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THERMOOXIDATIVE AND OXIDATIVE DESTRUCTION
OF THE WEATHERED AND URANIUM-RICH
ESTONIAN DICTYONEMA OIL SHALE

The Tremadoc Dictyonema (Oil) Shale (DS) is one of the most problematical
sedimentary rocks occurring in Estonia (Fig. 1). Due to its specific chemical
composition (e.g. high heavy metals content) it should have found use in the national
economy long ago already but investigations carried out so far have not yet yielded
results applicable to practice. This is why about 70 million tonnes of crushed shale
have been dumped in the Maardu phosphorite quarry. The weathering of DS in the
dumps leads to its self-ignition, 11-15 cases taking place per every million tonnes of
buried shale each year [1].

The thermal processing and burning of DS is difficult to carry out due to its low
organic and high pyritic and organic sulphur content. The concentration of sulphur
compounds in combustible gases and thermolysis products is high. As a result of the
inner burning of DS in dumps, also elemental sulphur and sulphur products are
released [2, 3]. Simultaneous leaching of uranium and other heavy metals compounds
is a serious environmental impact at Maardu as well.

Until now the composition and distribution of the weathering products of
geochemically active DS and pyrite have been dealt with in many researches [4-7].
The weathered as well as uranium-rich DS, however, have been investigated very
little. This work aimed at finding suitable methods for characterizing the weathered
and irradiated DS samples. The weathered, uranium-rich and X-ray irradiated
samples, some of them being also high-sulphur, were studied by thermooxidative and
oxidative destruction. The composition of the organic acids formed was determined
by gas chromatography. The research procedure has been described elsewhere
[8, 9].

Samples

Altogether nine DS samples, five from the Maardu deposit and four from north
eastern Estonia, were studied (Fig. 1). The U concentration of the DS from the
Maardu deposit is relatively low (20-50 ppm or g/t), decreasing even more during
weathering as a result of U leaching. So, the U content of the nonweathered DS
sample from Borehole M-30 is 39 ppm (Table 1). The nonweathered DS sample
from which extracts were removed before study (hereinafter nonirradiated sample)
was taken from the middle section of the southern region of the Maardu deposit. The
latter sample was exposed to X-ray irradiation at 25 °C for 133 h (hereinafter
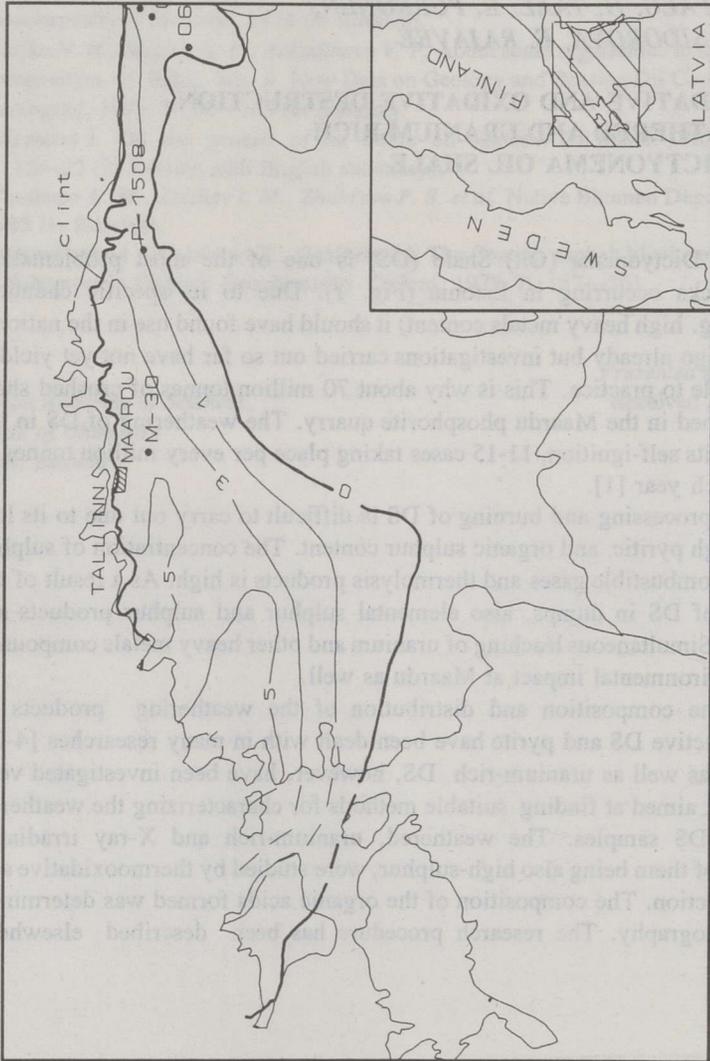irradiated sample). The procedure was carried out in a gamma contour of a nuclear

