{30} 7β(H)21α(H)-moretane
23	C_{31} 17α(H)21β(H)22(S)-hopane
24	C_{31} 17α(H)21β(H)22(R)-hopane
25	Gammacerane
26	C_{32} 17α(H)21β(H)22(S)-hopane

27	C_{32} 17α(H)21β(H)22(R)-hopane
28	C_{33} 17α(H)21β(H)22(S)-hopane
29	C_{33} 17α(H)21β(H)22(R)-hopane
30	C_{34} 17α(H)21β(H)22(S)-hopane
31	C_{34} 17α(H)21β(H)22(R)-hopane

2.5.4. Steranes

Steranes in the C_{27}-C_{29} range are widely used in petroleum correlation studies and source rock studies. The steranes present in petroleum are derived from mixtures of sterols (stanols, stenols, stanons and stenons) occuring in plants and animals (Philp et al, 1985). Different sterols or steroids (stanols, stenols, stanons and stenons) of extinct organisms are decomposed by microorganisms during early diagenesis, at shallow depths and low temperatures and pressures, and through various processes of defunctionalisation are converted into sterenes and steranes (Vitorović, Jovančićević, 2005; Al-Arouri et al., 1998; George et al., 1998; Figure 11). Epimerization reactions and migration of methyl groups from one ring juncture to another produce new steranes from the original 5α, 14α, 17α (20R) steranes (Waples, Dougle 1985; Al-Arouri et al., 1998; George et al., 1998; Figure 11). Furthermore, epimerization at the C-20 position converts 20R epimer into a mixture of 20R and 20S stereoisomers. Epimerization can occur in other positions of sterane molecules, such as epimerization which occurs simultaneously in C-14 and C-17 positions to produce isokeletal steranes. Migration of methyl groups across a ring juncture leads to rearranged steranes, also called diasteranes (Waples, Dougle 1985).

The most significant steranes identified in crude oils, their biological precursors, and characteristics of their depositional environments are reviewed in Table 6. High abundance of C_{27} sterane indicates lacustrine source, C_{28} sterane indicates marine source and C_{29} terrigeneous source. High ratios of steranes/hopanes and diasteranes/steranes are indicative of shale sample, while low ratios point to carbonates (Peters et al., 2005; Hughes, 1984; Nasir et al., 2013). High

value of $\sum C_{27}$diasteranes/$\sum C_{27}$steranes indicate high maturity of petroleum and high content of clays in their source rocks (Peters et al., 2005).

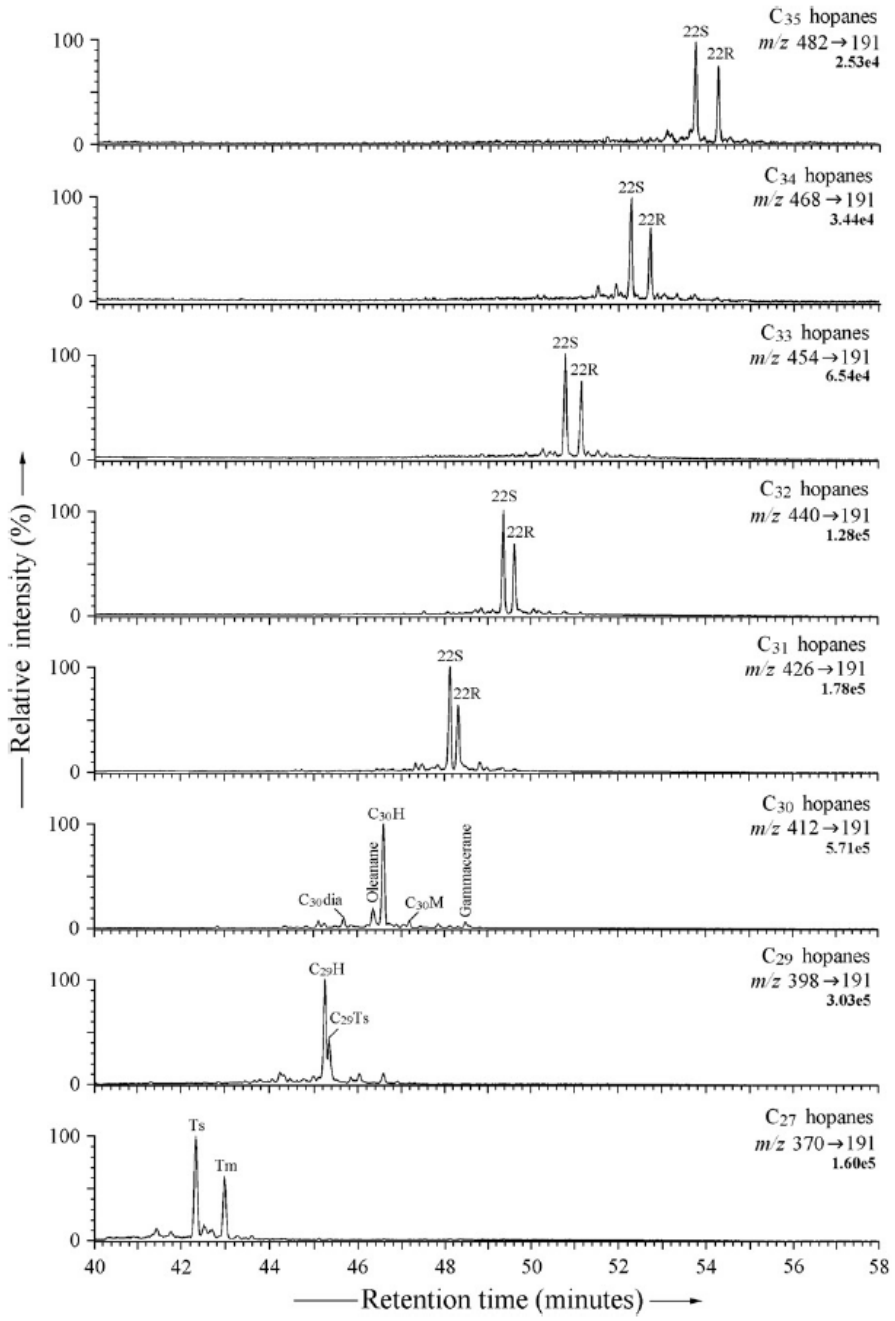

Figure 10. Analisys of C_{27} and C_{29}-C_{35} hopanes by GC-MS-MS technique (Šolević, et al., 2008).

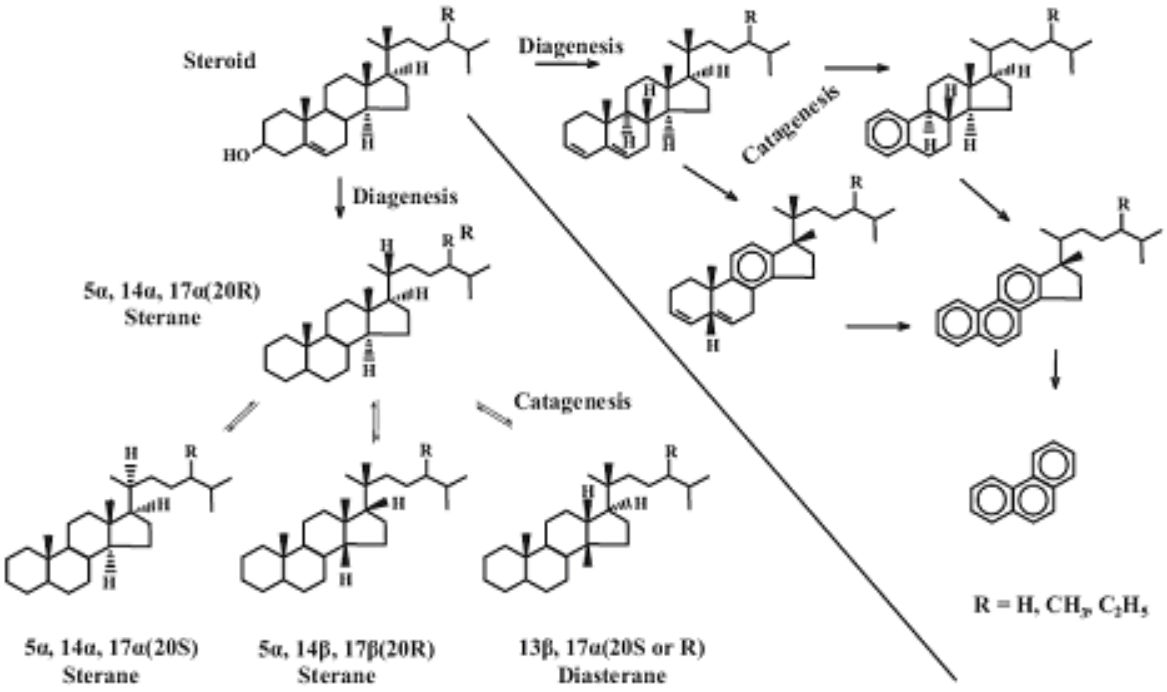

Figure 11. The most important structural and stereochemical changes of steroids in the geosphere (Al-Arouri et al., 1998; George et al., 1998).

Steranes in crude oils are found in trace amounts and their concentration is usually expressed in ppm (parts per million). Due to the low abundance of sterane biomarkers in crude oils, their identification and quantification requires application of GC-MS or GC-MS-MS analysis (ion fragmentogram m/z = 217 for steranes and m/z = 218 for diasteranes; Philp, 1985, Peters, Moldowan, 1993).

Typical example of sterane fragmentogram from the Kikinda crude oil is shown in Figure 12, and the corresponding peak identification is given in Table 7 (Šolević et al., 2008). GC-MS-MS technique allows the separation of the sterane carbon number and completely accurate quantification of all isomers. Using this instrumental technique C_{27}, C_{28}, C_{29} and C_{30}-steranes and diasteranes were identified in crude oils (Šolević et al., 2008; Figure 13).

Table 6. Review of petroleum sterane biological precursors, and characteristics of their environment of deposition (Peters, Moldowan, 1993).

Compound	**The biological precursor**	**Environments of deposition**	**Literature**
C_{27}-C_{29}- steranes	Algae and higher plants	different	Moldowan *et al.*, 1985; Volkman, 1986
C_{27}-C_{29}- diasteranes	Algae and higher plants	The rich clays	Rubinstein *et al.*, 1975
C30-4-desmethyl 24-n-propylcholestanes	Chrysophyta algae	Marine, Triassic age or younger	Moldowan *et al.*, 1985; Peters *et al.*, 1986
C_{28}-C_{30}- 4- methylsteranes	Dinoflagellates and some bacteria	Lake or marine, Triassic age or younger	Brassell *et al.*, 1986; Wolff *et al.*, 1986
C_{30}- dinosteranes	dinoflagellate	Marine, Triassic age or younger	Summons *et al.*, 1987; Goodwin *et al.*, 1988
C_{21}-pregnane and C_{22}-homopregnane	unknown	hypersaline	ten Haven *et al.*, 1986

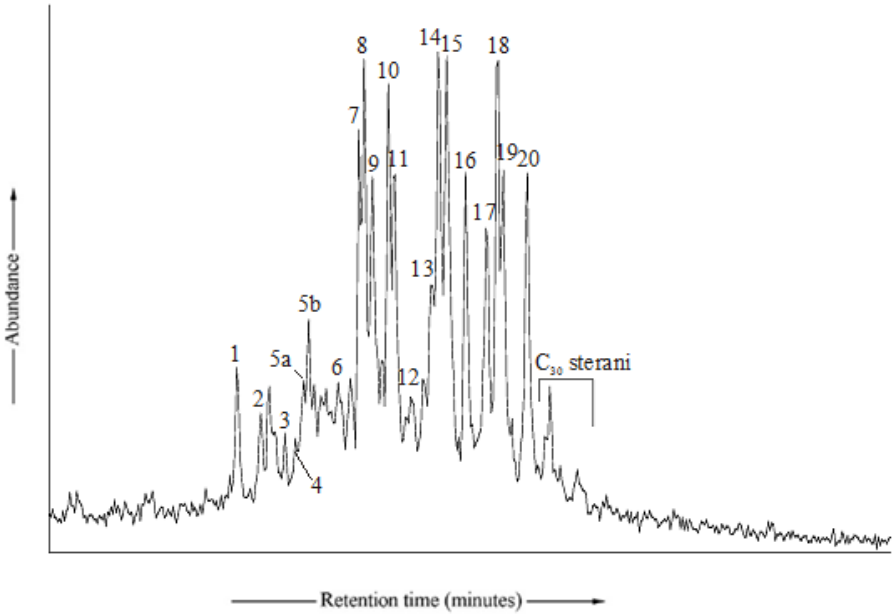

Figure 12. GC-MS fragmentograms of staranes (*m/z* = 217) from the Kikinda crude oil, Serbia (Šolević et al., 2008).

Table 7. Identification of the peaks in the chromatogram shown in Figure 12.

Peak	Compounds
1	C_{27} 13β(H)17α(H)20(S)-diasterane
2	C_{27} 13β(H)17α(H)20(R)-diasterane
3	C_{27} 13α(H)17β(H)20(S)-diasterane
4	C_{27} 13α(H)17β(H)20(R)-diasterane
5a	C_{28} 13β(H)17α(H)20(S)24(S)-diasterane
5b	C_{28} 13β(H)17α(H)20(S)24(R)-diasterane
6a	C_{28} 13β(H)17α(H)20(R)24(S)-diasterane
6b	C_{28} 13β(H)17α(H)20(R)24(R)-diasterane
7	C_{28} 13α(H)17β(H)20(S)-diasterane + C_{27} 14α(H)17α(H)20(S)-sterane
8	C_{29} 13β(H)17α(H)20(S)-diasterane + C_{27} 14β(H)17β(H)20(R)-sterane
9	C_{28} 13α(H)17β(H)20(R)-diasterane + C_{27} 14β(H)17β(H)20(S)-sterane
10	C_{27} 14α(H)17α(H)20(R)-sterane
11	C_{29} 13β(H)17α(H)20(R)-diasterane
12	C_{29} 13α(H)17β(H)20(S)-diasterane
13	C_{28} 14α(H)17α(H)20(S)-sterane
14	C_{29} 13α(H)17β(H)20(R)-diasterane + C_{28} 14β(H)17β(H)20(R)-sterane
15	C_{28} 14β(H)17β(H)20(S)-sterane
16	C_{28} 14α(H)17α(H)20(R)-sterane
17	C_{29} 14α(H)17α(H)20(S)-sterane
18	C_{29} 14β(H)17β(H)20(R)-sterane
19	C_{29} 14β(H)17β(H)20(S)-sterane
20	C_{29} 14α(H)17α(H)20(R)-sterane

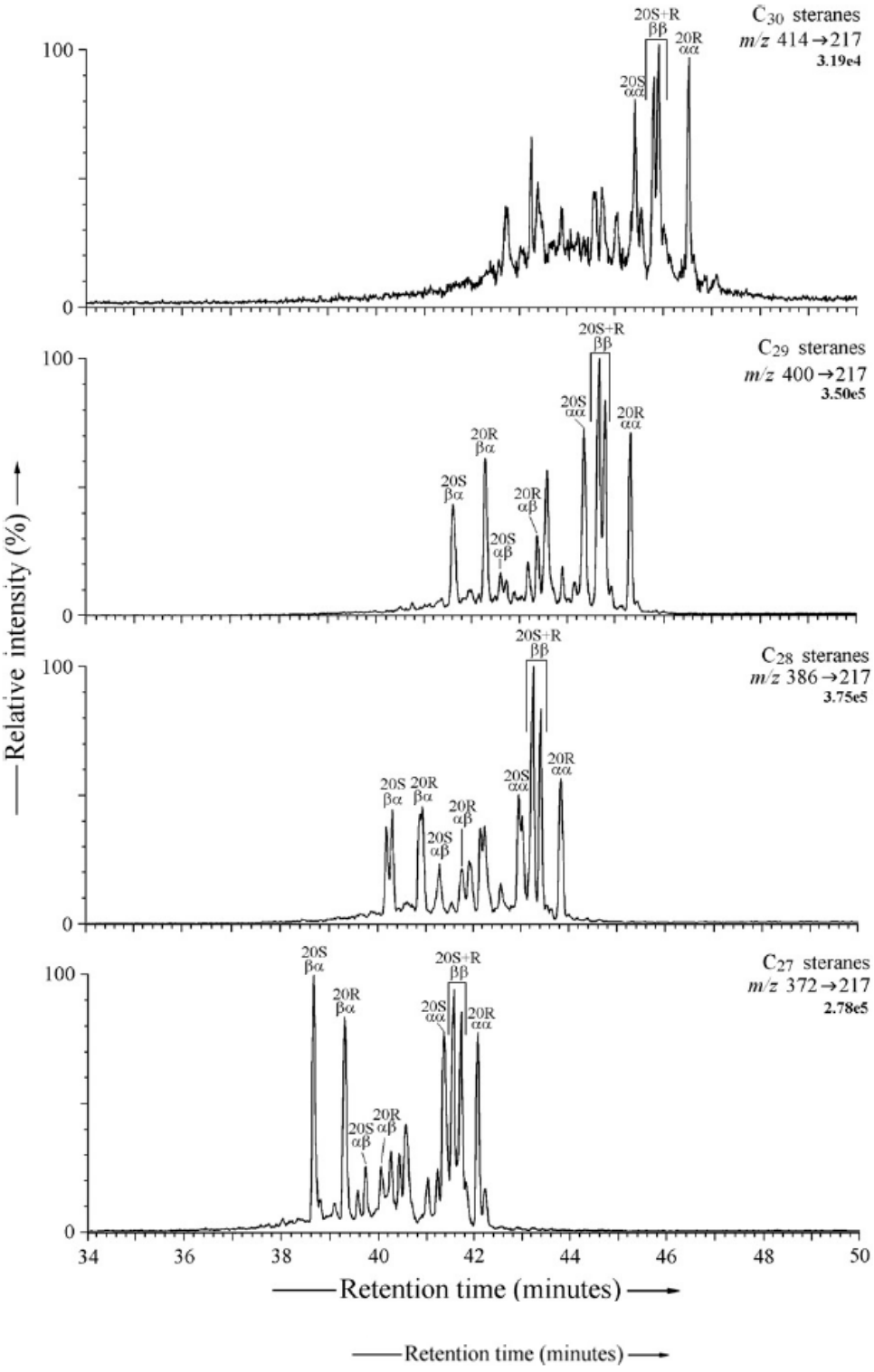

Figure 13. Identification steranes and diasteranes (C_{27}-C_{30}) by GC-MS-MS technique (Šolević, et al., 2008a).

2.5.5. Aromatic hydrocarbons in petroleum

Aromatic hydrocarbons (or aromatics, arenes) represent one of the most abundant group of compounds in crude oils. Their concentrations range from 15 % to 35 % and sometimes even reach the value of 50 % (Schwarzbauer, Jovančićević, 2015). Mono-, di-, tri- and polycyclic aromatic hydrocarbons have been identified in crude oils. Distribution of aromatic rings in crude oils is calculated as follows: 67 % of benzene, 18 % naphthalene, 8 % phenanthrene, 3 % chrysene and benzofluorene, 2% pyrene and less than 1 % of anthracene rings (Kuklinski et al., 1983; Ramadan, 2013). Monocyclic aromatic hydrocarbons are usually the most abundant aromatics in crude oils, while di- and triaromatics are represented in trace amounts. Distribution and abundance of di- and tricyclic aromatic hydrocarbons are often used for the assessment of thermal maturity level (Alexander et al., 1984, 1985; George et al., 1998, 2001; Golovko, 1997; Ivanov, Golovko, 1992; Radke et al., 1982a,b; Radke, 1987; Simons et al., 2003; Ramadan, 2013).

2.5.5.1. Bicyclic aromatic hydrocarbons

Content of bicyclic aromatic hydrocarbons in crude oils ranges from 1 % to 10 % (Golovko et al., 2002). A significant amounth of bicyclic aromatic hydrocarbons identified in oils is formed by decomposition during catagenesis (Schwarzbauer, Jovančićević, 2015).

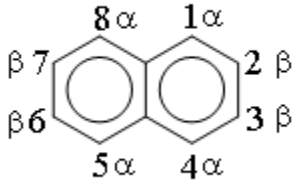

Figure 14. Structural formula of naphthalene

Alkylnaphthalenes are the most abundant (up to 90%) bicyclic aromatic hydrocarbons in crude oils. 1- and 2- methylnaphthalenes (MN), dimethylnaphthalene (DMN) and trimethylnaphthalene (TMN), with their isomers are identified in crude oils (Table 8). Except from naphthalene isomers, crude oils contain in much smaller concentrations biphenyls, biphenyl-alkanes and naphthenic-diarenes with maximum 6 - 8 saturated rings (Cumbers et al., 1987; Golovko, 2001; Golovko, Koržov, 1992; Grice et al., 1999a; Kamyanov et al., 1982; Schwarzbauer, Jovančićević, 2015).

Development of instrumental techniques enabled identification tetramethylnaphthalenes (TeMN) and pentamethylnaphthalenes (PMN), with their alkylated isomers (Table 8; van Aarssen et al., 1999; Bastow et al., 1998). Except from methylnaphthalenes, Ethylnaphthalenes (EN), n-Alkylnaphthalenes C_{13}-C_{32} are also present in crude oils (Table 8).

Table 8. Review of the most abundant alkylnaphthalenes in bicyclic aromatic fraction of crude oils.

Compounds	Isomers
Methylnaphthalenes (MN)	1-, 2-MN
Dimethylnaphthalenes (DMN)	1,2-, 1,3-, 1,4-, 1,5-, 1,6-, 1,7-, 1,8-, 2,3-, 2,6-, 2,7-DMN
Trimethylnaphthalenes (TMN)	1,2,4-, 1,2,5-, 1,2,6-, 1,2,7-, 1,3,5-, 1,3,6-, 1,3,7-, 1,6,7-, 2,3,6-TMN
Tetramethylnaphthalenes (TeMN)	1,2,3,5-, 1,2,3,6-, 1,2,3,7-, 1,2,4,6-, 1,2,4,7-, 1,2,5,6-, 1,2,5,7-, 1,2,6,7-, 1,3,5,7-, 1,3,6,7-, 1,4,6,7-, 2,3,6,7-TeMN

Pentamethylnaphthalenes (PMN)	1,2,3,5,6-, 1,2,3,5,7-, 1,2,3,6,7-, 1,2,4,6,7-PMN
Ethylnaphthalenes (EN)	1-, 2-EN
n-Alkylnaphthalenes C_{13}-C_{32}	1-, 2-*n*-propylnaphthalene – 1-, 2-*n*-dodecylnaphthalene

GC and GC-MS analyses are the methods used for identification and quantification of dicyclic aromatic hydrocarbons (Mrkić et al., 2011; Figure 15).

The largest number of maturation parameters of the dicyclic aromatic fraction is based on the distribution and abundance of naphthalene homologs, since these hydrocarbons are the most common diarenes in oil.

The first defined maturity naphthalene parameter was methylnaphthalene ratio, MNR = 2-MN / 1-MN (Radke et al., 1982). In a large number of papers it has been proven that the equilibrium of isomerisation 1-MN → 2-MN dose not establish even at the highest degrees of the thermal maturity. Test of 29 samples of coals of different ages from the regions of West Canada, Germany and Japan, resulted in establishment of two similar linear dependences of the MNR parameter with the measured vitrinite reflection index, Ro (Radke et al., 1984). They are represented by the following equations:

a) MNR = 3.31xRo - 2.14 and b) MNR = 5.88xRo - 4.82.

Due to the fact that 1,5-dimethylnaphthalene (DMN) is one of the isomers of the α-type that can be easily identified in petroleum, the first defined dimethylnaphthalene parameter was the dimethylnaphthalene ratio DNR = (2,6- + 2,7-DMN) / 1,5-DMN (Radke et al., 1982).

This ratio is based on isomerization of α-, 1,5-dimethylnaphthalene into thermodynamically stable β-isomers, 2,6- and 2,7-dimethylnaphthalene. For the same group of coal samples, as MNR parameter, two similar linear dependences were established between DNR and measured index of vitrinite, Ro (Radke et al., 1984):

a) DNR = 14.8xRo - 12.0 and b) DNR = 21.7xRo - 19.3.

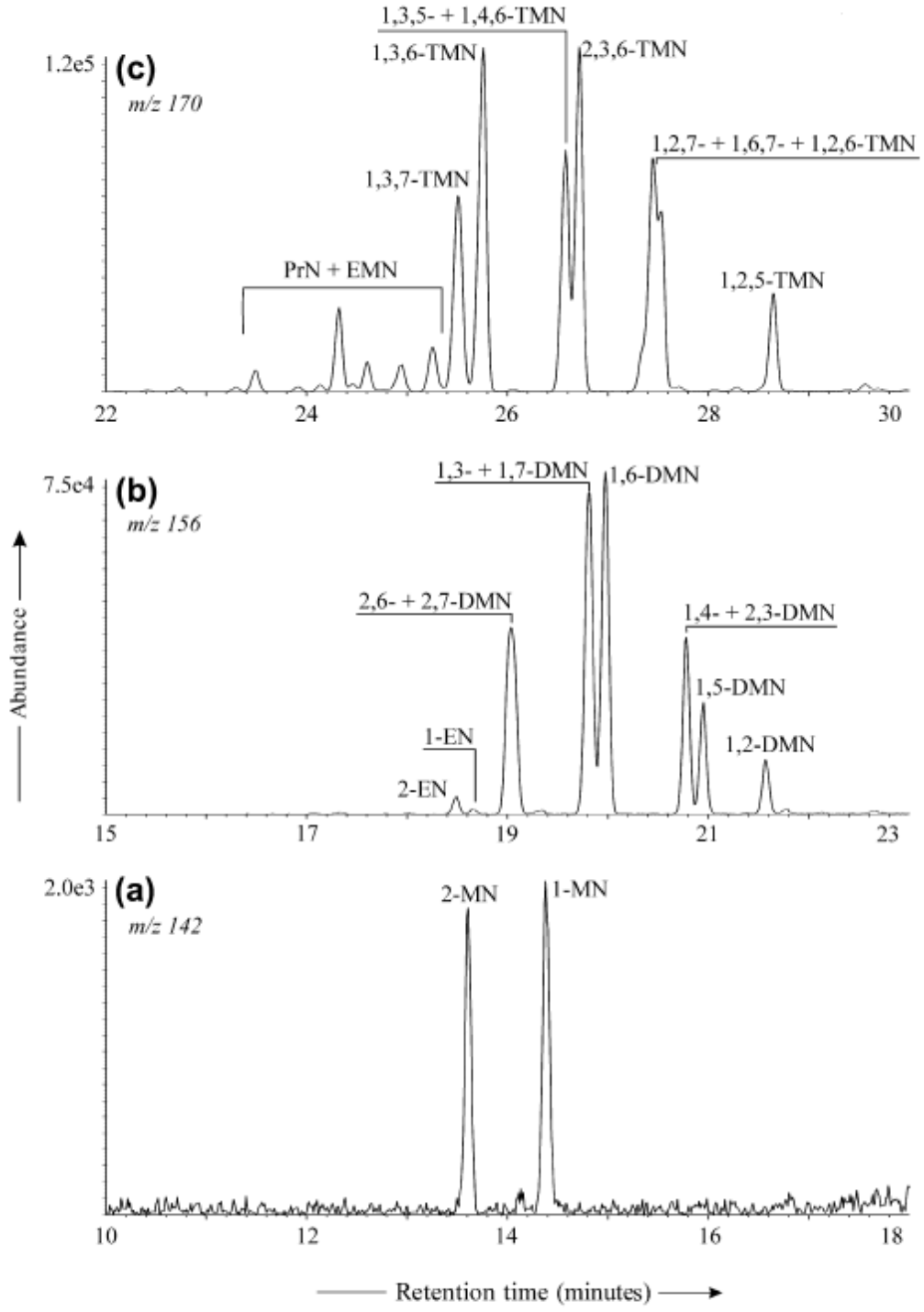

Figure 15. GC-MS chromatograms of methylnaphthalenes (m/z = 142), dimethylnaphthalenes and ethylnaphthalene (m/z = 156), trimethylnaphthalenes (m/z = 170) from the Pannonian Basin, Serbia (Mrkić et al., 2011).

Methylnaphthalene and dimethylnaphthalene, maturation parameters based on the distribution and abundances of bicyclic aromatic compounds in oils are shown in Table 9 (Radke et al., 1982b; Alexander et al., 1984; Yawanarajah, Kruge, 1994; Golovko, 1997; Ahmed, George, 2004; Stojanović et al., 2007).

Table 9. Review of maturation parameters based on the distribution and abundances of bicyclic aromatic compounds in oils.

