

Properties of the Jurassic Clayey Deposits of Southwestern Latvia and Northern Lithuania

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Abstract — Jurassic clay rich in organic matter from western Latvia is known already from early 19th century. Jurassic clays provide an interest because of high potential for innovative use due to its clay mineral composition jointly with organic material. Properties of the Jurassic clayey deposits were studied by using various physical and chemical methods. Material gained from field was tested by modern techniques such as UV-Vis, 3D fluorescence and FTIR — spectra, which show patterns of organic compounds in the clay material. AAS analyses characterized inorganic content. PXRD studies raised discussions about the origin of kaolin, illite and smectite and interactions among these clay minerals. Obtained results show that Jurassic clays with organic matter have future potential for possible use in cosmetic industry and as a sorbent material.

Keywords — Kaolin, natural clay, organoclays, 3D fluorescence.

I. INTRODUCTION

Outcrops of the Jurassic deposits in Venta Valley are already known since 1811, when Dionizas Poška came in Papile to collect fossils; later engineer Jan Ullman from 1825 to 1826 continued the investigation. Jurassic sediments consist of grey and white quartz sand, black and grey clay with an admixture of organic matter, brown coal and limestone concretions can also be found [1]. Jurassic clay with organic matter in Latvia previously was not of high interest for industrial use due to its relatively small amount and complicated exploitation conditions. This research was performed in order to improve knowledge on naturally formed clay with admixture of organic matter and to describe their properties in detail. Jurassic clay containing kaolinite, smectite, illite, and organic matter has been studied by various researchers in Latvia [2], [3], [4], [5], [6]. It is already known that selective prospecting of smectite and kaolinite enriched clay can be done in Pulvernieki and Strēļi prospects and that significant variations of mineral composition and texture take place in clay successions [4], [5], [6]. This means that more detailed research is needed in spatial and analytical directions.

The perspective use of Jurassic clay with organics in cosmetics and health care industries, as well as unclear diagenetic history of Jurassic deposits lead to innovative studies performed by using modern technological advances in physical chemistry. Results gained in this study will elaborate information about physical-chemical properties of organics-rich Jurassic clays in Latvia and provide an opportunity to compare organo-modified natural clay with organo-modified synthetical clay (organoclays). Research of organic matter has been done before with carbonate nodules from Callovian stage (Jurassic) and with fossil wood remains [7], [8] from the famous, fossil-rich locality of Łukow in the eastern part of

Poland [9]. This research provided new data about aspects of diagenetic transformations, sedimentation environment and organic chemical composition of the organic matter. The Jurassic deposits from Callovian and Oxfordian stages in many cases were transported to Latvia, Lithuania, and eastern Poland from north by Pleistocene glaciers. It is thought that the sediments originated from the bottom of European seas [10]. The Callovian deposits were researched also in Lithuania using material from outcrops as well as from drill-holes to retrieve a full scale picture of the type of organic matter and conditions of its formation [11]. The whole Lower to Upper Callovian sequence was investigated showed a clear change of facies from terrestrial to deep marine. Callovian deposits are important part of Jurassic system in Western Europe that provides geological information on significant climatic and environmental changes during that time. Research of organic matter has shown the presence of anoxic conditions in water during deposition of the Middle Callovian deposits in the Anglo-Paris Basin [12], [13], [14], [15]. However, some of the researchers even forced the ideas that during Late Callovian global sea-level rise took place [16], [17]. When Callovian depositional environments of the eastern European and Anglo-Paris Basins are compared, it should be mentioned that this is the first complex research of the Callovian sedimentary succession of Eastern Europe based on geochemical, organic, and petrographic analyses. Unlike the Callovian of the western part of Europe and the eastern part of the Paris Basin, in the section at Lithuania there was no evidence of anoxic conditions occurring in water column found, but periodically such episodes below the photic zone during maximum transgression in the Late Callovian basin were possible [11]. The compositions of the organic matter extractable by solvent from Middle Jurassic clays from Poland were characterized by a dominance of terrestrial material as a large amount of terrestrial organic matter which was eroded from the Fennoscandian Shield; oxic to suboxic depositional conditions were affirmed by low concentrations of C33–C35 homohopanes [18]. Samples of Jurassic clay with organic material were analyzed for the first time by the 3-D fluorescence method. These results showed interesting patterns of organic matter, 3-D spectra were similar to those of clays at Poland and Lithuania; the occurrence of some organic substances define their ancient origin which is one of oldest known biomolecules from coniferous material found in geological samples.

