Experimental geoecology

Maghidov S.Kh. Extraction of fluids and geological environment protection

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Abstract. Anthropogenic changes taking place in the bowels are considered as the sources of geoecological risks. Activity of oil and gas sector, causing changes in the geoenvironment, promotes induced seismicity. Besides, associated stratal water of oil deposits can pollute ground freshwaters, making them unfit for drink supply. Along with it the mineralized associated waters cause salinization of soils contributing decrease in their bioproductivity and result in desertification of territories. Irrational use of groundwaters have resulted in their depletion, depriving the next generations of the high-quality freshwater sources. All this things call for urgent and drastic measures of geoenvironment, ground freshwater and soil protection.

Key words: geological environment, fluids, groundwater, soil salinization, depletion, rational use of water resources, earthquakes.

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Changes taking place in the bowels, and artificial defluidization above all, present a great potential threat. Depths of oil and gas wells and their density per unit of area are almost everywhere growing, but output of hydrocarbons fall and the elastic potential of underground decrease. And this happens not only on the local sites, but in such major areas as the Russian Federation and the United States. Thus, over half a century of operation in Russia the share of oil flowing wells dropped from 80 percent to 10 percent. Similar trends are observed in the US and other countries. The density of the general fund of oil and gas wells in the US per thousand square kilometers has approached hundred and continues to grow. In some regions this figure is even higher. All this results in the fact that the lithosphere system loses its elastic and plastic properties becoming brittle and rigid geomaterial hindering the course of natural geodynamic processes. And this leads to the accumulation of stress and promotes the emergency of strong and super-strong earthquakes. Trend analysis of the reduction of seismic energy of earthquakes over time suggests a possible manifestations in the near future not only super-strong tectonic earthquakes, but also more powerful ones. Intensification of anthropogenic activities entailing disturbance of natural conditions in the deeper subsurface horizons permit to suggest the possibility of hyper tectonic earthquake with a magnitude of 10 and above in the near future, if drastic measures to protect the geological environment will not taken.

The modern technogenic activity inflicts no less damage to fresh underground water - the main reserve for drinking water supply in the future. In addition, in many regions there is a tendency of growing the fraction of fresh groundwater utilization, despite increasing pollution of underground hydrosphere due to intensive engineering activities [Goldberg, 1987; Plotnikov, 1983]. Higher quality of groundwater is still preserved, but at the current rate of pollution growth it can become equal or even exceed the surface waters by the content of toxic substances in a short term. This can be illustrated by the example of man-made contamination of Daghestan underground water. Currently in Northern Daghestan groundwater in the areas of thousands of square kilometers are polluted with arsenic. In Babayurt, Kizlyar, Nogai and some other areas the content of arsenic in groundwater exceeds maximum permissible concentration (MPC) 2-4 times on the average [Kurbanova, 2008]. In that work as a maximum permissible concentration the value of 0.05 mg/l is used for trivalent arsenic compounds, but for fishery ponds MPC of pentavalent arsenic compounds five times less. This means that the average arsenic content may exceed MPC up to 20 times. The authors of this work rightly qualify this situation as catastrophic. According to them, the processes contributing to the contamination of groundwater are in progress. Unless we take drastic measures, North Daghestan artesian basin will meet continuous arsenic contamination and become unfit for drinking.

In addition, groundwater of many artesian wells in the region contains significant amounts (2-4 MPC) of pollutants such as heavy metals, including manganese, phenols and other organic substances. Such course of events in this vast region will inevitably lead to enormous environmental, economic and social issues. As one of the main reasons, authors of the publication indicate infiltration of highly toxic water from bedding lower aquifers in freshwater of productive horizons. This explanation is the most logical and supported by the majority of the observed facts. This process can also occur naturally, because interstratal flows exist in areas not affected by anthropogenic activities. However, their intensity is in most cases many orders of magnitude below the catastrophic situation in Northern Daghestan.

Also in this area a few decades ago was introduced the method absurd and harmful from an environmental point of view, bypassing of lower deposited highly mineralized water in the overlying layers without withdrawal it on the surface. This method was first introduced at Maysky oil and gas condensate field. If two aquifers connect pipe, flow will continue as long as the pressure in them equalize. In addition, oil and gas enterprises of Republic Dagestan (RD) often pump stratal waters in the overlying horizons with less pressure not only to maintain reservoir pressure, but also to get rid of them. Proper control over this activity is practically absent, although there are many government agencies obliged to do it. Up until now, many abandoned wells operate in a self-flowing, salting and contaminating the soil and water sources. According to some estimates, about 80 % of extracted groundwater is not used in the national economy, and is discharged to the surface that results in depletion of hydro reserves and is one of the main sources both of primary and secondary salinization of ground and surface waters.

You would take into account the fact that the wells, liquidation or preservation of which have not met all technical requirements, may be the cause of the interstratal flows intensification with all the consequences. All this inflicts irreparable damage not only to the underground hydrosphere, but also landscapes and biogeocenoses of Daghestan. According to our estimates, for the entire period of operation in the RD, about roughly 30 million tons of salt were brought out with groundwater on the surface [Maghidov, 2005]. In that paper the approximate assessment of the amount of salt causing salinization in RD may be underestimated, since it does not take into account additional salinization due to receipt of salt from adjacent regions.

Such large-scale delivery of salt turns fertile land in the salt-marshes or alkaline soils with low biological productivity [Maghidov, 1997].

Thriftless and inefficient use of groundwater results not only in depletion of its reserves and also helps to reduce compressibility potential of bowels both in some regions and the RF as a whole. As a result of human activities during the past half-century, this parameter have decreased in Russia several times [Maghidov, 2011; Maghidov S., Musayev, 2011; Maghidov, 2013 a].

The dynamics of this process is shown in Figure 1. It is necessary at the same time take into account that intensive groundwater extraction for economic use reduces the compressibility potential as well. Figure 2 shows as an example the data on the use of groundwater in the national economy of Republic of Daghestan.

Such large-scale changes in the geological environment are very dangerous and can promote geo-environmental disasters of a planetary scale. This applies to the increase of seismicity level too. In some oil producing regions, it is considerably increased due to anthropogenic activities. Global changes in geohydrosystem can cause both strong and super-strong earthquakes. From Fig. 1 it is follow that intensive injection of water into reservoirs can slow and even reverse the decline of reservoir pressure.

Among the major problems associated with misallocation of water resources there is intense decline in stocks of fresh groundwater. Provision of groundwater varied in different regions, so the production level should be set at the levels to prevent their depletion. Table 1 presents the data on the North Caucasus Federal District.

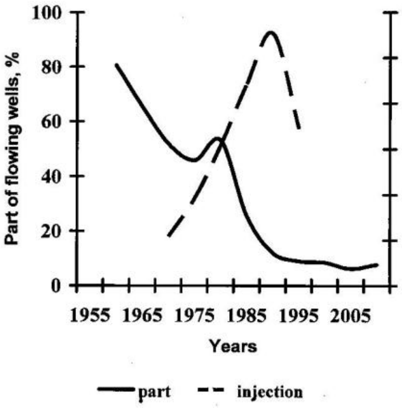

Fig.1. Injection of water into reservoirs in RF and compressibility potential of underground water

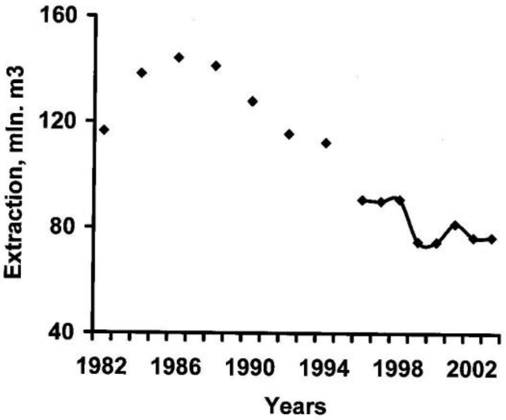

Fig.2. Mining of underground water in Republic of Daghestan.

