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Uranium and Rare-Earth Elements in Dictyonema Shale of the Baltic Sedimentary Basin (Kaibolovo-Gostilitsy Area)

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Abstract. The article presents the results of the study of dictyonema shales of the Baltic basin (Leningrad Oblast, Kaibolovo-Gostilitsy prospecting area) for uranium (updated data on uranium mineralization of dictyonema shales) and rare earth elements (for the first time – as a new promising raw material source). At the same time, updated author's data on the total metalliferous content of dictyonema shales was made In relation to uranium, its average content in dictyonema shales has been clarified, the distribution of uranium in the section of sedimentary strata according to new well profiles has been given, and the features of its distribution have been clarified, in comparison with earlier authors' publications on this object of research. For rare earth elements in dictyonema shales, the results on their concentrations on a much larger analytical material are presented (670 samples, instead of 88, data on which were published earlier). For the first time, the features of the distribution of rare earth elements over the prospecting area and in the section of sedimentary strata along the profiles of wells are illustrated. New data on the petrographic composition of dictyonema shales are presented. An additional study of mineral impurities of dictyonema shales was carried out using a new method of areal scanning of preparations with an electron probe microanalyzer using the "Feature" software module. The correlations between the concentrations of uranium and rare earths with other micro- and macroelements, the forms of uranium and rare earth elements in dictyonema shales, geochemical indicators, conditions and genesis of the formation of uranium and rare earth mineralization developed in them was clarified. Based on an earlier assessment of the resource potential of uranium and rare earths, a modern assessment of their prognostic mineral resources and possible recoverable industrial reserves and the cost of potential ore raw materials of the studied acute-deficient metals for energy and a number of important industries has been made. The authors express the opinion that the mineral resource base of uranium and rare earth elements in Russia can be significantly increased due to the presence of these critical metals in the dictyonema shales of the Baltic sedimentary basin, since only within the studied Kaibolovo-Gostilitsy prospecting area the largest uranium resources and large resources of rare earths have been discovered, which may increase even more with further geological research in the conditions of a developed infrastructure of the middle zone of the Russian Federation.

Keywords: dictyonema shales, black shales, metalliferous, mineralization in black shales, uranium, rare earth metals, prognostic mineral resources

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Introduction

Carbonaceous water-sedimentary rocks, the so-called black shales, have been of great interest to geologists for a long time. Black shales are carbon-containing clayey, carbonate-terrigenous, siliceous, usually schistose rocks, often enriched in ore elements. Black shale formations occur in deposits of different sedimentary facies (lacustrine, deltaic, littoral, lagoonal, shallow-water and depression-shelf, continental slope and foot, and possibly even bathyal). Black shales were formed in humid and arid climatic conditions (Yudovich and Ketris, 1988). Black shales can be stratigraphic materials that make it possible to mark certain epochs in the history of the stratisphere; they can often be used to correlate sections of remote regions; they are often associated with sharp changes in the abundance and taxonomic diversity of fossil flora and fauna (Zheng et al., 2020; Ofili et al., 2022). The most important feature of black shales is the presence in these sedimentary formations of large geochemical anomalies of U, Mo, V, Re, Se, Zn, Cu, Hg and a number of other rare and valuable elements. In the black shale formations of the world, industrial accumulations of uranium, noble and non-ferrous metals are also known (Belenitskaya et al., 2015, etc.). Therefore, recently, due to the growing needs of a number of industries and the development of new technologies, black shale is actively considered as a new promising non-traditional source of ores of acutely scarce (critical) metals. At the same time, the elements

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most in demand in "green" energy are of particular importance: uranium and rare earth elements (REE) – for nuclear power plants, wind turbine generators, hybrid cars, rechargeable batteries. REE are indispensable in modern military technologies, night vision devices, high-precision weapons, navigation equipment, mobile phones, televisions, etc. Rare earth metals include lanthanides, yttrium and scandium. Traditionally, lanthanides are divided into two groups: cerium and yttrium, which are distributed differently in rocks and ores of deposits.

However, questions of the conditions for the formation of black shale ore-bearing strata, the genesis of the mineralization developed in them, including uranium and rare earth mineralization are among those that have not been sufficiently studied (Neruchev, 2007, etc.).

Black shale sedimentary formations rich in organic matter, formed from the Middle Cambrian to the Late Ordovician, are known over a large area of Northern Europe under different names (Fig. 1).

In Sweden, it is alum shale (Andersson et al., 1985) in the area of Oslo (Henningsmoen, 1960) and Bornholm (Poulsen, 1966). In Estonia it is called graptolite mudstone, "Dictyonema shale" (Männil, 1966), in Poland (Szymanski, 1973) and Northwestern Russia (Vyalov et al., 2010, etc.) – kukersite as oil shale itself.

This huge sedimentary basin is known as the Baltic basin of dictyonema and oil shale; it extends from Norway, Denmark, Sweden and Estonia to the Leningrad region, where in the latitudinal direction it can be traced for about 300 km from the Narva river in the west to the Syas' river in the east. Further east, the Dictyonema shale (DS) is buried beneath Upper Devonian sediments. Dictyonema shales have a large area of distribution and, accordingly, enormous resources. Thus, the predicted resources of the DS with an average thickness of 2 m (up to a depth of 100 m) in the Izhora area alone are 5.7 billion tons (Kiselev et al., 2002).

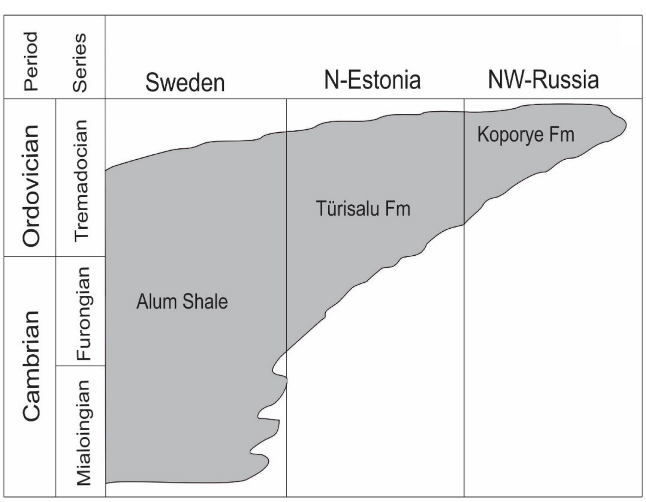

Fig. 1. Stratigraphy and distribution of black shales of the Baltic paleobasin according to (Ofili et al., 2022)

The origin of the Baltic-Scandinavian black shales and the nature of the distribution of high-metal concentrations in them remain little studied, despite their long history of exploration and exploitation (historically, uranium mining and enrichment were carried out in the USSR and Estonia).

The purpose of this article is an expanded and refined description of uranium and rare earth mineralization in the DS in the Leningrad region in comparison with our previous works within the Kaibolovo-Gostilitsy search area (Fig. 2). For this purpose, the following work was carried out: analysis of the features of the distribution of mineralization over the area and in the section of the formation, as well as the distribution of uranium and rare earth elements in the DS; clarification of potentially industrial concentrations of U and REE, forms of their occurrence and conditions of their formation; detailed assessment of predicted metal resources for areas of the exploration area; clarification of the initial cost estimate of potential uranium raw materials.

Materials and methods

We used our own original analytical information (database) obtained during our search work in 2012–2014 on the Kaibolovo-Gostilitsy area of the Leningrad region 1 (Report of the A.P. Karpinsky Russian Geological Research Institute (responsible by V.I. Vyalov) "Exploration work for rhenium in Dictyonema shales and phosphorites of the Baltic basin on the Kaibolovo-Gostilitsy area with an assessment of the forecast resources of rhenium in categories P2 – P1 "(State registration No. 41-12-289 of Rosgeolfond, 2014. V. 1–4, 1 graphic appendix)), as well as new research results obtained during the implementation of the Russian Science Foundation project No. 23-27-00427, https://rscf.ru/project/23-27-00427/.

Analytical determinations of uranium and REE concentrations were carried out at the Central Laboratory of the A.P. Karpinsky Russian Geological Research Institute (analysts V.L. Kudryashov and V.A. Shishlov) using inductively coupled plasma mass spectrometry (ICP-MS) according to the company's methods. The optimal methods of decomposition of the initial sample were used, as was used in the study of metals in coals (Oleinikova et al., 2015): acid decomposition for U, fusion with flux followed by dissolution in acids for REE. In total, more than 670 analyzes were carried out. X-ray fluorescence analysis was also performed. The structure and material-petrographic composition of the DS were studied on a Leica DM LP microscope in transmitted and reflected light, as well as on a Tescan VEGA II LMU scanning electron microscope with INCA ENERGY 450/XT energy-dispersive and wave-dispersive microanalysis systems (Oxford Instruments Analytical, UK) at the Research Center mineral resources and environmental

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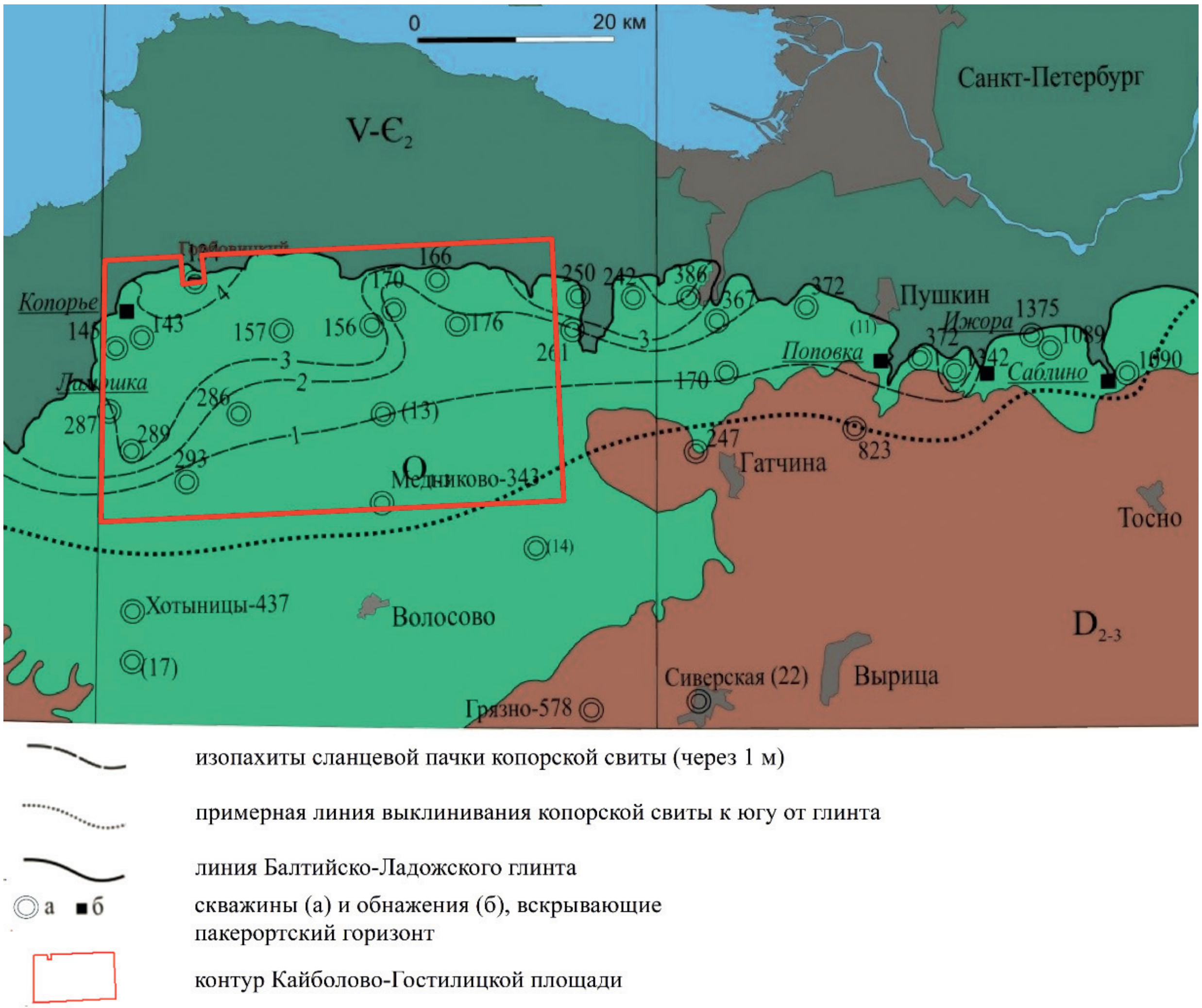

