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Diagenesis of Miocene pelitic sedimentary rocks in the Sava Depression (Croatia)

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ABSTRACT: Miocene pelitic sedimentary rocks from six wells in the Sava Depression (sub-basin in the south-western part of the Pannonian Basin System) were investigated in order to determine the degrees of diagenetic alteration. Qualitative and semiquantitative mineral compositions of samples and the content of smectite in illite-smectite (I-S) were determined by X-ray powder diffraction (XRD). Vitrinite reflectance and thermal alteration index (TAI) were measured in order to estimate the palaeotemperatures. Carbonate minerals, clay minerals and quartz are the main constituents of the pelitic sediments. Feldspars (albite), pyrite, opal-CT and hematite are present as minor constituents in some rocks. The mineral composition of the rocks, apart from previously known differences caused by various depositional environments and clastic material provenance, is dependent on the degree of diagenetic processes. At elevated temperatures and large burial depths the minerals formed by alteration processes or precipitated at the surface; smectite, kaolinite and calcite were gradually replaced by minerals formed by diagenetic processes, i.e. by illite-smectite, illite, chlorite, Ca-excess dolomite/ankerite and albite. Based on XRD data for smectite, I-S and illite, three stages of diagenetic development have been established. The early stage was characteristic of samples at depths <1.8 km containing smectite, I-S of the random *R*0 type and detrital illite. The middle stage begins with the appearance of the ordered *R*1 type of I-S at the depths >1.8 km and temperature above 80ºC. At depths >4.6 km with corresponding temperatures >190ºC, the late stage began, characterized by the presence of *R*>1 I-S with <10% smectite.

KEYWORDS: diagenesis, illite-smectite, Miocene, Pannonian Basin System, pelitic sedimentary rocks, Sava Depression, Croatia, thermal alteration index, vitrinite reflectance.

Mineralogical investigations of the Miocene pelitic sedimentary rocks in the Croatian part of the Pannonian Basin System (PBS) are scarce and have focused mainly on the determination of mineral compositions (Braun, 1991; Slovenec & Tadej, unpublished data, 1992; Tadej & Slovenec, 2001; Grizelj *et al.*, 2007). Investigations of the illitization process in smectite, which are widely used in the oil industry, have not been carried out so far in the Croatian part of the PBS. In the neighbouring sub-basins of the PBS the process is well documented (Kurzweil & Johns, 1981; Franců *et al.*, 1990; Hámor-Vidó & Viczián, 1993; Šucha *et al.*, 1993; Hillier *et al.*, 1995; Tanács & Viczián, 1995; Gier, 1998; Sachsenhofer *et al.*, 1998).

Due to the fact that both the migration of oil to oil-traps and the illitization process of smectite are temperature dependent (Hancock & Taylor, 1978), and the fact that the latter process can be calibrated with respect to temperature, the illitization process is widely used for the reconstruction of the thermal

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and tectonic evolution of sedimentary basins (Perry & Hower, 1970; Hoffman & Hower, 1979; Pollastro, 1993; Hillier *et al.*, 1995).

In the course of smectite-to-illite alteration processes, diocatahedral smectites gradually transform to I-S as intermediate phases in the transition to pure illite. The main controlling factors for the illitization of smectite are temperature and the availability of K^+. Contributing factors include: permeability, which accelerates the mineralogical transformation; organic matter, which appears to retard clay transformation; original detrital mineral composition; and the time for which the pelitic sedimentary rocks remain at a given temperature (Potter *et al.*, 2007). Generally less stable minerals transform to more stable phases at greater burial depths (e.g. Ca-feldspar to albite, and opal-A to opal-CT and quartz). Illite-to-smectite is the most common mineral transformation used for reconstruction of the thermal and tectonic evolution of sedimentary basins. Transition from the $R0$ to $R1$ type of illite-smectite, as well as from $R1$ to $R>1$ type illite-smectite, can be used for determining the thermal maturity of source rocks and their oil generation potential. According to Hoffman & Hower (1979) and Środoń (2007), disordered illite-smectite transforms to the ordered $R1$ type at temperatures of ~100ºC, while at ~170ºC the $R1$ type I-S transforms to the $R>1$ type. These transformation temperatures roughly correspond to the ‘oil window‘ temperatures.

The aim of the present study was to determine the sequence of diagenetic processes, i.e. to determine changes in mineral composition with increasing burial depths and to establish, by correlating clay mineralogy and palaeotemperatures, estimated from vitrinite reflectance studies, the depths and temperatures at which certain diagenetic changes took place. Investigations were carried out on samples from the deepest central part of the Sava Depression. Samples from six oil wells have been taken from the drilling core repository of the INA oil company. The greatest number of samples was available from the wells of Donja Jelenska-1 (DJ-1) and Gojilce-1 (Gj-1); therefore the results obtained from these wells are the most representative for the sedimentary column of the Sava Depression. Samples of specific stratigraphic horizons from the adjacent wells Mahovo-1 (Mah-1), Laktec-1 (Lak-1), Ježevo Duboka-3 (JeD-3) and Žutica-256D (Žu-256D) (Tables 1 and 2) were analysed for correlation purposes in order to obtain additional information on the mineral composition dependence on burial depth.

GEOLOGICAL SETTING

The Pannonian Basin System is one of the Mediterranean back-arc basins, whose development started in the Early Miocene as a result of continental collision and subduction of the European Plate beneath the Apulian Plate. It is surrounded by the Alps, Carpathians and Dinarides, and is composed of several smaller deep depressions (sub-basins), such as the Sava Depression, separated by elevations of the basement rocks (Fig. 1a) (Horváth & Royden, 1981; Royden, 1988). Two phases of development of the PBS have been recognized. The first (syn-rift) phase was marked by the subsidence of basins along faults and strong volcanic activity, while the second (post-rift) phase was marked by basin subsidence caused by cooling of the lithosphere (Horváth & Royden, 1981; Royden *et al.*, 1983; Royden, 1988).