Table 1. Operational resources and extraction of ground water by the regions of the North Caucasian Federal district of Russian Federation in 2008 and 2009 (average), thousands m3 per day.

	Resources for 1.01.09		**Average extraction (2008 and 2009)**	
	Total	Category A	**General**	Per capita, m^3/day
Russian Feredation	95494.7	29307.1	23381	0.165
Republic of Daghestan	1166	346.4	410	0.151
Republic of Ingushetia	100	-	50.4	0.099
Cabardino-Balkaria	1395	453	235	0.263
Northern Ossetia Republic	1679	666	471	0.672
Chechen Republic	1252	414	245	0.198
Stavropol Krai	1815	401	221	0.082

The table shows that Daghestan is the only North Caucasian region where the extraction of the underground waters has already exceeded the resources of category A. It's one more proof of irrational using of resources of ground freshwater.

The resources are divided onto 4 categories by the degree of being investigated: A, B, C1 and C2. Category A includes the most explored resources, and category C2 the least explored. Category C2 is also called reserve resources.

Table 2. Operational resources by the degree of exploration of the deposits, quality of waters and conditions of exploitation by 1.01.09.

Category of resources	A	B	C_1	C_2	Total
Republic of Daghetsan	346.4	248.1	381.8	189.4	1165.7
Russian Federation	29307	28185	25095	12907	95495

The more complete information about the resources with division by categories is given in the table 2 for Russia and Daghestan.

Dynamics of water extraction from underground sources in RD is also given in the work [Water resources of Daghestan, 1996]. In this paper, great concern has been expressed about the state of the water sector of the RD, and some measures are proposed to improve the situation.

Along with the depletion of compressibility potential and resources of underground water with their pollution, there is no less acute problem of soil contamination with groundwater. Researching this problem is not enough attention is paid to, although the degree of its importance is comparable with the above. All these problems are closely interconnected. So, lowering reservoir pressures in the productive aquifer promotes intensification of interstratal flows and pollution of fresh water with more saline and polluted. Depletion of groundwater is parallel to the elastic energy exhaustion stored in the bowels.

To meet the needs of RD agriculture, huge amounts of fresh water are also selected from surface sources without significant economic effect.

Selection of water for agricultural use per unit of area in RD exceeds the corresponding figures for the Russian Federation two orders and more.

Nevertheless, almost all plain land, especially in Northern Daghestan is salted in one degree or another. There are enough works on the problem of soil salinity and the related problem of area desertification in the northern zone of Dagestan [Mirzoyev, 2013; Zalibekov, 2000; Fedorov, 1991; Maghidov, 2013 b].

In [Fedorov, 1991] [12], with reference to the research conducted in 30 - 60s of the last century by known soil scientist S.V. Zonn it is noted that large areas of meadow and meadow-bog soils of coastal and adjacent areas of the Terek - Kuma plain 100% are converted in highly desertified land.

These data affirm the need for urgent and drastic measures to protect the geological environment and soils. In the first stage they should be the following:

a) forcing all the users of natural resources to the strict compliance of existing regulations related to subsurface and protection of geological environment;

b) assessment of the extent of man-made damage to geological environment and making probabilistic forecasts;

c) carrying out the respective geo-ecological research with recommendations for the rational use of natural resources.

In the second stage, one of the priorities should be probably considered the introduction of developed recommendations into environmental practices and the adoption of more strict laws in the sphere of subsoil use.

Questions relating to the protection of the geological environment and the rational use of water resources should have the most top priority for both government and non-governmental organizations.

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Martynov[1] K.V., Akhmedjanova[2] G.M., Kotelnikov[2] A.R., Tananaev [1] I.G., Myasoedov[1] B.F. Influence of replacement of phosphorus with silicon in kosnarite on its crystal-chemical and cationic exchange properties

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Abstract. Sodium-zirconium kosnarites in which phosphorus is partially replaced on silicon in an anion tetrahedron – $(Si,P)O_4$, were synthesized under hydrothermal conditions at a temperature

200°C and autoclave pressure – 1.55 MPa. It was shown that parameters and volume of Si-replaced kosnarite crystal cell increase at the same time with increase in a charge of a framework and cationic capacity of extra frame positions. Distribution of Na, K, Cs and Sr between phosphatic and silicon-phosphatic kosnarites and nitrate water solutions was studied by experimental and calculated methods. It was defined that isomorphic replacement of phosphorus with silicon displaces cationic exchange balance towards enrichment of a solid phase by strontium and at its absence – sodium, and its depletion by potassium, and caesium.

Key words: kosnarite, isomorphism, crystal structure, hydrothermal synthesis, cationic exchange.

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Complex orthophosphates with frame crystal structure similar to a mineral kosnarite – $KZr_2(PO_4)_3$ (s.g. R –3 c, Z=6) represent, in fact, multicomponent solid solution and are the unique compounds possessing ability cardinally to change the properties according to change of their chemical composition. For example, they can change electric conductivity in the range from dielectric to the conductor. Ability to change of their chemical composition is connected with extremely developed isomorphism of framework forming and extra frame cations. Thanks to this feature, and also resistance to influence of high temperature, radiation and chemically aggressive substances on compounds having kosnarite structure, it is possible to use them as a matrix material for immobilization of radionuclides in the form of structural isomorphic impurity, both for the purpose of radioactive waste disposal, and for creation of radioisotope sources. It has special value for radioisotopes of caesium and strontium which take extra frame positions in crystal structure of kosnarite and can be taken from water solutions by a method of a cationic exchange under soft hydrothermal conditions [Martynov, 2013].

To operate properties of kosnarite including characteristics of extra frame cations exchange, the maximum effect can be achieved by replacement of framework forming cations. Earlier we showed that partial replacement of titan and zirconium with aluminum in an octahedral position of kosnarite framework increases the capacity of its structure concerning extra frame cations, but at the same time limits their size [Martynov, 2012]. In a different way to modify framework composition of kosnarite which use to synthesize NaSICon, it is replacement of phosphorus with silicon in an anion tetrahedron – $(Si,P)O_4$. Thus at the same time with growth of a charge of a framework the cationic capacity of extra frame positions increases. Our and literary [Didisheim, 1986; Hazen, 1987] data testify that at traditional high-temperature solid phase synthesis, parameters and volume of unit cell of Si-replaced sodium-zirconium kosnarites increase together with increasing of silicon content (fig. 1). It creates potentially favorable conditions for occupying of extra frame positions by larger and charged cations like caesium and strontium, in Si-containing kosnarites. Received by us in this work results will show as far as this tendency remains at hydrothermal synthesis, and consequences following from it are sufficient for realization of primary occupying of extra frame positions by caesium and strontium against other alkaline cations (Na, K) in Si-replaced kosnarite in the course of a cationic exchange with water solutions.

