

PETROLEUM GEOCHEMISTRY

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Summary

The chapter reviews and describes the organic and inorganic geochemical features of oil and gas reservoirs. In particular indicators of oil origin and maturation have been considered and discussed. Genetic tracers derived by insoluble and soluble organic material have been described together with related analytical techniques. Biological markers able to describe relevant characteristics of source rocks and of depositional environments have been described as well. Organic geochemical methods for oil age-dating are discussed. Methods of geochemical stratigraphy able to contribute to the knowledge and modeling of reservoir's characteristics have been described. Inorganic geochemical features of petroleum have been compared to the diagenetic evolution of organic molecules. Geochemical features of oilfield waters associated with petroleum in reservoirs have been compared to oil, shale, sandstones and carbonate composition.

Chemical and isotopic compositions of natural gases which often accompany liquid hydrocarbons have been described. In particular, isotopic noble gases abundances utilized in hydrocarbon reservoir characterization studies have been listed and discussed. Finally, direct and indirect surface geochemical methods utilized in hydrocarbons exploration and secondary potential sources of petroleum represented by coal or by deep inorganic environments have been considered and discussed.

1. Introduction

Geochemistry studies the history of chemical elements in the Earth's crust and their behavior under different physicochemical natural conditions. Geochemistry is concerned with the laws governing the distribution of the chemical elements and their isotopes throughout the Earth. Petroleum geochemistry is a branch of geochemistry and studies the application of chemical principles to the study of the origin, generation, migration, accumulation and alteration of petroleum, and the use of this knowledge in exploration and production of oil and gas.

The determination of the most favorable petroleum exploration targets depends on the geochemical knowledge of source rocks and on the knowledge of generation, migration and accumulation processes combined with the geophysical and geological features of the sedimentary basin under evaluation.

2. Geochemical Analytical Techniques Utilized in Petroleum Geochemistry

Petroleum is a mixture of many organic compounds and is commonly analyzed from the organic and inorganic point of view through a variety of techniques. In particular the optical parameter of Vitrinite Reflectance is widely utilized to obtain indications on the maturity of potential source rocks. Organic compounds are usually analyzed by Gas Chromatography and by Pyrolysis. More detailed analysis of organic components may be carried out by means of Gas Chromatographic Mass Spectrometry. Atomic Absorption Spectro-Photometry and Inductively Coupled Plasma Spectrometry are commonly utilized to identify inorganic components at trace level concentrations. Mass Spectrometry is also widely utilized for isotopic investigations of crudes and natural gases. Particular devices, like sniffers etc., are also utilized during surface geochemical prospection.

3. Oil Composition and Origin

Petroleum originates by hydrocarbons that have been generated by thermal alteration after burial of organic matter in sediments. Crude oils are composed by organic compounds characterized by different molecular weight, size, shape, solubility and elemental composition. The average composition is the following:

85 % carbon
 13 % hydrogen
 2 % sulfur, nitrogen, oxygen.

Crude oils are basically composed of hydrocarbons (alkanes, naphthenes, and

aromatics) while most important non-hydrocarbon components are resins and asphaltenes. Other non-hydrocarbon compounds are metal-porphyrin complexes and trace elements. Distillation allows the separation of petroleum in groups characterized by different molecular weight: gas from C_1 to C_4 , gasoline from C_5 to C_{10} , kerosene from C_{11} to C_{13} , light gas oil from C_{14} to C_{18} , heavy gas oil from C_{19} to C_{25} , lubricating oil from C_{26} to C_{40} , residuum for $C_n, n > 40$, where n is the number of carbon atoms in the molecular structure. The three most important stages of petroleum formation are diagenesis, catagenesis and metamorphism.

Diagenesis comprises all the chemical and physical alteration of organic matter excluding effects of temperature T (T in the range from 50 to 60 °C), catagenesis implies the thermal alterations of organic matter (T in the range from 175 to 200 °C) and metamorphism implies high temperature thermal alteration ($T > 200$ °C). The largest amount of petroleum substances originated from organic matter in sediments subject to diagenesis and catagenesis, with temperature in the range from 60 to 150 °C.

