HAL
open science

Petroleum Geochemistry At the Dawn of the 21st Century

A. Y. Huc

To cite this version:

A. Y. Huc. Petroleum Geochemistry At the Dawn of the 21st Century. Oil & Gas Science and Technology - Revue d'IFP Energies nouvelles, 2003, 58 (2), pp.233-241. 10.2516/ogst:2003015 . hal-02043854

HAL Id: hal-02043854

https://ifp.hal.science/hal-02043854v1

Submitted on 21 Feb 2019

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Oil & Gas Science and Technology – Rev. IFP, Vol. 58 (2003), No. 2, pp. 233-241
Copyright © 2003, Éditions Technip

Petroleum Geochemistry at the Dawn of the 21st Century

A.Y. Huc[1]

1 Institut français du pétrole, 1 et 4, avenue de Bois-Préau, 92852 Rueil-Malmaison Cedex - France
e-mail: a-yves.huc@ifp.fr

Résumé — La géochimie organique pétrolière à l'aube du XXIe siècle — Après un bref historique de l'évolution de la géochimie organique pétrolière au cours des dernières décennies, cet article résume l'état actuel de la recherche dans ce domaine et présente les orientations dictées par les besoins des opérateurs. Aujourd'hui, les acteurs industriels s'intéressent à des prospects de plus en plus profonds (haute pression, haute température), à l'exploration des grands fonds marins, à la recherche de gaz et à la production des énormes réserves d'huiles lourdes de la planète. Dans ce contexte, l'enjeu est de contribuer d'une manière efficace à la prédiction quantitative des réserves en huile et gaz à l'échelle d'un bassin (volume, composition, incertitudes) et à la prédiction de la qualité des fluides contenus dans un gisement, et cela par une meilleure connaissance des événements géochimiques affectant leur préservation et leur altération.

Abstract — Petroleum Geochemistry at the Dawn of the 21st Century *— Following a short review of the evolution of petroleum organic geochemistry in recent decades, this paper depicts the present status of research in the field and describes the guidelines dictated by the needs of the operators. Today, the industrial players are interested in increasingly deep prospects (high pressure, high temperature), in the exploration of the deep offshore, the search for gas and in the production of the planet's enormous heavy oil reserves. In this context, the challenge is to contribute effectively to the quantitative prediction of the oil and gas reserves at the scale of a basin (volume, composition, uncertainties) and to predict the quality of the fluids present in a reservoir, through a closer knowledge of the geochemical events affecting their preservation and their alteration.*

1 BACKGROUND AND TRENDS

1.1 Geochemistry

Geochemistry is a discipline devoted to the study of the chemistry of geological objects. Accordingly, it shares its analytical and experimental approach with chemistry, and its consideration of time and space with geology. This specificity makes geochemistry an irreplaceable investigative tool for all phenomena that involve transformations or interactions of matter in the geosphere.

The geochemist must constantly adapt his analytical and experimental approach to the complex and often poorly isolated systems that he studies (chemical reactor of the size of a sedimentary basin, heterogeneous medium, generally open system, out-of-equilibrium reactions, absence of steady state conditions, number and chemical structure of reactants and products difficult if not impossible to define accurately, representativity of samples, extrapolation to geological dimensions of experiments conducted at laboratory space-time scales, etc.). He must also develop concepts that incorporate the scale and geological history of the problems investigated.

To contend with the difficulties inherent in the chemistry of geological material (contamination, trace species, structural complexities of certain substances, etc), geochemists have been forced to develop experimental protocols and very high technology specific analytical techniques that are routinely used today in the petroleum industry.

The contribution of geochemistry is considerable for the petroleum geosciences because it supplies information that serves to define quantitative constraints in domains where they are often lacking. Geochemistry has been instrumental in defining the concept of "petroleum system", which no explorer can do without today.

1.2 Petroleum Geochemistry

Petroleum geochemistry is concerned with the geological evolution of the very substances making up the sedimentary rocks: formation of kerogen (fossilized sedimentary organic matter), followed by its decomposition into hydrocarbons; fluid migration; hydrocarbon transformations within the reservoirs; transformations of the mineral suite of the reservoirs and their petrophysical consequences. This kind of geochemistry serves petroleum exploration because it develops tools to describe, understand and predict:

- the formation of oil and gas and their migration;
- the thermal history of the basins and the composition of the fluids that have passed through them;
- the distribution of porosities in the drains and reservoirs.

It also serves for the characterization and production of the hydrocarbons fields, because it provides the keys to a closer understanding of the distribution of important properties at the scale of the reservoir: composition of the fluids, and petrophysical properties (porosity, permeability, wettability, irreducible saturation, resistivity, water geochemistry, etc.).

The tools of geochemistry are measurement techniques, as well as conceptual and numerical models constructed in particular through the extrapolation of the laboratory experiments.

1.3 Petroleum Organic Geochemistry

1.3.1 The Origin of Oil, Oil/Source Rock Correlations and Kinetic Formalism

Between 1970 and 1980, organic geochemists played a decisive role in the evolution of ideas concerning the origin of fossil hydrocarbons, and the identification and formalization of the chemical processes involved in the formation of oil and gas.

The modern vision of the "petroleum system" is based on the presence of ingredients (all) necessary for the presence of hydrocarbon accumulation, manely, a source rock, a reservoir rock, a cap rock and a trap, and also on the fact that these elements must fit into a dynamic scenario in which the major role is held by the source rock, whose thermal history (primarily controlled by its burial over time) orchestrates the "petroleum" life of the basin.

