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Geochemical Assessment Methods of Outcropped Metasedimentary/ Metamorphic and Deeply Buried Sedimentary Oil and Gas Source Rocks by Hydrocarbon-Rich Waters and Soils: A Novel Graphical Approach and Case Studies

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INFORMATION

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ABSTRACT

This study presents the applied methods used for geochemical evaluation of metasedimentary/metamorphic (depleted/exhausted/spent source rocks) and deeply buried sedimentary source rocks from hydrocarbon-rich waters and soils. Someone can determine all parameters used in geochemical assessments of source rocks by conducting Total Petroleum Hydrocarbons (TPH) analysis in both water and soil. It is considered that our knowledge about the metamorphosed source rocks will increase as the applications of methods discussed in the study increase. Within the study's scope, the Pr/n-C17 versus Ph/n-C18 plot used to evaluate the source, depositional environment, redox conditions of the depositional environment, thermal maturity, and hydrocarbon generation potential of source rocks in petroleum geochemistry is also comprehensively revised. In the revised plot, the ranges for API gravity, specific gravity (SG), sulfur content (S), biodegradation parameter (BP), vitrinite reflectance (Ro%), and maximum temperature (T_{max}) values are defined. Thus, a new approach is developed to estimate American Petroleum Institute API gravities and S of petroleum fluids that might be discovered within reservoirs in any specified prospective area from surface geochemical surveys. Furthermore, humic and sapropelic coal ranges are separated. In this way, the plots' functionality and efficiency are developed, making petroleum geochemical assessments possible in only one diagram instead of using several graphs or charts.

1. Introduction

Oil and gas exploration requires figuring out petroleum source rocks' formations, which is crucial for further investigating geological evolution. Petroleum source rocks are closely associated with the governing factors such as dynamics, chemistry, biology, etc., of an ocean system realized through geological time affecting occurrence and accumulations conditions. Source rock is a sedimentary rock that generated oil, currently generating oil, or could generate oil (Tissot and Welte, 1984). Kerogens (organic matters) that reside in petroleum source rocks are classified into three major types, which are Type-I: Algal kerogen (best source, Lipid-rich), Type-II: Vegetable kerogen (good oil source, contains zooplankton/sapropelic), and Type-III: Woody kerogen (good natural gas source, coaly), relying on their chemical structure (Fig. 1) (Dow, 1977; Tissot and Welte, 1984). Ozdemir and Palabiyik (2019a) have stated that the petroleum source rock can form around the hydrothermal vent (black and white smokers) on the seafloor as a consequence of an uplifting mantle plume because both clastic and carbonate petroleum source, as well as crude oils in black and dark colors, are rich in metals (Fig. 2). They have also compared the occurrence and emplacement ages of the known source rocks of oil and gas production fields and ophiolites. Their study shows that the tectonic and magmatic events (such as the intrusion of a mantle plume, etc., as driven phenomena) causing the ophiolites and petroleum source rocks' formation are entirely in harmony the ages of the source rocks of oil and gas production fields. Furthermore, it has been observed that the distribution maps of the hydrocarbon production areas and ophiolites of the world are very well-matched. According to this study, the occurrence of petroleum source rock has a very close relationship with ophiolites.

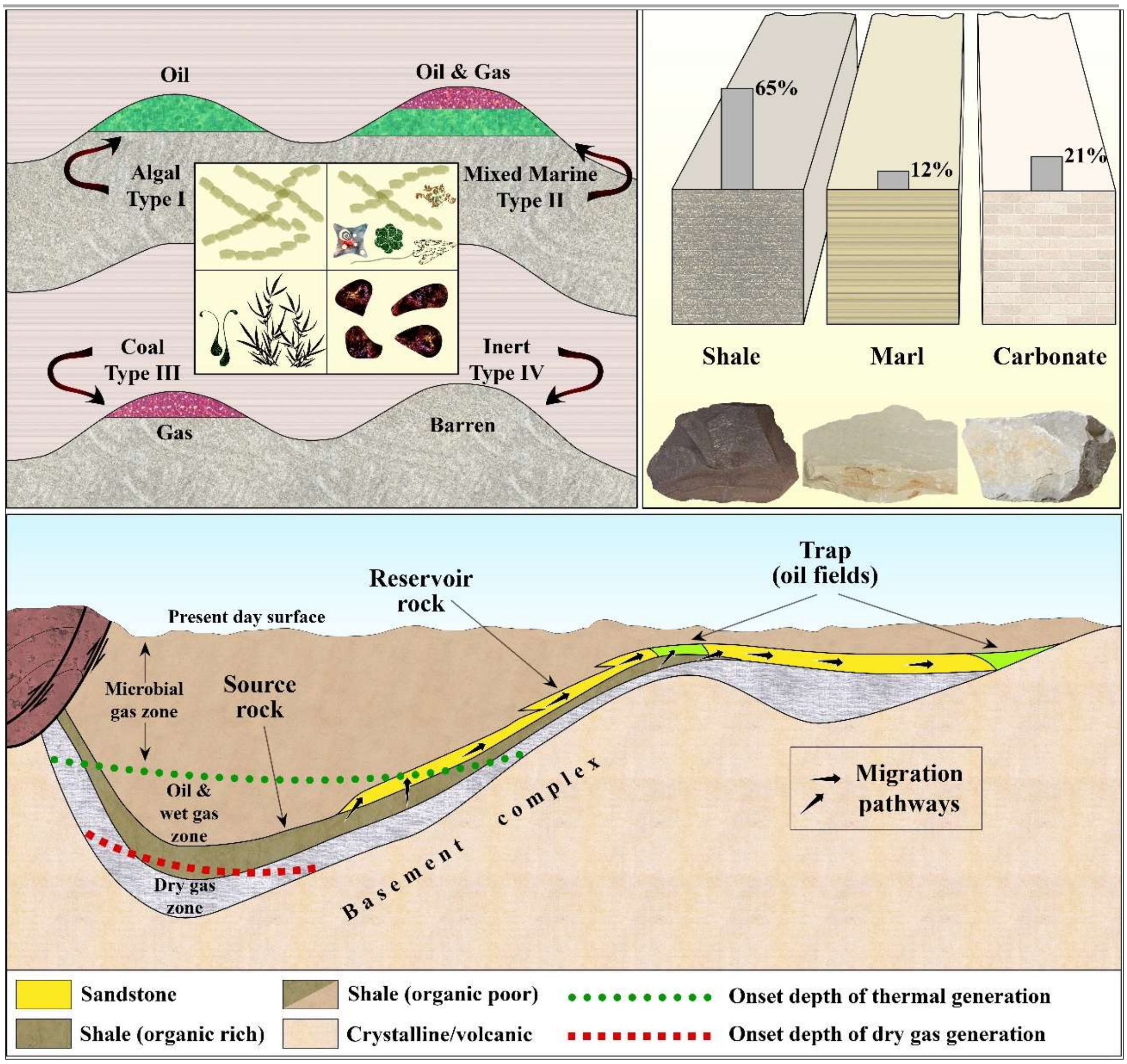


Fig. 1. Source rock types and components of a petroleum system

Several essential geological elements and processes in time and space have vital importance for the economic evaluation of the accumulation of petroleum (oil and/or gas) in the subsurface. Petroleum generation and its expelling from source rocks occur when the sedimentary organic matter (kerogen) is subject to sufficient thermal energy to break its chemical bonds. This heating is usually induced with burial by overburden strata. Petroleum migrates either along faults and/or through highly permeable formations as carrier beds once it is expelled. If petroleum migration creates an obstacle within a highly porous media (reservoir rocks) for further movement, it can cause an accumulation only in these strata.

These petroleum traps are created only when geologic movements result in subsurface topographies (structural and stratigraphic) that block migration and the reservoir rocks are covered by low permeability strata (seal rocks). The presence of these geologic elements is insufficient to form oil and gas reserves. Petroleum traps must exist at the instant of oil expulsion, and their integrity must be preserved until the exploitation once charged to constitute these elements and processes the "Petroleum System" (Fig. 1).

A source rock's characteristics are reflected in the molecular and isotopic composition of the petroleum that it generates. Therefore, geochemical analyses can determine which source rocks are present and their level of exposure to thermal stress. It should be proved with geochemical assessments if a basin has viable hydrocarbon occurrence and generation before detailed exploration activities. At this point, petroleum geochemistry is an essential branch of geoscience in understanding a petroleum system. Source rocks may be directly sampled and analyzed to reveal their source potential and thermal maturity. Often, source rocks of a basin do not outcrop at the surface. Besides, they may have been metamorphosed. For this reason, a geochemical evaluation cannot be made by taking samples from source rocks in such basins. In such basins, samples can be taken from some potential source rocks; however, they may not represent the actual source rock facies in the basin. Hence, in this study, the investigation of the geochemical assessment methods of metamorphosed and/or deeply buried source rocks in basins where the presence of hydrocarbon indicates (hydrocarbon-rich surface and subsurface waters, soils, and operable-size metallic ore deposits); nevertheless, in the areas where the source rocks don't outcrop is described in detail.

2. Metasedimentary/Metamorphic Oil and Gas Source Rocks

Source rocks can be divided into the types of potential (could generate oil), effective (currently generating oil), relic effective (generated oil) or spent (generated oil). A potential source rock can be defined as a rock that contains enough carbon- and hydrogen-rich organic matter to generate and expel hydrocarbons. It has adequate quantities of organic matter to generate petroleum. Still, it only becomes an effective source rock when it generates bacterial gas at low temperatures, or it reaches the proper level of thermal maturity to generate oil. An effective source rock is an organic-rich rock that is currently generating and has expelled hydrocarbons. It is generating or has generated and expelled petroleum. An active source rock is generating and expelling petroleum at the critical moment, most commonly, because it is within the oil window. A relic effective (inactive) source rock is an effective source rock that has ceased to generate and expel hydrocarbons owing to thermal cooling (uplift) before exhausting its organic matter supply.

Even though it has stopped generating petroleum, it still exhibits petroleum potential. Inactive source rock is not generating oil at present; nevertheless, it had been an active source rock in the past. A spent (exhausted, depleted) source rock is an active source rock that has exhausted its ability to generate and expel hydrocarbons either through insufficient remaining organic matter or reaching adequate maturity. A spent source rock has reached the post-mature stage of maturity and is incapable of further oil generation. A petroleum system is a system containing active source rock. Active source rocks include rocks or sediments that are generating petroleum without thermal maturation. Once-active source rock may now be inactive or exhausted (depleted, spent) (Dow, 1977; Barker, 1979; Peters and Casa, 1994; Law, 1999).

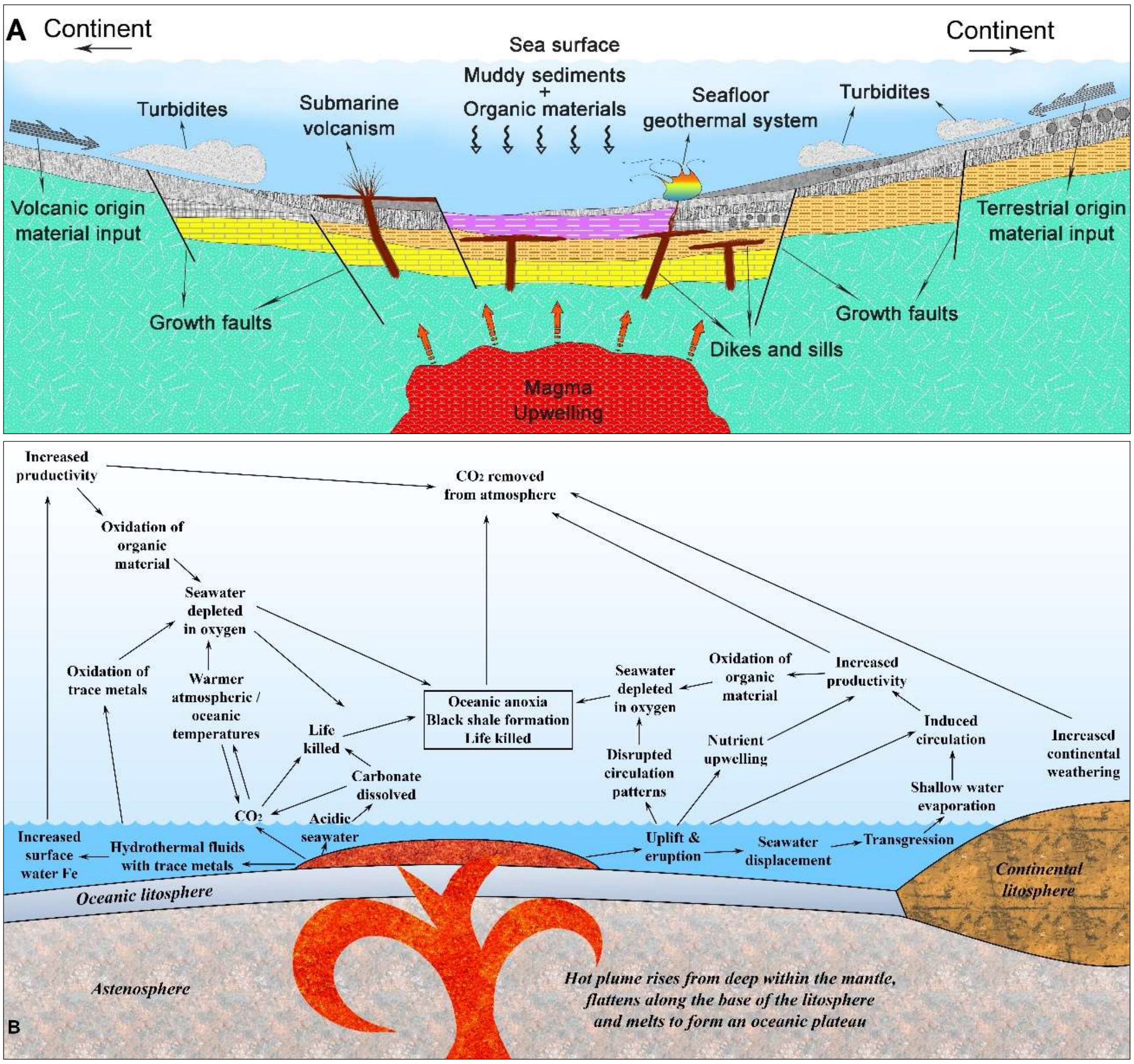


Fig. 2. Conceptual models of petroleum source rock formation: A) from Ozdemir (2019a, 2019b); Ozdemir and Palabiyik (2019a) and B) from Kerr (2005)

Fig. 3. An example for outcropped metamorphosed source rocks containing hydrocarbons (phyllites-schistes of Domuzdağ Complex, Kastamonu, Central Pontides, Turkey). TPH: 12.27 mg/kg, Pristane/Phytane (Pr/Ph) ratio = 0.91, Pristane/n-C17 alkane (Pr/n-C17) = 0.75, Phytane/n-C18 alkane (Pr/n-C18) = 0.53, %Ro = 0.70, T_{max} = 443 oC, BP = 0.62, Normal n-alkane ratio (NAR) = 0.90 (Palabiyik et al., 2020). According to these values, the source rock is in the mature oil zone (see Section 4.3 for the explanation)

In many studies, hydrocarbons/organic matter/carbonaceous material have been determined in metamorphic rocks with different degrees of metamorphism (Large et al., 1994; Rantitsch et al., 2004; Ader et al., 2006; Suchý et al., 2007; Judik et al., 2008; Kribek et al., 2008; Rantitsch and Judik, 2009; Suchý et al., 2015; Hu et al., 2015; Sawicka et al., 2018; Palabiyik et al., 2020; Sahinoglu et al., 2020; Ghasemlounia et al., 2020). Thus, in basins/regions where the presence of hydrocarbon indicates (oil and gas seeps, hydrocarbon-rich surface- and -subsurface waters, and soils), however, in the areas where the effective source rocks don’t outcrop, two possibilities might come into existence for the source of hydrocarbons: 1) In the region, there are effective petroleum source rocks (shale, mudstone, carbonate, etc.) wholly covered by stratigraphic or tectonically younger or older units. 2) In the region, petroleum source rocks that have been inactive or spent and oil and/or reservoir in which hydrocarbons generated from these source rocks are trapped, exist, which had been active in the past or spent. These inactive or spent source rocks in the region may be black, gray, and brown metamorphic rocks (phyllite, slate, schist, crystallized limestone, marble, and metasedimentary rocks), which are sedimentary (shale, mudstone, etc.) before metamorphism (Figs. 3-5).

Rocks with high total organic carbon (source rocks) alter under increasing temperature so that the organic molecules slowly mature into hydrocarbons (diagenesis). Source rocks are therefore broadly categorized as immature (no hydrocarbon generation), sub-mature (limited hydrocarbon generation), mature (extensive hydrocarbon generation), and overmature (a majority of hydrocarbons that have been generated). This fact makes an indicator to reveal the hydrocarbon potential using the source rock's maturity.

According to geological intervals, the geographical distribution of maturity levels of petroleum source rocks was presented in the studies of Ulmishek and Klemme (1990); Klemme and Ulmishek (1991).

Therefore, metasedimentary/metamorphic rocks containing organic matter/hydrocarbon/carbonaceous material can be used to evaluate the hydrocarbon potential of the region by organic geochemical methods, just like sedimentary rocks containing organic matter/hydrocarbon/carbonaceous material. In other words, all classic organic geochemistry/ petroleum geochemistry analyses applied in sedimentary rocks as the first stage of hydrocarbon exploration can also be applied on metasedimentary/metamorphic rocks containing hydrocarbon/organic matter. Therefore, it is possible to evaluate the hydrocarbon potential of the basin/region according to the results of this geochemical analysis. Indicator to reveal the hydrocarbon potential using the source rock's maturity. According to geological intervals, the geographical distribution of maturity levels of petroleum source rocks was presented in the studies of Ulmishek and Klemme (1990); Klemme and Ulmishek (1991).

Fig. 4. An example for outcropped metamorphosed source rocks containing hydrocarbons (schistes of Karakaya Complex, Ankara, Central Turkey). TPH: 3.67 mg/kg, Pristane/Phytane (Pr/Ph) ratio = 3.81, Pristane/n-C17 alkane (Pr/n-C17) = 2.38, Phytane/n-C18 alkane (Pr/n-C18) = 0.13, %Ro = 0.55, T_{max} = 437 °C, BP = 0.53, Normal n-alkane ratio (NAR) = 0.39 (Sahinoglu et al., 2020). According to these values, the source rock is in the early mature oil zone (see Section 4.3 for the explanation)

Fig. 5. An example for outcropped metamorphosed source rocks containing hydrocarbons (phyllites-schistes of Bozdağ Massif, Konya, Southwestern Turkey). TPH: 7.68 mg/kg, Pristane/Phytane (Pr/Ph) ratio = 0.34, Pristane/n-C17 alkane (Pr/n-C17) = 0.06, Phytane/n-C18 alkane (Pr/n-C18) = 0.09, $\%R_o$ = 1.5, T_{max} = 470 °C, BP = 0.11, Normal n-alkane ratio (NAR) = 0.23 (Ghasemlounia et al., 2020). According to these values, the source rock is in the wet gas - condensate / dry gas zone (see Section 4.3 for the explanation)

3. The Use of Operable-Size Metallic Ore Deposits as an Indicator for The Presence of Outcropped Metasedimentary/Metamorphic and Deeply Buried Sedimentary Petroleum Source Rocks

Ozdemir and Palabiyik (2019b-e) and Ozdemir et al. (2020a) have investigated the relationship between operable-size metallic ore deposits and hydrocarbons. They have indicated a close relationship between oil and gas reservoirs and metallic ore deposits in numerous studies published in the literature.

Moreover, it has been detected in many previous studies that a high amount of metal concentrations is encountered in both source rocks and petroleum resources. In ore deposits, in terms of both hand specimens and a microscopic scale, metallic ores are spatially associated with hydrocarbons. Organic matter in sediments can occur in different forms such as kerogen, bitumen, solid carbon, hydrocarbon gas, and more, in fractures and inclusions in significant amounts of free oil. On a regional scale, the same tectonic units of the basin bound hydrocarbon reservoirs or seeps along with the metallic ore deposits and the similar structures (primarily regional anticlines, domes, or paleo-highs) controls them. The study results show that the co-transportation process deposits hydrocarbons and metals derived from sediment pores during diagenesis by the same hydrothermal fluid.

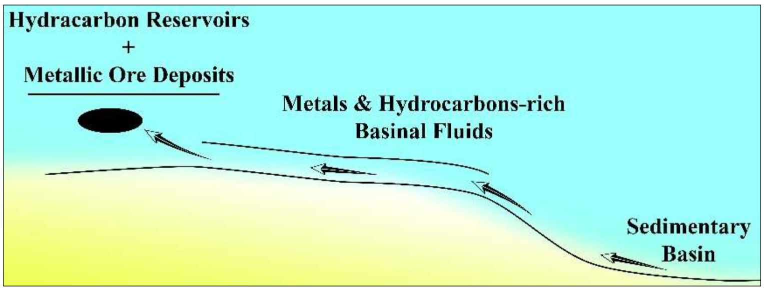


Fig. 6. Schematic representation of the formation of mineral deposits and hydrocarbon reservoirs by the migration of metal- and hydrocarbon-rich basin fluids formed in a sedimentary basin (Ozdemir and Palabiyik, 2019b)

Consequently, ore and organic matter in host rocks have a common source. In other words, anyone can use organic- and metal-rich sediments in a sedimentary basin as a source for both metallic ore deposits and hydrocarbon reservoirs. Metal- and hydrocarbon-rich fluids derived from sediments consolidated as a result of topographic uplift and the compression of the basin laterally migrate throughout aquifers and head towards the boundaries of the basin and paleo-highs along the faults in the main- and sub-basin. Thus, they constitute metallic ore deposits and hydrocarbon reservoirs characterized by different deposition and trapping mechanisms in separate compartments (Fig. 6).

