ANALELE ŞTIINŢIFICE ALE UNIVERSITĂŢII „AL. I. CUZA” IAŞI
Geologie. Tomul LVI, nr. 2, 2010

PALYNOLOGY, PALYNOFACIES AND THERMAL MATURATION OF THE KEROGEN FROM THE MOLDAVIDIAN DOMAIN (GURA HUMORULUI AREA)

DANIEL ŢABĂRĂ[1]

[5] “Al. I. Cuza” University of Iaşi, Faculty of Geography and Geology, Department of Geology, 20A Carol I Blv., 700505 Iaşi, Romania

Abstract

The present paper analyzes the palynofacies and maturation degree for bituminous rocks belonging to the Tarcău and Vrancea Nappes (Gura Humorului-Frasin area). The organic constituents discovered in the samples analyzed consist, in a large proportion, of amorphous organic matter, followed by phytoclasts and palynomorphs. The prevailing component in the palynological assemblage is marine phytoplankton from the Lower Dysodilic Shale, indicating an outer neritic setting. The type of sedimentary basin, inferred based on palynofacies criteria, is a distal suboxic-anoxic one.

The kerogen extracted from the rocks is Type II, and the TOC content indicates a fair to excellent genetic potential for petroleum. The maturation degree of the organic matter was determined based on optical criteria (Thermal Alteration Index and palynomorph fluorescence), a stage at the limit between the immature and the mature being identified.

Keywords: Oligocene, palynology, palynofacies, thermal maturation of kerogen, bituminous rocks.

Introduction

In the Eastern Carpathian area, the main types of bituminous rocks are menilites, brown marls and dysodilic shale belonging to the Tarcău and Vrancea Nappes. The organic content in relation to the oil production and the degree of maturation of organic matter were documented by Nacu et al. (1970), Balteş (1983), Stănescu and Morariu (1986), Grasu and Catană (1989), Ştefănescu et al. (2006), Grasu et al. (2007), and Belayouni et al. (2007).

---

[5] e-mail: tabara_d@yahoo.com

These bituminous rocks, which have a higher content of organic matter, have been formed under the anoxic conditions of the sedimentary basin stretching along the Carpathian Chain during the Oligocene.

The present paper aims to establish the palynofacies and the degree of maturation of the kerogen from the Bituminous Marls Formation and the Lower and Upper Dysodilic Shale Formation of the Tarcău and Vrancea Nappes (Gura Humorului-Frasin area).

Geological settings

The Carpathian Chain from Romania was the result of the collision between the African-Arabic and European plates, which led to the gradual closure of the Tethys Ocean during the Cretaceous and Miocene convergence events (Săndulescu, 1984). The author separates the deformation in the Romanian Carpathians into two episodes: (a) – in the Cretaceous period, when the Transylvanide and Dacide Units were formed; (b) – during the Miocene, when the Moldavide Unit in the Eastern Carpathians was formed. The Moldavide Unit includes, from west to east, the following tectonic nappes: Teleajen, Macla, Audia, Tarcău, Vrancea and the Pericarpathian Nappe (fig. 1).

The Paleogene-Miocene deposits included in various structural units of the Moldavide sometimes display considerable lateral facial variation. Thus, in the Tarcău Nappe three distinct lithofacies were separated (Băncilă, 1958; Ionesi, 1971): in the west, the Fusaru Lithofacies; in the center, the Moldoviţa Lithofacies (mixed), and in the eastern part – the Kliwa Lithofacies. In the lithological profiles from the Moldova Valley (between Gura Humorului and Frasin) that were analyzed, only the Kliwa Lithofacies of the Tarcău Nappe was intercepted (fig. 1).

The sedimentary deposits of the Kliwa Lithofacies consist of quartzarenites (of the Kliwa type), composed of mineral particles with a possible external source (cratonic). In the case of the bituminous rocks, the sedimentation consists mainly of pelitic, bituminous marls with a calcareous-clay substrate, dysodilic shales that are generally silty-clayey, and menilites containing a silicious material. Their sedimentation occurred in an anoxic environment, which led to the preservation of a larger quantity of organic matter. The source of this organic matter is considered to be autochthonous (marine), its accumulation being uniform throughout the External Flysch basin (Grasu et al., 2007).

In the Kliwa Lithofacies, the Oligocene has Kliwa Sandsone as the limit of the erosion, while in the Vrancea Nappe it is completed by the Upper Dysodilic Shale Formation and it ends with the Gura Șoimului Formation of Miocene age (fig. 1).

In the Eastern part of the Kliwa Lithofacies corresponding to the Tarcău Nappe, the Pietricica Lithofacies included in the Vrancea Nappe was identified. This structural unit is found under the Tarcău Nappe (fig. 1 – Geological section), occurring as a tectonic half-windows resulting from the erosion of the covering nappe. It was separated for the first time by Ionesi (1961) and called the Humor Half-windows.

Stratigraphically, the deposits assigned to the Vrancea Nappe are of Senonian, Paleogene and Lower Miocene age (Ionesi, 1971). These deposits are generally similar to those of the Kliwa Lithofacies. However, there are some differences, such as the reduction in the thickness of the Kliwa Sandstone (sometimes up to extinction) and the appearance of ruditic facies with “green schists” of the Central Dobrogea type (Ionesi, 1971; Grasu et al., 1999).

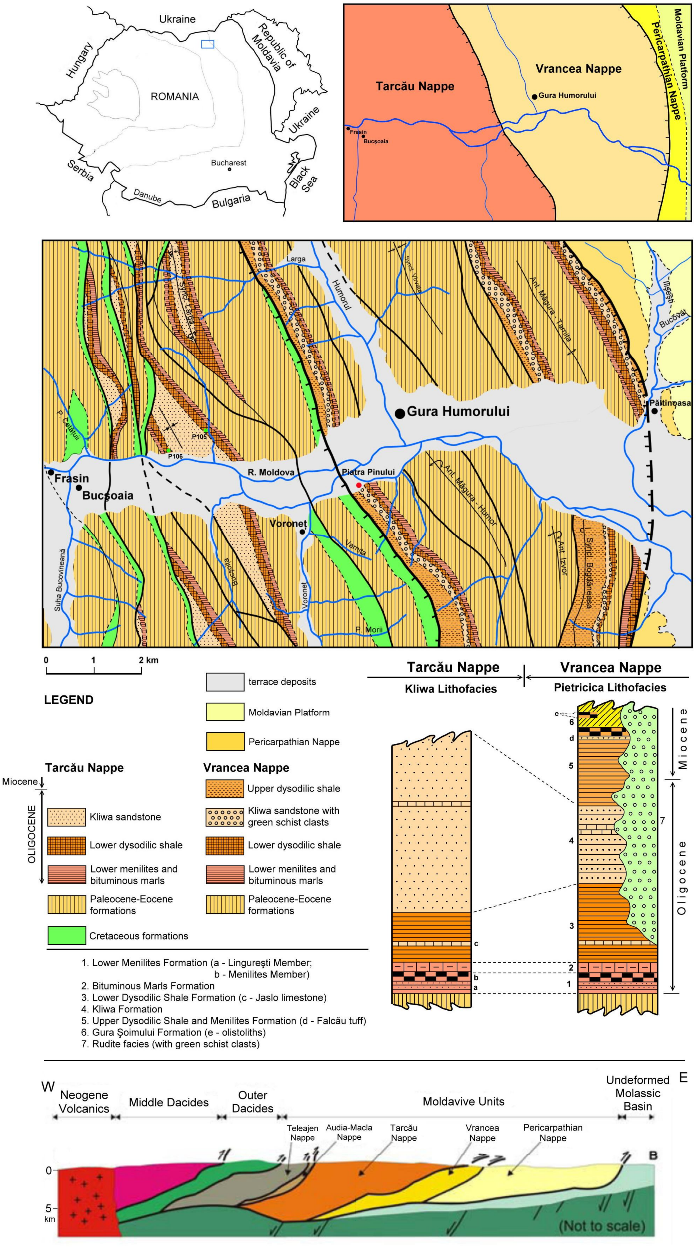


Fig. 1 Geological and tectonic sketch map of the Gura Humorului-Frasin area (geological map according to Ionesi, 1971, with modifications; lithological column according to Grasu et. al., 2007, and geological cross section according to Bădescu, 2005).

The lithological profile where deposits corresponding to the Pietricica Lithofacies from the Vrancea Nappe have been identified is upstream Gura Humorului, on the right side of the Moldova River, in the area of the Piatra Pinului paleontological reservation (figs. 1, 2).