Carbon in sedimentary rocks has undergone isotopic fractionation, with the heavier isotope ^{13}C concentrating in carbonate carbon and the lighter isotope ^{12}C in organic carbon. Organic carbon is characterized by 27 parts per thousand less ^{13}C than carbonate carbon. Petroleum $^{13}C/^{12}C$ values are in the range of organic carbon. Geochemical methods allowed recognizing genetic relationships of crude oils with parent organic matter and genetic uniformity of oils in different stratigraphic sequences. Concentration of trace elements in oil is often relatively high because trace elements are complexed in organic molecules. In particular vanadium and nickel are complexed by porphyrin derived from the original chlorophyll molecule. Most crude oil and gas are derived from organic matter with kerogen as the major intermediate. The knowledge of kerogen characteristics enables to understand the oil and gas genesis. Dispersed organic matter of rocks may be classified into insoluble and soluble in organic solvents (chloroform, benzene, alcohol, methanol, acetone and ethanol). The portion of organic matter which is insoluble in organic solvents is named kerogen while the soluble portion is named bitumen. The predominant pathway for the formation of crude oils is via the kerogen intermediate.

4. Insoluble Organic Material - Kerogen

Kerogen is a very heterogeneous and complex agglomerate of macerals. Macerals are discrete particles of insoluble organic materials which can be identified under the microscope and represent residual detritus from various sources of organic material. Major components of kerogen are carbon, hydrogen, oxygen, nitrogen and sulfur. Kerogens can be petrographically characterized in a way similar to the classification of coals. This led to the concept of classifying kerogens as types from I to IV and different kerogen types were constrained by well-defined boundaries on the $[H]/[C]$ versus $[O]/[C]$ plot (Tissot-Welte diagram) as shown in Figure 1. The Tissot-Welte diagram, derived from the coal petrographers' Van Krevelen diagram (Figure 2) is still used to assign kerogen types. It provides an indication of kerogens maturity level, and the nature of products that a particular kerogen may be expected to generate at appropriate levels of maturity.

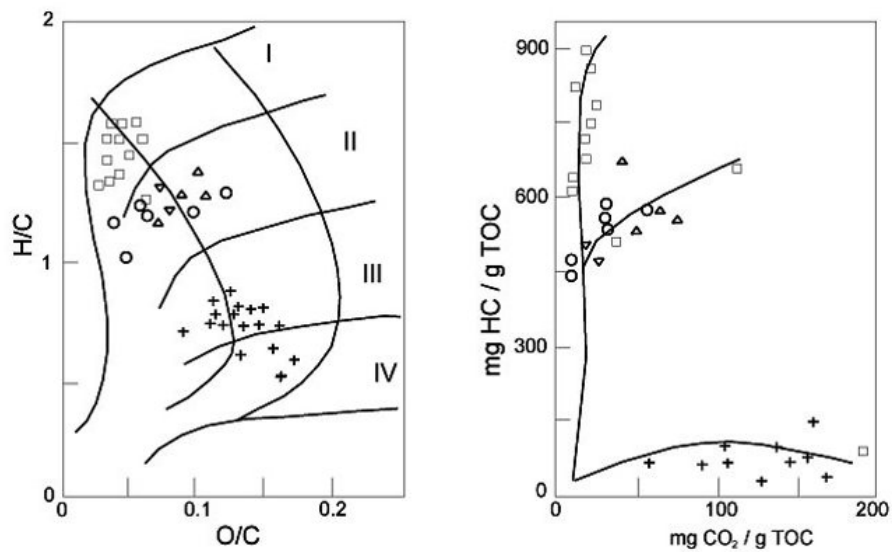


Figure 1. Maturation pathways of the dominant kerogen types in terms of their atomic [H]/[C] vs. [O]/[C] ratios in the Tissot-Welte diagram. Rock Eval pyrolysis allows measuring Oxygen Index (OI) and Hydrogen Index (HI) which are proportional to [H]/[C] and [O]/[C] values. (from Hunt J.M., , *Petroleum Geochemistry and Geology*. W.H. Freeman, New York, 1996).

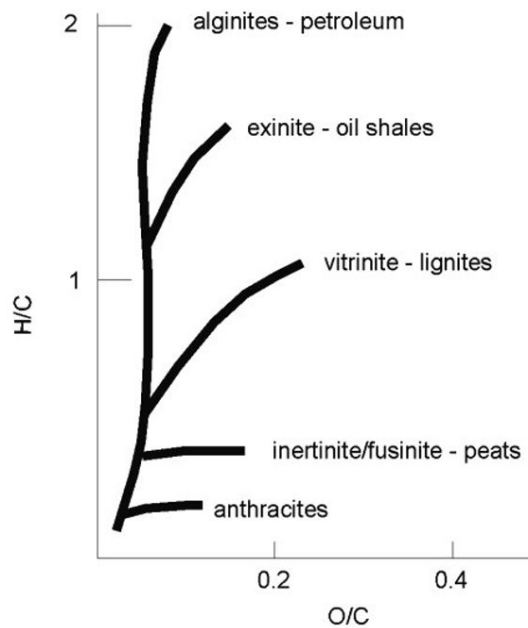


Figure 2. Classification of kerogens in the Van Krevelen diagram (from Van Krevelen D.W. *Coal*. Elsevier. New York, 1961).

