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Plenary Session

SOILS OF CLEMENTS MASSIF, EASTERN ANTARCTICA

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Preliminary results of the soil surveys in the Clemence Massif are discussed in presentation. The Clemence Massif situated in the central part of the Prince Charles Mountains, Mc. Robertson Land, Eastern (Continental) Antarctica, close to the edge of the Lambert glacier, 400 km far from the ocean (Cooperation sea). Mountains investigated are presented by gneisses and their debris's. Relief of the studied territory is mountain upland, surrounded by glaciers. Climatic conditions are very severe, mean January temperature is –3,1 C, while in March it decreases to –23 C, precipitations in snow form prevails. The first soil description of the Clemence Massif have been made by M. Andreev during the 58th Russian Antarctic Expedition. Investigations conducted shows that the soils of the massif presented by Regolith's ("Ahumic soils"), Leptosols and Lithosols. Their profiles are not developed, slightly differentiated, they doesn't show the evidence of well weathered solums and strong vertical differentiation. Soils with some humus content formed under mosses and lichens communities, while the regolith dominates in vegetation free areas. Cryogenic features are not well expressed in soil investigated due to small profile thickness. The mean organic carbon content in soils investigated is about 0,12–0,40 %, while the maximum rate is 4,74 %. In general, nitrogen content, also is very low — 0,01–0,03 %, which is caused by organic remnants composition and low degree of soil organic matter transformation. Thus, on the base of the data obtains, the soil of the Clements massive can be classified as a weak developed soils of continental polar deserts with low portions of organic Carbon and total Nitrogen, weak soil profiles, low degree of soil profile differentiation.

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ORGANO-MINERAL COMPLEXES AS THE TOOL OF ORGANIC MATTER DIFFERENTIATION AND PROTECTION IN SOILS AND PALEOSOLS

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Interactions between soil organic matter (OM) and mineral surfaces play the important role in OM protection. Solid state ^{13}C-NMR spectroscopy was applied to characterize the organic matter of: (1) different granulometric fractions (sand, silt and clay) separated from modern smectite — rich soil (vertisol); (2) the whole late Holocene steppe paleosoils and their predominantly smectitic clay fractions; (3) clay fractions of Carboniferous paleosoils with smectite, kaolinite or palygorskite dominant clay mineral. To study the possible mechanisms of OM protection we investigated the adsorption of humic acids by montmorillonite and palygorskite using batch-equilibration laboratory experiments.

The obtained data showed that the adsorption of HAs by montmorillonite and palygorskite resulted in fractionation of HAs depending on the clay type. The main trend is the enrichment of HA-montmorillonite complexes in alkyl — (polymethylene type structures) groups and HA-palygorskite complexes — in *O*-alkyl (polysaccharides) groups. In both cases the aromaticity of adsorbed HAs decreased and complexes gain the characteristics which are more typical for fulvic acids.

In vertisol (Limagne plain, France) the OM of the clay-size fraction is the richest among other fractions in alkyls and carboxyl-carbonyl groups. Silt and sand-size fractions show the gradual decrease of the abundance of these two groups and the increase of *O*-alkyls and aromatic C abundances (Alekseeva et al., 2014).

OM of smectite rich clay fractions from the top horizons of steppe soils (Volgograd region) in a comparison with the whole soil samples demonstrate the same tendency: they are richer in alkyls and carboxylic — C. The topsoils of the late Holocene paleosoils buried under the kurgan mounds 600–5000 years ago are characterized by the loss of organic carbon content by factor upto 4. Stabilization of OM in soil clay fractions resulted in its preservation and diagenetic loss only by factor 2. Under burial both kind of samples demonstrate the loss of alkyls and *O*- alkyls, both of them become richer in aryls (aromatic C) concentration; clay fractions additionally have larger content of carboxyl — C.

The protection of OC in soil clay fractions allows to investigate the humic substances which age is over 300 millions years. Clay fractions of the studied Carboniferous paleosols contain 0.5–5 % of OC. Their ^{13}C — NMR spectra showed that aryl-C is the main component of OM in case of smectitic and kaolinitic clay composition. In palygorskitic soils of this age fulvate type of humus containing the equal parts of alkyl-, O-alkyl- and aryl-C preserved due to the formation of chemical bonds between HA molecules and Si-OH groups of palygorskite (Alekseeva et al., 2010).