At the bottom, the geological cross section shows Lower Menilites alternating with grey marls, followed by black bituminous marls having a thickness of about 50 cm. Lower Dysodilic shales have the appearance of blackish-gray clay, with visible lamination and traces of sulfur on the strata surfaces. Sometimes, these contain impressions of fossil fish.

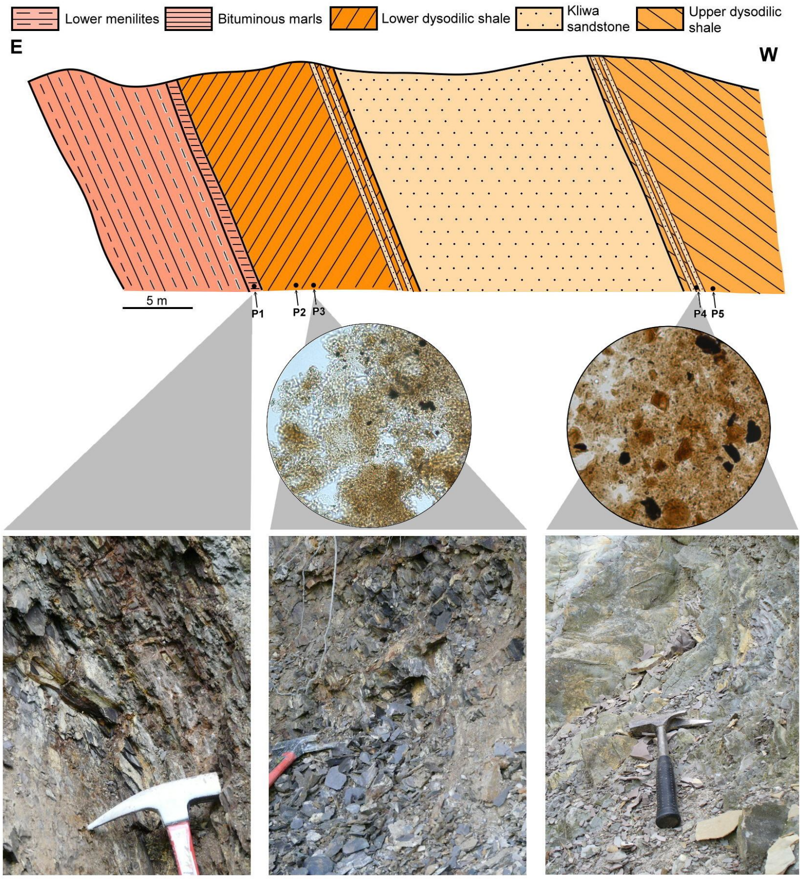


Fig. 2 Geological cross section through Oligocene deposits of the Vrancea Nappe (Piatra Pinului geological profile)

The Kliwa Sandstone of this geological section has a thickness of about 20 m, being placed in the quartzarenite category (Grasu et al., 1988). At the top of this formation, layers of sandstone with interbedded dysodiles can be noticed. The upper part of the sandstone layers displays a wavy surface due to the conservation of marine currents for which a wavelength of a few decimeters was measured.

The stratigraphic sequence ends with the Upper Dysodilic Shale Formation. The shales have a brown color, with visible lamination and Kliwa Sandstone intercalations of a few centimeters.

Materials, methods and sample location

For the present paper, two outcrops have been analyzed. The first one is located between Gura Humorului and Frasin, on the left side of the Moldova River (fig. 1). The Paleocene-Oligocene stratigraphic sequence corresponds to the Tarcău Nappe and it is disposed as a syncline, having the Kliwa Formation in the center. From this geological section, two samples collected from the Lower Dysodilic Shale Fm have been analyzed. One of these samples came from the western flank (P106), and the other from the eastern flank (P105) of the syncline (fig. 1).

A second geological profile is located in the Piatra Pinului Reservation (the Vrancea Nappe). 5 samples of bituminous marl and lower and upper dysodilic shale were analyzed from this area (fig. 2, tab. 1).

Tab. 1 Elemental geochemical analysis for bituminous rocks from the two analyzed cross sections

Location		Sample	TOC (%)	H (%)	O (%)	S (%)	H/C	O/C	Petroleum potential
Tarcău Nappe, Kliwa Lithofacies	TOC analysis	*P106 lower dysodilic shale	1.652	1.043	6.212				good
		*P105 lower dysodilic shale	4.316	1.32	7.094				excellent
Vrancea Nappe, Pietricica Lithofacies, Piatra Pinului section		P1 bituminous marls	8.905	1.66					excellent
		P2 lower dysodilic shale	2.032	0.957					very good
		*P3 lower dysodilic shale	2.911	1.1					very good
		*P4 upper dysodilic shale	1.963	0.889					good
	analysis on kerogen extracted from rock	P1 bituminous marls	47.697	5.422	15.79	4.194	1.36	0.248	
		P2 lower dysodilic shale	52.012	5.245	15.59		1.21	0.224	
		P5 upper dysodilic shale	44.07	5.48	18.14		1.492	0.308	

* analyzed palynological samples

The analyses for Total Organic Carbon (TOC), H, N, S, and O were performed using a EuroEa 3000 EuroVector elemental analyzer. The TOC content is used as an indicator of the potential of the hydrocarbon source rocks. Based on its values, the genetic potential of the source rocks can be established, being estimated between poor and excellent (Peters and Cassa, 1994). The analyzed samples were prepared in the laboratory through two methods:

- the first method consisted of crushing the samples down to a particle diameter of 0.1-0.3 mm. Subsequently, they were treated with HCl 2N for 24 hours in order to remove any carbonates. The remaining material was then washed with distilled water so as to remove any acid and later dried in an oven at 50°C. The samples thus treated, on which TOC analyses (tab. 1) have been carried out, are P105, P106 (Tarcău Nappe) and P1-P4 (Vrancea Nappe).
- a second method aimed at the extraction of the kerogen from the rock and the quantification of C_{org}, H and O. Afterwards, the H/C, O/C ratios were calculated and the results were projected onto a Van Krevelen diagram in order to identify the type of the kerogen from the samples analyzed (fig. 3a). Such analyses were conducted on 3 samples, namely P1, P2 and P5 from the Piatra Pinului geological profile.

The extraction of the kerogen from the rocks was described by Durand and Nicaise (1980; modified by Vandenbroucke 2003; Vandenbroucke and Largeau, 2007). The separation of the kerogen from the mineral fraction is performed using a series of chemical reagents, in an attempt at preserving as much of the original chemical composition of the organic matter as possible. The samples were crushed down to a particle size of about 0.1 mm, and then treated with an organic solvent (dichloromethane - DCM) so as to remove the soluble fraction (the bitumen) from the rock. The carbonates and silicates were destroyed by a solution of HCl 6N + HF 40% (1/3-2/3 v/v). The isolation of the kerogen from the minerals undestroyed by the acid attack was carried out through centrifugation in heavy liquid ($ZnCl_2$ with a density of 2). The kerogen extract was then washed with distilled water and treated once again with dichloromethane. The kerogen thus obtained was afterwards used in elementary analyses for C, H, O, N and S.

For the palynological analyses, 50 g of rock sample were used. These samples were first treated with HCl (37%) in order to remove carbonates, and then with HF (48%) so as to destroy silicates. The separation of organic matter was achieved through centrifugation in heavy liquid ($ZnCl_2$ with a density of 2).

The optical study of the organic matter was performed by means of a Leica DM1000 microscope with transmitted light (Osram 30W bulb type), and the reflected blue light (fluorescence) with a mercury lamp of the HBO 50W type. The rank of fluorescence of palynomorphs (Robert, 1985) and the Thermal Alteration Index (TAI - Pearson, 1984) were used to determine the degree of maturation of organic matter. As the maturation degree increases, palynomorphs display a green to bright yellow (equivalent to a vitrinite reflectance VR_0 up to 0.7%), orange ($VR_0 \approx 0.7$-0.9%) and red fluorescence color ($VR_0 \approx$ 0.9-1.2%) (Smojić et al, 2009). In the over-mature stage the fluorescence is not visible. Pearson (1984) established the following maturation scale in relation to the Thermal Alteration Index: TAI= 1-2 for the immature stage (up to 0,5% VR_0), TAI = between 2+ to 3+ (0.5-1.3% VR_0) for the mature stage, and TAI = 3+ up to 4-5 for the over-mature stage.

Considerations regarding the petroleum genetic potential

Bituminous rocks of Oligocene age are the main source rocks for hydrocarbons in the external flysch of the Eastern Carpathians.

