Physical chemical properties of geomaterials

Koroleva O.N., Ivanova T.N., Korobatova N.M., Korinevskaya G.G., Shtenberg M.V. Investigation of alkali borongermanate glasses by meanes of vibrational spectroscopic

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The coordination number of germanium can changed from 4 to 6 with standard pressure in systems with the small content of an alkaline cation. This leads to existence, along with tetrahedrons, both pentahedrons, and octahedrons where the germanium is central atom, surrounded with 5 or 6 atoms of oxygen, respectively. It is known that the coordination number of atom of boron in the alkaliboron systems can be equal 4 or 3 that is confirmed by experimental methods and corresponds to existence in structure of boron-containing glasses and meltns both triangles, and tetrahedrons with a different ratio bridging also a non-bridging of oxygen atoms. The purpose of this work was studying of structure and degree of polymerization of a borogermanium network depending on type of a cation and its contents. Glasses with structures $xM_2O \cdot xB_2O_3$ (100-2x)GeO₂, where M = Li, K μ x = 3, 5, 7, 10, 20, 30 mol. % have been synthesized by a furnace charge method from the corresponding oxides and carbonates. Research of the samples structure was carried out by the IR and Raman spectroscopy.

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Maghidov S.Kh. Man-made change in the balance of thermobaric conditions in the earth's interiors of the russian federation and global environmental risks.

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Abstract. Artificial subsoil defluidization due to oil and gas development as well as groundwater extraction for household needs result in accelerated depletion of interiors compressibility potential and unstable state of geo-hydrosystems that can cause environmental disasters and emergencies of regional and global scale.

Keywords: man-made changes, thermobaric conditions, compressibility potential, geo-ecological risks.

A number of studies have shown that there have been significant changes in the subsurface hydrosphere by nowadays as a result of increasing anthropogenic impact on the subsoil [Magidov S.Kh., 2014, Magidov S.Kh., 2015 (1-3)]. First of all, it's confirmed by the fact that compressibility potential of the Russian interiors has already been largely lost [Magidov S.Kh., 2014]. The share of flowing wells has been declined by more than a mathematical order for half a century of oil and gas deposits exploitation; their flow rates have been also substantially reduced. Similar trends are identified in the Russian Federation when producing the thermal waters, too. All this constitutes a violation of the balance of thermobaric conditions in the Earth's bowels and promotes the rise of global geo-ecological risks. Temperature and pressure parameters reducing contribute to forming the depressions and. respectively, to the Earth's surface subsidence. In some cases lowering speed can be tens of centimeters per year and the absolute value of the sinking is seven and more meters. Arising from it strains result in changes of seismic regime. In some cases such imbalance can become the main reason of strong man-made earthquakes [Magidov S.Kh., 2015 (2)]. When water injecting in productive oil-bearing beds for reservoir pressure maintenance (RPM) takes place, the areas of repression resulting in swelling of the Earth's surface local areas can be formed. The mentioned effect is usually relatively short-time due to being a side effect of measures aimed at oil recovery increasing. The surface heave can be associated not only with an increase of the reservoir pressure connected with efforts for RPM, but also with the interaction of injected water with clay minerals of the waterproof beds changing their volume. Figure 1 presents data on volumes of fluid withdrawal (oil + water + condensate) by oil and gas industry in the Russian Federation and the dynamics of water injection into oil and gas productive horizons for the RPM versus the curve of flowing wells share.



Fig.1. Groundwater extraction and injection and tendency of the flowing oil wells share in the oil and gas industry of the Russian Federation.

The figure shows that for the period of interest a bit more fluid was being injected in comparison with extracted volumes.

At the initial stage the increase in fluid injection into productive formations for RPM during the 70's -80's of last century allowed not only to stabilize the energy process of elastic exhaustion for hydrogeological systems in Russia, but also to reverse it [Magidov S.Kh., 2015 (3)]. But there was a sharp drop in the share of oil and gas flowing wells further, despite of the significant increase in the fluid injection volume. This indicator had been continuing to decline in the current decade and had dropped to a value of 5.6% by 2014. It leads to the obvious conclusion that the water injection in the earlier volumes no longer allows the recovery of reservoir pressure at an acceptable level. Probably, such a scenario is a confirmation of the thesis of the global nature of negative changes in the depths under the influence of human activities. It means that even intensive pumping of fluids in a separate field for the RPM can give only the short-term effect on the local site. Drop in reservoir pressure and, accordingly, the proportion of flowing wells will occur with time, due to the hydrogeological connection with regional hydrogeosystem. The same effect is likely to act in the interaction at the regional and global level. Thus, the other important conclusion follows from the above that the restoration of the original (preanthropogenic) conditions in the bowels at the global level will require excessive expenses which would make such a task almost impossible.

