

## HYDROCARBON GENERATION MODEL OF THE SOUTHERN ADRIATIC DEPRESSION

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**Abstract.** The anticline of the Divjaka gas field as unique focus of compelled data is an integral part of the Southern Adriatic Depression, which is composed of Middle Miocene to Pliocene deposits. There were discovered two levels of natural gas: the first level located in the Pliocene deposits, while the second one belongs to the Tortonian and Messinian sandstone bodies, named the "Divjaka suite". Vitrinite Reflectance has given good results for making out the geochemical model of hydrocarbon generation. This indicator is correlated with others indicators such as those of pyrolytic and hydrocarbon composition of the natural gas. Interpretation of these geochemical indicators enabled making out of three sections of hydrocarbon generation of methane gas as biogenic gas of the Pliocene deposits, mixed gas (biogenic and thermogenic) occurred in the Tortonian to Pliocene deposits and thermogenic gas of the Langhian and Serravallian deposits.

**Keywords:** anticline, depression, cuttings, vitrinite, maturity.

**Rezumat. Modelul generării hidrocarburilor din Depresiunea Adriatică de Sud.** Anticlinalul câmpului gazeifer de la Divjaka este parte integrantă a Depresiunii Adriatice de Sud, alcătuită din depozite ce datează din Miocenul Mediu până în Pleistocen. Aici au fost descoperite două niveluri cu gaze naturale: primul nivel este localizat în depozitele pliocene, în timp ce al doilea aparține Tortonianului și Messinianului, apărând în depozite de gresie cunoscute sub denumirea de "suita de Divjaka". Reflectanța vitrinitelor a dat rezultate satisfăcătoare pentru schițarea modelului geochimic al generării hidrocarburilor. Acest indicator este corelat cu alți indicatori, precum cel pirolitic și al compoziției hidrocarburilor. Interpretarea acestor indicatori geochimici ne-a dat posibilitatea de a stabili trei secțiuni ale generării hidrocarburilor, a gazului metan ca gaz biogen în depozitele pliocene, ca gaz mixt (biogen și termogen) format în depozitele totoniene și pliocene, și ca gaz termogen format în depozitele din Langhian și Serravallian.

**Cuvinte cheie:** anticlinal, depresiune, foraje, vitrinit, maturitate.

### INTRODUCTION

Improvements of the methodology of determination of Reflectance of Vitrinite of the Miocene-Pliocene deposits and its correlation with others geochemical parameters helps us establishing the geochemical model of hydrocarbon generation.

In determining the Reflectance of Vitrinite, it is very important to select and prepare proper samples. Achieving this objective based on multidisciplinary litho-stratigraphic studies on several surface sections, and deep wells drilled in the Divjaka gas field of the Albanian onshore part of the South Adriatic Depression. Samples were picked up from the drilled wells carrots and cuttings, stored in the storehouse. Initially, there were carried out the pyrolytic analysis of 1,112 samples and cuttings. Then, based on the content of organic matter expressed in organic carbon, there were selected samples (with organic carbon greater than 0.3%) to be processed for the evaluation of the Reflectance of Vitrinite and Maceral analysis. Sample picking up was performed in two ways: initially picked up samples from cores of the wells drilled in the core of the Divjaka anticline and then from the wells drilled on its eastern flank. Both groups of the wells have crossed similar geological sections. Preparation of polishing sections (pellets) and measurements of the Vitrinites Reflectance have followed methods of some European authors, advancing further more to approach the organic matter maturation of the lower stages.

### GEOLOGICAL SETTING

Divjaka gas field anticline is an integral part of the structural-anticline chain Kraps-Ardenic-Divjake-Durres of the South Adriatic Depression, which is composed of Serravallian to Quaternary deposits. Along this anticline chain, additionally to Divjaka field, gas appears within Kraps structural nose, Ardenica and Durrësi anticlines, which has different features owing to its individual palaeotectonic development. The structure of the Divjaka anticline has a regular shape of 15 x 5 km size according to the base of the Pliocene deposits. It is dissected by a longitudinal reverse fault of some hundred meters range along its western flank, as well as of some back thrusts of some tenths meters range along its eastern flank (Fig. 1).

Divjaka gas field geological reserves were estimated at about 65,053,356 m<sup>3</sup> dry gases. It was discovered in 1964 through Divjaka-2 wildcat and exploitation started in 1968 through Div 5 / a development well.

The gas-bearing deposits of Divjaka field belong to the sandstone bodies of the Tortonian-Messinian molasses deposits where there were identified 17 beds of 3.5 to 6.8 m effective thickness. Gas pools were also discovered in the Pliocene deposits of the fields in question (GJOKA & KURTI, 2003).