Over the last 40-50 years, many studies regarding the petroleum genetic potential of these rocks were conducted. A first paper that dealt with this aspect was devised by Nacu et al. (1970). Samples were collected from the Larga watercourse (fig. 1), where the Oligocene of the Kliwa Lithofacies from the Tarcău Nappe was identified. Lower Menilites have a low TOC content (0.62 to 0.69%), the dysodilic shale intercalation from this member, however, recording the highest percentage in C_{org} (13.15%). Bituminous Marl has values between 2.54 to 4.3% TOC, and Upper Dysodilic shale – from 2.25 to 11.85% TOC. Overall, Bituminous Marl, Upper Dysodilic shale and pelitic intercalations from the Lower Menilites displayed a very good to excellent petroleum genetic potential.

The characterization of the organic content of the bituminous rocks of the Kliwa Lithofacies (samples collected from the left side of the Moldova River, geological profile between Gura Humorului and Frasin) was presented by Belayouni et al. (2007). The Lower Menilites and the Dysodilic Shale Formation are rich in organic matter (TOC up to 10% in the Lower Dysodilic shale), the kerogen identified using Rock-Eval pyrolysis is type II, being considered thermally immature, as indicated by the HI (Hydrogen Index) parameters ranging between 178 and 490 mg HC/g TOC, and T max (411 to 430°C). Based on the considerations above, the authors believe that these rocks can be regarded as an excellent source of oil. The large amount of kerogen preserved in them is attributed to the anoxic conditions under which the sediments have accumulated. It also states that the origin of the organic matter is autochthonous (marine), and its accumulation is uniform throughout the External Flysch Basin. Organic matter of continental origin represents a very low percentage.

Balteş (1983) believes that the Lower Dysodilic shales have an Index of Organic Metamorphism (IOM) between 2 and 4, which shows that these rocks have generated heavy oils, dry gas and CO_2.

Stănescu and Morariu (1986) show that the Oligocene bituminous rocks from the External Flysch were subjected to a low geothermal gradient, favorable thermal conditions having been provided by the heat flow generated from the friction processes (along the overthrust) of the Tarcău and the Vrancea Nappe. Thus, the dysodilic shale from the Vrancea Nappe began to generate oil within the Upper Miocene – Pliocene interval.

References regarding the type of kerogen present in the Oligocene-Miocene bituminous rocks from the External Flysch were presented by Ştefănescu et al. (2006). It is estimated that the organic matter is type II, partially type III. The same view regarding the type of kerogen present in the Oligocene dysodilic shale from the External Flysch was shared by Pawlewicz (2007). According to the author, this organic matter displays a mature stage of hydrocarbon generation (VR_0 = 1-1.15%), with a TOC range between 0.35 and 2.5%.

Stoicescu (2004) offered a description of the Oligocene-Miocene palynofacies from the Vrancea Nappe (Slănic Oituz Half-Windows). The samples analyzed come from the

Upper Dysodilic shale and the Menilite Formation. The author state that the organic matter is represented mostly by continental phytoclasts (approx. 85%), amorphous organic matter and palynomorphs. The TAI established on the palynomorphs identified is between 1 and 3 (mostly between 2 and 2 +), the kerogen being in the early stage of maturation. It is concluded that the organic matter corresponding to this formation is type II, generating oil and gas condensate and having been accumulated in a marginal basin with dysoxic-anoxic conditions.

Results and discussions

1. Palynology

The palynological assemblages of Oligocene age from the Carpathian Flysch have been described by Olaru (1978) and Stoicescu (2004). From the area between the Bistriţa and Trotuş rivers, genera such as the following have been identified for the Oligocene: *Quercus, Betula, Corylus, Alnus, Pinaceae,* ferns and phytoplancton represented by *Deflandrea phosphoritica* Eis., *Wetzeliella rotundata* Balteş, *Thalassiphora delicata* Will. & Dow., *T. pelagica* Eis., *Cleistosphaeridium pectiniforme* Garlach. a.o. (Olaru, 1978). From the Slănic-Oituz Half-Windows (Upper Dysodilic Shale and Menilite Formation), Stoicescu (2004) cites species such as *Baculatisporites nanus* (Wolf, 1934), *Laevigatosporites gracilis* Wilson & Webster 1946, *Pinaceae, Monocolpopollenites tranquillus* (Pot. 1934) Th. et Pf. 1953, *Magnolipollis* sp., *Caryapollenites simplex* (Pot. 1931) Kr. 1960, *Tilia, Juglans* a.o. Among these, dicotyledonous angiosperms have a higher frequency. The palaeoclimate revealed by this palynological assemblage is a subtropical-temperate one (MAT from 16 to 18°C, MAP 1400 mm/year), which has a tendency of decreasing in temperature towards the end of the Oligocene.

The palynological assemblage identified came from the Tarcău Nappe (P105, P106 – Lower Dysodilic Shale Formation) and the Vrancea Nappe (P3 – Lower Dysodilic Shale Formation and P4 – Upper Dysodilic Shale Formation). Table 2 presents species of continental palynomorphs and phytoplankton identified in the analyzed samples.

Tab. 2 Taxonomic list of palynomorphs identified in the Gura Humorului-Frasin deposits of Oligocene age

Sample	Taxa	Plate index	TAI	Fluorescence λ (nm)
P3 – Lower dysodilic shale (Vrancea Nappe)	Phytoplancton			
	Spiniferites ramosus (Ehrenberg 1838) Mantell 1854			
	Dracodinium sp.	Plate I, fig. 4		
	Pollen			
	Sciadopityspollenites sp.	Plate II, fig. 7	2+	580
	Pityosporites sp.		2+	590
	Pityosporites sp.	Plate II, fig. 9		
P4 – Upper dysod. shale (Vrancea Nappe)	Phytoplancton			
	Tytthodiscus sp.			580
	Tytthodiscus sp.	Plate I, fig. 2		580
	Tytthodiscus sp.			580
	Tytthodiscus sp.			580
	Tytthodiscus sp.	Plate I, fig. 3		590

Sample	Taxa	Plate index	TAI	Fluorescence λ (nm)
P105 – Lower dysodilic shale (Tarcău Nappe).	Phytoplancton			
	Cordosphaeridium gracile (Eisenack 1954) Davey et Williams 1966	Plate I, fig. 5(a); Plate I, fig. 5(b)		570
	Cordosphaeridium inodes (Klumpp 1953) Eisenack 1963			
	Homotryblium plectilum Drugg et Loeblich Jr 1967			
	Cordosphaeridium sp.			
	Achomosphaera sp.			570
	Cordosphaeridium sp.			
	Homotryblium plectilum Drugg et Loeblich Jr 1967	Plate II, fig. 2		
	Spiniferites ramosus (Ehrenberg 1838) Mantell 1854	Plate I, fig. 1(a)		
	Dinoflagellate (indeterminable)	Plate I, fig. 1(b)		580
	Operculodinium sp.	Plate I, fig. 1(c)		
	Deflandrea phosphoritica Eisenack, 1938	Plate II, fig. 5		570
	Thalassiphora pelagica (Eisenack, 1954) Eisenack and Gocht, 1960	Plate I, fig. 7		570
	Spiniferites sp.			
	Thalassiphora sp.			580
	Pollen			
	Pityosporites microalatus (Potonie 1931) Thomson et Pflug 1953		2+	
P106 - Lower dysodilic shale (Tarcău Nappe).	Phytoplancton			
	Deflandrea sp.			550
	Spiniferites sp.			
	Lingulodinium pycnospinosum (Benedek 1972) Stover et Evitt 1978	Plate II, fig. 4		580
	Operculodinium centrocarpum (Deflandre and Cookson, 1955) Wall, 1967	Plate II, fig. 3		560
	Thalassiphora pelagica (Eisenack, 1954) Eisenack and Gocht, 1960	Plate II, fig. 10		580
	Wetzeliella sp.	Plate II, fig. 1		580
	Pollen			
	Angiosperm pollen	Plate I, fig. 6	2	570
	Pityosporites insignis (Naumova ex Bolchovitina 1953) Krutzsch 1971	Plate I, fig. 8	2+	590
	Pityosporites sp.	Plate II, fig. 8	3-	610
	Pityosporites sp.	Plate II, fig. 6	2	560
	Inaperturopollenites sp.		2-	540

Most species have been determined from the Lower Dysodilic Shale (P105 and P106 – Tarcău Nappe). The predominance of phytoplankton species (marine organic matter) such as *Cordosphaeridium gracile, Thalassiphora pelagica, Operculodinium centrocarpum, Spiniferites ramosus* a.o. is noted. Among the species from the continent, only examples of pollen, mainly of gymnosperms (*Pityosporites, Inaperturopollenites*), can be cited. Spores have not been identified in this palynological assemblage.