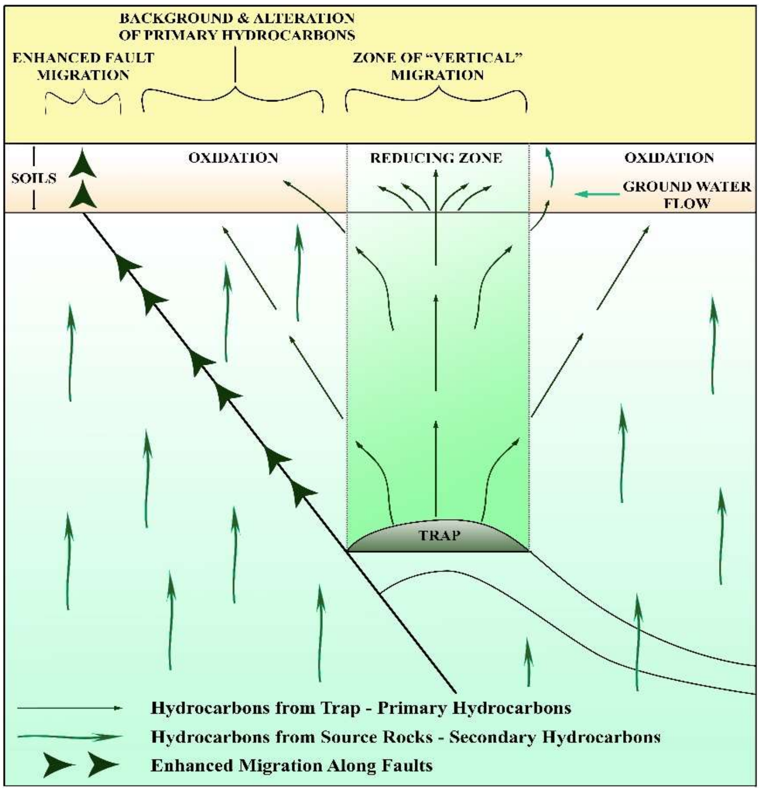


Fig. 7. The model for the formation of the hydrocarbon-rich waters and soils from the hydrocarbons and hydrocarbon-rich reservoir waters migrated from a working petroleum system which cause identifiable hydrocarbon enrichment in shallow waters and soils in the environment (from Potter II et al., 1996)

Metallic ores are deposited in faults, fracture zones, and unconformity surfaces in areas where ore fluids encounter suitable geochemical barriers whereas stratigraphic, lithological, and structural traps host hydrocarbons for their accumulations. TPH analysis in water in areas with no potential or effective source rock outcrops, but with operable-size metallic ore deposits can be geochemically evaluated for metamorphosed or deeply buried source rocks as can be understood from the studies of Ozdemir and Palabiyik (2019b-e) and Ozdemir et al. (2020a).

Besides, it is deduced that such deposits can be utilized within the context of a shallow and reliable indicator for petroleum exploration purposes, particularly in areas where metallic ore deposits that can form an economic deposit exist.

They have also claimed that the proposed alternative technique (reservoir-targeted) will be able to increase the success ratio of discovery by decreasing risks and costs of oil and gas exploration which has a 10-20% success ratio (very-high risk) with classical organic geochemical methods (source rock-targeted).

Table 1. The TPH permissible values recommended for surface and subsurface waters

TPH (mg/l)	Reference
< 0.05	Liu et al. (2018)
<0.1	Zemo and Foote (2003)
< 0.5	Ozdemir (2018)
<0.2	Ministry of Agriculture and Forestry of Turkey (2004a), Surface Water Quality Regulation of Turkey (Appendix 5, Table 2: Oil and Grease)
< 0.02	Ministry of Agriculture and Forestry of Turkey (2004b), Water Pollution Control Regulation of Turkey (Appendices Table 1: Oil and Grease)

Table 2. Intensity scale of the Geoaccumulation Index (I_{geo}) (Müller, 1979)

Pollution intensity	I_{geo}	I_{geo} class
Very heavily polluted	> 5	6
Heavily to very heavily polluted	4-5	5
Heavily polluted	3-4	4
Moderate to heavily polluted	2-3	3
Moderately polluted	1-2	2
Slightly to moderately polluted	0-1	1
Practically unpolluted	< 0	0

4. Geochemical Assessment Methods from Hydrocarbon-Rich Waters and Soils of Source Rocks

The main target of the conduction of soil geochemistry and hydro-geochemical survey for hydrocarbons within the surface or near-surface ground waters and soils leaking from source rocks or oil and gas reservoirs is to identify the various surface findings showing metamorphosed/deeply buried source rocks or the oil-and -gas fields in the subsurface.

The source of hydrocarbon enrichment in waters (surface and subsurface waters) and soils in basins are the migration phenomena of hydrocarbons from the depths to the surface/near-surface parts.

Concentration changes occur on the surface and in waters or soils associated with geological environments close to the surface, with the effect of hydrocarbons migrating from deep to the surface. This situation creates an increase in identifiable contents of hydrocarbons in water and soils (Potter II et al., 1996; Liu et al., 2018a, 2019; Ozdemir, 2018; Eymold et al., 2018; Kreuzer et al., 2018; Dultsev and Chernykh, 2020) (Fig. 7).

4.1. *TPH in water and soil analysis*

In recent years, TPH in water analysis has started to be used in petroleum geochemical exploration. Therefore, hydrocarbon-rich waters and organic geochemical properties in basins/regions, where source rocks are not exposed at the surface as outcrops (deeply buried basins) or has been exhausted (depleted or spent), can be determined by means of the technique mentioned above (Ozdemir et al., 2020a-c; 2021; 2022; Ozdemir and Palabiyik, 2022). Furthermore, recent studies have also revealed that source rock and gas samples can be analyzed by conducting all organic geochemical analyses and these methods can apply to the hydrocarbon-rich surface and subsurface waters determined by TPH in water analysis as well. Ultimately, the same analysis and interpretation results for the same basins/regions have been reached by using these different approaches (Liu et al., 2018a; Ozdemir, 2018).

TPH analysis used to determine the hydrocarbon content of surface waters, ground waters, the produced water from oil and gas fields, and soils is a routine analysis in environmental engineering applications. TPH limit values for water and soil samples have been proposed in many studies and standards (Table 1). Moreover, TPH permissible values have been reported in many standards for soils and sediments (US-EPA, 2009; Yang et al., 2015; Dumitru and Vladimirescu, 2017; Merchán-Rivera, 2017; Sari et al., 2018).

However, these standards' allowable pollution values, which are high, are valid for soils and sediments in regions where oil production areas and refineries are located. These values are the ones required for cleaning the soil from hydrocarbons. Masoud et al. (1996) proposed and classified permissible values for natural sediments. According to their study, the TPH permissible value for natural soils and sediments can be taken as 6 mg/kg in hydrocarbon exploration. Müller (1979) proposed an index called the I_{geo} to determine the degree of pollution in the soil. The value of 1.5 in the formula used to calculate this index is a correction factor for the background data variables due to lithogenic effects. Müller's I_{geo} (Table 2) is an assessment modeling used to analyze the sediment pollution intensity. The index establishes the relation among the contents found in the explored area and an equivalent reference value to the world average, which allows the calculation of different areas' pollution levels. Therefore, the index can also be used to classify hydrocarbon-rich waters.

$$I_{geo} = \log_2 \frac{[TPH\ value\ of\ the\ analyzed\ sample]}{[1.5(TPH\ value\ of\ the\ analyzed\ sample)*]} \qquad (1)$$

* In the formula, the TPH value for the reference soil sample according to Masoud et al. (1996) can be taken as 6 mg/kg, the TPH value for the reference water sample can be taken as 0.05 mg/l according to Table 1.

Gas chromatography (GC) analyses are conducted in the laboratory to determine TPH concentrations in waters and soils. The dominant peaks in these chromatograms are n-alkane types of hydrocarbons (Fig. 8). Geochemical assessment is performed by taking the distribution and size of the gas chromatograms (Ozdemir et al., 2020a-c; 2022) into account to observe hydrocarbon compounds' general distributions and obtain information about organic matter type, maturation, and depositional environments. TPH contents of water resources (cold and hot springs, water- and geothermal wells) and soils in the investigation area can be measured with a portable analyzer (Fig. 9). These instruments are used to obtain the preliminary evidence in the study area and select samples for analysis from the water resources studied. This approach allows for the right selection of the samples to be sent to the laboratory for analysis and optimum sampling. Besides, it provides an understanding of the existence of metamorphosed and deeply buried source rocks (thus, hydrocarbon generation) in the related area before laboratory analysis.

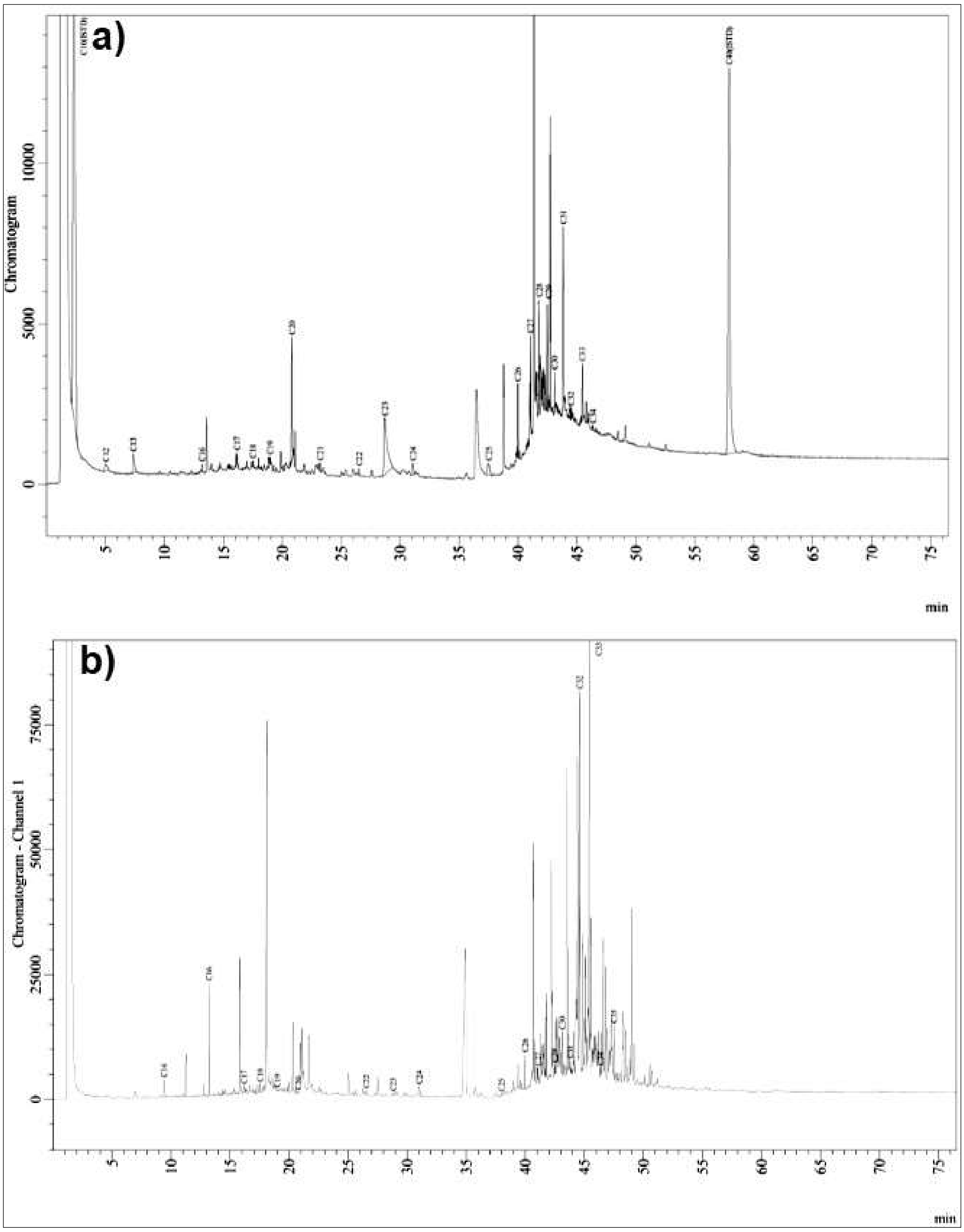


Fig. 8. TPH gas chromatograms of water (a) and soil (b) samples

The samples are collected for geochemical interpretation by using the scaled polyethylene bottles of 1 or 1.5 liters from the naturally flowing waters (cold water fountains) in the region (Fig. 10), which are taken from the untreated water resources not interacted with tap water (running water). It is crucial to collect and preserve the samples according to the standard procedures (ISO 5667-3, etc.). TPH analysis is carried out on water samples using the standard methods (ISO 9377-2, etc.) in the laboratory. Direct TPH concentrations of water samples (in mg/l) are determined with these analyzes, and geochemical parameters (CPI, NAR, etc.) are calculated from gas chromatograms. The TPH concentrations and computed parameters are finally utilized in geochemical assessments.

Soil samples are usually taken from the depths of 0 - 30 cm (Fig. 11) and placed in resealable zipper plastic storage bags and kept in these bags until the analysis. It is essential to collect and preserve soil samples according to standard procedures (ISO 10381:1 and 2, ISO 18400, etc.) similar to the water samples. TPH analysis is then performed on the samples in the laboratory using standard methods (ISO 14039, ISO 16703, etc.). Direct TPH concentrations of soil samples (in mg/kg) are determined after these analyses, and geochemical parameters are calculated from gas chromatograms. The TPH concentrations and parameters calculated are made use of in geochemical assessments.

Fig. 9. Various types of portable TPH analyzers

4.2. Geochemical assessment of hydrocarbons in waters and soils

4.2.1. Vitrinite reflectance (Ro%)

Since the maturity level of petroleum enables to determine the possible maturation stage of oil expulsion, a remarkable effect can be caused by its assessment for hydrocarbon exploration and prediction of the discovery of hydrocarbon accumulations along with their phase types at the deeper parts of geological intervals or undrilled sections of the basin (Chakhmakhchev et al., 1995; Sun et al., 2005; Chang et al., 2012).

Fig. 10. A view of the sampling procedure from a cold water fountain (pure and clean natural flowing waters) by using a scaled polyethylene bottle

Majority of the world's petroleum is biodegraded (Roadifer, 1987), and the level of maturity of biodegraded oils is a challenging issue. Even though the processes associated with biodegradation of crude oils within reservoir remain significantly obscure, their impacts on the composition and physical properties are well explained (Sun et al., 2005). The leading process to reduction of paraffin content and an increase in S content, oil density, acidity, and viscosity in the reservoir is considered as biodegradation of crude oils (Larter et al., 2003; Head et al., 2003). Usage of inconclusive or ambiguous molecular profiles to identify source or maturity is performed by consireably modifiying the molecular fingerprints and parameters of degraded oils (Sun et al., 2005). Low mature oil composition can be mostly similar to the partially biodegraded mature oils. Hence, it may be difficult to distinguish between them from gas chromatographic analysis alone (Volkman et al., 1983). The parameters such as provenance, sedimentation environment, catalytic effect of minerals, migration, and biodegradation are controlled by the values of individual maturation parameters within oils (Sainbayar et al., 2005; Sun et al., 2009; 2010). Even though the steranes and hopanes can be regarded as more resistant to biodegradation and their isomerization ratios are more trustable for maturity inspection, they are not useful for the samples indicating the maturity levels beyond peak oil generation (Ro~0.9%) because the reactions carried out by them have reached an equilibrium (Peters and Moldowan, 1993; Peters et al., 2005).

Fig. 11. Taking a sample from the soil with a resealable zipper plastic storage bag

Areas underlain by thermally mature generative source rocks in a basin are generative basins or depressions or else hydrocarbon kitchens. It has been statistically observed at a world scale that zones of high success ratios in finding oil and gas generally correlate in most basin types (such as intracratonic or rift basins) with the mapped "generative depressions". Cases of long-distance oil migration into shallow traps away from the "generative depressions" are generally located in foreland basins. As well as pointing to high petroleum potential zones within a basin, the determination of a thermal maturity degree of the source rock is also the primary tool to identify and broadly delineate plays. In petroleum geology, the maturity of a rock is a measure of its state in hydrocarbon generation. Maturity is evaluated using geochemical methods. Both optical and chemical methods can be used to determine the thermal maturity of source rock (Tissot and Welte, 1984). An analytical approach may not be sufficient to achieve a precise result, and so, the most reliable 2 or 3 methods are usually used. The data obtained from these methods can be classified as follows: (1) the amount of organic matter/oil or gas richness (2) the proneness of the organic matter (kerogen) to oil or gas, and (3) the maturation stage (immature, mature or overmature) (Hunt, 1995). Thermal maturity is the most important process in the evaluation of oil and gas potential.

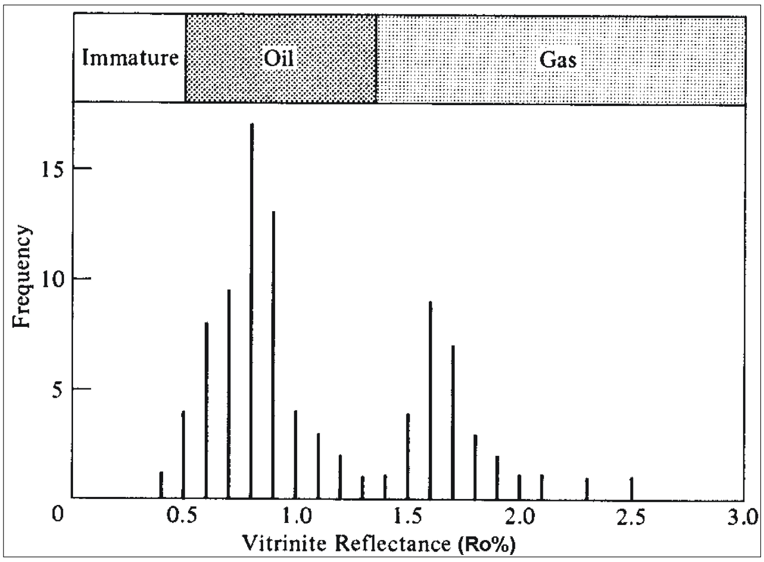


Fig. 12. Hydrocarbon generation according to % Ro values (Hunt, 1979)

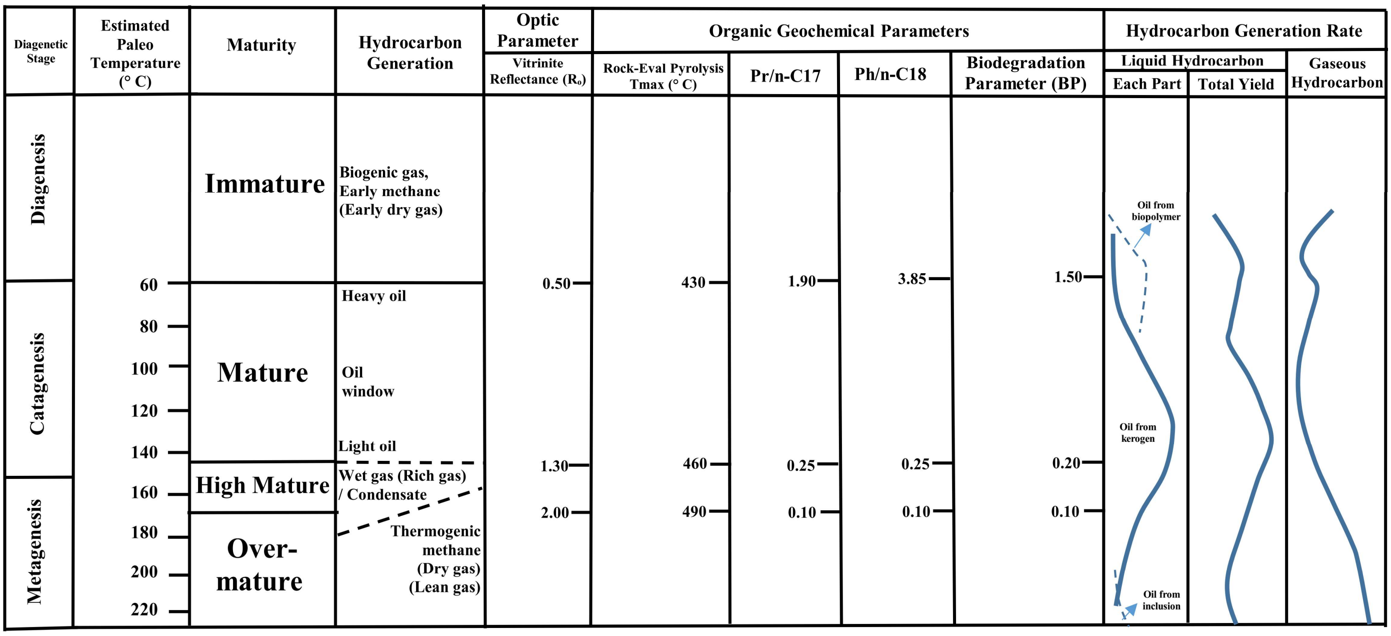


Fig. 13. Relationship between some maturity parameters for Type I-II and Type II-III kerogen (organic matter) and hydrocarbon generation stages (modified from Heroux et al., 1979; Thompson, 1982; Xia et al., 2019, also see references in the text). Pr/n-C17 and Ph/n-C18: isoprenoid/n-alkane hydrocarbons ratios, BP = (Pr+Ph)/(n-C17+n-C18). Oil and gas generation ranges are based on the literature

Geologists widely accept R_o% for measuring the thermal maturity of organic matter in sedimentary rocks (Down, 1977; Bostick, 1979; Murchison, 1987; Hunt, 1996). The Ro% values increase with increasing rank. The values between 0.50% and 1.30% suggest the oil generation window, while the values less than 0.50% are considered thermally immature (0.8-1.0% is the peak value of oil generation). However, Ro% values greater than 1.30% indicate gas window maturity (Figs. 12-14) (Tissot and Welte, 1984).

