Experimental geoecology

Konopleva I.V., Sevast'yanov V.S., Kuznetsova O.V., Vlasova L.N., Galimov E.M. Modeling of oil production from biota's organic matter in hydrotherm's conditions

V.I. Vernadsky Institute of Geochemistry and Analytical Chemistry RAS, Moscow (konopleva@geokhi.ru)

Abstract. An experiment on the thermohydrolysis of biota, which is considered as a source of oil in the Uzon volcano caldera (Kamchatka), was performed. Biota was sampled in a small thermal lake of the caldera. High-molecular n-alkanes C_{20}-C_{33}, resins and asphaltenes were detected in the biota organic matter. Its structure-group composition is typical for the early stages of diagenesis. As a result of the biota thermohydrolysis, medium-molecular *n*-alkanes C_{17}-C_{19} were formed, the content of PAHs and asphaltenes increased. The transformation of the biota organic matter as a result of the thermohydrolysis corresponds to deeper diagenesis and/or the initial stage of catagenesis.

Keywords: *biota thermohydrolysis, hydrocarbons, oil seeps, Uzon caldera, Kamchatka*

Oil seeps near hot springs of the hydrothermal fields in the caldera of Uzon Volcano (Kamchatka) were discovered. At present, most scientists consider a biogenic origin of the Uzon oil as the most reasonable hypothesis. The formation of the Uzon oil seeps is considered as a process of thermolysis or thermocatalytic processing of plant remains and the biomass of microorganisms that inhabit the caldera thermal lakes (Fursenko et al., 2014; Galimov et al., 2015).

The modern scientists have no common opinion about the time duration of the Uzon oil formation. According to the results of different measurements the age of the Uzon oil varies from 50 to 1000 years. Most scientists associate its origin with the organic matter buried in the caldera sediments (Bazhenova et al., 1998; Simoneit et al., 2009; Kontorovich et al., 2011). Some researchers believe that the Uzon oil seeps are formed as a result of an intensive transformation of lipids of the living matter, which passes for a very short time under aggressive environmental conditions without immersing to significant depths (Varfolomeev et al., 2011; Maryutina et al., 2013).

To reveal regularities of oil hydrocarbons formation in hydrothermal conditions, the sample of biota was taken from the caldera thermal lake and subjected to thermal hydrolysis. High temperature exposure allows to experimentally simulate the influence of low temperatures and the duration of geological time, and is widely used in oil formation modeling.

In this study the biota hydrocarbon molecular markers were investigated. Based on the data on their composition and distribution one can define the genesis and degree of organic matter transformation in diagenetic and catagenetic processes.

Objects and methods of research The sample of biota was collected from the water surface of thermal lake, which is situated within the bounds of the Central hydrothermal field. The sample consisted of organic and mineral matter. It was decarbonatizated, rinsed, and dried. This material was sealed in a platinum capsule and underwent to thermal hydrolysis at 300°C for 24 h. The chloroform extracts of biota and the hydrothermally altered biota (Biota_exp) were separated into five fractions. Asphaltenes were precipitated from the initial sample by pentane. Then, the asphaltenes free residue was separated in a chromatographic column filled by silica gel into fractions via stepwise eluation using a set of solvents with increasing polarity: *n*-hexane (methane-naphthenic fraction, MN), hexane–benzene mixture, 1:1v/v (naphthene-aromatic fraction, NA), benzene (fraction of benzene tars), and benzene–methanol mixture, 1:1v/v (fraction of alcohol-benzene tars).

Analysis of the molecular composition of the saturated hydrocarbon fractions of extracts was 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. The mass fragmentograms of hydrocarbons are obtained from the total ion current (TIC) and in the scanning mode by characteristic fragment ions (SIM). Hydrocarbons of the saturated fraction were identified by ions m/z 71.

Results and discussion The extract of biota consists of paraffin, naphthenic, aromatic hydrocarbons as well as resins and asphaltenes (Table 1). Resins and asphaltenes are uncommon for living organic matter. Their structures represent a polycyclic, strongly condensed aromatic systems connected to heterocycles. Oil content is significantly less than tar-asphaltene components (29.4 and 71.6%, respectively). The methane-naphthenic fraction (MN) exceeds the naphthene-aromatic (HA) by 4.7 times, and resins are twice more than asphaltenes. The high content of tar-asphaltene components in the structural-group composition is characteristic of immature organic matter of modern sediments at the stage of early diagenesis.

As a result of the thermobaric action on biota, a decrease in the proportion of saturated hydrocarbons was observed: the content of the MH fraction decreased by 2.8 times, the fraction of the NA fraction decreased 1.7 times. The total proportion of resinous components decreased slightly, but changes in their structural-group composition are noted. The content of the benzene fraction, whose composition is mainly represented by polyaromatic hydrocarbons, increased by 1.8 times. The proportion of alcohol-benzene resins, mainly represented by heteroatomic compounds, decreased by 1.2 times. In general, the ratio of alcohol benzene resins to benzene reduced almost threefold. The amount of asphaltenes increased by 1.8 times. At elevateds temperatures enrichment of the thermohydrolysis products with aromatic compounds was observed, followed by the formation of condensed polycyclic aromatic structures. Resins are unstable compounds, and their heating leads to aggregation of large molecules and formation of asphaltenes.

Table1. Structural-group composition of the biota and the thermohydrolysis products

sample	Group composition, %							MN/ NA	tars/ asphalte-nes
	oils			tars			asphaltenes		
	methane-naphthenic (MN)	naphthene-aromatic (NA)	sum	benzene	alcohol-benzene	sum			
Biota	24,4	5,2	29,6	6,7	40,5	47,1	23,3	4,7	2,0
Biota_exp	8,8	3,1	11,9	11,9	33,5	45,4	42,7	2,8	1,1

GC-MS data (TIC- background) for the saturated fraction of the biota are given in Figure 1. One can observe the noticeably expressed "naphthenic hump" on the chromatogram. Large homologous series of gopans is a sign of the significant contribution of components from bacterial cells to the biomass.

Based on the data on the distribution and composition of the *n*-alkanes one can reveal some specific features of organic matter, which are determined by a bioproducer origin. Only high-molecular weight *n*-alkanes range from C_{20} to C_{33} with a maximum at *n*-C_{27} have been identified in the saturated hydrocarbon fraction of the biota (Fig. 2). The presence of long-chain *n*-alkanes may indicate an input from terrestrial higher plants and/or bacteria to the biomass. The *n*-alkane distribution has comparable concentrations of even to odd homologs (CPI $_{20\text{-}32}$ =1,17).

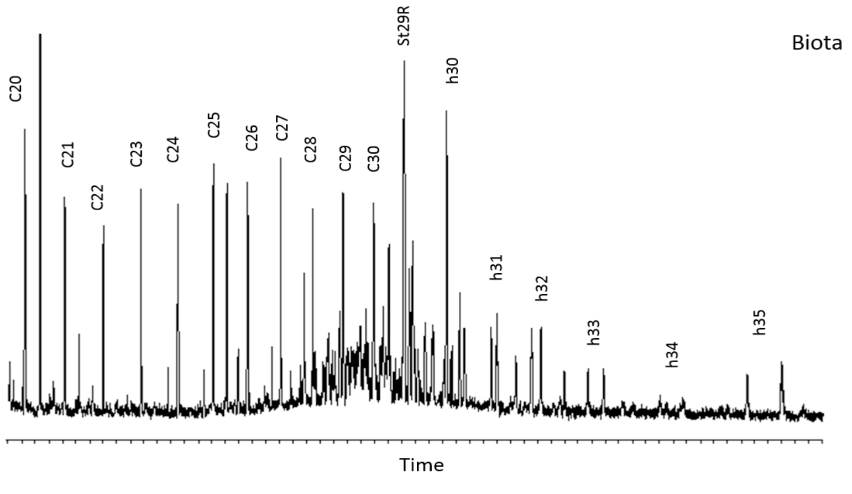


Fig. 1. Total ion current (TIC) chromatogram for the saturated fraction of the biota (GC-MS data)

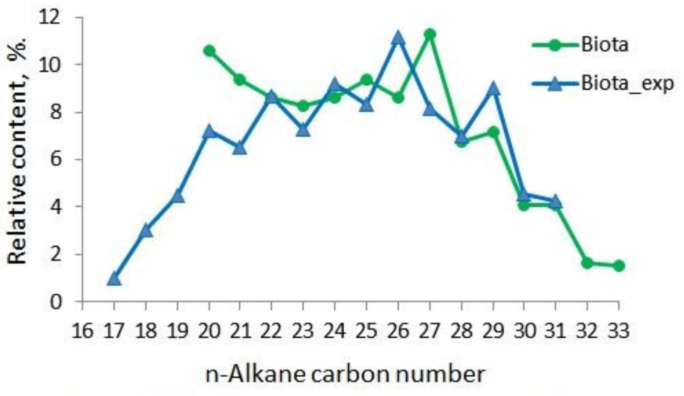


Fig. 2. Molecular-mass distributionof rvalkanes

As a result of the biota thermohydrolysis, medium-molecular weight alkanes C_{17}-C_{19} were produced. Their proportion accounted for 8.6%. (Table 2). The carbon preference index slightly decreased (CPI_{20-32}=0,94). A shift of the maximum to even *n*-alkanes C_{22}-C_{26} occurred. The second maximum was at *n*-C_{29}. The distribution curve of *n*-alkanes has acquired a "sawtooth" form. This distribution is characteristic for sediment organic matter in the early stage of diagenesis, the fossilization of which took place under reducing conditions. Fragments of fatty acids with even carbon number in the composition of esters dominate in lipids of living matter.

Hydrolysis of lipids leads to the formation of fatty acids that contain an unbranched chain with even carbon number. Subsequent reduction without separation of carbon leads to the formation of even homologues of the *n*-alkanes. The reducing conditions of thermal hydrolysis may be formed due to molecular hydrogen, which is a product of hydrocarbon destruction at a temperature of 300°C.

Table 2. Molecular-mass and group composition of *n*-alkanes

Sample	*n*-alkanes,%			CPI_{20-32}*
	C_{17}-C_{19}	C_{20}-C_{26}	C_{27}-C_{33}	
Biota	*not detected*	63,4	36,6	1,17
Biota_exp	8,6	58,4	33,0	0,94

* CPI-carbon preference index for *n*-alkanes

Conclusions It was shown that the transformation of the biota organic matter already begins in the surface layers of the thermal lake. Resins and asphaltenes, uncommon for living organic matter, are produced at the stage of the initial transformation of the biota organic matter at “the present moment” of geological time. Resins and asphaltenes are part of the sediment bitumoid and accumulate for the stage of diagenesis. Thus, one can conclude that the hydrothermal alterations of the biota organic matter are similar to the diagenetic processes.

Microbial processes are of great importance at the stage of early diagenesis. Microbial activity of thermophilic bacteria, widely represented in the caldera waters, elevated temperatures and the involvement of mineral substances, which present in the thermal lakes, lead to an accelerated transformation of the biomass, which consists of microorganisms and plant debris.

As a result of the biota thermohydrolysis, *n*-alkanes with medium carbon number in the chain were produced, and the dominance of even-numbered homologues was revealed. The content of benzene resins and asphaltenes in the structural-group composition of the thermohydrolysis products increased.

The conducted laboratory simulation showed that as a result of the thermohydrolysis, a transformation of the biota organic matter has occurred. It corresponds to the deeper processes of diagenesis and/or the initial stage of catagenesis.

References:

Bazhenova O.K., Arefiev O.F., Frolov E.B. (1998). Oil of the volcano Uzon caldera, Kamchatka. *Org.Geochem. Vol. 29, p. 421-428. doi:10.1016/S0146-6380(98)00129-6*

Varfolomeev S. D., Karpov G. A., Sinal, G. A., Lomakin S. M., Nikolaev E. N. The Youngest Natural Oil on Earth. *Doklady Chemistry, 2011, Vol. 438, Part. 1, pp. 144-*147. *doi: 10.1134/S0012500811050053*

Galimov, E. M., Sevastyanov, V. S., Karpov G. A. Kamaleeva A. I., Kuznetsova O. I., Konopleva I. V., Vlasova, L. N. Hydrocarbons from a Volcanic Area. Oil seeps in the Uzon caldera, Kamchatka. *Geochem. Int., 2015, Vol. 53, pp. 1019-1027. doi:10.1134/S0016702915120046*

Kontorovich A. E., Bortnikova S. B., Karpov, G. A., Kashirtsev V. A., Hotel E. A., Fomin A. N. Uzon volcano caldera (*Kamchatka*): a unique natural laboratory of the present-day naphthide genesis. *Russian Geology and Geophysics, 2011, Vol. 52, No. 8, pp. 768-772. doi: 10.1016/j.rgg.2011.07.002*

Maryutina T.A., Karpov G.A., Varfolomeev S.D. Basic Hydrocarbon Components and Chemical Composition of the Environmental Medium of the Youngest Oil on Earth. *Doklady Chemistry, 2013, Vol. 449, Part. 1, pp. 77-80. doi: 10.1134/S0012500813030026*

Fursenko E. A., Kashirtsev V. A., Kontorovich A. E., Fomin A. N. Naphthides of continental hydrotherms *(Uzon, Yellowstone, New Zealand)*: Geochemistry and genesis. *Russian Geology and Geophysics, 2014, Vol. 55, No. 5-6, pp. 726-736. doi:10.1016/j.rgg.2014.05.015*

Simoneit B.R., Deamer D.W., Kompanichenko V.N. Characterization of hydrothermally generated oil from the Uzon caldera, Kamchatka. *Appl. Geochem., 2009, Vol. 24, pp. 303-309. doi:10.1016/j.apgeochem.2008.10.007*

Kotelnikov A.R., Suk N.I., Martynov K.V., Akhmedzhanova G.M. Synthesis of matrix materials for fixation of radionuclides based on liquid immiscibility in the melts. UDC 621.039.736

*Institute of Experimental Mineralogy RAS, Chernogolovka Moscow district (*kotelnik@iem.ac.ru, sukni@iem.ac.ru)