Parameter	Abbr.	Formula	Author
Methylnaphthalene ratio	MNR	2-MN/1-MN	Radke *et al*., 1982b
Dimethylnaphthalene ratio 1	DNR 1	1,8-DMN/(ΣDMN in dicyclic aromatic fraction)	Alexander *et al*., 1984
Dimethylnaphthalene ratio 2	DNR 2	(2,6-+2,7-DMN)/1,5-DMN	Radke *et al*., 1982b
Dimethylnaphthalene ratio	DMNR	(2,6-+2,7-DMN)/(1,4-+1,5-+1,6-+2,3-+2,6-+2,7-DMN)	Yawanarajah , Kruge, 1994
α/β Dimethylnaphthalene index 1	α/β DN 1	(1,4-+1,5-+1,8-DMN)/ (2,3-+2,6-+2,7-DMN)	Golovko, 1997
Dimethylnaphthalene ratio	DNr-x	(2,6-+2,7-DMN)/1,6-DMN	Ahmed , George, 2004
Dimethylnaphthalene ratio	DNx	(1,3-+1,6-+1,7-DMN)/ (1,4-+1,5-+2,3-DMN)	Stojanović *et al*., 2007
Trimethylnaphthalene ratio 1	TNR 1	2,3,6-TMN/(1,3,5-+1,4,6-TMN)	Alexander *et al*., 1985
Trimethylnaphthalene ratio 2	TNR 2	(1,3,7-+2,3,6-TMN)/ (1,3,5-+1,3,6-+1,4,6-TMN)	Radke *et al*., 1986
Trimethylnaphthalene	TNR 3	1,3,6-TMN/1,2,5-TMN	Strachan *et al*.,

ratio 3			1988
α/β Trimethylnaphthalene index 1	α/β TN 1	(1,2,4-+1,2,5-TMN)/ (2,3,6-+1,2,7-+1,6,7-TMN)	Golovko, 1997
α/β Trimethylnaphthalene index 2	α/β TN 2	1,2,5-TMN/1,2,7-TMN	Golovko, 1997
Trimethylnaphthalene ratio	TMNr	1,3,7-TMN/(1,2,5-+1,3,7-TMN)	van Aarssen *et al*., 1999
Trimethylnaphthalene ratio	TNy	(1,3,6-+1,3,7-TMN)/ (1,3,5-+1,4,6-TMN)	Stojanović *et al*., 2007
Tetramethylnaphthalene ratio	TeMNR	2,3,6,7-TeMN/1,2,3,6-TeMN	George *et al*., 1998
Tetramethylnaphthalene ratio	TeMNr	1,3,6,7-TeMN/(1,2,3,5-+ 1,2,5,6-+1,3,6,7-TeMN)	George *et al*., 1998
Pentamethylnaphthalene ratio	PNR	1,2,4,6,7-PMN/ (1,2,3,5,6-+1,2,4,6,7-PMN)	Bastow *et al*., 1998
Ethylnaphthalene ratio	ENR	2-EN/1-EN	Radke *et al*., 1982b
Isocadalene/cadalene ratio	I/I+C	I/I+C	Alexander *et al*., 1994

2.5.5.2. Tricyclic aromatic hydrocarbons

Abundance of tricyclic aromatic hydrocarbons in petroleum is lower than abundance of dicyclic aromatic fractions (Grice et al., 1999b; Radke, 1987; Ramadan, 2013). Similarly to the

dicyclic aromatic hydrocarbons, triarenes also are formed mainly by degradation of kerogen during catagenesis (Schwarzbauer, Jovančićević, 2015).

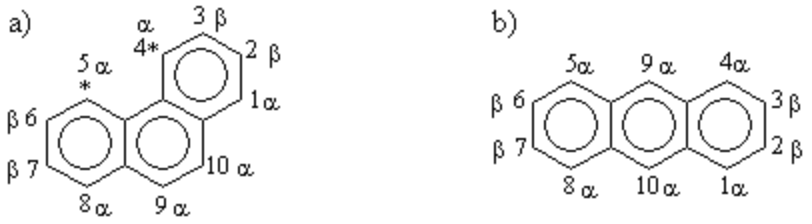

Figure 16. Structural formulas of phenanthrene (a) and anthracene (b).

In a tricyclic aromatic fraction of oil, the most abundant are phenanthrene (Figure 16) and its methyl derivatives. Five isomers of methylphenanthrenes, 4 isomers of ethylphenanthrenes and numerousisomers of dimethyl- and trimethil phenanthrenes are identified in crude oils (Golovko, 1997; Radke, 1987).

Table 10. Review of the most abundant alkylphenanthrenes in tricyclic aromatic fraction of crude oils.

Compounds	Isomers
Methylphenanthrenes (MP)	1-, 2-, 3-, 4-, 9-MP
Dimethylphenanthrenes (DMP)	1,2-, 1,3-, 1,6-, 1,7-, 1,8-, 1,9-, 2,3-, 2,6-, 2,7-, 2,9-, 2,10-, 3,5-, 3,6-, 3,9-, 3,10-, 4,9-DMP
Trimethylphenanthrenes (TMP)	1,2,3-, 1,2,8-, 1,3,6-, 1,3,7-, 1,3,8-, 1,3,9-, 1,7,10-, 2,3,6, 2,3,7-, 2,3,10-, 2,6,10-, 2,7,10-, 2,8,10-, 3,8,10-TMP
Ethylphenanthrenes (EP)	1-, 2-, 3-, 9-EP

Alkylphenanthrenes, naphthenic-phenanthrenes are also found in crude oils, but in smaller quantities (Golovko, 2001; Kamyanov, 1996; Petrov, 1984; Simoneit, 1977). Anthracene (Figure 16) and its alkyl-derivates are usually found in very low concentrations in crude oils (Schwarzbauer, Jovančićević, 2015).

GC and GC-MS analyses are used for the identification and quantification of tricyclic aromatic hydrocarbons (Figure 17; Mrkić et al., 2011).

Most of the parameters based on the distribution and abundances of tricyclic aromatic compounds are dependent on distribution of phenanthrene homologous series (Table 10). Methylphenanthrene dealkylation processes and $\alpha \rightarrow \beta$ isomerization are the one most often used for assessment of petroleum thermal maturity (Table 10; Angelin et al., 1983; Ishiwatari, Fukushima, 1979; Kvalheim et al., 1987; Radke, 1987; Radke et al., 1982a,b; Stojanović et al., 2001; Wilhelms et al., 1998).

The first defined phenanthrene maturation parameter based on the distribution and abundances of tricyclic aromatic compounds is methylphenanthrene index MPI 1:

$$MPI\ 1 = 1{,}5x(2\text{-}+3\text{-}MP)/(1\text{-}+9\text{-}MP+P)$$

During the study of sedimentary formations from the West Canadian basin, which predominantly contained type III kerogen, a significant agreement was found between MPI 1 and the measured vitrinite index Ro (Radke et al., 1982):

$$\%\ Rc = 0{,}40 + 0{,}60MPI\text{-}1.$$

Additionally, in order to classify the bitumen of sediments according to maturation, treshold values for MPI 1 and Ro parameters are proposed. They are represented by the following equations:

$Ro = 0{,}7(\pm 0{,}05)xMPI\ 1 + 0{,}22(\pm 0{,}04)$ (Boreham *et al*., 1988) and

$Ro = 0{,}291xMPI\ 1 + 0{,}293$ (Chandra *et al*., 1994).

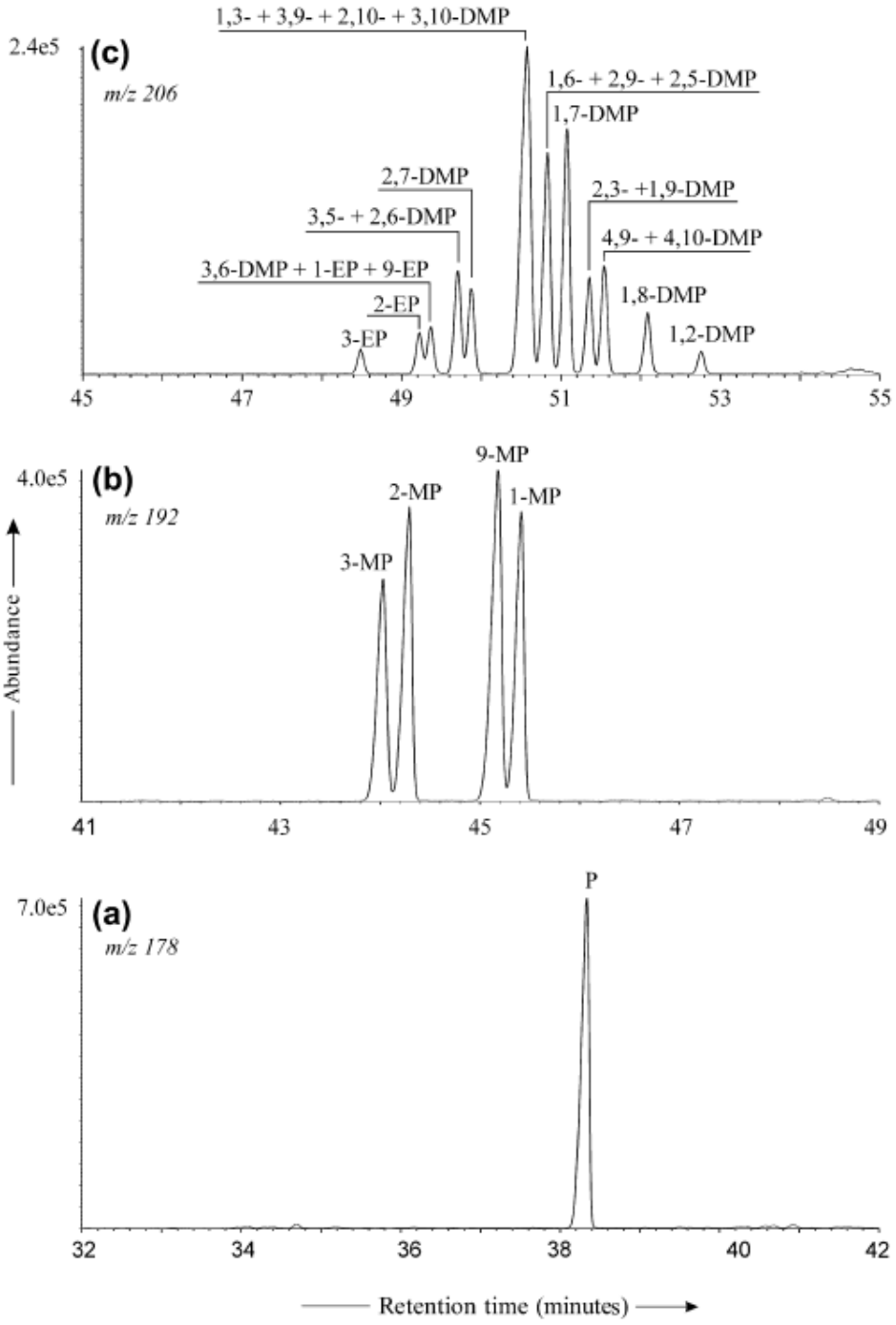

Figure 17. GC-MS chromatograms of phenanthrenes (P) (m / z = 178), Methylphenanthrenes (MP) (m / z = 192), Dimethylphenanthrenes (DMP) and Ethylphenanthrenes (EP) (m / z = 206) from the Pannonian Basin, Serbia (Mrkić et al., 2011).

Table 11. Review of maturation parameters of tricyclic aromatic fraction.

Parameter	Abbr.	Formula	Author
Methylphenanthrene index 1	MPI 1	1,5 · (2-+3-MP)/(1-+9-MP+P)	Radke *et al*., 1982a
Methylphenanthrene index 2	MPI 2	3 · 2-MP/(1-+9-MP+P)	Radke, 1987; Garrigues *et al*., 1988
Methylphenanthrene index 3	MPI 3	(2-+3-MP)/(1-+9-MP)	Angelin *et al*., 1983; Radke, 1987
β-Methylphenanthrene distribution fraction	MPDF	(2-+3-MP)/(1-+2-+3-+9-MP)	Kvalheim *et al*., 1987
Methylphenanthrene distribution fraction	F1	(2-MP + 3-MP)/ΣMPs	Kvalheim *et al*., 1987
Methylphenanthrene distribution fraction	F2	2-MP / ΣMPs	Kvalheim *et al*., 1987
Methylphenanthrene ratio 1	MPR 1	2-MP/1-MP	Radke *et al*., 1982b
Methylphenanthrene ratio 2	MPR 2	2-MP/9-MP	Radke *et al*., 1982b
3-Methylphenanthrene to retene ratio	/	3-MP/Retene	Wilhelms *et al*., 1998
Dimethylphenanthrene index 1	DMPI 1	4 · (2,6-+2,7-+3,5-+3,6-DMP+1-+2-+9-EP)/(P+1,3-+1,6-+1,7-+2,5-+2,9-+2,10-+3,9-+3,10-DMP)	Radke *et al*., 1982a
Dimethylphenanthrene index 2	DMPI 2	(2,6-+2,7-+3,5-DMP)/(1,3-+1,6-+2,5-+2,9-+2,10-+3,9-+3,10-DMP)	Radke *et al*., 1982b

2.5.5.3. Aromatic sulphur compounds in crude oil

Crude oil usually contains no more than 0.5 % of sulphur, although its content in some crude oils can reach up to 7 % (Vitorović, Jovančićević, 2005). The bulk of sulphur is built in asphaltene structures. However, some lighter sulphur compounds are found within malthene fraction of crude oils. Among them, the most important ones are benzothiophenes and dibenzothiophenes (Figure 18).

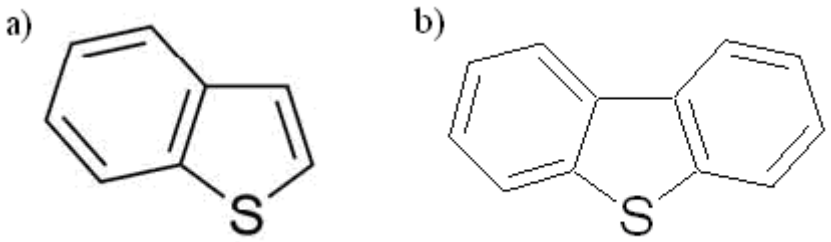

Figure 18. Structural formulas of benzothiophene (a) and dibenzothiophene (b)

The most abundant aromatic sulphur compounds in aromatic fraction of crude oils usually are dibenzothiophene and its methyl- and dimethyl-derivates. These compounds are produced by degradation of kerogen during the phase of catagenesis (Schwarzbauer, Jovančićević, 2015).

GC and GC-MS analyses are the instrumental techniques used for identification of aromatic sulphur compounds (Chakhmakhchev et al., 1997; Radke, 1988; Radke et al., 1986; Requejo et al., 1996). Characteristic m/z values of ion fragmentograms are: 184 for dibenzothiophene, 198 for methyldibenzothiophenes and 212 for dimethyldibenzothiophenes and ethyldibenzothiophenes, which correspond to their molecular masses.

Distribution and abundances of these compounds in crude oils are used for assessment of conditions in depositional environment, source rock lithology and thermal maturity level.

2.6. Statistical methods

Over the years, different statistical methods have become irreplaceable tool in organic geochemical analyses and interpretations. In this thesis two approaches were applied which are considered the best in the method comparison studies (Choudhary, Nagaraja, 2007): concordance correlation coefficient and mean-difference plot.

2.6.1. Concordance correlation coefficient

The concordance correlation coefficient (CCC), ρc was introduced and developed by Lin (Lin, 1989; Lin, 2000) as a measure of agreement between paired continuous measurements obtained by two analysts or by two measurement methods. This coefficient can be calculated as a product of two components:

$$\rho c = \rho \times Cb$$

The term ρ is the Pearson product-moment correlation coefficient. Being a measure of the closeness (or distance) of the results to the best-fit line, Pearson ρ is interpreted as a measure of precision.

The term Cb is a bias correction factor, interpreted as a measure of accuracy. It determines how far the best-fit line deviates from the line of perfect concordance (i.e., the line at 45° on a square scatter plot). The bias can have values: $0 < Cb \leq 1$. When Cb = 1, the best-fit line coincides with the 45° line. The lower the value of Cb, the greater the deviation is from the 45° line.

Similar to other correlation coefficients, ρc can have values between -1 and +1. ρc = +1 means perfect concordance; ρc = -1 means perfect negative concordance and ρc = 0 means no correlation (no linear relationship exists between two continuous variables). Regarding the values between 0 and ±1, some authors suggested different magnitude guidelines to express the strength of the agreement (Altman, 1991; McBride, 2005). However, it should be emphasized that the extent of the agreement depends on the samples to be analyzed, the methods to be used

and the features to be compared. Because of that there are no universal scales in the method comparison studies, but they are rather arbitrary and might be quite different from one case to another.

2.6.2. Mean-difference plot

The mean-difference plot is a graphical method to evaluate the agreement between two different instruments or two measurements techniques. This approach is based on the construction and the analysis of the plot, which is in the literature known as Tukey mean-difference plot (Cleveland, 1994; Chambers et al., 1983) or the Bland–Altman plot (Altman, Bland, 1983). The plot is constructed as a difference of two paired measurements against their average. Usually, at least three horizontal lines are drawn within this plot: the line at the mean difference, and the lines for the 95 % confidence interval for the mean (the mean difference ±1.96 times the standard deviation of the differences). The former two lines are called "limits of agreement", and they tell us how far apart the measurements by two methods (or two instruments) are more likely to be for most individuals.

The next step is a visual and the statistical analysis of the results in order to identify outliers and/or systematic bias between the paired measurements.

If a 1-sample t-test, shows that the mean value of the difference does not differ significantly from 0, this indicates a good agreement between the two methods and that they may be used interchangeably. If a 1-sample t-test, reveals that the mean value of the difference differs significantly from 0, this indicates the presence of fixed or proportional bias, meaning that the methods do not agree equally through the range of measurements.

The visual analysis of the results is probably the most important part of the method comparison studies. The purpose of this analysis is to estimate the degree of agreement (or disagreement) between two methods taking into the account the analytical significance of the difference between the results for the analyzed set of parameters, the precision of the analytical methods and the instruments used, and the nature of the samples.

3. Geological and petrological characteristics of the investigated oil fields

The crude oil samples investigated in this thesis originate from different parts of the Sirt basin in Libya. The Sirte (Sirt) basin is a prolific hydrocarbon basin in Libya. It is located on the northern margin of the African plate, covering an area of approximately 600.000 km^2 in north central Libya (Fig 19). Over twenty-three large oil fields and sixteen giant oil fields occur in this province (Ahlbrandt, 2001).

The Libyan crude oils investigated in this research originate from the oil fields: Amal, En Naga, Intisar, Messla, Nafoora, Samah, Sarir C, Waha and Zelten.

3.1. Geology and Petroleum Systems of the Sirte Basin

Libya is situated on the Mediterranean foreland of the Africa Shield. The northern part of the African continent has been center of a number of tectonic events within a north–south-directed compressional stress field (Ahlbrandt, 2001; Wennekers et al., 1996; Hassan et al., 2014).

North Africa (including Libya) underwent tectonic subsidence during the Late Cretaceous as a result of reversed dextral shear along the trans-tensional plate boundary of the European and African plates. As a result of these tectonic events, there are five major onshore sedimentary basins in Libya: the Sirt Basin, the Murzuq Basin, the Kufrah Basin, the Ghadamis Basin, and the Cyrenaica Platform (Figure 19; Gumati et al., 1991a; Hassan et al., 2014). Offshore is tectonically active area along the north-western coastline, and lies in the Tripolitana Basin (Figure 19).

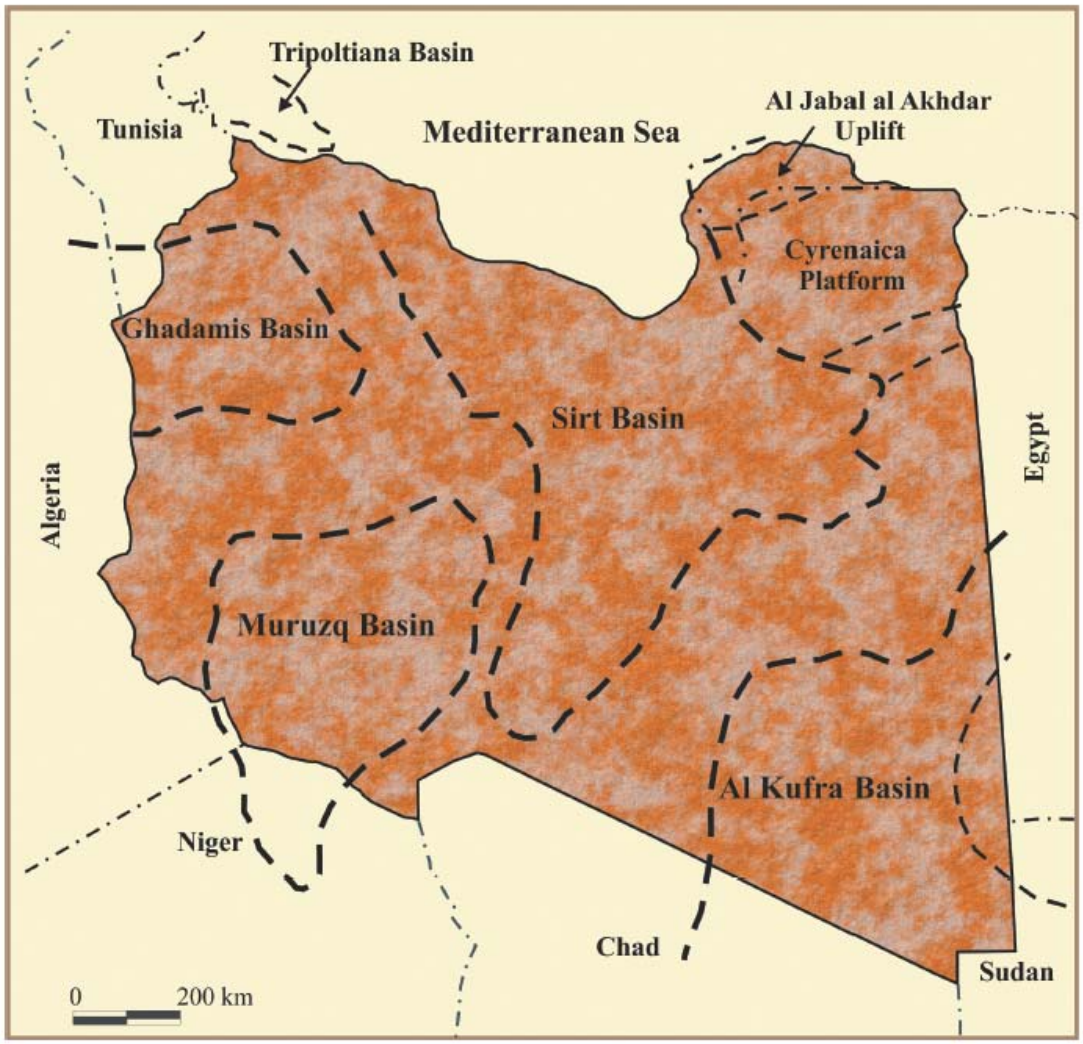

Figure 19. The geological basins of Libya (Hassan et al., 2014).

The Sirt basin is characterized by a Mesozoic-Cenozoic basin-fill, and a series of platforms and deep troughs (Gumati et al., 1996).

The Mesozoice Cenozoic systems of the Sirte basin are sourced by Upper Cretaceous to Oligocene shales that feed fractured basement and Cretaceous to Oligocene clastic and carbonate reservoirs in tilted fault block, drapes, horst, and Palaeocene reef in addition to stratigraphic traps (Abdunaser, 2015).

The Sirt Basin is unusual in that oil is produced from rocks of widely differing ages, including Precambrian (fractured basement), Cambrian–Ordovician, Triassic, Early and Late Cretaceous, Paleocene, and Eocene (Figure 20; Ahlbrandt, 2001; Hassan et al., 2014). The

Cambrian–Ordovician sandstone and quartzite are proven reservoirs in the Augila, Nafoora, and Amal fields. On the Bayda Platform, the Samah field is partly producing from the Ordovician Gargaf quartzite (Hassan et al., 2014). The Lower Cretaceous Nubian Sandstone (or Sarir Sandstone) forms the main reservoir for major giant oil fields (Abu-Attifel, Sarir and Messlah) (Clifford et al 1986). In the Sirt Basin some oil fields are also produced from carbonates of the Paleocene Zeltan Formation and Eocene carbonates, such as Intisar and Waha oil fields. The Zelten oil field (now known as the Nasser field) is produced from limestones of the upper Paleocene.

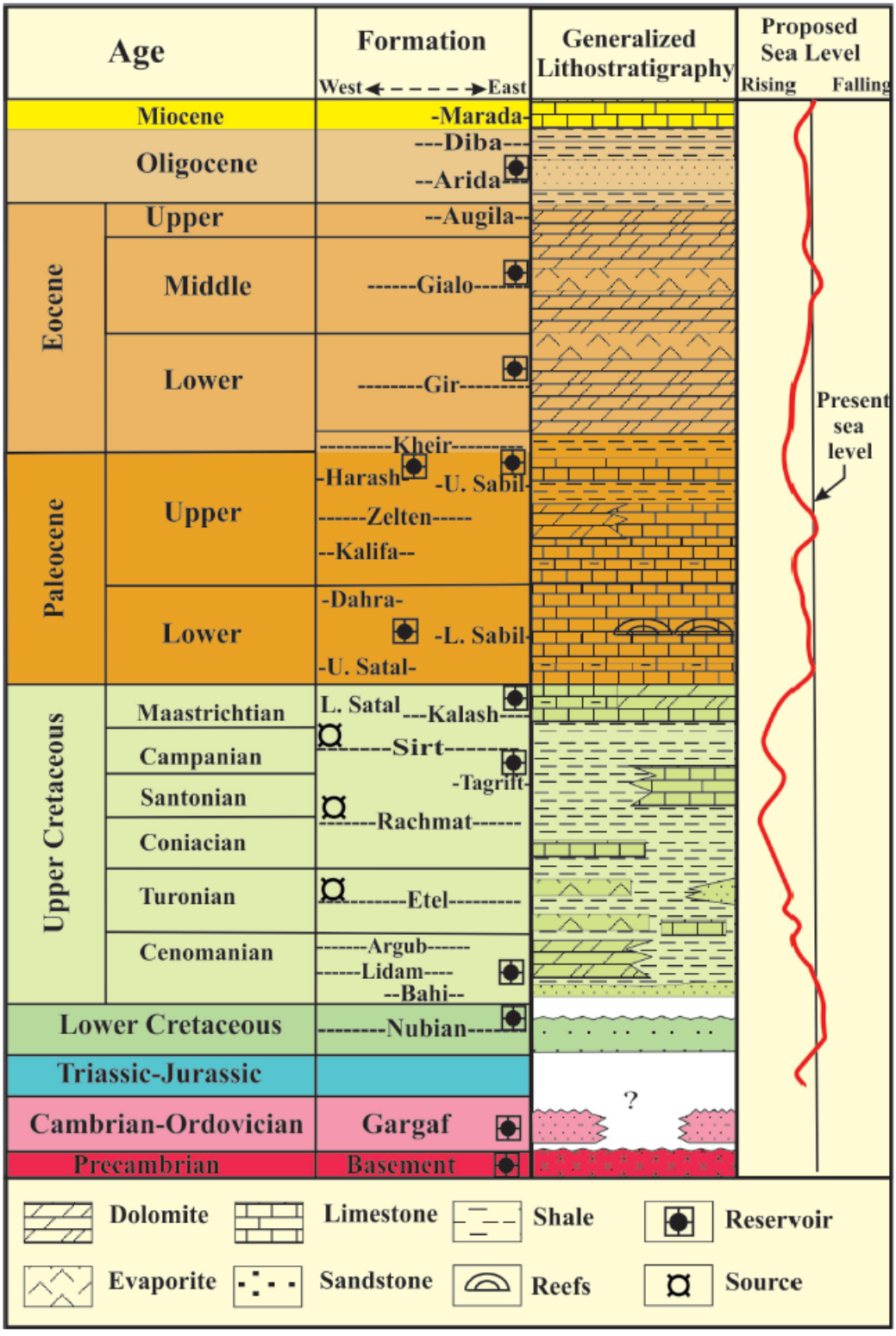

Figure 20. Summary of the stratigraphic section of the Sirt Basin, showing distribution of major reservoirs and source rocks (Hassan et al., 2014).

3.2. Geological settings and tectonic history of the Sirte Basin

The Sirte Basin (Sirt Basin), is located on the northern margin of the African plate in the north central part of Libya between latitudes14°00' - 20°00' E and longitudes 28°00' - 31°00' N (Ahmed et al., 2013). It is the youngest sedimentary basin in Libya and covers an area of approximately 600 km^2, extending offshore along the Mediterranean Sea. It is bordered in the east by the Cyrenaica Platform, in the west by the Ghadames Basin, in the south-east by the AI Kufrah Basin, in the south-west by the Murzuq Basin and in the north by the Mediterranean Sea (Figure 19; Hassan et al., 2014; Amjed Ahmed Ben, 2000).

The evolution of Sirt basin was developed during Latest Jurassic and Early Cretaceous. Tectonic evolution of the Sirt Basin involved thermal arching and repeated phases of rifting that culminated in the Late Cretaceous and Paleocene to Early Eocene, which were followed by thermal subsidence from Late Eocene the present. Rifting commenced in the Triassic - Early Cretaceous, peaked in the Late Cretaceous, and terminated in early Tertiary time (Abadi, 2002; Abugares 2007).

