

Experimental geoecology

Konopleva I.V., Sevast'yanov V.S., Kuznetsova O.V., Vlasova L.N., Galimov E.M. Experimental modeling of biota's organic matter catagenetic transformation. Relationship with oil genesis.

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An experiment on a thermal hydrolysis of the biota, which was sampled in the thermal lakes of the Uzon caldera on the Kamchatka, has been performed. The biota is considered as a source of Uzon oil seeps. The oil was sampled in the hydrothermal field. The biomarker composition of the biota, the thermal hydrolysis products and the oil was analyzed. The geochemical parameters on the composition of steranes and terpanes were calculated. It is shown that a thermal treatment of the biota leads to almost complete degradation of the biohopanes. As a result of the thermal hydrolysis, the sterane coefficients of maturity reached values close to those found for the oil structures. Similarity in the biomarker composition and distribution in the hydrothermal oil, the biota, and the thermohydrolysis products of the biota have been observed. The Uzon oil is the product of the thermal processing of the biota that inhabits the hydrothermal area.

Keywords: *biota thermohydrolysis, hydrothermal oil, biomarker analysis, Uzon caldera, Kamchatka*

“Young” oil sources were discovered in the Kamchatka volcanic activity zone, in the hydrotherms of the volcano Uzon caldera's area. The Uzon oil was formed by one estimate, about 1,000 years ago, according to others its age does not exceed 50 years. It's assumed that biomass of microorganisms and plant detritus in the caldera is a source of organic matter for oil.

This study was conducted to identify the nature of organic matter from which the hydrothermal oil was formed and also to find the genetic relationship of the Uzon oil with organic matter of the biota that inhabit the caldera's hydrothermal lakes. The research tasks included a study of the thermal effects' influence on the change in the composition of biota's organic matter. High temperatures allow one to experimentally simulate the influence of low temperatures and the duration of geological time on the course of natural processes.

Objects and methods of research

The oil was sampled by skimming from surface films on hot water in holes dug within the bounds of the central hydrothermal field. The sample of the biota, inhabiting in the thermal small lakes, was collected at the same hydrothermal area. The sample consisted of organic and mineral matter. It was decarbonatized, washed and dried. An experiment simulating a catagenetic transformation of the biota: a thermal hydrolysis in a platinum ampoule at 300°C for 24 hours was carried out. The oil samples (Uz1,

Uz2), chloroform extracts of the biota and the hydrothermally altered biota (biota1) were subjected to elution from a chromatographic column with n-hexane. The chromatographic column was filled by silica gel in advance impregnated with 10% AgNO₃ solution. Analyses of biomarkers in the eluents were performed by gas chromatography mass-spectrometry (GC-MS). The GC-MS was Thermo Fisher Scientific Trace GC coupled to mass spectrometer Polaris Q. We used a composite (30 m TR-MS and a 30 m TR-5MS), fused silica capillary column (60 m x 0.25 mm i.d., 0.25 μm film thickness) and He, as a carrier gas. The temperature program was as follows: 80°C hold for 1 min, ramp at 4°C/min to 200°C, 200°C hold for 1 min and then 3°C/min to 300°C and hold for 40 minutes. The MS was operated in the electron impact mode with 70 eV ion source energy and scan range from 50 to 650 Da at 3 scan/s. The temperature of the evaporator and interface was 300°C.

Results and discussion

The compounds in petroleum derived from formerly living organisms are called biomarkers. They show little or no changes in their structure from the parent organic molecules. The composition and distribution of biomarkers allows to determine the origin of oil, as well as to assess the extent of primary organic matter (OM) transformation, or the degree of maturity. Uzon oil is enriched by steranes with a biological configuration ($\alpha\alpha\alpha R$), their share accounted for 50 - 60% of the total isomers. Stigmastane (C₂₉) and ergostane (C₂₈) are predominating among the steranes. Terpanes are mainly represented by hopanes (C₂₇-C₃₅). The content of tricyclic terpanes is negligible. The steranes can have R- and S-configuration at the acyclic carbon atom C-20, resulting in two homologue series with 20R (20R $\alpha\alpha\alpha$ and 20R $\alpha\beta\beta$) and 20S (20S $\alpha\alpha\alpha$ and 20S $\alpha\beta\beta$) configurations. The biomolecules of the sterane with the C20R configuration are converted into more stable molecules with C20S, and the regular $\alpha\alpha\alpha$ steranes transform to more stable forms of isosteranes $\alpha\beta\beta$ due to isomerization transformations, which take place during the catagenetic process. The degree of catagenetic transformations of rock OM and oil, generated by this OM, is characterized by the parameters based on ratios of biomolecules and the new formed isomers: $k_1 C_{29} = \alpha\alpha 20S / (\alpha\alpha S + \alpha\alpha R)$; $k_2 C_{29} = \beta\beta (20S + 20R) / \beta\beta (S + R) + \alpha\alpha (S + R)$. The maturity coefficient $k_1 C_{29}$ increases to range 0,20-0,25 in poorly converted OM and reaches equilibrium values of 0,50 to 0,55 at the middle stages of catagenesis. Coefficient $k_2 C_{29}$ reaches values of 0.5-0.85 in the main zone of oil generation.