## MATERIALS AND METHODS

Among the main factors affecting the accuracy of measurement, we mention the preliminary sample processing, which includes:

- Picking up the samples from the cores and cuttings of Divjaka gas field drilled wells.
- Crashing of mineral matter and separation of the organic matter.
- Preparation of polish section.
- The procedure of the Vitrinite Reflectance measurement. Vitrinite Reflectance measurement can take place easily in cases of the coal and coal shale deposits, but the later lack in the Divjaka anticline. So, the assessment of the Vitrinite Reflectance is realized through dispersed organic matter, which, occurs in clay and siltstone beds of the Miocene-Pliocene deposits.

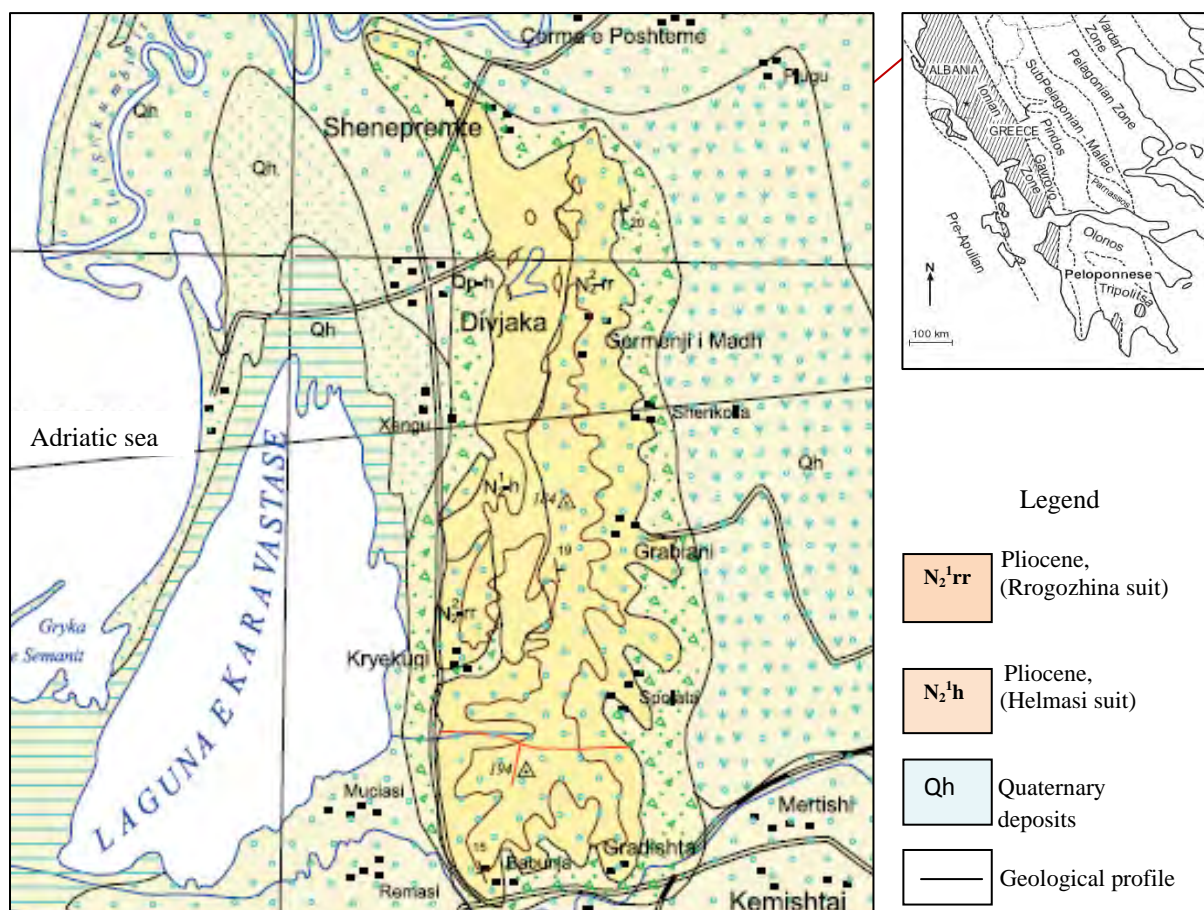


Figure 1. Geological map of Divjaka area. / Figura 1. Harta geologică a zonei Divjaka.

Samples picking up are based on the content of organic matter expressed in TOC, which in the Pliocene deposits goes up to 0.63, with an average of 0.32, while in those of the Tortonian-Messinian reaches the maximum value of 0.58, with an average of 0.28. The samples selected for study by means of the Vitrinite Reflectance were those that have higher TOC than the average. Also, picked up samples divided into two groups – those of the Divjaka anticline core wells and of the eastern flank ones.