The Sirte Basin was formed by block faulting which induced great subsidence that started during Late Cretaceous (Selley, 1997). The Sirte rift system consists of a point junction that failed to evolve into the spreading stage, Sarir-Hameimat arch and Tibesti-Sirt arch (AbuTumayam) (Figure 21; Hallett, 2002; Aboglila et al., 2010; Stoneley, 1998; Van Houten, 1983). The Sarir arch is characterised by predominantly east-west trending structural elements. These structures appear to be basement-controlled, and were reactivated principally during the earliest Cretaceous extension (Guiraud and Maurin, 1992). Sarir Hameimat arch is dominated by shear faults with subordinate normal faults. These are developed parallel to a deep seated wrench zone interrupted by numerous, right- lateral en-echelon faults that form flower structures (Abadi, 2002).

The NNW-SSE trending Sirte arch developed into a major depocentre primarily in the Late Cretaceous and Early Tertiary, while NNE-SSW trending Tibesti arch experienced only minor Tertiary subsidence (Stoneley, 1998; Saenz de Santa Maria, 1993).

NW arm is the main of Sirt arch and is dominated by normal faults with subordinate wrench faults. It consists of a series of sub parallel grabens separated by tilted fault blocks forming platforms.

Some parts of the Sirte Basin have originated from the collapse of the Tibesti-Sirt Arch during Late Jurassic to Early Cretaceous time. The Tibesti-Sirt Arch (AbuTumayam) may have collapsed due to the plate movements along a group of faults, possibly forming a failed triple junction whose arms trend eastward, northwestward, and northeastward (Mansour and Magairhy, 1996). The main troughs are, from west to east, the Hun Graben, Zallah (Tagrifet), Hagfa (Marada) and Ajdabiya (Marsa Al Brayqah) (Fig 21; Amjed Ahmed Ben, 2000; Hallett, 2002; Aboglila et al., 2010). The Sirt Basin is heavily fractured with major faults resulting in a number of major NW -SE trending reefs (North Sarir Trough, South Sarir Trough, the Hun reef, Zallah Trough, Abu Tumayam Trough, Maradah reef, Agedabia Trough, Hameimat Trough).

The Ajdabiya (Marsa Al Brayqah) Trough is the deepest, longest and widest trough in the basin, and contains more than 6 km of Upper Cretaceous and Tertiary sediments (Amjed Ahmed Ben, 2000). The platforms on intervening horst blocks are from the west to the east (Waddan platform, Al Zahara platform, Bayda platform, Zelten, Al Jahamah Platforms and Rakb High (Abadi, 2002).

The east-west-trending horsts and reefs of the Sarir-Hameimat arch and NNW-SSE arch were formed during the Triassic, Middle and Late Jurassic and Early Cretaceous Neocomian time, prior to the main northwest-southeast oriented horsts and reefs of the Sirt arm that evolved during Early Cretaceous Aptian time, and continued to Late Cretaceous. Maragh Trough (eastern Sirt Basin) was developed during the Permo-Triassic time. (Abadi, 2002; Bonnefous, 1972; El Hawat et al., 1996; Wennekers et al., 1996; Hallet, 2002).

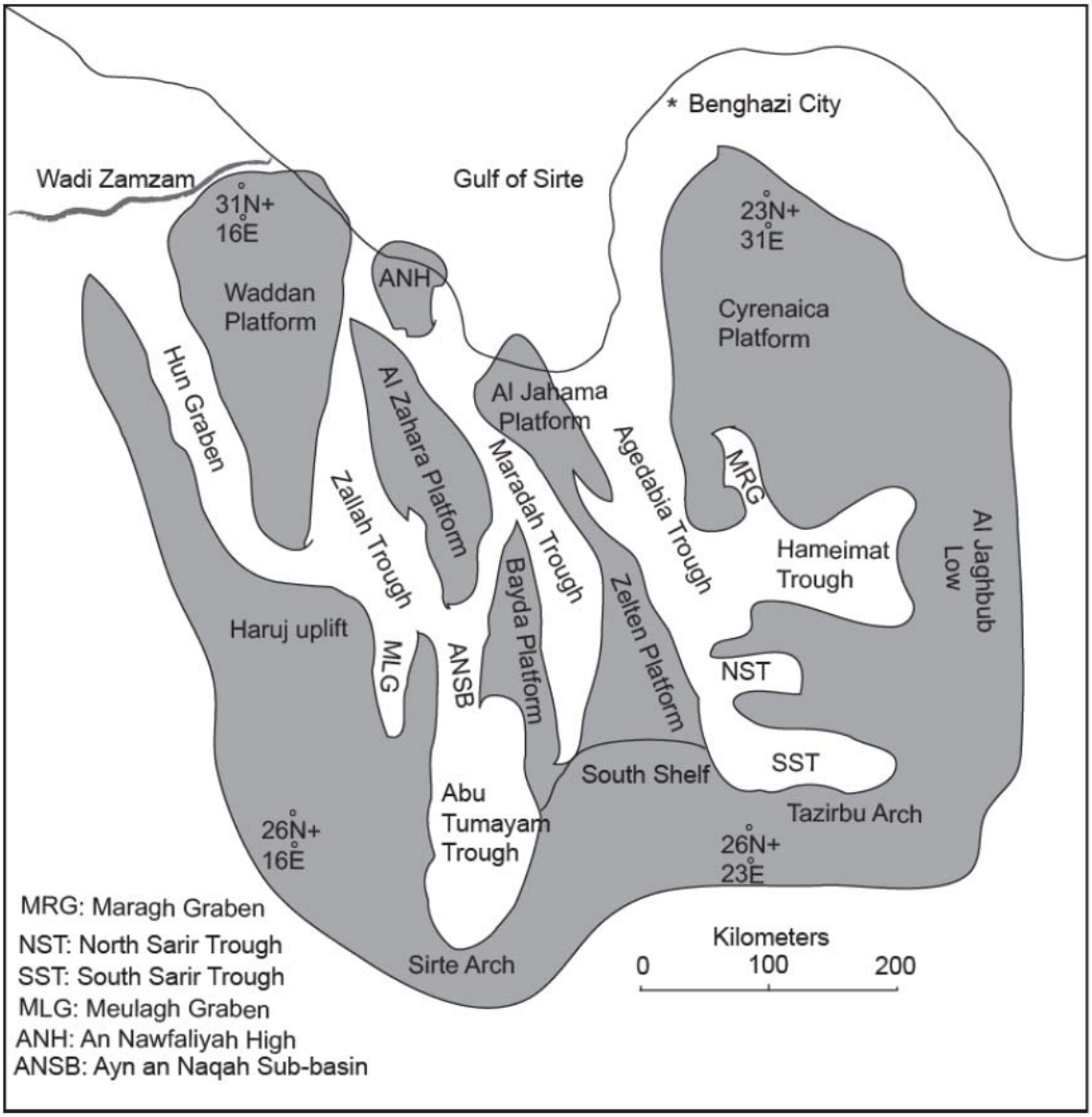

Figure 21. Tectonic framework of the Sirt Basin. (Hallett, 2002; Aboglila et al., 2010).

3.3. Stratigraphic framework of the Sirte Basin

Sediments of Sirt Basin had been classified in to Pre-rift, Syn-rift and Post-rift. The Pre-rift and Post-rift sediments were dominated by clastic sediments, whereas the Syn-rift sediments were dominated by carbonates (Saheel, et al 2010).

The Pre-rifting sediments

The Cambro - Ordovician is represented by Hofra (Gargaf) Formation and Sarir (Nubian) Formation. The former is bound by unconformable boundaries, where it is overlain by Bahi Formation and underlain by Basement igneous rocks (Saheel, et al., 2010).

The Hofra (Gargaf) Formation is quartzitic sandstone of Cambro-Ordovician age. The Ordovician rocks include sedimentary strata, volcanic, plutonic and metamorphic rocks. Upper and Lower Ordovician strata are present over most of the subsurface of the Sirt Basin (Amjed Ahmed Ben, 2000). The Amal Formation may be equivalent to the Hofra Formation in the western part of the Sirt Basin (Hedwi, 2010).

Sarir (Nubian) sandstone formation is represented by continental-marine clastic sediments. The Nubian or Sarir formation is particularly well known in the southeastern part of the basin where it is a prolific oil reservoir at as Sarir, Messlah, and many other fields (Hedwi, 2010).

The Syn-rifting sediments

They are represented by the Late Cretaceous to Late Eocene overlay by the Hofra Formation. These sediments are represented by Sarir, Bahi, Maragh, Lidam, Etel, Argub, Rachmat, Tagrifat, Sirte, Kalash, Satal, Waha, Hagfa, Beda, Khalifa, Zelten, Harash, Kheir, Al Gir, Gialo and Awjilah formations, from base to top (Ahmed et al., 2013; Saheel, et al., 2010).

The Bahi Formation is only present in the subsurface of the western Sirt Basin. It was deposited in a littoral or very shallow marine environment during the Cenomanian. The Bahi Formation forms the main reservoir in such fields as Haram, Bahi and Attahaddy. Also it is a major reservoir for the Nafurah-Augila, Waha, Ar Raqubah and Hateiba fields (Hedwi, 2010).

The Bahi and Maragh formations are similar. They demonstrated a passage from marine to non-marine environment. The Bahi and Maragh formations represent shallow marine, swamp, palaeosol, and alluvial fan (El Alami1996a; Hallett et al., 2002). Some oil fields in the eastern part of the Sirt Basin, such as the Amal, an Nafurah and Jakherrah oil fields, are producing from reservoirs in the Maragh Formation.

The Lidam Formation is a significant oil reservoir in several areas, particularly in the western Sirt Basin. It represents the first marine unit for the majority of the basin (Aboglila

et al., 2010). The Etel Formation is overlaid by marine sequence of thinbedded dolomites, anhydrites, shales and siltstones. It is limited to the central and southern parts of the Sirte Basin.

The Rachmat Formation provides a huge petroleum source for the oil fields located along the crest axis of the basement highs (such as the Augila, Nafoora and Amal field) (Belazi, 1989; Roberts, 1970; Hedwi, 2010).

The Waha Limestone is the main hydrocarbon reservoir of the Raqubah oil field in the eastern margin of the Dahra Platform and of the Waha field on the Zelten Platform. It represents one of the largest hydrocarbon reserves in the Sirt Basin (Hedwi, 2010).

The Waha, Lower Satal, Samah, and the time-transgressive Bahi Sandstone represent the Shallow-marine high-energy carbonates. Paleocene through early Oligocene sedimentation in the central basin yielded shales and carbonates. On the Sirt platforms, these carbonates formed reefs, banks, and mounds preserved within the Defa, Beda, Lower and Upper Sabil, Upper Satal, Zelten, and Dahra Formations (Hassan et al., 2014). The Samah oil field on the Beda or Bayda Platform and Attahaddy gas field produces from Cambro-Orovician quartzites (Hedwi, 2010). The Zelten Limestone forms the reservoir rock for the Zelten (Nasser) field located on the Zelten Platform.

Taqrifat formation represents open-marine, shallowing of the Upper Cretaceous. The age of the formation is late Santonian to early Campanian. This formatiom is a significant oil reservoir on the Awjilah and Nafurah fields and in the Latif area (Hallett et al., 2002).

The Khalifa Formation is the onset of rifting corresponded to a deepening in the basin with thick, deep marine sections deposited in troughs and carbonate buildups on the platforms (Aboglila et al., 2010).

The Post-rifting sediments

They represent the Lower Eocene - Miocene sediments which are mainly shallow marine carbonates (tidal to supra-tidal environment). These sediments are represented by Arida, Diba and Marada formations (Ahmed et al., 2013; Barr and Weegar, 1972 and Hallett, 2002).

The Marada Formation consists of anhydrite, sandstone, and sandy limestone with distal/marine facies, calcarenite and gypsum fine-to coarse-grained sands and sandstone are

dominant in the western and southeastern parts of the Sirt Basin (Aboglila et al., 2010; Hedwi, 2010).

The Arida formation represents continental sandstone in the southeast to marine shale and carbonates in the north of the basin (Hedwi, 2010).

3.4. Organic geochemical evaluation of the Sirt Basin

Oil in the Sirt Basin is generally sweet, with sulphur content between 0.15 and 0.66 % and with relatively small amount of gas. There is no evidence of oil biodegradation and oil gravity varies within the range from 32° to 44° API, The temperature in the reservoirs ranges from 52 °C to as high as 143 °C. Published studies suggest that most of the oil in the Sirt Basin was derived from the Sirte Shale (Upper Cretaceous, Campanian/ Turonian) at high level of thermal maturity (Abdunaser, 2015; Aboglila, 2010a; Hallett et al., 2002; Burwood, 2003). Type IV kerogen (oxidizing conditions) is found on the Az Zahrah-Al Hufrah, Al Jahamah, Zaltan and Waddan Platforms. Type III is around the trough margins, while type II in the centre of the troughs (El Alami et al,. 1989).

Most hydrocarbon reservoirs are pre-Tertiary clastic reservoirs and Tertiary carbonate reservoirs. Oil pools in the lower Cretaceous are paraffinic with pour points around 38 °C. Accumulations with a Palaeocene top seal have pour points up to 13 °C, and those with Ohgocene and Eocene top seals have a pour point less than 9 °C.

Oil accumulations have been found from depths of 700 m to the depths 4000 m with average thickness in the reservoirs of about 250 m (Hallett et al., 2002).

In Sirt Basin, the Upper Cretaceous principal source rock with different thicknesses are deep marine shales accumulated in troughs whereas shallow marine carbonates and clastics deposited in platforms represent the hydrocarbon reservoirs (Khaled et al., 2014). According to the published results, the most of the oil in the Sirt Basin was derived from the Sirte Shale (Upper Cretaceous, Campanian/ Turonian) with excellent oil generation characteristics. TOC values of the sediments from this area average between 2 and 5 %, but occasionally exceeds 10 %. Mereover, the entire northern part of the basin is lean, partly due to unsuitable kerogen facies and partly to the high level of maturity (El Alami et al, 1989; 1996a; 1996b).

Oil production in the Sirt Basin started in the late 1950s. Over 1600 exploration wells have been drilled in the basin leading to the discovery of 340 oil and gas fields within 18 reservoirs. More than 85 % of the hydrocarbons (with 500 million barrels of oil equivalent) in Libya have been discovered in Sirte Basin, making this province the 13th among the biggest world's petroleum provinces (Shaniba et al., 2012; Selley, 1997; Amjed Ahmed Ben, 2000).

3.5. Geological settings of the Intisar oil fields

The Intisar oil fields are located within the Ajdabiya Trough in the eastern part of the Sirte Basin (Figure 22).

Rapid subsidence during the Late Palaeocene in this area led to a situation in which carbonate deposition was replaced by shale deposition. However, in a few isolated areas reef growth was able to keep pace with the subsidence, and pinnacle reefs grew to a height of 385 m. Individual reefs reach up to 5 km in diameter (Hallett, 2002). The Intisar pinnacle reefs consist of algal-foraminifera limestone in the lower part and coral reefs in the upper part (Terry and Williams, 1969). The average porosity in these fields ranges from 15 % to 27 %. The permeability averages 87 mD, but can reach as much as 500 mD (Tawardos, 2011).

The reefs at the Intisar are stratigraphic traps. They are surrounded by Harash and Khayir Shales (Figure 23) which form both the seal and the trap (Ahlbrandt, 2001). The reservoirs have been charged by vertical migration through porous Kalash and Lower Sabil carbonates and into the overlying reefs (Brady, et al. 1980; Hallett, 2002). Peak oil generation began during the Late Oligocene/Miocene and may continue to the present day (Ahlbrandt, 2001).

There are ten pinnacle reefs in the Intisar group (Hallett, 2002). Most of the structures appear to have been filled to the spill-point. However, some of the reefs have developed rim-synclines which may have affected the migration pathways. As a consequence, at least one reef in the complex does not contain hydrocarbons at all (Brady, et al. 1980).

Total oil in the whole Intisar complex is estimated to be over 4 billion barrels (Tawadros, 2011). These oils are characterized by generally low content of sulphur (≤ 0.6 % and often < 0.2 %, wt %), and API gravity in the 25.8 – 51.4 º range (Burwood, et al. 2000).

According to the published organic geochemical data, Intisar oil was derived from the Upper Cretaceous (Campanian) Sirt Shales, which are considered the only source rocks with adequate potential in this area (Ahlbrandt, 2001; Burwood et al., 2003; Hallett, 2002).

Sirt Shale source kitchen is present in the Ajdabiya Trough (Figure 22). The effective thickness of organic shales (TOC > 1 wt. %) reaches 760 m in the Intisar area. Depth to peak oil generation is about 3800 m and the top of the gas window is at about 4200 m. The mature source area extends over a length of 190 km covering an area of approximately 7000 km^2 (Tawardos, 2011).

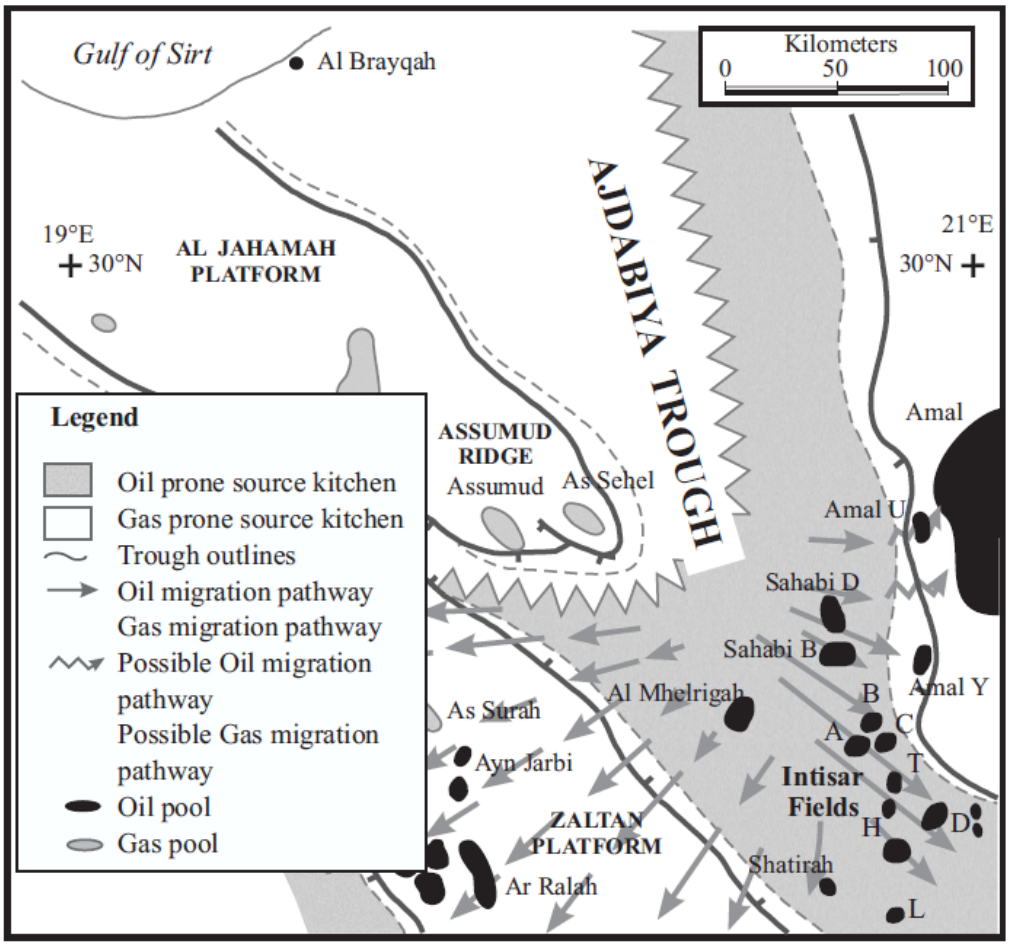

Figure 22. Petroleum Systems in the Ajdabiya Trough (modified after Hallet, 2002).

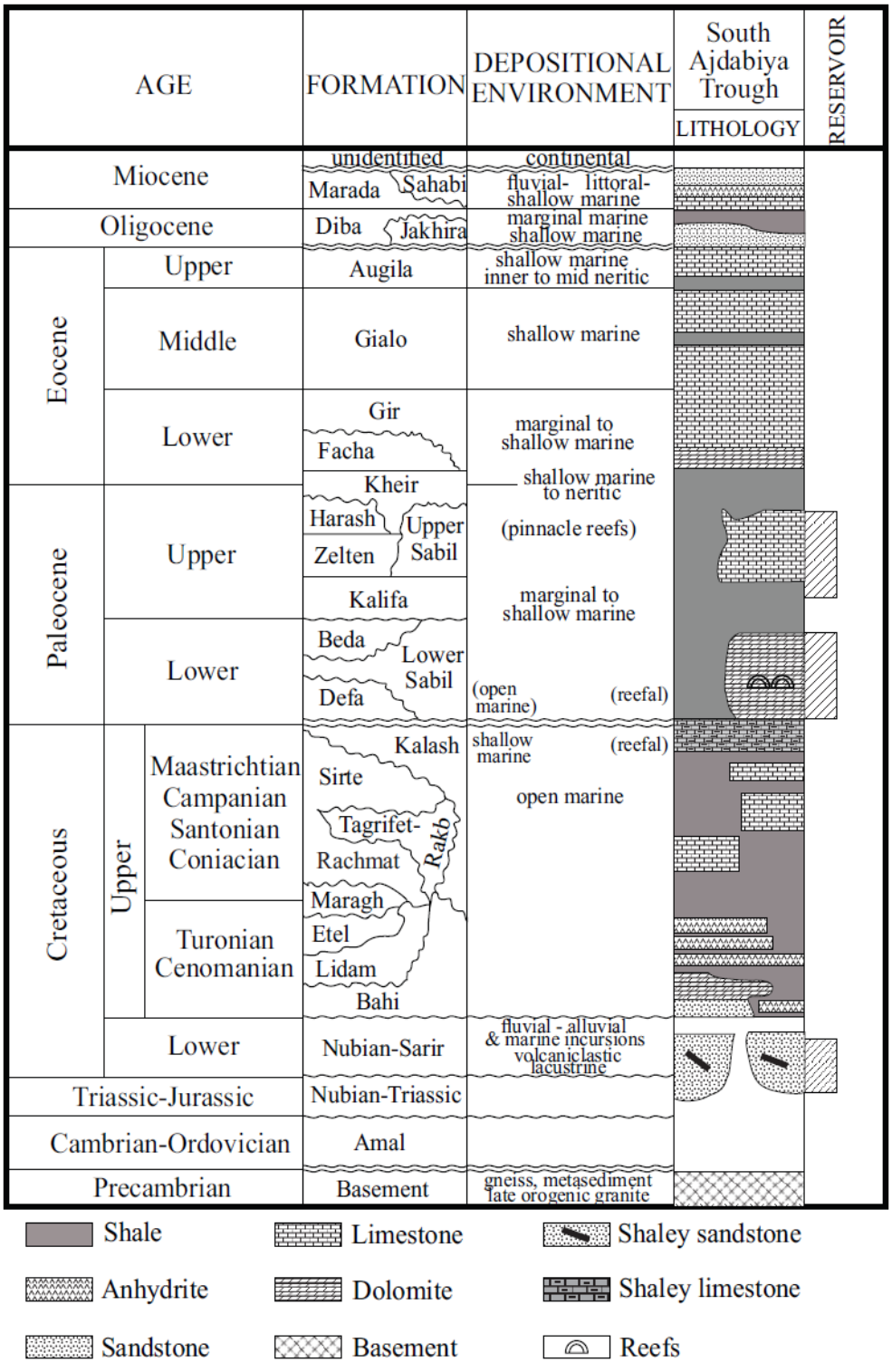

Figure 23. Stratigraphic section of the investigated part of the South Ajdabiya Trough showing depositional environment, lithologies of the formations and reservoirs (modified after Aboglila et al., 2010; Guiraud et al., 2005; Hassan, Kendall, 2014; Rusk, 2000).

Some authors believe that the Intisar reefs are sourced from the late Paleocene Sheterat Shale (Brady et al., 1980). However, this is considered unlikely since the Sheterat has neither the capacity nor the organic richness to generate the large amounts of oil found in the Intisar reefs (Hallett, 2002). Nevertheless, two other possible source rocks have been identified in the southeast Sirte basin. Oils have been identified that are carbon isotopically heavier and quite distinct in sterane-triterpane comparisons from the Sirte Shale source rock. These oils are waxy and appear to have an affinity to Lower Cretaceous non-marine shales and/or Etel formation evaporites (Turonian). Moreover, the oils in Amal field are also distinct and bear source/oil similarity to an adjacent nonmarine Triassic shale interval (Thomas, 1995).

As previously stated, the crude oil samples investigated in this thesis were taken from 4 different wells in the Intisar A (sample 'Intisar A21' from the reef core and sample 'Intisar A52' outside of reef), Intisar D (sample 'Intisar D21') and Intisar E (sample 'Intisar E25') fields.

The Intisar A oil field was discovered in April 1967. It contains original oil reserves of 750 million barrels (Elag et al., 2014). The Intisar A reef is 365 m thick and approximately 6 km in diameter. Porosity in the coral reef facies is 20 to 25 %. The coral reef unit, which forms a cap to the pinnacle, contains coral colonies in growth position which are surrounded by a micritic matrix. The original aragonite of the corals has been removed by solution leaving extensive moldic porosity (Hallett, 2002). Within the Intisar A oil field, fifty eight wells have been drilled so far. Most of the wells were drilled in the late 1960's to early 1970's. The reservoir characterization of this field was concentrated on the reef core only and not outside of reef, due to depletion of oil in the reef. New wells A48, and A51 - A58 were drilled outside of the reef core to test the reservoir quality in this part of the Intisar A oil field (Elag et al., 2014).

The Intisar D oil field was discovered in October 1967. It contains original oil reserves of 1.8 billion barrels. The Intisar D is one of five productive Paleocene pinnacle reefs that grew in an embayment bounded by three carbonate banks (Brady et al., 1980). It is roughly circular in plan and approximately 5 km in diameter. Its maximum thickness is 385 m. The reef is coral and algal with grain- and mud-supported biomicrites. Porosity averages 22 % and is mostly solution and intergranular. Measured permeability is as high as 500 mD and averages 87 mD. The main reservoir is remarkably homogeneous without any noticeable layering typical of other reefs in the area. The reef is full to spill point with a maximum oil column of 291 m (Brady et al., 1980; Hallett, 2002).

The Intisar E field was discovered in 1968. It comprises seven separate producing reservoirs designated Elgiza A and B, Upper Girs A, B and C, Lower Girs and Shoal. The reservoir structures are four way-dipping anticlines with varying closures from 15 to 46 m. All reservoirs are carbonates, particularly limestones, stacking on top of each other. As of December 2002, a total of 40 wells have been drilled in the field (Senturk et al., 2006).

4. The aim and the scope of the research

In this thesis 14 Libyan crude oils were investigated. These oils originate from the oil fields: Amal, En Naga, Intisar, Messla, Nafoora, Samah, Sarir C, Waha and Zelten.

This thesis consists of two distinctive parts.

In the first part of this thesis the values of parameters calculated from distributions and abundances of selected pentacyclic terpanes in crude oils from Libya and Serbia, which were originally derived from gas chromatography-mass spectrometry (GC-MS) were compared with quantification results based on gas chromatography-mass spectrometry-mass spectrometry (GC-MS-MS).

Although the knowledge on the discrepancies between GC-MS and GC-MS-MS results in quantification of sterane and terpane parameters is not a novelty for the organic geochemical scientific community, a detailed comparison of the results of the analysis of the same samples using these two techniques, has not been published so far.

In this thesis a comparison of the values of parameters calculated from distributions and abundances of selected pentacyclic terpanes in crude oils from Libya and Serbia, derived from gas chromatography-mass spectrometry (GC-MS) and gas chromatography-mass spectrometry-mass spectrometry (GC-MS-MS) quantification results was performed, using a large sample set of 70 oils. The parameters analyzed are the most often used terpane source and maturity parameters: C_{27}18α(H)-22,29,30-trisnorneohopane/(C_{27}18α(H)-22,29,30-trisnorneohopane + C_{27}17α(H)-22,29,30-trisnorhopane (Ts/(Ts+Tm)), C_{29}18α(H)-30-norneohopane/ C_{29}17α(H)21β(H)-30-norhopane (C_{29}Ts/C_{29}H), C_{29}17α(H)21β(H)-30-norhopane/ C_{30}17α(H)21β(H)-hopane (C_{29}H/C_{30}H), C_{30}17β(H)21α(H)-moretane/C_{30}17α(H)21β(H)-hopane (C_{30}M/C_{30}H), gammacerane index (GI = G x 100/C_{30}H) and oleanane index (OI = O x 100/C_{30}H). The aim was to investigate to which extent the measurements of the selected parameters by these two instrumental techniques agree and to understand the nature of their differences.

In the second part of this thesis four crude oil samples from the oil fields Intisar A, Intisar D and Intisar E (Sirte Basin, Libya) were investigated in order to define depositional environment, lithology, thermal maturity and geologic age of the corresponding source rocks.

Previous organic geochemical studies on the Intisar crude oils were conducted on the samples from the oil fields A, B, C, D and L (Burwood et al., 2003). That research was based on the stable isotope and quantified biomarker analyses, and statistical evaluation of the data. The isotopic and biomarker composition suggested that the Intisar oils were of marine-source provenance. The results of biomarker analyses revealed that these oils were not biodegraded, and that they originated from mature marine shales, dating of Late Cretaceous or younger.

