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Characterising the source rocks in petroleum systems using organic and stable isotope geochemistry: An overview^{+}

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ABSTRACT

Geochemical investigations for correlating the petroleum (oil and gas) with source rocks and that with petroleum itself, which can be produced from a similar or dissimilar source rock, is important for the assessment of generation potential of a prolific or potential petroleum system. Analytical advancements have synergized the hydrocarbon exploration methods, with exploration geochemistry becoming increasingly an integral part of source rock characterization. Geochemical studies investigate the presence and properties of hydrocarbons trapped in geological formations, or the potential to generate such hydrocarbons and provide source rocks properties, by measuring the compositional changes associated with hydrocarbon generation, migration, accumulation and production. These are critical for proper and efficient management of the hydrocarbon assets at all stages. The source rocks and the petroleum are primarily characterized utilizing the organic geochemical and stable isotope techniques. Organic geochemistry deciphers the source, depositional environment and thermal maturity of sedimentary organic matter from which the hydrocarbons are generated and the stable isotopes of carbon, nitrogen and hydrogen describe the paleo productivity, origin, evolution and correlation of organic matter with generated or in situ hydrocarbon components. The paper presents an overview of the stable isotopic and organic geochemical properties of shales from Damodar Valley basin of India in the light of its gas generation potential.

Key words: Source rocks; organic matter; kerogen; isotopes; biomarkers; thermal maturity; Damodar Valley; Permian; Shale Gas

INTRODUCTION

The unifying concept of petroleum system encompasses a combination of essential elements (source, reservoir, seal, and overburden rocks) and essential processes (basin and trap formation, deposition of source and reservoir rocks and generation-migration-accumulation of hydrocarbons) (Magoon and Dow, 1994). The geologic time when essential elements and processes are correctly placed is critical. Formation of an effective petroleum system is realized only when the organic matter preserved in a source rock, is converted into petroleum (oil and natural gas) and accumulated in a trap, following which there are reasonable chances of its exploitation. A petroleum system investigation includes the identification, naming, determining the level of certainty, and mapping the geographic, stratigraphic, and temporal extent of a petroleum system (Magoon and Dow, 1994; Kenneth et al., 2012).

Geochemical investigations for correlating the petroleum with source rocks and that with petroleum itself is important for the evaluating the generation potential of a prolific or potential play. Advancement in high resolution mass spectrometers for the determination of trace levels of compound specific organic components and their isotope ratios have synergized the hydrocarbon exploration methods, with exploration geochemistry becoming an increasingly integral part of it. Geochemical studies investigate the presence and properties of hydrocarbons trapped in geological formations or the potential to generate such hydrocarbons by providing highly specific information about the characteristics of a petroleum system from just a few rock, oil or gas samples (Eden and Mungo, 2013). It involves the chemical analysis of source rocks and measures the compositional changes associated with hydrocarbon generation, migration, accumulation and production, which are critical to proper and efficient management of the hydrocarbon assets at all stages (Eden and Mungo, 2013). The source rocks and the petroleum are primarily characterized using the organic geochemical and stable isotope techniques. Organic geochemistry deciphers the source, depositional environment and thermal maturity of sedimentary organic matter from which the hydrocarbons are generated and the stable isotopes of carbon, nitrogen and hydrogen describe the paleo productivity, origin, evolution and correlation of organic matter with generated hydrocarbon components (Mani et al., 2011).

This paper presents an overview on characterising the source rocks in petroleum and shale gas/oil systems, using organic and stable isotope geochemistry, with a case study describing the potential of gas generation from Permian shales of the Damodar Valley basin. The origin, evolution, qualitative and quantitative properties of sedimentary organic matter and its thermal decomposition kinetics, all of which are critical for resource assessment, are discussed in light of the Permian shales from Jharia sub-basin, which might be potential source rock for natural gas generation.

$^{+}$ Invited paper

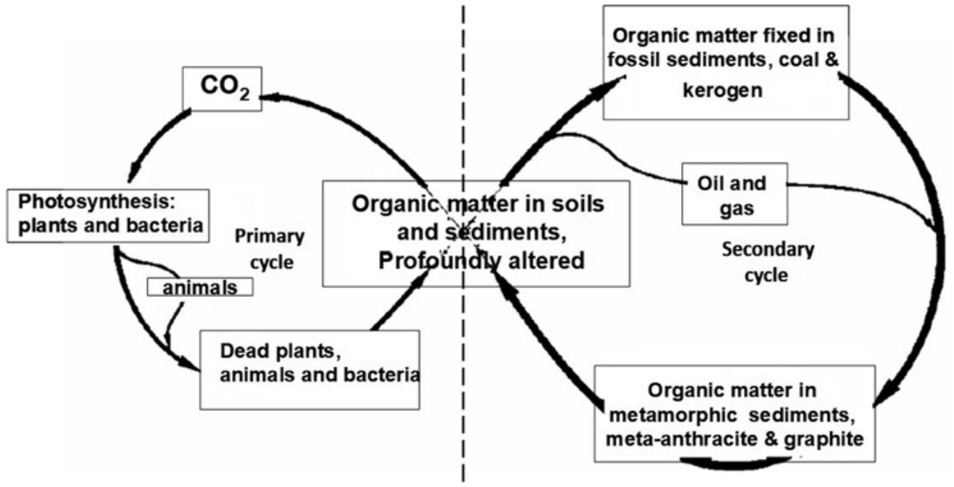


Figure 1. The organic carbon cycle (modified after Tissot and Welte, 1984).

ORGANIC MATTER – FROM SOURCE ROCKS TO TRAPS

Synthesis of organic matter

It is evident that organic matter in sediments upon exposure to subsurface temperature and pressure, transforms into hydrocarbons. The mass production of organic matter is achieved by universal process of photosynthesis, wherein autotrophic green plants, blue green algae and photosynthetic bacteria convert solar energy into chemical energy, utilizing the CO_2 and H_2O from the ambient environment to fix the carbon in the form of polysaccharide - glucose ($C_6H_{12}O_6$) with the release of free oxygen and water.

$$6CO_2 + 12\ H_2O \overset{h\nu}{\rightleftharpoons} C_6H_{12}O_6 + 6O_2 + 6H_2O$$

Oxygenation of primitive reducing atmosphere of early Earth supported the evolution of diverse lifeforms and is considered an important event in timeline of photosynthesis. Though the exact timing of the 'great oxidation event' is being constrained narrowly by present day research, the earliest evolution of free oxygen and production of organic matter has been reported to be much older than 2.5 - 3 billion years. Nearly 75 million petagrams (Pg) of carbon are distributed within various reservoirs of the Earth's crust, biosphere, and ocean (Petsch, 2014). Most of the carbon on Earth is concentrated in sedimentary rocks, a large part (~ 82%) of it in the form of inorganic carbonates and remaining (~18%) as organic carbon. A dynamic equilibrium between the oxidised (e.g. CO_2; HCO_3^-) and reduced ($C_6H_{12}O_6$; CH_4) forms of carbon is manifested in the global carbon cycling, which involves sequence of processes through which carbon compounds move from one carbon reservoir or sink to another.

Organic Carbon cycle

The atmospheric, hydrospheric and terrestrial reservoirs of carbon are in constant exchange with each other. Carbonates get precipitated in the aquatic reservoirs in the form carbonate sediments such as calcites. Dissolution of sedimentary carbonates produces carbonate and bicarbonate ions and carbon dioxide, which are in equilibrium in the surrounding waters.

$$\begin{gathered} CO_2(aq) + H_2O \rightleftharpoons H_2CO_3 \\ H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \\ HCO_3^- \rightleftharpoons H^+ + CO_3^{2-} \\ Ca^{2+} + CO_3^{2-} \rightleftharpoons CaCO_3 \end{gathered}$$

The terrestrial plants form the organic matter directly from the atmospheric reservoir by photosynthesis, while marine plants synthesize it from the dissolved CO_2 in the hydrosphere. Terrestrial and marine organic matter is largely destroyed by oxidation, and CO_2 is returned for recirculation in the system. The cycling of organic carbon is illustrated in the organic carbon cycle (Figure 1), which consists two sub-cycles, a primary and a secondary one.

The primary cycle is smaller with a lower turnover and shorter half-life of days to couple of years, whereas the secondary cycle has a larger turnover and half-life of millions of years. The two cycles are interconnected by a tiny leak of 0.01-0.1% of total organic carbon, which represents the oxidation of sedimentary organic matter to carbon dioxide (Tissot and Welte, 1984). For petroleum formation, the secondary cycle is significant. Once the organic matter completes the second cycle during formation of a sedimentary basin, upon increasing burial it is subjected to diagenetic and catagenetic reactions, which lead to formation of petroleum.

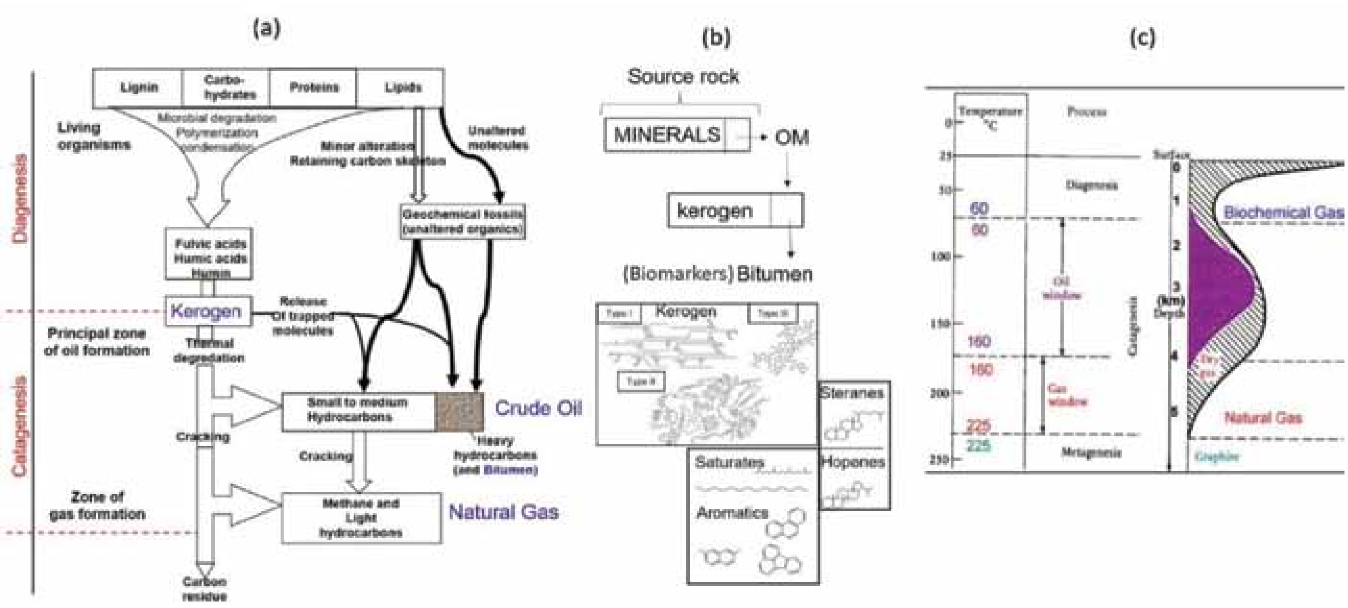


Figure 2. Thermal transformation of organic matter in source rock to petroleum and natural gas (modified after Hunt, 1996; Tissot and Welte, 1984).

