

Mineralogical characteristics of upper Jurassic Mikulov Marls, the Czech Republic, in relation to their thermal maturity

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ABSTRACT

The Upper Jurassic Marls of Mikulov present a formation that is considered to be the most promising strata to produce hydrocarbons in the Vienna basin. The marls are composed of dark pelagic marlstones that frequently contain layers of limestone with thickness reaching several hundreds of meters. Twenty-seven core samples from selected wells located in the south-eastern portion of the Czech Republic representing depths ranging from 2300 to 4500 m were analyzed by x-ray diffraction to assess bulk mineralogy and the progress of smectite illitization.

Bulk mineralogy of the Mikulov Marls comprises carbonates (mean value = 54.4 mass%), clay minerals (26.6 mass%), quartz (15.0 mass%), and feldspar (1.6 mean%). In the decreasing order, the clay mineral fraction is composed of illite/mica, kaolinite, illite-smectite, and chlorite. The amount of smectite in illite-smectite decreases with depth from 70% to 28%. There is a change from random to ordered interstratification at the depth of 3300 m. The transition from short-range ordering (R1) to long-range ordering (R3) occurs at depths greater than 4,500 m.

There was a good correspondence between thermal maturity parameters: the percentage of smectite in illite-smectite structures and vitrinite reflectance as a parameter of organic matter. The increase of the metamorphic grade was compared in respect to the geothermal gradient with adjacent basins.

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1. Introduction and regional setting

Sedimentary basins present important archives of past geological processes. Utilizing new approaches and scientific tools, we can reconstruct long-term changes and evolution that affected the history of Earth. Studying a geothermal gradient and maximum burial depth proves to be important not only for petroleum geologists but also for climatologists. There is a broad spectrum of units referred to as paleo-thermometers that serve for paleo-reconstructions in sedimentary basins (Allen and Allen, 2005; Littke et al., 2008). The most frequently applied thermal maturity parameters are vitrinite reflectance, maximum pyrolytic temperature, and an apatite fission track analysis (Suggate, 1988; Wagner and van den Haute 1992; Littke et al., 2008). Less common thermal maturity parameters are fluid inclusion data, conodont alteration index and clay mineral transformation ratio (Velde 1995; Samson et al., 2003). However,

every method has its limitations and cannot be applied in every environment, thus the correlation with other paleo-parameters is necessary.

Vitrinite reflectance is the most commonly used parameter; it provides information on the amount of eroded sediment and the paleo-gradient during the maximum burial (Allen and Allen, 2005). Unfortunately, it cannot be used in environments with a lack of terrestrial (plant derived) organic matter.

Illite-smectite reaction expressed as a percentage of expandable layers (% S) in illite-smectite (I-S), illite crystallinity (IC) and chlorite crystallinity (ChC) belongs to frequently used clay mineralogy parameters (Šrodoň and Eberl, 1984; Eberl et al., 1998; Frey and Robinson, 1999). The interpretation of changes in the clay mineralogical composition is a complex matter and requires a well-defined stratigraphy (Brindley and Brown, 1980; Hillier and Clayton, 1989; Hoffman and Hower, 1979; Eberl et al., 1998; Frey and Robinson, 1999; Moore and Reynolds, 1989; Pollastro, 1993; Šrodoň and Eberl, 1984). A systematic increase in illite in illite-smectite allows utilizing clay minerals as a paleo-thermometer in the same way as vitrinite reflectance (Weaver 1960; Kisch 1983;

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Środoń and Eberl, 1984; Frey and Robinson, 1999; Kotarba and Środoń, 2000; Środoń and Clauer, 2001). In sedimentary environments (basins) with abnormally high or low geothermal gradients, the kinetic response of clay mineral reaction can significantly differ from one produced by organic matter (Velde and Lanson, 1993; Hillier et al., 1995; Allen and Allen, 2005). Until recently, illite-smectite reaction progress was characterized by a simultaneous increase in illite in the interstratified I-S. Smectite starts to convert into illite at the temperature of 50 °C; the reaction does not terminate until 200 °C is reached. Increase in illite content in I-S and the ordering of I-S is referred to as “Reichweite” (R) and describes the number of neighbor-to-neighbor interactions. Random interstratifications are Reichweite 0 (R0), whereas Reichweite 1 (R1) marks are ordered or nearest-neighbor layer-only dependence and Reichweite 3 (R3) stands for structures ordered with non-nearest-neighbor layer dependence (Jagodźinski, 1949; Reynolds, 1980; Lanson et al., 2009; Meunier and Velde, 2013). Ordered I-S (R1) is present in the temperature range of 100–180 °C that generally corresponds to the “oil window” – the main temperature range for generating oil in sedimentary rocks (Tissot and Welte, 1984; Weaver and Broekstra, 1984; Pollastro, 1993; Środoń, 2003). There has been a significant increase in a number of papers in the last years describing the smectite illitization as a heterogeneous reaction involving a physical mixture of pure smectite and I-S or two phases of illite-containing mixed layers increased (e.g. Drits et al., 1997; Lindgreen et al., 2002; McCarty et al., 2008, 2009; Lanson et al., 2009; Meunier and Velde, 2013).