In this thesis organic geochemical characterization of the Intisar crude oils continues. The oils investigated in this research were taken from different parts of the oil field Intisar A (sampled from the reef core and sampled outside of the reef core), and from the oil fields Intisar D and Intisar E. The organic geochemical research on these oils was conducted in order to define depositional environment, lithology, thermal maturity and geologic age of respective source rocks. Accordingly, genetic relationships among these oils were investigated as well.

Standard organochemical instrumentation methods, gas chromatographic-mass spectrometric (GC-MS) analysis was used for preliminary analyzes of saturated biomarkers (*n*-alkanes, isoprenoids, steranes and triterpanes) and aromatic hydrocarbons (phenanthrene, methylphenanthrenes, methyl-dibenzothiophenes and trimethyl-naphtalenes). However, these instrumental techniques did not show sufficient selectivity in the identification and quantification of the individual compounds needed to calculate the key molecular parameters necessary for the above interpretations. Therefore, stereane and terpane biomarkers were additionally analyzed by gas chromatographic-mass spectrometric-mass spectrometric technique (GC-MS-MS).

In this thesis two statistical approaches were applied which are considered the best in the method comparison studies (Choudhary and Nagaraja, 2007): concordance correlation coefficient and mean-difference plot.

4.1. The research plan

In order to fulfil the assigned goals, the following research plan was created:

1. Elemental analysis of crude oils – determination of content of carbon, hydrogen, oxygen and nitrogen;
2. Separation of asphaltenes from crude oils, by precipitation with n-heptane;
3. Separation of maltene fractions of crude oils into fractions of saturated hydrocarbons, aromatic hydrocarbons and polar compounds with nitrogen, sulfur and oxygen (NSO compounds) using column chromatography;
4. Gas-chromatographic (GC) analysis of total alkane fractions;
5. Gas chromatographic – mass spectrometric (GC-MS) analysis of *n*-alkanes and aliphatic isoprenoid alkanes (fragmentograms of ions m/z = 71 and 183);
6. GC-MS analysis of steranes and diasteranes (fragmentograms of ions m/z = 217 and 218);
7. GC-MS analysis of terpanes (fragmentograms of ions m/z = 191);
8. Gas chromatographic – mass spectrometric – mass spectrometric (GC-MS-MS) analysis of C_{26}, C_{27}, C_{28}, C_{29} and C_{30} steranes (using transitions: m/z 358 → 217, m/z 372 → 217, m/z 386 → 217, m/z 400 → 217 and m/z 414 → 217);
9. GC-MS-MS analysis of the C_{28}, C_{29} and C_{30} methylsteranes (using transitions: m/z 386 → 231, m/z 400 → 231 and m/z 414 → 231);
10. GC-MS-MS analysis of the C_{27}, C_{29}, C_{30}, C_{31}, C_{32}, C_{33}, C_{34} and C_{35} terpanes (using transitions: m/z 370 → 191, m/z 398 → 191, m/z 412 → 191, m/z 426 → 191, m/z 440 → 191, m/z 454 → 191, m/z 468 → 191 i m/z 482 → 191);
11. GC-MS analysis of methylnaphthalene, dimethylnaphthalenes, trimethylnaphthalenes and tetramethylnaphthalenes (fragmentograms of ions: m/z = 142, 156, 170 and 184);
12. GC-MS analysis of phenanthrene, methylphenanthrenes, dimethylphenanthrenes and trimethylphenanthrenes (fragmentograms of ions: m/z = 178, 192, 206 and 220);
13. GC-MS analysis of dibenzothiophene, methyldibenzothiophenes, dimethyldibenzothiophenes and trimethyldibenzothiophenes (fragmentograms of ions: m/z = 184, 198, 212 and 226);

14. Interpretation of the results with the use of statistical methods, concordance correlation coefficient and mean-difference plot.

5. Experimental part

5.1. Precipitation of asphaltenes

Asphaltenes were separated from crude oils by precipitation with n-heptane. Approximately 1.5 g crude oil was measured in a small beaker on analytical balance (precision ± 0.0001 g). Crude oil was quantitatively transferred to a 250 ml round-bottom flask, using n-heptane or dichloromethane (Acros Organics, HPLC grade). Then the excess of n-heptane was added into the flask to make n-heptane to crude oil mass ratio 40 : 1. Known density of n-heptane (0.684 g/ml), e.g. for 1.5 g crude oil, total 87.6 ml n-heptane is needed. The mixture was left to settle overnight in the sealed flask, for 16 h in a dark place on room temperature.

After this time, a reflux condenser was attached to the flask and the mixture was heated in a boiling water bath for 15 - 20 min (boiling point of n-heptane is 98.4 °C). A sintered glass filter, vacuum rubber adaptors, Büchner flask and water jet pump were assembled into a filtration system. Hot n-heptane suspension was filtered through the sintered glass filter or by filter paper (previously dried to a constant weight) under low pressure. Precipitated asphaltenes were washed several times with hot n-heptane to remove adsorbed malthenes.

The filter with asphaltenes was dried at 100 °C to a constant weight and asphaltene content was calculated. Malthene solution was quantitatively transferred to a 500 ml round-bottom flask, using n-heptane. Excess solvent was removed using rotary evaporator and the remaining malthenes were transferred to a weighing bottle with a constant weight, using n-heptane. Residual solvent was evaporated to dryness at room temperature under a stream of air without heating and the mass of malthenes was calculated.

5.2. Column chromatography

Saturated and aromatic hydrocarbons ("hydrocarbon concentrate") were isolated from malthene fraction of crude oils using column chromatography (Figure 24) with Al_2O_3 and SiO_2 adsorbents.

Approximately 0.03 g of malthene fraction was measured in a small beaker on analytical balance (precision ± 0.0001 g). Malthenes were dissolved in as small volume of chloroform (Carlo Erba, p.a.) as possible and approximately 1 g silica gel (SiO_2; Merck, 70-230 mesh) was added. The beaker with sample was left overnight at room temperature under a stream of air and chloroform was allowed to evaporate, thus homogenous mixture of the sample and silica gel was formed.

Chromatography column was packed in a 50 cm long and 1 cm in diameter glass chromatography tube with a Teflon stopcock. Cotton wool, washed with n-hexane, was used as a column support and silica gel (SiO_2; Merck, 70-230 mesh) and alumina (Al_2O_3; Merck, 70-230 mesh) were used as adsorbents. Previously, adsorbents were activated - dried at 150 °C for 2 h. Proportion for 30 mg of organic material (8.65 g SiO_2 + 6.35 g Al_2O_3) was applied. Silica gel was introduced into the chromatography tube as n-hexane suspension, while alumina was introduced dry. Dry sample + silica gel mixture was quantitatively introduced to the top of the column.

Hydrocarbon concentrate (mixture of saturated and aromatic hydrocarbons) was sequentially eluted with four solvents: n-hexane (Carlo Erba, HPLC grade), n-hexane : benzene = 3 : 1 (v/v) mixture, n-hexane : benzene = 1 : 1 (v/v) mixture and benzene (Carlo Erba, p.a.). Proportion for 30 mg of organic material (30 ml n-hexane + 90 ml "3:1" mixture + 90 ml "1:1" mixture) was applied, while the volume of benzene used for elution was equal to the volume of chromatography column (sample + adsorbents). All the eluates were collected in the same round-bottom flask at the rate of 1 drop per second.

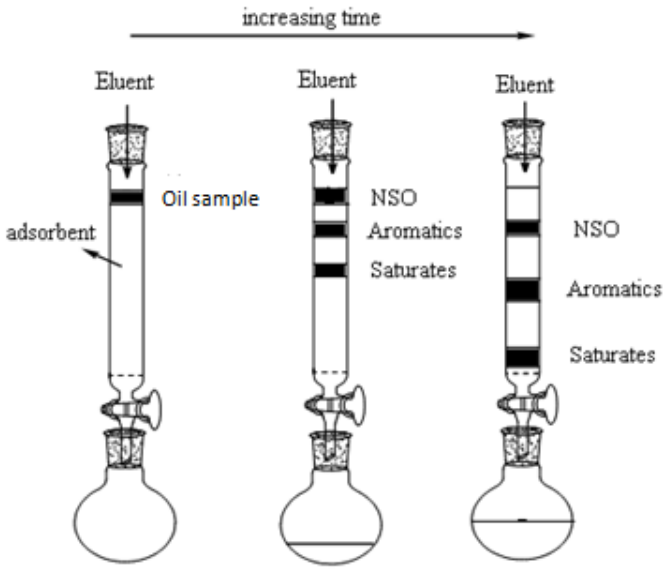

Figure 24. Column-chromatographic separations of fractions of crude oils. Saturated hydrocarbons move fastest, followed by aromatics and then by NSO- compounds.

After the experiment, excess of solvent was removed using rotary evaporator and the remaining extract (hydrocarbon concentrate) was transferred to a weighing bottle with a constant weight, using n-hexane. The residual solvent was evaporated to dryness at room temperature under a stream of air without heating. The mass of saturated hydrocarbons was calculated as: mass of saturated hydrocarbons = weighing glass with alkanes– empty weighing glass. The mass of aromatic hydrocarbons was calculated as: mass of aromatic hydrocarbons = weighing glass with aromatics – empty weighing glass.

The content of saturated and aromatic hydrocarbons was expressed in percentages.

Percentage of NSO compounds was determined from the difference (% NSO = 100 – % saturated hydrocarbons - % aromatic hydrocarbons).

5.3. Biomarker analysis

For GC-MS analyzes an Agilent 7890N gas chromatograph fitted with a HP5-MS capillary column (30 m x 0.25 mm, 0.25 μm film; temperature range: 80 ºC for 0 min; then 2 ºC min^{-1} to 300 ºC and held for 20 min) with helium as the carrier gas (flow rate 1 cm^3 min^{-1}) was used. The GC was coupled to a Hewlett-Packard 5972 MSD operated at 70 eV in the 45–550 scan range.

n-Alkanes and isoprenoids were identified on the basis of fragmentogram ions *m/z* = 71 and *m/z* = 183; Steranes and disteranes were identified on the basis of fragmentogram ions m/z = 217; Terpanes were identified on the basis of fragmentogram ion *m/z* = 191; Phenanthrene and its methyl isomers were identified on the basis of fragmentogram ions *m/z* = 178 and 192, while identification of methyl-dibenzothiophenes, was carried out from typical ion fragmentograms *m/z* = 198. The compounds in corresponding ion fragmentograms were identified by comparison with the reference data (Peters et al., 2005), as well as on the basis of NIST5a total mass spectra library. Integration of peak areas was carried out using GC-MS ChemStation Software.

GC-MS-MS analysis was conducted using an Agilent 6890N gas chromatograph connected to a Waters (Micromass) Quattro Micro GC tandem quadropole mass spectrometer. A Phenomenex ZB-5 column (30 m x 0.25 mm i.d., film thickness 0.10 μm) was used. The temperature programme was: 30 ºC min^{-1} from 70 to 100 ºC and 4 ºC min^{-1} from 100 to 308 ºC (hold 8 min). Specific GC-MS-MS analyzes were carried out for the characteristic ion transition for C_{26}-C_{30} steranes ($M^+ \rightarrow$ m/z 217), C_{28}-C_{30} methyl steranes ($M^+ \rightarrow$ m/z 231) as well as C_{27} and C_{28}-C_{35} terpanes ($M^+ \rightarrow$ m/z 191). In addition, the transition 412.41 → 191.18 (C_{30} hopane) was included in the analysis steranes in order to check the relative response of the detector. The transition m/z 414.42 → 259.24 was used to verify the presence tetracyclic polyprenoids (TPP).

6. Results and discussion

6.1. GC-MS vs. GC-MS-MS analysis of pentacyclic terpanes in crude oils from Libya and Serbia

In the first part of this thesis a comparison of the values of parameters calculated from distributions and abundances of selected pentacyclic terpanes in crude oils from Libya and Serbia, derived from gas chromatography-mass spectrometry (GC-MS) and gas chromatography-mass spectrometry-mass spectrometry (GC-MS-MS) quantification results was performed, using a large sample set of 70 oils. The parameters analyzed are the most often used terpane source and maturity parameters: C_{27}18α(H)-22,29,30-trisnorneohopane/(C_{27}18α(H)-22,29,30-trisnorneohopane + C_{27}17α(H)-22,29,30-trisnorhopane (Ts/(Ts+Tm)), C_{29}18α(H)-30-norneohopane/C_{29}17α(H)21β(H)-30-norhopane (C_{29}Ts/C_{29}H), C_{29}17α(H)21β(H)-30-norhopane/C_{30}17α(H)21β(H)-hopane (C_{29}H/C_{30}H), C_{30}17β(H)21α(H)-moretane/C_{30}17α(H)21β(H)-hopane (C_{30}M/C_{30}H), gammacerane index (GI = G x 100/C_{30}H) and oleanane index (OI = O x 100/C_{30}H). The aim of this research was to investigate to which extent the measurements of the selected parameters by these two instrumental techniques agree and to understand the nature of their differences.

6.1.1. Samples

Following the conclusion of some authors that a sample size of at least 50 should be used in the regression analysis (Ludbrook, 2010), a large data set of 70 crude oil samples was chosen for our present research. The crude oils were carefully selected to comprise samples different in source, maturity and biodegradation level. To this end, 14 crude oil samples from different parts of the Sirte Basin (Libya) were selected. In order to avoid erroneous conclusions that might be drown from analyses of the oils from one location, and in order to make the conclusions even more general, the samples from four oil fields from the Pannonian Basin (Serbia) were selected

and included in this research as well. All investigated oils are of Cretaceous or Tertiary age (Faraj et al., 2016; Mrkić et al., 2011; Šolević et al., 2008).

The crude oils from the Sirte Basin are in the literature described as mature to post mature oils. Most of them are of marine origin, although a mixed marine-terrestrial source is proposed for some oils as well. The Sirte Shale is considered the main source for most of the oils in this area (Burwood et al., 2003; Hallet, 2002). The Libyan crude oils investigated in this research originate from different parts of the Sirte Basin, from the oil fields: Amal, En Naga, Intisar, Messla, Nafoora, Samah, Sarir C, Waha and Zelten.

The Serbian crude oils investigated originate from the southeastern part of the Pannonian Basin, from the oil fields Elemir, Rusanda, Zrenjanin and Velebit. All these oils were generated from clay-rich source rocks containing mixtures of terrestrial and marine organic matter. However, they are different in their maturity level. The Zrenjanin oils have low level of thermal maturity, corresponding to calculated vitrinite reflectance, Rc of 0.60-0.70 % (Mrkić et al., 2011). The Elemir and Rusanda crude oils were generated from the source rocks at medium maturity level, equivalent to vitrinite reflectance between 0.70 and 0.80 % (Šolević Knudsen et al., 2015a,b). The source rocks of the Velebit oils are estimated to be of high maturity, consistent with a vitrinite reflectance of > 0.80 % Rc (Šolević et al., 2008). Another distinctive feature of the Velebit oils is that they are biodegraded. In a biodegradation-based classification (Peters et al., 2005), these oils were found to be altered to an index value of 3 to 4 (Šolević et al., 2008). Detailled analysis of these oils from the southeastern part of the Pannonian Basin was subject of several PhD thesis defended at the Department for applied chemistry of the Faculty of Chemistry, Univesity of Belgrade.

6.1.2. Analytical and instrumental metods

The saturated fractions were isolated from the crude oils according to the methods described in paragraph 5.2., and analysed by GC-MS and GC-MS-MS instrumental techniques described in paragraph 5.3. Characteristic terpane parameters were calculated from GC-MS and GC-MS-MS chromatogram peak areas (softwares: Agilent ChemStation and Waters MassLynx V4.0) and listed in Table 12.

Table 12. Values of terpane parameters in investigated oils

Parameter		Ts/(Ts+Tm)[a]		$C_{29}Ts/C_{29}H$[b]		$C_{29}H/C_{30}H$[c]		$C_{30}M/C_{30}H$[d]		GI[e]		OI[f]	
No.	Sample \ Technique	GC-MS	GC-MS-MS	GC-MS	GC-MS-MS	GC-MS	GC-MS-MS	GC-MS	GC-MS-MS	GC-MS	GC-MS-MS	GC-MS	GC-MS-MS
	Libyan oils												
1	Amal	0.56	0.65	0.53	0.50	0.54	0.61	0.14	0.07	7.46	5.30	N.D.[g]	N.D.
2	En Naga	0.63	0.68	0.73	0.60	0.50	0.60	0.13	0.07	8.24	5.05	N.D.	N.D.
3	Intisar AQLB3C	0.56	0.87	0.83	1.58	0.77	0.65	0.14	0.06	6.42	4.43	N.D.	N.D.
4	Intisar E25	0.49	0.54	0.44	0.37	0.67	0.74	0.07	0.04	10.78	3.71	N.D.	N.D.
5	Intisar A52	0.61	0.63	0.51	0.38	0.72	0.73	0.10	0.03	10.88	2.93	N.D.	N.D.
6	Intisar A21	0.65	0.74	0.74	0.63	0.45	0.58	0.07	0.04	9.91	3.04	N.D.	N.D.
7	Intisar D21	0.60	0.64	0.65	0.54	0.53	0.58	0.08	0.04	9.12	3.11	N.D.	N.D.
8	Messla	0.68	0.75	0.75	0.65	0.51	0.52	0.13	0.05	17.12	4.29	N.D.	N.D.
9	Nafoora	0.53	0.59	0.58	1.00	0.53	0.61	0.10	0.05	9.74	5.09	N.D.	N.D.
10	Samah 1	0.67	0.72	0.56	0.46	0.52	0.54	0.10	0.05	9.38	4.29	N.D.	N.D.
11	Samah 2	0.65	0.71	0.64	0.54	0.52	0.47	0.07	0.05	9.91	3.43	N.D.	N.D.
12	Sarir C	0.58	0.65	0.64	0.59	0.56	0.62	0.14	0.07	10.06	6.03	N.D.	N.D.
13	Waha	0.58	0.65	0.56	0.43	0.45	0.48	0.10	0.05	6.05	4.97	N.D.	N.D.
14	Zelten	0.51	0.58	0.47	0.37	0.49	0.53	0.11	0.05	6.67	3.74	N.D.	N.D.
	Elemir oils												
15	Elemir-2	0.38	0.46	0.22	0.22	0.51	0.61	0.11	0.07	3.54	2.64	10.73	14.35
16	Elemir-6	0.37	0.44	0.23	0.19	0.51	0.60	0.11	0.07	4.48	2.73	14.47	16.85
17	Elemir-10	0.40	0.44	0.15	0.21	0.69	0.63	0.11	0.06	4.35	2.79	11.41	15.33
18	Elemir-15	0.36	0.41	0.19	0.19	0.53	0.61	0.11	0.06	3.66	2.75	12.80	17.69
19	Elemir-18	0.35	0.40	0.20	0.19	0.52	0.62	0.10	0.06	3.28	2.41	13.00	18.38
20	Elemir-19	0.41	0.48	0.21	0.22	0.52	0.63	0.10	0.06	2.88	2.98	9.32	13.69
21	Elemir-33	0.37	0.44	0.20	0.21	0.51	0.63	0.11	0.06	4.56	2.96	13.40	14.38
22	Elemir-40	0.39	0.40	0.17	0.18	0.69	0.62	0.10	0.06	4.87	2.80	14.06	17.86
23	Elemir-43	0.41	0.46	0.15	0.22	0.63	0.64	0.16	0.06	3.71	2.81	9.89	13.40
24	Elemir-45	0.40	0.41	0.20	0.20	0.69	0.62	0.11	0.06	4.89	2.77	13.23	16.48
25	Elemir-48	0.36	0.43	0.20	0.20	0.51	0.61	0.12	0.06	3.08	2.44	11.75	14.76
26	Elemir-49	0.38	0.43	0.21	0.19	0.56	0.62	0.11	0.06	3.48	2.84	11.41	15.49
27	Elemir-51	0.37	0.43	0.17	0.21	0.54	0.62	0.14	0.06	3.25	2.80	10.31	16.03
28	Elemir-52	0.35	0.41	0.21	0.20	0.53	0.61	0.11	0.06	3.21	2.81	12.13	16.16
29	Elemir-54	0.37	0.43	0.19	0.21	0.53	0.62	0.11	0.06	3.11	2.82	11.62	16.15
30	Elemir-59	0.37	0.41	0.20	0.19	0.53	0.62	0.11	0.06	2.86	2.44	12.81	17.25
	Rusanda oils												
31	Rusanda-1	0.44	0.53	0.28	0.28	0.49	0.60	0.13	0.05	11.75	2.80	15.69	16.50
32	Rusanda-2	0.54	0.61	0.33	0.34	0.45	0.57	0.11	0.06	12.61	3.48	13.93	15.27
33	Rusanda-5	0.44	0.58	0.27	0.32	0.51	0.59	0.11	0.06	9.68	3.13	12.59	16.17
34	Rusanda-8	0.48	0.56	0.30	0.28	0.45	0.60	0.13	0.05	6.16	2.41	14.43	12.35
35	Rusanda-12	0.45	0.58	0.34	0.33	0.47	0.57	0.11	0.05	11.07	2.82	11.96	11.50
36	Rusanda-14	0.44	0.56	0.31	0.28	0.50	0.61	0.11	0.05	5.82	2.45	12.93	12.95
37	Rusanda-16	0.46	0.55	0.29	0.31	0.50	0.59	0.12	0.05	9.94	2.67	13.56	13.36
38	Rusanda-17	0.42	0.55	0.31	0.30	0.50	0.62	0.11	0.05	10.43	2.42	12.13	12.75
39	Rusanda istok-1	0.39	0.47	0.17	0.24	0.69	0.66	0.12	0.07	2.18	2.07	7.34	9.81

Table 12 continued

Parameter		Ts/(Ts+Tm)[a]		$C_{29}Ts/C_{29}H$[b]		$C_{29}H/C_{30}H$[c]		$C_{30}M/C_{30}H$[d]		GI[e]		OI[f]	
No.	Sample / Technique	GC-MS	GC-MS-MS	GC-MS	GC-MS-MS	GC-MS	GC-MS-MS	GC-MS	GC-MS-MS	GC-MS	GC-MS-MS	GC-MS	GC-MS-MS
	Zrenjanin oils												
40	Zrenjanin-4	0.26	0.25	0.27	0.20	0.61	0.66	0.18	0.11	4.26	4.27	20.85	28.72
41	Zrenjanin-6	0.24	0.26	0.24	0.19	0.53	0.67	0.15	0.10	3.52	3.72	20.42	28.60
42	Zrenjanin sever-2	0.25	0.28	0.20	0.16	0.56	0.69	0.16	0.09	3.20	3.44	15.11	20.12
43	Zrenjanin sever-3	0.25	0.27	0.18	0.16	0.59	0.70	0.14	0.09	2.81	2.97	14.41	19.75
44	Zrenjanin sever-5	0.25	0.25	0.17	0.17	0.61	0.69	0.16	0.09	2.99	3.04	15.61	21.35
45	Zrenjanin sever-7	0.24	0.27	0.18	0.16	0.60	0.69	0.15	0.08	2.91	3.28	15.99	21.78
	Velebit oils												
46	Velebit-1	0.51	0.63	0.20	0.46	0.55	0.49	0.11	0.06	12.92	6.78	13.95	23.12
47	Velebit-2	0.53	0.62	0.19	0.46	0.53	0.49	0.11	0.06	13.46	5.88	14.65	22.84
49	Velebit-3	0.56	0.63	0.21	0.42	0.52	0.50	0.11	0.06	12.2	5.92	14.24	23.66
49	Velebit-4	0.49	0.62	0.18	0.47	0.58	0.49	0.11	0.06	11.64	5.90	14.33	23.44
50	Velebit-5	0.53	0.63	0.20	0.41	0.60	0.51	0.10	0.06	10.71	6.40	15.65	22.84
51	Velebit-6	0.54	0.62	0.24	0.45	0.51	0.49	0.11	0.06	11.51	6.84	15.57	23.32
52	Velebit-7	0.54	0.64	0.24	0.52	0.56	0.49	0.12	0.06	15.11	6.79	14.26	22.86
53	Velebit-8	0.50	0.63	0.22	0.43	0.51	0.50	0.11	0.06	12.39	5.97	13.58	24.35
54	Velebit-9	0.55	0.62	0.19	0.42	0.54	0.51	0.10	0.06	10.14	6.58	14.36	23.52
55	Velebit-10	0.50	0.60	0.19	0.40	0.51	0.51	0.10	0.06	11.49	5.72	13.68	23.59
56	Velebit-11	0.50	0.61	0.24	0.46	0.54	0.49	0.13	0.07	14.09	6.65	15.27	22.77
57	Velebit-12	0.59	0.67	0.27	0.52	0.54	0.49	0.12	0.07	13.65	7.60	16.38	25.83
58	Velebit-13	0.58	0.66	0.24	0.46	0.60	0.51	0.11	0.06	11.70	7.06	13.77	22.52
59	Velebit-14	0.55	0.65	0.21	0.49	0.58	0.48	0.10	0.06	9.73	6.65	15.02	22.62
60	Velebit-15	0.60	0.67	0.21	0.47	0.65	0.49	0.13	0.05	13.72	6.69	18.01	23.76
61	Velebit-16	0.56	0.64	0.21	0.48	0.56	0.48	0.11	0.06	11.54	6.82	15.28	23.85
62	Velebit-17	0.60	0.67	0.26	0.50	0.54	0.49	0.10	0.06	12.58	6.82	13.44	23.00
63	Velebit-18	0.52	0.61	0.20	0.45	0.55	0.48	0.11	0.07	13.34	6.02	17.74	27.34
64	Velebit-19	0.54	0.59	0.19	0.42	0.54	0.48	0.12	0.06	10.70	6.02	19.02	28.30
65	Velebit-20	0.56	0.66	0.21	0.49	0.61	0.48	0.12	0.06	11.11	6.99	14.36	22.99
66	Velebit-21	0.52	0.64	0.28	0.48	0.55	0.48	0.11	0.06	11.74	6.83	16.95	25.32
67	Velebit-22	0.55	0.66	0.28	0.53	0.52	0.49	0.10	0.06	12.01	6.75	15.27	23.72
68	Velebit-23	0.59	0.66	0.25	0.54	0.60	0.49	0.14	0.06	13.85	7.44	14.53	23.81
69	Velebit-24	0.58	0.62	0.22	0.48	0.62	0.47	0.17	0.06	15.16	6.67	21.46	25.21
70	Velebit-25	0.54	0.67	0.35	0.50	0.65	0.50	0.19	0.05	31.68	7.45	25.00	22.92

[a] Ts/(Ts+Tm) = C_{27}18α(H)-22,29,30-trisnorneohopane/(C_{27}18α(H)-22,29,30-trisnorneohopane + C_{27}17α(H)-22,29,30-trisnorhopane; [b] $C_{29}Ts/C_{29}H$ = C_{29}18α(H)-30-norneohopane/C_{29}17α(H)21β(H)-30-norhopane; [c] $C_{29}H/C_{30}H$ = C_{29}17α(H)21β(H)-30-norhopane/C_{30}17α(H)21β(H)-hopane; [d] $C_{30}M/C_{30}H$ = C_{30}17β(H)21α(H)-moretane/C_{30}17α(H)21β(H)-hopane; [e] GI, Gammacerane index, GI = G x 100/$C_{30}H$; [f] Oleanane index, OI = O x 100/$C_{30}H$; [g] N.D. – Not determined due to the absence of oleanane in Libyan oils.

6.1.3. The analysis of concordance correlation coefficients

As a first step in the method comparison study, the concordance correlation analysis was conducted for the six organic geochemical parameters determined by GC-MS and GC-MS-MS instrumental techniques. As stated before, the parameters analyzed were: Ts/(Ts+Tm), $C_{29}Ts/C_{29}H$, $C_{29}H/C_{30}H$, $C_{30}M/C_{30}H$, gammacerane index (GI = G x $100/C_{30}H$) and oleanane index (OI = O x $100/C_{30}H$). The correlation analysis graphs are shown in Figure 25.

The concordance correlation analysis of the Ts/(Ts+Tm) parameter (Figure 25a; Table 13) showed high similarity between the values of this parameter determined by GC-MS and GC-MS-MS techniques. This observation is additionally confirmed by high Pearson correlation coefficient (ρ = 0.97; Table 13), indicating high precision in measurement of this parameter by these two instrumental techniques. High concordance correlation coefficient ρ_c = 0.82 (Table 13) with narrow 95 % confidence interval, ranging from 0.76 to 0.87 (Table 13) indicates that similar values of the Ts/(Ts+Tm) parameter determined by GC-MS and GC-MS-MS can be expected for wide range of the values.

However, visual inspection of the similarity graph (Fig 25a) revealed a slight deviation from the line of equality ($y = x$ line) with increase in the values of the Ts/(Ts+Tm) parameter. This deviation is also reflected in accuracy in determination of this parameter, as shown by bias correction factor C_b (accuracy < precision; Table 13). According to these results it might be presumed that when the values of the Ts/(Ts+Tm) parameter are higher, the values of this parameter determined by GC-MS-MS might be higher than those determined by GC-MS. Considering the fact that the Ts/(Ts+Tm) parameter increases with increase in oil maturity (Peters *et al*., 2005), it can also be concluded that in more mature crude oils a higher difference in Ts/(Ts+Tm) parameter determined by GC-MS and GC-MS-MS can be expected than in less mature oils.

