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Maturation changes of hydrocarbons in solid parts of peloids from Serbian spas – Catalytic influence of clay minerals

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Abstract: The study focused on inspecting the composition of *n*-alkane, sterane and terpane biomarkers in healing mud (peloid) organic matter in the Rusanda, Bujanovac and Vranje spas. It was assumed that the catalytic influence of minerals on changes in biomarkers could be effectively evaluated based on the distribution of their biolipid and thermodynamically more stable geolipid structural and stereochemical isomers. Quartz, illite, kaolinite, plagioclase, smectite and chlorite were identified in the samples by powder X-ray diffraction. *n*-Alkanes, terpanes and steranes were analyzed in the solid parts of the peloids using the gas chromatography–mass spectrometric, GC–MS, technique. In Rusanda and Bujanovac samples, *n*-alkanes were identified with distributions characteristic of immature sediments. In contrast, distributions of terpanes and steranes are typical for the mature organic matter of old sedimentary formations. It was concluded that the identified clay minerals do not have an obvious catalytic effect on the maturation of *n*-alkanes. At the same time, the presence of illite, chlorite, and smectite compensated for all other missing factors (heat, pressure and geological time) by catalytic action and, as a result, gave terpanes and steranes with distributions that are characteristic for petroleum, as the most mature form of organic matter in the geosphere.

Keywords: biomarkers; GC–MS analysis; maturity; smectite.

INTRODUCTION

The organic matter of sedimentary rocks changes through diagenetic and catagenetic processes. Under the influence of heat, pressure and mineral catalysts,

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changes occur towards forming more thermodynamically stable isomers of organic compounds. Most of these alterations are slow and take a long geological time, measured in millions of years. That is why geological time is justifiably considered the fourth necessary factor in these processes.[1–5]

Crude oil (petroleum) is considered to be the most mature form of organic matter in the geosphere. It is formed from an organic matter from the biosphere that undergoes intense transformations through geological time. Everything takes place in sedimentary formations, from recent to oldest, that is, to source and reservoir rocks for oil. At the end of those transformations that have passed through fulvic and humic acids, humin, kerogen and bitumen, the most mature form, crude oil, will be created. It is natural and expected that the hydrocarbons in it will have structural and stereochemical forms at the highest degree of thermodynamic stability. In organic geochemistry, the most attention is paid to the examination of changes in hydrocarbon biomarkers of the *n*-alkane type, as well as polycyclic alkanes of the sterane and terpane type.[1–5]

Heat and pressure are considered the most critical organic geochemical factors influencing the transformation of biomarkers. In catagenesis, the temperature ranges from 70 to a maximum of 150 °C, and the pressures are between 700 and 1300 bar. In such cases, minerals may act as catalysts, influencing the intensity and speed of biomarker transformations. Some changes cannot even occur if the organic matter is not in contact with certain minerals. For example, it is known that the transformations of steroids into the most thermodynamically stable sterane isomers, diasteranes, cannot take place without the catalytic action of silicate-type minerals, even when they are under the influence of heat at high temperatures and the influence of high pressure. The same applies to the transformation of the hopane isomer C_{27}-17α(H)-trisnorhopane (Tm) into the thermodynamic isomer C_{27}-18α(H)-trisnorneohopane (Ts).[3,6,7] Our earlier works also proved that these changes, and many others, are significantly influenced by the clay minerals, e.g., montmorillonite, illite, kaolinite and chlorite.[6–8]

This research studied the composition of *n*-alkane, sterane and terpane biomarkers in the organic matter of sediments used as healing mud (peloids) in the Serbian spas of Rusanda, Bujanovac and Vranje. These sediments contain a significant portion of clays and do not belong to formations located at greater geological depths and, therefore, were not exposed to high temperatures and pressures. Therefore, it was assumed that the catalytic influence of minerals on changes in biomarkers could be effectively evaluated based on the distribution of their biolipid and thermodynamically more stable geolipid structural and stereochemical isomers.