It is the recognition of this geochemical process of kinetic cracking (formalized as a first order kinetics) of the organic matter (kerogen) and the products of its transformation (primary and secondary cracking), present in the source rocks, which crystallized the idea of the "petroleum system". It also led to the development of the numerical basin models. It was at that time that the concept of "types" of kerogens, reflecting the variability of the properties of the fossilized organic matter in the sediments, and its fundamental role for the petroleum potential of the source rocks, was proposed.

One of the many benefits of the conceptual breakthrough achieved in this way was the availability to the industry of the Rock-Eval pyrolyzer which elegantly incorporated the knowledge about the properties of the sedimentary organic matter and its evolution through its thermal history, but above all, helped to translate them into simple and readily usable parameters for the exploration teams, such as the identification of potential "source rock" intervals, organic matter content, type and thermal maturity.

It was also at this time that molecular geochemistry was established by developing the concept of "biomarkers". These molecules, which are found in oils, have retained sufficiently well preserved chemical structures that help to affiliate them with biological molecules present in the tissues of living organisms whose remains generated the organic matter of the source rocks. The distribution of these

biomarkers can be considered as a genuine "fingerprint" for an oil. The comparison of this molecular imprint with those that can be obtained from organic extracts of source rocks existing in the same sedimentary basin then often enabled the explorer to recognize the actual source rock(s) that charge the reservoirs of a petroleum system (the "oil/source rock correlation" principle). The biomarkers, which, at the time of their fossilization, possess a spatial molecular configuration corresponding to those that are specific to the biomolecules from which they originated, also proved to be invaluable for estimating the thermal maturity of an oil. In fact, the unique initial molecular configuration is progressively replaced by a mixture of molecules due to the appearance of molecules of identical formulas but whose spatial configurations are thermodynamically favored (these molecules are either produced from the previous molecules by isomerization or added by liberation during the thermal cracking of the kerogen). The ratio of the molecules displaying a stable conformation increases through the thermal history of the source rock (formation of more stable and degradation of less stable molecules). This principle underlies the broad set of "molecular maturity parameters" available to the practitioner.

1.3.2 Understanding the Source Term, Quantifying and Predicting the Composition of the Hydrocarbons Formed

The second investigation phase (1980-1990) was aimed to better constrain the kinetic equations, which were crucially important for the basin models (1D, 2D), currently under development. The basic difficulty was to determine the quantitative kinetic parameters for organic matter (kerogens of different types and associated oils) which have an extremely complex chemical structure. The adaptation of "Rock-Eval" type "open system" pyrolyzers and the use of complementary "closed system" approaches, in anhydrous conditions or in the presence of water, helped to develop procedures to obtain these parameters, which have since been applied successfully by exploration professionals. It was also important to have a better handle on the composition of the fluids formed by cracking from the different "types" of source rocks, according to the advancement of the reaction. This made it possible, at any time in the history of the basin, to determine the composition of the fluids available for expulsion to the reservoir rocks. The results obtained, at the cost of huge experimental programs, are operational today, and have allowed the development of a new generation of operational numerical basin models (Temiscomp, Petromod, Basinmod, Sextant, etc.).

At the same time, it was necessary to understand the factors responsible for the existence of source rocks in the sedimentary stack of a basin and those controlling their regional extension, in order to reduce the risks of a permit and to supply information on the geological sections with a reasonable representation of the source term (the source rock) in the basin models. This led to major research efforts in the area of the sedimentology of source rocks.

1.3.3 Gas and Reservoir

In recent years, in response to major trends in the policy of the industry (greater interest in gas exploration, deep prospects, focus on production), the research programs were substantially refurbished:

- The formation of hydrocarbon gases, heretofore considered as by-products in the oil genesis schemes, was investigated *per se*.

  Significant breakthroughs were achieved in this field, particularly with the establishment of diagnostic methods and numerical models taking account of the variety of sources of natural gas: biogenic, produced by early or late cracking of kerogen, secondary cracking of the oil. The results of these studies, which have powerful implications for the appraisal of the gas potential of the basins, are currently undergoing validation. The displacement (migration) of the gas in the basins, which must account for aspects of physics that are negligible in the case of oil (solubility in water, diffusion) is the subject of ongoing research and the development of quantitative models. This specific behavior of gas is now included in certain four-phase (solid, water, oil, gas) basin simulators.

  One of the major risks in gas exploration is the presence of nonhydrocarbon species in variable amounts (CO_2, N_2, H_2S). In this area, where the knowledge is still rudimentary, emphasis is laid on the development of tools to diagnose the origin of these gases, and the design of the numerical models describing the formation of these gases, issued from the thermal decomposition of organic matter (CO_2, N_2, H_2S), and also from inorganic sources (mantle CO_2, thermal decomposition of carbonates, N_2 from ammoniacal nitrogen associated with clays, H_2S from low temperature bacterial sulfate reduction and from high temperature thermal sulfate reduction).
- The spatial change in the composition of the hydrocarbons present in the reservoirs is an irreplaceable source of information for understanding the supply history of a field: source of the oils, filling scenario (supply direction, mixture of several feeds, replacement of a pre-existing oil charge, etc). It also helps to constrain the state of connectivity of the reservoirs (compartmentalization) and thereby supplement the geometric information provided by geologic approaches. The aim is to identify a spatial heterogeneity of the composition (molecular imprint) of the oil which, if it exists, reflects the existence of permeability barriers that prevented the compositional homogenization since the charging time of the reservoir.