Preservation of organic carbon in sediments

The long-term fate of organic matter in sediments is mainly governed by tectonic activities. Phases of subsidence and increasing burial, or uplift and erosion define whether the organic content is preserved and thermally evolved into petroleum, or is eroded and oxidized back to carbon dioxide (Tissot and Welte, 1984). The average preservation rate of organic carbon is estimated to be less than 0.1%, and is controlled by the geological and geochemical conditions of sedimentation. Higher organic productivity, nutrient supply (brought by rivers, upwelling currents, and water mixing), low oxygen content of associated water column and sediments (less than 0.2 mL/L water), restricted water circulation, lack of bioturbation, very fine-grained sediment particles ($<2\ \mu$m), and an optimum sedimentation rate favour the preservation of organic matter in the sediments. The upper limit of the preservation rate of organic carbon, to be found in certain oxygen-deficient environments such as Black Sea, favourable for deposition of source rock-type sediments, is about 4% (Peters et al., 2005).

Thermal transformation of organic carbon

About 10 - 20% of petroleum is formed from the hydrocarbons, mainly lipids which has been synthesized naturally by the earlier living organisms. It constitutes carbon homologs, (≥ C15+ compounds) that have identifiable biological and chemical structure or 'biomarkers' (Hunt, 1996). These are soluble in organic solvents and constitute the bitumen part of organic matter. The carbon skeleton in biomarker compounds gets only minimal or slightly altered during the digenetic processes, thus providing useful information on paleo-events of its deposition and preservation. The second major source of petroleum is kerogen, which constitutes about 80–90% of hydrocarbons, and involves the conversion of the proteins, lipids, and carbohydrates of living organisms into organic matter of sedimentary rocks. Consecutive burial of organic matter at different depths in the subsurface causes various chemical and physical transformations in it, ultimately leading to the formation of liquid and gaseous hydrocarbons, through the stages of diagenesis, catagenesis, and metagenesis (Figure 2) (Hunt, 1996). Diagenesis occurs in recent sediments at shallow depths, where the temperatures are less than 60°C. The bio-polymers like carbohydrates and proteins transform into geo-polymers, or kerogen. Increased sedimentation leads to burial of previously deposited beds and exposure of sediments to subsurface conditions of increasing temperature (T~50 –150°C) and pressure (P~300 –1000 bars). Overburdened sedimentary column and tectonic activities govern the subsurface P–T conditions. Thermal degradation of kerogen results in the formation of petroleum, condensates, and wet gases. At still higher temperature (150°–200°C), organic matter is cracked to dry gas. Metamorphism is the last stage of evolution of sediments in the subsurface (Hunt, 1996).

Besides the prevailing depositional conditions and environment, the accumulation and preservation of organic matter also depends upon the sediment grain size. Clay type sediments adhere maximum organic material, followed by the carbonate matrices. As a result, amongst the sedimentary rocks, fine grained shales have the highest percentage of organic carbon, only seconded by

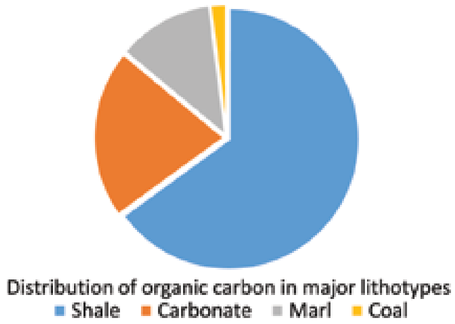


Figure 3. Distribution of organic carbon in different sedimentary rocks.

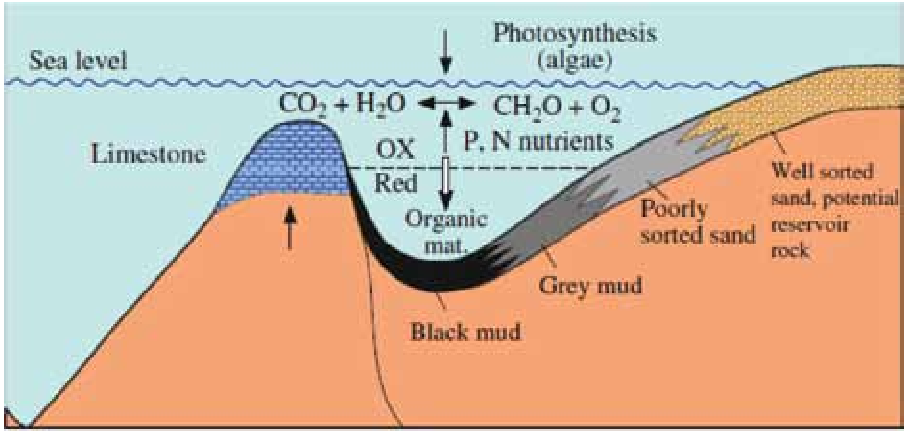


Figure 4. Depositional environment for potential source rock (after Bjørlykke, 2015).

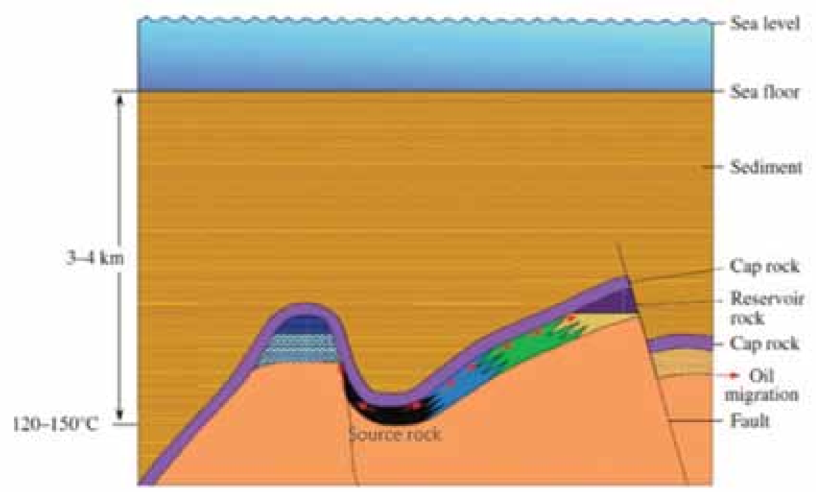


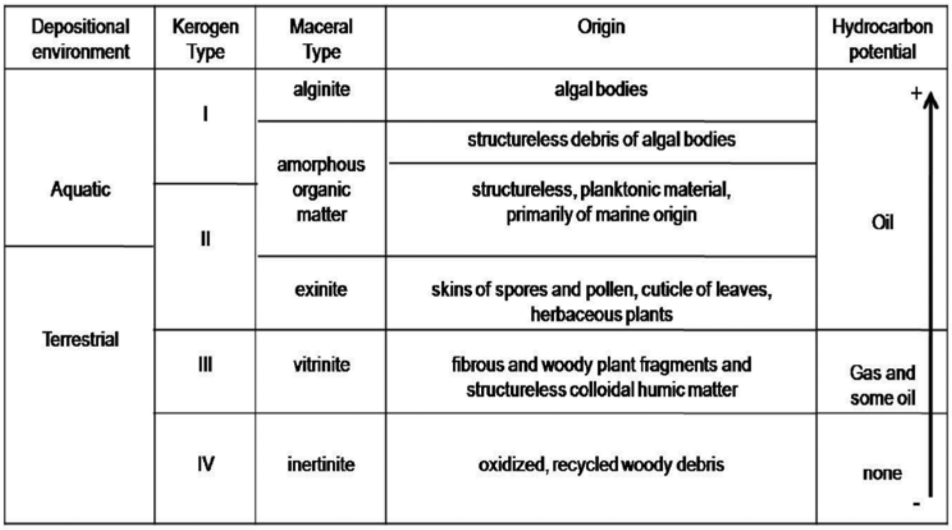
Figure 5. Schematic of essential elements of petroleum system (after Bjørlykke, 2015).

the carbonate rocks (Figure 3). The similar hydrodynamic behaviour of the organic matter tends to get deposited preferentially with fine-grained mud. Unlike sand, fine grained mud more readily excludes oxygen-rich water below the sediment-water interface, thereby enhancing anoxia when it develops. Oxygen deficit environment is essentially important for the preservation of organic matter.

Source, reservoir and trap rocks

The organic matter in sedimentary rocks, with increasing temperature and time, transforms into petroleum and natural gas. The black-grey colour of sedimentary rocks is primarily due to the presence of organic matter in it. It is well known that shale is the most abundant sedimentary

Table 1. Sources and types of kerogen with variable oil and gas generation potential



Depositional environment	Kerogen Type	Maceral Type	Origin	Hydrocarbon potential
Aquatic	I	alginite	algal bodies	+ Oil
		amorphous organic matter	structureless debris of algal bodies	
	II		structureless, planktonic material, primarily of marine origin	
Terrestrial		exinite	skins of spores and pollen, cuticle of leaves, herbaceous plants	
	III	vitrinite	fibrous and woody plant fragments and structureless colloidal humic matter	Gas and some oil
	IV	inertinite	oxidized, recycled woody debris	none -

rock, and black shales containing 1-3% of total organic carbon (TOC) and as high as 20% form important petroleum source rocks in the world. Some depositional controls favourable for good source rocks include major marine transgressions, warm equable climate, and anoxia (Figure 4).

