

<https://doi.org/10.3176/oil.1993.2/3.03>

UDC 622.337:543.54:543.51:621.039.8

E. B. BONDAR, H. A. TAAL, M. M. BITYUKOV

SOLID BITUMEN INCLUSIONS IN KUKERSITE OIL SHALE: STRUCTURE AND GENESIS

*This paper is dedicated
to our scientific adviser
Professor Ilmar Klesment*

Abstract

The supermolecular structure of the solid bitumen (SB) inclusions present in Ordovician kukersite oil shale has been studied and its similarity to that of crude oil asphalts has been demonstrated. Differences in the composition of the saturated hydrocarbons extracted with chloroform from SB and kukersite have been established. Among the *n*-alkanes of SB "even" homologues prevail, contrary to "odd" ones predominating in the extractable *n*-alkanes of kukersite. The different pristane to phytane ratio of SB (0.78) and kukersite (1.10) is indicative of different environments of their source organic matter deposition.

The relatively high content of isoprenoid and branched alkanes (predominantly 2- and 3-methylsubstituted) is characteristic of SB. In the composition of SB steranes diasteranes prevail, while regular steranes are abundant in kukersite. On the whole, the composition of the saturated hydrocarbon fraction of SB is similar to that of biodegraded and/or water washed crude oils. The $\delta^{13}\text{C}_{\text{PDB}}$ values of the extractable (-31.2‰) and insoluble organic matter of kukersite (-32.0‰) and its semicoking oil (-32.0‰) are even lower than those of the saturated hydrocarbon fraction of SB (-30.5‰). The $\delta^{13}\text{C}$ value of SB asphaltenes (-29.4‰) differs from that of asphaltenes isolated from the kukersite extract (-30.7‰), being similar to the $\delta^{13}\text{C}$ value of asphaltenes isolated from Baltic Cambrian oils (on an average -29.5‰).

Introduction

SB inclusions in kukersite have been investigated for over 40 years already but no unanimous opinion about their genesis has been formed yet. In two recent works [1, 2] an exhaustive bibliography of the previous works and different conceptions of SB genesis has been presented. Based on the results of lithological investigations as well as those of group and elemental composition of SB, the autochthonous genesis of the latter has been proposed. Contrary to the current opinion about the immaturity of kukersite organic matter the probability of local thermolysis of kukersite has been assumed [2]. On the other hand, the mineral composition of SB inclusions and kukersite as well as the elemental composition of SB and the extractable and insoluble organic matter of kukersite have been established to differ. No correlation between *n*-alkanes and *n*-alkenes-1 of kukersite semicoking oil and SB pyrolysate has been observed. The data obtained suggest the allochthonous origin of SB inclusions present in kukersite [1].

Experimental

Sample Location. The SB sample was taken from the lense found in the commercial kukersite layer B ("Estonia" mine, northeastern Estonia) (for the commercial zonation of kukersite see [3]). SB lenses (up to 25—30 cm long, 3—5 cm thick) bed in conformity with kukersite layers and are timed predominantly to the lower part of Kukruse horizon. By the appearance SB are coal-like black brittle rock.

Analytical Procedure. The SB sample was examined by scanning electron microscopy with a "TESLA BS 300" (acceleration voltage 25 kV, probe current 100 pA, decoration with gold). Thermal analysis was carried out in air (100 ml/min) using an OD-102 Q 1000 derivatograph; the heating rate was 283 K/min. The powdered SB was extracted with chloroform. From the extract obtained asphaltenes were precipitated with *n*-pentane. The *n*-pentane-extracted malthenes were separated into fractions by thin layer chromatography [4]. The saturated hydrocarbon fraction was analyzed using a "Hewlett Packard 5942A/5985A" GC-MS system equipped with a capillary column (10 m × 0.25 mm i.d.) coated with OV-101; the electron energy was 70 eV. The other fractions were not accessible to gas chromatographic analysis. The elemental composition was determined with a "Hewlett Packard 185 CNH" analyser. Carbon isotopic composition (relative to PDB standard) were obtained using a "Finnigan MAT Delta E" mass spectrometer. Infra-red spectra were recorded using a "UR-20 Jena Zeiss" i.r. spectrophotometer.

Results and Discussion

According to chloroform solubility (85.5 %) and elemental composition (Table 1), the SB under study may belong to the greemite subclass of asphaltite class and is similar to other SB findings in kukersite [1]. In coordinates H/C and (N+S)/O in the Hunt diagram [5] SB and greemites plots are grouped closer to petroleum asphaltenes and apart from pyrobitumens and coals (Fig. 1).