From the Lower Dysodilic Shale collected from the Vrancea Nappe (P3, geological section from Piatra Pinului), a limited number of species has been identified (tab. 2), and from the Upper Dysodilic Shale of the same geological profile only a few specimens of *Tytthodiscus* sp. were determined.

Based on the palynological analyses performed on those 4 samples (tab. 2), it can be concluded that the number of dinoflagellates is higher in relation to the species from the continent (spores and pollen).

2. Palaeoecological significance of dinocyst assemblage

The fossils dinoflagellate cysts are used for palaeoenvironment and palaeoecological interpretations, even if they are organisms that lived only in the photic zone of seas and oceans. Given these organisms, we can deduce the sedimentary palaeoenvironments, as well as the temperature and salinity of the water.

Dale (1996) and Sluijs et al. (2005) have suggested a dinoflagellate assemblage zonation along a distal-proximal direction of a sedimentary basin. The interpretations that derive from the dinoflagellates identified in the Lower Dysodilic Shale of the Tarcău Nappe are the following:

- the innermost neriting setting is indicated by the presence of the *Homotryblium plectilum* species (in low frequencies), which could be transported by some marine currents in a distal area from the shore (Brinkhuis, 1994; Jaramillo and Oboh-Ikuenobe, 1999).
- the species from the outer neritic setting are most numerous in the assemblage identified for the Lower Dysodilic Shale Formation. Among them, *Cordosphaeridium* div. sp., *Operculodinium centrocarpum, Lingulodinium, Spiniferites ramosus, Achomosphaera* a.o. *Cordosphaeridium* could be mentioned, indicating open sea conditions (Downie et al., 1971; Köthe, 1990). *Operculodinium centrocarpum* is a cosmopolitan taxon, currently living in high abundance in the North Atlantic, in cold temperate waters. Regarding the species presented above, De Vernal et al. (1989) suggests a relationship between process length and salinity. Thus, it is claimed that the length of the process decreases with the decrease in salinity. The dinoflagellates identified by us (see Plate II, fig. 3; Plate I, fig. 1) have a greater length of the process, indicating normal salinity.
- a lagoon environment, estuarine or low salinity is indicated by the presence of the *Deflandrea* genus (Islam, 1984; Köthe, 1990), often cited in the Oligocene from the Carpathian Flysch. Its presence indicates an environment rich in nutrients. Increased nutrient abundance can occur as a result of the introduction of shelf-stored nutrients in the photic zone through turbulent mixing associated with flooding events (Brinkhuis, 1994).
- a low-oxygen shelf environment can be assumed based on the presence of the *Thalassiphora pelagica* species (Köthe, 1990; Pross and Schmiedl, 2002). Changes in dinoflagellate assemblages as a response to oxygen depletion at the sediment surface and in the water column of epicontinental setting have been observed in early Oligocene sediments (Pross, 2001). Dinoflagellate assemblages from oxygen-depleted intervals within the Mainz Embayment, SW Germany, are characterized not only by reduced dinoflagellate diversities, but also by high abundances of *Thalassiphora pelagica*. However, it is noted that, in the analyzed profiles, we have not identified a higher frequency for this species.

3. Palynofacies analysis

In marine environments, the proximal-distal trend is one of the most important control factors in kerogen distribution. In addition to this control factor, the amount and type of kerogen dispersed in rocks also depend on the source of organic matter, lithology, tectonics conditions, sea level fluctuations, paleoproductivity, diagenesis (Oboh-Ikuenobe et al., 1998). For detailed marine environmental analyses, several kerogen distribution trends and parameters have been used (Tyson, 1995). These trends and parameters are based on percentages of kerogen categories.

a. Amorphous organic matter (AOM): represents a high proportion of all the analyzed samples.

A high value of AOM in sediment samples indicates a reducing environment (dysoxic or anoxic), with a high potential for preservation of planktonic organisms. This AOM can have both a marine origin, derived from bacterial degradation of planktonic organisms, and a continental origin resulting from the degradation of continental plant debris (Bombardiere and Gorin, 2000). We can distinguish between these two categories of AOM (derived from marine or continental sources) based on fluorescence. Thus, AOM derived from the degradation of phytoplankton has fluorescence, while AOM resulting from the degradation of plant debris is non-fluorescent. Another opinion on AOM fluorescence was expressed by Tyson (1995). According to this author, AOM presenting fluorescence derives from "well-preserved plankton/bacteria", and non-fluorescent AOM results from "degraded plankton/bacteria".

The AOM extracted from the samples of analyzed Lower and Upper Dysodilic Shale was found in the percentages presented in table 3.

Tab. 3 The percentage of AOM, phytoclasts and palynomorphs from the kerogen analyzed under the microscope

Sample	AOM %	Phytoclasts %	Palynomorphs %
P106	≈ 96 - 97	≈ 2	≈ 1
P105	≈ 95	≈ 3	≈ 2
P3	≈ 98	≈ 1	≈ 1
P4	≈ 75 - 80	≈ 18 - 23	≈ 2 - 3

The Lower Dysodilic Shale Formation (Tarcău and Vrancea Nappe) contains approx. 95 to 98% of the AOM from the total amount of kerogen. The AOM included in P3 (Lower Dysodilic Shale – Vrancea Nappe) represents a large portion of the sample, thus hiding most of the palynomorphs and phytoclasts. The dinoflagellates and pollen from the analyzed samples have been identified because they displayed fluorescence, thus being clearly distinguished even if they were covered/included in the predominant AOM without fluorescence. It is worth noting that all the AOM viewed in the samples is non-fluorescent, which leads to the conclusion that this would come from either phytoplankton found in an advanced stage of degradation, or from a series of degraded continental plant debris. The AOM identified is likely to display a "mixture" of the two sources mentioned above (marine and continental). This assertion is supported by the type of kerogen determined based on chemical criteria (H/C and O/C ratios projected onto a Van Krevelen diagram), which is Type II (mixed) (fig. 3a).

b. Phytoclasts: are relatively poorly represented in the Lower Dysodilic Shale (≈ 1-3% of kerogen), and exist in a higher proportion (≈ 18-23%) in the Upper Dysodilic Shale from the Piatra Pinului geological profile. This percentual difference between the two geological formations could be a link between them (tab. 3). A low percentage of phytoclasts (continental source of organic matter) would indicate distal depositional conditions of the sedimentary basin.

Among these phytoclasts we could mention black coal remains, brown-yellow fragments and a low percentage of plant tissue and amber. All these remains are non-fluorescent.

c. Palynomorphs: represent 1-3% of the total amount of kerogen, often masked by the AOM present in high percentage. We noted that most palynomorphs could be identified in reflected light (fluorescent), while in transmitted light they were hardly noticeable. Phytoplankton is predominant, often appearing bright yellow in fluorescent light (Plate I-III). Pollen is represented mainly by gymnosperms.

More details regarding the palynological assemblage and the interpretations made in relation to it are presented in the palynology chapter.

The AOM-Phytoclast-Palynomorph ternary plot of Tyson (1995) suggests sedimentation in a distal suboxic-anoxic basin, with AOM-rich kerogen hiding the palynomorphs (fig. 4).