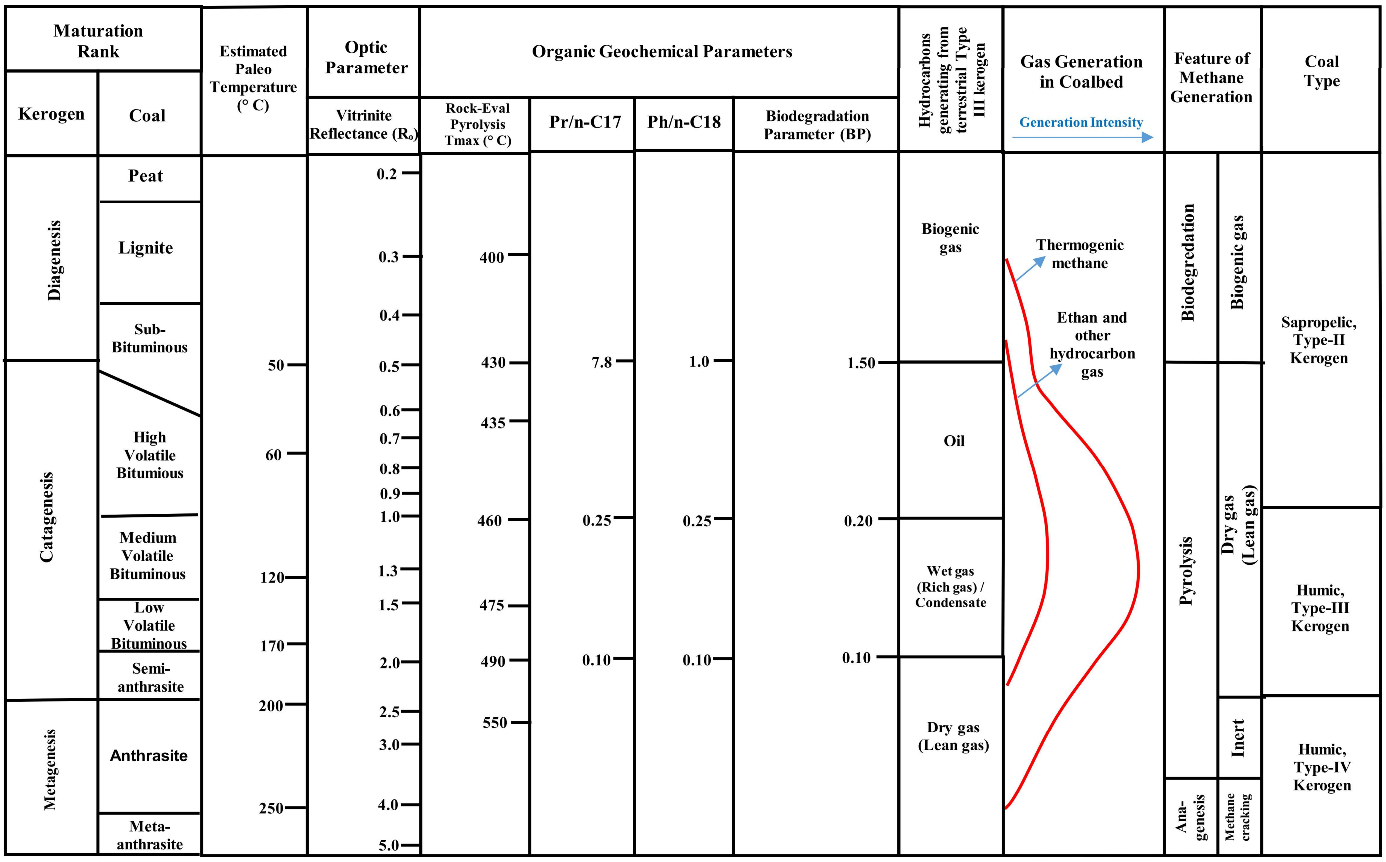


Fig. 14. Relationship between some maturity parameters for Type III kerogen (terrestrial organic matter) and coals and hydrocarbon generation stages (modified Rice, 1993; Zdravkov et al., 2011; Suárez-Ruiz et al., 2012; Zhou, 2013). Also see references in the text. Pr/n-C17 and Ph/n-C18: isoprenoid/n-alkane hydrocarbons ratios, BP = (Pr+Ph)/(n-C17+n-C18). Oil and gas generation ranges are based on the literaturee

4.2.2. Isoprenoids (Pr, Ph) and n-alkanes (n-C17 and n-C18)

Pristane/phytane (Pr/Ph) ratio is a proper correlation parameter. Even though Pr and Ph define other sources, they are derived from phytyl, which is the side chain of chlorophyll, especially in phototropic organisms. Under anoxic conditions, the phytyl side-chain breaks down to form the phytol, while phytol is also reduced to pristane under oxic conditions (Fig. 15) (Peters and Moldowan, 1993). Thus, the Pr/Ph ratio reflects the redox potential of the depositional environment. Pr/Ph values less than 1 indicate anoxic conditions, whereas the values greater than 1 indicate oxic conditions (Didyk et al., 1978; Hunt, 1995). Most marine and organic-rich sediments have Pr/Ph ratios in the range of 0.8-2.5, which indicate a gradual increase with increasing maturity within this range. However, the marine organic matter usually has a Pr/Ph ratio less than 1.5 at high maturity levels, while terrigenous organic matter input under oxic conditions shows ratios of Pr/Ph greater than 3 - 10 indicates that abundant woody material exists in the source rock for oils or that petroleum is derived from coal (Tissot and Welte, 1984). Pr/Ph ratios of oil samples are used to help define the environment in which source rocks have been formed. For example, Pr/Ph < 1: anoxic environment; Pr/Ph < 0.5: hypersaline environment (Volkman and Maxwell, 1986; ten Haven et al., 1987; Fu et al., 1990); Pr/Ph > 3: fluviodeltaic environment (also coal) (Hughes et al., 1995).

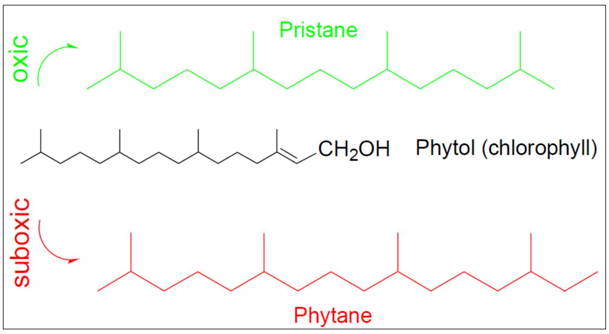
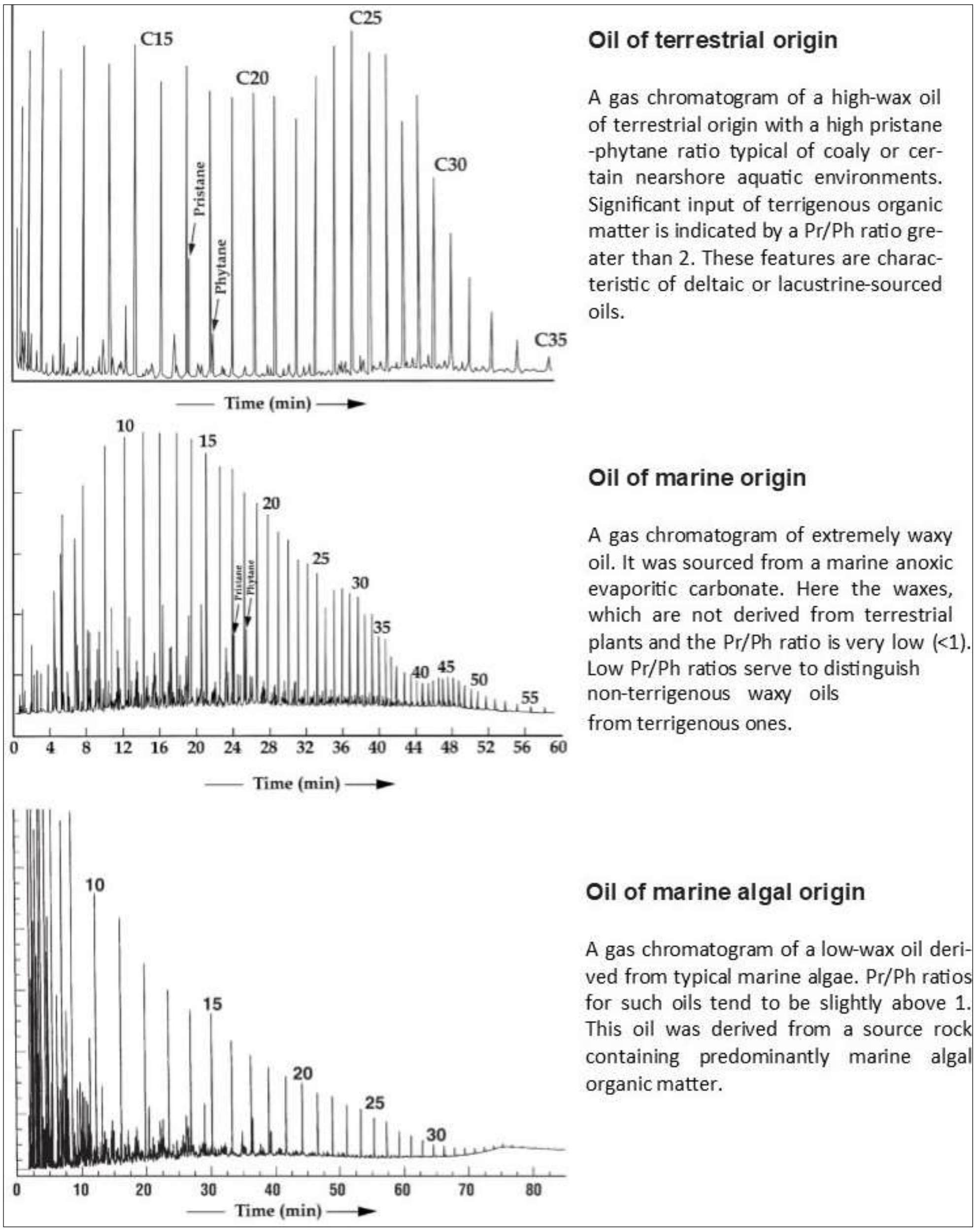


Fig. 15. Diagenetic origin of pristane and phytane (Peters et al., 2005)

The Pr/Ph ratio of marine oils are generally much less than 3. Oils have a moderate Pr/Ph ratio, whereas the Pr/Ph ratio of condensates ranges from moderate to high. A higher Pr/Ph ratio in condensates is attributed to migration fractionation (Dzou and Hughes, 1993). These parameters indicate predominantly terrestrial source input deposited in an oxic environment with variation in organofacies (Peters and Moldowan, 2005). The Pr/Ph ratio of Gippsland Basin oils (Australia) is between 5 and 6. The oils in the Gippsland basin indicated that the oil's paraffinic fraction was derived from coal, and the naphthenic fraction was derived chiefly from resin (Shanmugam, 1985). For this reason, the Pr/Ph ratio becomes high. The Pr/Ph values of the low-rank coals are high and, however, vary considerably.



Oil of terrestrial origin

A gas chromatogram of a high-wax oil of terrestrial origin with a high pristane-phytane ratio typical of coaly or certain nearshore aquatic environments. Significant input of terrigenous organic matter is indicated by a Pr/Ph ratio greater than 2. These features are characteristic of deltaic or lacustrine-sourced oils.

Oil of marine origin

A gas chromatogram of extremely waxy oil. It was sourced from a marine anoxic evaporitic carbonate. Here the waxes, which are not derived from terrestrial plants and the Pr/Ph ratio is very low (<1). Low Pr/Ph ratios serve to distinguish non-terrigenous waxy oils from terrigenous ones.

Oil of marine algal origin

A gas chromatogram of a low-wax oil derived from typical marine algae. Pr/Ph ratios for such oils tend to be slightly above 1. This oil was derived from a source rock containing predominantly marine algal organic matter.

Fig. 16. Pr and Ph peaks in gas chromatograms of marine and terrestrial oils (Waples and Curiale, 1999)

In contrast, the values are relatively low at the high-rank coals (thermally metamorphosed coals) (Figs. 16-17) (Amijaya, 2005). The Pr and Ph values are more abundant in immature samples, implying that they are primarily inherited from organisms rather than from thermally generated from kerogen and/or asphaltenes (Goossens et al., 1984; Koopmans et al., 1999). Isoprenoid/n-alkane ratios are commonly used in petroleum correlation studies. Samples containing high Pr indicate an oxidizing source, while high Ph content reflects a reducing source. Normal alkanes (n-alkanes) closest to isoprenoids in gas chromatograms are used in isoprenoid/n-alkane ratios. The n-C17 and n-C18 characterize Pr and Ph, respectively, as the double peaks in the chromatograms (Fig. 18).

Although the Pr/Ph ratio above 1.5 indicates settling conditions in an oxygenated environment according to a standard geochemical interpretation, it is well-known that it may be less than 1 for an anoxic depositional environment. Furthermore, lower values may show fewer oxic conditions than the other parts of the same sequence (Hartkopf-Fröder et al., 2007). The ratio of isoprenoid/n-alkane decreases with the increase in maturity as more n-alkanes are released from kerogen subjected to cracking (Tissot and Welte, 1984; Hunt,

1995) and is used as a measure of maturity for biodegradable oil and bitumen samples. It increases with biodegradation (Hunt, 1995) and is influenced by organic matter input and secondary processes as well.

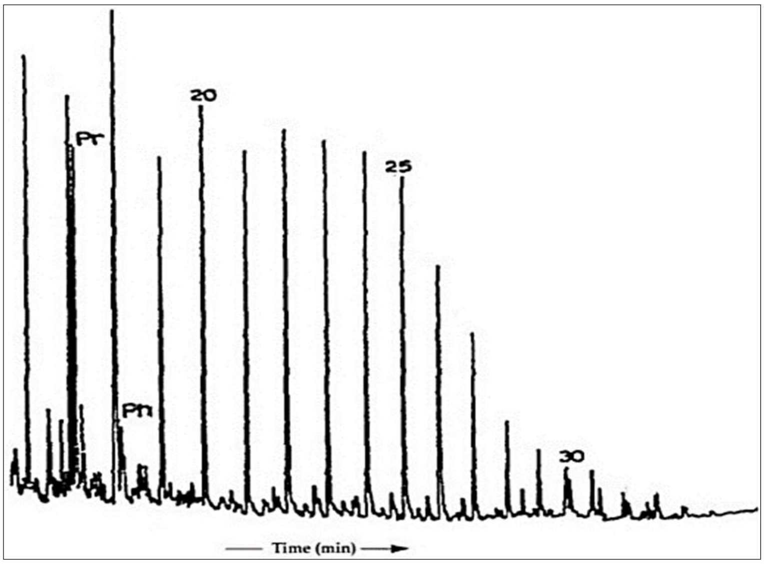


Fig. 17. Pr and Ph peaks in a hard coal gas chromatogram (from Alexander and Hazai, 1981)

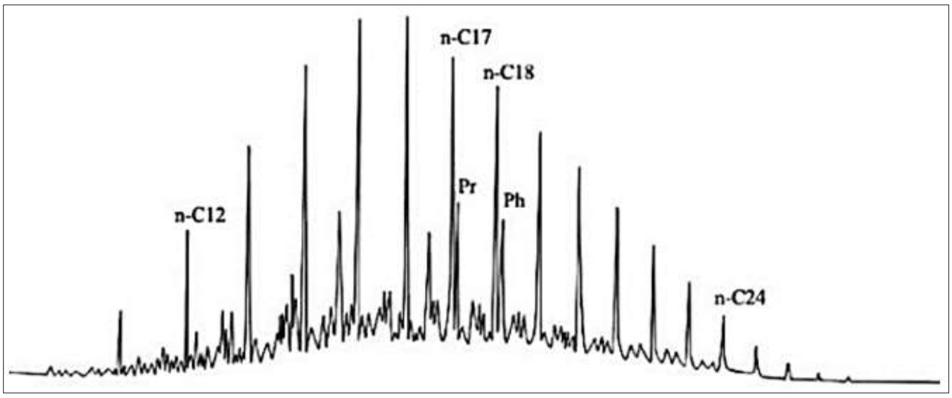


Fig. 18. Pristane (Pr), phytane (Ph), isoprenoids (n-C17 and n-C18) peaks in a gas chromatogram

The Pr/n-C17 and the Ph/n-C18 ratios in oils and condensates provide information about the generative kerogen (i.e., redox conditions during deposition and thermal maturity) (Didyk et al., 1978; Connan and Cassou, 1980; Hunt, 1995; Peters al., 2005; Azhar, 2012; Prosser et al., 2020; Volk, 2020). While the Ph/n-C18 value of shale source rocks is ≤ 0.3, the Ph/n-C18 value of carbonate source rocks is ≥ 0.3 (Connan, 1981; Palacas et al., 1984). Pr/n-C17 and Ph/n-C18 directly reflect the thermal maturity of the oils (Gomez, 2016). However, the isoprenoid/n-alkane (n-paraffin) ratios are often used to provide information not only on the depositional environment and source rock type but also on the secondary processes like biodegradation and maturation (Peters et al., 1999; Peters, 2000). An assessment of source, maturity, and biodegradation can be realized by using a plot of Pr/n-C17 versus Ph/n-C18. The n-alkanes are generated faster than isoprenoids with increasing maturity, resulting in a decrease in isoprenoid/n-alkane ratios (Pr/n-C17 and Ph/n-C18). Conversely, biodegradation removes n-alkanes more quickly, increasing isoprenoid/alkane ratios. Typically, two basic changing mechanisms occur during catagenesis; a gradual disappearance of the odd-even predominance and a shift toward the lower molecular weight range thanks to the synthesis of smaller molecules and cracking of larger molecules (Ahmed et al., 2004). The variation in the n-paraffin distribution through diagenesis and catagenesis is shown in Fig. 19.

Pr/n-C17 and Ph/n-C18 ratios decrease with the thermal maturity since more n-alkanes are released from kerogen by cracking and are more thermally stable than isoprenoids (Tissot et al., 1971; Tissot and Welte, 1984; Hunt, 1995; Ma, 2016). The early generation mostly produces isoprenoids (Pr and Ph) from original organic matter, while more n-alkanes are generated from kerogen by thermal cracking as the thermal maturity increases. The n-alkanes (n-C17 and n-C18) increase with depth and the distribution pattern of n-alkanes becomes similar to that of crude oils (Fig. 19). Fig. 15 shows the comparison of isoprenoid hydrocarbons (Pr, Pr) with n-alkanes (n-C17, n-C18). Relative decrease with the depth of isoprenoids (which result mostly from an early generation from original organic matter) compared to n-alkanes (which are produced continuously and predominantly during the burial of the sediment).

