Oil Shale, 2002, Vol. 19, No. 1
pp. 3-18

ISSN 0208-189X

https://doi.org/10.3176/oil.2002.1.01

CURRENT VIEWS ON THE ORIGIN OF ESTONIAN KUKERSITE KEROGEN

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A brief overview of current views on formation, characterization and classification of kerogens is given. On this background the results of geochemical investigations on G. prisca-derived kerogens, in particular Estonian kukersite kerogen obtained during last two decades are analysed, and changes in views about the origin of kukersite kerogen are underlined.

Biogeochemical studies driven by the environmental and petrochemical needs and carried out increasingly at the molecular level [1, 2] afforded during the last two decades a number of results on the origin of kerogens including Estonian kukersite kerogen (further 'kukersite' if not specified in other way). Experimental work and generalizations made have added new aspects to the previous views and opened new avenues of research. The aim of this article is to present on the background of general progress in the field the results on the origin of kukersite published in specialised journals in a short form to the readers of OIL SHALE. Naturally it reflects the author's attitude on this matter as well.

General Features of Kerogen Formation, Characterization and Classification

Kerogens are defined as insoluble sedimentary organic matter of any kind, in recent or ancient sediments, in dispersed or concentrated form [3]. This definition includes coals and during last decades the development towards convergence between the methods and philosophies of disciplines dealing with sedimentary organic matter, observed already in early eighties, has been progressively accelerated.

Kerogens are formed *via* transformations of biogenic organic matter throughout geological times. Two main pathways leading to kerogens are identified:

1) The classical degradation–recondensation pathway introduced nearly twenty years ago and including mainly biological degradation of original biomacromolecules into a mixture of monomers and random recombination of the latter into geomacromolecules followed by their insolubilization (Fig. 1). So formed material has no structural relation to floral or faunal remains and is termed as amorphous (in chemistry this term usually means non-crystallinic). The oil obtained upon pyrolysis of such kerogen has no relationship to the starting material of the kerogen. However, amorphous kerogen can contain a minor part of low-molecular lipid compounds so-called molecular fossils or biomarkers carrying information on the starting material and its transformation conditions [4, p. 74–92].

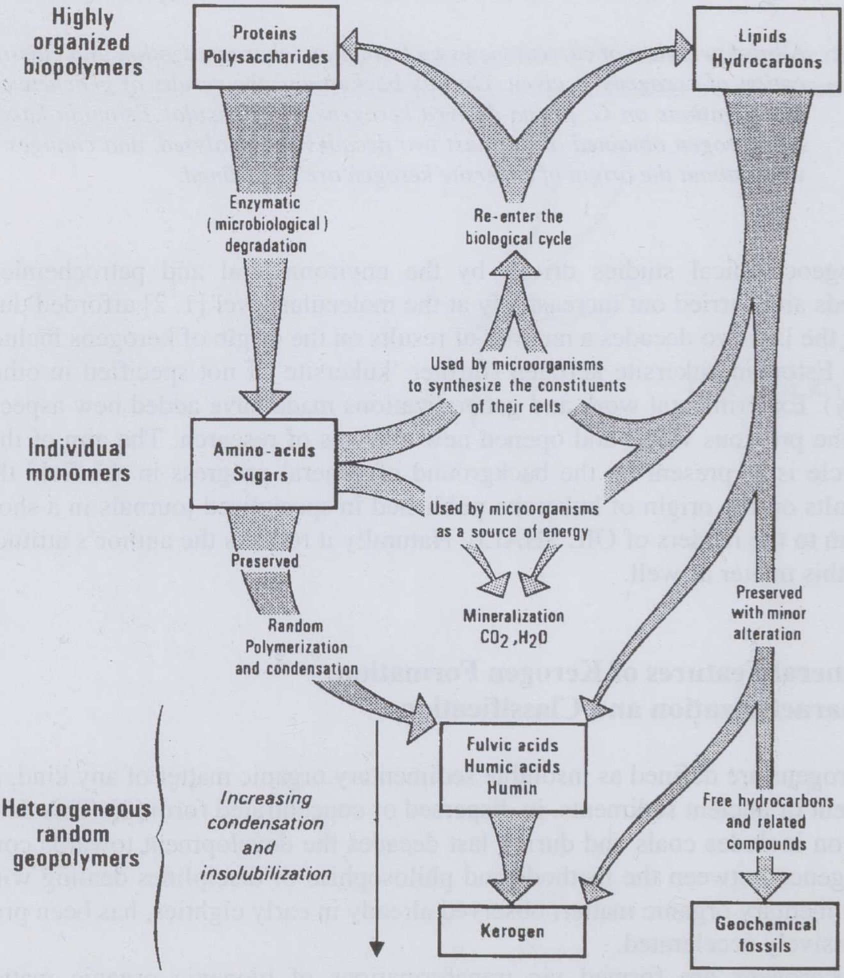

Fig. 1. Classical degradation-recondensation pathway model of kerogen [4]

