Oil Shale, 2003, Vol. 20, No. 3
pp. 253-263
ISSN 0208-189X

https://doi.org/10.3176/oil.2003.3.03

CURRENT KNOWLEDGE ON THE ORIGIN AND STRUCTURE OF ESTONIAN KUKERSITE KEROGEN*

Ü. LILLE**

Institute of Basic and Applied Chemistry
at Tallinn Technical University
15 Akadeemia St., Tallinn 12618, Estonia

A brief overview of the assumed microbial source material of Estonian kukersite kerogen and of the redox conditions in Ordovician epicontinental sea is given. The results of the investigations on the structure and pathways of the phenol formation in the retorting process are analyzed. The distribution of carbon types and oxygen functions are presented. It is concluded that further research into three-dimensional structure, glass-liquid transition and oxygen functions of this aliphatic but oxygen-rich kerogen is needed.

If we cannot determine the truth
then we should follow the most probable.

R. Descartes, 1637

More than three decades have passed since the UN Symposium on the development and utilization of oil shale research in Tallinn in 1968. During this time considerable changes in our understanding of the kerogens have taken place. They are caused by the convergence of the research, integration of research methods and extensive generalization of the experimental data. In this short report, it is not possible to discuss these developments. Therefore let as concentrate on the problems of origin and structure of Estonian kukersite kerogen, a topics open to debate during last decades, and on the ways the time as the best judge has made decisions on them.

Origin of Kerogen

Origin of Estonian Kukersite Kerogen [1]

In 1917 botanist (*sic!*) M. Zalessky [2], studying microscopically oil shale from Kukruse stage, introduced the term 'kukersite'. He described the oval bodies in kerogen, interpreted them as the remains of an extinct microorgan-

* Presented at Symposium on Oil Shale in Tallinn, Estonia, November 17–21, 2002.
** e-mail: *lille@chemnet.ee*

ism, and named this supposed organism *Gloeocapsamorpha prisca* due to morphological similarity with extant cyanobacterium *Gloeocapsa quaternata Kützing* occurring on moist rocks. About forty years later it was shown that these oval bodies are in fact cavities consisting of carbon dioxide, hydrogen and methane and interpreted as gas bubbles without any biological meaning [3, 4]. However, further microscopic research confirmed Zalessky's observations [5–8], and now there exists a general agreement between kerogen researchers that a line of Ordovician kerogens is derived from *G. prisca*.

The corresponding oil shales are termed as kukersites [9]. Along with the microscopic investigation including electron microscopy exceeding 10^4-fold magnification, the flash-pyrolytic (characteristic hydrocarbon pattern) and spectral data contribute to this agreement. The remains of *Gloeocapsamorpha prisca* consist of bright yellow, spherical to ovoid globules 20–500 μm in diameter [6]. These globules consist of a uniform or concentrically layered wall surrounding a number of ovoid cavities. These cavities, located in distinct order, are believed to represent the non-fossilizing cells of a colonial microorganism.

Different types of colonies give rise to several morphotypes identified in various kukersites, in our context most relevant are "closed-wall phenol-rich" and "open-wall phenol-poor" morphotypes from Estonian and North American (Wisconsin shales), respectively [6]. Their thick resistant organic walls (sheaths) are presumably the main source of kerogen. It consists of phenolic compounds (absorbance at 3050, 3200–3500 cm^{-1} in the IR spectra, 5-alkyl- and 5-alkenyl-benzene-1,3-diols in flash pyrolysates) [10, 11], which may have played a role analogues to that of the modern UV-blocking cyanobacterial pigment scytonemine. A recent study of microfossil-rich part of Estonian and Guttenberg kukersite kerogens using microscopic, spectral, pyrolytic and oxidative methods resulted in a reconstruction of *n*-alkylresorcinol-based polymer composing the *G. prisca* microfossils for these two kukersites (Fig. 1 [8]).