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NANOCLUSTER (QUATARON) CONCEPT OF CRYSTAL NUCLEATION AND GROWTH

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At the end of last century the author had proved the possibility of spontaneous formation and relative stable existence of special nano-size clusters in supersaturated media (solutions, vapor phase) and overcooled melts. These clusters were interpreted as prenucleation protomineral particles and were named clusters of “hidden” phase or QUATARONS [1]. On this basis a special quataron concept of cluster self-organization of matter at nano-level was formed within which a number of debatable questions of the nucleation theory, formation of crystalline and non-crystalline materials was solved [2, 3]. In particular, nucleation of crystals through quatarons explains the nature of the two-step mechanism of nucleation [4].

Next year new ideas on clusterization of substance in crystal-forming media and prenucleation clusters became extremely popular and find more and more experimental proofs. Owing to really specific character of their properties, these clusters are given special names by other authors — for example «DOLLOP» [5]. We, in turn, go further — we consider quatarons, dollops and other similar particles as the basic building units of growth of crystals. As a result a principally new concept of quataron growth of crystals, different from known concepts of microblock (Fedorov-Balarev) and atomic (Kossel-Stransky) growth of crystals was formed on this basis.

According to this concept growth of crystals is carried out by particles larger, than separate atoms and molecules, but these are not crystalline blocks. Clusters of "hidden" phase (quatarons) are these particles (growth units). With that, atomic growth can take place, when quatarons disintegrate on a growing face of a crystal to separate atoms, while microblock growth (growth by 3D nuclei) — when quatarons are transformed to crystalline nuclei in surrounding medium. The quataron concept developed by us allows to generalize nowadays popular ideas of nonclassical crystal nucleation and growth.

Thus, quataron concept of crystal nucleation and growth adopts features of basic crystallogenetic concepts, which pretend to be modern paradigm of crystal forming. Yet, accepting relative universalism of nanoclaster crystal growth it is impossible to deny multipath character of this process, and as a result dominant mechanism of crystal growth can vary depending on growth conditions.

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BACTERIAL BIOCALCIFICATION: FROM FUNDAMENTAL RESEARCH TO APPLIED PERSPECTIVES

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Microbially-induced calcification is considered as one of the main natural processes controlling CO_2 levels in the atmosphere and a major structural and ecological player in the modern and past ecosystems. In this study are presented the data of laboratory experimental work on $CaCO_3$ precipitation with pure cultures of the cyanobacteria *Gloeocapsa* sp. and of two anoxygenic phototrophic bacteria (APB), the haloalcaliphilic *Rhodovulum steppens* A-20s and the neutrophilic halophilic *Rhodovulum* sp. S-17–65. These bacteria represent two important groups of photosynthetic organisms in the past and at present time. APB is the oldest microorganism that could be dominant during the anoxygenic period of Earth's life (approximately 3.5 billon years ago) whereas the origin of oxygen evolving microorganisms (cyanobacteria) is placed at about 2.5–2.2 billion years ago as based on oxidation records of the Earth's crust. In modern ecosystems, cyanobacteria are the dominant primary producers. Nonetheless, the potential of APB are abundant in the modern microbial mats and stromatolites and thus may represent a considerable fraction of the standing biomass. However, biomineralization induced by these bacteria has not been thoroughly studied so far.

In this context, the aim of this study is to characterize the process of biological $CaCO_3$ precipitation and to assess the existence of metabolic processes protecting studied bacteria against carbonate mineralization on their surfaces. To this end, kinetic experiments, SEM and TEM imaging, EDX and XRD analyses, along with coupled CLSM and Raman microspectroscopy, zeta-potential measurements and Ca adsorption into bacterial surface were carried out.

The result of our study demonstrates the participation of studied bacteria in $CaCO_3$ precipitation and the existence of two different mechanisms of $CaCO_3$-nucleation: an unspecific supersaturation by APB and a specific nucleation at the cell wall by cyanobacteria *Gloeocapsa* sp..

In addition, by accelerating the naturally occurring carbonation of magnesium silicate minerals, it is possible to sequester CO_2 in the geologically stable mineral magnesite ($MgCO_3$). Reaction rate can be accelerated by decreasing the particle size, raising the reaction temperature, increasing the pressure, changing the solution chemistry, using a catalyst, and, hypothetically, by adding bacteria. The strain *Synechoccocus* PCC 7942 (freshwater cyanobacteria) was chosen for this study because many aspects of this species have been well studied (physiology, metabolism, surface properties, mineral precipitation). The results show that *Synechoccocus* PCC 7942 can accelerate silicate dissolution (Mg release) and then magnesium carbonate precipitation (by pH increasing during photosynthesis). Therefore, it is a potentially good candidate for large-scale CO_2 sequestration experiments.