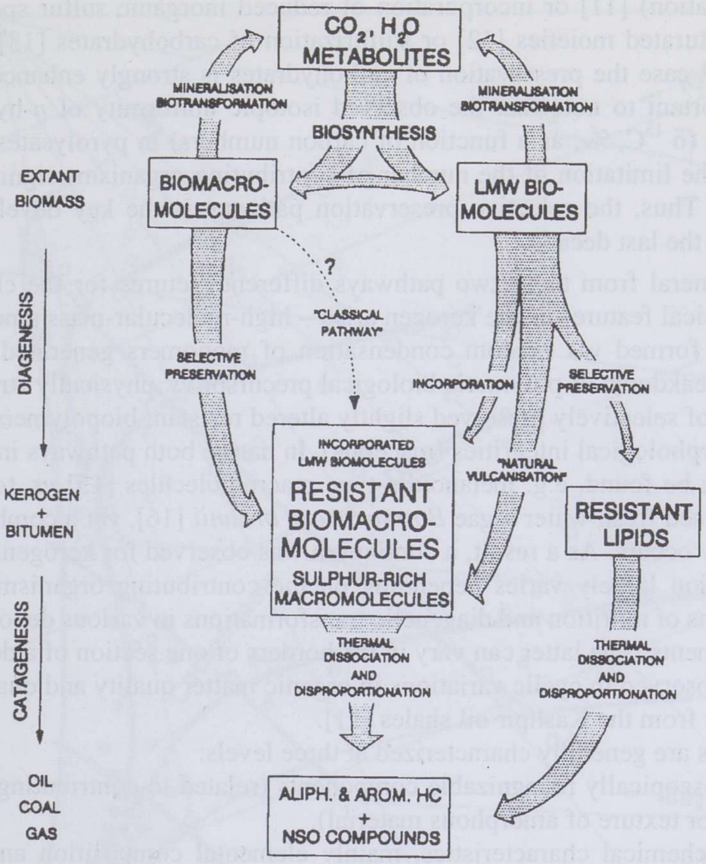

Fig. 2. Selective preservation pathway model of kerogen [5]

2) The selective preservation pathway implies relationships between the structure of the resistant biopolymers present in the contributing organisms and their fossil counterparts in the kerogen (Fig. 2) [5, 6]. The selective preservation concept has been long a common tool in the coal chemistry; experimental data obtained recently allow for the use of this concept to the kerogens as well. All known biopolymers range from extensively degradable under any depositional conditions to non-degradable ones [7]. Among the biopolymers identified so far the highest "preservation potential" is found for algaenans from algal cell walls, (see [8] as well) and cutans, suberans and lignins from vascular plants; the lowest one are carbohydrate-based polymers, proteins, nucleic acids. The preservation potential of organic compounds can be enhanced by adsorption of labile compounds onto minerals [9] or by encapsulation within an aliphatic organic matrix [10]. In specific depositional environments incorporation of low-molecular mass compounds into geomacromolecules may take place, e.g. cross-linking by oxygen (oxidative re-

ticulation) [11] or incorporation of reduced inorganic sulfur species in unsaturated moieties [12] or sulfurization of carbohydrates [13]. In the latter case the preservation of carbohydrates is strongly enhanced. It is important to note that the observed isotopic uniformity of *n*-hydrocarbons ($\delta\ ^{13}C$, ‰, as a function of carbon numbers) in pyrolysates allows for the limitation of the number of contributing organisms significantly [14] Thus, the selective preservation pathway is the key development over the last decade.

In general from these two pathways different pictures for the chemical and physical features of the kerogen arise – high-molecular-mass amorphous material formed *via* random condensation of monomers generated by the initial breakdown of polymeric biological precursor *vs.* physically structured mixture of selectively preserved slightly altered resistant biopolymers exhibiting morphological integrities (macerals). In nature both pathways in "pure" form can be found, e.g. melanoidin-type macromolecules [15] *vs.* torbanite as fossilised fresh-water algae *Botryococcus braunii* [16], yet a combination generally occurs. As a result, a continuum was observed for kerogens which constitution largely varies depending on the contributing organisms, their conditions of nutrition and diagenetic transformations in various depositional environments. The latter can vary in the borders of one section of a deposite, as it is observed in cyclic variations in organic matter quality and quantity in kerogens from the Kashpir oil shales [11].

Kerogens are generally characterized at three levels:

1) microscopically recognizable components (related to contributing organisms or texture of amorphous material),
2) bulk chemical characteristics, mainly elemental composition and other related data, e.g. Rock-Eval analysis, which give basis for the optical and chemical classification schemes respectively
3) molecular characteristics including relative importance of different structural elements and their connections [17].

Morphological approach to kerogen classification *via* light microscopy generally distinguishes between structured and unstructured kerogens [18]. The first ones comprise recognizable relics of microorganisms, plants and animals, the latters do not. Mostly three main maceral groups are defined in structured kerogens: hydrogen-rich – liptinite, preserved woody tissue – vitrinite, and hydrogen-poor oxidized – inertinite [19].

The kerogens are then represented on the corresponding triangular plots. Most kerogens have amorphous appearance (sometimes called sapropelic kerogens) and optical classification of these kerogens is still a problem (there are *ca* 20 optical classification schemes which are not treated here). Here we note that the meaning of the term 'sapropel' varies with the context: mainly it designates amorphous kerogen (degradation–recondensation pathway), which biological origin often cannot be established [17], sometimes potentially oil-generating kerogen comprising typical algal macerals and formed *via* selective preservation pathway [20].