Abstract. To study the possibility of processing glass matrixes in stable mineral forms, a study of the interphase distribution of elements (La, Ce, Sr, Cs) in the systems: aluminosilicate – fluoride melts, aluminophosphate –

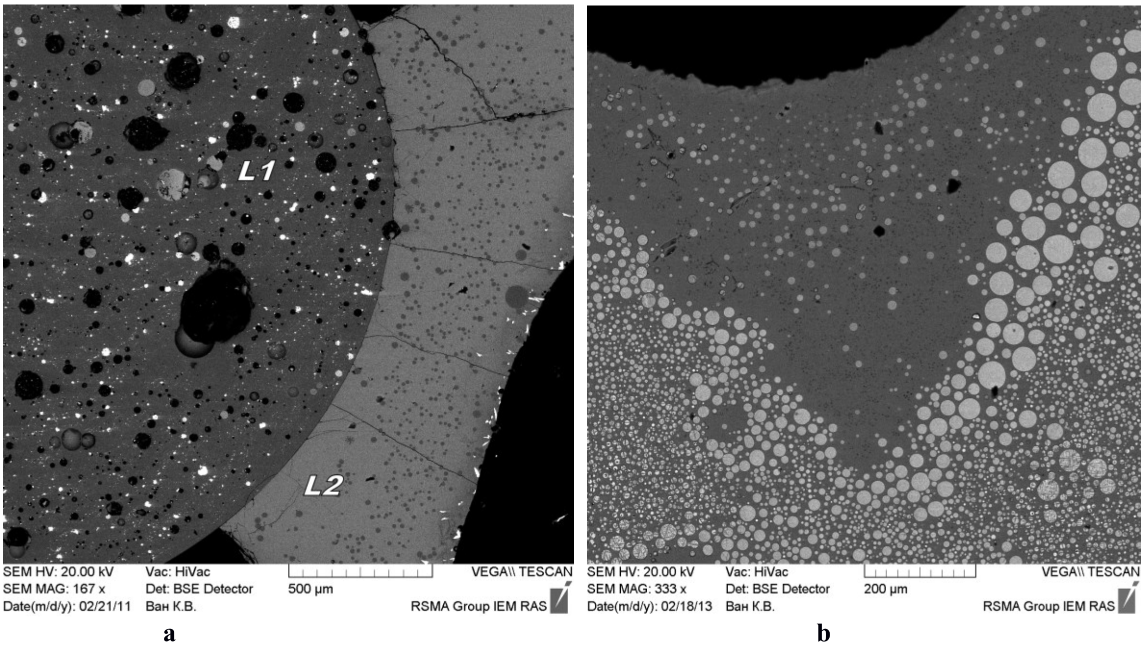
aluminofluoride melts, aluminophosphate – phosphate melts, borosilicate – borate melts and others has been produced. The approach to the immiscibility area was carried out by the following methods: (1) by addition of salts; (2) by adding salting out components in the melt (SiO_2 - in aluminophosphate, Al_2O_3 - in borosilicate); (3) by a change in temperature. As a result of the appearance of areas of liquid immiscibility, the elements were redistributed between the phases of the liquating system. It was observed the formation of very stable minerals – concentrators of RW elements, such as monazite, loparite, etc. This method can be used for industrial immobilization of radionuclides.

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

Previous studies show that as a result of the appearance of liquid immiscibility in the layering silicate-salt systems, a selective concentration of elements by melts of different composition occurs (Suk, 1997, 2017; Gramenitskiy et al., 2005). The revealed regularities can be used in the development of methods for the enrichment and extraction of certain ore elements from the corresponding rocks and sub-standard ores, as well as methods for processing borosilicate and aluminophosphate glasses used as matrixes for immobilization of radioactive waste. To study the possibility of processing glass matrixes in stable mineral forms, the interphase distribution of elements – imitators of radioactive waster (La, Ce, Sr, Cs) has been produced in systems: borosilicate – phosphate melts, borosilicate - aluminofluoride melts, aluminophosphate – silicate melts, borosilicate – borate melts and others.

Experimental method. The experiments were carried out using an ampoule method at a high gas pressure vessel, as well as in muffle furnaces KO-14. The starting material was model borosilicate glass, similar in composition to matrix materials containing REE (La, Ce), Sr, Cs, Li, Ti, premelted at T= 1200^{o}C, P = 1 kbar during 3 hours at a high gas pressure vessel or in KO-14 at T = 1200^{o}C, and reagents SiO_2, $NaPO_3$, and $(Na_{1.5}Li_{1.5})_3AlF_6$. The products of the experiments were analyzed on a digital scanning electron Tescan Vega II XMU (Tescan, Czech Republic) microscope with an INCA Energy 450 X-ray spectral microanalysis system with an INCAx-sight X-ray spectrometer (Oxford Instruments, England) and the INCA Energy+ software platform. The approach to the immiscibility field was carried out by the following methods: (1) addition of salts; (2) by addition of salting out components to the melt (SiO_2 – in aluminophosphate, Na_2CO_3 – in borosilicate); (3) by changing the temperature of the experiment.

The processing glass matrixes (borosilicate and aluminophosphate glasses) to stable crystalline mineral materials have been considered. In experiments with borosilicate and aluminophosphate glasses, phosphate and aluminofluoride phases with elements of RW imitators up to 10 wt. % were used as melts-concentrators. The composition of borosilicate glass (wt.%): SiO_2 – 51.54; B_2O_3 – 15.70; Al_2O_3 – 2.60; Li_2O – 3.64; Na_2O – 9.04; MgO – 1.97; CaO – 4.16; TiO_2 – 1.35; SrO – 1.02; Cs_2O – 3.65; La_2O_3 – 1.21; CeO_2 – 4.12. The composition of aluminophosphate glass (wt.%): Na_2O – 40.23; Al_2O_3 – 16.48; P_2O_5 – 36.50; SrO – 1.06; Cs_2O – 3.77; La_2O_3 – 1.25; Ce_2O_3 – 4.48.



a **b**

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

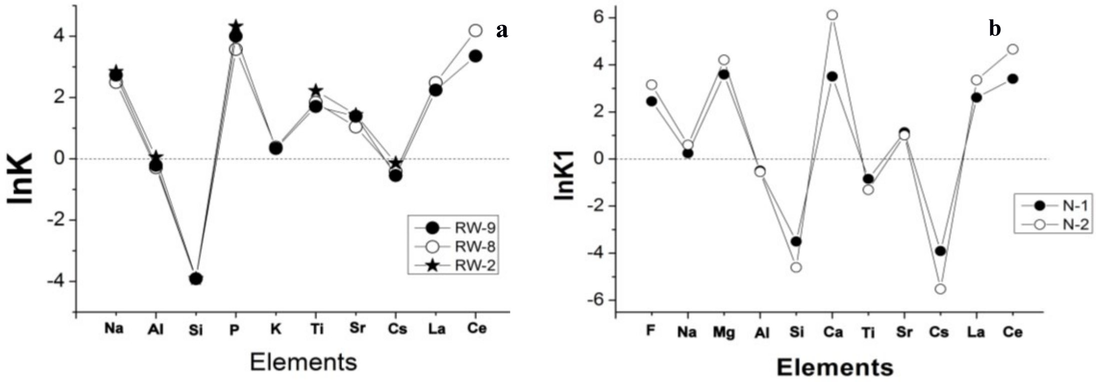


Fig. 2. Partition coefficients K = C_{L2} / C_{L1} of the elements (lnK) between the borosilicate glass (L1) and the phosphate phase (L2) in the dry system (a) and the partition coefficients of elements between the borosilicate glass and the aluminofluoride phase (lnK1) in dry (N-1) and water-containing systems (N-2) (b).

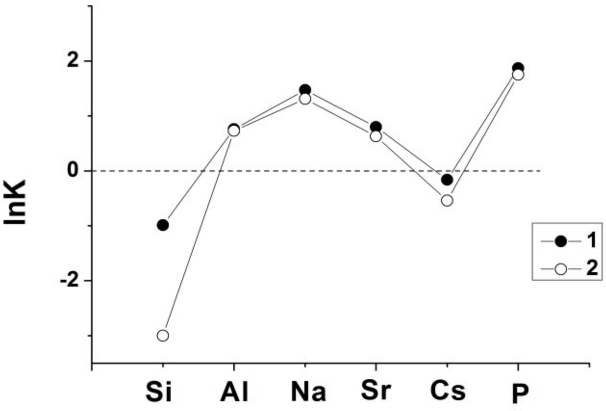


Fig. 3. Element partition coefficients between silicate and phosphate melts (lnK) in dry (1) and water-containing systems (2).

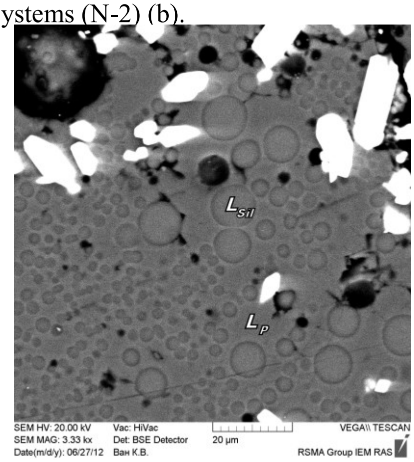


Fig. 4. Formation of monazite crystals in the aluminophosphate glass – SiO_2 system at 1200°C, P = 2 kbar under "dry" conditions. L_P - phosphate melt, L_{Sil} - silicate melt.

The addition of sodium phosphate or sodium aluminofluoride to the borosilicate glass, and SiO_2 to the aluminophosphate glass, resulted in the attainment of the immiscible field. Thus, during the experiments, liquid immiscibility between borosilicate and phosphate (or aluminofluoride), and also between silicate and aluminophosphate melts appeared (fig. 1). In this case, the elements were separated between phases: Si and Al enriched the phase of borosilicate glass, and Mg, Ca, Na, P – phosphate (or aluminofluoride) phase. From the element-imitators of RW, Sr, La and Ce enrich the phosphate (or aluminofluoride) phase, and Cs is concentrated in borosilicate glass (fig. 2, 3). In the water-containing borosilicate – phosphate system, as well as in the aluminophosphate glass – SiO_2 system, the rare earth elements are concentrated in the monazite phase, which is highly stable in natural processes (fig. 4).

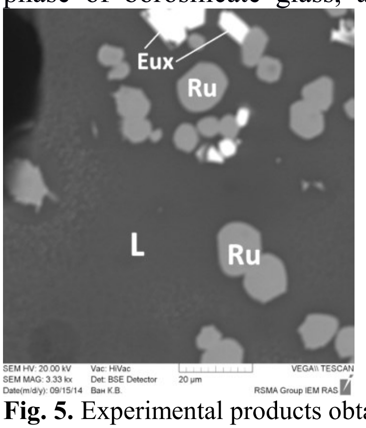


Fig. 5. Experimental products obtained by the salting out method at 2 kbar and 1100°C. Ru – niobium rutile, Eux – euxenite, L – glass. BSE-image.

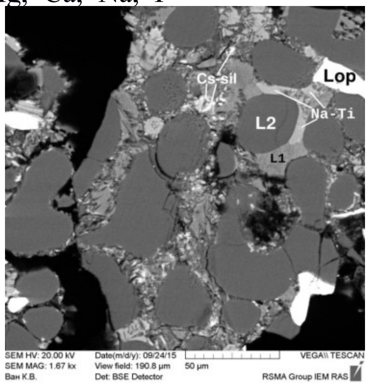


Fig. 6. Experimental products obtained by means of a liquation method (1300°C → 850°C). Lop –loparite, L1, L2 – glasses of liquidating melts. BSE-image.

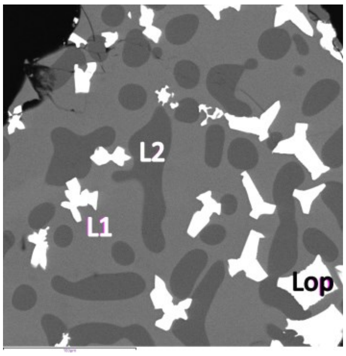


Fig. 7. Products of the experiment obtained by means of a liquation method (1300°C → 850°C → 650°C). Lop – loparite, L1, L2 – glasses of liquidating melts, Na-Ti – sodium titanate, Cs-sil – Cs-silicate. BSE-image.

Methods of fixation of radwaste elements from glasses into solid solutions of minerals have been experimentally developed. It is shown that by means of the salting out method it is possible to achieve crystallization of the melt (with the formation of niobium rutile and euxenite) using alumina as a salting out agent (fig. 5). The addition of Al_2O_3 destabilized the melt and, with a decrease of temperature, promoted liquation. When the immiscibility field is reached, the components of RW (Sr, La, Ce) redistribute into the borate glass and form loparite crystals (fig. 6), while cesium remains in the silicate melt. For the cesium fixation a directed crystallization method was proposed. In the residual borosilicate melt, elements such as Na, Al and Si are presented in significant amounts. It was suggested that at lower temperatures (600°C) crystallization of the own Cs phase will begin. The experiments have been carried out in the following regimes: 1300°C (exposure 1 hour) → 850°C (exposure 2 days) → 600°C (exposure 1 day) at atmospheric pressure. At these parameters, Cs was fixed in the form of cesium aluminosilicate $(Na_{0.58}Cs_{0.08})_{0.66}$ $(B_{1.34}Si_{0.45}Al_{0.31})_{2.1}$ (fig. 7).

Conclusions

1. As a result of the appearance of liquid immiscibility between borosilicate melt and phosphate (or aluminofluoride) phase, the elements are separated between phases. Wherein, from RW elements-imitators Sr, La and Ce are enriched the phosphate (or aluminofluoride) phase and Cs is concentrated in borosilicate glass.
2. When silica is added to the aluminophosphate melt, heterogenization into two liquids (silicate melt and phosphate melt) arises. At the same time, such RW elements as Sr and REE enrich the phosphate melt, in which crystallization of the mineral phase-concentrator of the RW elements – monazite – is carried out.
3. By various methods at temperatures of 1250 ÷ 650°C in "dry" conditions from borosilicate melt with elements – RW imitators, loparite – a very stable mineral matrix for fixation of radionuclides has been synthesized. For cesium immobilization the directional crystallization method with cesium concentration in the aluminosilicate crystalline phase was used.