Fig. 1. The scheme of the Estonian Dictyonema Shale basin with isopachytes (m) and the location of boreholes

reactor at the Institute of Physics, Latvian Academy of Sciences. The capacity ofartificial radiation was 462 rad/sec (4.62 Gy/sec), integral dose 220.8 Mrad or 2.21 MGy (± 15 %). The dark and light varieties of the weathered DS samples were taken from the denuded wall near the entrance to the Ülgase phosphorite pit. The organic content of the light variety is lower than that of the dark variety, its solubility in chloroform and benzene-methanol being higher (7 and 3 % on organic matter, respectively). The preliminary high concentration of sulphur (up to 10 %) in the extracts obtained decreased 2-4 times after treatment with mercury, which is indicative of the existence of elemental sulphur in weathered DS samples. The extracts from the nonweathered DS sample (3.2 % on organic matter) also contained elemental sulphur.

The U-rich samples were isolated from cores. Their Mo content is in most cases remarkable (Table 1). The sample, whose U content is 514 ppm, was taken from Borehole 0604 (Fig. 1) locating near Kuremäe. The core, containing anthraconite crystals was partly weathered and foliated.

Sample 355 whose U-content is 526 ppm was taken from Borehole 0613 7 km south of Sillamäe and 1 km east of Viivikonna kukersite oil shale quarry. The upper half of a 0.8 m core was investigated. The U content of the lower half of the core is 280 ppm, that of Mo, Th and Sr being 381, 152, 13 and 70 ppm, respectively.

Table 1. **Heavy Metal Content of DS Samples as Established by X-ray Fluorescence Spectrometry, ppm (g/t)**

Core	Nr.	U	Mo	Pb	Sr	Th
M-30	559	39	107	101	62	8
0604	15	514	91	150	71	10
0613	355	526	650	158	76	12
P-1508	510	530	870	94	64	7
0612	45	540	1466	183	41	8

Sample 510, whose U content is 530 ppm, was taken from Borehole P-1508 4 km east of Rakvere, where the thickness of the DS layer is only 30 cm. The average U content of the core is 364 ppm (Mo 537, Th 8, Pb 133 and Sr 120 ppm) while the minimum content of U (Sample 503) and Mo (Sample 508) is 133 and 75 ppm respectively.

Sample 45 with a U content of 540 ppm was taken from Borehole 0612 at a depth of 35.2-36.3 m. The sample investigated (35.75-35.95 m) was homogeneous, unlike that from the upper and lower parts of the core which contained anthraconite crystals. The lowest U content of the DS sample from that core was 175 ppm, that of Mo 108 ppm. The U content of the samples of the present DS in Orasoja sandstone (Sample 517, the same borehole) is surprisingly high, 1200 ppm. The samples studied contained 9.0-14.2 % of carbon and 0.4-6.2 % of total sulphur (analyzed by the method described in [10] (Table 2)).