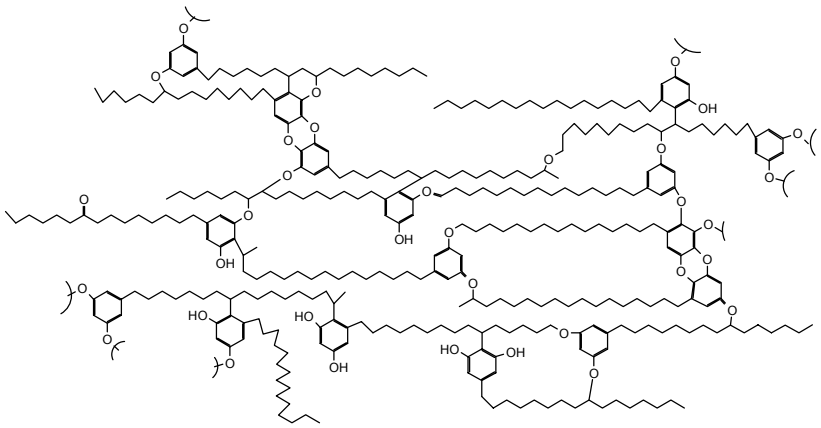

Fig. 1. Simplified reconstruction of the proposed *n*-alkyl-1,3-benzenediol-based polymer composing the *G. prisca* microfossils from Estonian kukersite kerogen [8]

In rich fauna of kukersite beds described by several researchers ([7] and citation therein) the inorganic skeletal material predominates. Moreover, elemental mapping demonstrates the fundamental role of authigenic mineralization in the preservation and replication of faunal remains in the presence of clay minerals [12]. Thus, the contribution of faunal remains to the formation of kerogen seems to be rather low.

Mineral matter accompanying the kerogen comprises mainly the minerals of limestone and clay, e.g. calcite, dolomite marl with some minor admixtures, e.g. pyrite, gypsum [4, 13]. The source of carbonate-rich minerals is the debris of fauna and precipitation from the seawater. These both sources of calcium carbonate are augmented through intensive photosynthesis, i.e. light-enhanced calcification and the shift of the carbonate solubility equilibrium in the seawater respectively [14]. However, this relationship is not so straightforward, in fact, the continental discharge controlled the carbonate accumulation in the littoral zone [15].

Redox Conditions and Microbial Mats in Ordovician Epicontinental Sea

Early Paleozoic including Ordovician phytoplankton activity was governed by organic-walled plankton, i.e. cyanobacteria [16] and sulfur bacteria [17] inhabiting in oxic and anoxic (euxinic) photic zones, respectively.

As shown in a recent detailed study of a single continuous core from the late Middle Ordovician [18], sediments deposited in oxic period are characterized by high pristane/phytane ratio, low homohopane index and low gammacerane ratio and abundant presence of *G. prisca* remains. (One must keep in mind the possibility of local anoxia discussed in [1, 18].) Sediments, in which contrary values of redox indicators are observed and whose organic matter consists of arylisoprenoids derived from sulfur bacteria, have been deposited in anoxic period. During the latter siliciclastic lithology (including argillites) dominated over carbonaceous ones. Fundamental changes in the dominant phototrophic sources of organic matter are probably related to the changes in ocean circulation and temperature regime.

Kerogen of Estonian black shale (alum shale) formed probably at such anoxic period. This euxinic more aromatic kerogen, enriched *ca* six-fold with nitrogen in comparison to the kukersite kerogen, is deposited in the same area and yields upon pyrolysis products which do not show the characteristic features of these of *G. prisca*-derived kerogens, and is believed to be formed by cyanobacteria [19]. This argillaceous metal-rich amorphous kerogen contains the remains of graptolite *Dictyonema* pointing to the largely dysoxic conditions.

We speculate here that the dominant role in its formation could have been played by green sulfur bacteria using in the process of photosynthesis hydrogen sulfide as electron donor. The elevated nitrogen content can be the result of intensive nitrogen fixation suppressed by the increasing atmospheric oxy-

gen concentration [20] or better protection *via* adsorption on siliciclastic minerals [21] (the analysis of this topic is beyond the borders of this report).

Multilayered microbial communities (microbial mats) along with tropical rain forests and coral reefs are among the most productive ecosystems in the world [11, 22]. Very intense carbon turnover (high production/biomass ratio) in microbial communities is an important difference between these ecosystems. It is noteworthy that cyanobacteria have played the major role in bringing about the increase in free oxygen in the Earth's atmosphere from far less than 1 % to about 20 %, and massive deposits of kerogen (e.g. Green River Formation [21] and petroleum [20]) are believed to be formed by masses of decayed cyanobacteria.