Generally, we needed 50-80 g of rock from carrots or cuttings, which were processed with hydrochloric acid (HCl) and fluorhydric acid (HF) for crashing the solid mineral. After water washing until neutral environment, the sample was processed with heavy liquid (cadmium iodide + potassium iodide) of the 2.1 g/cm<sup>3</sup> specific weight. This treatment was made to separate the organic matter from the minerals, which remained undestroyed by acids. The obtained organic matter filled a glass tube of 25 cc and was washed out with alcohol. In this way the product was ready for the preparation of pellets.

For the preparation of pellets, it was used a plastic holder bar of 20-25 mm diameter and 5-10 mm length. Along the ax of the plastic holder bar, it opened a channel of 2 mm diameter and 5-10 mm length, which served as supporter of the organic matter mixed with resin to keep its grains linked. Then the samples were put in the thermostat at a temperature of 50°C, for the resin solidification and preparation for polish in the Geopol-300 machine.

This process involves working out the organic matter with corrosive paper of the number 1,200 and polarization by polishing plates and diamante paste of 0.1 micron grain size. Polarization process undergoes a

control through the Microphotometr Leitz MPV3. Samples that appear to be badly polished undergo re-polishing starting with the diamond paste. This can be done by hand or by machine such as the Geopol-300, which can polish 12 pellets concomitantly. Then, it takes place the Vitrinite Reflectance measurement. The equipment calibration was carried out at 0.576% standard, which is suitable for low maturity organic matter. The same pellets underwent Maceral analysis using the observation under fluorescent light, for a detailed Liptinite determination, as well as for detecting macerals groups of Liptinite, Inertinite, and Huminite.

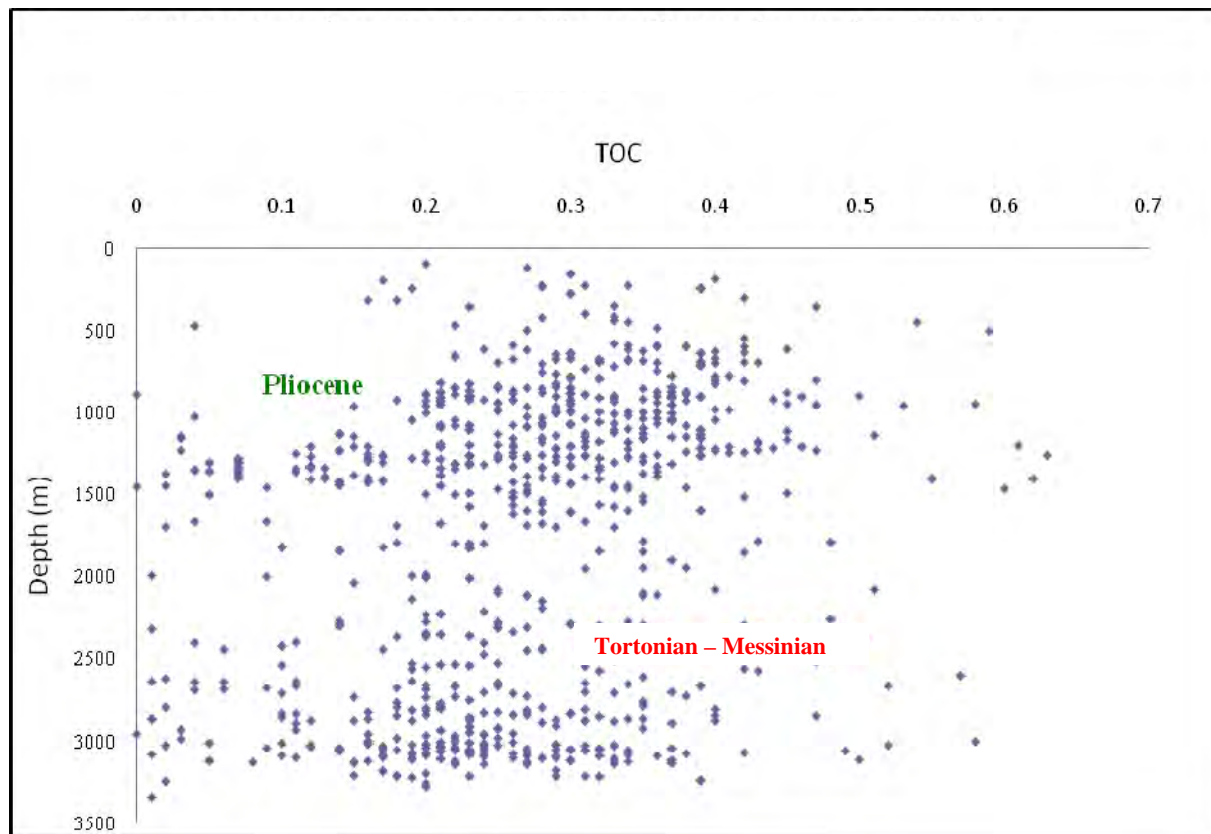


Figure 2. Content of organic carbon (TOC) vs depth in Miocene-Pliocene deposits from Dvjaka anticline.  
 Figura 2. Conținutul de carbon organic (TOC) versus adâncime în depozitele miocen-pliocene din zona Divjaka.