Techniques of hydrothermal synthesis of kosnarite, studying of cationic exchange equilibrium between kosnarite and water solution, researches of experimental products were similar to those which we used earlier [Martynov, 2012; Martynov, 2013]. According to X-ray diffraction patterns of products of hydrothermal synthesis carried out at a temperature 200°C it was found that for Si-replaced kosnarites synthesized under hydrothermal conditions, parameters and volume of a crystal cell grow with increasing of silicon content, but less intensively, than for products of solid phase synthesis (fig. 1). The reason of this at hydrothermal synthesis is that extra frame positions of kosnarite become partially populated by nonmetallic cations: proton – H^+, oxonium – H_3O^+ and ammonium – NH_4^+. Really, for these kosnarites according to results of X-ray spectral electron microprobe analysis we received the following compositions: $Na_{0.72}K_{0.03}Cs_{0.03}Zr_{2.16}P_{2.90}O_{12}$, $Na_{0.91}K_{0.14}Zr_{2.03}Si_{0.67}P_{2.43}O_{12}$ and $Na_{0.80}K_{0.11}Zr_{2.07}Si_{1.44}P_{1.82}O_{12}$. It means that the sums of the analyzed alkaline cations (hydrogen, nitrogen and oxygen aren't defined by this method), made respectively 78, 63 and 37 mol % from the cationic capacity of M(1)+M(2) crystal structural positions at these ratios of silicon and phosphorus as a part of a framework. Thus, at hydrothermal synthesis and a cationic exchange nonmetallic cations can compete for occupying of extra frame positions in structure of kosnarite, and with growth of extent of replacement of phosphorus with silicon this competition amplifies.

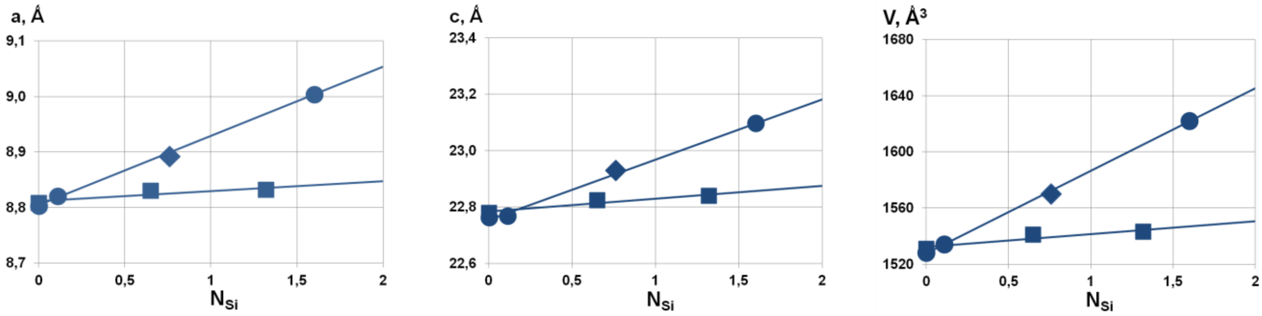

Fig. 1. Parameters and volume of an unit cell of kosnarites $Na_{1+N}Zr_2Si_NP_{3-N}O_{12}$ synthesized by hydrothermal (■) and high-temperature solid phase methods according to ours (♦) and literary (●) data. N_{Si} – number of formula units of silicon.

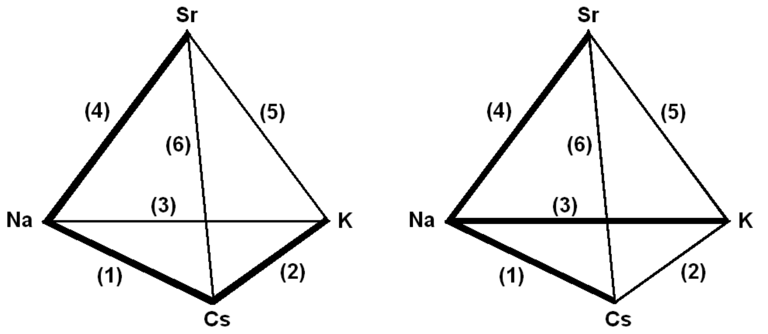

Fig. 2. Experimentally studied (fat lines) and calculated (thin lines) sections of the system Na-K-Cs-Sr: at the left – siliconless kosnarites, on the right – Si-replaced kosnarites.

For experimental studying of interphase distribution of alkaline and alkaline-earth cations (Na, K, Cs and Sr) between solid phase and water solution at a temperature 200°C we used siliconless or Si-replaced kosnarites having $N_{Si}=1$ and nitrate solutions with concentration of 1 mol/l for alkaline cations and 0.5 mol/l for strontium. Exchange equilibria have been studied in regional binary sections of four-component system which are represented in fig. 2. In the text and in figures the sections and kosnarite solid solutions corresponding to them are designated by numbers according fig. 2 or letters. The first two letters designate couple of extra frame cations, the others – framework composition: ZP – siliconless zirconium-phosphatic, ZSP – zirconium-silicon-phosphatic. Generally distribution of cations in the studied sections is described by exchange reaction

$$m\cdot n\cdot(M^{m+})_{1/m}Zr_2(P,Si)_3O_{12} + m\cdot N^{n+} =$$
$$=n\cdot m\cdot(N^{n+})_{1/n}Zr_2(P,Si)_3O_{12} + n\cdot M^{m+}.$$

Mole fractions of components in the solid phase – X^{ss} and water solution – X^{fl} are expressed as

$$X^{ss/fl}{}_N{}^{n+}= ([N^{n+}]/m)/([N^{n+}]/m+[M^{m+}]/n),$$

where $[N^{n+}]$ и $[M^{m+}]$ – molar concentration of components. Coefficients of interphase distribution are defined as follows:

$$Kd=[(X^{ss}{}_N{}^{n+})^{n\cdot m}/(1- X^{ss}{}_N{}^{n+})^{m\cdot n}]\cdot[(1- X^{fl}{}_N{}^{n+})^{n}/(X^{fl}{}_N{}^{n+})^{m}].$$