ION SUBSTITUTIONS AND NON-STOICHIOMETRY OF OXALATE AND PHOSPHATE MINERALS OF THE HUMAN BODY

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There are many uncertainties about the ionic substitutions and non-stoichiometry of minerals formed in living organism.This work summaries the long term data on the regularities of complicate substitutions in phosphate and oxalate minerals of a human body.

Owing to the presented resultsthe Ca-oxalates (whewellite $CaC_2O_4(1+x)H_2O$, weddellite $CaC_2O_4(2+x)H_2O$) and phosphates (apatite $Ca_{10}(PO_4)_6(OH)_2$, struvite $NH_4MgPO_46H_2O$, brushite $CaHPO_42H_2O$) are characterized by variable non-stoichiometry composition that reflects the non- stationarity of formation conditions [1–3].

Non-stoichiometry of calcium oxalates connect with variable quantities of water molecules. The amount of”zeolitic” water molecules (x) in the structure of weddellitefrom renal stonesvaries from 0.13 to 0.38 p.f.u.There is a significantpositive correlation between the x value andthe closest interatomic distance between coordination water molecules in the large channels (OW1–OW1) as well as positive correlation between the valueof the a parameter and the average distance of <Ca1–O> in Ca polyhedron.Obtainedlinearregression equationcan be used for determination of the“zeolitic” wateramount usingthe known unit cell a parameterwith mean-root-square error ±0.03 p.f.u.The significantvariations of whewellitecrystal lattice parameters can be explained by presence of additional water molecules, which are disorderly distributed and therefore cannot be found in the difference Fourier synthesis maps.

Variable composition of calcium and magnesium phosphates is caused by substitutions at all crystallographic sites. Thevacanciesaredetectedat Ca-sites (apatite, brushite) and at Mg-site (struvite). Isomorphic capacity of admixture ions in struvite and brushite crystals is limited by the content of these ions in the physiological solution and, in case of Mg replacement with Ca in struvite and Ca with K in brushite, is also essentially limited by the size differences of the host and admixture ions.The studied biological apatites are water-containing carbonated hydroxyapatites with Ca_2^+ and OH^- ion deficiencies. Whilethedominantrole in the structure belongs to water the influence of carbonate ions is less. The charge imbalance is mainly compensated by the vacancies at Ca-sites. The contribution of alkali cations is restricted. Owing to the variations in the unit cell parameters ion replacements in apatites of pathogenic origin are more intense in comparison with physiogenic dental enamel apatites. Among the pathogenic apatites major compositional variations are observed in renal stone apatites that indicate strong variability of formation conditions.

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THERMODYNAMICS AND KINETICS OF BIOLOGICAL FLUIDS CRYSTALLIZATION

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Processes of crystallization of slightly soluble compounds have always attracted the attention of researchers. This fact draws attention of scientists because these compounds are pathogenic minerals and they are of pathologic origin in human body. Furthermore, the studying these compounds gives perspective for the synthesis of modern biomaterials. There are very few researches concerning the crystallization of pathogenic compounds as well as the slightly soluble compounds from biological fluids necessary for human.

The main difficulty in studying of such systems is to determine their composition. Biological fluids consist of a number of components, both organic and inorganic. Crystallization of biological fluids is a genetically based process associated with the presence of certain organic and inorganic components. Biological fluids are complex polydisperse acellular structures with constituent components which have fragile bonds: saliva, serum, lymph, etc. Body fluids include lyotropic liquid crystals, and even the smallest changes in the functioning of the body are manifested in the changes in the crystal structural order. Elements in biological fluids instantly change its structure peculiarities after any impact of external and internal nature.

Studying of the processes of crystallization of slightly soluble compounds in human body for the purpose of prophylaxis and prevention of a number of diseases is a promising area of research.

This paper presents the results of studies of the nature of crystallization of slightly soluble compounds from solutions simulating the composition of human physiological fluids under close to the physiological conditions.

Thermodynamic calculations reflect the possibility of phase formation only using the data of their thermodynamic stability in standard conditions and it doesn't consider, in particular, the impact of kinetic factors on the process of solid phase formation.