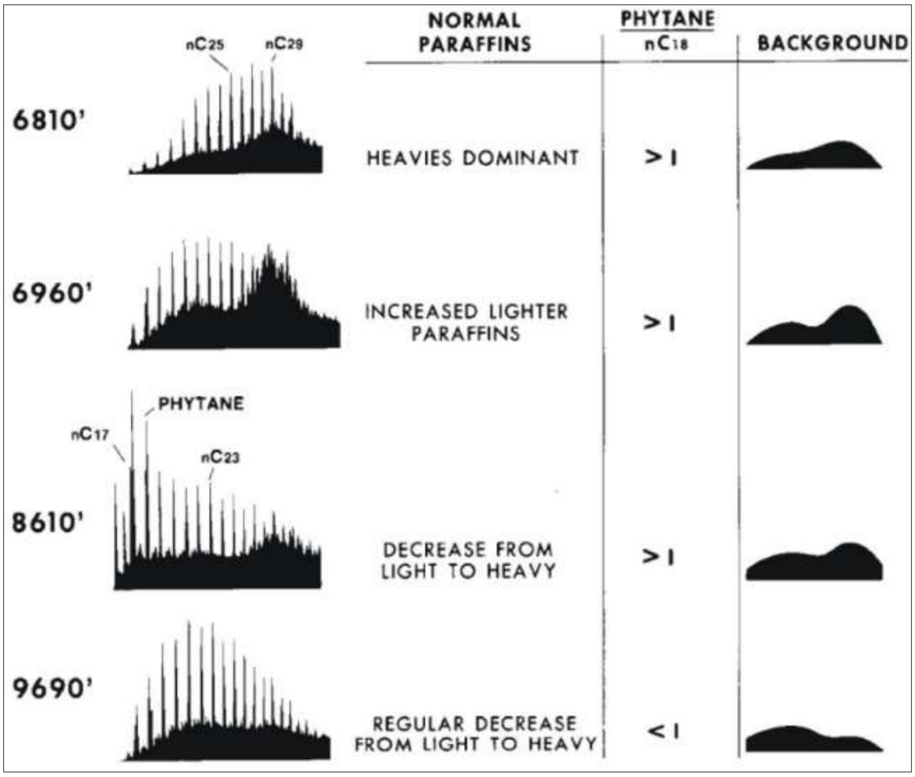


Fig 19. Changes in the n-paraffin distribution with depth through diagenesis and catagenesis (modified from Ahmed et al., 2004)

As maturity increases, n-alkanes are generated faster than isoprenoids in contrast to biodegradation, maturation, and diagenetic conditions (Waples, 1985). Isoprenoid hydrocarbons are usually more resistant to biodegradation than those of normal alkanes (Nwadinigwe and Alumona, 2018).

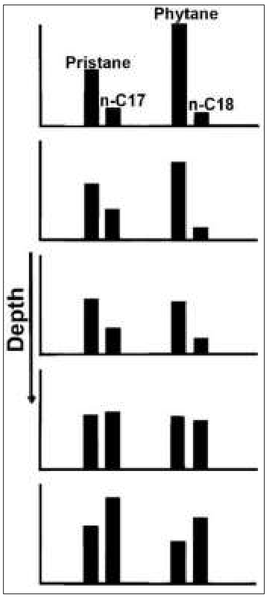


Fig. 20. The comparison of change by depth increase of the isoprenoids and n-C17, and n-C18 alkanes (from Tissot, 1971)

Both Pr/n-C17 and Ph/n-C18 ratios increase with biodegradation due to the loss of associated n-alkanes. On the other hand, they decrease with increasing maturity due to the increasing dominance of these n-alkanes (Figs. 20 and 21).

Biodegradation increases these ratios because aerobic bacteria generally attack the n-alkanes before the isoprenoids (Alexander et al., 1981; Peters et al., 2005; Pletsch et al., 2010; Nasir and Fazeelat, 2013). These parameters should be interpreted with caution because the Pr/n-C17 and Ph/n-C18 ratios are also affected by biodegradation. Their low ratios point out more mature samples because the isoprenoid breaks down earlier than n-alkanes during maturation as tertiary carbon-carbon bonds have lower stability than primary and secondary carbon bonds (Azhar, 2012).

These isoprenoid/n-alkane ratios can be determined in ranking the thermal maturity of oils and bitumens (Alexander et al., 1981; Peters et al., 2005). Therefore, the higher the Pr/n-C17 ratio means the decrease in the level of maturity of the crude (Nwadinigwe and Alumona, 2018).

Ko (2010) generated oils from Cameo coal, Mowry, Mancos, and Baxter shales at three different temperatures by conducting three sequential hydrous pyrolysis experiments and performed GC analysis of the generated oils. He observed that Pr/n-C17 and Ph/n-C18 ratios were changed during the analysis. Pr/n-C17 and Ph/n-C18 ratios of all the oil samples decrease with increasing maturity (Fig. 22).

Changes in Pr/n-C17 ratio with increasing degree of thermal maturity is shown in Fig. 23. The decrease in Ph/n-C18 ratio from 1.0 to 0.1 suggests that at least 90% of Ph in the original oils was decomposed during the transition from oils to condensates (Fig. 24) (Ishiwatari and Ishiwatari, 2004). The linear correlation between Pr/n-C17 and Ph/n-C18 ratios is substantial evidence that a range of maturity for oils is distinguishable with these parameters. It is strangely notable to emphasize that the linear relation between Pr/n-C17 and Ph/n-C18 is rather good, confirming the validity to assess and differentiate the maturity and biodegraded of oils (Fig. 25) (Asif et al., 2009; Chang et al., 2012).

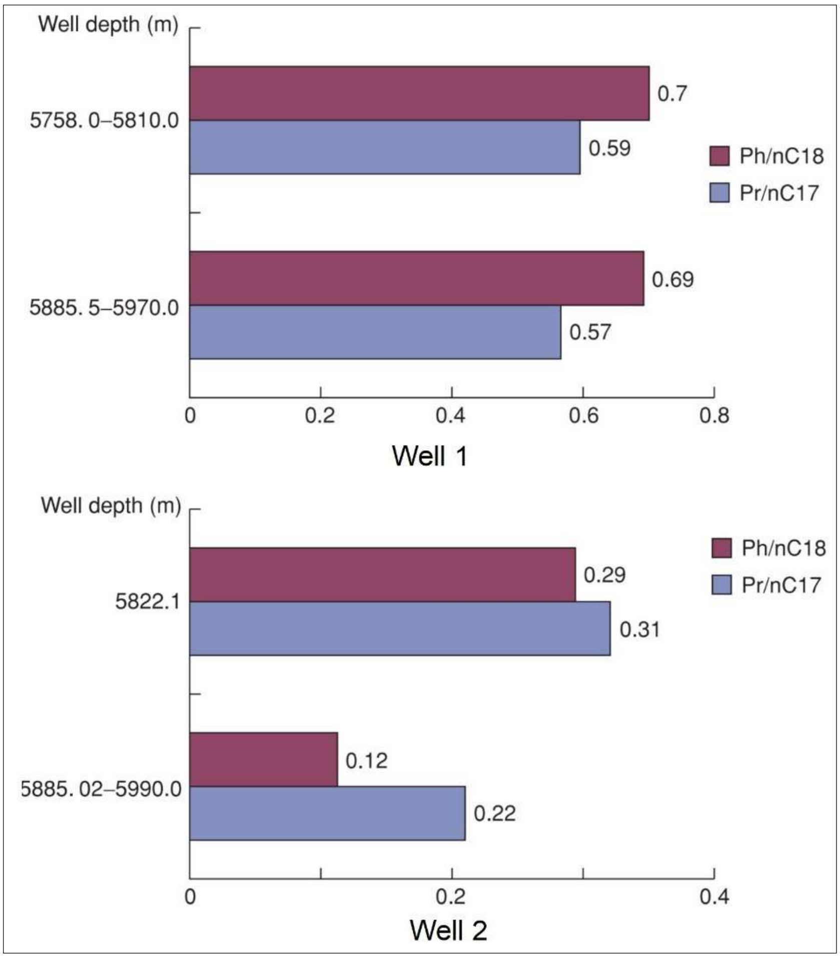


Fig. 21. Change characteristics with the depth of Pr/n-C17 and Ph/n-C18 ratios of crude oils from two deep wells of an oilfield (from Zhou et al., 2010)

On the other hand, Poturay and Kompanichenko (2019) have examined hydrocarbons' maturity in hydrocarbon-rich geothermal fluids. They divided the hydrocarbons in geothermal fluids into four groups in terms of maturity in the Pr/n-C17 versus Ph/n-C18 diagram.

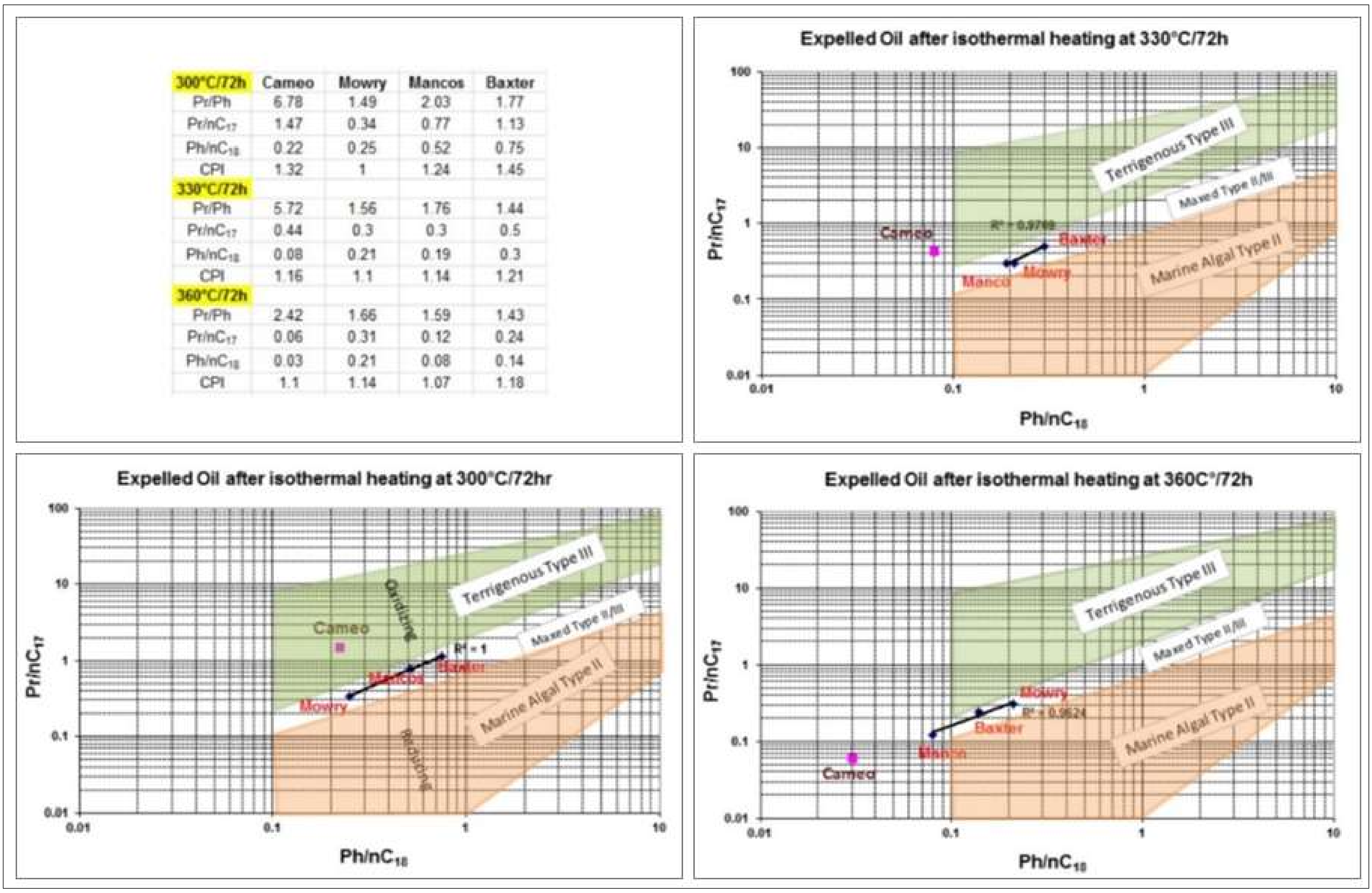
Zhou et al. (2010) chose Pr/n-C17 and Ph/n-C18 ratios as saturated hydrocarbon maturity parameters applied to immature, mature, and overmature stages. According to their research, Pr/n-C17 and Ph/n-C18 ratios show heterogeneity in spatial distribution and decrease with increasing maturity. They have less affected by secondary activities such as migration. The Pr/Ph ratio of isoprenoid hydrocarbon increases with rising crude oil maturity; Pr/n-C17 and Ph/n-C18 ratios distinctly decrease, whereas the proportion of light and heavy hydrocarbon significantly increases. Besides, it has been detected that the rise in Pr/n-C17 and Ph/n-C18 from down to top shows hydrocarbon migration from deep formations to shallow ones. They have also stated the hydrocarbon migration trend is evident with changes in Pr/n-C17 and Ph/n-C18 ratios. Additionally, Manzano et al. (1997) showed that hydrocarbons derived from deeper levels migrate to shallow levels with the thermal maturity level as indicated by the parameter Pr/n-C17.

Petroleum in the reservoir can react with sulphate ions in the pore water and can be oxidized into CO_2 by reducing sulphate into H_2S. Inter-steps of this redox reaction are elemental sulphur and polysulfides. “Thermochemical Sulphate Reduction” (TSR) was first proposed by Orr (1974).

It can explain the high H_2S concentrations found in some deep-seated gas reservoirs and the light isotopic composition of carbonate types of cement formed under the incorporation of CO_2 derived from the oxidized petroleum. Elevated temperatures are needed to induce TSR. This minimum temperature has controversially been discussed. Worden et al. (1995) postulated that TSR could take place at the temperatures as low as 140 °C, whereas most authors claim that higher temperatures require (e.g., Manzano et al., 1997; Machel, 1998). For oils that have been altered by TSR processes, low Pr/n-C17 values are typical. Hence, the ratio of Pr/n-C17 may be used as an independent maturation parameter that is not significantly affected by TSR (Manzano et al., 1997).

Pr/n-C17 and Ph/n-C18 values are less than 1 for all the samples from localities, which can be regarded as suspicious TSR sources. Therefore, a relationship between TSR processes and products of natural pyrolysis is conceivable (Volk, 2020).

Anyigba (2021) has investigated the effects of Pr/nC17 and Ph/nC18 ratios on oil API gravity with Boosted Trees Ensemble machine learning model. Boosted Trees Ensemble regression model was used to correlate API gravity and Pr/nC17 and Ph/nC18 ratios. A global data set of specifically 694 API gravity crude oils and their corresponding isoprenoid/n-alkane i.e. Pristane/nC17 (Pr/nC17) and Phytane/nC18 (Ph/nC18) geochemical biomarker parameters have been assembled from open literature and open access data reports. Inferential hypothesis testing on the data collected, indicates the effects of Pr/nC17 and Ph/nC18 ratios on API gravity are statistically significant at a 95% confidence level.



300°C/72h	Cameo	Mowry	Mancos	Baxter
Pr/Ph	6.78	1.49	2.03	1.77
Pr/nC$_{17}$	1.47	0.34	0.77	1.13
Ph/nC$_{18}$	0.22	0.25	0.52	0.75
CPI	1.32	1	1.24	1.45
330°C/72h				
Pr/Ph	5.72	1.56	1.76	1.44
Pr/nC$_{17}$	0.44	0.3	0.3	0.5
Ph/nC$_{18}$	0.08	0.21	0.19	0.3
CPI	1.16	1.1	1.14	1.21
360°C/72h				
Pr/Ph	2.42	1.66	1.59	1.43
Pr/nC$_{17}$	0.06	0.31	0.12	0.24
Ph/nC$_{18}$	0.03	0.21	0.08	0.14
CPI	1.1	1.14	1.07	1.18

Expelled Oil after isothermal heating at 330°C/72h

Expelled Oil after isothermal heating at 300°C/72hr

Expelled Oil after isothermal heating at 360C°/72h

Fig. 22. Pr/n-C17 and Ph/n-C18 plot for expelled oils generated from sequential hydrous pyrolysis of Cameo Coal, Mowry, Mancos, and Baxter Shales. With increasing thermal maturity, data points move towards the lower-left corner of the diagram (from Ko, 2010)

The prediction accuracy range of the BTE model is ±6°API. When the BTE model was applied to oils in the southeastern Anatolia basin of Turkey, it has a predictive accuracy of ±3°API. This corresponds to a percentage predictability of 85%. The model was applied to oils generated from Arabian gulf fields the model generally yields a predictive accuracy of ±4°API. This corresponds to percentage predictability of 80%.

The Pr/n-C17 vs. Ph/n-C18 plot, initially proposed by Lijmbach (1975), provides useful information about the source material type, thermal maturity, biodegradation, and depositional conditions of organic matter. The Pr/n-C17 vs. Ph/n-C18 plot is often used to deduce maturity proxy (Figs. 22 and 26) (Connan and Cassou, 1980; Shanmugam, 1985; ten Haven et al., 1987; Peters et al., 1999; Peters et al., 2005). Besides, the cross plot of Pr/n-C17 vs. Ph/n-C18 is the most commonly used biodegradation indicator based on this assumption for initial to moderate alteration levels (Peters et al., 1999).

4.2.3. Biodegradation parameter (BP)

One of the most remarkable parameters in terms of the oil recovery and quality in the subsurface is the API gravity, which is significantly reduced by proceeding biodegradation making the oils pastier (Aldahik, 2010). API gravity of oils derived from shales is medium-high, and oils derived from carbonate source rocks are low-medium (Hughes et al., 1984; Palacas et al., 1984; Tissot and Welte, 1984). Biodegradation is a secondary process that alters the molecular composition and bulk properties (such as API gravity) of petroleum in reservoirs (Connan, 1984).

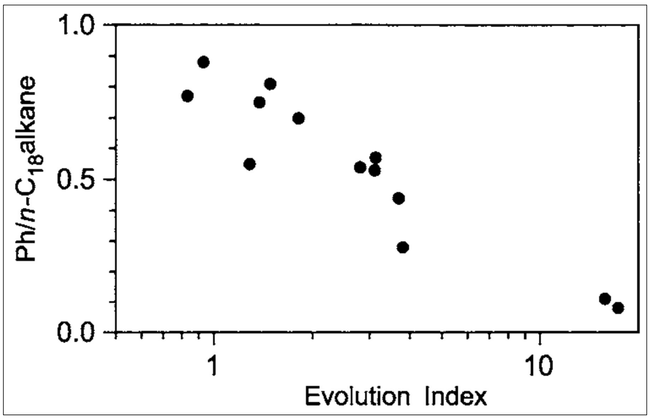


Fig. 23. The decrease in Ph/n-C18 alkane ratio with thermal maturity (Evolution Index, EI) for oils (Ishiwatari and Ishiwatari, 2004). EI values for Oils are 1 - 4. EI = 1 values indicate heavy oils. EI values for Condensates are EI > 10

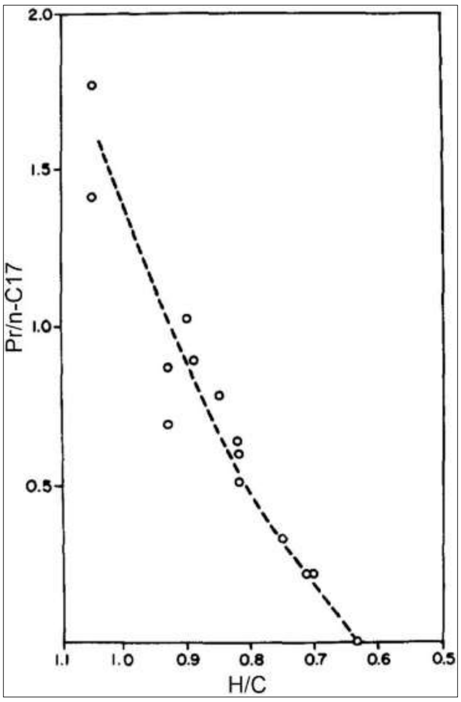


Fig. 24. The relationship between the Pr/n-C17 ratio and the hydrogen/carbon (H/C) ratio with increasing degree of thermal alteration (Ishiwatari et al., 1977)

The presence of saturated hydrocarbons in oils tends to reflect a high API value, representing a good oil quality. Biodegradation affects the quality of oil because of the loss of the saturated hydrocarbons leading to a decrease in API values (Figs. 27-29) (Connan, 1984; Wenger et al., 2001). The biodegradation level is directly correlated with the Pr/n-C17 and Ph/n-C18, and as expected, it is inversely proportional to the API gravity (de Abreu et al., 2020). In the analysis of crude oil for API gravity, the biomarkers such as isoprenoids/n-alkanes (Pr/n-C17 and Ph/n-C18) ratios are necessary. They are used to ascertain the levels of maturity and indicate the deposition environments of crude oils (Nwadinigwe and Alumona, 2018). In the meantime, a value of Ph/n-C18 less than 1 indicates non-biodegraded hydrocarbons (Hunt, 1995).