Fig. 2. Map of the distribution and thickness of the Dictyonema shale formation in the Baltic basin (Leningrad region) based on the A.P. Karpinsky Russian Geological Research Institute materials

conditions of the Southern Federal University. In 2023, at the Central Laboratory of the A.P. Karpinsky Russian Geological Research Institute (Karpinsky Institute), an additional study of mineral impurities of DS on rare earth elements was carried out using a new technique – area scanning of preparations with an electron probe microanalyzer using the Feature software module. The total carbon content was determined on an SC-144DR instrument (LECO Corporation, USA) using the infrared spectrometry method. The coulometric method was used to determine carbonate carbon (C_{carb}). The analysis was carried out on a carbon analyzer AN-7529 (OOO NPP ANALITPROMPRIBOR, Russia). Organic carbon (C_{org}) was determined by the difference between the total carbon content (C_{tot}) and carbonate content (C_{carb}). To determine uranium and REE in the OM of black shale, humic acids (their content was 15 wt.%), carboxylic acids, including fulvic acids, and other extractants with various solvents (hydrogen peroxide, benzene, HNO_3,) (analytics and original method by A.A. Gontsov, VNIGRIugol). The obtained analytical information was processed using correlation analysis (Spearman's rank correlation) of element contents. Geological-mineralogical, petrographic, geochemical studies of Dictyonema oil shale were carried out.

Brief geological characteristics of the research object

Dictyonema shales are part of the Lower Ordovician deposits of the Russian Platform, overlying the southern slope of the crystalline rocks of the Baltic Shield. They are a component of the deposits of the Pakerort stratigraphic horizon, the sediments of which, with plan-structural unconformity, lie on the eroded surface of Lower and Middle Cambrian rocks. The northern boundary of the distribution of DS runs along the Ordovician cliff, which stretches along the southern coast of the Gulf of Finland in the Baltic Sea and further to Lake Ladoga. In the area of the Ordovician clint, shales come to the surface, and 22–25 km to the south they were recorded in wells at a depth of about 100 m, and pinched out even further south. The DS layer is overlain by glauconite sandstones of the Lower Ordovician Volkhov Formation. It has a gentle slope, falling from northwest to southeast.

The depth of the shale roof varies from 0 in the near-clint zone to 107 m in the south. Figure 3 shows a map of the thickness of the DS formation (with a lower unit of interbedded dark brown shales, gray, sometimes brown siltstones and sandstones) of the Kaibolovo-Gostilitsy area – the object of the Karpinsky Institute prospecting work in 2012–2014.

Dictyonema shales are a relatively homogeneous rock in terms of mineral composition and organic matter (OM) content (up to 8–15%), which is represented by the remains of dictyonemas and lower algae. Average mineral composition (%): quartz (60–74), potassium feldspar (sanidine) (8–15), microcline, muscovite (2–8), chlorite (2–4) rarely present, and clay minerals in the mixture with OM, finely dispersed pyrite (3–8), marcasite (3) in interlayers and nodules (in the lower and middle parts of the DS formation); accessories – apatite, zircon, rutile, monazite, etc. There are anthraxolite nodules and ore minerals (galena, sphalerite, molybdenite, pitchblende, etc. in small quantities) (Vyalov et al., 2017).

History of studying the uranium potential of Dictyonema shales

The study of the metal content of DS in the Baltic basin began with the study of their radioactivity in the early 30s of the last century. These shales were studied as possible raw materials for the extraction of radium, and since the mid-40s, forecasting and prospecting work was organized aimed at clarifying the prospects for their uranium content: after the Second World War, due to competition for the atomic bomb, the Soviet Union conducted intensive searches for uranium deposits. As a result of the work carried out by the Northern Expedition of the First Main Geological Directorate of the USSR Ministry of Geosciences, the largest resources of low-grade uranium ores were discovered. It was found that Estonian graptolite mudstone, an unmetamorphosed black shale, contains abnormally high uranium content. In Sillamäe, in north-eastern Estonia, a uranium ore enrichment plant was built and put into operation in 1948. A total of 22,500 tons of elemental uranium was obtained from 271,575 tons of graptolite mudstone extracted from a mine near Sillamäe. Due to low concentrations and complex, low-gain technology, most of the uranium remained as solid waste (Soesoo et al., 2020). In 1952, mining of Estonian graptolite mudstone ceased, and between 1950 and 1977, more than 4 million tons of uranium ore were imported to the plant from Central Asia and Eastern Europe, mainly from Czechoslovakia and East Germany. The estimated amount of elemental uranium produced from this resource was 25,000 t (Soesoo et al., 2020). The plant operated as a Soviet top-secret facility until 1991. After Estonia gained independence, in 1997, it was privatized and renamed AS Silmet. Currently, the plant produces rare metals, rare earth metals and their compounds and

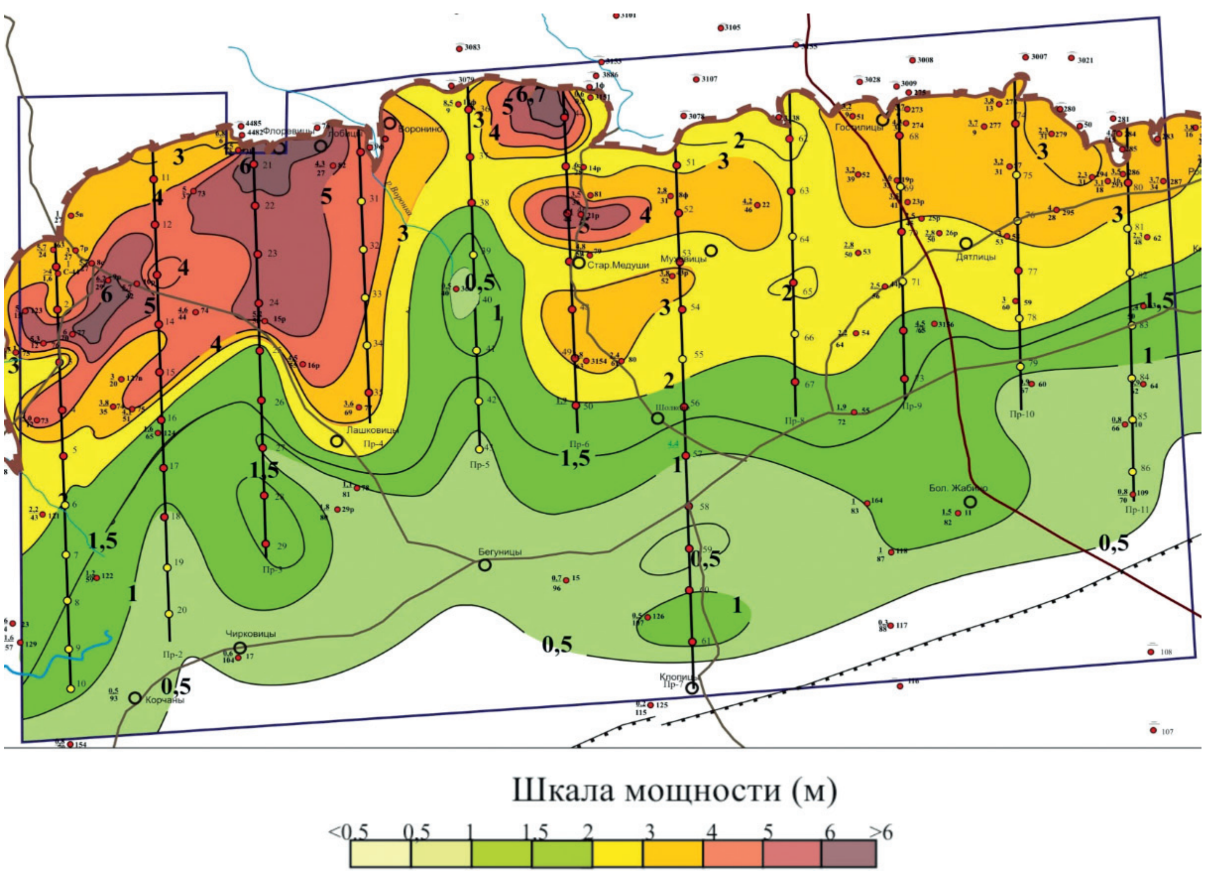

Fig. 3. Map of the thickness of the Dictyonema shale formation in the Kaibolovo-Gostilitskaya area

is one of the main producers of rare earth elements in the European Union.

In Russia, the study of uranium in DS was carried out during geological survey work on a scale of 1:200,000 (in 1946–1947 at the Krasnoselsky site with an area of 30 km^2, coordinates 59°42′00″ – 59°45′20″ N and 29°58′00″ – 30°06′00″ E), during prospecting and exploration studies in 1959 for phosphate raw materials in the obolus sandstones underlying the DS (Kotly-Koporye site, where associated searches for uranium were carried out, and later revision work (1962, ibid.)). As a result of the work, the five areas were delineated in the rank of non-industrial ore deposits with uranium reserves (thousand tons): Kotlovskoye – 6.2; Rannolovskoe – 2; Kaibolovskoye – 5.7; Kummolovskoe – 58; Krasnoselskoye – 13 (Vyalov et al., 2017). These prospecting and exploration works were accompanied by detailed lithological and mineralogical studies, which were carried out by employees of the All-Russian Research Institute of Mineral Raw Materials named after. N.M. Fedorovsky (Althausen et al., 1967, etc.). As a result, the structure of the Dictyonema shale formation was studied, the distribution of uranium in it and its occurrence form, as well as the content of accompanying components, were established. Among them, Mo, V, Ni, P, less frequently Zn, REE, Sc, Re, etc. were most often noted in elevated concentrations.