Analogs of phosphate and oxalate minerals were received in our model experiments as well as the differences in the conditions of their formation are revealed. The analysis of the obtained data showed that the pH of the solution has the greatest impact on the structure of a being forming solid phase. Thus the variation of initial concentrations of the components of the solution, in the range of values which are characteristical for biological liquid, leads to quantitative changes instead of changes in the structure of the deposit.

The investigation of the state of aggregation of the components of bioliquids on the pathology has been carried out. The studying of physical and chemical reaction mechanisms of bioliquids on external physical factors have been made, this is necessary for the fundamental knowledge about the nature and the development of a number of practical applications, based on this knowledge.

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MIMICKING A CALCITE-BASED FUNCTIONAL BIOMINERAL OF THE HUMAN BODY

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After having learned about the structural complexity of biomimetic fluorapatite-gelatin nanocomposite crystals [1], we investigated the morphogenesis and structure of a calcite-based nanocomposite, also grown by double-diffusion in gelatin-gel matrices [2,3] .

The outer shape of the as-grown specimens in their final state of morphogenesis is characterized by a bulbous (cylindrical) body with 3+3 rhombohedral faces at their ends, a morphology which is known from human otoconia (calcite-based biominerals in the inner ear, acting as receptor system for gravity and linear accelerations) [4] .

Biomimetic otoconia represent the first example of a perfect copy of a biomineral (functional material), not only in inner architecture but also in outer shape. Although the inner architecture of otoconia is highly anisotropic and is characterized by a more dense dumbbell-region (rhombohedral branches) surrounded by a more porous (less dense) belly area, the Bragg pattern (X-ray) of otoconia is representative for a single crystal.

The knowledge of the particular structure of otoconia opens up the chance for deeper understanding of their function as receptor organ for acceleration movements, as well as for degeneration effects under in vivo conditions leading to trouble with positional vertigo. Structural damage of otoconia may be caused by complexing agents, such as the antibiotic gentamicin [5]. The main advantage of biomimetic otoconia for experimental use under in vitro conditions is their bigger size (up to 400 μm) compared with human otoconia (~ 10 μm) .

At first glance, the morphology (habit) as well as the inner architecture of otoconia seem to correspond to the macroscopic symmetry (point group) –3m. In the ideal case, the density distribution within an otoconium also corresponds to this point group symmetry, However, significant signs have already been collected that the overall macroscopic symmetry of most of the otoconia (biogenic as well as biomimetic) is reduced by loss of the center of symmetry and sometimes even the three-fold rotation axis. This situation is indicated by varying sizes of the rhombohedral planes which immediately reflect different volumes of the branch areas within otoconia and which are assumed to cause non-centrosymmetric density distributions. These observations may contribute to deeper understanding of the function of otoconia.

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PARTICULARITIES OF SUPERPERIODICAL MOLECULAR PACKING IN CRYSTAL STRUCTURES OF ORGANIC SUBSTANCES OF BIOLOGICAL AND GEOLOGICAL ORIGIN

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Three types of superperiodic molecular packing in crystals of organic substances have been analyzed in a series of exemplary organic compounds occurring in both living organisms and their fossilized remnants. The analysis involves perusing the results obtained by the author and co-workers in the course of studying a number of organic compounds by means of X-ray diffraction methods, X-ray high-temperature techniques, and chromatographic analysis, as well as results of simulating the structures of naturally occurring mixtures by means of experimental preparation of blends having pre-determined molecular compositions. The factors that can facilitate formation of superperiodic structure are briefly considered below taking into account the concept of the closest molecular packing and the types of intramolecular bonding.

Superperiodic structure as the result of the closest packing of molecules having different sizes. This structure has been observed in substances having van der Waals intramolecular bonds. In the absence of directed intramolecular bonds (e.g. hydrogen bonds), this type of packing can be formed “on its own accord”, because the molecule having various lengths tend to pack themselves within the crystal in the closest possible fashion. Examples of compounds having such types of packing include numerous naturally occurring and artificially obtained polycomponent paraffin compositions of the following formula: $C^{n}H_{2}^{n+}{}_{2}$ (n = 17–36), i.e. ozokerites, ceresins, petroleum waxes and beeswaxes, paraffins occurring in mammalian brains, etc. [1, 2] .