Mikulov Marls represent one of the autochthonous sedimentary covers of the Bohemian Massif (Fig. 1). The unit lies directly on either the pre-Mesozoic basement or the older Upper and Middle Jurassic sequences; it is covered with the system of allochthonous nappes of the West Carpathian Flysch Belt (Pícha et al., 2006). Mikulov Marls are the result of a pelagic sedimentation process that took place under the wave base and in some cases under euxinic conditions during the Upper Jurassic (Eliáš 1981; Pícha et al., 2006). According to the rhabdospira micro-fauna, the stages represented by Mikulov Marls are the Oxfordian to the Kimmeridgian (Stráník et al., 1968; Vašíček, 1978; Eliáš, 1981). The laminae within Mikulov Marls represent layers of different grain size alternating those containing variable proportion of quartz, micrite and the clay component (Eliáš, 1981; Stráník et al., 1993). The thickness ranges from several meters in the erosional relics preserved within the deeply buried Paleogene valleys (Vranovice and Nesvácilka) to more than 1500 m. The overall thickness is sometimes tectonically enlarged by duplications (Eliáš and Wessely, 1990). Discrete blocks of Mikulov Marls were also found to form tectonic slices within the Carpathian thrust belt units (Pícha et al., 2006).

Mikulov Marls are supposed to be the main source rock for petroleum in the Vienna basin (Landwein, 1988; Eliáš and Wessely, 1990; Blížkovský et al., 1994; Ciprys et al., 1995; Krejčí et al., 1996; Pícha, 1996; Pícha et al., 2006). They are also considered to be amongst the possible sources of petroleum in the broader area of the southern Czech Republic, northern Austria and northwestern Slovakia (Franců et al., 1996; Krejčí et al., 1996).

The aim of this article is to evaluate the mineralogical composition of the Mikulov Marls formation and systematically document changes in clay minerals with emphasis on smectite-to-illite conversion. The conventional approach based on a peak position was used to determine the type of illite-smectite. This approach does not take into account the new improvement by the multi-specimen method for characterization of the illite-smectite structure. However, it allows the comparison of data presented in this paper with those previously published from the broader region and defining the beginning of the oil window and the geothermal gradient at the time of the maximum burial.

2. Materials and methods

A total of 27 core samples from 10 exploration wells were examined (Fig. 1). Of these, 25 samples represent a sedimentary sequence and are referred to as “autochthonous” elsewhere in this paper. Two samples, both coming from Well Bul 1 (2300 m and 2375 m), originated in the Jurassic tectonic klippe which was detached from the autochthonous sequence during the Carpathian orogenesis and incorporated into the West Carpathian nappe and are referred to as “allochthonous”.

All the 27 samples were examined for bulk mineralogy; 23 samples were selected for detailed identification of clay minerals. Three samples underwent a random vitrinite reflectance measurement.

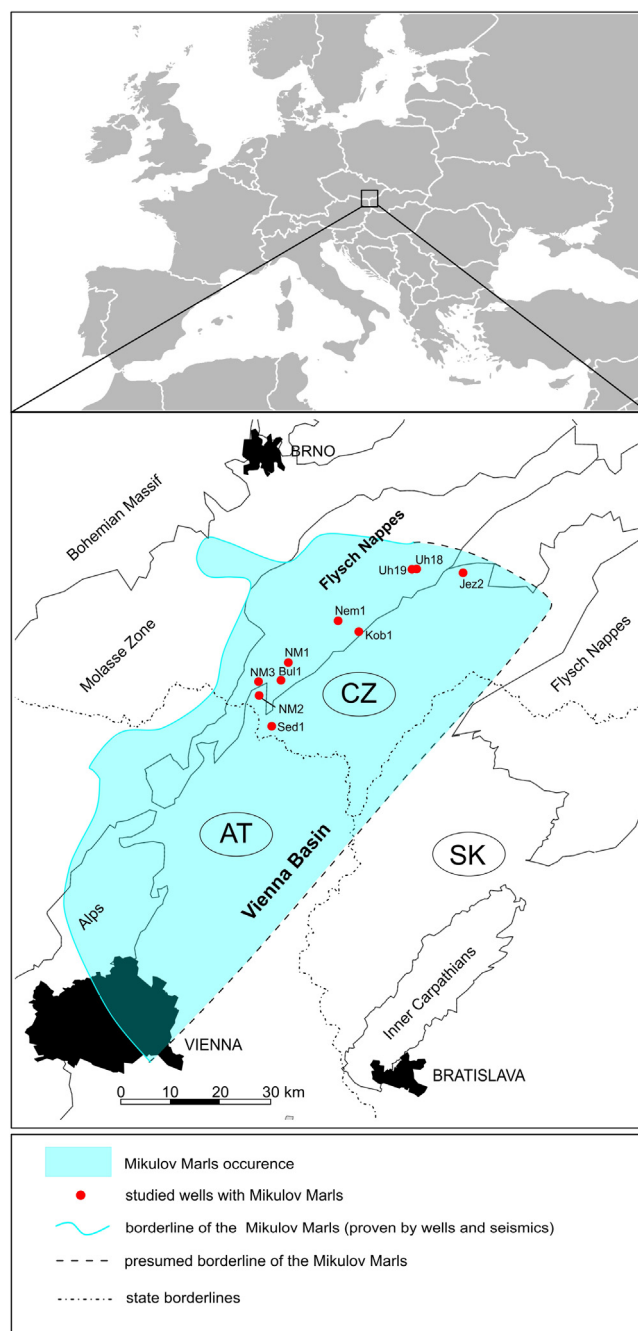


Fig. 1. The occurrence of Mikulov Marls in Central Europe with localization of studied wells.

Other vitrinite reflectance data were adopted from Geršlová et al. (2015).

2.1. Bulk mineralogy

The bulk mineralogical composition was determined by homogenizing the 27 samples, grinding them in an agate mill to obtain a fraction below 0.25 μm . All samples were prepared as texture-free specimens (the surface was made coarse with sandpaper) and analyzed using the Panalytical X'Pert PRO diffractometer (CuK α radiation, 40 kV, 40 mA, size of divergence slit 1° and receiving slit 0.2 mm step size: 0.0167.5 s per step, the measured interval being 1–70° 2 Θ). The X-ray diffraction patterns were interpreted using X'Pert Data Viewer and X'Pert High Score in accordance with Moore and Reynolds (1997). Semi-quantitative mineral estimates of the bulk sample were done using the method of Schultz (1964) with the accuracy of $\pm 10\%$.