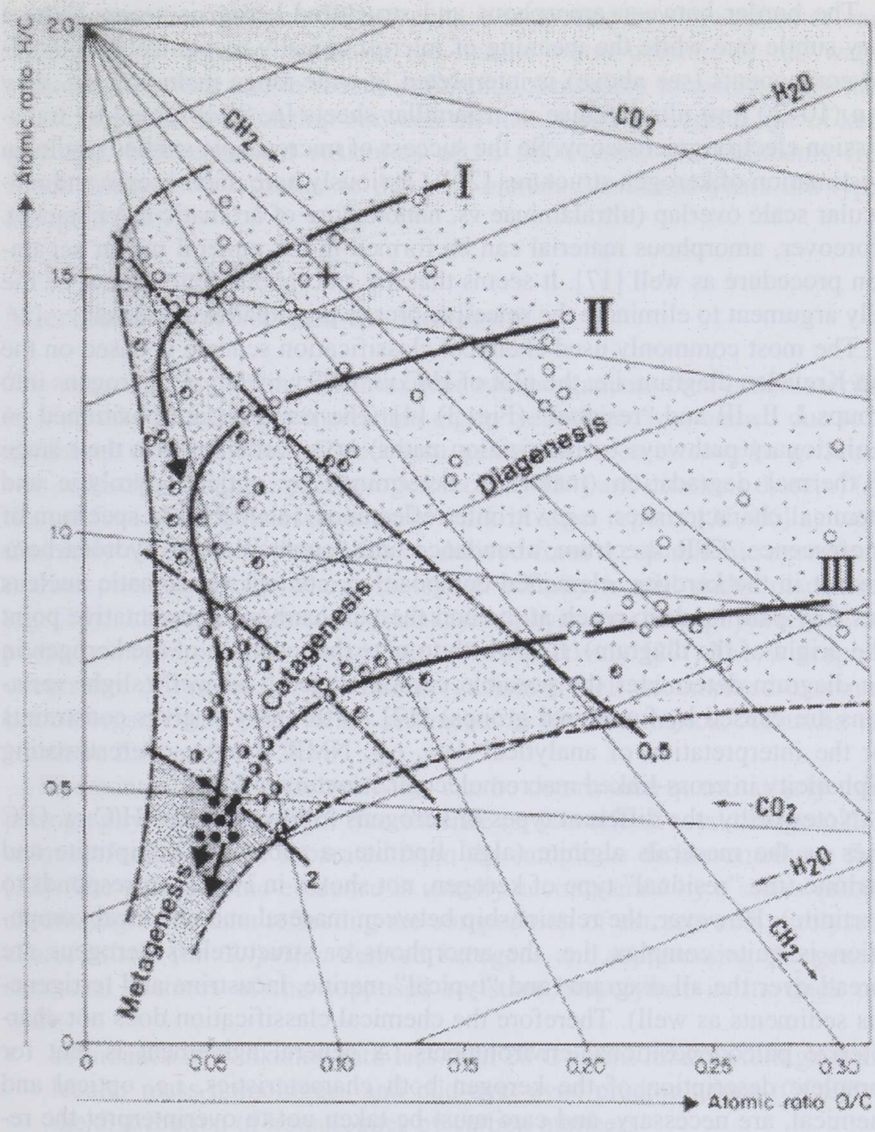

Fig. 3. Kerogen types (I, II, III) and evolution pathways from diagenesis to metagenesis (black arrows) in the van Krevelen diagram (modified from [4]). Vitrinite reflectants from zero (o) to four (●) and its iso-value lines are shown. The superimposed diagonal lines show the effects on the elemental composition of "formal" elimination of water, carbon dioxide or alkanes from the initial kerogen). Interrupted lines show the boundaries of the field of kerogen. + designates the location of kukersite

The border between amorphous and structured kerogens seems to be a very subtle one while the meaning of microscopically recognizable biological components (see above) is interpreted in wide range including e.g. very thin (10–20 nm) ultralaminae or trilamillar sheets [6, 8] observed by transmission electron microscopy. So the success of microscopic studies results in reestimation of kerogen structures [21]. Obviously here microscopic and molecular scale overlap (ultralaminae *vs.* nanotexture of aromatic layer stacks). Moreover, amorphous material can be formed in the mineral matter separation procedure as well [17]. It seems that the amorphous state cannot be the only argument to eliminate the selective preservation pathway model.

The most commonly used chemical classification scheme is based on the van Krevelen diagram, i.e. the plot of H/C *vs.* O/C which types kerogens into groups I, II, III and "residual" (Fig. 3) [4]. The kerogens are positioned on evolutionary pathways (carbonization paths) in accordance with their stage of thermal degradation (maturity), determined by optical, pyrolytic and chemical characteristics, e.g. vitrinite reflectance, intensity and spectrum of fluorescence, EPR spectrum, abundance and composition of hydrocarbons present in the kerogen, elemental composition, content of aromatic nucleus etc. Any path tends to reach at the end the pure carbon representative point (the origin of the diagram). It is worth to note that position of the kerogen in the diagram determines the possible carbon skeleton as well (slight variations are caused by functional groups) [17]. In this way it gives constraints for the interpretation of analytical data, e.g. NMR spectra, overestimating aliphaticity in cross-linked macromolecular structures [22].

Noteworthy, the different types of kerogens follow the same H/C *vs.* O/C lines as the macerals alginite (algal liptinite, a submaceral), liptinite and vitrinite (the "residual" type of kerogen, not shown in Fig. 3, corresponds to inertinite). However, the relationship between maceral and chemical composition is quite complex, i.e. the amorphous or structureless kerogens are spread over the all diagram (and "typical" marine, lacustrine and terrigeneous sediments as well). Therefore the chemical classification does not characterize paleodepositional environments. A general agreement is that for complete description of the kerogen both characteristics, i.e. optical and chemical, are necessary, and care must be taken not to overinterpret the results from either technique alone [17]. Since mixed-type kerogens are often encountered, the typing of kerogens is a complicated task [19].

The characterization of kerogens at a molecular level, hindered by its recalcitrant nature, involves the combined use of bulk spectral, isotopic, electron microscopic and thermal/chemical degradation methods, especially pyrolytic-GC-MS and selective oxidative/reductive cleavage [2, 23]. The modern degradative methods afford more detailed molecular information on structural elements and bonds in kerogens. The obtained characteristics, evaluated from the viewpoint of biogeochemical information, are represented as molecular models (this is the topic of another article).

We note that research on kerogens is supported by the studies of early diagenesis of organic matter in the marine water column, at the water–sediment interface and in recent sediments. According to recent study there is not any strict relationship between the nature and geological age of kerogen (e.g. bulk chemical structures of *ca* 5000 years old sediments from Black Sea are very similar to those of immature millions years old type I kerogen) [20].

Microfossil *G. prisca* and the Kukersite

The microfossil, remains of an extinct microorganism, first time described by Zalessky in kukersite more than eighty years ago, was named due to its similarity to the modern Gloeocapsa genus, *Gloeocapsamorpha prisca*. It was redescribed in the same kerogen recently [24] and citations therein] (see the confirmation of Zalessky's early work in short reports [25, 26] as well). Currently *G. prisca* is thought to be derived from a colonial nitrogen-fixing marine photoautotroph whose biological affinity is still under discussion, e.g. [12]; it has been related to extant cyanophytes or chlorophyta (e.g. *Entophysalis major* or *Botrycoccus braunii,* respectively [27]).The widespread occurrence of remains of this microorganism is well documented in a number of organic-rich Ordovician sediments in North America, Australia and Northern Europe [28–32].