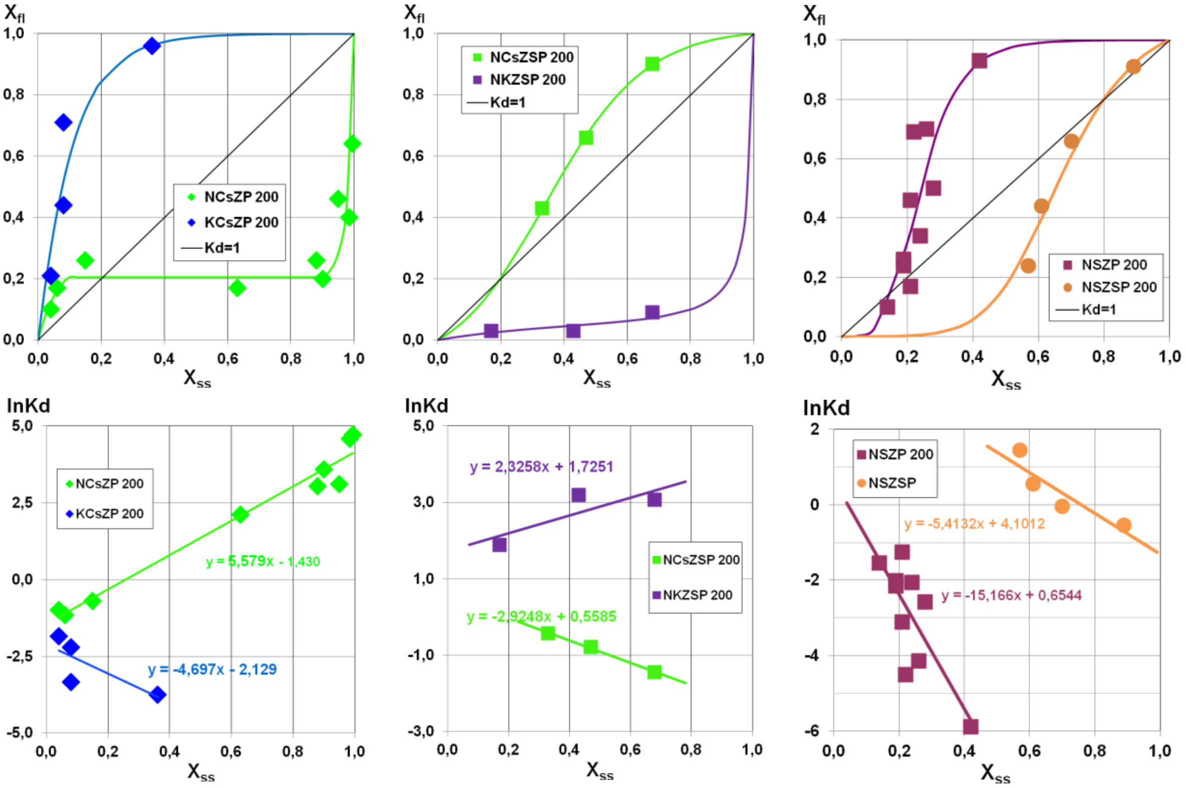

Fig. 3. The diagrams of interphase distribution (above) and dependences of lnKd from kosnarite composition (below) for distribution of elements between kosnarites and 0.5-1M nitrate water solutions at a temperature 200°C. Symbols – experimental data, lines – approximating curves.

In total, six sections were experimentally studied: three sections for each frame composition of kosnarite (fig. 3). To process experimental data about cationic exchange equilibria and calculate of thermodynamic mixture parameters of solid solutions we used a method of the analysis of Kd dependence from compositions of coexisting phases applied in [Martynov, 2013] which consists in the following. For distribution of elements between ideal (here – a liquid phase) and nonideal (a solid phase) solutions in case lnKd linearly depends on composition of nonideal solution:

$$\ln Kd = C_0 + C_1\cdot X,$$

one-parametrical model can be used to describe excess free energy of mixture of nonideal solution, and the thermodynamic equation for a constant of equilibrium can be written down in a look:

$R \cdot T \cdot \ln Kd = -\Delta G^0 - (1-X)^2 \cdot W + X^2 \cdot W$.

Ratios are thus fair:

$\Delta G^0 = - R \cdot T \cdot (2\ C_0 + C_1)/2$ and $W = R \cdot T \cdot C_1/2$

for an isovalent cationic exchange and

$W = R \cdot T \cdot C_1/4$

for a heterovalent cationic exchange with a ratio of cations charges – 2:1, where C_0 and C_1 – polynomial coefficients, W – model parameter, ΔG^0 – Gibbs free energy (isothermo-isobaric potential) of exchange reaction, X and (1-X) – mole fractions of components, R – universal gas constant, T – temperature in K. Coefficients of the polynoms describing dependences of lnKd from composition of kosnarites, were determined from experimental data by a method of linear regression. Sizes of the found thermodynamic parameters are presented in tab. 1, and curves approximating experimental data – in fig. 3. Thermodynamic parameters for the sections which weren't studied experimentally (three for each type of kosnarite, see fig. 2), were calculated proceeding from ratios:

$$\ln Kd_{(2)} = \ln Kd_{(1)} - \ln Kd_{(3)}$$
$$\ln Kd_{(3)} = \ln Kd_{(2)} - \ln Kd_{(1)},$$
$$\ln Kd_{(5)} = \ln Kd_{(4)} - 2\ \ln Kd_{(3)},$$
$$\ln Kd_{(6)} = \ln Kd_{(4)} - 2\ \ln Kd_{(1)}.$$

Results of these calculations are also given in tab. 1, and calculated diagrams of cationic distribution between kosnarites and water solutions for all sections of the studied four-component Na-K-Cs-Sr system are shown in fig. 4.

Table 1. Calculated sizes of Gibbs free energy of exchange reactions and energy of mixture model parameters for kosnarite solid solutions at 200°C. * – the sections studied experimentally**.**

Section	**NCsZP***	**NKZP**	**KCsZP***	**NSZP***	**KSZP**	**CsSZP**
ΔG^0, kJ/mol	-5.35	-22.96	17.61	27.26	73.18	37.95
W, kJ/mol	10.97	20.21	-9.24	-14.92	-35.13	-25.89
Section	**NCsZSP***	**NKZSP***	**KCsZSP**	**NSZSP***	**KSZSP**	**CsSZSP**
ΔG^0, kJ/mol	3.56	-11.36	14.92	-5.49	17.24	-12.60
W, kJ/mol	-5.75	4.58	-10.33	-5.32	-9.90	0.43

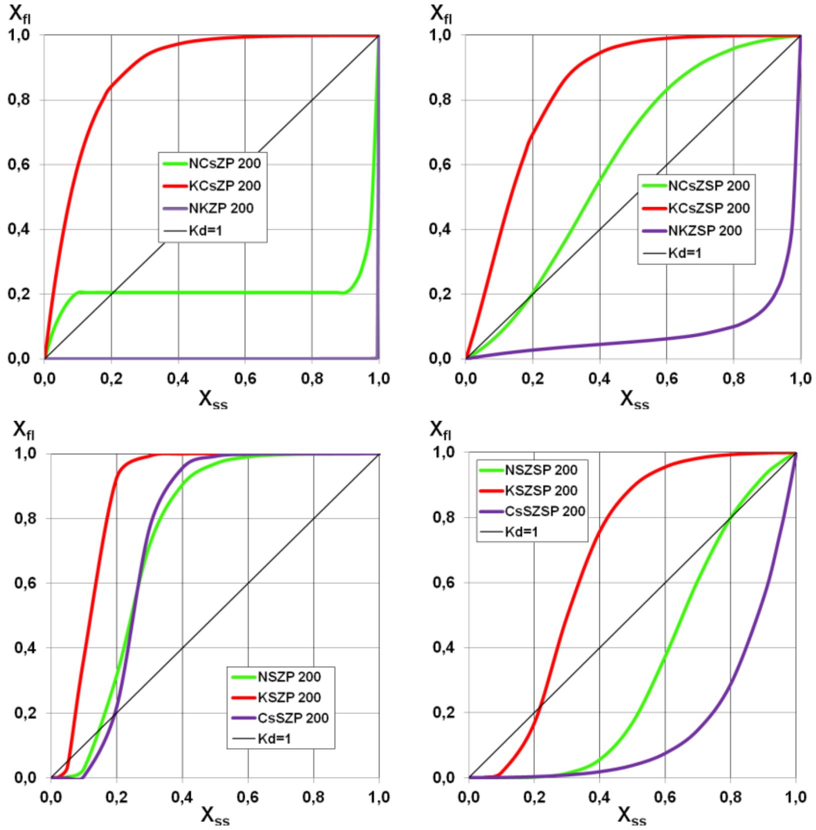

Fig. 4. Calculated diagrams of cationic interphase distribution between siliconless (at the left) and Si-replaced (N_{Si}=1) (on the right) kosnarites and 0.5-1M nitrate water solutions at 200°C.

Analyzing the positions of distribution isotherms for the same sections with siliconless and Si-replaced kosnarites, it is possible to make the following supervisions. Partial replacement of phosphorus with silicon leads to shift of distribution isotherms for Na-Cs and Na-K sections towards to enrichment of kosnarite by sodium, for sections of Na-Sr, K-Sr and Cs-Sr – towards to enrichment of kosnarite by strontium, and in K-Cs section the distribution isotherm practically doesn't change the position. Shift of isotherms for sections alkaline metal-strontium is especially remarkable because it shows that strontium can be selectively extracted from water solutions containing alkaline metals cations by means of Si-replaced kosnarite, especially against caesium. That is actually, Si-replaced kosnarite is possible to use for division of cations of Cs-Sr fraction.