Eight samples were selected for quantitative phase analysis; the general aim was to specify the amount of specific phyllosilicates. One gram of sample was mixed with 0.250 g Al₂O₃ (internal standard with nominal grain size 3.5 μm ; AL-OX-03-P, American Elements Corp). The mixture was mixed with about 4 ml of denatured alcohol and crushed for 5 min using a McCrone micronizing mill (ZrO stabilized with Y was used as the grinding element; Środoń et al., 2001; Eberl, 2003; Omotoso and Eberl, 2009). The randomly oriented sample was X-rayed from 5 to 65° two-theta using diffractometer Philips PW 1710 (Cu K α radiation, voltage 35 kV, current 20 mA, step size 0.02° 2 Θ , count time 2 s per step, using graphite monochromator). RockJock11 (Eberl, 2003) was used for quantitative analysis. It is a computer program that determines quantitative mineralogy in powdered samples by comparing the integrated X-ray diffraction (XRD) intensities of individual minerals in complex mixtures to those of the internal standard. The program automatically fits the sum of stored XRD patterns of selected pure standard minerals (the calculated pattern) to the measured pattern by varying the fraction of each mineral standard pattern, using the Solver function in Microsoft Excel to minimize a degree of fit parameter between the calculated and measured pattern (Środoń et al., 2001; Eberl, 2003). Measurement errors for common minerals should be $\pm 4\%$ (Eberl, 2003).

2.2. Clay minerals

In order to determine which clay minerals are locally present, 23 core samples were crashed and sieved to obtain fraction < 0.16 mm. Subsequently, modified Jackson treatment by Šucha et al. (1991) was applied. Samples were treated to remove carbonates (add 50 ml NaOAc = 136 g H₃COONa·3H₂O + 27 ml CH₃COOH into 1 l distilled water per 5 g of the sample), organic matter (add 50 ml NaOAc per 5 g of the sample; after heating up to 70 °C, 5–10 ml H₂O₂ was applied per 5 g of the sample, three times in the row after reducing the reaction) and Fe oxides and hydroxides (45 ml of the citric acid–sodium citrate buffer per 5 g of the sample; after heating up to 80 °C, 1–2 g of Na₂S₂O₄ was applied per 5 g of the sample three times in the row with 5 min periods). Fine clay fraction (< 0.2 μm) was separated by centrifugation. Excess of soluble salts was removed by dialysis. Orientated powder samples were prepared in the form of glass slides. The samples were analyzed in an air-dried state and saturated with ethylene glycol overnight at 70 °C (EG) using the Philips PW 1710 diffractometer (CuK α radiation, 35 kV, size of divergence slit 1° and receiving slit 0.2 mm, 20 mA, step size 0.2°, 1 s per step; measured interval was 2–50° 2 Θ). The amount of expandable, smectite layers (expandability) was identified based on the position of the basal I-S peaks 001 (6.5–6.7° 2 theta), 002/003 (about 16.7° 2 theta), 005/008 and 005/009 (between 44.3 and 46.4° 2 theta) after ethylene glyco-

lation (Środoń and Eberl, 1984; Dudek and Środoń, 1996; Moore and Reynolds, 1997). The reference intensity ratio method was used for semi-quantitative analysis of fine clay fraction (Moore and Reynolds, 1997).

2.3. Vitrinite reflectance

The measurement of vitrinite reflectance was carried out in the Institute of Rock Structure and Mechanics in the Academy of Sciences of the Czech Republic, Prague. The polished surfaces were prepared from rock chips and the reflectance measurement was performed in oil in non-polarized light (R_r) using the Opton Zeiss microscope-photometer, with 50 \times and 100 \times objectives and optical standards of 0.58%, 0.89%, 1.71%, 3.12% and 5.42% reflectance.

3. Results

3.1. Bulk mineralogy

There was an excellent correlation between the results obtained through the semi-quantitative Schultz method and quantitative RockJock11 processing (Table 1, Fig. 2).

Carbonates form the most abundant group of minerals in the studied sample set (average value: 54.4%, ranging from 37.0% to 74.8%). Calcite (50.6%) and dolomite (2.5%) predominate among the carbonates. Siderite (1.2%) occurs exceptionally and aragonite is found rarely. Clay minerals present the second most abundant mineral group, representing 26.6% of the samples (ranging from 16.7% to 37.8%). The major part of clay minerals consists of phyllosilicates such as muscovite, illite and interstratified I-S, followed by kaolinite and chlorite.

Quartz and feldspar form about 17.5% of the samples (quartz 15.9%, feldspar 1.6%). Pyrite is found in every sample and ranges from 0.4% to 2.4% (average value: 1.1%). Seldom occurring minerals include gypsum (less than 1.0%); which is found in one third of the samples.

3.2. Clay minerals

There were I-S, illite/mica, kaolinite and chlorite identified in the fraction < 0.2 μm through X-ray diffraction patterns. As the non-clay mineral, quartz was present in all the studied samples (Table 2). I-S, illite and kaolinite are the major components, the approximate percentage being 25–35% per substance. Chlorite is present as minor or trace phases, i.e. < 10 or less than 5%.