The content of *G. prisca* remains can be determined quantitatively using petrography under blue light fluorescence (± 10 vol% of total kerogen) [30], or microfossils can be separated from the sample as dichloromethane float [32]. The petrographic evidence is usually accompanied by a series of bulk chromatographic data reflecting the composition of extracts and pyrolysates characteristic for *G. prisca*-derived kerogens and representing the general structural features of the supposed resistant biopolymer in its thick cell walls:

- abundance of *n*-alkanes with less than 20 C atoms relative to higher molecular mass homologues and odd-over-even predominance (OOEP) in the distribution of homologues by carbon numbers
- substantial levels of alkylcyclohexanes, 2-methylalkylcyclohexanes and 2-methylalkylbenzenes
- low content of branched alkanes

Electron microscopic studies reveal difference in the organization of *G. prisca* colonies of the Baltic and North American kerogen samples, defined as "closed-wall phenol-rich" and "open-wall phenol-poor" types, respectively [28].

The first morphotype is characteristic for kukersite. This morphotype forms upon flash pyrolysis a phenol-rich pyrolysate including as most specific components homologues series of 5-alkyl-, 5-alkenyl-1,3-benzenediols and alkylhydroxybenzofurans [33]. Other series of *n*-alkanes (OOEP >1), *n*-alk-1-enes, alkyl- and methylalkylcyclohexanes, -benzenes and -thiophenes, and *n*-alkylmethylketones with characteristic distributions are observed as well (see earlier identification of 5-alkyl-1,3-benzenediols consisting up to 17 carbon atoms in the side chain showing OOEP in range of C11-C17 and reviewed recently in [34], and other compounds in retort oil [35, 36]).

In addition to series of mid-chain alkylketones [37], series of 3- and 4-alkylketones were recently found in the supercritical fluid extracts of kukersite [38]. Ketones with random position of the carbonyl group, characteristic for abiotic oxidation [39], are not found. However, the value of the pristane/phytane ratio (1.1) corresponds to oxidative conditions [40] and cross-linking *via* incorporation of oxygen into double bonds which positions are determined biologically cannot be ruled out.

In the pyrolysate of the second morphotype (North American kerogens) 5-*n*-alkyl-1,3-benzenediols are present in much lower relative abundance [28], and the Guttenberg Member samples have higher thermal maturity as determined by hopanoid epimerization in comparison to that of kukersite [32].

The comparison of micro-FT-IR spectra corresponding to *G. prisca* colonies and interstitial organo-mineral matrix shows higher contribution of hydroxyl groups/aromatic carbons and lower content of mineral matter (chiefly carbonates) in the former, therefore alkyl- and alkenylbenzenediols are likely formed from *G. prisca* colonies rather from some constituents of the matrix [41]. Interestingly, phenolic ether lipids consisting of alkenyl-1,3-benzenediols are typical structural units of the algaenan from the fresh-water green microalgae *Botryococcus braunii*, race A [42] while main components of race B are long-chain α-unsaturated aldehydes [43]. Laboratory tests with control cultures of *B. braunii* show the positive effect of water salinity on the content of phenols and the habitat of the closed-wall morphotype is supposed to be high-salinity water. Hence oxygen in the specific phenols of kukersite – 1,3-benzenediols – is derived from the starting material but not from oxidation during diagenesis as assumed in [44, 45] or formed *via* pyrolytic cleavage of carbohydrates as proposed in [46]. It can be noted that the biogenic origin of oxygen in the kukersitic benzenediols was assumed already in [47, 48].

Results of the stepwise chemical degradation of kukersite with alkaline potassium permanganate afforded information on aliphatic moieties [49] and similar elemental composition of oxidation residues was interpreted as showing the chemical homogeneity of kerogen [50, p. 117–146].

Ruthenium-ion-catalyzed oxidation (RICO) of dichloromethane float prepared from kukersite samples and termed as "botryoidal aggregates of *G. prisca*" (yield of float not shown) resulted in the formation of a characteristic set of mono-, di- and tricarboxylic acids interpreted as derived from alkylbenzenediol building blocks of kukersite [32]. No evidence was found in the latter study for the presence of a linear polyaldehyde characteristic for *B. braunii*. The given explanation is temptating since it overcomes the confusing discrepancy between the high aliphaticity of the kukersite as revealed by oxidative cleavage and its cyclic nature determined by its elemental composition. The relatively narrow signal previously observed at 30 ppm in the solid state ^{13}C NMR spectrum [33] corresponds to low abundance of alicyclic bridgehead carbons which is consistent with the dominance in the oxidation products of α,ω-dicarboxylic acids over the tricarboxylic ones.

The structure proposed in [32] for *G. prisca* microfossils in kukersite, i. e. *n*-alkylbenzenediol-based polymer formed possibly by a free-radical oxygen- or enzyme-catalyzed mechanism during senescence or diagenesis of the organism, can be true if the abundance of aromatic carbons is still *ca* twofold underestimated. This is an unreal assumption contradicting with the results of carbon-type analysis carried out recently. Furthermore, NMR studies of alkaline $KMnO_4$ oxidation residue did not reveal the increasing abundance of stable in this conditions aryl-aliphatic ether bonds suggesting the presence of covalently free phenolic hydroxyl groups in kukersite [51 and citations therein]. May be the above polymer formed mainly *via* cross-links in side chains is diluted with other non-aromatic compounds from the microfossil-free amorphous part of kerogen. Such explanation is consistent with the data on the presence of two morphotypes of kerogen [31].