To do this, a panoply of analytical methods and data processings designed to identify the presence of an heterogeneity and thereby constrain the image of a field is available today to the industry under the generic term of "reservoir geochemistry".

- The presence of solid or semi-solid organic phases (asphalts, bitumens) is fairly widespread in petroleum reservoirs (Ghawar, the world's biggest field, contains an accumulation of bituminous material several tens of meters thick in its central portion). Methodologies designed to locate these bitumens and to identify their extension have been developed and applied successfully. The source of these bitumens is still the subject of investigations that have already demonstrated the wide variety of geological situations causing their appearance. The thermal cracking of oils in place is one of these processes. It is accompanied by the formation of a solid carbonaceous residue (pyrobitumen), which alters the properties of the reservoir (reduced porosity and permeability, modification of grain surface properties, migration of fine solid particles). The growing interest of explorers in deep prospects evidently increases the "pyrobitumen risk", making a better knowledge of these products and their formation more necessary than ever.
- A special effort has been mounted in recent years to found a genuine "geothermodynamics", aimed to integrate the geochemical approach and the thermodynamic approach for the study of petroleum fluids. Promising results have been obtained, as for example, the formalization of phase changes occurring during the migration of the hydrocarbons, which takes account of the composition of the fluids as calculated by the compositional kinetic models discussed earlier (this formalism is incorporated today in certain basin models like Temiscom). Research projects underway adapt (meshes, time steps) the thermodynamic calculations of the engineering type to the geological evolution of the reservoir fluids. The aim of this new approach is to provide explorers and producers with diagnostic and predictive tools concerning the properties of the hydrocarbons trapped.
- Our knowledge of source rocks has grown considerably thanks to recent studies taking account of the sedimentology of these deposits in terms of sequential analysis and cyclostratigraphy. It is now becoming possible to define, indeed to predict, the arrangement, volume and internal heterogeneity of these particular sedimentary intervals, as well as the type of associated organic matter. This is a major advance in the assessment of the basins: *a priori* forecasting of the petroleum potential, and spatial relations between source rocks and drains at the scale of the petroleum system.
- The Rock-Eval 6, marketed in 1996, represents an undisputed advance over its predecessors. Beyond its entirely reviewed technology (high temperature furnace, sample loading robot, infrared detectors, etc), the new functionalities it features help to obtain original supplementary parameters, as for example, the quantification of the carbonates.

1.4 The New Situation

1.4.1 Quantifying Migration and Constraining the Geological History of a Reservoir

The needs of the industry which, while maintaining strong demand on the reservoir and gas, fits into a context of enlargement of the permit area as well as interest in new types of prospects (high pressure/high temperature, deep offshore, production of the enormous heavy oil reserves, etc), demand a scientific and technical investment that is capable of addressing the revival of activity in exploration/production while creating new challenges for petroleum geochemistry. In this connection, the state of knowledge fairly clearly determines the projects that must absolutely be undertaken:

- exploration: quantitative prediction of oil and gas reserves at the scale of a basin (volume, composition, uncertainties);
- reservoir: geological events affecting the qualities of a reservoir and the preservation and alteration of the composition of the fluids it contains.

- The interest directed to deeply buried objectives increases the risk associated with the composition of the fluid anticipated in a prospect. The accuracy of the compositional numerical models must therefore be enhanced and the stability of the hydrocarbons in high pressure/high temperature conditions better constrained. It is therefore necessary to add, to the now conventional approaches of the laboratory simulations (pyrolysis), which are sometimes difficult to extrapolate to natural conditions for the composition of the fluids, a theoretical approach relying on molecular numerical modeling applied to representative chemical species, whereof the behavior could serve as a reference for "lumping" operations.
- The quantitative prediction of reserves in a petroleum system is closely linked today to our ability to formalize the hydrocarbon retention and migration mechanisms in the basins. In fact, although explicitly accounted for in present approaches, the real mobility of all the petroleum products and the characteristics of the displacements are poorly constrained in terms of physics. The physical displacement thresholds (for example, factors limiting expulsion from the source rock), the flow of petroleum products during the different steps of migration, the losses and modifications of composition caused, represent essentially empirical information today. The advent of the 3D basin models, one of their *raisons d'être* being ultimate volumetric quantification, must be accompanied by progress in this field. This makes it necessary to:
  - quantify (with help from the thermodynamic approach) the role of adsorption/desorption mechanisms along the

migration chain: kerogen-mineral surface-petroleum products for expulsion from the source rock, adsorption or insolubilization by thermodynamic disequilibrium along the sedimentary drains for secondary migration;
- make better use of information connected with natural tracers present in the oils and gases (trace metallic elements, rare gases, etc.);
- integrate at the basin scale, the information potentially contained in the hydrocarbon flows reaching the surface (surface shows, mud volcanoes, etc.).

- The preservation of the fluids in a trap over geological time scales is an important factor for analyzing exploration risks. A reservoir is basically a transitory object. Its existence at a given moment depends on the residence time in the trap, the quality of the trap, and the dispersion or alteration mechanisms at play. The determination of the residence time is based on the possibility of dating the charging(s) by the hydrocarbons. This chronology is determined today:
  - from the results of numerical basin models (definition of the "critical moment" at which the hydrocarbons begin to reach the trap) which, to be usable, imply a good knowledge of the geological history of the source rock (burial sequences, heat flux history). The existence of erosional phases, a long history or poorly constrained thermal regimes, induce inaccuracy that sometimes makes the model unusable;
  - and whenever possible, from absolute dating of the start of filling, presumed to arrest the mineral diagenesis (for example, dating of the latest diagenetic shales by the K/Ar method).