The ordering expressed as Reichweite within the illite-smectite mixed layers splits the studied samples into three groups:

Group 1 contains samples with randomly ordered I-S (R0) and illite/mica and kaolinite as major minerals. This group includes samples referred to as Bul 1 2300 m; Jez 2 2320 m; Bul 1 2375 m; NM 2 2904 m; NM 3 2925 m; NM 3 3104 m; Bul 1 3300 m. The Bul 1 2300 and Bul 1 2375 samples have expandability of 40–60%. The remaining samples have expandability of 50–70% (Fig. 3A).

Group 2 has R1 ordering and expandability of about 30%. The group covers samples referred to as Kob 1 3179; Kob 1 3390; Kob 1 3599; Kob 1 3780; Kob 1 4054; Kob 1 4334; NM 1 3491; Bul 1 3500; Nem 1 3506; Sed 1 4305, Sed 1 4551 (Fig. 3B).

Group 3 contains ordered ($R \geq 1$) I-S with expandability of about 15% and disordered I-S (R0) with expandability of 40–60% in I-S structures (Fig. 3C). It covers samples referred to as Uh 18 2605 m; Uh19 2439 m; NM 1 3168 m; Bul1 3275 m.

Table 1
Mineralogical composition of Mikulov Marls (bulk mineralogy – mass%); results from RockJock11 are presented in bold italics.

Well	Depth (m)	Quartz (mass %)	Feldspar (mass %)	Calcite (mass %)	Dolomite/Ankerite/Siderite (mass %)	Gypsum (mass %)	Pyrite (mass %)	Clays –total (mass %)	
Bul 1	2300	18.9	3.8	33.5	1.9	1.6	0.4	1.9	37.8
Jez 2	2320	10.2	1.4	62.0	0.9	0.0	0.0	0.5	25.0
		10.0	2.0	62.0	0.5	0.0	0.0	0.5	24.0
Bul 1	2375	12.5	2.6	50.8	1.3	0.0	0.4	2.3	30.0
Uh	2439	6.7	0.6	69.8	4.3	0.7	0.0	1.2	16.7
19		7.0	0.5	68.5	7.0	0.0	0.0	0.5	16.5
Uh	2605	16.6	1.4	54.3	2.0	0.0	0.0	1.6	23.8
18		15.0	2.5	52.0	3.0	0.0	0.0	1.0	25.0
NM	2904	17.2	1.3	51.3	0.9	1.1	0.2	0.9	26.8
2		19.0	2.0	51.0	1.0	0.0	0.0	0.5	26.0
NM	2925	12.4	1.5	51.2	3.1	0.8	0.0	2.1	28.9
3		10.5	2.0	49.0	1.0	0.0	0.0	1.0	28.0
NM	3104	14.0	1.5	47.8	4.3	0.0	0.0	1.7	30.4
3		12.0	1.5	46.0	2.0	0.0	0.0	0.5	30.0
NM	3168	28.8	1.0	42.8	1.5	0.8	0.0	1.2	23.7
1		31.0	1.0	44.0	2.0	0.0	0.0	1.0	31.0
Kob 1	3179	15.8	1.2	44.5	4.6	1.9	0.0	1.0	30.8
Kob 1	3190	14.0	1.8	52.6	2.5	3.2	0.0	0.7	25.0
Bul 1	3275	16.6	2.4	53.4	4.0	2.37	0.0	0.5	20.7
Bul 1	3300	20.1	1.0	52.6	2.2	1.0	0.2	1.2	21.7
Kob 1	3390	13.8	1.8	51.1	1.8	2.8	0.0	0.6	28.0
NM	3491	17.3	1.1	55.7	1.9	0.0	0.0	0.7	23.0
1		17.5	1.0	55.0	2.0	0.0	0.0	0.5	23.0
Bul 1	3500	13.3	0.8	50.8	4.4	1.6	0.0	1.0	28.0
Nem 1	3506	14.1	0.8	53.7	0.7	1.0	0.0	0.6	29.0
Kob 1	3599	16.4	0.8	51.6	3.4	1.5	0.0	2.0	24.0
Kob 1	3780	17.0	1.7	52.4	2.2	3.8	0.0	0.4	22.5
Kob 1	4018	14.3	2.5	47.5	2.1	2.6	0.5	0.7	29.7
Kob 1	4054	16.9	1.3	51.0	3.0	0.0	0.4	2.4	25.0
Kob 1	4103	13.6	2.5	48.4	4.2	2.7	0.0	0.2	28.0
Kob 1	4131	18.2	1.8	51.7	1.2	1.6	0.3	0.9	24.1
Kob 1	4182	14.0	3.5	54.4	3.3	1.3	0.0	0.5	23.0
Sed 1	4305	17.5	1.1	47.7	2.3	0.0	0.0	1.1	30.1
Kob 1	4334	16.5	1.1	49.3	1.8	1.7	0.0	1.3	28.0
Sed 1	4551	21.6	1.3	43.3	1.4	1.6	0.6	1.2	29.0

3.3. Vitrinite reflectance

The mineral phase (68–75%) prevails over organic matter in all of the three samples. The dominant maceral group involves liptinite with admixtures of inertinite and vitrinite. Each of the samples are homogeneous, both lithologically and with respect to their maceral composition. Bituminite is the predominant maceral in Uh18 and Uh19 samples. Vitrinite reflectance varies in a narrow range of 0.61–0.70% R_r (Table 3).

