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Scientific paper

# Organic Geochemistry in the Rationalization of Oil and Gas **Exploration and Production**

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Key words: Source rocks, Organic facies, Maturity, Petroleum alteration.

#### Abstract

Organic geochemistry, a comparatively young scientific discipline integrated into the basic geological model can affect the reduction of oil and gas exploration risks. The correct use of these data, particularly on a regional level, so-called geochemical mapping, has been successful in discovering the hydrocarbon reservoir. By selecting relevant geochemical parameters (source, migration, temperature regime) it has been possible to obtain particulary useful information about marginal, markedly unfavourable parts of the basin, where exploration costs are very high.

The geochemical results are used as correlation parameters, not only in exploration, but also during hydrocarbon production. They enable determination of reservoir destruction, as well as composition change of reservoir hydrocarbons.

However, the combination of all geological and geophysical methods and techniques in the course of exploration process results in the maximum effect of geochemical prospection.

## 1. INTRODUCTION

Oil and gas exploration is a complex process requiring the application of numerous geological, geophysical and geochemical methods. Every method has certain disadvantages and its proper selection is imperative to gain the maximum benefits and reduce exploration risks (MURRIS, 1984).

The old theory that oil is so widespead in sedimentary basins that it "generates everywhere and migrates anywhere" has been abandoned long ago. The mechanisms of hydrocarbon generation, migration and accumulation are well known today and are considered universal, but depend on basic facts, i.e. sources, reservoirs, cap rocks and traps (DEMAISON, 1984).

Geochemistry, as a relatively new scientific discipline, is primarily used in the process of exploration for hydrocarbons, since it enables the determination of source rocks, evaluation of their generating potential, efficiency of expulsion and detection of migration phenomena. The genetic characterization of reservoir hydrocarbons is achieved by the application of geo-



Ključne riječi: matične stijene, organski facijes, zrelost, izmjenjenost ugljikovodika.

1 Tab.

### Sažetak

Organska geokemija, relativno mlada znanstvena disciplina, integrirana u osnovni geološki model može utjecati na smanjenje rizika pri istraživanju nafte i plina. Ispravna primjena ovih podataka posebno na regionalnom planu, tzv. geokemijsko kartiranje, pokazalo je uspjeh u otkrivanju ležišta ugljikovodika. Izborom relevantnih geokemijskih parametara (izvor, migracija, temperaturni režim), moguće je dobiti posebno korisne informacije u graničnim, izrazito nepovoljnim dijelovima bazena, u kojima su cijene istraživanja vrlo visoke.

Osim u istraživanju i tijekom proizvodnje ugljikovodika koriste se geokemijski rezultati kao korelacijski parametri. Njima je moguće također utvrditi destrukciju ležišta, kao i izmjenu sastava ležišnih ugljikovodika.

Maksimalan učinak geokemijske prospekcije postiže se kombinacijom svih geoloških i geofizičkih metoda i tehnika u istražnom procesu.

chemical analyses, as well as by their correlation, identification of alteration and transformation of hydrocarbons within accumulations.

An objective evaluation of the role and application of geochemistry is possible today and its importance in the hydrocarbon exploration process has also been defined. Greater efficiency in the search for hydrocarbon resources and discovery of hydrocarbon reservoirs can be achieved by incorporating geochemical data into basic geological models.

## 2. RESULTS AND DISCUSSION

The paper presents the results of geochemical investigation carried out to date in the Croatian part of the Pannonian basin, in the Dinarides and in the Adriatic offshore. The main oil and gas fields in Croatia are located in the south-western, marginal part of the Pannonian basin (Fig. 1). Research included the identification of source rocks, genetic characterization of hydrocarbons within accumulations, determination of alteration and destruction of hydrocarbons within reservoirs and explanation of the mechanisms for the appearance of high concentrations of chemically inorganic con-

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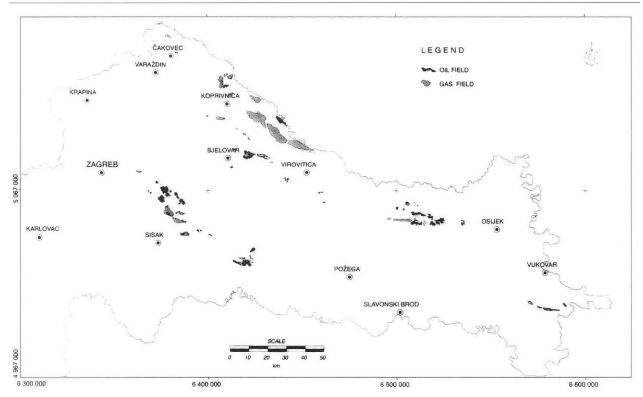


Fig. 1 Index map with oil and gas fields in the Croatian part of the Pannonian basin.