One of the major distinctive features of Jurassic clays is the presence of natural organic matter that reflects a wide range of environmental and geological processes. Organic matter in the clayey deposits consists of low molecular, low polarity organic substances (bitumens, waxes, etc.) and humic substances

(fulvic and humic acids) which are the basic result of degradation and polymerization of organic matter during microbial, chemical and photochemical reactions. Humic substances represent a polydisperse, complex mixture of high to low molecular weight species.

Fluorescence spectroscopy (FS) can be used as a non-destructive tool to quantify the decomposition degree of organic matter of any kind. FS also requires a small volume of aqueous sample at low concentration [19], [20]. This is a prominent analytical method for tracing the degradation of organic matter and it is used to characterize not only dissolved organic matter, but also humic substances [21]. FS provides important information on the chemical nature of humic substances (on their position, shift and intensity of fluorescence peaks) and all those data can be correlated to the structural information, such as functional groups, polycondensation, aromaticity, heterogeneity and various dynamic properties related to their intramolecular and intermolecular interactions [22]. The most recent and complete fluorescence technique is total luminescence spectroscopy (TLS) which is also known as excitation-emission matrix (EEM). EEM at present is the most advanced technique, as it provides “fingerprints” for a single compound or a mixture of fluorescent components. In EEM the general behavior of humic macromolecules can be described, even if the various structural units have very variable effects on the wavelength and intensity of fluorescence. The fluorescence intensity decreases with increasing molecular size of the humic macromolecule [23].

The aim of this work is to describe physical-chemical properties of Jurassic clay with organic matter found in territory of Latvia, to evaluate main groups of organic substances and mineralogical properties that could be assessed in future as unrecovered potential materials in cosmetic and remediation industries.

II. MATERIALS AND METHODS

A. Samples of Jurassic Clays

According to previous research, Jurassic clay found in Latvia consist of kaolinite, illite and small amount of smectite and has organic matter and sulfide admixture. Both organic matter and sulfide admixture give it black and dark grey colour; some fossils are also found in these clays as well. Samples for this study were collected at 3 sites: Lēģernieki outcrop, Zoslēni cliff and Papile (Fig. 1).

Jurassic clay sediments were collected in winter conditions from outcrops; previous research data was used in order to determine which samples are necessary for analysis later. Clayey sediments were black, contained silt and sand admixture and their texture was homogenous. Samples from Zoslēni outcrop contained larger proportion of coarser fractions.

B. Determination of Texture and Basic Physical-chemical Characteristics

Jurassic clay was lyophilized in order to prevent destruction of organic matter. Grain size was determined by sieving. Air-dried soil samples were sieved through sieves and fractions finer than 0.05 mm were determined by pipette analysis [24]. The samples were classified using USDA soil texture classes: fractions from 0.063 mm to 2.0 mm were classified as sand,

those from 0.002 mm to 0.063 mm were classified as silt, and those finer than 0.002 mm were classified as clay [25]. Fine fraction analysis was done by *Micromeritics SediGraph*. Cation base saturation analysis was performed by BaCl₂ extraction methodology. Soil pH_{KCl} was measured with a glass electrode in 1 M KCl (1:2.5 mass-to-volume ratio) in triplicate.



Fig. 1. Locations of sites where the samples were collected: **1** Lēģernieki (on Lēģiža bank: coordinates 376927; 6268406) and **2** Zoslēni (coordinates 373806; 6269967) outcrops in Latvia; **3** Papile (Lithuania: coordinates 422534; 6224725) outcrop in Lithuania.

0.1M BaCl₂ was used to determine \ base cation saturation parameters, samples were batch treated, filtrated and analyzed by atomic absorption spectrometry using *PerkinElmer Instrument AAnalyst 200*. In order to find out the amount of total organic carbon (TOC), *Shimadzu TOC-VCS_N* TOC analyzer with solid phase detection module *SSM-5000A* was used. Parameters are given in Table I.

C. LOI Studies of Organic Matter

Organic matter and carbonate minerals proportion in the sediments was determined by loss on ignition (LOI) method [26], which is based on sequential heating of samples in a muffle furnace.