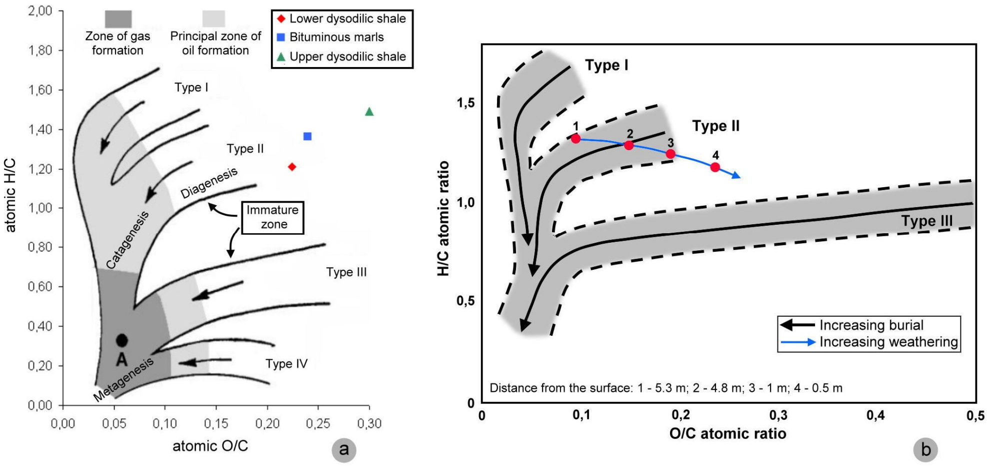
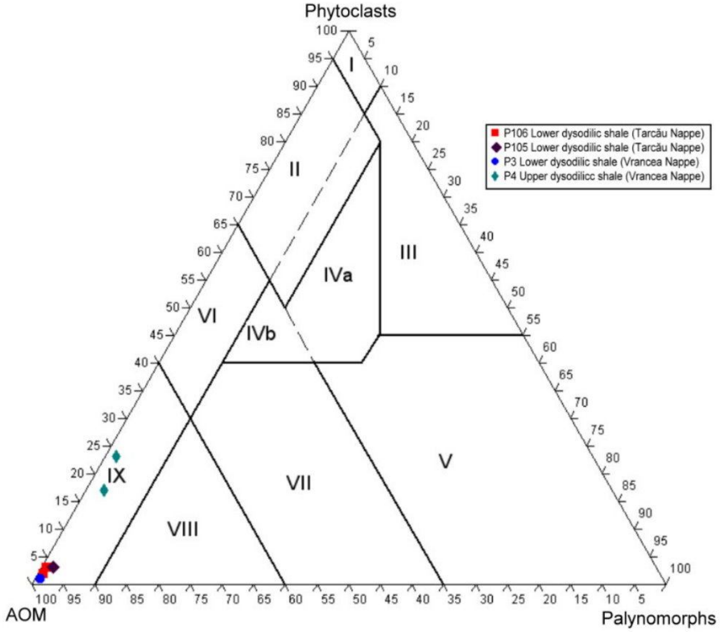


Fig. 3 (a) – Van Krevelen diagram, with examples of types of kerogen derived from chemical analyses; (b) – Development of H/C vs. O/C atomic ratio with decreasing outcrop sampling depth (after Durand and Monin, 1980).

4. Organic carbon content in bituminous rocks

In the present paper, analyses were peformed on 6 samples, 2 collected from the Lower Dysodilic Shale Formation from the Tarcău Nappe and 4 collected from the outcrop in the Piatra Pinului Reservation area (tab. 1). The petroleum genetic potential indicated by the TOC analyses is generally good to excellent, the maximum value (TOC = 8.9%) being registered in sample P1, collected from the Bituminous Marls which crop out on the Piatra Pinului Reservation (Vrancea Nappe).

Overall, the Bituminous Marls and Lower Dysodilic Shale contain a higher TOC percentage, compared to the Upper Dysodilic Shale.



Palynofacies field and Environment		Comments	Spores: Bisaccates	Microplankton	Kerogen type
I	Highly proximal shelf or basin	High phytoclast supply dilutes all other components.	usually high	very low	III, gas prone
II	Marginal dysoxic-anoxic basin	AOM diluted by high phytoclast input, but AOM preservation moderate to good. Amount of marine TOC dependent on basin redox state.	high	very low	III, gas prone
III	Heterolithic oxic shelf ("proximal shelf")	Generally low AOM preservation; absolute phytoclast abundance dependent on actual proximity to fluvio-deltaic source. Oxidation and reworking common.	high	common to abundant dinocysts dominant	III or IV, gas prone
IV	Shelf to basin transition	Passage from shelf to basin in time (eg increased subsidence/ water depth) or space (eg basin slope). Absolute phytoclast abundance depends on proximity to source and degree of redeposition. Amount of marine TOC depends on basin redox state. IVa dysoxic-suboxic, IVb suboxic-anoxic.	moderate to high	very low-low	III or II, mainly gas prone
V	Mud-dominated oxic shelf ("distal shelf")	Low to moderate AOM (usually degraded). Palynomorphs abundant. Light coloured bioturbated, calcareous mudstones are typical.	usually low	common to abundant dinocysts dominant	III>IV, gas prone
VI	Proximal suboxic-anoxic shelf	High AOM preservation due to reducing basin conditions. Absolute phytoclast content may be moderate to high due to turbiditic input and/or general proximity to source.	variable, low to moderate	low to common dinocysts dominant	II, oil prone
VII	Distal dysoxic-anoxic "shelf"	Moderate to good AOM preservation, low to moderate palynomorphs. Dark-coloured slightly bioturbated mudstones are typical.	low	moderate to common dinocysts dominant	II, oil prone
VIII	Distal dysoxic-anoxic shelf	AOM-dominated assemblages, excellent AOM preservation. Low to moderate palynomorphs (partly due to masking). Typical of organic-rich shales deposited under stratified shelf sea conditions.	low	low to moderate dinocysts dominant, % prasinophytes increasing	II>>I, oil prone
IX	Distal suboxic-anoxic basin	AOM-dominated assemblages. Low abundance of palynomorphs partly due to masking. Frequently alginite-rich. Deep basin or stratified shelf sea deposits, especially sediment starved basins.	low	generally low prasinophytes often dominant	II≥I, highly oil prone

Fig. 4 AOM-Phytoclast-Palynomorph plot, after Tyson (1995). Palynofacies analysis revealed an abundant AOM, indicating a distal suboxic-anoxic basin.

5. Thermal maturation of kerogen

The maturation degree of the organic matter extracted from the bituminous rocks analyzed was derived according to the TAI (inferred from pollen specimens), based on the fluorescence color of the dinoflagellates.

TAI is a numerical scale, based on the changes that the color of the palynomorphs (spores and pollen) undergoes as the temperature to which they are subjected increases (Pearson, 1984). The visual determination of palynomorph color showed a TAI between 2 and 2+ (frequently) (tab. 2), indicating a stage between immature and mature for the organic matter.

The fluorescence color of dinoflagellates is yellow to bright yellow, which corresponds to a wavelength of $\lambda \approx 580$ nm (frequently) (tab. 2). According to Raynaud and Robert (1976), organic matter that displays a fluorescence color between 580 and 630 nm is in a mature stage in terms of hydrocarbon generation. The bright yellow displayed by the majority of the palynomorphs is equivalent to a vitrinite reflectance (VR_0) up to 0.7% (Smojić et al., 2009).

Based on the optical analysis of the kerogen extracted from the analyzed rocks, we can conclude that it is at the limit between an immature and a mature stage of hydrocarbon generation.

The projection of the H/C and O/C ratios onto the Van Krevelen diagram indicated that the bituminous rocks analyzed from the Piatra Pinului geological profile are in an immature stage (fig. 3a). The position of the points on the diagram would indicate a beginning of rock diagenesis that contradicts the results obtained in the case of fluorescence and TAI, which point to the limit between an immature and a mature stage.

This discrepancy between the two analytical methods (chemical analyses for H, C, O, and optical analysis of kerogen in transmitted and fluorescent light) seems to be due to the method used in the sampling for chemical analysis. The samples analyzed in the present paper were collected from outcrops at depths of about 10 to 20 cm in the outcrop, therefore it is possible that the original chemical composition of the organic matter changed as a result of the influence of external factors such as oxidation and degradation phenomena. An experiment that revealed the phenomenon of change in the chemical composition with the sampling at depth of the outcrop has been proposed by Durand and Monin (1980). The experiment was performed on organic matter (Kerogen II) from the Lower Toarcian Shale of the Parisian Basin. Four samples were collected (from depths of 5.3 m, 4.8 m, 1 m and 0.5 m in the outcrop), and it was observed that the sample taken from the greatest depth had a much smaller O/C ratio, compared to that extracted from the surface (fig. 3b).

We believe that this “early diagenesis” of the sediments examined through the chemical analysis of the kerogen is due to the method used in sampling the outcrops, which may lead to errors. For good results to be achieved, it would be preferable that the samples derive either from boreholes or from a greater depth inside the outcrop.

Conclusions

The palynological, palynofacial and thermal maturation study of organic matter from the 7 samples belonging to bituminous rocks included in the Tarcău and Vrancea nappes that were analyzed revealed the following:

- the palynological assemblage is better represented in the Lower Dysodilic Shale Formation, being dominated by species of phytoplankton (*Cordosphaeridium gracile, Operculodinium centrocarpum, Thalassiphora pelagica, Deflandrea phosphoritica* a.o.). Among the continental palynomorphs we could mention the predominance of conifers. In the Upper Dysodilic Shale Formation (Piatra Pinului geological profile), only a few specimens of *Tytthodiscus* sp. were determined. The palaeoenvironment indicated by most phytoplankton species identified in the Lower Dysodilic Shale Formation (Tarcău Nappe) is an outer neritic setting. The presence of a lagoon and a poorly-oxygenated shelf environment inferred based on the presence of the *Thalassiphora pelagica* species could also be stated.