Thermooxidative Destruction

According to thermooxidation process course (Fig. 2), the DS samples studied can be divided into two groups: those with a low and high concentration of U. The DTA profiles of the former showed two exothermal peaks with the first maximum between
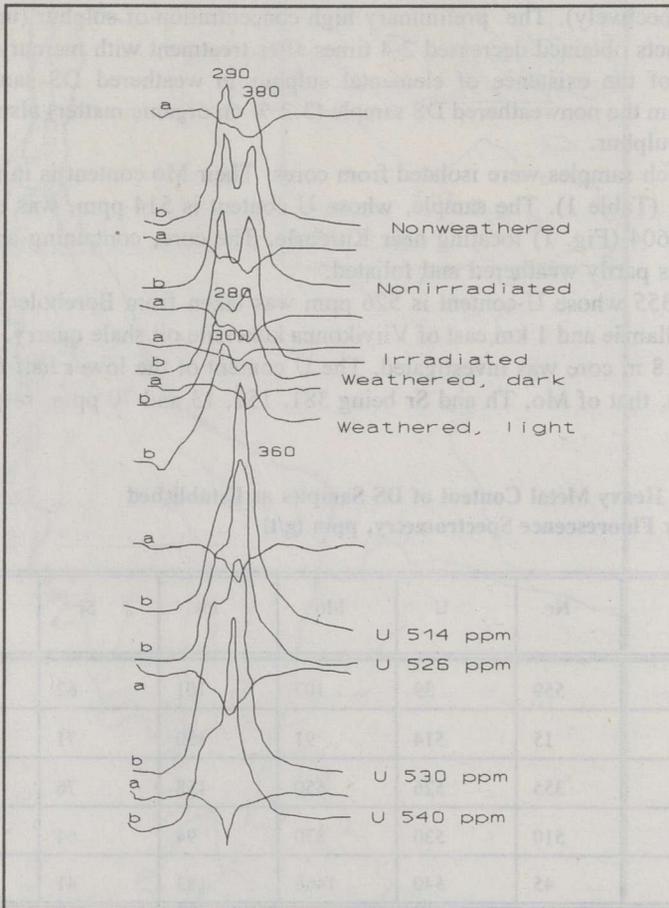

Fig. 2. DTG (*a*) and DTA (*b*) profiles of DS samples

280 and 300 °C and the second one between 360 and 390 °C. The U-rich samples were characterized by only one maximum between 340 and 380 °C with the exception of the sample with a U content of 530 ppm, its maximum being also at 290 °C. For all the samples studied the exothermal destruction began at 170 °C. All the preceding processes were endothermal and were related to the loss of the moisture of DS and a partial loss of the crystal water of the minerals contained in the samples (TG curves). The exothermal weight loss for the dry DS samples from the Maardu deposit ranged between 17 and 18 %. Only for the light variety of the weathered DS the weight loss was considerably lower, 14.7 %. The respective data for the U-rich samples taken from another area ranged from 12.1 to 21.6 %. The carbon and sulphur contents of these samples also varied largely, unlike those of the

samples from Maardu. Only the light weathered Maardu DS sample differs from the rest of the Maardu samples, as part of its organic matter and sulphur was lost in the weathering process (Table 2).

Table 2. **Results of Analysis of DS Samples, %**

Sample	C^d	S^d	Data of thermal analysis				
			Sample weight, mg	Water loss 20-170 °C	Exothermal loss >170 °C		
					In all	Step I, 170-330 °C	Step II, >330 °C
Maardu samples							
Nonweathered	12.2	2.8	105	3.3	17.2	34	66
Nonirreadiated	11.7	2.3	103	2.1	18.0	32	68
Irradiated	...	...	103	2.7	17.8	29	71
Weathered:							
dark variety	14.2	0.8	60	1.7	17.0	30	70
light variety	10.5	0.4	70	2.2	14.7	52	48
U-rich samples							
514 ppm	13.5	3.6	123	2.4	16.8	17	83
526 ppm	9.0	6.2	123	2.2	12.1	19	81
530 ppm	14.2	2.4	123	4.1	21.6	29	71
540 ppm	9.7	3.2	107	3.7	14.9	23	77

In the first step of thermooxidation (170-330 °C) only part of crystal water and organic matter and all of the elemental sulphur, whose amount was low in comparison with that of the decomposed organic matter, can be released. In the second step pyrite underwent oxidation together with the organic matter. When eliminating the effect of pyrite, the weight loss of the Maardu DS samples in the first exothermal step made 29-34 % of that observed in the course of the whole exothermal process. For the light weathered sample this value reached 52 %. The weight loss of U-rich samples in the first, less intensive exothermal step ofthermooxidation was considerably lower, except the sample with a U content of 530 ppm (Table 2). If we take into account the pyrite content, the weight loss of organic matter in the first thermooxidation step would increase only 1 %, for U-rich samples up to 4 % (sample with a U content of 526 ppm).