In a palaeogeographic sense, the PBS comprises the greatest part of the Central Paratethys, the sedimentation area that lost and re-established connections with the Mediterranean and the Indo-Pacific Ocean several times during the Miocene. A growing trend of isolation of the Central Paratethys led to the evolution of endemic fauna; therefore it was necessary to introduce local Miocene stratigraphic divisions (Fig. 2) (Rögl, 1996).

The Sava Depression, a sub-basin of the PBS, is located in its SW part (Fig. 1). The evolution of Neogene sedimentation in the area of the Sava Depression has been described in detail by several authors (Barić *et al.*, 2000; Lučić *et al.*, 2001; Vrbanac, 2002; Saftić *et al.*, 2003; Pavelić, 2005). According to them, the thickness of the Neogene deposits, together with the Quaternary deposits, exceeds 5.0 km; just over 1 km is formed of syn-rift sediments (Ottnangian-Lower Badenian) and the rest are post-rift sediments (Upper Badenian–Recent). Their deposition began in the Ottnangian, on the tectonized Palaeozoic-Mesozoic crystalline basement, in alluvial and freshwater lake environments. These oldest sediments are represented by breccias, conglomerates, sandstones and marls. At the beginning of the Karpatian a connection with marine areas was established; sandstones, marls and tuffs were deposited in marine environments on the Ottnangian sediments. Marine conditions persisted through the Badenian, and, during this period,

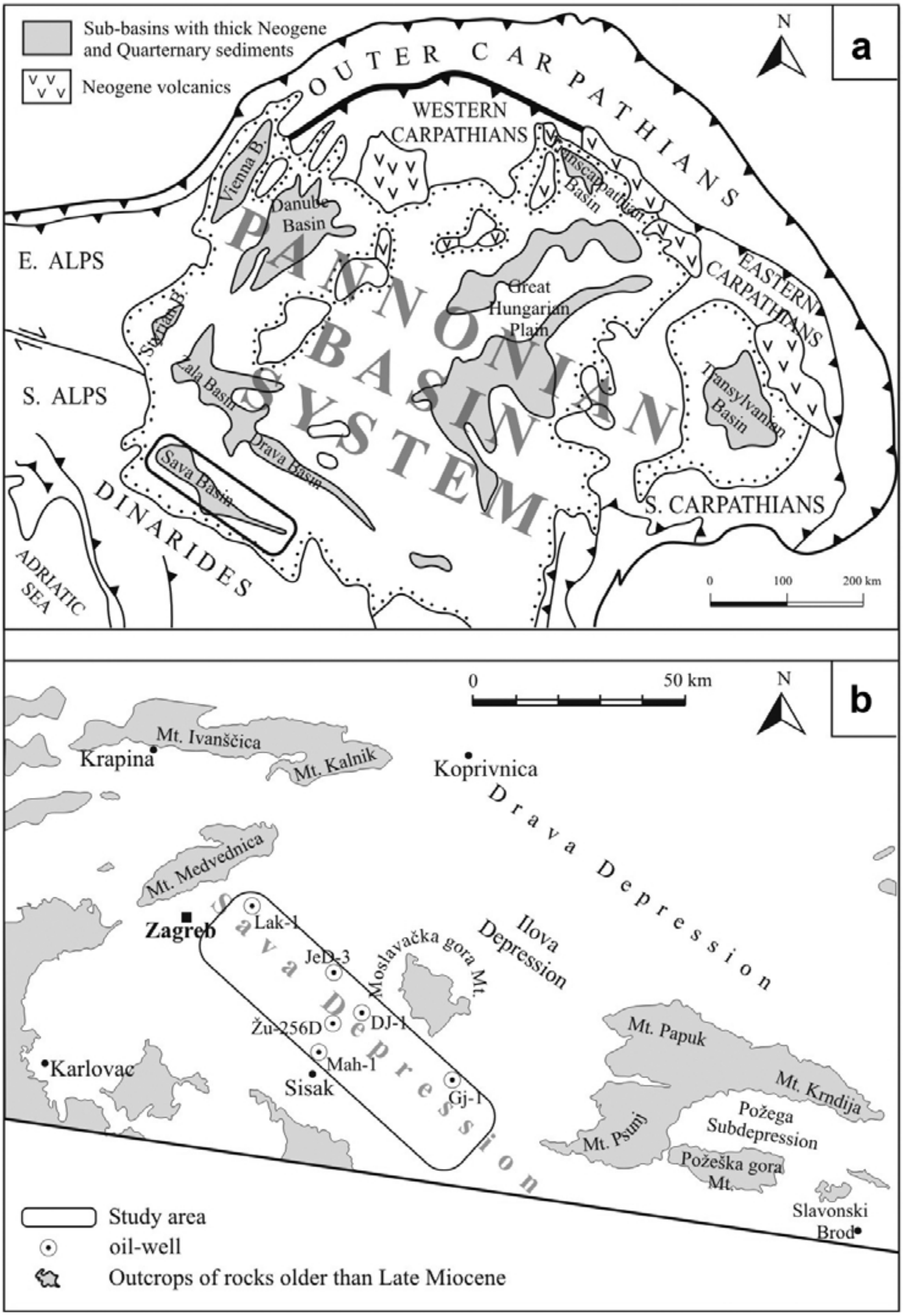

FIG. 1. (a) Tectonic sketch of the Pannonian Basin System and its surroundings (after Royden, 1988). (b) South-western part of the Pannonian Basin System with locations of the study-area (Sava Depression) and the oil-wells (Lak-1, Laktec-1; JeD-3, Ježevo Duboka-3; Žu-256D, Žutica-256D; DJ-1, Donja Jelenska-1; Mah-1, Mahovo-1; Gj-1, Gojilce-1).