- the palynofacial analyses revealed an abundance of AOM, often masking other constituents of kerogen (palynomorphs, phytoclasts). This AOM is non-fluorescent; its origin can be combined: marine (phytoplankton in an advanced stage of degradation) and continental (degraded debris of terrestrial plants). Out of the total amount of organic matter studied under a microscope, the AOM percentage is higher in the Lower Dysodilic Shale Formation (≈ 95-98%) and lower in the Upper Dysodilic Shale Formation (≈ 75-80%).

- the kerogen from the analyzed rocks is Type II, having been established based on chemical criteria (the projection of H/C and O/C atomic ratios onto a Van Krevelen diagram).

- AOM-Phytoclasts-Palynomorphs ratios (Tyson, 1995) suggest a distal suboxic-anoxic basin.

- the TOC content indicates a good to excellent petroliferous genetic potential (TOC = 1.65-8.9%). The maximum value corresponds to the bituminous marls from Piatra Pinului.

- the maturation degree of the kerogen, assumed based on TAI and palynomorph fluorescence, indicates a stage of organic matter at the limit between immature and mature.

Acknowledgments

The author wishes to thank his colleague Teaching Assistant Gabriel Chirilă, PhD for his help in drafting the present paper. He is also grateful to Prof. Em. Leonard Olaru, PhD for his revision of the present paper.

References

Balteş, N., 1983. Hydrocarbon source-rocks in Romania. Anuarul Institutului de Geologie şi Geofizică; Tectonică, petrol şi gaze, **LX**, 265–270.

Bădescu, D., 2005. Tectonic-stratigraphical evolution of the Eastern Carpathians during the Mesozoic and Neozoic age. Ed. Economică, Bucureşti, 312p. (In Romanian).

Băncilă, I., 1958. Geology of Eastern Carpathians. Ed. Ştiinţifică, Bucureşti, 368p. (In Romanian).

Belayouni, H., Di Staso, A., Guererra, F., Martin, M.M., Miclăuş, C., Serrano, F., Tramontana, M., 2007. Stratigraphic and geochemical study of the organic-rich black shales in the Tarcău Nappe of the Moldavidian Domain (Carpathian Chain, Romania). International Journal of Earth Sciences, **98**, 157–176.

Bombardiere, L., Gorin, G.E., 2000. Stratigraphical and lateral distribution of sedimentary organic matter in Upper Jurassic carbonates of SE France. Sedimentary Geology, **132**, 177–203.

Brinkhuis, H., 1994. Late Eocene to early Oligocene dinoflagellate cysts from the Priabonian type-area (Northeast Italy): biostratigraphy and paleoenvironmental interpretation. Palaeogeography, Palaeoclimatology, Palaeoecology, **107**, 121–163.

Dale, B., 1996. Dinoflagellate cyst ecology: modeling and geological applications. In: Jansonius, J., MacGregor, D.C. (Eds.), Palynology: Principles and Applications. American Association of Stratigraphic Palynologists Foundation, 1249–1275.

De Vernal, A., Goyette, C., Rodrigues, C.G., 1989. Palynostratigraphic contributions (dinocysts, pollen and spores) at the knowledge of Champlain Sea: Saint-Césaire section, Québec. Can. J. Earth Sci., **26**, 2450–2464. (In French).

Downie, C., Hussain, M.A., Williams, G.L., 1971. Dinoflagellate cyst and acritarch associations in the Paleogene of southeast England. Geosci. Man, **3**, 29–35.

Durand, B., Nicaise, G., 1980. Procedures of kerogen isolation. In: Durand, B. (Ed.), Kerogen, Insoluble Organic Matter from Sedimentary Rocks, Editions Technip, Paris, 35–53.

Durand, B., Monin, J.C., 1980. Elemental analysis of kerogens. In: Durand, B. (Ed.), Kerogen, Insoluble Organic Matter from Sedimentary Rocks. Editions Technip, Paris, 113–142.

Grasu, C., Catană, C., Grinea, D., 1988. Carpathian flysch. Petrography and economic considerations. Ed. Tehnică, Bucureşti, 208p. (In Romanian).

Grasu, C., Catană C., 1989. Variations of chemistry, mineralogy and content of the organic matter in Oligocene dysodiles from the Carpathians Flysch. The Oligocene from the Transylvanian Basin, Special issues, Cluj-Napoca, 363–369. (In French).

Grasu, C., Catană, C., Miclăuş¸ C., Boboş¸ I., 1999. Molasse of Eastern Carpathians. Petrography and sedimentogenesis. Ed. Tehnică, Bucureşti, 227p. (In Romanian).

Grasu, C., Miclăuş, C., Florea, F., Şaramet, M., 2007. Geology and economic exploitation of bituminous rocks from Romania. Ed. Universităţii "Al. I. Cuza" Iaşi, 253p. (In Romanian).

Ionesi, L., 1961. Geology of the Gura Humorului – Poiana Micului region. An. Şt. Univ. "Al. I. Cuza", Geologie-Geografie, **VII**, 2, p.355–382 (In Romanian).

Ionesi, L., 1971. Paleogene flysch from the Basin of Moldova River. Ed. Academiei, Bucureşti, 250p. (In Romanian).

Islam, M.A., 1984. A study of Early Eocene palaeoenvironments in the Isle of Sheppey as determined from microplankton assemblage composition. Tertiary Res., **6**, 11–21.

Jaramillo, C.A., Oboh-Ikuenobe, F.E., 1999. Sequence stratigraphic interpretations from palynofacies, dinocyst and lithological data of Upper Eocene–Lower Oligocene strata in southern Mississippi and Alabama, U.S. Gulf Coast. Palaeogeography, Palaeoclimatology, Palaeoecology, **145**, 259–302.

Köthe, A., 1990. Paleogene dinoflagellates from northwest Germany - biostratigraphy and Palaeoenvironments. Geol. Jahrb., **A118**, 3–111.

Nacu, D., Botez, C., Ionesi, L., Voiculescu, N., 1970. Some aspects of the geochemistry of organic matter in bituminous rocks from the basin of the Moldova Valley. St. şi Cerc. Geol., Geofiz., Geogr., Geologie, 2, **15**, 367–379. (In Romanian).

Oboh-Ikuenobe, F.E., Yepes, O., Gregg, J.M., 1998. Palynostratigraphy, palynofacies, and thermal maturation of Cretaceous –Paleocene sediments from the Côte D'Ivoire-Ghana transform margin. In Mascle, J., Lohmann, G.P., Moullade, M. (Eds.): Proceedings of the Ocean Drilling Program, Scientific Results, **159**, 277–318.

Olaru, L., 1978. Research on the stratigraphic distribution of microflora in the Paleogene flysch between Bistriţa and Trotuş Valleys. Instit. de Géol. et de Géof., Mémoires, **XXVII**, Bucureşti, 5–111. (In Romanian).

Pawlewicz, M., 2007. Total Petroleum Systems of the Carpathian–Balkanian Basin Province of Romania and Bulgaria. U.S. Geological Survey Bulletin, 2204–F, 17 p.

Pearson, D.L., 1984. Pollen/spore color 'standard'. Phillips Petroleum Company Exploration Projects Section (reproduced in Traverse, A., 1988. Palaeopalynology, Plate 1. Unwin Hyman, Boston).

Peters, K.E., Cassa, M.R., 1994. Applied Source Rock Geochemistry. In: Magoon, L.B., Dow, W.G. (Eds.). The petroleum system from source to trap, American Association of Petroleum Geologists, Memoire, **60**, 93–117.

Pross, J., 2001. Paleo-oxygenation in Tertiary epeiric seas: evidence from dinoflagellate cysts. Palaeogeography, Palaeoclimatology, Palaeoecology, **166**, 369–381.

Pross, J., Schmiedl, G., 2002. Early Oligocene dinoflagellate cysts from the Upper Rhine Graben (SW Germany): paleoenvironmental and paleoclimatic implications. Marine Micropaleontology, **45**, 1–24.

Raynaud, J.F., Robert, P., 1976. Methods of optical study of the organic matter. Bull. Centre Rech. Pau – SNPA, **10**, 109–127. (In French).