Despite the fact that significant resources of uranium ores were identified in the DS, due to low contents (on average 0.016%), work on uranium was stopped.

Regional metallogenic studies for uranium were also carried out at the Karpinsky Institute. It was found that the area of development of uranium-bearing Lower Ordovician rocks is in the zone of influence of mantle and crustal faults penetrating from the basement into the sedimentary cover. An assumption was made about the possibility of epigenetic redistribution of uranium in zones of influence of faults with the emergence of higher concentrations in relation to syngenetic accumulations.

Since 2009, the Karpinsky Institute has been conducting studies of Dictyonema shales for acutely scarce (critical) metals. In 2012–2014 in the Leningrad region, in the Kaibolovo-Gostilitsy area, the Institute's staff carried out prospecting work for rhenium, which was accompanied by massive sampling from the core of drilled wells, followed by analytical studies of samples of Dictyonema shale for a number of ore metals, including uranium. Based on precise quantitative methods, such as mass spectrometry, a high concentration of uranium has been confirmed, at the level of off-balance and industrial ores. Dictyonema shales are characterized by elevated contents of U and other strategically important metals (Vyalov et al., 2010; Vyalov et al., 2013a, Vyalov et al., 2013b). For the first time, the concentrations of rare and trace elements were established at the industrial level: Sc, Rb, REE, Cs, Re, etc. (Vyalov et al., 2010; Vyalov et al., 2013a; Vyalov et al., 2013b; Vyalov et al. , 2017).

The development of shale as an ore raw material can be profitable when extracting uranium along with other valuable metals. The state balance takes into account a number of deposits with similar uranium contents: Ulug-Tanzekskoye in Tyva, Dolmatovskoye and Khokhlovskoye in the Kurgan region (State balance of mineral reserves..., 2019a).

The ore component available for industrial extraction from black shale is highly scarce REE. Most of the deposits of rare earth metals taken into account by the State Balance of Mineral Reserves of the Russian Federation (State balance of mineral reserves..., 2019b) are complex, in which REE are associated components. When leaching uranium from Dictyonema shales, rare earth metals can be simultaneously extracted into solution (Patent RF No. 2477327, 2013). The technique described in this patent refers to a method for complex processing of carbon-silica black shale ores containing vanadium, uranium, molybdenum and rare earth elements. The method includes grinding the ore to a particle size of no more than 0.2 mm and two stages of leaching. Sulfuric acid oxidative leaching is carried out at atmospheric pressure. Autoclave oxidative sulfuric acid leaching is carried out at a temperature of 130–150 °C in the presence of an oxygen-containing gas and a nitrogen oxide-forming substance as an oxygen oxidation catalyst. From the resulting productive solution, ion-exchange sorption of uranium, molybdenum, vanadium and rare earth elements is carried out. The technical result is an increase in the degree of extraction of vanadium to 95%, uranium, molybdenum to 90%, an increase in the complexity of ore use due to the associated 80% extraction of rare earth elements.

All of the above determines the need to continue research into DS as a source of valuable complex scarce raw materials.

Research results

Additional diverse studies in 2023 showed that the petrographic composition of the DS (Fig. 4) is relatively consistent over the area, but gradually changes along the section.

The structure is silty, the texture is wavy-lenticular-layered, microlayered. The mineral part of the DS is 85–90%, consisting of 20–30% hydromica clay particles and 70–80% silty material, mainly quartz and feldspars. Quartz (sometimes in amounts up to 60%) with varying degrees of roundness of grains, potassium feldspars – sanidine, rarely – microcline. Inclusions of acidic plagioclase, chlorite, glauconite, apatite and opal, sulfides, and carbonate and phosphate nodules are rare.

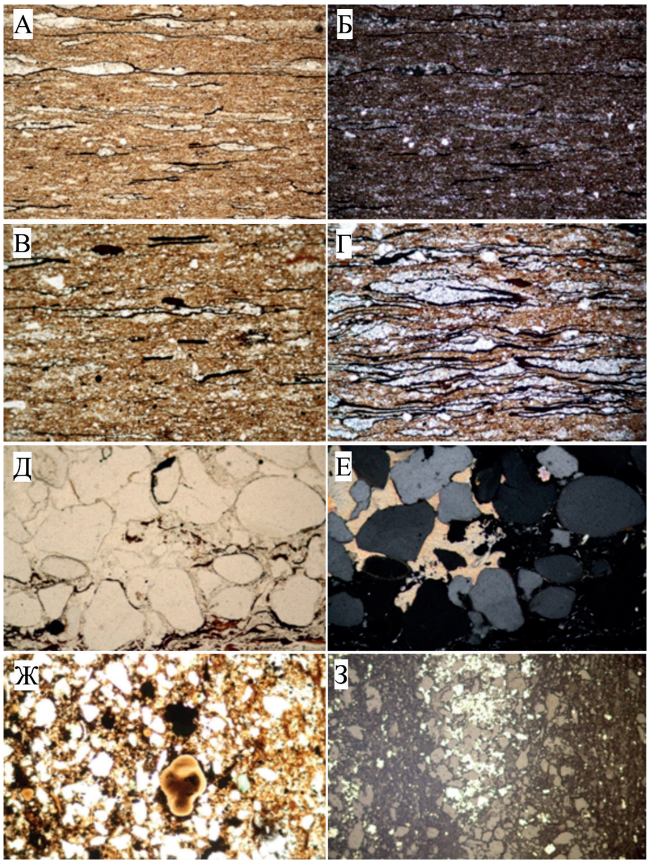

Fig. 4. Petrographic composition of Dictyonema shales: A – colloalginite with clayey matter (nicoli ‖, magnification ×50), B – the same (nicoli +, magnification ×50); B – graptolite thecae in the more clayey part of the shale (nicoli ‖, magnification ×100); G – aleurite nests (nicoli ‖, magnification ×200); D – silt layer. Quartz, calcite (nicoli ‖, UV ×200); E – the same (nicoli +, magnification ×200); F – phosphate nodules (in the center, nicoli ‖, magnification ×200); H – dissemination of sulfides, glauconite (in the center, reflected light, magnification ×200)

Accessory minerals include zircon, sphene, epidote, rutile, and monazite.

Organic matter consists of the remains of graptolites and lower algae (up to 15%). The bulk of the OM is composed of colloalginite of blue-green algae (from light yellow to brownish color) in a dispersed mixture with the clayey substance of shale – hydromicas (illite, etc.), sericite, muscovite and biotite, scattered throughout the thin section. The remains of graptolites in the form of elongated skeletal fragments (thecas) are clearly distinguished by their color (from dark brown to black) and clear outlines against the lighter background of the main mass (Fig. 4). Thecae are mainly represented by remains of very small sizes (from 0.01 to 0.06 mm), confined to silty interlayers about 0.02 mm wide, and less often by large remains up to 1 mm. Graptolite thecae occur throughout the formation section. Less common are oval bodies (from dark yellow to brown colors) – fragments of pseudovitrinite of unknown origin.

According to the petrographic type of oil shale, according to A.I. Ginzburg (Ginzburg, 1991), DS belong to the silty-clayey colloalginite type, and according to the composition of the kerogen-forming substance, they belong to the sapropelite class itself.

Uranium. The uranium content in the DS reaches the minimum industrial level (300 g/t) with a maximum concentration on average for a well of 880 g/t with an average content for wells of 188 g/t (this is updated data for 97 exploratory drilling wells in the DS formation with an average thickness 3.4 m taking into account the lower layer of interlayering). The uranium content according to furrow samples from exploratory drilling ranges from 7 to 1130 g/t.

Figure 5 shows the distribution of uranium in the DS layer without the lower layer of interbedding, in the so-called productive horizon of the DS layer with an average thickness of 1.8 m within the Kaibolovo-Gostilitsy area. The average uranium content turned out to be higher – 216 g/t.

The distribution of uranium over the area of the DS formation is heterogeneous; there are local areas of increased concentrations. It has been established that the concentration of uranium has an inverse relationship with the thickness of the shale formation. The lower the thickness of the DS formation, the higher the concentration of the element. When the thickness of the DS formation is reduced to 1 m or less (Fig. 3), the uranium concentration increases to > 250–350 g/t, in well 59 – > 436 g/t (well average) (Vyalov et al., 2017).

In the section of the formation, the most uranium-bearing layer is located approximately in the middle of the formation (Fig. 6, 7), in its productive horizon.

In Fig. 6 and 7 show some enrichment of obol sandstones with uranium in the form of trails, stripes or zones under its high concentrations in the Dictyonema shales – probably due to the removal of the element from the DS by groundwater, its redistribution during epigenesis.

In the underlying obolus sandstones (phosphorites), the uranium content is much lower (from 10–15 g/t, on average about 60 g/t).

Rare earth elements. The content of the sum of lanthanides and yttrium in DS ranges from 95 to 724 g/t, i.e. sometimes 2 or more times higher than the estimated standards (340 g/t according to (Vyalov, Nastakin, 2019)). The average total REE content in Dictyonema shales is 288.6 g/t. The distribution of REE over the area of shale formation development is presented in Fig. 8, and in the section of the formation – in Fig. 9, 10.

REE are distributed relatively evenly over the area of formation development; only occasionally are areas with contents above 250 g/t observed. Local areas with increased concentrations have a lens-shaped shape.