The generated hydrocarbons, after being expelled from source rocks migrate upward and laterally along faults and fractures until a trap is encountered. The density variations in natural gas and petroleum leads to formation of free gas cap on the top of the trap, oil reservoir in the middle and salt water at the bottom. In the trap, the reservoir rock is overlain by an impermeable caprock or seal (Figure 5).

Because of migration, the physical and chemical properties of petroleum formed deep in the basin and where it ends in the trap are different both vertically and horizontally.

SOURCE ROCK CHARACTERIZATION

Organic Geochemistry

Organic geochemistry provides analytical data for identification and mapping of petroleum source rocks. The maps generated from the organic geochemical data indicates the quantity, quality and thermal maturity of organic matter in a source rock and is important in determining the stratigraphic and geographic extent of a pod of active source rock in a petroleum system (Peter and Cassa, 1994). These characteristics of active source rocks lead to the determination of the amount of oil and gas available for traps and significantly assist in reducing the exploration risk. Carbon compounds manifest themselves on Earth in inorganic or oxidised forms, such as carbonates or carbon dioxide etc. and organic or reduced forms such as methane, carbohydrates which are produced by living organisms. Kerogen is the dispersed, amorphous, macromolecular organic matter. It is the precursor geo-polymer from which most of the hydrocarbons are generated in a source rock, with minor contribution from the bitumen, which is derived mainly from the lipid and fat content of once existing organisms. Thus, the source rocks are, in general, characterised by the organic richness, type and thermal maturity of the kerogen and the bituminous biomarkers present in it. Organic richness is characterised by the total organic carbon content, expressed in weight percent (% TOC). Higher the TOC, greater is the hydrocarbon generation potential. A TOC < 0.5% is considered to have poor generation potential, whereas that between 3-4% is considered very good to excellent.

Kerogen

The type or quality of organic matter is dependent upon the source of organic components and its environment of preservation, thus resulting in different kerogen types with varying capacity for oil and gas generation. Kerogen is classified under Type I, II, III and IV based on their Carbon (C), hydrogen (H) and oxygen (O) content (Van Krevelen, 1961). Type I and II have generated most of the world's oil. Type I is generated predominantly in lacustrine/marine depositional setting and is derived mainly from algal lipids (Table I). It contains several long aliphatic chains and the H/C ratio is originally high ($H/C > 1.5$) (Tissot and Welte, 1984; Peters et al., 2005). Type-II kerogen contains aliphatic chains and more number of aromatic and naphthenic rings compared to Type I. The range of hydrocarbon compounds generated and the oil and gas potential of Type-II kerogen are lower ($H/C= 1.2$ to 1.5) than Type I kerogen. Type-III kerogen has low H/C range ($H/C= 0.7$ to 1.0). It generates primarily gas, condensates and some waxes and contains mainly condensed poly-aromatics and oxygenated

Table 2. Thermal maturity and oil and gas generation potential (after Tissot and Welte, 1984)

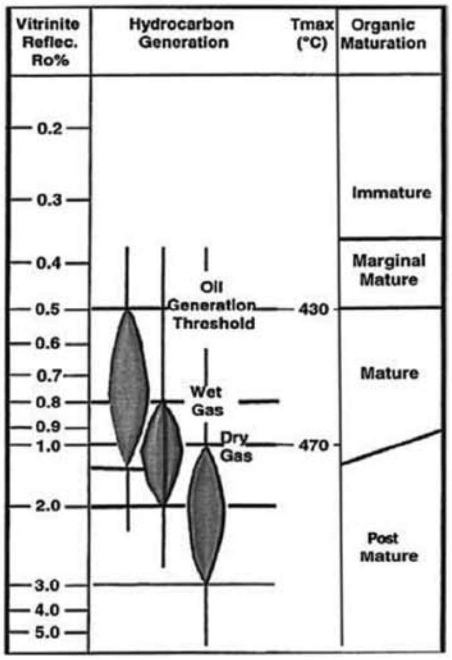


Table 3. Selected biomarkers along with their source and depositional environments

Hydrocarbon Biomarkers	Proxy information
n-Alkanes	
Long chain n-alkanes with predominance maxima at n-C_{27}, n-C_{29} and n-C_{31}	Terrigenous plant source
n-alkanes with n-C_{15}n, n-C_{17} and n-C_{19} predominance	Marine algae/ lacustrine source
Carbon Preference Index (CPI)	Thermal Maturity
Acyclic Isoprenoids	
Pristane (Pr) Phytane(Ph) ratios	
Pr/Ph < 2	Marine, fresh water and brackish water *(Reducing Environ)*
Pr/Ph < 2-4	Fluvio-marine and coastal swamp *(Oxic to suboxic)*
Pr/Ph up to 10	Peat swamp *(Oxic environment)*
Unusual distributions of n-alkanes and cyclohexylalkanes	Characteristic of *Gloeocapsomorpha prisca* found in early Paleozoic samples
Steranes	
C_{27} and C_{28} steranes	Algal source
C_{29} steranes	Higher plants
C_{30} steranes	Marine phytoplankton
Hopanes	
C_{35} homohopanes	Anoxic Depositional Environment
28,30-bisnorhopane	High in certain reducing environments
30-norhopanes	Carbonate Source Rock
Botryococcane	Lacustrine depositional settings
C35 homohopane	Degree of oxicity of marine sediments
Gammacerane	Stratified Column
Oleanane	Characteristic of angiosperms (flowering plants) found only in Tertiary and Upper Cretaceous rocks and oils
Dinosterane	Marine dinoflagellates, possibly distinguishing Mesozoic and Tertiary from Paleozoic source input
24-n-Propylcholestane	Marker for marine algae extending from at least the Devonian to the present.

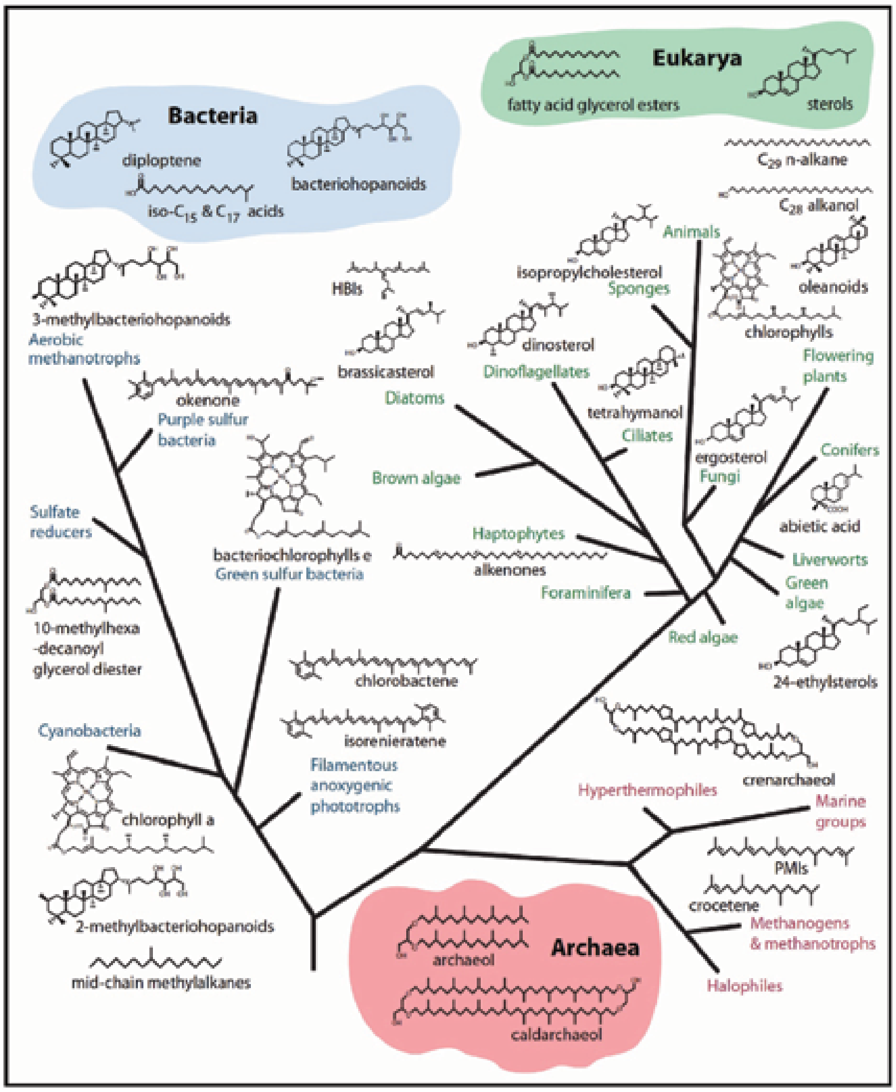


Figure 6. Biomarker tree of life showing the three domains of life (after Briggs and Summons, 2014)

functional groups, with minor aliphatic chains. The organic matter is mostly derived from terrestrial higher plants. Type IV kerogen is inert and generates only small amount of methane and CO_2 (Hunt, 1996).

Various thermal maturity parameters such as vitrinite reflectance, conodont index, Rock Eval Tmax etc. indicate the extent of heat experienced by the source rocks. High subsurface temperatures (60°- 200°C) eventually lead to the cooking and transformation of organic matter into the oil and gas (Table 2). Depending upon the thermal exposure, the rocks are categorised as immature, with no ability to generate petroleum in present condition; mature, in oil or gas condensate zone or post-mature, largely in gas generating window (Peter and Cassa, 1994).

Geochemical logs prepared from organic richness, type and thermal maturity of kerogen, help in identifying a potential, effective, and spent petroleum source rock, the thermal maturation gradient, including immature, mature, and post-mature zones, and in situ and migrated petroleum shows (Peters and Cassa, 1994).