Robert, P., 1985. Geothermal history and organic diagenesis. Bull. Centres Rech. Explor.-Prod. Elf-Aquitaine, Mém., **8**, 345p. (In French).

Săndulescu, M., 1984. Geotectonics of Romania. Ed. Tehnică, Bucureşti, 336p. (In Romanian).

Sluijs, A., Pross, J., Brinkhuis, H., 2005. From greenhouse to icehouse; organic-walled dinoflagellate cysts as paleoenvironmental indicators in the Paleogene. Earth-Science Reviews, **68**, 281–315.

Smojić, S.B., Smajlović, J., Koch, G., Bulić, J., Trutin, M., Oreški, E., Alajbeg, A., Veseli, V., 2009. Source potential and palynofacies of Late Jurassic "Lemeš facies", Croatia. Organic Geochemistry, **40**, 833–845.

Stănescu, V., Morariu, D.C., 1986. Oil generation in the major tectonic evolution of the basins from Romania. St. şi Cerc. Geol., Geofiz., Geogr., Geologie, **31**, 143–153. (In Romanian).

Stoicescu, A., 2004. The palynology and biostratigraphy of the Lower Miocene and bitumens from Slănic-Oituz half-windows. PhD. Thesis, „Al. I. Cuza" Univ, Iaşi, 163P. (In Romanian).

Ştefănescu, M., Dicea, O., Butac, A., Ciulavu, D., 2006. Hydrocarbon geology of the Romanian Carpathians, their foreland, and the Transylvanian Basin. In: Golonka, J., Picha, F.J. (Eds.), The Carphathians and their foreland: Geology and hydrocarbon resources, AAPG Memoire, **84**, 521–567.

Tyson, R.V., 1995. Sedimentary Organic Matter: Organic Facies and Palynofacies. Chapman & Hall, London.

Vandenbroucke, M., 2003. Kerogen: from types to models of chemical structure. Oil & Gas Science and Technology, **58**, 243–269.

Vandenbroucke, M., Largeau, C., 2007. Kerogen origin, evolution and structure. Organic Geochemistry, **38**, 719–833.

Received July, 2010
Revised: November, 2010
Accepted: November, 2010

CAPTION OF PLATES

Plate I

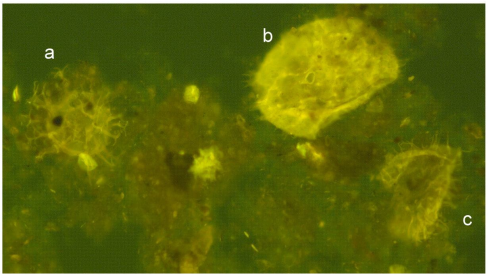
1a (incident blue light, fluorescence), 1b (Idem, transmitted light): a - *Spiniferites ramosus*; b - dinoflagellate (indeterminable); c - *Operculodinium* sp. (P105)
2a (incident blue light, fluorescence), 2b (Idem, transmitted light): *Tytthodiscus* sp. (P4)
3a (incident blue light, fluorescence), 3b (Idem, transmitted light): *Tytthodiscus* sp. (P4)
4a (incident blue light, fluorescence), 4b (Idem, transmitted light): *Dracodinium* sp. (P3)
5a (incident blue light, fluorescence), 5b (Idem, transmitted light): a - *Cordosphaeridium gracile*; b - *Cordosphaeridium inodes* (P105)
6a (incident blue light, fluorescence), 6b (Idem, transmitted light): Angiosperm pollen (P106)
7a (incident blue light, fluorescence), 7b (Idem, transmitted light): *Thalassiphora pelagica* (P105)
8a (incident blue light, fluorescence), 8b (Idem, transmitted light): *Pityosporites insignis* (P106)

Plate II

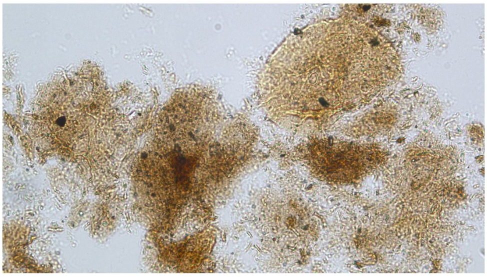
1a (incident blue light, fluorescence), 1b (Idem, transmitted light): *Wetzeliella* sp. (P106)
2a (incident blue light, fluorescence), 2b (Idem, transmitted light): *Homotryblium plectilum* (P105)
3a (incident blue light, fluorescence), 3b (Idem, transmitted light): *Operculodinium centrocarpum* (P106)
4a (incident blue light, fluorescence), 4b (Idem, transmitted light): *Lingulodinium pycnospinosum* (P106)
5a (incident blue light, fluorescence), 5b (Idem, transmitted light): *Deflandrea phosphoritica* (P105)
6a (incident blue light, fluorescence), 6b (Idem, transmitted light): *Pityosporites* sp. (P106)
7a (incident blue light, fluorescence), 7b (Idem, transmitted light): *Sciadopityspollenites* sp. (P3)
8a (incident blue light, fluorescence), 8b (Idem, transmitted light): *Pityosporites* sp. (P106)
9a (incident blue light, fluorescence), 9b (Idem, transmitted light): *Pityosporites* sp. (P3)
10a (incident blue light, fluorescence), 10b (Idem, transmitted light): *Thalassiphora pelagica* (P106)

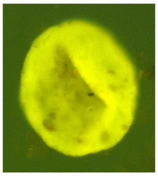
Plate III

1a (transmitted light), 1b (Idem, incident blue light, fluorescence): organic matter from P4 (Upper dysodilic shale, Vrancea Nappe)
2a (transmitted light), 2b (Idem, incident blue light, fluorescence): organic matter from P3 (Lower dysodilic shale, Vrancea Nappe)
3a (transmitted light), 3b (Idem, incident blue light, fluorescence): amorphous organic matter, P106 (Lower dysodilic shale, Tarcău Nappe)