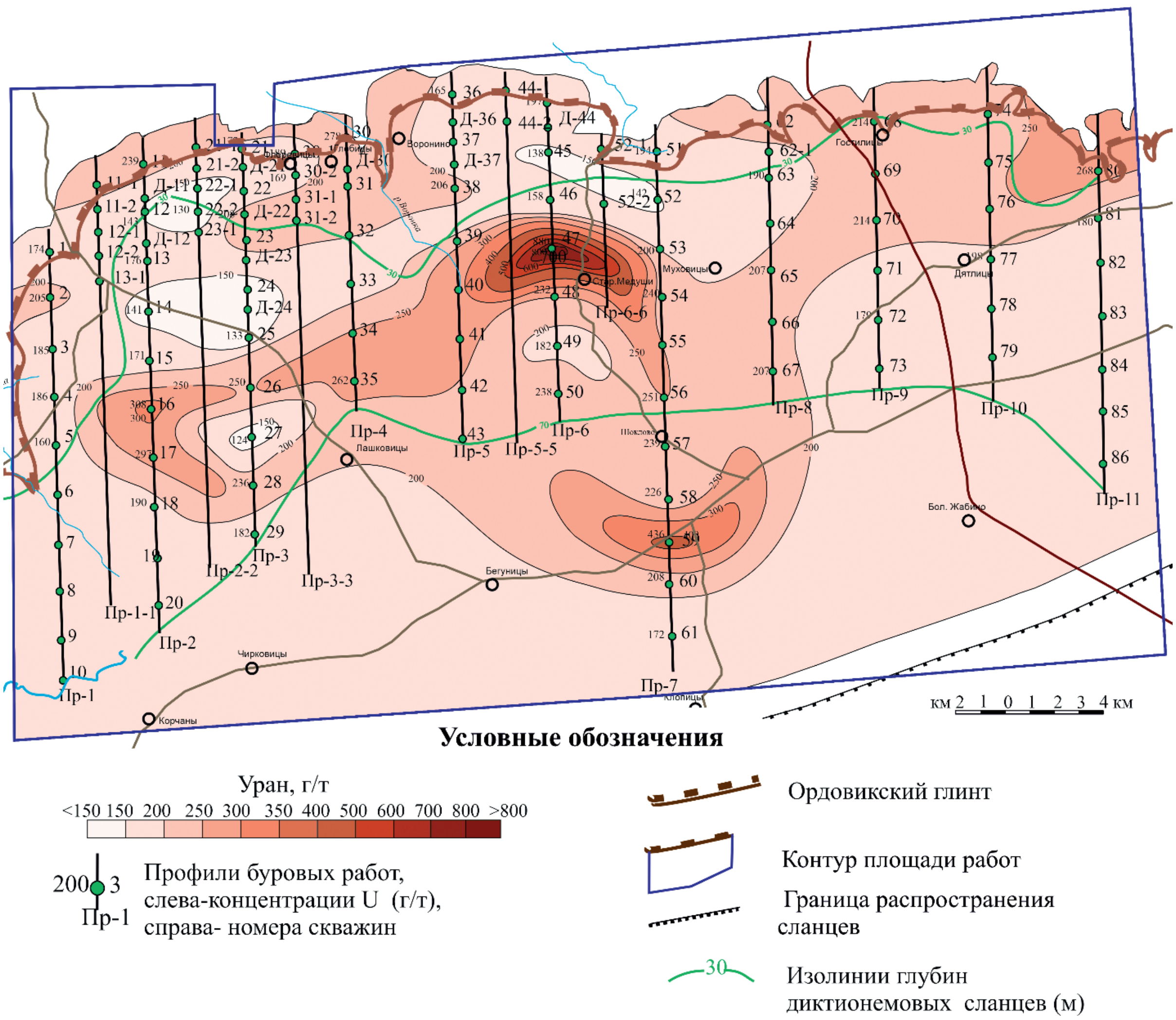

Fig. 5. Distribution of average uranium concentrations among wells in the productive horizon of the Dictyonema shale formation within the Kaibolovo-Gostilitskaya area according to (Vyalov et al., 2017)

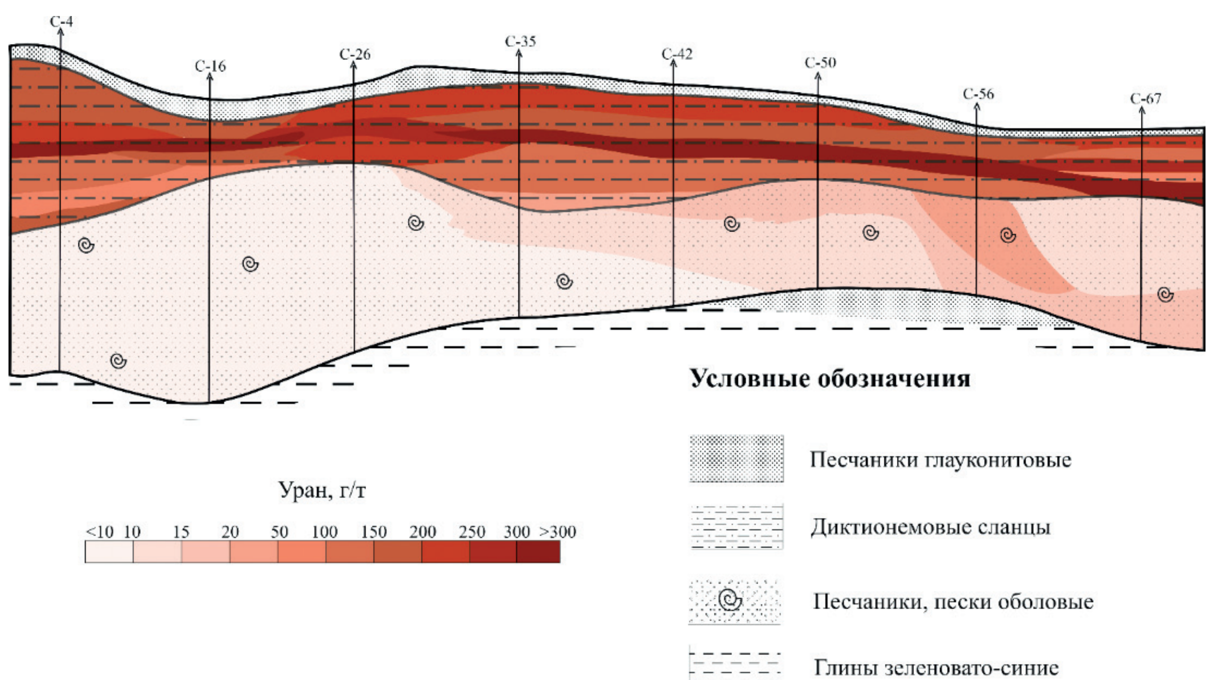

Fig. 6. Distribution of uranium in the section of Dictyonema shales formation and obolus sandstones along the profile of wells S-4 – S-67 according to (Vyalov et al., 2017). Horizontal scale 1:100,000, vertical for shales and sandstones 1:100, for supra-shale strata 1:1000

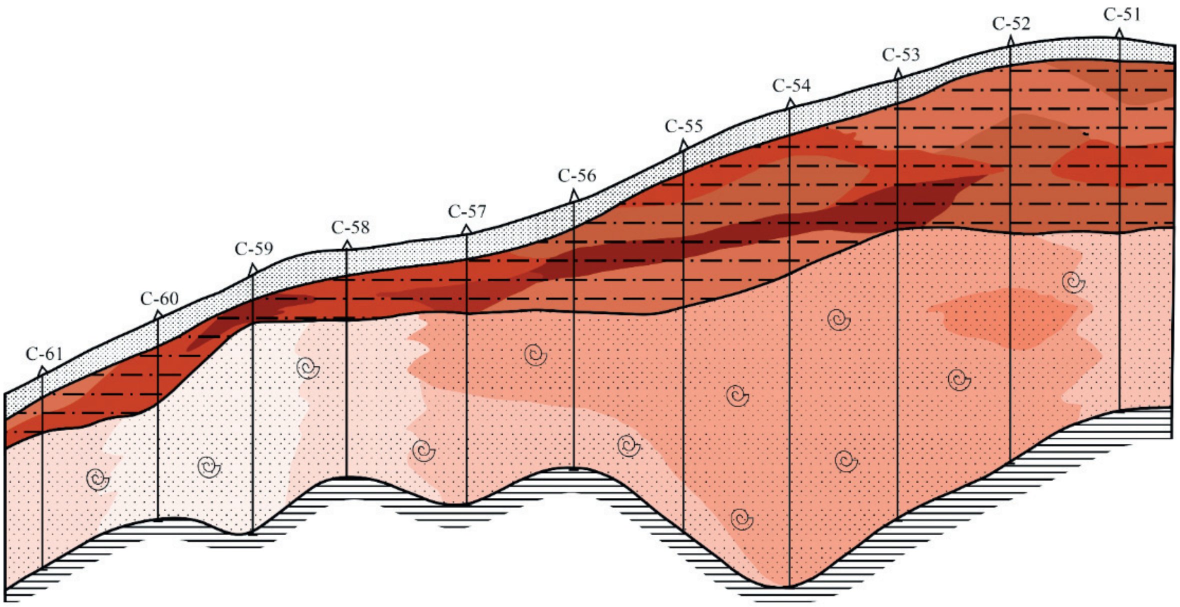

Fig. 7. Distribution of uranium in the section of the formation of Dictyonema shales and obolus sandstones along the profile of wells S-61 – S-51. For symbols, see Fig. 6. Horizontal scale 1:100,000, vertical for shales and sandstones 1:100, for supra-shale strata 1:1000

REE concentrations are higher in the underlying obolus sandstones.

Forms of occurrence and conditions of formation of uranium and rare earth elements in DS

Uranium. Previously, it was believed that the forms of uranium in the form of pitchblende constitute up to 10% of the total amount in DS, and in the composition of OM – up to 30%. Uranium was assumed to be present in significant amounts (30–40%) even in silicate and phosphate substances of the DS (Altgauzen et al., 1967; Davydova,Goldstein, 1967; Altgauzen, 1992; Mikhaylov et al., 2006).

Uranium in the form of an protoxidic-oxide form – pitchblende – was visually discovered during microprobing of concentric-zonal pyrite of Dictyonema shales in the form of rare small (several microns) mineral grains. According to microanalysis data, U is extremely unevenly present in iron sulfides, from 15.8 to 2780 g/t (Vyalov et al., 2013b). According to Professor S.I. Arbuzov (personal communication), uranium in iron sulfides cannot be present in the form of an isomorphic impurity due to its high charge and ionic radius. Consequently, it is present only in the form of micromineral inclusions. Uranium (usually in the form of pitchblende – raninite) forms mineral phases on the surface of pyrite or a fine-grained pitchblende-pyrite aggregate, which indicates the role of diagenesis and epigenesis in the distribution of uranium.

Based on the results of research in 2023, we detected uranium in apatite and monazite of Dictyonema shales in the form of an isomorphic impurity (Fig. 11, Table 1).

Table 1 shows that there is more uranium in apatite (0.47%) than in monazite (0.17% and, judging by the table data, this is coularite – a thorium-free supergene variety of monazite).

According to the results of rank correlation, uranium correlates with a number of associated metals (Vyalov et al., 2017). The average contents of a number of microelements in DS, determined using mass spectrometry carried out at the Central Laboratory of the Karpinsky Institute, are presented in Table 2 (Vyalov, Dyu, 2021).

With a large sample size n = 672, correlation coefficients (in descending order of r values): V (0.78), Rb (0.78), Ga (0.7), Cs (0.69), Sc (0.6), Ag (0.6), Mo (0.55), Cr (0.51), Sb (0.5), Cu (0.4), Ni (0.3) (Vyalov, Dyu, 2021).