Thus, kukersites (and possibly Estonian alum shale as well) are believed to be formed mainly by a massive accumulation of a single type of organisms, analogously to the formation of boghead, torbanite and tasmanites. The three latter originate from microalgae [16, 23]. The occurrence of these kerogens has strongly contributed to the formulation of selective preservation pathway of kerogen formation. However, until *G. prisca* is not biologically firmly defined it is not possible to link the chemistry of Estonian kukersite kerogen to some certain extant organism.

Biological Identification of *G. prisca*

Currently *G. prisca* is thought to be derived from a marine photoautotroph. The modern mat-forming cyanobacterium *Entophysalis* [21] (kingdom *Monera*) appears to be the morphologically nearest living organism to *G. prisca*. Its outermost thick sheaths have the highest preservation potential, especially following chelation by trace elements (the actual cell membrane as opposed to the sheats and its contents are completely degraded soon after the death). There is a complete continuum in morphology from the larger benthic mat colonies to the smaller planktonic ones [11].

Cyanobacteria, formerly and misleadingly called 'blue-green algae' are photosynthetic bacteria (in which chlorophyll a occurs along with characteristic pigments known as phycobilins), ancestors of red and green algae [20]. At present, the classification of cyanobacteria is not unequivocal, this phylum is classified according to phenotypic characteristics rather than the 16S rDNA phylogeny as such a scheme is not yet possible [24].

Some researchers suggest *G. prisca* to be freshwater/brackish green microalgae related to *Botryococcus braunii* [6, 25] (Phylum *Chlorophyta*, kingdom *Protista*) and the polymorphism of *G. prisca* and abundance of 5-alkyl-1,3-benzenediols could be the result of various salinity levels [6]. Noteworthy, green algae is unable to fix atmospheric nitrogen, many cyanobacteria among them *Gloeocapsa* have this possibility [5], corresponding ability of *G. prisca* is unknown.

Chemical Structure of Kerogen

Carbon Skeleton and Functional Groups

For generalization of numerous data on this matter, we used the method of modeling designing the two-dimensional chemical structure of kerogen (Fig. 2 [26]). The obtained structure was checked by simulation of its ^{13}C CP MAS NMR spectrum. We note that quantification of the NMR spectra of low-aromaticity kerogens is reliable under certain conditions of the experiment [27].

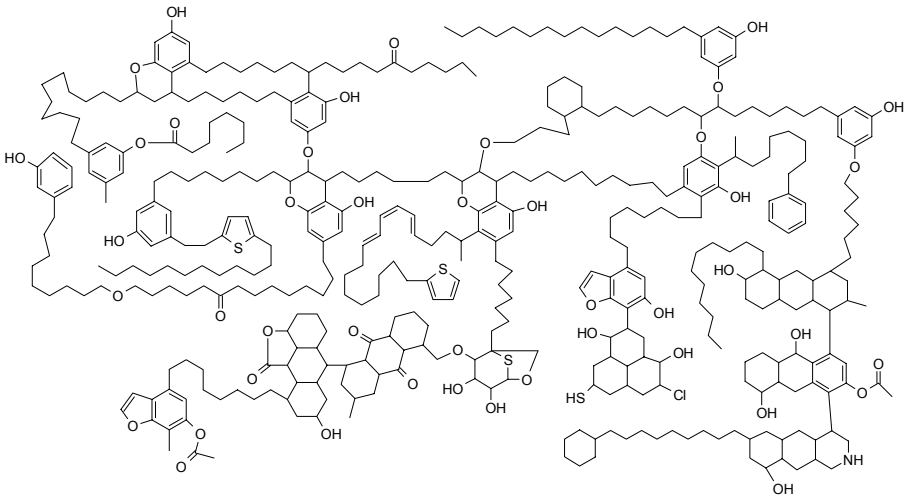

Fig. 2. Two-dimensional model of Estonian kukersite kerogen with the molecular mass 6581 D and empirical formula $C_{421}H_{638}O_{44}S_4NCl$ [26]

