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Plenary Session

ORNITOGENIC SOILS OF ANTARCTICA: DIVERSITY, CHARACTERISTICS, FUNCTIONING

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Ornitogenic soils are specific version of soil formation which is characteristic moreover for the Southern Hemisphere, but at the same time they are distributed in Northern Hemisphere, but in less grade. Ornitogenic soil formation usually implemented in the subsidence of the terrestrial soils by the guano and in the development of postornitogenic successions of soils and vegetation cover. At the same time ornitogenic transfer of the seeds and separate and able for vegetation plants result in initial colonization of both coastal and interland zones. This processes result in initialization of the pedogenesis. Ornitogenic processes also play an important role in redistribution of the trace elements in the ecosystems. Thus, the ornitogenic soil formation could be considered as specific version of the pedogenesis and as the global biogeochemical phenomena for South Hemisphere.

Antarctic pedogenesis is characterized by specificity which is caused by relative isolation of the ecosystems each from other and from others terrestrial biomes (Mergelov, Goryachkin, 2012, The soils of Antarctica, 2015). This isolation is not complete, namely the ornitohoria became the main process in redistribution of the compounds and energy in Antarctic. Plants redistribution caused not only with penguins, but also with scuas and other migrants birds. Their activity causes the partial isolation of the *Deshampsia antarctica*, while the ornitogenic transfer prevents the full isolation of this plant in Antarctic refugees (Parnikoza et al, 2014; Peter, 2008). Migration birds play an important role in the redistribution of the genetic information and in the transfer of generative and vegetative parts of lower and vascular plants, as well as invertebrates on the long distances. (Andrassy, 1998; Porazinska, Wall, 2002; Ryss et al., 2005; Yeates et al., 2009; McGill et al., 2015; Parnikoza, Abakumov et al, 2017). Due to this factor even the isolated moraines and nunataks are colonized by the mosses, lichens, algae's and cereals and also by nematodes. An accumulation of guano and nests construction result in formation of the specific polypedones with specific particle size distribution with prevailing of the coarse fraction and formation of specifics aggregate composition. The content of nitrogen is essentially higher in soils with pronounced ornitogenic effect not only on the territories of direct birds effect, but also in geochemically subrdirrected positions. That is why, the depressions of the relief can be considered as spatial continuation of the authomophous ornitogenic soils.

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ACCUMULATION OF CHEMICAL ELEMENTS BY SOILS AND PLANTS UNDER EXTREME CONDITIONS OF MINING

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Accumulation of chemical elements by soils and plants was studied at the Perevalnoe and Sakhalinskoe mercury mines in Krasnodar Krai, the Urup copper-zinc pyritic mine in the Karachay-Cherkess Republic, coal mines in Rostov Oblast, deposits of building materials (clay, gravel), oil and gas in Krasnodar Krai and Stavropol Krai and lead-zinc deposits in Kazakhstan. The conducted research showed that mining areas with extreme conditions of existence and interaction between biogenic and abiogenic systems represent rather large technogenic geochemical anomalies. Furthermore, the crystal-chemical characteristics of several elements, local climatic and landscape-geochemical conditions often influence the elemental composition of associations. In the cases studied, the mineralogical and geochemical parameters of the extracted raw materials, the degree of rock crushing, the way deposit mining and dump formation were the key factors.

In such a biogenic system as soils, in the extreme conditions of mining areas, *Ba*, *Co*, *Cu*, *Mo*, *Pb*, *Ti*, *V* and *Zn* make up a cluster of elements with concentrations exceeding the average Earth’s soil abundances. *Sr* is also accumulated in soils of the majority of investigated mines. When comparing to the average levels in soils of the North-Western Caucasus, the row is continued by *Cr*, *Ge* and *Sn*. At ore deposits, contents of Ag, Ba, Co, Cu, Mo, Pb and Zn are not just anomalous but exceed the abundances up to 225 times. Its accumulation depends mainly on geochemical features of the mined material, enclosing rocks and primary haloes.

Contents of *Ba*, *Li*, *Sr*, *Ti*, *W* and often *Pb* are increased in woody vegetation of all the investigated mines relative to the average levels of terrestrial trees. The enrichment factor (EF) of *Ba*, *Sr*, *Ti* and *W* is normally over 10 at the ore deposits, as well as at the mines of building materials. This can be largely explained by geochemical (including biogeochemical) features of the North-Western Caucasus. Relatively to the regional vegetation, the EF of *Ag*, *Co*, *Cu*, *Li*, *Mn*, *Mo*, *Sr*, *W* and *Zn* exceeds 1 in trees of almost all the mines. This allows assuming that, even under extreme conditions, the regional distinctive geochemical features of the North-Western Caucasus have a significant influence on the absorption of *Ag*, *Co*, *Cu*, *Mn*, *Mo* and *Zn* by woody vegetation.

Hornbeam is a ubiquitous tree of ore mining areas. The EF of the majority of elements is more than 1. At the Urup mine, the EF of *Ag* and *Zn* are over 10; at the mercury mines, the EF of *Ag* is over 10. In the studied stress situations, not more than 25–30% of the previously grown and surrounding flora species were able to inhabit the disturbed territory for 50–80 years. Its biomass is normally several times lower than in undisturbed natural conditions. Thus, the biological cycle of numerous chemical elements changes significantly under the impact of mining.

The influence of the geomorphology of the dumps, as well as the size of the fragments of rocks forming them on the biological cycle and the concentration of elements in soils and plants, is found. A fairly clear dependence of migration distance and joint accumulation of elements on such factors as ionic radius, A.E. Fersman's energy coefficients, ionisation and Cartledge potentials is revealed.

RESPONSE OF THE SOILS TO THE GLOBAL CLIMATE CHANGE AND CLIMATIC GRADIENTS AT ECOSYSTEM SCALE

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Soil formed *in situ* as a natural body, which records environmental changes by transformations according to the interactions of climatic, biotic, and anthropogenic factors, as conditioned by geologic and topographic settings, over geological and biological time scales. Climate change has the potential to alter soil ecosystem structure and function in non-linear ways. Soil can also influence climate on a smaller scale (soil climatic gradients). The monitoring of soil change an excellent environmental assessment, because every block of soil is a timed "memory" of the past and present biosphere dynamics.

Climatic changes is the major factor influencing mineralogical and chemical composition of soils and palaesols that does them by the irreplaceable archive which is potentially containing answers to important questions reflecting significant stages of evolution of biosphere. For carrying out the quantitative reconstruction of state variables of a surrounding medium, the independent methods reflecting a condition of a solid phase of soils (a magnetic, mineralogical, geochemical method, an isotope geochemistry) were used.

The complex investigation of three Luvic Phaezoem soils under secondary deciduous forest, grassland and cropland from Moscow region, Russia, were fulfilled with the main goal to study the state of solid phases of soils along local gradients of environmental change. Detailed study of mineralogy and chemistry (XRD, XRF), surface area, porosity, organic matter, carbon/microbial biomass, moisture content, monitoring of total soil respiration was performed.

In addition to the bulk and clay fraction, we separated and investigated the different sub-fractions of silt. The profile distribution of chemical elements such as Si, Al, Fe, K, for bulk sample looks very similar. On the contrary, in the case of the analysis of element concentration in different sub-fractions of silt and clay we observed the redistribution with a connection to the ecosystem and climatic conditions. The observed feedback of soils to local climatic gradients will be compared with results of investigation of Quaternary paleosols in the frame of global climate change. The aim of this study was to estimate the status of Quaternary palaesols using, clay mineral assemblages, geochemical indicators (coefficients based on ratios of different element concentrations), iron oxide magnetic mineralogy and clay-organic complexes. A variety of climatic proxies were observed and used to estimate the relative intensity of the Quaternary climatic change.: The possibility of the quantitative assessment of palaeotemperature for Holocene palaesols on the basis of palaesols weathering index (PWI) will be demonstrate. The received tool allows to calculate the index of aridity and to estimate in details shifts of borders of climatic zones throughout the late Holocene in the south of the East European Plain. Clay fractions of palaesols generally hold the highest content of soil organic matter (SOM), clay minerals protect efficiently SOM from decomposition. The clay fractions of palaesols were analyzed by solid-state 13C NMR spectroscopy: amounts of C-species demonstrate the changes in structure of organic matter versus climate of soil formation. Carbon isotope compositions (δ13C) of organic matter in clay fractions of palaesols suggest changes of the vegetation. Geochemical and mineralogical data of palaesols and clay-organic-complexes from palaesols are useful indicators of past environments and climate.

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ABOUT HUMIN

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Soil humic substances or humus is subdivided into main 3 groups based on their chemical properties: humic acids, fulvic acids and humin (or non hydrolysable part of soil organic matter – SOM). The experimental studies of humin remain still limited whereas its mean concentration in soils is 50% and in non-lithified sediments reaches 70%. These figures say about the considerable input of humin in a global organic carbon pool. Published data on humus composition of ~ 200 modern soils of different genesis and of > 100 Quaternary paleosols have been collected and processed. The content of humin in paleosols is comparable with that of modern soils (50±15% and 54±21% respectively). Thus humin does not accumulate under diagenesis and is not the inert part of soil organic matter. The existence of good negative correlation between humin and humic acids for modern soils (R^2=0.75), as well as for buried palaeosoils (R^2=0.72) shows the genetic relationships between these two groups of humus. The similar conclusion has been made by Rice and MacCarthy (1991) based on elemental composition of 600 soil humic acids, fulvic acids and humins.

The comparative study of humin in a number of soils of different genesis and their clay fractions (natural organo-mineral complexes) shows that humin content in clay fractions is smaller (60±15% for soils and 36±21% for clay fractions). Solid state ^{13}C NMR spectroscopy showed that irrespectively to soil genesis soil humin is aliphatic and enriched in *O*-alkyls and acetal groups. This reflects the presence of polysaccharides, lignin and other weakly decomposed plant residues in humin. To compare, total soil organic matter contains more aryls and carboxyls. The humification degree expressed as alkyls/*O*-alkyls is visibly smaller for humin samples (0.45±0.10) in a comparison with total soil organic matter (0.74±0.16). It is concluded that humin fraction is not homogeneous and consists from at least two distinct parts: clay–bound organic carbon, non-hydrolyzed being physically–chemically protected and weakly decomposed plant residues stable to hydrolysis.

Study of humin within clay fractions of Carboniferous palaeosols (Moscow sedimentary basin) shows that its concentration could be very different (from 0 to 55% from SOM content). Correlations between humin and other groups of humus have not been found. The conclusion has been made that both palaeosol genesis and mineralogy as well as diagenesis affect the status of fossil SOM (Alekseeva et al., 2016).

^{13}C NMR spectroscopic study of Carboniferous kerogen (Moscow sedimentary basin) showed the principal difference between terrestrial humin and kerogen where the dominant C groups are alkyls. The contents of *O*-alkyls and aryls are small, acetal groups are not detected. These results indicate the sapropel origin of organic matter in kerogen and reducing conditions of its development.

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MICROBIAL COMMUNITY IN SOILS OF SAINT PETERSBURG

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Introduction. Urbanization is the most intense factor that affects soils. Almost all forms of direct and indirect impact, including change of the structure and properties, soil profile destruction and formation, are connected with it. In megalopolises, the amount of the effectively functioning surface rapidly decreases, which increases intensity of the ecological situation. Effective performance of ecological functions by soils, on which the human life quality depends, is determined to a great extent by a microbial community (MC). The MC is the most important element of the biogeomembrane, the main structural ecological unit of the soil.

Objective: study of specific features of the microbial community structure in the megalopolis soil variously modified by the human economic activities.

Study subjects and methods. For a comparative analysis of the soil microbiome, samples from humus horizons of three soil groups were taken: native (section 4 and 7), anthropogenically modified (section 3, 9), and antropogenic (section 3, 5).

The microbiome was studied by extracting DNA and RNA from the soil and sequencing of 16SpPHK gene at GS Unior (Roche) sequencer. A comparative analysis of libraries was performed with QIIM software.

Results and discussion. At the initial stage of study of the taxonomic structure of the city soil MC, their affinity with native soils of the surrounding territory was established [Aparin et al., 2017].

Studied samples showed absolute predominance of bacteria at the domain level. Percentage of archaea represented by *o.Crenarchaeota* does not exceed 2%. In all samples, representatives of 9 bacterial phyla are detected: *Acidobacteria, Actinobacteria, Bacteroidetes, Chloroflexi, Firmicutes, Gemmatimonadetes, Planctomycetes, Proteobacteria, Verrucomicrobia*. Their content varies over a wide range (from 0.4 to 40%). Relative percentage of these phyla from the total amount is approximately 98%.

Acidobacteria dominate in phyla. Actinobacteria, Bacteroidete. They account for almost 70% in samples from sections 1 and 9 and 90% in section 4. Phylum of *Chloroflexi* ranks 4th showing the maximum range of content variety. All sections may be divided in 2 groups by the ratio of three dominant phyla. The first group includes sections 4, 5 and 7. Here, Proteobacteria rank first, Actinobacteria rank second, and Acidobacteria – third. In the second group (sections 1, 3 and 9) Actinobacteria dominate; Proteobacteria and Acidobacteria rank second and third, respectively.

At the family level, the structure of microbiom of studied soil is more indicative. The maximum number of families was also determined for three phyla: *Proteobacteria* (21)*, Actinobacteria* (18)*, Acidobacteria* (10). And the amount of attributed families in all the rest phyla did not exceed three units. Significant variety of bacteria content in the soil of different groups was found for 12 families; 7 orders and 1 class that were not attributed at the family level.

In native soils (sections 4 and 7), families of Conexibacteraceae, Syntrophobacteraceae and orders Ellin6513, Actinomycetales are absolutely dominant, and their content is higher in section 4 almost everywhere. The content of Intrasporangiaceae, Solirubrobacteraceae, Bradyrhizobiaceae, [Chthoniobacteraceae] families, orders iii1–15, 0319–7L14, Myxococcales, class Ellin6529 is minimal in section 4. Section 7 is distinguished from others by absolute domination of Bradyrhizobiaceae family in MC, while the content of Solirubrobacteraceae family and orders 0319–7L14, Ellin6529 is minimal. The maximal content of Gaiellaceae, Solirubrobacteraceae, [Chthoniobacteraceae] families, order iii1–15 and class Ellin6529 is in agrogenic soil (section 9), and the content of Enterobacteriaceae family is minimal. In section 5, Intrasporangiaceae family and order Myxococcales are dominant. In the sod introduced soil (section 3) Gaiellaceae family and order iii1–15 rank first.

COMPARATIVE ANALYSIS OF THE ELEMENTAL STATUS OF CHILDREN LIVING IN AREAS WITH DIFFERENT MORBIDITY OF CHILDREN'S POPULATION IN THE EURO-ARCTIC REGION

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In our studies have been shown the difference in prevalence of diseases of the musculoskeletal system and connective tissue (MSCTD) in the Apatity town and in the Lovozero village in children of 0–14 years old by 2.8 times, in prevalence of the overall morbidity of children of 15–17 years old in Apatity in 2.2 times. However, the primary incidence of urolithiasis (ULD) in children of 0–14 years old in the Apatity was lower than in the Lovozero in 2.7 times. This alternative type of morbidity of children's population in the Apatity and in the Lovozero was reason for studying of the mineral metabolism in children living in areas under different combined effects of the natural and man-made environment in the Arctic. For this purpose, 25 samples of hair for every comparison group from preschoolers in the Lovozero and in the Apatity (4.46±0.53 4.59± 0.85 years old, respectively) and adolescent (14.32±1.03 and 3.96± 0.35 years old, respectively) were taken for further analysis. Determination of chemical elements in biological samples was carried out by atomic-emission spectrometry and mass spectrometry with inductively coupled plasma. As a result of the study, significant ($p < 0.05$) differences in the content of microelements (μg/g) in hair of preschoolers from the the Lovozero and from the Apatity were found: in Mg, P, Cr, Cu, Zn, Se, Sr, Ba, Mo, Si, Ge, Sn, Ti. Also significant ($p < 0.05$) differences in the content of microelements in the hair of adolescent from the Lovozero and from the Apatity were found. To assess the possible metabolic activity of chemical elements and the trends in the formation of pathological processes in children's population in the Lovozero and in the Apatity, the most informative coefficients of the ratios of essential micro- and macro elements (Ca/P, Ca/K, Na/K, Na/Mg, Fe/Cu, Fe/Co, Ca/Mg) were calculated. A significant deviation from the optimum in the ratios of essential elements in hair children from the Lovozero and from the Apatity were revealed. In particular, ratios Ca/P was more than 2 times higher than in the optimum, the Ca/K ratio was almost 5 times less than the optimum, the Ca/Mg ratio was more than 7 times greater than the optimum; Na/K was almost 2 times less than the optimum, the Na/Mg ratio, on the contrary, was more than optimum almost 14.5 times; The Fe/Cu ratio was greater than the optimum by almost 3.5 times; the ratio of Fe/Co was 2.3 times higher of optimum in the hair of preschoolers in the Lovozero and in the Apatity. In adolescents, the direction of the deviation of the ratio of elements from the optimum was practically the same as in preschoolers from the Lovozero and from the Apatity, but with a decrease in the deviation from the optimum. Significant ($p < 0.05$) differences between the ratios of the elements in hair of children from the Lovozero and from the Apatity were found for Na/K, Fe/Cu, and for Ca/Mg. Deviations in the content of essential elements from the standards and their ratio from the optimum may be one of the reasons for the high incidence of the children's population in the Lovozero and in the Apatity due to diseases caused by a violation of mineral metabolism. We can assume that the deficit of Zn and Se, a lower content of Mo and an increased content of Ge in hair of preschoolers, the increasing content of Ni, Rb, Ge almost in 2 times, Hg in 3 times higher in hair of adolescents from the Lovozero than in hair of children from Apatity could contribute to the prevalence of incidence of ULD, which in the group of children 0–14 years old is 2.7 times higher in the Lovozero than in the Apatity. At the same time, the increasing in the content of Sr in almost 5 times, Sn, Ti in 2 times in preschoolers from in the Apatity, in comparison with preschoolers from the Lovozero could be associated with a high prevalence of MSCTD in children in the Apatity-Kirovsk district.

STABILITY OF ARSENATES AND ARSENITES IN NATURAL AND ANTHROPOGENIC ENVIRONMENTS

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Arsenic is widely distributed in the environment. Although arsenic is useful for industrial, agricultural, medical and other purposes, it exerts a toxic effect on a variety of organisms, including humans [1]. Drainage from mineralized and mined areas may have high dissolved arsenic concentrations, and of major interest as the natural sources of As in waters, soils and plants are likely to be the low-temperature oxidizing environments in the vicinity of ore bodies which contain As-bearing sulfides, and arsenides. Under oxidizing environmental conditions, arsenic occurs in the form of arsenate (AsO_4^{3-}) or arsenite (AsO_3^{3-}) oxyanions, i.e. As^{5+} or As^{3+}, respectively. The oxidation of arsenides can be catalyzed by bacteria such as *Acidithiobacillus ferrooxidans,* which also leads to the formation of various iron oxides and hydroxysulfates [2]. Newly discovered microorganisms that use arsenite and arsenate as a basis for their metabolism are thought to play an important role in regulating of arsenic redox reactions. Recent studies have pointed out the complex interplay among adsorption and precipitation of arsenic processes, changes in oxidation states and mineral stabilities mediated by microbial activities in surface and subsurface environments [3].

The most arsenites and arsenates were formed at chemical weathering of ores by oxygenated waters establishes conditions of increased Eh and low or neutral pH (at seasonal fluctuations of temperatures and atmospheric pressure). The interpretations are summarized on the Eh-pH diagrams, synthesized from equilibrium calculations, and reported geologic occurrences. The most recent thermodynamic data available [4] were used for the construction of diagrams from reactions which are balanced equations of Eh-pH relationships among species which are thermodynamically stable within the ranges of oxidation potential and pH considered for each reaction. The Eh-pH diagrams of systems Me–As–H_2O (Me=Co, Ni, Fe, Cu, Zn, Pb) were calculated and constructed using the Geochemist's Workbench (GMB9.0) software package. Eh–pH diagrams have been constructed for the average content of these elements in underground waters and for their contents in acidic waters of the oxidation zones of sulphide deposits [5]. The formation of arsenates and arsenites of Co, Ni, Fe, Cu, Zn, Pb in near-surface conditions are discussed. For the geologic purposes of this work ionic concentrations has been considered equivalent to ionic activities.

Eh-pH stability relationships have been determined for arsenic oxysalts (adamine, annabergite, scorodite, erythrite etc) and in order to interpret conditions of formation of these minerals and to compare their geologic stabilities of ore deposits. The understanding of mechanisms of arsenic behavior in the near-surface conditions is one of actual problems of modern mineralogy and geochemistry and it is very important for the solving of some environmental problems.

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OPTICAL METHODS DEVELOPMENT TO STUDY BIOGENIC-ABIOGENIC INTERACTIONS

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The methods based on the effects of Surface Enhanced Raman scattering /SERS/ and Spatially offset Raman spectroscopy /SORS/have great information value. In the present work, these methods are developed on the basis of the joint use of organic and inorganic nanodisperse semiconductor compounds. The electromagnetic theory of SERS on semiconductors is developed. It is determined that the amplification of Raman scattering by semiconductors is less than on metal substrates. A significant number of organic semiconductor structures are known, which exhibit the properties of biological catalysts. This makes them promising for the study Biogenic-Abiogenic interactions. In the work as model systems, diphthalocyanine, anatase and also a multicomponent system (MS), which was synthesized from plant material, were used. The MS used in experiments had pronounced antioxidant properties. The resulting composite material based on MS and TiO_2 possessed a pronounced photocatalytic activity, which allowed it to be used as a source of Reactive Oxygen Species (ROS).

It was found that ROS often participates in Biogenic-Abiogenic interactions. They can play a negative role, for example, by changing the pH of the medium, as a result of which processes of pathological mineral formation arise. They can also play a positive role, for example, as biocides, contributing to the purification of water and air. This circumstance is important in the tasks of preserving monuments of cultural heritage. ROS are also important components in the processes of formation of immunity in a biological cell. The paper presents the results of a study of chemiluminescent reactions involving ROS, which allowed to develop a highly efficient sensor of superoxide ion and Singlet Oxygen and a means of measurement in the gas phase.

The practical result of the work is the creation of a small remote Raman spectrometer, as well as high-performance sensors and sources of active oxygen species that can be used for research in the field of Biogenic-Abiogenic interactions. An illustration of the effectiveness of the use of sensors is the registration of the process in the kinetics of singlet oxygen release into the air environment by plants and microcrystals of ice and snow.

BIOFILM MINERALIZATION BY PARTICIPATION OF LITHOBIOTIC MICROBIAL COMMUNITY

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Metabolism of lithobiotic microbial community (microscopic fungi, bacteria, lichens) is an important factor of secondary mineral formation on the surface of different rocks and minerals. By the participation of microscopic fungi and lichens, oxalates are formed, and by the participation of bacteria – carbonates (mainly calcite) are also formed. There are bacteria (for example, the genus *Bacillus*) with the participation of which both carbonates and oxalates are formed. Among microbial crystalline hydrates of oxalic acid salts calcium oxalates are most common: the tetragonal dihydrate weddelite $CaC_2O_4 \cdot (2 + x)\ H_2O$ and monoclinic monohydrate whewellite $CaC_2O_4 \cdot H_2O$. Weddellite form dipyramidal and dipyramidal-prismatic crystals, whewellite – often irregular intergrowths, less often – fine crystals. We have found crystals of calcium oxalates in biofilms on the surface of the different Ca-bearing rocks and minerals: marbles and limestones (in Chersonese and St. Petersburg), shell sandstone (Kingessep, Leningrad region) etc. Determination of the species composition of biofilm microorganisms allow revealed that the crystallization of calcium oxalates is initiated by the lichens of the genera *Lecanora* and *Caloplaca*, as well as by numerous micromycetes producing oxalic acid.

Results of biomimetic syntheses with the participation of fungi *Aspergillus niger*, *Penicillium* sp. and bacteria of the genus *Bacillus* have given the general morphogenetic pattern of microbial crystallization. In addition to calcium oxalates, the biomimetic analogs of humboldtin group minerals $Me^{2+}C_2O_4 \cdot 2H_2O$, $Me^{2+} = Fe^{2+}$. Mg^{2+} Mn^{2+} (humboldtin, glushenskite and lindbergite) as well as of falottait $MnC_2O_4 \cdot 3H_2O$ and muluite $Cu\ (C_2O_4) \cdot (1\text{-}x)\ H_2O$ were obtained. It was shown that the fungus Ca-oxalate crystallization starts at pH ~5 from the formation of almost ideal dipyramidal and dipyramidal–prismatic (with dominant {101} pyramidal faces) tetragonal weddellite crystals. Then the prismatic faces {001} of weddellite crystals became more pronounced and calcium oxalate monohydrate, whewellite, appears as splitted spherulite-like aggregates. At the last stage there are almost ideal dipyramidal weddellite crystals of the new generation. As a result of laboratory experiments, it was established that the determining role in the formation of metastable weddellite crystals in biofilms besides oxalic acid play the citric acid released during the metabolic activity of micromycetes, as well as Fe^{3+} ions that fall into biofilms from the environment and also the value of the ratio $C_{Ca} / C_{C_2O_4}$, depending on the intensity extraction of acid by fungi and dissolution of underlying rock. The possibility of the incorporation of Sr-ions in the weddellite and the whewellite, which leads to the formation of appropriate isomorphic and isodimorphic series, is revealed. It was shown that crystallization with the participation of bacteria Bacillus *subtilis* begins from the formation of whewellite crystals in the acid medium. Then the formation of a globular secondary calcite crust begins, which is accompanied by shift of pH to the alkaline side. Tetragonal weddellite crystals are formed by the synergistic effect on marble of *Bacillus subtilis* bacteria and *Aspergillus niger* fungus. The formation of polycrystal pseudomorphosis of secondary calcite over whewellite in syntheses by participation of the bacterium *Bacillus subtilis* and the fungus *Penicillium* sp. indicates the possibility of complete replacement of the whewellite with calcite.

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KINETICS OF OMA DISSOLUTION WITH MEDICINAL DRUGS

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Recently, interest in extracerebral calcification in the human body has increased. Calcification processes are poorly described in the literature, and the regularities that occur during the crystallization of cardiotolites have been poorly studied. The purpose of this work is to investigate the dynamic dissolution of solid phases in various solvents and the preparation of the calcium antagonist group. Since the blood plasma has a complex composition, the values of the average concentrations of inorganic substances were used to calculate the systems, the values obtained from the literature data.

The results of XRF indicate that non-stoichiometric carbonate hydroxylapatite was obtained in the synthesis. IR spectroscopy also confirms the proximity of synthesized apatites to biogenic B-type carbonatopatites. Analysis of the kinetic curve of dissolution in a 0.9% NaCl solution showed that the maximum dissolution rate in samples with supersaturation of 10 and synthesis time of 4 and 8 weeks. In our opinion, this is due to the formation of a more soluble phase of the vitlockite. As a calcium antagonist, the drug Verapamil was chosen. Dissolution in the drug Verapamil showed that the reaction rates for the samples with a synthesis time of 4 weeks increased, and in the synthesis of 8 weeks with supersaturation of 50 the maximum dissolution rate. Comparing the dissolution in a 0.9% solution of NaCl, Tris buffer and Verapamil preparation, we can say that the effect of the drug Verapamil on the resorption of the samples is 2 times higher. Verapamil antianginal action, therefore along with antagonism with respect to calcium ions causes dissolution of the samples. Based on the results of XRD samples with glutamic acid, it was found that the variation in the concentration of the additive changes the phase composition and for some represents a mixture of phases. In the IR spectra of the samples, the transmission bands characteristic of phosphate and carbonate ions are recorded. Analyzing the kinetic parameters of dissolution in a 0.9% NaCl solution, the tris buffer is seen, an increase in the concentration of glutamic acid leads to a decrease in the rate of dissolution due to the predominance of the KHA phase. The X-ray diffraction analysis for samples with albumin addition showed that the phase composition changes not significantly when the synthesis time is varied and represents a mixture of carbonatopatite phases. Kinetic parameters of dissolution in a 0.9% solution of NaCl, Tris buffer, with the increase in the synthesis time, the reaction rate decreases in the tris buffer, this is due to the structural change in the position of substitution of the carbonate ion in the KGA from B-type to A-type. The maximum dissolution rate in a 0.9% NaCl solution for a sample with a synthesis time of 8 weeks.

To study the bioactivity, dissolution in the preparation of verapamil was carried out. It can be seen that the dissolution rate of a sample with alanine is 2.5 times higher than that of a sample without an additive. Due to alanine, the metatable phase of the vitlockite is formed. To study the effect of inorganic components, magnesium ions were chosen. As a result, the phase composition of the samples contains carbonate and vitlockite. Semiquantitative analysis showed the predominance of the vitlockite. Based on the results of dissolution in the preparation of Verapamil, the reaction rate changes with increasing synthesis time and with an increase in the addition of magnesium ions. It can be concluded that an increase in the magnesium additive affects the increase in the dissolution rate of the drug Verapamil and, as with the increase in the synthesis time, the phase is more soluble.

BACTERIAL MECHANISMS OF PATHOGENIC CRYSTALLIZATION IN THE HUMAN BODY

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The study of pathogenic organic-inorganic aggregates formed in the human body is one of the main tasks of medical mineralogy. Investigation of minerals and formation conditions of the urinary system stones allows to reveal the physiological solution components and microorganisms inhibiting and initiating crystallization of minerals in the urine. It provides a scientific basis for the development of biotechnology preventing lithiasis, including methods of urolithiasis prevention using known pharmacological and vitamin remedies, food supplements and mineral waters of appropriate composition. Experimental data obtained from the systems modeling composition of physiological solution show the effect of crystallization medium parameters (pH, temperature, concentration of inorganic and organic components) on the lithiasis. Moreover, the physiological solution parameters are not the equally affect as crystallization of various mineral phases, as the nucleation process, aggregation and crystallization of a single mineral phase. The presence of bacteria in the urine, indicating the inflammatory processes in the urinary system, leads to a change in a number of physico-chemical parameters of urine. This is reflected in the phase composition changes of the compounds formed, as well as in the variation of the crystallization kinetic parameters and aggregation.

The experimental simulation shows that the presence of bacteria and protein media contributes to changing the pH of the solutions and significantly affects the phase composition of human renal stones. Under conditions of oxalate mineralization, bacteria accelerate the nucleation of calcium oxalates by almost two times, and also increase the amount of oxalate precipitates along with phosphates and stabilize the calcium oxalate dihydrate – weddellite. The pH change under the action of bacteria is of great importance in the case of phosphate mineralization. Bacteria lead to the crystallization of brushite, struvite, apatite and (to a much lesser extent) whitlockite with addition of pathogens at a minimal composition of human urine; no octalcium phosphate have been detected. At a maximal composition of human urine, bacteria lead to a shift in the formation of struvite to a more acidic side, and also to the crystallization of apatite in a much larger amount.

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BIOMIMETIC SYNTHESIS OF HYDROXYAPATITE BASED COMPOSITES

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Application of biomaterials can be conceptualized as the use of materials to replace lost structures, augment existing structures or promote new tissue formation. Common degradable and non-degradable implant materials can be divided into synthetically produced metals and metal alloys, ceramics, polymers, and composites or modified natural materials. Whereas non-resorbable materials like steel or titanium alloys are commonly used for prosthetic devices, resorbable bone substitute materials are mainly investigated for their feasibility in bone replacement therapies. Various approaches used in the design of bone substitute materials have focused on the degradation and ultimate replacement of the material with new tissue. Whether or not a material is biodegradable, its surface properties will influence the initial cellular events at the cell-material interface. There is good demand for materials for bone and dental replacement. Study of finding a substitution for the bone parts and repairing seriously damaged portions of the human body is a challenging area of multidisciplinary research.

Hydroxyapatite (HAp, $Ca_{10}(PO_4)_6(OH)_2$, a bioceramic is the main constituent of the bones and teeth of vertebrates as well as almost all hard tissues of humans. Hydroxyapatite has a high affinity for natural tissue in situ and can be molded to fill spaces created by physical damage of bones and or teeth.

Synthesis of nano-HAp by various routes such as microwave, hydrothermal and sol-gel, will be discussed. Scaffolds for tissue engineering applications were biomimeticaly synthesized. Hydroxyapatite composites with various polymers such as collagen, gelatin, PVA and PMMA were prepared. The samples were analyzed by SEM, AFM, XRD, IR, DLS and photoluminescence techniques. Thermal and mechanical properties of the composites were analyzed. Bioactivity of the samples was tested using simulated body fluids. It was seen that the method of preparation of the samples influenced the bioactivity, antibacterial efficacy and drug delivering properties in a significant way. The surface roughness and wettability properties of the HAP incorporated composites were enhanced when compared to the pristine samples. Some of the fabricated composites exhibited better stability, mechanical property and haemocompatibility and hence could be used as a composite for tissue engineering and drug delivery.

ORGANIC ACIDS HAVING CHIRAL MOLECULES AS IMPORTANT MEMBERS OF BIOGENIC-ABIOGENIC INTERACTIONS

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Molecules of many organic substances, including organic acids and most of amino acids, include a chiral center. The center, as a rule, is a so-called asymmetrical carbon atom, which has four different substituents. Substances comprising chiral molecules can exist as levorotatory and dextrorotatory enantiomers (optical antipodes). Enantiomers are mirror images of each other that are non-superposable and all known physical properties of enantiomers are identical except for their ability to rotate plane-polarized light in opposite directions. The products of industrial synthetic processes contain, as a rule, equal proportions of levorotatory and dextrorotatory enantiomers. On the contrary, in the nature levorotatory enantiomers occur more frequently than dextrorotatory ones. In the abiocoen, many organic acids having chiral molecules can be preserved in the lithified rocks at great depths and high temperatures. Such conditions can initiate thermo-catalytic reactions that induce racemization processes resulting in equalizing the amounts of levorotatory and dextrorotatory enantiomers due to, for example, transformation of levorotatory enantiomers into dextrorotatory ones. Therefore, particularities of compositions and structures of acids having chiral molecules can reflect the deposition conditions and subsequent transformations of the initial organic matter and that can allow using such acids as indicators of sediment deposition conditions (duration, paleotemperature, geomorphology, etc.).