DEPRESSION	MURA	DRAVA west	DRAVA east	SAVA
Depth (m)	>3000	>3000	>2100	>2300
Thickness (m)	200-500	200-500	200-300	100-300
Age	Mid. to Low. Miocene	Mid. to Low. Miocene, Mesozoic	Mid. Miocene	Mid. to Low. Miocene
Lithology	mudstone, siltites	mudstone, siltites	marlstone	marly limestone limy marls
TOC (%) average	0.9	1.5	1.2	1.4
Kerogen type	III - (II)	III - (II)	II - (III)	II - (III)
Maturity (% $R_0$ )	0.7 - 1.8	0.5 - 2.2	0.4 - 0.9	0.6 - 0.8
$\delta^{13}C_{PDB}$ (%)	-25.8 to -28.7	-26.3 to -28.5	-22.3 to -26.2	-21.6 to -26.6

Table 1 Basic Source Rock Quality Data in the Croatian part of the Pannonian Basin.

stituents in gas and gas-condensate fields of the Mura and Drava depression.

In the Croatian part of the Pannonian basin, source rocks were identified in a large number of wells by geochemical analyses and the regional determination of sedimentation facies (Table 1). Source rocks are predominantly marly limestones and limy marls of Lower to Middle Miocene age, while bacteria-degraded algal matter and terrigenous lipids are the precursors of petroleum<sup>1</sup>.

Recent investigation established that thick, compact dark-gray to black carbonaceous fossiliferous mudstones, clayey mudstones and siltstones of Lower Miocene and Mesozoic age at depths exceeding 3,000 m in the Mura depression and in the western part of the Drava depression represent source rocks in these areas (Figs. 2 and 3). Terrestrial organic matter and longer exposure to high temperatures resulted in generation of gas-condensate and dry thermogenic gases (BARIĆ et al., 1990, 1996).

Geochemical characterization of hydrocarbons within the reservoirs (Fig. 4) confirmed that they genetically belong to the determined source rocks and at the same time established the relatively short source rock - accu-

<sup>&</sup>lt;sup>1</sup> Cornford, C. (1989): Petroleum Geochemistry of the Pannonian Basin.- Unpublished ECL Report, INA-Naftaplin Archive, Zagreb.

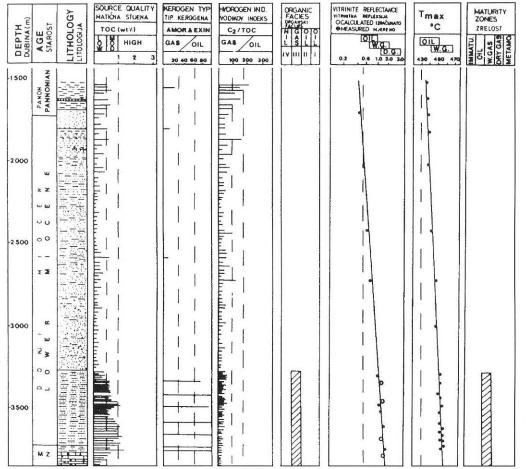


Fig. 2 Organic facies and maturity log of Mura-2 well (after BARIĆ et al., 1996).

mulation migration paths. The investigation confirmed that in some oil fields of the East Drava depression source rocks, fine-grained pellitic sediments also represent cap rocks, and in certain localities they simultaneously act as source and reservoir rocks due to secondary porosity (HERNITZ et al., 1995). Current results indicate that during further exploration in the Croatian part of the Pannonian basin the type of hydrocarbons can be predicted. The generating potential and volume of the determined source rocks are mostly in agreement with the size of the existing hydrocarbon accumulation. Geological and geochemi-

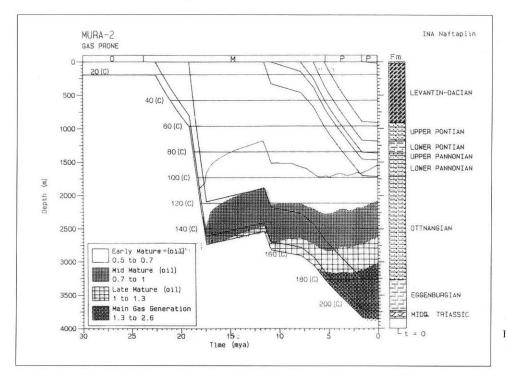


Fig. 3 Burial history curves for Mura-2 well (after BARIĆ et al., 1996).

LEGEND: +F - 70 B Mol 0 Kal -60 XM  $\triangle$ StG δ<sup>13</sup>C<sub>CH4</sub> [ppt] KB -50 1 Lč Mič -40 2.0 0 Lšn 0 Di -4.0 -30 TT(m) Okr TT(h)  $\square$ Gr -20 Leg -250 -200 -150 -100 -50 X Go δD<sub>CH4</sub> (ppt)

Fig. 4 Isotope ratios of natural gases in the western part of the Drava depression (genetic zonation after SCHOELL, 1983).

cal reinterpretation of certain areas has to be undertaken to evaluate further prospectivity of exploration areas and greater attention has to be paid to those localities in which source-rocks have been determined, but in whose vicinity hydrocarbon reservoirs have not been discovered.