EXPERIMENTAL

Samples

The present study examined samples of the solid part of peloids, which are used as "healing mud" in the Serbian spas of Rusanda, Bujanovac and Vranje. Peloids are two-phase systems consisting of a solid and a liquid part.[9] The solid part mostly comprises of clay minerals, and the liquid part is thermomineral water. It can contain various inorganic and organic components formed during geological, geochemical and biological processes. Peloid characteristics depend on the composition of the solid and liquid phases and the duration of the mixing process between these phases. This process is called maturation or aging.[8-11] Due to various biological and biochemical processes, depending on the habitat in which the clay is left to mature, during peloid formation, the amount of microorganisms (including microalgae) increases. Microalgae, together with the cyanobacteria that grow on them, improve the dermocosmetic properties of the peloid. It is described in the literature that they have soothing, regenerating, antioxidant, anti-inflammatory and antimicrobial effects. All of this together contributes to the strong positive cosmetic and healing properties of peloid.[9,11-16]

Earlier studies also proved that the presence of long-chain normal alkanes and some of their substituted derivatives contributes to the thermotherapeutic and anti-inflammatory effects of peloids.[17,18] On the other hand, the presence of steroid and terpenoid compounds contribute to analgesic, antioxidant and antitumor properties.[19-22] Other classes of organic compounds contribute to the healing effect. For example, polyunsaturated fatty acids protect against free radicals and have an anti-inflammatory effect,[17,18] and methyl esters of fatty acids contribute to antibacterial and antifungal activity.[21-23]

Methods

The solid parts of the peloid samples from the Serbian spas of Rusanda (Rus), Bujanovac (Bu) and Vranje (Vr) were dried under ambiental conditions. The organic matter was isolated using the Soxhlet method from the samples freed of hygroscopic moisture. An azeotropic mixture of methylene chloride and methanol (88:12 volume ratio) was used as a solvent. The saturated hydrocarbon fraction was isolated by column chromatography. Silica gel and aluminum oxide (2:1) were used as adsorbent and *n*-hexane was used as eluent.

Total aliphatic fractions were analyzed by gass chromatograpy–mass spectrometry (GC–MS, TIC mode), using an Agilent 7890A gas chromatograph (HP-5MS column, 30 m×0.25 mm, 0.25 μm film thickness, He carrier gas 1.5 $cm^3 min^{-1}$), coupled to an Agilent 5975C mass selective detector. For a more detailed analysis of *n*-alkanes, steranes and terpanes in aliphatic fractions, typical mass fragmentograms (*m*/*z* 71, 217 and 191, respectively) were extracted.

The mineral composition in the samples was determined using the powder X-ray diffraction method (PXRD). The data were collected at room temperature on a Rigaku SmartLab X-ray diffractometer using Bragg–Brentano geometry and CuKα radiation. The presence and type of clay minerals were determined from the oriented aggregates.

RESULTS AND DISCUSSION

The mineralogical composition of the samples was defined using powder X-ray diffraction (PXRD) method. Fig. 1 shows the X-ray diffractograms of Rus, Bu and Vr samples.

The Rusanda sample contained quartz, illite, plagioclase, calcite, chlorite and smectite, with possible presence of kaolinite, K-feldspar, dolomite and paragonite, Bujanovac – quartz, plagioclase, illite, kaolinite, chlorite and smectite, with possible presence of K-feldspar and dolomite and Vranje – quartz, analcime, illite, plagioclase, chlorite and smectite, with possible presence of calcite and clinoptilolite.