Such significant changes in subsurface thermobaric conditions occurred for a relatively short period will obviously entail perceptible change at first in geophysical properties of the geological environment (geological substrate) itself in the Earth's crust upper layers, that may affect the natural super-long geodynamic waves passing tentatively in the frequency range of 10^{-8} - 10^{-11} Hz. The generation of such waves can be caused by both geological and cosmic factors. Apparently, industrial activity will mainly affect the elastic and plastic properties of the conductive medium that can interfere with the steady natural geodynamic rhythms, introducing imbalance and promoting geo-disasters. The fact that this possibility can become a reality at present may be indicated by growing number of catastrophic events in the world, geomagnetic poles drift having been increased sharply in recent and change of the natural frequency of the geomagnetic field pulsation (Schumann frequency).

Apparently just the growth of disbalance in the Earth's bowels caused by intensive human activity nowadays is one of the main reasons for super-strong and hyper strong earthquakes [Magidov S.Kh., 2015 (1, 3)]. It should also be taken into account that such earthquakes can trigger supervolcano eruptions which may jeopardize the existence of mankind itself.

It's necessary to estimate the frequency of such earthquakes at least roughly because of absence of unambiguous instrumental data to determine the frequency of their occurrence. Such events can cause irreparable harm to modern civilization; therefore, the problem of prediction of this disturbed system behavior in the medium and long-term prospect and determination of the global geo-disasters probability becomes especially urgent.

It is impossible without the whole complex of geophysical and geochemical surveys as well as analog simulation of the behavior of geosystems disturbed by human-induced activities.

At the same time one should mention that there is the long-time urgent necessity not only in the preparation of the global scale overall programs for the geological environment protection, but also in taking severe and effective measures (administrative and legal) at the international level to rectify the current catastrophic situation in the Earth's interiors.

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UDC:550.47:574.21+574:24:57.042:573.4 Ermakov V.V., Khushvakhtova S.D., Tyutikov S.F., Danilova V.N., Safonov V.A., Krechetova E.A. Geochemical ecology of plants under conditions of polymetallic biogeochemical provinces.

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Keywords: Ardon river, metals, plants, phytochelatins, chlorophyll, carotene, tailings.

Abstract. The new data on the use of the biogeochemical indication for the detection of plant responses to extremal natural and man-made factors are presented. It is shown that in conditions with excess heavy metals in the environment the synthesis of phytochelatins and pigments are differentiated.

Introduction

The ore areas are optimal experimental grounds for carrying out works in the field of geochemical ecology. An interesting problem is the sustainability of plants to metals, homeostasis of certain plant communities, and mechanisms responsible for their sustainability to metals. These mechanisms involve synthesis of metallothioneins (MT), which are low molecular weight proteins enriched in cysteine, with a molecular weight of about 3000 daltons or less. Their synthesis is regulated by specialized genes, which bind several metals and facilitate their transfer and accumulation in organisms. The activation of synthesis of phytochelatins in the presence of excess concentrations heavy metals is likely one of the mechanisms commonly utilized by organisms to eliminate toxicity and regulate trace element exchange (Ermakov, 2015; Ermakov et al., 2015). However, in natural conditions, the activation of the synthesis of SH-compounds in plants growing on soils contaminated with metals is not sufficiently studied. In this connection, the determination of these compounds in natural environments and objects has an important informational value.

So this article focuses on the evaluation of the content of SH-compounds in plants growing on soils with different content of heavy metals, arsenic and selenium.

Sampling areas and methods

The Unal basin is located in mountain region of Northern Ossetia (the Caucasus) and belongs to Pb-Zn natural province with anthropogenic and natural transformation of the environment leading to risks of ecological damage. Activity of the Misursk Mining Combine and its Arkhon-Khosta tailings caused a significant local increase of Pb, Cd, Cu, Zn content in soils, water and biotic components relative to background values [1-5].

The basin of Ardon river (North Ossetia) with the Sadon group of several lead-zinc polymetallic deposits as an experimental site for studying the geochemical ecology of organisms under of the polymetallic biogeochemical provinces was selected (Fig. 1).