  It may be observed that no constraint is supplied by the fluid itself, and this is particularly problematic today insofar as the fluid present may not be the one emplaced during the last trap filling phase, which is the one dated by the K/Ar method.

  The use (hitherto unexplored) of certain radiogenic elements, for example, iodine 129 and xenon 129, which tend to display affinities with mobile hydrocarbons, and which could have descended from radioactive isotopes present in the source rocks (U, Th), could serve as a basis for an original methodology for dating the reservoir charging. Other "natural clocks" are also conceivable, all associated with radioactive decays yielding "daughter" isotopes like ^{4}He, ^{40}Ar, ^{187}O. One could understand the importance of developing a method for direct dating of the emplacement of hydrocarbon accumulations and its integration within the dynamic framework of the petroleum system: fitting of hydrocarbon formation models, information on the time-table of migration episodes, grouping of fields by supply periods, relationship to the structural history (activation of migration paths, temporal correlation with families of traps).

- The changes in composition of the fluids occurring in the traps during geological timescales have strong implications for the commercial value of the hydrocarbons of a reservoir as well as the conditions of their production. The knowledge of the mechanisms involved and their prediction at the regional scale thus appear to be necessary for taking industrial decisions. In this area of fluid alteration, which becomes crucial in a context of deep exploration, an approach that combines thermochemistry and experiments, supplemented by field data, should permit a decisive breakthrough. Many factors affect the composition of the fluids, and some of them are very poorly known. The thermal reduction of sulfates, for example, is a mechanism identified in numerous fields (deep Lacq, North Caspian, Abu Dhabi, Alberta, Gulf Coast) and which, in the presence of anhydrite, causes the oxidation of the hydrocarbons and the formation of H_2S. The economic consequences are considerable due to the alteration of the reserves and the presence of sour gas in the fields. Our knowledge about this process is embryonic and is mainly based on naturalistic observations. The reactions involved are not fully established, realistic experimental attempts have hitherto failed, and prediction remains empirical. Note that in this connection, the interactions occurring in the subsurface between hydrocarbons and sulfur species, ignored for many years, are becoming a research subject with many applications: prediction of the oil sulfur content, prediction of the presence of H_2S in the reservoirs.

  As opposed to deep objectives, shallow fields are subject to alterations by the action of bacteria, and this for example, is one of the processes which led to the Alberta and Orinoco heavy crudes and tar sands. This widely described biodegradation has never been the subject of a quantitative treatment due to the difficulty of modeling the biological factors, especially when they concern yet incompletely identified organisms, living in unusual environments. This represents a whole field of investigation barely touched by preliminary studies, which have nonetheless demonstrated the vast potential of coupling geochemistry with microbiology. Considerable advances achieved recently in microbiology (molecular genetics, study of "extremophiles") are opening attractive prospects for the study of the biodegradation of oils in reservoir conditions. The prediction of the spatial variation of composition and properties of the heavy oils in a reservoir would particularly help to optimize the architecture of the horizontal drains used for the cold production of these fields. In this respect, the understanding of the origin of gases (products of the biodegradation itself?) often dissolved in heavy oils is of prime importance because these gases impacted the natural foaming capacity of the oils and therefore the conditions of production.

- The need for a more accurate characterization of the oils produced during the history of a field, in order to anticipate water inflows, to identify the possible participation of a neighboring compartment, to better quantify the allocations during a multiple completion and sometimes to locate damage on a casing, leads the geochemist to place his molecular imprint techniques at the disposal of the producer. The geochemistry of organic deposits (paraffins, asphaltenes, diamandoids), actively contributes to the research effort aimed to explain and predict (at the exploration and production scale) the risks associated with the appearance of these mechanisms. "Reservoir geochemistry" and "Production geochemistry" are largely operational today and mobilize many geochemists in the oil companies.

This brief review of petroleum organic geochemistry and its evolution over the years, driven by advances in knowledge, technology and industrial orientations, illustrates the important technical role that it can and must play in taking decisions and reducing the risks during exploration, reservoir characterization and production. The considerable expertise of organic geochemistry, concerning the knowledge of hydrocarbons, their reactivity and their role in the biogeological cycle, must, even more than in the past, be placed at the service of public demand in the field of environmental conservation. Helping the operators to better evaluate the impact of petroleum activities and, alongside them, participating in installing the right prevention and remediation methods, should more than ever be included in the missions assigned to geochemists.

2 A TIMELY CONCERN INVOLVING GEOCHEMISTRY: THE DEEP OFFSHORE

Most of the oil majors are involved today in the exploration and production of fields in the deep ocean depths. The high cost of the operations reduces the number of boreholes drilled, and demands better predictability of the prospects with a minimum quantity of information. Many risks are at least partly associated with geochemistry (viable petroleum system, fluid composition, biodegradation, use of the information offered by surface shows, organic deposits during production, etc.). Reducing these risks hence demands rapid progress in areas still inadequately known, such as the habitat of source rocks in deep offshore conditions, the biodegradation of oils or the use of surface shows.

2.1 Biodegradation

The biodegradation of oils is currently one of the major risks in deep offshore operations. This mechanism of oil alteration by the action of bacteria is reflected by a decrease in the API density of the oils and often by an increase in their *in situ* viscosity. The merchant value of the oil and the insufficient yields can accordingly compromise the economic value of a discovery. Our knowledge of this mechanism is largely inadequate today in view of the industrial challenges.