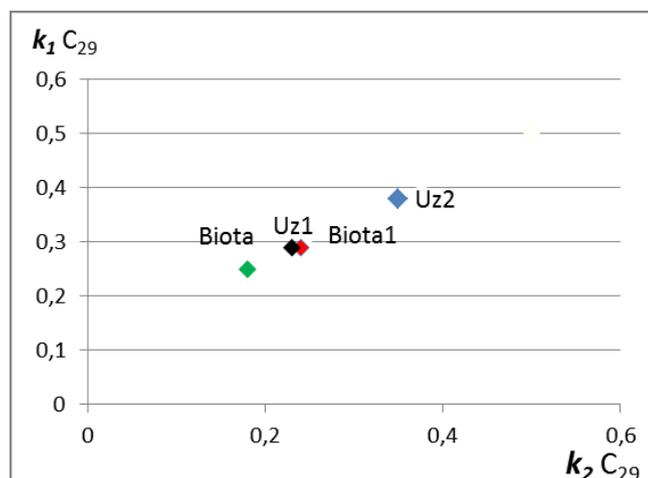


Fig.1. The distribution of the biota, the hydrothermally altered biota and the Uzon oils in the coordinates of the sterane maturity coefficients.

Fig. 1 shows distribution of the biota, the hydrothermally altered biota and the oils in the coordinates of the maturity coefficients. It is seen that the degree of catagenetic transformation increases in the row: biota <Uz1< biota 1 <Uz2. The maturity parameters k_1C_{29} and k_2C_{29} are significantly less than the thermodynamic equilibrium ones. The low values of k_1C_{29} (0,23-0,29) and k_2C_{29} (0,35-0,38) indicate the weak catagenetic transformation of the oil. The inhomogeneous heating in the oil formation zone because of the inhomogeneous heat flow in the hydrothermal fields is the probable reason of the observed variability in the values of the oil maturity degrees.

The results of the biomarker analysis are presented in the Table 1.

Table 1. The biomarker geochemistry parameters of the oils, the biota and the hydrothermally altered biota

n	Sample	Steranes		Hopanes				
		$C_{27}:C_{28}:C_{29}$ ($\alpha\alpha\alpha$)	Bio / iso-steranes C_{29}	$22S/(22S+22R)$ $\sum(C_{31}-C_{35})$	Ts/Tm	C_{35}/C_{34}	$\sum(C_{31}-C_{35})/C_{30}$	C_{29}/C_{30}
1	Biota	11:30:5	1,8	0,47	no	2,29	1,43	0,40
2	Biota	12:32:5	1,8	0,48	no	1,34	3,23	0,56
3	Uz1	10:43:4	1,6	0,50	0,16	1,72	1,02	0,91
4	Uz2	16:40:4	0,9	0,52	0,11	1,30	0,5	0,74

The biomarker geochemistry of the Uzon oils enables inferences about the organisms that contributed to the OM deposited under the sediments from which the analyzed oil was generated. The most important conclusion about the origin of oil can be made based on the sterane C_{27} - C_{29} composition. The predominance of the steranes C_{29} (44-47%) and C_{28} (40-44%) indicate an origin of the Uzon oil derived from terrestrial higher plants and algae.

Stigmastane (C_{29}) prevails in biota's OM. The identical sterane distribution of the Uzon oil ($C_{27}:C_{28}:C_{29} = 8:35:57$) was observed by Fursenko with co-workers in the earlier study.

Hopanes also used to determine the degree of catagenetic transformation of oils. Hopanes exist as three stereoisomers: $\alpha\beta$, $\beta\beta$ and $\beta\alpha$ -hopane. Hopanes in the $\beta\beta$ series are called *biohopanes*. Biohopanes are considered to be a source for oil hopanes $\beta\alpha$ and $\alpha\beta$ -series. The hopane ratios are also commonly used to determine the oil maturity rate. Homohopanes

range C_{31} - C_{35} have a chiral atom C-22, which is easily susceptible to epimerization, so oil homohopanes have 22R- and 22S-epimers, and only R-configuration is typical for biohopane. The number of 22S-epimers compared to 22R-epimers rises with increasing of the oil maturity and ratio $22S/(22S+22R)$ reaches equilibrium values of 0,6 at the middle stages of catagenesis. The maturation calculated as ratio $22S/(22S+22R)$ for homohopanes (C_{31} to C_{35}) increases in the row: biota <biota1<Uz1 <Uz2 from 0,47 to 0,52 (Table 1). Low values of this parameter indicate the Uzon oil weak transformation. The thermal hydrolysis of the biota did not affect the ratio of the S- and R-isomers of homohopanes range C_{31} - C_{35} . *Biohopanes* are characterized by the least thermodynamic stability compared with other epimeric series ($\beta\alpha$ and $\alpha\beta$). The hopane distributions of the biota and the oils under study are identical, except the biota contains biohopanes. The ratios of biohopanes to $\alpha\beta$ -hopanes

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for the biota are $\beta\beta\text{-C}_{29}/\alpha\beta\text{-C}_{29}=0,67$; $\beta\beta\text{-C}_{30}/\alpha\beta\text{-C}_{30}=0,05$; $\beta\beta\text{-C}_{31}/\alpha\beta\text{-C}_{31}=0,11$; $\beta\beta\text{-C}_{32}/\alpha\beta\text{-C}_{32}=0,04$. The products of the thermal hydrolysis and the oils contain only traces of bihopanes. (Fig. 2).

Comparing diagnostic ratios C_{35}/C_{34} , $\sum(C_{31}\text{-}C_{35})/C_{30}$ and C_{29}/C_{30} for the biota, the products of thermal hydrolysis and the oils (Table 1), one can catch a downward trend for the first two values and

upward one for the third with increasing maturity of organic matter. Relatively high value of $\sum(C_{31}\text{-}C_{35})/C_{30}$ for the hydrothermally altered biota caused by the decrease in the hopane C_{30} concentration due to its destruction under these thermal hydrolysis conditions.