Oxidative Destruction

All the samples presented in Table 2 were subjected to exhaustive alkaline $KMnO_4$ oxidation at 95 °C. Some of the samples, i.e. nonweathered, weathered and that of the highest content of U, were oxidized with the same oxidizer at 60 °C for 1 h and the last two samples also exhaustively at room temperature. The 70 % HNO_3 oxidation (20 g of shale per 30 ml acid) at room temperature for 110 days was applied to nonirradiated, irradiated and weathered samples, as well as to a U-rich one.

In the benzenecarboxylic acids (BCA) mixture all the homologs from phthalic to mellitic acid (with HNO_3 also benzoic acid) were determined by GLC. The acids grouped according to basicity (Fig. 3) showed that irrespective of different natural or artificial factors (weathering, irradiation) the distribution of the acids formed was unexpectedly similar in the identical oxidation conditions.

In mild permanganate (20 and 60 °C) and nitric acid oxidation all the samples afforded aliphatic dicarboxylic acids (DCA). In permanganate oxidation products DCA C_4-C_{11} were determined. The acids were of a similar distribution, the amount of C_4 being the highest, while that of each of its higher homologs was respectively lower. The same applies to the DCA mixtures contained in the ether-acetone extracts obtained by HNO_3 oxidation, while the hexane extracts contained DCA C_7-C_{20} with a slightly varying distribution (maximum C_{14} or C_{15}). The hexane extracts contained monocarboxylic acids (MCA) C_8-C_{22} of a varying bimodal distribution with maximums at C_{12}, C_{16} or C_{18}.

Based on the results of analysis, for one homologous series differences in acids distribution are insignificant, those in MCA/DCA and BCA/DCA ratios are more considerable, being 0.6 and 2.2, and 0.7 and 5.0, in weathered and U-rich samples, respectively.

To characterize the major HNO_3 oxidation products, i.e. those abbreviated in the scheme (Fig. 4), the elemental composition was determined and the carbon balance was calculated (Fig. 5). The carbon lost in the form of CO_2 (C_{x1}) and that of acetone- and alkali-insoluble residues (C_{x2}) were calculated as follows (in %): C_{x1} = 100 - (C_{SIP} + C_{E+A}); C_{x2} = C_{SIP} - (C_{AW} + C_{AF} + C_{RH}). The hexane extracts were omitted due to their very low yield.