Furthermore, it can also be noticed that deviation of this parameter from the line of equality is similar for the oils from the same oil field but it is different for the oils from different oil fields. In the case of Ts/(Ts+Tm) parameter, the discrepancies between the values determined

by GC-MS and GC-MS-MS instrumental techniques, for the oils originating from different oil fields, are not surprising. Actually, it is well known that Ts and Tm in GC-MS *m/z* = 191 chromatograms co-elute with some tri- and tetracyclic terpanes (Peters *et al*., 2005). Furthermore, the relative content of tri-, tetra- and pentacyclic terpanes in crude oils is influenced by the source rocks organic matter, but also by lithology and oxicity of the depositional environment (Peters *et al*., 2005). As a consequence, the difference between the values of the Ts/(Ts+Tm) parameter determined by GC-MS and GC-MS-MS instrumental techniques is different for crude oils from different oil fields. Because of that, it should be emphasized that, when GC-MS-MS results are to be used in organic geochemical interpretations, a regional calibration of GC-MS vs. GC-MS-MS relationship for each crude oil system investigated is highly recommended.

It is noticeable that the values of the Ts/(Ts+Tm) parameter for the Velebit oils follow, more or less, the same trend as for all other samples (Figure 25a). As stated earlier, the Velebit oils were shown to be biodegraded to the biodegradation level 3, and some samples even to the level 4. Accordingly, it can be concluded that Ts and Tm are not affected by biodegradation in oils biodegraded to the level 4, or if they are somewhat degraded, they are removed to the same extent, leaving their ratio unaltered. This conclusion is in accordance with published literature data (Peters *et al*., 2005).

The concordance correlation analysis of the $C_{29}Ts/C_{29}H$ parameter (Figure 25b; Table 13) indicated low correlation coefficient (ρ = 0.53; Table 13) and a wide 95 % confidence interval for CCC (0.35 - 0.67; Table 13). All these results point to the significant difference between the values of this parameter determined by GC-MS and GC-MS-MS instrumental techniques. However, visual examination of the similarity graph (Figure 25b) revealed a different correlation trend for the $C_{29}Ts/C_{29}H$ ratio in the Velebit oils and other samples.

In the case of the Velebit crude oils, the $C_{29}Ts/C_{29}H$ parameter, determined by two instrumental techniques, showed significant deviation from the line of equality ($y = x$ line) with systematic shift between the GC-MS and GC-MS-MS values (Figure 25b). These results indicate that the GC-MS-MS analysis may result in $C_{29}Ts/C_{29}H$ parameter values which are twice as higher than those determined by GC-MS technique. The obtained result can be attributed to the fact that among investigated samples, only Velebit oils were analysed by GC-MS with a heating

rate of 3 ºC min^{-1}, whereas for other oils a heating rate of 2 ºC min^{-1} was used. Since C_{29}Ts and C_{29}H have very similar retention times and eluted much closer than corresponding C_{27} homologues (Ts and Tm) it can be supposed that under heating rates higher than 2 ºC min^{-1} separation of C_{29}Ts and C_{29}H in routine GC-MS is not efficient, particularly in mature samples, such as Velebit oils, which are usually rich in C_{29}Ts, resulting in erratic values of C_{29}Ts/C_{29}H ratio.

Taking into account the different pattern of the Velebit oils, the concordance correlation analysis of the C_{29}Ts/C_{29}H parameter was repeated using the results for other oils from the analyzed data set (oils: Libya, Elemir, Rusanda and Zrenjanin; Tables 12, 13). This analysis revealed a high similarity between the values of this parameter determined by two instrumental techniques. High CCC coefficient (0.94; Table 13) reflects both, high precision and accuracy in measurement of this parameter by these two techniques. A narrow 95 % confidence interval for CCC, ranging from 0.90 to 0.96 indicates that similar values of the C_{29}Ts/C_{29}H ratio determined by GC-MS and GC-MS-MS can be expected in wide range of values. However, visual inspection of the similarity graph revealed a slight deviation from the line of equality ($y = x$ line) for the Libya crude oil samples. These results indicate that a difference in the strength of the agreement between these results can be expected for crude oils originating from different oil fields and, again point to the importance of regional calibration of GC-MS and GC-MS-MS results in organic geochemical studies. Difference in the strength of the agreement for C_{29}Ts/C_{29}H ratio in different basins could be attributed to the fact that certain oleanane/taraxastane derivatives such as 18α(H)-28-noroleanane and 19α(H)-24,28-bisnortaraxastane may co-elute with C_{29}H under routine GC-MS equipped with 25 m column (Nytoft *et al*., 2002). This influence can be particularly expected in deltaic oils of Late Cretaceous or younger age, rich in oleanane/taraxastane. On the other hand, C_{29}14α(H)17α(H)20(R)-sterane has almost identical retention time as C_{29}Ts. Contribution of this sterane to C_{29}Ts peak can be detected by presence of 217 fragment in the mass spectra of C_{29}Ts. This co-elution can be expected rather in marine oils, which are generally characterized by predominance of steranes over hopanes. Nevertheless, from the results of this study, a general conclusion can be drown that calculation of C_{29}Ts/C_{29}H ratio either by GC-MS or GC-MS-MS does not significantly influence geochemical interpretation, if routine GC-MS is performed with column heating rate at 2 ºC min^{-1}.

Table 13. Concordance correlation analysis

Parameter	Sample size	Concordance Correlation Coefficient (CCC)	CCC 95 % Confidence interval	Pearson correlation coefficient ρ (precision)	Bias correction factor C_b (accuracy)
Ts/(Ts+Tm)[a]	68	0.82	0.76-0.87	0.97	0.85
$C_{29}Ts/C_{29}H$[b]	68	0.53	0.35-0.67	0.59	0.90
$C_{29}Ts/C_{29}H$[c]	44	0.94	0.90-0.96	0.98	0.96
$C_{29}H/C_{30}H$[d]	68	0.27	0.05-0.47	0.29	0.94
$C_{30}M/C_{30}H$[e]	68	0.10	0.06-0.14	0.68	0.15
GI[f]	68	0.29	0.19-0.37	0.73	0.39
OI[g]	55	0.33	0.22-0.43	0.79	0.41

[a] Ts/(Ts+Tm) = C_{27}18α(H)-22,29,30-trisnorneohopane/(C_{27}18α(H)-22,29,30-trisnorneohopane + C_{27}17α(H)-22,29,30-trisnorhopane; [b] $C_{29}Ts/C_{29}H$ = C_{29}18α(H)-30-norneohopane/C_{29}17α(H)21β(H)-30-norhopane;
[c] Velebit oils were excluded from the analysis; [d] $C_{29}H/C_{30}H$ = C_{29}17α(H)21β(H)-30-norhopane/C_{30}17α(H)21β(H)-hopane; [e] $C_{30}M/C_{30}H$ = C_{30}17β(H)21α(H)-moretane/C_{30}17α(H)21β(H)-hopane;
[f] GI, Gammacerane index, GI = G x 100/$C_{30}H$; [g] Oleanane index, OI = O x 100/$C_{30}H$.

In the case of all other parameters investigated ($C_{29}H/C_{30}H$, $C_{30}M/C_{30}H$, GI, and OI; Table 12) concordance correlation analysis of the results calculated from two instrumental techniques revealed poor agreement with concordance correlation coefficients lower than 0.33 (Table 13) and significant deviation from the line of equality (Figure 25c-f).

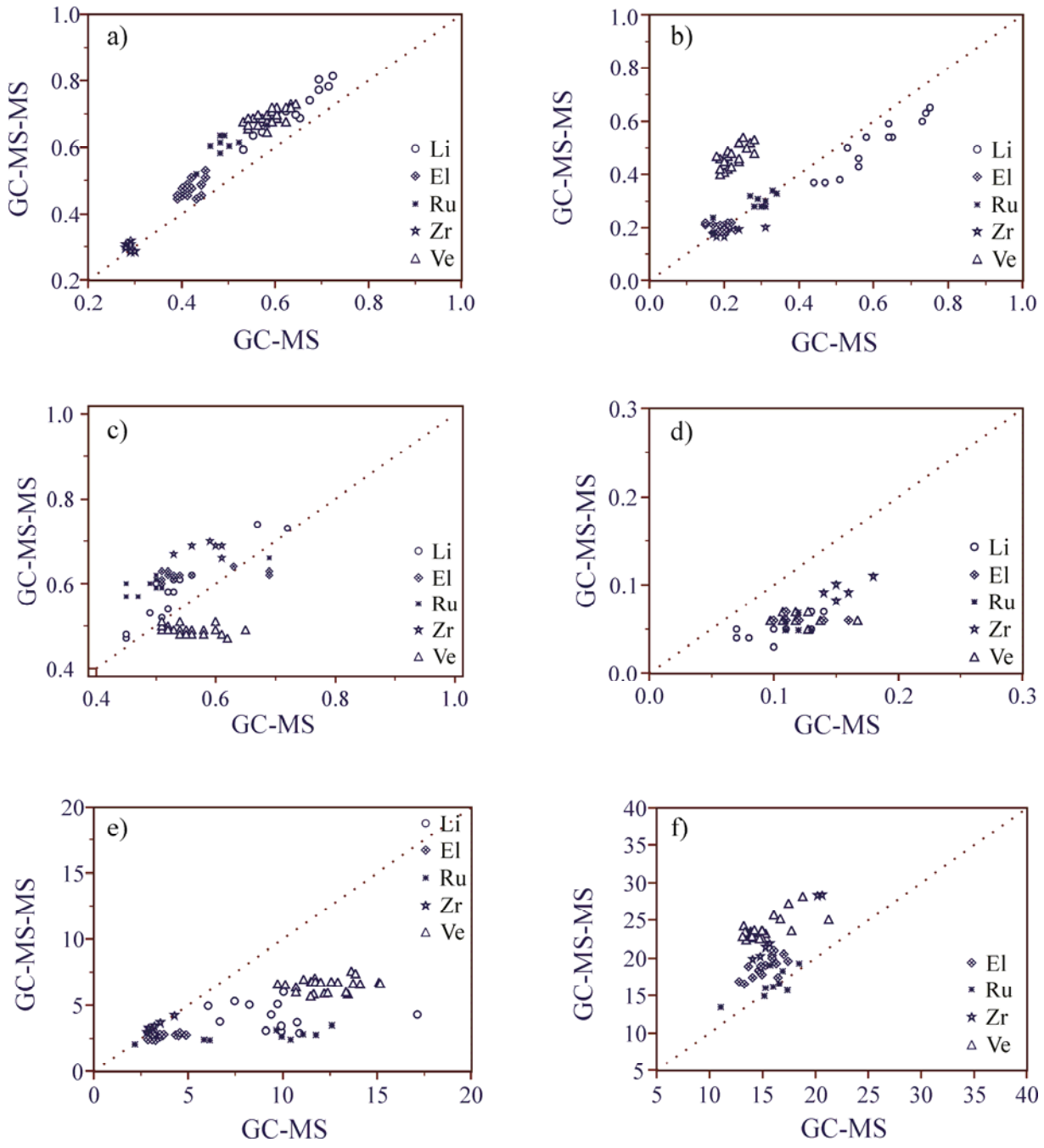

Figure 25. Concordance correlation analysis scatter diagrams for parameters: Ts/(Ts+Tm) (a); $C_{29}Ts/C_{29}H$ (b); $C_{29}H/C_{30}H$ (c); $C_{30}M/C_{30}H$ (d); GI (e) and OI (f).
Li – Libya oils; El – Elemir oils; Ru – Rusanda oils; Zr – Zrenjanin oils; Ve – Velebit oils.

6.1.4. The analysis of the mean-difference plots

Further investigation comprised construction of difference plot for each parameter (the plot of the difference between the values of the parameter calculated from GC-MS and GC-MS-MS results for each sample against their mean) and their visual and statistical analysis. The difference plots for the geochemical parameters analysed are shown in Figure 26.

The statistical analysis comprised a one-sample t-test of the difference for the paired measurements of the organic geochemical parameters analyzed. The purpose of this test was to determine if the difference between the values determined by GC-MS and GC-MS-MS is statistically considered different from zero. The results are shown in Table 14.

Table 14. One-sample t-test of the difference

Parameter	Sample size	Arithmetic mean	Lower limit	Upper limit	Significance level (P)[b]
Ts/(Ts+Tm)	68	0.07	0.01	0.14	< 0.0001
$C_{29}Ts/C_{29}H$[a]	44	- 0.03	- 0.13	0.08	0.0018
$C_{29}H/C_{30}H$	68	0.02	- 0.14	0.18	0.0493
$C_{30}M/C_{30}H$	68	- 0.06	- 0.09	- 0.02	< 0.0001
GI	68	- 4.10	- 10.10	1.90	< 0.0001
OI	55	5.60	- 0.70	12.00	< 0.0001

[a] Velebit oils were excluded from the analysis; [b] If the calculated P-value is lower than 0.05 the conclusion is that, statistically, the sample mean is significantly different from zero; For the abbreviations of parameters, see the legend of Table 12.

The t-test of the difference of the Ts/(Ts+Tm) parameter (Tables 12, 14) showed that the mean value of the difference between GC-MS-MS and GC-MS results is statistically significantly different from 0. These results indicate that these two methods do not agree equally through the investigated range of measurements. The visual analysis of the difference plot (Figure 26a) revealed that the GC-MS-MS gives higher values for the Ts/(Ts+Tm) parameter (Figure 26a), and that the difference from the GC-MS results for this parameter is in the range from 0.01 to 0.14, with the arithmetic mean at 0.07 (Table 14). Although the statistical analysis

indicated significant difference in calculation of Ts/(Ts+Tm) parameter based on GC-MS and GC-MS-MS analyses, from the organic geochemical point of view these differences can not be considered significant. Ts/(Ts+Tm) ratio depends on both, depositional environment and maturity and therefore is usually used in geochemical research only to confirm other biomarker ratios. Accordingly, it can be concluded that the differences observed in this research probably would not affect geochemical interpretation.

In the difference plot is also visible that the difference between GC-MS-MS and GC-MS results is similar for the oils from the same oil field but it is different for the oils from different oil fields. These results are in agreement with the previous concordance correlation analysis and confirm the importance of the analysis of the agreement between GC-MS-MS and GC-MS results in organic geochemical interpretations.

Considering the fact that the concordance correlation analysis of the $C_{29}Ts/C_{29}H$ revealed a different pattern for the Velebit oils (most probably affected by the higher heating rate during GC-MS analysis), these samples were excluded from the further analysis of this parameter. The t-test of the difference of the $C_{29}Ts/C_{29}H$ ratio (Tables 12, 14) showed that the mean value of the difference between GC-MS-MS and GC-MS results is statistically significantly different from 0. These results imply that these two methods do not agree well in the investigated range of measurements.

The visual inspection of the difference plot (Figure 26b) indicated a similar pattern for the oils originating from the same oil basin. On one hand, the results for the Serbian oils are centered around the zero line demonstrating low difference in the values of this parameter obtained from different instrumental methods and good agreement between them. On the other hand, the results for the oils from the Libyan Sirte basin indicate a systematic shift between the GC-MS-MS and GC-MS values. The values of the $C_{29}Ts/C_{29}H$ ratio in the Sirte oils determined by GC-MS-MS are lower and the difference from the GC-MS results for this parameter is in the range from 0.08 to -0.13, with the arithmetic mean at -0.03 (Table 14). Even though the statistical analysis suggested a significant difference in calculation of $C_{29}Ts/C_{29}H$ parameter based on GC-MS and GC-MS-MS analyses, these differences can not be considered significant in geochemical investigations. Since $C_{29}Ts/C_{29}H$ ratio as an analogue to the Ts/(Ts+Tm) ratio depends on both, depositional environment and maturity it is therefore usually used in geochemical research to

confirm other biomarker ratios. Because of that it can be concluded that the observed difference would not significantly influence geochemical interpretation.

The t-test of the difference of the $C_{29}H/C_{30}H$ parameter (Tables 12, 14) revealed that the mean value of the difference between GC-MS-MS and GC-MS results is statistically significantly different from 0, suggesting a possible disagreement between these two methods for the investigated set of measurements. The observed differences could be attributed to already discussed co-elution of certain compounds with $C_{29}H$, as well as to contribution of 30-nor-17α(H)-hopane (Peters *et al*., 2005) and some other non-identified compounds to $C_{30}H$ peak.

The visual analysis of the difference plot (Figure 26c) showed that the difference between the GC-MS-MS and GC-MS results is scattered around the zero line within the ± 0.16 range (Table 14). In organic geochemical research the $C_{29}H/C_{30}H$ ratio is used for distinction of anoxic carbonate or marl sourced oils having the value of this parameter ≥ 1 from other samples. Accordingly, it can be concluded that the observed differences between the GC-MS-MS and GC-MS results in most cases would not significantly influence the geochemical interpretation.

In the difference plot (Figure 26c) a similar pattern for the oils from the same oil field is noticeable, indicating that this parameter is influenced by both, origin and maturity of crude oils. However, a considerably different pattern for the oils from the different oil fields is noticeable as well. According to these results it can be concluded that the agreement between the GC-MS-MS and GC-MS results in analysis of the $C_{29}H/C_{30}H$ parameter can vary from one oil field to another in both, the sign and magnitude.

The t-test of the difference of the $C_{30}M/C_{30}H$ parameter (Tables 12, 14) showed that the mean value of the difference between GC-MS-MS and GC-MS results is statistically significantly different from 0, implying a possible disagreement between these two methods for the investigated set of measurements. The difference between GC-MS-MS and GC-MS results for this parameter is in the range from -0.02 to -0.09, and the arithmetic mean is at -0.06 (Table 14). In geochemical interpretations the $C_{30}M/C_{30}H$ ratio is used as maturity and age indicator. Its values usually range from 0.05 to 0.20 in oils, having boundary value for interpretation of 0.10. Considering all these facts, it can be concluded that the differences we observed between the

GC-MS-MS and GC-MS results in the analysis of the $C_{30}M/C_{30}H$ parameter should be considered important in geochemical studies.

The examination of the difference plot (Figure 26d) revealed that the values of the $C_{30}M/C_{30}H$ parameter determined by GC-MS-MS are lower than those determined by GC-MS. This analysis (Figure 26d) also revealed a very similar pattern for all oils investigated indicating a systematic difference between the two analytical methods, which is in this case very similar for all oils investigated regardless of their origin.

Possible influence of co-elution in GC-MS traces on $C_{30}H$ peak has already been discussed. However, $C_{30}M$ peak can also be affected by co-elution of $C_{30}17\alpha(H)21\alpha(H)$-hopane or $C_{31}17\alpha(H)22(S)$-diahopane during GC-MS analyses, particularly under conditions of poor column performance.

The t-test of the difference of the GI (Tables 12, 14) indicated that the mean value of the difference between GC-MS-MS and GC-MS results is statistically significantly different from 0. These results suggest that these two methods do not agree through the investigated range of measurements. Visual inspection of the difference plot (Figure 26e) showed that the lower values measured by GC-MS-MS, comparing to GC-MS should always be expected. Furthermore, from this figure is obvious that a proportional difference exists between these results, with an increase in the differences between GC-MS and GC-MS-MS results corresponding to larger values. All these results demonstrate significant disagreement between the GC-MS-MS and GC-MS results in GI analysis. The reason for this disagreement can be explained with the fragmentation pattern of gammacerane during GC-MS analysis. Due to its high symmetry, gammacerane molecule always gives two identical fragments in *m/z* 191 mass chromatograms. Because of that, the gammacerane peak always suggests much larger values and the correction of the results is usually needed for proper interpretation (Seifert and Moldowan, 1979). Furthermore, some authors found that gammacerane co-elutes with a C_{31} methylhopane, which can be another source of unrealistically high gammacerane index values measured from GC-MS (Schoell *et al*., 1992). Finally, it shoud be stated that under conditions of poor column performance, gammacerane can nearly co-elute with the 22R epimer of $C_{31}17\alpha(H)21\beta(H)$-homohopane, which can additionally result in unrealistically high values of gammacerane ratio.

It can be concluded that the difference between GC-MS-MS and GC-MS results in analysis of GI is both, statistically and geochemically significant. Due to the all aforementioned reasons the GC-MS analysis always gives higher results requiring careful geochemical interpretation.

The t-test of the difference of the OI (Tables 12, 14) indicated that the mean value of the difference between GC-MS-MS and GC-MS results is statistically significantly different from 0. These results also indicated a possible disagreement between these two methods for the investigated set of measurements. The visual analysis of the difference plot (Figure 26f) showed that the GC-MS-MS method always gives higher values of this parameter comparing to the GC-MS results. Furthermore, a proportional difference between these results can be noticed, with an increase in the differences between GC-MS and GC-MS-MS results corresponding to larger values. All these results point to the significant disagreement between these two methods. These differences can be explained by co-elution and peak overlapping in GC-MS analyzes but also by better separation, higher precision and better selectivity of the GC-MS-MS system used.

The visual analysis of the difference plot (Figure 26f) also revealed that the difference magnitude between GC-MS-MS and GC-MS results in OI determination depends on the oil field studied. For the Rusanda oil samples the difference is close to 0 indicating a good agreement between the two methods and that they may be used interchangeably for the analysis of these crude oils. However, for the oils from the other oil fields the difference between GC-MS-MS and GC-MS results is higher and they are increasing in the following order Elemir < Zrenjanin < Velebit. For these three oil fields the difference between two analytical methods is not only statistically but also geochemically significant, and can significantly affect geochemical interpretation. Considering the fact that Oleanane in crude oils is an indicator for both source input and geologic age (Moldowan et al., 1994; Peters et al., 2005), these results are not surprising. Nevertheless these results also stress the importance of regional calibration between GC-MS-MS and GC-MS results for each oil field and each parameter to be analysed.

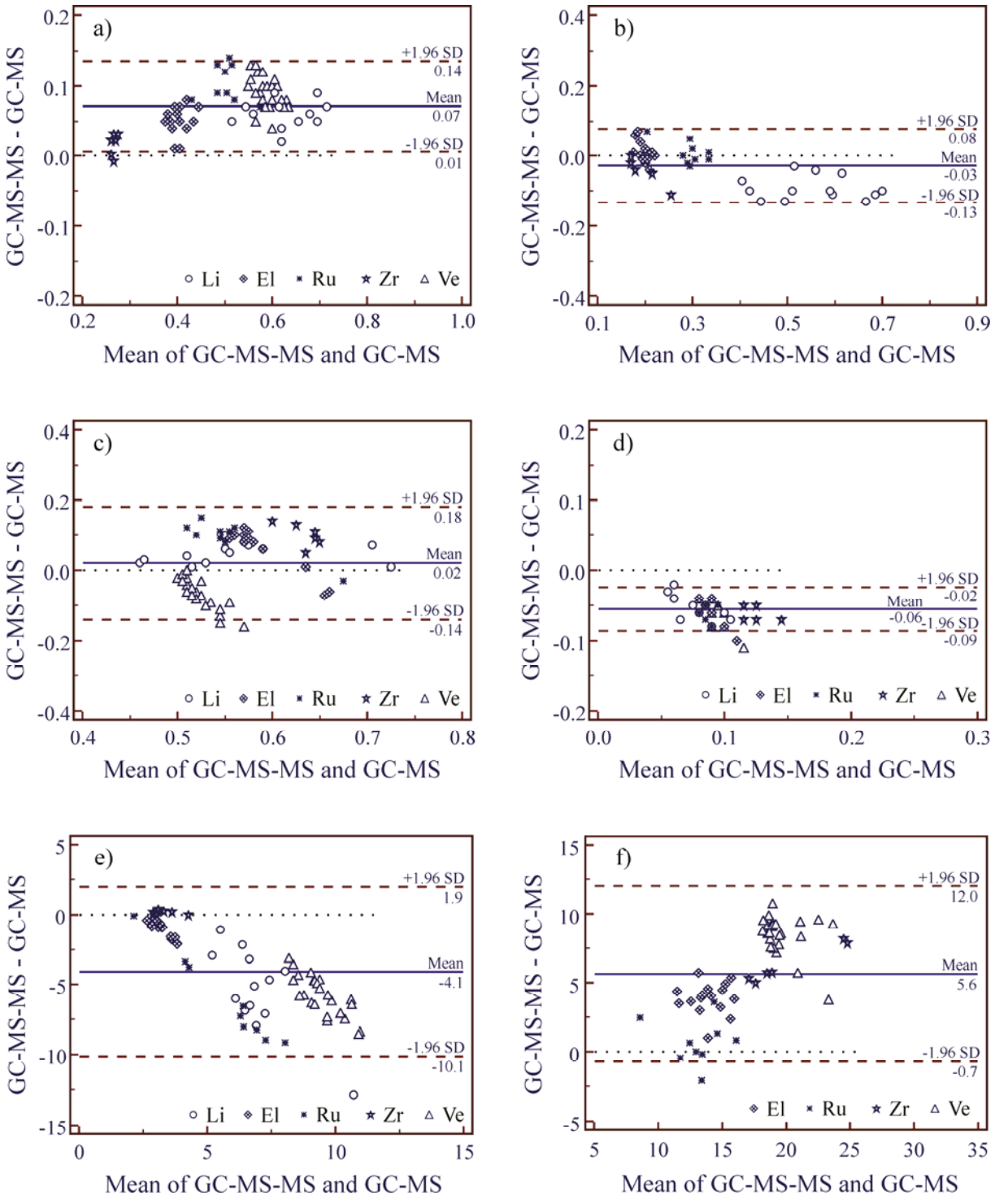

Figure 26. Mean-difference plots for parameters: Ts/(Ts+Tm) (a); $C_{29}Ts/C_{29}H$ (b); $C_{29}H/C_{30}H$ (c); $C_{30}M/C_{30}H$ (d); GI (e) and OI (f).
Li – Libya oils; El – Elemir oils; Ru – Rusanda oils; Zr – Zrenjanin oils; Ve – Velebit oils.

6.2. Organic geochemistry of crude oils from the Intisar oil field (East Sirte Basin, Libya)

In the second part of this thesis four crude oil samples from the oil fields Intisar A, Intisar D and Intisar E (Sirte Basin, Libya) were investigated in details in order to define depositional environment, lithology, thermal maturity and geologic age of the corresponding source rocks.

6.2.1. Samples

The Intisar structure is located in the eastern part of the Sirte Basin (Figure 22). It represents a group of genetically related oil fields in close proximity to each other. Nine structures containing hydrocarbons have been discovered so far, and they are designated: Intisar A, B, C, D, E, H, L, N and T (Hallet, 2002).

Previous organic geochemical studies on the Intisar crude oils were conducted on the samples from the oil fields A, B, C, D and L (Burwood et al., 2003). That research was based on the stable isotope and quantified biomarker analyses, and statistical evaluation of the data. The isotopic and biomarker composition suggested that the Intisar oils were of marine-source provenance. The results of biomarker analyses revealed that these oils were not biodegraded, and that they originated from mature marine shales, dating of Late Cretaceous or younger.

In this thesis the organic geochemical characterization of the Intisar crude oils continues. The oils investigated in this research were taken from different parts of the oil field Intisar A (sampled from the reef core and sampled outside of the reef core), and from the oil fields Intisar D and Intisar E. The organic geochemical research on these oils was conducted in order to define depositional environment, lithology, thermal maturity and geologic age of respective source rocks. Accordingly, genetic relationships among these oils were investigated as well.

6.2.3. Analytical and instrumental metods

The saturated and aromatic fractions were isolated from the crude oils according to the methods described in paragraph 5.2., and analysed by GC-MS and GC-MS-MS instrumental

techniques described in paragraph 5.3. Characteristic organic geochemical parameters were calculated from GC-MS and GC-MS-MS chromatogram peak areas (softwares: Agilent ChemStation and Waters MassLynx V4.0).

Mass chromatograms *m/z* = 71 of all Intisar crude oil samples investigated in this research, showing the distribution of *n*-alkanes and isoprenoids is shown in Figure 27. Figures 28, 29 and 30 are ion chromatograms characteristic of the phenanthrene and methylphenanthrenes, methyl-dibenzothiophenes, and trimethyl-naphtalenes respectively.

GC-MS mass chromatograms *m/z* = 191 and *m/z* = 217, of all Intisar crude oil samples investigated in this research, are shown in Figures 31 and 32.