Biomarkers

Biological markers or biomarkers are complex organic compounds composed of carbon, hydrogen, and other elements occurring in sediments, rocks, and crude oils. These compounds originate from formerly living organisms and show little or no change in structure from their parent organic molecules in living organisms. Biomarkers are important because select lipids and their hydrocarbon remnants derived from earlier organisms carry a high degree of taxonomic specificity, which allows the reconstruction of past organismic diversity from the sedimentary inventory of fossil biomarkers (Figure 6, Table 3). Biomarkers help in deciphering the source, depositional environment and thermal maturity of the organic matter and are particularly used in source rock to oil and oil to oil correlation studies.

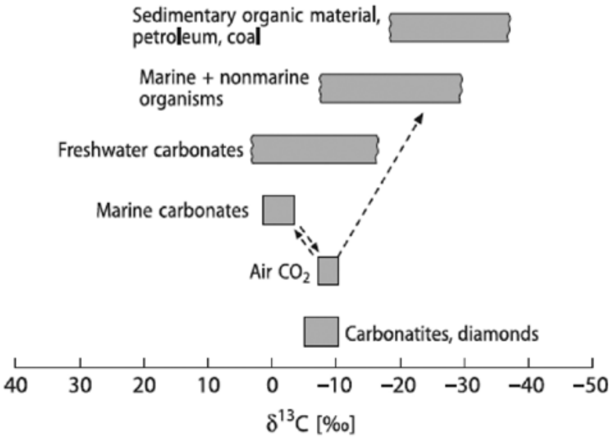


Figure 7. Range of carbon isotope values in different reservoirs (after Schidlowski, 1987)

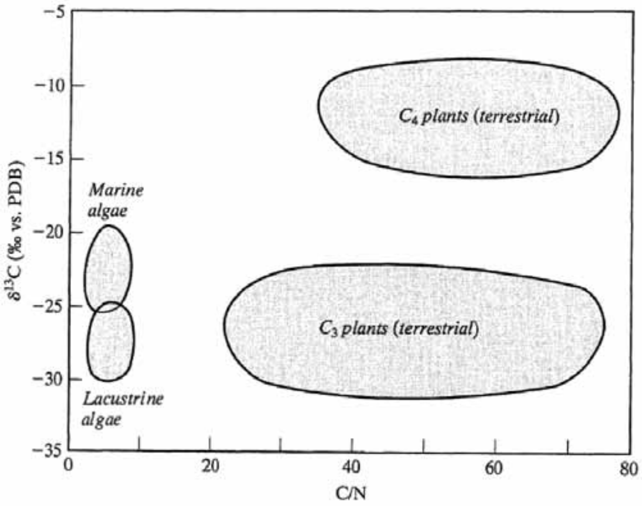


Figure 8. Carbon and nitrogen isotope ranges for organic matter sourced from different biological mass (after Sharp, 2007)

Stable isotope geochemistry

Isotopes of carbon, hydrogen, nitrogen and oxygen have been used to study diverse aspects of organic matter burial, productivity, storage and cycling on the Earth. The isotopic variations documented in the sedimentary shales and carbonates, provide information on the productivity, gross carbon storage and development of prolific source rocks in sedimentary basins. As a result of kinetic isotope effects, the transformation of inorganic carbon into living matter entails a marked bias in favour of light isotopes (^{12}C), with heavy species (^{13}C) retained in the inorganic reservoir (Schidlowski, 1987). This isotopic discrimination leads to the preferential accumulation of ^{12}C in all forms of biogenic (reduced) carbon as compared with the inorganic (oxidized) carbon pool of surficial environment, mainly in form of the atmospheric carbon dioxide and dissolved marine carbonate (Schidlowski, 1987). When the biogenic materials and carbonates are incorporated in newly formed sediments, the kinetic isotope effect, associated with the autotrophic carbon fixation, is propagated from the surficial exchange reservoir into the rock section of the carbon cycle (Schidlowski, 1987). Over geological time, this effect has ultimately brought about a conspicuous isotope disproportionation of Earth's primordial carbon into a light and heavy crustal carbon reservoir (Figure 7).

The hydrocarbon components generated from different organic matter types differ in isotopic compositions due to the characteristic parent source material (Figure 8). Depending upon the different enzymatic process used for carbon fixation in photosynthesis, there may even be different isotopic values for terrestrially derived organic matter, in addition to the variability of marine and lacustrine organic signatures. Plants using C3 Calvin cycle show less efficient carbon fixation and observe large ^{13}C depletions compared to plants adopting C4 cycle (Figure 9).

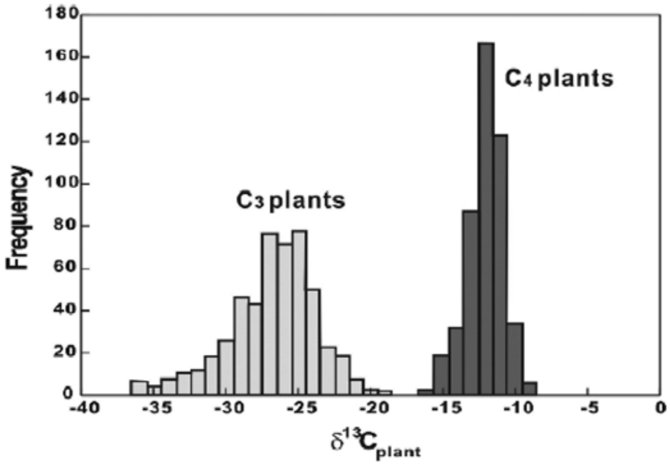


Figure 9. Carbon isotope values of C_3 and C_4 plants (after Sharp, 2007)

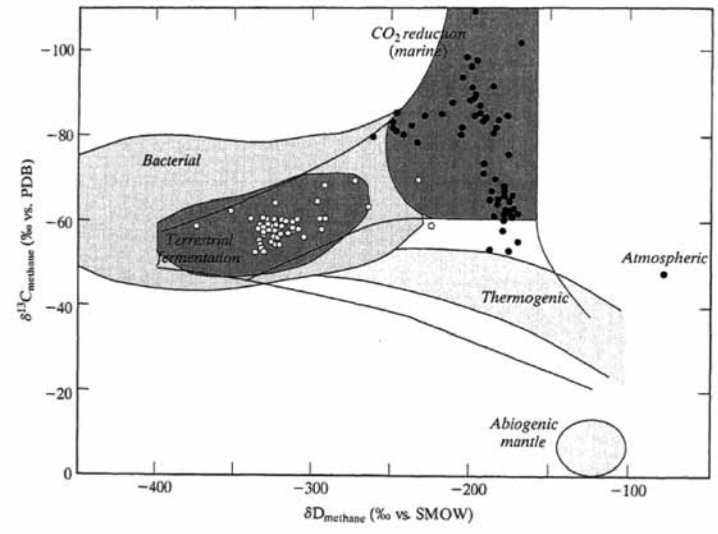


Figure 10. Schematic showing varying sources of methane (After Hoefs, 1996)

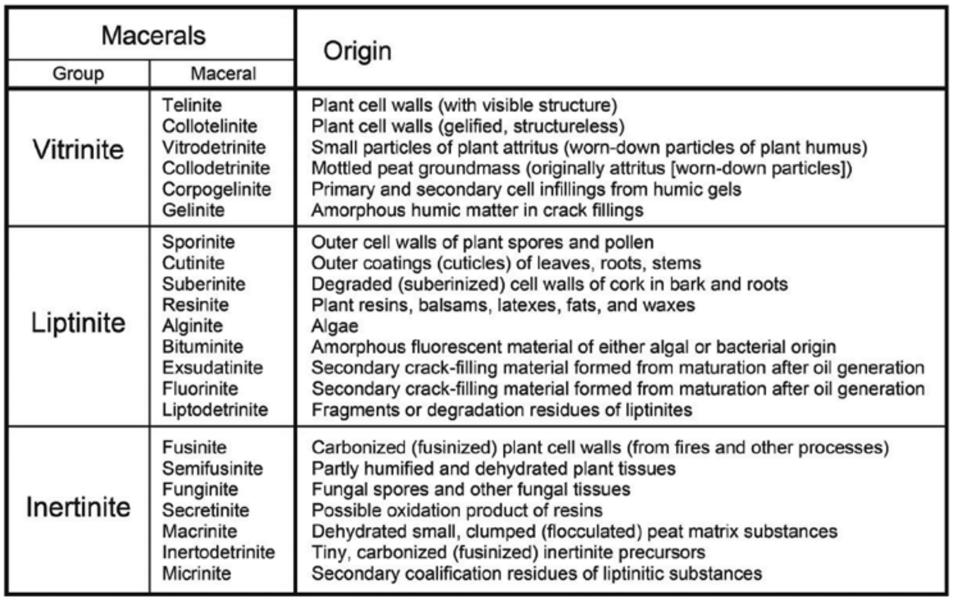
The isotopic variations provide significant information on the origin and correlation of petroleum and natural gas. The gas systems originating from a respective source of organic matter have been classified into two distinct types, namely biogenic (or microbial) and thermogenic (Figure 10). There can also be mixtures of the two gas types. Occurrence of thermogenic gas in the subsurface establishes the possibility or presence of a source rock and provides information on the elements of the petroleum or gas system, which otherwise lacks in biogenically produced gases.

Organic Petrology

Organic petrology comprises of the visual examination of organic matter under microscope and is useful for the characterization of the source rocks. The study of macerals or organic constituents in sedimentary rocks, such as coal, petroleum source-rocks and oil shales (with abundant organic matter) and limestone, sandstone and shale (with minor dispersed organic matter), provide important information about kerogen type, its thermal maturity level, and the hydrocarbon generation potential. Reflectance measurements and overall observations of organic matter (OM) under the microscope with white and UV light in oil immersion or dry environment, allow identification of maceral composition of source rocks and understanding of interplay between OM and minerals for in-depth evaluation of source rock potential in conventional and unconventional exploration and production.