The HNO_3-treated DS samples have been arranged so that the sample with a minimum C_{x1} + C_{x2} value is placed first and that with the respective maximum value last (Fig. 5). The other samples have been placed between these points according to their C_{x1} + C_{x2} values. As seen in Fig. 5, the higher the C_{x1} + C_{x2} value, the lower the amount of ether-acetone extracts and the higher the amount of the "regenerated" humic acids. It is noteworthy that the yield of "regenerated" humic acids was the highest for the U-rich sample, while their H/C ratio was very low (0.66). The H/C ratio of the "regenerated" humic acids obtained from other DS samples is about 1, except for the nonweathered sample (1.32). At the same time, the H/C ratio of the ether-acetone extracts separated from different DS samples in different yields varied very little (1.06-1.24).
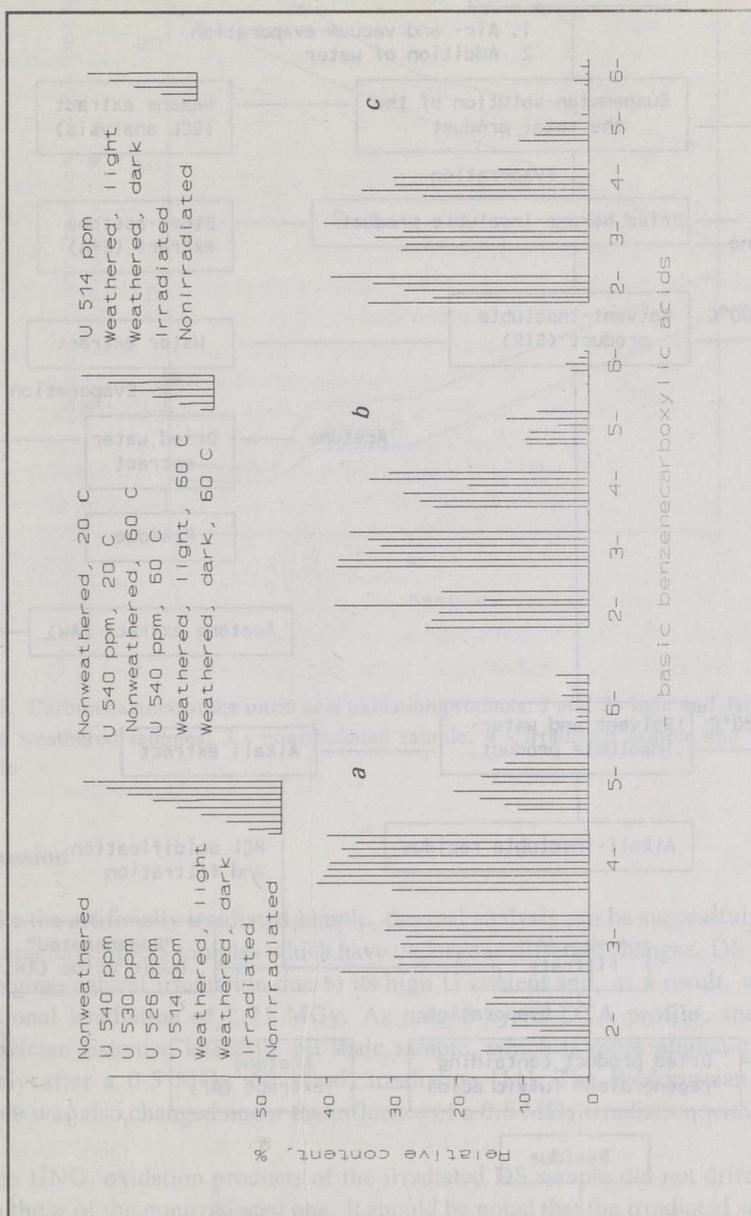
Fig. 3. The relative distribution of benzenecarboxylic acids in the products formed under hard (*a*) and mild (*b*) permanganate oxidation as well as mild (*c*) nitric acid oxidation
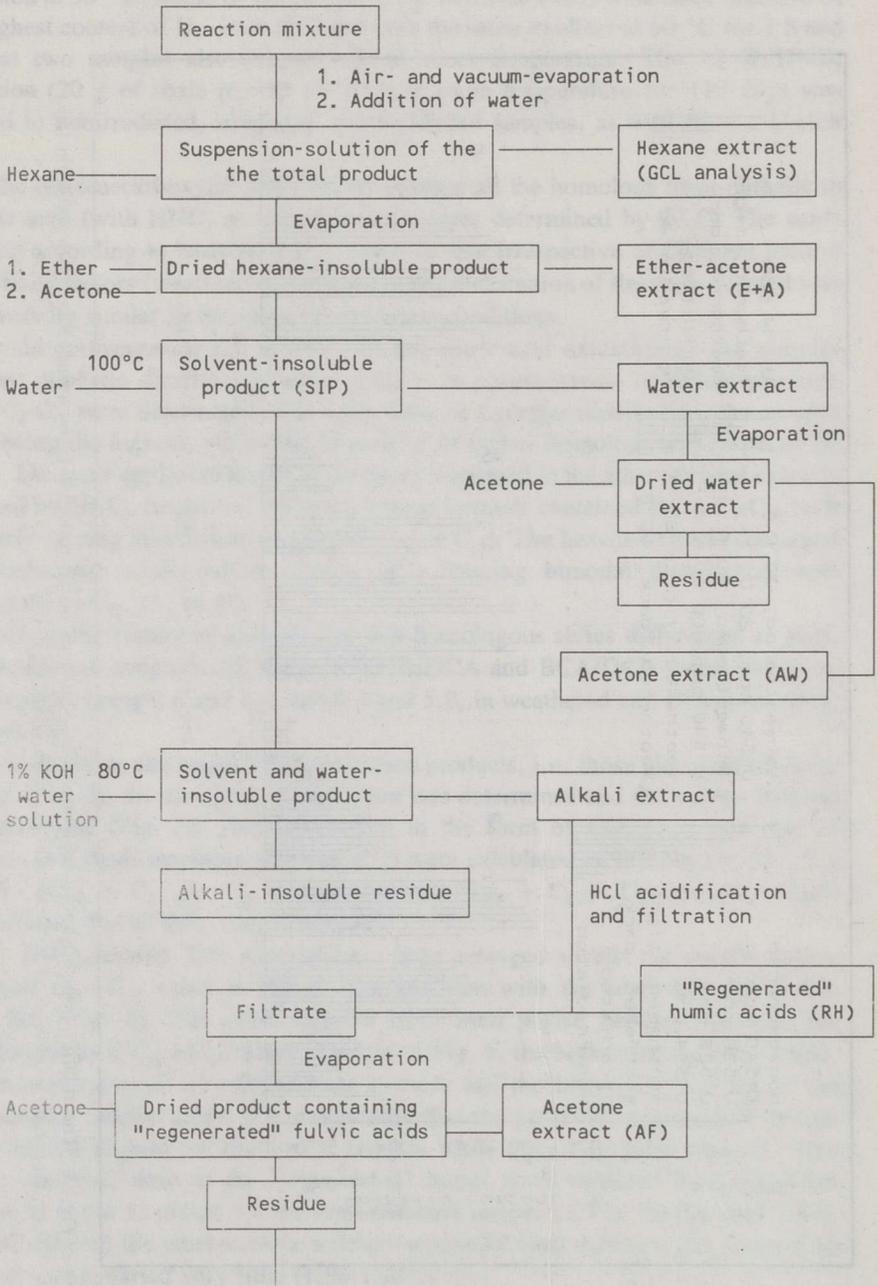
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                    ┌─────────────────────┐
                    │   Reaction mixture  │
                    └─────────────────────┘
                          1. Air- and vacuum-evaporation
                          2. Addition of water