Scanning electron microscopic examination demonstrated SB to consist of associates (up to 50 μ in diameter) (Fig. 2). The same microheterogeneity is distinctive of petroleum as a system and persists in each of its fraction from light cuts to asphaltenes [6, 7]. After dissolution in chloroform the supermolecular structure of SB is destroyed and the chloroform extract becomes quite homogeneous (Fig. 2). Changes in the structural order were established by differential thermal analysis (DTA) (Fig. 3). The behaviour of the chloroform extract of SB during DTA is similar to that of petroleum asphaltenes [8].

Table 1. Comparison of the Elemental Composition (wt. %) of SB and Kukersite Organic Matters (OM)

Organic matter	C	H	N	O + S	H/C _{at}
SB chloroform extract	86.2	8.7	1.7	2.7 0.7	1.21
Kukersite chloroform extract	83.3	11.6	-	5.1	1.67
Kukersite insoluble OM	79.9	9.7	0.3	11.0	1.46

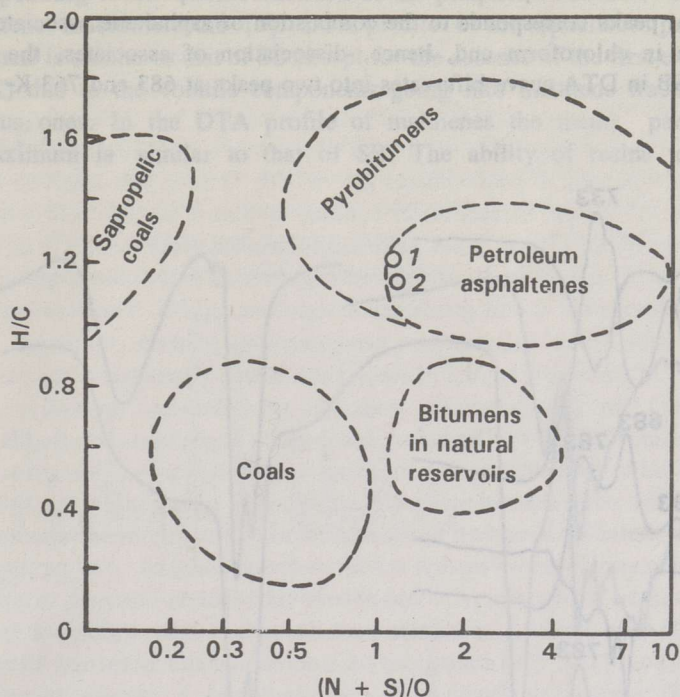


Fig. 1. Atomic H/C ratio vs atomic (N+S)/O ratio (Hunt diagram): 1 - SB, 2 - greemite [5]

The high molecular mass of petroleum asphaltene molecules is due largely to an electrostatic association of individual asphaltene units. In the medium of a solvent with a sufficiently high dielectric constant the break-down of π -electron interactions between individual asphaltene units and, hence, a lower-degree association take place [9]. In DTA profile of SB an exotherm at 603 K corresponds to the release and

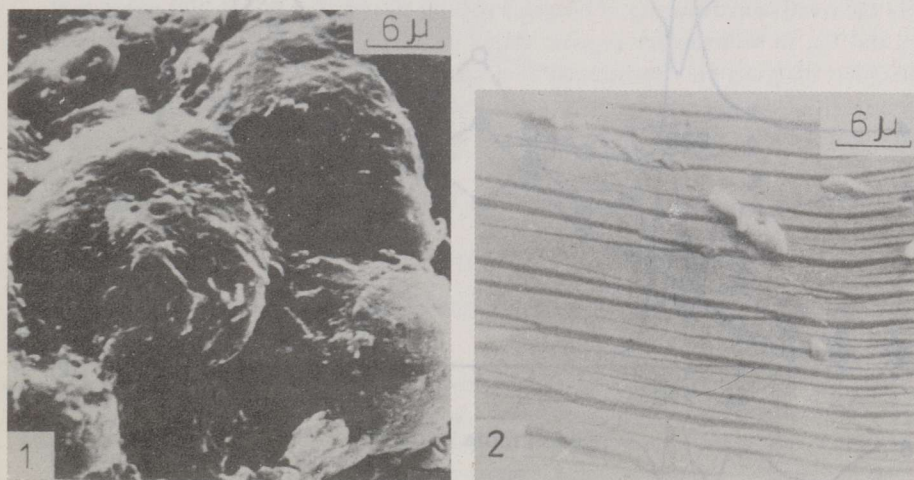


Fig. 2. Scanning electron photomicrographs of SB (1) and its chloroform extract (2)

combustion of volatile compounds. An exotherm at 733 K presented in the form of two coalescent peaks corresponds to the combustion of asphaltene associates. Due to dissolution in chloroform and, hence, dissociation of -associates, the second exotherm of SB in DTA curve bifurcates into two peaks at 683 and 763 K