4. Discussion

4.1. Mineralogical characteristics

According to the classification by Pettijohn (1975), the majority of the studied samples of Mikulov Marls belong to the group of argillaceous marlstones (Fig. 2). The X-ray analysis shows that the mutual proportion of carbonates (37.0–74.8%) and quartz (6.7–28.8%) presents mineral phases that feature the highest sensitivity to changes. The minor mineral components in all samples stay in stable proportions. The relatively high quantity of pyrite points to the reduction environment and support the conclusion previously suggested by Eliáš (1981) and Pícha et al. (2006) regarding the restricted circulation during sedimentation. The scarcity of terrestrial organic matter particles (vitrinite) in Mikulov Marls indicates that the depositional environment was distant from the shoreline. Taking into account that carbonate compensation depth (CCD) was much shallower in the Jurassic than today (Bosselini and Winterer, 1975), it is assumed that Mikulov Marls were deposited in the depths below 3 km.

The illite/mica group followed by kaolinite prevails in the clay fraction with no evidence for changes within the studied interval of depth. The amount of illite/mica in the clay fraction fluctuates around 20% in the studied samples of Mikulov marlstone. Schicker and Gier (2012) found that the illite/mica percentage increases with depth. The same authors also observed a decrease in the kaolinite content based on depth. Unlike in our samples, the kaolinite content oscillates around 3–5% within the studied interval of depth (2300 to 4551 m). On the contrary, there is an increase of up to 9.8% in kaolinite content in the depth of 4000 m. Kaolinite is perfectly compatible with the deduced diagenetic conditions. It begins to be transformed at the deeper part of the diagenetic grade, near the anchizone (Merriman and Peacor 1999)

The chlorite amount occurs only in trace amounts within the studied depth section, or is detected in the values of 0.5–1% with no significant changes with depth. Schicker and Gier (2012) describe the increase in chlorite content with depth to range from 0.5% to 12%.

4.2. Smectite-illite transformation

The bulk rock composition is one of the key parameters influencing the kinetics of the illite-smectite reaction and thus their presence. There are well-marked differences in sediments of the same age and different lithology that were affected by the same temperature; they are described in the literature referring to the illitization process (Meunier and Velde, 2013). The X-ray analysis of Mikulov Marls provides a good evidence of homogenous mineralogical composition of all studied samples (see 4.1 above); as a result, the lithology effect on the illitization process can be re-

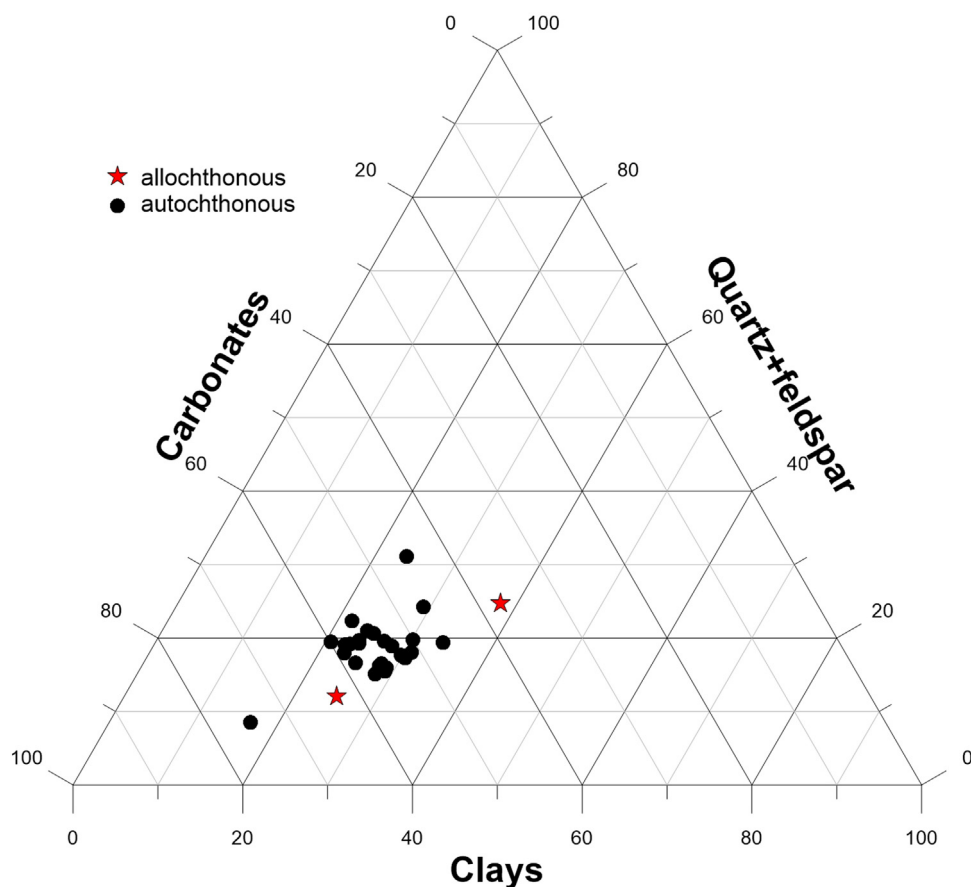


Fig. 2. Bulk mineralogical composition of Mikulov Marls – based on Schultz method.

Table 2

Clay mineral composition of Mikulov Marls. +++ – more than 25%, ++ – 5–25%;+– less than 5%.