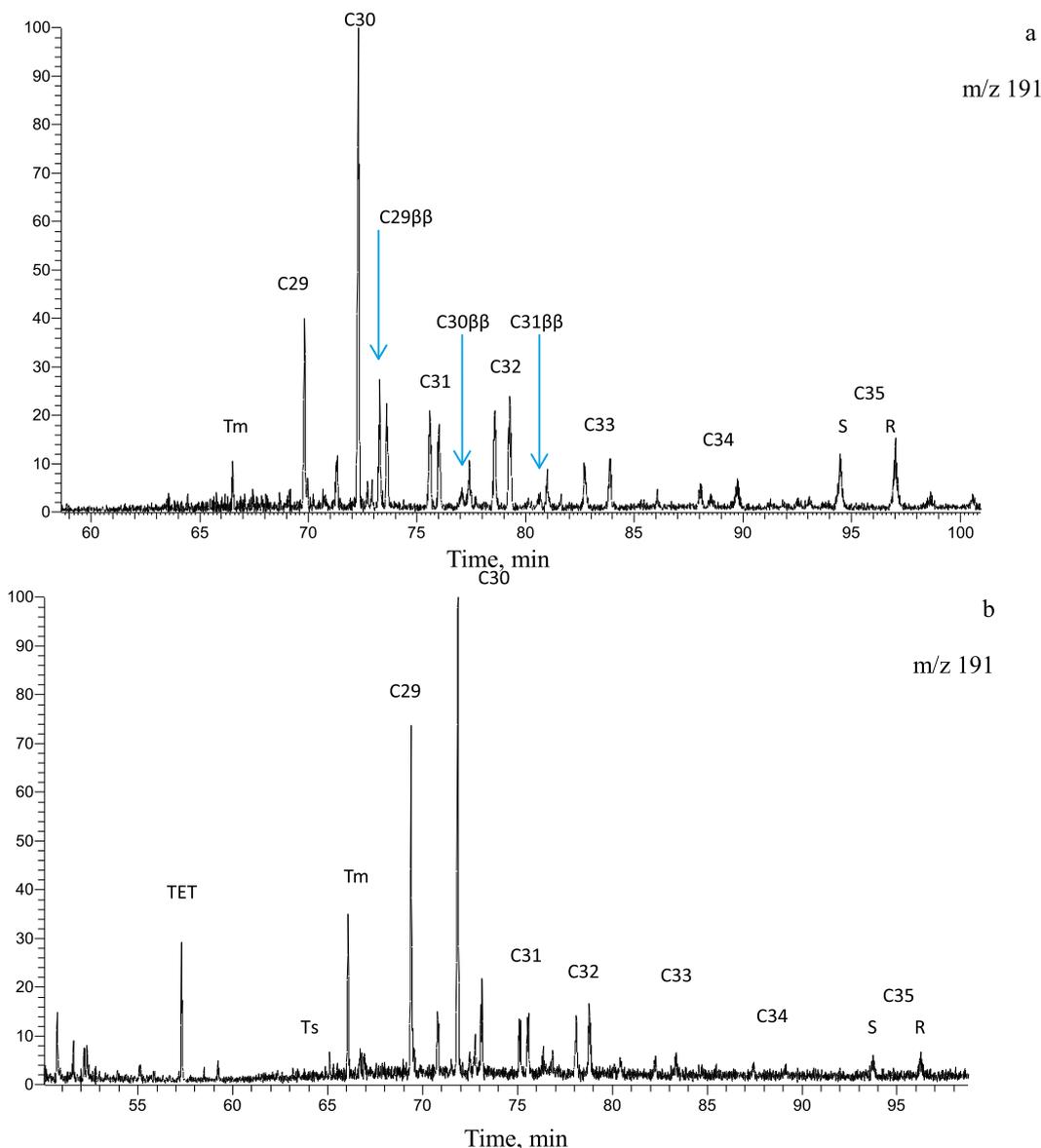


Fig. 2. Mass-fragmentograms of terpanes in the saturated fractions of the biota (a) and the oil (Uz1) (b)

Tricyclic terpanes are usually related to marine source of organic matter, and are a qualitative indicator of the oil maturity. Their absence in the oil samples indicates a terrestrial source of organic matter and/or an initial stage of the Uzon oil catagenesis.

The ratio Ts/Tm is commonly used to determine the oil maturity degree. It's assumed that Tm is a biological structure. The low Ts/Tm ratio (<1) is evidence that the maturity of the Uzon oil is weak. The biota and the products of the thermal hydrolysis contain no Ts. (Table 1).

Conclusions As a result of the thermal hydrolysis conducted in laboratory conditions, biota's organic matter has undergone a transformation of bihopanes to oil hopanes, which is similar to natural catagenesis. The transformation of biosteranes to isosteranes was not observed, but isosteranes converted in favor of S- and $\beta\beta$ -epimers. The Uzon oil is characterized by low maturity. As a result of the experiment, the biota's thermal hydrolysis products reached the degree of maturity of the oil Uz1 according to the parameters k_1C_{29} and k_2C_{29} . The Uzon oils are different in the degree of

maturity. The sterane distributions indicate a terrigenous origin of the Uzon oil.

The result of the research revealed similarities in the biomarker composition and distribution of the oils, the biota and the biota's thermal hydrolysis products, which is the argument in favor of the hypothesis of genetic relationship between the Uzon oil and organic matter of the biota that inhabits the caldera thermal waters.

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Zharikov A.V.¹, Lebedev E.B.², A forecast of possible changes in physical properties of enclosing rocks of underground radioactive waste depository on the base of the experimental data. UDC 621.39:754.716

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Abstract. On the base of the data on physical properties of the rock samples from Enisseyskiy site and their comparative analysis with the results obtained for the analogues areas at ambient and at high temperature, as well, a prediction of their possible changes under heating due to HLW thermal generation is done.

