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LATE-EPIGENETIC (HYPERGENETIC?) BITUMENS IN OIL SHALES

Worked out for oil-parent rocks (approaching the main oil-formation zone, oil-generating and oil-generated), the division of bitumens into types (syngenetic, epigenetic, as well as their derivatives - mixed, residual, para-autochthonous) and the distinctive features established for them enable us to estimate, also quantitatively [1], the contribution of individual varieties to total bitumen in sedimentite. The above-mentioned sediments are, as a rule, timed to depths where the effect of hypergenesis may be neglected.

Typical oil shales are not deep-deposited (usually at a depth of down to some hundreds of metres) and from the mesocatagenesis stage they will lose one of the main features - the ability of organic matter (OM) to produce a substantial amount of liquid organic products on thermal decomposition (owing to realization of this potential).

Systematic investigations on oil shales have revealed that the existing criteria allow attribution of the soluble part of OM of many oil shales to none of the bitumen types distinguished for oil-parent rocks. Thus, the yield of bitumen on the OM of Suzak oil shales of Uzbekistan [2] and Devonian shales of the Komi Republic [3] reaches 14 and 22 %, respectively. Proceeding from the law of Uspenskii and Vasoevich [4], this suggests that the soluble part of OM of the above shales should belong to epibitumens. However, by the heteroelements (8-23 %) and heteroatom compounds (50-90 %) contents they are considered to be syngenetic. The same applies to the Irati Permian shales of Brazil: the yield of bitumen on organic carbon is 17.4 %, the nonhydrocarbon compounds content of bitumen is 52.3 % [5].

Then, although in elemental and group chemical composition bitumens of most oil shales should be considered syngenetic, very often they so differ in individual chemical composition from the insoluble part of OM (IOM) that their genetic relationship is difficult to assume. For example, if, based on data of different investigations, in the kukersite OM aliphatic chains C_7-C_{17} prevail [6, 7], then in bitumen chains C_{19}-C_{25} do [8, 9]. The n-alkanes of bitumen of Estonian Vendian shale are characterized by the concentration maximum in the C_{25}-C_{27} range, with 'odd' homologues predominating [10]. The latter phenomenon gives evidence of a terrigenous origin of bioproduction [11] which, however, did not exist in the Vendian.

The kerogen of Central Asian Lower Eocene shale is, in general, homogeneous in composition, also petrographically, and is highly transformed, but bitumens of shales from different localities and even different beds of the same location considerably differ, leaving retained the specific features of the initial biological material: the carbon preference index (CPI) of n-alkanes, aliphatic ketones and saturated fatty acids is 1.3-1.6, ~1.2 and 1.7, respectively. It is not clear either how chemically unstable unsaturated aliphatic hydrocarbons may have remained in the bitumens of Ordovician kukersite [12] and dictyonema shale [9], as well as the black shales of Rumania [13], but in Precambrian formations, unsaturated steroids do [14]. It is difficult to explain the

presence of oleic and other unsaturated fatty acids in the bitumens not only of dictyonema shale [15], but also in highly-metamorphosed Riphean shales of East Siberia [10]. It is known that Precambrian deposits were formed in reducing medium [16], but in recent deposits unsaturated acids disappear already in the upper sediment layers [17, 18]. As to saturated fatty acids, then apart from the age and degree of catagenetic transformation of most shales, including Precambrian graphitoids, their bitumens are abundant in the C_{16} and C_{18} acids which are typical of lower organisms, but usually, fatty acids of bitumens are similar in composition to those found in recent sediments [17, 19]. It is also difficult to account for the presence of carbohydrates and carbohydrate structures in Lower Paleozoic shales [20-22] and Precambrian sediments [23, 24], whose low biochemical and thermal stability is well-known,as well as the presence of amino acids not only in Phanerozoic shales and shale-like rocks [25-26], but also in Precambrian shales [14, 24, 27-29].

Moreover, among the amino acids of thermally degraded Irkutsk Riphean shales, which have been subjected to thermal decomposition, one of the thermally most unstable acid, lysine, prevails [29], whereas the thermal instability of the former complicates even their analysis by thin-layer chromatography [30].