The entity of mixtures in enantiomeric systems can be various. These can be physical mixtures (conglomerates), or solid solutions, or equimolar and non-equimolar homomolecular and heteromolecular discrete compounds

[1]. The results obtained during the study of solid phases formed in chiral binary systems of various types by means of PXRD, SCXRD, TRPXRD, DSC, IR, and other methods, are discussed. The system composed of R- and S- enantiomers of 3-chloromandelic acid ethanolamine salt was chosen as an exemplary system with an eutectic [2], the system of L- and L-*allo*-diastereomers of amino acid threonine represented a system with continuous solid solutions [3], the system of phenylglycine L- and D-enantiomers was an exemplary system containing an equimolar compound (racemate) [4], the system of S- and R-enantiomers of malic acid represented a system containing an equimolar compound (racemate) and several non-equimolar homomolecular discrete compounds [1, 5], and the system of L-enantiomers of valine and isoleucine was the example of a system containing a non-equimolar heteromolecular discrete compound [6]. All the above experimental systems were also examined to determine the limits of the corresponding solid solutions.

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ELECTRON MICROSCOPY STUDY OF BIOLEACHING OF SHUNGITE ROCKS

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In recent years, special attention is drawn to the methods of microbiological processing of hard-to-rich rocks, which are characterized by minimal technological equipment, high yield and practical absence of losses of allocated elements, relatively low operating costs and environmental safety. At present, the search for effective microorganisms capable of converting hard-to-reach components into soluble forms without additional environmental risks and significant economic costs is very relevant. In this regard, it is of interest to study microorganisms found in shungite rocks, that are able to effectively decompose sulfides, even extremely small and shielded by shungite carbon, and increase at times leaching of various elements, which are characteristics of the action of thionic bacteria.

Microorganisms detected in shungite rocks are fibrous formations and have a number of characteristic morphological features, which are revealed by scanning electron microscopy (SEM), microanalysis (EDS) and transmission electron microscopy (TEM) (see figure). Shungite bacteria have significantly smaller dimensions (diameter of the order of 0.5 μm and length within 5–10 μm) and a hollow multisection structure as compared with the thionic bacteria described in the literature. These microorganisms concentrate iron on themselves during the sulfide leaching according to EDS. Figure b shows an image of a shungite bacterium that has captured metal sulfide. It is seen that the metal is deposited in the form of nanoscale inclusions on the inner wall of the bacterium. It is interesting to note that the continuation of the process leads to the metallization of bacteria and, apparently, to their death, since the bacteria clusters are fixed on the surface of the shungite rock and do not change their configuration for a long time. Also, with the help of electron microscopy, the processes of reproduction of bacteria by the formation of dendrid-like structures and their subsequent separation are noted.

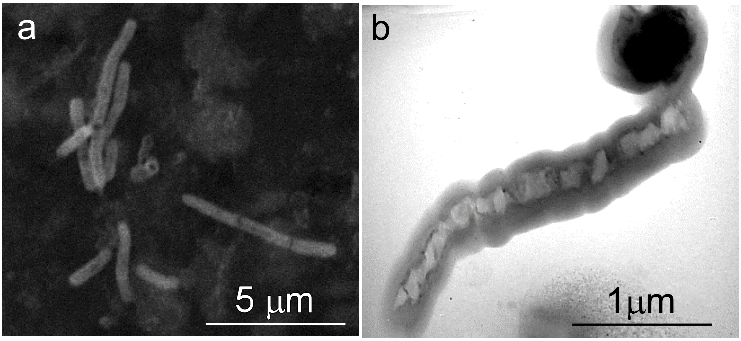

Figure. SEM (a) and TEM (b) images of Shungite bacteria.

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NANOSTRUCTURED BIOMINERALS AND BIOMIMETIC MODELING OF THEIR CHARACTERISTICS.

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Biomineralization is a process of controlled formation of mineral biocomposites, the formation of which takes place with the participation of living organisms. The process of biomineralization takes place in the formation of physiogenic and metabiogenic minerals. Usually biomineral nanocomposites include two main components: organic and mineral. The organic subsystem consists of proteins or polysaccharides, and the mineral subsystem includes various salts or oxides of chemical elements. The formation of the mineral component occurs after the appearance of the organic base (matrix) as a result of filling of the matrix cavities with a mineral substance. Water is a constant component of mineral-forming solutions and one of the building blocks of a living organism in the process of biomineralization. Shells of sea mollusks, spicules of sea glass sponges, bones and teeth of human organisms are examples of biomineral materials.

Biomineralization technology, developed in the process of evolution by living organisms, provides the ability to synthesize crystals under natural conditions from their negligible concentration in the hydrosphere and does not impose special requirements on the purity, temperature and acidity of the environment. This unique feature of the process of biomineralization opens wide horizons for the creation of new low-energy and environmentally friendly biomimetic technologies for the production of materials.

The purpose of the report is to consider the features of natural biomineralization processes and the possibility of using them to create biomimetic technologies.

The role of the biomatrix in the processes of biomineralization and features of self-organization of living matter controlled by proteins are considered. Two approaches to the modeling and reproduction of the biomineralization process in living nature are singled out and considered: the biological direction of modeling and the chemical and biochemical modeling. Examples of sol-gel technologies for biomimetic modeling of biosilicate nanocomposite structures are given. Some aspects of the use of the obtained structures are considered, in particular, in photonics and chemosensors [1,2].

As an example of a biological direction, the possibilities of obtaining materials by direct bioorganic synthesis, in particular, the use of functional active proteins isolated from the spicules of glass sponges are considered. Examples of the developed methods of biosynthesis of nanocrystals of silicon dioxide, silver, gold nanoparticles, and also bimetallic nanoparticles are given [3].

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MINERALOGY AND LANDSCAPE CHARACTERISTIC OF SOME GEOPHAGIC CLAYS FROM SOUTH AFRICA

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In the regions of Asia and Africa geophagic clays are traditionally used by population based on historical and traditional motivations including ethno- medical ones. The aim of the present research was to reveal the general common properties of some geophagic clays based on their mineral composition and landscapes specificity, in which they were sampled. In addition to asses the potential source of the minerals for geoghagic clay, the mineral association of the hard rocks, located in geophagic loose material, was also studied. Mineralogy of the samples was investigated using X-ray diffractometry, FTIR spectroscopy, and optical microscopy.

The studied samples were collected in two provinces of South Africa: Free State and Limpopo. The round trip was approximately 1500 km starting in Free State: Bloemfontein – Clarens – Phuthaditjhaba and in Limpopo Province: Polokwane – Thohoyandou. The studied sites were located in the areas of High-veld (elevation ~ 1800 m) as well as Low-veld (elevations ~ 800–900 m).

The key studies were situated in the stepped table mountain on the Paleozoic nondislocated deposits and on the plateau with detached table mountains (High-veld) and the stratal plains of midland depressions (Low-veld). The geophagic clays were sampled from (i) loose sediment accumulations between boulders of polymict sandstone; (ii) outcrops of arkosic sandstone cemented by clayish material; (iii) clayish oxidized tuff; (iv) calcareous sediment from alluvial valley; and (v) fine earth accumulations in the residual outcrops of bedrocks.

In the fine size fraction separated from loose sediment accumulations and polymict sandstone kaolinite is predominant besides that smectite(s) and small proportion of mica are also present. Oppositely, in the rock cement from arkosic sandstone predominance of smectite(s) was found; mica and kaolinite were also identified. The identities of the mineral associations confirm that sandstone is the source of clay minerals for the loose geophagic material.

In the clayish oxidized tuff enriched by Fe-oxides besides smectite(s) and mica, chlorite was found. Despite the fact that loose material from alluvial valley is calcareous, whereas it is calcite free in the outcrops of bedrocks (the study sites were located close together), their fine size fractions are characterized by the same association of phyllosilicates including mica and kaolinite and predominance of smectite(s).

It was shown that location of geophagic materials is spread widely in the studied provinces. Using material as geophagic is more historically and traditionally determined than by the type or specificity of landscape, which can not be characterized by common features. Whereas it was revealed that despite the differences in location and rock geneses, the most common mineral in the studied geophagic materials is smectite(s) – mineral being able to play a role of sorbent.

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ORGANO-MINERAL INTERACTIONS IN SUBAERIAL SEGMENT OF SILICATE ROCKS: NANOSIMS AND SEM-EDX STUDY FROM EAST ANTARCTICA

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The subaerial segment of quartz- and feldspar-containing hard rocks in East Antarctica is often inhabited by cryptoendolithic communities involved in a variety of organo-mineral interactions. A number of such interactions especially those with engagement of cyanobacteria have occurred in geosystems far in advance the vascular plants established and employed sophisticated weathering potential including rhizosphere effects. Endolithic systems are among the best natural models we have in hands to explore organo-mineral interactions of a very old “phylogenetic age”, and East Antarctica provides the most pristine specimens lacking the noise from many advanced plant communities.

Endolithic organisms have been intensively studied worldwide for decades. Here we present data novel approach combining NanoSIMS (nanoscale secondary ion mass spectroscopy) and SEM-EDX techniques to study weathering mechanisms and organic matter stabilization patterns in cryptoendolithic systems of East Antarctica dominated by cyanobacteria. We explored the spatial distribution of elements detected by NanoSIMS as $^{12}C^{-}$, $^{12}C^{14}N^{-}$, $^{16}O^{-}$, $^{28}Si^{-}$, $^{32}S^{-}$, $^{27}Al^{16}O^{-}$, $^{56}Fe^{16}O^{-}$ secondary ions directly at the surface of biofilm-to-mineral biogeochemical interfaces. By high resolution imaging we were able to demonstrate distinct biogeochemical interface patterns at submicron scale. Preferential organic matter occurrence was detected in micrometer size defects on mineral surfaces, larger etching pits and attributed to clay minerals, yet not fully covered by organic matter. Such secondary ions as $^{12}C^{-}$ and $^{12}C^{14}N^{-}$ were often distinctly colocalized with mineral components indicating the prevalence of sorption mechanisms and the development of organo-mineral associations. The role of aluminum rich areas over silicon ones in sorption was clearly emphasized. We found that nitrogen rich organic matter was more frequently directly colocalized with mineral compounds, mainly aluminum which is consistent with the "onion" layering model of organic matter accumulation in common soils. Based on correlations between $^{12}C^{-}$ and $^{12}C^{14}N^{-}$ secondary ions we conclude that several different generations of organic matter are present in parallel in the endolithic systems. Due to increased resolution of NanoSIMS we revealed some distinct areas where organic matter and Al, Si, Fe-containing species were co-localized, clearly pointing to the formation of mineral-associated organic matter, in contrast to the lower resolution EDX data only pointing towards their "cohabitation".

We observed surprisingly diverse types of organo-mineral interactions and propose different potential pathways for organic matter stabilization in cryptoendolithic systems some of which have quite old ^{14}C ages. Relatively simple systems of microbial origin that exist and replicate on Earth over geological time scales demonstrate the principles of organic matter stabilization strikingly similar to those known for modern full-scale soils of various climates.

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THE INFLUENCE OF THE ENVIRONMENT ON THE EVOLUTION OF HUMAN, THE FORMATION OF SOCIETY, SCIENCE AND CULTURE

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The evaluation of the environmental impact on the evolution of hominids and the history of human cultures is the key problem of the Earth Science and related sciences. Human influence on the environment is measurable. The other thing is the influence of the environment on anthropogenesis.

The systematic approach to the study of the geodynamics impact on human communities avoids the «geodynamic» determinism. Almost all of the facts and structures associated with geodynamics are open dissipative systems (Nesterov, 2001). Energy and substance are exchanged through their boundaries. It is important for us that paleoclimatic rhythm served as a context (and for a number of causal relationships the driving force) of the hominids evolution, the appearance of human and the history of cultures. The geodynamic processes most clearly affected the early stages of society and still evident for present. The importance of regularities of evident and hidden disasters makes us to consider geoecological problems in historical retrospective. The fundamental feature of the Cenozoic paleogeography is the frequent and sharp fluctuations in the global climate in the context of the global cooling, which began in the late Cretaceous. In the era of political instability or excessive economic tension, an extreme natural event can disrupt the unstable equilibrium and lead to disaster immediately or gradually. Probably, the Minoan eruption played such a role for one of the ancient Greek civilizations, the Minoan civilization. The natural disaster destroyed the forces of the Minoan civilization, which, although recovered from the consequences and continued its previous policy, but 50 years later was conquered by the stronger Achaeans. So, one of the first powerful civilizations was obliterated under the determining influence of natural factors.

The processes of anthropogenesis are usually explained by social and economic factors; however, to understand the relationship of biological and social, it is important to mention that the results of social and labor activity, according to the laws of genetics, could not be recorded in genes (Dubinin, 1963). There for, it can be concluded that the causes of anthropogenesis should be biological and depend on the natural features of the human ancestral home. The place of human origin should be sought where the geographical conditions of the environment contributed to genetic changes.

The human body can be considered as a geoindicator, integrating the transformations of the natural environment. Vladimir Vernadsky was the first who came to this conclusion, despite the negligible content of many chemical elements in the environment, they are present in plant and animal organisms constantly and not by chance. The most important role was played by natural and anthropogenic changes in the geochemical context. The microelement composition of bone tissue from archaeological excavations contains a lot of information. It reflects the trace element composition of the bone and blood at the time of death. This is due to the fact that the biological function of the bone system is determined by its ability to quickly give blood to its compounds, and thus contribute to the maintenance of homeostasis of the internal environment (Mavopulo, 2000).

Specific landscape-geochemical conditions determine the specificity of accumulation, and, consequently, the possibility of getting into the human body through trophic chains and other ways, and individual elements. A feature of the Geochemistry of technogenesis (Fersman, 1937) XXI century is an intensive metallization of the biosphere. The geochemical appearance of a person living in the second half of the XX-early XXI century, has fundamentally become different, it appeared rare earth, radioactive and other isotopes.

GEOCHEMICAL FEATURES OF BIOLOGICAL WEATHERING OF GRANITE

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Weathering is the process of destruction and change of minerals and rocks under the influence of physical, chemical and biotic factors. Weathering is divided into mechanical, chemical and biogenic. Usually all types of weathering are closely related.

Physical weathering – disintegration of rock without significant changes in the composition of the debris, leads to granulation and coarsening of the surface, the appearance of crusts and peeling cracks. This process increases the surface of the stone, which enhances the chemical decomposition reactions of the rock and prepares the surface to be populated by microorganisms.

Chemical weathering is the process of chemical transformation of minerals and rocks under the influence of water, oxygen, carbon dioxide, organic acids, as well as due to biochemical processes. Chemical weathering is accompanied by extraction of calcium, sodium, potassium and magnesium silicates from crystal chemical structures. As a result of chemical weathering forms new phases of clay minerals (hydrology, montmorillonite, beidellite, etc.).

Biogenic weathering is associated with the impact on the rocks of plant and animal organisms. Biogeochemical impact on rocks begins with the settlement of microorganisms, lichens and mosses on the surface defects of the stone. The biochemical component actively affects the mineral substance, on the one hand, producing organic acids, and, on the other hand, can contribute to the extraction of minerals from minerals, which also contributes to the destruction of them.

Bio-inert interactions lead to the emergence of primitive soils. Carbon dioxide and humic acids released during the decomposition of organic residues fall into water, which as a result increases its destructive ability. Plant cover promotes the accumulation of moisture and organic substances in the soil, thereby increasing the exposure time of chemical weathering. Bacteria, which are common everywhere, form substances such as nitric acid, carbon dioxide, ammonia and others, contributing to the rapid dissolution of minerals contained in rocks.

The study of the geochemical features of the biological destruction of granite was carried out using the methods of scanning electron microscopy and microprobe analysis, confocal microscopy, ICP MS analysis. Model experiments on the solubility of granite with and without surface biofilm were carried out. For comparison, the geochemical features of the crust and subcortical granite were studied. The dynamics of the behavior of chemical elements in the process of dissolution was studied for 30 days with regular selection of the solution at certain intervals. During of the experiment the pH of the solution and particle size (nanosizer “Nanosight”) were recorded.

The migration coefficients of chemical elements were calculated as the ratio of their content in the crust to the biofilm compared to the crust without biofilm. On the basis of the coefficients a number of chemical elements mobility in the process of biological granite weathering was established: Ca, K, Mg, Na, Zn, Mo, Ni, Ba.

The studies were carried out in the resource centers of SPBU “Geomodel”, “methods of substance analysis”, “development of cellular and molecular technologies”.

PALLADIUM (II) BIOSORPTION BY MICROFUNGUS

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Biochemical reactions exposure in platinum-metal minerals formation is usually viewed in outline, it seems for lack of experimental data specified the geochemical part of living matter in the elements transformations. The metals concentration by microorganisms occurs both as by the effect of intracellular accumulation in the result of biochemical reactions, so as by sorption interaction mechanisms of the cell wall (CW) surface with metal ions. The sorption capacity of microfungus CW is based on the variety of functional groups presented.

The carboxyl, amine and hydroxyl functional groups of CW of the microfungus *Penicillium canescens* Sopp., originally isolated from the Paleocene brown coals (Raichikhinskiy deposit, Amurskaya Oblast), contribution to Pd(II) biogenic sediments was evaluated. To achieve this, the CW product based on [1] was extracted from fungic biomass, thereafter the products with derivatized carboxyl, amine and hydroxyl groups were prepared thereof. Carboxyl groups derivatization was carried out by methylating with (trimethylsilyl) diazomethane (2M in ethyl ether) in toluene over methanol. Amino- and hydroxyl groups were derivatized by acetic anhydride acetylizing over pyridine. For acetylating amino groups without hydroxyl the reaction was carried out over methanol [2].

The results revealed that Pd(II) sorption by the initial non-derivatized CW product causes a pH drop level. When the Pd(II) sorption methylated by the CW carboxyl groups, the solution pH drop level became slower, however, it didn’t affect the metal sorbed. When the Pd(II) sorption by CW with acetylated amino groups, the fractional change of solution pH level was observed in comparison with the non-derivatized CW sample, and the metal sorbing was noticeably dropped in 0.5–1 hours after it had been incubated. Simultaneous acetylation of both amino and hydroxyl groups had the greatest effect on Pd(II) sorbing drop. In this case the solution pH drop level was less than with the initial non-derivatized CW or acetylated in the amino groups only, but was greater when incubating by methylated CW.

Thus, it was revealed, that largely hydroxyl groups and amine groups in a less are engaged in the Pd(II) ions sorption in a weak acid medium (pH ~ 6), the most typical for natural environment. Hydroxyl groups account for about 22% of the total metal sorbed, NH_2 group accounts for 14%. The part of carboxyl groups remains questionable under these conditions, whereas according to the literature data, amine, carboxyl, hydroxyl and phosphate groups are involved in Pd(II) sorption.

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EFFECTS OF BIOMINERALIZATION IN SOL-GEL DERIVED EPOXY-TITANATE COATINGS USED TO PROTECT MARBLE FROM BIODEGRADATION

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Sol-gel compositions based on organosilicon compounds and epoxy resins are successfully used to protect cultural heritage monuments against to adverse weather conditions, biological colonization and for their restoration. As a rule, the surface of stone objects is impregnated with these compositions. This is a fairly long and time-consuming procedure. Simple and economical ways of hydrophobizing stone surfaces and protecting them from biodestructors, primarily molds, have been developed by us. Coatings were prepared using sols based on silicon or titanium alkoxides and epoxy resin with additives of soft biocides (detonation nanodiamond, photosensitizers). They create a thin protective layer or impregnate an upper layer of a surface and inhibit the development and growth of micromycetes. Interesting phenomena characteristic for epoxy-titanate coatings were found during laboratory tests on the biostability (bioreceptivity) to the micromycetes: *Cladosporium sphaerospermum, Ulocladium chartarum, Paecilomyces variotii*. Coatings were obtained by deposition from sols based on titanium tetrabutoxide and epoxy resin Eponex 1510, both without biocide additives and with additives (0.1–0.5 wt.%) of detonation nanodiamond (DNA) or photosensitizer TiO_2 (Degussa®). Coatings were inoculated by spore suspension of micromycetes. Infected glasses were kept in moist chambers for 7 days and were periodically exposed with ultraviolet light (2 hours a day). Initially, the yellowish coloration was characteristic for epoxy-titanate coatings, which disappeared on the second day of incubation. This color disappeared after 3-month exposure in the open air. An interesting phenomenon of the formation of crystals in droplets of suspensions of micromycete spores was found on the 2nd day of incubation for a coating obtained from a sol with 0.1 wt% TiO_2. However, these crystals disappeared within 7 days. The effect of phase separation and, possibly, the formation of new crystallization centers around the newly emerging spores of the micromycete *Ulocladium chartarum* was manifested with the use of detonation nanodiamond as a soft biocide in the structure of the epoxy-titanate coating. The described phenomena, undoubtedly, are connected with the life activity of mold fungi. In this case, the addition of TiO^2 powder to the sol triggered the formation of crystals on the coating surface. However, this happened precisely under the influence of micromycetes (all three species). In the future, these crystals were dissolved again under the influence of the products of the life activity of fungi. Titanium oxides are known for their ability to initiate crystallization, for example, in melts. The phenomena of crystallization in melts and solutions are very similar. Therefore, it was the epoxy-titanate coatings that proved to be the most sensitive to the products of the life of micromycetes (compared to, for example, epoxy-siloxane coatings, where such phenomena were not observed). The effect of changing the surface of the coating around the resulting micromycetes is also associated with biomineralization. The report will also present the results of a study of the structure of coatings.

INORGANIC PHOSPHATE-SOLUBILIZING CULTIVABLE BACTERIA AND FUNGI

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MSU

Phosphorus (P) is among the main limiting macronutrients for plants and other groups of biota. In soils P can be found both in inorganic (Pi) and in organic (Po) forms. Pi is mainly presents as insoluble unavailable for plant roots compounds, such as Ca phosphates (in alkaline and neutral soils) or Fe, Al and other metal`s phosphates (in acid soils). It is well acknowledged that numerous microorganisms (PSM) possess an ability for phosphate solubilizing. It is common both for bacteria and fungi (Illmer et al.,1995; Fomina et al., 2006; Richardson and Simpson, 2011; Taktek et al., 2015; Fontaine et al., 2016). The main PSM mechanisms for Pi solubilizing include pH changing (acidification, organic acids production), metal cations chelation and siderophore production (for Fe phosphate solubilization) (Khan et al. 2007; 2014; Uroz et al., 2009; Jones and Oburger, 2011; Ingle and Padole, 2017). 2011; Kaur and Reddy, 2017). However often PSM mode of action remains obscure.

Solubilization of P-containing compounds thus making P available for plants is considered among the main functions of arbuscular and ectomycorrhizal mycobionts. Mycorrhizosphere and symbiotic fungi hyphosphere-inhabiting bacteria are known to take part in this process (Lapeyrie et al., 1991, Wallander, 2000, Landeweert et al., 2001, Frey-Klett et al., 2005). The role of mycobionts *per se* in P-solubilization is questionable.

Soil mycorrhizal and litter saprobic agaricomycetes are prevailing within wood mycobiota. Their mycelia provide hyphosphere niche in soil –specific microhabitats where the fungi deal with mineral and organic soil matter along with soil borne biota. Hyphosphere is considered as a match for rhizosphere in its impact on life in soil (Voronina and Sidorova, 2017).

Previously we found out that in mycorrhizal agaricomycete hyphosphere is significantly richer in cultivable bacteria solubilizing tricalcium phosphate compared to litter saprobes` hyphosphere and bulk soil. The ability for tricalcium phosphate solubilizing is critical for PSM screening.

The report summarizes the data on P-solubilizing ability in cultivable bacteria and fungi isolated from 8 dominant and frequent fungal species` hyphosphere and bulk soil. The modified NBRIP media (Nautiyal, 1999) with Al phosphate or tricalcium phosphate as a single P source was used due to acid soils predominance at the area of research (the Moscow Region). P-solubilizing ability was detected as zones of soluble P encircling the growing colonies. It was shown that the strains capable of Al phosphate solubilizing are significantly less numerous than those capable of tricalcium phosphate degrading. To reveal the Al phosphate PSM the more prolonged (10–12 days) incubation is needful. The most of active strains were obtained from mycorrhizal agaricomycete hyphosphere. Conspecific strains strongly varied in their solubilizing activity towards Al phosphate, which was not the case for for tricalcium phosphate solubilizing. The most active Al phosphate solubilizers were *Penicillium simplicissimum* and Pseudomonas spp. strains. The distinction between mycorrhizal and litter saprobic agaricomycetes in selective accumulation of PSM in the hyphosphere was corroborated.

CRACKING THE STRUCTURAL AND GENETIC BASIS OF TOOTH BIOMINERALIZATION IN CICHLID FISHES: HOW TO DEVELOP THE MOST EFFICIENT TEETH?

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The teeth of cichlid fishes provide a powerful model for how vertebrates optimize dental hard tissues for ecologically relevant tasks. Cichlid fishes have undergone explosive speciation in a very short time span, evolving tuning morphological specializations. Dramatic variability in the shapes and inner structures of their teeth and jaws are central to their diversification. The main task of this research work is to determine the structure-property relationships of dental hard tissues of Cichlid fishes (so called “soft” and “hard” diet species) through detailed investigation of the composition, hierarchical structure and their mechanical performance. The most exiting are those Cichlid species that have repeatedly evolved exceptionally robust teeth to crush snails, and we are using an interdisciplinary framework to clarify the structural, chemical, mechanical and molecular genetic bases of these particularly mechanically durable teeth. Thus, we elaborate and combine an exciting evolutionary model system with cutting-edge spectroscopy, microscopy, diffraction techniques and next-generating sequencing methodology to analyze structural, chemical and genetic basis of the exceptionally hard teeth of cichlid fish. Our new understanding of tooth morphogenesis in cichlids could also advance strategies for synthesizing biomimetic materials for biomedical application.

VARIABILITY OF BIOGEOCHEMICAL CYCLE CAPACITIES UNDER THE INFLUENCE OF LOCAL BURIED RELIEF HETEROGENEITIES (CASE STUDY OF SOUTH MESHCHERA FOREST ECOSYSTEM)

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Study of biological productivity and associated element cycles makes an integral part of forest carbon-depositing capacity assessment, forecast of wood increment under varying climate conditions, calculation of natural ecosystem anthropogenic pollution resistance. However, in most cases, biological productivity is considered as an independent variable (biocentric approach) and the lithogenic factor is underestimated. It leads to dramatic underestimation of landscape element internal contingency as well as to misunderstanding of real causes of biological productive process changes in time and space.

The objective of the present study was to analyze interrelation of heavy metal (HM) (Cu, Zn, Cd) biogenic migration parameters with the largest lithogenic base heterogeneities under flat relief conditions. Studies were carried-out in landscapes of the south part of Meshchera mixed forest natural province (the key territory covers the lands of Solotcha forestry station, 389.6 km^2) using drilling records (archive materials, 1 well per 16 km^2), biogeochemical sampling data (authors' research, approximately 250 samples in total) as well as forest mensuration materials.

In the course of the study there have been identified stable spatial heterogeneities in wood increment as well as in long-term immobilization and recycling migration of heavy metals correlated with local buried relief heterogeneities. The mentioned heterogeneities mainly formed already in the Mid-Mesozoic and some were formed in the Late Paleozoic and quite often do not correspond to present-day relief. In total, there were identified 11 such heterogeneities, which have the rank of landscape areas. The most important of them are area I – Solotcha inselberg massif (absolute elevation – 126 m, base – buried ledge formed by Jurassic clays), area II – Peredeltsy swampy plain (absolute elevation – 115 m, base – large Late Paleozoic erosion cut) and area III – Boriskovo non-swampy low plain (absolute elevation – 113 m, base – Late Paleozoic erosion inselberg, formed by limestone).

Despite of lower location, area III specifically represents the geographic optimum of South Meshchera mixed forests. Here, one may observe maximal diversity of forest stand species composition and species productivity – both moisture demanding and non-demanding species – is in average 1.7 times higher than in area II and 1.1–1.4 times higher than in area I which shows lowest hydromorphous characteristics. Owing to high proportion of limestone (2,600 n/m^3, which is 1.33 times higher than for Jurassic clays), the limestone ledge forms a positive gravity anomaly which reduces area III humidification and conduces to drastic biocycle capacity increase. For instance, Cd accumulation in wood increment is 1.5–2.0 times higher than for areas I and II and for Zn this value is 2.5–5.0 times higher than in areas I and II. The minimal intensity of bioproductive processes is observed in area II (thalweg of buried erosion cut). The spatial regularities of biogeochemical processes, which we identified in the study, are also typical for other humid forest landscapes in the conditions of low-contrast relief.

MICROBIOLOGY OF THE FOOTPRINT TUFF (SITE G, LOCALITY8), LAETOLI, TANZANIA

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East Africa is one of the most important paleoanthropological and paleontological localities on Earth. The Laetolil beds and closely located Olduvai Gorge (northern Tanzania) are among the world’s premiere areas for *Australopithecus afarensis, Paranthropus boisei,* and *Homo habilis* remains, as well as for numerous non-hominin fossils. Laetoli is also unique in its preservation of footprint trails within Tuff 7 (also known as

Footprint Tuff) left by *Australopithecus afarensis*, dating to about 3.66 Ma.

In line with plans of the Ngorongoro Conservation Area Authority of Tanzania to create the Laetoli Footprints Museum we have studied Laetoli Tuffs and the purpose of a microbiological study was to characterize microorganisms living inside these tuffs, under and over the Footprint Tuff, and to estimate their potential involvement in destructive processes.

Samples for the study were collected from the vertical walls of several pits and from the surface of the Footprint conservation mound. Two types of samples have been used to identify microorganisms. The first type is so-called replica samples – they were collected from the pit walls using a non-destructive print method into sterile plastic containers with artificial media Czapek-Dox agar on the inner surface of their lid. The second type of samples is small fragments of tuffs and soil collected from the pit walls and placed inside sterile plastic containers. All necessary precautionary measures were taken to avoid sample contamination.

Scanning electron microscopy, mycological study and molecular genetics analyses have shown that different microorganisms (micromycetes, bacteria and archea) are present in all of the studied tuff and soil samples. Thirty-one species of microfungi, as well as sterile white and dark mycelia were identified. They occur as hyphae and mycelia inside the tuffs, and are concentrated in circum-granular and intergranular pores, microcracks and cavities. The number of micromycetes is moderate and does not exceed 7000 CFU per gram of substrate.

There are some dominant groups of microorganisms, which are capable of affecting the rocks and artificial materials in the project area. The most typical microfungi are from genera *Aspergillus* and *Fusarium*. They are known as active destructors of different natural and artificial substrates and can colonize building materials, particularly during rain seasons. All of these microorganisms are also known as potential human pathogens. The destructive impact of *Aspergillus* is related to its physical action on the substrate (growth through the material), as well as its acid production. Increasing environment humidity (atmospheric humidity, evaporation from soil and tuffs, condensation inside buildings) will stimulate the reproduction of these fungi.

The application of molecular genetic methods to the Laetilil tuffs and soil revealed a large group of different bacteria (21 phyla). The microbiota consists mostly of Actinobacteria, Proteobacteria, Bacteroidetes and Cyanobacteria. Their relative distribution shows the preferential occurrence of Bacteroidetes in the upper part of stratigraphic sections (soil), and concentration of Actinobacteria and Proteobacteria within the tuffs. Exposure of the Footprint tuff could lead to the development of photosynthetic microorganisms like Cyanobacteria. They are considered to be the most aggressive microorganisms due to their photoautotrophic nature.

With all available data, we conclude that microbiological activity within the study area appears to be moderate and the Footprint Tuff does not presently require any treatment with biocides. However, the presence of black biofilms on the surface of the Footprint conservation mound concrete shows that biodestruction does occur.

We would like to thank the Tanzania Commission for Science and Technology for granting permission to conduct research.

GEOMETRY, CLASSIFICATION AND NOMENCLATURE OF CAPSIDS OF ICOSAHEDRAL VIRUSES

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Icosahedral (regular, spherical) viruses build highly ordered capsids of *–3–5m* and *235* symmetry point groups (s.p.g.’s). Geometrical and physical principles in their construction from protein globules were found by Caspar & Klug (1962). In general, the facets of mega-icosahedra look like triangles differently (for different capsids) oriented on the 2D dense hexagonal packing of protein globules. It was announced that icosahedral capsids can exist with triangulation numbers $T = P f^2$ only, where $P = h^2 + hk + k^2$, h and k – any pair of integers with no common factors, and f = 1, 2, 3, *etc*. (The proof of the above statement was first published by Schmalz *et al*., 1988). As a result, the whole variety of icosahedral capsids was divided as follows: P = 1 (*i.*e. h = 1, k = 0, any f, s.p.g.*–3–5m*), P = 3 (*i.*e. h = k = 1, any f, s.p.g.*–3–5m*), and “skew classes” (*i.*e. h > k > 0, s.p.g. *235*). It was shown by Voytekhovsky (2016) that icosahedral capsids and fullerenes form homological series with combinatorial geometry of the latter being well investigated. This allowed us to describe the geometry of icosahedral capsids in more details.

The series of capsids-isomers were found, *ex*. for T = 49 (h = 5, k = 3, s.p.g. *235* and h = 7, k = 0, s.p.g.*–3–5m*) and T = 91 (h = 6, k = 5 and h = 9, k = 1, both s.p.g.'s *235*). That is, the nomenclature of icosahedral capsids should be based not on the triangulation numbers but on the (h, k) symbols which uniquely determine their geometry.

The classification of icosahedral capsids by the s.p.g.'s *–3–5m* (with symmetry planes) and *235* (without them) is correct but extremely approximate. In more details, their *–3–5m* variety consists of the (t, 0) and (t, t) homological series (t = 1, 2, 3, *etc*.) connected by the dual transformations (h, k) → (h + 2k, h – k).

The *235* variety of "skew classes" also consists of the (t h, t k) homological series (t = 1, 2, 3, *etc*.), where (h, k) is capsid-generator with h and k – any pair of integers with no common factors and h – k being not divisible by 3. For any *235* homological series of capsids, another one is connected with it by the dual transformation (h, k) → (h + 2k, h – k).

The simplest generators (1, 0), (2, 1) and (3, 1) are related to bacteriophage φX174, papovavirus and rotavirus, respectively. They generate the majority of the known icosahedral capsids as their homological series and duals.

A matrix equation is found to describe the transition (h_1, k_1) → (h_2, k_2) between any two icosahedral capsids. This is a rare case of biological organization for which such a general result is obtained.

The following questions are of interest for the future studies: on the limits of h and k for real icosahedral viruses, on the frequency of *–3–5m* and *235* viruses, and on the viruses-isomers occurrence.

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GEOMETRY OF BIOLOGICAL COATINGS: GENETICS OR INVARIANTS OF POLYGONAL TILINGS?