First samples were oven-dried for 12–24 h at 105 °C until weight was constant, then samples were combusted at 550 °C for 4 h. LOI was then calculated using the following equation:

$$LOI_{550} = 100(DW_{105} - DW_{550})/WS \quad (1)$$

where LOI₅₅₀ is the percentage of loss on ignition at 550 °C or the percentage by weight of the organic matter and DW₅₅₀ is the weight of the sample after heating at 550 °C [26], [27].

In the third step, samples were combusted at 900 °C for 2 h and LOI was calculated as:

$$LOI_{900} = 100(DW_{550} - DW_{900})/WS \quad (2)$$

where LOI₉₀₀ is the percentage of loss on ignition at 900 °C or the percentage by weight of the carbonate and DW₉₀₀ is the weight of the sample after heating at 900 °C. The remaining sample, after heating at 900 °C, is the residual mineral matter (LOI_{res}) [26], [27], [28].

D. Determination of Major and Trace Elements in Jurassic Clay

- Metallic elements from clay samples were extracted using HNO₃/H₂O₂ solution [29], [30]. Clay sample pretreatment was done as follows: 10 mg of dry samples

of clayey sediments from fraction less than 0.25 mm were weighed in 50 mL glass beakers,

- 25 mL of 50 % HNO₃ and 5 mL of 30 % H₂O₂ were added.
- Then samples were heated on a heating block at 170° C until 15 mL of solution were left. Additionally 25 mL of 50 % HNO₃ were added and heated until boiling point. Sample solutions were filtrated into polypropylene tubes and filled with ~ 25 mL deionized water. Trace elemental analysis (Al, Na, Mg, K, Ca, Fe, Cr, Mn, Co, Ni, Cu, Zn, Cd, Pb, As, Mo) was carried out by atomic absorption spectrometry (*Perkin-Elmer AAnalyst*) using appropriate wavelengths.

E. PXRD Spectra

Mineral composition of Jurassic clayey deposits was determined by performing and interpreting XRD spectra. Powder X-ray powder diffraction (PXRD) analyses for dry, finely ground clay samples were performed on a Bruker *D8 Advance* diffractometer (generator 40 kV, 40 mA) with 0.6 mm divergence slits, 0.2 mm detector slit, Copper K_α radiation ($\lambda = 0.15418$ nm), 2θ interval from 3° to 60°, scan speed 0.5 s per step, step 0.02°, detector – *LynxEye* (1D-position sensitive). The procedure of activation and enrichment of these clays was followed by the extraction of a smectite concentrate. Extraction of a smectite concentrate with water soluble organic coagulant (KOHIDRAC) results in complete removal of carbonates [31]. This allowed determining spectra on clay mineralogy without minerals sized larger than 1 μ m. The proposed method is based on dispersing smectite containing clay in sodium phosphate solutions, resulting in phosphate stabilized clay suspensions.

Regeneration thermal treatment for samples was also performed as published in [32]. After heating at elevated temperature (450 °C) the reflections are shifted and after treatment with acetone and HCl mixture the characteristic montmorillonite reflection is partially restored [32].

F. Sample Preparation for UV-Vis and 3-D Fluorescence

10 mg of clay powder were extracted with 50 ml of 8 % NaOH solution for 24 h in a horizontal shaker at room temperature. The samples were filtered to remove any suspensions, and their pH was normalized to 7. Extracts of the samples (humic substance solutions) were analysed using 3D fluorescence spectroscopy.

G. UV-Vis Spectroscopy

UV-Vis spectroscopic measurements of the samples were performed on a *Shimadzu UV-1800* spectrophotometer using 1 cm quartz cuvette. The absorption spectra were recorded in the range from 200 nm to 800 nm. Spectral ratios E₂/E₃ [33] and E₄/E₆ [34] were calculated from absorbance at 280 nm 360 nm, and 465 nm and 665 nm. Absorbance ratio of E_{270/400} was calculated from UV-Vis absorbance at 270 nm and 400 nm.

H. 3-D Fluorescence

Clay organic matter can be characterized as chromophoric dissolved organic matter with high phenolic group content. Chromophoric dissolved organic matter absorb the ultraviolet light and can be characterized by its specific ultraviolet absorbance (SUVA). SUVA correlates with the aromaticity and

reactivity of the organic matter. 3D fluorescence spectroscopy was recorded using a TL spectrometer *HORIBA Aqualog*. The spectra were recorded at a 5 nm bandpass excitation in a clear quartz cuvette. The EEM fluorescence spectra were obtained by subsequently scanning the emission spectra from 250 nm to 600 nm at 250-800 nm excitation wavelengths with 5 nm increments.