True, both hydrocarbonates and amino acids are usually identified in the hydrolysis products of organic matter of the rock: owing to the high activity the connection of the above compounds with the organic matter macromolecular matrix is natural, but it is not likely that their thermal stability may sufficiently increase as a result. And, finally, in addition to differences between bitumens and IOM in chemical composition, a distinct discrepancy is often observed between the compositions of the individual group components of bitumens, especially the degraded n-alkanes with CPI near 1, and the fatty acids present in unaltered biosynthetic production with the C_{16} and C_{18} acids prevailing (Tchagansk Jurassic shales [31], Ukhta [3] and Selennyakh Devonian shales, etc.). In the bitumen of highly-metamorphosed Precambrian shales from the Irkutsk Region, besides the n-alkanes and acids of the above types, also methyl n-alkyl ketones with CPI≤9 are present, approaching ketones of plant origin [32], but in the C_{14}-C_{20} range, isoprenoid alkanes make 50-80 % of the concentration of n-alkanes, although it has been established that with advancing catagenesis their content in bitumen rapidly diminishes [33]. The saturated aliphatic ketones of kukersite bitumen are characterized by two concentration maxima, viz.at C_{18}-C_{20} and C_{24}-C_{26}, n-alkanes, by one at C_{19}-C_{25}, with even-numbered ketones predominating [8].

It is therefore natural to assume that besides syn- and epibitumens, oil shales contain also soluble organic compounds of different origin.

In addition to the conventional mechanism, we shall now consider another two possible pathways of bitumens generation and transformation.

First, introduction of OM and the change in bitumen composition caused by ground waters filtrated through the deposit.

There are numerous data indicating a significant contribution of ground waters to the mineral formation in oil shales [34-38], but no systematic investigations have been carried out of their effect on oil shale organic matter. It is believed that catagenetic transformation of organic matter of some non-metamorphosed metal-bearing black shales was influenced by aqueous solutions at a temperature of up to 60 °C [37]. It has been established that in the karsts [39] and faults [40] formation regions the kukersite kerogen has considerably been transformed. The n-alkanes of kerogen bitumen have little in common with the aliphatic chains of IOM, but are very similar to those of near-lying sandstone of the Leetse horizon, Estonia, mine water and soil of the oil-shale basin during the nonvegetative period [9] that gives evidence of a hydrotransport origin of the paraffins of shale bitumen. A relationship between the compositions of soil n-alkanes

and the corresponding bitumen fraction of Estonian Vendian shale is observed [10]. In the extractable part of OM of the Leetse sandstone, as in both kukersite and dictyonema shale, unsaturated aliphatic hydrocarbons (HC) have been identified. It should be pointed out that by mining kukersite 8 m^3 mine water per 1 t of shale is pumped out [40]; of course, only a small portion of it may be filtered directly through the undisturbed oil-shale layer.

The rate of OM transformation increases in contact with thermal water: kerogen may be degraded directly to the oil [41], both HC and oxygen compounds are formed from dispersed OM [42]. It is also believed that the formation of shungite deposits is associated with redeposition of carbonaceous material from hydrothermal solutions [43]. Thus, introduction and transformation of OM by ground waters may contribute to the formation of bitumen of oil shales.

Another possible pathway of bitumen neogenesis may lie in microbial activity (bacteria, actinomycetes, lower fungi, etc.) on oil shales, including their bitumen.

Assimilation of oil HC with microbes has long been known [44]. This is observed in oil deposits at a depth below 1300 m (4, p. 451), whereas mainly paraffinic HC are subjected to biodegradation and oil is enriched with naphthenic HC and asphalt-like compounds [45-47]. The bituminous sands of Canada are believed to be the product of oil biotransformation [46]. Moreover, microorganisms have been shown to contribute to the extraction of bitumen from them [48]. In recent sediments, bacteria have been detected at a depth of 140 m [49], but the biochemical formation of methane is possible at 300-350 m, to say the least [50]. Microbes have also been found in coals which have been shown to serve as a nutritive medium for them [51]. Obviously similarly, microbes may assimilate oil shale bitumens, anyway, their alkane fraction.