The leaves of most common plants colt's foot (*Hippóphaë rhamnoides*), buckthorn (*Hippóphaë*

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rhamnoides), willow (*Salix spp.*) and dandelion (*Tarexacum officinales*) were selected as biological objects.

Plant leaves homogenized in cold to a pulp in a mixture of methanol and 0.1 M phosphate buffer (pH=6,8) and after centrifugation in upper phase were determined S-containing compound phytochelatins: oxidized glutathione (G-G), reduced glutathione (GH), metallothioneins (MT), cysteine (Cys) and derivatives of glutathione (X). In addition, the pigments of leaves (chlorophyll a, chlorophyll b, carotene) were extracted. In a separate charge determined by A moisture content of biological objects were measured in separate mass of the leaves. Determination of 13 microelements in 56 samples of the leaves by means of the method of flame AAS (KVANT-2A) and flameless AAS (KVANT.Z.E) was carried out after acid mineralization of samples, including various metals, arsenic and selenium. The content of different phytochelatines was measured in 56 samples of leaves.

For the separation of various biologically active sulfur compounds applied high performance liquid chromatography (HPLC) with pre-derivatization of the substances by means of

N-9 (acridinyl)maleimide (NAM) and ophthalaldehyde (OFA) and their separation on columns of BioSep type. The phytochelatins determination was performed according to our developed method of HPLC-NAM-OFA spectrofluorimetry [1, 2, 4], and pigments - according to the standard technique [5].

Results

Concentrations of copper, zinc, lead and cadmium in plants on the background landscapes in mg/kg are: a 4.9-21.9 (Cu), a 12.1-120.5 (Zn), < 0.3-3.9 (Pb) from 0.02- to 2.93 (Cd). And maximum values refer to the leaves of the willow - the concentrator of zinc and cadmium. On industrial sites the plant contain the following concentration of metals in mg/kg: 16.2-148.5 (Cu), of 21.3-711 (Zn), 26.4-239 (Pb), 2.8-18.9 (Cd). Content of As and Se on the industrial sites increased: arsenic concentrations from 1.49 to 9.22 mg/kg, and selenium - from 0.5 to 21 mg/kg.

Plants respond differently to an excess of metals in the studied landscapes. In the most contaminated sites, the content of pigments and their ratios in the leaves of colt's foot (*Tussilago farfara*), dandelion (*Tarexacum officinales*) and willow (*Salix spp.*) are not violated. Not a change in the water metabolism of plants, as the moisture content of the plants selected relative to the background and contaminated sites, almost the same. Nevertheless, in areas susceptible to contamination or secondary accumulation of metals, the level of chlorophyll a content significantly increased in leaves of sea buckthorn and willow. Significantly increased content of pigments in the leaves of dandelion in conditionally background areas may be due to local (focal) accumulation of pollutants.

However, the impact of metals affects the synthesis of chlorophyll a, chlorophyll b, their ratio, the ratio of total chlorophyll to carotene in the leaves of sea buckthorn. The concentration of chlorophylls a and b increased almost 2-fold in plants grown on anthropogenic sites.

Industrial pollution of the floodplain of the river Ardon in the area Unal tailings affects on the synthesis of phytochelatins in the leaves of the willow, sea-buckthorn and to a lesser extent in the leaves of colt's foot (Fig. 2).



Fig. 2. Comparative levels of phytochelatins in the leaves of the willow in relative to the background (1-4, 10-16) and anthropogenic (5-9) areas in the floodplain of the Ardon river. 7-8 – areas within Unal tailings of Misur MPP. Phytochelatins: a – the amount of phytochelatins, b - glutathione oxidized, c - reduced glutathione, d – metallothioneines, d – the amount of thiocontaining substances, e – unknown compounds.

The phytochelatin concentrations in the leaves of the dandelion rise in the area of pollution, but the maximum values reach in the area (village Ramonovo). Apparently, this is due to the secondary formation of biogeochemical anomalies, which was found before or with the influence of other factors that you need to find out. But most adequately on the level of metals in the environment and foliage reacts willow. Namely, the willow is concentrator and an indicator of the levels of cadmium and zinc in soil [3].

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Asavin A.M.¹, Ignatov Yr.A.¹, Litvinov A.V.² Experimental calibration of MDS-type gas sensors by gas mixtures and vacuum.