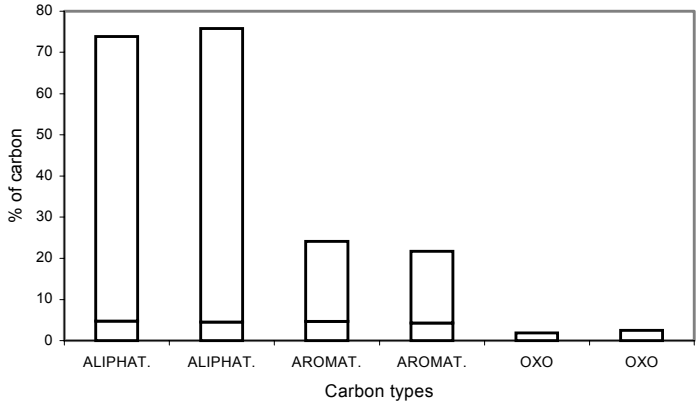

Fig. 3. Distribution of carbon types in the kerogen model (left columns), and in the intact kerogen (right columns). Carbons attached to oxygen are shown shaded horizontally. Carbonyl carbon includes carboxylic as well

The comparison of carbon types in the model and intact kerogen is shown in Fig. 3. We can observe the consistency of both data demonstrating the well-known low aromaticity of Estonian kukersite kerogen.

The distribution of aromatic carbon types again shows the adequacy of the model (Fig. 4). On the contrary, the structure proposed for *G. prisca* microfossils in [8] (right columns) consists of *ca* twice quantity of oxygenated carbons compared to these of the intact kerogen and no protonated carbons in the *meta* position to oxygenated carbons. The question arises, whether the proposed structure does not represent the real structure or the microfossils do not represent the whole kerogen (the yield of the used dichloromethane float is not shown by the authors of this serious research article).

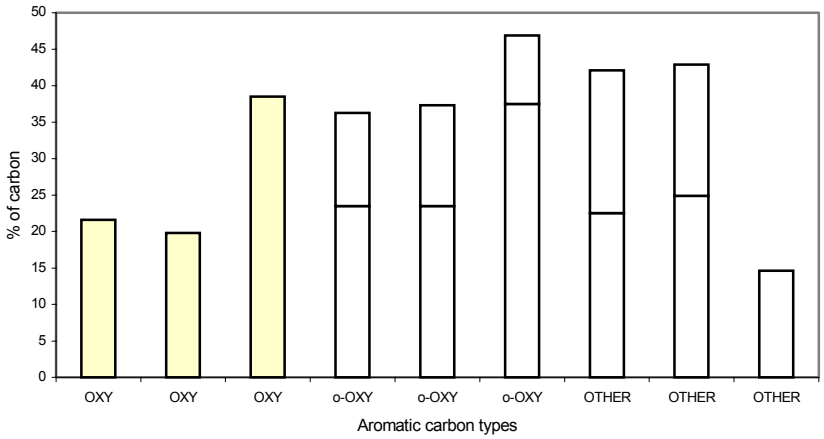

Fig. 4. Distribution of aromatic carbon types in the kerogen model (left columns), in the intact kerogen (middle columns) and in the proposed structure of the resistant polymer from *G. prisca* microfossils [8] (right columns). Protonated and branched carbons are shaded horizontally and vertically, respectively

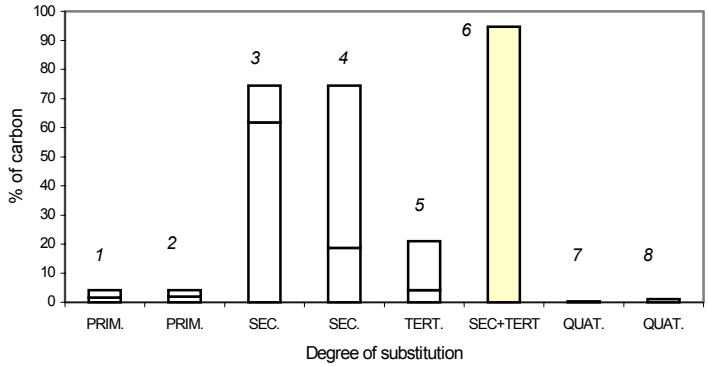

Fig. 5. Distribution of CH_n carbons in the kerogen model (columns *1*, *3*, *5*, *7*), and its comparison with the results of NMR [30] (columns *2*, *6*, *8*) and chemical determinations/statistical calculations [28] (column *4*). Carbons in the cycles and chains are shaded horizontally and vertically, respectively, blank – this ratio is not determined