In addition, there are some data evidencing that oil shale organic matter as a whole is subjected to microbial attack [52, 53]. It has been reported that in the kukersite sample collected in the sterile conditions the aerobe *Clostridium pasteurianum* has been detected, causing butyric fermentation and binding to the air nitrogen [54]; it has been shown that the kukersite kerogen is subjected to the action of sulphate-reducing bacteria [55]. In combination with the methane-producing microflora they also assimilate organic matter of many other shales [56]. The hypergenetic transformation of the Kasphir shale is accompanied by enrichment of its bitumen with the asphalthenic fraction [57], probably also in the presence of microorganisms. In bitumens of many shales, including Precambrian and Lower Cambrian shales [58], alkanes of thermally unstable iso-structure, which are typical of bacterial bioproduction, are abundant [59]. The *n*-alkanes present in bitumens of some shales are believed to be of bacterial origin [60].

Thus, it is beyond doubt that organic matter of shales is sensitive to microbial attack, but their bitumens bear signs of their recent activity. Most of oil shales are deposited near the earth's crust where the conditions for microbial activity are favourable, the upper temperature limit of their distribution being 60-70 °C [45] which almost corresponds to the beginning of realization of liquid and gaseous organic products-generating potential by oil shale kerogen.

Assuming the presence of varieties in oil shale bitumens originating from recent bioproduction, introduced into the deposit by filtrating waters or synthesized *in situ* by bacteria on the basis of sedimentite as substrate, several specific features of the composition of the extractable part of oil shale organic matter may be explained. Thus, an abnormally high bitumen content of organic matter of some shales (e.g. Central Asian Suzak shales) may be considered as being the result of its neogenesis; at the same time, the prevalence of heteroatom compounds in bitumens is natural, as is the nonconformity of its composition with that of IOM. In fatty acids as an immediate biosynthetic product chemical features of the starting biomaterial should be preserved

better than in *n*-alkanes that is really observed in bitumens of most shales. The presence of saturated dicarboxylic acids in bitumens of several shales [61-63] may be the result of biochemical oxidation of monocarboxylic fatty acids [64] and paraffins [4, p. 449] that is also observed in recent sediments [65, 66]. Natural is also enrichment of bitumens with isoprenoid alkanes at their relatively high degree of biotransformation (Estonian dictyonema [67] and other shales) as *n*-alkanes are assimilated by bacteria in the first place. In that case the presence of unsaturated HC, unsaturated fatty acids, amino acids, carbohydrates, steroids and other chemically and thermally unstable products of biosynthesis in bitumens of shales, even Precambrian graphitoids, may be considered to be normal.

And, finally, the secondary transformation of OM of the shale of the deposits already formed may be the cause of an entirely different composition of Estonian kukersite and dictyonema shale whose deposits overlap horizontally and their formation temporally (Ordovician). The problem has long been discussed. As a result of the break in sedimentation after the formation of the dictyonema shale layer, evidenced by erosion of the surface of these layers by water and the belonging of an overlying horizon to the products of new transgression [68], favourable conditions for the development of hypergenetic processes, including microbiological neogenesis of bitumen and transformation of IOM, might have been created. Judging by the relative concentration of minor elements in dictyonema shale and kukersite, total (aerobic and anaerobic) oxidation losses of OM [69] were more noticeable with the former; it is not precluded that they may have taken place not only at the sedimentogenesis stage, but also considerably later. Conservation of the kukersite OM, besides other factors, may have been favoured by an early cementation of its preferably carbonate mineral matter, obviously also in the presence of microbes [70, 71]; the primarily low penetrability of clays is changed more slowly (their porosity at a depth of 500 m makes about 50 % of initial [72]).

Proceeding from the foregoing it should be expedient to distinguish another two bitumen types of oil shales in addition to autochthonous syngenetic and allochthonous epigenetic (of oil type, preferentially hydrocarbon) types: the allochthonous-epigenetic type formed as a result of introduction of OM with subsurface and surface waters and relatively rich in high-polar heteroatom compounds owing to their higher water solubility, and the autochthonous-epigenetic type, the product of microbial activity on the basis of shale as substrate and possible chemical (oxidation, hydrolysis, reduction) transformation of OM by aqueous solutions.

The above bitumen types may be conditionally regarded as hypergenetic, having in mind hypergenesis in a wide sense, i.e. as transformation of rocks not only in the very upper part of the Earth's crust, but also in deeper horizons, more precisely, within the whole zone of minimum penetration of surface waters, sometimes down to some hundreds of metres [73]. At the same time it is believed that under favourable conditions hypergenesis may take place over the whole geological history of sediment after sedimentogenesis.