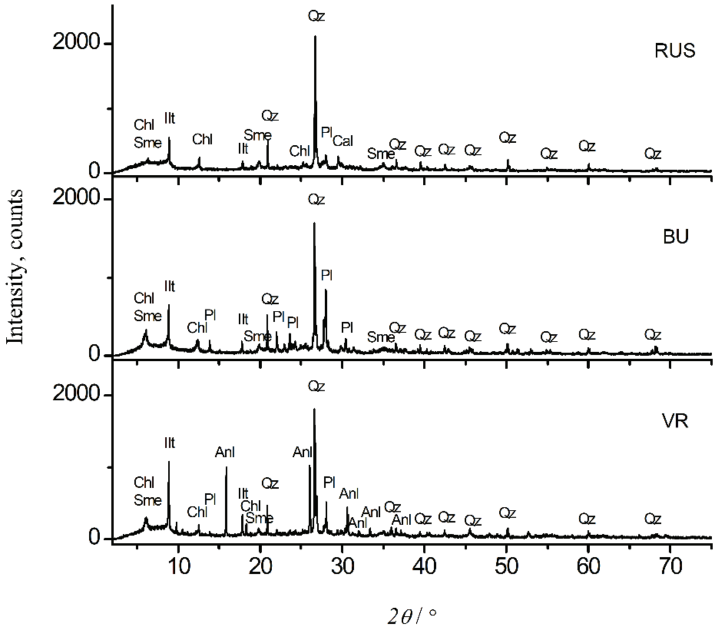

Fig. 1. X-Ray diffractograms of the investigated samples Rusanda, Bujanovac and Vranje. Ilt – illite, Chl – chlorite, Sme – smectite, Qz – quartz, Pl – plagioclase, Anl – analcime.

Previous studies of the effect of minerals on thermal changes in sedimentary organic matter have shown that smectite, illite, chlorite and kaolinite can have catalytic properties.[5–8] Smectite, chlorite and illite were identified in the investigated samples (Fig. 1).

Fig. 2 shows fragmentograms of *n*-alkanes obtained by GC–MS analysis of isolated fractions of saturated hydrocarbons (*m*/*z* 71). Table I demonstrates commonly used organic geochemical parameters calculated based on their distributions.

The distribution of *n*-alkanes of the Rusanda sample shows a bimodal character. The most abundant member in the homologous series is *n*-C_{29}. However, within the short-chain *n*-alkane series, a maximum at *n*-C_{17} is observed. In contrast, within the long-chain *n*-alkane group, a strong dominance of odd homologs is noticed ($CPI_{\text{full range}} = 2.77$; Table I) and unambiguously originate from the organic matter of higher terrestrial plants with a low degree of thermal maturity.[5] The short-chain *n*-alkanes mainly originate from algal precursor biomass.[5] Given the proximity of the Rusanda oil field, these *n*-alkanes may be part of an allochthonous organic matter originating from migrated crude oil.