Let us turn to the largest group of carbons, the aliphatic ones (Fig. 5). Unfortunately, methylene and methine groups, and especially the formers in the chains and cycles, cannot be distinguished by the NMR spectra. In accordance with the designed model, up to 80 % of the methylene groups are located in chains with the average length about 7.5 methylene groups. Based on statistical calculations, strong dominance of methylene groups in cycles was suggested [28]. Our model studies taking into account especially the high straight to branched chain ratio in oxidation products of kerogen showed that a different interpretation of the elemental composition of kerogen is possible as well. This result shows the less extent of cross-linking in the kerogen structure, a fact consistent with the low maturity of this kerogen.

The determination of the methylene group distribution between chains and cycles in amorphous solids is a complicated problem and needs further research, especially the dipolar-dephasing behavior of the kerogen in the ^{13}C NMR MAS experiment. By our experience it cannot be reduced only to the determination of the ratio of "mobile"/"rigid" carbons based on comparison of "protonated" and "non-protonated" spectra as follows from [29].

The distribution of oxygen functionalities is shown in Fig. 6. Based on the stability of model *sec*.-dialkylethers of 1,3-benzenediols in the conditions of alkaline $KMnO_4$ oxidation [30] the suggested dominating role of such structural unit in the structure of Estonian kukersite kerogen [31] is unrealistic but aliphatic ether bonds are probably involved in the cross-linking. This new knowledge is reflected in the model consisting of free phenolic hydroxyl groups and dialkyl ether bonds. The presence or absence of aryl-alkyl monoethers needs further research.

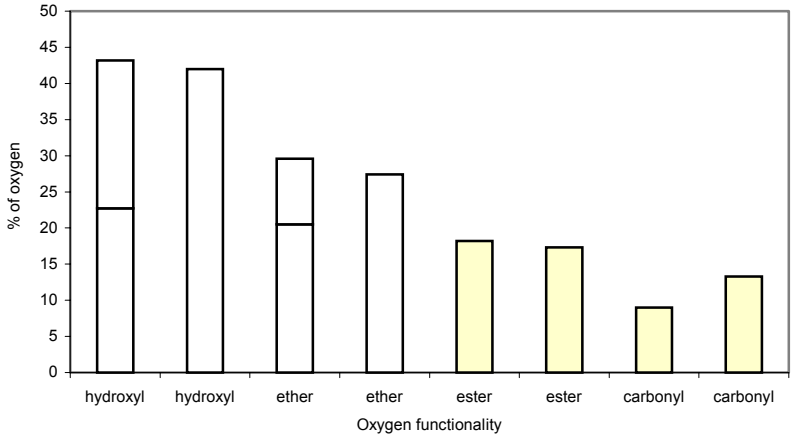

Fig. 6. Distribution of oxygen in the kerogen model (left columns) and its comparison with the results of chemical determinations (right columns) [28, 33]. Hydroxyl and alkoxy groups attached to aliphatic and aromatic carbons are shaded horizontally and vertically, respectively

As for the chemical determinations of functional groups in the kerogen there is a growing evidence on limitations of these methods caused by the three-dimensional structure of the kerogen [30, 32]. The latter is so far badly understood.

Formation of Phenols Present in Retort Oil

We return now to Fig. 3 and turn attention to the carbon attached to oxygen shown in the lower part of the columns. Simple calculation shows that the quantity of oxygen bound to aromatic carbon (*ca* 4.5 % from the total carbon) is high enough to form pyrolytic oil abundant of phenols (with average molecular mass e.g. *ca* 200) and other oxygen compounds. Nearly the same quantity of oxygen is bound to the aliphatic carbon. From this oxygen only a minor part is located in alcoholic hydroxyl groups, and it will be consumed totally by the formation of pyrolytic water (3–5 % from the kerogen). Therefore, the transformation of this oxygen into phenolic hydroxyl groups in the process of kerogen pyrolysis as supposed in [33] is unrealistic.

The pathways of phenol formation upon pyrolysis of the kerogen and an abundance of aromatic carbons in its structure, intensively discussed in fifties and sixties [4, 34] are nowadays relatively clear, the phenols originate from the phenolic structures already present in the kerogen, they are released and modified *via* further transformations in the process of pyrolysis (see [35] as well). These processes and especially the glass-liquid transition of the kerogen need further research. Notably, trace amounts of 5-alkyl-1,3-benzenediols can be detected in the oxidative degradation products of the kerogen at the temperature as low as 75 °C [30].