## RESULTS AND DISCUSSIONS

Initially, we determined the amount and type of organic matter through pyrolysis analyses. From the organic carbon content (TOC) point of view, the Pliocene deposits are richer than those of Tortonian-Messinian. Thus, the organic carbon content amounts up to 0.63% in Pliocene deposits, which has an average of 0.32%, while in the Tortonian-Messinian deposits, it reaches 0.58% and an average of 0.28% (Fig. 2).

The type of organic matter was determined by the hydrogen index, which ranges from 6 to 400 and displays an average of 55.76 in 1,112 of samples and cuttings. Dominantly, the organic matter is of the third type, whereas just 16 samples belong to the second type. The types of organic matter appear clearly separated in the figure 3, HI versus T maximum. The assessment of the level of organic matter maturity cannot rely on T<sub>max</sub>, because its values have large fluctuations. This forced us to evaluate the maturity of the organic matter according to the Vitrinite Reflectance.

Maceral analysis has confirmed the presence of the third type of organic material. Macerals of the Liptinit group includes Sporinite, Cutinite and very little Alginite, Resinite, therefore they are mostly of continental origin. These macerals constitute 6-26% of the organic matter. Within the Huminite macerals, there predominates the Textinite, less Collinite and Corpocollinite, which represent 20-57% of organic matter, while the Semifusinite are dominant macerals, which constitute 7-55% of organic matter of the Inertinite group.

Presumably, the organic matter of the Miocene and Pliocene deposits belongs to the third type, which has come from the continent and is able to generate gaseous hydrocarbons (Fig. 3).

The carried out measurements confirmed that the Vitrinite Reflectance of the Pliocene deposits is less than 0.3% at the dome of Divjaka anticline and more than 0.3% along its eastern flank, while for the same depth the Vitrinite Reflectance is higher in the Miocene than in the Pliocene deposits.