Keywords: physical properties, HLW depository, high temperature

At the present time the National Operator for Radioactive Waste Management is developing an underground research laboratory to study possibilities of final isolation of high and medium

level wastes in the Enisseyskiy site (Nizhnekanskiy massif, South-Western part of the Enissey ridge, Krasnoyarsk region) The geologic structure of the site is represented by schist-gneiss thickness intersected by the gabbro-dolerites dikes [Kochkin et al., 2017].

The underground water is the main agent for radioactive nuclide transport in geological media. So the general requirement for the site which will be chosen for underground HLW depository is to minimize a risk of their escape to the biosphere. So, it is very important to study carefully rock transport properties, first of all its permeability as a main factor governing natural and technogenic fluid dynamics in the geologic media.

It is found that the gneisses and dolerites composing the most part of the section are strong enough (the mean compressive strength is ~120 MPa) and low porous (the mean porosity value is ~ 0,4 %). The values of true permeability have to be clarified, but taking into account the data obtained for the analogues sites and rocks [Petrov et al., 2005; Zharikov et al., 2003, 2013], obviously, are also low (~10⁻²⁰ -10⁻¹⁸ m²). The contrasting differences in permeability (preliminary estimates ~ 50 %, possibly more) and in strength (average ~ 70 % for compressive strength) between gneisses and dolerites is the main feature of the section. It should be noted that the most part of the rocks are layered anisotropic and this is manifested for permeability and physico-mechanical properties, as well. As the dip of the rocks in this area is relatively shallow, their anisotropy lead to significant differences between the rock physical properties in lateral and vertical directions. The permeability of rocks normally to bedding is much lower that almost eliminates upward filtration, and the compressive strength, on the contrary, is higher. This is a very favorable factor for the safe HLW isolation. However, the compressive strength in the rocks dip direction is much lower and that, on the contrary, is an unfavorable factor for the stability of mining excavation.

The decompacted rocks related to the contacts with the dikes, the dikes of the second phase with porphyry structures, as well as zones of alterations may occur on the general background of massive and strong rocks. In order to characterize such zones, to refine the true permeability values of occurring rocks, and to establish the spatial distribution of reservoir properties nearby the HLW disposal site it is necessary to conduct further detailed laboratory studies. Thus, to avoid significant systematic errors, it is necessary to use special methods for measurements of low- permeability and techniques for sample preparation [Malkovsky et al., 2004, 2009].

Basing on the results of determinations of the filtration properties of the rocks from the Enisseyskiy

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site and the analysis of the experimental data obtained for analogues samples at ambient and at high temperatures [Balashov & Zaraisky, 1982, Zaraisky, 2007, Zharikov et al., 2003, 2013], a prediction of their changes with heating is made. The most conservative estimate is taken into account: heating up to maximum temperatures of 600 – 700 °C not only in dry conditions but also in conditions of water saturation. Moreover, in the last case the processes of pressure solution, which can lead to microcrack sealing and pores colmatation, are not active. It is found that changes in transport and physico-mechanical properties of rocks are caused by

their composition (the higher quartz content leads to the more intensive decompression) and by their microstructure changes under heating (opening of intergranular boundaries).

The intensity of changes in physical properties of rocks varies with temperature increase and depends on fluid saturation. The same factors characterize the reversibility of the changes in physical properties under heating.

Heating of the nearfield rocks during the first decades after HLW loading will lead to permeability and porosity increase.

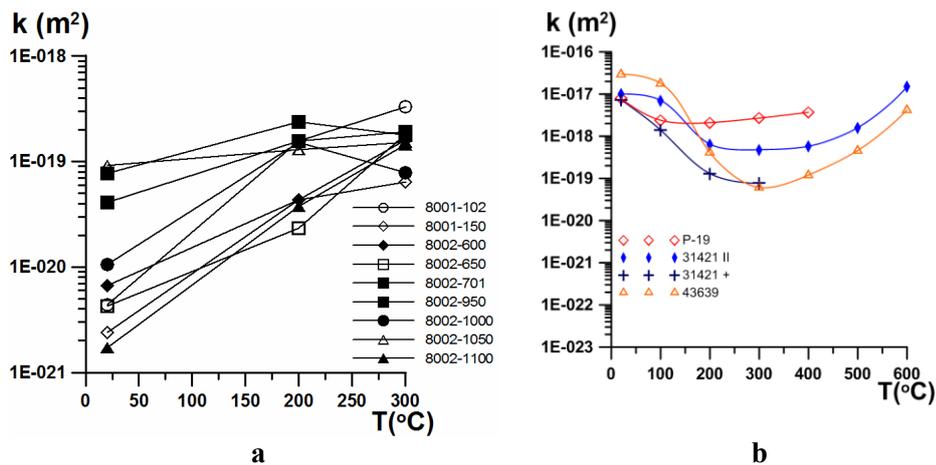


Fig. 1. Dependences of permeability of metavolcanites from PA Mayak – a and gneisses of the Kola series – b on temperature at constant pressure. [Zharikov et al., 2003, 2014]