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GI FIC KSC RAS

Many organisms use in their skeletons and coatings the same mathematical (precisely geometric or crystallographic) ideas (*ex*., convex polyhedra and polygonal tilings) as inorganic objects do (Voytekhovsky, 2015). Biologists usually look for genetic causes of this. But, is it always the case? Let us look at some examples.

The geometry of fullerenes is a hot field of stereochemistry and mathematics, especially for icosahedral (of -3–5m and 235 symmetry point groups) fullerenes. Icosahedral viruses follow the same idea when building capsids from 20 triangle fragments of 2D hexagonal dense packing of protein globules. The mathematical system of icosahedral fullerenes is, in fact, the morphological system of icosahedral viruses and is written in matrix equations (Voytekhovsky, 2016).

Morphological variability of polyhedral colonies of *Volvocaceae* follows the combinatorial regularities of polygonal sphere tilings. It was shown that in 3D Euclidean space for each colony of *Pandorina morum* (*Müll*.) *Bory* only three forms are possible. One of them has no plane of symmetry and, thus, has two enantiomorphous varieties (Voytekhovsky, 2001).

The strong analogy between the fullerenes and radiolarian skeletons (*Heliosphaera inermis, H. tenuissima, H. actinota, H. echinoides, H. elegans; Circogonia dodecahedra; Haliomma capillaceum, Ethmosphaera siphonophora Hkl*., *etc*.) is found. The computer algorithms are created to classify the variety of fullerenes-isomers. It seems that the classes obtained are of taxonomic significance for related *Radiolaria* (Voytekhovsky, Stepenshchikov, 2016).

The main morphological features of *Ostraciontidae* and *Diodontidae* fishes are found to be dual to each other as the crystallographic tilings by Dirichlet and Delaunay. Taken the bases of needles on the quasi-spherical surface of *Diodontidae* as the Delaunay (R, r)-system of points, then the related Dirichlet polygonal tiling looks like the bone coating of *Ostraciontidae*. This emphasizes the taxonomic proximity of *Ostraciontidae* and *Diodontidae* among *Tetraodontiformes*

(Voytekhovsky, 2009).

Thus, the geometric invariants should be distinguished among the structures fixed in the genome of many organisms in the course of their evolution. Some fundamental morphological principles are equally effective in both biological and mineral creatures.

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Section 1

Methods for studying the interactions between biogenic and abiogenic components

INSTRUMENTAL CONTROL OF THE GAS EXCHANGE OF HIGHER PLANTS AT BIOTIC STRESS

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Phytopathogenic fungi Cahliobolus sativus has a hemibiotrophic type of nutrition [1, 2]. This phytopathogen cause helminthosporiosis in cereals. To reduction of such fungal illnesses, higher plants have developed immunity. It means a number of chemical compounds, which can activate when “foreign markers” get onto plant tissues. Consequently searching of ecological technologies of processing of plants, for the purpose of initiation of education at them induced immunity, is relevant task.

The first reaction of the plant to the pathogen is known to be accompanied by the formation of reactive oxygen species (ROS), for example, production of singlet oxygen ($^1O_2$) and superoxide radical ($O_2\cdot^-$) which stand at the beginning of electron transport chain (ETC). Generally, the period of such reaction can be quite short. It is predetermining some problems with registration of changing of gas exchanging of higher plants. ROS can be consider as sensitive indicators of secondary metabolic processes. In line with above, itself great relevance to control of the ROS in the metabolism of plants with the aim to explore mechanics of metabolism and of the mechanics of the induced immunity to phytopathogen. At this project, we use the new approach to the identification key points of pathogenesis, which is based on monitoring of ROS (gaseous phase) by solid-state heterogeneous chemiluminescence.

This method is based on heterogeneous reaction of interaction of molecules $^1O_2$ and $O_2\cdot^-$ with sensor composite material. This reaction is accompanied with chemiluminescence, measured by a photodetector in the visible region of the spectrum (the maximum is 463 nm). The intensity of chemiluminescence is proportional to the concentration $^1O_2$ in the analyzed gas mixture and the quantum yield of chemiluminescence intensity is proportional to the concentration $O_2\cdot^-$. The most important property of chemiluminescent analyzers is their extremely high selectivity to the component and high sensitivity. Selectivity of this analyzer ROS derived from the principle of operation of the chemiluminescence method. At this project presents the experimental data to assess the possibility of using ROS as an indicator of the processes of formation of stable immunity to pathogens in higher plants.

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ANALYZER OF SINGLET OXYGEN AND THE PROSPECTS OF ITS APPLICATION IN THE STUDY OF BIOCOSE SYSTEMS

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Singlet oxygen ($O_2(^1\Delta_g)$) is a metastable active form of oxygen, which is formed in atmospheric air, both as a result of the transfer of excitation energy from the chromophores to triplet oxygen, and during biochemical processes of dismutation. The molecules of $O_2(^1\Delta_g)$ are quite reactive, and already under normal physical conditions effectively enter into chemical interactions. In view of the wide distribution of triplet oxygen in the earth’s atmosphere, metastable $O_2(^1\Delta_g)$ also takes an active part in a variety of biological and chemical processes. In nature, it performs protective and signaling functions. In the cells of living organisms, it is involved in a variety of secondary metabolic processes. For this reason, the concentration of $O_2(^1\Delta_g)$ is an important parameter of many open systems, by the modification of which it is possible to study the processes taking place in these systems. Development of composite catalytic materials for efficient photosynthetic active oxygen species are also interfaced with the necessity of using an objective analytical methods and control devices.

To solve the problem of determining the concentration of $O_2(^1\Delta_g)$ analyzer was developed based on the method of multi-photon excitation of the chromophore in the form of a molecular hybrid. This method has high selectivity, sensitivity, and a small constant time for the determination of $O_2(^1\Delta_g)$, whose concentration in ambient air is usually at the level of μg/m^3, and can vary by several orders of magnitude during a short period of time. The metrological characteristics of the singlet oxygen analyzer are provided by a special internal calibrator – a photocatalytic generator of $O_2(^1\Delta_g)$.

The paper presents data on the efficiency of photocatalytic properties of new composite materials used in the synthesis of metastable $O_2(^1\Delta_g)$, based on hydroxylapatite.

POSSIBILITIES AND PERSPECTIVES OF BIOGENIC INTERACTIONS INVESTIGATION IN STROMATOLITIC BUILDUPS.

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GIN RAN

Up to now biogenic interactions in stromatolites have been predominantioly estimated visually, for it was impossible to get any relevant information about organisms' contribution to stromatolites formation. A new technique with a use of electron microscope with EDS – accessory can detect immediate participants of the process. The method has been tested with use of both traditional and new approaches and proved to be capable to reveal numerous ultramicrotextures which are not detectable with using of other techniques. Development and widespread use of the new technique discover wide perspectives in solutions to many important issues of natural science. Use of it gives possibilities for:

1. Determine biogenic ultramicrotexture – stromatolit builders, the first organisms on the Earth, by their morphologic criteria and elementary composition.
2. Determination in each stromatolite taxon the most prevalent biogenic ultramicrotextures, that is dominant cyanobacteria, and determination of their functions in building of rock microtexture and buildings morphology, on the ground of those the stromatolites classification has been created
3. Discover a pattern of carbon distribution in organisms and

concomitant biophile elements, confined to a bios, their influences onto physic and chemical characteristics of sedimentation formation (pH, Eh, time, velocity etc)

4. Determine a cause for a dominant change in a community within a stromatolite reef. Analyze this process development in each investigated buildups and in Precambrian stromatolites on the whole.
5. Create a classification of biogenic ultramicroformations in stromatolites and determine their spatial–terminal distribution in Precambrian sequences. Assess a perspective for use of obtained results in stratigraphy.
6. Determine relationships of biogenic ultramicrotextures with host rocks. Assess secondary transformations in stromatolites and redistributions of micro and macro elements in biogenic and non-biogenic compositions of stromatolites.
7. Visual recreation of origination, vital activity and growth of a cyanobacterial community within constant sedimentation, analyze long–term interaction between biogenic and abiogenic processes and causes for stromatolite buildups degradation
8. Reveal consistent patterns of stromatolites reef formation and its existence conditions, numerous direct and opposite relations within reef building, consistency of reef building in a ecosystem as well as determine additional geochemical criteria's of biogenic sedimentation.

The technique can be of importance in solutions to more common issues, such as living and non–living environment interactions at early stage of life, contribution of stromatolites reefs in relief formation and their influences onto climatic and ecological conditions of the.

EXPERIENCE OF APPLYING THE TECHNIQUES OF SCANNING ELECTRON MICROSCOPY FOR STUDIES OF INTERACTION BETWEEN BIOLOGICAL AND NON-BIOLOGICAL OBJECTS

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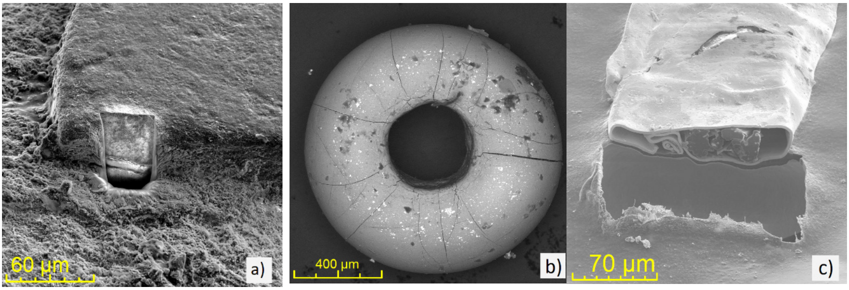
TESCAN Ltd. (CIS)

Scanning electron microscopy (SEM) is attractive technique for investigation of convergence between biological and non-biological materials because of high spatial resolution, almost non-destructive testing with similar effectivity for biogenic and abiogenic substances. In addition, a SEM offers both visual and quantitative information about micro-objects on a sample. Electron images provide us with visual information, while local compositional (EDS) and micro-texture (EBSD) data could be obtained simultaneously.

There are presented a few examples of SEM application for observation of artificial objects degradation inside natural environment:

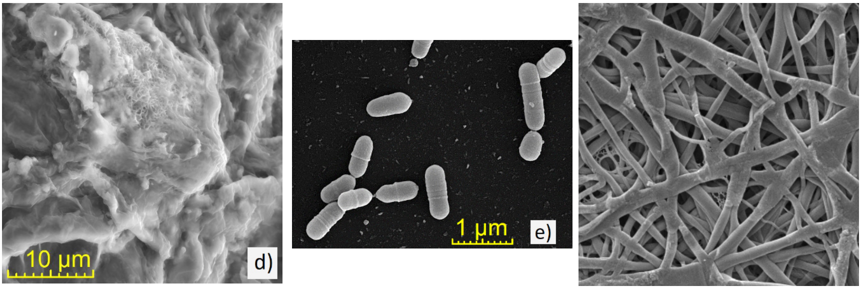
a) surface of a stone bead, 6 thousands years old, North Caucasus. A local cross-section by a FIB-SEM was made in order to observe a superficial layer of about 40 µm thickness. The cause of the superficial layer is unknown; b) a glass bead, ~ 200 years old; c) a FIB-SEM cross-section of a gold fiber from the ancient Chersonese.



A few examples are given to illustrate artificial object's degradation within life forms:

d) calcification of an artificial biomaterial; e) Streptococcus bacteria on a dental filling;

f) structure of a biopolymer fiber for surgery.



WETTING CONTACT ANGLE HYSTERESIS ON THE WATER-AIR BOUNDARY OF A FEW CLAY MINERALS*

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Surface properties of clay minerals create the base to distribute soil organic matter and determine sorption/desorption processes, permeability and wettability for a number of liquids. The studying of surface properties of such natural medium like clays and soils forces difficulties due to anisotropy of their inside spaces. There the areas with abruptly different characteristics (hydrophilic or hydrophobic, with oxidizing or reduction potential) may be in close in a micro scale. Each clay mineral forming the rock possesses specific slightly studied surface properties. We have aimed to find the connection of clay minerals' composition with theirs wettability. Samples for the studying were prepared from following clays: A) muscovite-chlorite, B) muscovite-kaolinite, C) montmorillonite, D) kaolinite, E) phyllite, F) fine silica powder. They were treated according to the operation set described by (Shein et al., 2016), and were sieved through 0,05 mm. In addition, the same series of clays had been taken for the studying after microbial growth on them during several months. Microorganisms were selected due to their ability to grow on hydrophobic liquids (like crude oil, oleicy acid). We used magnitude of wetting contact angle at the water-air bound (CA) to characterize wettability of clay samples. Also, the time of spreading of water drops on the samples' surface was observed. The research was based on the background that wettability of solids is the result of an entropic process leading to a decrease in energy of the system at the bound of three phases: solid, gas and liquid. The cosine of CA is described by the formula: $\cos\theta = \frac{\sigma_{13} - \sigma_{12}}{\sigma_{23}}$, where indexes 1, 2 and 3 correspond to solid, liquid and gaseous phases. As a result, the series of clays showed dispersion of CA in the range from 10 ° (on fine silica powder) to 130 ° (on muscovite – kaolinite clay). It was assumed that this dispersion is concerned the presence of kaolinite, because of its particles have larger average diameter compared to another minerals studied. Consequently, it caused a decrease in surface per volume unit, and smaller wettability. Simultaneously, the observation of smaller wettability of powder samples than that for the polished solid was confirmed. The series of clays after microbial growth on them showed the tendency to increase CA. Microorganisms highlighted with crude oil medium reliably caused an increase in CA compared to ones highlighted with soil surface. Besides, the treatment of membrane filters with sterilized liquid medium reliably led to smaller CA compared to the treatment with the same liquids contained living microbial cells. Surface tension at bounds of “clay samples / air” and “clay samples / water”, before and after microbial growth, was calculated.

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TIME AND SPACE OF BIOLOGICAL MORPHOGENESIS

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Our perception distinguishes biological objects from their environment due to a more complex structure and motion both independent of external gradients. This means that living objects and the environment are different spatio-temporal systems. Thanks to the discovery of the accelerated expansion of the universe with the physical nature of time can be characterized as the process of energy supply to the universe, and the physical nature of space as the process of its scattering in it. Since the influx of energy and its scattering can not go in one direction, these processes determine the general anisotropic space-time structure of phenomena with the leading role of time.

The minimal entropy of living objects indicates that, as living beings, we perceive objects that most fully absorb this energy and then dissipate it as in the form of the energy of their chemical, morphological and behavioral connections, and in the form of the energy of their movement.

Thanks to this, there is a general similarity between the principle scheme of the morphogenesis of various organisms – prokaryotes and eukaryotes, plants and animals, as well as living objects and crystals. In addition, there is a similarity of the tree-like structure of ontogeny and phylogenesis.

ACTIVE INTERACTIONS IN A SYSTEM OF OIL AND MICROORGANISMS

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The interaction of oil and microorganisms in an oil reservoir occurs at the water/oil interface. Water with dissolved mineral and organic compounds serves as the habitat for microorganisms and provides their life processes. Most microorganisms are capable of enzymatic oxidation of petroleum hydrocarbons, the latter serving as a source of nutrition and energy. Interaction of microorganisms with oil changes its physical-chemical composition due to accumulation of metabolic products that promote emulsification of oil, increase its viscosity and density.

At high pressure and low temperature, typical for oil production and transportation in the Arctic regions, water-oil emulsions and associated gas form gas hydrates [1]. Hydrates are a class of clathrate compounds, with gas enclosed in cavities of frame formed by water molecules connected by hydrogen bonds. Changes in the physical-chemical properties of oil in the process of biodegradation affect the hydrates nucleation and growth.

We studied the probability of gas-hydrates nucleation using samples of light oil from the Kazanskaya (KN) field of Western Siberia with an association of microorganisms. The latter were extracted from crude oil and added to the samples. Biodegradation was carried out for 30 and 60 days, the obtained samples of biodegraded oil are marked as KN30 and KN60 respectively. Destructive changes in oil composition were investigated by infrared spectrometry (IR). Within the biodegradation process, emulsions were formed with contents of oil compounds and viscosity (cf. table) different from the native oil.

Table. Component composition of Kazanskaya oil samples, crude and biodegraded.

Sample of Kazan oil	Content,% rel.				
	Saturated HC	Aromatic HC	Resins	Asphaltenes	Light HC
crude KN oil	68.7	7.8	8.1	5.5	9.9
KN30	60.2	10.9	8.8	5.7	8.4
KN60	54.5	12.5	9.3	7.0	3.7

The acid content increased by 70% in KN60 sample and by 87% in KN30 compared to the crude oil. The oxidation degree of samples KN30 and KN60 were 0.3 and 0.6, respectively. The main products of naphthenic oxidation are acids, hydroxy acids and a small amount of resins resulting from oxidative condensation. For each of the emulsions, the nucleation of methane hydrate was investigated for 24 samples at pressure of 12 MPa, with a linear decrease in temperature from + 20 °C to –15 °C. The probability of hydrate formation with crude KN oil is 0, KN30–20%, KN60–12%. Thereby, the processes of oil biodegradation increase the probability of hydrates nucleation which depends on the degree of biodegradation for the oil-microorganism system.

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Section 2
Geochemistry of biogenic-abiogenic systems

SOIL GEOCHEMISTRY IN THE NOVOROSSIYSK URBAN AND INDUSTRIAL AGGLOMERATION

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Novorossiysk city is located in the foothills of the North-Western Caucasus on the Black Sea coast. The Novorossiysk industrial agglomeration consists of the city over 300,000 people, the eldest Russian cement factory “Novoroscement”, the largest regional seaport, as well as other enterprises and transport infrastructure objects. Open-pit mining of marl deposit in the agglomeration is a source of raw material for Portland cement manufacturing.

The research is devoted to monitoring the environmental impact of deposit mining, i.e. soil pollution. Fugitive dust emission from dumps is the key environmental pollution driver of the industry. Soil sampling (over 80 samples) was carried out twice, in 2014 and 2015. The samples were taken from the uppermost 10-cm soil horizon. All spectral emission analyses of the samples were carried out in the certified “Kavkazgeolsyomka” laboratory.

Soil pollution was assessed separately in geochemical landscapes of residential areas, wastelands, and industrial sites. The joint effect of cement factory emissions, relief features and building height led to certain dispersion in mean concentrations in soils of landscapes with various geomorphological conditions. The comparison between the *maximal* average concentrations and the *minimal* ones in the *residential area* shows that for 8 out of 22 studied elements the former is more than 1.5 times as much as the latter: *Pb* (4.5 times), *Sr* (1.7), *Ag* (2.2), *Cu* (1.7), *Zn* (2.5), *Ga* (1.5), *Sn* (1.6), and *Yb* (1.5). In soils of *wasteland* landscapes, under different morphological conditions, the excess of maximal average contents over minimal ones by more than 150% was recorded for four elements only: *Zn* (1.7 times), *Pb*, *Co*, and *Ag* (1.6). We note that the maximal average contents of these elements in soils of *wastelands* are significantly lower than those in soils of *residential areas.* The distribution of the majority of chemical elements’ average contents is more uniform in soils of *industrial areas*, including the main pollution source – the cement factory. The largest exceed of maximal average contents over minimal ones was recorded for two elements only: *Sn* (2.9

times) and *Pb* (1.7). The maximal average content of these elements in soils of *industrial areas* is higher than that in soils of *wastelands*, but lower than in *residential areas*.

Thus, *residential areas* mostly tend to be affected by the technogenic impact, resulting in the intensive soil pollution. The *maximal* for the entire city *average polluting element contents* were established in these areas. The greatest number of *unevenly distributed average element contents* was recorded in soils of *residential areas* under the influence of geomorphological and anthropogenic factors in combination. There has been a six-fold increase in the number of elements with the maximal mean contents, i.e. the number has changed for 18 *(Cu, Zn, Pb, Mo, Ba, Co, Ni, Ti, V, Cr, Ga, Li, Sr, Y, Yb, Sc, Zr,* and *Nb)* in soils of *transaccumulative* and *trans-superaquatic* landscapes of residential areas located below. This pollution is associated with relief characteristics: the average contents in soils of upper slope parts were mainly due to the impact of pollutants precipitating after the sorption by cement industrial emissions.

The urban soil pollution under the impact of mining and processing industry is determined by the local factors of chemical element migration and accumulation: geomorphological structures of urban area and types of land use. The data obtained characterise the ecological and geochemical state of Novorossiysk urban environment, and allow developing the measures for improvement.

ASSESSMENT OF HEAVY METALS AND ARSENIC POLLUTION OF SOILS DURING POSTAGROGENIC EVOLUTION

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At present, in connection with the increasingly increasing anthropogenic impact on the environment, a great practical and scientific interest is the study and assessment of soil contamination with heavy metals. In agricultural soils, xenobiotics fall both through air transport and when organic and mineral fertilizers are enriched with impurity elements, as well as with sewage sludge used as fertilizers.

This study was aimed to estimate the regularities of heavy metals

(Mn, Cu, Zn, Cd, Cr, Pb, Ni, Co) and arsenic accumulation in soils during postagrogenic evolution of former arable lands in various bioclimatic zones of the European part of Russia. The chronosequence studies were carried out in southern taiga (sod-podzolic soils, Kostroma region), zone of deciduous forest (grey forest soils, Moscow region), forest steppe zone (dark-grey forest soils, Belgorod region) and steppe zone (chernozems, Kursk region). Each chronosequence included arable, abandoned lands of different ages, and native (forest or steppe) cenosis.

The carried out researches have shown that in the soils of all chronosequence we have considered, the concentrations of heavy metals and arsenic do not exceed the established values of maximum permissible concentrations (MPC) and tentative allowable concentration. The only exception is the 35-year-old land abandoned in the Kostroma region. Here we observe a significant excess of MPC on Mn by 1.2 times ($p < 0.05$). The content of heavy metals in soils largely depends on the concentration of the xenobiotics themselves, as well as on factors such as the pH of the medium, the content of clay particles and organic matter. In soils with low sorption capacity (acidic and sandy), accumulation will not occur even under high loads. Thus, according to the study, the lowest concentrations of all the metals we studied and As are characteristic of acidic sandy-loamy sod-podzolic soils of the Kostroma region (pH = 4.1–4.4). The maximum values were noted in the loamy soils of Moscow (pH = 5.0–5.3) and Belgorod (pH = 4.5–5.7). The chernozems of the Kursk chronological range (pH = 5.7–7.1) also occupy a leading position in the content of Zn, Cr, Ni and Co. As for the changes in the content of heavy metals and arsenic with increasing period of abandonment, no reliable dependencies were revealed during the studies conducted. The content of elements within a single chronosequence in all types of soils studied is relatively stable, minor fluctuations, rather, are the result of spatial heterogeneity of the soil cover and different levels of initial contamination. Thus, the content and behavior of heavy metals and arsenic in the soil is more influenced by the type of soil associated with a certain bioclimatic zone, and its characteristics (acidity, granulometric composition, enrichment with organic matter) than features of agricultural use of soils (arable, abandoned lands of different ages, and native (forest or steppe) cenosis) within a single soil type.

HEAVY METALS IN THE SOILS OF SUPERAQUAL LANDSCAPES OF SAINT PETERSBURG, RUSSIA

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The problem of urban influence on the biogeochemical processes in natural landscapes is actual for modern city agglomerations. The accumulative (superaqual) landscapes located in lowlands are among the most vulnerable ones. The studied superaqual landscapes in Saint Petersburg are situated in the coastal zone of the Finnish Gulf. The accumulation of different chemical elements are typical for these landscapes. The aims of the study were to investigate the soils of the superaqual landscapes and to determine the content of heavy metals (HM) in these soils, then to assess the level of HM accumulation in the soils of the superaqual landscapes in comparison with soils of the adjacent watershed. The two protected natural areas – "Yuntolovsky" and park "Sergievka" were chosen as the study location.

According the data obtained the soil cover of the low marine terrace of the Finnish Gulf consists of marsh layered (Gleyic Fluvisols) and marsh clay-mud gley soils (Gleyic Histic Fluvisols). The most common soils of the Littorina terrace are humus gley soils (Mollic Gleysols) and peat gley soils (Histic Gleysols). The main soil-forming processes are organic matter accumulation and gleization, the sedimentation process takes place in the soils of the submerged part of the low marine terrace. The majority of the studied soils have low pH, the exception is the alluvial soils which have neutral reaction. The organogenic horizons have high cationic exchange capacity and low base saturation. All these data confirm the belonging of the studied landscapes to the acid gleyic, where Fe, exchangeable H and organic C are the typomorphic elements. The marsh soils have high base saturation due to their role of final link of terrestrial migration of elements. The elements of vigorous (P, S) and strong (Ca, Mg, Zn) biological accumulation retain on the biogeochemical barrier on the border of terrestrial and aquatic landscapes. All of considered soils have elevated content of organic matter, which could concentrate many elements because of high absorption capacity.

The soil cover of the studied accumulative (superaqual) landscapes usually keeps its native structure and function. At the same time, these landscapes are exposed to technogenic influence due to geochemical connection with contaminated urban landscapes, atmospheric deposition of heavy metals and also because of recreational impact. The positive anomalies of Zn (the total content 200–600 mg/kg) are widely distributed in the studied soils. Their formation could be explained by widespread occurrence of this metal in urban environment, the relatively high mobility of Zn and also by its ability to biological concentration.

The study was carried out using the equipment of the Resource Center of the St. Petersburg State University “Chemical Analysis and Materials Research Centre”.

HEAVY METALS IN THE SOILS OF THE LIPETSK TECHNOGENIC BIOGEOCHEMICAL PROVINCE

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Ferrous metallurgy predominates in the structure of industrial production in the Lipetsk region. Ferrous metallurgy accounts for 70% of the region’s industrial output. Technogenic load of metallurgical enterprises on urban landscapes leads to a change in the chemical composition of soils and forms of heavy metal compounds.

The aim of the work is to study the distribution of heavy metals in soils in urbanized landscapes and to study the forms of their compounds in soils.

The information obtained is necessary for the formation of a database of ecological and geochemical indicators characterizing the ecological state of Russian soils.

The following tasks have been accomplished in the course of the work:

1) The total contents and forms of compounds of heavy metals in soils of different landscapes of Lipetsk were studied,

2) The estimation of ecological-geochemical condition of soils of investigated landscapes is given.

3) Areas of environmental risk were identified.

The research was carried out in the sphere of influence of the Starolipetsk metallurgical plant “Svobodny Sokol” and the Novolipetsk Metallurgical plant.

The total content of heavy metals in soils was determined by the atomic absorption method after the acid microwave decomposition of the sample. Forms of heavy metal compounds were determined using sequential extraction procedures (Tessier et al., 1979). Acetate-ammonium buffer (pH 4.8) was used to assess the availability of soils with microelements.

In the study area, three ranges of soils were identified:

1 – loamy soils with alkaline reaction medium, adjacent to the metallurgical plant “Svobodny Sokol”,

2 – soils of the Voronezh river floodplain, which are an accumulative landscape,

3 – soils on bog sands near the Novolipetsk metallurgical plant.

Soils with insufficient availability of mobile microelements have been identified near the metallurgical plant “Svobodny Sokol”.

The total concentrations and concentrations of mobile forms of zinc and lead in the floodplain soils exceed the maximum allowable concentrations (total concentration of zinc –290 mg / kg, mobile form of zinc –37 mg / kg; total concentration of lead –157 mg / kg, mobile form of lead –7,5 mg / kg).

The total contents of heavy metals in sandy soils in the impact zone of the Novolipetsk metallurgical plant were Zn-780 mg / kg, Pb – 125 mg / kg, Cd –3,4 mg / kg.

Fractionation analysis (Tessier et al., 1979) showed that heavy metals in Lipetsk soils are mainly in the residual fraction and the fraction bound to iron and manganese oxides.

Zones of ecological risk are the soils of the Voronezh river floodplain and forest park landscapes on the sands in the impact zone of the Novolipetsk metallurgical plant.

MICROMORPHOLOGICAL STRUCTURE, MINERAL AND CHEMICAL COMPOSITION OF SOILS FROM TECHNOGENIC LANDSCAPES OF TUNGSTEN MINE

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In the areas of mineral deposits development, the processes of mining technogenesis are activated that accompanied by the formation of technogenic dispersion halos of chemical elements and changes in the migration cycles of chemical elements in geosystems. Soil, as a component of the landscape, reflects the processes occurring in the biogeosystem. The direction and intensity of these processes are related with the chemical composition of the soils. Physical and chemical properties of the soils depend on their mineral composition.

The purpose of our research is the study of the micromorphological structure, mineral and chemical composition of soils from technogenic landscapes of the Dzhidinsky tungsten-molybdenum combine (Western Transbaikalia). Object of the research is the alluvial swamp soils covered by tailings after dressing of sulfide-bearing ore for a long time. At the top of the soil profile, there is a dark gray organogenic horizon with a width up to 30 cm. Amount of organic matter of high degree of decomposition reaches 47–52% in the organogenic horizon. The underlying horizons have different degrees of gleization. The reaction of the soil is strongly acidic in the upper part and acidic in the lower part of the profile.

The main rock-forming minerals of the skeletal part of the soil are quartz and feldspar (mostly plagioclase, partially replaced by sericite). Also there are muscovite, biotite, amphibole, pyroxene. Chlorite, epidote, potassium feldspar, apatite, zircon, titanite, rutile, garnet, fluorite and ore minerals are accessory. Shape of the mineral grains is rounded and semi-rounded, sometimes is angular. Skeletal material is well sorted. The indicators of cryogenesis has been determined; there are polygonal structure, cryogenic microaggregate and cryoturbation. The plant residues of average and strong degree of disintegration are ferruginous. The charred plant residues are found. New formed minerals are presented by glandular spots, flakes, microorgans, small iron-manganese nodules, full and fragmented ferruginous films on the surface and fractures of mineral grains and fragments of rocks.

The tailings dam of Dzhidinsky tungsten-molybdenum combine overlying the soils for a long time had an impact on microstructure of the soil: density of the microaggregates and amount of ferruginous flakes and micromortgages have been increased, solid ferrous film on the surface of the grains of the skeleton has been appeared. These changes are present in all genetic soil horizons. In addition, the intensity of ferruginization signs increases to the down of the soil profile. Association of chemical elements and their absolute concentration relative to the values of the local background has been determined.

The association of Cd, Zn, F, Mo, Cu, Ni, As, Co, Pb is on the area of the former bulk tailing dump. The concentrations of these elements, except for Pb, are decreased to the down of the soil profile. The Cd, Pb, Zn, Ni, Cu, F, Mo, Co are the geochemical association of elements in the organogenic horizon of alluvial swamp soils in the area of the former tailing dump; whereas Cd, Ni, F, Zn, Cr, Cu, Co, As are in gley horizons.

The studies have been carried out with the support of the fundamental project of RAS (0340–2016–0006) and RFBR (grant 16–05–01041).

ASSESSMENT OF VERTICAL MIGRATION OF POLLUTANT ELEMENTS IN SOILS OF THE ORENBURG TECHNOGENIC PROVINCE

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The paper presents an analysis of the results of studies conducted in the 1980s in the territory of the Orenburg region. In this territory there are outcrops to the earth's surface of ores of various heavy metals, which increases the content of these elements in soil-forming rocks and soils. Action of numerous enterprises of ferrous and non-ferrous metallurgy, chemical and petrochemical industry led to the emergence of the technogenic province in the region.

The purpose of the work is to evaluate the parameters of long-term vertical migration of pollutant elements in the soils of the region. Knowledge of migration parameters allows retrospective and long-term forecasts of soil profile contamination. The migration parameters are necessary for monitoring the soils of the region. The presence of migration parameters will supplement the database of similar parameters for soils of different regions.

The parameters of migration models were assumed to be constant in depth and time as a result of long-term averaging of real fluctuations in soil conditions and the rates of soil processes. The parameters found are called "apparent". Work on the study of migration was carried out on soil sections of southern chernozem and gravelly mountain chernozem. Chemical analyzes of soil samples of the sections were carried out. The upper horizons of soils underwent the most severe changes. It was found that the upper layers of the soils near the Mednogorsk copper-sulfuric acid plant underwent strong acidification. The emissions of sulphide oxides by the plant have led to acidification of soils. The pH of the copper plant near the Copper decreased to 3.7–4.4. The upper 20 cm of southern chernozem (7 km from the Mednogorsk plant) and 10 cm of mountain chernozem (0.5 km from the plant) were acidified most strongly. The upper layers of soils near the Orsk-Khalilov Metallurgical Combine contain high levels of alkaline earth metals and iron.

It is shown that the diffusion and convection-diffusion models with parameters averaged over time and depth of the soil in most cases adequately described the distribution of heavy metals and fluorine along the soil profile in the eastern part of the Orenburg region. The “apparent” coefficients of diffusion of Cr, Ni, Cu, Pb, F in these soils are found in the range $(0.2–2.7)\cdot10^{-8}$ см^2/s. These coefficients are in the ranges of values obtained for analogous soils by other authors.

It is of interest to forecast the profile contamination of the substances studied for 2020. The forecast was calculated from the assumption that the average intensity of airborne pollution did not change significantly. The results of the forecast are quite interesting. The convective-diffusion model in all cases showed a lower predicted total contamination of the soil profiles in comparison with the diffusion model. According to the diffusion model, contamination of soil profiles in all cases should increase by 2020. The exception is lead contamination of southern chernozem at a distance of 7 km from the Mednogorsk plant. According to the convection-diffusion model, it is assumed that there is no additional pollution for Ni (2 km south of the Orsk-Khalilov plant) and for Cu (7 km from the Mednogorsk plant).

ANTHROPOGENIC GEOCHEMICAL TRANSFORMATION OF SOILS AND HERBAL VEGETATION IN THE CITY OF SERPUKHOV (Moscow region)

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Long-term anthropogenic impact on depositing components of urban environment (soils, plants) causes transformation of their trace element composition. The soil cover reflects the perennial pollution of the urban environment, annual herbaceous plants also contains information on the current fallout of pollutants from the atmosphere. Spatial analysis of anomalies in soils and vegetation enables to identify sources and set of priority pollutants and also rates of their accumulation in landscape's components. In this paper, these problems were solved using the example of the city of Serpukhov.