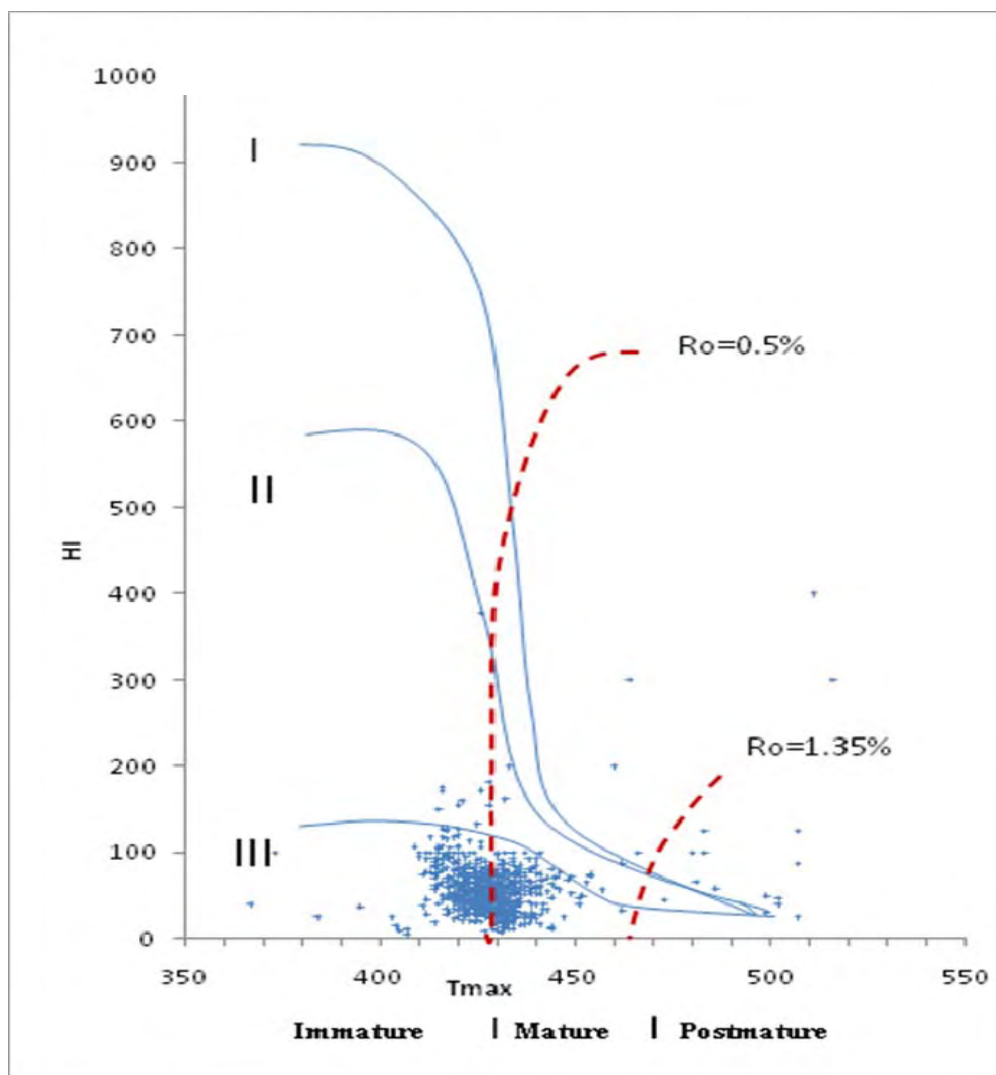


Figure 3. Type of organic matter from rock-eval data (hydrogen index,  $T_{max}$ ) in Divjaka region.  
 Figura 3. Tipul de materie organică din datele de evaluare a rocilor (indicele hidrogen, temp. max.)  
 în regiunea Divjaka.

Hydrocarbon composition of the natural gas of the Miocene and Pliocene deposits is different. Thus, the natural gas of the Pliocene deposits is very dry ( $C_1/C_2 > 335$ ), whereas the gas of the Miocene deposits is fatty ( $C_1/C_2 < 101$ ). So, hydrocarbon composition of natural gas (PRIFTI, I. & MUSKA, K. 1999) associates the Vitrinite Reflectance and other changes.

Based on the Vitrinite Reflectance, we made up certain models, which include the maturity profiles of the two drilled wells groups, which have different paleotemperature and paleogeothermal gradients. At the same time, this modeling shows the characteristics of hydrocarbon generation models to find out the spatial position of deposits penetrated by the studied wells.

After making up the maturity profiles of both groups of wells of Divjaka anticline dome and its eastern flank, it was calculated the Vitrinite Reflectance according to the equations of the dependence to the highest correlation ratio. The values of the organic matter maturity enable us making up its models, which show the separated depth intervals of hydrocarbon generation in Divjaka region (Fig. 4, 5).

There are two maturity profiles for each well group. As for the continuation of the isolines / isorefectances toward more plunged sectors and the eastern syncline, it is applied the isorefectances dissection of the deposits of the newer geological age, as those of the Pliocene.

In other words, the maturity of the organic matter occurred before and during the folding processes until Divjaka region became a continental area. Pliocene deposits generate biogenic hydrocarbon gas. They have a maturity of  $R_o = 0.3\%$ , which grows further toward syncline structures. Whereas, the Tortonian and Messinian deposits are more matured since their Vitrinite Reflectance exceeds the value of  $0.4\%$  and have generated mixed gas, i.e. biogenic gas and thermogenic gas.