A change to the original diagram resulted from the introduction of the Rock Eval pyrolysis system. Development of the Rock Eval technique for characterization of the source rocks provided a relatively rapid alternative method for determination of two indices that could be used to replace the [H]/[C] and [O]/[C] ratios. This technique is a

pyrolysis method whereby a sample is exposed to a temperature programmed pyrolysis from ambient temperature to 600 °C and the pyrolysis products are detected without any chromatographic separation. The result is represented by three peaks S1, S2 and S3 reported in Figure 3. Modern versions of the Rock Eval technique produce some additional peaks.

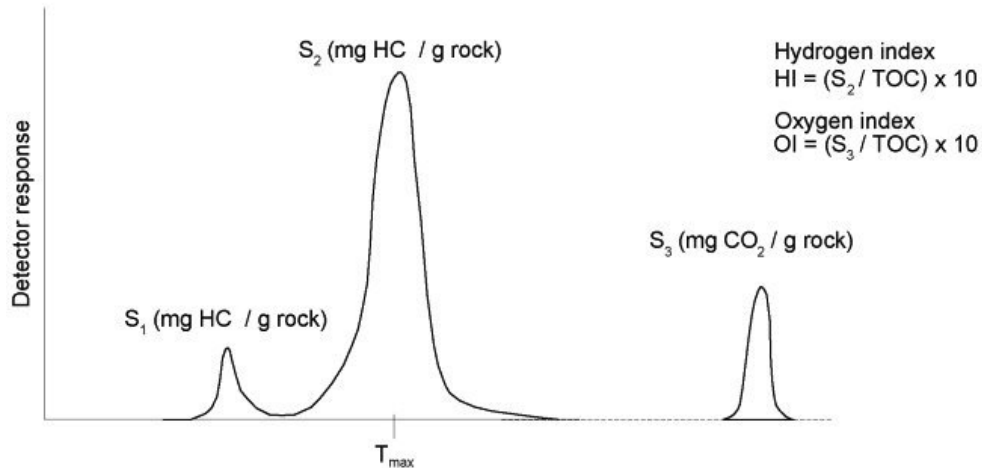


Figure 3. Peaks generated by Rock Eval pyrolysis. Hydrogen index (HI) and oxygen index (OI) may be obtained by peak evaluation (from Philp R.P., *Formation and Geochemistry of Oil and Gases. Treatise on Geochemistry. Vol.7 (Mackenzie F.T. Ed.; Holland H.D. and Turekian K. Ex.Ed). Elsevier, Oxford, 2004).*

Peak S1 corresponds to the material which is normally solvent extracted from a source rock. Peak S2 corresponds to the products formed from the thermal breakdown of the kerogen and peak S3 is derived from oxygen-containing molecules within the kerogen. From these three parameters, plus the total organic carbon content of the sample, two important parameters are developed, namely, the so-called Hydrogen Index (HI), which is the S2 peak normalized to the Total Organic Carbon (TOC), and the Oxygen Index (OI), which is the S3 peak normalized to the TOC. It has been shown that the HI and OI are directly proportional to the [H]/[C] and [O]/[C] ratios and, therefore, a plot of HI to OI can be used to replace the [H]/[C] and [O]/[C] values on the Tissot-Welte diagram. Another important feature related to the generation of oil or gas is the maturity level of the source rock. Organic matter has to reach a certain level of maturity before starting the thermal degradation and to convert into liquid or gaseous hydrocarbons. The threshold level for oil generation varies depending upon kerogen type. The determination of maturity levels is critical to the success of every oil exploration program. Recovery of immature, but organic-rich, source rocks indicate good source potential for such rocks if buried more deeply in other parts of the basin. At the other extreme an over-mature source rock indicate a mature part of the basin not capable of generating additional liquid hydrocarbons, but possibly gas. There are several available indicators that can be used to estimate the relative maturity of a source rock. The traditional method is measuring the maturity of vitrinite.

The chemical composition of the maceral vitrinite, derived from higher plant debris, changes as the level of maturity increases. With increasing maturity, the ability of

vitrinite to reflect light increases and hence a vitrinite reflectance scale which correlates the degree of reflectance with maturity has been developed. Maturity changes of vitrinite have been studied by coal chemists for a long period of time. A similar approach was adopted by the petroleum geochemists. The vitrinite reflectance scale is summarized in Figure 4 which indicates step values of this scale representing the start of oil generation, peak oil generation, the start of gas generation and the start of graphitization.