On the basis of the foregoing, the following genetic bitumens types of oil shales may be distinguished, in different combinations forming the really existing bitumens:

(1) syngenetic (primary autochthonous);
(2) allochthonous-epigenetic of oil migration type;
(3) water-introduced allochthonous-epigenetic not associated with the oil formation processes;
(4) autochthonous-epigenetic (microbial and chemogeneous).

The problems of microbial actions on oil shale OM and transfer of organic compounds by waters filtering through a deposit have not yet been thoroughly investigated; further study in this field is necessary.

REFERENCES

1. *Жузе Н. Г.* К оценке эпигенетичных примесей в битумоидах и балансовых потерь при вторичной миграции нефти. Л., 1982 (Рукопись деп. в ВИНИТИ, № 2474 - 82).

2. *Уров К. Э., Авазматов Х. Б., Листрем А. И.* Геохимические особенности нижнеэоценовых горючих сланцев Западного Узбекистана // Накопление и преобразование органического вещества современных и ископаемых осадков. М., 1978. С. 133-140.

3. *Уров К. Э., Листрем А. И.* Сравнительная характеристика органического вещества девонского и юрского горючих сланцев Ухтинского месторождения // Химия тв. топлива. 1977. № 2. С. 71-77.

4. *Неручев С. Г.* Нефтепроизводящие свиты и миграция нефти. - Л., 1962.

5. *Hunt J. M.* Petroleum geochemistry and geology. - San Francisco, 1979.

6. *Bondar E., Veski R.* Investigation of production of stepwise nitric acid oxidation of kukersite kerogen. 3. Aliphatic mono-and dicarboxylic acids [in Russian; with English summary] // Eesti NSV TA Toim. Keemia. 1981. V. 30, No. 3. P. 172-179.

7. *Уров К. Э.* Термическое разложение керогена в присутствии галогенидов аммония // Химия тв. топлива. 1978. № 1. С. 27-31.

8. *Pais R., Klesment I., Pobul L.* Hydrocarbons and oxygen compound in the bitumen of oil shale kukersite [in Russian; with English summary] // Eesti NSV TA Toim. Keemia. 1979. V. 28, No. 3. P. 182-189.

9. *Уров К. Э., Клесмент И. Р.* Углеводороды в осадочном покрове на территории Эстонского сланцевого месторождения // Исследования органического вещества современных и ископаемых осадков. М., 1976. С. 292-298.

10. *Urov K., Listrôm A., Jaanus A.* A comparative study on the organic matter of Precambrian shales of Estonia and Irkutsk Region [in Russian; with English summary] // Eesti NSV TA Toim. Keemia. 1979. V. 28, No. 2. P. 71-79.

11. *Mathews R. T., Igual X. P., Jackson K. S., Johns R. B.* Hydrocarbons and fatty acids in the Evergreen Shale, Surat Basin, Qweensland, Australia // Geochim. Cosmochim. Acta. 1972. V. 36, No. 8. P. 885-896.

12. *Urov K., Rändur A., Klesment I., Eisen O.* Aliphatic hydrocarbons in kukersite-shale and in the vicinity // Eesti NSV TA Toim. Keemia, Geol. 1976. V.25, No. 3. P. 179-186 (in Russian).

13. *Filipescu M. G., Botez C., Movillanu A., Nacu D., Cabe I.* Unele aspecte privind coloratia sisturilor negre de la Covasna // Bul. Instr. politehn. Iaşi. 1972. Sec. 2. V. 18, No. 3-4. P. 9-19.

14. *Сидоренко Св. А., Теняков В.А.* Геологические, геохимические и генетические аспекты интерпретации химической природы углеродистого вещества биолитогенных образований докембрия // III Всесоюз. совещ. «Геохимия горючих сланцев»: Тез. докл. Таллинн, 1982. С. 159-161.

15. *Bondar E., Veski R.* Unsaturated fatty acids in the extracts from Ordovician Dictyonema oil shale [in Russian; with English summary] // Eesti NSV TA Toim. Keemia. 1980. V. 29, No. 4. P. 251-255.

16. *Сердюченко Д. П., Созинов Н. А.* Роль углеродистого вещества в формировании седиментогенных месторождений докембрия // Литология и осадочная геология докембрия: X Всесоюз. литол. совещ. Тез. докл. М., 1973. С. 349-351.