There are three major maceral groups, liptinite, vitrinite and inertinite (Table 4). The liptinite group is derived from the resinous and waxy parts of plants, the vitrinite group from coalified woody tissue, and the inertinite group is derived from charred and biochemically altered plant cell wall material.

Table 4. Macerals classification and sources (after Kentuky.edu, 2018)



Macerals		Origin
Group	Maceral	
Vitrinite	Telinite	Plant cell walls (with visible structure)
	Collotelinite	Plant cell walls (gelified, structureless)
	Vitrodetrinite	Small particles of plant attritus (worn-down particles of plant humus)
	Collodetrinite	Mottled peat groundmass (originally attritus [worn-down particles])
	Corpogelinite	Primary and secondary cell infillings from humic gels
	Gelinite	Amorphous humic matter in crack fillings
Liptinite	Sporinite	Outer cell walls of plant spores and pollen
	Cutinite	Outer coatings (cuticles) of leaves, roots, stems
	Suberinite	Degraded (suberinized) cell walls of cork in bark and roots
	Resinite	Plant resins, balsams, latexes, fats, and waxes
	Alginite	Algae
	Bituminite	Amorphous fluorescent material of either algal or bacterial origin
	Exsudatinite	Secondary crack-filling material formed from maturation after oil generation
	Fluorinite	Secondary crack-filling material formed from maturation after oil generation
	Liptodetrinite	Fragments or degradation residues of liptinites
Inertinite	Fusinite	Carbonized (fusinized) plant cell walls (from fires and other processes)
	Semifusinite	Partly humified and dehydrated plant tissues
	Funginite	Fungal spores and other fungal tissues
	Secretinite	Possible oxidation product of resins
	Macrinite	Dehydrated small, clumped (flocculated) peat matrix substances
	Inertodetrinite	Tiny, carbonized (fusinized) inertinite precursors
	Micrinite	Secondary coalification residues of liptinitic substances

Liptinitic organic matter generates more of the oil compared to the vitrinite, which is gas prone. The intertinite is generally comprises the recycled organic matter with no oil or gas generative property (Table 1).

Kerogen Kinetics

The petroleum evaluation in a sedimentary basin involves a quantitative approach, taking into account the amount of oil and gas generated by primary cracking of kerogen when temperature increases through time (Tissot and Espitalie 1984). The degradation of kerogen into hydrocarbons is described by a series of n parallel chemical reactions, each of which obey a first order kinetics, characterized by Arrhenius Law.

$$\frac{dXi}{dt} = -ki.Xi \qquad \text{......................1}$$

1. $\frac{dXi}{dt}$ = hydrocarbon generation rate
   Xi= residual petroleum potential
   t=time (sec)

where ki is

$$ki = A\exp(-\frac{Ei}{RT}) \qquad \text{................ 2}$$

2. A= Arrhenius constant; s^{-1}
   Ei =activation energy; kcal/mole
   R = molar gas constant; 0.00199 kcal/mole
   T = absolute temperature in degree Kelvin
   ki =rate constant for a reaction i

Combining Eq. 1 and 2,

$$\frac{dXi}{dt} = A\exp(-Ei/RT).Xi$$

Xi = The residual petroleum potential

$$Q = \sum_{i=1}^{n}(Xio - Xi)$$

where, Xio is the value of Xi at t=0

The activation energy and associated kinetic parameters are integrated with the burial and thermal history of the basin which are used in basin modelling studies to predict the amount and timing of generated hydrocarbons as function of time and temperature (Tissot and Espitalie, 1984).

ANALYTICAL METHODOLOGY

A range of geochemical analyses, comprising of organic and isotopic composition determination, are performed to determine the properties of source rocks. Kerogen, being insoluble in organic solvents is generally studied using petrological and pyrolysis methods. The biomarkers are studied using solvent extraction and chromatographic techniques. The kinetic parameters of thermal decomposition of kerogen are then combined with geological data for deciphering comprehensive maturity models for hydrocarbon generation and expulsion in sedimentary basins.

Rock Eval Pyrolysis

Rock Eval pyrolysis is a routinely used technique for source rock characterization. It involves thermal cracking of sedimentary organic matter in accordance with a programmed temperature pattern in an open system pyrolyzer to estimate the petroleum generation potential of the source rocks. The process occurs in two ovens, pyrolysis and oxidation (combustion), respectively of the Rock Eval

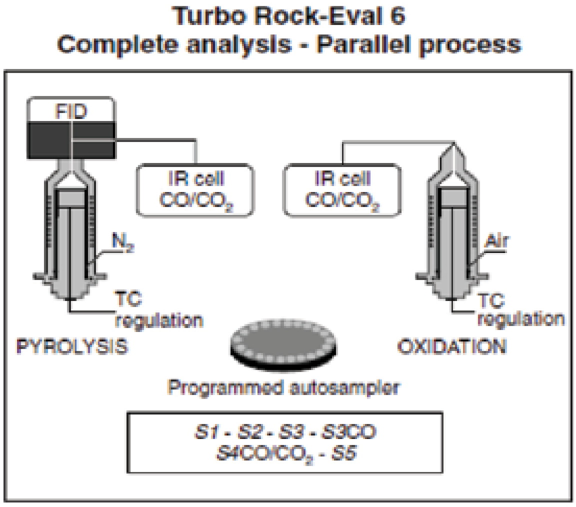


Figure 11. Schematic of Rock Eval 6 Pyrolyzer (after Behar et al., 2001)

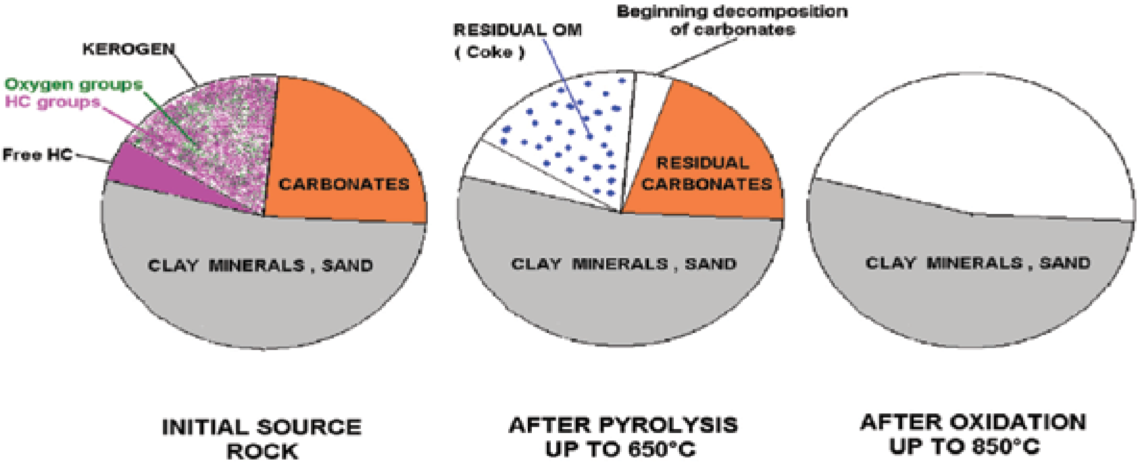


Figure 12. Evolution of a typical source rock during pyrolysis and oxidation in a rock eval pyrolyser (after Tissot and Espitalie, 1984)

pyrolyzer (Figure 11). The pyrolyzed hydrocarbons, both the thermo-labile ones (given by peak S1) and those obtained during the cracking of organic matter (given by peak S2), are detected by a flame ionization detector (FID). The residual rock, recovered after pyrolysis, is combusted in oxidation oven up to 850°C. The CO and CO_2 released during pyrolysis and oxidation processes are monitored online by an infrared cell. This enables the determination of organic and mineral carbon content of samples, defined as the TOC and MinC, respectively. The Tmax value is a thermal maturity parameter. It corresponds to the temperature at which the maximum amounts of hydrocarbons are released from the thermal degradation of kerogen, i.e., the temperature at which S2 peak reaches its maximum.

Among the other calculated parameters of Rock Eval, the hydrocarbon potential or HI is defined by 100 × S2/TOC. The OI is defined as 100 × S3/TOC, where S3 is the CO_2 released during the pyrolysis. These indices help in establishing the kerogen type and its maturity (Behar et al., 2001; Espitalié et al., 1987; Peters and Cassa, 1994; Mani et al, 2014). Figure 12 depicts the evolution of a typical source rock during pyrolysis and oxidation in a rock eval pyrolyser.

Depending upon the type of kerogen, the hydrocarbon generation capacity is different. Higher H/C ratios have greater possibility of generating oil. Thus, Type I kerogen is oil prone and generates significant amount of petroleum. With decrease of hydrogen content, and/or increase of O/C ratios, more and more gas prone behaviour of source rocks is exhibited (Figure 13)

Gas chromatography–mass spectrometry (GC-MS)

The composition and concentration of volatile gases and the biomarkers components in a source rock are determined using Gas chromatography. The gas chromatography–mass spectrometry (GC–MS) is a separation technique (GC),

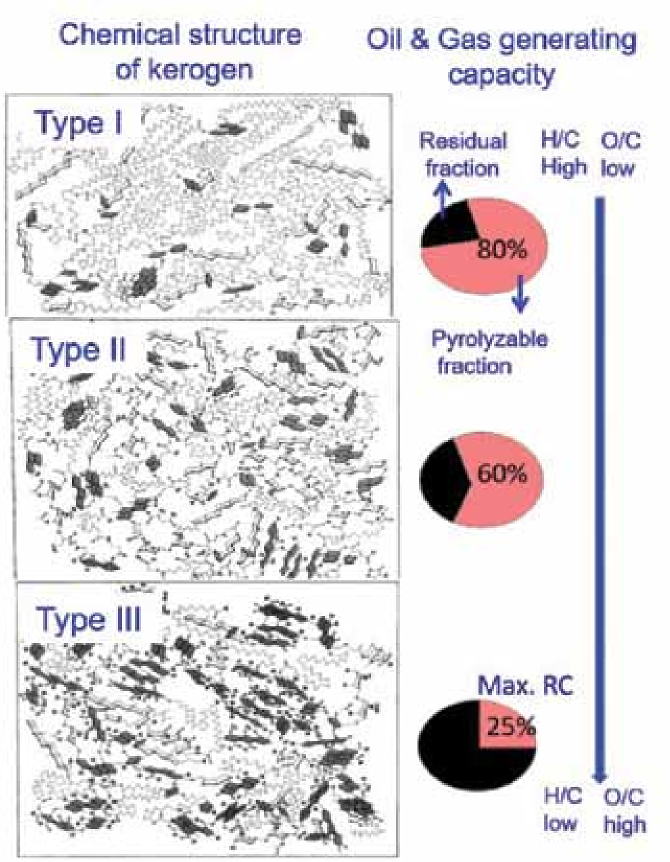


Figure 13. Chemical structure and hydrocarbon generating capacity of kerogen (after Vandenbroucke, 2003)

coupled with analytical power of mass spectrometre (MS). It is used to detect compounds using the relative gas chromatographic retention times and elution patterns of components of a mixture in combination with the mass spectral fragmentation patterns, which is the characteristic of a compound's chemical structures (Sneddon et al., 2007). A typical GC–MS system performs the following functions: (1) separation of individual compounds in a mixture by gas chromatography; (2) transfer of separated components to the ionizing chamber; (3) ionization; (4) mass analysis; (5) detection of the ions by an electron multiplier; and (6) data acquisition, processing, and display by a computer system (Figure 14).