What we know:

By definition, biodegradation demands the presence of active microorganisms, at least during a part of the geological history of a reservoir. Hence temperature is a crucial factor, and the experience gained makes it possible today to propose guides to the limits beyond which biodegradation is a minor risk (75°C) or none at all (95°C). The consideration of the temperature of a field, or even better, the modeling of the regional thermal history, is hence an indispensable prerequisite to assessing the "biodegradation" risk in exploration.

What we do not know:

Conventionally speaking, biodegradation was considered as the result of the activity of aerobic bacteria in the presence of oxygen supplied by meteoric waters. The latest studies tend to show that the alteration of the oil is probably the result of anaerobic organisms. It is extremely important to verify this new concept, because the circulation of meteoric waters, the only ones that could contain oxygen, in contact with the oil accumulation, would become a non necessary prerequisite. This does not necessarily mean that the circulation of an aquifer is not instrumental to renew the nutrients and the electron acceptors, while preventing the self-poisoning of the system by eliminating the toxic products resulting from microbial activity. The microbial mechanisms involved in this anaerobic degradation (sulfate-reduction, fermentation, methanogenesis), the electron acceptors necessary (sulfates, metals, etc.), and the limiting factors, other than temperature (nutrients, trace elements, salinity?) remain theoretical. Basically, the kinetics of the mechanism is unknown. A better prediction of biodegradation, relying on a deterministic model, therefore depends on the answers provided to these questions.

In this respect, basin models should ultimately be enriched with biodegradation modules. Already, the functionalities of these models, explicitly taking account of the hydrodynamism, the thermal history, the formation of the hydrocarbons and their composition, help to calculate a number of boundary conditions of the prospects and to assess the age of filling of the fields, parameters whose knowledge contributes to a better understanding of the risks associated with biodegradation, or to the effective testing of the assumptions made.

2.2 Source Rocks

The presence, distribution and quality of the source rocks condition the viability and effectiveness of a petroleum

system. Beyond the deep sea extension of source rocks already accounted by the models recognized in the systems explored in shallower depths (*i.e.* lacustrine source rocks of Neocomian and Barremian age of the Western African and Brazilian margins, for example), the problem of the occurrence of source rocks deposited under a large depth of water must be faced, with even greater insistence with increasing distance form the continental shelf. The accumulation of organic matter in a deep setting is still little investigated, but seems possible. For instance sediments rich in marine organic matter have been deposited since the Late Miocene offshore Namibia, with a thickness of up to tens of meter, and to water depths exceeding 3000 m. A type III source rock model associated with Miocene low sea level deposits has been proposed for the Mahakam delta system (Indonesia) in order to explain the discoveries made in the deep Strait of Macassar.

2.3 Surface Shows

The seepage of hydrocarbons on the surface (surface shows) has always been regarded with close attention by explorers because they offer invaluable indications at the regional scale concerning the existence of an active petroleum system. The geochemistry of these surface shows has never truly been developed and its practical application (surface geochemistry) mainly consists in systematically mapping surface manifestations reflecting the arrival of hydrocarbons, using different direct techniques (for example, macro-show records, analysis of soil or sediment gases) and indirect methods (*e.g.* microbiology). This prospecting technique, often challenged when addressing traces, recently enjoyed a revival of interest aroused by the deep sea exploration of relatively shallow prospects, of which the low grade cap rocks permits substantial dismigration. Extensive reconnaissance surveys of the shows, by coring, have thus been carried out in recent years. In such situations, however, it is clear that not only the mapping but also the composition of the fluids dissipated at the surface potentially offer invaluable information to anticipate the quality of the oils in the reservoir. Technological breakthroughs in the field of sampling, and conceptual breakthroughs in the interpretation of the composition of the shows, are necessary to make the most of this information.

2.4. Organic Deposits

The circulation of oceanic waters at the global scale involves downwelling of the polar waters towards the deep ocean floor and their rise in the tropical and equatorial upwelling zones. The consequence of this hydrodynamic system is the low temperature (~4°C) of the ocean floor waters. The production facilities installed in great depths are hence exposed to the formation of temperature sensitive organic deposits like paraffins or waxes. Hence the prediction of the "paraffin" risk is a major economic challenge, considering that remediation operations cost up to twenty times more below 2000 m. The genetic origin of the oils containing these paraffinic molecules, often combined with type III source rocks (continental organic matter) and type I rocks (lacustrine organic matter) is therefore important to take into account in an early stage of field assessment. Besides, some oils may contain very high molecular weight paraffins (up to 100 carbon atoms) which already raise problems by obstructing the production facilities in conventional operating conditions. The origin of these molecules, which mainly appear to be inherited from lacustrine source rocks (type I), is far from established. Recent analytical advances (high temperature chromatography) which have demonstrated the existence of these hydrocarbons, and the beginning of their identification, have shown that their composition, unlike the lower molecular weight paraffins primarily formed of *n*-alkanes (linear hydrocarbons) was complex and often included branched (and cyclic?) molecules, sometimes predominant. The thermodynamic properties of these compounds are still unknown, making the existing paraffin (*n*-paraffins) precipitation models inappropriate. A research effort addressing the characterization and origin of these molecules, as well their thermodynamic properties, hence appears to be indispensable.