References:

Gramenitskiy E.N., Schekina T.I., Devyatova V.N. Phase relations in fluoride-bearing granite and nepheline-syenite systems and element distribution between phases (experimental investigation). M.: GEOS. 2005. 188 p.
Suk N.I. Behaviour of ore elements (W, Sn, Ti и Zr) in layering silicate-salt systems. Petrologiya. 1997. V. 5. N 1. P. 23-31. Petrology. V. 5. N 1. P. 20-27.
Suk N.I. Liquid immiscibility in alkaline magmatic systems. 2017. M.: “KDU”, “Universitetskaya kniga”. 238 p.

Kubrakova I.V., Tyutyunnik O.A., Silant’ev S.A. Fate of palladium and platinum under water-rock interaction in acid media UDC 543:550:4

Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences, Moscow, (kubrakova@geokhi.ru)

A comparative study of the mobility of palladium and platinum in highly-salt acidic chloride media, similar in composition to the derivatives of sea water, was carried out. In dynamic conditions, the interaction of model solutions containing chloride forms of palladium and platinum with natural oceanic serpentinites, is considered. Due to the high neutralizing potential of the serpentinites, the stability of the pH of a solution interacting with an ultrabasic substrate has been demonstrated for at least 6 months.

The obtained data on the composition of the solutions formed and on the leaching kinetics of the components demonstrate the transfer of palladium and the complete retention of platinum by serpentinites. It is assumed that the transport of palladium through the rock is realized in the form of its strong complex with thiosulfate ion, formed during the oxidation of small amounts of sulfides contained in the rock. The results obtained are used to explain the increased mobility of palladium in the process of transformation of mantle peridotites under oceanic crust conditions.

Keywords: *palladium, platinum, species and migration, experimental modeling, serpentinites, mid-oceanic ridges, underwater weathering, hydrothermal systems of mid-oceanic ridges*

A comparative study of the mobility of palladium and platinum in high salt acidic chloride media, similar in composition to the derivatives of sea water, is presented. In dynamic conditions, the interaction of model solutions containing chloride forms of palladium and platinum with natural oceanic serpentinites is considered.

Material and methods of research Samples of serpentinites were collected during the dredging of the ocean floor in the region of the foot of the western side of the rift valley of the Mid-Atlantic Ridge, at 12°58'N, 44°52'W, during the Serpentine expedition aboard the French sea vessel "Purcua Pa?». The composition of serpentinites was analyzed by chemical silicate analysis and atomic-emission spectrometry with inductively coupled plasma (ICP-AES) (Table).

Table. The composition of harzburgite serpentinites used in the experiment

Mass %	Al_2O_3	CaO	Cr_2O_3	Fe_2O_3 tot	FeO	K_2O	MgO	MnO	Na_2O	TiO_2	P_2O_5	SiO_2	NiO	LOI
SeDr 3-2-1	0.73	1.72	0.36	6.46	2.34	0.047	36.4	0.093	0.0808	0.010	0.013	36.0	0.34	15.2
SeDr 5-1-4	0.54	5.10	0.31	7.18	2.49	0.025	33.9	0.110	0.11	0.032	0.027	35.0	0.27	16.6

ppm	Ba	Sr	Pb	Co	Cu	Mo	S	Sc	V	Y	Zn
SeDr 3-2-1	40.0	188	45	133	10	0.89	764	9.7	42	1.7	60
SeDr 5-1-4	3.10	911	1.8	125	28	1.40	735	7.0	43	1.7	57

The behavior of palladium and platinum was investigated during the interaction of an acidic solution (C_{Cl} = 1M) containing palladium and platinum chlorides with samples of harzburgite serpentinites while passing the solution through a column filled with crushed rock for 180 days. The solution obtained was analyzed by the ICP-AES for the content of Al, Ca, Mg, Fe, Ti, P, Cu, Ni, Co, Cr, Ba, Sr, Zn, Si, S. Platinum, palladium was determined by the ETAAS. The determination of sulfur anions in solutions was carried out by ion exchange chromatography.

Results and discussion The main factor governing the speciation of elements and their behavior in solutions is pH. In our experiments, the acidity of the solution was practically constant throughout the experiment (pH 7-8) (Fig. 1), which indicates a high buffering capacity of serpentinite. Elemental composition of the eluate also remained fairly stable throughout the experiment. Significant concentrations were observed for Ca, Mg, Si, Sr, Ni, Cu, S, and Fe.

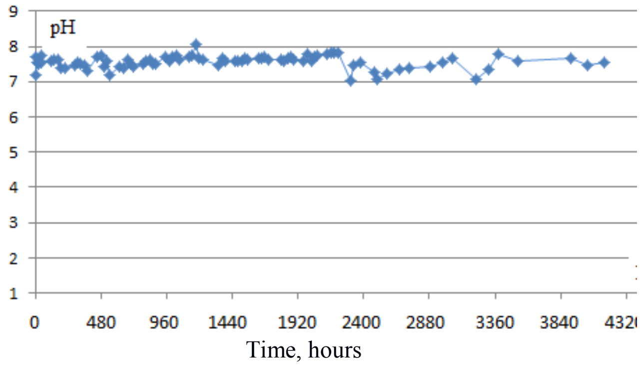


Fig.1. Change in pH during "solution-serpentinite" experiment

It has been established that in the course of the experiment there is a transfer of palladium, initially introducing to the rocks as a chloride. After 180 days of elution, which corresponded to a solution-rock ratio (10: 1500), 100 and 80% palladium on the column was found in the eluate. In this case, for a more carbonatized sample, the main peak at the output curves was observed after 6-7 days (for less carbonatized sample after 20).

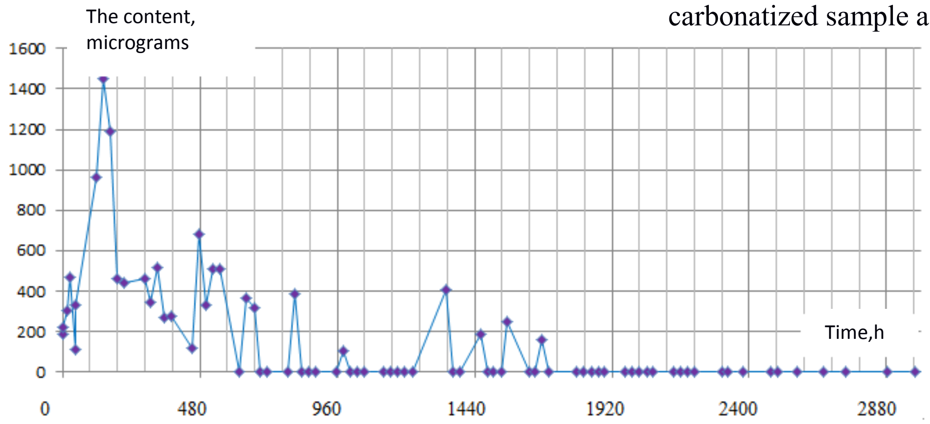


Fig.2. The change in palladium content in the eluate during the "solution-serpentinite"

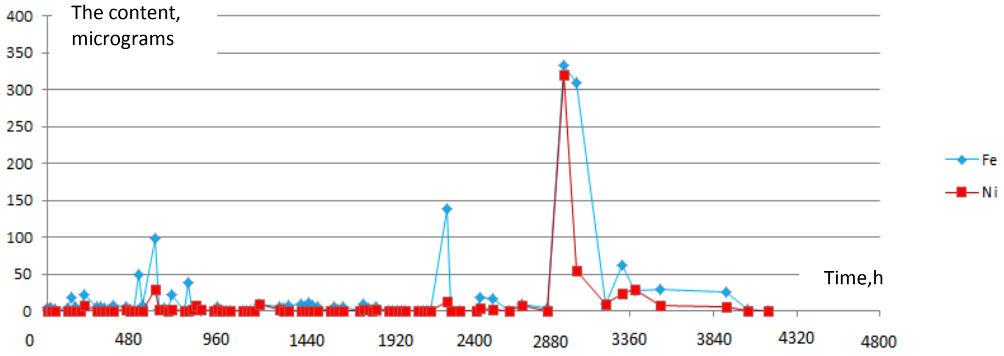


Fig. 3. Output curves of iron and nickel in the solution-serpentinite

The different release times with increasing degree of carbonatization of serpentinites are due, most likely, to the different porosity of these structures, to the increase in rock permeability, and to more efficient filtration of the fluid through the altered substrate. Another factor affecting the migration ability of palladium and platinum in contact with serpentinites is the amount of sulphides [1]. We believe that the transfer of palladium under the experimental conditions could take place in the form of a palladium-thiosulfate ion compound formed during the experiment; this ion appears as the solution passes through the rock due to the oxidation of the sulfides contained in the rock upon their release from the silicate matrix [2]. For example, the dissolution of pentlandite was recorded in the experiment (Fig. 3).

Platinum does not form strong coordination compounds with thiosulfate under these conditions. Therefore, probably, in our experiment platinum was not found in any of the eluates. The obtained data indicate the possibility of fractionation of palladium and platinum in the process of hydrothermal transformation of an oceanic ultrabasic substrate containing sulphides.

Experiments confirm the increased mobility of palladium (in comparison with platinum) in the interaction of rocks with acidic chloride solutions, which are similar in composition to low-temperature aqueous-salt solutions of marine origin, and the possibility of its transfer during serpentinization, i.e. the possibility of fractionation of palladium and platinum in the hydrothermal process. Thus, the conclusion [3] on the possibility to use the data on the distribution of PGE (and other siderophiles) in abyssal peridotites is found to support the reconstruction of geochemical trends in the change in the composition of the protolith of these rocks during its hydrothermal transformation and halmyrolysis.

Conclusions

Experiments modelling the interaction of serpentinites with a hydrothermal fluid of marine origin were performed for ultrabasic rocks of the oceanic crust. Data on the composition of solutions formed and on the leaching kinetics of the components demonstrate the transfer of palladium and the complete retention of platinum by serpentinites. It is assumed that the transport of palladium through the rock is realized in the form of its strong complex with thiosulfate ion, formed during the oxidation of sulfides contained in the rock. The experiment demonstrated the stability of the pH of the solution interacting with the ultrabasic substrate for at least 6 months and confirmed the high neutralizing potential of serpentinites. Thus, pore solutions circulating in the bottom layer with serpentinites should have a high pH, which is a geochemical indicator of the presence of extended underwater outcrops of serpentinites within the inner oceanic complexes.

The results obtained are used to explain the increased mobility of palladium in the process of transformation of mantle peridotites under oceanic crust conditions [4].

References:

Barnes S.J., Liu W. Pt and Pd mobility in hydrothermal fluids: Evidence from komatiites and from thermodynamic modeling // *Ore Geology Reviews − 2012.* 44**.** −P. 49–58.
Tyutyunnik O.A., Kubrakova I.V., Pryazhnikov D.V Formation and sorption behavior of the palladium thiosulfate under natural conditions (model experiments) // Geochemistry International − 2016. V.54, № 1. − P. 85-91.
Silantyev S.A., Kubrakova I.V., Tyutyunnik O.A. Distribution of Siderophile and Chalcophile Elements in Serpentinites of the Oceanic Lithosphere as an Insight into the Magmatic and Crustal Evolution of Mantle Peridotites // Geochemistry International. − 2016, V. 54, №. 12. − P. 1019–1034.
Kubrakova I.V., Tyutyunnik O.A., Koshcheeva I.Ya., Sadagov A.Yu., Nabiullina S.N. Migration Behavior of Platinum Group Elements in Natural and Technogeneous Systems // Geochemistry International – 2017. V. 55, № 1.− P. 108

Lapitskiy S.A., Drozdova O.Yu. Microelements in the streams of the catchment basin of the lake tsipringa (Northern Karelia): lithology and landscape

UDC 550.47

M.V. Lomonosov Moscow State University, Department of Geology, Moscow lapitsky@geol.msu.ru; drozdova_olga@yahoo.fr

Abstract. 26 streams draining the Archean granites and early Proterozoic intrusions of the Tsipringa basin were investigated. Sampling was conducted for 4 years in the summer low-lying period. In the samples studied, the contents of the main cations and anions, microelements and dissolved organic carbon were determined. The obtained results were compared with the composition of bedrock, precipitation (meteoric water), groundwater and feeding bogs to assess their effect on the trace element composition of the studied watercourses.

Keywords: *microelements; streams; weathering; boreal zone; catchment basin; rocks; North Karelia*

The boreal regions of the Russian Arctic play a crucial role in the transport of elements from continents to the ocean at high latitudes (Zakharova et al., 2007; Vasyukova et al., 2010). In view of the importance of these circumpolar zones it is necessary to perform detailed regional studies of geochemistry of trace element in boreal landscapes (Ilina et al., 2016). The composition of natural waters is a function of variety of processes and is controlled by climate, biological activity, topography, composition of parent rock and time of interaction with them. If all these factors are taken together it becomes very difficult to understand their influences on weathering processes as they exhibit very complex relationships (Sayyed, 2014). In this paper, the influence of the composition of rocks, groundwater, precipitation and runoff from the catchment area on the geochemical composition of streams flowing into Lake Tsiprings was assessed (Fig. 1).

The mouth reaches of streams of Tsipringa lake basin were sampled during extensive field campaigns in July of 2009 – 2014 during the summer base-flow period. The samples were immediately filtered through sterile, single-use filter units (Sartorius) with pore sizes 0.22 µm.

Water temperature, pH, conductivity were measured in the field. Major anion concentrations (Cl^-, SO_4^{2-}, NO_3^-, PO_4^{3-}) were measured by ion chromatography (Dionex ICS-2000) with an uncertainty of 2%. Alkalinity was measured in situ by titration with HCl using phenolphthalein as indicator. The dissolved organic carbon (DOC) was determined using analyser liquiTOC trace (Elementar) with an uncertainty of 3% and a detection limit of 0.1 mg/L. Concentration of elements was measured by ICP-MS (Agilent 7500ce).