Conclusions

1. Microscopic and geochemical data evidence that Estonian kukersite kerogen is formed along with other kukersites from a single extinct photosynthetic microorganism which seems to be related morphologically to cyanobacteria but chemically to green algae.
2. This kerogen represents a highly aliphatic macromolecule. According to NMR data, the ratio of aliphatic and aromatic carbons is *ca* 4-5, tentative ramification of known data on the distribution of aliphatic carbon shows the predominance of secondary carbon in the alkyl chains.
3. Heteroatomic functional groups are represented mostly by oxygen-containing ones, more than two third of these groups are hydroxyl and alkoxy groups. These groups are attached to aromatic and aliphatic carbons, quantitative estimation of these structural elements is only tentative.
4. For further interpretation of available data on the structure of kerogen, the knowledge of its three-dimensional structure is necessary.

REFERENCES

1. *Lille, Ü.* Current views on the origin of Estonian kukersite kerogens // Oil Shale. 2002. Vol. 19, No. 1. P. 3–18.
2. *Zalessky, M.* On marine sapropelite of Silurian age formed by a blue green alga // Bulletin De L'Académie Des Sciences De Russie, VI Série. 1917. Vol. 11, No. 1. P. 3–18 [in Russian].
3. *Dilaktorskij, N.* Zur Frage von der Struktur des Kerogens // Proc. Estonian Acad. Sci., Chem. 1960. Vol. 9, No. 2. P. 130–133 [in Russian, abstract in German].
4. *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. – Tallinn : Estonian Acad. Sci., 1965 [in Russian, summary in English].
5. *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, No. 6. P. 735–759.
6. *Derenne, S., Metzger, P., Largeau, C. et al.* 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, No. 3. P. 299–313.
7. *Kõrts, A.* Ordovician oil shale of Estonia – origin and paleoecological characteristics // Global Perspectives on Ordovician Geology / B.D. Webby and J.R. Laurie (eds.). Rotterdam : Balkema, 1992. P. 445–454.
8. *Blokker, P., van Bergen, P., Pancost, R.D. et al.* The chemical structure of *Gloecapsomorpha prisca* microfossils: Implications for their origin // Geochim. Cosmochim. Acta. 2001. Vol. 65, No. 6. P. 885–900.
9. *Hutton, A.C.* Organic petrography of oil shales // Composition, Geochemistry and Conversion of Oil Shales / C. Snape (ed.). Dordrecht, Boston, London : Kluver Academic Publishers, 1995. P. 17–33.
10. *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, No. 5. P. 626–628.
11. *Stasiuk, L.D., Kybett, B.D., Bend, S.L.* Reflected light microscopy and micro-FTIR of upper Ordovician *Cloeocapsomorpha prisca* alginite in relation to paleoenvironment and petroleum generation, Saskatchewan, Canada // Org. Geochem. 1993. Vol. 20, No. 6. P. 707–719.
12. *Orr, P.J., Derek, E.G., Kearns, S.L.* Cambrian Burgess shale animals replicated in clay minerals // Science. 1998. Vol. 281, No. 21, August. P. 1173–1175.
13. *Bauert, H., Kattai, V.* Kukersite oil shale // Geology and Mineral Resources of Estonia / A. Raukas and A. Teedumäe (eds.). Tallinn : Estonian Academy Publishers, 1997.
14. *Osborne, P.L.* Tropical Ecosystems and Ecological Concepts. – Cambridge : University Press, 2000.
15. *Zhmur, S.I.* Origin of Ordovician oil shales in the Baltic syneclise, paper 2: kukersites // Lithology and Mineral Resources. 1990. Vol. 24, No. 2. P. 244–251.