Well	Depth (m)	Illite	Kaolinite	IS	Chlorite	Quartz	I-S Reichweite	%Smectite
Bul 1	2300	+++	+++	+++	+	+	0	50±10
Jez 2	2320	+++	+++	++	+	+	0	42±5
Bul 1	2375	+++	+++	+++	+	+	0	60±5
Uh 19	2439	+++	+++	++	+	+	0, ≥1	45±15, 15±2
Uh 18	2605	+++	+++	++	+	+	0-1, ≥1	39±4, 12±2
NM 2	2904	++	+++	++	++	++	0	72±7
NM 3	2925	+++	+++	++	+	+	0	57±7
NM 3	3104	+++	+++	++	+	+	0	50±10
NM 1	3168	+++	+++	++	++	+	1, 0	34±7, 80±20
Kob 1	3179	+++	+++	+++	+	+	1	30±5
Bul 1	3275	+++	+++	+++	+	+	0, ≥1	45±7, 17±7
Bul 1	3300	+++	+++	+++	++	+	0	50±10
Kob 1	3390	+++	+++	+++	++	+	1	30±5
NM 1	3491	+++	+++	+++	++	+	1	30±5
Bul 1	3500	+++	+++	+++	++	+	1	32±8
Nem 1	3506	+++	+++	+++	+	+	1	30±5
Kob 1	3599	+++	+++	+++	++	+	1	25±5
Kob 1	3780	+++	+++	+++	+	+	1	30±10
Kob 1	4054	+++	+++	+++	++	+	1	33±7
Sed 1	4305	+++	++	++	++	+	1	30±5
Kob 1	4334	+++	+++	+++	+	+	1	25±5
Sed 1	4551	+++	++	++	++	++	1	28±8

Table 3

Random vitrinite reflectance (%) and maceral composition (vol.%) of organic matter in the Mikulov Marl (other data in Geršlová et al., 2015).

Well	Depth (m)	Rr (%)	∑Vitrinite macerals	∑Liptinite macerals	∑Inertinite macerals	∑Minerals
Jez 2	2320	0.61	3.4	24.0	4.9	67.7
Uh 19	2439	0.70	0.8	22.0	2.4	74.8
Uh 18	2605	0.69	2.0	26.6	2.4	69.0

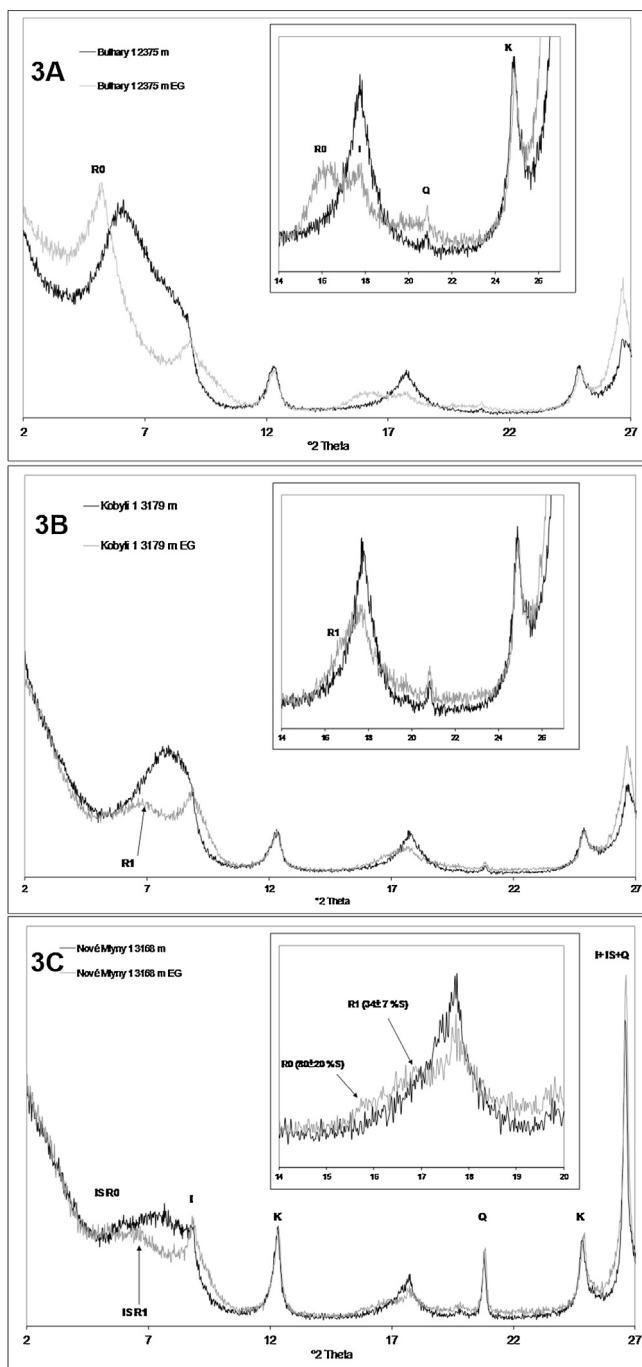


Fig. 3. XRD patterns of oriented samples with fine clay fractions in an air-dried state and after saturation by ethylene glycol (EG) (R0,R1–ordering type, I–illite/mica, K–kaolinite, Q–quartz, Ch–chlorite): (A) detailed examples of samples with randomly ordered interstratified illite-smectite (IS R0), (B) detailed examples of sample with ordered interstratified illite-smectite (IS R1), (C) detailed examples of sample with two types of interstratified illite-smectite (IS R1 and R0).

oned in the same manner. Other important factors influencing the presence of smectite and illite-smectite in sediments involve retrograde reactions under diagenetic conditions and low-intensity tectonic events (Jiang et al., 1990; Nieto et al., 1994, 2005). In such cases the other maturity parameters have to be used to identify the appropriate paleogeothermal gradients (Bauluz, 2013).

According to the degree of illitization the studied samples can be divided into two groups: the randomly ordered R0 (more than 50% of smectite interlayers in I-S) and ordered R1 (less than 50% of smectite interlayers in I-S). It may be noticed (Fig. 4) that the

samples of R0 group form two clusters within the studied section: a shallower cluster from 2300 to 2605 m and a deeper cluster from 2904 to 3300 m.