Over and above the technology employed, the "deep offshore" challenge has only been faced thanks to the concepts and geological models developed in recent decades, to which geochemistry has made a powerful contribution. However, as stated earlier, the specificities of the petroleum systems concerned, and the conditions of existence of the deposits and their production, demand additions to this body of knowledge and the rapid availability of prediction guides and tools for the operators, unfortunately still lacking.

ACKNOWLEDGEMENTS

This document considerably benefited from the critical reading and the constructive comments of Mireille Vandenbroucke and Alain Prinzhofer.

REFERENCES

General Readings

Bordenave, M.L. (1993) *Applied Petroleum Geochemistry*, Éditions Technip, Paris.

Durand, B. (1980) *Kerogen: Insoluble Organic Matter from Sedimentary Rocks*, Éditions Technip, Paris.

Engel, M.H. and Macko, S.A. (1993) *Organic Geochemistry, Principles and Applications*, Plenum Press, New York and London.

Hunt, J.M. (1995) *Petroleum Geochemistry and Geology*, W.H. Freeman and Company, New York, 2nd edition.

Tissot, B.P. and Welte, D.H. (1984) *Petroleum Formation and Occurrence*, 2nd edition, Springer-Verlag.

Source Rocks

Demaison, G. and Moore, G.T. (1980) Anoxic Environments and Oil Source Bed Genesis. *AAPG Bull*., **64**, 1179-1209.

Duval, B.C., Cramez, C.and Vail, P.R. (1998) Stratigraphic Cycles and Major Marine Source Rocks. In *Mesozoic and Cenozoic Sequence Stratigraphy Of European Basins*, De Graciansky, P.C., Hardenbol, J., Jacquin, T. and Vail, P.R. eds., *SEPM Special Publication*, **60**, 43-51.

Hedges, J.I. and Oades, J.M. (1997) Comparative Organic Geochemistries of Soils and Marine Sediments. *Organic Geochemistry*, **27**, 319-361.

Huc, A.Y. (1988) Sedimentology of Organic Matter. *Dahlem Workshop Report on «Humic Substances and their Role in the Environment»*, F.H. Frimmel and R.F. Christman eds., John Wiley and Sons Ltd, Chichester, 1988, 215-243.

Huc, A.Y. (1995) Paleogeography, Paleoclimate, and Source Rocks. *AAPG Studies in Geology*, **40**, Tulsa, USA.

Huc, A.Y., Vandenbroucke, M.. Bertrand, P., Gayet, J.and Stow, D.A.V. (2001) Organic Sedimentation in Deep Offshore Settings: The Quaternary Sediments Approach. *Marine and Petroleum Geology*, **18**, 513-517.

Katz, B.J. and Pratt, L. (1993) : Source Rocks in a Sequence Stratigraphic Framework. *AAPG Studies in Geology*, **37**.

Katz, B.J. (1995) *Petroleum Source Rocks*, Springer-Verlag.

Tyson, R.V. (1995) *Sedimentary Organic Matter*, Chapman and Hall, London.

Kinetics and Modeling of Hydrocarbon Composition

Behar, F., Vandenbroucke, M., Tang, Y., Marquis, F.and Espitalié, J. (1997) Thermal Cracking of Kerogen in Open and Closed Systems: Determination of Kinetic Parameters and Stoichiometric Coefficients for Oil and Gas Generation. *Org. Geochem*., **26**, 5/6, 321-339.

Braun, R.L. and Burnham, A.K. (1990) Mathematical Model of Oil Generation, Degradation, and Expulsion. *Energy and Fuels*, **4**, 132-146.

Espitale, J., Ungerer, P., Irwin, H. and Marquis, F. (1988) Primary Cracking of Kerogens. Experimenting and Modelling C_1, C_2-C_5, C_6-C_{14} and C_{14+} Classes of Hydrocarbons Formed. *Org. Geochem*., **13**, 893-899.

Lewan, M.D. (1997) Experiments on the Role of Water in Petroleum Formation. *Geochimica and Cosmochimica Acta*, **61,** 3691-3723.

McNeil, R.I. and BeMent, W.O. (1996) Thermal Stability of Hydrocarbons: Laboratory Criteria and Field Examples. *Energy and Fuels*, **10**, 60-67.

Pepper, A.S. and Corvit, P.J. (1995) Simple Kinetic Models of Petroleum Formation. Part I: Oil and Gas Generation from Kerogen. *Marine and Petroleum Geology*, **12**, 3, 291-319.

Pepper, A.S. and Dodd, T.A. (1995) Simple Kinetic Models of Petroleum Formation. Part I: Oil and Gas Cracking. *Marine and Petroleum Geology*, **12**, 3, 321-340.

Sweeney, J.J., Burnham, A.K. and Braun, R.L. (1987) A Model of Hydrocarbon Generation from Type I Kerogen: Application to Uinta Basin, Utah. *AAPG Bull*., **71**, 8, 967-985.

Tissot, B.P. and Espitalié, J. (1975) L'évolution de la matière organique des sédiments : application d'une simulation mathématique. *Revue de l'Institut français dupPétrole*, **30**, 743-777.

Ungerer, P. and Pelet, R. (1987) Extrapolation of Kinetics of Oil and Gas Formation from Laboratory Experiments to Sedimentary Basins. *Nature*, **327,** 52-54.

Ungerer, P. (1990) Kinetic Modelling of Oil Formation and Expulsion. *Org. Geochem.*, **16**, 1-3, 1-25.