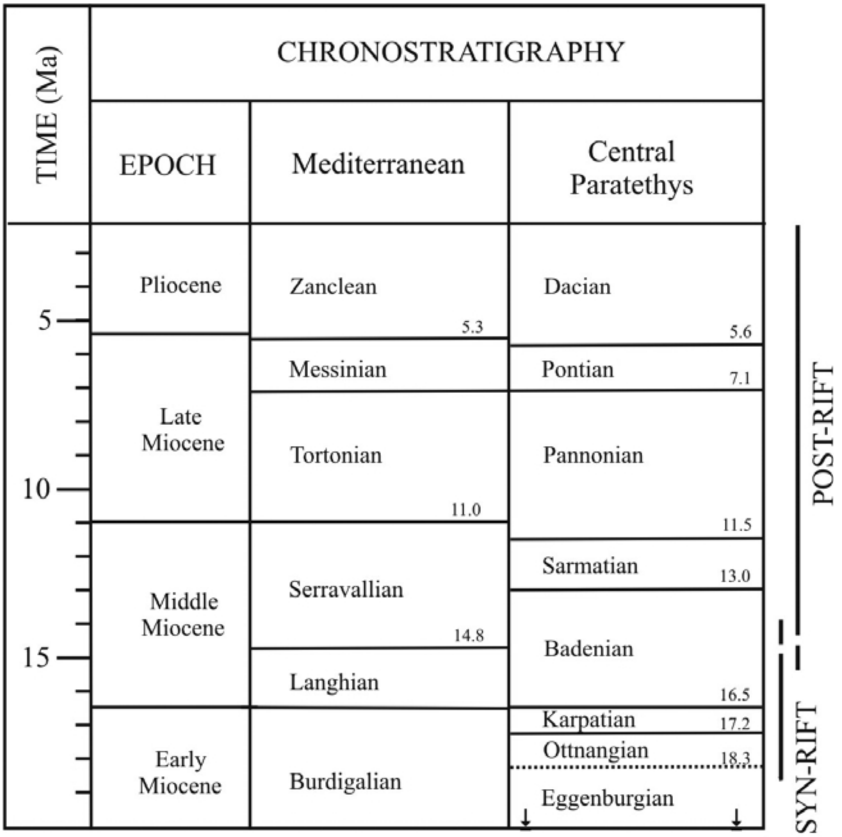

FIG. 2. Chronostratigraphic correlation of the Mediterranean and the Central Paratethys (after Rögl, 1996).

lithothamnium limestones, sandstones and marls are the dominant sediments, but at times pyroclastic rocks were also deposited as a result of enhanced volcanic activity. During the Sarmatian, connections of the PBS with marine areas were significantly reduced. The marls and sandstones were deposited in environments of reduced salinity, in most cases continuously on the Badenian strata. At the beginning of the Late Miocene, the brackish Pannonian Lake was formed in the area of the PBS. In the Sava Depression, clayey limestones and sandstones were deposited at the beginning of the Late Miocene (Early Pannonian). During the Late Pannonian, sedimentation of sandstones and marls gradually began. At the end of the Miocene (Pontian), the Sava Depression became shallower and it was gradually filled by sands from progradation of deltaic systems. During the Pliocene and Quaternary, clays, sands and gravels were deposited in freshwater lakes, swamps and fluvial environments. The depression is now at maximum burial depth and no uplift or erosion is occurring (Saftić *et al.*, 2003).

MATERIALS AND METHODS

Twenty-seven samples of Miocene (Ottnangian-Pontian) pelitic sedimentary rocks taken from wells in the Sava Depression were investigated. The carbonate fraction of the samples was dissolved by acetic acid buffered with ammonium acetate (1 M) to pH 5, while organic matter was removed by treatment with H_2O_2 (10%). The suspensions were saturated with NaCl (1 N), the excess salt being removed by centrifuging in distilled water.

In spite of the fact that the <0.2 µm fraction is the best choice for the determination of smectite % in I-S (Środoń & Eberl, 1984), due to a lack of available material, the <2 µm fractions were separated by centrifugation. It should be emphasized that patterns recorded on coarser fraction are of poor quality and readings from them are inaccurate.

X-ray powder diffraction (XRD) patterns were recorded from the random and oriented mounts of air-dried material, after ethylene-glycol treatment and after heating to 400ºC and 550ºC. A Philips vertical X'Pert goniometer equipped with Cu tube was used. Experimental conditions for qualitative and semiquantitative analysis were: 45 kV, 40 mA, X-celerator detector, primary beam divergence 1/2º, anti-scatter slit 1º and detector anti-scatter slit 5.5 mm.

Illite-smectite type and smectite % in I-S were determined by peak position methods (Środoń, 1981, 1984). The semiquantitative analysis was performed according to Schultz (1964).

The isolation of organic matter was made by the standard HCl-HF/$ZnCl_2$ procedure (Schwab, 1990). In samples that contained vitrinite, its reflectance (%R_o) and thermal alteration index (TAI) were measured while, in those lacking vitrinite, only TAI was determined. TAI values were converted to %R_o values using the table of Barić (2006). The diagram of Bostick *et al.* (1979) was used for the estimation of palaeotemperatures from the vitrinite reflectance data.