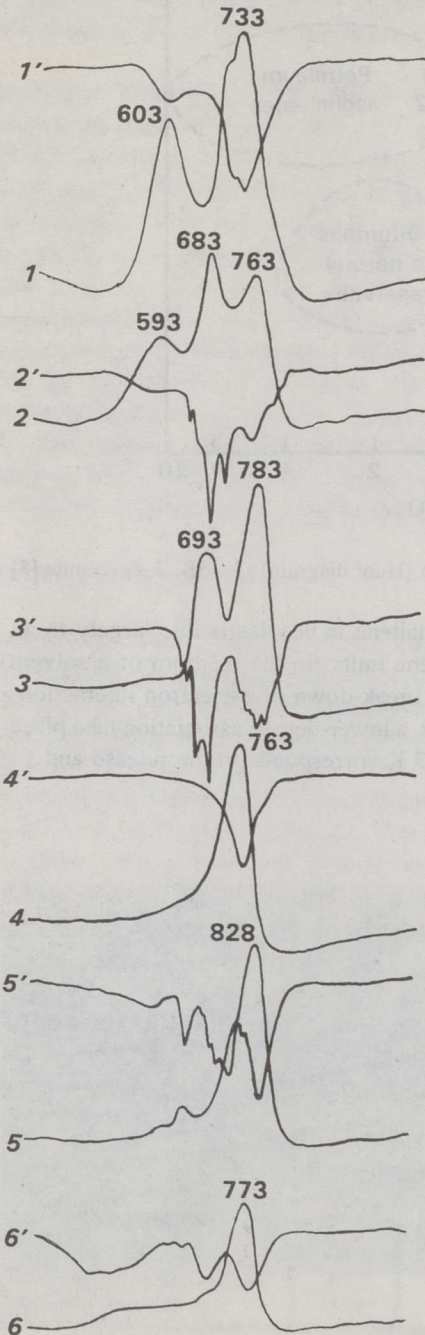


Fig. 3. DTA and TG (numbers with prime) profiles of SB (1), its chloroform extract (2), asphaltenes (3), pyrolysis residue (4), and malthenes (5) and kukersite chloroform extract (6). Exomaxima temperatures are given in K

corresponding to the thermooxidation of the peripheral and basic structure of the asphaltene macromolecule [9]. DTA profile of the asphaltenes precipitated with *n*-pentane is similar to that of SB except for the absence of the first exomaximum (at 593 K) due to the volatile components going into malthene fraction as well as resinous ones. In the DTA profile of malthenes the main, partially resolved exomaximum is similar to that of SB. The ability of resins to convert into