Superperiodic structure as the result of the closest packing of dimer molecules having different sizes. This structure has been found in substances having both hydrogen and van der Waals intramolecular bonds. The packing of this type is formed by so-called “combined dimers”. The dimer consists of two molecules having unequal lengths and interlinked by hydrogen bonds to form the dimer structure. Examples of such compounds include even and odd fatty acids in the series of the following general formula: $C^{n}H_{2}^{n}O_{2}$ (n = 11–24) [3, 4] .

Superperiodic structure as the result of the closest packing of molecules having similar dimensions, but different configurations. This structure occurs in substances having both hydrogen and van der Waals intramolecular bonds. The packing of this type can be encountered in enantiomers or chiral substances. Despite having similar dimensions, such molecules are not identical due to their different configurations. Various stoichiometric ratios of the dextrorotatory and levorotatory molecules facilitate formation of a number of discrete types of superperiodic packing (e.g. four-layer packing, etc.) of molecules in the crystal structure. Examples can be represented by numerous discrete compositions in the system of malic acid enantiomers [5] .

The investigations were performed using the equipment of the Saint-Petersburg State University Resource Centers “X-ray diffraction studies” and “Geomodel”.

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LINKAGE OF POROSITY OF BASIC AND ULTRABASIC ROCKS TO SOIL CLAY MINERALOGY IN COLD HUMID CLIMATES OF RUSSIA

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Pore space characteristic of rocks strongly affect diffusion transport and permeation transport and hereby chemistry of pore solution. In order to assess the dependence of soil characteristics, especially mineral association, from the kind and pore space characteristics of the parent hard rock was studied. The soils are represented by recent ones of Holocene age from northern taiga and mountainous tundra zones of cold humid climates of Northern Eurasia (Russia). Mineral association of the basic (amphibolite and meta-gabbro amphibolite) and ultrabasic (serpentinous dunite) rock samples from the lithic contact of the soils were studied in thin sections by optical microscopy. Three supplementing methods for the determination of the pore space characteristics were applied to investigate rock weathering. The methods are (i) mercury intrusion porosimetry (MIP) for quantification of the total porosity and pore size distribution, (ii) a modification of this method, the intrusion of a molten alloy (Wood‘s metal) and subsequent electron microscopy on polished sections for determination of the micromorphology of the connective pores and detection of closed pores, and (iii) scanning atomic-force microscopy (AFM) for getting quantitative data of pore dimensions. The quantitative mineralogical composition of the samples was also determined with X-ray diffraction and Rietveld analysis.

Based on the data obtained, in the rock samples zones of phyllosilicate accumulation are observed in regions with higher porosity indicating the dissolution of primary minerals in rocks and creating new voids, most pronounced in the ultrabasic rock. Despite similar values for total porosity of rock samples (8–14 vol.%), they show considerable difference in pore size distribution, reflecting the presence of phyllosilicates. In the ultrabasic rock strongest enriched in phyllosilicates ~90% of the porosity is due to pores with radii <100 nm. Whereas in the basic rocks the portion of pores with radii <100 nm and especially <10 nm is significantly lower. The content of clay minerals in the fine size fractions of soils from the basic rocks correlates to the portion of smallest pores in the parent rock. Inherited phylosilicates are clearly traceable in the soil from meta-gabbro amphibolite as opposed to soil derived from amphibolite, which lack phyllosilicates in the whole profile. Thus, the rock sensitivity to weathering is affected by (i) high value of the small pores, especially with the size range <10 nm radius; (ii) elongated form of the pores and surface roughness; and (iii) the zones with phyllosilicates accumulation in regions with higher porosity. Thus, the specificity of pore space characteristics is a decisive factor for the clay mineral association in soils formed from basic and ultrabasic hard rocks.

USE OF MEMBRANE TECHNOLOGIES TO STUDYING BIOINERT INTERACTIONS

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Membrane technologies are important in the process of conducting research related to the environment, and in particular in the study bioinert interactions. Membrane — a selective barrier between two phases. Membrane methods allow you to implement a wide range of separation processes, and solutions for different tasks require different types of membranes with different structures.

Various membranes are widely used for filtering microorganisms from environmental objects (soils, minerals, etc.) for their subsequent detection and study of interactions bioinert.