Thus, our assumptions based on the crystal-chemical analysis of Si-replaced kosnarite structure, came true only partly. Really, partial replacement of phosphorus with silicon in tetrahedrons of kosnarite framework promotes occupation of extra frame positions by more charged cations, in our case – strontium. However, large cations (potassium and caesium) give way to smaller sodium in Si-replaced kosnarite even more willingly, than in siliconless one. Apparently, the increasing electrical potential difference between the frame and the charge-compensating cations taking place at replacement of phosphorus with silicon, the same as earlier established for replacement of the titan and zirconium with aluminum [Martynov, 2012], is the factor defining an optimum ratio of a charge and the size of kosnarite extra frame cations.

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Martynov K.V., Konstantinova L.I., Konevnik Yu.V., Proshin I.M., Zakharova E.V. Tritium diffusion through pore solution of crystal rocks (gneiss, lamprophyre)

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Abstract. Diffusion of tritiated water (*HTO*) containing: 75 mg/l of $CaCl_2$, 272 mg/l of $NaHCO_3$, 70 mg/l of $MgSO_4 \cdot 7H_2O$, pH=7.8 through samples of gneiss and lamprophyre was experimentally investigated. The received results testified to steady state diffusion of *HTO* through the studied rocks. Effective diffusivities – D_e^{HTO} were found: $2.3 \cdot 10^{-8}$ cm^2/sec for lamprophyre and $1.6 \cdot 10^{-9}$ cm^2/sec for gneiss. These sizes were correlated with values of connected porosity of samples – ε, defined by a water saturation method: 0.036 for lamprophyre and 0.002 for gneiss. The formation factor – δ/τ^2, reflecting porosity structure, was close for both rocks: 0.027 for lamprophyre and 0.033 for gneiss, despite an essential difference in their mineral composition and structure.

Key words: migration of radionuclides, tritiated water, matrix diffusion, porosity structure.

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The modern concept of the closed nuclear fuel cycle provides solidification and disposal of radioactive waste in special repositories located in stable geologic formations for reliable isolation of these materials from the biosphere until the radioactivity contained in them has diminished to a safe level. At disposal of high or middle level radioactive waste a creation of multibarrier protection, against possible carrying out of radionuclides to the biosphere by underground waters circulating in rocks is an indispensable condition. However, the volume and the guaranteed period of validity of engineering barriers aren't comparable to these parameters for containing rocks. Therefore, studying of rocks as main barrier to migration of radionuclides has paramount value for justification of long-term safety of radioactive waste repository.

In our country a possibility of construction of radioactive waste repository is studied on Yeniseiskiy site close to The Mining Chemistry Plant (Krasnoyarsk Krai) in the massif of archean gneisses and schists. The main way of circulation of underground waters in crystal rocks is the fracture filtration. Interaction of underground waters and rock minerals happens not in volume of rock, but on a surface of fractures. The main mechanism limiting of radionuclide advection by flowing underground waters is a sorption on fractures surface. Other factor influencing on radionuclides migration through the massif of rocks is diffusion in the rock matrix. Pore (rock matrix) diffusion increases the capacity of rocks for sorption of radionuclides owing to involvement in this process of a pores surface which significantly exceeds a fractures surface. Thus, barrier properties of crystal rocks depend on sorption and diffusive interaction of radionuclides transferred by underground waters filtering through fractures with a fractures surface and pore solutions.

For diffusive experiments we chose examples of rocks selected on Yeniseiskiy site from metamorphic (biotite-plagioclase gneiss) and dike (lamprophyre) complexes which represented the fresh pieces of a drill core taken from the depths respectively 475 and 208 meters. Previously the structure, chemical and mineral compositions of rocks were studied by methods of optical microscopy (Olympus BX51), X-ray fluorescent spectrometry (XRFS) (PANalytical Axios Advanced) and scanning electronic microscopy (SEM) with electron microprobe analysis (EMPA) (Tescan Vega II XMU with X-ray energy dispersive spectrometer Oxford Instruments INCAx-sight). The total chemical composition of rocks (macrocomponents) is presented in tab. 1, optical and SEM images of polished petrographic thin sections – in fig. 1 and 2.

Biotite-plagioclase gneiss represented medium-grained massive rock having hypidiomorphic structure and consisting mainly from quartz (40-50%), plagioclase $Na_{0.56}Ca_{0.40}K_{0.01}Al_{1.38}Si_{2.65}O_8$ (20-30%) and chloritizated $(Mg_{2.81}Fe_{1.75}Mn_{0.08}Al_{1.29})[Si_{2.87}Al_{1.13}]O_{10}(OH)_8$ biotite (до 20%) $K_{0.98}(Mg_{1.50}Fe_{0.97}Mn_{0.03}Al_{0.41}Ti_{0.11})[Si_{2.90}Al_{1.10}O_{10}](OH_{1.99}Cl_{0.01})$. Ore minerals (to 10%) were presented by magnetite and titanomagnetite $(Ti_{0.30}Fe^{2+}_{1.29}Mn_{0.01})(Fe^{3+}_{1.39}V_{0.01}Cr_{0.01})O_4$, the accessory – rutile, zircon, apatite, orthite.

Table 1. Total chemical composition of rocks according to XRFS (macrocomponents), wt.%

Type of rock	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	MnO	Fe_2O_3	P_2O_5	S	LOI 950°C	**Total**
Gneiss	3.36	2.57	17.09	60.97	2.64	3.43	0.71	0.08	6.33	0.07	<0.02	1.52	98.77
Lamprophyre	5.40	6.91	15.12	51.57	1.62	5.83	0.95	0.12	7.57	0.67	0.23	3.43	99.42

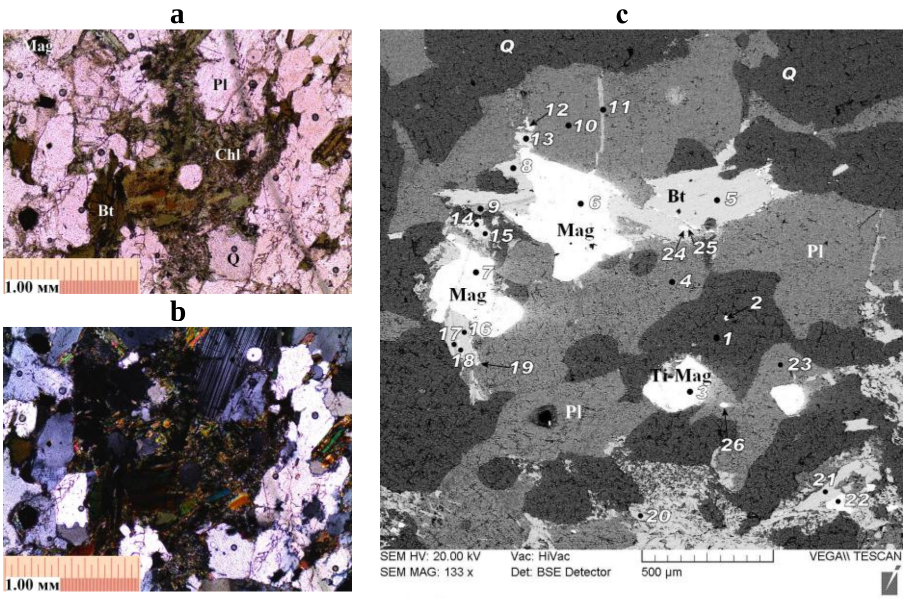

Fig. 1. Petrographic thin section images of biotite-plagioclase gneiss in bright field illumination (**a**) and in cross-polarized light illumination (**b**) and SEM-image of its surface in backscattered electrons (**c**). Q – quartz, Pl – plagioclase, Bt – biotite, Chl – chlorite, Mag – magnetite, Ti-Mag – titanomagnetite.