          ┌──────────────────────────┐              ┌──────────────────────┐
          │ Suspension-solution of the│──────────────│ Hexane extract       │
Hexane────│   the total product       │              │ (GCL analysis)       │
          └──────────────────────────┘              └──────────────────────┘
                          Evaporation
 1. Ether  ┌──────────────────────────────┐          ┌──────────────────────┐
 2. Acetone│ Dried hexane-insoluble product│──────────│ Ether-acetone        │
           └──────────────────────────────┘          │ extract (E+A)        │
                                                       └──────────────────────┘
          100°C  ┌──────────────────────┐             ┌──────────────────────┐
Water ──────────│ Solvent-insoluble    │─────────────│ Water extract        │
                │ product (SIP)        │             └──────────────────────┘
                └──────────────────────┘                  Evaporation
                                        Acetone ──── ┌──────────────────────┐
                                                     │ Dried water          │
                                                     │ extract              │
                                                     └──────────────────────┘
                                                     ┌──────────────────────┐
                                                     │ Residue              │
                                                     └──────────────────────┘
                                                     ┌──────────────────────┐
                                                     │ Acetone extract (AW) │
                                                     └──────────────────────┘
 1% KOH  80°C ┌──────────────────────┐              ┌──────────────────────┐
  water ──────│ Solvent and water-   │──────────────│ Alkali extract       │
 solution     │ insoluble product    │              └──────────────────────┘
              └──────────────────────┘
              ┌──────────────────────┐                  HCl acidification
              │ Alkali-insoluble     │                  and filtration
              │ residue              │
              └──────────────────────┘              ┌──────────────────────┐
                ┌──────────────┐                    │ "Regenerated"        │
                │ Filtrate     │────────────────────│ humic acids (RH)     │
                └──────────────┘                    └──────────────────────┘
                     Evaporation
Acetone── ┌──────────────────────────┐   ┌──────────────────────┐
          │ Dried product containing │   │ Acetone              │
          │ "regenerated" fulvic acids│───│ extract (AF)         │
          └──────────────────────────┘   └──────────────────────┘
                ┌──────────────┐
                │ Residue      │
                └──────────────┘
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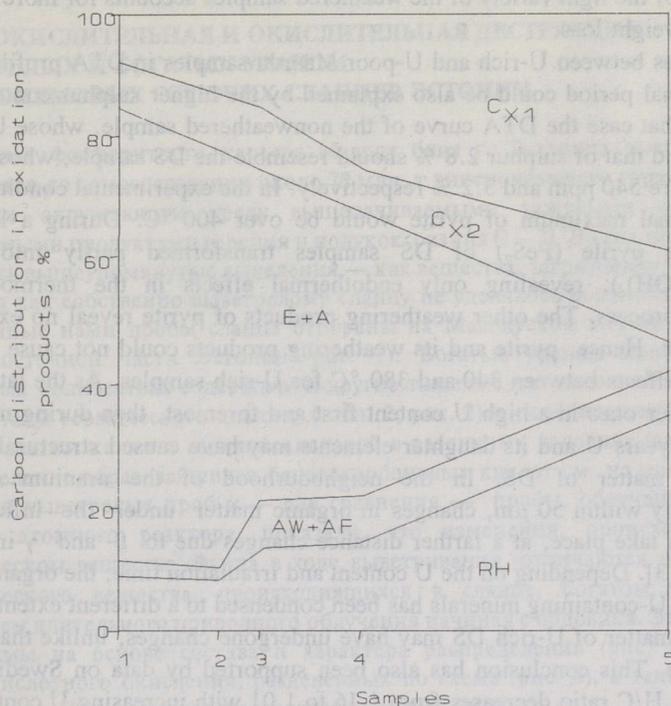*Fig. 4.* Scheme of separation of nitric acid oxidation products