All membranes can be divided into two types: porous and nonporous. For filtering bacteria and viruses often are used for microfiltration membranes, porous (pores> 50 nm) and ultrafiltration (2 nm <pore size <50 nm). Using non-porous membranes with pores less than 2 nm is impractical solutions ecological problems. Morphology, or rather, the physical state of the polymer membrane material (crystalline or amorphous crystalline, glassy or rubbery) directly determines it, s permeability.

Use of microfiltration membranes typically provides a relatively high flow and good retention of viral particles due to electrostatic interactions. However, the pore size microfilters are often much larger than the size of many viruses that use of ultrafiltration applications. In some cases, there is a need for ultrafilters with a smaller pore size.

Ultrafiltration membranes can also be considered as porous membranes. However, their structure is substantially more asymmetric compared with the structure of microfiltration membranes. In some cases, there is a need for ultrafilters with a smaller pore size. Ultrafiltration membranes consist of a thin upper layer at the porous substrate, the mass transfer resistance is almost entirely determined by the upper layer.

We have successfully applied for the separation membrane technology bioinert material soil. For definitions of various microorganisms and viruses used microfiltration membranes and ultrafiltration membranes. In the study we used the technology concentrating microorganisms in a tangential flow. Besides the standard developed by us using membranes with optimal membrane pore structure based on aromatic polyamide compounds.

Thus, the wider adoption of membrane technology could bring new data in the study of fundamental and applied aspects bioinert interactions in the lithosphere, biosphere and technosphere.

SOILS INSIDE THE ROCKS: STRUCTURE, GENESIS AND RESEARCH TECHNIQUES

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Soils inside the rocks develop under the influence of endolithic communities occupying structural cavities in the interior of solid rocks. Scientific rationale for endolithic organisms was provided by Friedmann

(1982) revealing that bacteria, algae, fungi and specific lichens find their ecological niche within few upper centimeters of the rocks, thus escaping in hot/cold deserts and high mountains the intensive UV-radiation, moisture deficit and wind abrasion. The most suitable rocks for endolithic colonization are sandstones, various granitoids, marbles and any others with a significant content of translucent and/or transparent mineral grains which make the primary organic matter production possible inside the rock (dark basalts are more subjected to epilithic colonization) .

Our studies in East Antarctica oases show that the system "endolithic organisms — parent rock" has all characteristic features of soils: (1) the rock (parent material) layer subjected to the action of external abiogenic factors, (2) the living organisms functioning in this rock and synthesizing/decomposing organic matter, (3) the in situ transformation of initial rock under the impact of abiogenic and biogenic factors with accumulation and removal of the transformation products and development of the vertical heterogeneity composing the microprofile. It is very important that endolithic pedogenesis is capable to produce autochthonous fine earth. The other crucial feature related to pedogenesis is the presence of organomineral horizon — the hotspot of biota-rock interactions.

Microtomography data shows that different layers of endolithic system are connected with the fissure network which serve as the transport system for elements migration.

Our measurements in Larsemann Hills oasis (East Antarctica) indicate that the carbon content in endolithic organomineral horizons developed in granitoid rocks varies from 0.2 to 3.7 %, the nitrogen content — from 0.02 to 0.47 %, and the mean residence time of organic matter reaches 480 ± 25 yrs. The values of $\delta\ ^{13}C$ obtained for the dated samples attest to a somewhat heavier isotopic composition (–21.0 to –23.7 ‰) of the organic matter in comparison with the values typical of C3 plants, as well as with the values obtained for the endolithic material from the Dry Valleys of Antarctica (Hopkins et al., 2009). Our preliminary estimate of average endolithically generated organic C stocks in granites of Larsemann oasis in East Antarctica is 0.037±0.019 g C/cm^2.

The major products of the endolithic pedogenesis are the silty–sandy fine earth and abundant amorphous Fe–Al–Si–C-containing films with admixtures of K, Na, Mg, Ca, S that are formed on the walls of the fissures inside the rocks and on the lower face of exfoliation plates; precipitation of these film is specified by the mechanical and oxidation geochemical barriers at the air/rock interface.

The study of endolithic weathering front with the approaches of soil science needs more systematization and understanding of the place these objects occupy in the soils world. It can turn out that endolithic soils are the most spatially abundant soil bodies in extreme environment of Antarctica, some highlands and deserts. Besides such objects should be recognized as an early-Earth “protosoils”.

The data on major features of endolithic soils studied by contemporary microtomography, SEM/TEM and isotopic techniques will be discussed in the presentation.

WAS THERE LIFE ON MARS, WILL CONTINUE LIFE ON EARTH?