17. *Matsuda H., Koyama T.* Early diagenesis of fatty acids in lacustrine sediment. I. Identification and distribution of fatty acids in recent sediment from a freshwater lake. // Geochim. Cosmochim. Acta. 1977. V. 41, No. 6. P. 777-783.

18. *Van Vleet E. S., Quinn J. G.* Early diagenesis of fatty acids and isoprenoid alcohols in estuarine and coastal sediments // Geochim. Cosmochim. Acta. 1979. V. 43, No. 3. P. 289-303.

19. *Simoneit B. R. T.* Diterpenoid compounds and other lipids in deep-sea sediments and their geochemical significance // Geochim. Cosmochim. Acta. 1977. V. 41, No. 4. P. 289-303.

20. *Виноградов А. П., Бойченко Е. А.* Пектины в древних породах // Рефераты научно-исследовательских работ за 1944 г. АН СССР. Отд. хим. н. С. 173.

21. *Nappa L., Fomina A.* Products of a hydrolysis of kukersite kerogen [in Russian; with English summary] // Eesti NSV TA Toim. Füüs.-mat. ja Tehn. ser. 1965. V. 14, No. 1. P. 163-165.

22. *Бурлов В. В., Яковлев В. И., Кутуев Р. Х., Проскуряков В. А.* К вопросу об углеводных структурных элементах керогена прибалтийского горючего сланца Л., 1977 (Рукопись деп. в ВИНИТИ, № 3425-77).

23. *Swain F. M., Pakalns G. V., Bratt J. G.* Possible taxonomic interpretation of some Palaeozoic and Precambrian carbohydrate residues // Advances in Organic Geochemistry 1966, Oxford. 1968. P. 461-483.

24. *Prashnowsky A. A., Oberlies F.* Über Lebenszeugnisse im Präkambrium Afrikas und Südamerikas // Advances in Organic Geochemistry 1971, Oxford. 1972. P. 683-698.

25. *Наппа Л. А., Фомина А. С., Кивимяги Э. К., Куузк М. Г., Иконописцева С. Г.* Азотистые вещества диктионемового сланца ЭССР // Химия тв. топлива. 1975. № 4. С. 98-103.

26. *Семенова З. В., Кожевина Л. П., Тутурина В. В.* Аминокислотный состав гидролизатов сапропелита // Химия тв. топлива. 1975. № 5. С. 49-53.

27. *Хейр П. Е.* Геохимия протеинов, пептидов и аминокислот // Органическая геохимия. - Л., 1974. С. 330-355.

2 . *Войткевич Г. В., Зеленщикова К. Х., Лебедько Г. И., Пояркова И. Ф.* Остатки жизнедеятельности организмов в докембрии юго-восточного склона Воронежского кристаллического массива // Докл. АН СССР. 1975. Т. 224, № 3. С. 689-690.

29. *Urov K. E., Klesment I. R.* A comparative geochemical characterization of organic matter of the Precambrian and Lower-Paleozoic oil shales [in Russian; with English summary] // Geokhimia. 1979. No. 11. P. 1679-1686.

30. *Likussar W., Gagliardi E., Fischer J.* Dünnschichtchromatographie von Aminosäuren in Bitumina. III. Tiroler Ölschiefer // Sci. pharm. 1981. V. 49, No. 4. P. 441-449.

31. *Klesment I., Pobul L., Kuusik M.* Characterization of bitumen of the Tñhagansk oil shale (Orenburg Region) [in Russian; with English summary] // Eesti NSV TA Toim. Keemia. 1981. V. 30, No. 3. P. 187-193.

32. *Eglinton O., Hamilton R.* Leaf epicuticular waxes // Science. 1967. V. 156, No. 3780. P. 1322-1335.

33. *Albrecht P., Vandenbroucke M., Mandengué M.* Geochemical studies on the organic matter from the Douala Basin (Cameroon). I. Evolution of the extractable organic matter and the formation of petroleum // Geochim. Cosmochim. Acta. 1976. V. 40, No. 7. P. 791-799.

34. *Илларионов И. К.* Роль подземных вод в образовании гипергенного сидерита месторождений фосфоритов и горючих сланцев Среднего Поволжья // Тр. Воронежск. ун-та. 1957. Вып. 58. С. 35-48.

35. *Тихомирова Е. С.* К вопросу о геохимической подвижности элементов при образовании сульфидных конкреций в сланценосных отложениях Волжского и Прибалтийского бассейнов // Докл. АН СССР. 1960. Т. 135. № 6. С. 1501-1504.