Source rock sequences have been determined in deep exploration wells of the Adriatic offshore,

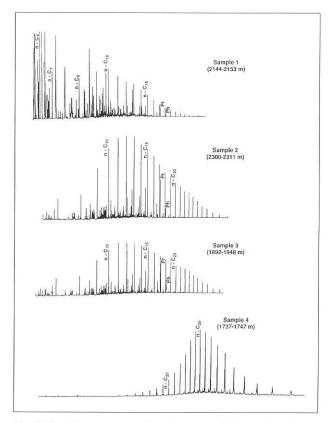


Fig. 6 Gas chromatograms of condensates and bitumen in the Mura depression.

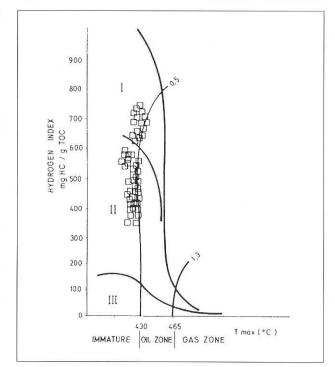


Fig. 5 HI - T<sub>max</sub> diagram showing types and maturity of kerogen in the Dugi Otok Basin (Adriatic offshore).

although their regional distribution has not been fully defined. The organic matter in those sediments has not yet reached the stage of maturity, i.e. the oil window (Fig. 5). Poor physical characteristics of cap rocks, which permit migration of hydrocarbons, are a special problem, as bituminous impregnations and bitumenfilled stylolites confirm (BARIĆ et al., 1988).

Geochemical analyses were used for determination of the alteration of reservoir hydrocarbons. The most frequent cases are caused by processes of evaporative fractionation (THOMPSON, 1987; SILVERMAN, 1965). Fractionation phenomenon caused by structural deformation or a low degree of regional seal effectiveness (DEMAISON & HUIZINGA, 1991) are manifested in the separation of the saturated gas phase from gassaturated liquid. Separation results in dispersion and dismigration of light hydrocarbons, while residual hydrocarbons remain in the reservoir and, depending on the quantity of waxes or resin-asphaltene components, increase the viscosity and cause difficulties in production. The reservoirs in the Mura depression are characterized by different degrees of alteration through evaporative fractionation and in some cases by the total destruction of hydrocarbons (Fig. 6).

Alteration of hydrocarbons in a reservoir can be influenced by water action, too (TISSOT & WELTE, 1984). Water washing processes usually characterize shallow accumulations with active hydrodynamic flows. Those processes only slightly affect the composition and physical properties of oil. A higher stage of degradation is the result of the combined action of water and microorganisms, known as biodegradation. Depending on their intensity, partial or full alteration of

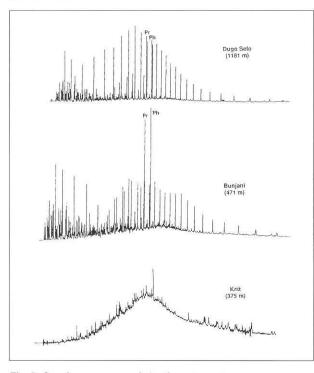


Fig. 7 Gas chromatograms of oils (Sava depression) altered by water action.

certain types of hydrocarbons is possible. Different levels of biodegradation have been established at the Bunjani field, while total alteration from paraffinic-aromatic to naphtenic-aromatic type characterizes the Križ field oil (Fig 7).

Studies researching the origin of chemically inorganic constituents (H<sub>2</sub>S and CO<sub>2</sub>) in the Molve-Kalinovac-Stari Gradac field gases, as well as in the exploration localities of Vučkovec and Vukanovec, were conducted in our geochemical laboratory. It was determined that H<sub>2</sub>S was the result of the thermocatalitic reduction of dissolved sulphates with the simultaneous partial sulphurization of reservoir hydrocarbons. The processes are thermodynamically controlled, and cyclic, but higher emissions and degasification can be predicted by continuous monitoring of fluid during production (BARIĆ & JUNGWIRTH, 1995). Carbon dioxide in gases is of inorganic origin, and occurs as a result of the thermal decomposition of reservoir carbonates or carbonates from the deeper parts of the basin. Changes of equilibrium in reservoir systems are the result of decreased formation pressure, primarily caused by exploitation, but can also result from the breakthrough of formation water with large quantities of dissolved  $CO_2$ , which causes an increase in the  $CO_2$  levels in gases of some wells.

## **3. CONCLUSION**

A short review of the results indicates that in the forecasting and estimation of the further prospectivity of exploration areas, a relatively large amount of existing geochemical data has to be used in addition to other geological and geophysical methods, to lower the risk involved in finding new hydrocarbon reservoirs. The results also indicate that geochemistry can be successfully applied in solving the problems arising in the process of hydrocarbon production.

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