The interval between 2904 and 3300 m shows a continuous increase in smectite content in I-S and the transition from R0 to R1 is observed at the depth of 3100 m. The maturity increase observed in the same depth interval was described by Geršlová et al. (2015) using two parameters from organic matter. Both methods supports the conclusion that the studied interval of Mikulov Marls represent the geothermal gradient at the time of maximum burial.

Five samples (ranging from 2300 to 2605 m) are beyond the expected diagenetic trend. Two samples from Bul1 (2300 and 2375 m depths) marked with the red star (Fig. 2) are part of the Mikulov marlstone block inside the West Carpathian flysch nappe. The block has been incorporated by overthrusting into its position. Therefore, the clay mineralogical composition of these two particular samples was influenced by tectonic processes and their current position does not represent the original position in the sediment sequence. With no evidence found as to the presence of other I-S phases, the difference between the current position of both samples and the diagenetic trend defined earlier in the present paper suggests the minimum amount of uplift that equals 500 m.

The samples from Uh18 and Uh19 contain ordered I-S (R1) with expandability of 12% and 15% and disordered I-S (R0) with expandability of 39% and 45% in I-S structures. Both of the samples (Uh18 and Uh19) are, according to the recent 3D seismic interpretation, situated within a small-scale, approx. 2000 m wide and 800 m deep, post-Jurassic graben formed close to the eastern slope of the Nesvackilka paleo-valley (Adamek, 2005; Pícha et al., 2006). As illite-smectite is a *meta*-stable system and prone to retrograde diagenesis, the presence of ordered and disorder I-S can be related to the proximity of the tectonically active zone (Nieto et al., 2005). The clay composition could be affected by the fluid circulation along the dense network of faults within this structure. Therefore, these samples do not show any progressive trend of illitization. The influence of fluid migration is also supported by the presence of the elevated amount of bituminite in both samples when compared to the previous study on organic matter from Mikulov Marls (Geršlová et al., 2015). The shallow-seated sample Jez2 (2320 m) contains randomly ordered I-S (R0) with expandability of 42% and vitrinite reflectance of 0.61%Rr, with no indication of post diagenetic processes (Fig. 4). The agreement between clay minerals and organic matter maturity suggests an uplift of as many as 500 m (Fig. 4).

The changes in the clay composition (Fig. 4) reflect the geothermal gradient. This was studied by Franců et al. (1990) in the Vienna Basin and Transcarpathian Depression and by Hillier et al. (1995) in the Pannonian Basin (Fig. 5). The increase in %S with depth defined for I-S is comparable to the trend described in the Vienna Basin, where the low geothermal gradient is expected. The transition from R0 to R1 was found between the depths of 3200 m and 3500 m.

These findings are in agreement with the local geological concept that is expecting the maximum burial of Jurassic Mikulov Marls during the Miocene when the West Carpathian nappes overthrust the region (Krejčí et al., 1996; Pícha et al., 2006; Krejčí et al., 2001). The Jurassic sedimentation (terminated with Kimmedgian Mikulov Marls, followed by Tithonian Erstbrunn Limestones) was followed by a major regression and hiatus. A Cenomanian global transgression is documented in presence of Upper Cretaceous strata known from numerous wells. A following Paleogene sedimentation in the area is found predominantly in two large paleovalleys as pelitic sedimentary fill (few hundred meters to more than 1500 m). The most significant event in terms of thermal maturation came in the early Miocene. The area was loaded by the West Carpathians thrust belt and the Vienna basin (Pícha et al., 2006). At that time or slightly afterwards the Jurassic Marls were exposed to the maximum temperature and reached their current thermal maturity. This

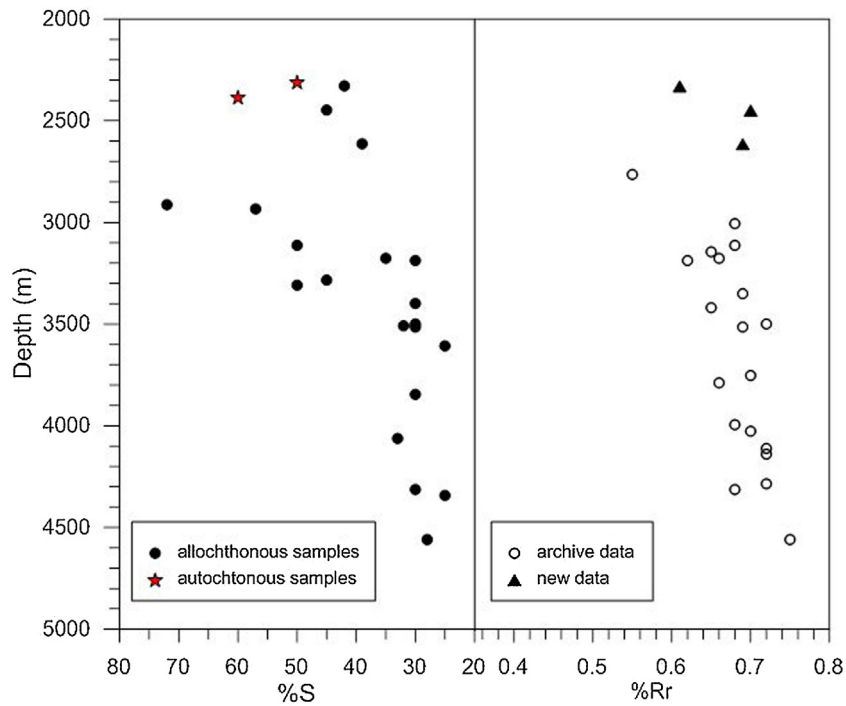


Fig. 4. Depth trends of illite-smectite (%S) transformation and vitrinite reflectance (%Rr) for Mikulov Marls.