36. *Srivastava R. N.* Phosphatic nodules in the carbonaceous shales of Lower Tal Beds // Misc. Publ. Geol. Surv. India. 1972. No. 15. P. 215-254.

37. *Альтгаузен М. Н.* Катагенетическое перераспределение вещества древних металлоносных черных сланцев // III Всесоюз. совещ. «Геохимия горючих сланцев». С. 10-11.

38. *Зыков И. А., Горький Ю. И., Рогачева Л. П., Лосева С. В., Жицкая З. В.* О влиянии состава горючих сланцев Припятского прогиба на их физические свойства и содержание некоторых элементов // Там же. С. 75-76.

39. *Левин А. С.* О вторичных изменениях горючих сланцев Ленинградского месторождения // Изв. АН СССР. Сер. геол. 1976. № 1. С. 125-129.

40. *Бауков С. С.* Кукерситы Эстонской ССР и Ленинградской области // Формации горючих сланцев (методы изучения и генетическая классификация). Таллинн, 1973. С. 17-38.

41. *Simoneit B. R. T.* Hydrothermal effects on diatomaceous sediments in Guaymas Basin, Gulf of California: genesis of petroleum and degradation of protokerogen // III Всесоюз. совещ. «Геохимия горючих сланцев». С. 163-164.

42. *Sokolova N. T., Karyakin A. V., Efimova N. F., Kremneva M.A.* Disseminated organic matter in the hydrothermal mineral-formation [in Russian; with English summary] // Geokhimia. 1979. No. 11. P. 1687-1697.

43. *Фирсова С. О., Бочек Л. И., Сидоренко Св. А.* Оптическое изучение углеродистых веществ (шунгитов и графитов) докембрия // III Всесоюз. совещ. «Геохимия горючих сланцев». С. 184-186.

44. *Таусон В. О.* К вопросу об усвоении парафина микроорганизмами // Журн. Русск. ботан. о-ва. 1925. Т. 9, С. 161-176 (Приводится по: Таусон В.О. Основные положения растительной биоэнергетики. М.-Л., 1950. С. 138).

45. *Philippi G. T.* On the depth, time and mechanism of origin of the heavy to medium-gravity naphthenic crude oils // Geochim. Cosmochim. Àcta. 1977. V. 41. No. 1. P. 33-52.

46. *Rubinstein I., Strausz O. P., Spyckerelle C., Crawford R. J., Westlake D. W. S.* The origin of the oil sand bitumens of Alberta: a chemical and a microbiological simulation study // Geochim. Cosmochim. Àcta. 1977. V. 41, No. 9. P. 1341-1353.

47. *Забродина М. И., Арефьев О. А., Макушина В. М., Петров Ал. А.* Химические типы нефтей и превращение нефтей в природе // Нефтехимия. 1978. Т. 18, № 2. С. 280-290.

48. *Zajic J. E., Gerson D. F.* Microbial extraction of bitumen from Athabasca oil sand // Oil Sand and Oil Shale Chem. Proc. Symp. 2nd Ann Joint Meet. Chem. Inst. Can. and Amer. Chem. Soc., Montreal, 1977. New York, 1978. P. 145-161.

49. *Smith P. V.* Studies of origin of petroleum: occurence of hydrocarbons in recent sediments // Americ. Assoc. Petrol. Geol. Bull. 1954. V. 38, No. 3. P. 377-404.

50. *Авров В. П., Галимов Э. М.* О микробиологической природе метановой залежи, обнаруженной на значительной глубине // Докл. АН СССР. 1968. Т. 179, № 5. С. 1203-1205.

51. *Ponsford A. P.* Microbiological activity in relation to coal utilisation. Part II. Coal and hydrocarbons // Monthly Bull. Brit. Coal Utilis. Res. Assoc. 1966. V. 30, No. 2. P. 41-71.

52. *Findley J., Appleman M. D., Yen T. F.* Degradation of oil shale by sulfuroxidizing bacteria // Appl. Microbiol. 1974. No. 3. P. 460-464.

53. *Yen T. F.* Microbial oil shale extraction // Microb. Energy Convers. Proc. Semin., Göttingen, 1976. Oxford, 1977. P. 309-328.