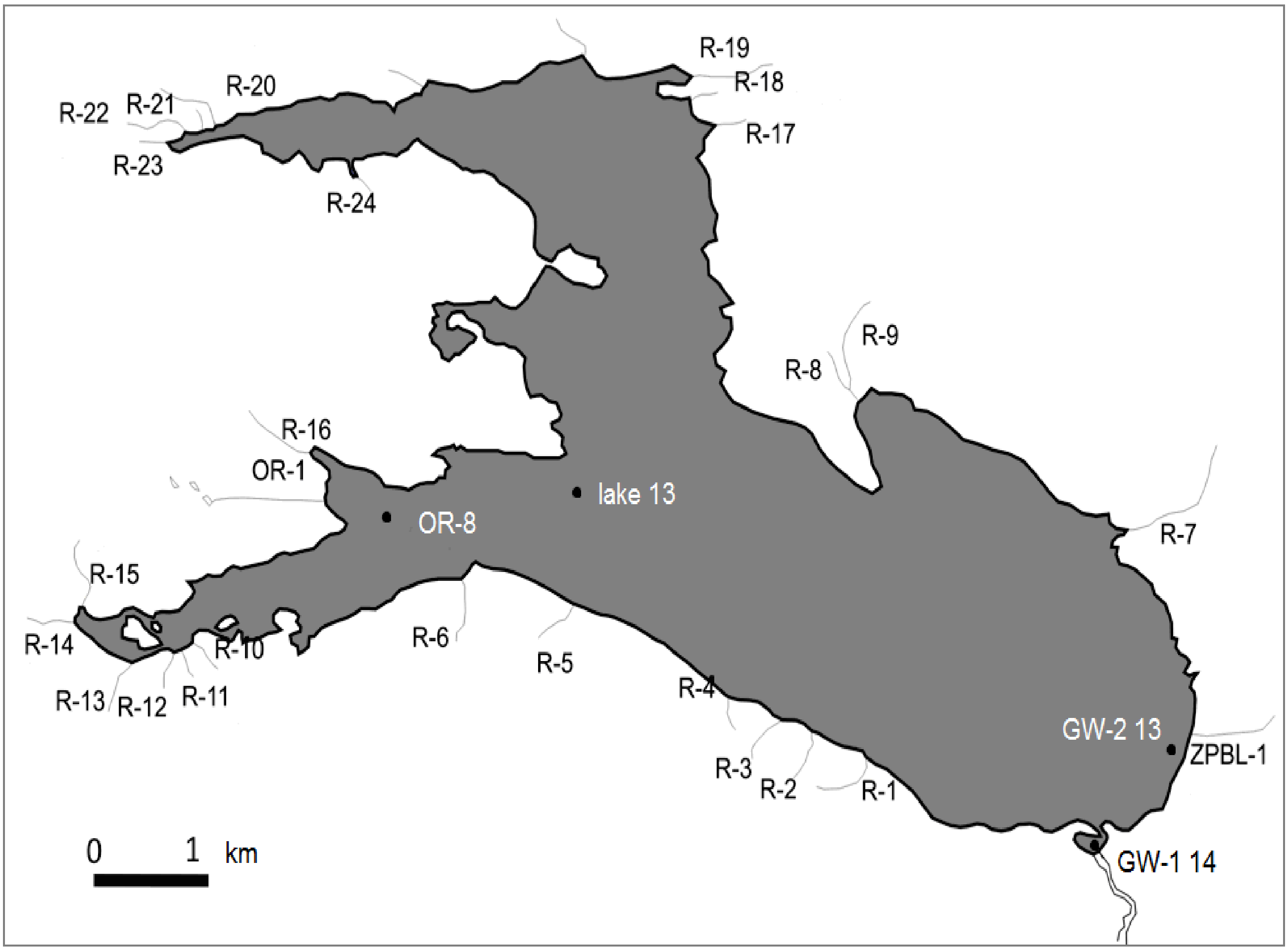


Fig. 1. The scheme of the location of the studied streams (R)

The most of streams were characterized by sufficiently low values of electrical conductivity (20-50 µSm cm^{-1}) with dissolved solid (TDS) 10-30 mg L^{-1}. Typical values of TDS for the rivers of this region are 15-30 mg L^{-1} (Zakharova et al., 2007); the concentration of river suspended matter is very low (Ilina et al., 2014). The pH ranging of streams was from 3.7 to 7.5. The average DOC concentration was 14 ±4 mg L^{-1} (from 4 to 45 mg L^{-1}). The inorganic non-balanced charge ($(\sum+-\sum-)/\sum+$) calculated for most samples is ≤ 0.1.

To assess the influence of the mineral and chemical composition of rocks, the groups of streams flowing through rocks of different lithologies were compared:

- group I: olivines, metaolivinites, peridotites, pyroxenites, olivine gabbro-norites (14 streams);
- group II: biotite granite-gneisses and their biotite, amphibole gneisses and amphibolites (4 streams);
- group III: metagabbro (8 streams).

The significant differences in the composition of streams were revealed only between groups I and III (Fig. 2).

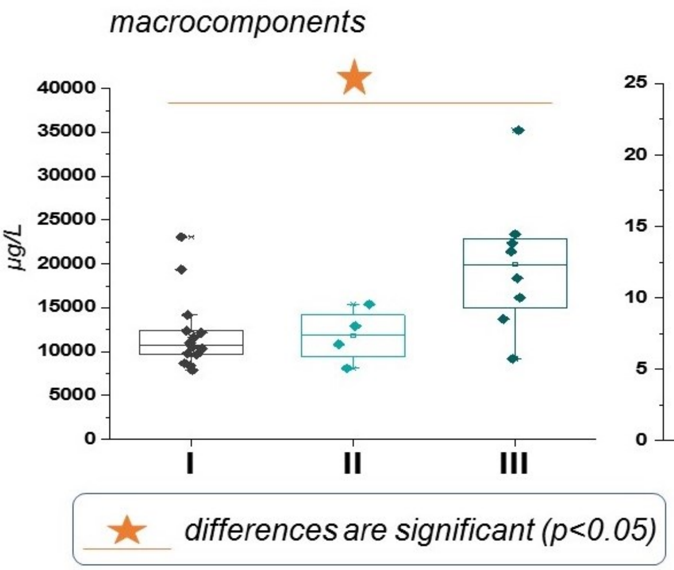


Fig. 2. Comparison of groups of streams by composition

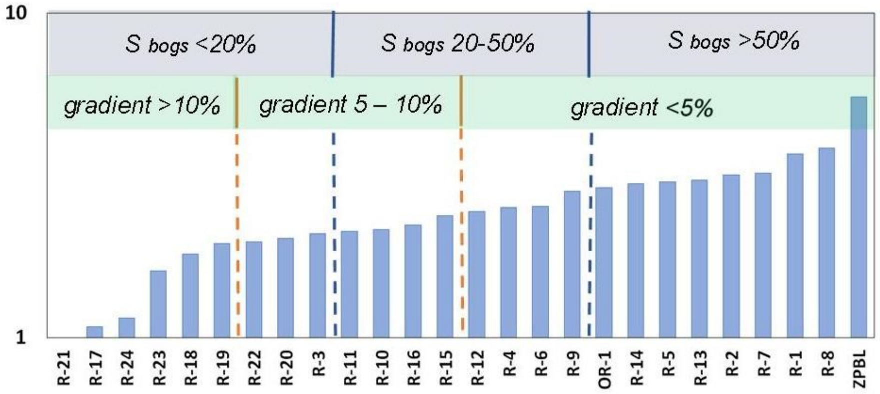


Fig. 3. Trace elements contents in the streams as a function of bogs amounts in the catchment area (S_{bogs}) and gradient

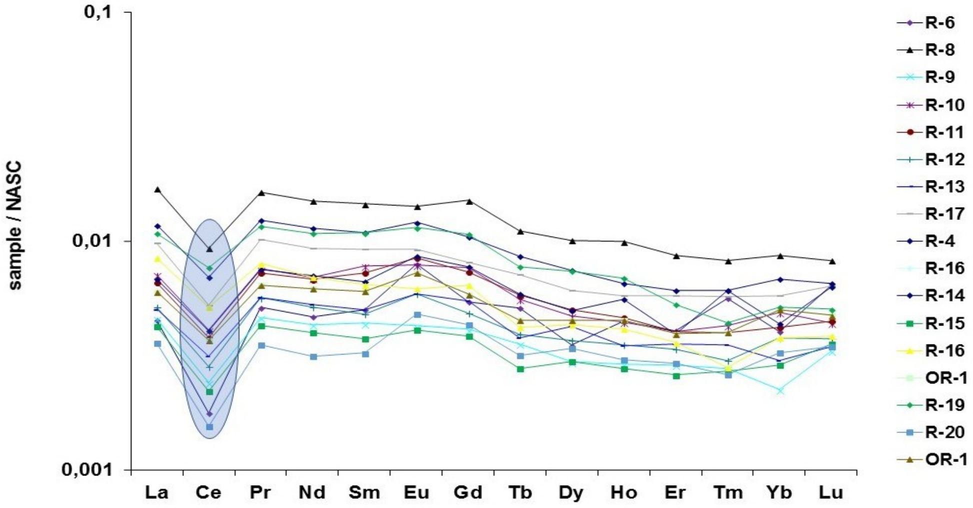


Fig. 4. REE patterns normalized to NASC for streams of Tsipringa lake basin

Further, the composition of the streams within the groups was estimated. It was found that with the same type of lithologic composition of underlying rocks, climate and biological activity, the composition of the streamflows depends on local topography. Thus, for example, the largest content of trace elements was characteristic for streams with bog feeding (bog area more than 50% of the catchment area), and the smallest - for streams with a gradient more than 5% (Fig. 3).

For most the studied streams the presence of «Ce minimum» is characteristic (Fig. 4). The presence of «Ce minimum» is linked to its oxidation on Fe oxyhydroxide colloids and particles (Ingri, et al., 2000; Pourret et al., 2008; Pédrot et al., 2015). Such a minimum is not observed in streams with bog feeding (partially suboxic waters with high concentrations of colloidal and suspended Fe).

It should be noted that all streams are characterized by very local catchment basins, and the residence time (migration) of elements is limited.

As such, in boreal landscapes, trace elements transport in small streams is determined by local topography and landscape (the presence of feeding bogs) rather than by bedrock lithology.

The work was executed at Russian Foundation for Basic Research and CNRS support (№№ 16-55-150002-CNRS_a, 18-05-00162_a).

References:

Ilina S.M., Drozdova O.Yu., Lapitskiy S.A., Alekhin Yu.V., Demin V.V., Zavgorodnyaya Yu.A., Shirokova L.S., Viers J., Pokrovsky O.S. Size fractionation and optical properties of dissolved organic matter in the continuum soil solution-bog-river and terminal lake of a boreal watershed (North Karelia, Russia) // Org. Geochem. 2014. Vol. 66. P. 14–24.

Ilina S.M., Lapitskiy S.A., Alekhin Y.V., Viers J., Benedetti M., Pokrovsky O.S. Speciation, Size Fractionation and Transport of Trace Elements in the Continuum Soil Water–Mire–Humic Lake–River–Large Oligotrophic Lake of a Subarctic Watershed // Aquat. Geochem. 2016. Vol. 22. № 1. P. 65–95.

Ingri J, Widerlund A, Land M, Gustafsson O, Andersson P, Ohlander B. Temporal variations in the fractionation of the rare earth elements in a boreal river; the role of colloidal particles // Chem. Geol. 2000. Vol. 166. P. 23–45.

Pédrot M, Dia A, Davranche M, Gruau G. Upper soil horizons control the rare earth element patterns in shallow groundwater // Geoderma. 2015. Vol. 239–240. P. 84–96.

Pourret O, Davranche M, Gruau G, Dia A. New insights into cerium anomalies in organic-rich alkaline waters // Chem. Geol. 2008. Vol. 251. № 1–4. P. 120–127.

Sayyed M.R.G. Lithological control on the mobility of elements during chemical weathering // Comunicações Geológicas. 2014. Vol. 101. № 1. P. 63-69.

Zakharova E.A., Pokrovsky O.S., Dupré B., Gaillardet J., Efimova L.E. Chemical weathering of silicate rocks in Karelia region and Kola peninsula, NW Russia: Assessing the effect of rock composition, wetlands and vegetation // Chem. Geol. 2007. Vol. 242. P. 255–277.

Vasyukova E.V., Pokrovsky O.S., Viers J., Oliva P., Dupré B., Martin F., Candaudap F. Trace elements in organic- and iron-rich surficial fluids of the boreal zone: Assessing colloidal forms via dialysis and ultrafiltration // Geochim. Cosmochim. Acta. 2010. Vol. 74.P. 449–468.

Makarova M.A.[1], Karaseva O.N.[2] Investigation of adsorption accumulation of microcomponents in various horizons of laterate bauxite-bearing weatherin profile

[1]Lomonosov Moscow State University, Department of Geology, Moscow,
[2]D.S. Korzhinskii Institute of Experimental Mineralogy RAS, Chernogolovka, Moscow district IEM RAS, (frolikovam@gmail.com)

Abstract. Experiments on the adsorption of trace elements on various types of rocks of lateritic weathering cores have been conducted under static conditions. Results on the adsorption of trace elements were obtained as a function of pH (3, 4.5, 5.5, and 7) and of the initial concentration of the solution (1ppm-20ppb). As adsorbents, samples of rocks of the bauxite profile (from the top downwards along the section) were used: cuirass, bauxites, laterites of transition zone. It is determined that against a background of high Al content in the solution, as a result of partial dissolution of gibbsite at pH 3, an insignificant desorption of most trace elements is observed. Significant adsorption was revealed for Ga, Sc. Microelements Be, Y, As, U, Pb, REE are adsorbed almost completely at pH 4.5-7. The partial adsorption is observed for Co, Ni, Cu and Cd. The absorption values of V, Th, and Bi by the solid phase, regardless of the rock and the pH, were 98-100%. The experimental data are in good agreement with the accumulation of trace elements in the profile of lateritic bauxiton weathering crusts.