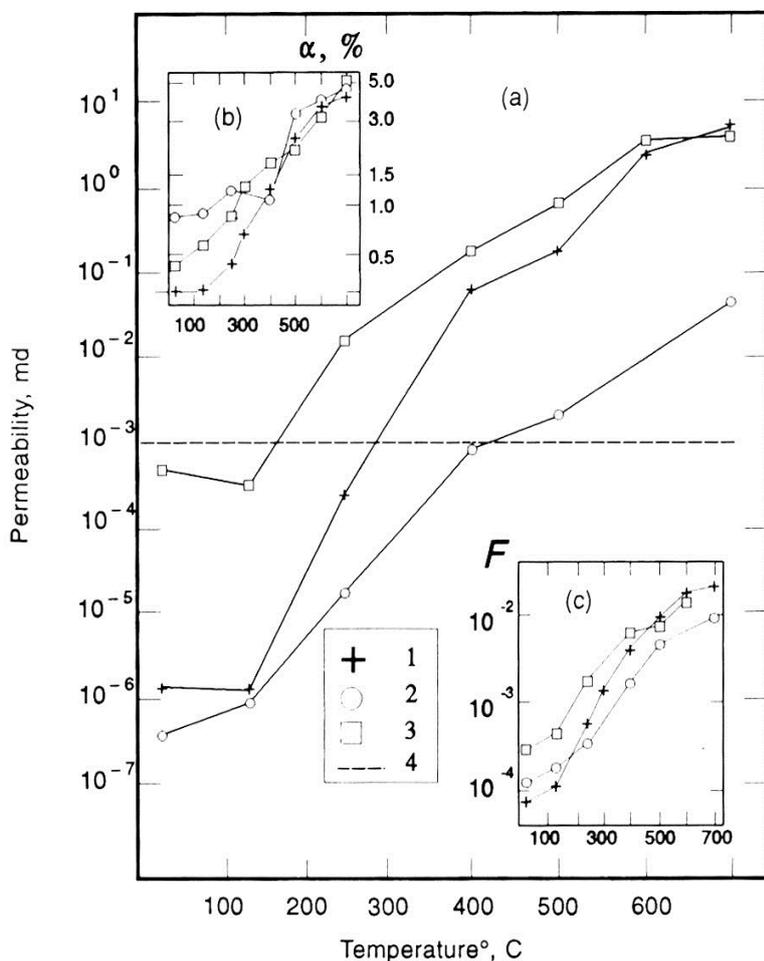


Fig. 2. Porosity, permeability and form factor of granite and gabbro-dolerite with heating [Zaraisky & Balashov, 1995]

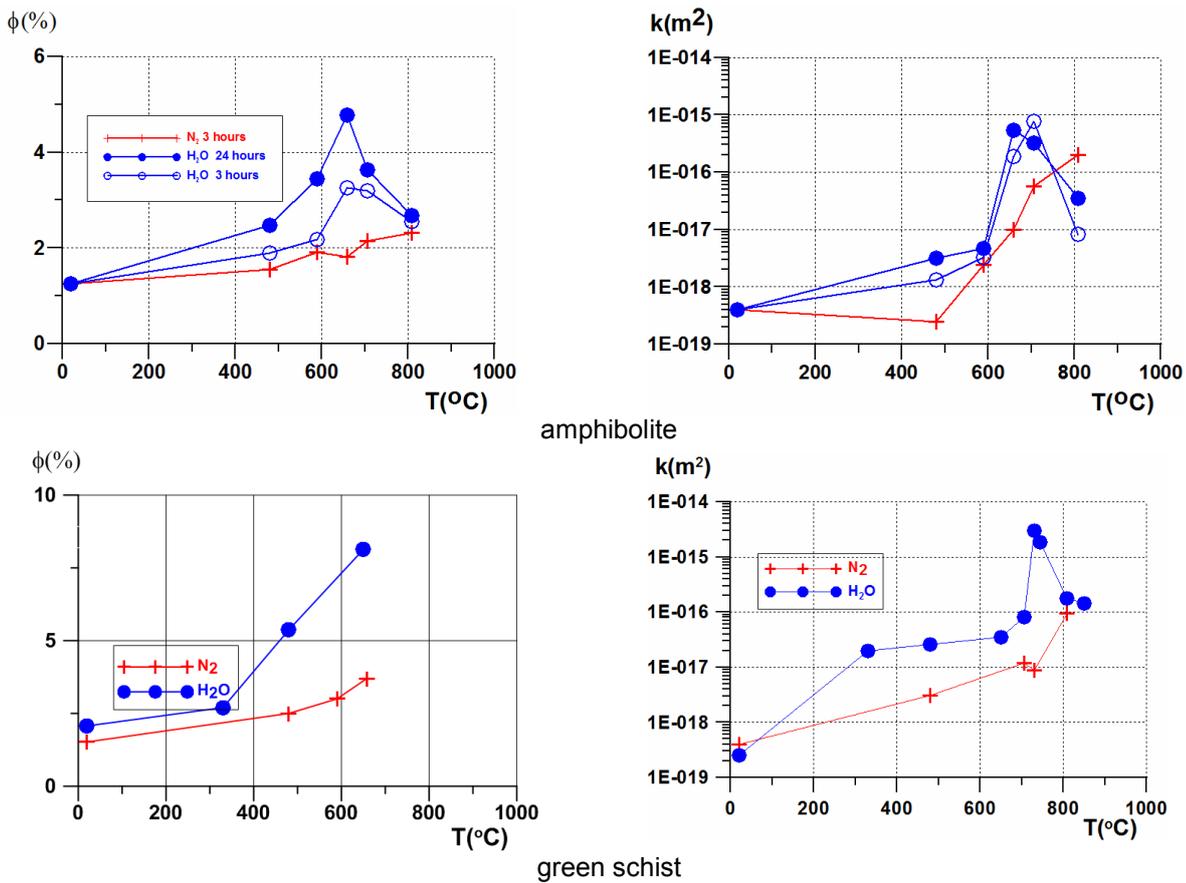


Fig. 3. The porosity and permeability of amphibolite and green schist with heating [Zharikov et al., 1993, 2000].