However, the main point of the interpretation of the RICO results is not the putative structure of this polymer but its possible secondary nature stated as follows: "... it still remains unclear if the poly(*n*-alkyl resorcinol) is a biopolymer or a structure that is formed from free *n*-alkylresorcinols after the organism died. The inner morphology of the Kukersite *G. prisca* microfossils clearly shows the voids of the original cells embedded in concentrically layers of organic matter" [32]. In this place it is proper to cite a statement made 70 years ago by Kogerman [52, p. 129–131], the father of Estonian oil shale chemistry: "... the greater part of the molecules of kerogen of kukersite are built up either of concentric layers or of long spiral chains".

During *ca* six decades after Zalessky's early finding in 1917 there was little progress in the geochemical studies of kukersite and his views on the role of *G. prisca* are met by most kukersite researchers with severe criticism. Indeed, there was a general agreement concerning the marine origin of kukersite, the latter was often related to amorphous kerogens and to contribution of all marine organisms living at that time, in its genesis. *G. prisca* was estimated only as a diagnostic minority [53, p. 137–147] or globular particles in the kerogen are even thought to be of synthetic [52, p. 64–65] or physical (gelation, droplet and air bubble formation) origin [44, 46, 54, 55], i.e. they represent secondary structures disappearing upon liquefaction in benzene at 290 °C [56].

Noteworthy, that the assumption made in the most recent study [32] discussed above: "It is also possible that *G. prisca* microfossils are composed of a cell wall or sheath component that polymerised during senescence or diagenesis of the organism" supports the idea on the synthetic origin of globular particles in the kerogen. In this way the bridge between the new paradigm of selective preservation of remnant biochemical compounds and secondary structures in the kerogen can be formed.

The bulk isotopic composition of the total organic matter of kukersite, its extractable organic fraction, pyrolysate and alkanes in it fall in a rather narrow range ($\delta\,^{13}C$ values minus 31–32 ‰), benzenediols are slightly lighter (minus 35.1 ‰) [40]. These observations point to the homogeneity of kukersite with respect to source input though the reason of lighter isotopic composition of benzenediols is not clear.

G. prisca is typically associated with high total organic matter content in the sediments and the latter exerts control on sedimentary conditions creating local anoxia in case of abundant deposition [30]. This is in accordance with the view of productivity-induced changes in oxygenation conditions [11]. Sulfate reduction inextricably intertwined with organic matter decomposition [57] and enhanced by local anoxia results in the formation of reduced sulfur species. Iron ions (pyrite formation) and reactive components of organic matter (see above) compete for these sulfur nucleophiles. In accordance with this, one can observe a rough correlation between the pyrite and organic matter contents in the kukersite seams (Kukruse stage) [58 and citations therein] and the occurrence of series of cyclic sulfur compounds in the flash pyrolysates of kukersite and *G. prisca*-derived Guttenberg kerogen (Wisconsin, USA). The presence of sulfur compounds in the latter is interpreted as the result of incorporation of reduced sulfur species into unsaturated moieties of the hypothetical precursor for the fossil biopolymer of *G. prisca*, similar to the algaenans of *Botryococcus braunii*, race A [12].

The possible presence of carbohydrates in kukersite has been described [59]. However, keeping in mind the mentioned above "light" isotopic composition of kukersite, the abundance of carbohydrates ($\delta\,^{13}C$ value minus 18 ‰ [13] in kukersite should be rather low.

With respect to bulk chemical characteristics as high hydrogen content, alicyclic nature of the carbon skeleton and low aromaticity [60, 61] kukersite represents type I/II kerogen (Fig. 3). Conspicuously most kukersite samples analyzed in recent researches for their elemental composition have increased oxygen content (*ca* 13–14 %) in comparison to its typical value 10.2–10.8 % in all main seams [62]. Possibly this reflects inadequate analytic techniques of oxygen determination or in some cases the efforts to obtain better-preserved *G. prisca* colonies [31]. Anomalous H/C and O/C values are presented in excellent monograph [4, p. 263] as well.

Well-preserved microfossils in kukersite serve as basis for its petrographic classification as *G. prisca*-derived kerogen [63]. Characteristic units of this microfossil-rich part of kerogen are long alkyl chains connected preferably at 5th position of 1,3-dioxygenated benzene nucleus. These units seem to form a polymer *via* cross-links preferably in alkyl chains. These cross-links comprise apparently aliphatic C–C and C–O bonds. Such polymer is capable of forming the main characteristic compounds observed in the thermal and oxidative cleavage products of kukersite including slight OODP of *n*-alkanes in the pyrolysate. There are only a few data on the composition and abundance of microfossil-poor part of kerogen and the relationship between primary and secondary structures is not clear.

From the viewpoint of secondary structure formation one can consider the appearance of macromolecular droplets from biopolymers over geological times by a mechanism parallel to that of the coalescence mechanism resulting in lignin droplets in steamed wood. Such possibility is supported by the excellent morphological research of the fate of biological macromolecules on three different microscopic levels [64]. From this viewpoint is of interest the occurrence of anisotropic domains on the carbonization path of kerogens, though kukersite modelled as purified cell wall of fossil alga *B. braunii* remained isotropic [65].

At the end it is necessary to remember a good remark: "Making correct and definitive connections between biogenic organics and their fossil products in the sediments is never easy or complete" [66]. In this connection we remind that kerogens from other geological periods form upon pyrolysis 5-alkyl-1,3-benzenediols as well e.g. Pripyat deposite (Devon) in Belarus [45], as a rule the quantification of *G. prisca* abundance in the studied samples of kukersite is not made and often in organic-rich formations cyclic variations in organic matter quality and quantity are observed [11]. As follows from the chemical classification scheme of kerogens, the close elemental composition of all main kukersite seams does not necessarily reflect the similar morphological integrities.

Future researches including the petrographic quantification of microfossils in various seams and full characterization of distinct morphostructural varieties etc. should afford new insight in the origin and particularly in the structure of kukersite. In tackling this complicated task more international teamwork is clearly needed [1]. From the viewpoint of organic chemist the problem is really a very complicated one since the starting material, reaction conditions and reaction product are all not fully understood.