Fig. 5. Carbon balance of the nitric acid oxidation products: *1* and *2* - light and dark varieties of the weathered samples, *3* - nonirradiated sample, *4* - irradiated sample and *5* - U-rich sample

Discussion

Unlike the artificially irradiated sample, thermal analysis can be successfully applied to characterizing DS samples which have undergone different changes. DS may have undergone natural irradiation due to its high U content and, as a result, withstands additional irradiation of 2.21 MGy. As judged by its DTA profile*, the Middle-Ordovician Estonian kukersite oil shale sample, which is more aliphatic, changed already after a 0.5 MGy (50 Mrad) irradiation [11]. The Byelorussian oil shale sample was also changed under the influence of a 0.5 MGy irradiation with electrons [12].

The HNO_3 oxidation products of the irradiated DS sample did not differ in yield from those of the nonirradiated one. It should be noted that the irradiated sample lies between U-rich and nonirradiated ones, while the weathered DS varieties located on the opposite side (Fig. 5). This allowed a conclusion to be made that changes in organic matter of DS due to weathering and irradiation are different. The organic and sulphur content of the light variety of the weathered samples are lower than those of the dark variety or the nonweathered sample, while the case is vice versa.

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*Analyzed by H. Taal.

with the extractable matter. During the first exothermal step of thermooxidation the weight loss of the light variety of the weathered samples accounts for more than half of its total weight loss.