RESULTS

XRD analysis revealed that the main components of the pelitic sedimentary rocks under study are carbonate minerals and clay minerals together with ubiquitous quartz (Table 1). Carbonates are represented by calcite, which is present in all analysed samples, aragonite, dolomite and excess Ca-dolomite/ankerite. The last two were found as important components only at greater depths.

The clay mineralogy varied with the sampling depth. In samples which are close to the surface, smectite or *R*0 type I-S were the dominant clay minerals (Table 1). Minor constituents were illite, kaolinite and chlorite, the last two present only in some samples. With increasing sampling depth, a decrease of smectite in I-S and ordering of I-S, at first from *R*0 to *R*1 and then to *R*>1, were observed (Table 2, Fig. 3). The sharp change from the *R*0 type (containing 75% smectite) to the *R*1 type of I-S, with ~20% smectite, was observed at depths of ~1.8 km (Fig. 4). In the DJ-1 well, transformation from the *R*1 to *R*>1 type (<15% smectite) took place at depths of 3.6 to 3.8 km (Table 2, Fig. 4). The occurrence of the ordered type of I-S (*R*1) in the JeD-3 and Žu-256D wells is more or less in accordance with the *R*0 to *R*1 transformation depth in the well Gj-1 (Fig. 4); namely, in the Žu-256D-2 sample two expandable phases were identified (Fig. 5). In the borehole Mah-1, the *R*1 type occurred at a depth of ~1.6 km, but at depths close to 1.8 km the *R*0 type occurred again.

In the DJ-1 well, represented by the greatest number of samples, the quartz content increased, and a general decrease of calcite content, especially in the Badenian samples, was observed with increasing sampling depth (Fig. 6). The chlorite quantity increase with depth is apparent but not prominent.

Some samples contained smaller amounts of other minerals: feldspar (albite), pyrite, hematite and opal-CT. Opal-CT was found only in samples of the Sarmatian rocks which contained diatoms.

Since the temperature profiles for the wells were not available, palaeotemperatures were estimated from the vitrinite reflectance and TAI data. These data showed that with increasing depth the organic matter maturity increased, reaching the lower boundary of the metagenesis zone, i.e. temperatures of 190ºC, at the bottom of the investigated section of the well DJ-1 (Table 2).

DISCUSSION

The mineral composition of the investigated rocks from the boreholes in the Sava Depression varies significantly. In order to determine the reasons for these differences, the mineral content of subsurface samples was compared with equivalent pelitic sedimentary rocks taken at outcrops located on the slopes of Medvednica, Moslavačka Gora and Psunj, mountains situated close to the Sava Depression (Fig. 1). Investigations of the surface samples (Grizelj, 2008) showed that they also contain carbonates, the type and quantity of which is dependent on the depositional environment and the terrigenous material input to the basin. Depending on the sedimentary environment, high-Mg calcite and aragonite are present along with calcite, which is the most common carbonate mineral. High-Mg calcite and aragonite are mainly present in the samples of Sarmatian age, while in the Badenian and Pannonian age samples these minerals are less common (Grizelj, 2008). Carbonates were mainly deposited by chemical and bio-precipitation, but some carbonate minerals

TABLE 1. Semiquantitative mineral compositions obtained by XRD according to the procedure described by Schultz (1964). The clay mineral contents were determined on the <2 µm fraction of the insoluble rock residue while the content of other minerals (in wt. %) was determined on bulk samples.

Borehole	Sample	Depth (m)	Qtz	OCT	Clm	Cal	Arg	Dol	Ank/ Ca-Dol	Pl	Py	Hem	S	I-S (*R*0)	I-S (*R*>1)	I/Ms	K	Chl
Gojilce-1	Gj-1-1	839	6		23	11[m]	54	2	2	2				***		**	*	+
	Gj-1-2	872	4		15	16	59	2	3		1		***			**	*	*
	Gj-1-3	938	11	14	46	10		2			17			***		**	*	
	Gj-1-4	1456	20		40	30		3		5	2			***		**		*
	Gj-1-5	1845	11		65	12				12					***	**	*	*
	Gj-1-6	1933	9		61	3		7		9	11				**	**		*
	Gj-1-7	2131	23		49	11				15		2			***	**		*
Donja Jelenska-1	DJ-1-1	2442	10		50	4		29		7					**	**		**
	DJ-1-2	3039	4		34	56		3		3					*	***		**
	DJ-1-3	3232	3		29	56		9		1	2				**	***		*
	DJ-1-4	3296	5		22	63		3	3	2	2				**	***		*
	DJ-1-5	3450	5		17	70			2	3	3				*	***		
	DJ-1-6	3518	9		17	58			6	6	4				**			***
	DJ-1-7	3831	10		28	50			5	3	4				**	**		
	DJ-1-8	4231	14		29	45			3	6	3				**			***
	DJ-1-9	4607	15		38	37			2	7	1				*	***		**
	DJ-1-10	4822	21		42	25		2		8	2				*	***		**
	DJ-1-11	5000	21		54	9			4	11	1				*	***		**
Mahovo-1	Mah-1-1	1564.4	12		54	20		8		6	+				*	**	**	*
	Mah-1-2	1860.9	12		18	65			2	2				***		**		*
Laktec-1	Lak-1-1	1077	3		21	70		4			2			*		**	**	*
	Lak-1-2	1204	5		26	42			24	3				**		**	*	*
	Lak-1-3	1248.5	13		45	30			8	4				***		**		*
Ježevo	JeD-3-1	2403	5		19	72			2	2					**	***		
Duboka-3	JeD-3-2	2822	12		19	41		10		8	5				**	***		
Žutica-256D	Žu-256D-1	2257	13		34	29	5	2		3	14			***		**	*	
	Žu-256D-2	2364	10		25	49			8	3	5			$\underline{**}$		**	*	

[m], high-magnesium calcite; Qtz, quartz; OCT, CT opal; Clm, clay minerals; Cal, calcite; Arg, aragonite; Dol, dolomite; Ank/Ca-Dol, ankerite/high-calcium dolomite; Pl, plagioclase; Py, pyrite; Hem, hematite; S, smectite; I-S (*R*0), illite-smectite *R*0 type; I-S (*R*>1), illite-smectite *R*>1 type; I/Ms, illite/muscovite; K, kaolinite; Chl, chlorite; ***, dominant (>50%); **, abundant (20–50%); * subordinate (1–20%); +, traces (<1%); $\underline{*}$, two types of I-S.