The permeability of basic rocks, obviously, will increase monotonically, while the permeability of gneisses may firstly decrease, reaching a minimum, and then start to increase. (Fig. 1). Taking into account that the average permeability of initial dolerites is decimal order lower than of gneisses it can be assumed that at temperatures of about 200 $^{\circ}\text{C}$ the differences between the permeability values of the main rock types will decrease. Heating to higher temperatures will lead to increase of permeability for the both lithological rock types. Moreover, the permeability of acid rocks, obviously, will increase faster than of basic ones. At temperatures > 400 $^{\circ}\text{C}$ the porosity and permeability will reach maximum values. Probably, it can be expected that the porosity will increase by several times, and the permeability by several orders in the comparison with the initial values.

In the presence of aqueous fluid the trend pattern will be the same, but the porosity values will exceed by several times, and the permeability values - by several decimal orders obtained in dry conditions (Fig. 2, 3). With heating in the water presence up to ~ 200 $^{\circ}\text{C}$ porosity can increase by 1,5 – 2,0 times, up to $\sim 400^{\circ}\text{C}$ – by 2-4 times, and up to 700°C – by 5-10 times in comparison with initial. Permeability can increase much more significantly. With heating up to

200 $^{\circ}\text{C}$ permeability of acid rocks will increase by 2 orders, of basic rocks – by 1, with heating up to 700 $^{\circ}\text{C}$ by 6 and 5, correspondently.

In case of heating under dry conditions at temperatures < 250 $^{\circ}\text{C}$ the properties of rocks after cooling can return to the initial values. With heating to higher temperatures (250 – 500 $^{\circ}\text{C}$) after cooling the gneisses will undergo a residual decompression, and the dolerites – will not. With heating to much higher temperatures, all rocks except gabbro will not return to the initial state after cooling.

Thermophysical and physico-mechanical properties of host rocks, their relation with microstructural characteristics and possible changes after heating are considered. It is determined that the deformation character is analogous to permeability behavior: the gradients dramatically increase after 200 $^{\circ}\text{C}$. At the same time the heating up to 200 $^{\circ}\text{C}$ leads to the decrease of strength and elastic modulus, but then the decreasing of these parameters goes slowly.

In case of dry rocks heating up to 200 $^{\circ}\text{C}$ their thermal properties will change slightly. An increase of specific heat capacity (20 - 30 %) and a decrease in temperature conductivity (50 - 60 %) and heat capacity (20 - 30 %) are possible.

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It was found that under heating the influence of porosity on deformation and thermophysical properties of rocks enhances. Thus, at higher temperatures the pattern of their changes will be similar to the changes of porosity one. However, to establish more accurate correlations calls the further studies.

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Kotelnikov A.R.¹, Kovalsky A.M., Tikhomirova V.I., Akhmedzhanova G.M., Suk N.I.¹, Bychkov A.M.², Kolpakova T.G.¹. Mineral matrix materials for fixation of radionuclides.

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Abstract. For immobilization of radwaste elements in the Earth crust we for the first time enunciate the principle of phase and chemical accordance in the system matrix – enclosing rock. This principle allows producing motivated synthesis of specific mineral matrixes. Mineral matrixes for immobilization of alkaline, alkaline-earth and rare earth elements – radionuclides were experimental synthesized. Besides that the methods of fixation and separation of noble metals (radwaste components) and halogenides (Br and I) were developed and tested. The problem of processing of glass matrixes (borosilicate and aluminophosphate glasses) to the stable crystalline mineral materials is considered. Methods of radwaste elements fixation from glasses to mineral solid solutions have been developed.

Keywords: *experiment, radioactive waste, mineral matrix, borosilicate and aluminophosphate glasses*

During more than semicentennial period of exploitation of nuclear piles through to recent time a lot of radwaste is accumulated. Existent methods of radwaste immobilization into glasses are not in accord with specification of defensive keeping of matrix materials because glasses are metastable phases.

In this paper two main problems of radwaste immobilization are considered:

1. synthesis of mineral matrix materials for radwaste fixation (based on the solid solutions of rock-forming and accessories minerals);
2. remaking of glass matrixes into stable mineral matrixes.

Determination of first problem provides for formation of matrix materials stable in conditions of long-time keeping in rocks of Earth crust. For development of mineral matrixes principle of phase and chemical correspondence in the system matrix – country rock which allow producing of task oriented synthesis of determine mineral matrixes has been represented.

Following specifications to matrix materials have been developed:

1. capacity to join and refrain as solid solutions most number of radionuclides and products of their disintegration during a long time (for geological scale);
2. to be stable materials in relation to the processes of physics-chemistry weathering in conditions of dumping (longtime keeping);
3. to have a complex of physics-chemistry properties which any matrix material must have: mechanical resistance, high thermal conductivity, small coefficients of heat expansion, stable to radiation damage;
4. technological scheme of their producing must be maximum simple;
5. matrix material in terms of quantity must satisfy to conception of phase and chemical correspondence in the system matrix – solution – country rock.

Table 1. Compositions of radwaste (after 5 years exposition in the pools-settling sumps)

Z ¹⁾	Elements	mass.% ²⁾	Z	Elements	mass.%	Z	Elements	mass.%
11	Na	19.94	32	Ge	0.00091	50	Sn	0.05
12	Mg	0.56	33	As	0.00037	51	Sb	0.03
13	Al	4.54	34	Se	0.13	52	Te	0.07
14	Si	0.84	35	Br	0.06	53	I	0.29
15	P	0.01	37	Rb	1.29	55	Cs	7.10
19	K	6.74	38	Sr	1.75	56	Ba	2.66
20	Ca	0.85	39	Y	2.02	57	La	1.46
24	Cr	0.09	40	Zr	9.70	58	Ce	6.64
25	Mn	1.12	41	Nb	0.02	59	Pr	2.03
26	Fe	4.47	42	Mo	6.17	60	Nd	7.10
28	Ni	0.83	43	Tc	1.63	62	Sm	1.28
	Sum	39.99	44	Ru	3.77	63	Eu	0.38
			45	Rh	1.00	64	Gd	0.06
			46	Pd	1.29	65	Tb	0.003
			47	Ag	0.03	66	Dy	0.00009
			48	Cd	0.03		Sum	58.52
			49	In	0.03			
						92	U	0.66
						93	Np	0.02
						94	Pu	0.03
						95	Am	0.57
						96	Cm	0.02
							Sum	1.30

1) Z – element number; elements Z= 11÷28 – constructional and technological; Z= 32÷66 – fission-produced; Z= 92÷96 actinides.