Keywords*: bauxites, bauxite-bearing weathering profile, adsorbtion trase-elements*

The study of the weathering crust is of great theoretical and practical interest, since they play a huge role in the formation of the sedimentary shell of the Earth and serve as a unique source of information on the composition and patterns of evolutionary changes in the lithosphere, atmosphere and hydrosphere. Many of the world's minerals are associated with the weathering crust and the products of their redeposition. Much research in these areas (Ginzburg, 1963, Slukin, 1980, Novikov, 2007, Mamedov, 2010, Bronevoy, 1975, Zhukov, Bogatyrev, 1989, Bogatyrev, 1988, 2009, Bugelsky, 1979) was conducted, but, despite this, there are still many uncertainties regarding the redistribution of trace elements in the lateritic bauxite-bearing weathering crust. The study of the differential mobility with respect to individual microelements and the maximum capacity of the lateritic weathering crust as complex geochemical barriers remains a topically (может, now или today). Our work is devoted to solving this problem.

The Sangaredi area conditionally distinguished by us occurs in the northwestern Guinea, partly occupying the left bank area of middle and upper Cogon River. It is confined to the axial zone of Bove Syncline formed of Ordovician, Silurian, and Devonian sedimentary deposits and Mesozoic igneous rocks of trappean complex (Mamedov et al., 2016).

The surface of the all parent rocks are intensely lateritized. In this region lateritic weathering crusts cover positive landform and the mild slopes almost completely. Only steep slopes and floors of modern valleys are free of the lateritic mantles. Whatever their bedrock the lateritic weathering mantles usually show a two-horizon profile. The lower horizon mainly consists of clays grading in the mineralogical composition from polymineralic in the lower part to essentially kaolinitic in the upper part. The upper horizon is mainly composed of iron and aluminum oxides and hydroxides and includes the laterites of transition zone, the bauxite horizon, and the cuirass. This horizon can be considered as the properly lateritic mantle. The lithologically and geochemically zoned weathering profile corresponds strictly to groundwater and ground air regimes.

Experiments on the adsorption of trace elements under static conditions were carried out in a so-called «batch method»: 0.5 g of adsorbent was placed in tubes of 50 ml, an aliquot of the multi-element solution (68B Solution A High-Purity Standards) was added, then the suspension was stirred for several hours using a shaker. The concentrations of the initial solution of microelements were 0.395 - 1.2 mg / L, the concentration of the suspension was 20 g/l, pH 3. As samples were used samples of rocks of the profile of lateritic bauxiton weathering crusts (from top to bottom along the section): ferrous cuirasses (SiO_2 content 6.12%, Al_2O_3 38% Fe_2O_3 31.5%), bauxites (SiO_2 content 0.79%, Al_2O_3 43.2%, Fe_2O_3 28.9%), glandular laterites of the transition zone (SiO_2 content 5.58%, Al_2O_3 34.8%, Fe_2O_3 37.9%). After sampling and centrifugation, the concentrations of trace elements in the solution were measured by ICP-MS on an ELEMENT 2 device from Thermo Finnigan in the Laboratory of experimental geochemistry at the Lomonosov Moscow State University. The values of adsorption for each trace element were calculated from the difference between the initial concentration of the trace elements in the tube and the measured concentration in the solution: $C_{ads} = (C_{ads1} - C_{ads0}) / C_{ads1}$. Thus, the values of the adsorption of trace elements were obtained as a function of the initial concentration of the multi-element solution (1200, 800, 400 ppb) and the different proportions of the main components of lateritic bauxite weathering crusts, aluminum, iron, and silicon.

It was obtained that desorption of the most of trace elements even at pH 3 was insignificant (i.e. at high concentrations of Al in solution due to complete dissolution of solid).

It was determined that against a background of high Al content in the solution, as a result of partial dissolution of gibbsite at pH 3, an insignificant desorption of most trace elements was observed. Adsorption of Re, Cs, U, Tl, Pb is approximately equals to 5-10%. For elements of groups of rare earths, the difference between the initial concentration and the final concentration in the solution was within the error range. Significant adsorption was obtained for Ga, Sc, Th (Fig. 1). This may be due to both the lower content of iron-containing minerals, which are the main adsorbents of trace elements in the natural medium, and the dissolution of gibbsite at pH 3, which predominates in these samples. The values of the absorption of V and Bi by the solid phase in all the samples were 98-100%.

The results of the experiment on the sorption of trace elements by bauxite are well reproduced (Figure 2) in the natural redistribution of microelements in the bauxite horizon of the lateritic weathering profile (Makarova and Shipilova, 2017): the estimate is based on the concentration coefficients obtained on an isovolumetric basis by the ratio of the absolute content of the element in bauxite to the indigenous breeds.

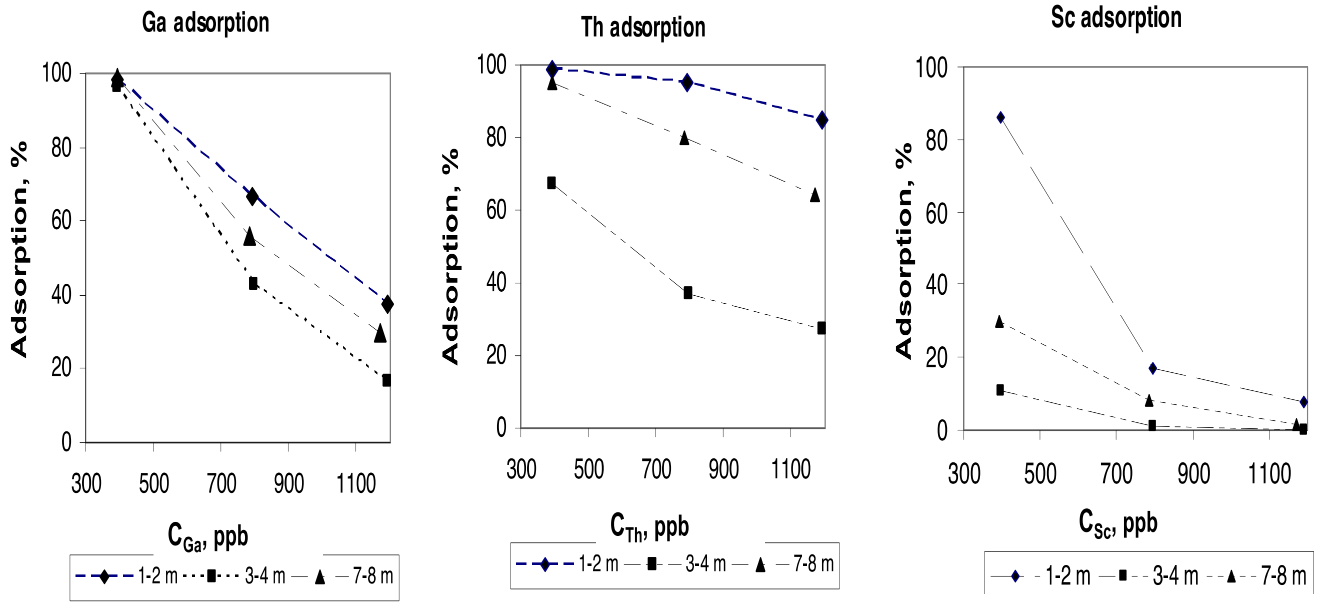


Fig. 1. Dependence of the adsorption of the microelement on the sorbent composition: 1-2 m - ferrous cuirass, 3-4 m - classical bauxite, 7-8 m - ferrous laterite of the transition zone

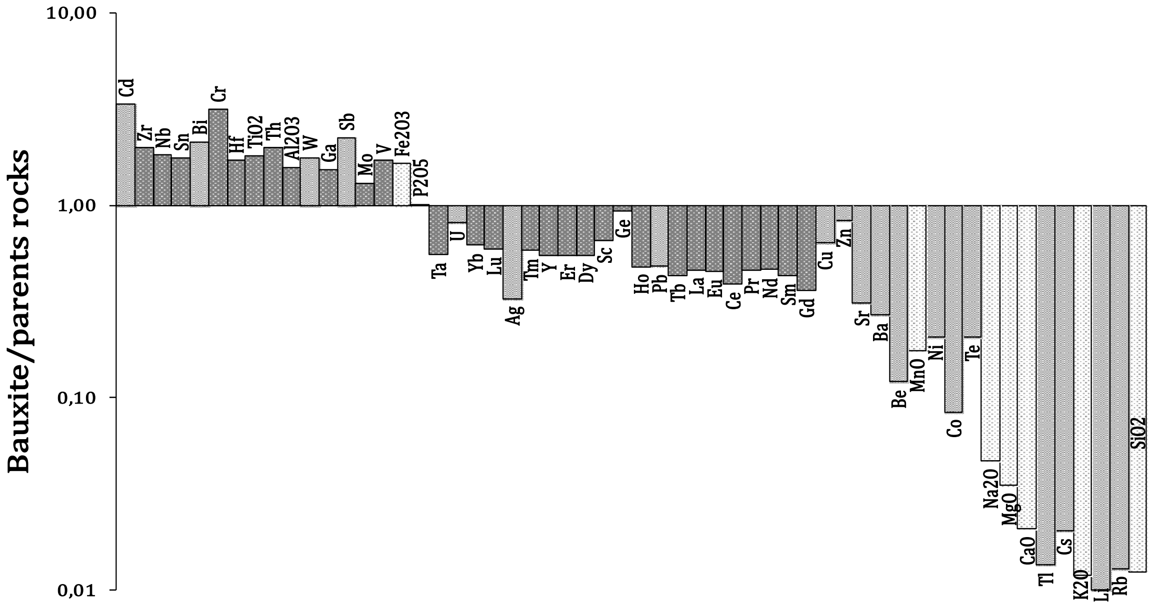


Fig. 2. Spider diagram for elements-impurities and petrogenic elements in bauxites normalized to the parent rock (light elements denote main elements, dark elements-hydrolysates), values above 1 characterize accumulation, and less than 1-carry out

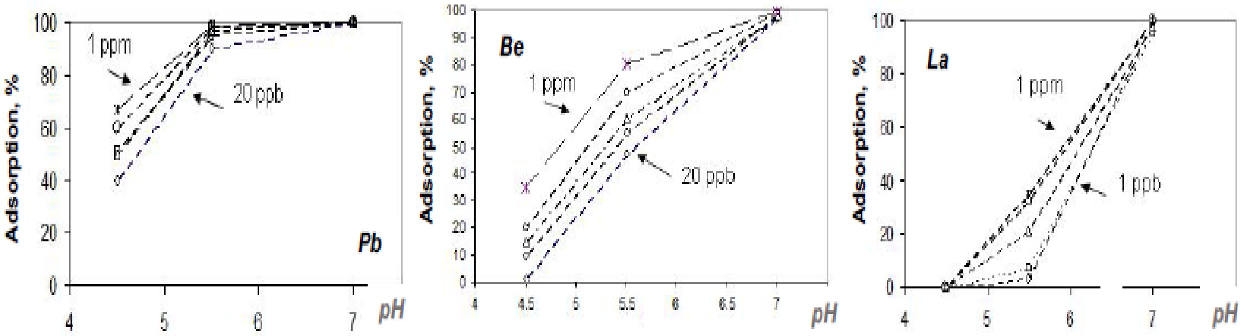


Fig. 3. Dependence of the adsorption of trace elements on bauxite on the acidity of the solution

Static experiments were also conducted to determine the acidity of the solution for sorption of the elements by bauxite: an aliquot of a multi-elements solution of a certain pH was added to tubes with a finely dispersed bauxite slurry (~ 5 g/l), covered, mixed for 24 hours with a shaker, then a solution from each tube was filtered, and analyzed by ISP-MS. Thus, the results of adsorption of trace elements as a function of pH (4.5, 5.5, and 7) and on the initial concentration of multi-elements solution were obtained: (1000, 500, 100, 50, 20 ppb).

It has been found that trace elements Be, Y, As, U, Pb and lanthanides are adsorbed almost completely in the pH range studied (Fig. 3). Bi and Th were not observed in solution even at their high initial concentration (Fig. 4). Partial adsorption is observed for Co, Ni, Cu and Cd. Although the natural profile for Co and Ni is characterized by an absolute outflow in lateritic weathering (Mamedov et al., 2017).

As expected, there is no adsorption of alkaline and alkaline-earth elements: Li, Rb, Sr, Cs, and also Re and Tl, that is, with lateritic weathering, absolute removal is typical for these elements. What is well reproduced in the natural distribution along the lateritic weathering profile (Fig. 5).

As a result of the obtained experimental data on the adsorption values on rocks of various horizons of the lateritic weathering crust, groups of elements experiencing outgrowth in lateritic weathering were obtained, and elements for which accumulation in the lateritic cover as a whole are characteristic. The obtained groups are in good agreement with the natural distribution of trase elements in the lateritic weathering profile. Whatever the parent rock, the absolute loss with the lateritic weathering is typical of Co, Ni, Sr, Tl, Rb, Cs, and Li.Most of trace elements accumulate in the lateritic weathering profile. Zr, Nb, Ta, Ga, Hf, V, Sc, Th, Bi, U, Zn, Mo, Ag, Cr, Cd, Sb, and Te starts accumulating in laterites of the transition zone, with the process similar in intensity to the aluminum and iron accumulation.