Conclusion

In the light of kerogen formation pathways formulated during the last two decades one can conclude that kukersite is a *G. prisca*-derived "phenol-rich" kerogen formed *via* selective preservation pathway. This pathway is supplemented with oxidative cross-linking to form insoluble three-dimensional network. Sulfurization of unsaturated bonds and carbohydrates could play a minor role as well. Besides the structured component kukersite comprises amorphous part though chemically it behaves mainly as homogeneous matter. The abundance of *G. prisca* remains has not been determined quantitatively and the impact of amorphous part of kerogen into overall kerogen structure is not clear. The nature of mentioned cross-links is not determined as well. Further research using quantitative petrographic and chemical structural methods is needed to afford new information on the origin and structure of this kerogen.

Acknowledgements

The author is grateful to Estonian Science Foundation for financial support (Grant No. 4182) and to Dr. O. Parve for the possibility of co-operation with target financed theme 0350315s98.

REFERENCES

1. *Hedges, J.I., Eglinton, G., Hatcher, P.G., Kirchman, D.L., Arnosti, C., Derenne, S., Evershed, R.P., Kögel-Knabner, I., de Leeuw, J.W., Littke, R., Michaelis, W., Rullkötter, J.* The molecularly-uncharacterized component of nonliving organic matter in natural environments // Org. Geochem. 2000. Vol. 31. P. 945–958.
2. *Rullkötter, J., Michaelis, W.* The structure of kerogen and related materials. A review of recent progress and future trends // Org. Geochem. 1990. Vol. 16. P. 829–852.
3. *Durand, B.* Sedimentary organic matter and kerogen. Definition and quantitative importance of kerogen // Kerogen. Insoluble Organic Matter from Sedimentary Rocks / B. Durand (ed.). Editions Technip., Paris, 1980. P. 13–34.
4. *Tissot, B.P., Welte, D.H.* Petroleum Formation and Occurrence. – Springer-Verlag, Berlin–Heidelberg–New York–Tokyo, 1984.
5. *Tegelaar, E.W., de Leeuw, J.W., Derenne, S., Largeau, C.* A reappraisal of kerogen formation // Geochim. Cosmochim. Acta. 1989. Vol. 53. P. 3103–3106.
6. *Derenne, S., Largeau, C., Casadevall, E., Berkaloff, C., Rousseau, B.* Chemical evidence of kerogen formation in source rocks and oil shales *via* selective preservation of thin resistent outer walls of microalgae: Origin of ultralaminae // Geochim. Cosmochim. Acta. 1991. Vol. 55. P. 1041–1051.
7. *De Leeuw, J. W., Largeau, C.* A review of macromolecular organic compounds that comprise living organisms and their role in kerogen, coal and petroleum formation // Organic Geochemistry. Principles and Applications / M.H. Engel and S. H. Macko (eds.). Plenum Press, New York–London, 1993. P. 23–72.
8. *Gelin, F., Volkman, J.K., Largeau, C., Derenne, S., Sinninghe Damste, J.S., de Leeuw, J.W.* Distribution of aliphatic, nonhydrolyzable biopolymers in marine microalgae // Org. Geochem. 1999. Vol. 30. P. 147–159.
9. *Salmon, V.S., Derenne, S., Lallier-Verges, E., Largeau, C., Beaudoin, B.* Protection of organic matter by mineral matrix in a Cenomanian black shale // Org. Geochem. 2000. Vol. 31. P. 463–474.
10. *Mongenot, Th., Riboulleaua, A., Garcette-Lepecq, A., Derennea, S., Poueta, Y., Baudinb, F., Largeau, C.* Occurrence of proteinaceous moieties in S- and O-rich Late Tithonian kerogen (Kashpir oil shales, Russia) // Org. Geochem. 2001. Vol. 32. P. 199–203.

11. *Riboulleau, A., Derenne, S., Largeau, C., Baudin, F.* Origin of contrasting features and preservation pathways in kerogens from the Kasphir oil shales (Upper Jurassic, Russian platform) // Org. Geochem. 2001. P. 647–665.
12. *Douglas, A.G., Sinninghe Damste, J.S., Fowler, M.G., Eglinton, T.I., de Leeuw, J.W.* Unique distribution of hydrocarbons and sulphur compounds released by flash pyrolysis from the fossilised alga *Gloeocapsomorpha prisca*, a major constituent in one of four Ordovician kerogenes // Geochim. Cosmochim. Acta. 1991. Vol. 55. P. 275–291.
13. *Sinninghe Damste, J.S., Kok, M.D., Köster, J., Schouten, S.* Sulfurized carbohydrates: an important sedimentary sink for organic carbon? // Earth and Planetary Science Letters. 1998. Vol. 164. P. 7–13.
14. *Eglinton, T.I.* Carbon isotope evidence for the origin of macromolecular aliphatic structures in kerogen // Org. Geochem. 1994. Vol. 21. P. 721–735.
15. *Zegouagh, Y., Derenne, S., Largeau, C., Bertrand, P., Sicre, M.A., Saliot, A., Rousseau, B.* Refractory organic matter in sediments from the North-West African upwelling system: abundance, chemical structure and origin // Org. Geochem. 1999. Vol. 30. P. 101–117.
16. *Largeau, C., Derenne, S., Casadevall, E., Kadouri, A., Sellier, N.* Pyrolysis of immature torbanite and of the biopolymer (PRB A) isolated from extant alga *Botryococcus braunii*. Mechanism of formation and structure of torbanite // Org. Geochem. 1986. Vol. 10. P. 1023–1032.
17. *Whelan, J.K., Thompson-Rizer, C.L.* Chemical methods for assessing kerogen and protokerogen types and maturity // Organic Geochemistry. Principles and Applications. P. 289–353.
18. *Senftle, J. T., Landis, C. R., McLaughlin, R. L.* Organic petrographic approach to kerogen characterization // Ibid. P. 355–374.
19. *Cornford, C., Gardner, P., Burgess, C.* Geochemical truth in large data sets. 1: Geochemical screening data // Org. Geochem. 1998. Vol. 29. P. 519–530.
20. *Brown, S.D., Chiavary, B., Ediger, V., Fabbri, D., Gaines, A.F., Galletti, G., Karayigit, A.J., Love, G.D., Snape, C., Sirkecioglu, O., Toprak, S.* Black Sea sapropels: relationship to kerogens and fossil fuel precursors // Fuel. 2000. Vol. 79. P. 1725–1742.
21. *Largeau, C., Derenne, S., Casadevall, E., Berkaloff, C., Corelleur, M., Lugardon, B., Raynaud, J. F., Connan, J.* Occurrence and origin of “ultralaminalar” structures in “amorphous” kerogens of various source rocks and oil shales // Org. Geochem. 1991. Vol. 16. P. 889–895.
22. *Poirier, N., Derenne, S., Rouzaud, J.N., Largeau, C., Mariotti, A., Balesdent, J., Maquet, J.* Chemical structure and sources of the macromolecular, resistant organic fraction isolated from a forest soil (Lacadee, South-West France) // Org. Geochem. 2000. Vol. 31. P. 813–827.
23. *Larter, S.R., Horsfield, B.* Determination of structural components of kerogens by the use of analytical pyrolysis methods // Organic Geochemistry. Principles and Applications. P. 271–288.
24. *Foster, C.B., Reed, J.D., Wicander, R. Gloeocapsamorpha prisca* Zalessky, 1917: A new study. Part 1: taxonomy, geochemistry and paleoecology // Geobios. 1989. Vol. 22. P. 735–759.