As the individual organic compounds elute from the GC column, they enter the MS. During ionization, they are bombarded by a stream of electrons leading to the fragmentation into ions. The mass of the fragment, divided by its charge is the mass to charge ratio (*m/z*). Almost always, the charge is +1, and *m/z* ratio represents the molecular weight of the fragment. In general, MS are configured with magnetic sector or quadrupole type mass analyzers. A quadrupole GC–MS has a group of four electromagnets that focus each fragment through a slit into the detector. These are programmed to direct only certain fragments, one at a time (scan), until the complete range of *m/z* is recovered. This produces a mass spectrum, which is a graph of the signal intensity (relative abundance) versus the *m/z* ratios (essentially the molecular weight). Each compound has a unique fingerprint, and the software is equipped with a library of spectra for unknown compounds (Sneddon et al., 2007).

The homologous series of saturated and aromatic fractions are identified by characteristic masses of the fragmented ion and their retention times in the chromatographic column e.g. alkanes by *m/z* = 57; steranes by *m/z* = 271; hopanes by *m/z* = 191 etc. The individual compounds or their isomers in a series are identified by the characteristic fragmentation pattern of the molecular ions, its retention time, and use of respective biomarker standards and/or published mass spectra.

Isotope ratio mass spectrometry (IRMS)

Isotope ratio mass spectrometry (IRMS) has been widely used to determine the ratio of stable isotopes of several low molecular weight elements such as carbon ($^{13}C/^{12}C$) and oxygen ($^{18}O/^{16}O$) in geological samples. Stable isotopes provide important information on the origin and source of hydrocarbon gases and in oil to oil and oil to source rock correlation studies. Such studies are performed using

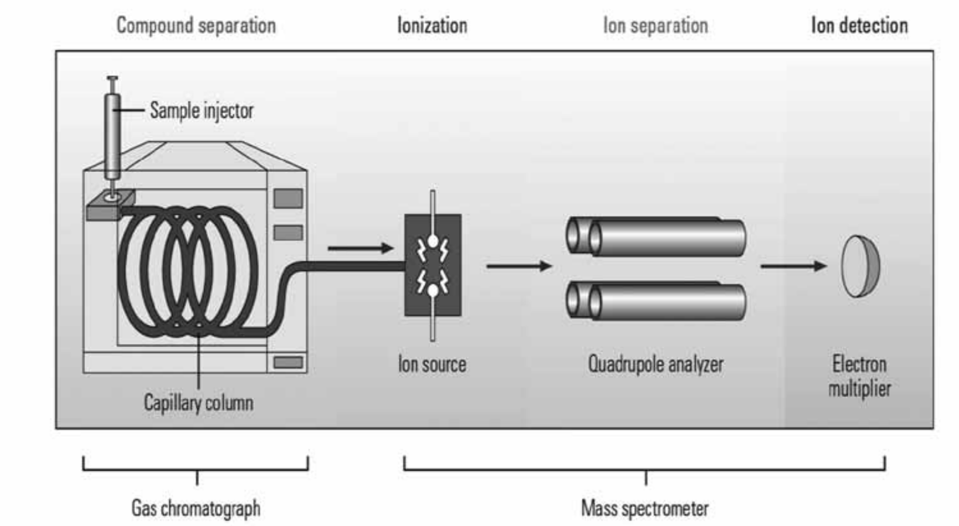


Figure 14. Components of a Gas Chromatograph-Mass Spectrometer.

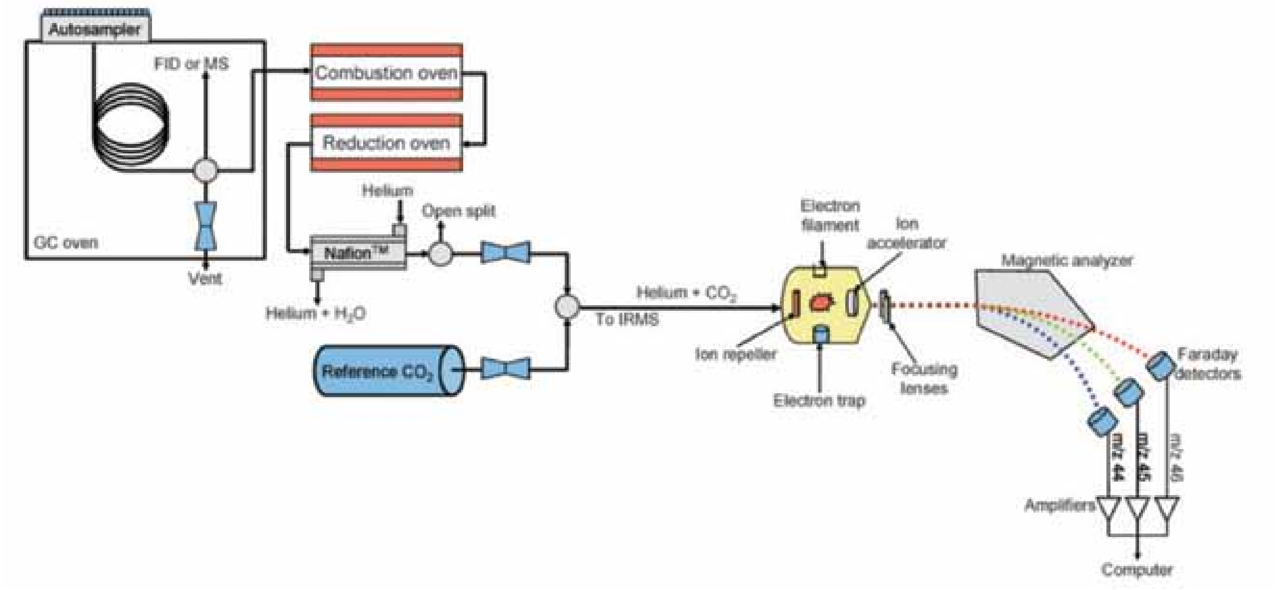


Figure 15. A schematic of Gas Chromatograph-Combustion-Isotope Ratio Mass Spectrometer (GC-C-IRMS)

hyphenated techniques, which include the separation power of a gas chromatograph coupled to the mass spectrometer, along with the introduction of a sample combustion interface into the gas chromatograph-IRMS (Platzner, 1997). Broadly, a mass spectrometer comprises of the (1) ion source for the fragmentation of the sample molecule into ions and (2) mass analyzer for separating and detecting the ion beam according to the mass of the respective ions (Figure 15). In GC–C–IRMS, the separated products of the sample mixture, carried in the stream of helium, are eluted at the output of the gas chromatograph and passed through an oxidation/reduction reactor and then are introduced into the ion source of mass spectrometer for the ratio determination. An open split-coupling device ensures that only a part of the sample/reference gas containing carrier gas is fed into the ion source, thus reducing the volume constraints and sample size. Continuous Flow-IRMS is a standard term used for the IRMS instruments, that are coupled online to preparation lines or instruments.

This includes the (1) Gas Chromatography–Combustion–IRMS (GC–C–IRMS), used for the compound specific isotope ratio determination of individual hydrocarbon components, (2) Gas Bench–IRMS (GB–IRMS), used for the C and O isotope ratio determinations on carbonates, and (3) Elemental Analyzer–IRMS (EA–IRMS), for the determination of bulk isotopic compositions of the coexisting organic matter.