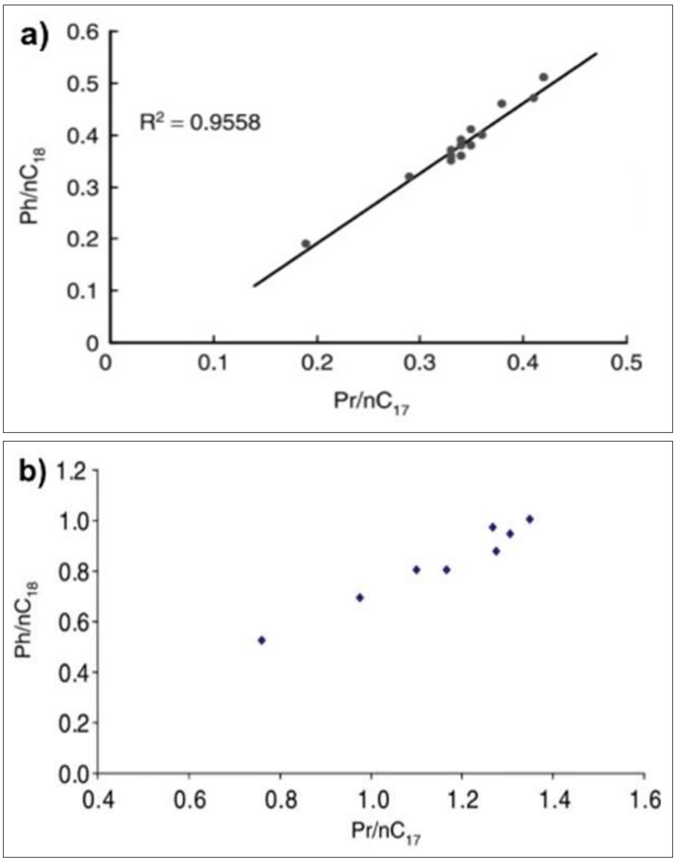


Fig. 25. The linear correlation between Pr/n-C17 and Ph/n-C18: a) Chang et al., 2012 and b) Asif et al., 2009)

The Pr/n-C17 and Ph/n-C18 ratios are reliable indicators of biodegradation (Winters and Williams, 1969). A plot of Pr/n-C17 vs. Ph/n-C18 shows a consistent trend with biodegradation (Figs. 26, 30). The ratio values increase with rising biodegradation. API gravity decreases as Pr/n-C17 increases (Fig. 31). The API gravity and viscosity of biodegraded oils have been reported to be remarkably altered relative to non-biodegraded oils (Wenger et al., 2001).

(Pr+Ph)/(n-C17+n-C18) ratio is considered as a BP (Isoprenoid coefficient, Ki), based on the preferential degradation of n-alkanes over isoprenoids (Fig. 26) (Koopmans et al., 2002; Asif et al., 2009; Hu et al., 2014; Samoilenko et al., 2019; Kayukova et al., 2020). It was also used in an oil correlation study (e.g., Abboud et al., 2005).

The viscosities [μ(50)] of crude oils have strong correlations with the biomarker B [(Pr+Ph)/(n-C17+n-C18)] with increasing biodegradation, and the correlation coefficients are 0.96. A linear correlation between μ (50) and the ratio of

(Pr + Ph)/(n-C17 + n-C18) because the denominator of this parameter is the sum concentration of two compounds of n-alkanes. In contrast, the numerator is the sum concentration of the two acyclic isoprenoid types that are relatively more resistant to biodegradation. It is well-known that the process of biodegradation can change the chemical composition and physical properties of crude oil (Erstad et al., 2009; Wardlaw et al., 2011).

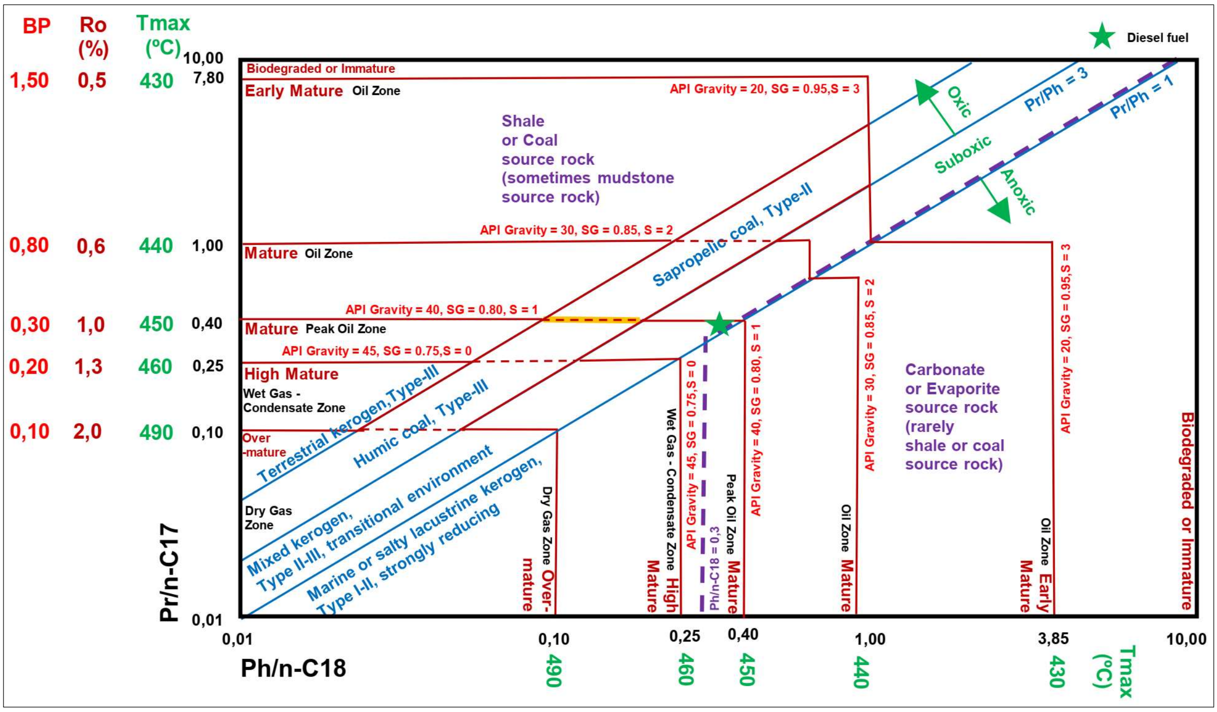


Fig. 26. The Pr/n-C17 vs Ph/n-C18 plot used to assess source rock type, maturity, depositional environment and redox conditions, biodegradation degree of organic-rich rocks/hydrocarbons/oils (modified from Shanmugam, 1985; Pletsch et al., 2010; Petersen et al., 2016; Böcker et al., 2017; Poturay and Kompanichenko, 2019; Ozdemir et al., 2020a). API: American Petroleum Institute, S: (%), SG: (gr/cm3), BP: (Pr+Ph)/(n-C17+n-C18), Ro: Vitrinite reflectance (%) T_{max}: (°C). Data: Lijmbach (1975), Connan and Cassou (1980), Shanmugam (1985), Dzou and Hughes (1993), Chandra et al. (1994), Abdullah (1999), Betchel et al. (2001), Matuszewska (2002), Amijaya (2005), Oforka et al. (2012), Onojake et al. (2015), Ma (2016), Gomez (2016), El Diasty et al. (2016), Adepojua et al. (2018), Nwadinigwe and Alumona (2018), Hakimi et al. (2018a, 2018b, 2019) and other literatures (also see other references in text)

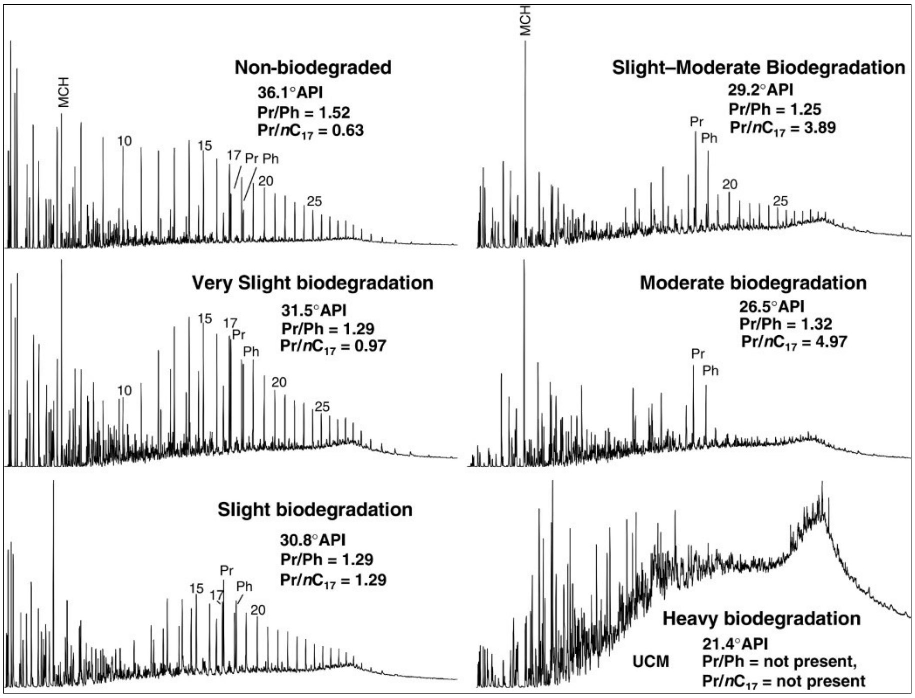


Fig. 27. Gas chromatograms, API gravities, Pr/Ph, and Pr/n-C17 ratios are shown systematic changes as a result of increasing biodegradation of crude oils. The oils in the figure were generated from the same source rock under comparable thermal conditions (from Peters et al., 2005)

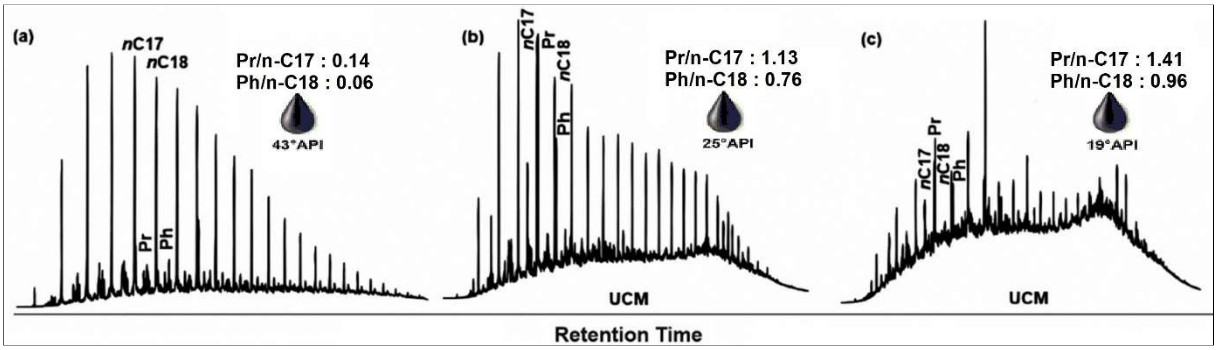


Fig. 28. Chromatographic profile showing the distribution of the n-alkanes and isoprenoids (Pr and Ph) in addition to the Pr/n-C17 and Ph/n-C18 ratio values for the oil samples (a), (b), and (c). The oil sample (a) has low Pr/n-C17 and Ph/n-C18 ratio values due to the higher abundance of n-alkanes and no Unresolved Complex Mixture (UCM), which are typical characteristics of a non-biodegraded and light oil. On the other hand, oil samples (b) and (c) have more pronounced UCM and a low abundance of n-alkanes, resulting in high Pr/n-C17 and Ph/n-C18 ratio values in agreement with their low API and high biodegradation levels. The oil sample (c) is the most biodegraded, showing a very low abundance of pristane and phytane, in addition to the n-alkanes, and markedly higher UCM, likely related to its high amount of NSO (nitrogen, sulfur, and oxygen compounds) compounds (de Abreu et al., 2020)

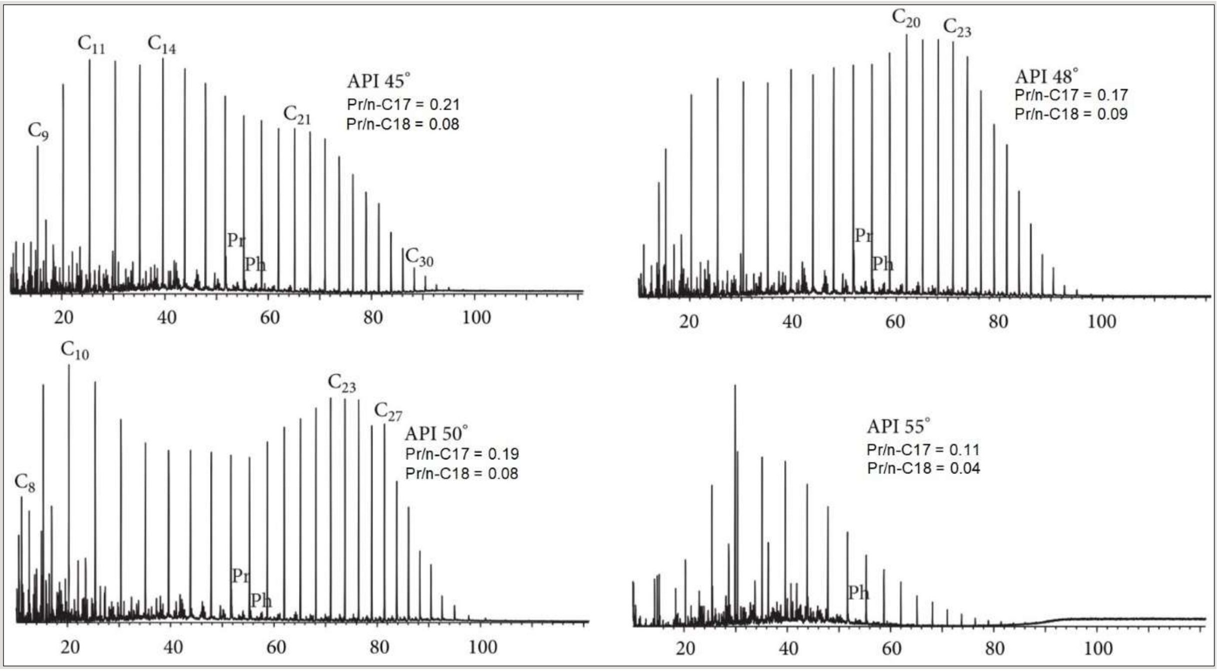


Fig. 29. Chromatographic profile showing the distribution of the n-alkanes and isoprenoids in addition to the Pr/n-C17 and Ph/n-C18 ratio values for some condensates with different API gravity (from Nasir and Fazeelat, 2013)

Some of the compositions are consumed with increasing biodegradation. For instance, the components of n-alkanes (n-C17, n-C18) and acyclic isoprenoids (Pr, Ph) are almost completely consumed when crude oil is suffered from severe biodegradation. In this case, it is difficult to obtain an accurate value of the parameters, and it is inappropriate to use the BP to predict the viscosity value of heavy to severely biodegraded oil (Hu et al., 2014). A plot of (Pr+Ph)/(n-C17 +n-C18) vs. API gravity shows an inverse correlation (Fig. 31) (Asif et al., 2009). Oil quality in a petroleum reservoir, gas-oil and oil-water contacts, etc., can be predicted with petroleum geochemistry (Peters and Fowler, 2002). Crude oil with high viscosity often suffers from bacterial biodegradation process that can considerably change the crude oil's chemical composition, and the oil becomes more and more viscous. The degree of biodegradation can be estimated by analyzing various BP such as (Pr+Ph)/(n-C17+n-C18), etc., (Fig. 26) (Peters et al., 2005). Oil API gravity largely depends on the maturity and source type.

Nevertheless, a four-level classification of the BP values in Fig. 26 is presented below based on the current worldwide database to assess biodegradation degree in the process of geochemical assessment organic-rich rocks/hydrocarbons/oils:

I. No biodegradation: ≤ 0.30 = BP; unaltered/fresh non-biodegraded oil or negligible biodegradation, typically API > 35.
II. Low biodegradation: $0.30 \leq \text{BP} \leq 0.80$; incipient biodegradation; loss of light saturate (normal) compounds; typically, 28 < API < 35.
III. Moderate biodegradation: $0.80 \leq \text{BP} \leq 1.5$; typically, 20 < API < 28.
IV. Heavy biodegradation: BP > 1.50; typically, API < 20.

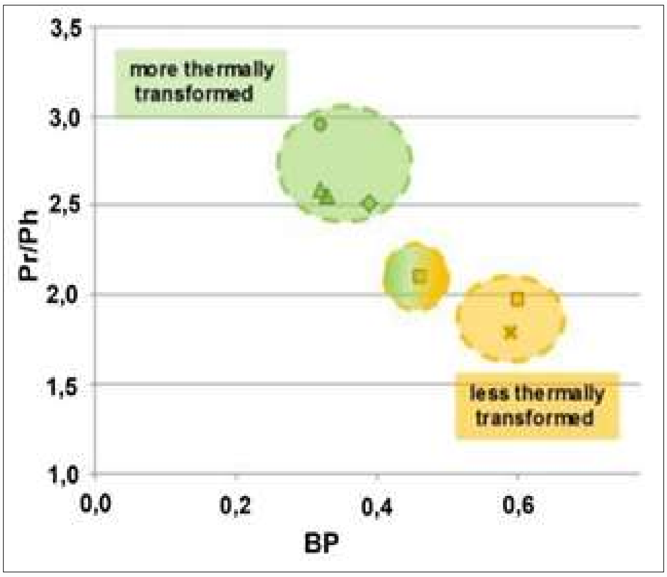


Fig. 30. Pr/Ph ratio vs BP diagram for oils from fields of Gydan Peninsula (West Siberia, Russia) (Samoilenko et al., 2019)

4.2.4. Other geochemical assessment parameters

4.2.4.1. Carbon Preference Index (CPI)

The CPI is an indicator of the source of n-alkanes. The index can apply to any range of the carbon sequence. CPI, a ratio between the amounts of n-alkanes having odd and even carbon numbers, is determined by measuring the heights or areas of the peaks in gas chromatograms (Fig. 32). The dominant peaks in these chromatograms correspond to the n-alkanes. In the calculation of CPI, different formulas have been suggested by various researchers (Bray and Evans, 1961; Tissot and Welte, 1984; Marzi et al., 1993). The CPI is used to interpret the type of organic matter, the sedimentation environment, and thermal maturity. CPI value of mature hydrocarbons is equal to 1 or close to 1 (Waples 1985). A high value reflects the immature, early mature, or organic matter derived from higher terrestrial plants (Tran and Philippe 1993). CPI < 1 represents a reducing environment, while CPI > 1 indicates an oxidizing environment. The values of oils and bitumens associated with hypersaline carbonate or evaporitic environments are less than 1 (Tissot and Welte 1984; Peters and Moldowan, 1993).

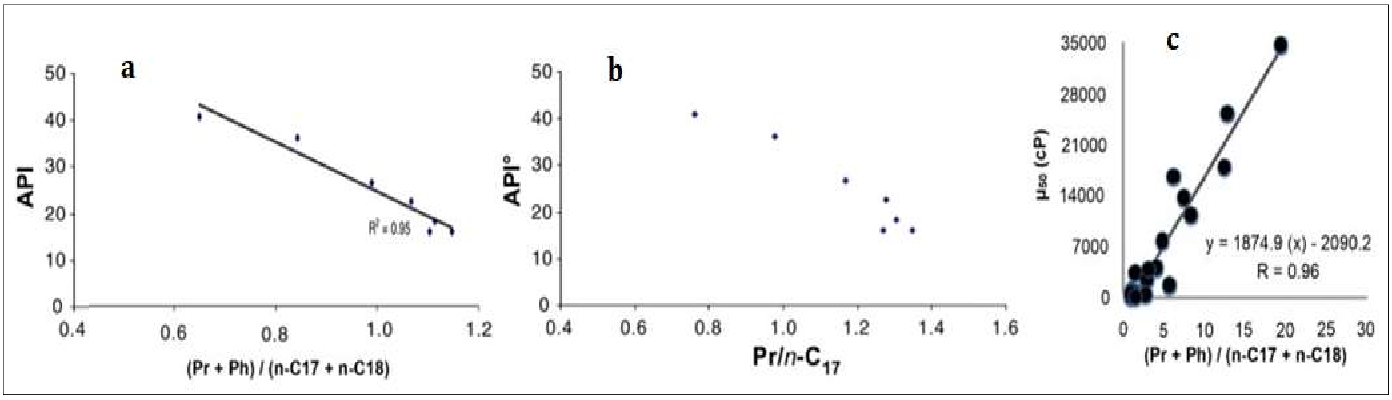


Fig. 31. Relationship between API gravity, viscosity and BP [BP: (Pr + Ph)/(n-C17 + n-C18)]. API gravity is controlled by the Pr/n-C17 ratio rather than any other biodegradation factor (a, b: Asif et al., 2009, c: Hu et al., 2014)

The CPI values calculated for the same samples using different formulas and carbon ranges may be quite different. The value should be used with caution in maturity assessment since different researchers can apply it to different carbon sequence ranges using different formulas. The CPI values of oils derived from both immature and terrestrial organic matters are much higher than 1 whereas both immature and hypersaline carbonates and evaporites' values are lower than 1 (Fig. 33). Moreover, the relationship between CPI and Ro% values of coals is non-linear (Fig. 34) (Alexander and Hazai, 1981; Amijaya, 2005; Havelcová et al., 2012; Zamansani et al., 2019; Kara-Gülbay et al., 2019).