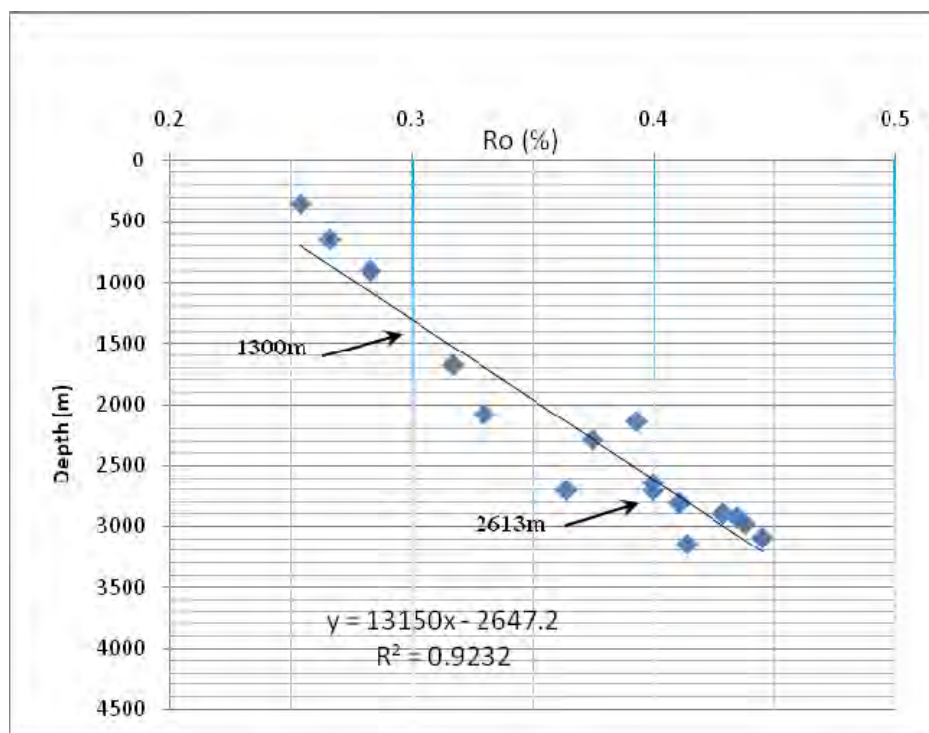


Figure 4. Reflektanța of vitrinites vs depth (m) in east part of Divjaka anticline.  
 Figura 4. Reflectanța vitrinitelor versus adâncime (m) în partea de est a anticlinalului Divjaka.

Hydrocarbon composition of natural gases obviously confirms that the Tortonian and Messinian deposits generate wet gas?. Thus the ratio  $C_1/C_2$  ranges from 38 to 102 for the Miocene deposits, meanwhile in the Pliocene deposits it varies from 335 to 1,837 (Fig. 6), because the Tortonian-Messinian deposits are more matured and hydrocarbon gas is generated in biogenic and thermogenic conditions, while in the Pliocene deposits, it is generated only in the biogenic conditions.

The results obtained from both maturity profiles have been put on the seismic profile no. 116/81, where it is determined the isorelectance  $Ro = 0.3\%$  (Fig. 7). It is noted that the isorelectance dissects the newer deposits toward the eastern syncline of Divjaka gas field. This phenomenon means that the maturity of organic matter has continued to take place also after the sedimentation of the Pliocene deposits. But the maturing process stopped when the region turned into continental conditions. Subsequently, the assessment of the geothermal gradient relies on the paleotemperatures calculated according to the Vitrinite Reflectance values.

The maturity gradient is evaluated from the calculated Vitrinite Reflectance ( $Ro$ ) and real sections of drilled wells. Evaluation of the paleogeothermal gradients must rely on known temperatures, which are fossilized in the Vitrinite Reflectance that have undergone the sedimentary section during its geological development.

Paleotemperatures calculation utilizes a modification of the Lopatin method by Middleton. This modeling presents the relationship between the Vitrinite Reflectance and the time-temperature history of the rocks (LOPATIN 1976; PRIFTI 1995).

$$Ro^a = R_{init}^a + bt \exp(cT)$$

where  $Ro$  = Vitrinite Reflectance

$R_{init}$  = initial reflectance (0.20 or 0.15)

$a = 5.5$ ,  $b = 2.8 \times 10^6$

$c = 0.065$ ,  $t$  = time (Ma)

$T$  = temperature ( $^{\circ}C$ )

This calculating method relies on age determination of each sample. It is noted that the paleotemperatures are about  $100^{\circ}C$  higher than the current temperatures, while paleogeothermal gradient is  $220^{\circ}C/1,000$  m for the Tortonian-Messinian deposits and lower for the Pliocene ones. The paleotemperatures and paleogradients data have been good enough for making up the curves of the sink of the eastern syncline of Divjaka gas field.

Finally, the paleogeothermal gradient of Divjaka region is reconstructed through examination of the coalification gradient, which have right direction tendency to each other.