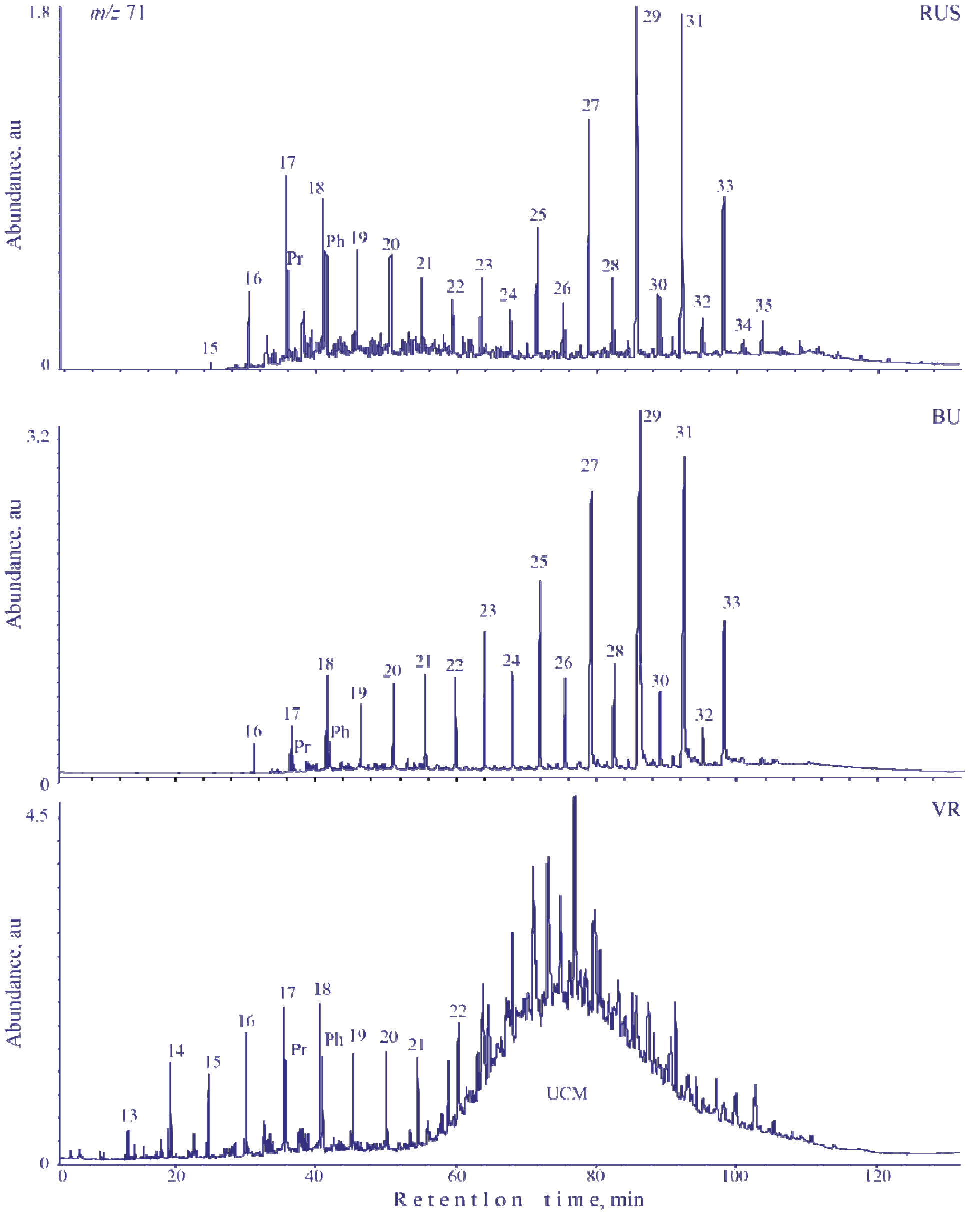

Fig. 2. Fragmentograms of *n*-alkanes obtained by GC-MS analysis of isolated saturated hydrocarbon fractions (*m*/*z* 71). *n*-Alkanes are labelled according to their carbon number; Pr – pristane; Ph – phytane; UCM – unresolved complex mixture.

TABLE I. Parameters calculated from *n*-alkane distributions; *CPI* – carbon preference index

Sample	The range of *n*-alkanes	The most abundant *n*-alkane	*CPI*
Rus	C_{16}–C_{37}	C_{17}, C_{29}	2.77
Bu	C_{16}–C_{33}	C_{29}	3.78
Vr	C_{13}–C_{22}	C_{18}	0.91

n-Alkanes of the Bujanovac extract are characterized by the dominance of odd homologs in the C_{16}–C_{33} range with the most abundant *n*-C_{29} (*CPI* = 3.78; Fig. 2, Table I). This distribution is characteristic of organic matter of terrestrial origin and a low degree of maturation. In the Vranje sample, only lower *n*-alkanes in the C_{13}–C_{22} range and with a slight dominance of even homologs were identified (*CPI* = 0.91; Table I). The second part belongs to the "unresolved complex mixture" (UCM).[24] Considering that there are no oil deposits near this location, it can be assumed that these *n*-alkanes are autochthonous. In that case, it can be concluded that they have an algal origin.

Fig. 3a and b show fragmentograms of steranes (*m*/*z* 217) and terpanes (*m*/*z* 191) of investigated samples. The peak identification is given in Tables II and III, and the values of some maturation parameters calculated from the distributions of steranes and tepanes are given in Table IV.

The distribution and abundance of terpanes in the *m*/*z* 191 fragmentogram for the Rusanda sample (Fig. 3a) are typical for the mature organic matter of sedimentary rocks, usually found in bitumens of source rocks for oil or in oils themselves.[1–5] Numerous parameter values from Table IV confirm this unequivocally. Hopane is distinctly more dominant than moretane (parameter 1), 22*S* isomers are more abundant than the corresponding 22*R* isomers (parameters 2 and 3), C_{27}-18α(H)-trisnorneohopane (Ts), a typical geoisomer, is present in a lower concentration than Tm, but is still present (parameter 4; Table IV).