III. RESULTS AND DISCUSSION

Results on physical parameters and chemical content are given in Tables I and Tables II. Jurassic clay which is found in Zoslēni outcrop contains very low content of clay minerals – these sediments cannot be classified as clay sediments. Papile and Lēģernieki sites have better represented clay fraction with 12 % and 20 % content on average, respectively. Sieving, sedigraph, as well as activation and enrichment procedures prior to XRD analysis were performed. Base cation saturation partly depicts cation exchange capacities (CEC) of samples. However, due to 2–3 % organics content in Jurassic clayey deposits this comparison should be done with precaution as full picture can be gained only by full CEC analysis.

TABLE I
PHYSICAL CHEMICAL PARAMETERS OF THE STUDIED JURASSIC DEPOSITS

Parameters / Soil	Zoslēni	Papile	Lēģernieki
Sand and silt (%)	98	88	80
Clay (%)	2	12	20
pH _{KCl}	6.9	7.4	7.2
Base cation saturation (mmol g ⁻¹)	0.11	0.16	0.15
Organics (%)	2	3	2

TABLE II
AVERAGE CONCENTRATIONS OF MAJOR ELEMENTS AND TRACE ELEMENTS IN JURASSIC CLAYEY DEPOSITS

	Element concentration ($\bar{x} \pm s$), mg/kg		
	Zoslēni	Papile	Lēģernieki
Al	5530 ± 3449	14598 ± 4222	14015 ± 2313
Na	127 ± 156	615 ± 292	535 ± 111
Mg	1092 ± 1689	15330 ± 9670	5523 ± 1466
K	751 ± 572	4241 ± 1794	2282 ± 733
Ca	5005 ± 8886	37949 ± 23070	20255 ± 3151
Fe	2775 ± 3405	13893 ± 2626	7466 ± 1155
Cr	8 ± 6.50	34 ± 5.21	19 ± 2.85
Mn	32 ± 58	208 ± 74	130 ± 20.6
Co	1 ± 1.27	6 ± 0.56	4 ± 1.18
Ni	2 ± 3.18	21 ± 3.25	10 ± 2.95
Cu	1 ± 1.81	7 ± 1.70	5 ± 1.41
Zn	6 ± 6.26	41 ± 5.24	21 ± 4.73
Cd	< 0.02	< 0.02	< 0.02
Pb	2 ± 0.32	5 ± 0.91	3 ± 0.73
As	< 81	< 81	< 81
Mo	< 2	< 2	< 2

Major elements in samples from 3 different sites are common for clay sediments containing various minerals. Al, Na, Mg, K, Ca and Fe are typical for clay minerals. Large standard

deviations observed are explained with complicated interlayering in outcrops as well as large amount of sand, silt, carbonate minerals and other deposit material present together with clay. Trace elements present in clays include those with potential toxicity (Cr, Mn, Co, Ni, Cu, Zn, Cd, Pb). Are however, these amounts are very close to the geochemical background level or are even under the detection limit. As, Mo and Cd were found under the detection limit of the method.

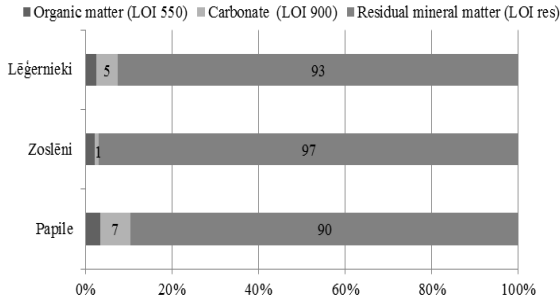


Fig. 2. Organic matter and carbonate mineral proportions in samples of Jurassic clay.

Results depicted in Fig. 2 affirm that the samples consist mainly as the admixture of non-carbonate minerals (~ 90%). This is also proved by PXRD analyses (Fig. 3 and Fig. 6). The host deposit mainly consists of quartz (SiO₂) and muscovite (KAl₂(OH)₂(AlSi₃)O₁₀). A small part (1–7 %) of admixtures consists of carbonates: dolomite (CaMg(CO₃)₂) and calcite (Ca(CO₃)). Gypsum (CaSO₄·2H₂O) here it is thought to have an anthropogenic origin as Papile outcrop has been stabilized by using cement.