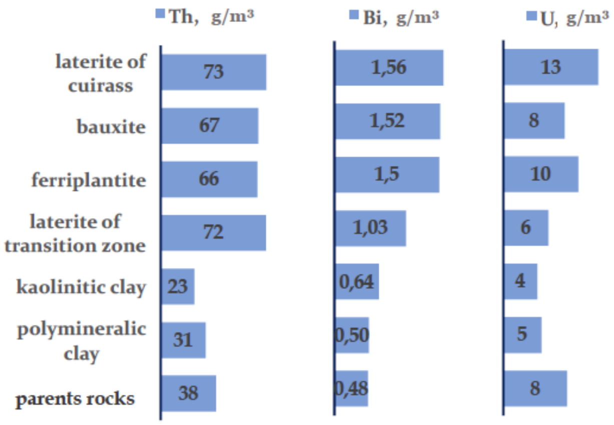


Fig. 4. Absolute content of impurity elements, for which accumulation is characteristic for lateritic weathering

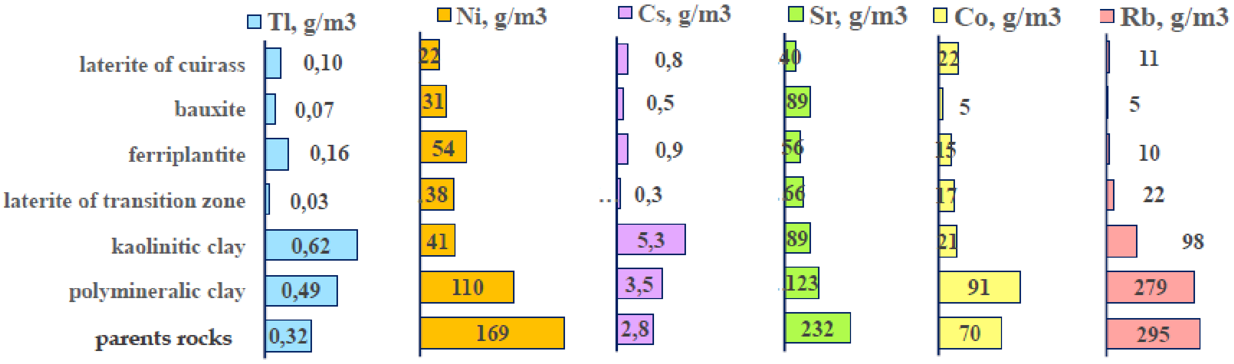


Fig. 5. Absolute content of impurity elements experiencing outflow above the clay horizon in the weathering profile

References:

Makarova M.A., Shipilova E.S. Geochemical regularities in the formation of bauxites in various parent rocks (Guinea Republic) // Geology in the Developing World: Sat. sci. tr. (based on the materials of the X International Scientific and Practical Conference of Students, Applicants and Young Scientists): in 2 tons / ot. Ed. RR Gilmutdinov; Perm. state. nat. Issled. un-t. - Perm, 2017. - T.1. -from. 92-94.

Mamedov V.I., Makarova M.A., Gomesh J. Correa and others. Features of the bauxite-bearing lateritic integuments of the Sangaredi region (Republic of Guinea) // International Scientific and Research Journal. - 2016. - No. 7 (49). - P. 114-135. DOI 10.18454 / IRJ.2016.49.178

Mamedov V.I., Makarova M.A., Shipilova E.S. Behavior (output and accumulation) of chemical elements in bauxite-bearing weatherin profile at sangaredi deposit, Republic of Guinea // 17th International Multidisciplinary Scientific Geoconference SGEM 2017. Conference proceedings,. — Vol. 17 of Science and Technologies in Geology, Exploration and Mining. — STEF92 Technology Ltd Sofia Bulgaria, 2017. — P. 35–48. DOI 10.5593 / sgem2017 / 11 / S01.005

Molchanov*[1] *V.P.*, *Medkov*[2] *M.A.*, *Dostovalov*[3] *V.A. **An experimental scheme of extraction of useful components (strategic metals, extra pure graphite and carbon nanostructures) from the graphite-bearing rocks using hydrometallurgical and plasmachemical methods.** UDC 553.22+551.2

[1]Far East Geological Institute, Far Eastern Branch of the RAS, Vladivostok, Russia, (vpmol@mail.ru),
[2] Institute of Chemistry, Far Eastern Branch of the RAS, Vladivostok, Russia,[3] Far Eastern Federal University, Vladivostok, Russia.

Abstract. A new promising source of minerals has been discovered in the south of the Far East. The metalliferous high-carbon rocks of the Ruzhinskaya area are found to contain significant reserves of graphite, gold, platinum, and carbon nanostructures (fullerenes, nanotubes, and diamond-like carbon). To extract the strategic metals from these rocks, a hydrometallurgical method was tested. The developed scheme has enabled also the extraction of extra pure graphite (99.7%) which served as an initial material for plasmachemical study. The test has yielded carbon nanoparticles, some possibly inherited from native graphite rocks. The information obtained is going to be used for the development of a resource-saving technology of useful components extraction.

Keywords: *Primorye, high-carbon rocks, technologies for extraction of useful components, hydrometallurgy, plasma chemistry, ultrapure graphite, diamond-like carbon.*

A new perspective source of minerals has been discovered in the south of the Russian Far East (Khanchuk et al., 2007; Khanchuk et al., 2010). The high carbonaceous rocks of the Ruzhinskaya square incorporate enormous resources of as crystalline graphite as carbon nanostructures, gold, platinum and rare earths. The quantity and quality of useful components concentrated in the graphite rocks of this area indicate that in the nearest future they will determine prospects of the Russian Far East mineral raw material base development.

The main task of the investigation was to study effects of various factors on a graphite-bearing rock in order to devise physicochemical principles of profitable and environmentally acceptable technology of mineral extraction. As is known, graphite of the Ruzhinskaya square represents several varieties (Khanchuk et al., 2013) depending on formation conditions. The first variety is a result of gas-condensate crystallization from a deep reducing fluid and is characterized by the presence of diamond-like carbon. The second variety is a product of metamorphic recrystallization of sedimentary protolith and is distinguished by the presence of fullerenes and nanotubes. The plasma experiments for synthesis of carbon nanoindividuals from the high-clean graphite extracted from ore formations of the Ruzhinskaya square were carried out having regard to these facts.

Commonly, the initial material for plasma chemical synthesis of carbon nanostructures is crystalline graphite (Dubrovsy, Bezmelnitsyn, 2004). This carbon modification corresponds to a condition of thermodynamic equilibrium, therefore production of the thermodynamically non-equilibrium (unstable) carbon modifications is possible only in conditions of substantial departure from the thermodynamic equilibrium. Such conditions are easily created under intensive energy supply causing sputtering and atomization of the condensed carbon. Subsequent dispersion of carbon vapor in the space of buffer gas goes with the vapor cooling that leads to occurrence of chemically unstable state of the carbon vapor in which content of free carbon atoms many times exceeds the equilibrium value defined by a value of gas temperature. The further condensation of carbon vapor in the buffer gas under the considered non-equilibrium conditions can bring into formation of the thermodynamically equilibrium graphite structure and multiple carbon nanostructures as well.

The initial material for the experiment was a sample of high carbon rock from the Ruzhinskaya square with gold content 0,1-0,2 g/t and the total REE concentration up to 100 g/t. The sample was separated into silicate and graphite components by flotation, with the pine oil as a foaming agent, the terpene alcohols as a basic reagent and the long-chain amines as a collector. During the flotation, a bulk of graphite as well as compounds of rare earth elements, silicon, aluminum, iron, magnesium, calcium, sodium, and titanium were concentrated in the foam, whereas ore minerals (gold, platinum) – in the slime (Khanchuk et al., 2015). According to X-ray fluorescent analysis, the flotation yielded industrial graphite with the ash content of 4-7 % that corresponds to 829-73 State Standard (the graphite available for making lubricants, coats of current-conducting rubber of the increased hardness, and so on.). However, graphite used in plasma chemistry as the initial raw material is required to have the lesser ach content. To lower the ach content, graphite is usually subjected to acid treatment or alloying with soda. In our case, the high ash content of the graphite is conditioned essentially by the presence of rare earths, silicon, aluminum, iron, magnesium, and calcium. In this connection, the treatment of the foam with ammonium hydrogen difluoride and subsequent acid leaching of the fluorinated product seemed to be the most appropriate decision for picking impurities. The physicochemical basis of fluoridation with ammonium hydrodifluoride is in the ability of oxygen-containing compounds of the transition and many non-transition elements to form easy-to-process ammonium fluometallates when interacting with NH_4HF (Fig.1).

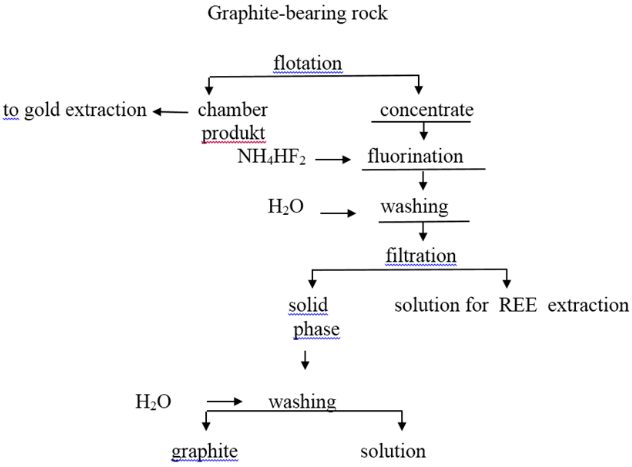


Figure 1. Scheme of graphite purification

In the fluorination, 25 g of the graphite concentrate was mixed with 5 g of NH_4HF_2, dissolved in 5 ml of water. The dense paste was being slowly heated to 190-200o C; the temperature was then raised 400°C and remained for 2 hours. As a result of this standing, 2.8 g of $(NH_4)2SiF_6$ was desublimated in the nickel condenser and 0.8 g of a mixture of NH_4HF_2 and NH_4F in the fluoroplastic one. The NH_4HF_2 - NH_4F mixture can be further recycled. The sublimated ammonium fluorosilicate had high purity. The admixtures content did not exceed 10-4 mass. %. The non-volatile residue in the reaction container was remixed with 5 g of NH_4HF_2 dissolved in 5 ml of water. The obtained paste was heated to a temperature of 190-200°C and hold at this temperature for 2 hours. The weight of the fluorinated product was 24.7 g.

The X-ray diffraction data showed that the admixtures in the doubly fluorinated product represented water-soluble fluoammonium salts of aluminum, titanium, and iron and insoluble fluorite. The leaching process consisted in double dissolving of the fluorinated product in water at the liquid-to-solid ratio of 1:10, settling of the suspension and discharging of the transparent solution. The remained portion was filtered and the resulting filtrate was evaporated to dry salts. The mass of the yielded product was 1.44 g. According to the X-ray diffraction data, the product was a mixture of complex aluminum, iron and titanium fluoammonium salts. The ash-content of the graphite purified in this way was 0.56%.

The graphite purity can be raised by acid leaching because in this case the main admixtures are insoluble calcium and magnesium fluorides. The graphite obtained at this stage was subjected to water leaching and then treated with the 10% hydrochloric acid solution at the liquid-to-solid ratio of 1:8 or with the 15% nitric acid solution at the liquid-to-solid ratio of 1:5 for an hour at 700°C. The mixture was filtered, washed with water and dried. The purity of graphite in this case comprises 99.98% (Khanchuk et al., 2016).

There is an assumption that the REE enter into the structure of natural graphite at nanolevel. In this connection it was important to determine the composition of solution of the acid leaching of fluorinated product. For this purpose nitric solution was evaporated to dryness. In the residue obtained there have been discovered high concentrations of REE (Tab. 1) that clearly confirms our conclusions about the close bonds between the rare-earth components and natural graphite.

Table 1. Rare earth elements content in the evaporated filtrate, g/t

element	content	element	content
Y	67.2	Gd	18.2
La	640.2	Tb	2.3
Ce	263.4	Dy	12.6
Pr	33.2	Ho	2.5
Nd	102.4	Er	7.0
Sm	16.8	Tm	0.9
E	3.75	Yb	5.3

Extra pure graphite can find a wide application as a constructive material in atomic power and heat engineering, as well as a starting material for preparing colloid graphite, graphitic oxide and extended graphite for use in microelectronics (production of electronic components), aircraft construction and automobile industry (fuel system parts, fuel pipes), defense industry.

The extra pure graphite was taken for making rods and a charge which were later used for producing the electric-arc plasma. The charge is a mixture of graphite powder and a collector looking like shavings of low carbon steel.

For experimental use, a plasma chamber was built. The hermetic right-angled chamber with internal dimensions 1000x800x80 mm is equipped with feed and evacuation system for buffer (and cooling, if necessary) gas, quartz windows for optical observations and measurements, and built-in thermo inlets for voltage supply on the plasmatron located inside the chamber. This laminar plasmatron worked as a generator of low temperature plasma. Coefficient of the plasma-generating gas (argon) compression consisted n=0.5-0.8. For electrodes, graphite rods of natural material were used. Electric arcing caused the charge melting.

Plasma chemical method application allowed obtaining the dispersive materials, which then have been studied with the help of Dron equipment, microprobe analyzer, atomic-force and scanning electron microscopes. The results of the study showed that the powder contained high amounts of fullerenes, carbon nano-tubes and diamond-like graphite.

The comparison of native carbon nanotubes discovered in the Ruzhinsky graphite (Fig. 2) and the synthetic nanoforms synthesized from the same material exhibits their great outward and inward resemblance. This similarity may be because of some carbon nano individuals (first of all diamond-like carbon) which could pass from the native graphite-bearing rocks. It seems that the study of native and synthetic carbon nano-objects generation should develop in two complementary ways. The developed technology for obtaining carbon nanomaterials with desired features will be in demand in various fields of science and technology. The designing of new techniques for the mass production of diamond-like carbon and carbonaceous nanotubes to be used, for example, in composite material (Rakov, 2003), or nanotubes with given parameters for electronics and metrology (Soh et al., 1999) becomes perspective.