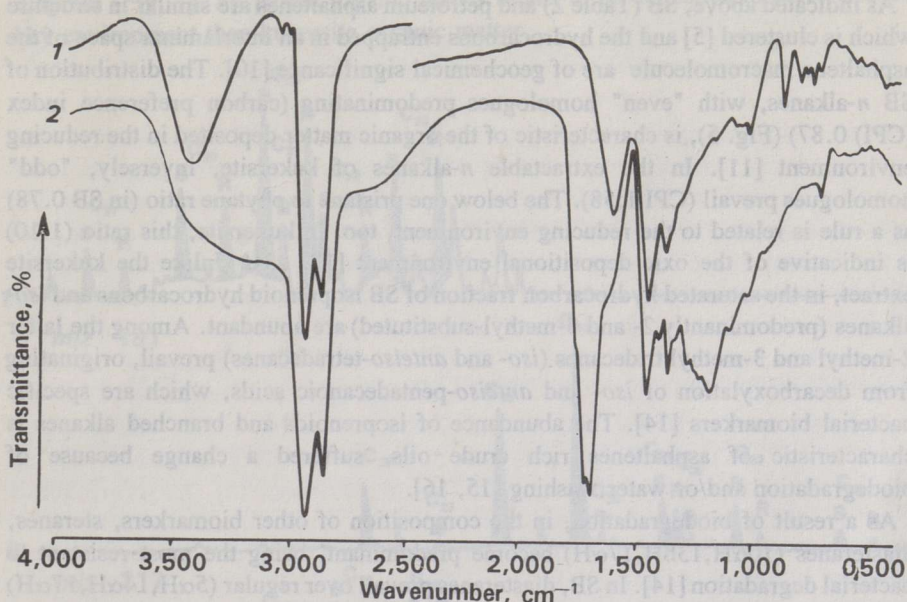


Fig. 4. Infra-red spectra of SB (1) and kukersite (2) chloroform extracts

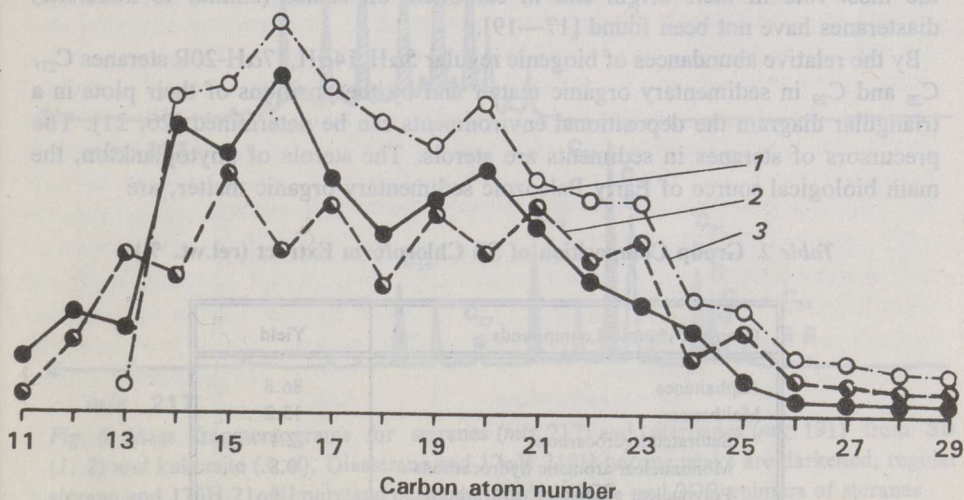


Fig. 5. The relative distribution of *n*-alkanes of SB (1) and kukersite (2) chloroform extracts and Ladushkin crude oil (3) [24]

asphaltenes upon the Friedel-Crafts alkylation already under mild conditions in the presence of catalyst (metal ions in SB) has been confirmed [9].

A comparison of the DTA curves of the chloroform extracts of SB and kukersite shows them to differ (Fig. 3). The same applies to their infra-red spectra (Fig. 4). In the spectrum of the former the absorption band of the carbonyl group (at 1720 cm^{-1}) is absent, being intensive in that of the other. The absorption band of methylene groups in long aliphatic chains (at 720 cm^{-1}) is of low intensity in the spectrum of the chloroform extract of SB contrary to that of kukersite (Fig. 4).

As indicated above, SB (Table 2) and petroleum asphaltenes are similar in structure which is clustered [5] and the hydrocarbons entrapped in an interlaminal space of the asphaltene macromolecule are of geochemical significance [10]. The distribution of SB *n*-alkanes, with "even" homologues predominating (carbon preference index (CPI) 0.87) (Fig. 5), is characteristic of the organic matter deposited in the reducing environment [11]. In the extractable *n*-alkanes of kukersite, inversely, "odd" homologues prevail (CPI 1.58). The below one pristane to phytane ratio (in SB 0.78) as a rule is related to the reducing environment, too. In kukersite, this ratio (1.10) is indicative of the oxic depositional environment [12, 13]. Unlike the kukersite extract, in the saturated hydrocarbon fraction of SB isoprenoid hydrocarbons and *iso*-alkanes (predominantly 2- and 3-methyl-substituted) are abundant. Among the latter 2-methyl and 3-methyl tridecanes (*iso*- and *anteiso*-tetradecanes) prevail, originating from decarboxylation of *iso*- and *anteiso*-pentadecanoic acids, which are specific bacterial biomarkers [14]. The abundance of isoprenoids and branched alkanes is characteristic of asphaltenes rich crude oils, suffered a change because of biodegradation and/or water washing [15, 16].

As a result of biodegradation, in the composition of other biomarkers, steranes, diasteranes (10 α H, 13 β H, 17 α H) become predominant, being the most resistant to bacterial degradation [14]. In SB, diasteranes prevail over regular (5 α H, 14 α H, 17 α H) steranes, which are abundant in kukersite (Fig. 6). As to the occurrence of diasteranes in sedimentary organic matter, the catalytic effect of clay minerals plays the most role in their origin and in carbonate oil shales (similar to kukersite) diasteranes have not been found [17—19].

By the relative abundances of biogenic regular 5 α H, 14 α H, 17 α H-20R steranes C₂₇, C₂₈ and C₂₉ in sedimentary organic matter and by the positions of their plots in a triangular diagram the depositional environments can be determined [20, 21]. The precursors of steranes in sediments are sterols. The sterols of phytoplankton, the main biological source of Early Paleozoic sedimentary organic matter, are

Table 2. Group Composition of SB Chloroform Extract (rel.wt. %)

Group of chemical compounds	Yield
Asphaltenes	86.8
Malthenes:	13.2
Saturated hydrocarbons	2.1
Mononuclear aromatic hydrocarbons	0.8
Polynuclear aromatic hydrocarbons	1.6
Neutral heteroatomic compounds	3.1
Polar heteroatomic compounds	5.6

represented mainly (up to 70 % by weight) by C_{27} sterols, whose concentration in zooplankton is high too. Phyto- and zooplankton are a suitable source of C_{28} sterols too but the highest concentrations of C_{28} sterols are characteristic of fungi and protozoa [20]. The source of C_{29} sterols, being the most abundant in higher plants, in the Early Paleozoic could be marine invertebrates, i.e. crustaceans, known from the Cambrian. Despite the uniformity of biological sources of Early Paleozoic organic matter, the relative abundances of biogenic regular $5\alpha H, 14\alpha H, 17\alpha H$ -20R steranes C_{27} , C_{28} and C_{29} in SB and kukersite do not coincide in the triangular diagram (Fig. 7). SB parent organic matter seems to be deposited in more shallow bay environment than kukersite organic matter.