Serpukhov is a large industrial city in the Moscow region. 147 factories (machine-building and metal working enterprises (making 35% of industrial products), food (22%) and chemical (21%) industries) are located in the city. Their emissions contain heavy metals and metalloids (HMMs): Cd, Cu, Ni, Zn, Ba, As, V, Cr. Vehicles emit Pb, Zn, Cu, Sb, Mn, Cr, contributing significantly to the pollution of the city. 118 samples of topsoils and 69 samples of leaves of dandelion *Taraxacum officinale* were collected on a grid with a step of 500–600 m in 2016. Data on undisturbed soils in the Prioksko-Terrasniy Reserve and urbanized background for dandelion on outskirts of the city were used to indicate geochemical changes in the urban environment. The HMM content in the samples was determined in the All-Russian Scientific Research Institute of Mineral Resources by mass-spectral and atomic-emission methods with inductively coupled plasma (ICP-MS, ICP-AES).

The priority pollutants for soils – Cu, Pb, Zn, Sb, Ni, Cr, W, Sn, Bi – were identified. This set is caused by the industrial specialization of the city and the impact of vehicles. The accumulation of cationic elements Cu, Pb, Zn, Ni and Bi is enhanced because they are inactive in neutral and alkaline conditions of the soils of Serpukhov. The most pronounced anomalies of HMMs in the topsoils have been formed near the sources operating for a long time.

Leaves of dandelions in the city are enriched in Bi (enrichment factor EF10.2), V, Pb, W, Cr (EF 3–1.9) relative to the urbanized background. Plants growing near roads are the most contaminated, Bi (EF 9.2), V, Pb, As (EF 6.2–4.3) and Cr, Ni, W, Sc, Co (EF 3.6–1.8) are accumulated in dandelion's leaves of the traffic zone. Most of elements enter plants with emissions of motor vehicles, and Bi – mostly with construction dust; they are absorbed predominantly through the foliar uptake. Plants receive mainly essential elements (Cu, Zn, Fe, Mn, Mo) from soils. Toxic ones, such as Bi and Pb are absorbed weakly, their coefficients of biological absorption Ax do not exceed 0.0001.

The multi-elemental contamination of soils and plants depends on the type of land use. The level of soil and plant contamination of traffic zone is the highest, as it produces the bulk of pollutants. In the industrial zone, the rate of HMM accumulation in plants is higher than in soils due to substantial emissions of modern enterprises in the atmosphere.

The work was supported by the Russian Foundation for Basic Research and the Russian Geographical Society (project No. 17–05–41024).

MONITORING LONG-LIVED RADIONUCLIDES (^{3}H, ^{14}C) AND HEAVY METALS IN SNOW COVER OF URBAN AREAS AS INDICATORS OF ENVIRONMENTAL POLLUTION (ST. PETERSBURG, RUSSIA)

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Environmental pollution by radionuclides and heavy metals remains one of the most pressing problems of environmental safety. Of particular interest are the radiologically significant isotopes radiocarbon and tritium. These radionuclides are formed under natural conditions or as a result of nuclear reactions. Emissions of carbon-containing substances during the burning of fossil fuels reduce the concentration of radiocarbon in the environment (Suess effect). In other cases, for instance the burning of modern organic or waste products, the emission of radiocarbon is increasing. Other dangerous pollutants are heavy metals that emerge in the environment as the result of industrial activities and the development of transport, as well as traffic. It is particularly important to conduct research in the territory of big cities. The fastest and most effective method of environmental monitoring is to examine snow cover. Snow effectively absorbs impurities from the atmosphere and accumulates not only wet atmospheric fall-out, but also dry dust emissions from transport and industrial sources.

To monitor the distribution of pollutants, observation points in the central districts of St. Petersburg, Russia. The research was conducted for four years. The entire area of investigation was divided into four polygons: 1)“Vasilevskii Island” (an area of 11 km^2, 34 points of samples); 2)“Central,” is located in the historical center of St. Petersburg

(13.6 km^2, 45 points); 3)"Right Bank," is located on the right bank of the Neva River (22.2 km^2, 48 points); "Pushkin" as a relatively successful ecological suburb (2.9 km^2, 6 points). The concentration of the main water-soluble forms of heavy metals was determined by means of an XRF-spectrometer "Spectroscan MAKS-GV". Evaluation of snow pollution by heavy metals was completed with a Zc parameter. Measurement of the radiocarbon and tritium activity was performed using a low-background scintillation counter, Quantulus 1220. An areal distribution of pollutants was charted in ArcGIS (Spatial Analyst GIS ArcGIS).

Comparison of the spatial distribution of radiocarbon and heavy metals in the snow cover of the city is an important indicator for determining the various pollution sources. Zones that are characterized by high concentrations of heavy metals and low concentrations of radiocarbon, as a rule, are related to the areas of highways, for example, Nevskii Prospect – where the reduction of radiocarbon concentration is a result of intensive traffic. Zones in which higher values of radiocarbon and heavy metals were recorded may be associated with PAH emissions that occur as a result of industry. One such zone has been identified at the territory of the "Right Bank" polygon (Irinovskii Prospect). Here the environment is influenced by a nearby factory that produces reinforced concrete and iron fittings. Increased values of both parameters in the central district can be related to the location of the Vitebskii railway, i.e. with the cargo-loading zone. At the "Vasilevskii Island" territory, an anomaly was detected at the end of the 8-liniii. This area has always had a predominantly industrial history.

Further monitoring studies and charting of digital maps will provide an opportunity to increase the accuracy of mapping the pollution in St. Petersburg and to identify the areas with the most stable levels of pollution caused by long-lived radionuclides and heavy metals.

ASSESSMENT OF MERCURY LOAD OF THE TERRITORY OF ALTAI REGION ACCORDING TO BIOINDICATOR RESEARCHES

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Mercury is an element of the first hazard class and has hypertoxicity and migration properties as well as specific forms of transformation in environment components. Mercury belongs to the group of thiol poisons and is mutagenic. It methylates forming high-toxicity chemical combinations and is known to be the one of the most dangerous environmental contaminants (Ermakov, 2010).

Studies on mercury concentration in leaves of poplar and soil and uneven-aged needles, and peculiarities of mercury accretion depending on needles age, climate and landscape references of the region, were held in the west part of Altai region. Mercury concentration in the needles samples was analyzed by the atomic absorption spectroscopy method using RA-915+ mercury analyzer with PYRO-915 pyrolytic attachment (pyrolysis method). Mercury concentration was calculated on 1 gram of dry basis.

Average mercury concentration in the needles on studied territory varies between 13 and 17 ng/n regardless of age of the needles. Obtained average concentrations are background concentrations and correspond with those of other regions (Republic of Buryatia, Irkutsk and Tomsk Region) (Lyapina, 2015). The data obtained by other researchers (Anoshin et al., 1995) show that the older the needles the more mercury it contains. However, in our study it is featured that the maximum concentration is settled in 4 years old needles. At that, any further significant differences in mercury concentration in needles were not observed. Spatially mercury concentration increases from the north-east to the south-west of the studied area. To identify interconnection between mercury concentration in needles and climate references correlation coefficient was calculated. This coefficient shows correlation between mercury concentration in needles and air temperature and amount of precipitations both in vegetation period and during the year. Consequently, the following results were obtained: mercury concentration is inversely related to the temperature both in vegetation period and during the year for the majority of locations of the studies region. All mercury concentrations retrieved from needles samples are background concentrations regardless of the age of needles. That is why for calculation of geoecological characteristics the data for reference sites were used. All these data are contained in sources of literature (Yanin, 1992). Mercury concentration ratio in studied samples does not exceed 7,5 in comparison with background and is 4,4 on average. Maximum excess over estimated temporarily allowable concentration is 2,2.

Average mercury concentration in leaves of poplar on studied territory varies between 38 and 40 ng/n. Spatially mercury concentration increases from the south-west to the north-east of the studied area. In addition, it is connected with prevailing wind pressure and the influence of transboundary transport.

Average mercury concentration in the soil on studied territory is 39 ng/n. Spatially mercury concentration increases from the north to the south of the studied area.

Data from the correlation analysis show the flow of mercury into the needles partly from the substrate in the northwest paradise it studies

This area is located in agricultural region where ploughing and cereal crops growing are carried out actively. Higher mercury concentration is probably connected to application of pesticides and herbicides.

COPEVOLUTION OF THE BIOLOGICAL AND BIOXIC MEDIA

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Charisma of geology in relation to a society is that it creates not only conditions for the emergence of life on the Earth itself but also is responsible for maintaining the conditions under which the existence of life is possible.

Geological processes have not only created a unique, perhaps for the entire Universe, inhabitance, but also continues to support it in an extremely narrow, in terms of physics and chemistry, range of temperatures and pressures prevailing on the surface of the planet and the gas composition of its atmosphere.For the evolution of life, lasting more than four billion years, it can be argued that not only the material system changes, but also a number of factors and processes of its evolution. The relations, existing from the very beginning of co-evolution of biological and bio-axial environment, can be called a permanent ecological crisis. Permanent ecological crisis of our planet's biosphere stimulates appealing to the history of ecological crises of the past. They happened in the history of the Earth long time before the appearance of a human being and it led to the extinction of many systematic groups. The most famous crisis happened at the end of the Cretaceous period and caused the extinction of dinosaurs and their accompanying Mesozoic biota, opened the way to the development of angiosperms, higher insects, mammals and birds in the Cenozoic. All global ecological catastrophes in the history of the Earth were caused by different natural planetary and cosmic reasons-periodically repeated cosmic events (in particular, the finding of the Solar system in certain parts of the galactic orbit, etc.), successive epochs of mountain formation and movement of various parts of the lithosphere (orogenesis and riftogenesis), accompanied by changes in the atmosphere and climate, transgressions (onset) and regressions (retreat) of the world ocean, etc. The reasons for them are not largely fully established yet, but it is important to emphasize that all these disasters were natural. Now, the most important factor of the global environmental crisis on the Earth is a human being, and this fact makes the main difference between this crisis and all the previous ones. The current environmental crisis is thus unnatural as it is caused by a man.

The formation of the system of environmental fears is mainly connected with the ideas of the Global Environmental Crisis. In our point of view, the global environmental crisis is largely a subjective reality rather than an objective one: the threat of a demographic explosion and related predictions by Malthus about the depletion of food resources; the greenhouse effect due to the increased release of carbon dioxide into the atmosphere with the promise of global warming; perceptions of irreversible environmental pollution; the imminent depletion of energy resources; and much more. All this is largely a consequence of our lack of understanding of the laws of evolution of Nature and the mechanisms of natural processes regulating (compensating) the development of the environment. Often environmental horror stories are speculative (in this case, the purpose justifies the means), due to the need to attract attention and funds to environmental issues. In fact, the Earth passed over all this and much more repeatedly for its almost five billion-dollar history. There was a radiative increase in large populations of living organisms, and global warming, including the participation of the greenhouse effect due to increased volcanic activity. Both in the past and today, the processes of natural regulation have been included. Excess carbon dioxide stimulates the formation of carbonate rocks that bind carbon dioxide. The consumption of hydrocarbons is growing at an arithmetic rate and this is frightening. However the increase in reserves is rising exponentially. Prediction and discovery of gas condensate fields put the problem of depletion of hydrocarbon resources for 5–6 centuries aside, during which alternative sources of energy will appear.

NOx EMISSION, NITROGEN DEPOSITIONS AND TROPHIC STATUS OF FORESTS: RETROSPECTIVE AND ACTUAL ESTIMATIONS FOR MOSCOW REGION, RUSSIA

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Nitrogen emissions by industry and vehicles, mostly in the form of nitrogen oxides (NOx), were considered as a factor of forests eutrophication and degradation in North and Central Europe in the eighties and nineties (De Vries et al., 2015). Calculations made in the frame of Convention on LRTAP show similar levels of reactive nitrogen depositions for European forests and forested lands in the central regions of the European Russia, especially in Moscow region (Klein et al., 2004; EMEP, 2015). In spite of this, in Russian literature there is the prevailing opinion about the low nitrogen deposition fluxes in forest ecosystems (Menyailo et al., 2018). Doubtless, it is typical for background regions of Russia. But in forests of urban-industrial regions with intensive nitrogen oxide emissions and high nitrogen loads during long time, it is difficult to expect the absence of eutrophication effects.

To reveal possible effects of high nitrogen loads on forest ecosystems we analyzed the rare literature data on N concentrations in the air as well as in rains and forest soils in Moscow region, and compared they with the dynamics of trophic status of some forest ecosystems in the same region (Priputina et al., 2016). The results shown similar trend of changes in nitrogen deposition and the trophic status of the considered forest ecosystems. The growth in nitrogen availability of forest soils in the 1960–1980s determined the favorable conditions for the invasion of new species in plant communities, which had a higher demand for nitrogen nutrition. The influence of increased atmospheric nitrogen income on the trophic status and dynamics of the species diversity of forests in the Moscow region coincides with the character of changes caused by natural succession of these forest types mentioned in (Rysin et al., 2003).

This work is a part of researches on the theme of state assignment of IPBSS № AAAA-A18–118013190176–2.

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TYPES OF MINERALIZATION OF DINOSAUR BONESOF THE KUNDUR LOCALITY (AMUR REGION)

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The paper discusses the problems of paleontology including mineralization processes of dinosaur bones: the degree of transformation of the primary bone microstructure, identifying the features of accumulation and redistribution of chemical elements and other indicators. Various limb bones along of dinosaur were used for the study. The dinosaur locality Kundurwas discovered in the southeastern part of the Zeya-Bureya sedimentary basin (Lower Zeya depression), near its borders with the adjacent uplifted areas: the Lesser Khingang Mountains and the Turan uplift. The site extending over several hundred square, dinosaur bones form large bonebeds.The studies has been established two types of bone mineralization can be distinguished (fig.1).

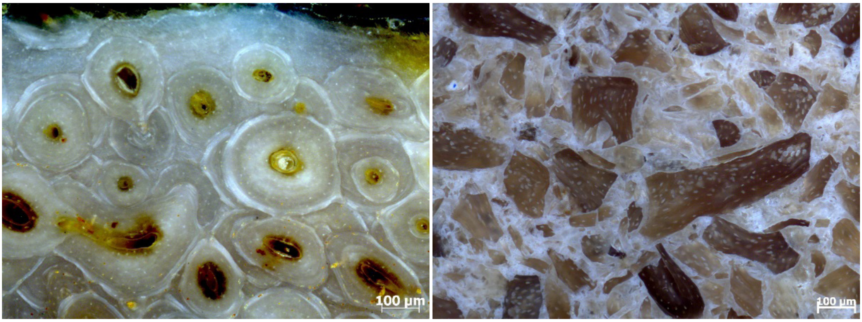

Fig.1 Two types of mineralization of dinosaur bones

The first type characterized by a high degree of preservation of the primary microstructure of the boneand more organized arrangement of the primary osteons.The transverse sections of all the bones examined show a well differentiated centrally located medullary cavity surrounded by an outer relatively compact cortex. Most of the vascular channels show centripetal deposition of osteonal bone and form primary osteons. Although the long bones is diagenetically altered, a reticular pattern of the primary osteons is evident.An interesting feature noted in all the partially changed bones examined is the extensive secondary reconstruction in the form of closed canal of osteon.Bone cross sectional geometry reveals that most of the adult limb bones of dinosaur are comparable with that of the present day terrestrial vertebrates.

The second type of mineralization is characterized by a high degree of destruction of the structure of bones and more phase modification. The diamond crystal is detected in fossil bones of Raman micro-spectroscopy. This may indicate an impact event.

These two groups also differ in the chemical composition of the basic and rare elements.

COMPARISON OF BALANCE SHEET RESULTS BY THE ARITHMETIC MEAN METHOD WITH THE RESULTS OF CALCULATIONS BY THE GEOMETRIC MEAN METHOD

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When analyzing the processes during the evolution of the organic matter of coal as its catagenesis, we will proceed from the fact in the article [1] by M. L. Levenshtein “Osnovnye problemy reginalnogo metamorizma ugley” (“The main problems of regional metamorphism”) on page 118 “metamorphism of organic matter and formation of hydrocarbon fluids should be considered as two sides of a single process”. Only we go beyond not only hydrocarbon fluids, but in general all the fluids including carbon dioxide and water. To analyze each contribution of hydrocarbon fluids, carbon dioxide and water, passing from one state to another, we must take into account the evolution of this transition. Set forth in [2, pp. 5–6] “… since the basis for further processing was oxygen, and accounting for nitrogen and sulfur, due to the heterogeneity of the materials, sometimes introduced errors into the calculations, the sum of C + H + O was taken as 100%” we select three points on the Van Krevelen diagram in order to show the independence of the solution when using the geometric mean method [3, Fig. II.5.1. The general scheme of the evolution of kerogen from diagenesis to metagenesis in the van Krevelen diagram].

We illustrate this process using the example taken from [2, Tables

2 and 3 p.7, selectively] (see the table and the figures selectively ([2] numbers in Tables 2 and 3):–3, 9, 4 and 7). We follow the example of calculation described in [6, p. 7]. In [6], the basic equations in accordance with the simplified scheme of Uspensky are the following (the author's designations are retained): x = C–ClM (1) y = H-H1M (2) u = O-O1M, (3) where C, H, O and C1, H1, O1–the elemental composition of the coals of two consecutive matched stages …; x, y, u–loss of C, H and O in a given interval,% of the organic mass of coal α,.β, γ. And **M**–yield of residual coal (ie coal of the second stage),% of OM (organic matter–*S.R.*) of coal of the first stage. Denoting the amounts of H_2O, CO_2 and CH_4 released through α, β and respectively, we can represent the loss of carbon, hydrogen and oxygen in the form of the following equations:

$$x = \frac{12}{44}\beta + \frac{4}{16}\gamma,\ y = \frac{2}{18}\alpha + \frac{4}{16}\gamma \quad , \quad u = \frac{16}{18}\alpha + \frac{32}{44}\beta$$

The transformation of equations (1)–(6) leads to a system of three equations with four unknowns (α, β, γ and **M**). The correctness of the calculations is controlled by the equalities: x + y + u = α + β + γ = 100 –**M** (in%). Under the condition of autonomy of coal substance transformation, the values of x, y and u should be greater than zero (or at least not negative–S.R.), and M–less than 100%. Equating the values of α, β, and γ to zero successively, we can calculate the corresponding values of **M**. The largest of them must be discarded, since one of the quantities α, β or γ would then acquire a negative value … Then, with the values taken, we get zero generation of water when the ratio is:

$$H_2O = \frac{24H - 8C + 3O}{24H1 - 8C1 + 3O1} \quad CO_2 = CH_4 =$$

for methane in hydrocarbon fluids.

For paraffins we will repeat the mathematical calculations with the only difference that in the composition of hydrocarbon fluids we will replace methane with paraffins. So we have:

$$x = \frac{12}{44}\beta + \frac{12}{14}\gamma \ \ \mathrm{y} =, \ u = \frac{16}{18}\alpha + \frac{32}{44}\beta$$

Zero values for paraffins generate water this ratio will be equal to:

$$H_2O = \frac{48H - 8C + 3O}{48H1 - 8C1 + 3O1} \quad CO_2 = \ CH_2 =$$

The author hopes that as a result of a broad discussion, geologists-coal miners and especially geochemists (only to mention Ya. Yudovich, a recognized authority in the field of geochemistry in general and especially coal geochemistry in particular) will find another reference to the work, in which the difference between the arithmetic mean and the geometric mean (in the geochemical sense) would be clarified, otherwise the author retains the primacy in interpreting these two averages in the geochemical sense.

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THE TIME OF PREPARATION AND DEFENSE OF THE DISSERTATION WORK. RYABINKINA S.V. “QUANTITATIVE ASSESSMENT OF THE SCALE OF METHANE GENERATION BY COALS OF THE PECHORA BASIN”.

Ryabinkin S. V.[1], Virtanen K. S.[2]

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In the Komi Archives of the Scientific Center of the Ural Branch of the Russian Academy of Sciences in Fund 2, inventory 4, file 271, sheet 4, a document is kept. It is called a statement. At the top, handwritten to the Chairman of the Specialized Council, D. 200.21.01, Academician N. Yushkin. from Ryabinkin Sergey Vladimirovich. “ This statement about the request to take a Ph.D. thesis … for protection in your Academic Council. The work is for the first time. “ On his hand, Academician Nikolai Pavlovich Yushkin made a decree to “A.I. Eliseev, Ya.E. Judiovich – For examination” and a handwritten signature and date – 05.05.94 [1]

But then the fun begins. A. I. Yeliseyev, who, together with Y. Yudovich, was appointed an expert. In it, noted, A. I. Yeliseyev that the work was carried out at a high scientific and methodological level, the theme and content of the thesis fully correspond to the chosen specialty – 04.00.17 – geology, prospecting and exploration of oil and gas fields … the protected half-notes of the thesis were published by the author in the publications of the Institute of Geology and repeatedly reported at scientific conferences and meetings of various levels (including international and …) [1] and gave the conclusion – "… the work is worth considering at the special council D.201.210.01 and it can be rekamendovana to protection "[1].So thought and acted Alexander Ivanovich Eliseev. As for Yakov Elievchcha Yudovich, he ignored his appointment (Ya.E. Yudovich) as an expert. Alexander Alexandrovich Eliseev put in his place. So Ya. Yudovich would have done – express his attitude to the work, whether positive or negative is important – but Ya. Yudovich chose a different path, without expressing any relation to the dissertation work of Ryabinkin S. V., he hid behind Y. A. Tkachev. Practise what you preach.

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HEAVY METALS AND METALOIDS IN MACROMYCETES FROM THE ZONE OF ACCUMULATED ENVIRONMENTAL HARM IN PETROZAVODSK (REPUBLIC OF KARELIA)

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Studies of macromycetes were carried out in the zone of accumulated industrial pollution in the center of Petrozavodsk (the former site of the Onega Tractor Plant). Chemically altered soils, as well as all the representatives of higher fungi (species *Verpa bohemica* (Krombh.) Schroet. and *Leccinum scabrum* (Bull.: Fr.) S. F. Gray) were studied in detail in this area. The risk of chemically contaminated fungi as food was assessed, a comparative polyelement analysis of morphological parts of *L. scabrum* fruiting bodies (including comparison with background area), species of macromycetes, macromycetes and soil substrate was carried out.

Soils of the former industrial site, located on the bank of the Lososinka river in the central part of the modern city of Petrozavodsk, are characterized by a high level of contamination with heavy metals and metalloids (Pb, Cu, Zn, As, W, Mo, Cr, Ni, As, etc.). In case of non-acceptance of the normatively provided measures for neutralization of toxicants, in this territory there will be a danger for the biota, falling into the impact zone.

The studied species of macromycetes from the contamination zone concentrate chemical elements (including toxicants) in different degrees in comparison with background determinations (*L. scabrum*) and soil substratum. In general, potentially hazardous elements (Pb, W, Bi, Cu, Zn, Sb, etc.) accumulate in fungi selected in the contamination zone in larger quantities than in the background (control) area. At the same time, a more detailed analysis is needed in background areas for some heavy metals, including Sr, Co, Cr, Y, Sn, Mo, Ni and Mn, as well as Cd, Tl and Mo.

Both spring and autumn types of polluted macromycetes can represent of danger, when consumed as a food. The main toxicants in them accumulate in different ratios: *V. bohemica* has more Cu and Zn, while *L. scabrum* as a whole more strongly accumulates Pb and Cd.

We established that large quantities of Pb, W, Ba, Bi, Sb and Zn are present in the caps of the *L. scabrum* from contamination zone. The spectrum of elements with increased concentrations in stems is somewhat wider: Ba, Pb, Bi, W, Sb, Zn, U, Ag, Tl, Cu. The content of Cd in the control samples of *L. scabrum* is large enough (especially in the cap), therefore contamination with this toxicant within the impact zone is confirmed by its maximum content (2,47 mg/kg air-dry sample) and exceeding the MPC (in terms of the initial product is 0,1 mg/kg).

The possible using of the studied species of macromycetes in zones of technogenic contamination for bioremediation purposes automatically excludes their further applying as food products. Therefore, in addition to the study of fungi, especially with regard to contaminated sites, which are accessible to the population, it is necessary to search and identify plant species that are not used for food, but grow well and actively accumulate heavy metals.

CHEMICAL CONTENT OF MICROBIOTA COMMUNITIES IN MINE WATERS FROM TUNGSTEN DEPOSITS

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The various associations of microorganisms and water-plants (biomates) are widely widespread in mine and subdump waters of geotechnogenic landscapes of tungsten deposits of East Transbaikalia. The aleak in them processes of vital functions result in the selective accumulation of chemical elements from an environment or, vice versa, assist passing of weakly soluble forms of potentially toxic elements to the movable easily soluble forms and migrations of them in surrounding landscapes [1].

For territory of abandoned tungsten mine Dzhidinskoe at West Transbaikalia seven samples of biomates are took. Samples are consisted by thread water-plants, associating with a sulphur, brown or whitish substances. They characterize the next technogenic situation: 1) mine waters flowing out from “Western” adit, unsealing lowermost horizons of vein tungsten deposit; 2) the river Modoncul after an inflow in her mine waters; 3) brook of Gudzhirka, draining the dumps of rock waste of mine. As control samples, the microcommunities of pure Morgenshen brook and biomates of the river Dzhida are considered. The chemical composition of the samples is determinated in dry matter by the method of ICP−MS. Morphology and quality chemical composition of microbiota studied by means of scan electronic microscope of LEO 1430vp.

Chemical composition of microbal associations of surface-water of technogenic and natural landscapes differentiates substantially. So, content of iron in the biomates of mine and subdump waters arrives at a 20 g/of kg, while in control samples it makes a 0,7–1,5 g/of kg. The highest content of aluminium is marked in biomates from the river Modoncul. In the same sample, content of beryllium on three orders exceeds his content in the microbal associations of “clean” landscapes. A copper is concentrated by the biomates of both mine and subdump waters, its content in that on two orders exceeds control. The highest content of lead is marked in the biomates of mine brook, and tungsten and bismuth – in subdump waters of Gudzhirka brook. An only chemical element, content of that in the associations of microbiota both natural and technogenic landscapes, is at one level is an arsenic.

The obtained data allow us to consider the biomates, formed on territory of tungsten deposits, as a kind of filters that can be used in the schemes of reclamation of the territories of mining.

The studies have been carried out with the support of the RFBR (Grant № 16–05–01041).

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CHANGES IN THE ACIDITY OF RAINWATER IN CONTACT WITH THE URBAN ATMOSPHERE

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Rainwater is the main agent of the chemical weathering; it takes part in the majority of the chemical reactions on rock surfaces at the natural and urban conditions. One of frequent occurrence reaction is calcite – gypsum transformation on marble or limestone surfaces in a modern urban environment causes irreparable losses of cultural heritage monuments. The present investigation is devoted to the mechanism of this transformation: the reaction of calcite – gypsum transformation was realized experimentally to identify the sulphur dioxide role in the process, and variations in the acidity of rainwater were measured.

Gypsum formation on a carbonate rock surface is often described by reaction

$$CaCO_3 + H_2SO_4 + 2H_2O = CaSO_4 \cdot 2H_2O + H_2O + CO_2.$$

Nevertheless, the reasons of the sulphuric acid appearance is still under discussion. It is known the main source of sulphur in an urban atmosphere is the gas SO_2 from traffic fumes; it needs transforming to SO_3 and then to H_2SO_4 in water. The fact is that reaction between gases $2SO_2 + O_2 = 2SO_3$ can be realized at a temperature over 450°C and with a catalyst. Therefore, the question is: when and where sulphur dioxide turns to sulphuric acid. According our hypothesis the follow reactions chain is occurred: $SO_2 + H_2O \leftrightarrow H_2SO_3$, $2HSO_3^{-} + O_2 \leftrightarrow 2SO_4^{2-} + 2H^{+}$, or $SO_3^{2-} + H_2O \leftrightarrow H_2SO_4$ [1]. It can be realized in a rainwater volume in contact with the atmosphere.

At the experiment, the calcite crystals and marble fragments were put in vials with distilled water contacted with atmosphere artificially enriched of sulfur dioxide at 40°–50°C during four weeks. These reactions led to gypsum crystals formation on calcite surfaces and in water around them. Analysis of the residual solution shows an acid solution appearing in the vials (pH=1). Identification test with $BaCl_2$ detects the presence of sulfate ions.

The experiment results confirm the metasomatic reactions can be realized on carbonate rocks surfaces in the absence of sulphuric acid at the beginning of the process.

The first stage of study of changes in the rainwater acidity took part at the period the 15–30 of November 2017 on the meteorological site of Herzen University Geography faculty. The rainwater was collected in 5 jars: in the jars № 1–3 it stayed all period of experiment, and the jars № 4–5 were emptied after each measure. Beside this, there was a jar№ 6 contained some distilled water in contact with atmosphere, but protected from rainwater. pH values were measured every day by pH-meter. This method allowed receiving pH data of new precipitations, and observing a dynamic of pH change in collected still water. The experiment results show new rainwater is neutral (pH ~ 6,75); but pH value change over time in collected rainwater and in distilled water from 6,75 to 5,8.

This confirms the hypothesis of a gradual change in the acidity of rainwater caused by the dissolution of gases. The results can be used to reconstruct the environmental conditions of gypsum formation and to develop methods for the protection and conservation of limestone and marble in modern urban conditions.

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SOIL GEOCHEMISTRY IN THE POLYMETALLIC DEPOSITS AREA OF NORTH-WESTERN ALTAI

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The North-Western Altai is represented by a set of ridges forming the Ob-Irtysh watershed in the north-west of the Altai-Mountains located on the border of Russia, Mongolia, China and Kazakhstan. On the one hand, there are no industrial enterprises in the region that could impact the ecosystem components. At the same time, some deposits, ore occurrences, diffuse halos of ferrous and non-ferrous metals are present here. Altai is one of the richest regions of Russia in mineral reserves. The study area is characterized by insignificant anthropogenic impact and background natural pollution since the deposits mining has not started yet.

High concentrations of zinc, lead, copper (the main ore–forming elements) and accompanying them cadmium were found in the soils of the mountain-tundra belt (see Table). Almost uniform intra-profile distribution of these metals is evidence of their natural origin.

Table. Elements content in soils of North-Western Altai

Profile, soil	Soil depth (cm)	Zn	Cu	Cd	Pb
09-Charysh-07. Mountain-tundra, Gorky Belok ridge	Ад (0–8)	561.7	41.1	3.1	79.3
	AB (8–23)	700.8	33.7	3.0	61.0
	B (с 23)	646.6	34.0	2.0	69.3
Average content in mountain tundra soils		216.0	28.8	1.60	33.9
16-Charysh-08. Leached chernozem, Charysh river valley	Ад (0–8)	95.5	41.4	1.45	26.6
	A (8–32)	97.7	42.0	1.64	27.3
	AB (32–56)	92.9	40.0	2.38	28.2
	B (56–72)	93,4	33.0	1.15	26.5
	BC (72–100)	90.6	39.0	1.16	22.5
	C (с 100)	112.8	34.3	1.47	25.2
Clark in the earth’s crust by A. P. Vinogradov (1962)		83	47	0.13	16
Background content in soils of North-Western Altai		66.7	23.0	0.13	16.0
AC (HS2.1.7.2511–09)		110	66	1	65

Anomalous concentrations of heavy metals are peculiar only to soils developed, probably, directly above the deposits, ore bodies of which are close to the surface. The pollution is local; the average content of elements in the soils of the mountain-tundra is relatively low. The content of these elements in soil specimens sampled in the river valley is within the background and below the MPC (except for cadmium). High Cd concentrations are due to its high mobility in the hypergenesis zone.

CARBON ISOTOPE RATIOS IN THE APATITE-PROTEIN COMPOSITES OF CONODONT ELEMENTS – PALAEOBIOLOGICAL PROXY

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Conodonts were the Palaeozoic and Triassic extinct group of the marine animals possessing discussed affinities. The only mineralized parts of conodonts are tooth-like elements disposed in a bilaterally symmetrical apparatus. The conodont elements are composed of complex fluorapatite-protein nanocomposites. The mineral component of conodont elements is represented by apatite-(CaF) with minor content (about 1% wt.) of CO_3 ions (Frank-Kamenetskaya et al., 2015). Organic matter is composed of collagen-like protein similar to type IV collagen (Журавлев, 2017), consisting less than 4% of a conodont element. D.J. Over and L.E. Grossman (1992) reported $\delta\,^{13}C_{org}$ in conodont elements of the Late Devonian genus *Palmatolepis* (from –24.5‰ to –24.0‰), Early Carboniferous siphonodellids (–26.3‰ and –27.3‰), and Late Carboniferous *Streptognathodus elegantulus* (from 23.0‰ to –24.0‰). Some data on trophic differentiation of the Late Visean (Early Carboniferous) conodonts based on $\delta\,^{13}C_{org}$ were published later (Nicholas et al., 2004). The study material comprises conodont elements of the middle Frasnian genus *Youngquistognathus* (n=1), and latest Famennian-Tournaisian species: *Polygnathus parapetus* Druce (n=10), *Hindeodus crassidentatus* (Branson et Mehl) (n=1), and *Ligonodina* sp. (n=1). Conodont elements were extracted from host rock, washed with ethanol and distilled water, and then used for analysis of carbon isotope values with DELTA V Advantage mass spectrometer equipped with the Thermo Electron Continuous Flow Interface (ConFlo III) and Element

Analyzer (Flash EA 1112). δ $^{13}C_{org}$ values are reported relative to the PDB standard. Isotope analyzes were performed at the CKP "Geonauka" of Institute of Geology Komi SC UrB RAS (Syktyvkar, Russia). δ $^{13}C_{org}$ values in conodont elements range in wide interval from –30.4‰ up to –22.5‰. δ $^{13}C_{org}$ values are distributed in the studied specimens as following: *Youngquistognathus* sp.–24.05‰, *Polygnathus parapetus* from –30.4 up to –22.5‰, *Hindeodus crassidentatus* –29.0‰, and *Ligonodina* sp.–23.47‰. Intraspecific variations of δ$^{13}C_{org}$ values in *Pol.parapetus* demonstrate weak facies trend (sea-ward increasing). Significant variations in δ $^{13}C_{org}$ values suggest low metabolism level and probably seston-feeding for conodonts. This supposition is supported by data on Sr/Ca (mol/mol) values in mineral component of lamellar tissue of conodont elements ranging from 0.0025 to 0.0081 (mean 0.0054) that is characteristic of marine primary consumers (Peek & Clementz, 2012).

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Section 3

Biomineralization and nature-like materials and technologies

SYNTHESIS OF ZN-SUBSTITUTED B-TCP

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Currently Russia and other countries are actively engaged in the calcium phosphate materials creation and study, capable of releasing drugs intended for the bone diseases treatment. Of particular interest is the use of β-tricalcium phosphate (β-TCP). By structure, bioactivity and mechanical properties, it is similar to dehydrated hydroxyapatite, but an order of magnitude higher than its resorbability.