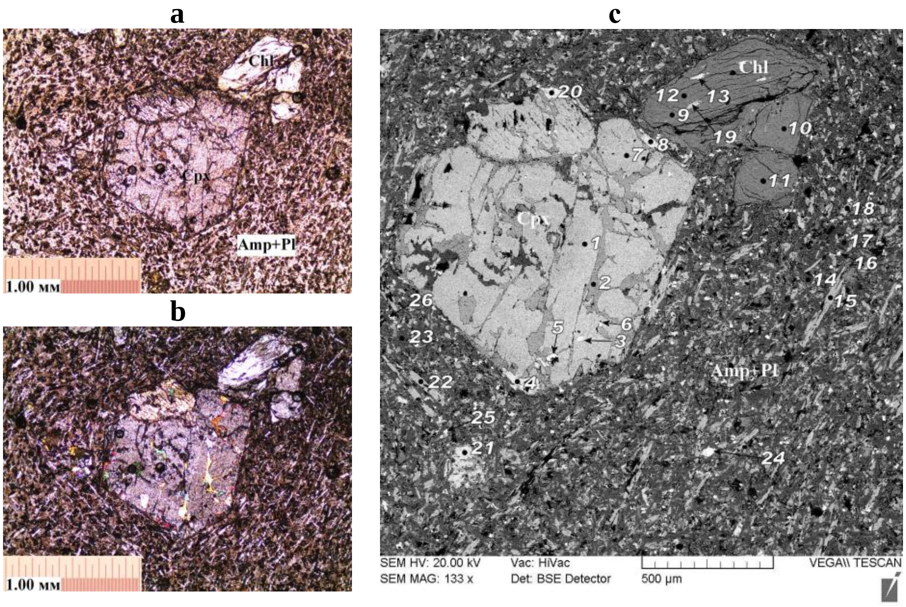

Fig. 2. Petrographic thin section images of lamprophyre in bright field illumination (**a**) and in cross-polarized light illumination (**b**) and SEM-image of its surface in backscattered electrons (**c**). Cpx – clinopyroxene, Chl – chlorite , Amp – amphibole, Pl – plagioclase, Py – pyrite

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Lamprophyre had the expressed porphyritic structure and massive texture. Phenocrysts composed to 30% of rock and were presented equally clinopyroxene $(\mathrm{Ca_{0.87}Mg_{0.82}Fe_{0.21}Al_{0.08}Ti_{0.02}})[\mathrm{Si_{1.94}Al_{0.06}}]\mathrm{O_6}$ and completely chloritizated biotite $(\mathrm{Mg_{3.22}Fe_{1.24}Ca_{0.06}Mn_{0.02}Al_{1.16}})[\mathrm{Si_{3.44}Al_{0.56}}]\mathrm{O_{10}(OH)_8}$. Groundmass consisted from amphibole $(\mathrm{Na_{0.55}K_{0.17}})(\mathrm{Na_{0.12}Ca_{1.85}Fe^{2+}_{0.04}})(\mathrm{Fe^{2+}_{1.02}Mg_{3.06}Al_{0.30}Fe^{3+}_{0.25}Ti_{0.37}})[\mathrm{Si_{6.11}Al_{1.89}O_{22}}](\mathrm{OH})_2$ and plagioclase $\mathrm{Na_{0.92}Ca_{0.02}Al_{1.02}Si_{3.05}O_8}$. Ore and accessory minerals were presented by titanomagnetite $(\mathrm{Ti_{0.07}Fe^{2+}_{1.07}})(\mathrm{Fe^{3+}_{1.84}V_{0.01}Cr_{0.02}})\mathrm{O_4}$, epidote $\mathrm{Ca_{1.89}}(\mathrm{Al_{1.98}Fe^{3+}_{0.99}})[\mathrm{Si_{3.08}O_{12}}](\mathrm{OH})$, pyrite, titanite and apatite. Calcite and quartz formed thin veins in clinopyroxene grains.

The isotope ^3H (tritium) was chosen as a tracer for studying of diffusive characteristics and structure of porosity of rocks from Yeniseiskiy site. The choice of tritium was dictated mainly by that this radionuclide is present in water solutions as a neutral non-sorbing species *HTO* (tritiated water). Besides, diffusivity of tritium are of interest as this radionuclide is a component of some kinds of radioactive waste and, being rapidly migrating, can create real danger to the biosphere. The only mechanism of a retardation for tritium as non-sorbing radionuclide is its diffusion from fracture flowing waters in pore space of rock matrix.

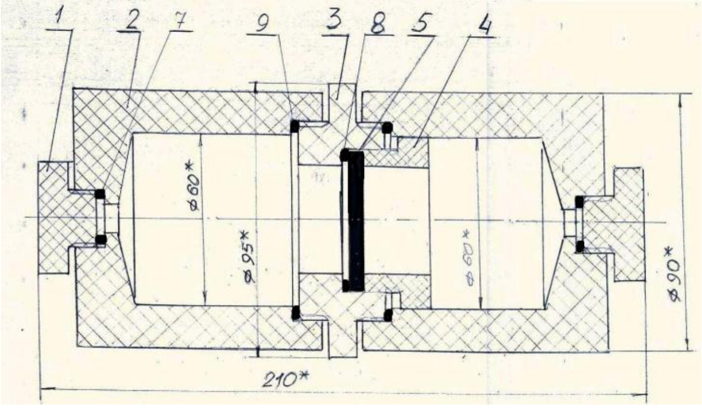

Fig. 3. Design of diffusive cell: 1 – plug, 2 – body, 3 – sample holder, 4 – clip (teflon), 5 – sample, 7, 8, 9 – sealing rings (silicone rubber)

Table 2. Chemical composition and pH value of model underground (pore) water**.**

Component	Na^+	Mg^{2+}	Ca^{2+}	Cl^-	SO_4^{2-}	HCO_3^-	pH
Content, mg/l	75	6.8	27	48	27	198	7.8

Diffusion experiments of *HTO* through flat examples of rocks with a diameter of 30 mm and 3 mm thick carried out in teflon cell (fig. 3) at a temperature 30±1°C in the TS-80M-2 thermostat. Samples were between the 150-170 cm^3 cameras filled with the model underground water corresponding on a chemical composition and pH value to deep underground water on Yeniseiskiy site (tab. 2). Tritium tracer with specific activity of 100 Bq/ml was added in one camera (source), another camera (recepter) – didn't contain it. The pore space of samples before experiments was forcibly filled with the distilled water. In the course of experiments aliquots of 0.5 ml for measurement of 3H activity by method of liquid scintillation spectrometry (Perkin Elmer Liquid Scintillation Analyzer Tri-Carb 3180 TR/SL) were selected from both cameras periodically. In connection with the considerable duration of experiments the correction owing to ^3H radioactive decay was introduced in the measured values of activity:

$$\boldsymbol{A=A_m\cdot exp(\lambda\cdot t)},$$

where $\boldsymbol{A}$ – activity accepted in calculations, $\boldsymbol{A_m}$ – measured activity, $\boldsymbol{\lambda}$ - constant of radioactive decay, $\boldsymbol{t}$ – time from the experiment beginning. Experimental results are shown in fig. 4 as the total relative tritium activity which has passed from the source camera into the reception camera through the sample against the time.