Also of interest are the correlations between the contents of uranium and REE not only with other microelements of the DS, but also with the amount of C_{org}, C_{tot}, C_{carb} and S. The correlation was carried out on 72 DS samples (furrow samples) taking into account the number of analyzes performed for carbon and sulfur, the results are presented in Table 3.

As can be seen, the above bindings between uranium and other elements are well demonstrated in a much smaller (almost an order of magnitude) sample, which indicates their stability.

M.N. Altgauzen noted that the source of uranium in the DS was seawater, into which it fell from the demolition area (Altgauzen, 1992).

The variety of positive correlations between uranium and a number of valuable metals is apparently due to the common source of their entry into the sediment – sea water, in which many elements are dissolved.

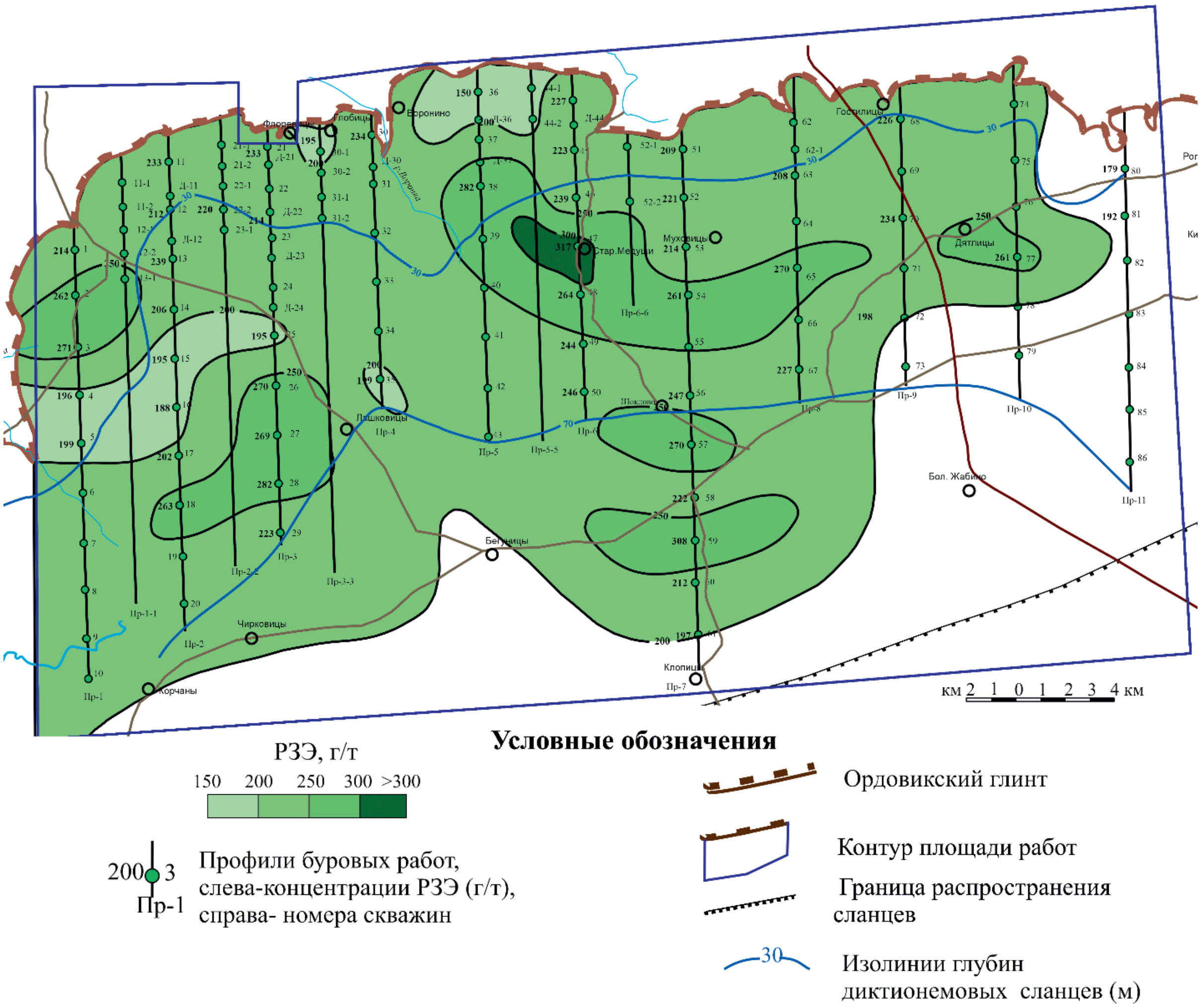

Fig. 8. Distribution of average REE concentrations among wells in the Dictyonema shale formation within the Kaibolovo-Gostilitskaya area

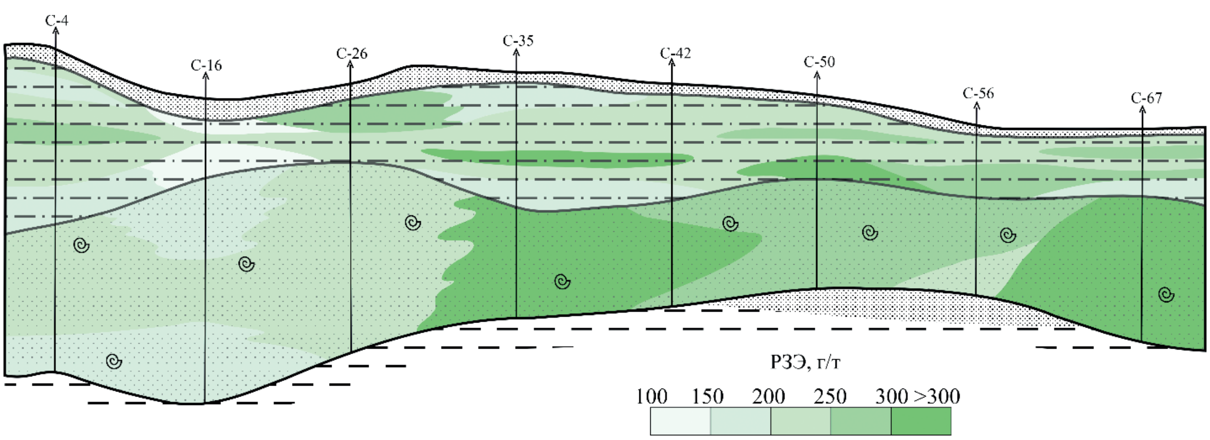

Fig. 9. REE distribution in the section of the Dictyonema shales and shell sandstones along the profile of wells S-4 – S-67. For symbols, see Fig. 7. Horizontal scale 1:100,000, vertical for shales and sandstones 1:100, for supra-shale strata 1:1000

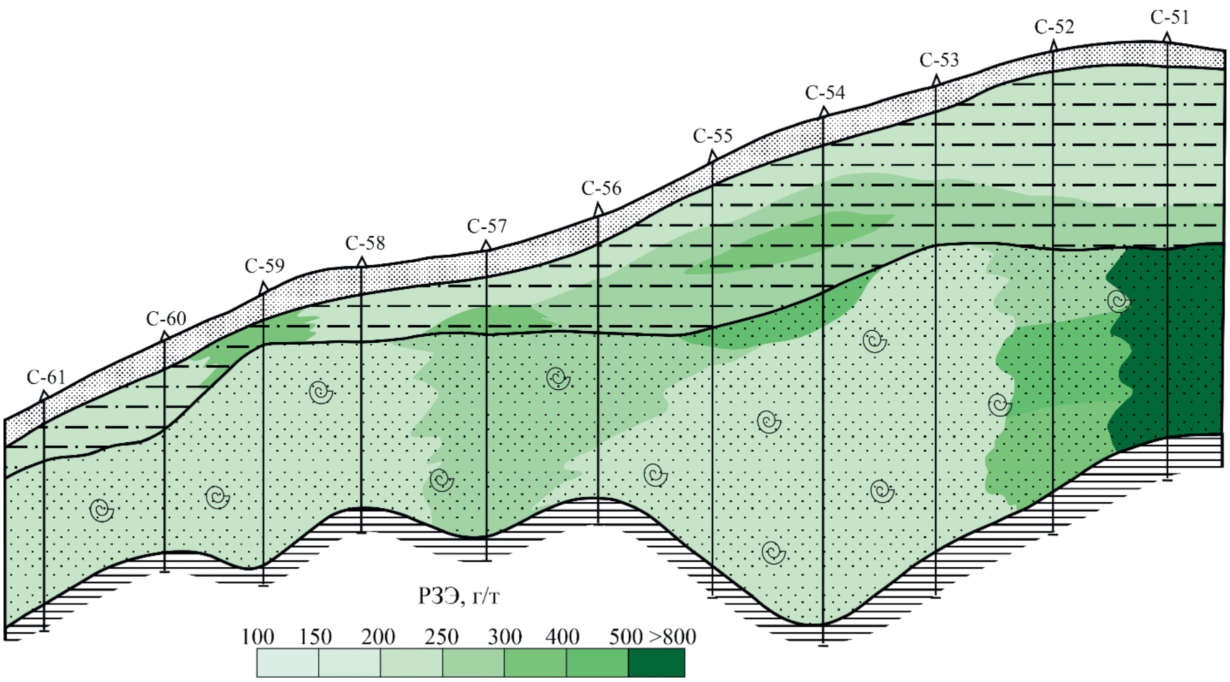

Fig. 10. REE distribution in the section of the Dictyonema shales and shell sandstones along the profile of wells S-61 – S-51. Horizontal scale 1:100,000, vertical for shales and sandstones 1:100, for supra-shale strata 1:1000

On the correlation between uranium and organic matter of DS. It is known that all types of aquatic organisms tend to accumulate uranium dissolved in water, thereby increasing its concentration in relation to the aquatic environment by tens and hundreds of times (Neruchev, 2007).

The sorption properties of OM were manifested both as a result of the intravital accumulation of metal (and many other trace elements) by graptolites and blue-green algae, and during the subsequent sorption of uranium (and many other metals) by dead OM in bottom sediments (Klyucharev, Soesoo, 2018).

Table 3 also shows a significant correlation between uranium and C_{org}, i.e. actually with OM. There is a strong relationship between C_{org} and C_{tot} (Fig. 12), therefore C_{tot} also significantly correlates with uranium.

Consequently, the amount of total carbon in the DS is determined primarily by organic carbon, i.e. OM.

In humic acids (HA) isolated from a DS sample with a uranium content of 156 g/t, the concentration of the element was 64.5 g/t (Vyalov et al., 2013a). The yield of HA is 15%, therefore, uranium makes up only 6.2% of the total amount. But HA are not all OM; there are also fulvic acids, so the amount of uranium in OM will be slightly higher (about 10%) for the studied DS sample. Hence a certain part of the uranium is obviously found in the OM.