TABLE 2. Results of XRD, vitrinite reflectance (*R*o) and thermal alteration index (TAI) measurements for the <2 µm fractions arranged by borehole, depth and stratigraphic age.

Borehole	Sample	Depth (m)	Stratigraphic age	— Analytical peak (°2θ Cu-*K*α) —				%S	*R*	%*R*o (N)	TAI	*T*(°C)
Gojilce-1	Gj-1-1	839	Pannonian	5.17;	15.83;	31.55;		87	*R*0	0.35 (1)	2^-	50
	Gj-1-2	872	Pannonian	5.08;	15.81;	31.95;		100	–	–	2^-	50
	Gj-1-3	938	Badenian/Sarmatian	5.54;	–	–	–	–	*R*1/*R*0?	–	2^-	50
	Gj-1-4	1456	Badenian	5.22;	15.98;	31.61;		77	*R*0	0.34 (7)	2^-	50
	Gj-1-5	1845	Ottnangian/Karpatian		17.08;	26.65;	33.86;	22	*R*1	–	2	80
	Gj-1-6	1933	Ottnangian		16.95;	26.69;	33.78;	28	*R*1	0.53 (13)	–	80–90
	Gj-1-7	2131	Ottnangian		16.95;	26.68;	34.68;	16	*R*1/*R*>1	–	–	–
Donja Jelenska-1	DJ-1-1	2442	Pontian		16.96;	26.70;	33.73;	28	*R*1	0.55 (10)	2^+	100
	DJ-1-2	3039	Pontian		16.99;	26.67;	34.66;	16	*R*1/*R*>1	–	$2^+–3^-$	100–120
	DJ-1-3	3232	Pannonian/Pontian	7.01;	16.89;	26.63;	34.59	17	*R*1/*R*>1	–	3^-	120
	DJ-1-4	3296	Pannonian		16.93;	26.63;	34.56;	18	*R*1/*R*>1	–	3^-	120
	DJ-1-5	3450	Badenian		17.17;	26.67;	34.70;	15	*R*>1	–	3	150
	DJ-1-6	3518	Badenian	6.62;	17.02;	26.65;	33.87	22	*R*1	–	3	150
	DJ-1-7	3831	Badenian	6.95;	17.11;	26.68;	34.32	15	*R*1/*R*>1	–	3^+	170–180
	DJ-1-8	4231	Badenian		17.07;	26.70;	34.80;	12	*R*>1	–	3^+	170–180
	DJ-1-9	4607	Badenian		17.10;	26.67;	34.92;	9	*R*>1	–	$3^+–4^-$	190
	DJ-1-10	4822	Badenian		17.19;	26.70;	34.87;	10	*R*>1	–	$3^+–4^-$	190
	DJ-1-11	5000	Badenian		17.24;	26.71;	34.89;	9	*R*>1	–	$3^+–4^-$	190
Mahovo-1	Mah-1-1	1564.4	Pannonian		16.99;	26.71;	33.69;	25	*R*1	–	–	–
	Mah-1-2	1860.9	Badenian	5.16;	16.12;	31.68;		67	*R*0	–	–	–
Laktec-1	Lak-1-1	1077	Karpatian	5.22;	16.22;	31.68;		64	*R*0	–	–	–
	Lak-1-2	1204	Karpatian	–	–	–	–	–	*R*0?	–	–	–
	Lak-1-3	1248.5	Karpatian	5.16;	16.03;	31.55;		72	*R*0	–	–	–
Ježevo Duboka-3	JeD-3-1	2403	Pannonian	6.79;	16.80;	26.63;	33.58	30	*R*1	–	–	–
	JeD-3-2	2822	Badenian		17.05;	26.65;	34.63;	17	*R*1/*R*>1	–	–	–
Žutica-256D	Žu-256D-1	2257	Badenian/Sarmatian		16.62;	26.56;	33.02;	38	*R*1	–	–	–
	Žu-256D-2	2364	Badenian	–	–	–	–	–	–	*R*0 & *R*1 -	–	–

%S, smectite in I-S (Środoń, 1981;1984); *R* – type of I-S; %*R*o, vitrinite reflectance; N, number of measurements; TAI, thermal alteration index (Pearson, 1990); *T*, temperature; ?, not determined unambiguously.