16. *Tissot, B.P., Welte, D.H.* Petroleum Formation and Occurrence. – Berlin, Heidelberg, New York, Tokyo : Springer-Verlag, 1984.
17. *Douglas, A.G., Sinninghe Damste, J.S., Fowler, M.G. et al.* Unique distribution of hydrocarbons and sulphur compounds released by flash pyrolysis from the fossilized alga *Gloeocapsomorpha prisca*, a major constituent in one of four Ordovician kerogens // Geochim. Cosmochim. Acta. 1991. Vol. 55, No. 3. P. 275–291.
18. *Pancost, R.D., Freeman, K.H., Patzkowsky, M.E. et al.* Molecular indicators of redox and marine photoautotroph composition in the late Middle Ordovician of Iowa, USA // Org. Geochem. 1998. Vol. 29, No. 12. P. 1649–1662.
19. *Klesment, I., Urov, K.* Role of bacterial lipids in the formation of geolipids and kerogens // Proc. Estonian Acad. Sci., Chem. 1980. Vol. 29, No. 4. P. 241–245 [summary in Russian].
20. *Raven, P.H., Johnson, G.B.* Biology. – St.Louis, Baltimore, Boston, Chicago, London, Philadelphia, Sydney, Toronto : Mosby Year Book, 1992.
21. *Tyson, R.V.* Distribution of the palynomorph group: phytoplankton subgroup, cyanobacteria and *Rhodophyta* // Sedimentary Organic Matter / R.V. Tyson (ed.). London, Glasgow, Weinheim, New York, Tokyo, Melbourne, Madras : Chapman Hall, 1995.
22. *Guerrero, R., Mas, J.* Multilayered microbial communities in aquatic ecosystems: growth and loss factors // Microbial Mats: Physiological Ecology of Benthic Microbial Communities / Y. Cohen and E. Rosenberg (eds.), American Society for Microbiology. Washington, DC, 1989. P. 37–51.
23. *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, No. 1. P. 1–70.
24. Bergey's Manual of Systematic Bacteriology. – Springer, 2001.
25. *Guy-Ohlson, D. Botryococcus* as an aid in the interpretation of paleoenvironment and depositional processes // Review of Paleobotany and Palynology. 1992. Vol. 71, No. 1. P. 1–15.
26. *Lille, Ü., Heinmaa, I., Pehk, T.* Molecular model of Estonian kukersite kerogen as evaluated by ^{13}C MAS NMR spectroscopy // Fuel. 2002. Vol. 82, No. 7. P. 799–804.
27. *Miknis, F.P.* Solid-state ^{13}C NMR in oil shale research: an introduction with selected applications // Composition, Geochemistry and Conversion of Oil Shales. P. 69–91.
28. *Aarna, A.J., Lippmaa, E.T.* On the structure of the Baltic oil shale kerogen // Tallinna Polütehnilise Instituudi Toimetised (Transact. Tallinn Polytech. Inst.). A-63. Tallinn, 1955. P. 3–50 [in Russian].
29. *Trewhella, M.J., Poplett, I.J.F., Grint, A.* Structure of Green River oil shale kerogen. Determination using solid-state ^{13}C n.m.r. spectroscopy // Fuel. 1986. Vol. 65, No. 4. P. 541–546.
30. *Lille, Ü., Heinmaa, I., Pehk, T.* Investigation into kukersite structure using NMR and oxidative cleavage methods: On the nature of phenolic precursors in the kerogen of Estonian kukersite // Oil Shale. 2002. Vol. 19, No. 2. P. 101–116.

31. *Raudsepp, H. T.* On the origin of phenols in the oil shale retorting oil // Tallinna Polütehnilise Instituudi Toimetised (Transact. Tallinn Polytech. Inst.) A-73. Tallinn, 1956. P. 120–132 [in Russian].
32. *Cody, G.D., Saghi-Szabo, G.* Calculation of the ^{13}C NMR chemical shift of ether linkages in lignin-derived geopolymers: Constraints on the preservation of lignin primary structure with diagenesis // Geochim. Cosmochim. Acta. 1999. Vol. 63, No. 2. P. 193–205.
33. *Aarna, A.J., Urov, K.* Study of the structure of oil shale kerogens using dehydrogenation by sulfur. Report 2 // Tallinna Polütehnilise Instituudi Toimetised (Transact. Tallinn Polytech. Inst.) A-228. Tallinn, 1965. P. 27–40 [in Russian].
34. *Gubergritz, M. J.* (ed.). Thermal Conversion of Kukersitic Oil Shale. – Tallinn : Valgus, 1966 [in Russian].
35. *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.