A similar judgment can be made for steranes (Figure 3b) where the geolipid isomers that are formed from the biolipid isomers, C_{27}–C_{29} 14α(H),17α(H)(20*R*), are found with them in ratios that are typical for oil. This can be said for 20*S* isomers (parameter 5; Table IV), $\beta\beta$ isomers (parameter 6), as well as for disteranes. As expected, the concentration of $C_{27}\beta\alpha$(20*S*) disterane is lower than C_{27} $\alpha\alpha$(20*R*) sterane. However, the ratio of relative concentrations of these two isomers in the Rusanda sample is typical for mature organic matter (parameter 7; Table IV).

The distributions of terpane and sterane isomers in the Bujanovac and Vranje samples are not identical to those in the Rusanda sample. However, their fingerprints (*m*/*z* 191 and 217, Fig. 3) are typical petroleum. The ratios of geolipid isomers, thermodynamically stable, and the corresponding biolipids from which they were formed during maturation processes, shown through parameters 1–7 from Table IV, unequivocally confirm this.

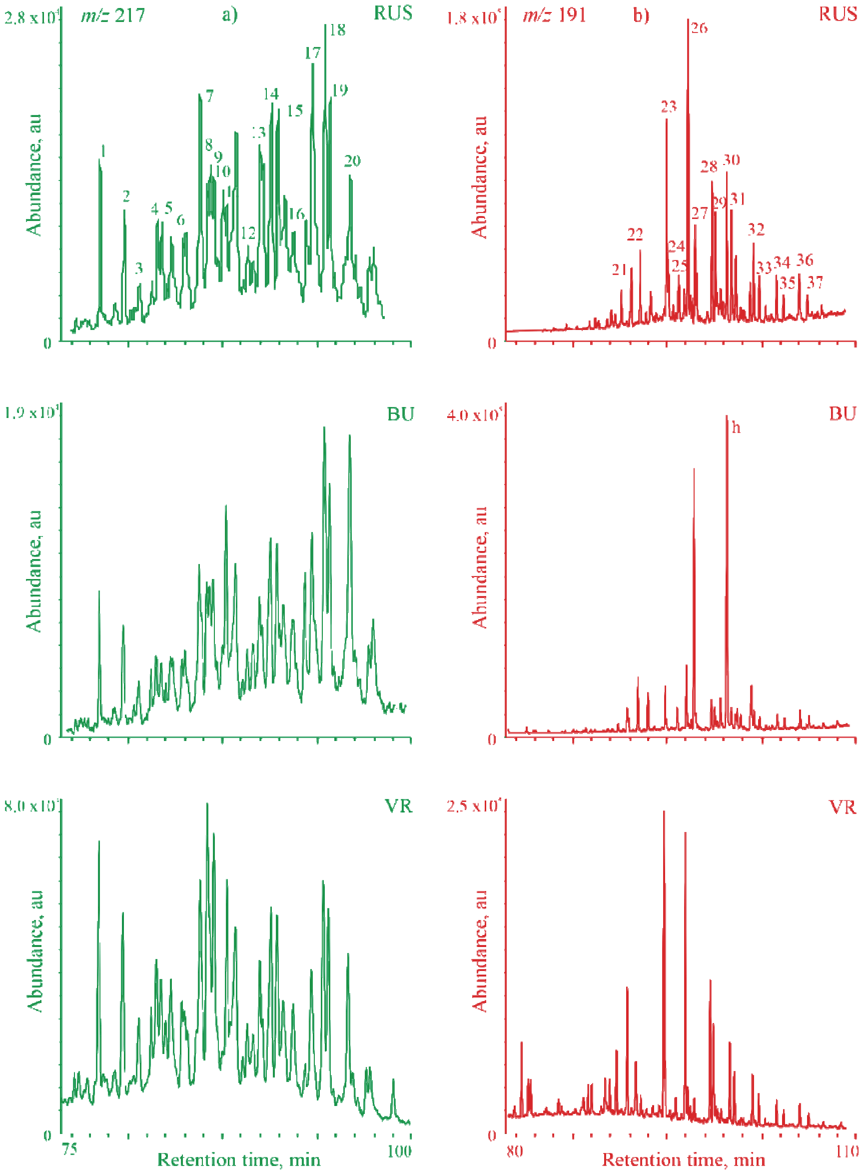

Fig. 3. Fragmentograms of steranes (m/z 217, a) and terpanes (m/z 191, b) obtained by GC–MS analysis of isolated saturated hydrocarbon fractions.