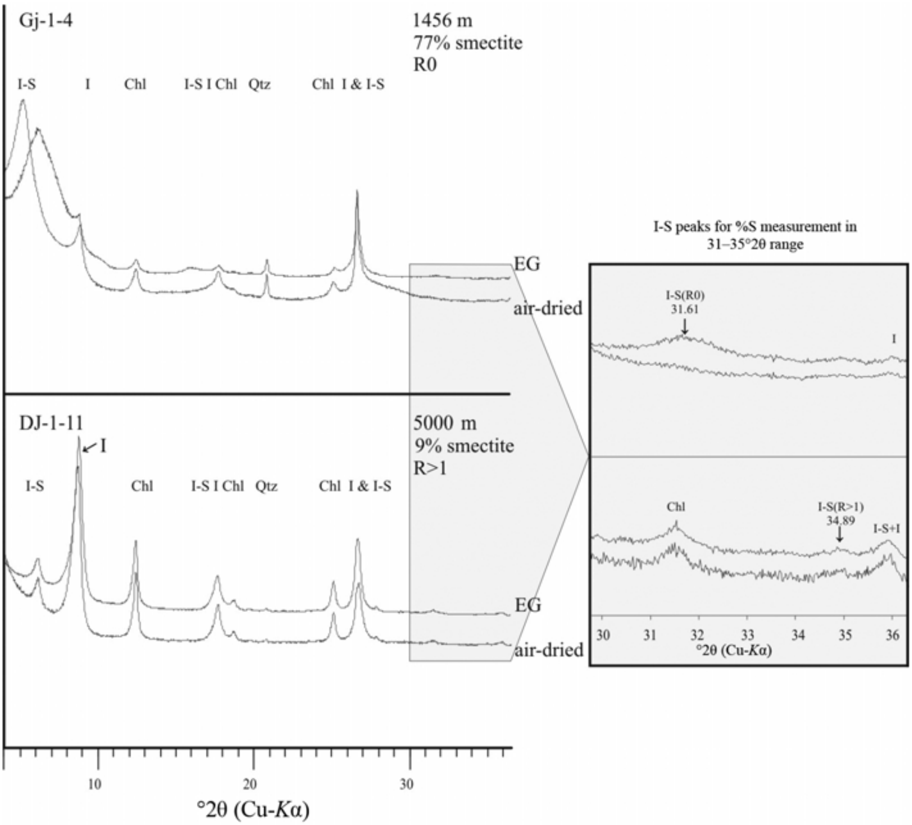

FIG. 3. XRD patterns of Na-saturated air-dried and glycolated (EG) <2 μm fractions of representative pelitic sedimentary rocks from the Gj-1 and DJ-1 wells. Sample depth, % of smectite in I-S, and type of ordering of I-S are indicated for each sample. I = illite, S = smectite, I-S = illite-smectite, Chl = chlorite. Positions of diagnostic I-S peaks, in the 31–35°2θ range, used for %S determination are shown on the right.

present in surface samples, e.g. dolomite, are of detrital origin. Concerning the clay mineralogy, no systematic differences were observed between surface samples of different age or sampling position. Smectite or I-S with >85% of the smectitic component were the dominant clay minerals in surface samples. Their minor constituents were ubiquitous detrital illite and kaolinite which were present in almost all samples. In some samples minor chlorite was also present.

The results of this study show that the mineral composition of pelitic sedimentary rocks from boreholes is, apart from previously mentioned factors, also dependent on diagenetic changes. Dolomite and excess-Ca dolomite/ankerite, as well as albite, were found as important components only at greater depths. Therefore it can be presumed that their occurrence is a result of diagenetic processes that, according to the vitrinite reflectance and TAI data, took place at temperatures between 50 and 190ºC. The quartz and clay mineral contents increase and the calcite content decreases with increasing depth in the Badenian samples in the DJ-1 well (Fig. 6). According to the investigations of surface samples (Grizelj, 2008), Badenian age samples are characterized by uniform composition with a relatively high calcite content, and they differ from the Pontian age samples which contain more of the siliciclastic component. Investigated samples from this well reflect variations in the primary mineral composition.

As expected, the most remarkable changes with sampling depth were recorded in the clay mineralogy. The samples close to the surface contained smectite or *R*0 type of I-S as dominant clay minerals (Table 1). With increasing depth, illitiza-

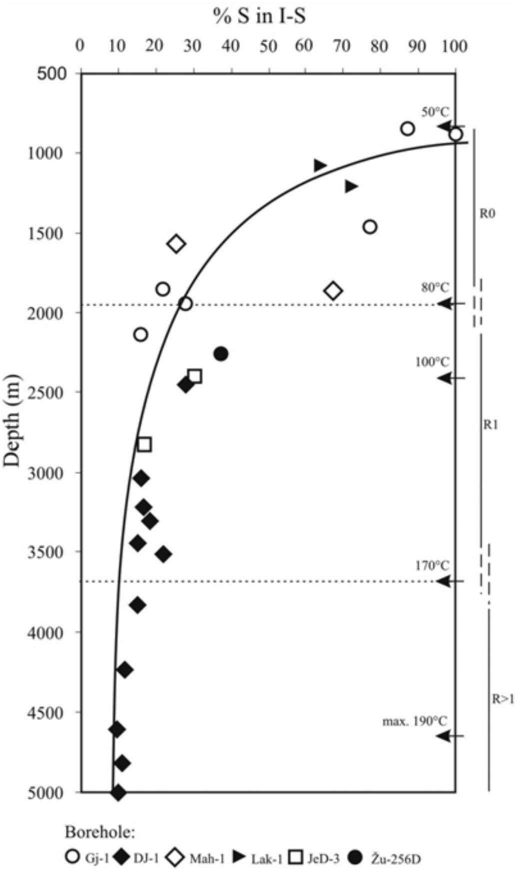

FIG. 4. Variation of %S in I-S with depth of sampling in the boreholes from the Sava Depression. The temperatures shown were estimated from vitrinite reflectance and TAI data.