Kerogen is a key intermediate in the formation of oil and gas. Kerogen types and maturity levels play an important role in determining the characteristics of the products that will be generated from a specific kerogen.

Maturation rank		% Volatiles in coal (d.a.f.)*	Max. paleo Temp. °C	Microscopic parameters					Chemical parameters											
Kerogen	Coal			Vitrin. refl. %Ro	TAI	SCI	Conodant alteration index	Fluorescence		CPI	Pyrolysis		C wt. %	H wt. %	HC wt. %	Hydro-carbon products				
								Color of alginite	λ_{max} (nm)		T max	P.I.								
Diagenesis	Peat	60	0.2	1 Yellow	1	1 Yellow	Blue green	500	5	400	0.1	67	8	1.5	Bacterial gas					
	Lignite		0.3				2					Greenish yellow	3	70		8	1.4			
	Catagenesis	Sub-bitumin C	46	0.4	2 Orange	2	2	Golden yellow	540	2	425	0.2	75	8	1.3	Immature heavy oil				
				B				0.5					3	2	2		80	7	1.1	
		High volatile bituminous	33	0.6	3 Brown	3	3	3	Dull yellow	600	1.5	435	0.3	85	6	0.85	Wet gas and oil			
B				0.7										4	4	4		87	5	0.7
A				0.8										5	2	2		80	7	1.1
Medium volatile bitumin	25	0.9	4 Brown/black	4	4	4	Orange	640	1.2	450	0.4	85	6	0.85	Condensate					
		A										1.0	6	6		6	87	5	0.7	
		0.9										7	3	3		3	87	5	0.7	
Low volatile bitumin Sem-anthrac.	13	1.3	5 Black	5	5	5	Red	680	1.0	475	0.5	90	4	0.5	Dry gas					
		1.5										8	4	4		4	90	4	0.5	
		1.5										8	4	4		4	90	4	0.5	
Metagenesis	Anthracite	4	2.0	5 Black	5	5	Nonfluorescent		500	550		90	4	0.5	Dry gas					
			2.5									9	4	4		4	94	3	0.38	
	Meta-anthrac.		3.0									94	3	0.38						
			4.0									96	2	0.25						
			5.0									96	2	0.25						

* Dry ash free

Figure 4. Vitrinite reflectance correlation chart. Vitrinite reflectance indicates the maturity of a potential source rock (from Hunt J.M., *Petroleum Geochemistry and Geology*. W.H. Freeman, New York, 1996).

5. Soluble Organic Material

The soluble part of the dispersed organic matter is called bitumen which is composed by oils, resins and asphaltenes. Soluble compounds such as steranes and terpenes in crude oils are considered biomarkers. Biomarkers are compounds in ancient sediments

characterized by carbon skeletons correlated to precursor molecules present in organisms and plants living at the time of deposition. For example, sterols are very abundant in many living organisms and plants and, upon burial diagenesis and thermal maturation, are ultimately converted into steranes. The only significant change that occurs is loss of the hydroxyl group and of the double bond present in the sterols. Therefore, a precursor to product relationship can be established between the sterol and the sterane. Similar precursors to product relationships have been recognized in a large number of other compounds as in the conversion from chlorophyll to porphyrins. The concentration of individual biomarkers in a crude oil are relatively low but their information content is significant and related to source, depositional environments, maturity, age of migration, and extent of biodegradation. Biomarker fingerprints are extensively utilized for the purpose of undertaking oil and source rock correlation studies.

6. Source Rocks and Depositional Environment

Source rocks are usually composed by fine-grained sediments like shales and carbonates. Sedimentary rocks are subjected to the effect of time and temperature. Hydrocarbon generation from kerogen of sediments is closely related to temperature, kerogen type and time. Peak oil generation occurs when carbon content of kerogen is between 77 and 87 % while peak gas generation occurs when carbon is between 85 and 92%.

The utility of biomarkers as indicators of depositional environments arises from the fact that certain types of compounds are associated with organisms or plants that grow in specific types of depositional environments. In some situations it has been possible to characterize depositional environments through a composite of biomarker parameters. For instance, gammacerane has long been used as an indicator of hypersalinity. Oils or extracts from evaporative environments, particularly lacustrine environments, typically have terpene chromatograms where gammacerane is the most abundant component in the chromatogram. Relatively high concentrations of pristane (Pr) are found in oxic type environments and high concentrations of phytane (Ph) are found in reducing type environments. Thus, the [Pr]/[Ph] ratio evolved as an indicator of the possible toxicity of the depositional environment. This information can be used to predict the location of better source rocks in vertically drained basins, especially in deltaic-type environments with relatively young source rocks. With long-distance vertical migration, some of the biomarker parameters may become less effective.