2) Element contents calculated on the dry balance.

In our work we decided to apply method of so called “wet” process which allows producing control fixation of radionuclides on the mineral sorbents at normal conditions and allows to distinct decrease PT-parameters of matrix materials synthesis.

Total scheme of process can be presented by following way: water solution of radwaste elements → separation into element group → sorption from water solutions, precipitation and substitution reactions → phase transformation → mineral matrix for location in the rocks of Earth crust.

We suppose original methods of synthesis of mineral matrix materials based on the sorption reactions, metasomatic substitution reactions and reactions of precipitation from water solution which produce at room temperature and pressure. Follow phase transformation transverses these materials into high stable mineral matrix materials geochemically compliant with rocks of assumed fields of location and dumping of matrixes with radionuclides. Compositions of radwaste are presented in Table 1.

More dangerous radionuclide groups are: (1) alkaline and alkaline-earth elements (Rb, Cs, Sr, Ba); (2) rare earth and transuranium elements (La...Dy; U...Am); (3) halogenides (Br, I); (4) precious metals (Ru, Rh, Pd, Ag).

Mineral matrixes have been experimentally synthesized for immobilization of alkaline, alkaline-earth and rare earth elements – radionuclides. Methods of fixation and segregation of precious metals (radwaste components) and halogenides (Br,

I) have been developed and tested, too. Examinations carried out showed high stability of synthesized materials to hydrolytic dissolution.

Problems of glass matrixes (borosilicate and aluminophosphate glasses) remaking into stable crystalline mineral materials are considered.

This study is based on the selective extraction of elements by melts of different compositions during the process of liquid immiscibility arise in them. As melts – concentrator phosphate and aluminofluoride phases are used.

In the run of experiments liquid immiscibility between borosilicate and phosphate (or aluminofluoride) melts and between silicate and aluminophosphate melts appeared (fig. 1). Herewith partition of elements between phases took place. Among elements – radwaste imitators Sr, La and Ce enrich phosphate (or aluminofluoride) phase and Cs concentrates in borosilicate glass (fig. 2). In water-bearing borosilicate-phosphate system and in the system aluminophosphate glass – SiO₂ REE concentrate in monazite phase which is high stable in natural processes (fig. 3).

Methods of fixation radwaste elements from glasses to solid solutions of minerals have been experimentally developed. We supposed and tested two methods of remaking of borosilicate glass matrixes: method of salting out and liquation method. It has been shown that used method of salting out melt crystallization with formation of Nb-bearing rutile and euxenite can be obtained. As salting out agent aluminium oxide was used (fig. 4).

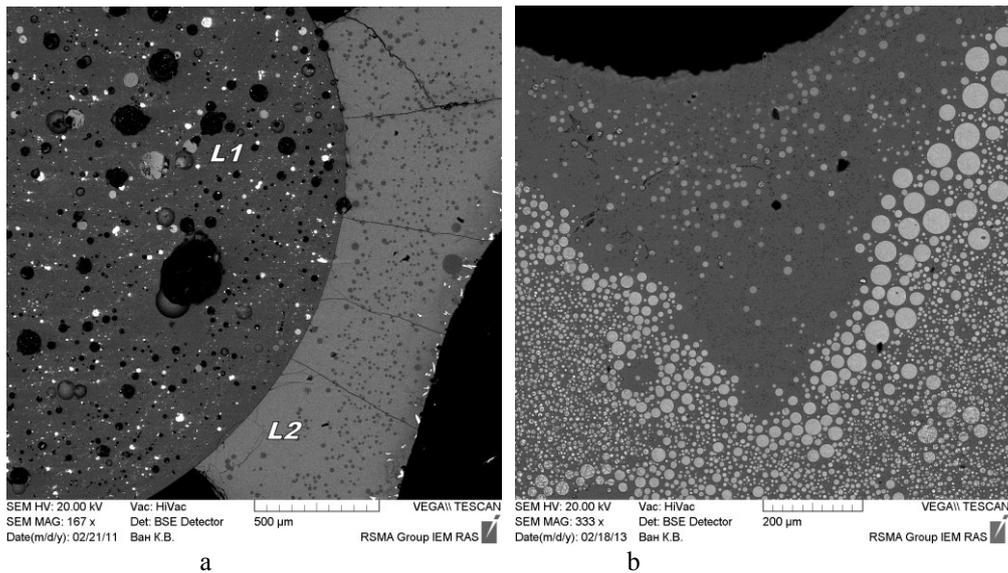


Fig. 1. Liquid immiscibility between borosilicate and phosphate (a) melts (L1 – borosilicate melt, L2 –phosphate melt) at T=1200°C, P=1 kbar and between borosilicate (dark) and aluminofluoride (light) melts (b) at T=800°C, P=1.5 kbar.