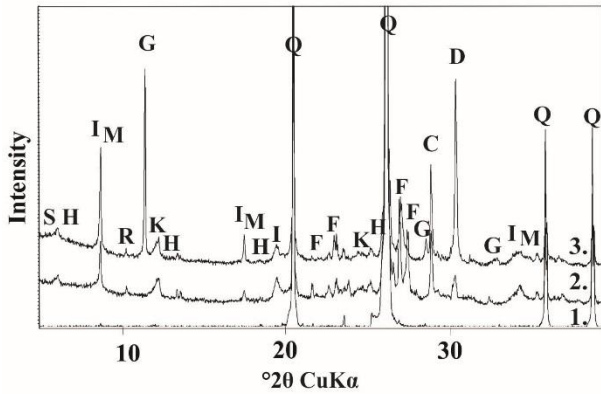


Fig. 3. PXRD patterns for raw Zoslėni (1.), Lėgėrnieki (2.) and Papile (3.) deposits. Abbr.: S – Ca or Na smectite; R – hornblende; M – mica; F – feldspars; H – clinocllore; I – illite; K – kaolinite; G – gypsum; Q – quartz; C – calcite; D – dolomite.

Enriched clay fractions by using above mentioned KOHIDRAC methodology show patterns that have Ca and Na smectites, illite, clinocllore and kaolinite appearing in approximately similar intensities (Fig. 4).

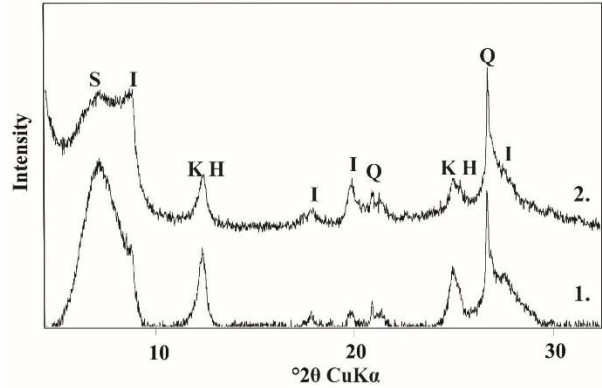


Fig.4. PXRD patterns of Papile-3 (1.) and Papile-1 (2.) enriched clay fractions.

In natural samples clinocllore is hardly distinguishable from kaolinite. Therefore the spectra were zoomed and double peaks could be seen melted together — so appearance of clinocllore and kaolinite is disputable, if discussions arise on details (Fig. 5).

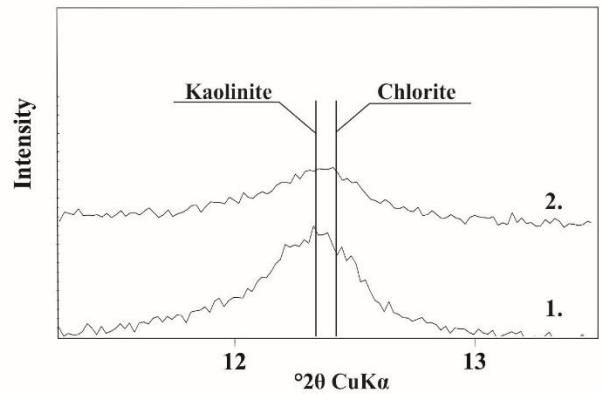


Fig. 5. Kaolinite and clinocllore XRD double peak (in all samples).

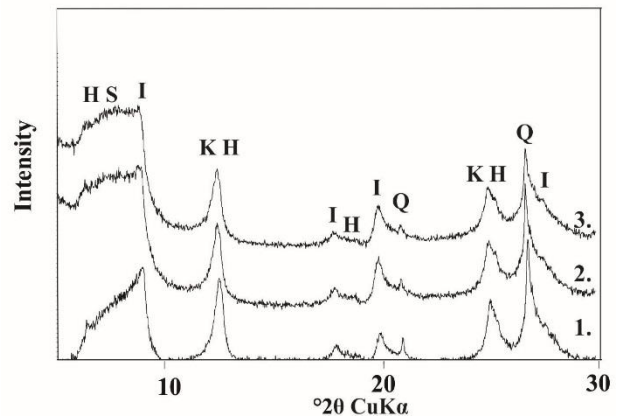


Fig. 6. PXRD patterns of Lėgėrnieki-2 (1.), Lėgėrnieki-8 (2.) and Lėgėrnieki-11 (3.) enriched clay fractions.