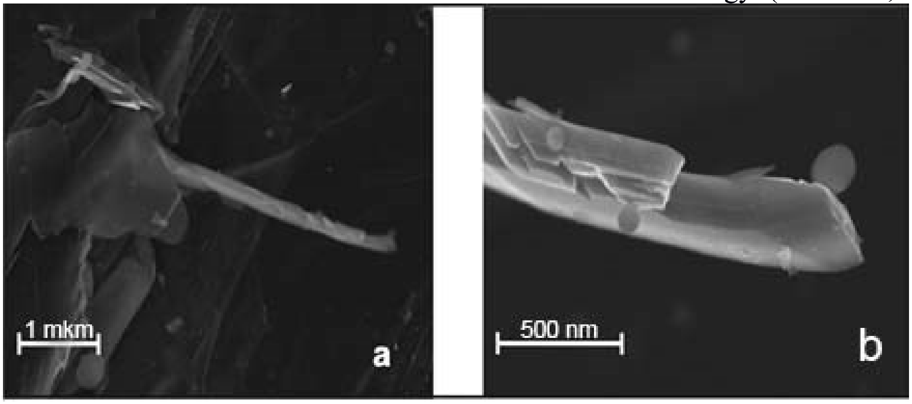


Figure 2. The image of carbonaceous nanostructure on native graphite – a, the enlarged image of the laminated carbonaceous nanotube with fullerite-like structures – b.

The fulfilled investigations made it possible to create a brand new integrated technology for a useful components extraction. At its first stage, flotation methods are needed to have noble metals and industrial graphite extracted. At the second stage the industrial graphite is treated by ammonium hydrofluoride to remove impurities, first of all rare earths. Then the obtained ultrapure graphite is subjected to plasma chemical procedure with the object of separating out the carbonaceous nanostructures (fullerenes, nanotubes, diamond-like carbon).

The fulfilled investigations made it possible to create a brand new integrated technology for a useful components extraction. At its first stage, flotation methods are needed to have noble metals and industrial graphite extracted. At the second stage the industrial graphite

The work was supported by RFBR grant № 17-05-00910.

References:

Khanchuk A I, Plyusnina L P, Molchanov V P and Medvedev E I. Noble metals in high-carbon rocks of the Khanka terrane, Primorye// Tikhookeanskaya Geologiya . 2007. Vol. 26. №1. P. 70-80.

Khanchuk A I, Plyusnina L P, Molchanov V P and Medvedev E I. Carbonization and geochemical specialization of graphite-bearing rocks of the Northern part of the khankai terrane, Primorye // J. Geochemistry. 2010. № 2. P. 115-125.

Khanchuk A I, Molchanov V P, Medkov M A, Gordienko P S and Dostovalov V A. Obtaining carbon nanostructures from natural graphite // Dokl. Earth Sciences. 2013. Vol. 452. № 2. P. 202-205.

Dubrovsy R, Bezmelnitsyn V.N. // Fullerens, nanotubes and cabon nanostructures 2004. Vol.101.P. 712.

Khanchuk A I, Molchanov V P, Blokhin M G, Elovsky E V, Medkov M A, Epov D G and Krysenko G F. DISTRIBUTION OF LANTHANIDES DURING TREATMENT OF HIGH-CARBON ROCKS WITH AMMONIUM HYDROGEN DIFLUORIDE // Doklady Chemistry. Vol. 460. № 1. P. 29-32.

Khanchuk A I, Krysenko G F, Epov D G, Voit A V, Molchanov V P and Medkov M A. Obtaining low-ash crystalline graphite from high-carbon rocks of the South of the Far East // J. Chem.Technol. 2016. Vol. **7. P.** 293-297.

Rakov E G. Methods of continuous production of carbon nanofibers and nanotubes / / J. Chemical technology. 2013. № 10. P. 2-7.

Soh H.T., Morpurgo A., Kong J. et. al. Integrated Nanotube Circuits: Controlled Growth and Ohmic Contacts to Single-Walled Carbon Nanotubes // Appl. Phys. Lett. 1999. V. 75. P. 627-629.

Tyutyunnik O.A., Anosova M.O., Grebneva-Balyuk O.N., Kubrakova I.V., Silant’ev S.A.

Methods of the study of microelement composition of ultrabasic rocks

UDC 543.4:550.4

Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences, Moscow, (NMlab@geokhi.ru)

For a complete characterization of different types of abyssal peridotites, a set of analytical methods was used, including the determination of the content of rock-forming elements by spectrophotometry and ICP-AES, as well as the determination of trace elements by ICP-AES, ETAAS and HR-ICP-MS. Parameters of the total composition of peridotites were used for qualitative assessment of the relative contribution of magmatic and hydrothermal processes in the existing picture of the distribution of their siderophile and chalcophilic elements.

***Keywords**: analytical techniques, determination of microcomponents, siderophile elements, chalcophile elements, oceanic lithosphere, hydrothermal process*

The composition of geochemical objects and the nature of the distribution of various groups of elements in them are the basis for the classification of geological material and conclusions about its origin and evolution.

One of the most complete sources of information on the main trends in the evolution of the Earth's mantle material is the ultrabasic rocks of the ocean floor, which carry geochemical signs of crustal and mantle processes. Especially important is the distribution of siderophilic (Au, Pt, Pd, Co, Ni, Cr) and chalcophilic (Ag, Cd, Sb, Pb, Zn, Cu, As, S) elements in rocks, which allows to evaluate the nature of variations of element’s content and on this basis - the contribution of magmatic and hydrothermal processes.

In this work, a complex of analytical methods including the determination of the content of rock-forming elements by spectrophotometry and ICP-AES, as well as the determination of trace elements using the ICP-AES, ETAAS and high-resolution ICP-MS are used to fully characterize the various types of abyssal peridotites.

A procedure A sample (1 g) was dissolved in high-purity HF, HCl and HNO_3 and treated with HCl to obtain the chloride forms of the elements. The insoluble residue was fused with sodium peroxide and, after treatment with HCl, was combined with the sample solution. In the solution obtained, Co, Cr, Cu, Ni, S, Sr, Zn, were determined by ETAAS; Ag, As, Cd, Pb, Sb by ICP-AES. Noble metals (Pt, Pd, Au) were determined by ETAAS after preconcentration on a powdered complexing sorbent POLYORGS-IV, which was introduced into an atomizer in the form of aqueous suspension (DLs: Au, Pd -1 ng/g, Pt 2.5 ng/g). For the determination of silicon, a sample of 0.1 g sample was fused with borax and soda, leached with 1M HCl and determined spectrophotometrically (KFK-3, Russia). Standard reference materials of silicate rocks after similar sample preparation were used as reference samples. The determination of the macrocomponents was carried out by the ICP-AES after acid decomposition using HF, $HClO_4$, HCl, a sample mass 0.1 g, also using standard reference materials.

To determine Pt, Pd, Rh, Ir, Ru and Au with reduced detection limits, a procedure for the determination by HR-ICP-MS (Element 2, Finnigan MAT, Germany) was developed after separation of matrix elements on the AG50W (Bio Rad) cation exchange resin with an external calibration. An aliquot of the decomposed sample (10 ml) was evaporated in a glass beaker, treated with *aqua regia*, then with conc. HCl and transferred to 5 ml of 0.3M HCl. The solution was passed through a pre-prepared column of cation exchanger AG-X8 (5 ml), eluting with 0.3M HCl. 15-20 ml of eluate were collected, evaporated to wet salts and transferred to a nitrate medium (5-10 ml) for ICP-MS.

Results The correctness of the determination of elements was checked by analyzing the sample of the ultrabasic rock OPY-1 (GeoPT 20) (Webb, 2007). The data obtained are presented in Table 1. It can be seen that these results are in good agreement with the statistically processed data obtained in 74 laboratories.

Table 1. The results of the determination of elements in the sample of the ultrabasic rock OPY-1

OPY-1	The obtained results	GeoPT 20 [1]	Method of determination
	%	*%*	
SiO_2	44.1	44.05	Spectrophotometry
TiO_2	0.38	0.38	ICP-AES
Al_2O_3	8.10	7.95	ICP-AES
Fe_2O_3	11.90	11.84	ICP-AES
MnO	0.18	0.18	ICP-AES
MgO	21.64	21.43	ICP-AES
CaO	7.9	7.80	ICP-AES
Na_2O	1.10	1.11	ICP-AES
K_2O	0.05	(0.049)	ICP-AES
P_2O_5	0.030	(0.029)	ICP-AES
LOI	4.71	4.65	Gravimetry
	ppm	*ppm*	
Ag	0.031		ETAAS
As	2.05	(2)	ETAAS
Cd	0.063	0.06	ETAAS
Co	92.9	86.46	ICP-AES
Cr	2421	2421	ICP-AES
Cu	43.6	43.65	ICP-AES
Ni	876	871	ICP-AES
S	0.028	(0.025)	ICP-AES
Sb	<0.1	(0.1)	ETAAS
Sr	16	15.99	ICP-AES
Pb	0.62	(0.5)	ETAAS
Zn	61.9	61.81	ICP-AES

Table 2. The composition of the solution before and after separation of the matrix

Element	OPY-1 ppm, (1 g/100 ml)	OPY-1, ppm after passing through the cation exchanger
Al	359	35.78
As	0.005	<0.005
Ba	0.058	0.014
Be	0.0008	<0.0005
Ca	79.6	0.08
Co	0.865	0.003
Cr	24.2	11.4
Cu	0.43	0.002
Fe	124	0.05
Hf	<0.01	0.02
K	86.1	0.5
Li	0.44	0.038
Mg	216	0.1
Mn	0.002	0.001
Mo	<0.001	0.007
Na	574	10.8
Ni	8.71	<0.005
P	3.00	<0.01
Pb	<0.005	<0.005
Rb	<0.01	<0.01
S	0.039	0.035
Sc	0.28	0.001
Sr	0.16	0.009
Ti	4.04	3.7
V	1.67	0.005
W	<0.01	<0.01
Y	0.094	0.005
Zn	0.62	0.01
Zr	0.17	0.12

Table 3. Isotopes of precious metals and possible interferences from oxide and argide ions

Isotope	Interferences	Isotope	Interferences
^{99}Ru	^{59}Co^{40}Ar	^{191}Ir (37.3%)	
^{101}Ru (17.07%)	^{61}Ni^{40}Ar, ^{85}Rb^{16}O	^{193}Ir (62.7%)	^{177}Hf^{16}O
^{102}Ru (31.61%)	^{62}Ni^{40}Ar, ^{86}Sr^{16}O, ^{102}Pd (0.96%)	^{194}Pt (32.9%)	^{178}Hf^{16}O
^{103}Rh (100%)	^{87}Sr^{16}O, ^{87}Rb^{16}O, ^{63}Cu^{40}Ar	^{195}Pt (33.8%)	^{179}Hf^{16}O
^{105}Pd (22.23%)	^{65}Cu^{40}Ar	^{196} Pt (25.3%)	^{180}Hf^{16}O, ^{180}W^{16}O
^{106}Pd (27.33%)	^{90}Zr^{16}O, ^{88}Sr^{18}O, ^{66}Zn^{40}Ar	^{198} Pt (7.2%)	
		^{197}Au (100%)	^{181}Ta^{16}O

Table 4. Results of PGEs and gold determination in OPY-1, ng / g

	^{101}Ru	^{105}Pd	^{197}Au	^{103}Rh	^{191}Ir	^{198}Pt
OPY-1(1)	2,4	11,7	1,09	1,48	0,88	13,3
OPY-1(2)	2,5	12,8	1,01	1,80	0,98	12,0
OPY-1(3)	3,6	12,8	1,04	0,86	0,83	11,3
Average value, the obtained results (HR-ICP-MS)	**2,82**	**12,4**	**1,05**	**1,38**	**0,89**	**12,2**
S	0,65	0,63	0,04	0,48	0,08	0,99
RSD, %	23	0,05	3,8	35	8,5	8,1
Detection limit	0,5	1,0	0,2	0,5	0,1	0,5
GeoPT 20 [1]	**4,89**	**12,2**	**1,0**	**1,53**	**1,06**	**12,9**
Average value, the obtained results (ETAAS)		**10**	**5**			**11**

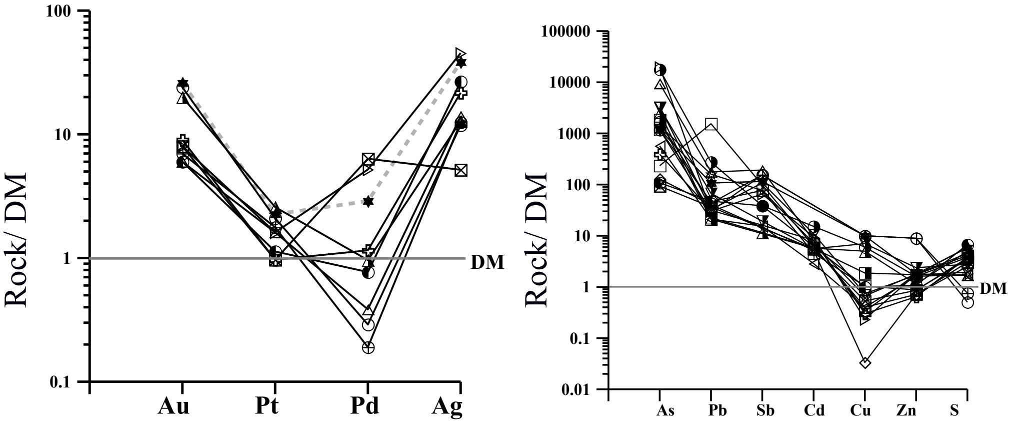


Fig.1. Distribution of normalized to DM values of the content of (a) siderophilic and (b) chalcophilic elements in abyssal peridotites [3].