Modification of the powdered TCP will give it additional properties. The authors developed a technique for the synthesis of zinc-substituted TCP powder, suitable for the drug delivery agents development. The choice of zinc is based on the fact that Zn^{2+} in the form of impurity elements is present in the bone tissue, which can have a beneficial effect on the osseointegration processes [1].

Objective: synthesis of β-TCP in the zinc ions presence (change in the concentration of Zn ions from 1 to 15 mass%).

The synthesis of Zn-substituted β-TCP was carried out according to the reaction described in [2] at room temperature:

$$2(NH_4)_2HPO_4+(3\text{-}x)Ca(NO_3)_2\times 4H_2O+xZn(NO_3)_2 \rightarrow Zn_xCa_{(3\text{-}x)}(PO_4)_2+4NH_4NO_3+4(3\text{-}x)H_2O+2HNO_3$$

All samples were examined by X-ray analysis, FTIR spectroscopy, optical microscopy, bioresorbability, and other methods.

With the help of XRD analysis and FTIR spectrum analysis, it was found that there are groupings characteristic of β-TCP in the structure of the sample. A study of the solid phase morphology showed that the particles of the obtained Zn-substituted β-TCP samples are porous aggregates.

Sample dissolution was carried out in acetate buffer with pH = 5.5. As a result of the experiment, the concentration of calcium ions was determined as a function of the dissolution time. It was found that when the addition of zinc ions increases, the solubility increases. This is explained by the difference in the values of the solubility products of calcium and magnesium phosphates ($SP(Ca_3(PO_4)_2=2.0\cdot 10^{-29}$ and $SP(Zn_3(PO_4)_2=9.1\cdot 10^{-33}$).

Supernatants after the separation of β-TCP and Zn-β-TCP were investigated for the presence of orthophosphate ions, as well as calcium and zinc ions. According to the synthesis results it is established that when the Zn ions concentration increases, the Ca/P ratio in the sediment decreases. This dependence characterizes the isomorphous substitution of calcium ions for zinc. Substitution is possible in accordance with the Goldschmidt rule, which states that isomorphous mixtures are formed if the ionic radii of interchangeable structural units differ by not more than 15% of the smaller value for the identity of the charge sign. Thus, comparing the radii of calcium and magnesium ions ($r(Ca^{2+}) = 0.100$ nm and $r(Zn^{2+}) = 0.060$ nm), we can conclude that continuous isomorphism is possible.

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FEATURES OF THE CRYSTALLIZATION OF CALCIUM PHOSPHATES FROM THE MODEL SALIVA SOLUTION IN THE PRESENCE OF AMINO ACIDS

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At present, a large amount of information has been accumulated on the effect of the composition of the biological solution on the phase composition of precipitation and on the kinetics of the crystallization of calcium phosphates. However, there is little data on the nature of their crystallization in physiological solutions. The rate of nucleation and growth of particles from supersaturated model solutions of saliva ($S = 25, 30, 35$, pH 7.0, $T = 298$ K) in the presence of amino acids (neutral, basic, acidic) has been studied. It is shown that at the physiological concentration and relatively low supersaturation of the system, the amino acids inhibit the stages of the crystallization process. A greater effect is seen at the nucleation stage in the range: glycine> glutamic acid> serine-aspartic acid> alanine. The simultaneous presence in the solution of a large number of active sites and the diffusion difficulties of mass transfer (due to a smaller initial supersaturation) cause a predominant flow of the nucleation stage without active growth of the particles. The laser diffraction method established a decrease in the size of the particles formed, in this case the amino acids are adsorbed on the surface of the sediments without changing their phase composition. The smallest aggregates are formed from a salivary model solution in the presence of alanine (physiological concentration) and the largest ones in the presence of glutamic acid. Isothermal distillation is the predominant growth mechanism with low supersaturation and additive concentration, with an increase in the concentration of precipitating ions and amino acids is aggregation. It was found that the amino acids are part of the precipitate by IR-spectroscopy. On the IR spectra there are vibration bands $-NH_2$ 1640–1630, 1530–485 cm^{-1},–COOH 1335–1330, 2120–2080 cm^{-1}. In addition, phosphate bands of 563 cm^{-1}, 602 cm^{-1} correspond to deformation vibrations of PO_4^{3}-, and the band of 1034 cm^{-1} corresponds to valence vibrations of this group, 3410 cm^{-1} refers to -OH oscillations, a low-intensity 868 cm^{-1} band corresponds to deformation fluctuations of carbonates. The XRD data of precipitation obtained in the presence of amino acids show that a mixture of calcium phosphates is formed. It is hydroxyapatite and brushite. It was noted that the content of glycine in the initial medium increases the proportion of CaHPO4□2H2O in the composition of the precipitate. With other acids, the composition is approximately the same, with a lower content of CaHPO4□2H2O. The change in the concentration of amino acids and the initial supersaturation does not lead to a change in the phase composition of the samples.

Conclusion

Thus, the study of the effect of amino acids on the formation of calcium phosphates from a model saliva solution with the use of modern physicochemical methods.

Acknowledgments

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Crystal chemical characterization and formation mechanism of human cardiovascular apatite deposits

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Apatite is the main mineral component of teeth, bones and one of the most common minerals in pathologic masses in human body. Cardiovascular system as one of the potential sites for the pathologic masses formation attracts a lot of attention because of the high impact of Pathological Cardiovascular Deposits (PCD) on the atherosclerosis and arteriosclerosis progression. As far as these diseases are the main cause of death in the industrial countries, deep research of PCD can be considered extremely significant.

According to the previously published studies, PCD are composite masses formed with collagen and mineral, mainly hydroxyapatite. PCD apatite is poorly crystalline, defective carbonated apatite mainly of B-type with the presence of a wide range of foreign elements such as Na, Mg, K, Cl, Fe, S, etc. in their structure.

Ion substitutions in the PCD apatites require further study. Their influence on the unit cell parameters, while important for the understanding the difference between PCD and other pathogenic apatites, also hasn't been studied yet. Also, there is no one dominant point of view among theories of the PCD formation. Existing correlation of the PCD formation with other diseases makes the aim of figuring out the real mechanism even more complicated.

Main goal of the present work was to refine crystal chemistry peculiarities of the PCD apatite and to advance in understanding of their formation mechanism. We tried to figure out differences of PCD apatites and other pathogenic apatites, as well as to establish the influence of the aorthic stenosis state on the crystal chemical characteristics of apatite.

Summarized crystal chemistry data concerning pathological mineralized deposits of the human cardiovascular system are presented. Samples of the valve deposits have been taken from several patients and studied with wide specter of the instrumental methods (XRD, FT-IR, Raman, EDX, SEM). All the data gathered evidence that pathological cardiovascular deposits apatite is similar to the other bioapatites and can be described as non-stoichiometric water-bearing B-type carbonated hydroxyapatite. PCD apatite is characterized by higher concentration of B-type carbonate ion (up to ~6 wt%), that leads to the increasing influence of the carbonate-ion on the unit cell parameters in comparison with water and other substitutes. Unit cell parameters of the PCD apatites therefore differ from the parameters of other pathogenic apatites: parameter ***a*** is decreased, parameter ***c*** is increased. Minor variations of the blood chemical composition cause small dispersion of the unit cell parameters in comparison with other pathogen apatites of the human body. Also, the mechanism of the PCD formation has been suggested.

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EGULARITIES OF POLYSACCHARID SORPTION ON THE SURFACE OF HYDROXYLAPATITE

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OmSU

Interaction of implants with surrounding bone tissue is an actual problem of modern medicine. In the body environment, the implant material interacts with the components of biological fluids, tissues (proteins, polysaccharides, cells, etc.). In connection with this, in the development of biomaterials, it is important to investigate the processes that occur directly on the surface of the implant in an in vivo medium.

The aim of the work was to study the sorption of high-molecular hyaluronic acid on carbonate hydroxylapatite, synthesized from the prototype of human synovial fluid. Hyaluronic acid is the main structure-forming glycosaminoglycan, which concentrates around itself water, components of the intercellular substance and even cells into a single system.

Objects of the research: adsorbent–carbonate–containing hydroxylapatite (CHA), adsorptive–high molecular weight hyaluronic acid (HHA, high molecular weight sodium hyaluronate, qualification “h” with a concentration of 0.025–0.25 wt.%). A solution of HHA was added to the CHA sample, pH adjusted to 7.40 ± 0.05, and shaken for 30 minutes. The contact time was 48 hours at 298 K. After a predetermined period, the solid phase was filtered off. In the filtrate, the residual concentration of HHA was determined spectrophotometrically.

On the obtained adsorption isotherm T = f (C) (Fig. 1), two sections can be distinguished. Within the initial section of the isotherm (Henry section) at concentrations of HHA not more than 0.105 wt.%. quantitative sorption is observed. Further, the exponential section is the slowing down of the adsorption of *G* and the content of the solution in the HHA solution exceeds 0.200 wt.%, saturation begins.

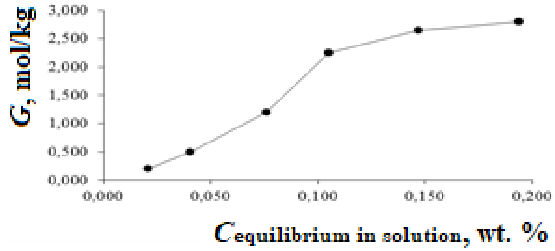

Fig. 1. Isotherm of HHA adsorption on CHA

The experimental data were processed from the position of the Langmuir and Freundlich theories (Table 1).

Таблица 1. Уравнения адсорбции ВГК на КГА

Model	The equation	R^2
Langmuir	$G = 5,263\frac{2,160\cdot C}{1 + 2,160\cdot C}$	0,364
Freundlich		0,970

It has been established that the adsorption of HHA at pH = 7.4 has a good correlation in the linear coordinates of the Freundlich model. According to this theory, the adsorption of the polysaccharide is not limited to the monomolecular layer, and the active centers of the HHA serve as embryos for subsequent crystallization of the CHA.

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SYNTHESIS OF CALCIUM CARBONATES IN THE PRESENCE OF YELLOW COMPONENTS

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One of the most common diseases associated with pathogenic biological formations in the human body is cholelithiasis. In Russia, every year, 5–6 people fall per 1000 population (about 1 million people a year). The prevalence of cholelithiasis is highest in the age group of 50–60 years and is 14% for men and 20.2% for women.

The most common among the inorganic components in gallstones is calcium carbonate, in three polymorphic modifications (aragonite, calcite and waterite). The crystallization of one or another modification of calcium carbonate is determined by the specific physicochemical and kinetic factors of the mineral-forming media.

In this regard, the purpose of our work is: synthesis of calcium carbonate and the study of the effect on its morphology and the properties of additives of different nature.

With the help of XRF it was found that calcium carbonate synthesized in the presence of glutamic acid, glycine, urea, proline and 1% bile, have calcite morphology. The concentration of added additives does not affect the composition and does not change the form of XRF. An increase in the bile concentration (5–100%) affects the morphology of calcium carbonate. For the precipitation obtained in this range of bile, a modification of calcium carbonate in the form of a vaterite is recorded.

Glutamic acid increases the particle size, in comparison with the unmixed sample, only in the case of a concentration of 0.004 mol/l. Glycine, as an additive, also increases the crystallite size. The greatest increase was observed at a concentration of 0.004 and 0.01 mol/l. Anomalous dimensions are characteristic for the sample, which crystallized in the presence of urea. The maximum concentration of the additive increases the crystallite size by 1.6 times. Proline, also affects the particle diameter and increases their size, but the maximum increase occurs at a concentration of 0.004 and 0.02 mol/, unlike other additives.

In the case of bile, the crystallite size increases only at a concentration of 1%. The increase in concentration does not change the particle size. The samples are anomalous at a concentration of 70 and 100%, their dimensions are smaller than in the case of unalloyed calcium carbonate. From this it can be concluded that it is possible that the amino acids exert a different effect on the $CaCO_3$ particles during the crystallization stage.

BET showed that the sample in the presence of glutamic acid is characterized by the largest crystallite size, with the lowest specific surface area. However, this dependence is not observed for all samples.

A sample containing bile has a particle diameter similar to that of unalloyed calcium carbonate, which should contribute to the equality of specific surfaces. But this sample has the most developed specific surface.

To dissolve the synthesized phases of calcium carbonate, a solution of 0.9% sodium chloride was used. From the kinetic equations obtained, it was found that the initial dissolution rate of calcium carbonate after 1 day of synthesis is higher than the speed of subsequent samples.

In the EDTA solution, the release of Ca^{2+} ions is much slower. In the case of dissolution in EDTA solution, it is established that the presence of additives reduces the dissolution rate of the sample by several tens of times.

PHYSICO-CHEMICAL MODEL OF EDUCATION OF POORLY SOLUBLE COMPOUNDS IN NEFRON OF THE KIDNEY

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The study of crystallization in biological media is one of the promising areas of research in the field of crystallization from solutions. To date, the problem of the formation of pathogenic organomineral aggregates in the human body remains relevant throughout the world due to a steady increase in the incidence rate, which is 0.5–5.5% per year.

For the first time, a physico-chemical model for the formation of sparingly soluble compounds in the nephron of the kidney was proposed on the basis of a mathematical description of an ideal displacement reactor. It is assumed that the process of formation of kidney stones predominantly proceeds in the structural-functional unit of the human kidney – nephron. In view of the peculiarities of the structure of the nephron (a considerable excess of length over the diameter), the mathematical apparatus of the ideal displacement reactor was used, which is widely used to describe the reaction processes taking place in thin long tubes. Given the specific processes that occur in different regions of the nephron, but also differences in the geometric parameters of the system for correct mathematical description of boundary conditions are introduced in different parts of the length of the nephron, but the form of the equations describing the process remains unchanged.

Calculation of the hydrodynamic flow in different parts of the nephron showed that low values of linear flow rate and the Reynolds number in the entire interval nephron length match laminar regime of the flow, hence, there is no back mixing environment that favors the correct model of the selected type. It is found that the residence time in the stream exceeds the nephron induction period of calcium oxalate crystallisation, in this connection, to describe the kinetics of the process used experimentally determined constants skorosti.Sravnitelny analysis of the effect of crystallization processes and reabsorption to change the amount of calcium ions in model solution showed that the predominant the process is the reabsorption of calcium ions and its removal from the system. The results confirm the hypothesis that under normal conditions of the organism under low ion concentration sediment-forming mineral aggregates in the kidney is predominant protsessom.Vid concentration profile of the ions Ca^{2+} caused a parallel process water reabsorption, which leads to occurrence of the maxima and minima on the curve. It should be noted that the maximum concentration of calcium ions was obtained for the descending section of the Henle loop, which can serve as confirmation of the hypothesis that organomineral aggregates are formed in this nephron section. It is established that under physiological conditions in normal formation of the solid phase is not a predominant process, but with increasing concentration of sediment-ions, which corresponds to a particular state of the organism, the occurrence of local high supersaturation in the downstream section of Henle’s loop may lead to nucleation of the solid phase and further growth in the subsequent departments of the nephron.

BIOMIMETIC SYNTHESIS, STRUCTURE AND PROPERTIES OF Sr-KGA IN THE PROTEIN MATRIX OF GELATINE

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Modern materials used in orthopedics and traumatology, as possible should mimic natural tissues of the body. Therefore, it is extremely desirable process is inclusion in structure calcium phosphate of ions contained in the biological fluids. Usage methods for the preparation of biomimetic calcium phosphate from model solutions of body fluids (SBF, simulated body fluid), saliva (saliva) and plaque fluid (plaque fluid). Biomimetic method of deposition is phosphate from body fluids prototypes. However, the processes crystallization of calcium phosphate in the multicomponent solution modeling a human ionic composition of biological fluids differ significantly affect the synthesis of resulting products are and their structural and morphological characteristics. This paper presents the method of synthesis Sr- carbonate hydroxyapatite (Sr-KGA) in protein matrix of gelatine from human synovial fluid. In this study, the gelatine introduced to the Sr-KGA system to prepare the gelatine /Sr–KGA composites. The testing and evaluation of its performance were conducted. It was found that the composite has structural characteristics of natural bone, is a quite promising substitute material for bone tissue. In this study, the phase identification of the composites was performed on an D8 Advance ray diffractometer using a Cu-Ka radiation $\lambda = 1.54056$ Å, 40 kV and 35 mA). FT-IR spectra of the samples were collected using a IRPrestige–21 “Shimadzu” spectrometer at room temperature, measured for powder specimens (2.0 mg) diluted with KBr powder (100 mg, spectroscopic grade) and the mixture was pressed into a disk for spectrum recording. The spectra were collected in 36 scans at a resolution of 4 cm-1 from 4000 cm^{-1} to 500 cm^{-1}. The microstructure of the composites was studied using JSM-6390 LV JEOL, scanning electron microscope. On XRD of the samples is evident that four intense peaks of crystal phases at 25.9°, 32°, 39.7° and 49.5° (2θ), which are assigned to (002), (211), (310) and (213) of crystalline carbonate-Sr-hydroxylapatite, respectively. The results infrared spectroscopy of samples the characteristic bands of hydroxyapatite were determined at 3420 cm^{-1}or 3430 cm^{-1} (structural OH^- ions, stretching and vibration mode); 1040 cm^{-}1or 1035 cm^{-1} (1000–1100 cm^{-1}, PO_4 bend ν_3); 960 cm^{-1}, 962 cm^{-1} (PO_4 bend ν_1); 604 cm^{-1}, 603 cm^{-1}, 602 cm^{-1} and 565 cm^{-1}, 564 cm^{-1}, 563 cm^{-1} (550–650 cm^{-1}, PO_4 bend ν_4).

The morphology of the samples was examined with JSM-6390 LV. Homogeny morphology is formed in these composites and smooth micro-scale tiny particles are formed. In comparison with Sr-KGA sample the surface of gelatine /Sr−KGA is not smooth enough.

Conclusion

SEM and XRD study shows inorganic phase, low crystallinity carbonate hydroxylapatite, uniformly dispersed in organic phase. The bioresorption studies and mechanical test show that the material has good biocompatibility, and is a potential bone repair material.

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STUDY OF METAL CO-PRECIPITATION WITH CALCITE IN THE PRESENCE/ABSENCE OF BIOPOLYMER

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Processes of calcite dissolution-precipitation play an important role in many natural systems, mostly regulating the mobility of anthropogenic toxic metals. The influence of calcite precipitation rate on the incorporation of microelements has been studied on many systems (e.g. Tesoriero and Pankow, 1996; Lorens, 1981). However, neither the effect of metal and biopolymer incorporation on the calcite precipitation rate nor the simultaneous co-precipitation of metals and biopolymers have not practically been studied. In our previous studies (Lakshtanov et al., 2015, Karaseva et al., 2018), precipitation of calcite in the presence of biopolymers (alginate and polyaspartate) was studied. It was shown that both polymers inhibit calcite growth. Inhibition is stronger at higher concentration and lower supersaturation. In the present work, we studied the cross-coupling between calcite precipitation rate and incorporation of metal ions (Cd^{2+} and Sr^{2+}) both with and without of dissolved biopolymer polyaspartate (pAsp).

Calcite precipitation rate in the presence of metal ions and biopolymer was measured using the constant-composition method (pH-start titration system), described elsewhere (Lakshtanov et al., 2011). By this method, we can maintain a constant supersaturation in the solution. The experiments were performed at 25 °C in a double walled glass vessel with a constant overhead stirring for supersaturations corresponding to Ca^{2+} concentrations from 1.5 to 2.25 mM, at pH =8.5.

Distribution coefficients, D_{Me}, for Cd^{2+} and Sr^{2+} were determined at the different calcite growth rates.

$$D_{\mathrm{Me}} = \frac{X_{\mathrm{MeCO_3}} / [\mathrm{Me}^{2+}]}{X_{\mathrm{CaCO_3}} / [\mathrm{Ca}^{2+}]},$$

where X_{MeCO3} и X_{CaCO3} are the mole fractions of $MeCO_3$ and $CaCO_3$ in the solid, $[Me^{2+}]$ and $[Ca^{2+}]$ are aqueous activities.

Our results show that D_{Sr} are 3 orders of magnitude lower than D_{Cd}. The structural similarity of otavite and calcite promotes a high degree of incorporation of cadmium into calcite. In the concentration range investigated (0.25–0.5 mg/L), pAsp inhibits calcite growth and decreases metal incorporation into calcite. The distribution coefficients of Cd and Sr decrease by 2–4 and 5–10 times, respectively. Effect of Sr on calcite precipitation rate is negligible due to its weak incorporation into calcite. In contrast, surface precipitation of cadmium carbonate on calcite decreases calcite growth rate.

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SYNTHESIS OF HYDROXYAPATITES FROM Ti-CONTAINING SOLUTIONS AND THEIR PHOTOCATALYTIC PROPERTIES

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According to a number of researchers Ti-containing hydroxyapatites have photocatalytic activity comparable to activity of anatase. Mechanism of entry of titanium ions into apatite is almost unexplored and nature of this activity remains controversial. In the work presented hydroxyapatites were synthesized from solutions containing $TiCl_3$ (Ti/Ca = 0–0.06, pH = 8–9, T=90 °C). 3 series of apatites were synthesized: 1st series had Ti/Ca in solution 0,005–0,060 and was made by fast precipitation; 2nd series had Ti/Ca in solution 0,002–0,009 and was made by fast precipitation as well; 3rd series had Ti/Ca in solution 0,020–0,060 and was made by slow precipitation. Synthesized precipitates were studied with a wide set of methods (X-ray analysis, Raman spectroscopy, EDX analysis, diffuse reflection spectroscopy) in order to confirm that precipitates are monophasic and make sure that titanium ions occurred into apatite.

X-ray analysis confirmed that hydroxyapatite was formed in all 3 series of precipitates. Any other phases weren't detected. We obtained significant changes in lattice parameters relatively pure hydroxyapatite: increase of a and reduction of c. We made an assumption of possible nature of this effect.

Raman spectroscopy detected anatase in all samples of 1st and 2nd series, and in samples of 3rd series with Ti/Ca =0,060. The anatase had crystalline size less than 6–7 nm. In 3rd series of samples anatase was not detected in samples with Ti/Ca < 0,06.

EDX analysis detected anatase in all synthesized samples. It also showed that titanium ions are spread irregularly, and there are many areas that don't contain titanium ions at all.

Diffuse reflection spectroscopy showed that spectra of hydroxyapatite changes its shape and becomes more similar to anatase spectra with increase of Ti/Ca in solution. Also band gap energy of samples was estimated by Tauc method using Kubelka-Munk transformation of experimental diffuse reflectance spectra R(λ). Band gap energy Eg of Ti-modified apatites (3,7–3.3 eV) occurred to be less than band gap energy of pure hydroapatite (Eg = 4.8 eV).

So, the investigation showed that synthesis of hydroxyapatites from Ti-containing solution causes red shift of their absorption edge, which could make them promising photocatalysts. However, we failed to synthesize monophasic samples, and the detected effect partially or completely associated with anatase, which forms in process of synthesis.

The research was supported by RFBR grant № 18–29–12114 and following resource centers of SPBU Research park:

Centre for Geo-Environmental Research and Modelling (GEOMODEL)
Centre for X-ray Diffraction Studies
Nanophotonics Centre
Centre for Optical and Laser Matetials Research
Centre for Microscopy and Microanalysis.

INFLUENCE OF BIOLEACHING ON SURFACE ACIDITY OF SHUNGITE ROCKS

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Shungite rocks are ancient Precambrian rocks containing shungite–carbonaceous matter and mineral components present in the form of micro–and nano–crystals, as well as layers and clusters that intercalate carbon. In the process of its transformation shungite rocks have undergone numerous transformations, and are carriers of a variety of fossilized biomorphs. Recently, however, functioning bacteria have been found in some shungite rocks that can effectively decompose sulfides. The use of such bacteria makes it possible not only to remove undesirable impurities harmful to a number of industries, but also to change the properties of rocks and carbonaceous matter at low operating costs with environmental safety.

One of the main parameters of carbon materials as sorbents is the content of functional groups of acidic and basic character, which can be determined by adsorption of dyes methylene blue (MB) and methanyl yellow (MY). It was previously shown that the bacteria found not only remove sulfides, but also change the structural state of carbon and its electrical conductivity, that may be associated with the extraction of carbon interlayer and cluster impurities. Removal of impurities can lead to the appearance of free bonds and change the content of the functional groups of acid and basic character.

To study the effect of bioleaching on the surface properties was selected shungite rocks with the same carbon content (47–48%) and different composition of rock-forming minerals. For all species under the influence of bacteria there is a different change in the sorption of MB and MY both in relation to the raw rocks and to the control samples aged in water without bacteria under the same conditions. In parallel, water analysis using bacteria and without them was carried out with using of ICP MS (inductively coupled plasma mass spectrometry). It is shown that for all species in the presence of bacteria more intensive leaching of Al, P, Ti, V, Cr, Fe, Ni, Cu, Zn, Ga, Ge and other elements occur (see in the table leaching of Fe, for example).

Table. Adsorption of MB and MY by shungite rocks with/without bacteria, and the corresponding leaching of iron.

Traits	Shungite rocks								
	Karnavolok			Maksovo			Podsosonje		
	Raw	Water	Germ	Raw	Water	Germ	Raw	Water	Germ
pH	5.7	5.4	5.4	3.5	2.7	2.4	4.5	2.9	2.6
MB mg/g	23.2	23.8	25.1	10.7	10.8	11.1	10.3	8.4	11.3
MY mg/g	12.8	11.0	9.9	8.0	4.5	5.7	8.1	6.3	6.5
Fe mcg/l	-	33	69	-	34210	49800	-	34100	49700

The work is performed in the framework of the PFNI GAN research of IG KarRC RAS and RFBR (17–05–01160).

SOLUBILITY OF HYDROXYAPATITE AS A FUNCTION OF SOLUTION COMPOSITION (EXPERIMENT AND MODELLING)

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The solubility of hydroxyapatite has been the subject of extensive investigations for several decades. Initially, the interest in this topic was caused by the need for study of the impact of external factors on dental enamel and the need for the development of dental materials and means of protecting the enamel, so solubility of hydroxyapatite was studied under acid conditions. Hydroxyapatite is a biocompatible substance, so in recent years, a huge number of works has been published dedicated to the development of artificial implants based on it. The phenomena of calcification of soft tissues also attract a lot of attention recently. To date, many works on the solubility of hydroxyapatite in water were published, but these data are poorly fit together. The difficulties have been attributed to factors such as incongruent dissolution. Difficulties of study of hydroxyapatite solubility are caused by long duration of setting chemical and phase equilibria and extremely low solubility. Study of influence of electrolyte and protein composition of body fluids on the solubility of hydroxyapatite to date has not been carried out. Low solubility of hydroxyapatite complicates the study of phase equilibria, because even a small sampling can shift the equilibrium in the system. In this regard, it is important to provide non-destructive analysis of the composition of a solution that is in contact with hydroxyapatite. Such analysis is a direct ionometry with membrane electrode selective to calcium ions. The use of calcium ion-selective electrode allows measuring the composition of the solution in a continuous manner in time directly in the cell without sampling. This method has an important additional advantage that the signal of the sensor depends on the activity rather than the concentration of calcium ions in solution. It is the activity rather than the concentration that determines the heterogeneous equilibria in solution.

Main goal of the present work was to get reliable data on the solubility of hydroxyapatite as a function of the solution composition. The obtained data demonstrate that that the concentration of calcium ions in solution non-monotonously changes over time: the respective curves contain a maximum. This may be evidence in favor that dissolution of hydroxyapatite is an incongruent process. It was shown that equilibrium can be achieved in three weeks. The logarithm of activity of calcium ions exhibits a direct relation on the logarithm of activity of hydrogen ions.

The lack of reliable experimental data hampered the development of molecular and thermodynamic modelling in these systems. The modelling of the chemical equilibria in solution that served as a prototype of the blood plasma with application to calcification of the tissues is performed in this study. The concentrations of molecular–ionic forms containing calcium and hydrogen cations and phosphate anions in the range of ionized-calcium and total phosphorus concentrations from 0.5 to 3.0 mM, and at the solution pH of 4.0–8.0 were calculated. The activities of the ionized species were described in approach to the Debye–Huckel theory. The full set of the equilibria taking into consideration the dissociation of water, phosphoric acid, and formation of both inert and ionic calcium phosphates was considered.

The study was supported by the Russian Foundation for Basic Research (Grant No. 18–29–12114).

THE FORMATION OF CALCIUM AND MAGNESIUM PHOSPHATES OF THE RENAL STONES DEPENDING ON THE COMPOSITION OF THE CRYSTALLIZATION MEDIUM

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Complicated ecological state in the modern urban environments leads to the increasing of the pathological stones formation diseases, so interest to the causes and mechanisms of their progression persists. Physiological fluid (ie urine) is normally supersaturated towards main inorganic components of the pathological minerals, but they don’t precipitate. That is usually explained by the influence of the amino acids and albumens that inhibit genesis and growth of the crystals, but these amino acids and albumens are presented both in the normal and unhealthy urine Main aim of the present study was to determine conditions of the Ca and Mg phosphates precipitation in the urine model solutions under the crystallization medium variations.

Syntheses were carried out by precipitation: 1 l of the 1 mol/l $CaCl_2$ and NaH_2PO_4 solutions is mixed at the 37°C during 5–20 days. Starting concentrations of the main components could be equal or fixed towards PO_4^{3-} (13 or 33 mmol/l) with concentration of Ca^{2+} varying (1–20 mmol/l). pH values varied in the 5.0–8.5 range. Other inorganic components were added according to the minimal or maximum their concentrations in the normal human urine (mmol/l): Mg^{2+} – 11 and 5.3, $(NH_4)^+$ – 24.6 and 13.1, K^+ – 102 and 21.7, Na^+ – 73–60, SO_4^{2-} – 69 and 21.7, Cl^- – 80–67, CO_3^{2-} – 33. Precipitate was filtered, washed with distilled water and dried at the 22–25°C. Morphology of the crystals was studied by the light microscopy, phase composition was determined by the XRD, chemical composition of the monophase samples was analyzed by the EDX analysis.

Three calcium phosphates were synthesized in the system without other components: brushite (DCPD $CaHPO_4x2H_2O$), octacalcium phosphate (OCP $Ca_8(HPO_4)_2(PO_4)_4x5H_2O$) and apatite ($Ca_{10}(PO_4)_6(OH)_2$). In the system containing other components with concentrations typical for the minimal values of the healthy human urine DCPD, OCP, whitlockite ($Ca_9Mg(HPO_4)(PO_4)_6$) and small amounts of apatite were found. In the systems with maximum values of the non-main components only DCPD and struvite ($(MgNH_4)PO_4$ x $6H_2O$) were found. Different Ca phosphates crystallize at different starting values of the solution pH. In the system with only Ca and phosphate ions DCPD crystallizes at the pH range of 5.0–6.5; OCP crystallizes at the pH range of 6.3–7.2; apatite crystallizes at the pH values higher than 7.0. Whitlockite crystallizes instead of apatite in the system with minimal amounts of other elements. Struvite crystallizes instead of apatite in the system with maximal amounts of other elements, at the pH values higher than 7.2. Struvite crystallizes in the system with the maximal Mg concentration only (11 mmol/l), while whitlockite crystallizes in the system with minimal Mg concentration (5.3 mmol/l). Ca phosphates solubility decreases with the increasing of the final pH value in the all systems. DCPD solubility changes from 20 to 4–2 mmol/l at the pH values 5.0–6.5. OCP solubility equals 1.7–0.3 mmol/l, apatite solubility is about 0.2–0.1 mmol/l, whitlockite solubility is 1.5–0.5 mmol/l, struvite solubility is about 7.0–5.5 mmol/l. pH value during the crystallization process changes alongside with the decreasing of the main components concentrations (change of the pH value can reach 1.0), so that two or even three phases of Ca phosphates can be presented in the precipitate.

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CARBONATE DEPOSITION BY ACTINOMYCETES *IN VITRO*

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One of the debatable questions in lithology is the process of formation of carbonate deposits in nature. Thus the aim of our experimental work was the bacterial production of carbonates *in vitro*. Calcite and low-magnesium calcite were obtained by the depositional activity of bacteria from the group of pseudomonas as a result of our earlier experiments. When XRD investigation of the new-formed calcite the presence of numerous weak reflections both of magnesium calcite with $d/n_{104} = 2.94Å$ and magnesite were detetermined at the diffraction patterns of gelled samples (culture 1–2a). With increasing of the concentration of $MgSO_4$ as magnesium source up to 2.42 g/l the presence of small amounts of magnesium calcite (or dolomite) with $d/n_{104} = 2.89Å$ and calcium magnesite with $d/n_{104} = 2.79Å$ was determined besides of low magnesium calcite. However, during the repeated XRD investigation of the sample reflections of high-magnesium carbonates were absent on the diffraction patterns. We could to solve the problem during examination of samples by scanning electron microscope SEM (JSM-6390LV JEOL, carbon deposition) and enego-dispersive spectroscopy EDS (Inca Energy 450)

Thus in the samples from the bottom of Petri dishes the spherical formations in size up to 50 μm were observed and considered to be an interlacing of mineralized filamentous covers of microorganisms. According to the results of EDS the fossils are composed of high-magnesium calcium carbonate and belong to the group of actinomycetes.

The mycelium covers were mineralized. In places of accumulation (spherical formations) it was enough of crystalline substance for determination by XRD analysis. However under the influence of X-rays these fragile structures were disintegrated and dissipated. So the newly formed material was not sufficient for the sensitivity threshold of XRD device.

This year the aim of our work was to determine and study the revealed actinomycetes as well as to obtain of crystalline calcium carbonate with their help. Cultivation was carried out on the nutrient medium Variant 3, (modified), g/l: KNO_3–0.5; $Na_2HPO_4x12H_2O$ – 0.25; Ca succinate – 5.0 (succinic acid – 3.54; $CaCl_2x2H_2O$ – 3.3); Oxoid agar – 15.0; pH 7.1. After 30 days of cultivation the samples were dried naturally and prepared for the SEM and EDS investigations. Now such cultures of actinomycetes have been isolated for the work: Streptomyces xanthophaeus IB St L4; Str. atroolivaceus IB StAK4–1; Str. atroolivaceus IB St L6–3; Str. avidinii IB St L1–1; IB StAK3–2; BAM IB StBO77; IB StHA1–1. Formation of $CaCO_3$ was distinguished in all Petri dishes. There are hemispherical or rarely spherical formations corresponded to metabolite drops in the peripheral part of the colony. Sometimes the cavities are filled with calcium carbonate crystals. The experiments are expected to continue with the addition to the nutrient medium of a source of magnesium in the ratio of Ca to Mg: 1: 1, 1: 2, 1: 3.