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Abstract. The paper discusses the methodological error calibration of gas sensors in the measurement evaluation of pollution in the atmosphere. A method for determination of the zero value for the comparison of measurements of different sensors. The high sensitivity of the sensors used by MDS at a hydrogen determination.

Keywords: gas sensor, atmosphere pollution, hydrogen in atmosphere.

Gas sensors based on the phenomenon of changes in conductivity into the nano-layered condensator packet metal-insulator-semiconductor (MDS) depending on the composition of the atmosphere and through his good gas molecules sorption on the surface MDS layer.

The sensitivity and performance of the sensor depends on the electrode material used. For example, the structure of the sensing element may consist of a silicon wafer on which the film was coated with the tantalum oxide, is then deposited metal film catalytic (Pd, Pt, Ni) of about 30 nm thick. This layered MIS capacitor pack is heated, there is a certain gas molecules adsorption on nano-layers with the result that the measured voltage in the thermistor is directly proportional to the concentration of adsorbed that gas pollutant. Thus, one can construct a calibration curve of the concentration of a specific evaluation, the pollutant gas from the measured voltage.



Fig. 1 Schema MDS-sensor:

 $\begin{array}{l} 1-\text{film Pd; } 2-\text{film Ta}_2O_5; \ 3-\text{film SiO}_2 \ (\text{dielectric}); \ 4-\text{Si film (semiconductor}); \ 5-\text{metal electrod}; \ 6-\text{dielectric} \\ \text{layer; } 7-\text{thermal element; } 8-\text{electric contact heater; } 9,11\\ -\text{electric contact of MDP-condensator; } 10-\text{thermally} \\ \text{sensitive resistor} \end{array}$

Type of gas to be measured depends on the material used. For example, if the electrode material is palladium, the sensor has a very high sensitivity to gases: H_2 , H_2S , NO_2 , etc. If a film made of platinum, the sensor sensitivity is reduced by several times, and its performance deteriorates. The film of iridium, according to the literature, provides increased sensitivity and speed to NH_3 .

The principal problem in the operation of such sensors is the question of the impact on the individual calibration curve of the sensor different factors: impurities in the atmosphere gas mixtures, concrete structure of the MDS assembly, operating time period, external conditions in the atmosphere. These is the reasons of the difficulty to compare data from different sensors.

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Fig.2 Calibration curve and equation signal as a function of H_2 concentration (A) and CH_4 (B).

Each sensor kit with circuitry of the device is unique because the high sensitivity measurement, instability of the spray technology and influence of the electronic scheme. And as result, its instability depending on the measuring system and requires individual calibration. In fig 2. We can see the different type of the function for H_2 and CH_4 curves. Also we can calculate the error of the measure concentration by this function. Average error for that function about 5-10 rel. % concentration of the gas pollutant. If we include also about 5 rel.% of the error of voltage measure the total error of measure grow to 10-15 rel.%. Here is the minimum of the error with very good value of R^2 parameter (closely to 1).

The next problem is the compare the point of zero between different sensors (Fig.3). We have to find a justified signal value that corresponds to the point where the gas concentration is zero pollution. In opposite case we couldn't compare measurement from different sensors.

Before our research the point of zero were calibrated as sensor signal in the office room during night time.

But this is not fully correct assumption. Now we offer calculate zero point as sensor signal in vacuum camera. In the fig 3 shows vacuum camera about 45 l volume which can hold 2 sensor simultaneously. We put sensors into camera and make several measurements during 6-8 hour period. On the graphic (Fig. 4) several minimum points corresponds condition with vacuum in camera and maximum pick on graphic corresponds moment when the door camera is open.

We observed high difference between zero points from sensors N12905 and N5757 (2300 and 950 mv).



Fig. 3. Result of observation H2 from two points wich closely to each other



Fig. 4. Equipment for testing gas-sensor readymounted into experimental gas mixtures and vacuum.



Fig. 5. Graphic level of signal sensors N12905 and N5757 for H_2 measure in vacuum camera. Red ellipse mark zero point values.

Accordingly, we believe that in the calculation of the true concentration of hydrogen in atmosphere should be deducted from the value of the measured signal, values of these constants.

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UDC 556 Alekhin Y.V., Makarova M.A., Shipilova E.S., Makarov M.I. The study of migration forms of trace elements in natural waters of West Africa

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Abstract. The paper discusses the main results of the study of forms of microelements migration underground, surface and atmospheric waters of various horizons vertical zoning boksitonostnogo lateritic weathering profile using the method of cascade filtration.