Migration of Hydrocarbons

Doligez, B. (1987) Migration of Hydrocarbons in Sedimentary Basins. *Colloques et séminaires*, 45, Éditions Technip, Paris.

England, W.A. and Fleet, A.J. (1991) Petroleum Migration. *Geological Society Special Publication*, 59, Geological Society, London.

Migration Tracers

Ballentine, C.J. and O'Nions, R.K.(1994 The Use of Natural He, Ne and Ar Isotopes to Study Hydrocarbon-Related Fluid Provenance, Migration and Mass Balance in Sedimentary Basins. *Geofluids*, **78**, 347-361.

Battani, A., Sarda, P. and Prinzhofer, A. (2000) Basin Scale Natural Gas Source, Migration and Trapping Traced by Noble Gases and Major Elements: The Pakistan Indus Basin. *Earth Planet. Sci. Lett.*, **181,** 1-2, 229-249.

Bosch, A. and Mazor, E.(1988) Natural Gas Association with Water and Oil as Depicted by Atmospheric Noble Gases: Case Study From the Southeastern Mediterranean Coastal Plain. *Earth Planet. Sci. Lett.*, **87**, 338-346.

Zartman, R.E, Wasserburg, G.J. and Reynolds, J.H. (1961) Helium and Argon in Some Natural Gases. *Journal of Geophysical Research*, **66,** 277-306.

Basin Modeling

Burrus, J. (1997) Contribution à l'étude du fonctionnement des systèmes pétroliers : apport d'une modélisation bidimentionnelle. *PhD Thesis*, École des Mines de Paris.

Rudkiewicz, J.L, Penteado, H.L.B, Vear, A., Vandenbroucke, M., Brigaud, F., Wendebourg, J. and Düppenbecker, S. (2000) Integrated Basin Modeling Helps to Decipher Petroleum Systems. In *AAPG Memoir*, 73, *"Petroleum Systems of the South Atlantic Margins"*, 27-40.

Schneider, F., Wolf, S., Faille, I. and Pot, D. (2000) A 3D Model for Hydrocarbon Potential Evaluation: Application to Congo Offshore. *Oil & Gas Science and Technology - Rev. IFP*, **55**, 3-13.

Ungerer, P., Burrus, J., Doligez, B., Chenet, P.Y. and Bessis, F. (1990) Basin Evaluation by Integrated 2D Modelling of Heat Transfer, Fluid Flow, Hydrocarbon Generation and Migration. *AAPG Bull*., **74,** 309-335.

Welte, D.H., Horsfield and B., Baker, D.R. (1997) *Petroleum and Basin Evolution. Insights from Petroleum Geochemistry, Geology and Basin Modeling*, Springer-Verlag, Berlin, Heildeberg.

Molecular Markers

Connan, J. (1987) Regard sur la géochimie organique pétrolière d'aujourd'hui. *Bulletin des centres de recherches Exploration-Production Elf-Aquitaine*, **11,** 2, 181-219.

Moldowan, J.M., Albrecht, P. and Philp, R.P. (1992) *Biological Markers in Sediments and Petroleum*, Prentice Hall, New Jersey, USA.

Peters, K.E. and Moldowan, J.M. (1993) *The Biomarkers Guide*, Prentice Hall, New Jersey, USA.

Geochemistry of Gases

Clayton, C. (1991) Carbon Isotope Fractionation During Natural Gas Generation from Kerogen. *MarineaAnd Petroleum Geology*, **8,** 232-240.

Cramer, B., Poelchau, H.S., Gerling, P., Lopatin, N.V. and Littke, R. (1999) Methane Released from Groundwater: The Source of Natural Gas Accumulations in Northern West Siberia. *Marine and Petrol. Geol*., **16**, 225-244.

Prinzhofer, A. and Huc, A.Y. (1995) Genetic and Post-Genetic Molecular and Isotopic Fractionations in Natural Gases. *Chemical Geology*, **126**, 281-290.

Prinzhofer, A. and Pernaton, E. (1997) Isotopically Light Methane in Natural Gases: Bacterial Imprint or Segregative Migration? *Chemical Geology*, **142**, 193-200.

Prinzhofer, A., Mello, M.R. and Takaki, T. (2000) Geochemical Characterization of Natural Gas: A Physical Multivariable Approach and its Applications in Maturity and Migration Estimates. *AAPG Bull*., **84**, 8, 1152-1172.

Ricchiuto, T. and Schoell, M. (1988) Origin of Natural Gases in the Apulian Basin in South Italy: A Case History of Mixing of Gases of Deep and Shallow Origin. In *Advances in Organic Geochemistry*, Mattavelli, L. and Novelli, L. eds., 311-318.

Schoell, M. (1983) Genetic Characterization of Natural Gases. *AAPG Bull*., **67**, 12, 2225-2238.

Alteration of Hydrocarbons in Reservoirs

Anisimov, L.A. (1978) Conditions of Abiogenic Reduction of Sulfates in Oil and Gas Bearing Basins. *Geokhimiya*, **1**, 1692-1702.

Behar, F., Ungerer, P., Kressman, S., Rudkiewicz, J.L. (1991) Thermal Evolution of Crude Oils in Sedimentary Basins: Experimental Simulation in a Confined System and Kinetic Modeling. *Revue de l'Institut français du pétrole*, **46,** 2, 151-181.

Bernard, F., Connan, J. and Magot, M. (1992) Indigenous Microorganisms in Connate Water of Many Oil Fields: A New Tool in Exploration and Production Techniques. *SPE, Paper 24811*.