7. Maturity Indexes and Biodegradation Processes

During crude oil maturation the percent of naphthenes decreases with respect to paraffins plus aromatics, and the percent of four-, five- and six-ring naphthenes decrease, while one-ring naphthenes increases. Selected biomarkers have been used to evaluate the relative maturity of suspected source rocks and the oils they may have generated.

The maturity parameters can be divided into a number of groups. The first group includes those parameters based on changes in distributions of stereoisomers or optical

isomers; the second group includes the parameters resulting from thermal degradation of certain molecules in a predictable manner (e.g., the cleavage of side chains from the tri-aromatic steroid hydrocarbon); finally, the third group contains various porphyrin ratios that depend on ring opening of the porphyrin which occurs with increasing maturity. The most recent set of biomarker maturity parameters are those based on changes in the relative distribution of various methylated diamantoid structures. Biomarkers ratios can be particularly important in samples that may not contain vitrinite, preventing the determination of a vitrinite reflectance value.

Various hypotheses concerning mechanisms of crude oil biodegradation have been introduced. These include: (a) the concept of paleopasteurization of reservoirs; (b) anaerobic, rather than exclusively aerobic degradation of crude oils in reservoirs; and (c) different mechanisms for degradation of surface seeps versus deep reservoirs.

Paleopasteurization explains why it is possible to observe reservoirs of non-degraded crude oils at relatively shallow depths in the subsurface where one might expect the oils to be degraded. In general, biodegradation in crude oils has not been reported in reservoirs that have experienced temperatures above 80 °C. For paleopasteurization to occur, a reservoir should have been exposed to temperatures above 80 °C at some time during its history. Above that temperature, the reservoir is effectively sterilized and subsequent uplift, or overburden erosion, leading to the temperature falling below 80 °C, will mean that the oil which enters the reservoirs at lower temperatures will not experience any additional biodegradation. In this way the sterilized sediments are not re-colonized by hydrocarbon degrading bacteria.

8. Age of Oil and Migration Processes

Many attempts have been made to age-date oils through the use of geochemical parameters. The main idea behind these attempts has been to find a compound, or class of compounds, that can be associated with a particular plant or organism, based on the fossil record. In particular a method is based on the changes in the percentage of naphthenes, paraffins and aromatics in gasoline-range hydrocarbons related to paraffin and aromatic hydrocarbons. The age of oil is calculable by the extent to which paraffins and aromatics have been formed from the naphthenes. A further method experimented in some test area considers the relative proportions of steranes in crude oils derived from marine source rocks with known ages. A calibration based on the ratio of the $[C_{27}]/[C_{78}]$ steranes versus geologic time has been set up. In this ratio a strong increase has been evidenced as the samples became progressively younger as a result of the increase in the concentration of the C_{23} steranes. Comparison with information on the increase in diversity of phytoplankton with time shows a good correlation with the sterane ratio and provides an explanation for this increase. Oil compositions change with migration distance. Changes occur as a result of geochromatography due to the fact that smaller molecules move faster and further than large molecules. Oils that have migrated for greatest distance are enriched in the lighter components and numerous attempts have been made to quantify such changes. The lighter components of a crude oil are in general isotopically heavier and, therefore, if the molecular distribution of crude oils changes one can expect isotopic changes to occur.

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Biographical Sketch

Giovanni Martinelli is Senior Hydrogeologist of the Environmental Protection Agency of the Emilia-Romagna Region (ARPA), Bologna, Italy. He holds a MS Degree in Geology and Geochemistry from the University of Modena (Italy). He specialized in general and applied geothermics in Laboratory Research Methodologies and in International Cooperation and Policies in Developing Countries.

He was Scholarship Holder of the Emilia-Romagna Region in the period 1980-1984 at the International Institute for Geothermal Research of National Research Council, Pisa, Italy. From 1985 to 1986 he has worked as Expert in Hydrology of the Emilia-Romagna Regional Government. In 1987 has worked as Senior Hydrogeologist in Mozambique (Italian Ministry of Foreign Affairs Expert). In the period from 1988 to 2002 he has worked as Expert in Fluid Geochemistry of the Emilia-Romagna Regional Government. Since 2001 he is Senior Hydrogeologist of the Environmental Protection Agency of the Emilia-Romagna Region (ARPA), Bologna, Italy.