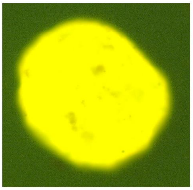


1a

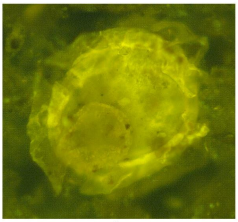

1b

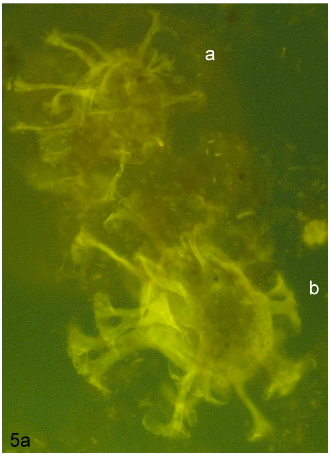

2a


2b

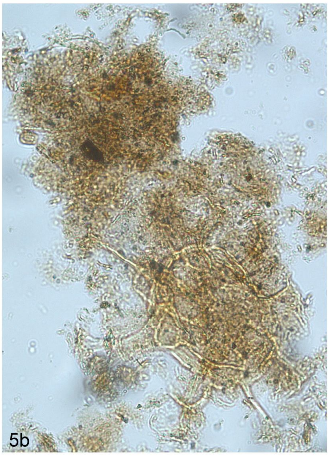

3a

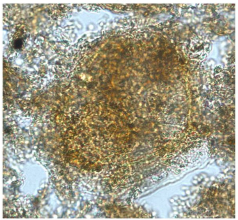

3b

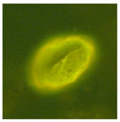

4a

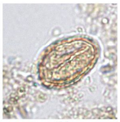


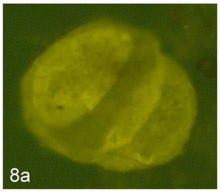
5a

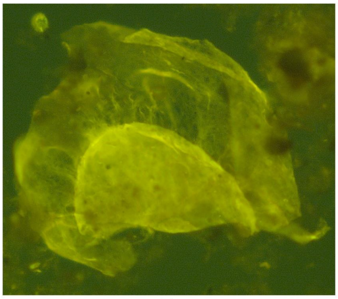

5b

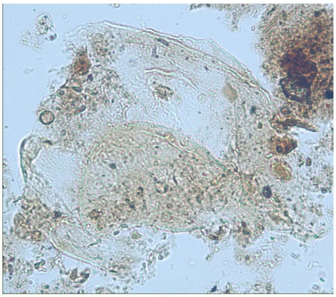

4b

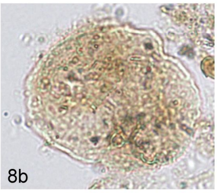

6a


6b

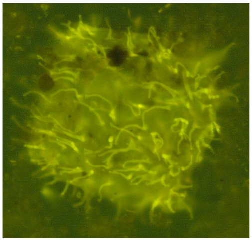

8a

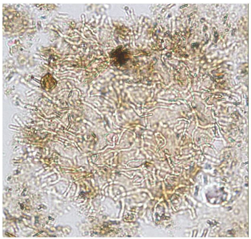

7a

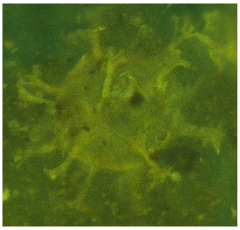

7b

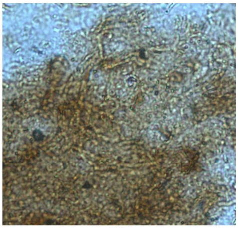

8b

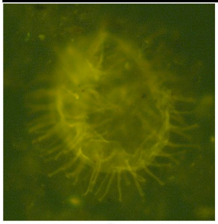
50 µm

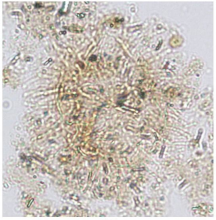

1a

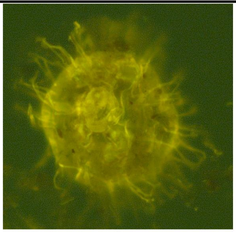

1b

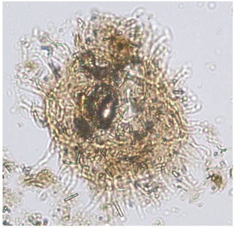

2a

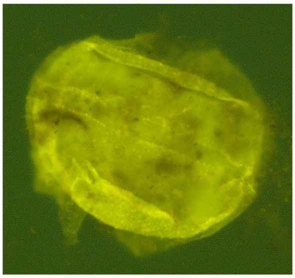

2b

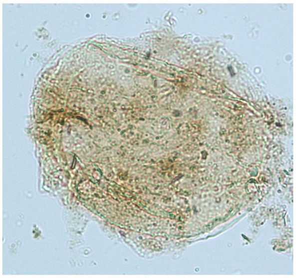

3a

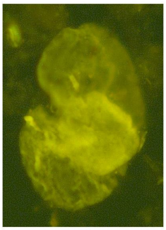

3b

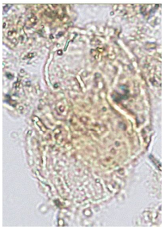

4a

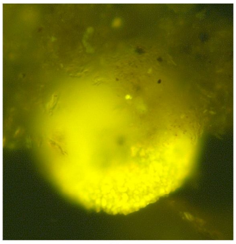

4b

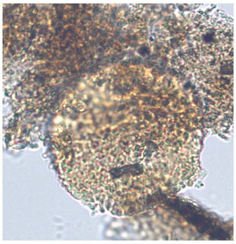

5a

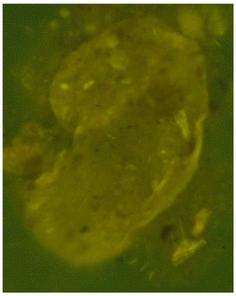

5b

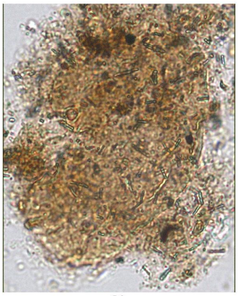

6a

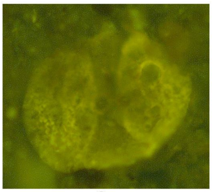

6b

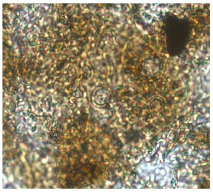

7a

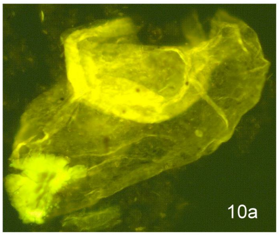

7b

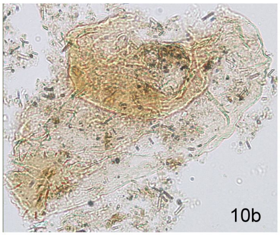

8a


8b

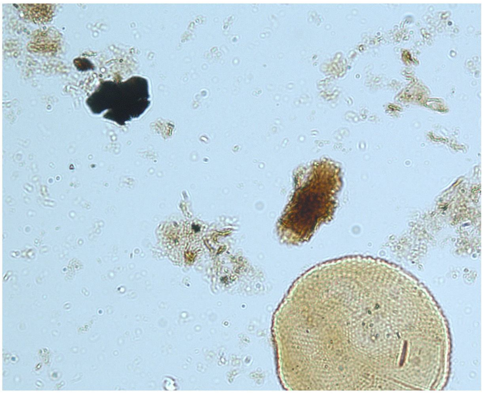

9a

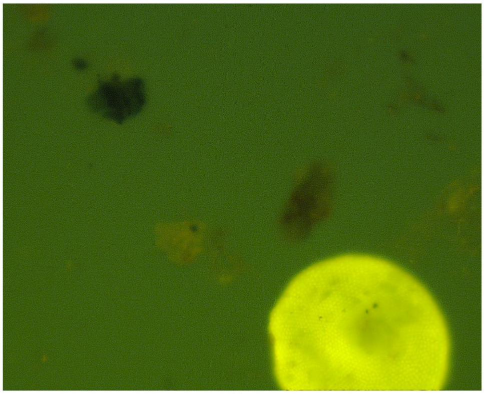

9b

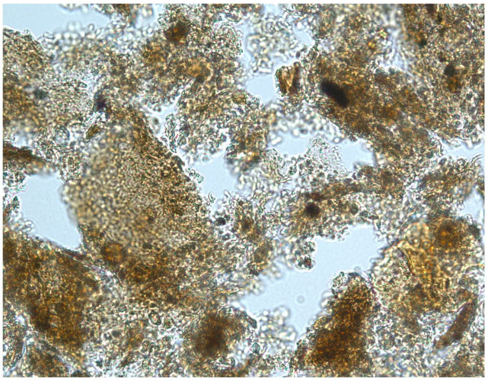

10a

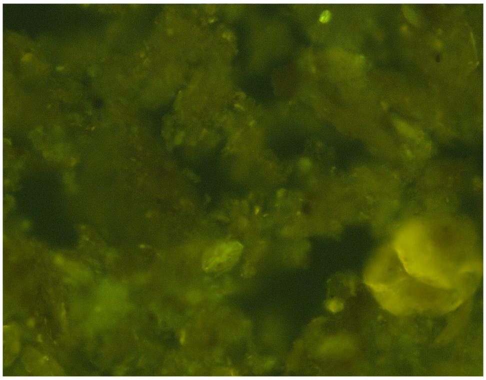

10b

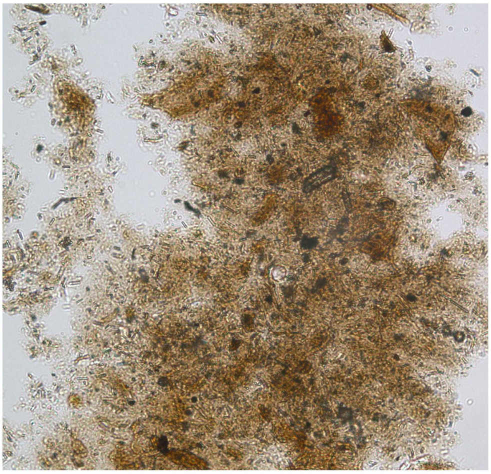
50 μm

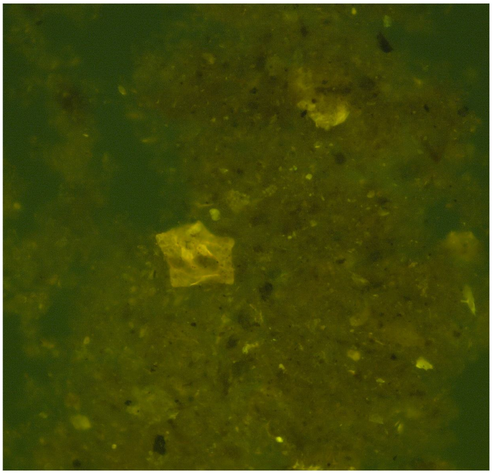

1a


1b


2a


2b


3a


3b