4.2.4.2. Natural n-alkane Ratio (NAR)

The term "petrogenic sources" identifies unburned fossil sources such as crude oil and coal. These kinds of sources were formed very slowly at moderate temperatures (between 100 °C and 300 °C) millions of years ago (Beyer et al. 2010). The NAR parameter has been proposed to evaluate the source of hydrocarbons (natural or petroleum n-alkane) in the environment (Mille et al., 2007). The ratio is zero or close to zero for natural petroleum hydrocarbons and crude oil. In other hydrocarbon sources, it is higher. The following formula is used to calculate the NAR parameter:

$$NAR = \frac{[\sum n - alk(C_{19-32}) - 2\sum even\, n - alk(C_{20-32})]}{\sum n - alk(C_{19-32})} \qquad (1)$$

4.2.4.3. Fractionation Index (FI)

In some basins, the presence of gas-condensates is associated with a fractionation-migration process rather than thermal maturation or source rock-related effects (Dzou and Hughes, 1993; Kato et al., 2006). In particular, the Fractionation Index (FI = n-C10/[n-C16+n-C25]) can be used to estimate the API gravity of hydrocarbons derived from terrestrial organic matter (fluvio-deltaic source rocks) or primarily marine source rocks.

However, they have high terrestrial organic material input (Fig. 35) because oils and gas-condensates derived from such source rocks may have higher Pr/n-C17 and Ph/n-C18 ratios as well as API gravity than the oil and gas-condensate ranges shown in Fig. 26 due to fractionation-migration from deep to shallow levels (e.g., Kato et al., 2006).

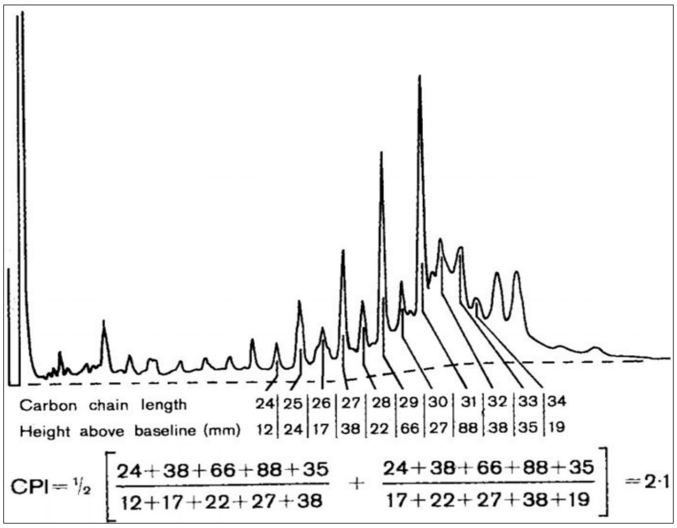


Fig. 32. Measurement of peak heights in gas chromatograms and calculation of CPI (Thompson, 1982)

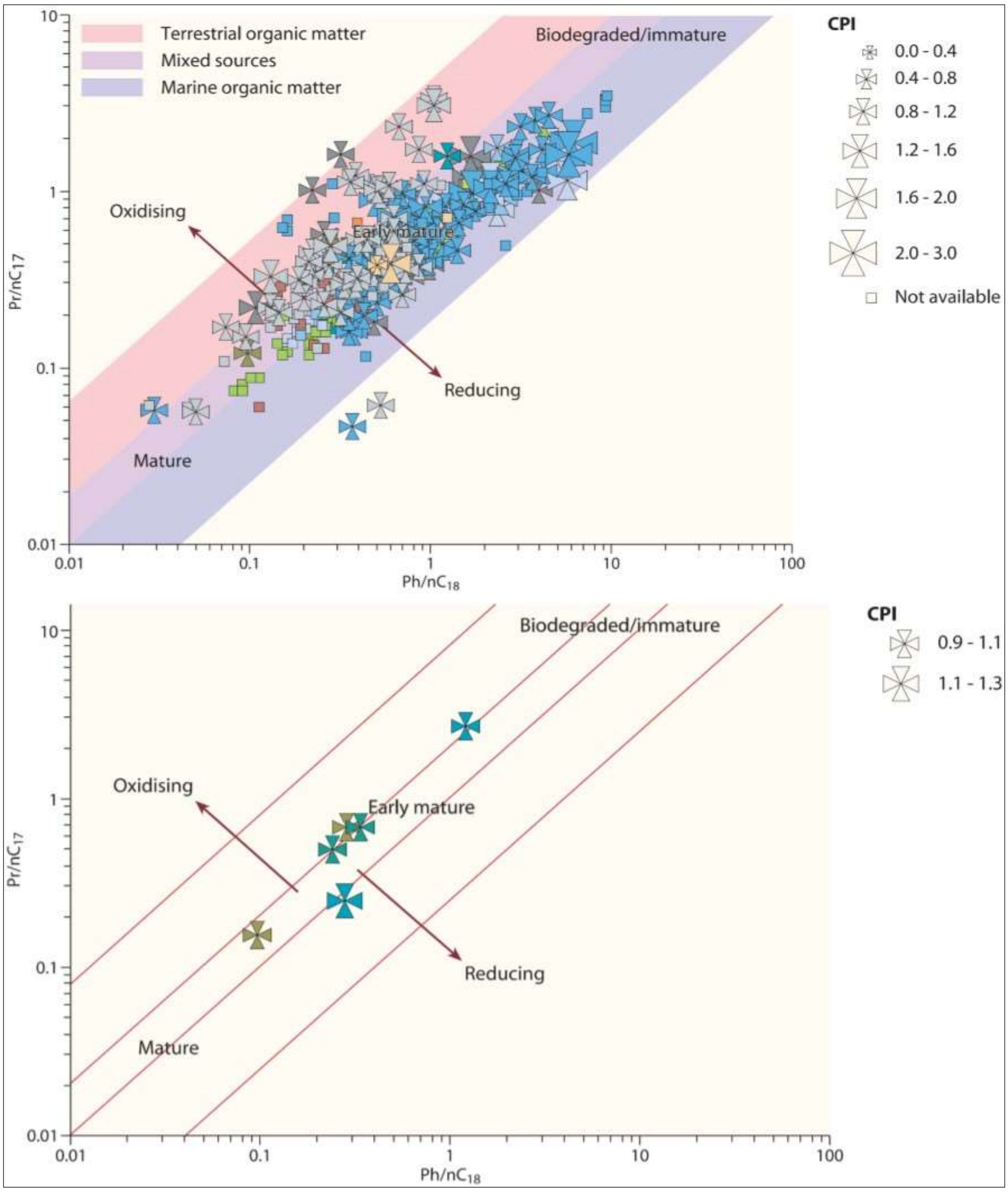


Fig. 33. Relationships between Pr/n-C17 versus Ph/n-C18 plot, CPI values and maturity (Pletsch et al., 2010)

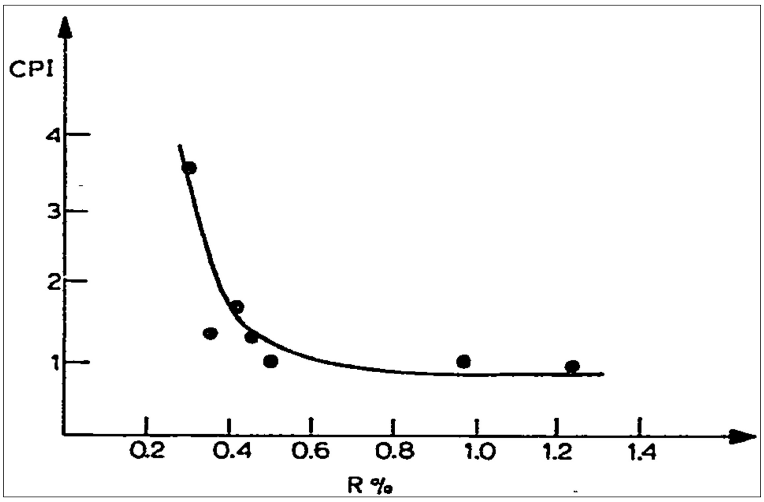


Fig. 34. The relationship between CPI and %Ro values of the coals (Alexander and Hazai, 1981)

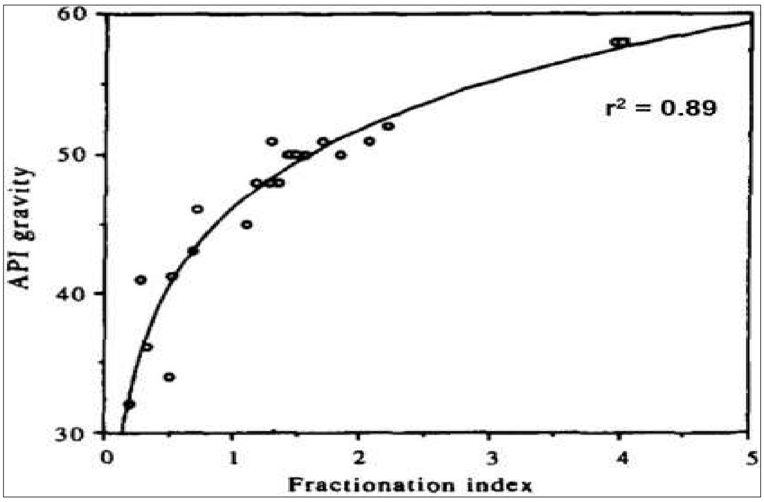


Fig. 35. The relationship between API gravity and Fractionation index (from Dzou and Hughes, 1993)

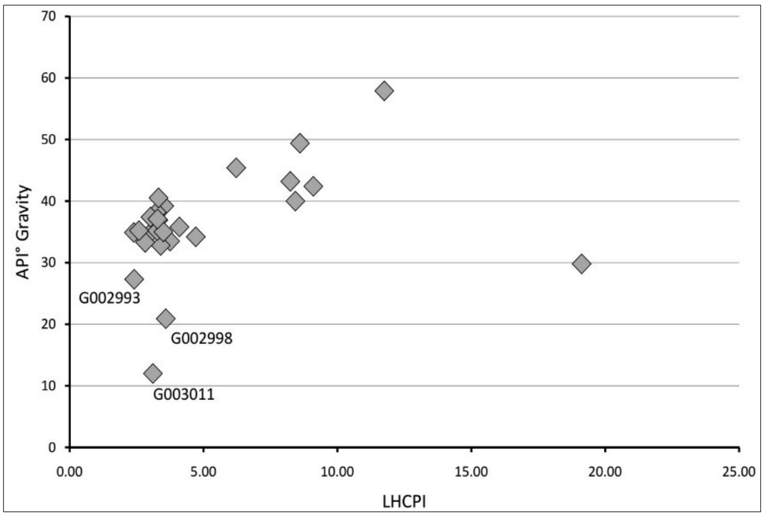


Fig. 36. Changes in LHCPI values with increasing maturity (Aldahik, 2010)

The index may need to be taken into account in all geochemical assessments because all hydrocarbons may be exposed to the fractionation-migration event (Dzou and Hughes, 1993).

4.2.4.4. Light Hydrocarbon Preference Index (LHCPI)

The LHCPI=[n-C17+n-C18+n-C19]/[n-C27+n-C28+n-C29]) reflects the relative dominance of short-chain over long-chain hydrocarbons (Chaffee et al., 1986; Littke et al., 1998). In this framework, this parameter indicates the maturation level of crude oils and source rocks as well. LHCPI values increase with increasing maturity (Fig. 36). Marine oils are characterized by LHCPI values higher than 1, whereas coal-derived and terrestrial oils have LHCPI < 1 (Aldahik, 2010). In particular, this index can be used to interpret origin of oils.

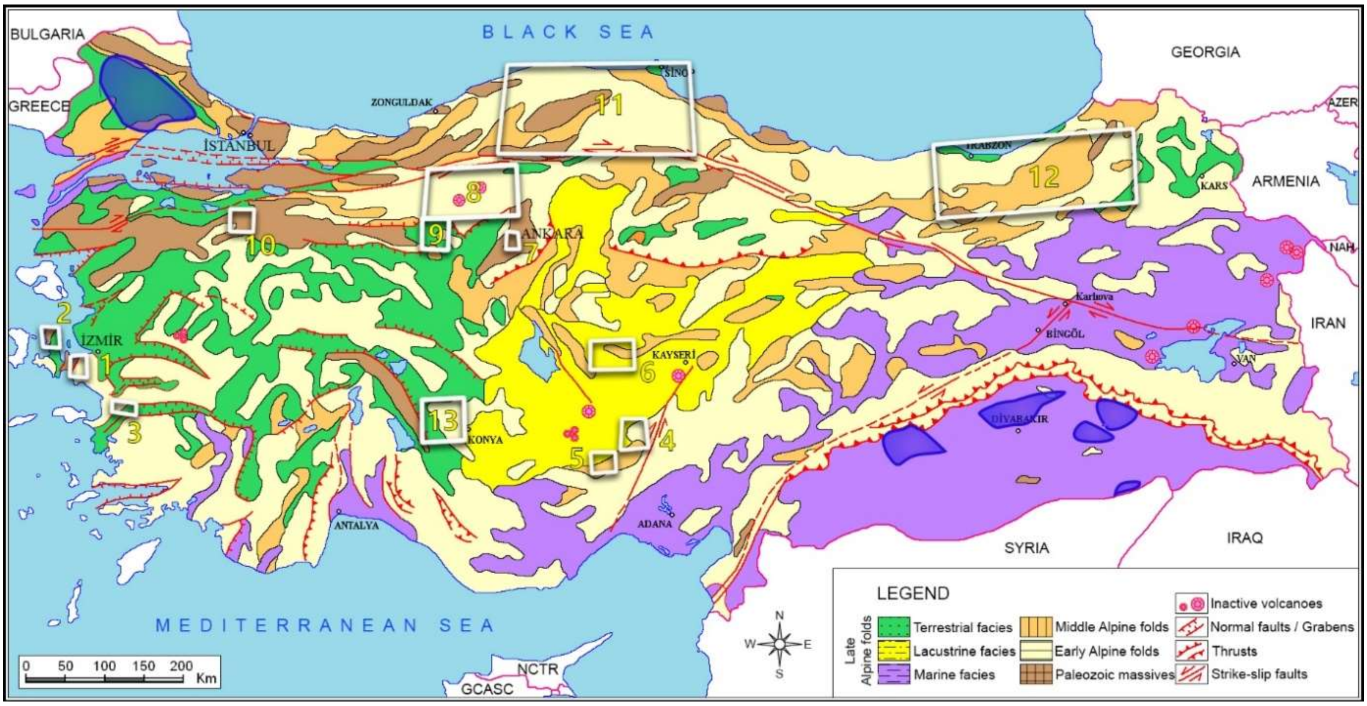


Fig. 37. Location map of study areas. 1: Seferihisar High, 2: Karaburun Peninsula, 3: Büyük Menderes Graben, 4: Ulukışla Basin, 5: Niğde Massif, 6: Kızılırmak Graben, 7: Hasanoğlan and Mamak regions, 8: Northern Ankara, 9: Beypazarı Neogene Basin, 10: Uludağ Massif, 11: Central Pontides, 12: Eastern Pontides, 13: Muhsine Graben, blue polygons: oil and gas production fields of Turkey. Locations of the metamorphic source rocks given in Figs. 1 and 3 (Area 7: Karakaya Complex, Area 11: Domuzdağ Complex and Area 13: Bozdağ Massif). The white polygons show the dimensions of the study areas

Table 3. TPH analysis results of the water samples and calculated geochemical parameters

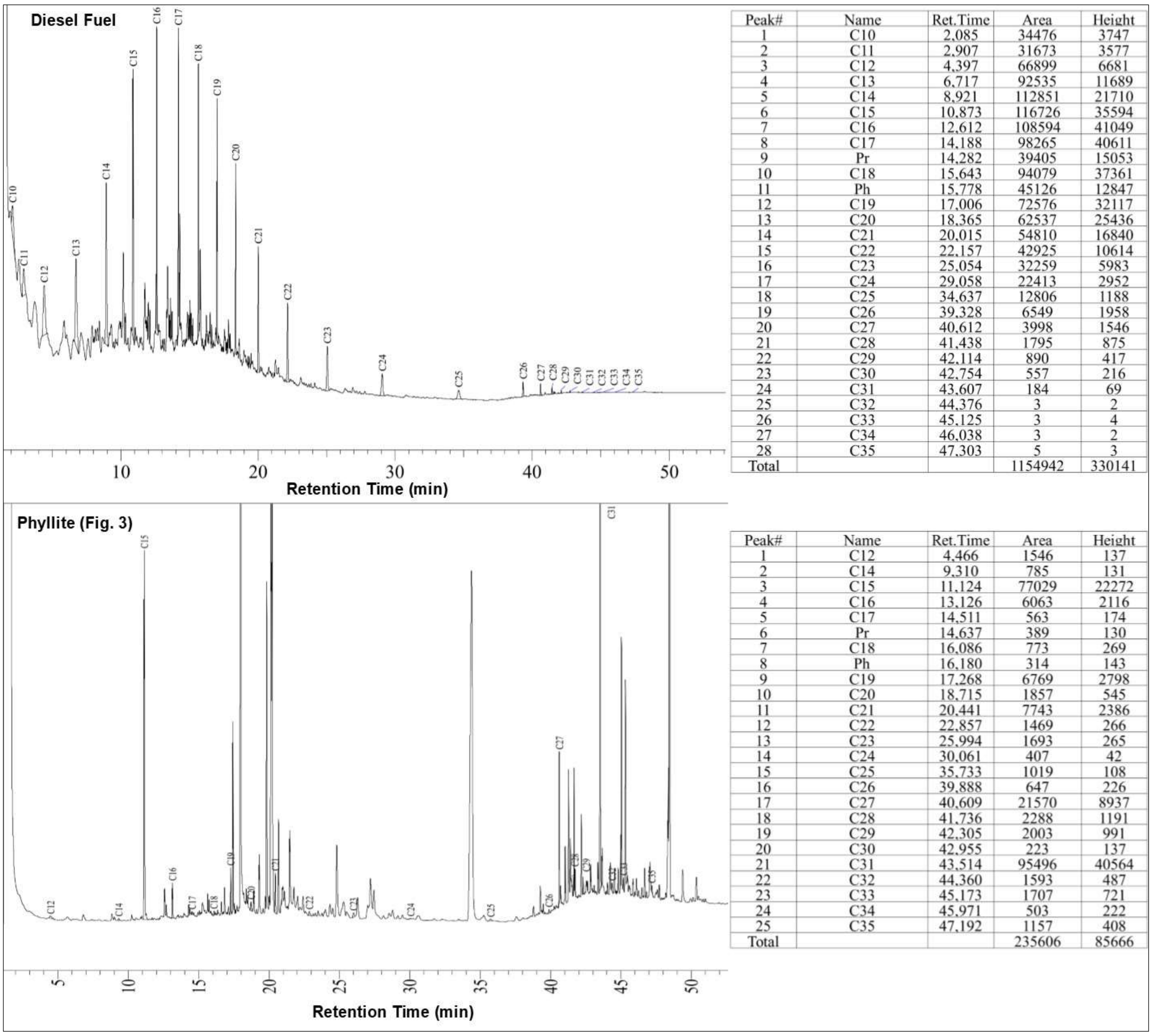
Area (Fig. 37)	Basin/Region	Number of samples	TPH (mg/l)	I_{geo}	Reference
1	Seferihisar High	25	0.40 - 0.79	2.41 - 3.39	Ozdemir et al. (2020a)
2	Karaburun Peninsula	23	0.40 - 0.71	2.41 - 3.38	Ozdemir et al. (2020c)
3	Büyük Menderes Graben	14	5.44 - 114.76	< 0 - 2.94	Ozdemir (2019c)
4	Niğde Massif	15	0.41 - 0.75	2.41 - 3.32	Ozdemir et al. (2021)
5	Ulukışla Basin	31	0.04 - 0.23	< 0 - 1.63	Sahinoğlu et al. (2020b)
6	Kızılırmak Graben	25	0.41 - 0.97	2.41 - 3.69	Ozdemir et al. (2022)
7	Hasanoğlan and Mamak	12	7.51 - 45.31	< 0 - 1.59	Ozdemir (2019a,b)
8	Northern Ankara	69	0.05 - 0.78	< 0 - 3.07	Sahinoğlu et al. (2020a)
9	Beypazarı Neogene Basin	25	0.46 - 1.00	2.52 - 3.74	Ozdemir et al. (2020b)
10	Uludağ Massif	24	0.40 - 0.82	2.41 - 3.45	Palabiyik et al. (2020a)
11	Central Pontides	100	0.05 - 0.83	< 0 - 3.47	Palabiyik et al. (2020b)
12	Eastern Pontides	21	0.04 - 0.08	< 0 - 0.10	Ozdemir and Palabiyik (2020)
13	Muhsine Graben	38	0.10 - 0.21	0.38 - 1.49	Ghasemlounia et al. (2020)

Table 4. TPH analysis results of the soil samples and calculated geochemical parameters

Area (Fig. 37)	Basin/Region	Number of samples	TPH (mg/kg)	I_{geo}	Reference
5	Ulukışla Basin	19	5.25 - 103.54	< 0 - 3.52	Sahinoglu et al. (2020b)
8	Northern Ankara	45	2.80 - 55.55	< 0 - 2.63	Sahinoglu et al. (2020a)
11	Central Pontides	50	7.01 - 107.24	< 0 - 3.57	Palabiyik et al. (2020b)
12	Eastern Pontides	7	10.16 - 61.89	0.14 - 2.79	Ozdemir and Palabiyik (2020)
13	Muhsine Graben	38	4.28 - 18.83	< 0 - 1.07	Ghasemlounia et al. (2020)

4.3. Re-Os isotope system

It is frequently possible to identify the source rock by using various methods (some of which include isotopic analysis), while standard correlation techniques can determine the age of the source rock. However, the age of other processes, especially the time of descent and migration, is difficult to predict. In applying the Re-Os system to the source rocks, the close relationship of both rhenium and osmium with organic matter is taken into consideration (Ravizza and Turekian, 1989; Ravizza et al., 1991; Cohen et al., 1999; Creaser et al., 2002). Both rhenium and osmium pass from seawater to anoxic deposits during or immediately after deposition due to the reactions at the water-sediment interface or the reduction reactions below the interface, and are collected in organic matter (Marques, 2012). This process constitutes the basis for the Re-Os system to be a good geochronometer for source rocks and fluids. Re and Os are present in many crude oils in measurable abundances (Li, 2017).