54. *Кожевников А. В., Первунинская Н. А.* Бактерии в горючих сланцах // Тр. ВНИИПС. 1960. Вып. 9. С. 295.

55. *Юсупова И. Ф.* Органическое вещество кукерсита в гидрогенных процессах // III Всесоюз. совещ. «Геохимия горючих сланцев». С. 206-207.

56. *Германов А. И., Борзенков И. А., Юсупова И. Ф.* Преобразование органического вещества осадочных толщ в подземной биосфере при биогенных сульфатредукции и метанообразовании // Седикахиты на разных этапах литогенеза. М., 1982. С. 79-82.

57. *Гонцов А. А., Курбатова Е. Г., Хрусталева Г. К.* Об устойчивости керогена горючих сланцев при гипергенезе // Всесоюз. совещ. «Геохимия горючих сланцев» Тез. докл. Таллинн, 1978. С. 36-37.

58. *Корчагина Ю. И., Дымова Н. Л., Митюшин Н. В., Фадеева Н. П., Храмова Е. В.* Углеводороды в древних толщах (на примере докембрийских и нижнекембрийских отложений Сибирской платформы) // Седикахиты на разных этапах литогенеза. С. 101-108.

59. *Tissot B. P., Welte D. H.* Petroleum formation and occurrence. - Berlin etc., 1978.

60. *Клесмент И. Р., Уров К. Э.* К биогеохимии горючих сланцев по данным о составе их битумоидов и нерастворимой части органического вещества // Геохимия современных и ископаемых осадков. Мат. VIII Междунар. конгр. по органич. геохимии. М., 1982. С. 179-186.

61. *Palu V., Bondar J., Veski R., Fomina A.* n-Alkanes, monocarboxylic and α, ω-dicarboxylic acids in the extract of Mandra oil shale // Comptes rendus de l'Académie bulgare des Sciences. 1979. V. 32. No. 4. P. 505-508.

62. *Pobul L., Klesment I.* Study of balkhashite. 1. The composition of bitumen [in Russian; with English summary] // Eesti NSV TA Toim. Keemia. 1981. V. 30, No. 2. P. 75-83.

63. *Pobul L., Klesment I., Kuusik M.* Investigation of the organic matter of Kenderlyk oil shale [in Russian; with English summary] // Eesti NSV TA Toim. Keemia. 1982. V. 31, No. 1. P. 25-32.

64. *Черкасова Л. С., Мережинский М. Ф.* Обмен жиров и липидов. - Минск, 1961. С. 309.

65. *Johns R. B., Onder O.* Biological diagenesis: dicarboxylic acids in recent sediments // Geochim. Cosmochim. Àcta. 1975. V. 39. P. 129-136.

66. *Volkman J. K., Johns R. B., Gillan F.T., Perry G. J.* Microbial lipids of an intertidal sediment. I. Fatty acids and hydrocarbons // Geochim. Cosmochim. Àcta. 1980. V. 44, No. 8. P. 1133-1143.

67. *Клесмент И. Р., Риккен Ю. Т., Уров К. Э.* Особенности органического вещества диктионемовых сланцев // Горючие сланцы / ЭстНИИНТИ. 1976. № 6. С. 20-25.

8. *Котлуков В. А.* Общая характеристика этапов сланцеобразования на территории Европейской части СССР // Прогноз горючих сланцев Европейской части СССР. Таллинн, 1974. С. 7-14.

69. *Неручев С. Г., Климова Л. И.* О возможности биогенного накопления в осадках P, V и U и некоторых других элементов и определении аэробных окислительных потерь органического вещества // Накопление и преобразование седикахитов. М., 1979. С. 39-56.

70. *Friedman G. M.* The making and unmaking of limestones or the downs and ups of porosity // J. Sed. Petr. 1975. V. 45, No. 2. P. 379-398.

71. *Sayles F. L., Manheim F. T.* Interstitial solutions and diagenesis in deeply buried marine sediments: Results from the Deep Sea Drilling Project // Geochim. Nosmochim. Àcta. 1975. V. 39, No. 1. P. 103-127.

72. *Вассоевич Н. Б.* Опыт построения типовой кривой гравитационного уплотнения глинистых осадков // Новости нефтяной техники (Геология). 1960. № 4 С. 11-15.

73. Геологический словарь. Т. 1. - М., 1973. С. 159.

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