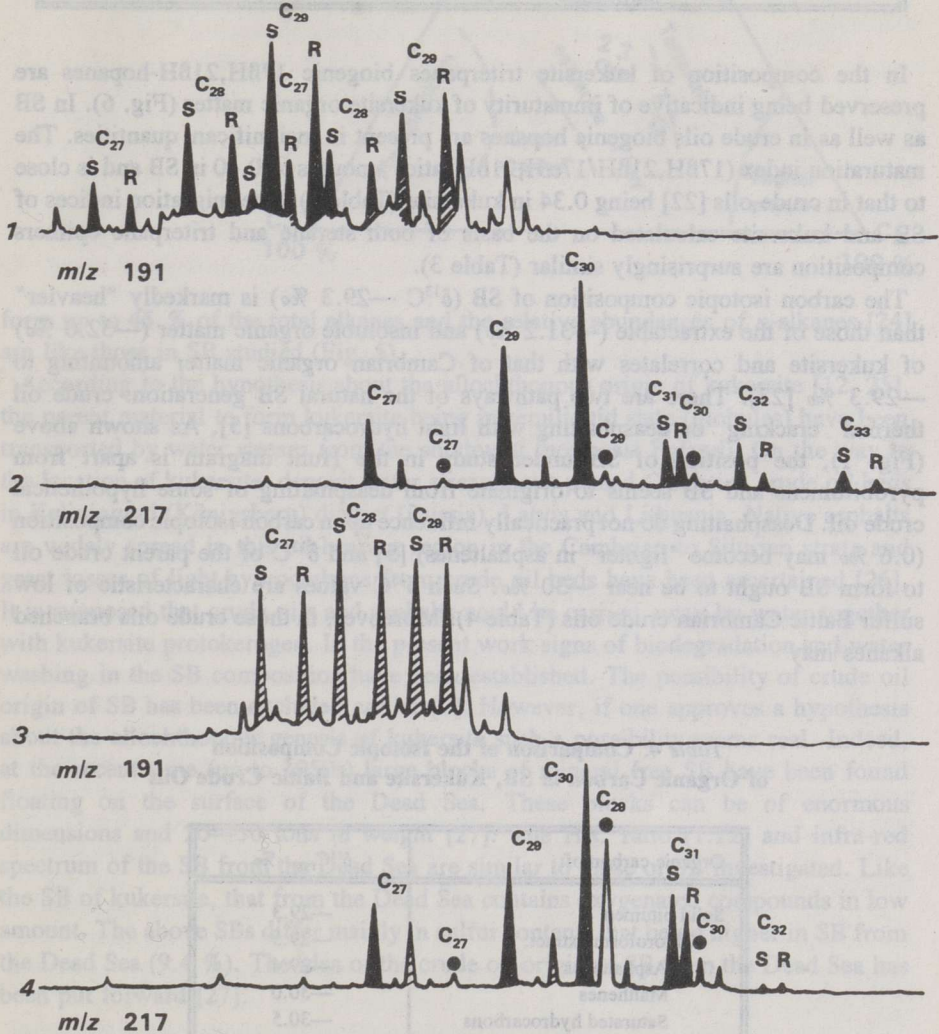


Fig. 6. Mass fragmentograms for steranes (m/z 217) and triterpanes (m/z 191) from SB (1, 2) and kukersite (3, 4). Diasterane and $17\alpha H, 21\beta H$ -hopane peaks are darkened, regular sterane and $17\beta H, 21\alpha H$ -moretane peaks are shaded, 20S- and 20R-epimers of steranes and 22S- and 22R-epimers of hopanes are marked with S and R, $17\beta H, 21\beta H$ -hopane peaks are marked with points

Table 3. Some Geochemical Parameters of SB and Kukersite

Parameter	SB	Kukersite
CPI of <i>n</i> -alkanes	0.87	1.58
Pristane/phytane	0.78	1.10
Pristane + phytane/ <i>n</i> -C ₁₇ + <i>n</i> -C ₁₈	0.77	0.40
5 α H,14 α H,17 α H-2OR C ₂₇ : C ₂₈ : C ₂₉	27 : 23 : 50	29 : 35 : 36
17 β H,21 β H/17 α H,21 β H	0.10	0.34
C ₃₁ 17 α H,21 β H 22S/22S + 22R	0.58	0.63
C ₂₉ 5 α H,14 α H,17 α H 20S/20S + 20R	0.47	0.50