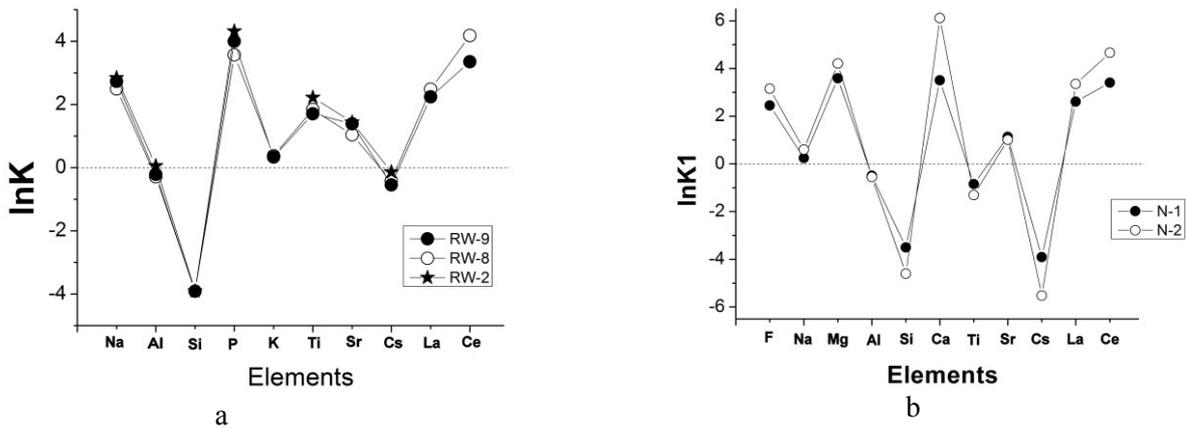


Fig. 2. Partition coefficients $K=C_{L2}/C_{L1}$ of elements ($\ln K$) between borosilicate glass (L1) and phosphate phase (L2) in dry system (a) and partition coefficients of elements between borosilicate glass and aluminofluoride phase ($\ln K1$) in dry (N-1) and water-bearing (N-2) system (b).

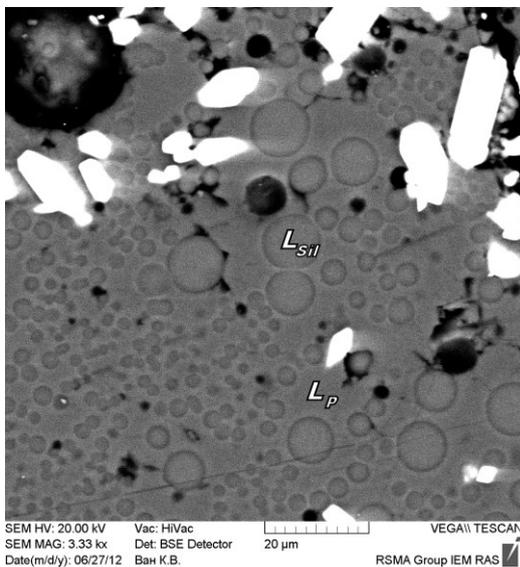


Fig. 3. Formation of monazite crystals in the system aluminophosphate glass – SiO₂ at 1200°C, P=2 kbar in dry conditions. L_p – phosphate melt, L_{sil} – silicate melt. BSE-image.

Liquation method of element partition is that as a result of liquation borosilicate melt depleted in SiO₂ from which loparite, sodium titanate and silicate of cesium crystallize is formed (fig. 5).

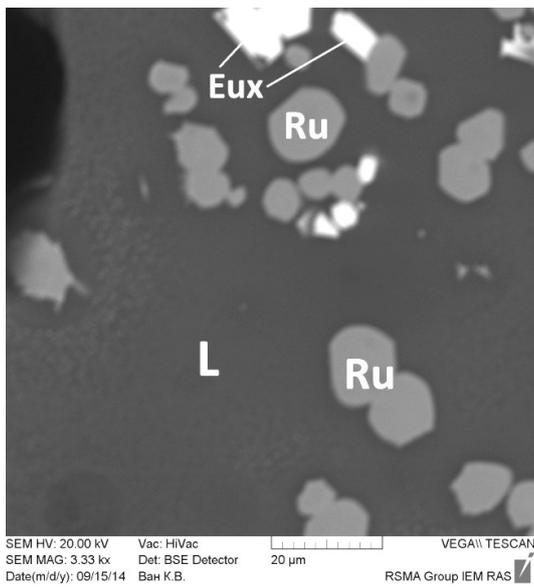


Fig. 4. Experimental products obtained used method of salting out at 2 kbar and 1100°C. Ru – Nb-bearing rutile, Eux – euxenite, L – glass. BSE-image.

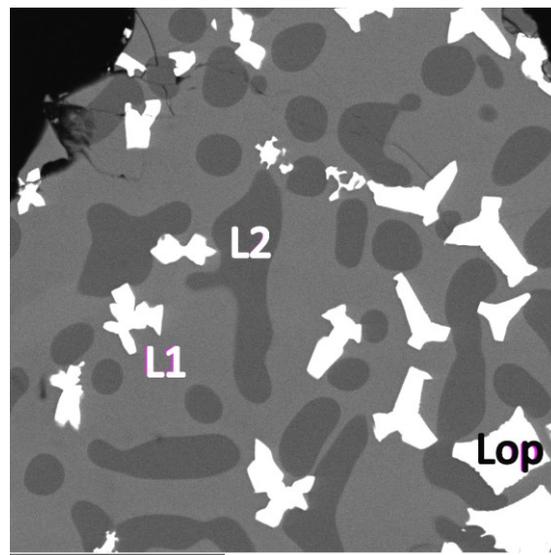


Fig. 5. Experimental products obtained used liquation method (1300°C → 850°C). Lop – loparite, L1, L2 – glasses of liquating melts. BSE-image.