Connan, J. (1984) *Biodegradation of Crude Oils in Reservoirs, Advances in Petroleum Geochemistry*, eds. J. Brooks and Welte, **1**, 299-335.

Cross, M. (1999) Rates and Mechanisms of Thermochemical Sulphate Reduction. *PhD Thesis*, University of Manchester.

Deroo, G., Tissot, B., Mc Grossan, R.G. and Der, F. (1974) Geochemistry of Heavy Oils of Alberta, Oil Sand, Fuel of the Future. *Can. Soc. Pet. Geol. Mem.*, **3**, 148-189.

Goldstein, T.P. and Aizenshtat, Z. (1994) Thermochemical Sulfate Reduction, A Review. *J. Therm. Anal.*, **42,** 241-290.

Hanin, S., Adam, P., Kowalewski, I., Huc, A.Y., Carpentier, B. and Albrecht, P. (2002) Bridgehead Alkylated 2-Thiaadamantanes: A Novel Markers for Sulfurisation Processes Occurring under High Thermal Stress in Deep Petroleum Reservoirs. *J. Chem. Soc. Chem. Commun., 1750-1751*.

Huc, A.Y., Nederlof, P., Debarre, R., Carpentier, B., Boussafir, S. and Laggoun-Desfarge, F. (2000) Pyrobitumen Occurrence and Formation in a Cambro-Ordovician Sandstone Reservoir, Fahud Salt Basin, North Oman. *Chemical Geology*, **168**, 99-112.

Lafargue, E. and Barker, C. (1988) Effect of Water Washing on Crude Oil Composition. *AAPG Bull*., **72**, 263-276.

Machel, H.G. (2001) Bacterial and Thermochemical Sulfate Reduction in Diagenesis Settings-Old and New Insights. *Sediment. Geol.*, **140**, 143-175.

Orr, W.L. (1977) Geologic and Geochemical Controls on the Distribution of Hydrogen Sulfide in Natural Gas. In *Advances In Organic Geochemistry*, R. Campo and J. Goni eds., Enadimsa, 571-597.

Schenk, H.J. and Horsfield, B. (1995) Simulating the Conversion of Oil into Gas in Reservoir: The Influence of Frequency Factors on Kinetics Predictions. *17th International Meeting on Organic Geochemistry*, 4-8 September, San Sebastian, Spain, AIGOA, 1102-1113.

Winters, J.C. and Williams, J.A. (1969) Microbiological Alteration of Crude Oil in the Reservoir. Symposium on Petroleum Transformation in Geological Environments. *Div. Pet. Chem. Am. Chem. Soc., Paper Petro.*, **86**, E22-E31.

Woorden, R.H., Smalley, P.C. and Oxtoby, N.H. (1995) Gas Souring by Thermochemical Sulfate Reduction at 140°C. *AAPG Bull*., **79**, 6, 854-863.

Reservoir Geochemistry

Cubit, J.M. and England, W.A. (1995) The Geochemistry of Reservoirs. *Geological Society Special Publication*, 86, Alden Press, Oxford, UK.

England, W.A. (1990) The Organic Geochemistry of Petroleum Reservoirs. *Organic Geochemistry*, **16,** 1-3, 415-425.

Fowler, M.G. and Peters, K.E. (2002) Application of Petroleum Geochemistry to Exploration and Reservoir Management. *Organic Geochemistry*, **33,** 1, 5-36.

Huc, A.Y., Carpentier, B., Guehenneux, G. and Magnier, C. (1999) Geochemistry in a Reservoir and Production Perspective. *SPE, Paper* 53146.

Kaufman, R.L., Ahmed, A.S. and Elsinger, R.L. (1990) Gas Chromatography as a Development and Production Tool for Fingerprinting Oils from Individual Reservoirs: Applications in the Gulf Coast Of Mexico. *Gulf Coast Section of The Society of Economic Paleontologists and Mineralogists Foundation, 9th Annual Research Conference Proceedings*, 263-282.

Lomando, A.J. (1992) The Influence of Solid Reservoir Bitumen on Reservoir Quality. *AAPG Bull.*, **76,** 8, 1137-1152.

Smalley, P.C. and England, W.A. (1992) Assessing Reservoir Compartimentalisation During Field Appraisal: How Geochemistry Can Help. *SPE, Paper 25005.*

Rock-Eval

Behar, F., Beaumont, V. and Penteado, H. (2001) Rock-Eval 6 Technology: Performances and Developments. *Revue de l'Institut français du Pétrole*, **56,** 111-134.

Espitalié, J., Laporte, J.L., Madec, M., Marquis, F., Leplat P. and Paulet, J. (1977) Méthode rapide de caractérisation des roches mères, de leur potentiel pétrolier et de leur degré d'évolution. *Revue de l'Institut français du pétrole*, **32**, 23-45.

Espitalié, J., Marquis, F. and Barsony, I. (1984) *Geochemical Logging; in Analytical Pyrolysis-Techniques and Applications*, K.J. Voorhees ed., Boston, Butterworth, 276-304.

Lafargue, E., Marquis, F. and Pillot, D. (1998) Rock-Eval 6 Applications in Hydrocarbon Exploration, Production, and Soil Contamination Studies. *Revue de l'Institut français du pétrole*, **53**, 4, 421-437.

Peters, K. (1986) Guidelines for Evaluating Petroleum Source Rock Using Programmed Pyrolysis. *AAPG Bull*., **70**, 318-329.

Final manuscript received in January 2003