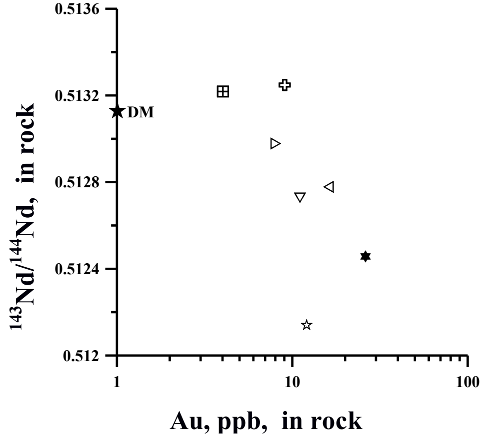


Fig. 2. Covariations of the Au content and ^{143}Nd/^{144}Nd ratio of the abyssal peridotites

ETAAS procedure, which has proven itself in the determination of Pt, Pd and Au, does not make it possible to determine Ir, Rh, and Ru in samples of ultrabasic rocks. To expand the range of PGEs under determination, high-resolution mass spectrometry was used as the detection method with the preliminary separation of matrix components on cation-exchange resins. This approach is often used in a combination with isotope dilution technique, providing the highest accuracy and precision in the determination of Ir, Ru, Pt, Pd.

We developed the method for determining the PGEs (except osmium) with external graduations, which requires quantitative recovery of platinum elements from the solution. In the model experiments, conditions were found that make it possible to obtain a practically quantitative yield from the column of Pt, Pd, Rh and Au and an 80% yield of Ir. It was shown by the ICP-AES method that after the separation of the matrix components by cation exchange (Table 2), the anion-forming elements such as Cr, Ti, Hf, W, Zr creating mass spectral interferences under the determination of PGEs can remain in the solution (Table 3). After measuring the PGEs and gold for all isotopes, the obtained data are analyzed and, taking into account our results and literature data [2], the isotopes most free from interferences are chosen: ^{101}Ru, ^{105}Pd, ^{197}Au, ^{103}Rh, ^{191}Ir, ^{198}Pt. The results obtained, as well as the detection limits calculated taking into account the value of the blank test and its standard deviation, are given in Table. 4. It can be seen from the table that good agreement of the results was obtained for all elements except ruthenium. The results of the determination of ruthenium are understated, probably because of the loss of volatile ruthenium tetraoxide upon acid decomposition in an open system. Such losses can be avoided by using in the initial stage decomposition in closed vessels (autoclave or microwave). The somewhat understated values for Ir and Rh are apparently associated with incomplete extraction from the cation exchanger, but the differences obtained do not exceed the determination error (25%) for this level of concentrations.

A comparison with ETAAS determination of Pt, Pd, and Au after sorption preconcentration also shows good agreement of the results.

Thus, a technique for determining the PGE, which extends the number of elements analyzed, has been developed. The agreement of the results allows us to consider our data as sufficiently reliable for this level of concentrations and to believe that further geochemical conclusions are not explained by possible systematic deviations.

The research was carried out within the framework of the Program of Fundamental Scientific Research of State Academies for 2013-2020 (Project Number in the state task 0137-2016-0010) with the support of the Russian Foundation for Basic Research (Grants No. 15-05-00021a and No. 18-05-00001a).

References:

1. Webb P. C., Thompson M., Potts P.J., Burnham M. GEOPT20 – AN INTERNATIONAL PROFICIENCY TEST FOR ANALYTICAL GEOCHEMISTRY LABORATORIES – REPORT ON ROUND 20 / January 2007 (Ultramafic rock, OPY-1) GeoPT20 Report. http://www.geoanalyst.org/wp-content/uploads/2017/10/GeoPT20Report.pdf
2. Men'shikov V.I., Vlasova V.N., Lozhkin V.I., Sokol'nikova Iu.V. Determination of platinum-group elements in rocks by icp-ms with external calibration after cation exchange separation of matrix elements by ku-2-8 resin// Analytika and Kontrol'. – 2016. V.20. № 3. - P.190-201
3. Salters V.J.M., Stracke A. Composition of the depleted mantle // Geochem. Geophys. Geosystems. – 2004. 5, 0 doi 1.1029/2003GC00059
4. Silantyev S.A., Kubrakova I.V., Tyutyunnik O.A. Distribution of Siderophile and Chalcophile Elements in Serpentinites of the Oceanic Lithosphere as an Insight into the Magmatic and Crustal Evolution of Mantle Peridotites // Geochemistry International. – 2016. V. 54. № 12. - P. 1019–1034.

Tyutyunnik O.A., Kiseleva M.S., Kubrakova I.V. Analytical solutions for the environmental control of sulfide ore deposit areas

V.I. Vernadsky Institute of Geochemistry and Analytical Chemistry RAS, Moscow (NMlab@geokhi.ru)

To improve the efficiency of monitoring of natural systems at risk of technogeneous pollution, a set of methods based on the use of microwave sample preparation and analysis of samples by instrumental methods (ICP-AES, ETAAS) has been developed. Metrological characteristics of the determination of sulfur and its forms, as well as the toxic elements (including mercury), are confirmed by analysis of standard reference materials of soils and rocks.

It is shown that the high efficiency of modern methods of sample preparation combined with an express determination of a wide range of elements in the complex samples provides the possibility to obtain large volumes of analytical information necessary for solving environmental problems.

Keywords: *analysis of environmental objects, microwave sample preparation, atomic spectrometry methods, toxic elements*

To predict the environmental hazard of technogenic processes, a study of a huge number of various samples (ores, overburden, natural waters, technological solutions, organisms exposed to technogenic impact) is necessary. In the development of sulfide deposits, the assessment of anthropogenic load is based primarily on data on sulfur-containing minerals present in overburden and dump rocks and determining the degree of possible acidification and the content of toxic microcomponents (mercury, arsenic, selenium, lead, cadmium, etc.) in them, capable of release. To fully characterize the degree of technogenic impact on the ecosystem, data on the content of toxic elements in soils and biological components are also required. Thus, reliable and rapid methods for the determination of toxic elements in various natural materials are needed for analytical support of environmental monitoring. This work is devoted to the development of such techniques based on the use of microwave systems for sample preparation and analysis of samples by instrumental methods. General questions and the current state of microwave sample preparation in geochemical and ecological studies are described earlier [1].

Microwave decomposition of samples was carried out using laboratory systems MARS6 and MarsXpress (CEM Corp., USA) with EasyPrepPlus and XP-1500Plus vessels at 180-200 ° C. Ten samples were loaded simultaneously. The solutions were analyzed by ICP-AES (Iris Intrepid II XDL, Thermo Electron Corp., USA) or ETAAS (AA-7000 (Shimadzu Corp., Japan)). The mercury was determined by the "cold vapour" technique.

Determination of total sulfur and its forms Determination of the total sulfur content, as well as of it's sulphate, sulphide and organic forms in rocks, was carried out after chemical isolation by treatment with appropriate reaction mixtures (individual acids or a mixture of acids).

To avoid losses of sulfur in the form of volatile compounds, heating of the samples in hermetically sealed vessels XP-1500Plus was used. Under conditions of microwave heating, such vessels allow not only to eliminate the loss of volatile components, but also to reduce the consumption of reagents, to reduce the risk of cross-contamination of the sample, and to minimize the time of obtaining a given component in a form convenient for determination.

The control of the correctness of the results was carried out by analyzing sulfide-containing silicate rocks reference materials (RMs) (Table 1). The reliability of the results obtained was confirmed by the coincidence of the obtained and certified values, as well as by the data of the direct CHNS-analysis.

Table 1. The results of determination of the total sulfur content (%) in RMs

Reference material	ICP-AES	CHNS-analysis	Certified
SdAR-H1	0,45±0,04	0,48±0,04	(0,46)
CDO-5	0,11±0,02	-	0,1

SdAR-H1 – river sediment, CDO-5 – bottom sediments

In addition to sulfur, geoecological tests involve the identification of a wide range of macro and microelements, including potentially dangerous ones. The approach proposed makes it possible to use the solutions obtained for the complete characterization of the elemental composition of rocks, ores, technogenic solutions, soils, etc. Examples of the determination of certain accompanying trace in RMs are given in Table 2.

Determination of mercury and other toxic elements Sulphide ores are rich not only sulfur but also heavy metals, which also belong to priority, mutagenic and toxic pollutants of the environment. Metal ions, depending on environmental conditions, exist in different degrees of oxidation and are part of inorganic and organometallic compounds, can be present in the form of true solutions, a colloidal dispersed state, or be part of mineral and organic suspensions. Therefore, the behavior and transformations of heavy metals in nature are under close ecological control; special attention is paid to mercury.

Table 2. Results of ICP-AES determination of some microelements (μg / g) in RMs

Element		SdAR-H1	DBC-1	SdAR-1
Be	found	22,4	3,90	2,65
	certified	22,07±0,61	3,87±0,25	2,52±0,17
Cd	found	25,8	0,075	5,16
	certified	25,2±0,42	(0,08)	5,27±0,33
Cu	found	1100	20,4	298
	certified	1159±8,1	21,35±1,08	302±10,227
Mo	found	61,5	2,5	12,09
	certified	64 ±2,74	2,51±0,175	12,6±0,7
Pb	found	4212	55	997
	certified	3893±89,73	53,5±2,35	979,3±27,8
S	found	4450	238	1185
	certified	(4550)	(200)	(1200)
Zn	found	3820	23,1	953
	certified	3684±85,61	21±1,06	932±26,6

SdAR-H1 – river sediment; DBC-1 – clay; SdAR-1 – modified river sediment

In the paper [2] we have developed methods for preparing natural objects for the determination of mercury and other toxic elements (As, Cd, Pb, Se, etc.) using various procedures of microwave decomposition of samples under high pressure conditions. The decomposition of samples of different nature (natural high-colored waters, soils, bottom sediments, biological objects) was carried out in EasyPrep vessels with partial removal of the gas phase. The use of such vessels makes it possible to increase the mass of degradable samples to 2 g (which increases the representability of the decomposable sample and makes it possible to reduce the detection limits of elements) and to eliminate the loss of volatile elements. The duration of preparation of a series of samples is about 30-40 minutes. Aqueous solutions obtained after acid decomposition can be analyzed by various instrumental methods (ETAAS, ICP-AES, ICP-MS). According to this scheme, ores and sulphide-containing rocks were analyzed; the correctness of the results was confirmed by analysis of the CRMs (Table 3).

Table 3. Determination of mercury (μg/g) in RMs of soils, rocks, bottom sediments using the "cold vapour" technique after microwave sample preparation (*n*=3, *P*=0.95)

Sample	Found	Certified
SDPS-2	0,122±0,007	0,130±0,020
SCT-2	0,355±0,014	0,420±0,100
Bil-1	0,030±0,004	(0,030)
DBC-1	0,72±0,08	0,712±0,014

SDPS-2 - soil sod-podzolic sandy loamy; SCT-2 - soil of typical chernozem; Bil-1 – Baikal's sludge; DBC-1 - clay

Table 4. Results of AAS determination of elements in solutions after microwave decomposition of tissues of hydrobionts by the "add-found" method. (*n*=3, *P*=0.95)

Element	Add, ng/ml	Found, ng/ml	RSD, %
Hg	0	0,24	7,2
	0,25	0,49	5,1
As	0	34,8	3,5
	10	45,3	5,2
Cd	0	0,084	1,6
	0,05	0,14	1,4
Pb	0	1,8	2,8
	1,0	3,1	3,0
Se	0	6,19	1,3
	5,0	11,3	2,6

Table 5. The results of the determination of elements in CRMs after acid extraction with partial removal of gaseous reaction products (n=3, P=0,95), μg / g. m =1,0 g, T =180 ^{0}C

Reference material		As	Cu	Pb	Zn	Cd	S	Ce	Se	Hg
SCT-2	Found	22,6±0,7	106,0±3,5	93,3±4,3	183±3	1,6±0,1	409±11	66,9±2,5	-	0,170±0,008
	Certified	21±5	110±10	90±10	180±20	1,8±0,4	500±100	70±20	-	0,180±0,090
Bil-1	Found	17,9±1,2	44,2±1,7	18,3±3,2	90,4±3,5	0,4±0,1	1597±38	75,0±2,0	1,05±0,1	0,045±0,014
	Certified	18±3	52±7	21±3	96±14	-	1650±130	80±5	(0,97)	(0,030)
DBC-1	Found	10,6±1,6	21,87±0,93	51,8±2,8	20,7±1	0,02±0,01	231±5	110,7±3,5	2,9±0,1	0,638±0,074
	Certified	9,0±0,3	21,35±0,24	53,5±2,3	21,0±0,6	(0,09)	(200)	119,9±4,7	3,0±0,2	0,712±0,014

SCT-2 - RM of soil of chernozem typical; Bil-1 - RM of Baikal's sludge; DBC-1 – clay; Estimated values are given in parentheses.

The possibility of determining toxic elements in tissues of hydrobionts according to the developed methods was confirmed in the work [2] by the method of additives (Table 4).

In the paper [3] new technical solutions promising for microwave sample preparation of complex natural objects have been experimentally studied and presented: decomposition of heavy mineral substances at T = 270 ° C; preparation of samples for the determination of components in the form of volatile compounds (for example, the determination of osmium); decomposition under conditions of partial removal of gaseous reaction products; simultaneous decomposition of different in composition and mass of samples. The efficiency of these solutions in determining the toxic elements that form volatile compounds during preparation is confirmed by the soil analysis (data given in Table 5).

The proposed set of analytical methods increases the efficiency of monitoring natural systems that are at risk of anthropogenic pollution. The high productivity of modern methods of sample preparation combined with the rapid instrumental determination of a wide range of trace elements in complex samples provides the possibility to obtain large volumes of analytical information necessary for solving environmental problems.

References:

Kubrakova I.V., Toropchenova E.S. Microwave sample preparation for geochemical and ecological studies //J. Analyt. Chem.- 2013. V. 68, № 6. - P. 467-476.

Tyutyunnik O.A., Getsina M.L., Toropchenova E.S., Kubrakova I.V. Microwave preparation of natural samples to the determination of mercury and other toxic elements by atomic absorption spectrometry //J. Analyt. Chem. - 2013. V. 68, № 5. - P. 377-385.

Kiseleva M.S., Tyutyunnik O.A., Nikulin A.V., Kubrakova I.V. Microwave Treatment of Natural Objects Using New Technical Solutions //Zavodskaya laboratoriya. Diagnostika materialov. - 2014. V.80, № 6. - P.7-11 (in Russian).