All 12 samples with its clay fraction (less than 1 μm) of Lėgėrnieki deposit have similar mineralogy (Fig. 6).

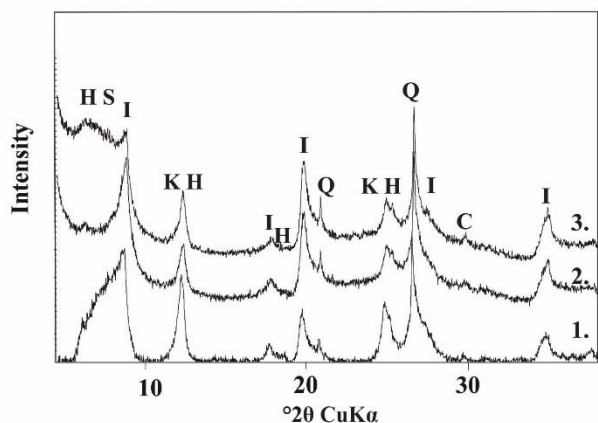


Fig. 7. XRD patterns of untreated (1.), thermally treated (2. at 450 °C) and regenerated (3.) Lėgėrniki-8 enriched clay fractions.

After heating at elevated temperature (450 °C) the 001 reflection has shifted from $2\theta = 7.2^\circ$ to $2\theta = 8.8^\circ$ presenting the evidence that pseudo-illitization caused by dehydration has taken place. After treatment with acetone and HCl mixture the characteristic montmorillonite reflection is partially restored. The small reflection in pattern 3. (Fig. 7) at $2\theta = 8.8^\circ$ implies a partial preservation of illite structure.

XRD patterns for Ca and Na smectites are to be distinguished because Ca-smectite peaks often are not detectable or are similar to chlorite peaks. This is possible with this regeneration thermal treatment method (Fig. 7).

UV-Vis and EEM fluorescence spectroscopy

It is well known that the UV-Vis spectra of humic substances exponentially increase with decreasing wavelength, between 200 nm and 800 nm (Fig. 8) [35]. The obtained spectra of the analyzed samples are relatively non-informative, therefore absorption ratios at different wavelengths were used to characterize humic substances.

TABLE III

UV-VIS ABSORPTION RATIOS OF HUMIC SUBSTANCES FROM JURASSIC CLAYEY SEDIMENTS

UV absorption ratios	Zoslėni	Papile	Lėgėrniki
E_2/E_3	1.12	1.10	1.14
E_4/E_6	1.11	1.10	1.11
$E_{270}/400$	1.17	1.09	1.20

Table III shows that Jurassic clayey deposit samples are relatively similar in values at all ratios — E_4/E_6 , E_2/E_3 and $E_{270}/400$. Comparing the findings to those found in literature about humic substances from peat [36] the absorbance ratios of the Jurassic clay samples can be evaluated as relatively low. The low E_4/E_6 ratio may be attributed to the absorption by

aromatic C = C functional groups, also, additionally, the high degree of the aromatic ring condensation as well as the large molecular weight of humic substances [37].

The E_2/E_3 ratio characterizes humification process — the humification degree increases with decreasing value [38]. Ratios E_2/E_3 and $E_{270}/400$ strongly correlate and show degradation of phenolic/quinoid core of humic substances [35] as well as proportion between the lignins and other materials at the beginning of humification [39].

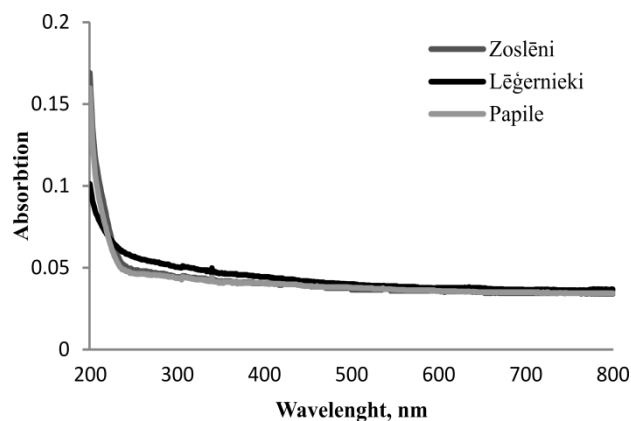


Fig. 8. UV-Vis spectra of the humic substances from clay samples.