25. *Baukov, C., Paap, J.* On the maternal substance of kukersitic kerogen // Vsesoyusnoe Soveshchanie "Geokhimiya Goryuchikh Slantsev" (Proc. of All-Union Conf. "Geochemistry of Oil Shales"). Tallinn, 1978. P. 16–18 [in Russian].
26. *Stefanova, E.I., Lebedeva, H.P., Fadeeva, N.P.* The use of scanning electron microscopy in the search for organic microcomponents in oil shales // Ibid. P. 88–89 [in Russian].
27. *Stasiuk, L.D., Kybett, B.D., Bend, S.L.* Reflected light microscopy and micro-FT-IR of upper Ordovician *Cloeocapsomorpha prisca* alginite in relation to paleoenvironment and petroleum generation, Saskatchewan, Canada // Org. Geochem. 1993. Vol. 20. P. 707–719.
28. *Derenne, S., Metzger, P., Largeau, C., van Bergen, P. F., Gatellier, J.P., Sinninghe Damste, J.S., de Leeuw, J. W., Berkaloff, C.* Similar morphological and chemical variations of *Gloeocapsomorpha prisca* in Ordovician sediments and cultured *Botryococcus braunii* as a response to changes in salinity // Org. Geochem. 1992. Vol. 19. P. 299–313.
29. *Reed, J.D., Illich, H.H., Horsfield, B.* Biochemical evolutionary significance of Ordovician oils and their sources // Org. Geochem. 1986. Vol. 10. P. 347–358.
30. *Pancost, R.D., Freeman, K.H., Patzkowsky, M.E., Wavrek, D.A., Collister, J.W.* Molecular indicators of redox and marine photoautotroph composition in the late Middle Ordovician of Iowa, USA // Org. Geochem. 1998. Vol. 29. P. 1649–1662.
31. *Kõrts, A., Veski, R.* Scanning electron microscopy of *Gloeocapsomorpha* as produced from kerogen oxidation // Oil Shale. 1994. Vol. 11, No. 4. P. 293–303.
32. *Blokker, P., van Bergen, P., Pancost, R.D., Collinson, M.E., de Leeuw, J.W., Sinninghe Damste, J.S.* The chemical structure of *Gloecapsomorpha prisca* microfossils: Implications for their origin // Geochim. Cosmochim. Acta. 2001. Vol. 65. P. 885–900.
33. *Derenne, S., Largeau, C., Casadevall, E., Sinninghe Damste, J.S., Tegelaar, E.W., de Leeuw, J.W.* Characterization of Estonian kukersite by spectroscopy and pyrolysis: Evidence for abundant alkyl phenolic moieties in an Ordovician, marine type II/I kerogen // Org. Geochem. 1990. Vol. 16. P. 873–888.
34. *Lille, Ü.* On the origin of 5-alkyl-1,3-benzenediols in the retort oil of Estonian kukersite // Oil Shale. 1999. Vol. 16, No. 3. P. 301–307.
35. *Raudsepp, H.* Oil shale phenols // Goryuchie slantsy. Khimiya i tekhnologiya (Oil Shales. Chemistry and Tecnology) / Academy of Sciences of the Estonian SSR. Tallinn, 1956. P. 107–113 [in Russian].
36. *Eisen, O.* Methods for the Analysis of Solid Fuels and Chemical Composition of the Estonian Shale Oil (doctor thesis) / Academy of Sciences of the Estonian SSR. – Tallinn, 1967 [in Russian].
37. *Klesment, I.* Application of chromatographic methods in biogeochemical investigations. Determination of the structures of sapropelites by thermal decomposition // J. Chromatogr. 1974. Vol. 91. P. 705–713.
38. *Luik, H.* Investigation of Supercritical Carbon Dioxide Extracts from Kukersite and Dictyonema Argillite : Final Report of ESF Grant Project Nr. 3784, Institute of Chemistry at Tallinn Technical University. Tallinn, 2001 [in Estonian].