Features of the distribution of uranium (and REE) in the mineral matter of DS can be studied on the basis of correlations with rock-forming oxides. The average contents of macroelements oxides in DS ash are given in Table 4.

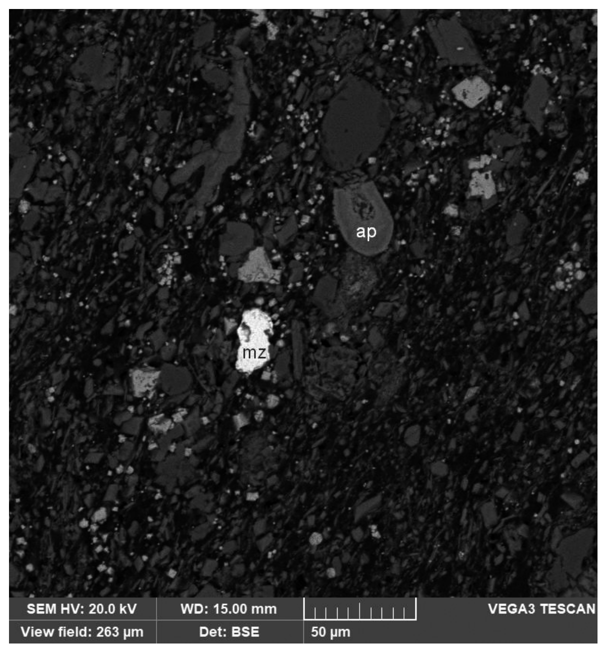

Fig. 11. Apatite (ap) and monazite (mz) in the composition of Dictyonema shales

Monazite	% wt	Apatite	% wt
O	27.59	O	37.95
Al	0.3	F	3.86
P	13.41	Na	0.84
La	13.83	P	15.5
Ce	31.1	S	1.08
Pr	2.9	Ca	39.44
Nd	9.94	Fe	0.32
Gd	0.75	Ce	0.53
U	**0.17**	**U**	**0.47**
Total	100	Total	100

Table 1. REE and U contents in accessories of Dictyonema shales according to microprobing data

Element	X_{av}	σ	min	max	Element	X_{av}	σ	min	max
Li	15.4	4.9	3.0	34.2	Rb	79.3	21.6	9.0	127.0
Sc	8.0	2.5	0.3	28.3	Sr	70.6	31.5	38.6	414.0
Co	12.3	5.8	1.1	56.9	Zr	115.9	83.5	32.0	366.0
Ni	128.5	62.2	6.0	512.0	Nb	10.6	2.6	0.3	16.5
Cu	68.6	50.3	12.0	263.0	Mo	153.0	108.0	1.7	562.0
Ge	1.7	1.3	0.7	19.2	Cs	2.0	1.1	0.2	17.1
Ag	1.5	0.7	< 0.01	6.8	Ba	3.3	1.2	0.02	7.4
Sb	6.6	3.5	0.1	23.5	Ta	0.8	0.2	0.02	1.6
Te	0.3	0.3	< 0.01	1.53	W	12.2	66.4	0.5	1400
Re	0.11	0.1	0.01	1.3	Th	10.7	2.4	3.0	17.7
Be	1.8	0.8	0.12	7.3	U	166.3	63.0	7.0	829.0
V	718.8	356.5	14.0	1600	REE	265.1	59.9	95.0	724.3
Cr	49.6	18.3	14.2	137.0	PGM	0.02	0.02	< 0.002	0.1
Ga	11.6	3.4	1.5	20.4	TiO_2	0.6	0.07	0.4	0.8

Table 2. Trace element composition of Dictyonema shales according to mass spectrometry data in g/t (n = 672) (Vyalov, Dyu, 2021). X_{av} – average value; σ – standard deviation; min – minimum value; max – maximum value; PGMs – platinum group metals

	S	C_{tot}	C_{carb}	C_{org}	Li	Sc	Co	Ni	Zn	Ge
U	0.05	0.24	–0.14	0.28	0.65	0.62	0.13	0.37	–0.01	0.32
REE	–0.12	–0.3	–0.25	–0.23	–0.16	0.11	–0.01	–0.07	–0.21	0.21
	Ag	Sb	Re	Be	TiO_2 %	V	Ga	Rb	Sr	Y
U	0.66	0.37	0.31	0.45	0.55	0.67	0.56	0.53	–0.17	0.24
REE	0.27	0.13	0.08	0.16	0.24	0.24	0.04	0.03	0.21	0.89
	Zr	Nb	Mo	Cs	Ba	Ta	Th	U	REE	PGM
U	0.2	0.59	0.59	0.48	0.46	0.31	0.7	1.00	0.2	0.24
REE	0.53	0.17	0.08	–0.07	0.12	0.34	0.44	0.2	1.0	–0.19

Table 3. Correlation of U and REE with carbon species, sulfur and other elements. n = 72, r = 0.22 – critical correlation coefficient – the correlation is positive starting from 0.22, negative – from –0.22, p = 0.95. Green color – correlation from 0.22 to 0.29, yellow color – correlation from 0.30 to 0.69, orange color – correlation from 0.70 to 0.99

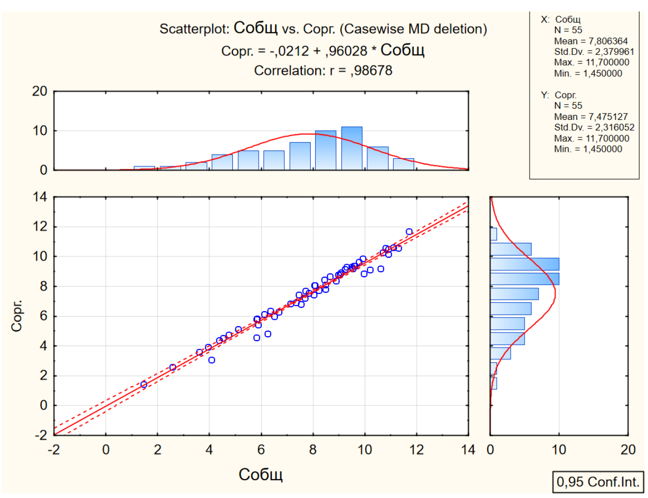

Fig. 12. Correlation between C_{org} and C_{tot}

According to the results of correlation analysis (sample of 90 samples, significant correlation coefficient r = 0.23), uranium is interrelated with the following macroelements: Mg (0.59), Al (0.57), K (0.52), Fe (0.45), Na (0.37) (Vyalov, Du, 2021).

Table 5 presents new data on the correlation of uranium, rare earth elements with oxides of macroelements (with a sample of n = 55 determined by the number of analyzes performed (XRD) for macroelements).

The set of oxides of rock-forming elements that interact positively with uranium remained the same even when the sample was reduced from 90 to 55.

It is likely that uranium is sorbed on clay minerals that are part of the DS. How can we explain the binding between uranium and TiO_2? This may be due to the fact that hydrated rutile (in sediments) exhibited high adsorption activity towards the water-soluble form of uranium (UO_2^{+2}) and can act as its sorbent, as shown in (Razvorotneva, Markovich, 2012).

The uranium content has a significant negative correlation not only with SiO_2, but also with the ash content of the DS (Table 5), since silica is the main ash-forming component (Table 4).

Table 6 shows the correlation between macronutrient oxides, DS ash content, carbon species and sulfur. With an increase in silica and ash contents, the contents of total carbon, organic carbon, and even carbonate carbon decrease (Table 6, Fig. 13).

An increase in silica content leads to an increase in the ash content of the DS and a decrease in the amount of OM concentrating uranium, which is an indirect reason for the negative relationship between uranium and SiO_2.

The correlation of uranium content is also negative with CaO. Consequently, alkaline environmental conditions were not conducive to the precipitation of uranium. Thus, both silicate (quartz) and carbonate substances DS cannot contain uranium in a noticeable amount. This does not reject the assumption that

SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	LOI
58.3	0.55	8.41	5.89	0.03	0.99	2.3	0.11	5.03	0.42	18.1

Table 4. Contents of main petrogenic oxides and loss on ignition (LOI) in Dictyonema shales in% (Vyalov, Dyu, 2021)

Oxides	U	REE
Ash	–0.46	0.26
SiO_2	–0.43	0.16
Al_2O_3	0.49	–0.13
TiO_2	0.64	0.06
Fe_2O_3 tot	0.22	0.24
MnO	–0.37	–0.04
MgO	0.29	–0.19
CaO	–0.36	–0.06
Na_2O	0.27	–0.29
K_2O	0.44	–0.19
P_2O_5	–0.1	0.19
LOI	0.49	–0.22

Table 5. Correlations of uranium, rare earth elements with oxides of macroelements. Note: LOI – loss on ignition. Significant r = 0.27, n = 55 p = 0.95. Green color – connection from 0.27 to 0.29, yellow color – connection from 0.30 to 0.69

up to 30–40% uranium can be contained in silicate and phosphate substances of DS (Altgauzen et al., 1967; Davydova, Goldstein, 1967; Altgauzen, 1992; Mikhaylov et al., 2006): as assumed above, it can be sorbed on clays; in DS phosphates, uranium was experimentally established in apatite and accessories from the demolition area (monazite).

Iron (according to its values in the oxide form, according to XRD data) has a high correlation with sulfur (Table 6, Fig. 14), which indicates the predominant localization of iron in sulfides, which was noted in petrographic studies.