The UV-Vis and EEM or 3D fluorescence spectroscopic results described further show that the Jurassic clay samples have a high degree of aromatic condensation and organic material humification.

Two general peaks were detected using EEM fluorescence spectroscopy of humic substances extracted from clay (Fig. 9). The first peak was centered at an Ex/Em wavelength pair of 330–360 nm/430–530 nm and is related to fulvic acid-like substance Fig. 8. UV-Vis spectra of humic substances from Jurassic clay samples compounds [40], [20]. In several cases the fulvic acid-like compounds had another, less pronounced peak at 400–420 nm/470–550 nm (Fig. 9). The second main peak had its own Ex/Em wavelength pair at 430–470 nm/520–560 nm, which is associated with humic acid-like substances [40], [20]. All of the EEM spectra have been spectrally corrected for instrument biases, corrected for inner filter effects and Raman calibrated. As a result all of the Rayleigh scatters and most of the Raman scatters have been removed. Fig. 9 depicts results of 3-D fluorescence analysis for organic matter in order to see trends and differences of organic matter substances.

The fluorescence intensity decreases, if the substance has a high content of electron acceptor groups (–COOH); in turn the content of electron donor groups — such as –OH, –NH₂, and –OCH₃ — significantly increases the fluorescence intensity, especially in aromatic compounds.