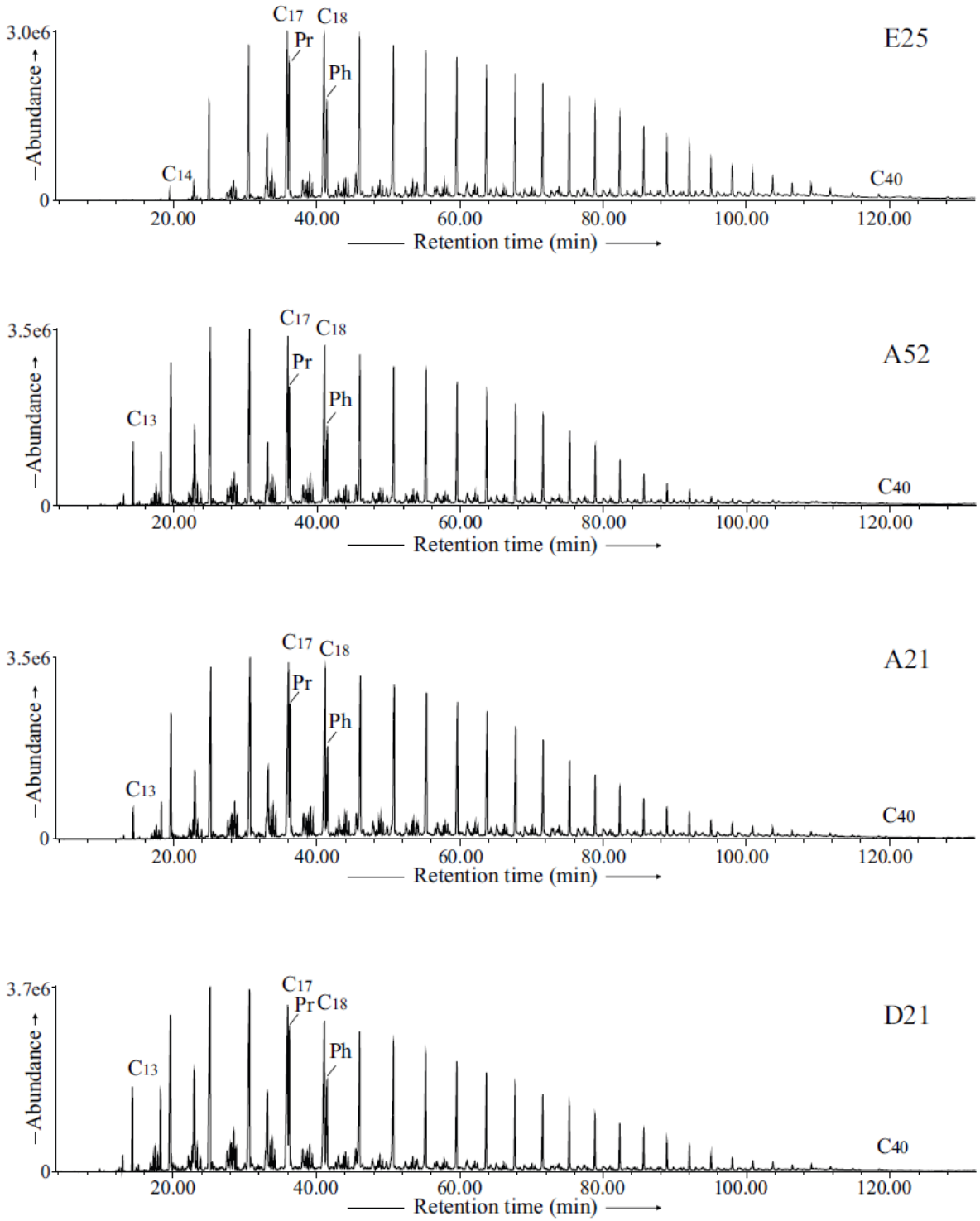

Figure 27. Mass chromatograms *m/z* = 71 of all Intisar crude oil samples investigated in this research.

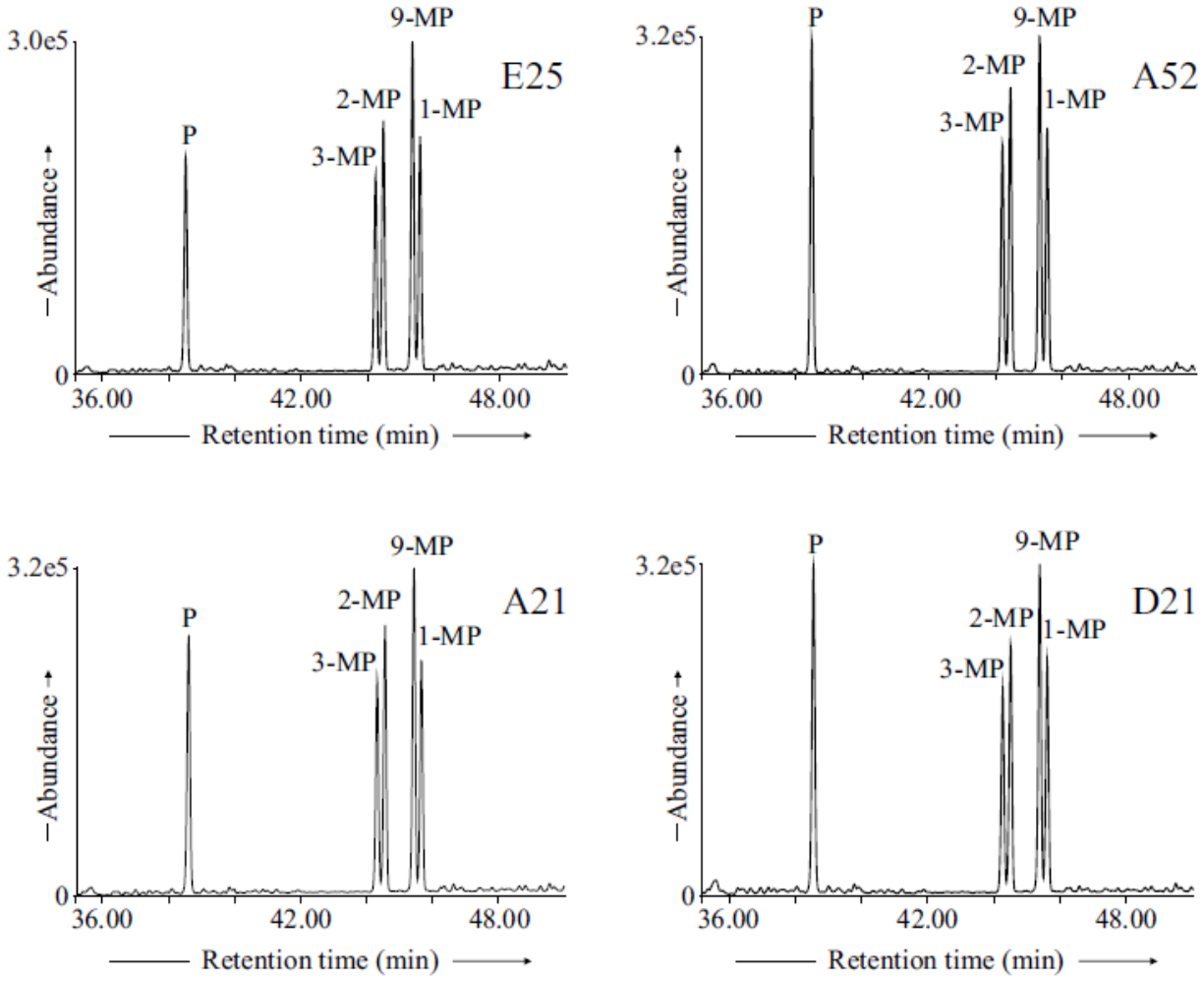

Figure 28. Mass chromatograms *m/z* = 178 + 192 of all Intisar crude oil samples investigated in this research (P – phenanthrene; MP – methylphenanthrene).

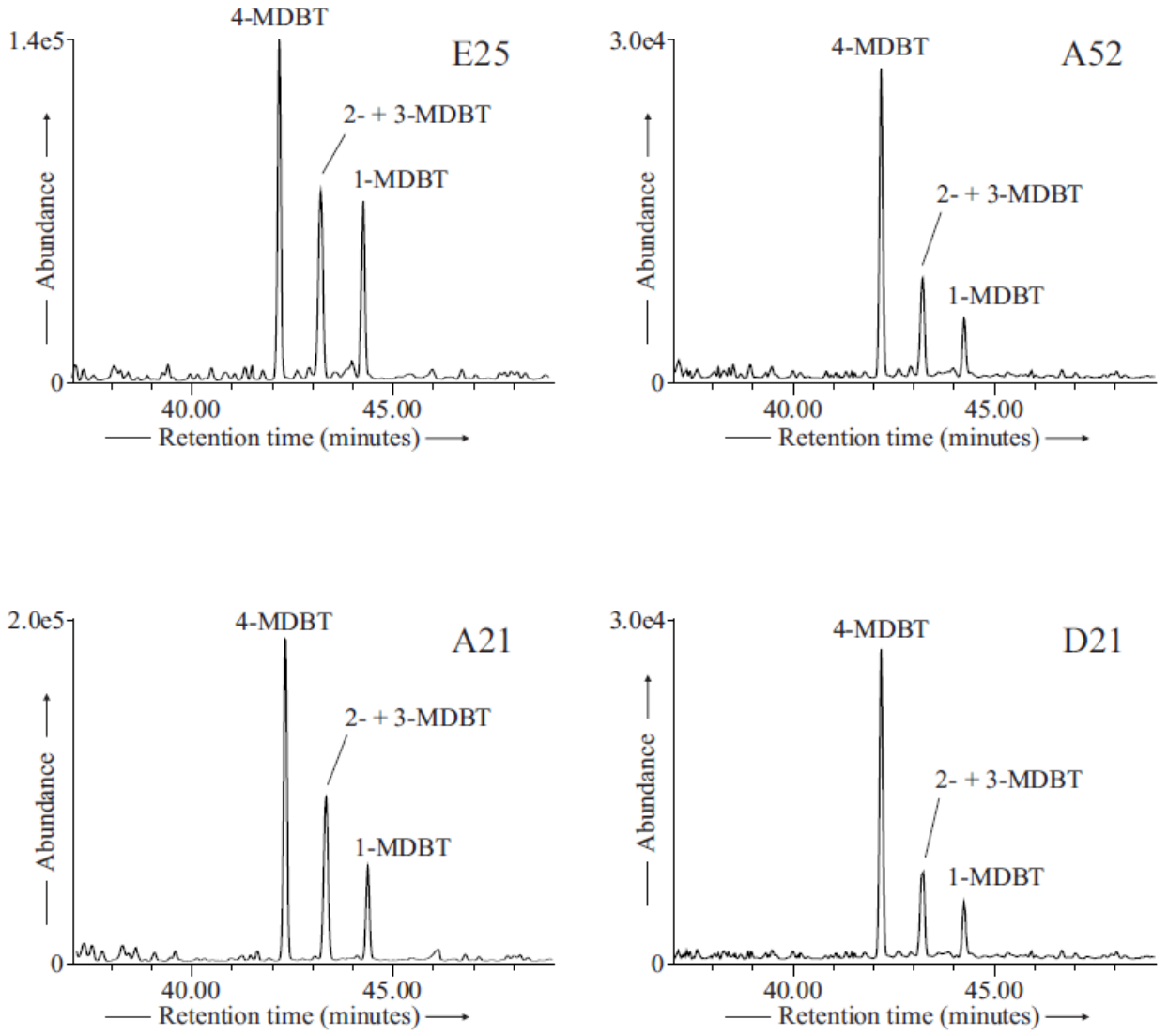

Figure 29. Mass chromatograms *m/z* = 198 of all Intisar crude oil samples investigated in this research (MDBT - methyldibenzotiophene).

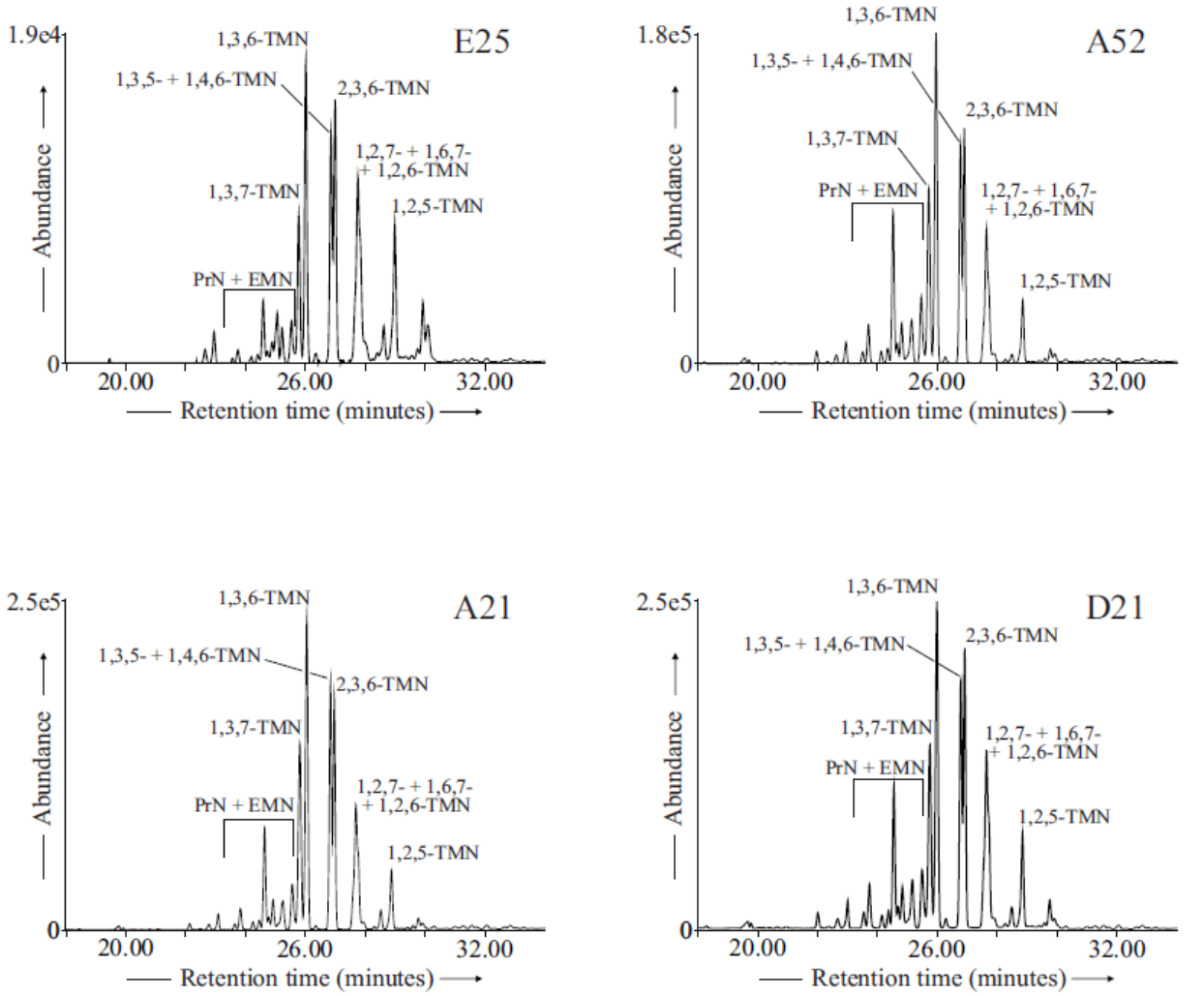

Figure 30. Mass chromatograms *m/z* = 170 of all Intisar crude oil samples investigated in this research (TMN - trimethylnaphthalene; PrN - propylnaphthalene; EMN - ethylmethylnaphthalene).

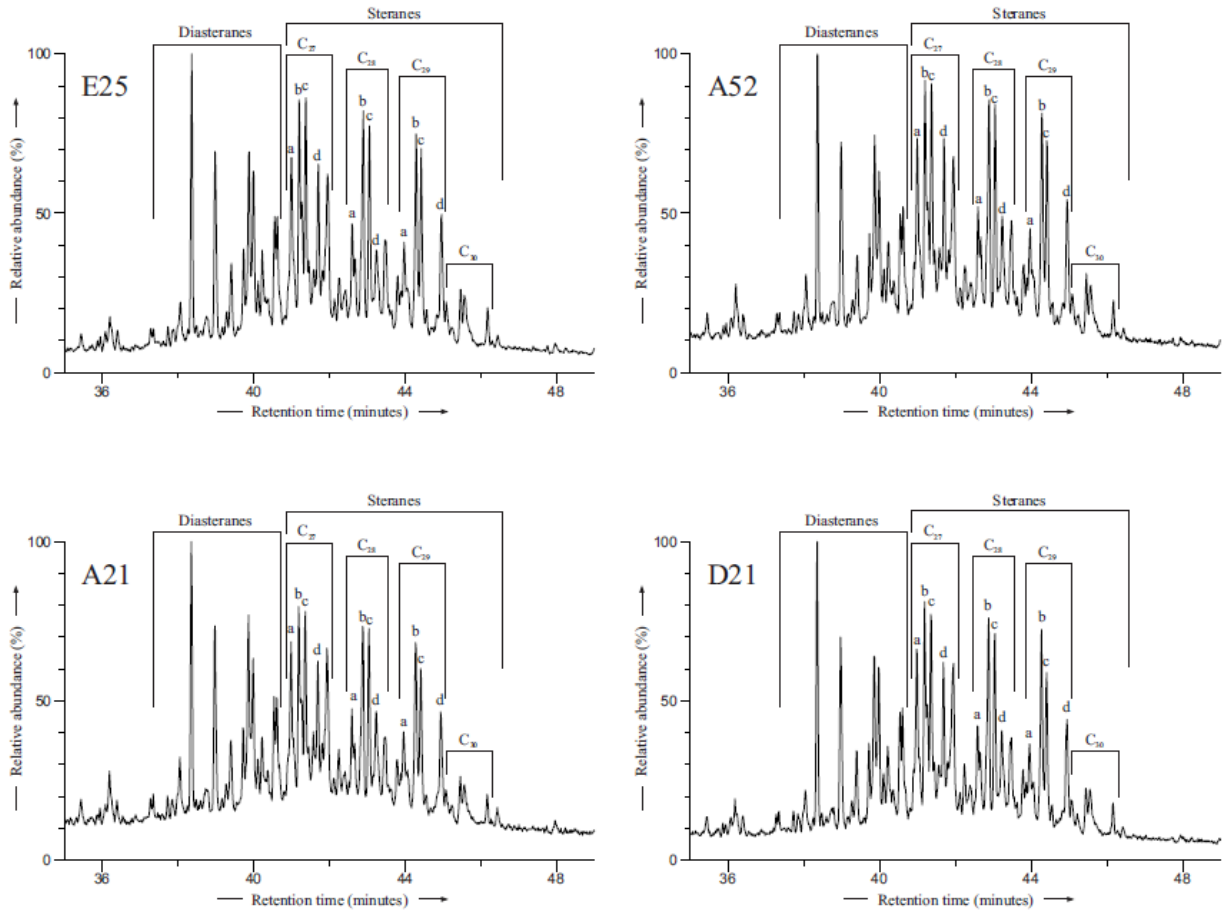

Figure 31. Mass chromatograms *m/z* = 217 of all Intisar crude oil samples investigated in this research (a - 14α(H),17α(H),20(S) - steranes; b - 14β(H),17β(H),20(R)-steranes; c - 14β(H),17β(H),20(S)-steranes; d - 14α(H),17α(H),20(R)-steranes).

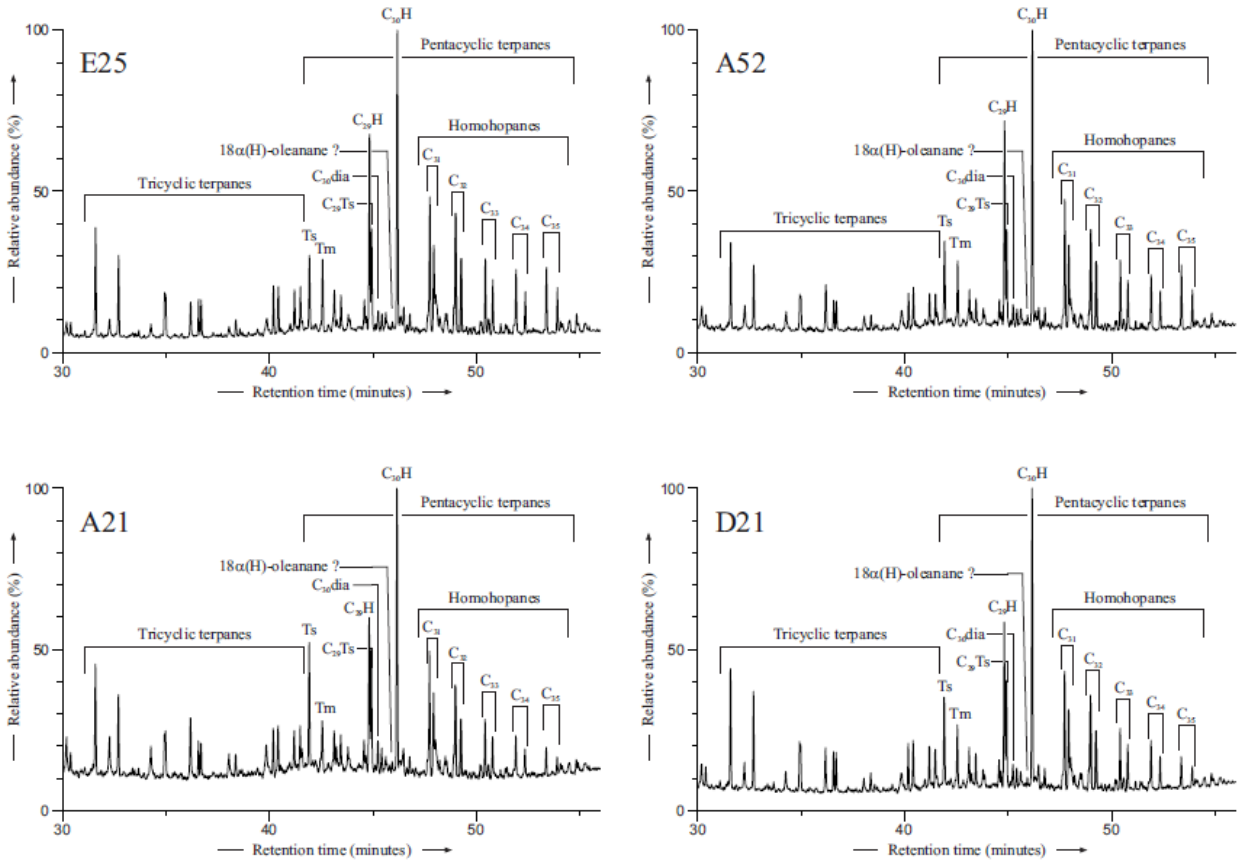

Figure 32. Mass chromatograms *m/z* = 191 of all Intisar crude oil samples investigated in this research (Ts - 18α(H),22,29,30-trisnorneohopane; Tm - 17α(H),22,29,30-trisnorhopane; C_{29}Ts - C_{29}18α(H),30-norneohopane; C_{30}dia - C_{30}17α(H)-diahopane; C_{29}H - C_{29}17α(H),21β(H)-hopane; C_{30}H - C_{30}17α(H),21β(H)-hopane).

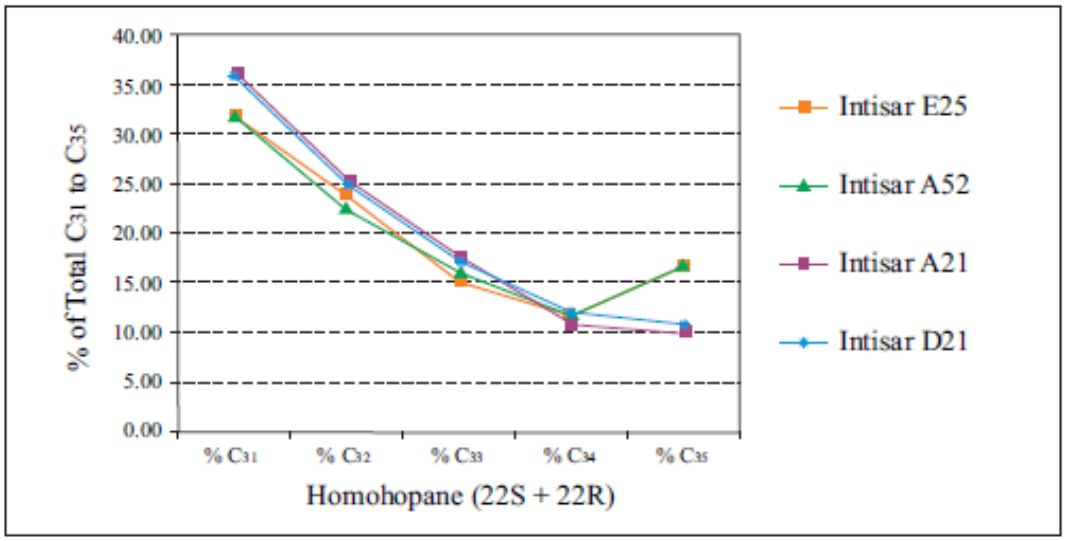

Figure 33. Distribution of $C_{31} – C_{35}$ homohopanes in the Intisar crude oils investigated in this research.

6.2.4. General characteristics of the investigated oils

The well depths and group parameters of the investigated Intisar oils are shown in the Table 15.

API gravity is a bulk physical property of oils that can be used as a crude indicator of thermal maturity (Peters et al., 2005). Based on the API gravity values (Table 15), the investigated crude oils can be classified as light crude oils. However, two of these samples (Intisar A52 and Intisar D21), having API gravity about 46º can be classified as more similar to condensates. Accordingly, these two samples are expected to be more mature than the samples with lower API gravity values.

Sulphur content is a bulk parameter commonly used to support inferred genetic relationships among crude oils (Peters et al., 2005). According to the values of sulphur content in the Intisar oils (Table 15) it can be presumed that some of these samples might be genetically different. Oil samples Intisar A21 and Intisar D21 have low content of sulphur (% S about 0.3) which is similar to reported literature values for the Intisar oils (Hallett, 2002; Tawardos, 2011).

However, oil samples Intisar E25 and Intisar A52 have sulphur content about 0.8. The difference between these values implies a possible genetic difference between these two groups of samples. However, this difference in sulphur content is not sufficient to make any firm conclusions, and it should be supported by other results

Table 15. Well depth and group parameters of the Intisar oils.

	Well depth (m)	API gravity (°)	% S	% Asphaltenes	Bulk composition			CPI*	*n*-Alkane max.	Pr/Ph
					% Saturated	% Aromatic	% NSO			
Intisar E25	2244	35.69	0.78	2.50	63.90	18.50	17.60	1.01	*n*-C17	1.41
Intisar A52	2462	45.93	0.83	0.70	68.30	16.30	15.40	1.02	*n*-C15	1.56
Intisar A21	3685	33.60	0.32	0.10	74.70	16.10	9.20	1.04	*n*-C16	1.52
Intisar D21	2999	45.67	0.29	0.40	73.90	15.50	10.60	1.03	*n*-C15	1.71

* the CPI parameter is calculated for the whole n-alkane range, using the equation by Bray and Evans, 1961.

All samples investigated have low content of asphaltenes. Saturated hydrocarbons dominate over aromatics and NSO-compounds. These results support presumption on high maturity of the Intisar oils (Peters at al., 2005; Tissot and Welte, 1984; Waples, 1985).

Total alkane chromatograms of all Intisar crude oil samples investigated in this research are shown in Figure 27. Total alkane chromatograms of all samples investigated are unimodal, dominated by lower *n*-alkane homologues and without any unresolved complex mixures (UCMs), showing that the Intisar oils were not biodegraded. Lower homologues of *n*-alkanes dominate over the higher ones in all samples. *n*-Alkane maximum is in the C_{15} to C_{17} range (Table 15). CPI (carbon preference index) values for all samples are close to 1 (Table 15). These results indicate significant proportion of algal biomass in precursor material of the source rocks and/or high level of thermal maturity (Peters et al., 2005).

Pristane/phytane is one of the most widely used biomarker parameters for the assessment of redox conditions during sediment deposition. Values of the pristane/phytane ratio < 1 are typical of anoxic depositional environment of source rocks while values of the pristane/phytane ratio > 1 point to the oxic conditions during deposition of sediment (Didyk et al. 1978; Peters et al., 2005). Pristane/phytane ratios for all Intisar crude oil samples investigated in this research are in the 1.41 to 1.71 range (Table 15), averaging at 1.55. These results indicate intermediate (suboxic) conditions during deposition of precursor organic material. Additionally, pristane/phytane ratios values 1 – 2 are also found to be typical of marine shale (Hughes et al., 1995; Peters et al., 2005). However, it should be stressed that pristane/phytane ratios are also influenced by the precursor organic matter type, maturity and salinity (Goosens et al., 1984; Alexander et al., 1981; ten Haven et al., 1987). Accordingly, interpretations based on this ratio should always be confirmed by other organic geochemical parameters.

6.2.5. Geologic age of the source rocks

Geologic age of the source rocks of the Intisar oils was evaluated using the age-specific biomarker ratios: nordiacholestane ratio and oleanane index.

Nordiacholestane ratio (NDR; Holba et al., 1998) is calculated as a ratio of abudances of C_{26} 24-nordiacholestanes and C_{26} 27-nordiacholestanes. Application of NDR as an age diagnostic ratio is based on the evidence that C_{26} 24-nordiacholestanes, directly or indirectly, originate from diatoms. Values of the NDR can be used to differentiate between Jurassic (NDR > 0.20), Cretaceous (NDR > 0.25), and Oligocene-aged or younger samples (NDR > 0.50; Holba et al., 1998). Nordiacholestane ratio for the Intisar oils (average value = 0.35) suggested Cretaceous or younger age of their source rocks.