There is a correlation between uranium and iron (with a sample of n = 90, r = 0.45 (Vyalov, Dyu, 2021)), and with a sample of n = 55, r = 0.22, a weak correlation was obtained (Table 5). This suggests a close association of uranium with sulfides; it has been established that

Oxides	Ash	S	C_{tot}	C_{carb}	C_{org}
SiO_2	0.88	–0.42	–0.86	–0.38	–0.82
Al_2O_3	–0.84	–0.08	0.83	0.12	0.84
TiO_2	–0.66	–0.1	0.56	–0.01	0.58
Fe_2O_3 tot	–0.19	0.93	–0.07	0.13	–0.09
MnO	0.43	–0.03	-0.20	0.36	–0.27
MgO	–0.52	0.11	0.61	0.46	0.55
CaO	0.35	0.01	–0.1	0.4	–0.17
Na_2O	–0.48	0.3	0.49	0.29	0.46
K_2O	–0.84	–0.07	0.85	0.14	0.86
P_2O_5	0.21	0.24	–0.29	–0.21	–0.26

Table 6. Correlation between macronutrient oxides, ash content of Dictyonema shale, carbon species and sulfur. Note. Significant r = 0.27, n = 55, p = 0.95. Green color – connection from 0.27 to 0.29, yellow color – connection from 0.30 to 0.69, orange color – connection from 0.70 to 0.99

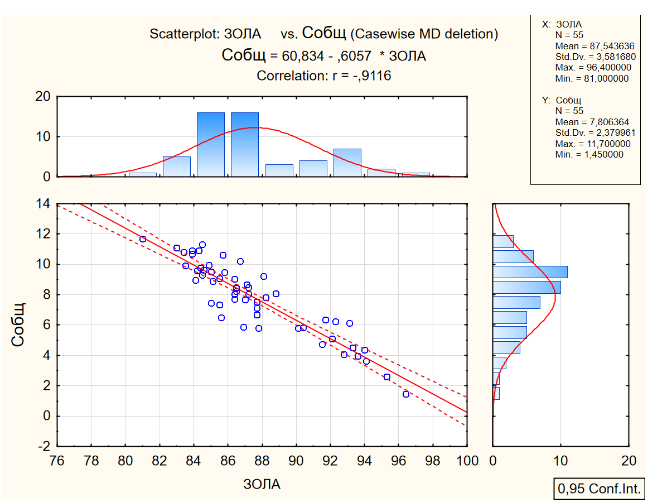

Fig. 13. Correlation C_{tot} – ash content of Dictyonema shale

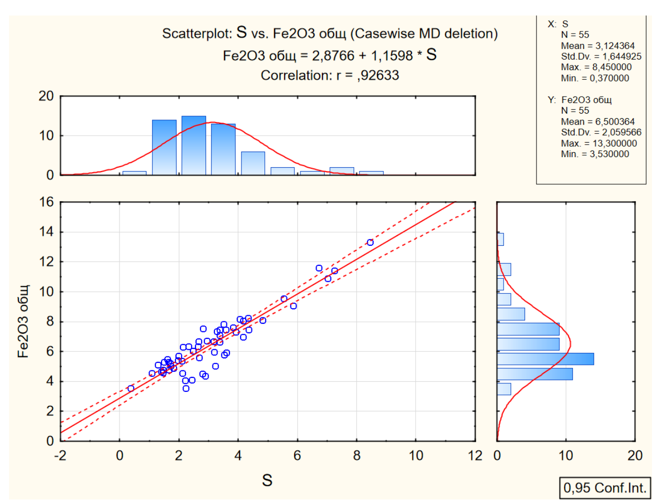

Fig. 14. Correlation of S and Fe_2O_3

uranium is extremely unevenly, from 15.8 to 2780 g/t, diagnosed during microanalysis of pyrite (Vyalov et al., 2013b).

A reducing environment is favorable for the accumulation of U, as well as V, Mo and other valuable metals from bottom waters. The large amount of organic matter in the sediment allows the development of bacteria that reduce the sulfates of seawater and release hydrogen sulfide, which reacts with iron to form pyrite. Note that the content of total sulfur in the DS of the Baltic basin was determined in the amount of 2.26–3.81%, pyrite sulfur – 1.46–2.98%, sulfate – 0.26–0.48%, organic sulfur – 0, 22–0.6% (Kivimägi, Loog, 1973).

It seems that uranium is most associated with shale OM, since its content in the stratigraphically lower layer of obolus sandstones (phosphorites) is significantly lower by several times – up to an order of magnitude or more, usually only 10–15 g/t, apparently due to the practical absence in them OM (and OM is a U concentrator, as shown above). However, in the obolus sandstones the sedimentation environment was alkali-type or slightly alkaline, which also did not contribute to the precipitation of uranium.

Rare earth elements. The occurrence of REE in the mineral part of the DS is similar to uranium: they can be found in the form of impurities in apatite or in its own mineral – monazite (Table 2, Fig. 11), which was noted earlier (Vyalov et al., 2014, etc.). However, in apatite from REE only Ce (0.53%) is detected, and in monazite the spectrum of REE is much wider – it is not only the predominant Ce (31.1%), but also La, Pr, Nd, Gd. This is due to the formation of apatite during sedimentation and diagenesis, with the solubility and mobility of Ce in water, while monazite is accessory, brought from the area where weathered igneous rocks were demolished.

The conditions for the formation of rare earth mineralization (applicable to uranium) in the DS were reconstructed based on calculations of geochemical indicators (Vyalov et al., 2014), the values of which were later refined using more factual material (Vyalov, Dyu, 2021): Ce/Y = 1.8; Ce/Ce* = 3.7; La/Yb = 9.8. The Ce/Y ratio allows one to distinguish between continental and marine sediments, which is due to the fractionation of REE during sedimentation. As is known (Yudovich, Ketris, 2011), with depth the Ce content decreases due to its oxidation and precipitation with Mn-Fe-hydroxide phases, while at the same time the content of other rare earth elements increases. There is almost 2 times more light lanthanide (Ce) in the DS than heavy lanthanide (Y), which suggests accumulation conditions near the continent. The cerium anomaly Ce/Ce* (3.7) indicates sedimentation in a passive continental margin setting. Based on the value of the La/Yb ratio, equal to 9.8, we can conclude that acidic magmatic formations predominate in the feeding areas – sources of uranium and other metals from the demolition area (granitoids of the Baltic crystalline shield).

The behavior of REE in DS differs from uranium: there is a binding between REE and the ash content of DS, and the correlations with C_{org}, C_{tot}, C_{carb} and S are negative (with carbon varieties – significant, with sulfur – below the critical value). REE are strongly correlated with other small trace elements (Y, Zr) than uranium; there is a low correlation with Ta, Th and a weak correlation with V, Ti, Ag (Table 3). Directly with uranium, REE have a weak positive correlation, slightly below critical values, explained by their co-occurrence as impurities in phosphates.

Rare earth elements in DS have a positive correlation with phosphorus (r = 0.19 at n = 55, Table 6), (r = 0.45 at n = 40 (Vyalov et al., 2014)), which indicates localization of REE in phosphorite varieties of two types: carbonate-fluorine-apatite shell fragments (Ca, F, P) and apatite in the form of small crystals, diagnosed by electron microscopic studies (Vyalov et al., 2014). There is probably a correlation between REE and manganese and iron because Ce, which predominates in the REE composition (and not only it) was deposited with Mn–Fe-hydroxide phases.

The answer to the question whether REE are included in the organic matter of DS has been established experimentally. DS was extracted with various solvents (see above). The extractants were analyzed using mass spectrometry. The results are presented in Table 7.

Thus, in humic acids, as well as in carboxylic acids including fulvic acids extracted from DS, a low (compared to the total concentration in the sample) REE content was found, which indicates an insignificant effect of OM on their concentrations. (According to preliminary data, at least 5% of the amount of REE may be contained in the OM of Dictyonema shales, for the studied sample with a total low REE content of less than 65 g/t without yttrium. We assume that in shales with a higher REE content their relative proportion in the OM may be slightly higher).

It should be noted that in the DS the relative amount of heavy, or yttrium, lanthanides (Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) in the total concentration of all lanthanides (light, or cerium, – La, Ce, Pr, Nd , Sm, Eu and the indicated heavy ones) is 15.6% (according to Table 1 (Vyalov et al., 2014)). Thus, we can conclude that in DS the share of heavy (and most valuable) lanthanides is significantly higher than in the world's confirmed reserves of REE, where the share of heavy REEs accounts for only about 7% (Review of the rare earth elements..., 2018).

Resources of uranium and rare earth elements in DS. Table 8 shows the metal content of the characterized rocks, shows the concentrations and resources of U and REE of the Kaibolovo-Gostilitsy area, specified by sections (Fig. 15).

As can be seen from Table 8, in the studied exploration area and its sections, incl. promising for priority development (quarries), concentrated huge resources of uranium and rare earth elements, comparable with early estimates (Vyalov et al., 2013; Vyalov et al., 2017). Based on their potentially industrial recoverable reserves, the Kaibolovo-Gostilitsy area can be considered a unique deposit of these scarce metals, rather poor individually, but potentially industrial complex ores.

The updated forecast uranium resources in the productive horizon DS within a given area in categories P_2 and P_1 are estimated at 630.9 thousand tons. With the conversion factor of forecast uranium resources into industrial reserves K_p = 0.2 and the uranium recovery factor K_i = 0.8, they will amount to 109.94 thousand tons. Valuation of industrial uranium reserves (at the world spot price as of March 22, 2022, $59.75/lb (https://www.tadviser.ru/index.php/Article:Uranium_market)) is $14.5 billion.

The predicted resources of REE in the DS within the area under consideration in category P_3 are 777 thousand tons. At K_p = 0.2 and K_i = 0.6, industrial reserves are 93.24 thousand tons. The potential value of recoverable industrial reserves of REE was estimated at about 470 billion roubles (Balakhonova et al., 2013).

Discussion and conclusions

Based on the results of analysis using the mass spectrometry method of DS samples from wells in the Kaibolovo-Gostilitsy area, it was established that potentially industrial mineralization of uranium and rare earth elements is developed in the shales, which is promising for development with their joint complex extraction. Contents of uranium and rare earth elements

Fractions	La (19)	Ce (25.4)	Pr (2.58)	Nd (8.74)	Sm (1.4)	Eu (0.44)	Gd (1.08)
B-1	6.42	8.38	0.80	2.64	0.46	0.11	0.43
B-2	13.65	22.60	2.42	8.70	1.51	0.32	1.48
B-3	18.55	24.95	2.44	8.15	1.32	0.34	1.23
B-4	20.95	27.50	2.72	9.60	1.57	0.41	1.58
B-5	23.40	30.65	3.05	10.12	1.79	0.42	1.63
B-6	4.67	9.28	1.04	4.02	0.73	0.16	0.80
Detection limit	0.01	0.01	0.01	0.01	0.01	0.005	0.01
Fractions	Tb (0.17)	Dy (0.87)	Ho (0.18)	Er (0.61)	Tm (0.11)	Yb (1.03)	Lu (0.16)
B-1	0.05	0.30	0.06	0.20	0.04	0.32	0.05
B-2	0.19	1.16	0.24	0.76	0.12	0.93	0.15
B-3	0.15	0.80	0.19	0.53	0.10	0.95	0.14
B-4	0.19	0.90	0.18	0.57	0.10	0.94	0.15
B-5	0.19	1.00	0.21	0.59	0.11	0.98	0.15
B-6	0.10	0.50	0.09	0.23	0.03	0.21	0.03
Detection limit	0.01	0.01	0.01	0.01	0.005	0.01	0.002

Table 7. Contents of elements in fractions of Dictyonema shale, g/t (next to the element index in parentheses its content in an ordinary sample of shale subjected to extraction is indicated). Note. B-1 – humic acids, B-2 – residue after treatment with HNO_3, B-3 – residue after treatment with hydrogen peroxide, B-4 – residue after extraction with benzene, B-5 – residue after removal of humic substances, B-6 – water-soluble carboxylic acids, incl. fulvic acids (collected on activated carbon)