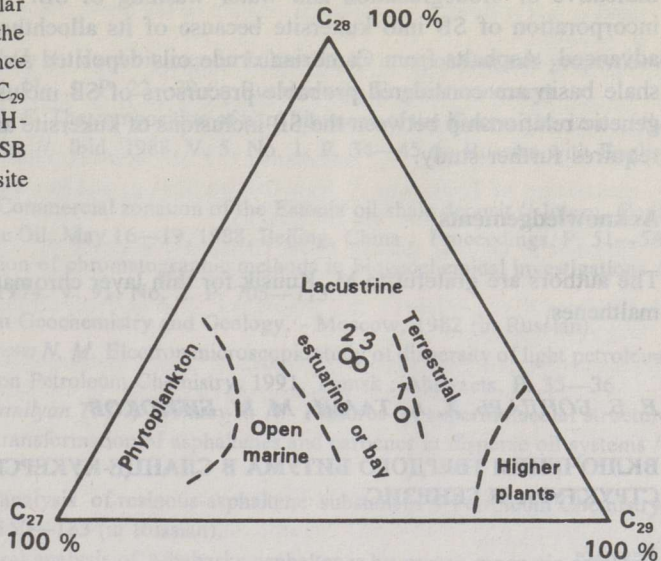
In the composition of kukersite triterpanes biogenic 17 β H,21 β H-hopanes are preserved being indicative of immaturity of kukersite organic matter (Fig. 6). In SB as well as in crude oils biogenic hopanes are present in insignificant quantities. The maturation index (17 β H,21 β H/17 α H,21 β H ratio) amounts to 0.10 in SB and is close to that in crude oils [22] being 0.34 in kukersite (Table 3). The migration indices of SB and kukersite calculated on the basis of both sterane and triterpane epimers composition are surprisingly similar (Table 3).

The carbon isotopic composition of SB ($\delta^{13}\text{C}$ -29.3 ‰) is markedly "heavier" than those of the extractable (-31.2 ‰) and insoluble organic matter (-32.0 ‰) of kukersite and correlates with that of Cambrian organic matter amounting to -29.3 ‰ [23]. There are two pathways of the natural SB generation: crude oil thermal cracking or deasphalting with light hydrocarbons [5]. As shown above (Fig. 1), the position of SB under study in the Hunt diagram is apart from pyrobitumens and SB seems to originate from deasphalting of some hypothetical crude oil. Deasphalting do not practically influence upon carbon isotopic composition (0.6 ‰ may become "lighter" in asphaltenes) [5] and $\delta^{13}\text{C}$ of the parent crude oil to form SB ought to be near -30 ‰. Such $\delta^{13}\text{C}$ values are characteristic of low sulfur Baltic Cambrian crude oils (Table 4). Moreover, in those crude oils branched alkanes may

Table 4. Comparison of the Isotopic Composition of Organic Carbon in SB, Kukersite and Baltic Crude Oils

Organic carbon of:	$\delta^{13}\text{C}_{\text{PDB}}$, ‰
Solid bitumen	-29.3
Chloroform extract:	-29.5
Asphaltenes	-29.4
Malthenes	-30.0
Saturated hydrocarbons	-30.5
Kukersite total organic matter:	-32.0
Semicoking oil	-32.0
Extractable organic matter:	-31.2
Asphaltenes	-30.7
Saturated hydrocarbons	-31.2
Cambrian organic matter [23]	-29.3
Baltic Cambrian crude oils [23]	-30.3
Asphaltenes [23]	-29.5

Fig. 7. Triangular diagram of the relative abundance of C_{27} , C_{28} and C_{29} $5\alpha H, 14\alpha H, 17\alpha H$ -2OR steranes of SB (1) and kukersite samples (2, 3)



form up to 45 % of the total alkanes and the relative abundances of *n*-alkanes [24] are like those in SB studied (Fig. 5).

According to the hypothesis about the allochthonous origin of kukersite [12, 25], the parent material to form kukersite being in semiliquid state (globules) have been transported by water stream from the southwest (northeast Poland). On the way to the location of kukersite deposit water stream have passed Cambrian crude oil beds in Kaliningrad (Königsberg) district (Russia), Latvia and Lithuania. Native asphalts are widely spread in this oil-bearing region in the Cambrian to Silurian strata and great losses of light hydrocarbons from crude oil beds have been ascertained [26]. It is supposed that crude oils and asphalts could be carried away by water together with kukersite protokerogen. In the present work signs of biodegradation and water washing in the SB composition have been established. The possibility of crude oil origin of SB has been excluded earlier [2]. However, if one approves a hypothesis about the allochthonous genesis of kukersite such a possibility seems real. Indeed, at the recent time (up to 1950s) large blocks of mineral free SB have been found floating on the surface of the Dead Sea. These blocks can be of enormous dimensions and 20—50 tons in weight [27]. The H/C ratio (1.22) and infra-red spectrum of the SB from the Dead Sea are similar to those of SB investigated. Like the SB of kukersite, that from the Dead Sea contains oxygenated compounds in low amount. The above SBs differ mainly in sulfur content, that being higher in SB from the Dead Sea (9.4 %). The idea of the crude oil origin of SB from the Dead Sea has been put forward [27].