Keywords: cascade filtration, lateritic weathering crust, bauxite, organic matter, trace components.

Insufficient knowledge of matter redistribution mechanisms (in particular forms of migration) in the lateritic profile - is an actual problem, which involved many scientists. Now days, there are new approaches to solve this problem. One of them is a new method for studying the changes in the molecular weight distribution of organic matter, colloids, iron hydroxides and Micro Component composition - the method of cascade filtration (Ilvin, 2011). This technique allows to study the nature of the distribution agents and behavior of trace elements in natural waters in detail. The object of the study ise groundwater and surface water, selected within the plateau of Fouta Djalon-Mandingo (West Africa). Water samples were taken from the piezometric wells, which are associated with distribution zones lateritic weathering crusts horizons: bauxite horizon 7m and 12m, 3m clay horizon, horizon bedrocks silty mudstone, and surface and atmospheric waters.

Cascade filtration method was used to solve the problem of the balance of different elements, its evaluation of the migration, the study of transformation and patterns of differences in true colloidal and dissolved forms of migration of certain metals with organic matter in natural waters. Cascade filtration is the method of separation of solutions into size fractions, during wich one sample is filtered through a series of partially permeable membranes with decreasing pore diameter. Sequential filtering samples through filters of different sizes allows you to get the distribution corresponding to the natural organic matter (7.5 µm, 1 µm, 0.45 µm, 0.22 µm, 0.046) and gives a more accurate distribution of organic matter in the subsequent filtration stages, where pore sizes (10 kDa and 1 kDa) comparable to

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the size of the molecules of fulvic acid (0.003 mm and 0.0014 mm, respectively), as there is no large particles clogging the filter.

Depending on the behavior of the chemical elements in cascade filtration we have isolated three groups. The first group includes Hf, Tl, W, Ta, U, Nb, Bi, Ga, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu throughout cascade filtration content of these elements does not change (Figure 1).



Fig. 1 The contents of the elements of the 1st Group for various stages of the test cascade filtration of water (the first points correspond to the original sample)

Almost horizontal trends for the first group with low coefficients of excretion and lack of correlations with organic matter testifies to the difference of the organic matter from the water DOC of boreal zone of Russia, which is characterized by a large number of polycarboxylic (humic and fulvic) acids (Alekhin, 2015). For tested water area apparently typical organic substance in the form of simple low molecular weight carboxylic acids. Trace elements of the first group are preferably in solution in a neutral (uncharged) forms complex with organic substance (OS), hydroxo as behave indifferently kilodaltons and reverse osmosis membranes.

The second group elements include Al, Fe, Th, Y, La, Ce. These chemical elements for parallel and serial filtration, behave differently with respect to the first group (Fig. 2-4). The concentrations of these elements with each subsequent stage of cascade filtration gradually reduced, i.e. they are in the form of complexes with iron colloids, and aluminum.

The third allocated contact group include Cd, Sb, Cu, As, Co. This group of elements is characterized by a sharp increase in concentration (Fig. 5) in the last two stages of filtration (filters kilodaltons) i.e. characterized ionic forms.



Fig. 2. The content of Al for the different stages of KF study treatment (first points correspond to the original sample)



Fig. 3 The content of Fe for the different stages of KF study treatment (first points correspond to the original sample)



Fig. 4 The content of elements in group 2 for the different stages of KF study treatment (first points correspond to the original sample)



Fig. 5 The content of the elements of the 3rd group for the different stages of KF study treatment (first points correspond to the original sample)

Correlation analysis of microcomponents with the basic elements of lateritic weathering crusts bauxite (aluminum and iron) did not reveal any significant correlations. We can only talk about trends (quite insignificant, $R^2 = 0.5-0.7$) in the correlations of Al with Y, Nd, Co, Sn, Cs, Cr, Ga.

The lack of correlations with organic matter shows that the study area is characterized by water rapidly decaying organic substance in the form of low molecular weight carboxylic acids and other simple molecules of OS (Fig. 6).



Fig. 6 The content of organic matter for the various stages of the test cascade filtration of water (the first points correspond to the original sample)

For water of laterite weathering crust is not necessary to use the method of cascade filter of a large volume sampling for the isolation of large quantities of organic matter and associated minerals in the early stages. It is enough to use a normal parallel filtration of small sample volumes to isolate fractions required dimension.

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