Oleanane in crude oils is used as an indicator for both source input and geologic age. Its presence in the oils indicates contribution of angiosperms (flowering plants), and it is restricted to Upper Cretaceous or younger sediments (Moldowan et al., 1994; Peters et al., 2005). The analysis of the GC-MS *m/z* = 191, and GC-MS-MS 412 → 191 data of the Intisar oils showed presence of a small peak eluting at the retention time exactly the same as the retention time of

18α(H)-oleanane (Figure 32). This result might indicate low values of oleanane index, and, accordingly, Upper Cretaceous age of the investigated oils. However, presence of some other compounds (presumably hopanes) could also be detected in GC-MS *m/z* = 191 traces of crude oils, at the retention time exactly the same as the retention time of 18α(H)-oleanane. In the absence of oleanane, this might lead to their misidentification as oleanane, and furthermore to misinterpretation of the geologic age of the investigated oils (Moldowan et al., 1991). Due to the fact that these results were not convincing enough to indubitably prove the presence of 18α(H)-oleanane in the Intisar oils, and accordingly, their Upper Cretaceous age, these samples were further thoroughly analysed.

Considering that the compounds detected in GC-MS *m/z* = 191 traces were present in a very low concentration, it was not possible to isolate them in order to confirm their structure. However, recent research showed that oleanane-containing oils always contain some other, "novel" (not yet identified) compounds. These novel compounds can be seen in oils with oleanane but not in those without. Furthermore, they are much easier to detect than oleanane itself (Nytoft, H.P., unpublished data). Detailed analysis of numerous mass spectra from different GC-MS-MS traces showed that these "oleanane accompanying" compounds were not present in the Intisar oils. These results gave us an indirect proof that 18α(H)-oleanane was absent in these samples as well. Accordingly, we can not confirm Upper Cretaceous or younger age of the Intisar oils.

It can be concluded that the analysis of the age-specific biomarker ratios suggested Cretaceous, most probably Lower Cretaceous age for the Intisar oils.

6.2.6. Maturity assessment

The maturity assessment of the Intisar oils was done using typical sterane isomerization maturity parameters, and vitrinite reflectance equivalent (Table 16).

Table 16. Maturity parameters of the Intisar oils.

	C_{29}αα(S/(S+R))	C_{29}(ββ/(ββ+αα))	Rc (MPI1)	Rc (MDR)	Rc (F1)	Rc (F2)	Rc (TNR2)
Intisar E25	0.48	0.63	0.90	0.64	0.82	0.79	0.88
Intisar A52	0.49	0.65	0.90	0.88	0.88	0.85	0.85
Intisar A21	0.50	0.65	0.92	0.74	0.87	0.85	0.85
Intisar D21	0.51	0.65	0.85	0.93	0.84	0.80	0.88

Rc (MPI-1) = % Rc = 0,40 + 0,60MPI-1 (Radke, Welte, 1983)
Rc (MDR) = % Rc = 0,073 × MDR + 0,51 (Radke, 1988)
Rc (F1) = % Rc = 2,242 × F1 – 0,166 (Kvalheim et al., 1987)
Rc (F2) = % Rc = 3,739 × F2 – 0,112 (Kvalheim et al., 1987)
Rc (TNR2) = % Rc = 0,40 + 0,60 TNR2 (Radke et al., 1986)

Sterane maturity parameters C_{29}(ββ/(ββ+αα)) and C_{29}αα(S/(S+R)) are considered the most often used molecular parameters in evaluation of thermal maturity. Application of these molecular maturity parameters in petroleum geochemistry is based on the relative enrichment of thermally more stable isomers compared to the biologically-inherited forms with increasing thermal maturity. C_{29}αα(S/(S+R)) isomerization ratios for C_{29}-steranes rise from 0 to reach an equilibrium value of ~ 0.5 near the main oil generation window (Peters et al., 2005). C_{29}(ββ/(ββ+αα)) parameter increases from non-zero values to ~ 0.70 around peak oil generation, making it effective at higher levels of maturity (Seifert and Moldowan, 1986).

Values of the C_{29}αα(S/(S+R)) parameters of the Intisar oils indicate that these isomerization ratios have reached equilibrium (Table 16), indicating high level of thermal maturity of these oils (Peters et al., 2005). This conclusion is confirmed by high values of the C_{29}(ββ/(ββ+αα)) parameters (Table 16).

Vitrinite reflectance (Ro) is a nonbiomarker parameter used as an indicator of maturity in hydrocarbon source rocks. Its equivalent (Rc) calculated using characteristic compounds in oils is used in the literature to estimate source rock thermal maturity at the time of hydrocarbon expulsion. The vitrinite reflectance equivalent of the Intisar oils was calculated using values of aromatic parameters: MPI-1 (based on the relative abundances of phenanthrene and methyl-phenanthrenes; Radke, Welte, 1983), MDR (based on the relative abundances of 4- and 1-methyl-dibenzothiophenes; Radke, 1988), F1 and F2 (based on the relative abundances of

methyl-phenanthrenes; Kvalheim et al., 1987), and TNR2 (based on the relative abundances of trimethyl-naphtalenes; Radke et al., 1986). All equations gave similar values of calculated vitrinite reflectance equivalent in the 0.8 – 0.9 % range (Table 16), proving that the Intisar oils were generated during the main phase of oil generation.

6.2.7. Precursor organic matter type

Evaluation of the precursor organic matter type of the Intisar oils was based on the abundance and distribution of regular sterane isomers C_{27}–C_{29}ααα(R), C_{30} steranes and tricyclic terpanes.

The use of distribution of C_{27}–C_{29} regular steranes in the evaluation of the depositional environment of organic matter is based on the evidence that C_{27} steranes originate dominantly from marine plankton, C_{28} steranes from yeast, fungi, plankton and algae (Volkman, 2003), while C_{29} steranes originate from higher plants (Volkman, 1986) and from brown and green algae (Volkman, 2003). Distribution of C_{27}–C_{29} regular steranes in all Intisar samples was found to be uniform (Figure 31), indicating a mixed origin of these oils. Marine C_{30} steranes (4-desmethylsteranes; Holba et al., 2003) are present in low concentration in all samples (Figure 31), which is another evidence of marine influenced depositional environment of the Intisar oils. Finally, high contribution from marine material to the source rocks was additionally supported by the relatively high abundance of the tricyclic terpanes (Figure 32; Aquino Neto et al., 1983).

6.2.8. Lithology and depositional environment of the source rocks

Evaluation of the lithology and depositional environment of the source rocks of the Intisar oils was based on the rearranged sterane and hopane biomarker ratios: $\sum C_{27}$diasteranes/$\sum C_{27}$steranes, C_{30}diahopane/C_{30}hopane, C_{29}Ts/C_{29}hopane, Ts/(Ts+Tm) and C29H/C30H (Table 17). All these ratios are used as indicators of thermal maturity, but also depend significantly on the lithological composition of the source rocks (Peters et al., 2005).

These parameters for Intisar oils have high values (Table 17; Peters et al., 2005), confirming high maturity of these oils but they also indicate a high content of clays in their source rocks.

Table 17. Indicators of the source rock lithology and depositional environment.

	C_{27} dia/ster	C_{30}dia/C_{30}H	C_{29}Ts/C_{29}H	Ts/(Ts+Tm)	C_{29}H/C_{30}H
Intisar E25	1.65	0.08	0.37	0.54	0.74
Intisar A52	1.53	0.08	0.38	0.63	0.73
Intisar A21	1.84	0.13	0.63	0.74	0.58
Intisar D21	1.73	0.09	0.54	0.64	0.58

C_{29}/C_{30}H ratios for all samples are similar in values (Table 17), pointing to the similar conditions during deposition of organic material in the Intisar oils' source rocks. Additionally, values of this ratio lower than 1.0 suggest clastic nature of the respective source rocks (Moldowan et al., 1985).

6.2.9. Redox conditions during deposition of the source rocks

The assessment of the redox conditions during deposition of the Intisar oils' source rocks was based on the interpretation of organic geochemical parameters which are indicators of the availability of oxygen in the environment: pristane/phytane ratio and C_{35} homohopane index (Peters et al., 2005).

Pristane/phytane ratio, as discussed earlier, had similar values for all these oils (Table 17) and indicated suboxic conditions during deposition of precursor organic material.

The relative distribution of C_{31}-C_{35} 17α,21β(H)-29-homohopanes 22R+22S in crude oils can be used as an indicator of the redox potential during deposition of source rocks (Peters and Moldowan, 1991). High C_{35} homohopane indices (expressed as ratio of C_{35}/(C_{31}-C_{35})) are indicators of highly reducing marine conditions during deposition, whereas low C_{35} homohopane

indices are typical of oxic conditions. Contrary to all previous results which showed great similarity between Intisar oils, values of the C_{35} homohopane indices revealed some difference between the samples investigated and divided them in two groups based on the redox conditions in the environment during deposition of their source rocks (Figure 33). Samples Intisar E25 and Intisar A52 have C_{35} homohopane index values > 0.1, consistent with the anoxic marine environment. On the contrary, values of C_{35} homohopane indices for samples Intisar A21 and Intisar D21 are lower, suggesting oxic conditions during deposition.

According to these results it can be concluded that samples from the oil field Intisar A actually originate from two source rocks different in the redox conditions in the environment during their deposition. Additionally, these results suggest that the oil sample Intisar A21 (sample from the reef core) is more similar to the sample from the oil field Intisar D, while the oil sample Intisar A52 (outside of the reef core) is more similar to the sample from the oil field Intisar E. Based on these similarities, a common source can be presumed for the oils from the oil field Intisar D and from the reef core in the oil field Intisar A. Similarity between the oil samples from the oil field Intisar E and outside of the reef core in the oil field Intisar A implies that these samples originate from the same source rock.

These results clearly indicate existence of at least two source rocks for the Intisar oils. Furthermore, presence of two oil families accumulated in different parts of one oil field sugests that these oils probably have had different migration pathways.

Finally, these results demonstrate that C_{35} homohopane biomarker indicators of oxicity and anoxia might be more sensitive, and potentially, more reliable in these assessments than other biomarker ratios.

7. Conclusions

In the first part of this thesis a comparison of the values of parameters calculated from distributions and abundances of selected pentacyclic terpanes in crude oils, derived from gas chromatography-mass spectrometry (GC-MS) and gas chromatography-mass spectrometry-mass spectrometry (GC-MS-MS) quantification results was performed. The parameters analyzed are the most often used terpane source and maturity parameters, which were applied to a large sample set of 70 oils. Two statistical methods were used: concordance correlation coefficient and mean-difference plot.

The analyses of the Ts/(Ts+Tm), $C_{29}Ts/C_{29}H$ and $C_{29}H/C_{30}H$ parameters indicated a good agreement between the results obtained by the GC-MS-MS and GC-MS methods and that they may be used interchangeably in determination of these parameters. However, it was also noticeable that the agreement between the GC-MS-MS and GC-MS results in analysis of these three parameters can vary from one oil field to another in the sign and/or magnitude. Although these differences were found to be statistically significantly different they are not geochemically significantly different because in most cases they would not affect geochemical interpretations.

The analyses of the $C_{30}M/C_{30}H$ parameter, GI and OI showed that the difference between the GC-MS-MS and GC-MS results is both, statistically and geochemically significant. The difference between two analytical methods in determination of these three parameters can significantly affect geochemical interpretation. Because of that $C_{30}M/C_{30}H$ parameter, GI and OI require careful analysis and interpretation depending on the analytical methods used.

The results obtained in this study point to the importance of comparison between GC-MS-MS and GC-MS results in organic-geochemical studies. Considering the fact that most of the organic geochemical parameters were originally defined on the basis of the results of GC-MS analysis, whenever GC-MS-MS results are to be used in organic geochemical interpretations, a regional calibration of GC-MS vs. GC-MS-MS relationship for each petroleum system is highly recommended.

In the second part of this thesis organic geochemical characteristics of crude oils from the Intisar oil field were evaluated using biomarker ratios for the saturated and aromatic hydrocarbon fractions of 4 crude oil samples.

Total alkane chromatograms showed that the Intisar oils were not biodegraded, and indicated significant proportion of algal biomass in precursor material of the source rocks and/or high level of thermal maturity.

The analysis of the age-specific biomarker ratios suggested Cretaceous, most probably Lower Cretaceous age for the Intisar oils.

Source parameters, i.e., the distribution of regular steranes, C_{30} steranes and tricyclic terpanes, indicated a mixed origin of these oils.

Sterane maturity parameters indicated high level of thermal maturity of these oils consistent with a vitrinite reflectance of 0.8 – 0.9 % Ro.

Numerous rearranged sterane and terpane biomarker ratios indicated a siliciclastic nature for the source rocks but also confirmed high maturity of these oils.

Pristane/phytane ratios for all Intisar crude oil samples indicated similar, intermediate (suboxic) conditions during deposition of precursor organic material. However, analysis of C_{35} homohopane indices offered a more precise assessments of the redox conditions during deposition of the Intisar oils' source rocks.

These results clearly indicate existence of at least two source rocks for the Intisar oils, different in the redox conditions in the environment during their deposition. Furthermore, presence of two oil families accumulated in different parts of one oil field sugested different crude oil migration pathways in this region.

8. References

Abadi, A., 2002. Tectonics of the Sirt Basin, Interferences from Tectonic Subsidence Analysis, Stress Inversion and Gravity Modeling. PhD Thesis.

Abdunaser, K .M., 2015. Review of the petroleum geology of the western part of the Sirt Basin, Libya. Journal of African Earth Sciences **111**, 76-91

Aboglila, Salem .Abdulghni-O., 2010. Organic and isotopic geochemistry of source-rocks and crude oils from the East Sirte Basin (Libya). Ph.D. Curtin University of Technology, Department of Chemistry.

Aboglila, S., Grice, K., Trinajstic, K., Dawson, D., Williford, K.H., 2010a. Use of biomarker distributions and compound specific isotopes of carbon and hydrogen to delineate hydrocarbon characteristics in the East Sirte Basin (Libya). Organic Geochemistry **41**, 1249–1258.

Abugares, Miloud .M., 2007. Deposition, diagenesis, and reservoir development of the Cretaceous Lidam formation, SE Sirt Basin, Libya., Durham theses, Durham University. Available at Durham E-Theses Online: http://etheses.dur.ac.uk/2599/

Ahlbrandt, T .S., 2001. The Sirte Basin is Province of Libya-Sirte-Zelten Total Petroleum System. US Geological Survey Bulletin 2202-F. <http:// geology.cr.usgs.gov/pub/bulletins/b2202-f/> (accessed 20.4.2009).

Ahmed, M .El Kammar., Selim, S .Selim., Mosab, .A .Abukliesh., 2013. Source Rock Evaluation Of The Upper Cretaceous Sirte Formation In Eastern Sirte Basin, Libya. J Am Sci **9**, 166-175, (ISSN: 1545-1003). http://www.jofamericanscience.org. 22

Ahmed, M., George, S .C., 2004. Changes in the molecular compositions of crude oils during their preparation for GC and GC-MS analyses. Organic Geochemistry **35**, 137-155.

Al-Arouri, K .R., McKirdy, D .M., Boreham, C .J., 1998. Oil-source correlations as a tool in identifying the petroleum systems of the Southern Taroom Trough, Australia. In: Horsfield, B. et al. (Eds.) Advances in Organic Geochemistry 1997, Part 1. Pergamon Press, Oxford, pp. 713-734.

Albrecht, P., 1986. Évolution géochimique des polyterpènes et des stérols, Prix Roussel, Institut Scientifique Roussel, Paris.

Alexander, R., Kagi, R., Woodhouse, G.W., 1981. Geochemical correlation of Windalia oil and extracts of Winning Grop (Cretaceous) potential source rocks, Barrow Subbasin, Western Australia. American Association of Petroleum Geologists Bulletin 65, 235–250.

Altman, D.G., 1991. Practical statistics for medical research. Chapman and Hall, London, UK.

Altman, D.G., Bland, J.M., 1983. Measurement in medicine: the analysis of method comparison studies. Statistician 32, 307-317.

Alexander, R., Kagi, R .I., Larcher, A.V., Woodhouse, G .W., 1983. Aromatic hydrogen exchange in petroleum source rocks. In: Bjorøy, M. et al. (Eds.) Advances in Organic Geochemistry 1981. Wiley and Sons, Chichester, pp. 69-71.

Alexander, R., Kagi, R .I., Rowland, S .J., Sheppard, P .N., Chirila, T .V., 1985. The effects of thermal maturity on distributions of dimethylnaphthalenes and trimethylnaphthalenes in some ancient sediments and petroleums. Geochimica et Cosmochimica Acta **49**, 385-395.

Alexander, R., Kagi, R .I., Sheppard, P .N., 1984. 1,8-Dimethylnaphthalene as an indicator of petroleum maturity. Nature **308**, 442-443.

Alexander, R., Kagi, R .I., Singh, R .K., Sosrowidjojo, I .B., 1994. The effect of maturity on the relative abundances of cadalene and isocadalene in sediments from the Gippsland Basin, Australia. Organic Geochemistry **21**, 115-120.

Amjed Ahmed Ben, Salem., 2000. Hydrocarbon prospectivity to the north-west of the assumood, field, Sirt Basin, Libya, Durham theses, Durham University. Available at Durham E-Theses Online: http://etheses.dur.ac.uk/4379/

Angelin, M .L., Collignan, A., Bellocq, J., Oudin, J .L., Ewald, M., 1983. Investigation of polycyclic aromatic hydrocarbons in source rock bitumens and petroleums by high pressure liquid chromatography. Comptes Rendues de l' Académie des Sciences Paris, Series II 296, 705-708.

Aquino Neto, F .R., Trendel, J .M., Restle, A., Connan, J., Albrecht, P .A., 1983. Occurrence and formation of tricyclic and tetracyclic terpanes in sediments and petroleums.

Barr, F.T., Weegar, A .A., 1972. Stratigraphic nomenclature of the Sirte basin, Libya. Petrol. Explor. Soc. Libya, p179.

Bastow, T .P., Alexander, R., Sosrowidjojo, I .B., Kagi, R .I., 1998. Penta-methylnaphthalenes and related compounds in sedimentary organic matter. Organic Geochemistry **28**, 585-595.

Belazi, H .S., 1989. The geology of the Nafoora Oil Field, Sirt Basin, Libya. Journal of Petroleum Geology **12**, 353-366.

Blanc, P., Connan, J., 1994. Preservation, degradation, and destruction of trapped oil. In: Magoon, L., Dow, W., (Eds.), The Petroleum System – From Source to Trap. The American Association of Petroleum Geologists, 237–251.53-366.

Bland, J.M., Altman, D.G., 1986. Statistical methods for assessing agreement between two methods of clinical measurement. Lancet 1, 307-310.

Bonnefous, J., 1972. Geology of the quartizitic 'Gargaf Formation' in the Sirt Basin, Libya. Bull. Centre Rech., Pau-SNPA **6**, 225-261.

Bordenave, M .L., 1993. Applied petroleum exploration. Editions Technip, Paris.Bourbonniere, R .A., Meyers, P .A., 1996. Sedimentary geolipid records of historical changes in the watersheds and productivities of Lakes Ontario and Erie, Limnology and Oceanography **41**, 352-359.

Brady, T.J., Campbell, N.D.J., Maher, C.E., 1980. Intisar 'D' Oil Field, Libya, *in* M.T. Halbouty, ed., Giant oil and gas fields of the decade, 1968-1978: AAPG Memoir 30, 543-564.

Brassell, S .C., Eglinton, G., Mo, F .J., 1986. Biological marker compounds as indicators of the depositional history of the Maoming oil shale. Organic Geochemistry **10**, 927-941.

Bray, E.E., Evans, E.D., 1961. Distribution of n-paraffins as a clue to recognition of source beds. Geochimica et Cosmochimica Acta **22**, 2-15.

Brocks, J .J., Summons, R .E., 2004. Sedimentary hydrocarbons, biomarkers for early life.In: Schlesinger W.H. (Ed.), Treatise on Geochemistry, Biogeochemistry. Schlesinger Elsevier - Pergamon, Oxford, **8**, 63-115.

Burwood, R., 1996. Geochemical evaluation of east Sirte Basin petroleum systems and oil provenance Proceedings of First Magrebian Conference on Petroleum Exploration, Benghazi, GSPLAJ, November **28**, 18-20.

Burwood, R., Redfern, J., Cope, M., 2003. Geochemical evaluation of East Sirte Basin (Libya) petroleum systems and oil provenance. In: Burnham, T., MacGregor, D.S., Cameron, N.R. (Eds.), Petroleum Geology of Africa, vol. 207. Geological Society Special Publication, London, 203–214.

Cleveland,W.S., 1994. The Elements of Graphing Data (2nd ed.). Hobart Press, Summit, NJ, USA.

Chambers, J.M., Cleveland, W.S., Kleiner, B., Tukey, P.A., 1983. Graphical Methods for Data Analysis. Belmont, Calif.: Boston: Wadsworth International Group; Duxbury Press Chapman and Hall/CRC Press

Choudhary, P.K., Nagaraja, H.N., 2007. Measuring Agreement in Method Comparison Studies – A Review. In: Balakrishnan, N, Kannan, Nandini, Nagaraja, H. N. (Eds.), Advances in Ranking and Selection, Multiple Comparisons, and Reliability: Methodology and Applications. Springer Science & Business Media. pp. 215-244

Chakhmakhchev, A., Suzuki, M., Takayama, K., 1997. Distribution of alkylated dibenzothiophenes in petroleum as a tool for maturity assessments. Organic Geochemistry **26**, 483-490.

Clark, J .P., Philp, R .P., 1989. Geochemical characterization of evapporite and carbonate depositional environments and correlation of associated crude oils in the black Creek BASIN, Alberta; Canadian petroleum Geologistis Bulletin **37**, 401-416.

Clifford, A .C., 1986. African oil-past, present and future. In: M. T. Halbouty (ed.): Future petroleum provinces of the world. AAPG, Mem. **40**, 339-372.

Connan, J., Bouroullee, J., Dessort, D., Albrecht, P., 1986. The microbial input in carbonate-anhydrite facies of a Sabkha paleoenvironment from Guatemala: a molecular approach. Organic Geochemistry **10**, 29-50.

Cumbers, K .M., Alexander, R., Kagi, R .I., 1987. Methylbiphenyl, ethylbiphenyl and dimethylbiphenyl isomer distributions in some sediments and crude oils. Geochimica et Cosmochimica Acta **51**, 3105-3111.

De Grande, S .M .B., Aquino Neto, F .F., Mello, M .R, 1993. Extended tricyclic terpanes in sediments and petroleum, Organic Geochemistry **20**, 1039-47.

Ekweozor, C .M., Okogun, J .I., Ekong, D .E .U., Maxwell, J .R., 1979. Preliminary organic geochemical studies of samples from the niger delta (Nigeria): II. Analyses of shale for triterpenoid derivatives. Chemical Geology **27**, 29-37.

Ekweozor, C .M., Udo, O .T., 1988. The oleananes: Origin, maturation and limits of occurence in Southern Nigeria sedimentary basins. Organic Geochemistry **13**, 131-140.

El- Alami, M., Rahouma, S., BUTT, A .A., 1989. Hydrocarbon habitat in the Sirte Basin northern Libya. Pet. Res. Journ. Tripoli **1**, 17-28.

El- Alami, M .A., 1996a. Petrography and reservoir quality of the Lower Cretaceous sandstone in the deep Mar Trough, Sirt Basin. First Symposium on the Sedimentary Basins of Libya, Geology of the Sirt Basin. Elsevier, Amsterdam **2**, 309-322.

El- Alami, M .A., 1996b. Habitat of oil in Abu Attiffel area, Sirt Basin, Libya. First Symposium on the Sedimentary Basins of Libya, Geology of the Sirt Basin, Elsevier, Amsterdam **2**, 337-348.

El-Hawat, A .S., Missallati, A .A., Bezan, A .M., Taleb, M .T., 1996. The Nubian Sandstone in Sirt Basin and its correlatives. In: Salem, M.J., El-Hawat, & A.M. Sbeta, A.S. (eds.).The Geology of Sirt Basin, vol. II. Elsevier, Amsterdam.

Elag, M., Cengiz T.V., Atila Sefunc, A., Sharif, A., 2014. Application of Seismic Attributes and Facies Modeling to Analyze The Reservoir Characterization In Intisar "103A" Field, Sirt Basin, Libya. AAPG Datapages/Search and Discovery Article 90194 © 2014 International Conference & Exhibition, Istanbul, Turkey, September 14-17, 2014. Retrieved from: http://www.searchanddiscovery.com/abstracts/html/2014/90194ice/abstracts/1945909.html (accessed 17. 12. 2015)

Engel, M .H., Macko, S .A., 1993. Organic geochemistry, Principles and Applications. Plenum Press, New York.

Faraj, M.A.M., Šolević Knudsen, T., Nytoft, H.P., Jovančićević, B., 2016. Organic geochemistry of crude oils from the Intisar oil field (East Sirte Basin, Libya). J. Pet. Sci. Eng. 147, 605-616.

Fu, J., Sheng, G., Peng, P., Brassell, S .C., Eglinton, G., Jigano, J., 1986. Peculiarities of salt lake sediments as potential source rocks in China. Organic Geochemistry **10**, 119-126.

Garrigues, P., De Sury, R., Angelin, M .L., Bellocq, J., Oudin, J .L., Ewald, M., 1988. Relation of the aromatic hydrocarbon distribution pattern to the maturity of organic matter in ancient sediments from the Makaham Delta. Geochimica et Cosmochimica Acta **52**, 375-384.

George, Sn .C., Lisk, M., Summons, R .E., Quezada, A .R., 1998. Constraining the oil charge history of South Pepper oilfield from the analysis of bearing fluid inclusions. In: Horsfield, B. et al. (Eds.) Advances in Organic Geochemistry 1997, Part 1. Pergamon Press, Oxford, pp. 631-648.

George, S .C., Ruble, T .E., Dutkiewicz, A., Eadington, P .J., 2001. Assessing the maturity of oil trapped in fluid inclusions using molecular geochemistry data and visually-determined fluorescence colours. Applied Geochemistry **16**, 451-473.

Golovko, A .K., 1997. Нефтяные алкилароматические углеводороды. Докторская диссертация, 02.00.13, Томск.

Golovko, A .K., Kontorovič, A .E., Pevneva, G .S., 2002. Алкилнафталины в нефтях Западной Сибири. Геохимия **14**, 282-293.

Golovko, A .K., Koržov, Y .V., 1992. Бифенилы и бифенилалканы в нефти Оленьего месторождения. Нефтехимия **6**, 747-757.

Golovko, J .A., 2001. Углеводородный состав Западно-Сибирских и Сахалинских нефтей различных генетических типов. Кандидатская диссертация, Томск.

Gong, J., 2004. Framework for the Exploration of Libya: An Illustrated Summary. AAPG Datapages/Search and Discovery Article 10061 (2004). Retrieved from: http://www.searchanddiscovery.com/documents/2004/libya/index.htm?q=%2Btext%3Agas (accessed 17. 12. 2015)

Goodwin, N .S., Mann, A .L., Patience, R .L., 1988. Structure and significance of C304-methyl steranes in lacustrine shales and oils. Organic Geochemistry **12**, 495-506.

Goosens, H., De Leeuw, J.W., Schenck, P.A., Brassell, S.C., 1984. Tocopherols as likely precursors of pristane in ancient sediments and crude oils. Nature 312, 440–442.

Grice, K., Fisher, S .J., Trolio, R., Alexander, R., Kagi, R .I., 1999b. Changes in the molecular composition of a condensate with increasing biodegradation in intertidal coastal sediments. Geochemistry, Istanbul, September 6-10, 1999. TÜBITAK, Istanbul, pp. 359-360.

Grice, K., Troilo, R., Fisher, S .J., Alexander, R., Kagi, R .I., 1999a. Geochemistry of alkylbiphenyls in crude oils and sediments. In: Abstracts of 19th International Meeting on Organic Geochemistry, Istanbul, September 6-10, 1999. TÜBITAK, Istanbul, pp. 61-62.

Guiraud, R., Maurin, J .C., 1992. Early Cretaceous rifts of Western and Central Africa: an overview. Tectonophysics **213**, 153-168.

Guiraud, R., Bosworth, W., Thierry, J., Delplanque, A., 2005. Phanerozoic geological evolution of Northern and Central Africa: An overview. Journal of African Earth Sciences 43, 83-143.

Gumati, D., Kanes, W .H., Schamel, S., 1996. An evaluation of the hydrocarbon potential of the sedimentary basins of Libya: Journal of Petroleum Geology **19**, 95–112.

Gumati, Y .D. and Nairn, A .E., 1991a . Tectonic subsidence of the Sirt Basin, Libya. J. Petrol. Geol **14**, 93-102.

Hallett, D., 2002. Petroleum Geology of Libya. Elsevier, Amsterdam, The Netherlands.

Hassan, S .Hassan, Christopher, C .G .Kendall., 2014. Hydrocarbon Provinces of Libya: A Petroleum System Study. University of South Carolina, Department of Geological Sciences, 701 Sumter St., EWS 617, Columbia, South Carolina, 29208, U.S.A.