Conclusions

The similarity of SB inclusions in kukersite with crude oil asphalts has been demonstrated. By the composition of the saturated hydrocarbons, CPI of *n*-alkanes, pristane to phytane ratio, $\delta^{13}C$ values, sterane and triterpane compositions, SB and the extractable and insoluble organic matter of kukersite differ. The geochemical parameters calculated on the basis of SB composition data are indicative of the

different genesis of SB and kukersite organic matter. Biomarkers composition is indicative of biodegradation and water washing of SB. A hypothesis about the incorporation of SB into kukersite because of its allochthonous genesis has been advanced. Asphalts from Cambrian crude oils deposited southwest of kukersite oil shale basin are considered probable precursors of SB inclusions of kukersite. The genetic relationship between the SB inclusions of kukersite and the Baltic crude oils requires further study.

Acknowledgements

The authors are grateful to M. Kuusik for thin layer chromatographic separation of malthenes.

Е. Б. БОНДАРЬ, Х. А. ТААЛЬ, М. М. БИТЮКОВ

ВКЛЮЧЕНИЯ ТВЕРДОГО БИТУМА В СЛАНЦЕ-КУКЕРСИТЕ: СТРУКТУРА И ГЕНЕЗИС.

Резюме

Хотя включения твердого битума (ТБ) в кукурсите изучаются уже более 40 лет, до сих пор нет единого взгляда на них генезис.

Исследовали ТБ из линзы в слое В кукурсита (шахта «Эстония»). По растворимости в хлороформе (85,5%) и элементному составу (С 86,2, Н 8,7, N 1,7, (O+S) 3,4%, Н/С 1,21) этот образец ТБ можно отнести к классу асфальтитов, подклассу греэмитов.

С помощью растровой электронной микроскопии установили, что надмолекулярная структура исследуемого ТБ подобна таковой нефтяных асфальтенов. При дифференциальном термическом анализе ТБ ведут себя аналогично нефтяным асфальтенам и отлично от битумоида и керогена кукурсита.

Среди *n*-алканов, экстрагированных из ТБ, преобладают четные гомологи, в отличие от *n*-алканов, экстрагируемых из кукурсита, в составе которых преобладают нечетные гомологи. В ТБ и кукурсите разное отношение пристан/фитан (0,78 и 1,10 соответственно), что связано с разными условиями накопления их материнского органического вещества. Для алканов ТБ в отличие от кукурсита, характерно относительно высокое содержание изопреноидных и разветвленных алканов (преимущественно 2- и 3-метилзамещенных), а в составе стеранов преобладают диастераны, а не регулярные стераны, как в кукурсите. Такие же особенности характерны для состава нефтей, подвергшихся биодegradации и вымыванию водой.

По изотопному составу ($\delta^{13}\text{C} -29.5\text{‰}$) углерод ТБ «тяжелее», чем углерод битумоида (-31.2‰), керогена (-32.0‰) и смолы полукоксования кукурсита и близок к углероду асфальтенов, выделенных из кембрийских нефтей Балтики (-29.5‰).

Согласно гипотезе об аллохтонном генезисе кукурсита, его протокероген в виде глобул был транспортирован водным потоком к месту его залегания с северо-востока Польши. Предполагается, что при этом могли быть захвачены битумы, широко распространенные в Калининградской области, Литве, Латвии в отложениях от кембрийского до силурийского возраста. Эти битумы не пирогенетические — они образовались за счет деасфальтизации нефтей легкими углеводородами. Вопрос генетической связи между включениями ТБ в кукурсите и кембрийскими нефтями Прибалтийского региона требует дальнейшего изучения.