Peak#	Name	Ret.Time	Area	Height
1	C10	2,085	34476	3747
2	C11	2,907	31673	3577
3	C12	4,397	66899	6681
4	C13	6,717	92535	11689
5	C14	8,921	112851	21710
6	C15	10,873	116726	35594
7	C16	12,612	108594	41049
8	C17	14,188	98265	40611
9	Pr	14,282	39405	15053
10	C18	15,643	94079	37361
11	Ph	15,778	45126	12847
12	C19	17,006	72576	32117
13	C20	18,365	62537	25436
14	C21	20,015	54810	16840
15	C22	22,157	42925	10614
16	C23	25,054	32259	5983
17	C24	29,058	22413	2952
18	C25	34,637	12806	1188
19	C26	39,328	6549	1958
20	C27	40,612	3998	1546
21	C28	41,438	1795	875
22	C29	42,114	890	417
23	C30	42,754	557	216
24	C31	43,607	184	69
25	C32	44,376	3	2
26	C33	45,125	3	4
27	C34	46,038	3	2
28	C35	47,303	5	3
Total			1154942	330141

Peak#	Name	Ret.Time	Area	Height
1	C12	4,466	1546	137
2	C14	9,310	785	131
3	C15	11,124	77029	22272
4	C16	13,126	6063	2116
5	C17	14,511	563	174
6	Pr	14,637	389	130
7	C18	16,086	773	269
8	Ph	16,180	314	143
9	C19	17,268	6769	2798
10	C20	18,715	1857	545
11	C21	20,441	7743	2386
12	C22	22,857	1469	266
13	C23	25,994	1693	265
14	C24	30,061	407	42
15	C25	35,733	1019	108
16	C26	39,888	647	226
17	C27	40,609	21570	8937
18	C28	41,736	2288	1191
19	C29	42,305	2003	991
20	C30	42,955	223	137
21	C31	43,514	95496	40564
22	C32	44,360	1593	487
23	C33	45,173	1707	721
24	C34	45,971	503	222
25	C35	47,192	1157	408
Total			235606	85666

Fig. 38. The TPH gas chromatograms and integration tables of the commercial diesel fuel and a phyllite soil sample from Domuzdağ Complex of the Central Pontides (Turkey)

In the meantime, Re-Os geochronology provides the following information (Hannah et al., 2014):

- Geologically consistent radiometric ages are for source rocks, allowing regional and global correlations.
- The same unit(s) dates by Re-Os geochronology provide detailed information about depositional conditions and hydrocarbon potential.
- Initial $^{187}Os/^{188}Os$ ratios provide a new tracer for paleoclimatology and paleoenvironmental conditions at the site of deposition.
- Cautious and targeted geological sampling and a holistic interpretation of Re-Os analytical results open unprecedented opportunities for the timing of hydrocarbon maturation and/or expulsion.

Re-Os isotope system has undergone remarkable developments over the past two decades and is used as a valuable geochronometer in petroleum geology to determine the direct dating of source rocks/hydrocarbons/oils (Cohen, 2004; Marques, 2012; Stein and Hannah, 2014; Ozdemir and Palabiyik, 2019f). Thus, the system provides vital information for the geological interpretation of hydrocarbons/oils' occurrence environments and source rocks (Ozdemir and Palabiyik, 2019f). It has been used in many studies to determine the geological age of source rocks (Ravizza and Turekian, 1989; Cohen et al., 1999; Creaser et al., 2002; Selby and Creaser, 2003, 2005; Kendall et al., 2004, 2006, 2009; Azmy et al., 2008; McArthur et al., 2008; Selby et al., 2009; Xu et al., 2009, 2013, 2014; Rooney et al. 2010; Finlay et al., 2010; Baioumy et al., 2011; Georgiev et al., 2011, 2012; Cumming et al., 2012; Cumming, 2013; Harris et al., 2013; Cumming et al., 2014; Stein et al., 2014; Tripathy et al., 2014; Wright, 2015; Liu, 2017; Liu et al., 2018b).

Researchers have recently succeeded in dating hydrocarbon migration and maturation using Re-Os isotopes (Creaser et al., 2002; Finlay et al., 2011; Lillis and Selby, 2013; Cumming, 2013; Liu, 2017). A study conducted on numerous oil samples from the United Kingdom Atlantic margin has indicated that Re-Os isotopic system actually may track the source of oil and that the obtained ages correspond to ages of generation events as well (Finlay et al., 2011). The Re-Os geochronometer has successfully constrained the timing of oil generation, TSR and thermal alteration of crude oil for petroleum systems worldwide. The osmium isotope composition has also been used as an oil-source correlation tool (Liu, 2017). Re and Os can be found in measurable amounts in most crude oil and organic-rich rocks (Ozdemir and Palabiyik, 2019f). It is thought that the Re-Os dating of hydrocarbons in soil samples containing high amounts of hydrocarbons can be performed. However, it is found at low levels in hydrocarbon-rich water samples. Hence, the hydrocarbons in the samples can be correlated with the geological history of the studied area. Furthermore, Paul et al. (2009) and Pierson-Wickmann et al. (2002) used the analysis method to determine the Re-Os isotope ratio of soils described in the surface and subsurface waters research in detail.

Table 5. The calculated geochemical parameters according to TPH analysis results of the water samples (see Table 3 for references)

Area (Fig. 37)	Basin/Region	Number of samples	Pr/n-C17	Ph/n-C18	Pr/Ph	NAR	BP
1	Seferihisar High	25	0.00 - 0.21	0.03 - 0.36	0.04 - 6.12	0.06 - 0.31	0.02 - 0.17
2	Karaburun Peninsula	23	0.02 - 0.34	0.02 - 0.29	0.14 - 27.43	0.00 - 0.37	0.04 - 0.43
3	Büyük Menderes Graben	14	0.25 - 0.50	0.31 - 0.69	0.25 - 0.50	-	0.23 - 0.44
4	Niğde Massif	15	0.19 - 1.00	0.03 - 0.16	3.23 - 24.50	0.01 - 0.19	0.06 - 0.25
5	Ulukışla Basin	31	0.04 - 28.00	0.13 - 18.17	0.00 - 2.00	0.01 - 0.64	0.08 - 8.88
6	Kızılırmak Graben	25	0.19 - 0.40	0.04 - 0.14	3.63 - 18.50	0.00 - 0.36	0.17 - 0.32
7	Hasanoğlan and Mamak	12	0.25 - 1.90	0.09 - 0.99	0.23 - 0.97	0.01 - 0.39	0.15 - 1.61
8	Northern Ankara	69	0.03 - 3.17	0.04 - 4.59	0.02 - 19.27	0.01 - 0.76	0.07 - 1.75
9	Beypazarı Neogene Basin	25	0.06 - 0.36	0.04 - 0.13	5.14 - 17.17	0.02 - 0.32	0.06 - 0.29
10	Uludağ Massif	24	0.08 - 0.38	0.05 - 0.15	3.33 - 10.67	0.15 - 0.50	0.09 - 0.28
11	Central Pontides	100	0.01 - 12.46	0.01 - 12.82	0.02 - 33.75	0.01 - 0.92	0.04 - 3.37
12	Eastern Pontides	21	0.38 - 8.50	0.46 - 7.87	0.07 - 2.70	0.03 - 0.84	0.42 - 6.70
13	Muhsine Graben	38	0.05 - 0.69	0.03 - 1.12	0.08 - 4.70	0.23 - 0.74	0.06 - 0.54

Table 6. The calculated geochemical parameters according to TPH analysis results of the soil samples (see Table 4 for references)

Area (Fig. 37)	Basin/Region	Number of samples	Pr/n-C17	Ph/n-C18	Pr/Ph	NAR	BP
5	Ulukışla Basin	19	0.09 - 8.34	0.46 - 1.69	0.08 - 2.08	0.06 - 0.74	0.31 - 1.78
8	Northern Ankara	45	0.07 - 2.51	0.05 - 1.77	0.06 - 9.94	0.12 - 0.93	0.06 - 0.90
11	Central Pontides	50	0.02 - 1.26	0.01 - 12.82	0.01 - 10.29	0.54 - 0.96	0.02 - 8.46
12	Eastern Pontides	7	0.12 - 1.16	0.01 - 0.99	0.18 - 4.94	0.32 - 0.83	0.30 - 0.68
13	Muhsine Graben	38	0.06 - 1.14	0.05 - 1.10	0.31 - 2.32	0.03 - 0.96	0.08 - 1.09

Table 7. Source, maturity, depositional conditions of hydrocarbons in water and soil samples in the investigated areas

Area (Fig. 37)	Basin/Region	Kerogen type	Depositional environment	Redox conditions	Maturity
1	Seferihisar High	II, II-III	Marine - Transitional	Anoxic - Suboxic	Mature, High Mature, Overmature
2	Karaburun Peninsula	II, II-III, III	Marine - Transitional - Terrestrial	Anoxic - Suboxic - Oxic	Mature, High Mature, Overmature
3	Büyük Menderes Graben	II, II-III	Marine - Transitional	Anoxic - Suboxic	Mature
4	Niğde Massif	III	Terrestrial	Oxic	Mature, Overmature
5	Ulukışla Basin	II, II-III, III	Marine - Transitional - Terrestrial	Anoxic - Suboxic - Oxic	Early Mature, Mature, High Mature
6	Kızılırmak Graben	III, II-III	Terrestrial - Transitional	Oxic - Suboxic	Mature, High Mature
7	Hasanoğlan and Mamak	II, II-III	Marine - Transitional	Anoxic - Suboxic	Early Mature, Mature
8	Northern Ankara	II, II-III, III	Marine - Transitional - Terrestrial	Anoxic - Suboxic - Oxic	Early Mature, Mature, High Mature
9	Beypazarı Neogene Basin	III	Terrestrial	Oxic	Mature, High Mature, Overmature
10	Uludağ Massif	II-III, III, II	Transitional - Terrestrial - Marine	Suboxic - Oxic - Anoxic	Mature, High Mature
11	Central Pontides	II, II-III, III	Marine - Transitional - Terrestrial	Anoxic - Suboxic - Oxic	Early Mature, Mature, High Mature
12	Eastern Pontides	II-III, II, III	Transitional - Marine - Terrestrial	Suboxic - Anoxic - Oxic	Early Mature, Mature
13	Muhsine Graben	II, II-III, III	Marine - Transitional - Terrestrial	Anoxic - Suboxic - Oxic	Mature, High Mature, Overmature

4.4. Geochemical assessment of some hydrocarbon-rich waters and soils in Turkey

Ozdemir and Palabiyik (2019g) have claimed that Turkey has high potential in terms of mature and overmature rich-petroleum source rocks that occurred during the Paleozoic-Miocene interval of Turkey, according to their paleo-geographic and paleotectonic maps and interpretations. Palabiyik and Ozdemir (2019) have also reported that many shows of surficial active and passive hydrocarbons exist across the country. However, effective and mature source rocks across the country have not been determined so far in geochemical studies conducted by different researchers using classical methods. Based on these studies, it has been suggested that there is no hydrocarbon potential in the onshore areas of the country, except for areas with limited production in Southeastern Anatolia and Thrace basins. Ozdemir and Palabiyik (2019g) have also stated that the majority of onshore Turkey has been covered by the alluviums, young volcanic rocks, ophiolites, and ophiolitic melanges. For this reason, they have emphasized that the possibility of exploring the onshore of the country is extremely limited with classical geochemical methods and that it would be more appropriate to use the TPH in water analysis in future hydrocarbon exploration.

To sum up, according to paleogeographic and paleotectonic data in the literature (Ozdemir and Palabiyik, 2019g), the authors combine the TPH analyses and geochemical assessments conducted on waters and soils in some basins/regions of Turkey, in which the source rocks (not outcropped, deeply buried and/or metamorphosed) should locate or hydrocarbons shows or operable-size metallic ore deposits exist. The authors also come up with and describe a new approach to analyze the data mentioned above.

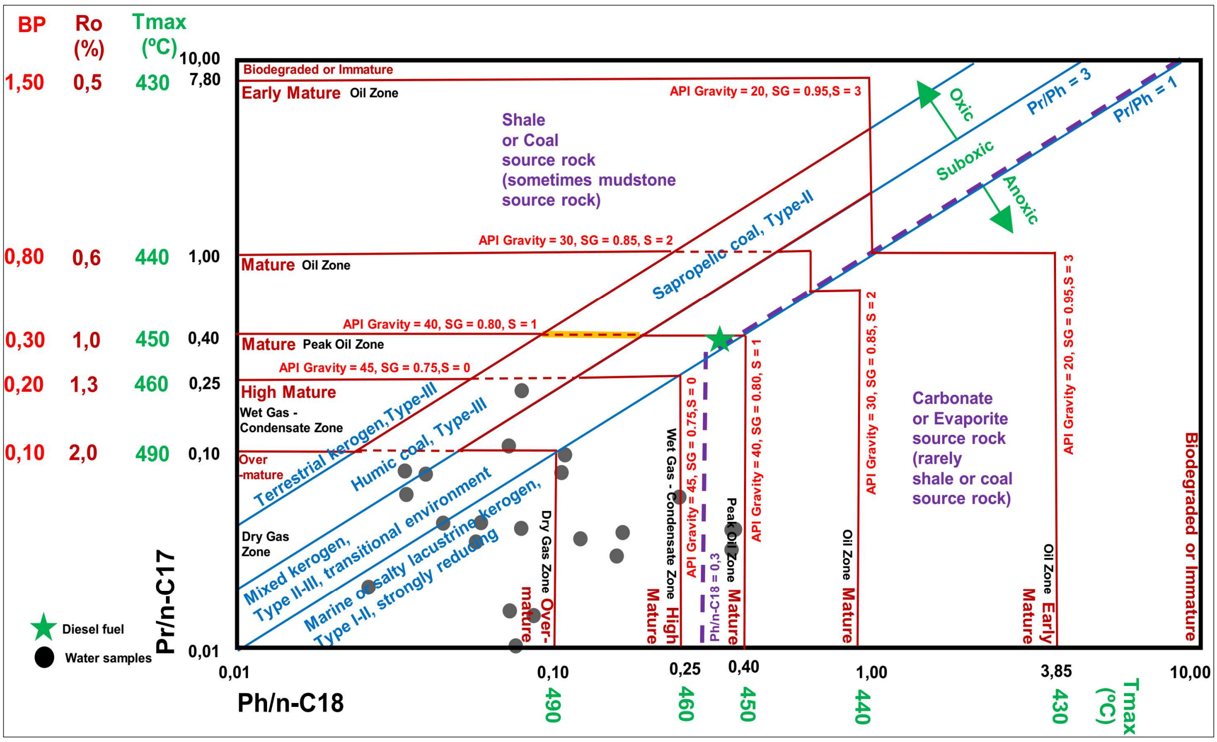


Fig. 39. Revised Pr/n-C17 vs Ph/n-C18 plot of water samples of the Seferihisar High (Fig. 37, Area 1) (data: Ozdemir et al., 2020a)

Turkey's geological structure under the impact of the active tectonic belt can be simply described as massive continental crust blocks that constitute the center of the country, surrounded by various mobile orogenic belts. These mobile orogenic belts are the most potential target areas for oil and gas exploration. In this study, the geochemical evaluations of 424 natural water resources and 159 soil samples collected from 13 regions coinciding with these mobile orogenic thrusts and fold belts are presented (Fig. 37).

Both water and soil samples have been collected from the regions' same locations. Based on the samples' TPH analysis results, the concentrations, biodegradation degree, sources, maturity, and redox conditions of depositional environments of hydrocarbons are evaluated by geochemical methods. All the water and soil samples are rich in mature and overmature hydrocarbons. Hydrocarbons in waters and soils are petrogenic hydrocarbons that are not biodegraded. As a result, these mature and overmature hydrocarbons detected in large areas on a scale of kilometers are evidence for deeply buried effective mature and metamorphosed source rocks and the working petroleum systems in the investigated regions.

4.4.1. Hydrocarbon concentrations

The TPH values of all the samples taken from water resources and soils in the study areas are higher than the permissible hydrocarbon values that should be found in waters (Tables 3 and 5). According to the I_{geo} values, the samples are in the class of waters and soils that are heavily polluted and unpolluted by hydrocarbons (Tables 4-6).

4.4.2. Source, maturity, depositional conditions of hydrocarbons

The chromatograms obtained from TPH gas chromatography analysis of the water and soil samples illustrate the retention times, peak heights, and areas of carbon atoms between 10 and 40 of n-alkanes (Fig. 8). Chromatogram retention times of the n-alkanes containing carbon atom of 10 to 40-alkanes of diesel fuel has been taken as a reference for the calibration of chromatogram retention times for the n-alkane types of hydrocarbon in water and soil samples collected from 13 basins/regions of Turkey (Fig. 37). In other words, the retention times of n-alkanes containing 10 to 40 carbon atoms of the diesel sample are referred to determine the locations and prepare integration tables of n-alkanes in chromatograms of the water and soil samples in Turkey for which the GC analysis has been conducted. The revised Pr/n-C17 vs. Ph/n-C18 plot is used to interpret the maturity of hydrocarbons, the depositional environment, and redox conditions of source rocks that derived hydrocarbons in the water and soil samples of the 13 regions investigated in this study in terms of geochemical parameters (Tables 5, 6) (Figs. 38, 26). According to the positions of the samples in this plot, source rocks that derived hydrocarbons were deposited in marine (Type-II kerogen), transitional (Type II-III kerogen), and terrestrial (Type-III kerogen) environments. Moreover, the hydrocarbons in the samples are predominantly mature and overmature petroleum hydrocarbons (Table 7).