Hassan, H.S., Kendall, C.C.G., 2014. Hydrocarbon provinces of Libya: A petroleum system study, In: L. Marlow, C. Kendall and L. Yose, (Eds.), Petroleum systems of the Tethyan region: AAPG Memoir 106, 101–141.

Holba, A.G., Dzou, L.I.P., Masterson, W.D., Hughes, W.B., Huizinga, B.J., Singletary, M.S., Moldowan, J.M., Mello, M.R., Tegelaar, E., 1998. Application of 24-norcholestanes for constraining source age of petroleum. Organic Geochemistry 29, 1269-1283.

Holba, A .G., Dzou, L .I., Wood, G .D., Ellis .L., Adam .P., Schaeer .P., Albrecht .P., Greene .T., Hughes, W .B., 2003. Application of tetracyclic polyprenoids as indicators of input from fresh-brackish water environments. Organic Geochemistry **34**, 441-469.

Hughes, W.B., 1984. Use of thiophenic organosulfur compounds in characterizing crude oils derived from carbonates versus siliciclastic sources. In: petroleum geochemistry and source rock potential of carbonate rocks, J. G. Palaces ed. American Association of the Petroleum Geologists, Studies in Geology **18**, 181-196.

Hughes, W .B., Holba, A .G., Dzou, L .I .P., 1995. The ratios of dibenzothiophene to phenanthrene and pristane to phytane as indicators of depositional environment and lithology of petroleum source rocks. Geochimica et Cosmochimica Acta **59**, 3581-3598.

Hunt, J .M., 1996. Petroleum Geochemistry and Geology. New York, 394-743.

Ishiwatari, R., Fukushima, K., 1979. Generation of unsaturated and aromatic hydrocarbons by thermal alteration of young kerogen. Geochimica et Cosmochimica Acta **43**, 1343-1349.

Ivanov, V .I., Golovko, A .K., 1992. Фенантреновые углеводороды в нефтях СССР. Сибирский химический журнал **1**, 94-102.

Jiamo, F., Guoying, S., Jiayou, X., Eglinton, G., Gowar, A .P., Rongfen, J., Shanfa, F., Pingan, P., 1990. Application of biological markers in the assessment of paleoenvironments of Chinese non-marine sediments. Organic Geochemistry **16**, 769-779.

Jiamo, F., Guoying, S., Pingan, P., Brassell, S .C., Eglinton, G., Jigang, J., 1986. Peculiarities of salt lake sediments as potential source rocks in China. Organic Geochemistry **10**, 119-126.

Killops, S .D., Carlson, R .M .K., Peters, K .E., 2000. Hightemperature GC evidence for the early formation of C40+ n-alkanes in coals. Organic Geochemistry **31**, 589–597.

Killops, S., Killops, V., 2005. Introduction to Organic Geochemistry, 2nd ed. Oxford: Blackwell Publishing.

Kamyanov, V .F., 1996. Закономерности в составе нефтей. Томск.

Kamyanov, V .F., Golovko, A .K., Korobicina, L .L., Kurakolova, E .A., 1982. Высококипящие ароматические углеводороды нефтей. Издательство ТФ СО АН СССР, Томск.

Khaled K., Darwish .M., Abu Khadra, A and Burki, M., 2014. Geochemical Evaluation of Campanian Sirte Shale Source Rock, Arshad Area, Sirt Basin, Libya. Journal of Applied Geology and Geophysics (IOSR-JAGG) **3**, 84-101.

Kuklinski, A .Y., Puškina, R .A., Gevorkova, V .L., 1983. Ароматические углеводороды высококипящих фракций нефтей. Нефтехимия **23**, 28-33.

Kvalheim, O .M., Christy, A .A., Telnæs, N., Bjørseth, A., 1987. Maturity determination of organic matter in coal using the methylphenanthrene distribution. Geochimica et Cosmochimica Acta **51**, 1883-1888.

Lin, L.I.K., 1989. A concordance correlation coefficient to evaluate reproducibility. Biometrics, 45, 255-268.

Lin, L.I.K., 2000. A Note on the Concordance Correlation Coefficient. Biometrics 56, 324-325.

Ludbrook, J., 2010. Linear regression analysis for comparing two measures or methods of measurement: but which regression? Clin. Exp. Pharmacol. Physiol. 37, 692-699

Mackenzie, A .S., Patience, R .L., Maxwell, J .R., Vandenbroucke, M., Durand, B., 1980. Molecular parameters of maturation in the Toarcian shales, Paris Basin, France-I. Changes in the configurations of acyclic isoprenoid alkanes, steranes and triterpanes. Geochimica et Cosmochimica Acta **44**, 1709-1721.

Mansour, A .T., Magairhy, I .A., 1996. Petroleum geology and stratigraphy of the southeastern part of the Sirt Basin, Libya. In: Salem MJ, El-Hawat AS, and Sbeta AM(editors), The geology of the Sirt Basin. Elsevier, Amsterdam: pp 485-428.

Maslen, E., Grice, K., Dawson, D., Le Metayer, D., 2010. Stable carbon isotopic compositions of individual aromatic hydrocarbons as source and age indicators in oil from Western Australian Basins. Organic Geochemistry. Submitted.

McBride, G.B., 2005. A proposal for strength-of-agreement criteria for Lin's concordance coefficient. NIWA Client Report: HAM2005-062.

Mello, M .R., Gaglianone, P .C., Brassell, S .C., Maxwell, J .R., 1988a. Geochemical and biological marker assessment of depositional environments using Brazilian offshore oils. Marine and Petroleum Geology **5**, 205-223.

Mello, M .R., Telnaes, N., Gaglianone, P .C., Chicarelli, M .I., Brassell, S .C., Maxwell, J .R., 1988b. Organic geochemical characterisation of depositional palaeoenvironments of source rocks and oils in Brazilian marginal basins. Organic Geochemistry **13**, 31-45.

Milner, C .W .D., Rogers, M .A., Evans, C .R., 1977. Petroleum transformations in reservoirs. Journal of Geochemical Exploration **7**, 101-153.

Mohamed, E., Cengiz, T.V., Atila, S., Abdelwahab, S., 2014. Application of Seismic Attributes and Facies Modeling to Analyze The Reservoir Characterization In Intisar "103A" Field, Sirt Basin, Libya. AAPG Datapages/Search and Discovery Article #90194 © 2014 International Conference & Exhibition, Istanbul, Turkey, September 14-17, 2014

Moldowan, J.M., Fago, F.J., Huizinga, B.J., Jacobson, S.R., 1991. Analysis of oleanane and its occurence in Upper Cretaceous rocks. In: Manning, D.A.C. (Ed.), Organic Geochemistry: Advances and Applications in the Natural Environment. 15th Meeting of the European Association of Organic Geochemists. © 1991 Manchester University Press, 195-197.

Moldowan, J.M., Dahl, J., Huizinga, B.J., Fago, F.J., Hickey, L.J., Peakman, T.M., Taylor, D.W., 1994. The molecular fossil record of oleanane and its relation to angiosperms. Science 265, 768-771.

Moldowan, J .M., Seifert, W .K., Gallegos, E .J., 1983. Identification of an extended series of tricyclic terpanes in petroleum; Geochimica Acta, **47**, 1531-4.

Moldowan, J .M., Seifert, W .K., Gallegos, E .J., 1985. Relationship between petroleum composition and depositional environment of petroleum source rock. American Association of Petroleum Geologists Bulletin **69**, 1255-1268.

Moldowan, J .M., Sundararaman, P., Salvatori, T., Alajbeg, A., Djukić, B., Lee, C .Y., Demaison, G .J., 1992. Source correlation and maturity assessment of select oils and rocks from the central Adriatic Basin (Italy and Yugoslavia). In: Moldowan, J.M., Albrecht P., Philp, R.P. (Eds.) Biological Markers in Sediments and Petroleum. Prentice Hall, New York, pp. 370-401.

Montgomery, S., 1994. Sirte Basin, North-Central Libya, prospects for the future: Petroleum Frontiers, Petroleum Information Corporation **11**, 94 .

Mrkić, S., Stojanović, K., Kostić, A., Nytoft, H .P., Šajnović, A., 2011. Organic geochemistry of Miocene source rocks from the Banat Depression (S.E. Pannonian Basin, Serbia). Organic Geochemistry **42**, 655-677.

Nasir, Shagufta., 2013. Applications of Biological Markers to Characterize Petroleum and Source Rocks of the Southern Indus Basin. PhD thesis. Department of chemistry, University of Engineering and Technology, Lahore – Pakistan.

Niessen, W .M .A., 2001. Current practise of Gas chromatography-Mass spectrometry; Copyright by Marcel Dekker, Inc.

Novaković, Milan .D., 2013. Influence of bioremediation conditions on biodegradation of satutated and aromatic hydrocarbons in oil-type pollutants. PhD thesis. Faculty of Chemistry, University of Belgrade.

Nytoft, H.P., Bojesen-Koefoed, J.A., Christiansen, F.G., Fowler, M. G., 2002 Oleanane or lupane? Reappraisal of the presence of oleanane in Cretaceous-Tertiary oils and sediments. Org. Geochem. 33, 1225-1240.

Ourisson, G., Albrecht, P., Rhomer, M., 1982. Predictive microbial biochemistry-from molecular fossils to procaryotic membranes; Trends in Biol. Sciences, 236-239.

Palanna, O .G., 2009. Tata McGraw-Hill Education private limited, 7 West Patel Nagar, New Delhi 110 008 - Chemical Engineering.

Philp, R .P., 1985. Fossil fuel biomarkers. Applications and spectra. Elsevier, Amsterdam.

Philp, R .P., Gilbert, T .D., 1986. Biomarker distributions in Australian oils predominantly derived from terrigenous source material. Organic Geochemistry **10**, 73-84.

Peters, K .E., Moldowan, J .M., 1991. Effects of source, thermal maturity and biodegradation on the distribution and isomerization of homohopanes in petroleum. Organic Geochemistry **17**, 47-61.

Peters, K .E., Moldowan, J .M., 1993. The Biomarker Guide, Interpreting Molecular Fossils in Petroleum and Ancient Sediments. Prentice Hall, New Jersey.

Peters, K .E., Moldowan, J .M., Schoell, M., Hempkins, W .B., 1986. Petroleum isotopic and biomarker composition related to source rock organic matter and depositional environment. Organic Geochemistry **10**, 17-27.

Peters, K .E., Walters, C .C., Moldowan, J .M., 2005. The Biomarker Guide, Second Edition: I. Biomarkers and Isotopes in the Environment and Human History. Cambridge University Press, Cambridge.

Petrov, A .A., 1984. Углеводороды нефти. Наука, Москва.

Püttman, W., Villar, H., 1987. Occurrence and geochemical significance of 1,2,5,6-tetramethylnaphthalene. Geochimica et Cosmochimica Acta **51**, 3023-3029.

Radke, M., 1987. Organic geochemistry of aromatic hydrocarbons. In: Radke, M. (Ed.) Advances in Petroleum Geochemistry. Academic Press, London, pp.141-205.

Radke, M., 1988. Application of aromatic compounds as maturity indicators in source rocks and crude oils. Marine and Petroleum Geology **5**, 224-236.

Radke, M., Garrigues, P., Willsch, H., 1990. Methylated dicyclic and tricyclic aromatic hydrocarbons in crude oils from the Hadil field, Indonesia. Organic Geochemistry **15**, 17-34.

Radke, M., Leythaeuser, D., Teichmüller, M., 1984. Relationship between rank and composition of aromatic hydrocarbons for coals of different origins. Organic Geochemistry **6**, 423-430.

Radke, M., Welte, D .H., 1983. The methylphenanthrene index (MPI): a maturity parameter based on aromatic hydrocarbons. In: Bjorøy, M. et al. (Eds.) Advances in Organic Geochemistry 1981. Wiley and Sons, Chichester, pp. 504-512.

Radke, M., Welte, D .H., Willsch, H., 1982a. Geochemical study on a well in the Western Canada Basin: relation of the aromatic distribution pattern to maturity of organic matter. Geochimica et Cosmochimica Acta **46**, 1-10.

Radke, M., Willsch, H., Leythaeuser, D., Teichmüller, M., 1982b. Aromatic components of coal: relation of distribution pattern to rank. Geochimica et Cosmochimica Acta **46**, 1831-1848.

Radke, M., Willsch, H., Welte, D .H., 1986. Maturity parameters based on aromatic hydrocarbons: influence of the organic matter type. Organic Geochemistry **10**, 51-63.

Ramadan, Muftah Mohamed Ali., 2013. The study of influence of biostimilation factors on microbiological degradation of main components in petroleum type pollutant. PhD thesis. Faculty of Chemistry, University of Belgrade.

Requejo, A .G., Sassen, R., McDonald, T., Denoux, G., Kennicutt, M .C., Brooks, J .M., 1996. Polynuclear aromatic hydrocarbons (PAH) as indicators of the source and maturity of marine crude oils. Organic Geochemistry **24**, 1017-1033.

Revill, A .T., Volkman, J .K., O, Leary, T., Summons, R .E., Boreham, C .J., Banks, M .R., Denwer, K., 1994. Hydrocarbon biomarkers, thermal maturity and depositional setting of tasmanite oil shales from Tasmania, Australia. Geochimica et Cosmochimica Acta **58**, 3803-3822.

Riva, A., Caccialanza, P .G., Quagliaroli, F., 1988. Recognition of 18β(H)-oleanane in several crudes and Tertiary-Upper Cretaceous sediments. Definition of a new maturity parameter. In: Mattavelli, L., Novelli, L. (Eds.) Advances in Organic Geochemistry 1987. Pergamon Press, Oxford, pp. 391-400.

Roberts, J .M., 1970. Amal field, Libya. In: Halbouty, M.T. (ed.), Geology of giant petroleum fields: American Association of Petroleum Geologists Memoir **14**, 438–448.

Robinson, W .E., 1969. Kerogen of the Green River Formation., in: Eglinton, G., Murphy, M.T.J. (Ed.), Organic geochemistry-methods and results. Springer-Verlag, Berlin Heidelberg, New York, pp. 619-637.

Rubinstein, I., Sieskind, O., Albrecht, P., 1975. Rearranged steranes in a shale: Occurrence and simulated formations. Journal of the Chemical Society, Perkin Transaction **1**, 1833-1836.

Rullkotter, J., Philp, R .P., 1981. Extended hopanes up to C_{40} in Thornton bitumen; Nature **292**, 616-618.

Rusk, D.C., 2000. Libya: petroleum potential of the under-explored Basin centers - a 21st century challenge. Pratt II Conference "Petroleum Provinces of the 21st Century", January 12-15, 2000, San Diego, California

Saenz De Santa Maria, F., 1993. Tectonic and sedimentary evolution of the Sirt Basin, an overview (Abst.). First symposium "Geology of the Sirt Basin", Tripoli, October 1993.

Saheel, Ahmed .S., Abdul Rahim Bin Samsudin., Umar Bin Hamzah., 2010. Regional geological and tectonic structures of the Sirt basin from potential field data. American journal of scientific and industrial research **13**, 448.462

Schoell, M., McCaffrey, M.A., Fago,, F.J., Moldowan, J.M., 1992. Carbon isotopic composition of 23,30-bisnorhopanes and other biological markers in a Monterey crude oil. Geochim. Cosmochim Acta 56, 1391-1399.

Schwarzbauer, J., Jovančićević, B., 2015. Fossil matter in the Geosphere (Fundamentals in Organic Geochemistry) . Institute of Geology and Geochemistry of Petroleum and Coal, RWTH, Aachen University, Germany. Department of Chemistry, University of Belgrade, Belgrade, Serbia.

Seifert, W .K., Moldowan, J .M., 1980. The effect of thermal stress on source-rock quality as measured by hopane stereochemistry. Physics and Chemistry of The Earth **12**, 229-237.

Seifert, W .K., Moldowan, J .M., 1986. Use of biological markers in petroleum exploration. In: Johns, B.R. (Ed.) Methods in Geochemistry and Geophysics, Volume 24. Pergamon Press, Oxford, pp. 261-290.

Seifert, W .K., Moldowan, J .M., 1981. Paleoreconstruction by biological markers; Geochim.Cosmochim.Acta **45**, 783-794.

Seifert, W.K., Moldowan, J.M., 1978. Application of steranes, terpanes and monoaromatics to the maturation, migration and source of crude oil, Geochimica et Cosmochimica Acta, 42, 77-95.

Seifert, W.K., Moldowan, J.M., 1979. The effect of biodegradation on steranes and terpanes in crude oils. Geochim. Cosmochim Acta 43, 111-126.

Selley, R .C., 1997. The Sirt Basin of Libya. In: Selley, R.C., (ed.), African Basins, Sedimentary Basins of the World, 3, Elsevier, Amsterdam, 27-37.

Senturk, E., Lahwel, M., Elghmari, M., 2006. Re-Development A Mature Field For Production Acceleration, Intisar 103E Field, Libya. Society of Petroleum Engineers, Europec/EAGE Annual Conference and Exhibition, 12-15 June, Vienna, Austria http://dx.doi.org/10.2118/99872-MS

Shaniba, Salah Abdurzak., 2012. Depositional and tectonic controls on architecture of the carbonate platform of upper Paleocene Khalifah Formation, Sirte Basin, Central Libya. Masters Theses. Paper 6930.

Simoneit, B .R .T., 1977. Diterpenoid compounds and other lipids in deep-sea sediments and their geochemical significance. Geochimica et Cosmochimica Acta **41**, 463-476.

Simoneit, B.R.T., 2005. A review of current applications of mass spectrometry for biomarker/molecular tracer elucidations. Mass Spectrom. Rev. 24, 719-765.

Simoneit, B .R .T., Schoell, M., Dias, R .F., Aquino Neto, F .R., 1993. Unusual carbon isotope composition of biomarker hydrocarbons in a Permian tasmanite. Geochimica et Cosmochimica Acta **57**, 4205-4211.

Simons, D-J .H., Kenig, F., Schröder-Adams, C .J., 2003. An organic geochemical study of Cenomanian-Turonian sediments from the Western Interior Seaway, Canada. Organic Geochemistry **34**, 1177-1198.

Smyth, M., 1983. Nature of source material for hydrocarbons in Cooper Basin, Australia: Bulletin of the American Association of petroleum Geologists **67**, 1422-1426.

Stojanović, K., 2000. Fenantren i metilfenantrenski izomeri u aromatičnoj frakciji nafti naftnih polja ostrva Sahalin Rusija – primena u proceni maturisanosti. Magistarski rad. Hemijski fakultet, Univerzitet u Beogradu.

Stojanović, K., Jovančićević, B., Pevneva, G .S., Golovko, J .A., Golovko, A .K., Pfendt, P., 2001. Maturity assessment of oils from the Sakhalin oil fields in Russia: phenanthrene content as a tool. Organic Geochemistry **32**, 721-731.

Stojanović, K., Jovančićević, B., Vitorović, D., Golovko, J., Pevneva, G., Golovko, A., 2007. Hierarchy of maturation parameters in oil-source rock correlations. Case study: Drmno depression, Southeastern Pannonian Basin, Serbia and Montenegro Journal of Petroleum Science and Engineering **55**, 237–251.

Stojanović, K., Jovančićević, B., Vitorović, D., Golovko, Y., Pevneva, G., Golovko, A., 2007a. Evaluation of saturated and aromatic hydrocarbons oil-oil maturity correlation parameters (SE Pannonian Basin, Serbia). Journal of the Serbian Chemical Society, 72, 1237–1254.

Stoneley, R., Pusey, W .C., Heritier, F., 1998. Statistical analysis of syn-rift sediments: anexample from the sarir sandstone, messlah field, Sirte Basin, Libya. Journal of Petroleum Geology **21**, 329-342.

Strachan, M .G., Alexander, R., Kagi, R .I., 1988. Trimethylnapthalenes in crude oils and sediments: effects of source and maturity. Geochimica et Cosmochimica Acta **52**, 1255-1264.

Summons, R .E., Volkman, J .K., Boreham, C .J., 1987. Dinosterane and other steroidal hydrocarbons of dinoflagellate origin in sediments and petroleum. Geochimica et Cosmochimica Acta **51**, 3075-3082.

Šajnović, Aleksandra., Ksenija, Stojanović., Vladimir, Simić and Branimir, Jovančićević., 2012. Geochemical and Sedimentation History of Neogene Lacustrine Sediments from the Valjevo-Mionica Basin (Serbia). Geochemistry - Earth's System Processes.

Šolević, Tatjana .M., 2008. Novi pristupi u pronalaženju i karakterizaciji izvornih stena na osnovu raspodele policikličnih zasićenih i aromatičnih ugljovodonika u naftama. Doktorska disertacija. Hemijski fakultet. Univerziteta u Beogradu, Beograd.

Šolević, T., Stojanović, K., Bojesen-Koefoed, J., Nytoft, H .P., Jovančićević, B., Vitorović, D., 2008a. Origin of oils in the Velebit oil-gas field, SE Pannonian Basin, Serbia – Source rocks characterization based on biological marker distributions. Organic Geochemistry **39**, 118-134.

Šolević Knudsen, T., Nytoft, H.P., Stojanović, K., Marković, D., 2015a. Organic geochemistry of crude oils from the Elemir oil field (SE Pannonian Basin, Serbia). 9th International Conference "Oil and Gas Chemistry", Tomsk, Russia, September 22-25, 2015. Proceedings, pp. 264-268.

Šolević Knudsen, T., Nytoft, H.P., Stojanović, K., Marković, D., 2015b. Organic geochemistry of crude oils from the Rusanda oil field (SE Pannonian Basin, Serbia). 27th International Meeting on Organic Geochemistry (IMOG 2015), Prague, Czech Republic, September 13-18, 2015. Book of Abstracts, pp. 513-514.

Tawadros, E., 2011. Geology of North Africa. November 2011. CRC Press.

ten Haven, H.L., De Leeuw, J.W., Rullkötter, J., Sinninghe Damste, J.S., 1987. Restricted utility of pristane/phytane ratio as a palaeoenvironmental indicator. Nature 330, 641–643.

ten Haven, H .L., de Leeuw, J .W., Sinninghe Damste, J .S., Schenck, P .A., Palmer, S .E., Zumberge, J .E., 1988. Application of biological markers in the recognition of palaeohypersaline environments. Geological Society, London, Special Publications **40**, 123-130.

Terry, C.E., Williams, J.J., 1969. The Idris 'A' bioherm and oilfield, Sirte Basin, Libya – its commercial development, regional Palaeocene geologic setting and stratigraphy. In: *The Exploration for petroleum in Europe and North Africa (ed. P. Hepple)*. Institute of Petroleum, London, and Elsevier, Amsterdam, p. 31-48.

Thomas, D., 1995. Exploration limited since ’70s in Libya’s Sirte Basin. Oil and Gas Journal vol. 93, no 11, p. 99-104.

Tissot, B .P., Bienner, F., 1974. Advances in organic geochemistry, 1973: actes du 6. Congres international de geochimie organique, 18-21 septembre, Rueil-Malmaison, France. Editions Technip.

Tissot, B .P., Welte, D .H., 1984. Petroleum Formation and Occurrence, 2nd Ed. Springer-Verlag, Heidelberg.

van Aarssen, B .G .K., Bastow, T .P., Alexander, R., Kagi, R .I., 1999. Distributions of methylated naphthalenes in crude oils: indicators of maturity, biodegradation and mixing. Organic Geochemistry **30**, 1213-1227.

Van Hooten., 1980. Latest Jurassic- Early Cretaceous Regressive Facies, Northeast Africa Craton. AAPG Bull., **64**, 857-867.

Van Houten, F .B., 1983. Sirte Basin, North Central Libya; Cretaceous rifting above a fixed mantle hotspot? Geology **11**, 115-1 18.

Venkatesan, M .I., 1989. Tetrahymanol: its widespread occurrence and geochemical significance. Geochimica et Cosmochimica Acta **53**, 3095-3101.

Vilela, M.J., Gharsalla, M., Elghmari, M., Majdoub, A.A., 2007. Performance Evaluation of a Reservoir Under EOR REcovery: Intisar D Reef, Concession 103, Libya. Society of Petroleum Engineers, Middle East Oil and Gas Show and Conference, 11-14 March, Manama, Bahrain http://dx.doi.org/10.2118/104619-MS

Vitorović, D., Jovančićević, B., 2005. Osnovi organske geohemije, Hemijski fakultet Univerziteta u Beogradu, Beograd.

Volkman, J .K., 1986. A review of sterol biomarkers for marine and terrigenous organic matter. Organic Geochemistry **9**, 83-89.

Volkman, J .K., Allen, D .I., Stevenson, P .L., Burton, H .R., 1986. Bacterial and algal hydrocarbons in sediments from a saline Antarctic Lake, Ace Lake; Organic Geochemistry **10**, 671-81.

Waples, Dougle .W., 1985. Geochemistry in petroleum exploration. Boston

Wenger, L .M., Isaksen, G .H., 2002. Control of hydrocarbon seepage intensity on level of biodegradation in sea bottom sediments. Organic Geochemistry **33**, 1277–92.
Wenneker et al., 1996. The Geology and Hydrocarbons of the Sirt Basin: A Synopsis. The Geology ofJhe Sirt Basin.I, Elsevier, Amsterdam, Netherland, 3-56.

White, William .M., 2013. Geochemistry. United States: www.wiley.com/go/white/geochemistry

Wilhelms, A., Telnæs, N., Steen, A., Augustson, J., 1998. A quantitative study of aromatic hydrocarbons in a natural maturity shale sequence - the 3-methylphenanthrene/retene ratio, a pragmatic maturity parameter. Organic Geochemistry **29**, 97-105.

Wolf, G .A., Lamb, N .A., Maxwell, J .R., 1986. The origin and fate of 4-methyl steroid hydrocarbons. I. 4-methylsteranes. Geochimica et Cosmochimica Acta **50**, 335-342.

Zengler, K., Richnow, H .H., Rosselló-Mora, R., Michaelis, W., Widdel, .F., 1999. Methane formation from long-chain alkanes by anaerobic microorganisms. Nature **401**, 266-269.

Yawanarajah, S .R., Kruge, M .A., 1994. Lacustrine shales and oil shales from Stellarton Basin, Nova Scotia, Canada: organofacies variations and use of polyaromatic hydrocarbons as maturity indicators. Organic Geochemistry **21**, 153-170.

Zengler, K., Richnow, H .H., Rosselló-Mora, R., Michaelis, W., Widdel, F., 1999. Methane formation from long-chain alkanes by anaerobic microorganisms. Nature **401**, 266-269.

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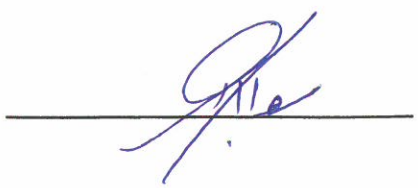

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Наслов рада ОРГАНСКО-ГЕОХЕМИЈСКА КАРАКТЕРИЗАЦИЈА И КОРЕЛАЦИЈА УЗОРАКА СИРОВЕ НАФТЕ ИЗ НАЈЗНАЧАЈНИЈИХ НАФТНИХ ПОЉА БАСЕНА СИРТЕ (ЛИБИЈА)

Ментор ДР БРАНИМИР ЈОВАНЧИЋЕВИЋ, ПРОФЕСОР ХЕМИЈСКОГ ФАКУЛТЕТА УНИВЕРЗИТЕТА У БЕОГРАДУ И ДР ТАТЈАНА ШОЛЕВИЋ КНЕЖЕВИЋ, ВИШИ НАУЧНИ САРАДНИК ИХТМ-ЦЕНТАР ЗА ХЕМИЈУ

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1. **Ауторство**. Дозвољавате умножавање, дистрибуцију и јавно саопштавање дела, и прераде, ако се наведе име аутора на начин одређен од стране аутора или даваоца лиценце, чак и у комерцијалне сврхе. Ово је најслободнија од свих лиценци.

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3. **Ауторство – некомерцијално – без прерада**. Дозвољавате умножавање, дистрибуцију и јавно саопштавање дела, без промена, преобликовања или употребе дела у свом делу, ако се наведе име аутора на начин одређен од стране аутора или даваоца лиценце. Ова лиценца не дозвољава комерцијалну употребу дела. У односу на све остале лиценце, овом лиценцом се ограничава највећи обим права коришћења дела.

4. **Ауторство – некомерцијално – делити под истим условима**. Дозвољавате умножавање, дистрибуцију и јавно саопштавање дела, и прераде, ако се наведе име аутора на начин одређен од стране аутора или даваоца лиценце и ако се прерада дистрибуира под истом или сличном лиценцом. Ова лиценца не дозвољава комерцијалну употребу дела и прерада.

5. **Ауторство – без прерада**. Дозвољавате умножавање, дистрибуцију и јавно саопштавање дела, без промена, преобликовања или употребе дела у свом делу, ако се наведе име аутора на начин одређен од стране аутора или даваоца лиценце. Ова лиценца дозвољава комерцијалну употребу дела.

6. **Ауторство – делити под истим условима**. Дозвољавате умножавање, дистрибуцију и јавно саопштавање дела, и прераде, ако се наведе име аутора на начин одређен од стране аутора или даваоца лиценце и ако се прерада дистрибуира под истом или сличном лиценцом. Ова лиценца дозвољава комерцијалну употребу дела и прерада. Слична је софтверским лиценцама, односно лиценцама отвореног кода.