tion of smectite took place. (Table 2, Fig. 4) Vitrinite reflectance and TAI measurements revealed that sediments found in the Gj-1 well at depths ~1.8 km, where the sharp change from *R*0 type (75% smectite) to *R*1 type (~20% smectite) of I-S was observed, were exposed to temperatures ~80ºC (Table 2, Fig. 4). According to the same data, temperatures in the DJ-1 well at depths of 3.6 to 3.8 km , where the transformation from *R*1 to *R*>1 type (<15% smectite) of I-S was recorded, were ~170ºC (Table 2, Fig. 4). Usually *R*0 transforms to *R*1 at temperatures close to 100ºC (Hoffman & Hower, 1979; Pollastro, 1993, Środoń, 2007), i.e. slightly higher than those determined for the Sava Depression. Temperatures ~100ºC have also been determined as *R*0 to *R*1 transformation temperatures in neighbouring sub-basins of the PBS (Franců *et al.*, 1990; Hámor-Vidó & Viczián, 1993; Hillier *et al.*, 1995; Tanács & Viczián, 1995; Sachsenhofer *et al.*, 1998). Sample Gj-1-5, for which the temperature of 80ºC has been assumed by the TAI method, represents the Ottnangian-Karpatian boundary, while sample DJ-1-7, for which the temperature of 170 to 180ºC has been estimated, is of Badenian age. Examples of lower *R*0 to *R*1 transformation temperatures have been given by Velde *et al.* (1986) for Niger Delta sediments and by Bjørlykke (1998) for North Sea sediments. Velde *et al.* (1986), Chang (1986) and Bjørlykke (1998) argue that the transformation at lower temperatures is possible due to the large content of potassium in the rock. Bjørlykke (1998) considers the exposure time to elevated temperatures as another important factor in the process of illitization. Therefore, the influence of longer exposure to elevated temperatures and availability of potassium on the process of illitization in the investigated Miocene pelitic sedimentary rocks have to be taken into consideration.

On the depth plot, the %S data are scattered around the curve representing the transformation trend of smectite to *R*0 I-S, and from *R*0 to *R*1, and *R*>1 (Fig. 4). Possible causes for such scatter could be variable geothermal gradient in the Sava depression (Barić *et al.*, 2000) or differences in the original mineral composition of the sediments that were exposed to diagenesis.

Another possible reason for the deviation could be the presence of more than one structure containing expandable layers. Two such phases were identified in the Žu-256D-2 sample (Fig. 5). Usually, the presence of more than one phase can not be recognized by standard peak position methods used for the determining the composition of I-S. For these purposes, profile fitting methods should be used (Lanson *et al.*, 2007). Part of the smectite is probably authigenic, i.e. it is an alteration product of volcanic glass. This can be presumed in spite of the fact that no evidence for the volcanic activity, except for the presence of smectite, was found in the investigated pelitic sediments. This presumption is based on the fact that volcanism in the area was intensive during the Lower and Middle Miocene (Pamić, 1997; Pamić *et al.*, 1995; Barić *et al.*, 2000; Lučić *et al.*, 2001), while in the Upper Miocene less intense volcanic activity has been recorded in the wider area of the PBS (Balogh *et al.*, 1983; Szabó *et al.*, 1992;

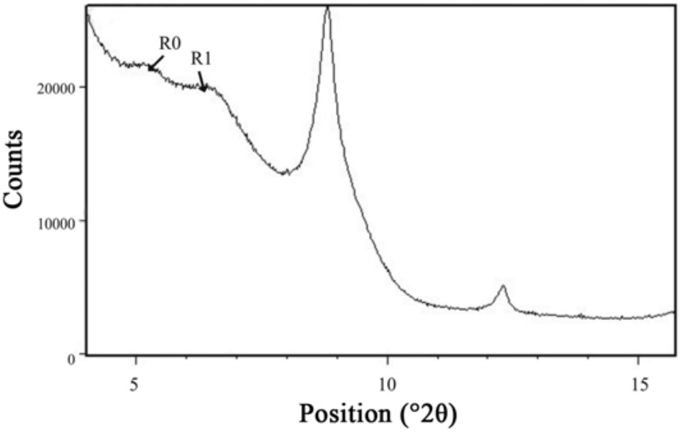

FIG. 5. XRD pattern of the <2 μm fraction of the ethylene-glycol treated sample Žu-256D-2.

Pamić, 1997; Pamić *et al.*, 1995; Harangi, 2001). Most probably some samples which deviated from linearity also contained some detrital expandable material (I-S) with different composition/degree of ordering.

The temperature determined for the *R*1 to *R*>1 transformation (170ºC) is in good agreement with published results (Hoffman & Hower, 1979).

The temperatures estimated from the vitrinite reflectance and TAI measurements (Table 2) are in accordance with the thermal gradient for the Sava Depression which is 30−60ºC/km (45ºC/km on average) (Barić *et al.*, 2000) and the unpublished geochemical measurements of Stanković *et al.* (Rock-Eval pyrolisis $T_{\max}$, TAI and vitrinite reflectance) for samples from the Gj-1 borehole, which showed that the organic matter in samples from the depths of 1840−1940 m reached the katagenetic stage of transformation.

According to Grizelj (2008), the content of K_2O in the analysed samples from the Gj-1 and DJ-1 boreholes generally increases with depth, and there is no difference in the composition trends between the whole-rock samples and the <2 μm fraction. Therefore she presumed that almost all of the K is incorporated in illite.