APPLICATION OF THE LUMINESCENT LABELS FOR THE STUDYING OF THE INTERACTION BETWEEN BONE TISSUE AND APATITE IMPLANT IN VIVO

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Apatites doped with rare-earth elements (REE) demonstrate luminescent properties, so they can be utilized for the non-destructive research of the implants in the living organisms. Among other REEs europium is one of the most prospective because of the high luminescent intensity, composition of the spectrum and antibacterial properties, that are typical for the Eu-doped apatite (Iconaru et. al., 2013). Apatite is one of the most wide-used materials in the medicine, but all the nuances of the interactions between bone tissue and implants are still not clear. Interaction of the apatite implant and the bone tissue *in vivo* was studied in the present work. Eu-doped and control apatite implants were implanted into the proximal section of the rabbit tibia (n=9) synthesized according to the previously reported method (Nikolaev et al 2017). Bone samples were taken out at the 15th, 45th and 90th day. Obtained bones were studied with X-Ray microtomography and photoluminescent methods.

All the data gathered showed that implants hasn't changed much. X-Ray microtomography showed that apatite particles halo doesn't scatter and it's form doesn't depend on the experiment time.

Photoluminescent mapping shows the luminescence of the both apatite and Eu-doped apatite of the implant (Fig. 1), with implant having strict border. That allows to say that apatite implant hasn't changed or recrystallized during 90-day term in the living organism.

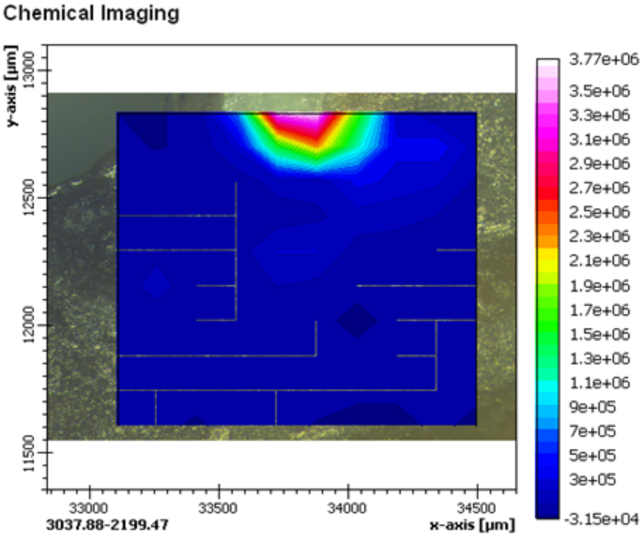

Fig. 1. Photoluminescence of the apatite implant in the rabbit bone. 90 days exposition.

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LITHOBIONTIC COMMUNITIES WITH PREVENTION OF CYANOPROKARIOTES AND THEIR ROLE IN BIOMINERALIZATION PROCESSES

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Cyanoprokaryotes, like the primary oxygen phototrophic microorganisms on Earth, created the initial primary production and carried out oxygenation of the planet. Today, cyanobacteria continue to play a central role in the carbon and nitrogen cycle (Kleinteich et al., 2017). They are considered to be the pioneers of the colonization of mineral substrata, and their development leads to weathering of minerals and rocks (Hauer, 2007). In contrast to biodegradation, the important role of cyanoprokaryotes is the biomineralization of carbonate in fresh water, including the accumulation of travertine or limestone tuff. About 80% of the earth's crust minerals are biominerals (Barskov, 2002). The biomineralization process is an environmentally important landscape-forming process that creates new environments with different microenvironments, which in turn support a variety of specialized biological communities (Golubić et al., 2008). Involvement of cyanobacteria in deposition of carbonate in freshwater including the build-up of travertine or calcareous tufa occurs worldwide (Pentecost 2005). Carbonate precipitation by bacteria is a complex process involving metabolic pathways associated with photosynthesis, nitrogen and sulfur cycles, and stoichiometric interactions between positively charged Ca^{2+} ions and the negatively charged bacterial cell wall (Zamarreno et al, 2009).

We have described the diversity of cyanoprokaryotes in places of modern travertine formation and have studied the minerals composition and species of microorganisms of travertines and alms from the water systems of the south of the Leningrad Region (r. Rivkuzi, Gatchina geysers, reservoirs in Pushkin's and Peterhof parks). It is shown that the mineral composition of carbonate deposits is represented by calcite and aragonite. The appearance of aragonite in the sediment is associated with an increased content of magnesium in the solution and, as a consequence, in the carbonate sediment (MgO> 1 wt.%), and also a calmer hydrodynamic conditions. Cyanobacteria (29 taxa), diatoms (6 taxa) and green algae (3 taxa) were found. The most widely distributed cyanobacterial species is the genus *Phormidium*. This genus, together with other (mainly filamentous cyanobacteria, mostly *Leptolyngbya* spp.) forms the basis of the studied biofilms. The special role of *Dichothrix baueriana* for the crystallization of calcite was first established.

The work was carried out using the equipment of the resource centers of St. Petersburg State University (RC Microscopy and Microanalysis, RC «Geomodel», RC X-ray Diffraction Studies) and was supported by the Russian Foundation for Basic Research (project No. 16–05–00986).

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BIOMINERALIZATION OF CALCIUM PHOSPHATE USING BIOMIMETIC METHOD

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Biomineralization is the process by which the living organisms produce minerals for the development of their mineralized tissue. Various biominerals such as silicates in algae and diatoms, carbonates in invertebrates and calcium phosphate and carbonates in vertebrates have been identified in living organisms. In human beings biomineralization results in the development of hard tissues such as bone and dentine. Biomineralization of bone is orchestrated by several bone cells and proteins. Bone mineral is grown on the orderly packed self-assembled collagen fibril with their c-axes aligned with long axes of collagen fibril. Several methods have been practised in vitro to mimic the biomineralization process. For mimicking biomineralization, SBF solution having the ionic concentration and composition approximately equal to that of human blood plasma has been developed to mimic the biomineralization. Among the different SBF solutions, m-SBF has been comparatively stable and useful in the formation of bone-like mineral. The nucleation of biomineral using SBF is influenced by the presence of the functional groups on the surface of the material, such as carboxyl (–COOH), phosphate (–H_2PO_4) and silanol (–SiOH) groups. The carboxyl group act as the nucleating site for the growth of apatite crystal. Here we have used tannic acid as the source of carboxyl group (–COOH) which act as the nucleating site for the growth and synthesis of biomineral.

Scanning Electron Microscopy (SEM), Energy Dispersive X-ray spectroscopy (EDX), X-Ray Diffraction analysis (XRD) and Fourier-transform infrared spectroscopy (FTIR) reveals the mineralization of calcium phosphate using tannic acid. Thus the synthesized biomineral exhibited better stability and haemocompatibility and hence can be used as a biomineral for assisting hard tissue repair.

Keywords: Biomineralization, bone mineral, collagen fibril, tannic acid.

THE ROLE OF AMINO ACIDS IN THE METABOLISM OF CALCIUM IONS

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Calcium ions play a key role in the alive organisms. They take part in muscle contraction, increase the permeability of the cell membrane for the potassium ions, affect on the sodium conductivity of cells, on the work of ion pumps, promote the secretion of the hormones, participate in the cascade mechanism of blood coagulation. Moreover, they serve as important intermediaries in intracellular communication of signals. The free concentration of Ca^{2+} in the cells depends on a number of factors, in particular, on their complexation with proteinogenic amino acids. The disruption of the regulation of these compounds provokes the appearance of pathological changes in organism. They can be cause of the emergence of about 150 diseases. This phenomenon is associated with a number of factors of exogenous and endogenous nature, which are actively manifesting itself in the last decade [1, 2]. That is why the purpose of this study is to find out the key characteristics of complexation between Ca^{2+} and ——— of proteinogenic amino acids. As a method of analysis, potentiometric E-titration is chosen. The object of study is 14 proteinogenic amino acids, different from each other by the structure and by the functional groups. After the obtaining and processing the integral E-curves (Fig. 1) of the potentiometric titration, the most important characteristics of complexation – stability constants, enthalpy, entropy, Gibbs energy of complexation are obtained. Also, the kinetics of complexation is considered. We have done this by entering a semi-quantitative criterion δ (the higher its value, the more stable the complex is). The data are presented in the Table. 1:

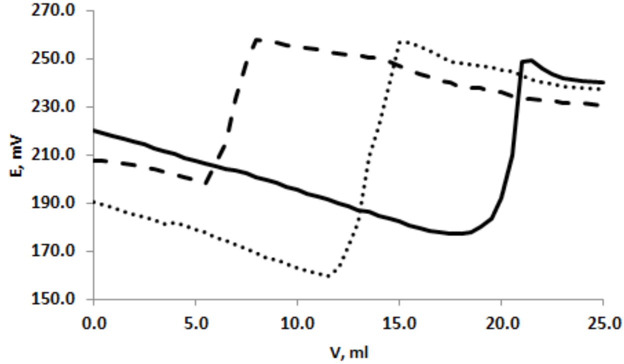

Fig. 1. Integral E-curves: an aqueous mixture of Ca^{2+} and valine – a solid line, an aqueous mixture of Ca^{2+} and methionine – a dashed line, an aqueous mixture of Ca^{2+} and glutamic acid – a dashed line.

Table. 1. The main parameters of the complexation in the system "Ca^{2+} – amino acid»

Amino acid	K_{st}	H^o_{298}, kJ/mole	S^o_{298}, J/mole · K	G^o_{298}, kJ/mole	δ
Met	0,42	-36,8	-123,3	-0,09	2,1
Glu	1,04	-38,4	-124,2	-1,38	2,2
Val	1,74	-35,8	-114,8	-1,55	2,8

Among the investigated complexes, the largest energy effect occurs when Ca^{2+} forms a complexing ions with glutamic acid and valine. This is due to the presence of an additional -COOH group in glutamic acid and to the presence a smaller number of carbon atoms in the carbon skeleton of valine molecules. When compared the formation and destruction of the complexes, the most stable are complexes with the valine, the most labile – with the methionine.

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BIOGENIC–ABIOGENIC SYSTEMS BASED ON MICROALGAE CELLS IMMOBILIZED IN A MATRIX.

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Monitoring of aquatic environments requires in real time obtained information, long before the appearance of visible signs of pollution. In recent years, organisms, which have high sensitivity to adverse factors, are widely studied as bio-indicators for water monitoring. The important objects for environmental monitoring of water are natural bio-indicators – living objects, such as microalgae, capable of responding to changes in the condition their habitat. A promising method of measuring the microalgae concentration and their living conditions is the analysis of fluorescence of pigments; primarily it is laser-induced fluorescence (LIF) of chlorophyll-a.

Recently, variants of algal biosensors have been developed for the detection of pesticides, volatile organic compounds and heavy metals, based on the analysis of the metabolic activity of a living organism.

However, it should be noted that the use of living cells in a free state not been widely used to create chemosensors, because the state of the environment significantly affects the metabolism and cell cycle of development and makes it difficult to adequate interpretation of the results. Stability of the characteristics of microorganisms when used for analytical purposes can be achieved by immobilization of cells in the matrix, ensuring their retention and effective functioning for a long time.

There are systems in which, as matrices were used porous glass [1], silica gel [2], filter paper coated by Ca-alginate gel [3], cryogel of polyvinyl alcohol [4]. At the same time, the process of searching some matrices that are inert to biological objects does not lose relevance, and a study of the effect of microalgae immobilization on their fluorescent characteristics is an important task both in studying the properties of immobilized algae and in creating sensors for the ecological state of water bodies.

The report presents the results of creation of organo-inorganic systems by biomimetic immobilization of microalgae cultures of marine phytoplankton into inorganic matrices with preservation of their optical activity. These systems have optical transparency and the ability of laser-induced fluorescence. It is shown that the immobilization of microalgae increases their stability and reduces the effect of temperature on the LIF signal, primarily the temperatures characteristic of their habitat. The report discusses perspectives of biogenic–abiogenic systems applying for detect to the presence in water of some water pollutants.

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EFFECTS OF SO_2 & HF EMISSIONS OF AN ALUMINIUM SMELTER ON THE GYPSUM & FLUORITE FORMATION IN STOMATA OF URBAN TREE LEAVES

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Aluminum industries are a source of polluting air by the main acid forming component such as sulfur dioxide and hydrogen fluoride.

Gaseous sulfur and fluorine compounds can be transported for considerable distances from the source of emissions and precipitate with atmospherically condensation on plants. The aim of our research is to determine poplar leaves reaction on the emissions of acid forming components from the aluminum industries by scanning electron microscopy.

Biological materials of study are poplar leaves *(Populus Balsamifera L.).* Samples of poplar leaves were collected in September 2015 in the influence areas of the Novokuznetsk aluminum plant. Sampling step was 2 × 2 km. Plant material was dried and was researched in the International Scientific and Educational Center "Uranium Geology" at the School of Earth Sciences and Engineering at the Tomsk Polytechnic University by scanning electron microscopy Bruker XFlash 4010. Samples were inspected in low vacuum, back-scattered electrons mode by X-ray spectral analysis.

In stomata of poplar leaves we were detected newly formed mineral phases of gypsum, fluorite by SEM. In addition, we found calcite in conductive tissue of leaves. Probably gypsum was formed in a result of the weak sulfuric acid interaction with ions. These ions contain in excess in transpiration moisture of leaves stomata. Fluorite was formed in a result of the aqueous caustic hydrogen fluoride interaction with calcium cation. Calcite can be a result of calcium hydro carbonate precipitate at leaf's drying time. All cells of phloem sieve tubes in dry poplar leaf were filled with phytogenic calcium. Thus, there is biogeochemical calcite barrier on the surface leaves. Different chemical reactions neutralize toxic SO_2 and HF with inert minerals forming. These minerals are gypsum and fluorite.

The main part in these processes is physiologically active calcium. It detoxifies acid forming component via transforming to stable, inactive mineral complexes in the stomatal apparatus of the leaves. Poplar leaves have great importance functions. They can clean and improve environment. They are a natural filter of atmospheric air which can trap aerosol contamination in the aluminum industries areas locating.

THE FORMATION OF CALCIUM OXALATE HYDRATES BY THE INTERACTION BETWEEN MICROORGANISMS AND APATITE ON THE BASE OF FIELD AND LABORATORY RESEARCH

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Dissolution and tunneling of ivory was observed on the surface of walrus tusks (Pinzari et al, 2013). Authors supposed the possibility of formation of calcium oxalates on the surface of ivory under the influence of microorganisms.

In the thalli of crustose lichens developing on various rocks, crystals of calcium oxalates have been found by many researchers. (Wadsten, Moberg, 1988, Gerhrmann et al, 1988).

In our research the calcium oxalates (whewellite and weddellite) in the thalli of the crustose lichens Myriolecis dispersa (Pers.) Śliwa et al. and Myriolecis hagenii (Ach.) Śliwa et al., which develop on the surface of quartz dolomite sandstone shells (the Kingisepp phosphorite deposit, Leningrad region), were detected by using SEM, XRD and EDX analysis.

A series of biomimetic experiments were carried out to check this assumption and study the regularities of transformation of apatite under the influence of microscopic fungi. The present work continues our research on the participation of microorganisms in mineral formation.

The biomimetic experiments aimed on researching the effects of the influence of microfungi *Aspergillus niger* (active producer of organic acids) on fragment of mammoth tooth (apatite-Ca(OH)-organic composite), piece of single crystal abiogenic apatite-Ca(F) (Sludyanka deposit, Russia), powder of synthetically precipitated apatite-Ca(OH), carbonated apatite-(CaOH), apatite-Ca(F) and carbonated apatite-(CaF) were carried out.

Experiments were held at room temperature in liquid Czapek-Dox medium. In addition the experiments were done with a lack of nutrients in the moist chamber (in conditions very close to nature). The exposures varied from 7 to 120 days. The synthetic products were studied under scanning electron microscope, as well as by EDX analysis and X Ray powder diffraction methods.

All experiments showed the formation of calcium oxalates (weddellite (Ca(C2O4)2H2O) and whewellite (Ca(C2O4)H2O). The transformation of “hydroxyapatite–oxalates” is more intense than “fluorapatite-oxalates”, which is well explained by their solubility ratio. The transformation of fluorapatite powder is more intense than single crystal fluorapatite. The morphology of dipyramidal-prismatic tetragonal weddellite crystals changed during experiments. The prism face was gradually growing (faster on carbonated apatite- (CaOH) slower on the mammoth tooth), which can be explained by the increase of (C2O4)2- and Ca2+ ions in the crystallization medium. After that with the aging of cultures the prism faces disappear (faster on the surface of mammoth tooth). The formed weddellite was unstable and lost water transforming to whewellite which was detected as rose like intergrowths or as packs of pseudohexagonal crystals.

The researches were carried out in the research resource centers of St. Petersburg State University: «Molecular and cell technologies», « X-ray Diffraction Studies», «Resource Center Microscopy and Microanalysis» The study was supported by Russian Foundation for Basic Research (project 13–05–00815-a, project 16–05–00986-a) and also Saint-Petersburg State University for research grants 1.37.151.2014.

Section 4
Biomineralogy and organic mineralogy

THERMAL PROPERTIES AND INFRA-RED SPECTROMETRY OF AMBER AND AMBER-LIKE FOSSIL RESINS IN NORTHERN EURASIA

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The application of physical and physicochemical methods of analyzing the composition of amorphous organic minerals with polymer structure, including fossil resins, allows to recommend derivatography at low heating rates (about 1 deg min-1) and infra-red spectrometry (frequency range 2000–400 cm-1) for their identification.

DTA curves of the samples from the Baltic region and Ukraine are characterized by a wide and relatively weak endoeffect with a maximum within the range 98–130 °C (160–185 °C for Belarussian specimens). With increasing temperature, this effect gives way to a relatively strong exothermic rise, which is followed by a sharp endothermic doublet within the temperature range 311–330 °C (320–340 °C for Belarussian samples). Two wide exothermic effects within the ranges 350–365 and 478–508 °C (355–370 and 490–520 °C for Belarussian samples) are separated by flat endoeffect with a maximum at 400–425 °C (395–420 °C for Belarussian samples). Further heating results in melting of the polymer as recorded in the thermogram by the endothermic effect at 540–565 °C (575–605 °C for Belarussian samples).

The DTA curves of Siberian fossil resins are similar to the general configuration and position of the main thermal effects. Some discrepancies arise as a wide, low-temperature exoeffect probably related to the partial molecular reorganization at a maximum temperature of about 150 °C for transparent varieties of Siberian fossil resins and 190 °C for translucent resins. The maximum of the second exoeffect at ~290 °C that indicates oxidation of resins occupies the same position in both thermograms, but is much wider for opaque varieties, where oxidation usually starts at 265 °C in comparison to 285 °C for transparent resins. The melting of both transparent and opaque fossil resins begins at 330–340 °C and is recorded in sharp endoeffects. The melting is accompanied by oxidation of melting products, as is confirmed by the spectrum of effects in the interval 330–385 °C, which is especially complex in the case of transparent varieties. Thermograms of Siberian fossil resins are similar to thermograms of those from the Far East; in particular, both demonstrate a complex set of effects in the range 300–400 °C.

Temperatures of softening *(T_s)* and flow *(T_f)* are more informative for identification of fossil resins than the melting temperature. T_s of Belarussian resins is 120–180 °C and T_s of Baltic amber is 130–170 °C, while T_f of Belarussian and Baltic resins are 370–420 °C and 370–410 °C, respectively. According to these distinguishing features, all samples are similar and belong to the group of thermally stable and viscous resins. On the contrary, T_s of Siberian and Far East resins fall within the intervals 110–140 and 120–180 °C and T_f are 150–190 and 160–250 °C. Thus, these samples are thermally unstable and belong to the group of brittle resins. The data obtained for Sakhalin resins are markedly different: T_s is 180–230 °C and T_f is 380–400 °C, so that these samples belong to the group of viscous resins.

The IR spectra of amber samples from Belarus, the Baltic region, and Ukraine are similar in the frequency range 2000–400 cm^{-1}. They consist of the same absorption bands and differ only in intensity. Interpretation of IR spectra indicates the presence of carboxyl, peroxide, hydroxyl, and complex ester functional groups as well as single and double bonds in the structure of the studied fossil resin varieties. Hence, these resins may be identified as succinite. According to the IR spectra, fossil resins from Siberia fit gedanite from the Baltic region. Two retinite varieties of the so-called Yantardakh and Begichevo types are distinguished by IR spectra among the resin samples from the Khatanga Basin. Fossil resins from the Far East correspond to retinite, which is widespread in Primorye, and rumanite found on the southeastern shore of Sakhalin.

LIMITS OF SOLID SOLUTIONS AND CRYSTAL MORPHOLOGY IN THE SYSTEM OF L–VALINE – L–LEUCINE ENANTIOMERS

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Proteinogenic amino acids are building blocks of proteins and, consequently, they are sufficiently abundant in the biosphere. In contrast to proteins, amino acids survive the death of their hosting living cells intact and, eventually, become a part of the geosphere. Some amino acids occurring in the fossils (bones, teeth, mollusk shells, etc.) are used for dating of the hosting sedimentary rocks [1]. The fact that almost all the proteinogenic amino acids (19 out of 20) are chiral compounds, i.e. their molecules can exist as enantiomers (mirror-related optically active stereoisomers), is crucial for many applications, especially those concerned pharmaceutical industry [2]. Enantiomers can behave differently in chiral (e.g. biochemical) media. One of the enantiomers can have therapeutic activity, while the other can be inert or even can produce an adverse effect [3]. Bulk chemical syntheses produce equal amounts of both enantiomers. So there is an essential task of chiral resolution. The task is insolvable without deep understanding of phase relationships in enantiomeric systems.

Crystal chemistry and phase equilibria were studied in the model system of levorotary enantiomers of different amino acids L-valine — L-leucine. Powder XRD and optical microscopy investigation methods were used to study initial reactants (99% purity) of L-valine (L–Val) $C_5H_{11}NO_2$ and L-leucine (L–Leu) $C_6H_{13}NO_2$, as well as 12 samples composed of their mixtures (mol. ratio). The samples were obtained from aqueous solutions via isothermal evaporation method.

It is found that the L–Val — L–Leu system contains limited solid solutions in the vicinity of the system components (ssV and ssL, respectively). It is to be noted that isomorphic capacity of Val (~7.5 mol.%) is higher than that of Leu (~5 mol.%). A non-equimolar discrete compound V_2L (Val: Leu = 2:1) is supposedly discovered as a part of the samples in the compositional range of 55–70 mol.% of Val. In the vicinity of this compound limited solid solutions (ssV_2L) are also formed presumably. Consequently, the system can contain two-phase regions of the following two types: ssV + ssV_2L and ssV_2L + ssL. A non-equimolar discrete compound of this type (2:1) was found earlier in the L-valine — L-isoleucine (V_2I) system by the present authors [4, 5], and the crystal structure of the compound (V_2I) having the above ratio of the constituent amino acids was also determined.

As the composition of the crystals formed in the L–Val — L–Leu system changes, the crystal habitus undergoes transformation from isometrically prismatic (pure L-valine) to needle-shaped (pure L-leucine).

The investigations were performed using equipment of the Resource Centre “Centre for X-ray Diffraction Studies” of SPSU. Financial support was provided by the RFBR (Project: 18–35–00183) and SPSU (Project: 3.10.75.2018).

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MINEROGENESIS ON THE TIMAN MACROPHYTES

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The study of systems of bio-nutrient interaction under continental cold-water conditions is actual due to the wide spread, variety of manifestation, and complexity of biogeosystems, including higher photosynthesizing plants, algae colonies (*Cyanobacteria*, *Charophyceae*, etc.), and microorganisms. Investigations of contemporary mineral formations were carried out on *Charophyceae* from Chermanty and Paras'kin lakes, and on calcified crusts occurring on *Potamogetonáceae* from the Vym River. Areas with hydrobiontolites were identified in the basin of the Vym River (the right tributary of the Vychegda River), within the Timan anteclise. The sulfate-carbonate-terrigenous and carbonate-terrigenous Permian deposits compose the geological structure of the territory. Researches of present mineral phases were carried out at the Centre of collective usage "Geonauka" (IG of Komi SC UB RAS) (Syktyvkar).

The biochemogenic carbonate sedimentation is observed in the region of excess moisture under conditions of moderate cold climate, in fresh and subsaline water of sulfate and hydrocarbonate-sulphate calcium composition (mineralization 0.6–1.7 g/l) and neutral-alkaline conditions (pH 6.9–8.2). In this area, lake water in the basin of the Vym River has an exceeding equilibrium content of HCO_3^- (88–164 mg/l) over CO_2 ($CO_{2\ \text{design value}}$= 0.5–12.64 mg/l), and therefore, segregation of abiogenic (chemogenic) calcite $CaCO_3$ (solid) is possible, providing that calcium content (73–420 mg/l) exceeds the total carbonate alkalinity $2m_{Ca^{2+}} > m_{HCO_3^-} + 2m_{CO_3^{2-}}$. The chemical composition of hydrobiontolites reflects modern carbonate sedimentation: the proportion of CaO in *Charophyceae* is 29–50, on mineral deposits of *Potamogetonáceae* – 68–92 wt.%. Sulfur (SO_3 1.07–1.4 wt.%) is determined in the biomineral formations, which is caused by a considerable sulfate amount in water; the accumulation of amorphous silica (SiO_2 6.0–26 wt.%) is associated with the development of *Diatomeae* on the surface of macrophytes. It has been established that calcite is the main mineral constituent in all the analyzed samples. In the study of macrophytes, intercellular and extracellular carbonatization as incrustations on the outer walls was detected. The SEM study showed that calcite occurs as structureless accumulations among a plenty of *Diatomeae*, druses, and monocrystals. A complex hierarchical structure and morphological peculiarities of the surface of calcite crystals indicate a probable bacterial origin of calcite.

THE STRUCTURE AND COMPOSITION OF THE DOGS ODONTOMA

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Odontoma form is a result of malformation tooth tissues. Odontoma is benign tumors which develop in jaws bone and represents the conglomerate of different tooth tissues. Tumors of the oral cavity are high prevalence for dog (around 99% of total tumors of gastrointestinal tract and 10–15% of total organism tumors). More predisposed to their occurrence males and young animals. Mainly odontomas are located in the field of incisors, canines, premolars of maxilla and mandibular angle.The genetic mutations, trauma and infections are main reasons of etiologic and pathogenetic factors of odontoma formation. In possible the appearance and progress of odontoma is one of these defects. We are studied the pathological lesion of the dog jawbone for diagnostics, classification and determination of possibility formation reasons.

The objects are odontomas in molars M1 area (left and right) of mandibla. Odontomas were removed for medical reasons from young (7 month) male dog of the Black Russian Terrier (BRT) during a period of mixed occlusion. The BRT is a young breed of dog with large amount original breeds in creating history (more than 17). In this regard there is a high risk of genetic defects in dog organism. The samples were scanned by Skyscan 1172. In all cases used conditions are source voltage – 100 kV, source current – 100 μA, Al filter 0.5 mm, pixel size – 4.69 μm, frame averaging – 3, rotation step – 0.4 deg. The morphology of odontoma was studied by SEM TESCAN VEGA 3. The composition of odontoma was determined using a Hitachi S-3400N scanning electron microscope equipped with an Oxford Instruments Energy Dispersive Spectrometer X–Max20.

The size of odontoma is 10–12 mm and the size of its single forming element is varying from 2–3 mm to 7–8 mm. Odontoma consists of chaotic different constituent parts: enamel, dentin, cement, pulp of teeth and fibrous tissue. The hard odontoma is progress from single or few teeth germs. It’s appearing during the period of permanent tooth formation. Soft odontoma consist of low differentiated teeth tissues which typical for growing teeth germs. Perhaps the soft odontoma is early stage of hard odontoma. There are three forms of hard odontoma: simple (full and incomplete), complex (composite and mixed) and cystic. The simple odontoma is caused with malformation of single germ. The complex odontoma is caused with disorder of few teeth germs because it consists from hard tissues on the different progress stages. The simple odontoma is formed by a few chaotic mixed hard tissues, which sufficiently for growth only single teeth. Germs of some tooth which tissues are calcified, high differentiated and chaotic situated are formed the complex odontoma. Complex odontoma there are composite and mixed. Complex composite odontoma including some right formed tooth (odontoids) with pulp in central part, but which have a deformation part. Odontoids (elemental parts of odontoma) are formed of hard tooth tissue. Studied formations are classified as a hard, complex, composite odontomas.

Microtomography investigation shown, that the low part of odontoma is similar in structure of tooth root. The two root canals are bringing together in the apical part. The root part of odontoma was formed by dentin with cement and connective tissues are covered outside. The pulp cavity is cover by predentin. In pulp cavity we can see the elements of pulp. The high part of odontoma (more than 2/3) was formed by chaotic separate parts with different size which are unit by fibrous tissue. Most of them were formed by canine tooth type with pulp cavity in central part. We are observing some elements like unformed parts of enamel and dentin (size is ≤ 1 mm) located at the upper part of odontoma.

The resistances degree of tissues is characterized by the Ca/P coefficient (KCa/P). The results of microprobe analysis are shown that the KCa/P of odontoid for enamel and dentin are 1.56 and 0.80; the KCa/P of odontoma tissues is 1.58 and 1.03 accordingly. The enamel KCa/P of odontoid and odontoma totally is satisfy of normal hard tooth tissues, but the dentin KCa/P is less.

PINEAL GLAND CALCIFICATION IN BLUE FOX (*VULPES LAGOPUS* L., CANIDAE, CARNIVORA, MAMMALIA)

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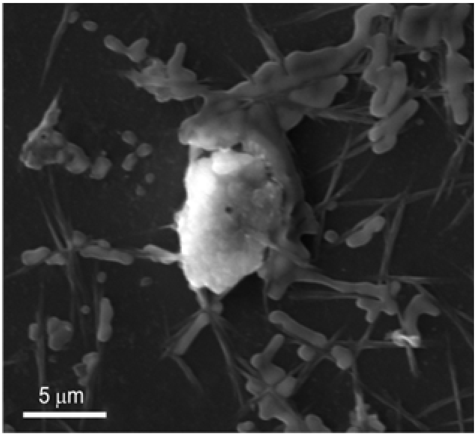
The calcified concretions (*corpora arenaceae*, acervuli, brain sand, etc.) are often found in the pineal gland of mammalian brain. Their morphology, mineral and chemical compositions, in general, are studied in human (Bocchi, Valdre, 1993; Baconnier, Lang, 2004; Kim et al., 2012) and are still a matter of debate. Moreover, the number, structure and distribution of concretions show interspecific differences. The solid-state concrements of pineal gland were studied in juvenile and adult blue foxes (*V. lagopus* L., Canidae, Carnivora, Mammalia) of different ages. Pineal glands were removed immediately after skinning and then fixed by immersion in 10% neutral buffered formalin for subsequent analysis. At light microscopic level the concretions were detected in blue foxes of all studied ages but not in all individuals. Acervuli had been observed in the parenchyma of distal part of the gland, in the capsule surrounding it and in the protruding septae. Morphologically concretions looked like as single deposits with laminar structure or as mulberry-like concrements.

The scanning electron microscopy (SEM) study revealed that the concretions are presented by single grains of hydroxyapatite with the size up to 7 µm (Fig.) or their aggregates with the size up to 25 µm. Noteworthy, that the minerals detected in human pineal concrements are hydroxyapatite (Bocchi, Valdre, 1993) and calcite (Baconnier, Lang, 2004). The aspects concerning the biogenesis of the calcium concretions need to be further investigated.



The study was carried out under state order (project № 0221–2017–0052) using the equipment of the Core Facility of the Karelian Research Centre of the Russian Academy of Sciences and according to EU Directive 2010/63/EU for animal experiments with the special permission of Local Ethic Committee of Institute of Biology.

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Fig. SEM image of calcified concretion in pineal gland of blue fox *V. lagopus* L.

Section 5

Medical geology

ASSESSMENT OF THE CONTRIBUTION OF THE HYDROCHEMICAL PROPERTIES OF THE DRINKING WATER IN THE PREVALENCE OF DISEASES AT THE KOLA NORTH

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The aim of the study is to reveal the contribution of the hydro chemical properties of drinking water in the prevalence of diseases of the population in certain areas of the Kola North. To identify the most significant characteristics of drinking water associated with the prevalence of diseases, 33 water quality indicators were taken into consideration, including: conductivity at 20 °C and control (pure water) at 25 °C (Cond20; Cond25, µS/cm, respectively); NH4 (µgN/l); Ca (mg/l); Mg(mg/l); Na (mg/l); K (mg/l); Alk (µeq /l) -alkalinity of natural waters; SO4(mg/l); NO3(µgN/l); Cl(mg/l); TN(µgN/l); PO4(µgP/l); TP(µg/l); Color; Chemical Oxygen Demand (COD-Mn) (mg/l); Si (µg/l); TAl (µg/l); TFe (µg/l); TCu (µg/l); TNi (µg/l); TCo (µg/l); TZn (µg/l); TMn (µg/l); TSr (µg/l); TPb (µg/l); TCr (µg/l); TCd (µg/l); TAs (µg/l); O2(mgO/l); Suspended solids (mg/l); Dry residue (mg/l). Drinking water samples for hydrochemical analysis were obtained from drinking sources located in the territories of the Murmansk region, including towns the Monchegorsk, the Olenegorsk, the Kovdor, the Lovozero village. The data of the Statistical Digest «Morbidity of the population of the Murmansk region 2006–2010», as well as the data of the Murmansk Regional Medical Information and Analytical Center for 2011–2016 were used in the work. To determine the relationship between the hydro chemical and elemental characteristics of drinking water and the diseases of the population (regardless of the areas where they lived), a factor analysis of the primary data array was carried out. As a result of this analysis, the original variables space was reduced to 4 main factors or «super factors». Well-known heuristics the "Criterion of the Kaiser» and the «Criterion of a stony scree» were used for selection of «super factors». Results of the factor analysis of the initial data using the maximum likelihood method (the way of rotation of the axes the «varimax normalized») have revealed that the first major factor (explaining 31.8% of the total alterability of the variables) includes in its structure two groups of indicators. First group are presented by diseases: congenital malformation in children of 0–14 years old and neoplasm in adults; the second group includes the physical-chemical parameters of drinking water, which most strongly affect the listed diseases – conductivity (Cond20, Cond25), alkalinity (Alk), total phosphate and polyphosphates (TP, PO4,), total strontium (TSr), pH, Si, total plumbum (TPb), Na, SO4, total cadmium (TCd), K. From the structure of the second factor, explaining 20.1% of the total alterability of variables, one can conclude that the diseases of the skin and subcutaneous tissue in adults, diseases manifested in symptoms and indicators of deviations from norm in children of 15–17 years old, congenital malformation in adults, neoplasm in children of 0–14 years old, depended mainly on the content in drinking water of N, Mn, Cu, Ni, Co, Zn and As. The content of Al, Mn, Pb and NH4 in water influences on the prevalence of urolithiasis disease, the diseases of the skin and subcutaneous tissue, congenital malformation in adults, neoplasm in children of 15–17 years old. The relative share of the third major factor in the total pool of variations was 15.3%.The combination of ions Al, Si, NH4, NO3 and Cr were associated with the prevalence of congenital malformation and diseases manifested in symptoms and indicators of deviations from norm in children of 15–17 years old. The share of the fourth major factor in the overall alterability of variables was relatively low – 9.4%. Thus it was revealed that the hydro chemical properties of water and its elemental composition make a significant contribution to prevalence of diseases of the population at the Kola North. The mechanisms of the separate and combined effects of water quality indicators on the human body require further study.