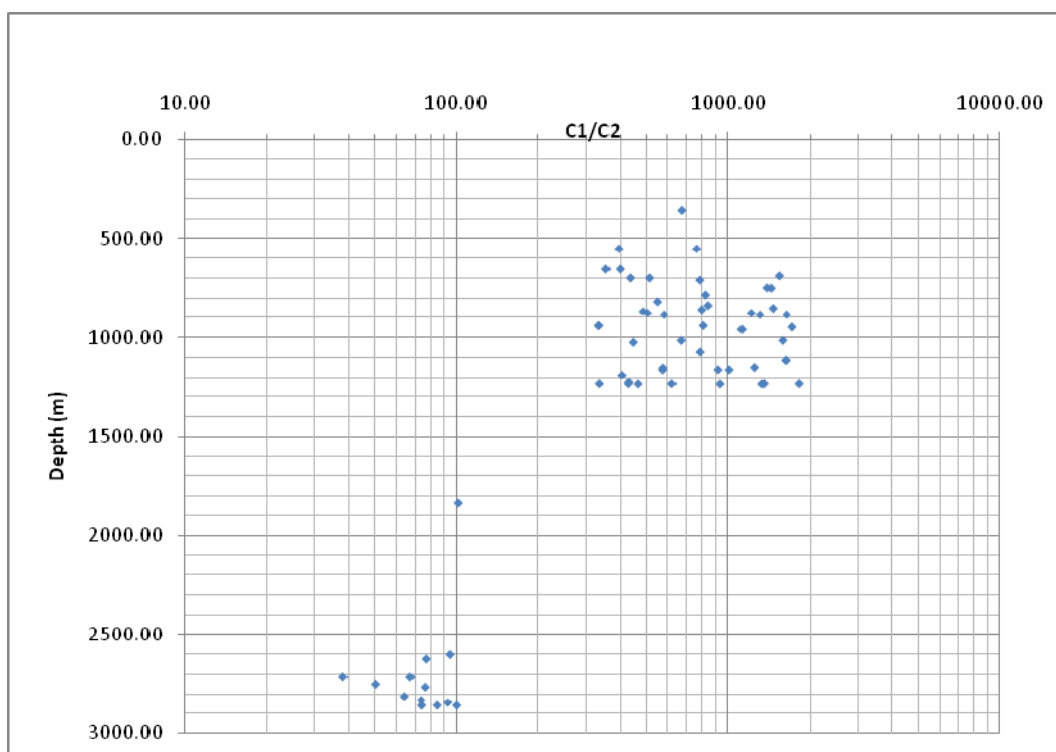


Figure 5.  $C_1/C_2$  vs depth, in deeper section generated wet gas.  
 Figura 5.  $C_1/C_2$  versus adâncime în secțiune mai adâncă generează gaz umez.

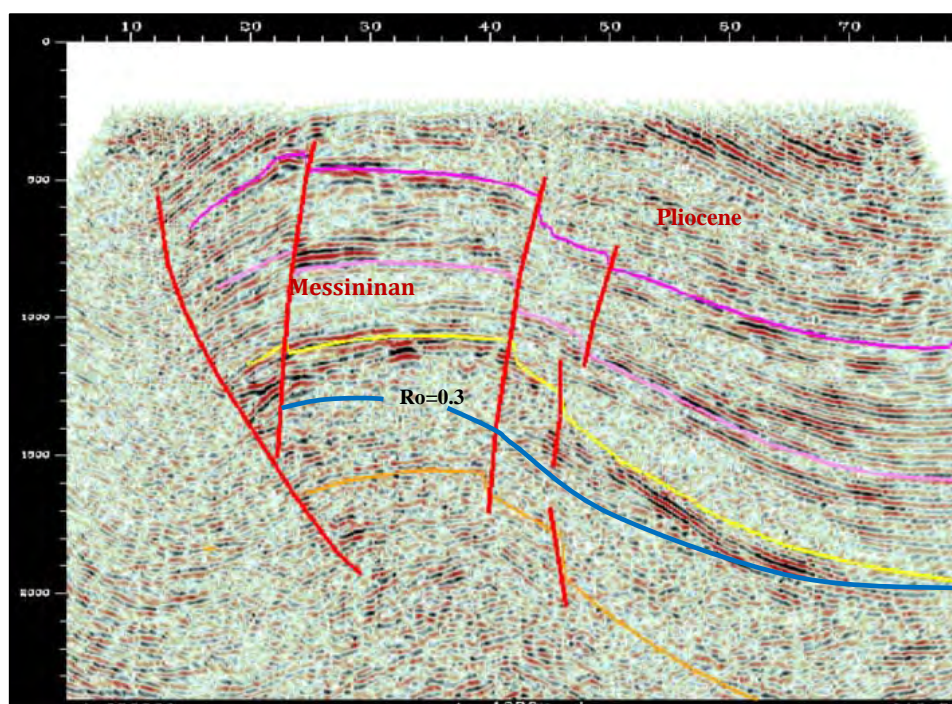


Figure 6. Seismic section 116/81 and level  $Ro=0.3$  % in Divjaka anticline.  
 Figura 6. Secțiunea seismică 116/81 și nivelul  $Ro=0,3$  % în anticlinalul Divjaka.