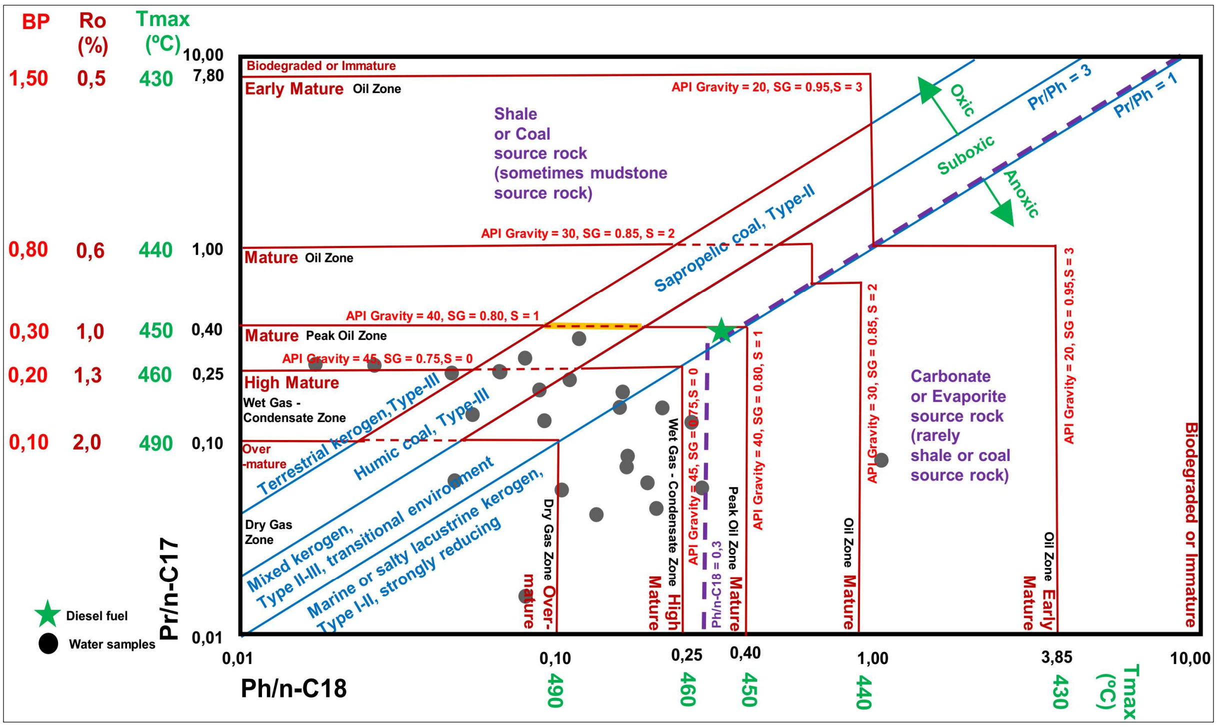


Fig. 40. Revised Pr/n-C17 vs Ph/n-C18 plot of water samples of the Karaburun Peninsula (Fig. 37, Area 2) (data: Ozdemir et al., 2020c)

4.4.2.1. *Seferihisar High (Fig. 37, Area 1)*

According to the Seferihisar High water samples' positions in the revised Pr/n-C17 vs. Ph/n-C18 plot (Fig. 39), the source rocks that derived the hydrocarbons in the samples have been predominantly deposited in an anoxic marine environment (Type-II kerogen). Some of them have been deposited in suboxic transitional (Type II-III kerogen) and oxic terrestrial (Type-III kerogen) environments. The hydrocarbons were predominantly derived from carbonate or evaporitic type source rocks, and the remaining ones were originated from shale-type source rocks and humic coals. The n-alkane hydrocarbons in the samples have different maturity levels: mature (Rock-Eval Pyrolysis T_{max} = 450-460 °C, [Ro%] = 1.0-1.1, Peak Oil Zone), high mature (Rock-Eval Pyrolysis T_{max} = 460-490 °C, [Ro%] = 1.3-2.0, Wet Gas/Condensate Zone), and overmature (Rock-Eval Pyrolysis T_{max} > 490 °C, [Ro%] > 2, Dry Gas Zone). BP values are < 0.30. According to these values, the hydrocarbons in the samples have unaltered/fresh non-biodegraded or negligible biodegradation levels. Therefore, the oils that are present with hydrocarbons expected to be predominantly gas reservoirs that might be discovered in the region should be expected to have API gravity > 35 (light oil), SG < 0.80 gr/cm^3, and very low S will be < 1%.

According to the positions of the Karaburun Peninsula water samples in the revised Pr/n-C17 vs. Ph/n-C18 plot (Fig. 40), the source rocks that derived the hydrocarbons in the samples have been predominantly deposited in an anoxic marine (Type-II kerogen) and suboxic transitional (Type II-III kerogen) environments. Some of them have been deposited in oxic terrestrial (Type-III kerogen) environments.

The hydrocarbons were predominantly derived from carbonate or evaporitic, and shale types of source rocks, while some of them were derived from humic coals. The n-alkane kinds of hydrocarbons in the samples have different maturity levels: mature (Rock-Eval Pyrolysis T_{max} = 450-460 °C, [R_o%] = 1.2-1.25, Peak Oil Zone), high mature (Rock-Eval Pyrolysis T_{max} = 460-490 °C, [R_o%] = 1.3-2.0, Wet Gas/Condensate Zone), and overmature (Rock-Eval Pyrolysis T_{max} > 490 °C, [R_o%] > 2, Dry Gas Zone). The BP values are < 0.30.

According to these values, the hydrocarbons in the samples have unaltered/fresh non-biodegraded or negligible biodegradation levels. Thus, the oils that are present with hydrocarbons expected to be predominantly gas reservoirs that might be discovered in the region should be expected to have API gravity > 35 (light oil), SG < 0.80 gr/cm^3 and very low S will be < 1%.

4.4.2.2. Niğde Massif (Fig. 38, Area 4)

According to the positions of the Niğde Massif water samples in the revised Pr/n-C17 vs. Ph/n-C18 plot (Fig. 41), the source rocks that derived the hydrocarbons in the samples have been deposited in an oxic terrestrial (Type-III kerogen) environment. The hydrocarbons have predominantly derived from humic coals, and some of them have been originated from shale-type source rocks. The n-alkane hydrocarbons in the samples have different maturity levels: mature (Rock-Eval Pyrolysis T_{max} = 450-460 °C, $[R_o\%]$ = 1.1-1.3, Oil/Gas Zone) and overmature (Rock-Eval Pyrolysis T_{max} > 490 °C, $[R_o\%]$ > 2, Dry Gas Zone). The BP values are < 0.30. According to these values, the hydrocarbons in the samples have unaltered/fresh non-biodegraded or negligible biodegradation levels.

Consequently, the oils that are present with hydrocarbons expected to be predominantly gas reservoirs that might be discovered in the region should be expected to have API gravity > 40 (light oil), SG < 0.80 gr/cm^3, and very low S (< 1%).

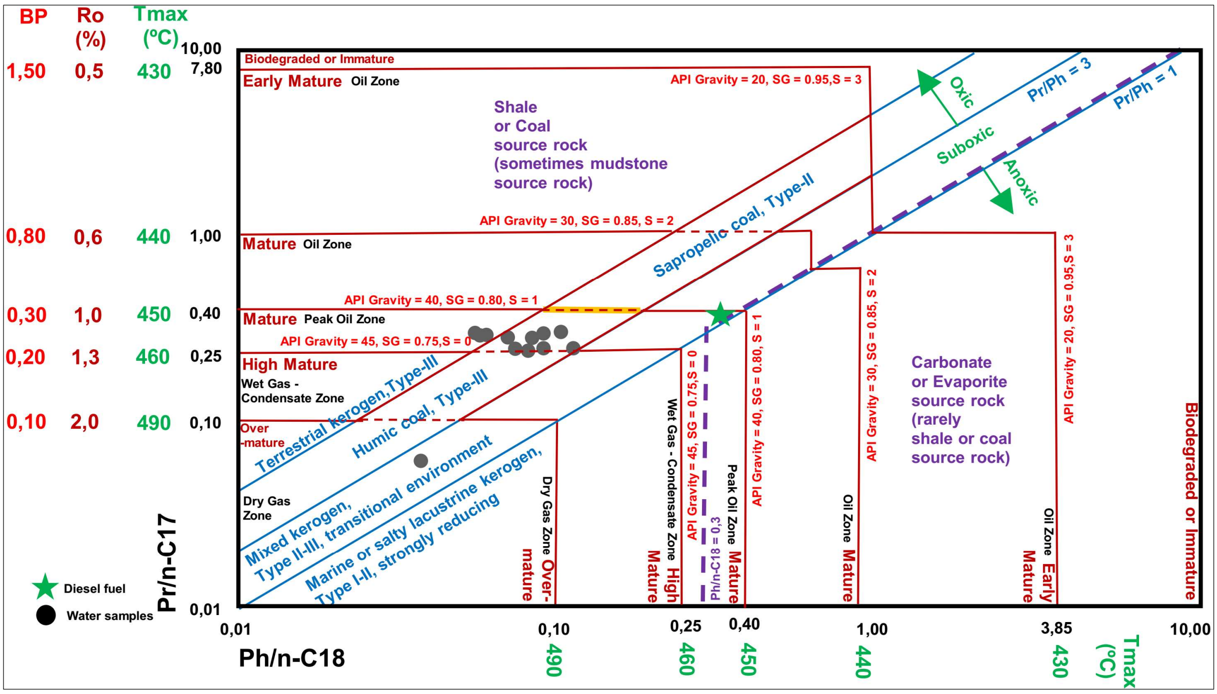


Fig. 41. Revised Pr/n-C17 vs Ph/n-C18 plot of water samples of the Niğde Massif (Fig. 37, Area 4) (data: Ozdemir et al., 2021)

4.4.2.3. Kızılırmak Graben (Fig. 37, Area 6)

Geochemical analyses and assessments of hydrocarbon-rich water and soil samples collected from the same areas are compatible with each other. According to the positions of water samples of the Kızılırmak Graben in the revised Pr/n-C17 vs. Ph/n-C18 plot (Fig. 42), the source rocks that derived the hydrocarbons in the samples have been predominantly deposited in an oxic terrestrial (Type-III kerogen) environment. Some of them have been deposited in suboxic transitional (Type II-III kerogen) environment. The hydrocarbons have been predominantly derived from humic coals, while some of them have been derived from shale-type source rocks. The n-alkane hydrocarbons in the samples have different maturity levels: mature (Rock-Eval Pyrolysis T_{max} = 450-460 °C, $[R_o\%]$ = 1.0-1.3, Oil/Gas Zone) and high mature (Rock-Eval Pyrolysis T_{max} = 460-470 °C, $[R_o\%]$ = 1.3-1.5, Wet/Dry Gas Zone). The BP values are ≤ 0.30. According to these values, the hydrocarbons in the samples have unaltered/fresh non-biodegraded or negligible bio-degradation levels. Ultimately, the oils that are present with hydrocarbons expected to be predominantly gas reservoirs that might be discovered in the region should be expected to have API gravity > 35 (light oil), SG ≤ 0.80 gr/cm^3, and very low S (<1%).

4.4.2.4. Beypazarı Neogene Basin (Fig. 37, Area 9)

According to the positions of water samples from the Beypazarı Neogen Basin in the revised Pr/n-C17 vs. Ph/n-C18 plot (Fig. 43), the source rocks that derived the hydrocarbons in the samples have predominantly been deposited in an oxic terrestrial (Type-III kerogen) environment. The hydrocarbons have predominantly been derived from humic coals, while some of them are originated from shale-type source rocks. The n-alkane hydrocarbons in the samples have different maturity levels: mature (Rock-Eval Pyrolysis T_{max} = 450-460 °C, $[R_o\%]$ = 1.0-1.3, Oil/Gas Zone), high mature (Rock-Eval Pyrolysis T_{max} = 460-470 °C, $[R_o\%]$ = 1.3-1.4, Wet/Dry Gas Zone) and overmature (Rock-Eval Pyrolysis T_{max} > 490 °C, $[R_o\%]$ > 2, Dry Gas Zone). The BP values are ≤ 0.30. According to these values, the hydrocarbons in the samples have unaltered/fresh non-biodegraded or negligible biodeg-radation levels. Finally, the oils that are present with hydrocarbons expected to be predominantly gas reservoirs that might be discovered in the region should be expected to have API gravity > 40 (light oil), SG ≤ 0.80 gr/cm^3, and very low S (<1%). No effective sedimentary petroleum source rocks outcropped exist in all 13 regions studied.

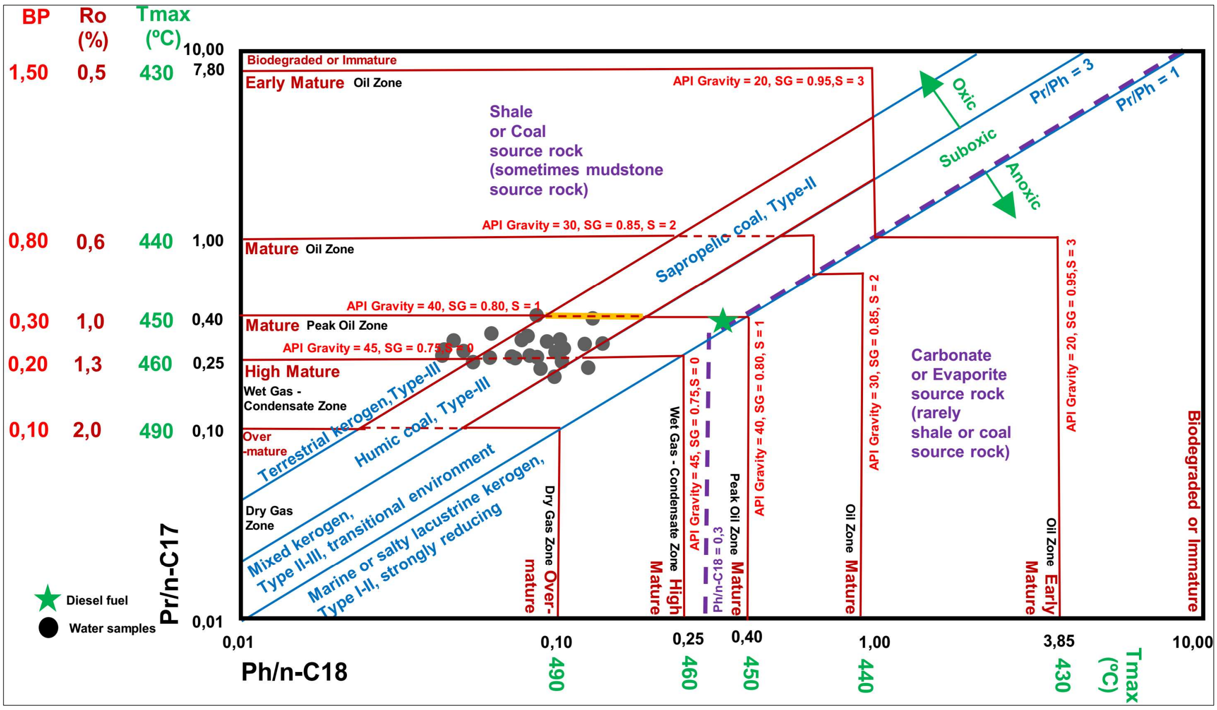


Fig. 42. Revised Pr/n-C17 vs Ph/n-C18 plot of water samples of the Kızılırmak Graben (Fig. 31, Area 6) (data: Ozdemir et al., 2022)

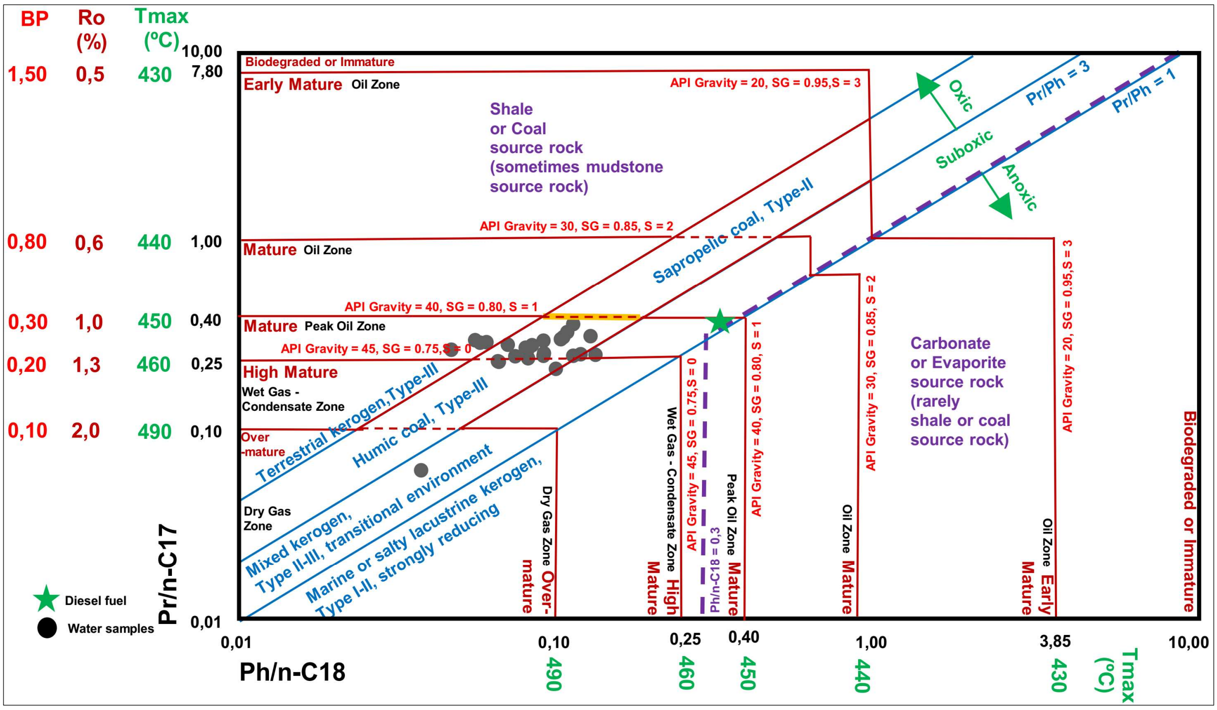


Fig. 43. Revised Pr/n-C17 vs Ph/n-C18 plot of water samples of the Beypazarı Neogene Basin (Fig. 31, Area 9) (data: Ozdemir et al., 2020b)

There are metasedimentary/meta-morphic rocks (meta-shale, phyllite, slate, etc.) in and around the investigated areas. The first possibility for this situation is that source rocks, which were sedimentary (shale, mudstone etc.) in the past, underwent metamorphism under the effect of Alpine Orogeny and are observed as metasedimentary/metamorphic rocks today (Figs. 3-5). The second possibility is the presence of deeply buried effective sedimentary source rocks in the explored areas. Ultimately, high amounts of erosion (tectonothermal event/high heat flow), which probably occurred during the Alpine Orogeny, or intensive magmatic intrusions should have caused thermal maturation and hydrocarbon generation of the source rocks deriving the hydrocarbons in the water and soil samples.

In the light of the results of the studies performed in 13 different basins/regions of Turkey where the effective source rocks do not outcrop, it is understood that the hydrocarbon potential of a basin can be evaluated with geochemical studies based on GC analysis conducted on water and soil samples after palaeogeographic and paleotectonic data of the basin are inspected if the hydrocarbon seeps and/or operable-size metallic ore deposits come into existence in the basin.

4. Conclusions and Recommendations

The following conclusions have been drawn as a consequence of these detailed investigations. Within the scope of the research, the Pr/n-C17 vs. Ph/n-C18 plot, which is used to evaluate the source, depositional environment, redox conditions of the depositional environment, and maturity of hydrocarbons, has been revised. In the revised plot, the ranges of API gravity, specific gravity, S, BP, Ro% and T_{max} parameters have been defined. Thus, a new approach is presented for the estimation of API gravities and S of oils that may be discovered in reservoirs in exploration areas from surface geochemical surveys. Moreover, humic and sapropelic coal ranges have been separated. In this way, the plots' functionality and efficiency are developed, making petroleum geochemical assessments possible in only one diagram instead of using several graphs or charts.

Geochemical analyses and assessments of hydrocarbon-rich water and soil samples collected from the same areas are compatible with each other.

As a result of the geochemical interpretation based on the TPH analyses performed on various hydrocarbon-rich water and soil samples in the area in which macro and micro-scale hydrocarbon shows exist, the presence of a working petroleum system in the related area can be reliably proven.

It is possible to geochemically evaluate the hydrocarbon potential of outcropped metasedimentary/metamorphic rocks by conducting TPH analysis in soil samples alone.

Deeply buried source rocks in the basins/regions covered by alluviums, volcanic rocks, ophiolites, ophiolitic melanges (such as Turkey), desert dunes and evaporites (such as the Arabian Peninsula), etc., the hydrocarbon potential of a basin/region can be geochemically inspected by jointly applying TPH in water and soil analyses.

Outcropping metasedimentary/metamorphic or deeply buried sedimentary source rocks in areas containing operable-size metallic ore deposits can be geochemically evaluated with TPH in water and soil analyses, and the hydrocarbon potential of the basin/region can be investigated.

In many studies, hydrocarbons/organic matter/carbonaceous material have been determined in metamorphic rocks with different degrees of metamorphism. Therefore, metasedimentary/metamorphic rocks containing organic matter/hydrocarbon/carbonaceous material can be used to evaluate the hydrocarbon potential of the region by organic geochemical methods, just like sedimentary rocks containing organic matter/hydrocarbon/carbonaceous material. In other words, all classic organic geochemistry/petroleum geochemistry analyses applied in sedimentary rocks as the first stage of hydrocarbon exploration can also be applied on metasedimentary/metamorphic rocks containing hydrocarbon/organic matter. Therefore, it is possible to evaluate the hydrocarbon potential of the basin/region according to the results of this geochemical analysis. TPH in water and soil analyses enable geochemical assessment and interpretation of petroleum systems in wildcat basins with complex geological structures (destroyed by metamorphism and tectonism) (such as the Alpine mobile belt).

Since groundwaters interact with all shallow and deep source rocks of the basin through faults and fractures, incorrect basin hydrocarbon potential assessment studies performed by taking surficial samples from potential source rocks that do not represent the real source rock facies in the basin can be prevented by TPH in water analyses.

According to this study's results, it can be deduced that geochemical exploration/source rock evaluation processes will be fast, cost-effective, and low-risk with TPH in water and soil analyses. It can also be regarded as a reliable geochemical survey method since both water and soil samples are jointly used.

The geological age of hydrocarbons can be directly determined by Re-Os isotope studies to be carried out, especially on hydrocarbon-rich soil samples. Although amounts of Re and Os in water samples are low, it is considered that Re-Os isotope analysis can also be performed in the water samples with future developments.

Petroleum geochemistry interpretations have been recently carried out on water and soil samples based on GC analyses and their results up to now. In the future, it is envisioned that organic geochemical studies and interpretations can be conducted and supported with other methods such as GC-mass spectrometry (GC-MS) and Rock-Eval Pyrolysis.

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