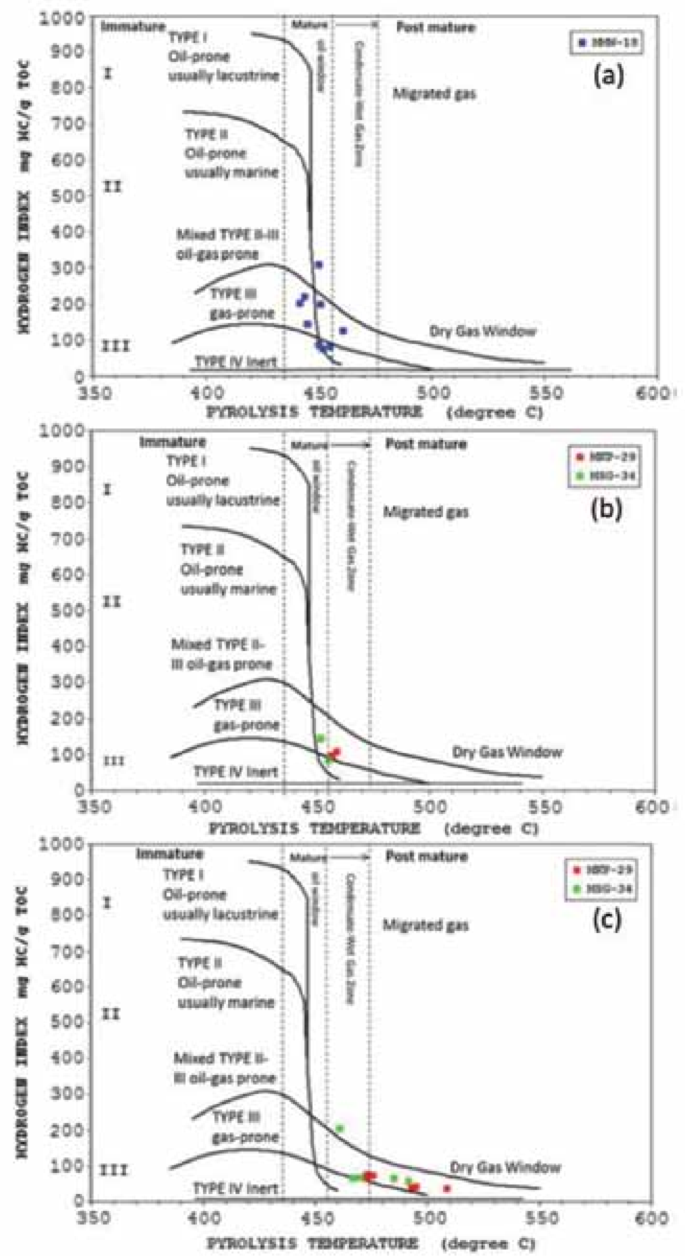


Figure 16. Kerogen type and thermal maturity of shales from Raniganj formation (MMW-18 borewell, represented in blue) (Figure a). Barren Measure formation (MKP-29 borewell represented in red and MSG-34 borewell represented in green) (Figure b); and Barakar Formation (MKP-29 borewell represented in red and MSG-34 borewell represented in green) (Figure c) of Damodar valley (Mani et al., 2015)

CASE STUDY

Gas generation potential of Permian shales in Damodar Valley basin

Jharia sub-basin, Damodar Valley:

Organic matter rich and thermally mature Permian shales are widely distributed in the Gondwana basins of Indian sub-continent. Gas shows have been reported in the wells drilled in the Raniganj area of Damodar Valley, which forms an important coal repository among the Indian Gondwana basins (Padhy and Das, 2013). Barakar and Raniganj are the main coal-bearing formations in the basin, and a marine/lacustrine succession that got deposited between these continental depositions resulted in the coal-devoid Barren Measure formation (Chandra, 1992). Thermal maturity of the coals surrounding the Barren Measure shale formation suggests it to be within the gas window (Padhy and Das, 2013), making it a potential shale gas target.

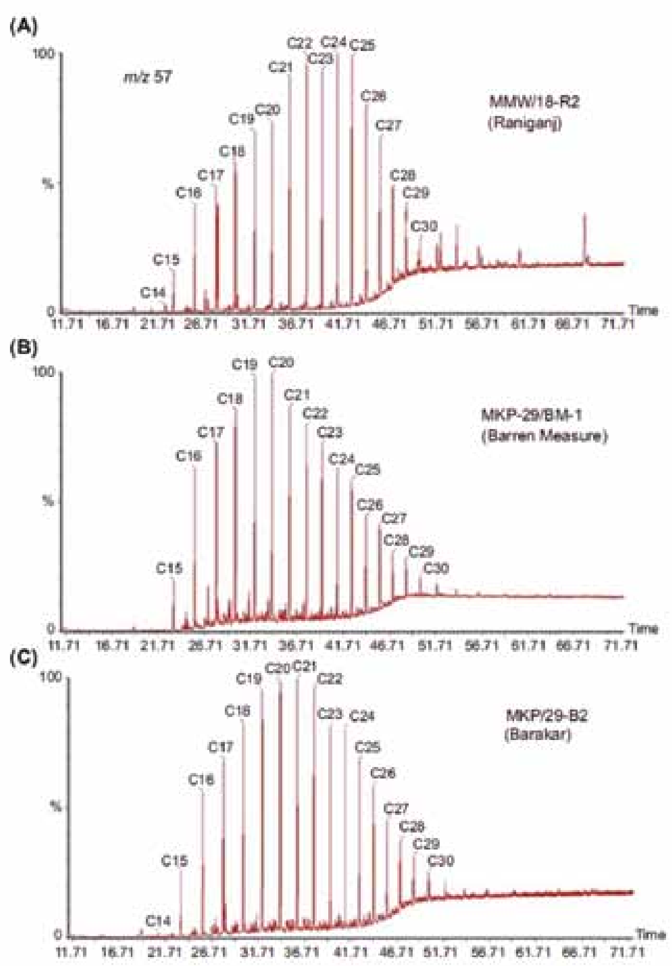


Figure 17. Saturated hydrocarbons (*n*C13 to *n*C30) in organic extracts of shales from Damodar Valley Basin (Mani et al., 2017)

The Permian shales from the Jharia sub-basin of Damodar Valley were studied for their organic matter properties, to infer the gas generation potential (Mani et al., 2015, 2017). Rock Eval pyrolysis of the shales showed excellent organic richness with TOC content ranging between 2.86% and 23.09%. Organic matter is characterized by Type II/III and Type III kerogen, and the thermal maturities span between the mature (oil window-gas condensate) and post-mature (dry gas) zone for hydrocarbon generation. The Raniganj and Barren Measure shales are in the late oil generation window, and the Barakar shales show post-mature stage for oil (Figure 16).

The bulk and compound specific carbon isotope ratios of hydrocarbon gases from the flash combustion and thermal desorption studies, respectively, of these shales indicate a thermogenic gas from the terrestrial organic matter, except for Barren Measure, where a lacustrine/marine source has been inferred (Mani et al., 2015). The isotopic compositions vary in a narrow range and are nearly similar for most of the studied samples (−40.4 to −44.8‰). The exposure of organic matter to high subsurface temperatures has not enriched or altered the δ^{13}C values significantly (Mani et al., 2015).

The organic matter in the shales was extracted and the aliphatic and aromatic biomarker constituents in it were studied using GC-MS (Mani et al., 2017). The total organic extract contains high proportion of saturated hydrocarbons in the range *n*C13 to *n*C30 and acyclic isoprenoids in all the samples (Figure 17).

The aromatic fractions in the organic extracts of the Raniganj, Barren Measure, and Barakar shale, in general, contain naphthalene, phenanthrene, biphenyl, and their alkylated derivatives, along with a low abundance of dibenzothiophene and its homologs. The ratio obtained by dividing the sum of odd carbon-numbered alkanes to the sum of even carbon-numbered alkanes has been defined by carbon preference index (CPI) (Didyk et al., 1978). It gives information on the maturity of the organic matter. The CPI of Damodar basin shales range from 0.9 to 1.1, which indicates no even or odd carbon preference and suggests the organic-rich sediments to be thermally mature. This is also corroborated by the unimodal peak

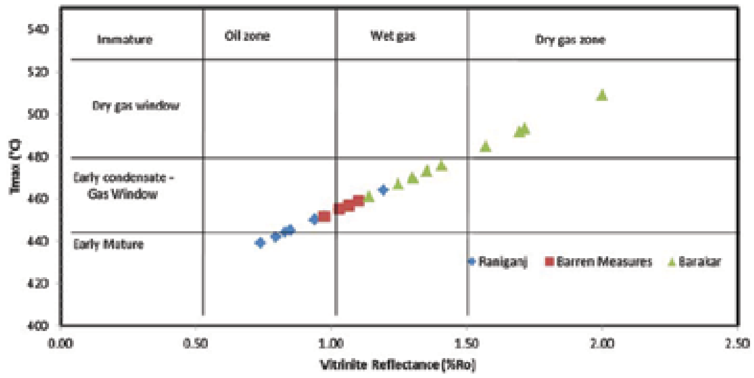
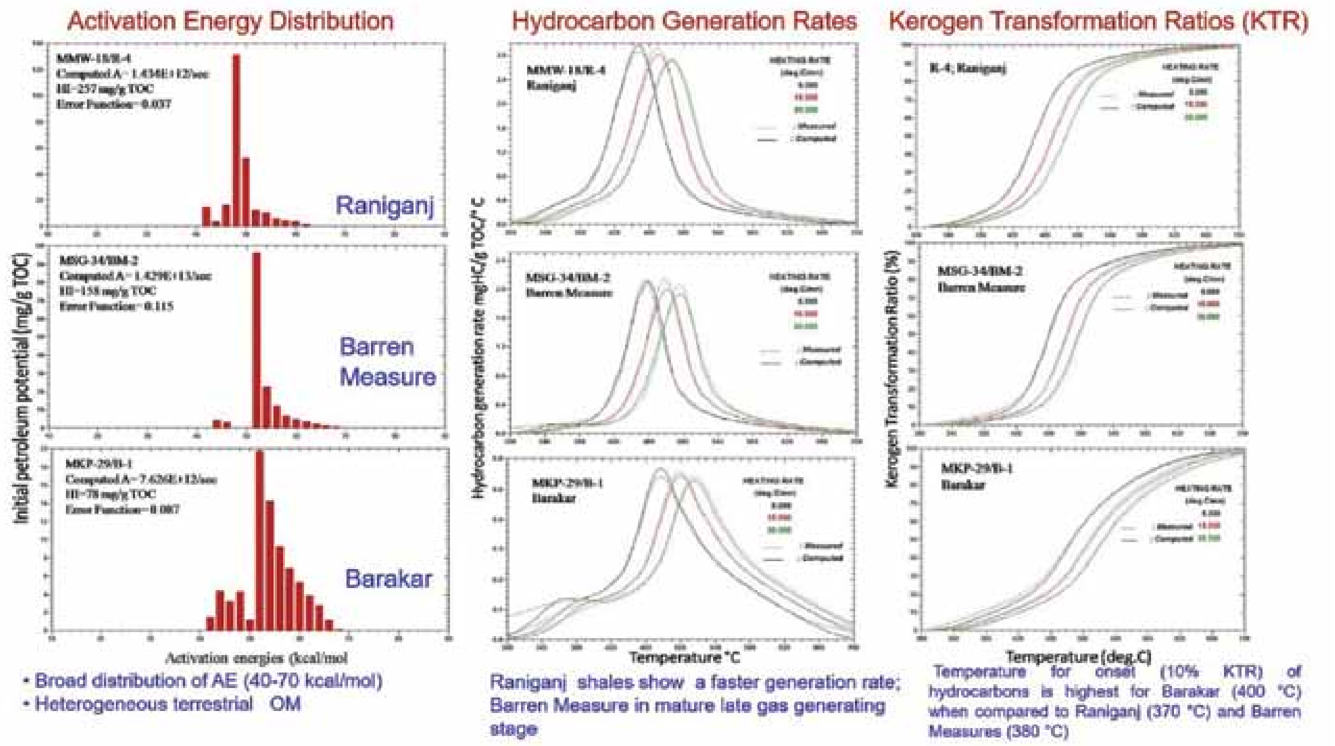