Results of XRD analysis of smectite, I-S and illite compared with the data of Weaver (1989)

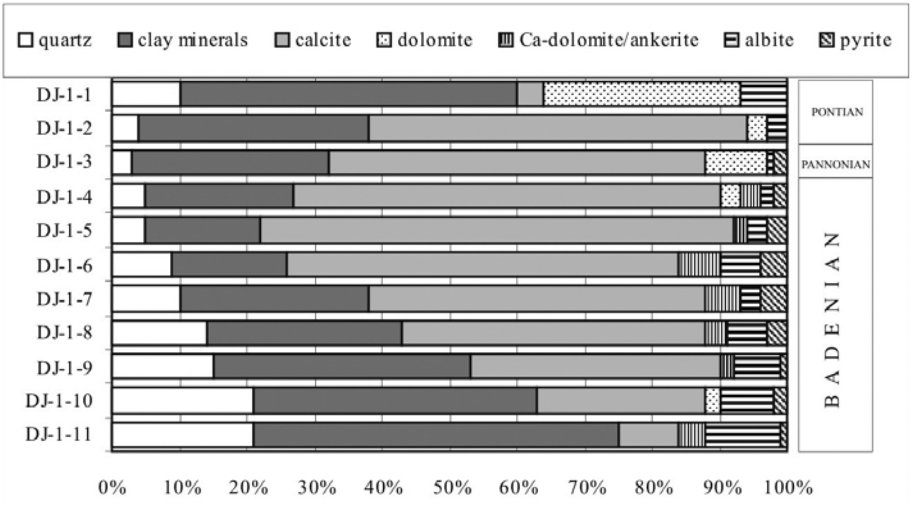

FIG. 6. Mineral composition and stratigraphic age of the samples from the DJ-1 well.

show that the diagenetic processes in the Sava Depression proceeded in three stages. The first (early) stage of diagenesis occurred at depths <1.8 km that are characterized by the dominance of smectite, or by the presence of disordered *R*0 type I-S and detrital illite. The second (intermediate) stage is marked by the appearance of the ordered type of I-S at depths >1.8 km and temperatures of 80ºC. Samples that have reached the third (late) stage of diagenesis are characterized by the presence of I-S with <10% smectite, and were found at depths of 4.6 km and temperatures of 190ºC. The poorly visible trend of increasing chlorite quantity with depth indicates that chlorite is at least partially of diagenetic origin.

In the part of the Sava Depression investigated here kaolinite was found only at depths shallower than 2.4 km (Table 1). Kaolinite at this maximum depth was found in the well Žu-256D; its disappearance at greater depths was also recorded in neighbouring sub-basins of the PBS. In the Hungarian part of the PBS, kaolinite disappearance at depths of 2−3.5 km was interpreted by Varsányi (1975), Viczián (1975) and Hillier *et al.* (1995) to be the result of sorting of the detritus during sedimentation and/or changes of the depositional environment. Kaolinite is a regular constituent of equivalent pelitic sediments found at the surface (Grizelj, 2008); therefore it is reasonable to presume that at greater depths kaolinite underwent diagenetic transformation in the process of albitization and/or illitization (Weaver, 1989; Bjørlykke *et al.*, 1995; Deer *et al.*, 2001). The disappearance and transformation of kaolinite in the sedimentary column is a process that is still the subject of discussion. Weaver (1989) reported that transformation and disappearance of kaolinite have been observed between 90 and 190ºC. In rocks that contain kaolinite as a major component the mineral can sometimes be preserved up to a temperature of 270ºC (Frey, 1987) in contrast to rocks that contain smaller quantities of kaolinite which are transformed at lower temperatures. Similar results were obtained by Środoń *et al.* (2006). They found that the stability of kaolinite is dependent not only on temperature but also on the availability of chemical elements (Fe, Mg and K) needed for illitization and/or chloritization, as well as on the porosity of the rocks.

The analysed pelitic sedimentary rocks contain calcite as a major component, which may have resulted in high pH of the pore waters, favouring the alteration of kaolinite.

CONCLUSIONS

Carbonate minerals, clay minerals and quartz are the main constituents of pelitic sediments in the Sava Depression. Feldspar (albite), pyrite, opal-CT, and hematite are present as minor constituents in some rocks.

The mineral composition of the pelitic sediments investigated are, apart from depositional environment and the clastic material provenance, also dependent on the degree of diagenetic processes. In samples which are close to the surface, smectite or the *R*0 type of I-S are the dominant clay minerals. Minor constituents are illite, kaolinite and chlorite, the last two present only in some samples. With increasing sampling depth, progressive illitization of smectite and evolution of ordering of I-S from *R*0 to *R*1 and then to *R*>1 were observed. At the same time the content of kaolinite decreased. As a result of these processes, the dominant components of the <2 μm fraction of pelitic sediments taken from greater depths were illite and chlorite. Advancement of the illitization process is primarily dependent on temperature, mineral composition (K availability) and exposure times to elevated temperatures. The lack of K-feldspars indicates that all K is present in illite and/or muscovite.

Ankerite/Ca-excess dolomite and albite are present in addition to illite, and probably quartz and chlorite, as minerals that formed by diagenetic processes.

XRD analysis of smectite, I-S and illite revealed that pelitic sediments from the Sava Depression have been subjected to three subsequent stages of diagenesis:

An early stage is characteristic of sediments at depths <1.8 km. In these sediments, smectite, disordered *R*0 type of I-S and detrital illite are present.

The appearance of the ordered type of I-S containing ~20% smectite at depths >1.8 km, and corresponding temperatures close to 80ºC, mark an intermediate stage of diagenesis.

The late stage of diagenesis was recorded in rocks at depths >4.6 km that were exposed to temperatures of 190ºC and which are characterized by the presence of I-S containing <10% smectite.

The depth and corresponding temperature at which the disordered *R*0 type of I-S transformed to the ordered *R*1 type, as well as the depth at which the *R*1 type transformed to the *R*>1 type correspond to ‘oil window‘ temperatures.

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