Analysis of biomarkers in the solid parts of peloids showed that *n*-alkanes have distributions that are characteristic of immature sediments (Fig. 1). This is an expected result considering that these sediments were not exposed to the temperatures and pressures that are characteristic for the creation of mature forms of the organic matter, e.g., the bitumen of the source rocks for oil or oil itself.

TABLE II. Identification of peaks from Fig. 3a

Peak	Compound
1	C_{27} 13β(H)17α(H)20(*S*)-diasterane
2	C_{27} 13β(H)17α(H)20(*R*)-diasterane
3	C_{27} 13α(H)17β(H)20(*S*)-diasterane
4	C_{27} 13α(H)17β(H)20(*R*)-diasterane
5a	C_{28} 13β(H)17α(H)20(*S*)24(*S*)-diasterane
5b	C_{28} 13β(H)17α(H)20(*S*)24(*R*)-diasterane
6a	C_{28} 13β(H)17α(H)20(*R*)24(*S*)-diasterane
6b	C_{28} 13β(H)17α(H)20(*R*)24(*R*)-diasterane
7	C_{28} 13α(H)17β(H)20(*S*)-diasterane + C_{27} 14α(H)17α(H)20(*S*)-sterane
8	C_{29} 13β(H)17α(H)20(*S*)-diasterane + C_{27} 14β(H)17β(H)20(*R*)-sterane
9	C_{28} 13α(H)17β(H)20(*R*)-diasterane + C_{27} 14β(H)17β(H)20(*S*)-sterane
10	C_{27} 14α(H)17α(H)20(*R*)-sterane
11	C_{29} 13β(H)17α(H)20(*R*)-diasterane
12	C_{29} 13α(H)17β(H)20(*S*)-diasterane
13	C_{28} 14α(H)17α(H)20(*S*)-sterane
14	C_{29} 13α(H)17β(H)20(*R*)-diasterane + C_{28} 14β(H)17β(H)20(*R*)-sterane
15	C_{28} 14β(H)17β(H)20(*S*)-sterane
16	C_{28} 14α(H)17α(H)20(*R*)-sterane
17	C_{29} 14α(H)17α(H)20(*S*)-sterane
18	C_{29} 14β(H)17β(H)20(*R*)-sterane
19	C_{29} 14β(H)17β(H)20(*S*)-sterane
20	C_{29} 14α(H)17α(H)20(*R*)-sterane

TABLE III. Identification of peaks from Fig. 3b

Peak	Compound
21	C_{27} 18α(H),22,29,30-trisnorhopane, Ts
22	C_{27} 17α(H),22,29,30-trisnorhopane, Tm
23	C_{29} 17α(H)21β(H)-hopane
24	C_{29} 18α(H),30-norhopane
25	C_{29} 17β(H)21α(H)-moretane
26	C_{30} 17α(H)21β(H)-hopane
27	C_{30} 7β(H)21α(H)-moretane
28	C_{31} 17α(H)21β(H)22(*S*)-hopane
29	C_{31} 17α(H)21β(H)22(*R*)-hopane
h	C_{30} hopene
30	C_{32} 17α(H)21β(H)22(*S*)-hopane
31	C_{32} 17α(H)21β(H)22(*R*)-hopane
32	C_{33} 17α(H)21β(H)22(*S*)-hopane
33	C_{33}17α(H)21β(H)22(*R*)-hopane
34	C_{34} 17α(H)21β(H)22(*S*)-hopane
35	C_{34} 17α(H)21β(H)22(*R*)-hopane
36	C_{35} 17α(H)21β(H)22(*S*)-hopane
37	C_{35} 17α(H)21β(H)22(*R*)-hopane

TABLE IV. Sterane and terpane maturation parameters

Sample	Terpanes (hopanes)				Steranes (diasteranes)		
	C_{30} moretane / C_{30} hopane	$C_{31}(22S)$ / $C_{31}(22R)$	$C_{31}(22S)$ / $C_{31}(22R)$	Ts / Tm	$C_{29}\alpha\alpha(20S)$ / $C_{29}\alpha\alpha(20R)$	$C_{29}\beta\beta(20R)$ / $C_{29}\alpha\alpha(20R)$	$C_{27}\beta\alpha(20S)$ disterane / $C_{27}\alpha\alpha(20R)$ sterane
Rus	0.19	1.24	1.44	0.76	1.98	1.54	0.36
Bu	0.23	1.32	1.69	0.75	0.84	1.01	0.45
Vr	0.13	1.40	1.34	0.54	1.25	1.29	0.63
Parameter	1	2	3	4	5	6	7