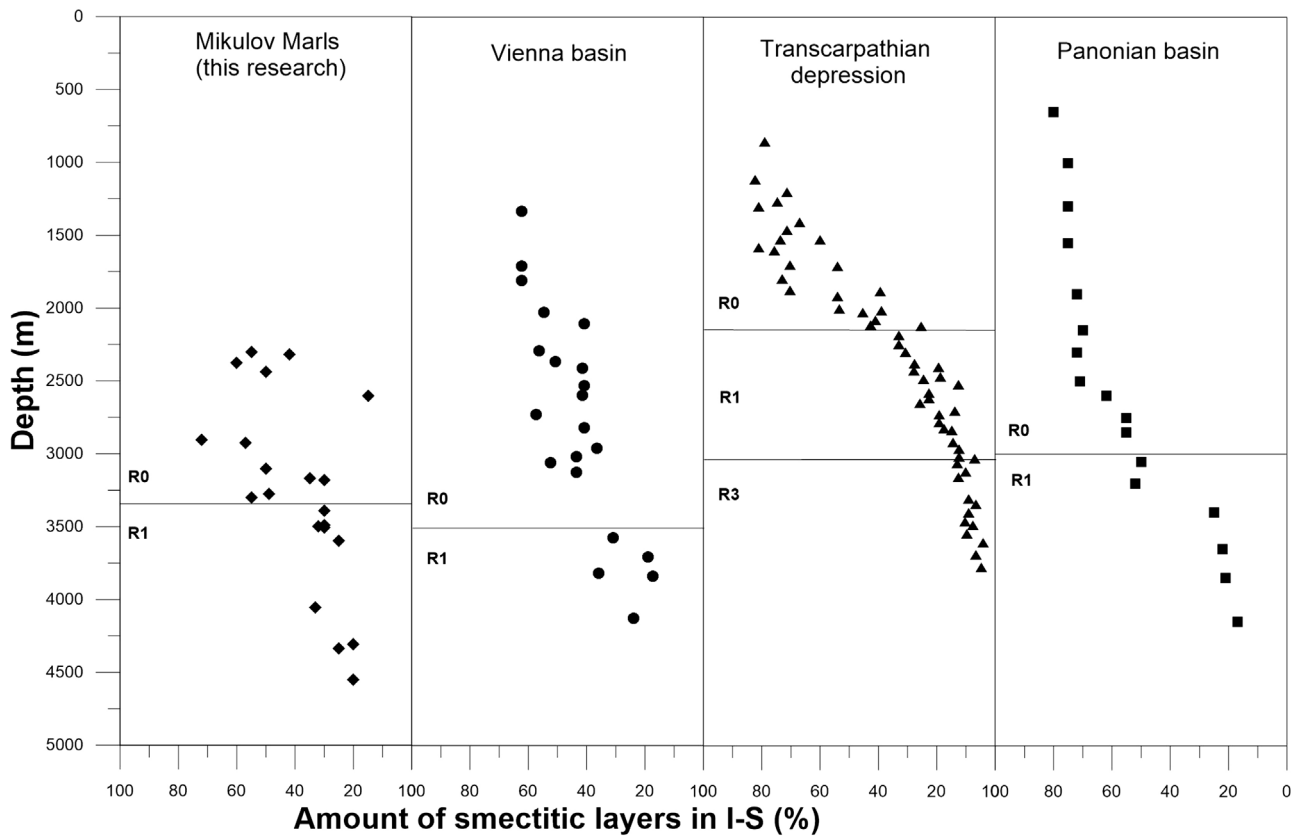


Fig. 5. Comparison of smectite illitization depth changes from Mikulov Marls with trends from adjacent basins (modified from: Francú et al., 1990; Hillier et al., 1995).

is supported by the comparable progress in smectite illitization with depth in Jurassic Mikulov Marls and in Miocene sediments from Vienna Basin.

5. Conclusion

The present systematic study of mineralogical composition of Mikulov Marls provides new information on the important source rock in the areas of Bohemian Massif and the Western Carpathians. The studied samples are highly homogenous in terms of mineralogical composition with predominance of carbonates (37.0–74.8%), clays (16–60%) and quartz (6.7–28.8%). According to these mineralogical findings Mikulov Marls belong to argillaceous marlstones. The formation of Mikulov Marls as pelagic marlstones (with prevalence of calcite matter) is supported by (1) the lack of the terrestrial organic matter that implies remoteness from the coast; and (2) the fact of the shallower CCD (carbon compensation depth) depth in the Upper Jurassic (Graciansky et al., 2011).

The clay fraction consists of: illite/mica > kaolinite > illite-smectite > chlorite. Unlike observations of Schicker and Gier (2012), results of this study do not confirm any significant increase in clay content with depth in the samples of Mikulov marlstone from the Czech Republic. Since very few data have been published on the marlstone formations, further research is necessary for the recognition of differences between Mikulov Marls found in Austria and in the Czech Republic.

In case of autochthonous samples is boundary between the immature zone and the oil window (the illite-to-smectite transition from “Reichweite” R0 to R1) set to the depth between 3100 and 3300 m. The transformation from R1 to R3 – corresponding to the shift from the oil window to the gas window – sets these transitions to depths greater than 4500 m. For Mikulov Marls, the geothermal gradient based on smectite illitization is comparable to the one in the Vienna Basin and supports the geological concept that expects maximum burial of Jurassic Mikulov Marls during the Miocene when the West Carpathian nappes overthrust the region (Krejčí et al., 1996; Pícha et al., 2006; Krejčí et al., 2001).

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