THE ROLE OF FUNDAMENTAL SCIENCE (THERMODYNAMICS, COMPUTER MODELING) IN MEDICAL AND ENVIRONMENTAL STUDIES

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The problem of formation of chemical composition of water under natural or anthropogenic influence attracts scientists all over the world. Chemical composition of water has a major impact on population health (L. I. Elpiner, I. S. Zektser, 1999; A. V. Skal'niy, 2004; T. Moiseenko et al., 2010 and a number of other Russian and foreign researchers). In 1980–1990, a number of scientists established the toxicity of aluminum to the aquatic environment and to humans. As with most metals, the toxicity of aluminum depends on the form it is in the water environment. It was found that the greatest toxicity comes from inorganic monomer aluminum. Among the most toxic forms of it are free (hydrated) ions or aqua complexes $[Al(H_2O)_6]^{3+}$ and hydro complexes $Al(OH)^{2+}$ and $Al(OH)_2^+$ (Linnik, Zhezherya, 2013). In the work of A. V. Skal'niy (2004) lists not only the 15 vital elements and presented their forms, including calcium (Ca^{2+}), iron (Fe^{2+}), copper (Cu^{2+}), phosphate (PO_4^{3-}).

We have selected and analyzed spring water and drinking water of Apatite-Kirovsky district (Murmansk region). We have studied the forms of migration of elements using physical and chemical modeling (PC Selector). Some of the environmental and physiological elements are presented in the table. The analysis of the results shows that only calcium is in the form necessary for a person.

The study was carried out with the financial support of RFBR and the Ministry of education and science of the Murmansk region within the framework of the scientific project 17–45–510640 "Geochemical assessment of groundwater in the Khibiny massif (age and identification of the origin of groundwater, chemical composition, forms of migration of elements)".

Table – Changes in migration forms depending on the temperature of some ions of one of the springs located in the vicinity of Apatite ($T^{o}C$, $P = 1$ bar)

$T^{o}C$	**Cu^{2+}**	**$CuOH^{+}$**	**$Fe(OH)_3$**	**$Fe(OH)_4^{-}$**	**FeO^{+}**	**$HFeO_2$**	**FeO_2^{-}**
3	1.77E-03	1.16E-03	8.68E-02	3.28E-02	5.82E-02	8.79E-01	0.0117
25	1.19E-03	1.89E-03	9.81E-02	7.30E-02	1.56E-02	8.82E-01	0.0231
37	8.82E-04	2.28E-03	1.07E-01	1.13E-01	7.81E-03	8.45E-01	0.0334
	$Al(OH)_2^{+}$	**$Al(OH)_2F$**	**AlO_2^{-}**	**$HAlO_2$**	**$Al(OH)_3$**	**$Al(OH)_4^{-}$**	**pH**
3	1.58E-05	1.43E-04	6.96E-02	3.63E-03	2.53E-03	1.19E-01	8.27
25	6.55E-06	6.62E-05	8.15E-02	2.20E-03	2.01E-03	1.03E-01	8.02
37	3.96E-06	4.42E-05	8.96E-02	1.76E-03	1.79E-03	9.07E-02	7.92
	PO_4^{3-}	**$H_2PO_4^{-}$**	**HPO_4^{2-}**	**Ca^{2+}**	**$CaCO_3$**	**$Ca(HCO_3)^{+}$**	**$CaSO_4$**
3	1.38E-06	2.76E-03	2.64E-02	21.6	0.453	0.804	0.571
25	1.30E-06	3.82E-03	2.53E-02	21.5	0.678	0.738	0.622
37	1.23E-06	4.47E-03	2.47E-02	21.4	0.872	0.769	0.686

MODELING AS A NEW PERSPECTIVE IN THE STUDY OF GASTRO-INTESTINAL TRACT

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In this article, an attempt to study the system of “gastric juice–water” with the help of physical and chemical modeling (equilibrium thermodynamics, PC “Selector”). The table presents the results of the interaction of 1000 g of the model analogue of gastric juice (Afendulov, 2008; Korotko, 2007) and water from 10 to 320 g (1st well, “Marcial waters” (Mazukhina, 2012) and groundwater of Apatity (Mazukhina et al, 2018). Analysis of the results (for two types of water) shows similarities in the behavior of the predominant forms of migration of aluminum (Al^{3+}), iron (Fe^{2+}), the presence of H_2S, CO_2, CH_4 and changes in pH and Eh values with variations in the water system from 10 to 320 g. The difference: the system “the gastric juice–Marcial water,” noted the presence of NH^{4+}, concentrations of iron and aluminum is higher by several orders of magnitude than in the “gastric juice–underground water”. Thus, new prospects in the study of the gastrointestinal tract are opened by modeling.

Table – Results obtained in the course of modeling

Marcial water, mg/ l						
Water, g	**Na^+**	**$Al(OH)^{2+}$**	**Al^{3+}**	**Fe^{2+}**	**$FeCl^+$**	**NH_4^+**
10	1,13E+03	3,66E-08	1,25E-04	1,22E-01	1,03E-02	7,97E+01
30	1,10E+03	2,21E-07	7,15E-04	3,80E-01	3,22E-02	7,80E+01
100	1,03E+03	1,03E-06	3,05E-03	1,13	9,20E-02	7,31E+01
320	8,65E+02	4,68E-06	1,03E-02	3,00	2,23E-01	6,11E+01
	H_2S	**CO_2**	**CH_4**	**Cl^-**	**Eh**	**pH**
10	3,41	3,52E+02	1,39E+01	4,91E+03	0,0917	1,243
30	3,86	3,50E+02	1,39E+01	4,80E+03	0,0913	1,249
100	5,20	3,45E+02	1,40E+01	4,51E+03	0,0897	1,274
320	8,63	3,29E+02	1,44E+01	3,77E+03	0,0852	1,342
Groundwater, wells the city of Apatity						
	Na^+	**$Al(OH)^{2+}$**	**Al^{3+}**	**Fe^{2+}**	**$FeCl^+$**	**NH_4^+**
10	1,13E+03	1,49E-08	5,56E-05	5,41E-04	4,21E-05	
30	1,10E+03	4,59E-08	1,65E-04	1,62E-03	1,25E-04	
100	1,04E+03	1,95E-07	6,33E-04	5,83E-03	4,40E-04	
320	8,67E+02	9,24E-07	2,33E-03	1,69E-02	1,14E-03	
	H_2S	**CO_2**	**CH_4**	**Cl^-**	**Eh, B**	**pH**
10	3,06	2,68E+02	1,24E+01	4,91E+03	0,0925	1,221
30	3,04	2,65E+02	1,22E+01	4,81E+03	0,0921	1,229
100	3,00	2,55E+02	1,16E+01	4,51E+03	0,0906	1,252
320	2,89	2,29E+02	1,01E+01	3,77E+03	0,0863	1,324

The study was carried out with the financial support of RFBR and the Ministry of education and science of the Murmansk region within the framework of the scientific project 17–45–510640 “Geochemical assessment of groundwater in the Khibiny massif (age and identification of the origin of groundwater, chemical composition, forms of migration of elements)”.

FEATURES OF THE GEOCHEMICAL ENVIRONMENT AND THE HEALTH OF THE POPULATION OF THE MINING REGION

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In the vicinity of mining complexes containing quarries and processing plants, biogeochemical zones with a high content of a number of toxic metals are formed.

In the Trans-Ural zone of the Republic of Bashkortostan, located in the Southern Urals, there is a large number of deposits of polymetallic ores, which have been developed for a long time and continue to be developed now. Large enterprises operating since the middle of the 20th century are the Uchalinsky Mining and Processing Plant (Uchalinsky District), its Sibai Branch (Sibay), the Bashkir Copper (Khaybullinsky District), and others. The main and most difficult for recycling types of waste of mining industry are overburden and the finely ground rock (tailings) which left over after mineral processing and stored as a watery mix in tailing dams. Dumps and tailings contain a significant amount of toxic metals, which are dangerous sources of secondary environmental pollution.

Objective: to study the level of environmental contaminations with toxic metals and investigate the state of health of the region's population.

The study was conducted between 2010 and 2017 on the territory of the city of Sybay, Khaybullinsky and Uchalinsky districts of the Republic of Bashkortostan.

Sampling of soils and water was carried out in accordance with generally accepted methods.

Analysis of water and soils on the content of heavy metals was carried out by atomic absorption, hair analysis was carried out in the accredited testing laboratory of the Center for Biotic Medicine (Moscow, Russia).

The state of health of the population was assessed on the basis of statistical data of territorial medical and preventive institutions in comparison with the average indicators for the Republic of

Bashkortostan.

As a result of the research, an increased content of copper, zinc, cadmium, cobalt, manganese in soils was revealed. The content of mobile forms of metals was several times higher than the permissible values.

The content of lead, cadmium, cobalt, copper, zinc, nickel and chromium in drinking water is in most cases within the maximum permissible concentration. At the same time, the concentration of iron and manganese in some cases is much higher than the permissible values.

The population living in this region is largely exposed to various toxic substances entering water and food, as a result of which they accumulate in the biological environments of people.

The raised level in hair of toxic elements (cadmium, lead, etc.) is revealed.

The primary morbidity of the Sibay population is higher than the average republican indicators for blood diseases, cardiovascular and circulatory, urogenital and respiratory systems.

The indicators of oncological morbidity in Sibay exceeded the corresponding indicators of the adjacent rural areas. The results of the study suggest a causal relationship between the increased morbidity of the population and the effect of metal ions, which in a large number present in all environmental objects.

PREMISES AND ONTOGENY OF MINERAL PATHOGENIC FORMATIONS IN HUMANS

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Biogeneous mineral concrements of various localization as stones in human body are alien pathogenic formations that cause a set of dangerous diseases. Among these biogeneous formations are calcifications, bilious and salivary stones. Still there is no consensus on the issue of their origin, but many medical workers connect them with an infectious etiology. It allows to assume a complex of reasons to generate this pathological process resulting in serious clinical consequences.

In medical practice patient diagnosis is based on clinical data, laboratory and tool research data, the latter ones result from pathophysiological basis and allow to give more definite interpretation of this or that disease, including radiological symptoms as manifestations of a pathological process course. Therefore it was interesting to investigate concrements morphology and mineral structure from the mineralogical point of view, in terms of minerals ontogeny, their priming source the crystallization nutritious, and spatial geometry for future modeling of their growth.

Biogeneous mineral concrements of different origin have been studied on mineralogical approach for their composition, structure and morphology. Among them are calcifications of various localization; bilious and salivary stones calcifications, other mineral formations. We believe mineralogical base of crystal growth theory as biogeneous stones arise and grow in human body.

We implemented a complex of physical testing methods, among them are optical microscopy, X-ray powder diffraction, XPD, X-ray Computed microTomography, μXCT. General data on morphology and composition we studied using optical microscopy. X-ray powder diffraction detected crystalline phase composition, but concrements also contained amorphous phases. So we used X-ray Computed microTomography, its advantages for studding biogeneous minerals analysis are obvious: the method is non-destructive and permits fast quantitative estimation of internal structure characteristics, i.e. without crushing; testing under room temperature. Thereby X-ray Computed microTomography allows to visualize internal volume of any object without destruction, thus determine its morphology and phase segmentation.

Actually mineral concrements display heterogeneous phase composition and morphology, irregular forms twisting edges, and usually have organic tissues in central part. Calcifications consist of 5–6 phases, two belong to an organic fabric (possibly proteins and lipids), other 3–4 mineral phases are wivewnit, hydroxlapatite, hydroxlcarbonateapatite and calcite of different density. The formed and young arising calcifications 30 microns size have been compared. Both organogeneous calcifications have considerable similarity of phase composition, but the young one also contained less than 0,15 wt.% slightly crystallized hydroxlapatite. Thus the young calcification has already initiated the development of atherosclerotic process. XCT tomograms of the salivary stone display morphology similarity to the one of mineral substance, for example ferromanganese nodules or pearls, but differ in phase composition. XPD of various salivary stones detected composition similar to calcifications, but gallastones were of different phase composition.

Biogeneous concrements calcifications, salivary stones and gallstones differ in phase composition and morphology, mechanisms of their nucleation and grows. The used mineralogical approach is alike histology in medical and biological studies, but may better promote disease courses explanation, revealing mechanisms of the calcification process development, being aimed at the human health protection.

Section 6
Biomineral interactions in soil

MODELING OF BIOGENIC WEATHERING OF ROCKS IN SOIL COLD ENVIRONMENTS

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Morphologically simple and microbially dominated ecosystems termed "biofilms" have existed and prevailed on Earth for a remarkably long period of biosphere evolution inducing biogenic processes of rock weathering. In the present research we aimed at conducting a modeling laboratory experiment with two examples of easily weatherable rocks sampled in the soil profiles from the cold regions of Eurasia: (i) meta-gabbro amphibolite (forest zone of the Polar Urals) and (ii) traprock (dolerite) (tundra-forest zone of Central Siberia Plateau). Meta-gabbro amphibolite is mostly composed by plagioclase and hornblende; besides quartz as a result of replacing some of the melanocratic minerals due to metamorphism, small proportions of epidote and chlorite were identified. In dolerite well-crystallized plagioclases and pyroxenes and secondary products from dolerite weathering – fine-crystalline aggregates of smectite(s) were identified by optical microscopy. As indicated by the intrusion of a molten alloy (Wood's metal) and subsequent electron microscopy the pores are well connected in both rocks. Based on small angle neutron scattering (SANS) data, both samples are characterized by a porous structure with fractal phase boundary (solid phase – pore); fractal dimension is 2.18 ± 0.07 in meta-gabbro amphibolite and 2.72 ± 0.06 in dolerite confirming that a higher specific surface area is in dolerite.

A model biofilm combining one heterotroph and one phototroph component (Gorbushina and Broughton, 2009) was used for a laboratory l experiment: 0.5g of pulverized (<200μm) rock was added to reactor flasks which contained 10 ml nutrient solution (CNPS); biotic runs (done in triplicates) were inoculated with both organisms, abiotic runs were left uninoculated. It was concluded after 3 month runtime of the experiment that the model biofilm clearly enhanced rock weathering: biotic runs showed a higher removal of Si from the samples, especially in case of dolerite. Besides, elemental uptake by the biofilm inhibited the entry of nutrients from the rock into solution: (i) the Mg solution concentration for both samples and (ii) the concentrations of Ca and K only for dolerite are higher in the abiotic run compared to the biotic runs. Biofilm visualization on the rock surface in polished sections also illustrated their stronger progress growth namely on dolerite confirming its higher sensitivity to biogenic weathering due to mineral association and porosity as well as higher specific surface area providing surfaces for biotic – abiotic interaction.

Reference: Gorbushina A. A., Broughton W. J. (2009) Microbiology of the atmosphere-rock interface: how biological interactions and physical stresses modulate a sophisticated microbial ecosystem. Annu. Rev. Microbiol. 63, 431–450.

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BIOGENIC FORM OF MIGRATION OF ELEMENTS IN OLIGOTROPHIC BOGS

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In peat soils, due to the accumulative direction of peat formation, the processes develop upward. Our own results and materials of other authors allow us to consider that the mineral substrate (mineral soil), which has undergone bogging, is the source of mineral nutrition for the soil-forming vegetation of bogs. Thus, our studies in the southern taiga subzone of Western Siberia to study the properties of oligotrophic bogs have made it possible to reveal their mesotrophic character due to the high content of calcium, magnesium and some other biogenic elements in the oligotrophic part of the profile, the mineral nutrition of which is carried out solely by atmospheric precipitation. However, these elements are found in large numbers in the underlying ancient soil, from where they migrate after the growing peat profile. The main quantity of ash elements in peat is accumulated at the initial stage of peat formation, when the mineral substrate, which is some carbonate clay in this case, serves as their source. From this layer, saturated with calcium, the root system of the next layer of peat-forming agents consumes calcium and other mineral elements. This is how the elements are redistributed along the profile of peat soils with a gradual decrease in their concentration closer to the surface. As a result, oligotrophic peat soils with signs of mesotrophic type of peat formation are formed on the investigated territory. Previously, this process has been called the biogenic form of migration of elements and described by Bakhnov V. K. Such reasoning is also valid for the content of iron, since the investigated territory is located in the area of occurrence of iron ores. Thus, the ancient soil, which underwent waterlogging, acts as a soil-forming rock in relation to the peat soil formed on it, and thereafter a close genetic connection is maintained between them. Let's consider the formation of a peat profile from the position of the movement of substances in the soil profile (soil-forming process). It is believed that the migration flow to soil-forming rocks in peat soils is very poorly expressed due to the large water-retaining capacity and weak soil filtration. This is probably true for a fairly flat surface, but the marshy terrain is non-uniform. As a result, there is an intra-marshy flow of gravitational waters, so autonomous, transit and trans-cumulative geochemical microlandscapes are formed. Thus, for example, there is an intra-marshy flow of water down the profile of peat bogs. Peat soil is divided into layers, the capacity of which is determined by the uniformity of the botanical composition of peat. Our studies on oligotrophic bogs have shown that microflora is present throughout the profile of peat soils. Let's consider this provision on a concrete example (table). Table. Limits of fluctuations in the concentration of microscopic fungi (A); reserves of fungal matter (B) and carbon share B (%) in oligotrophic peat soil

Soil	A (mg/g)			B (kg/m^2)			C (%)		
	Deposit depth, cm								
	50	100	300	50	100	300	50	100	300
Peat soil	2–26	5–30	11–36	0,05–0,7	0,2–0,9	0,5–1,2	0,2–3	0,3–2	0,3–1

In the theory of the peat-forming process, the leading role should be given to the transformation of peat-forming plants into peat, the origin of the organic and mineral parts in peat and their transformation, the processes of accumulation, transformation and movement of substances in the peat profile, and the disclosure of the forms of their accumulation and migration.

HEAVY METALS IN THE SOILS NEAR NICKEL–CUPPER INDUSTRIAL COMPLEX: SPATIAL DISTRIBUTION AMD TEMPORAL VARIATION

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Acid extractable Ni, Cu, Co, Cd, Pb, and Zn contents was determined in the topsoil of six catenas in the in impact zone of the "Severonikel" industrial complex (IC), which is the largest source of SO_2 and heavy metals in northern Europe. The aim of monitoring studies was to reveal the spatial and temporal regularities of variation in the degree of soil contamination by heavy metals (HMs). The sampling system made it possible to characterize the spatial distribution patterns of the topsoil contamination by heavy metals (HMs) in three aspects: the geographical aspect (with due account for the position of the experimental plots in relation to the source of emissions), the landscape aspect (with due account for the catenary position of the experimental plots), and the ecosystem aspect (in dependence on the degree of soil degradation of the separate spots or presence of pioneer mosses within ecosystem. The long series of observations allowed us to trace the long-term variability in HM concentrations, and the multiple character of monitoring made it possible to identify the factors affecting this variability.

The concentrations of major contaminating HMs in the upper organic horizon within the local impact zone of the "Severonikel" IC in 2001–2011 were hundreds (for Cu and Co) and thousands (for Ni) of times higher than those in the background soils. The concentrations of Mn and Zn in the upper organic soil layers and in illuvial horizon exposed to the surface did not exceed their background concentrations.

The differences between minimum and maximum concentrations of content of acid-extractable HMs in the soil samples varied from 1.5 to

6–7 times during the survey period. The organic matter content in the sample exerted the most considerable effect on the concentrations of Ni, Cu, and Co. At the same time, the high concentrations of HMs in the upper soil layer in 2008 with extremely small atmospheric precipitation and their low concentrations in 2007 with the highest atmospheric precipitation suggest that the processes of HM accumulation in the soils are dynamic and may be reversible. Heavy metals not only enter the soils with atmospheric precipitation; some part of HMs previously accumulated in the soil may be leached off from the upper soil layer by the subsequent less concentrations portions of atmospheric precipitation.

The distribution patterns of Ni, Cu, and Co in the upper soil layer on the examined plots do not always correspond to the distance from the source of emissions and the degree of contamination of the snow cover. This is related to the fact that the sorption capacity of the upper soil layer becomes smaller in the most considerably contaminated and degraded ecosystems because of the significant loss of organic matter and the approaching of the soil to the complete saturation with the major contaminants (Ni and Cu).

Despite considerable differences in soil conditions, we failed to find some general regularities in the distribution of HMs in the upper soil layer in dependence on the catenary position of the plots.

The objective assessment of the degree of soil contamination by HMs cannot be based on data of one sampling because of the great variations in the contents of HMs and their long-term dynamics.

BACTERIOMORPHIC STRUCTURES IN THE PERMIAN PEDOGENIC AND SEDIMENTARY CARBONATES OF MIDDLE VOLGA REGION BY SEM DATA

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Scanning electron microscopy (SEM) in recent years has become an ordinary method of studying many geological objects, including carbonate rocks. This work presents the results of the study of sedimentary and pedogenic carbonates of the Middle Volga region in the framework of a comprehensive study of the reference sections of the Permian system from the point of view of identifying global and regional biotic and abiotic markers.

The surface micromorphology and composition of sedimentary and pedogenic carbonates were studied using SEM Auriga Cross Beam (Carl Zeiss) with an X–Max energy dispersive attachment (Institute of Nanotechnologies and Nanomaterials, KNRTU, Kazan); fresh chips were used, more than 30 samples were studied.

Among the Middle Permian sedimentary carbonates, various structural-genetic types have been studied: massive and thin-layered dolomitic marls; micritic dolomites; thin-layered limestones with lacustrine fish, ostracods, bivalves; nodular, micritic lacustrine-palystrine limestone with root traces and ostracod fauna. Coeval pedogenic carbonates were also represented by both calcitic and dolomitic nodules of different sizes [1].

There is no one object among the studied carbonate rocks and nodules in which bacteriomorphes are not found. They are represented in most cases by rod-like and filamentous forms, close to Actinomycetes or Corynebacteria. The initial stages of growth are represented by coccoid forms, which often coalesce with each other, forming chains. The thickness of the filaments/rods is usually 80–100 nm, in some cases under them there are traces of biocorrosion in the form of grooves that repeat the shape of the rods [1]. Commonly, cocci, filaments and rods cover the surface of mineral grains or grow through it, creating the impression that the mineral grains are entirely made up of them. This is inherent not only for the calcite/dolomite micritic grains, but also for larger (spar) grains of secondary calcite. Thus, bacterial activity occurred not only in the stage of sedimentogenesis, but continued in early diagenesis.

The similarity of the bacterial forms present in sedimentary carbonates of different composition (subaquatic conditions) with those of pedogenic carbonates (subaerial conditions) may indicate the extreme shallowness of the continental lake basins of the Middle Permian of Volga-Ural region and makes the habitat conditions of microorganisms comparable in soils and lake muds.

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PLANT RESIDUES TRANSFORMATION IN THE NATIVE SPRUCE BILBERRY FOREST AND DECIDUOUS-SPRUCE FOREST STANDS OF DIFFERENT AGE (KOMI REPUBLIC, RUSSIA)

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The paper deals with plant waste chemical composition and its decomposition-caused changes during natural re-forestation after industrial cutting of spruce forests. The studies were conducted at the soil station of the Institute of Biology Komi SC UrD RAS (middle taiga, the Ust-Kulom region, Komi Republic). The station concerns impacts of clear cutting on changes in typical podzolic texture differentiated soils. Plant waste decomposition was studied at three plots as SP(sample plot)1 – virgin bilberry spruce forest; SP2 – young forest; SP3 – middle-aged deciduous-coniferous community. SP2 and SP3 were formed instead of forests clear-cut in winter of 2001/02 and 1969/70, correspondingly. Plant material transformation was assessed in microcosms isolated into nylon bags with 1-mm cell size. Material at SP1 and SP2 was living part of moss layer and at SP3 – fallen birch and asp leaves. Plant material was exposed for two years. At different destruction stages, plant material was assessed for total carbon (Ctotal), total nitrogen (Ntotal), water-soluble organic carbon (Cwso), and combined amino acids (AAs).

The initial destruction rate at SP1 was by 1.7–2.3 times higher than that at SP2 and SP3. After two exposition years, plant waste lost weight by 40–44% at every plot due to total organic carbon loss. AAs were dominated by mono amino carboxylic and mono amino acidic acids. They made 80.3–83.2% of total AAs. The most popular amino acids were amino aspartic and glutamic acids (25.2–27.0% of total AAs). This is typical of numerous plants and forest litter in boreal forests. Methionine, cystine, and histidine were found in small concentrations. Towards the end of experiment, we fixed certain changes in absolute concentrations of amino acids in different plant materials. Transformed mossy waste at SP1 and SP2 was similar by total content of amino acids; total content of amino acids in study material was by 1.3 higher at SP3 towards the end of exposition.

Changes in ratios of oxy amino acids to heterocyclic amino acids (AAo/AAhc), as well as of aliphatic to cyclic amino acids (AAa/AAc) during plant waste transformation at SP2 for 2 exposition years were poor. At SP1 both values decreased towards the end of experiment. At SP3, AAc tended to accumulate during plant waste decomposition as the AAo/AAhc value of 1.7 at initial experimental stages increased to 1.8 towards the end of exposition and the AAa/AAc value – from 5.7 to 6.1, correspondingly.

MICROORGANISMS OF TECHNOGENIC LANDSCAPES BY THE EXAMPLE OF NEPHELINE-CONTAINING SANDS, MURMANSK REGION

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Nepheline-containing sands compose the polymineral tailings of apatite–nepheline ores extracted in the Kola Peninsula for production of phosphate fertilizers. The oldest storage, which was organized in 1956, was abandoned in the 1970s. The working storage areas are regularly replenished with freshly pumped sands from the concentrating plants and represent active sources of dust in the environment. Because of the specific particle-size distribution (the predominance of fine sand and coarse silt), the sands are subject to wind and water erosion and pass into the aerosol state at a wind velocity of 4–10 m/s.

Sand transfer removes seeds and fertilizers and hampers the mechanical fixation of plants. Along with the unfavorable hydrothermal conditions and the absence of organic matter, this results in the extremely slow natural overgrowing of the tailings. The sands are considered to be nontoxic for biota, but they contain no organics and no nitrogen; less Si;

and more P, K, Na, and Al as compared to the zonal soils – acid Al-Fe-humus podzols. They have a slightly alkaline reaction and a low water capacity (2–4% in the 0- to 1-m layer), and they are subject to significant daily temperature variations.

Microorganisms are biocatalysts of processes of primary soil formation and one of the primary factors, which determine the specificity of this process. The investigation of biological characteristics was carried out in sands of different duration of storage in tailing dumps apatite-nepheline processing plants.

The total population density of bacteria ranged within 0.34–0.60 billion CFU/g in the sands without vegetation cover and within 2.6–7.2 billion CFU/g in the reclaimed sand under the different plant communities using the method of fluorescent microscopy with accounting for the unviable cells as well. The bacterial complex of the newly formed soils was characterized by the predominance of oligotrophs transforming nitrogen-free organic compounds. In distinction from the acid podzols, neutrophilic actinomycetes were abundant in these soils.

Microfungi mycelium length varied from 5 to 280 m/g in the recultivated nepheline sands. Low biodiversity of fungi in the initial sands of the apatite-nepheline industry and absence of species-dominants in their complex were pointed out. Nepheline sands recultivation (carried out 50 years ago) gave preconditions for the formation of fungi complexes, typical for regional podzol soils on the moraine sediments. Species diversity of the microfungi complexes in the recultivated nepheline sands is represented by 27 species which belong to 11 genera, 6 orders, 4 classes and 3 divisions, while only 11 species were isolated from the freshly pumped sands. The largest number of fungi species belonged to the *Penicillium* genera. *Mortierella longicollis*, *Phoma eupyrena*, *Penicillium* daleae were found to be the most commonly seen genera.

In total, 55 algae and cyanobacteria species referring to 5 divisions were found in the nepheline-containing tailings: Chlorophyta (18 species), Charophyta (6), Ochrophyta (16), Haptophyta (1), Cyanobacteria (14). The highest species abundance was observed in biological crusts on the sands surface. There were even typical of humid habitats algae from Conjugatophyceae class: the species of the genera *Cosmarium*, *Cylindrocystistis*, *Mezotaenium*. In general, the cyanobacteria-algae cenosis is the nepheline sands differ significantly from that of the zonal podzols on moraine deposits, where the green algae of Chlorophyceae and Trebouxiophyceae dominate.

The obtained data will help to better understand the processes of primary soil formation on nepheline sands.

Strains of microscopic fungi, algae and cyanobacteria are deposited to Herbarium of the Institute of the Industrial Ecology Problems of the North.

AEROBIC, ANAEROBIC AND PHOTO DEGRADATION OF BIOCHAR

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The inherent stability of biochar against oxidation led to the assumption that biochar is chemically and biologically inert to such an extent, that its mineralization rate was thought to be negligible. The main focus in such studies has been on CO2 evolution. Here we include the analysis of liquid products resulting from char solubilization. The ability of some microorganisms to metabolize coal is well known since the studies conducted by Potter (1908).The inoculation of coalbeds with methanogens to enhance methane production is a commonly used process referred to as Microbially Enhanced Coalbed Methane production. Here we study the rate of biochar degradation in anaerobic conditions, assuming that in such conditions it should be highly-degradable. This assumption is based on the lack of report on any significant accumulations of char in sedimentary basins.

The incubation study was conducted in closed columns installed in a laboratory at room temperature and filled with silica sand amended by addition of 10%wt biochar. The biochar used was produced from pine wood pyrolized at 450ºC. Microbial inoculation was done with a filtered suspension produced from rotting pine wood.

The anaerobic degradation trial was conducted in 500 ml Erlenmeyer flasks containing 50 grams of granulated methanogenic consortium to investigate the effect of pH and increasing biochar loads (expressed as chemical oxygen demand -COD), on the biodegradation of biochar. The trial consisted of three main treatments assessed over three periods each with increasing biochar loads. Sampling was done four times within each incubation period. The substrate feed and the effluent parameters monitored with every feed included the following: COD reduction (APHA, 1998), pH, alkalinity (as $CaCO_3$), total biogas produced and its composition.

Biochar is H_2O_2 degradable via hydroxylation and carboxylation reactions resulting in aromatic ring cleavage and the release of carboxylic acids. Basidiomycetes should therefore be able to degrade the highly aromatic structure of biochar.

This study has clearly shown that biodegradation of biochar in aerobic conditions produces not only gaseous, but also liquid products, which were previously disregarded in biochar degradation studies.The greatest COD removal efficiencies were attained from digesters with starting pHs of 7 and 8. The increase in COD input had no significant effect on COD removal efficiencies in any treatment. The methanogenic consortium produced CO_2 throughout the trial, whilst methane production was erratic at starting pH=7, but occurred more often compared to the other treatments. When methane production did occur the biogas composition consisted of ±70% methane and ±26% CO_2. Anaerobic degradation rates of up to 33% of initial char (as COD) input per week were observed.

EVIDENCE OF ORGANO-MINERAL INTERACTIONS INSIDE MICRO- AND FULL-SCALE PALEOSOLS FROM BARBERTON GREENSTONE BELT (3.5–3.2 Ga) AND HEKPOORT FORMATION (2.2 Ga), SOUTH AFRICA

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Continental shallow-water sediments and subaerial deposits from Barberton Supergroup (3.57–3.22 Ga) and Hekpoort Formation (~2.2 Ga) in South Africa continue to be in the focus of intensive research by geologists, geobiologists and paleopedologists as well preserved archives of organo-mineral interactions from the Paleoarchean and Paleoproterozoic. Here we present the new data on micro- and full-scale paleosols based on the three groups of objects.

Firstly, the paleosol profile in the greenstone exposure of Barberton

Supergroup with a set of distinct pedofeatures. The most striking ones are the slickensides with microridge texture and thin dark grey coatings. Sometimes coatings exhibit mottled patterns with dark areas enriched presumably in kerogen. We interpret this Paleoarchean paleosol as Vertisol.

Secondly, the Waterval Onder paleosol from Hekpoort Formation that was originally described by G. Retallack (1986, 1993 and 2013) and interpreted also as Vertisol. We will present new results of mezo- and micromorphological study including SEM-EDX data on cutans covering ped surfaces and weathering patterns presumably of biochemical origin in this Vertisol which contains microfossil complex of Paleoproterozoic organisms.

Thirdly, the microprofiles of subaqueous soil-like bodies with subparallel reddish-brown thin-layered texture in shallow-water silts and sandstones from the Moodies Group (~3.21–3.22 Ga). SEM-EDX examination revealed a goethite botryoidal microstructure. Some of thin layers were interpreted as a shallow-water analogue of BIF (deep-water ocean banded iron formation) that was possibly formed within a short-time period (one season or less) and has a number of features complying with biogenicity criteria.

This study was supported by Russian Science Foundation, Project No. 14–27–00133 (paleosols research) and Russian Foundation for Basic Research, Project No. 16–04–01776 (search for the ancient analogues of endolithic systems).

Section 7

Biodeterioration of natural and artificial materials

DESTRUCTION OF WHITE STONE IN THE URBAN ENVIRONMENT

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The natural stone that is used in the construction of every city has its own characteristics determined by its geological location. These differences contribute to the historical architecture of different cities giving them their unique appearances. For example, Moscow’s unofficial name “white stone city” comes from the fact that white stone constructions are of significant value among the architectural monuments of Moscow. A unique monument of the ancient white-stone architecture of Moscow that was preserved to this day is the homestead of the Romanov boyars (the museum of the “Chambers of the Romanov Boyars “).