## CONCLUSIONS

1. The following maturity levels of the organic matter and depth intervals of gas generation appear in the Tortonian-Messinian and the Pliocene deposits of the Southern Adriatic Depression studied in the drilled wells of Divjaka gas field of Albania onshore:

a. Biogenic gas generation zone with  $R_o$  between 0.2% and 0.3% has taken place in the Pliocene deposits down to 2,400 m depth and in the Messinian-Tortonian deposits down to 1,300 m depth.

b. Generation zone of the mixed gas (a combination of biochemical and thermal processes) with  $R_o$  between 0.3% and 0.4% occurred down to the depth 2,600 m (the Messinian-Tortonian deposits) in the anticline dome and down to the depth 3,900 m in the Pliocene deposits of its eastern flank. Older than the Pliocene deposits, they are more matured in the anticline flank and the syncline structure.

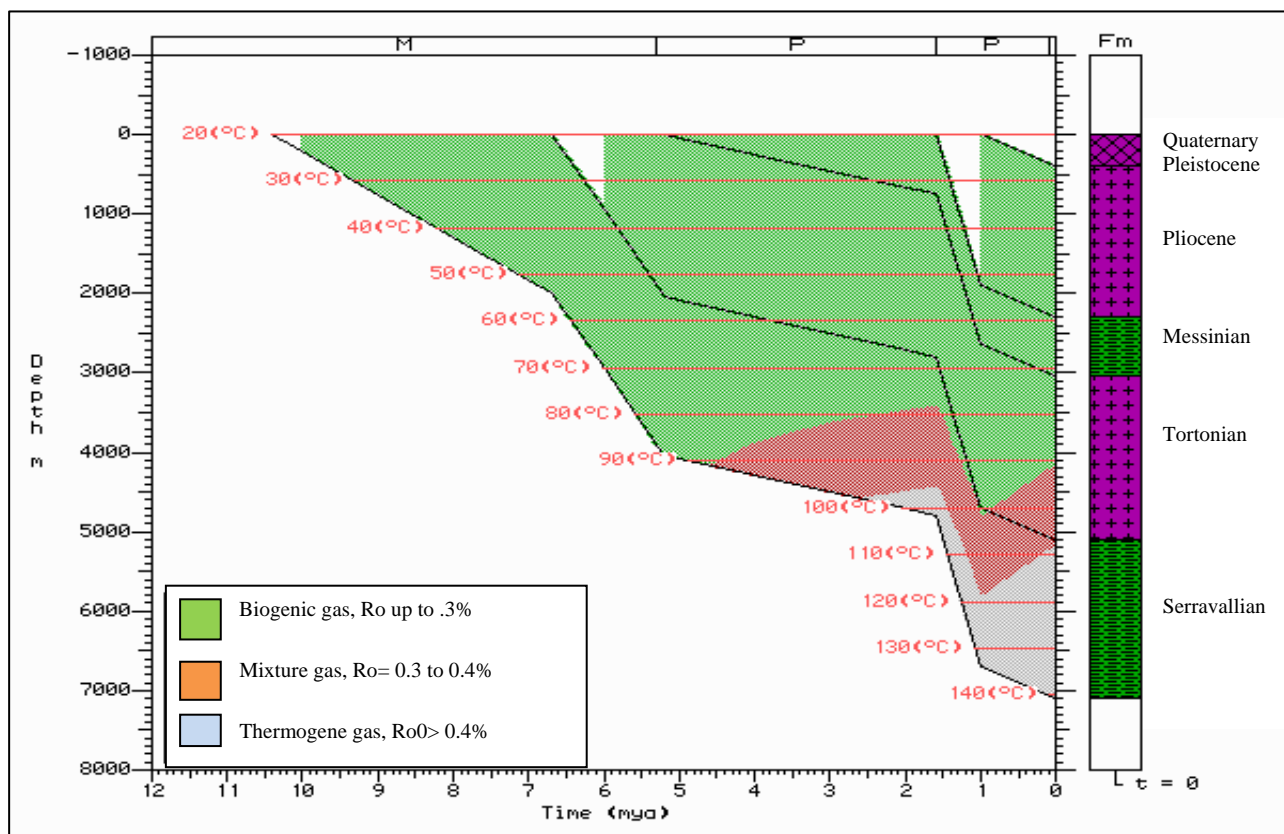


Figure 7. Generation zone of eastern part of Divjaka anticline.  
Figura 7. Zona de generare din partea estică a anticlinalului Divjaka.

c. Generation Zone of the early thermogenic gas, which has  $R_o$  between 0.4% and 0.5%. This generation zone lies below the depth of 2,600 m in the dome of Divjaka structure and under 3,900 m in its eastern flank, where it is documented the presence of the Langhian-Serravallian deposits.

2. Generally, the natural gas of the onshore South Adriatic Depression including Divjaka field belongs to the third type of the organic matter of Huminite type and corresponds dominantly to biogenic and mixed gas (biogenic and thermogenic) zones of generation (VELAJ & PRIFTI, 1996).

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