Figure 18. Thermal maturity of Permian shales from Damodar Valley Basin using Vitrinite reflectance and Rock Eval Tmax plot (Mani et al., 2015)



- Broad distribution of AE (40-70 kcal/mol)
- Heterogeneous terrestrial OM

Raniganj shales show a faster generation rate; Barren Measure in mature late gas generating stage

Temperature for onset (10% KTR) of hydrocarbons is highest for Barakar (400 °C) when compared to Raniganj (370 °C) and Barren Measures (380 °C)

Figure 19. Kinetic parameters of Hydrocarbon generation obtained from the pyrolysis of shales from Damodar Valley Basin (Mani et al., 2015).

distribution of the n-alkanes. The differences of pristine to phytane (Pr/Ph) ratios, which indicate the oxygenation conditions during the deposition of the Damodar Valley shales, suggest that these shales were deposited in fluvio-marine and coastal swamp depositional environment under oxic to sub-oxic conditions. The ratios of α/β isomers in aromatic biomarkers are maturity dependent and their concentrations are useful in the calculation of temperature-sensitive maturity parameters. Such isomeric ratios, expressed in form of indices such as Methylphenanthrene indices (MPI-1), dimethylnaphthalene ratios (DNR-1 and DNR-2), and trimethylnaphthalene ratio (TNR-1) are high in Jharia shales, suggesting a mature to highly mature state of kerogen. The high maturity of the shales is also supported by the Tmax parameter of Rock Eval pyrolysis. Vitrinite and inertinite are the dominant macerals in the Jharia shales. Liptinite occurs sparsely (Mani et al., 2015). The Raniganj and Barren Measure shales show vitrinite and inertinite macerals, with lesser occurrence of liptinite. The random reflectance (Rr%) varies between 0.99 and 1.22 for Raniganj shales and 1.1–1.41 for the Barren Measure. The Barakar shales consist mainly of vitrinite and inertinite with a random reflectance ranging between 1.11 and 2.0.

Further, the mineral matrix is characterized by abundant clay minerals with siderite and pyrite. The kinetic parameters obtained during pyrolysis studies indicate that Raniganj has lower activation energies (ΔE = 42–62 kcal/mol) in comparison to Barren Measure and Barakar (ΔE = 44–68 kcal/mol) (Figure 19, Mani et al., 2015). Temperature for onset (10%), middle (50%), and end (90%) of kerogen transformation is least for the Raniganj shales (Mani et al., 2015). It is followed by the Barren Measure and Barakar shales.

Thus, the organic geochemical and stable isotopic studies carried out on the Permian Gondwana shales from Jharia sub-basin of Damodar Valley, in particular, those from the Barren Measure formation, demonstrate excellent properties of a potential shale gas system (Mani et al., 2015). These shales possess abundant organic matter in highly mature stage for generation of gaseous hydrocarbons. Integration of organic geochemical, stable isotope, mineralogical and petrological data with the stratigraphic extent, thickness and structural features such as faults and fractures associated with the shale horizons is important for the shale gas exploratory studies in the basin.

SUMMARY

Source rock characterization using geochemical logs and maps is necessary in a sedimentary basin analysis with the objective of identifying the pod of active or potential source rock. A source rock can be described as potential (could generate oil), effective (generated or currently generating oil), or spent (generated oil). A spent source rock can still generate gas. The pod of active source rock contributes hydrocarbons to the petroleum system. Source rock assessments include determination of its richness, kerogen type, thermal maturity, product generated, time, and provenance or depositional environment. The organic richness of the source rock organic can be poor, fair, good, very good, or excellent and the kerogen can be described as type I, II, III, or IV, based on petrological and geochemical analyses. The source rocks can be immature, mature, and postmature, based on parameters like vitrinite reflectance, Tmax, and thermal alteration index. Geochemical logs of closely spaced Rock-Eval pyrolysis and TOC, vitrinite reflectance, lithology, and related data are indispensable tools in the sedimentary basin evaluation process. Useful geochemical logs require adherence to systematic sampling and proper procedures for sample preparation, analysis, and interpretation. The logs generated from such datasets aid in identify petroleum source rocks (as potential, effective, or spent), the thermal maturation gradient (including immature, mature, and postmature zones), and in situ and migrated petroleum shows. These rapid and inexpensive screening methods generate libraries of geochemical logs that progressively reduce the risk associated with petroleum exploration as the study region becomes more thoroughly sampled. Logs from various locations can be used to map the pod of active source rock, regional variations in organic facies, and the volume of generated petroleum. This information can be used as input to refine mathematical basin models. As hydrocarbons have become more difficult to discover and recover, the ever more precise forms of analysis to differentiate between a viable prospect and a dry hole can be provided essentially by exploration geochemistry.

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Compliance with Ethical Standards

The author declare that she has no conflict of interest and adhere to copyright norms

REFERENCES

Bjørlykke, K., 2015. Introduction to Petroleum Geology Chapter 1 In: K. Bjørlykke (ed.), Petroleum Geoscience: from sedimentary environments to Rock Physics, DOI 10.1007/978-3-642-34132-8_1, # Springer-Verlag Berlin Heidelberg.

Briggs, D. and Roger E. Summons, 2014. Ancient biomolecules: Their origins, fossilization, and role in revealing the history of life. BioEssays 36(5).

Behar, F., Beaumont, V., Penteado, H.L. and De, B., 2001. Rock-Eval 6 technology: performances and developments oil & gas science and technology. Rev. IFP, 56 (2), 111–134.

Chandra, D., 1992. Jharia Coalfield. Mineral resources of India 5. Geological Society of India, Bangalore, pp. 149.

Didyk, B.M., Simoniet, B.R.T., Brassell, S.C. and Eglington, G., 1978. Organic geochemical indicators of paleoenvironmental conditions of sedimentation. Nature, 272, 216–222.

Eden, H. and Mungo, D., 2013. Geochemistry-the dark horse upstream. Geo Expro 10(1), 22-25.

Espitalie, J., Marquis, F. and Sage, L., 1987. Organic geochemistry of the Paris Basin. In: Brooks, J., Glennie, K. (Eds.), Petroleum Geology of North West Europe. Graham and Totman, London, 71–86. http://www.uky.edu/KGS/coal/coal-macerals.php#

Hunt, J.M., 1996. Petroleum Geology and Geochemistry. W. H. Freeman and Company, San Francisco, p. 617.

Mani, Devleena, Patil, D.J. and Dayal, A.M., 2011. Stable carbon isotope geochemistry of near surface adsorbed alkane gases in Saurashtra basin**.** Chem. Geol., 280(1-2), 144–153.

Mani, Devleena, Dayal, A.M., Patil, D.J., Mateen Hafiz, Naveen Hakoo and Bhat, G.M., 2014. Gas potentiality of Proterozoic and Phanerozoic shales from NW Himalaya, India: Inferences from new pyrolysis data, Int. J. Coal Geol., 128-129, 81-95,

Mani, Devleena, Patil, D.J., Dayal, A.M. and Prasad, B.N., 2015. Thermal maturity, source-rock potential and kinetics of hydrocarbon generation in Permian shales of Damodar Valley basin, Eastern India, Marine and Petrol. Geol., 66, 1056-1072.

Mani, Devleena, Kalpana, M.S., Patil, D.J. and Dayal, A.M., 2017. Organic matter in gas shales: Origin, evolution and characterization. Chapter in Shale Gas: Exploration, Environmental and Economic impacts, 3, 25-52.

Magoon, L.B. and Dow, W.G., 1994. The petroleum system: From source to trap: AAPG Memoir 60, 655 pp.

Padhy, P.K. and Das, S.K., 2013. Shale oil and gas plays: Indian sedimentary basins. Geohorizons, 18(1), 20-25.

Peters, K.E., Walters, C.C. and Moldowan, J.M., 2005. The Biomarker Guide: Biomarkers and isotopes in the environment and human history, 1, Cambridge Press, pp. 1115.

Peters, K.E. and Cassa, M.R., 1994. Applied source rock geochemistry. In: Magoon, L.B., Dow, W.G. (Eds.), The Petroleum system from source to trap, AAPG Memoirs, 60, 93-120.

Peters, Kenneth E., David J. Curry, and Marek Kacewicz, 2012. An overview of basin and petroleum system modeling: Definitions and concepts, in Peters, Kenneth E., David J. Curry, and Marek Kacewicz, eds., Basin modeling: New horizons in research and applications: AAPG Hedberg Series no. 4, p. 1-16.

Petsch, S.T., 2014. Weathering of Organic Carbon, Treatise on Geochemistry, 217-238. doi 10.1016/B978-0-08-095975-7.01013-5.

Schidlowski, M., 1987. Application of stable Carbon isotopes to early biochemical evolution on Earth. Annual Rev. Earth Planet. Sci., 15, 47-72.

Sharp, Z., 2017. Principles of stable isotope geochemistry, 2nd Edition doi 10.5072/FK2GB24S9F

Sneddon, J., Masuram, S. and Richert, J.C., 2007. Gas chromatography-mass spectrometry-basic principles, instrumentation and selected applications for detection of organic compounds. Anal. Lett. 40:6, 1003–1012. http://dx.doi.org/10.1080/00032710701300648.

Tissot, B.P. and Welte, D.H., 1984. Petroleum formation and occurrence. A new approach to Oil and Gas, 2nd Edition, Springer Verlag.

Vandenbroucke, M., 2003. Oil and gas science and technology – Rev. IFP, 58(2), 243-269.

Van Krevelen, D.W., 1961. Coal typology-Chemistry-Physics-constitution. Elsevier, Amsterdam.

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