Differences between U-rich and U-poor Maardu samples in DTA profiles during the exothermal period could be also explained by the higher sulphur content of the former. In that case the DTA curve of the nonweathered sample, whose U content is 39 ppm and that of sulphur 2.8 % should resemble the DS sample, whose content of U and S are 540 ppm and 3.2 % respectively. In the experimental conditions used the exothermal maximum of pyrite would be over 400 °C. During a long-term storage, the pyrite (FeS_2) of DS samples transformed partly into jarosite ($KFe(SO_4)_2(OH)_6$), revealing only endothermal effects in the thermooxidative destruction process. The other weathering products of pyrite reveal no exothermal effects either. Hence, pyrite and its weathering products could not cause intensive exothermal effects between 340 and 380 °C for U-rich samples. As the latter differ from the other ones in a high U content first and foremost, then during more than 500 million years U and its daughter elements may have caused structural changes in organic matter of DS. In the neighbourhood of the uranium minerals, approximately within 50 μm, changes in organic matter under the influence of α-irradiation take place, at a farther distance changes due to ß- and γ-irradiation take place [13]. Depending on the U content and irradiation time, the organic matter surrounding U-containing minerals has been condensed to a different extent. Hence, the organic matter of U-rich DS may have undergone changes, unlike that of low-uranium one. This conclusion has also been supported by data on Swedish Alum Shale whose H/C ratio decreases from 1.16 to 1.01 with increasing U content from 18 to 440 ppm [4]. This is confirmed by differences between U-rich and other samples in the distribution and composition of the products obtained in the HNO_3 oxidation process.

Conclusions

1. The organic matter of the U-rich DS samples studied underwent structural changes under the influence of natural irradiation by uranium and its daughter elements to such an extent that it could be observed in the DTA profile of thermal analysis as well as in the distribution and composition of HNO_3 oxidation products.
2. The weathered DS samples can be distinguished from the nonweathered ones by thermal analysis and HNO_3 oxidation.
3. Due to a long-term natural irradiation by uranium the organic matter of DS has changed sufficiently enough so that no further changes can take place under the influence of a weak (2.21 MGy) artificial irradiation, while the organic matter of kukersite and Byelorussian oil shale changes under the influence of a 0.5 MGy irradiation.

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ТЕРМООКИСЛИТЕЛЬНАЯ И ОКИСЛИТЕЛЬНАЯ ДЕСТРУКЦИЯ ВЫВЕТРЕЛЫХ И БОГАТЫХ УРАНОМ ДИКТИОНЕМОВЫХ ГОРЮЧИХ СЛАНЦЕВ ЭСТОНИИ

На отвалах фосфоритного карьера Маарду близ г. Таллинна выветривается и нагревается до самовозгорания около 70 млн. т диктионемового горючего сланца, загрязняя окружающую среду выщелачиваемыми тяжелыми металлами и выделяемыми продуктами горения и полукоксования [1—3]. До сих пор в основном изучались вышеупомянутые выделения — как вещества, загрязняющие природу, в то время как собственно выветрелому сланцу не уделялось должного внимания.

Изученные нами пробы сланца отобраны на Маардуском месторождении и в северо-восточной части Эстонии (рис. 1). Богатые ураном пробы сланца в различных количествах содержали и другие тяжелые металлы (табл. 1).

Результаты термического анализа (табл. 2; рис. 2) и окислительной деструкции перманганатом калия и азотной кислотой в различных условиях (относительное распределение образовавшихся бензолкарбоновых кислот см. на рис. 3) богатых ураном и выветрелых проб и — для сравнения — пробы, облученной в гамма-контуре атомного реактора, показали, что изменения, происходившие в органическом веществе сланца в ходе выветривания, отличаются от изменений органического вещества, происходивших в сланце, богатом ураном, под действием длительного природного облучения начиная с ордовика. Эти изменения различимы на основе состава и характера распределения (рис. 5) продуктов азотнокислотного окисления, разделенных по схеме (рис. 4), а также на основе морфологии ДТА кривых термического анализа (рис. 2).

Дополнительное искусственное облучение (2,21 МГи) не вызывало существенных изменений в органическом веществе маардуского сланца даже с низким содержанием урана (судя по данным термического анализа и окислительной деструкции), в то время как органическое вещество кукерсита [11] и белорусского горючего сланца [12], судя по данным термического анализа, претерпевало изменения уже при дозе 0,5 МГи.

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