The results of experiments testified to steady state diffusion of *HTO* through both studied rocks without delay stage which is typical for sorbing species. Effective diffusivities – $\boldsymbol{D_e}$ were determined from experimental data by a method of linear regression using expression of Fick's first law for steady state diffusion:
$\boldsymbol{[A_r\cdot d]/[(a_s-a_r)\cdot S]=D_e\cdot t}$, where $\boldsymbol{A_r}$ – activity of tritium in the reception camera, $\boldsymbol{a_s}$ и $\boldsymbol{a_r}$ – specific activities respectively in the source camera and in the reception camera, $\boldsymbol{d}$ and $\boldsymbol{S}$ – thickness and section area of a sample. The sizes of $\boldsymbol{D_e}$ represent tangents of tilt angles of the straight lines approximating experimental data on charts of fig. 4. Their values in the standard units are given in tab. 3. The size of $\boldsymbol{D_e^{HTO}}$ for lamprophyre is more than the same for gneiss more than on a decimal order.

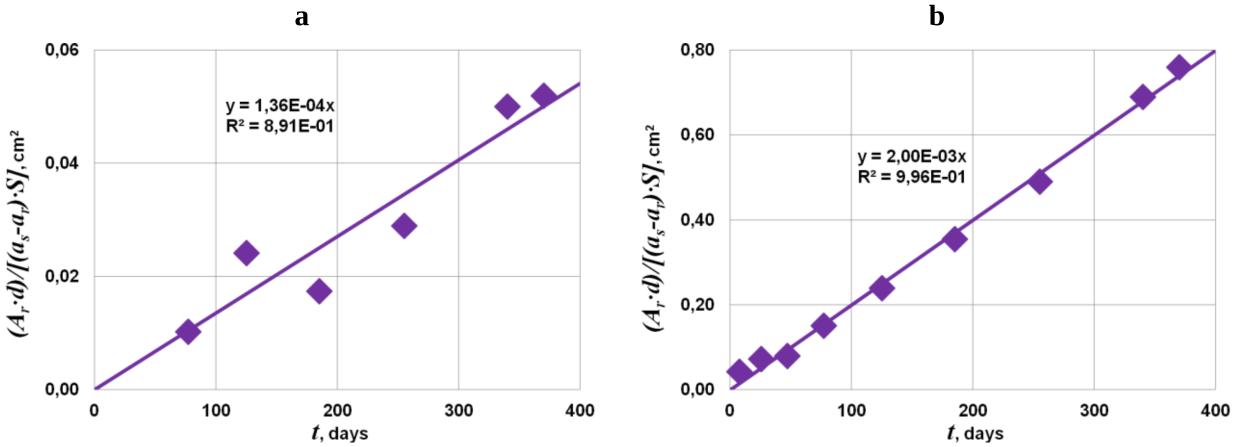

Fig. 4. Experimental data on *HTO* diffusion through gneiss (**a**) and lamprophyre (**b**).

Before diffusive experiments we determined values of connected porosity – ε of rocks examples by water saturation method in accordance to the GOST state standard 26450.1-85. The received results are presented in tab. 3. Like as the sizes D_e^{HTO}, values ε for studied rocks differ more than on a decimal order. It can quite be explainably different genesis of rocks. Gneiss was formed at high lithostatic pressure as a result of metamorphic recrystallization of the sedimentary deposits shipped deeply. Its hypidiomorphic structure (fig. 1), being characterized close contact of mineral grains with each other and the minimum intergrain porosity became result of its origin. Lamprophyre dikes were formed at a small depth what its porphyritic structure testifies about (fig. 2). Lamprophyre fine-crystalline groundmass consisting of extended amphibole and plagioclase grains, crystallized from melt (magma) with reduction of crystal phases volume concerning magma volume. At low lithostatic pressure it promoted formation of the developed porosity.

The size of *HTO* effective diffusivity through granite in the pore solution modeling composition of underground water, received [Skagius, 1986] are close to our assessment for gneiss (tab. 3). For our research, comparison with granite is interesting because of its mineral structure and the origin different from genesis of gneiss and lamprophyre investigated by us. Granite crystallizes from a melt like lamprophyre, but crystallization happens deeply at high general pressure, similar to formation of gneiss. The last factor is defining for porosity formation. Therefore connected porosity of gneiss and granite was identical.

Table 3. Effective diffusivities of *HTO* and porosity characteristics of rocks.

Type of rock	D_e^{HTO}, cm²/sec	ε	δ/τ^2
Gneiss	$1.6\cdot10^{-9}$	0.002	0.033
Lamprophyre	$2.3\cdot10^{-8}$	0.036	0.027
Granite [Skagius, 1986]	$1.8\cdot10^{-9}$	0.002	0.038

Except the size of connected porosity, porosity structure is of great importance for matrix diffusion. Porosity structure is expressed through a formation factor – δ/τ^2, connecting diffusivity in free solution – D_w and effective diffusivity for pore diffusion:

$$D_e = \varepsilon \cdot D_w \cdot \delta/\tau^2,$$

where δ – constrictivity, τ – tortuosity of pore channels. To estimate the size each of a component of formation factor it is rather problematic, but they make clear physical sense. Size of constrictivity defines a part of the connected porosity behind a deduction, so-called, dead-end pores. Tortuosity reflects how bigger way on the average a particle passes thanks to diffusion through real pores in comparison with the hypothetical rectilinear pore channel.

As value of tritium diffusivity in free water is known: $D_w^{HTO} = 2.4\cdot10^{-5}$ cm²/sec at 298K, we calculated sizes of formation factor for the rocks studied by us and for granite also. Despite an essential difference in mineral composition and structure, values of formation factor for all considered crystal rocks (gneiss, lamprophyre, granite) appeared close (tab. 3). Thus, distinction in *HTO* effective diffusivities through pore solutions of metamorphic and magmatic crystal rocks is defined generally by the size of connected porosity.

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Razvorotneva[1] L.I., Markovich[1] T.I., Gilinskaya[1] L.G., Isupov[2] V.P. Role of iron-containing minerals in uranium mobilization

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Abstract. Iron-containing minerals are effective sorbents for the extraction of soluble forms of uranium. Sequential chemical fractionation method was used to study the distribution of uranium between the main components of the absorption complex lake sediments of Northwestern Mongolia. More than 40% of the uranium binds iron-hydroxide form of precipitation. Redox interaction between the U^{+6} and the impurity ions Fe^{+2}, located in the octahedral sites of montmorillonite was identified by EPR.

Key words: radionuclides, sorption, geochemical barriers, uranium

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To develop the ways to minimize the impact of radioactive contamination (both natural and man-made sources) on the environment it is need to study not only the forms of radionuclides, but the mechanisms of their interaction with natural systems. Figuring out geological and physicochemical conditions of the mobilization of uranium in lake waters and sediments is important in the view of the development of methods to search hydromineral uranium deposits. The key objects for researching are highly mineralized lakes of uranium ore regions in Mongolia and Transbaikalia [Isupov, 2013].