However, the distributions of terpanes and steranes in all three examined samples are surprising. These biomarkers have distributions that are characteristic of mature organic matter of old sedimentary formations (Fig. 3; Table IV) despite insufficiently high temperatures and pressures and, most likely, insufficiently long geological time.

The investigated samples characterize the significant presence of clay minerals (Fig. 1). The conclusion is that illite, smectite and kaolinite, with their strong catalytic effect, actually compensated for all other missing factors, and, as a result, gave terpanes and steranes with distributions that are characteristic even for oil, as the most mature form of organic matter in the geosphere.

CONCLUSION

The composition of *n*-alkane, sterane and terpane biomarkers in the organic matter of sediments used as medicinal mud (peloids) in the Serbian spas of Rusanda, Vranje and Bujanovac was investigated. These sediments are clays that do not belong to formations located at greater geological depths, and therefore were not exposed to high temperatures and pressures. Therefore, it was assumed that the catalytic influence of minerals on changes in biomarkers could be effectively evaluated based on the distribution of their biolipid and thermodynamically more stable geolipid structural and stereoisomers.

Quartz, illite, montmorillonite, plagioclase and chlorite were identified in the samples. Previous tests have shown that all identified minerals in the investigated samples, except quartz, can catalyze the maturation changes of organic matter in sediments.

Analysis of biomarkers in solid parts of peloids showed that *n*-alkanes have distributions that are characteristic of immature sediments. Based on these results, it could be concluded that the identified minerals do not have an obvious catalytic effect on the maturation processes of normal alkanes. Instead, they indicate the precursor biomass from which they originated. Terpanes and steranes in all three examined samples, Rusanda, Bujanovac and Vranje, have distributions characteristic of mature organic matter in old sedimentary formations. Based on this result, it can be concluded that illite, kaolinite, smectite and chlorite, with their strong catalytic effect, actually compensated for all other missing factors (heat, pressure and most likely, geological time), and as a result gave terpanes and steranes with distributions that are characteristic even for oil, as the most mature form of organic matter in the geosphere.

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ИЗВОД

МАТУРАЦИОНЕ ПРОМЕНЕ УГЉОВОДОНИКА У ЧВРСТОМ ДЕЛУ ПЕЛОИДА СРПСКИХ БАЊА – КАТАЛИТИЧКИ УТИЦАЈ МИНЕРАЛА ГЛИНЕ

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Проучаван је састав биомаркера типа нормалних алкана, стерана и терпана у органској супстанци седимената који се употребљавају као лековито блато (пелоиди) у српским бањама Русанда, Врање и Бујановац. Пошло се од претпоставке да би се каталитички утицај минерала на промене биомаркера ефикасно могао да се процени на основу расподела њихових биолидних, и термодинимачки стабилнијих геолипидних структурних и стереохемијских изомера. У узорцима су рендгено–дифракционом анализом идентификовани кварц, илит, плагиоклас, монтморионит и хлорит. Гаснохроматографско–масеноспектрометријском техником у чврстим деловима пелоида анализирани су нормални алкани, терпани и стерани. У узорцима из Русанде и Бујановца идентификовани су нормални алкани са расподелама које су карактеристичне за нематурисане седименте. Закључено је да идентификовани минерали немају очигледно каталитичко дејство на матурационе процесе нормалних алкана. Терпани и стерани у сва три испитивана узорка имају расподеле које су карактеристичне за матурисане органске супстанце старих седиментних формација. Закључено је да су илит, каолинит, смектит и хлорит каталитичким дејством заправо надокнадили све друге недостајуће факторе (топлота, притисак и највероватније, геолошко време), и као резултат дали терпане и стеране са расподелама које су карактеристичне чак и за нафту, као најматурисанији облик органске супстанце геосфере.

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