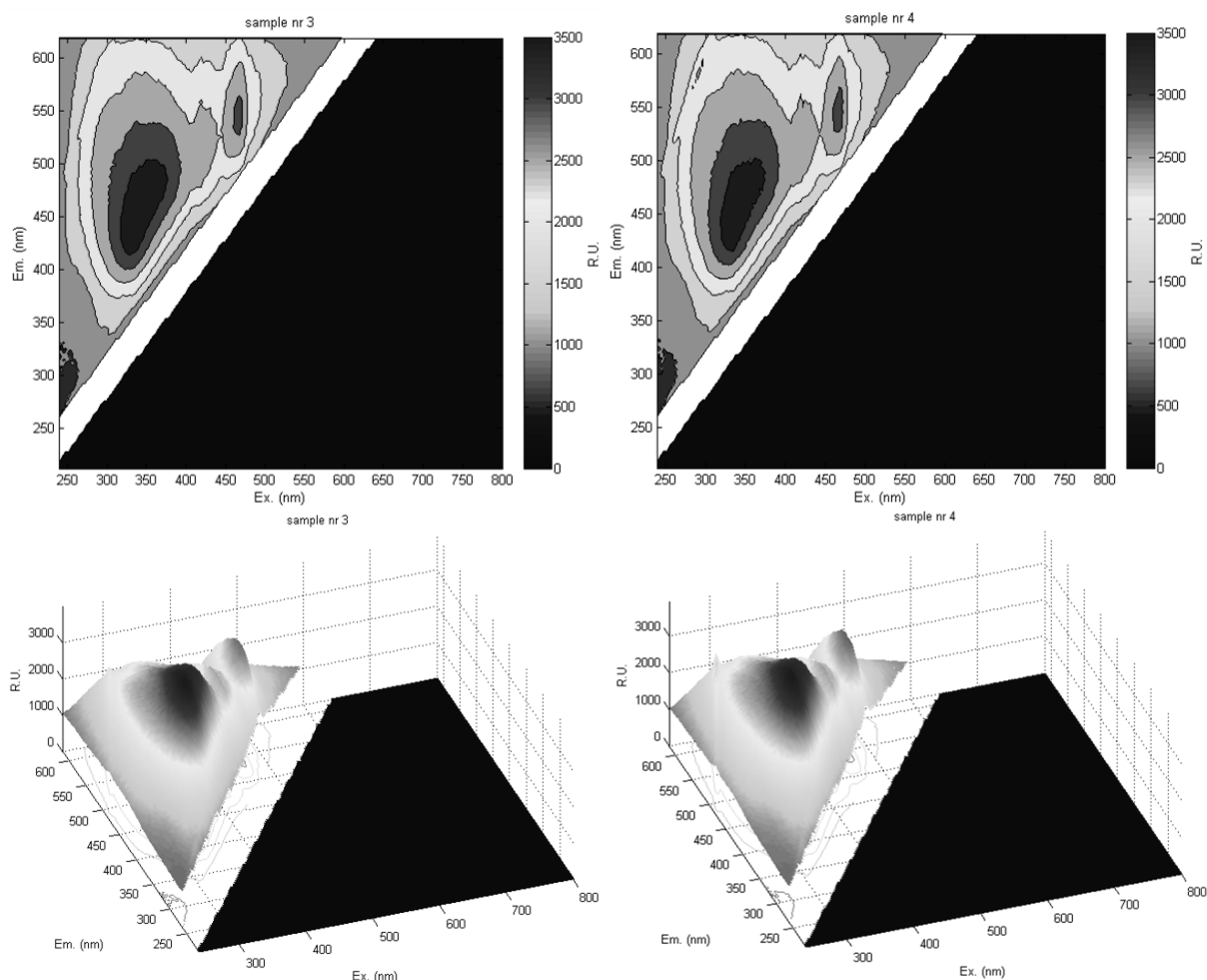


Fig. 9. EEM spectra of organic matter of clay from Papile samples from Oxfordian age outcrop.

The carboxyl-containing substituents and hydroxyl-, alkoxy- and amino- groups tend to shift the fluorescence maxima to longer wavelengths; at the same time, a decrease in the number of aromatic rings, reduction of conjugated bonds in a chain structure and conversion of a linear ring system to a nonlinear system can cause the fluorescence maxima to shift towards shorter wavelengths [23].

IV. CONCLUSION

Kaolinite, illite, smectite, and chlorite are in approximately similar proportions in fraction less than 1 μm in the studied Jurassic clayey deposits. The organic matter consists of organic molecules, including humic substances (fulvic and humic acids). It has a high degree of aromatic condensation and organic material humification. Our study has shown that EEM spectra of clay organic matter provides possibility to characterize both low-polarity and polar (humic substances) organic substances of natural organic matter. Therefore, it is possible to analyze very sensitive data that otherwise can be lost, leading to misinterpretation of results. Humic substances in the studied clayey deposits consist predominately of humic acids.

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Juris Burlakovs, Rūta Ozola, Juris Kostjukovs, Ivars Kļaviņš, Oskars Purmalis, Māris Kļaviņš. Dienvidrietumu Latvijas un Ziemeļlietuvās juras mālaino nogulumu īpašības.

Pētījumā gūtie rezultāti sniedz ziņas par Juras perioda mālaino nogulumu īpašībām, un palīdz salīdzināt šī perspektīvā derīgā izrakteņa īpašības. Juras sistēmas Kelovejas un Oksfordas stāvu nogulumi atrodami urbūmu serdēs, atradnēs, kā arī pleistocēna ledāja atrauņos jeb glasioloslakācijās. Līdz šim plašāki pētījumi notikuši Polijā un Lietuvā, salīdzinoši mazāk informācijas apkopots par Latvijas Juras māliem un to raksturojošām īpašībām. Šī pētījuma ietvaros paraugi tika ievākti Zoslēnu, Papiles un Lēģernieku atradnēs; to galvenās atšķirības saistās ar mālu frakcijas īpatsvaru salīdzinājumā ar pārējo nogulumu materiālu. Juras mālaino nogulumu sastāva īpatnības raksturotas, izmantojot granulometriskās analīzes, karsējuma zudumu, rentgendifraktometrisko un atomabsorbciometrijas metožu kompleksu; detalizēti pētīti arī nogulumu sastāvā esošie organiskie savienojumi, izmantojot UV-Vis un 3-D fluorescenci. Mālu sastāvā esošās organiskās vielas pamatā ir humusvielas, savukārt māla frakcijas neorganisko materiālu veido smektīts, illīts, kaolinīts un hlorīts aptuveni līdzīgās proporcijās, ko pierāda rentgendifraktometriskā izpēte. Agrākie pētījumi Polijā un Lietuvā liecina, ka dabiskās organiskās vielas, kas atrodamas Juras mālos, atspoguļo nogulumu veidošanās apstākļus. Juras māli var tikt izmantoti tālākos praktiskā pielietojuma pētījumos, kā arī, lai precizāk raksturotu attiecīgā perioda paleoģeogrāfiskos apstākļus.