Water of soda lakes located in the uranium ore areas in Western Mongolia contains elevated concentrations of uranium reaching units mg per liter. Shaazgay Nuur lake is located in the basin of the southern highlands Harhirinskogo (Northwest Mongolia) at the level of 1696-1700 m. Shaazgay Nuur Lake attractiveness as an object of study is due to both a high uranium concentration in the water of the lake (at the level of 1 mg/l) and the fact that the catchment area of the lake is located within the Tsagaan Shibetinskoy potential uranium ore zone. Our study indicates that a deposit of uranium occurs due to its accumulation not only in the lake waters, but also in the bottom sediments. The uranium content in cores varies from $5.18 \cdot 10^{-5}$ g/g (0-5 sm) to $10.42 \cdot 10^{-5}$ g/g of (5-10 sm), which is 50 to 100 times higher the weight concentration of uranium in water. Shaazgay Nuur lake water is supersaturated with respect to various carbonates including calcite, dolomite and strontianite, and also ferrihydrite $Fe(OH)_{3(s)}$. Additional amount of these minerals may fall over time with evaporative concentration of salts or fluctuating temperatures. The distribution of uranium content between the main components of the absorption complex sediments was studied by the method of sequential chemical fractionation (Table 1). It should be noted that with increasing depth of precipitation the role of metabolic processes decreases, and the number of surface complexes (associated with the hydroxide groups) increases.

Table 1. The amount of uranium (%) located in various forms of binding by the bottom sediments of Shaazgay Nuur lake.

Uranium binding forms	Kern (0-5) sm	Kern (5-10) sm
Water-soluble forms	17	12
Exchange forms	33	26
Carbonate forms	12	15
Hydroxide forms	34	43
Organic forms	4	4

Determination of the forms of components (true dissolved and suspended) revealed that iron hydroxide slurry transforms $UO_2{}^{+2}$ from solution into a solid phase due to the high sorption ability. At the same time there is a combination of two processes: sorption and gravity. Experimental leaching of uranium by ammonium acetate buffer confirmed the efficiency of (34 and 43 %) sorption barrier based on superfine iron hydroxides. The presence of iron in the lacustrine sediments increases their sorption potential, but the process is strongly dependent on the pH of the aqueous phase. It is experimentally shown that the optimum pH range is 5,5-8,2. The formation of surface complexes proceeds according to the following scheme:

$> FeOH + UO_2^{+2} = > FeOHUO_2^{-2}$
$> FeOH + UO_2^{+2} + H_2O = FeOHUO_3^{+}\ 2H^{+}$

For sorption experiments the uranium saline $UO_2\ (NO_3)_2\ 6H2O$ with a concentration of 25 µg/l was prepared. The amount of uranium in the solution was determined by high resolution ICP-MS by FINNIGAN MAT (Germany) with a standard solution 10090a977 by "Merk". The determination error is 1-5%.

The suspension $Fe(OH)_3$ (from 0.02 mM/g of $FeCl_2$ + NaOH) was prepared at pH 7.8 during 48 hours. The resulting precipitate was separated by centrifugation at 15 000 rpm for 20 minutes. Then, the precipitate was thoroughly washed and dried by freeze-drying with liquid nitrogen to maintain the parameters of the primary structure. Sediment surface measured by the BET method (by ASAP- 2400 ("Micrometrics", USA) by nitrogen adsorption at 77 K) was 48.3 m^2/g.

The X-ray analysis shows that the formed sediment contains fine-grained phases of FeOOH and UO2 with a low degree of crystallinity [Ho, 1985]. The leaching step method revealed that uranium can be adsorbed from solutions by both amorphous and crystal (goethite) forms of sediments.

In the aqueous medium uranium exists in the complexes according to the reactions:

$UO_2^{2+} + H_2O = UO_2OH^{+}$
$2UO_2^{2+} + 2H_2O = (UO_2)_2(OH)_2^{2+} + 2H^{+}$
$3UO_2^{2+} + 5H_2O = (UO_2)_3(HO)_5^{+} + 5H^{+}$

In the soda lakes uranium presents in the form of soluble carbonate complexes: $(UO_2)_2CO_3(OH)_3^{-}$, $UO_2(CO_3)_2^{2-}$, $UO_2(CO_3)_3^{4-}$ [Hun Jang, 2007]. At pH 7-8 the form $UO_2(CO_3)_2^{2-}$ dominates. In an alkaline environment, carbonate ions are the predominant ligands and higher solubility of uranium (U(IV)) caused, in particular, by its tendency to form anionic carbonate complexes.

In carbonate and, particularly, bicarbonate mediums (pH 9.4 and Eh 107 mV) uranium is in the form of highly charged carbonate complexes $UO_2(CO_3)_3^{4-}$, a slow recovery of the carbonate complexes of hexavalent uranium compounds Fe^{+2} is observed. It is known that the degree of oxidation of uranium has a significant influence on its mobility in the environment and, accordingly, on the environmental impact. Unlike high mobile U(VI), under reducing conditions, U(IV) becomes nonmobile due to the formation of sparingly soluble minerals, such as uraninite (UO_2). Studies on the sorption of uranium in mineral sediments of soda lakes have shown that carbonate complex formations markedly reduce the adsorption of uranium.

The process of uranium immobilization on mineral surfaces, containing in their structure iron ions, was studied by the method of electron paramagnetic resonance (EPR). Signals of paramagnetic ions (EPR studies were performed on radiospectrometer "Kadiopak" SE/X254, f_{mod} . = 100 kHz, T = 293 K) are indicators in the study of isomorphism of the surface structure. The most common are iron ions in the two- and trivalent state. In the studied samples of clay minerals ions of Fe^{+3} in the octahedral sites are recorded. In the EPR spectrum of montmorillonite with sorbed on it uranyl ion the wide (80 - 120 mT) symmetric line of complexes with iron in g = 2,05 is determined. During the experimental annealing of samples the intensity ion spectrum of structural Fe^{+3} increases (5 times). This indicates the occurrence of oxidation of bivalent iron, which is also included in the structure of the clay mineral, to the trivalent state.

In the bottom sediments of Shaazgay Nuur lake the X-ray analysis revealed the presence of alkali and, to a lesser extent, alkaline-earth bentonites. The intense spectrum of Fe-containing impurity phase – hematite – was observed in alkaline bentonites. Table 2 shows that the paramagnetic centers found in samples of bentonite clays are also participants of chemisorption processes.

Table 2. Change of the number of paramagnetic centers (PMC) (relative units) in the processes of uranium immobilization by alkaline and alkaline-earth bentonites.

Deposit composition	Center type	Number of PMC in the initial sample	Number of PMC after uranium sorption (UO_2^{+2})
Alkaline bentonite	Fe^{+3} structural	247	478
Alkaline-earth bentonite	Fe^{+3} structural	281	334
	Fe^{+3} Hematite	23220	25015

Following should be noted :

1) Changing the number of EPR centers after uranium immobilization confirmed their participation in the absorbing complex and the appearance of the redox barrier (with the appearance of U(IV)).

2) The efficiency of barrier performance with Fe^{+3}-(structural) in alkaline bentonites is higher (46 %) than in alkaline (20 %).

3) The contribution of the impurity phase - hematite – in the sorption process is less significant.

4) A number of wide lines (60 mTl) with different g-factors is determined in the spectra of alkali bentonites after UO_2^{+2} sorption. They are caused by complexes of Fe^{+3} ions in neighboring cationic positions that lead to the effect of superexchange.

Thus, in the lake sediments uranium presents in the form of adsorbed, complex, precipitated or recovered compounds. It has different mobility in the environment depending on the variety of forms. So, carbonate complex compounds, due to good solubility in water, can migrate over long distances. Fixation of uranium by bottom sediments may be caused by their composition, physico-chemical properties of the structure, dispersion and porosity. Controlling the sorption sorbent phases include oxides and hydroxides of iron and clay minerals containing iron ions in its structure. The mechanism of the contact of dissolved uranium with mineral phases may be different: adsorption, chemisorption, ion exchange, or a combination of several mechanisms. Any change in the composition or precipitation conditions (pH, ionic strength, Eh, etc.) leads to a change of the mechanism of uranium immobilization.

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