REFERENCES

1. Kattai V. A., Kundel H. A. Hard bitumen in kukersite, its composition and properties // Oil Shale. 1987. V. 4. No. 1. P. 22—29 (in Russian with English summary).
2. Klubov B. A., Urov K. E. The composition of hard bitumens of the Kukruse horizon of the Baltic oil shale basin // Ibid. 1988. V. 5. No. 1. P. 34—45 (in Russian with English summary).
3. Kattai V., Puura V. Commercial zonation of the Estonia oil shale deposit // Intern. Conf. on Oil Shale and Shale Oil, May 16—19, 1988, Beijing, China : Proceedings. P. 51—58.
4. Klesment I. Application of chromatographic methods in biogeochemical investigations // J. Chromatography. 1974. V. 91. No. 2. P. 705—713.
5. Hunt J. M. Petroleum Geochemistry and Geology. - Moscow, 1982 (in Russian).
6. Litvinov I. A., Likhterova N. M. Electron microscopic study of dispersity of light petroleum cuts // Intern. Conf. on Petroleum Chemistry, 1991, Tomsk : Abstracts. P. 35—36.
7. Rogacheva O. V., Danilyan T. D., Gimaev R. N. Features of supermolecular structure formation and phase transformation of asphaltenes and carbenes in disperse oil systems // Ibid. P. 314—315.
8. Pokonova J. V. The analysis of resinous-asphaltene substances // Petroleum Chemistry. Leningrad, 1984. P. 150—183 (in Russian).
9. Speight J. G. Structural analysis of Athabaska asphaltenes by proton magnetic resonance spectroscopy // Fuel. 1971. V. 50. No. 2. P. 102—112.
10. Douglas A. G., Grantham P. J. Fingerprints gas chromatography in the analysis of some native bitumens, asphalts and related substances // Advances in Organic Geochemistry. Paris, 1973. P. 261—276.
11. Guoying S., Shanfa F., Dehan L., Negosian S., Hongming Z. The geochemistry of *n*-alkanes with an even-odd predominance in the Tertiary Shahejie Formation of northern China // Advances in Organic Geochemistry. Oxford, 1979. P. 115—121.
12. Klesment I. R., Bondar E. B. Biogeochemical aspects of evolution of sapropelites according to data of molecular paleontology // Oil Shale. 1988. V. 5. No. 2. P. 129—146 (in Russian with English summary).
13. Bondar E. B., Bityukov M. M., Kuusik M. G. Geochemical peculiarities of kukersite oil shale of the Estonia deposit periphery // The 3rd All-Union Conf. on Carbon Geochemistry, 1991, Moscow : Abstracts. P. 17—18 (in Russian).
14. Ueta N., Ishizuka I., Yamakava T. Gas chromatographic grouping of bacteria // The First Intern. Conf. of Culture Collections University of Tokyo, 1970, Tokyo : Proceedings. P. 371—381.
15. Connan J., Restle A., Albrecht F. Biodegradation of crude oil in the Aquitaine basin // Advances in Organic Geochemistry. Oxford, 1979. P. 1—177.
16. Tissot B. P., Welte D. H. Petroleum Formation and Occurrence. - Moscow, 1981 (in Russian).
17. Sieskind O., Joly G., Albrecht P. Simulation of the geochemical transformation of sterols: superacid effect of clay minerals // Geochim. Cosmochim. Acta. 1979. V. 43. No. 10. P. 1675—1679.
18. Bondar E. Variations in the composition of steranes and triterpanes in oil shales of different origins and stages of maturity // Intern. Conf. on Oil Shale and Shale Oil, May 16—19, 1988, Beijing, China : Proceedings. P. 85—91.
19. Bondar E. B. Catalytic transformations of sterols in oil shales // All-Union Symp. on the Problems of Catalysis in Coal Chemistry, 1990, Donetsk : Abstracts. P. 94—96 (in Russian).
20. Huang W.-Y., Meinschein W. G. Sterols as ecological indicators // Geochim. Cosmochim. Acta. 1979. V. 43. No. 5. P. 739—745.

21. Boreham C. J., Powell T. G. The Toolebuc oil shale: an organic geochemical investigation // The Second Australian Workshop on Oil Shale, 1984, Brisbane : Proceedings. P. 50—55.
22. Petrov A. A. Petroleum Hydrocarbons. - Moscow, 1984 (in Russian).
23. Yeryomenko N. A., Pankina R. G., Botneva T. A. et al. Stable Isotopes in Petroleum Geochemistry. - Moscow, 1974 (in Russian).
24. Gurko N. N., Stepina L. F., Ankudinova V. P. About some regularities in the hydrocarbon composition of Baltic oils // New Data on Geology and Bearing Oil Capacity of Baltic. Leningrad, 1975. P. 80—103 (in Russian).
25. Klesment I. On the genesis of the Baltic oil shales // Oil Shale. 1985. V. 2. No. 1. P. 12—22 (in Russian with English summary).
26. Kħalimov E. M., Akishev I. M., Zhabreva P. S. et al. Native Bitumen Deposits. Moscow, 1983 (in Russian).
27. Nissenbaum A., Aizenshtat Z., Goldberg M. The floating asphalt blocks of the Dead Sea // Advances in Organic Geochemistry. Oxford, 1979. P. 157—161.

Presented by L. Mõlder
Received April 27, 1993

Estonian Academy of Sciences,
Institute of Chemistry
Tallinn, Estonia