39. *Jenish-Anton, A., Adam, P., Schaeffer, P., Albrecht, P.* Oxygen-containing subunits in sulfur-rich nonpolar macromolecules // Geochim. Cosmochim. Acta. 1999. Vol. 63. P. 1059–1074.
40. *Bondar, E.B., Taal, H.A., Bityukov, M.M.* Solid bitumen inclusions in kukersite oil shale. Structure and genesis // Oil Shale. 1993. Vol. 10, No. 2/3. P. 111–122.
41. *Derenne, S., Largeau, C., Landais, P., Rochdi, A.* Spectroscopic features of *Gloeocapsomorpha prisca* colonies and of interstitial matrix in kukersite as revealed by transmission micro-FT-i.r. : location of phenolic moieties // Fuel. 1994. Vol. 73. P. 626–628.
42. *Metzger, P.* Phenolic ether lipids with an alkenylresorcinol moiety from a Bolivian strain of *Botryococcus braunii* (A race) // Phytochemistry. 1994. P. 195–212.
43. *Metzger, P., Largeau, C., Casadevall, E.* Lipids and macromolecular lipids of the hydrocarbon-rich microalga *Botryococcus braunii*. Chemical structure and biosynthesis. Geochemical and biotechnological importance // Progress in the Chemistry of Organic Natural Products. 1991. Vol. 57. P. 1–70.
44. *Raudsepp, H.T.* On the genesis of Estonian oil shale-kukersite // Genesis tverdyh goryuchih iskopaemyh (Origin of Fossil Fuels). / H. M. Karavaev and N. G. Titov (eds.). Academy of Sciences of USSR, Moscow, 1959. P. 69–76 [in Russian].
45. *Klesment, I., Bondar, E.* Biochemical aspects of evolution of sapropelites according to data of molecular palaeontology // Oil Shale. 1997. Vol. 14, No. 1. P. 19–40.
46. *Fomina, A.S.* On the genesis of Baltic kukersite oil shales // Genesis tverdykh goryuchih iskopaemyh (Origin of Fossil Fuels). P. 77–91 [in Russian].
47. *Lille, Ü.E.* On the genesis of phenols in thermal degradation of kukersite kerogen // Khimia Tverdogo Topliva (Chemistry of Fossil Fuels). 1969. No. 4. P. 107–110 [in Russian].
48. *Lille, Ü.E., Bitter, L.A., Kundel, H.A.* On the structural similarity of shale oil alkylresorcinols and natural alkylresorcinols // Khimia Tverdogo Topliva (Chemistry of Fossil Fuels). 1972. No. 6. P. 137–138 [in Russian].
49. *Bajc, S., Ambles, A., Largeau, C., Derenne, S., Vitorovic, D.* Precursor biostructures in kerogen matrix revealed by oxidative degradation : oxidation of kerogen from Estonian kukersite // Organic Geochemistry. 2001. Vol. 32. P. 773–784.
50. *Fomina, A.S., Pobul, L.J., Degtereva, Z.A.* The Chemical Nature of Baltic Kukersite Oil Shale and Its Properties as a Chemical Raw Material / Academy of Sciences of the Estonian SSR. – Tallinn, 1965 [in Russian].
51. *Lille, Ü.* Molecular Model of Estonian Kukersite Kerogen : Final Report of ESF Grant No. 4182, Institute of Chemistry at Tallinn Technical University. Tallinn, 2002.
52. *Kogerman, P.N.* On the Chemistry of the Estonian Oil Shale "Kukersite". – Tartu, 1931.
53. *Dobryanskij, A.F.* Oil Shales of USSR. – Leningrad–Moskva, 1947 [in Russian].
54. *Aarna, A.J.* On the genesis of Estonian oil shales // Genezis tverdykh goryuchikh iskopaemykh (Origin of Fossil Fuels). P. 57–68 [in Russian].

55. *Klesment, I.R.* On the genesis of Baltic oil shales // Oil Shale. 1985. Vol. 2, No. 1. P. 12–22 [in Russian, summary in English].
56. *Nappa, L., Klesment, I., Vink, N.* The influence of different factors on the low temperature liquefaction process of the organic matter of kukersite oil shale // Proc. Estonian Acad. Sci. Chem. 1986. Vol. 35, No. 2. P. 83–91 [in Russian, summary in English].
57. *Berner, R.A.* Sulphate reduction, organic matter decomposition and pyrite formation // Phil. Trans. R. Soc. Lond. 1985. Vol. A 315. P. 25–38.
58. *Bauert, H., Kattai, V.* Kukersite oil shale // Geology and Mineral Resources of Estonia / A. Raukas and A. Teedumäe (eds.). Estonian Academy Publishers, Tallinn, 1997. P. 313–326.
59. *Fomina, A., Nappa, L.* On the role of carbohydrate component in the genesis of phenols in the semicoking of solid fuels // Oil Shale. 1984. Vol. 1, No. 2. P. 189–197 [in Russian, summary in English].
60. *Aarna, A.J., Lippmaa, E.T.* On the structure of the Baltic oil shale kerogen // Transact. of Tallinn Polytechn. Inst. Vol. A, No. 63. Tallinn, 1955. P. 3–50 [in Russian].
61. *Maremäe, E.* Investigation of the Structure and Composition of Natural Macromolecular Substances Using Solid Phase High-Resolution Power Nuclear Magnetic Resonance : Final Report of ESF Grant Project Nr 2914, National Institute of Chemical and Biological Physics. Tallinn, 2000 [in Estonian].
62. *Torpan, B.K.* Elemental composition of kukersite // Transact. of Tallinn Polytechn. Inst. 1954. Vol. A-57. P. 22–26 [in Russian].
63. *Hutton, A.C.* Organic petrography of oil shales // Composition, Geochemistry and Conversion of Oil Shales / C. Snape (ed.). Kluver Academic Publishers, Dordrecht–Boston–London, 1995. P. 17–33.
64. *Kallavus, U., Gravitis, J.* Comparative investigation of the ultrastructure of steam exploded wood with light, scanning and transmission microscopy // Holzforschung. 1995. Vol. 49. P. 182–188.
65. *Bonnamy, S.* Carbonization of various precursors. Effect of heating rate. Part 1: Optical microscopy studies // Carbon. 1999. Vol. 37. P. 1691–1705.
66. *Summons, R.E.* Biogeochemical cycles. A review of fundamental aspects of organic matter formation, preservation, and composition // Organic Geochemistry. Principles and Applications. P. 3–21.

Presented by J. Kann
Received November 9, 2001