	Full territory, without detailed area	Western area, without detailed area	Detailed area	Quarries area	Eastern area
			Data		
S, km^2	593.4	159.4	46.6	10.8	270
Thickness of layer of DS, m	1.8	1.67	3.60	4.69	2,08
Sp. wt of DS, g/cm^3	2.403	2.403	2.403	2.403	2,403
Metals			Average content, g/t		
U	219.3	197.2	168.7	179.7	226,3
REE	264.4	260.4	243.9	253.0	265,7
			Predicted resources, t		
Metals	Full territory, (without detailed area) category P_2	Western area, (without detailed area) category P_2	Detailed area category P_1	Quarries area category P_1	Eastern area category P_2
U	562875	126144	68008	21873	305397
REE (on TR_2O_3)	678633	168874	98323	30794	358569

Table 8. Uranium and REE contents and their predicted resources in the productive horizon of the Dictyonema shale formation of the Kaibolovo-Gostilitskaya area

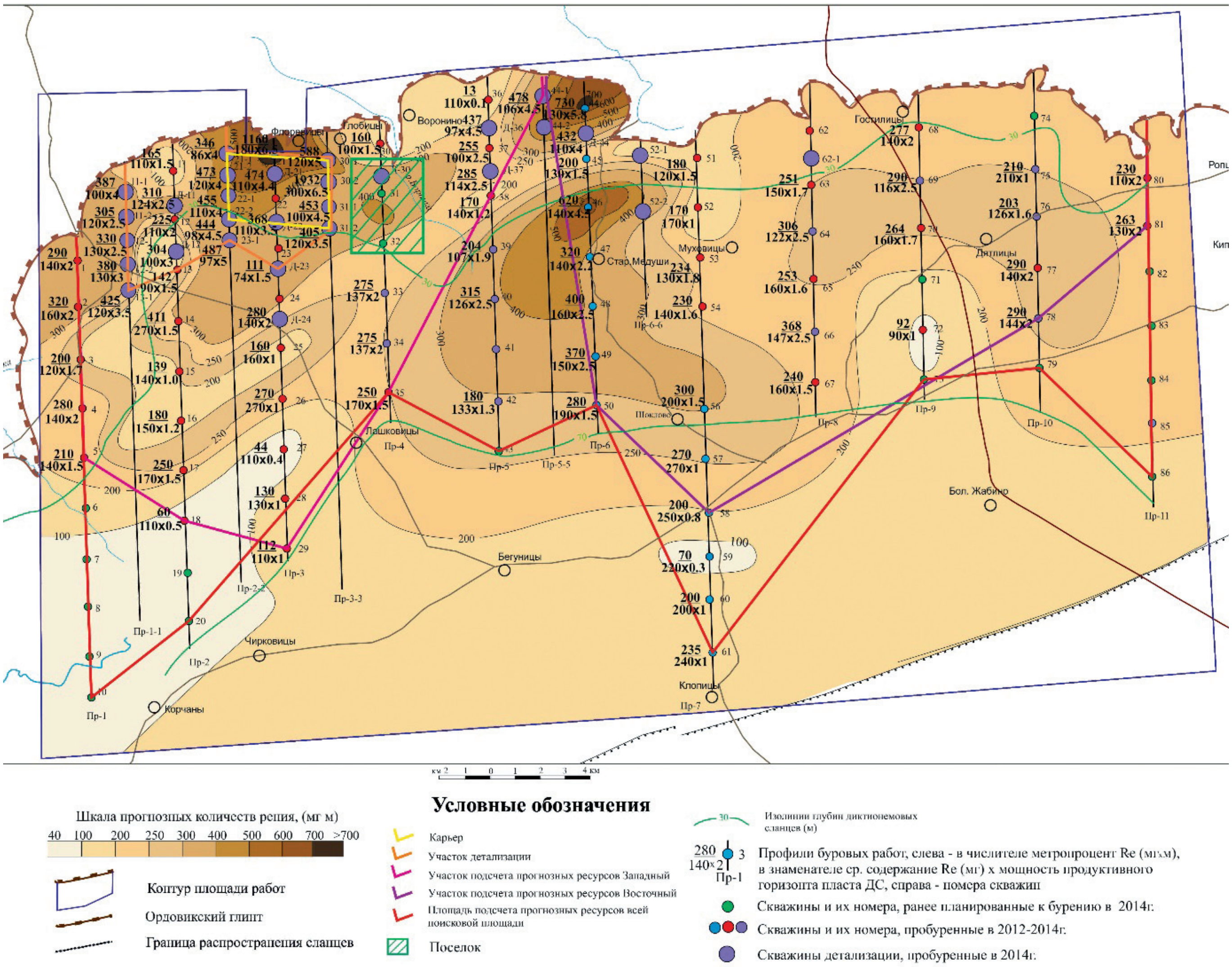

Fig. 15. Areas for calculating predicted U and REE resources

in DS on the territory of the Leningrad region can reach the minimum industrial concentrations specified in the State Balance of Mineral Reserves of the Russian Federation for industrial types of ores for uranium and rare earths (State balance of mineral reserves..., 2019a, 2019b).

Uranium and REE in DS are found in accessory minerals – apatite and monazite – in noticeable quantities (according to microanalysis data, uranium is up to 0.47% and 0.17%, respectively (Table 4). However, in the petrographic composition of DS, monazite accessory elements are rare (less 1%). Apatite makes up the first percent. The contribution of uranium from accessory monazite or apatite to its total concentration in shales seems to be low. Uranium is partially sorbed on clays, as it correlates with a number of macroelements of the clay substance. According to microanalysis data, U is extremely unevenly, from 15.8 to 2780 ppm (Vyalov et al., 2013b), associated with iron sulfides, which indicates the large role of diagenesis and epigenesis processes in its concentration and distribution in DS. Negative correlation of uranium with ash content of DS, silica, positive correlation of uranium with C_{org}, its noticeable concentrations in the fractions of humic and carboxylic acids isolated from shale, including fulvic acids, clearly indicate the significant role of OM in its accumulation.

The high content of uranium in carbonate-fluorine-apatite of shell fragments (0.47%) indicates the processes of its capture from sea waters during the replacement of carbonate detrital material with phosphorus. The genesis of phosphorites in the Baltic sedimentary paleobasin was associated with the phenomenon of coastal upwelling, which ensures high biological productivity of phytoplankton (Vyalov et al., 2014).

For comparison, we note that in the black shales of the Bureinsky massif (graphite and graphite shales), the mineral carriers of REE are monazite and, probably, xenotime (Cherepanov, Gostishchev, 2017). But in the DS of the Baltic basin, the REEs of a single monazite are unlikely to contribute a significant proportion to their total concentration. The connection of REE with phosphorus unambiguously indicates the localization of REE in phosphorites (in fragments of obolus shells transformed into phosphorite and in fine-crystalline apatite). The DS contains only a few percent of these phosphorites. Thus, the contribution of REE in apatites to the DS is more significant than in monazite, but predominantly Ce is found in apatite.

Sorption of REE by clay matter, according to the negative correlation of REE with Al, did not occur, and the positive correlation of REE with calcium, sodium, magnesium indicates the accumulation of REE in an alkaline environment.

In humic acids, as well as in carboxylic acids, including fulvic acids extracted from DS, the REE content is found to be low compared to the total concentration in the shale sample. With a low amount of OM from Dictyonema shales (8–15%) and the content of humic acids from the extracted sample (15%), this indicates an insignificant role of OM in the REE concentration.

It was noticed (Vyalov et al., 2014) phosphate substitution and decrystallization of sclerotia with the formation of small apatite crystals in the DS, which clearly occurred during the process of diagenesis. All this shows the great complexity of the processes of accumulation of uranium and rare earth elements during the formation of DS.

The studied metals accumulated in sediments of future DS in Early Ordovician time in the conditions of a bay-strait-shaped shallow sea basin with normal salinity. The area of demolition was the acidic magmatic formations of the Baltic shield – sources of uranium and rare earth elements, and many other metals during the weathering of these rocks. A large amount of organic material and the reducing hydrogen sulfide conditions that existed at that time created favorable conditions for the sorption of uranium from bottom waters. However, it could be concentrated during diagenesis and the formation of apatite as an impurity in this mineral.

In dictyonema sediments, which were formed in a shallow sea in a reducing hydrogen sulfide environment, REE – containing phosphatized fragments of shells of brachiopods of the genus *Obolus* – appeared, apparently, during the erosion and redeposition of the Dictyonema shales and obolus sandstones lying stratigraphically below.

The studies have shown that the Dictyonema shales of the Baltic sedimentary paleobasin are a potentially valuable complex ore mineral raw material for scarce strategic metals (U and REE) and represent a large potential unconventional mineral resource base of uranium and REE even within the studied Kaibolovo-Gostilitsy area. The source of this raw material (the Baltic sedimentary basin) is located in favorable infrastructure conditions (Leningrad region). Moreover, the resources of uranium and REE in the future can be increased many times over at the expense of other areas of this paleobasin in comparison with those already assessed in the studied exploration area.

Acknowledgements

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Уран и редкоземельные элементы в диктионемовых сланцах Прибалтийского бассейна (Кайболово-Гостилицкая площадь)

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В работе представлены результаты многолетних исследований диктионемовых сланцев (ДС) Прибалтийского бассейна (Ленинградская обл., Кайболово-Гостилицкая поисковая площадь) на уран и редкоземельные элементы (РЗЭ) – в качестве перспективного нетрадиционного источника дефицитного стратегического сырья для энергетики и целого ряда важнейших отраслей промышленности. Приведены новые данные по вещественно-петрографическому составу и металлоносности ДС, актуализированы и дополнены сведения по особенностям уранового оруденения ДС. Детализированы особенности распространения урана в пласте ДС по площади и в разрезе по профилям скважин. Впервые представлены данные по концентрациям РЗЭ в ДС, полученные на большом аналитическом материале (672 проб). Отмечены особенности распределения РЗЭ по площади поискового участка и в разрезе осадочной толщи по профилям скважин. Проведено дополнительное изучение минеральных примесей ДС по новой методике площадного сканирования препаратов электронно-зондовым микроанализатором с применением программного модуля Feature. Уточнены корреляционные связи между концентрациями урана и РЗЭ с другими микро- и макроэлементами, в том числе изучены связи урана и РЗЭ с $C_{орг}$, описаны разнообразные формы нахождения урана и РЗЭ в ДС, показана роль органического вещества в их концентрации, детализированы условия формирования уранового и редкоземельного оруденения в черных сланцах. Оценено содержание урана в ДС в пределах отдельных участков Кайболово-Гостилицкой площади, уточнена стоимостная оценка возможных извлекаемых промышленных запасов потенциального рудного сырья изученных остродефицитных металлов. Обосновано положение о том, что минерально-сырьевая база урана и РЗЭ в России может быть значительно увеличена за счет их наличия в ДС Прибалтийского осадочного палеобассейна в условиях развитой инфраструктуры средней полосы Российской Федерации.

Ключевые слова: диктионемовые сланцы, черные сланцы, металлоносность, оруденение в черных сланцах, уран, редкоземельные элементы, прогнозные ресурсы

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