Since every monument is an element of a complex natural and man-made city system, it is affected by all the processes happening in this system. Violation of ecological balance in the urban environment leads to accelerated weathering of the stone and the appearance of new types of damage. This area of the city belongs to the most challenging areas in terms of engineering geology. There are often occurrences of flooding and chemical contamination of soils and ground waters. The main cause of the pollutants in the air such as methane, carbon dioxide, nitrogen and sulfur oxides, vanadium pentoxide, etc., is the proximity of the highway and HPP-1.

The study of processes of limestone weathering was carried out on samples taken from various zones of the monument. All the samples were divided into three groups from stable to completely destroyed structure. As the result, it was found that the CaO content (54.3%) drops sharply to 18.9% in the samples that have their structural stability completely lost. Distinctive feature of these samples is the appearance in the mineral composition of a large number of salts (up to 44.7%), clay minerals (up to 2%) and weathering products of pyrite-bearing rocks – hematite and halotrichite. The intensive development of the microbiological component contributes to the increase finely dispersed fraction content in the destroyed stone. Studies on the stone walls of the monument showed that it was colonized by mold fungi (Penicillium sp, Aspergillus sp, Cladosporium sp, Alternaria sp, Tritirachium sp) and bacteria (Bacillus sp, Rhodococcus sp, Mycobacterium sp.). The dominant in the number of species were genera Penicillium (5 species) and Aspergillus (2 species), known as biodestructors of stone materials. Their content varies from the site of selection and can reach values of $5 \cdot 10^4$–10^5 CFU / g for fungi and $5 \cdot 10^4$ CFU / g for bacteria.

Finally, studies have shown that the exposure of this monument to both natural and man-made processes has contributed to the partial destruction of it. The change in water balance is one of the main factors. Water containing ions SO_4^{--}, NO_3^{-}, Cl^{-}, salts and microorganisms has more aggressive impact on the carbonate rock. Consequently, the damage to the stone is caused by dissolution and leaching of limestones, crystallization and hydration of salts and acidifying activity of micromycetes.

AT THE BEGINNING OF GEOLOGICAL MICROBIOLOGY (ON THE130th ANNIVERSARY OF THE BIRTH OF L.D.STURM)

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The name of Leonilla Dmitrievna Sturm (1888–1970) can be named among the names of the first women-microbiologists who worked in the field of geological microbiology and microbial ecology. Being the pupil of V. L. Omeliansky she was always devoted to the best traditions of Russian microbiology presented by S. N. Winogradsky, V. L. Omeliansky, S. P. Kostychev, B. L. Issatchenko etc. Her investigations were linked with the study of the biodiversity and biogeochemical role of microorganisms sapropels and in oil reservoirs. The scientific biography of L. D. Sturm can be divided in two main periods. The first period (1921–1939, Petrograd/Leningrad – Moscow) can be characterized by her investigations in soil microbiology and especially in the microbiology of sapropels and other lake sediments. Her most important works were executed at the Biological Station of the Committee of Sapropel (in Zaluchie). During the second period (1939–1965, Moscow) the scientific interests of L. D. Sturm were focused on the problems of petroleum microbiology, mainly in the oil reservoirs of the “Second Baku”. In 1949 she was awarded with the order of Lenin and in 1951 she received the degree of Doctor of biological sciences. The works of

L. D. Sturm largely contributed to the development of the geological microbiology.

RED-LISTED SPECIES OF VASCULAR PLANTS AND LICHENS IN GEOLOGICAL NATURE MONUMENTS IN THE VOLOGDA REGION, NORTH-WEST RUSSIA

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A specific type of protected areas is geological nature monuments (GNM), which feature non-living things – regionally rare rock species, fossils, landforms, tectonic occurrences, etc. Such areas would almost always contain bedrock or parent rock outcrops that are at least partially unvegetated, which means there are vacant ecological niches. Often, such land areas would be noted for phytobiota and mycobiota of unusual composition, and be the habitat for the species whose competitive capacity is low, wherefore they cannot survive or remain very rare in the rest of the region occupied by zonal vegetation.

Surveys of four geological nature monuments (GNM) yielded the findings of 28 vascular and 5 lichen species red-listed in the Vologda Region.

GNM “Devyatinskiy Perekop” (area – 37 ha) is a canal, ca. 1 km long, excavated through a mass of Upper and Middle Carboniferous monolithic limestone late in the 19th century as part of the ancient Mariinsky canal system, together with limestone spoil heaps from canal excavation. After the Volga-Baltic canal had been reconstructed early in the 1960’s, Devyatinskiy Perekop was drained. The territory was no longer in use, and was growing naturally vegetated. Surveys of limestone spoil heaps and the relatively vertical canal walls detected 15 red-listed vascular plant species. Some of the species belong to high conservation categories (*Gymnocarpium robertianum* – endangered, *Anemone sylvestris*, *Coeloglossum viride*, and *Epipactis atrorubens* – vulnerable); most of them are represented by numerous robust populations.

GNM “Tagazhma River Valley” (area – 740 ha) comprises a 10 km long river valley stretch with Carboniferous limestone outcrops. Tagazhma River is rich in rapids and features the Vologda Region’s largest waterfall Padun, 1.5 m high. Surveys have revealed 7 protected vascular species, including the vulnerable *Cinna latifolia*, as well as red-listed lichen *Chaenotheca trichialis.*

GNM "Patrov Stream Valley" (area – 20 ha). Lower Carboniferous sand and limestone outcrop in the sides of the stream-eroded gully, forming precipitous walls up to 25 m high. There are 5 known red-listed vascular species.

GNM Mount "Andomskaya Gora" (area – 150 ha). It features a 30–35 m high abrasion scarp representing Devonian outcrops (multicolored clays) containing fossils of invertebrates, plants, crossopterygians and placoderms. Records include 10 red-listed vascular species, including vulnerable psammophytes *Dianthus arenarius*, *Festuca arenaria*, *Lathyrus maritimus*, and *Rumex graminifolius*, as well as red-listed lichens *Ramalina baltica*, *R. farinacea*, *R. pollinaria*, and *Gyalolechia flavorubescens*.

Thus, several GNM, occupying a trifling area, were found to harbor a disproportionately large number of red-listed species of vascular plants and lichens.

EVALUATION OF THE EFFECT OF THE EQUIPMENTS DESIGN PARAMETERS ON THE DEGREE OF CHANGE OF THE NATIVE STRUCTURE OF PEAT

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In the production of high-quality peat products from excavated peat, it is necessary to take into account a wide range of factors that can be conditionally combined into the following groups: properties of excavated raw materials, meteorological conditions, parameters of machines and mechanisms used in the extraction and processing of raw materials. In the first group, the degree of peat processing can be identified as a determining factor, significantly affecting the technological processes of drying, energy costs and, ultimately, the quality of the products.

In the practice of field manufacture of peat products in the form of different in shape and size pieces, mechanisms on the basis of screw extruders are applied the most widely due to high processing ability, simple design and freedom to choose a moulding adjutage. However, in many cases, screw moulding machines are inefficient in terms of energy indicators, especially in regard of the specific energy costs per ton of products. Therefore, attempts to create other, more efficient and productive processing-moulding devices, continue aiming at manufacturing field raw material products with the pre-defined particle-size distribution. The use of roller-disc grinders is one of the promising directions for creating such devices. Its principle of action allows combining the separation of peat raw material and primary processing for the production of various peat-based goods. To determine the degree of peat processing in a roller-disk device, we determine its relative deformations when passing through the space between two adjacent rolls with disks connected to the rolls through the hubs. Processing in such a mechanism is carried out due to shear strains, which arise as a result of sliding layers of peat relative to each other, and also due to crushing deformation when narrowing in the space between two adjacent rolls. In determining the relative strains that arise in this case, we assume that the conditions of continuity and invariability of the volume are satisfied.

In research the theoretical analysis of the parameters of a roller-disc recycling device is performed with the assumption of constancy of characteristics of processed peat raw materials, the continuity of the material flow through the processing surface and the equality of the contact angle at all surfaces.

The presented technique can be applied to the calculation of the processing degree of peat raw materials on devices equipped with a roller-disk screening surface, which will further determine the energy cost for manufacturing peat products with the use of similar machines.

CRUSTS AND INCRUSTATIONS ON NATURAL AND ARCHITECTURAL OBJECTS

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Crusts and incrustation on the following objects are represented: rock art (“patina” of petroglyphs on metamorphic rocks), on alkali rocks in Siberia (Sangilen, Batagol); on granite facing stones and statues in urban environment (Kamenny and Moskvoresky Bridges, pedestals of sculptures); on limestone blocks of white stone cathedrals, on brick, terracotta and glazed ceramic products.

Devlet E. G. (2002) summarized the material on rock art (petroglyphs). Complex studies of Siberia petroglyphs were performed at Cemerovo University and Moscow State Research Institute of Restoration (Ageeva, Rebrikovba, 2003, R. V. Lobzova, S. M. Kropachev, A. V. Koganovich 2004, 2005, 2014). Rocks and "patina" studies using methods of petrography and electron microscopy showed important influence of mineral substrate, it structure and texture features, and also physics and mechanical properties of rock material on the formation of cave drawings planes. Despite on the different substrate (sandstones, shales, limestones) the mineral composition of the drawing plane are uniform: iron-manganese and iron oxides compounds are prevail. Under "patina" at a zone of leaching quartz grains, which are the most stable during the weathering, are cemented by silica, less often – by clay substance.

Different types of lower bio-forms are formed in deepenings of rocks, containing feldspathoids and carbonates (nepheline syenites of the Sangilen massif, Batagol). In cracks of such rocks carbonate deposits are formed with different thickness, color shades and forms – colloform reniform aggregates, stalactite-like deposits, thin films, often enveloping biological forms, sometimes forming structures such as calcareous onyx.

At the objects of cultural heritage, many years of materials science and biological research were carried out by A. G. Bulakh et. al. (2005), O. V. Frank-Kamenetzkaya et. al. (2010), D. Yu. Vlasov (2006). It was established that, only 15 types of bio-forms from 150 known are dominated on the monuments of Saint-Petersburg.

We studied different monuments of Moscow. It was determined that, crust and incrustation forms on the granite facing stone differ zonal structure and are associated with leaching and redeposition of the carbonate substance from cement and lime solutions; iron oxides – from reinforced concretes. The largest biogenic subject to degradation is limestone and marble, least of all – glazed ceramic products.

FUNGAL COMPLEX OF STONE MATERIALS IN INTERIORS OF CULTURAL HERITAGE

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Colonization of stone building materials by micromycetes have received a lot of attention in recent years, as fungi are shown to play one of the leading roles in their deterioration (Warscheid, Braams, 2000). The aim of our work was to characterize the fungal complex of stone building materials, i.e. limestone and plaster, in interiors of cultural heritage, to make a distinction of the development of fungal species in the studied materials and to reveal physiological characters, i.e. pH preferences and organic acids production, of actively developing fungal species. For this purpose, samples of limestone and plaster were taken from the interior walls and columns of 14 objects of cultural heritage located in Russian cities and villages. Altogether 117 samples were analyzed. Two agar media, Czapek and Starch Czapek, were used for isolation of fungi. Isolated strains were characterized by morphological and molecular data, that is, by sequencing the ITS and LSU rDNA regions. Fungal development in studied materials was estimated primarily by abundance of isolated species and in addition by their frequency of occurrence. To elucidate the pH growth optimum of the strains MYA-based media buffered at five pH levels, i.e. 4, 5, 7, 9 and 10 were used (Grum-Grzhimaylo et al., 2016). For carbonate dissolution test, $CaCO_3$ glucose agar was used (Pangallo et al., 2012).

In general, species from the isolated fungal complex possess different physiological and ecological characters and realize various life strategies. Indeed, the most abundant (abundance from 29% to 7%) and thus the most actively developing in materials were stress-tolerant microfungi, i.e. *Acremonium charticola*, *A. furcatum*, *Lecanicillium* sp., *Parengyodontium album*, *Purpureocillium lilacinum* and *Sarocladium kiliense*. Counts of these species in the obtained samples were high (10^4 CFU/g and more). They were all strong alkalitolerants except *A. furcatum*, which was alkaliphile. We propose that tolerance to osmotic stress and high pH values in conjunction with high enzymatic activities give these fungal species an advantage in developing on limestone and plaster for a long period. In addition, *A. charticola* and *Lecanicillium* sp. were able to dissolve $CaCO_3$ and thus were potentially very harmful for materials. Moreover, while actively developing in materials, fungi can deteriorate them mechanically or by means of other mechanisms (Unković et al., 2018). Another group of isolated species included generally plant-associated pathogenic fungi and airborne soil species, i.e. *Aspergillus flavus*, *A. versicolor*, *Cladosporium langeronii*, *Fusarium* sp., *Mortierella alpina*, *Penicillium chrysogenum*, *Penicillium* sp., *Pseudogymnoascus pannorum*, *Talaromyces funiculosus* and *Verticillium zaregamsianum*. These species were less abundant than that of the previous group (abundance from 4% to 0.2%), their counts in samples were 10^3 CFU/g and more. According to Dornieden et al. (2000), they are presumably the first inhabitants on surfaces of stone walls. When organic sources are expended, these species disappear, thus, in contrast to the previous group, they cannot stay on mineral substrates for a long period. Nevertheless, the majority of them were alkalitolerant, and *P. chrysogenum* displayed high calcite solubilization activity. The abundance of remaining species was less than 0.2% and these species were isolated in low amounts (10^2 CFU/g and less). Seemingly, they have got into samples with surface contamination and didn't play any role in deterioration process.

Our research will be helpful in planning the restauration works.

BIOCHEMICAL COMPOSITION OF ROCK-INHABITED COMMUNITIES IN ANTHROPOGENIC AND NATURAL AREAS

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To understand the mechanisms of microorganisms-rock interaction, it is important to study of rock-inhabited communities at the molecular level. Currently the metabolomic approach allowing analyzing various biological objects as a system of small molecules has proved very productive.

The aim of this study is a comparative analysis the different types of rock-inhabited communities using the metabolomic approach.

Type of analyzed stratification includes: lichen communities; biofilm formed by fungi; biofilm formed by algae; primary soil at various stages of its formation with mosses. To studies in natural conditions the Ruskeala marble quarry was chosen. Studies in urbanized area were conducted in the Museum Necropoleis in St. Petersburg. Extraction of biofouling samples was performed by methanol. Analysis of extracts was carried out by GC–MS on Agilent instrument with a mass-selective detector MSD5975.

More than 200 different compounds were found in the samples from the quarry: mono, di and trisaccharides, carbonic acids, amino acids, polyols, phenolic compounds, diterpenes, sterols, ethanolamine, glycerol-3-P, urea. About 100 different low molecular weight organic compounds of these classes were detected in the samples from the urban environment. In general samples collected in St. Petersburg characterized by less content of compound. This is mainly due to the lower content of species-specific secondary metabolites. At the same time, the concentration of certain compounds especially polyols was significantly higher in biofilms in the urban environment. Patterns of molecules distribution, depending on the type of biofouling, were generally similar for samples taken in a quarry and in museum necropolises. In biofilms with algae, the amount of mono- and disaccharides, amino acids and organic acids was higher in comparison with other types of biofouling. In samples with fungi the concentrations of polyols are higher. In the fouling with lichens, sugar alcohols and phenolic compounds predominated. In the primary soil with a moss cover, the greatest variety of low molecular weight metabolites was observed; however, their quantity was usually lower than in other samples of surface layers.

The results of this study show the possibility of using a metabolic approach for following research of rock-inhabited communities and contribute to an understanding of their biochemical activity in different environmental conditions.

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BACTERIAL DEPOSITING OF ZINC SULPHIDES IN THE CENTRAL HEATING SYSTEM

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The results of this investigation of technogenic minerals – Zn sulfides – that formed as sediment at the fittings of city hydronic heating system are presented. Object of our work is cream-colored powder from inner part of corroded heating fitting and radiator. The morphology, mineralogy and surface chemistry of this matter were studied by X-ray diffraction (XRD), X-ray fluorescence spectroscopy, scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS).

According to XRD data the phase composition of the inner precipitate is presented by two modifications of ZnS – wurtzite (hexagonal modification) and sphalerite (cubic modification) with a small addition of hemimorphite $Zn_4Si_2O_7\,(OH)_2$.

Reflections of these minerals on XRD patterns are broadened because of different size of their microcrystallites. When investigating of the sample with the photoluminescence method we observed blue luminescence that is specific for organic components.

On the SEM images of the sediment we can see tabular crystals of zinc sulfides of two generations. Additionally the spherical aggregates and chains of small globules (≈10 μm) with the same composition as ZnS crystals were observed. Their morphology and size make it possible to consider these formations to be the biomorphosis of the covers of elementspecific bacteria. Some of them look like at the SEM images as semitransparent, slightly segmented cylinders. The different length of the filaments indicates that these were bacteria whose cells are capable to form chains. Probably they formed a common mucous cover consisted of polysaccharides that subsequently was mineralized. Similar globules of zinc sulphides have been described in the numerous works of other researchers who note that such formations are specific for microbially-depended precipitation of ZnS.

The results of our investigation provide clear evidence that hydronic heating systems have been found to provide a breeding ground for bacteria associated with microbiologically influenced corrosion. In the sediment Zn sulfides are presented by tabular crystals of several generations, spheres, spherical aggregates and biomorphs on the bacterial cells that probably activated fitting corrosion and promoted Zn sedimentation as sphalerite, wurtzite and hemimorphite.

We recommend using of various microorganisms for water disinfection at heating systems with great caution (as it is now become popular) at least until you have studied the ways of their impact on all elements of the closed systems.

BIOLOGICAL WEATHERING OF INTRUSIVE ROCKS OF EGYPT

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One of the unique places in the world, where numerous stone monuments of ancient civilization are concentrated, is Egypt. Many monuments for thousands of years were exhibited here in the open air. The stone used to build the ancient temples and pyramids was mined in Egypt itself. Some of the most common and resistant to weathering stone materials are intrusive rocks. Two mica granites has a coarse-grained structure, microgranites and dolerites are fine-grained.

Granite and dolerite are very heavy stones, but it is destroyed under the influence of time. Destruction of a natural stone is a multifactorial process. Mechanical communications between stone particles collapse under the influence of water, a wind, because of a temperature drop. The most common forms of destruction of intrusive rocks are granular disintegration (chipping) of the surface layer and peeling of the surface crust. Rock-forming minerals such as, micas, pyroxenes, amphiboles and field spars are collapse. Rocks were covered by mosses and lichens, but the most common were fungi.

It is known that in the arid climate, specific communities of fungi are formed, which have increased resistance to insolation, salinity, temperature changes, desiccation, nutrient deficiencies and lack of moisture. Such conditions for many micromycetes can be considered extremely close to the species existence boundary.

The studies were carried out using scanning electron microscope, confocal microscope, and microprobe analysis.

In the samples of coarse-grained granite, 21 species of micromycetes were identified. 11 species of micromycetes were found on fine-grained rocks. The development of fungi is confined to the structural spaces formed under the exfoliating fragments of the rock. When the coarse-grained rock is weathering, cavities with a large space are formed in comparison with the fine-grained rock. On the photographs of scanning electron microscopy it is evident that hyphae of fungi are weaved by weakened elements of the rock.

Thus, species diversity of fungi is numerous on coarse-grained rock, the number of propagules in damaged granite sites reached 2800 colony-forming unit (cfu) per 1 gram of substrate.

Aspergillus niger, *Aspergillus fumigatus*, *Aspergillus flavus* species were isolated with the highest frequency.

The proportion of dark-colored micromycetes was high (about 70%) then light-colored one.

The study was carried out in the resource centers of SPbU “Geomodel”, “Methods of microscopy and microanalysis” and “ Methods of chemical analysis”.

Section 8

Biomineral interactions in extreme environment

ANTARCTIC SPORES INACTIVATION BY VUV EMISSION

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In the work, spores of various types of microfungs were obtained from the Antarctic habitat *(Aureobasidium pullulans, Cladosporium herbarum, Geomyces pannorum, Penicillium aurantiogriseum, Rhodotorula colostri*), which were irradiated with vacuum ultraviolet (VUV) radiation. VUV radiation (10 nm $<\lambda<$190 nm) plays an important role in astrobiological studies related to the origin of life on the surface of the Earth and the development and survival of microorganisms under extreme conditions on a stony substrate, which can be indicative of the conditions of transport of microorganisms to the surface of meteorites in space.

VUV irradiation of microorganisms is known to lead to their inactivation2. Potential mechanisms of the effects of VUV radiation on the micromycetes coincide with the mechanisms of action of ionizing radiation: destruction of chitin of the cell wall, the destruction of the phospholipid membrane, degradation of DNA. These processes can occur both as a result of direct absorption of VUV emission quanta, and as a result of exposure to highly reactive VUV products of water photolysis and lipid oxidation products.

The change of the cell wall structure by VUV radiation was studied by IR spectrometry and atomic force (AFM) microscopy. The intensity of the IR transmission spectra of the irradiated samples increases in the bands corresponding to the absorption of proteins λ=1313 cm-1,1376 cm-1, 1400 cm-1, and polysaccharides λ=1454 cm-1, indicating the destruction of the cell wall material. Studies on AFM indicate the absence of mechanical destruction in macromolecular scales at distances $d \geq 0.1 \mu m$.

The study on the effect of VUV radiation on the DNA molecule has been indicated DNA degradation: in the VUV irradiated samples appear low molecular weight fragments and a peak corresponding to fragments with a length of 20 000 pairs of nucleotides.

It is shown that VUV radiation is one of the factors affecting the viability of the propagule of microorganisms on the surface of a rocky substrate. Inactivation of the propagules of microfungi under the influence of VUV radiation can be caused both by destruction of the cell wall and by change of the DNA structure.

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MICROFUNGI IN THE PRIMARY SOILS OF THE ARCTIC (BOLSHEVIK ISLAND, SEVERNAYA ZEMLYA ARCHIPELAGO)

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Studies of soil microfungi by methods of plate dilution (pure culture) and molecular methods were carried out on soil samples selected on Bolshevik Island (Severnaya Zemlya Archipelago) near the AARI station (Cape Baranov). Metagenomic analysis was used (by regions ITS1 and ITS2 for fungi and genes for 16S rRNA for bacteria). This allows not only to expand information on the diversity of soil microorganisms (identify poorly cultivated or noncultivated forms), but also to determine the core of microbiota in the Polar regions.

With the use of culture methods 56 species of microfungi were isolated from the primary soils of this area. At the same time, in the soil of areas subjected to anthropogenic pollution, a change in the species composition and number of microfungi occurred. The abundance indices (CFU number) in anthropogenic polluted soils were significantly higher (by an order of magnitude), in comparison with natural habitats. These results were confirmed by the use of a metagenomic analysis of soil samples selected in the polluted and “control” soils at areas of island Bolshevik. In total, 88 taxa of microfungi were identified in soil samples using metagenomic analysis, 52 of which were recorded on anthropogenic polluted soils. It is important that metagenomic analysis confirmed the nucleus of the mycobiota of soil communities obtained by classical methods.

When the rank of the identified taxa declined, the number of differences in the results obtained by the two different methods increased. Using metagenomic analysis in control (unpolluted soils), a high proportion of fungi of the genus *Emericella* was noted, while in polluted soils they were not detected. The metagenomic data confirmed the presence of species from the genus *Penicillium* in anthropogenic polluted soils (with a relatively low share of participation), whereas in of control soils samples they were not detected at all. Other differences of the compared communities of micromycetes are also noted.

It is interesting to note the finds of yeast from the genus *Mrakia (Basidiomycota*), which were characterized by a significant share in anthropogenic polluted soils. The yeast *Mrakia* was also isolated in the pure culture from soil dilutions methods.

In general, the results of our studies allow to conclude that it is necessary to combine cultural and molecular genetic methods for studying soil microbial communities in the polar regions. It should be noted that a significant portion of the nucleotide sequences obtained from soil samples were not identified, which requires further research.

The work was supported by the Program of basic research of the Russian Academy of Sciences, Project “Biological diversity and dynamics of the flora and vegetation of Russia” and project RFBR N16–04–01649.

HOMEOTHERAPY AS A FACTOR FOR ENSURING THE LIFE OF THE HUMAN ORGANISM

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The main pollutants in large industrial cities are heavy metals, which, entering the environment with emissions of enterprises and transport, sewage, fuel combustion, pesticides and mineral fertilizers, accumulate in the human body. One of the urgent problems for the Donetsk region is the deterioration of the environmental situation and the quality of the human environment, because of the work of metallurgical and coke plants, boiler houses that work on coal. With prolonged exposure to heavy metals, asthenovegetative syndrome develops, complaints of constant headache, sleeplessness at night and drowsiness during the day, tearfulness, depressed mood, phobias, increased anxiety and self-doubt occur. The structures of the body that undergo the largest changes are soft tissues, bones, nervous system, blood and as a consequence, the manifestation of neurological pathological syndromes, pathologies of the respiratory system, digestion, blood circulation, hematopoiesis. At the same time in pharmacology has long been known the fact that the same substances in large and small doses have exactly the opposite effect, i.e. reduction of doses of drugs selected by the principle of "similarity", naturally increases the therapeutic effect. The article is based on the experience of using monopreparations made on the basis of lead and mercury salts in patients-workers of industrial enterprises, in which the clinical picture was within the framework of the pharmacological characteristics of these homeopathic preparations. After a 3-month course of homeotherapy, correction of vegetative lability, variability of pulse and blood pressure was noted. In 86% of patients receiving the above drugs, significantly decreased manifestations of gingivitis, sleep improved, daily activity increased. Thus, the use of subminimal doses of medications selected according to the principle of "similarity" naturally increases the therapeutic effect. Important is the absence of side effects of homeopathic drugs and contraindications to their use.

MINERAL COMPONENT OF THE BONE TISSUE OF ICE FISH *CHAMPSOCEPHALUS GUNNARI*

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Icefish is the common name for the 8 families of the Pesciform suborder Nototheniodei that live in the continental shelf waters surrounding Antarctica. Some of them are secondary pelagic organisms and therefore don't have swim bladder. Due to this fact they had to evolve some adaptation to compensate decreased buoyancy, and one of the ways to do so was to reduce the bone density (Eastman et. al., 2014). With the light (i.e. presumably poorly mineralized) bones icefish has been called a good model for the osteoporosis research (Maher, 2009). Water temperature of the Antarctic seas can fall up to –1.9 ^{o}C, but low temperature of the habitat also should have influenced the bone formation as well, while the formation of the bone tissue and apatite at the sub-zero temperature hasn't been investigated so far. So, the main purpose of this research was to study the nanostrusture of the Icefish bones and execute extreme biomimetics synthesis corresponding to the formation of the bones in the organism of Antarctic fishes.

Bones of Champsocephalus gunnari were extracted using fly maggots, with further treating with NaOH and 6% H_2O_2, according to the reported technique (Hill 1975). Dried bones were studied with the multiple instrumental methods, such as XRD, IRS, RAMAN spectroscopy, HR-TEM and EDX analysis (Nikolaev et al 2017). X-ray diffraction showed that mineral component of the icefish bone is presented by the poorly-crystallized apatite. Calculation of the CSD lengths along c axis showed that apatite crystals are about 15 nm, which correlates with the TEM data. This value is significantly smaller than CSD length of natural apatite (which was used as standard and has ~100 nm CSD length). Unit cell parameters of the apatite (a = 9,37 A, c = 6,87 A, ± 0,01 A) have a distinct difference if compared with stoichiometric apatite (a = 9,418 A, c = 6,884 A). IR- and RAMAN spectroscopy both confirm that apatite is the mineral component of the bone tissue. Spectra contain bands corresponding to the B-type carbonate ion, water molecules, OH-groups and hydrophosphate ions. Transmission electron microscopy showed that icefish bone has nanocrystalline structure with apatite as mineral phase. Apatite crystals have 5–10 nm size, and this value correlates with CSD lengths calculations. EDX & EELS scanning showed the presence of Ca, P, O, C and Mg in the bone. Element mapping with EDX didn't reveal any regularities in distribution of Ca, P, o or C in the bone.All the data gathered prove that the mineral component of the *Champsocephalus gunnari* can be defined as non-stoichiometric water-containing carbonated B-type hydroxyapatite with vacancies at the Ca site.

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FRAMBOIDAL PYRITE: EXTREME BIOMINERALIZATION FROM THE ARCTIC TO THE ANTARCTIC

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Authigenic pyrite in the bottom sediments of the seas is formed, as a rule, during the early diagenesis stage. Structure and morphological characteristics of authigenic pyrite are used as redox proxy in ancient and modern sedimentary systems. Authigenic pyrite often takes the form of the framboids in the bottom sediments of the seas. Framboids are subspherical aggregates of crystals of submicron sizes (crystallites). Framboidal pyrite in sedimentary deposits has a biochemical origin, since its formation is associated with the vital activity of sulfate-reducing bacteria. In the bottom sediments of normally aerated seas, such conditions are created, as a rule, in the reductive diagenesis zone at a depth of 20–25 cm below the sediments-water interface. However, the boundary between the oxidized and reduced zones may vary depending on the hydrological and geological conditions of the sea. It has been established that the framboidal pyrite in anoxic marine basins (the Black Sea, the Cariaco Basin in the Caribbean Sea) is formed already in the water column and in the surface layer of bottom sediments. Detailed lithological, mineralogical, geochemical and microbiological studies were carried out in the Laptev and the White Sea (Arctic), the Caspian and Black Sea, as well as in the Cooperation Sea (Antarctica). These seas are located in different geographic zones, which radically differ in climatic, hydrological, geochemical and other natural conditions. The structural features and character of the distribution of framboidal pyrite in the bottom sediments of the seas were studied. Hydrological, lithological, geochemical, and biological parameters influencing the intensity of the formation of authigenic pyrite under extreme conditions are determined: at the extremely low temperatures (in the Arctic and Antarctic), in the hydrogen sulphide zones (in the Caspian and Black Seas) and in the methane sipes areas (in the Laptev Sea). Some features of the processes of formation of the framboidal pyrite are established: (1) the extremely low temperatures of the lower layer of the water column are not a limiting factor for the bacterial sulfate reduction and diagenetic processes leading to the formation of a framboidal pyrite; (2) the formation of the framboidal pyrite actively proceeds in the bottom sediments saturated with biogenic components – opal frustules of diatoms (in the White and Caspian Seas, in the Cooperation Sea) and calcite plates of coccolithophoride (in the Black Sea); (3) framboids of pyrite are formed inside diatomic frustules without species or generic selectivity: for example, pyrite framboids are observed in the Cooperation Sea (Antarctica) at a depth of 700 m (in the fluffy layer) in the frustules of the pennate diatoms (Fragilariopsys sublinearis, F. rhombica, Pinnularia quadratarea) and centric diatoms (Corethron criophilum, Asteromphalus parvulus, A. flabellatus, Chaetoceros atlanticus, Rhizosolenia antennata f. semispina, Actinocyclus curvatulus, A. actinochilus, Coscinodiscus asteromphalus, C. radiatus); (4) the framboids of pyrite are observed in the bottom sediments of normally aerated marine basins (for example, in the White Sea) both in deep horizons (deeper than 20 cm), where the processes of diagenesis occur, including sulphate reduction, and in the oxidized surface layer, in the diatom frustules, where are reducing microzones, enriched planktonic organic matter, iron and sulfur; (5) framboidal pyrite in the areas of methane sipes (in the Laptev Sea) is formed in carbonate concretions in association with other authigenic minerals (magnesian calcite, aragonite, phosphate minerals), during the formation of concretions by bacterial sulfate reduction and the process of anaerobic oxidation of methane with the participation of methane-oxidizing microorganisms.

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INFLUENCE OF TEMPERATURE ON MICROMYCETES ISOLATED FROM MINERAL BUILDING MATERIALS

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Investigations of colonization of building materials by mould fungi are very important in connection with both negative deterioration consequences and health effects. Artificial and natural mineral materials are also exposed to fungi. In appropriate conditions micromycetes might be very abundant on plaster, on mortar and on concrete plates though from the biological point of view is an extreme environment. They get inside with dust and adapt to the external conditions. Biodeterioration of building materials is primarily dependent on the availability of water and nutrients. PH of mineral substrates also plays a significant role in the processes. After construction, concrete is usually immune to biological attack because of high alkalinity, but once the pH of the concrete surface decrease it colonized by microorganisms including fungi. It is known that micromycetes can develop in a wide range of temperatures. Unfortunately the influence of this factor on biocorrosion of mineral building materials is not well understood.

In mycological examinations of buildings mould fungi often were found in the fissures of concrete walls exposed to freezing. When the buildings were for a long time in a state of construction or reconstruction subject to repeated freezing and thawing many fungal colonies covered concrete or plaster surfaces of walls and ceilings. Most frequently genera *Aspergillus, Cladosporium, Penicillium, Verticillium and Ulocladium* were dominated. Giant colonies of *Aspergillus flavus* were found on concrete ceiling panel of an unheated building. *Ulocladium* species were isolated from damaged plaster of an Ice Arena interior wall.

The aim of this research was to determine the temperature effects on vital activity in laboratory experiments. As model organisms strains of *Aspergillus, Cladosporium, Ulocladium* able to overgrow plaster specimens were selected. For the fungi cultivation Czapek-Dox agar medium with 0.1% glucose as source of carbon was modificated with 10% of cement, medium pH was adjusted to 8.0. The medium without cement served as a control. Temperature of cultivation varied from 5 to 30 ˚C. As evaluation criteria radial growth rate, lawn biomass and length of substrate hyphae were used. Deterioration capability of fungi towards mineral substrates estimated by both color change of indicator bromocresol purple and clarification of chalk agar.

The fungi were able to grow actively in a wide temperature range (from 5 to 25 ˚C), for majority temperature optimum is about 15 ˚C. When the temperature decreases many of them become more resistant to biocides and other negative influence. They can penetrate into deeper layers of plaster. In laboratory conditions the fungi while growing on nutrient media with cement powder at low temperature were more submerged into substrate than at moderate ones. At 5 ˚C depth of penetration into the substrate of *Ulocladium* species was 1.5 times more than at 15 ˚C.

The growth rate of *A. niger* strains isolated from blackened areas on outdoor marble was almost the same in a wide temperature range (from 10 to 30 ℃). Acidification activity of *A. niger* after many freeze-thaw cycles was higher than before this manipulation.

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