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The Problem.There is a need for conceptual detail of some terms of the field of genetic. In particular, the process of organogenesis can mean as the transformation of a biological substance into the rock, and the formation of any natural endogenous compounds hydrocarbons nothing to organics, in the conventional sense, no. Therefore, in principle suitable specification — in the first case, the use of the term vitagenesis expressing the emergence and development of living organisms in that they produced the rock, which in this case referred to as vitagenious (eg coal, peat, coquina). The term organogenesis has a broader meaning and includes, in particular, hydrocarbon compounds all matter how they have origins (e.g. endogenetic oil, combustible gases). Organogenetic substance occurs in terrestrial lavas, meteorites, comets, where they have their synthesis.

Mars is so far the only foreseeable space of the planets, which has some properties to allow for comparative analysis with the Earth. Mars is like a dwarf Earth stopped in its development in the early stages The planet’s surface is covered with desquamationeous eluvium consisting of visible particles of dust and disintegrated particles of bedrock in mineral constituents: calcium feldspar, fayalite, augite, pigeonite, hypersthene, hematite, goethite and exogenous gypsum, jarosite, dolomite, montmorillonoid.. While never met organic compounds, no liquid and solid hydrocarbons, as well as evidence of the existence of any cellular forms. By analogy with other celestial bodies can assume that it has organospheare, as evidenced by the rare traces of methane on the surface of the planet. Evolved barely noticeable carbon dioxide from the interior of the planet, nitrogen, methane, inert gases and some other passing along the faults can form not yet met some organic compound. Doubtless that life is never existed on Mars.

Earth has a mantle, the term substance responsible for the physical properties of basic and ultrabasic complexes of Mars. It overlaps with the earth crust, upper part of which consists with granitogneisse rocks unique for the solar system planets. Many of its minerals, as many other peculiarities is also unique and associated with emerging and developing of life until the level of human civilization. Earth has a complex history of the characteristic feature of which is the divergence of planetary geological processes, the emergence of new biological formations, and the increasing complexity. And there is no alarming symptoms extinction of life on Earth.

But..Àafter about 1–2 Goals postantropazoic era will have evolutionary “ incorrect “ converse with positions anthropology direction. The genus Homo as a biological unit will irreparably degrade to the extinction, because of the innumerous reasons. One of the consequences of past civilization is man-made changes in the atmosphere with a sharp increase in carbon dioxide. Since CO_2 — gas providing basic implementation of photosynthesis his relative surplus provides intensive development postantropozoic photosphere.

In excess of carbon dioxide evolution intensifies almost all marine animals with carbonate exoskeleton — corals, sponges, echinoderms, mollusks, etc., as well as plankton and nekton.

Certainly, humanity anticipates its deadlock and is searching Earth-like planets, which should be as like her, having identical terrestrial atmosphere, hydrosphere, edaphosphere, in the future will be the only Mars, where no provisions for “accommodation “ Homo does not exist and it will remain uninhabited. In the known and unknown universe planetary systems may exist of such planets, which are similar in structure to the Earth, have their granitogneiss sheath and the biosphere, to the level of advanced civilization capable of leading the search for cosmic “ neighbors “. Preserving these civilizations produced signals, their physical expression, while traveling in the course of billions, or hundreds of millions of years more than problematic, all the more that the existence of civilization — a few thousand years at most — make up a negligible amount from the travel time of the signal. Therefore, the idea of interplanetary communications in its present form makes no sense and is using it in the usual harmful, as it allows to treat Alma mater as a winning place of temporary residence and thereby approximate time of ecological collapse. Mankind was born, and will end its days on Earth as all terrestrial species.

PICOCYANOBACTERIA: A LEADERSHIP IN THE GLOBAL CARBONIC VITALIZATION

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The main focus of bio-inert interactions is the global carbonic ‘vitalization’, i.e. the channeling of abiotic carbon, preferentially represented by carbon dioxide and carbonates, into biotic matter. This enzymes-driven process is performed by some representatives of the prokaryotic biosphere, including simple plastids, which synthesize carbon skeleton-possessing (organic) molecules from carbon skeleton-lacking (inorganic) precursors. Corresponding metabolic function is known as autotrophy or C1-nutrition and, in terms of ecology, as primary production. A leadership in the global carbonic vitalization belongs to cyanobacteria, especially to the members of marine and freshwater plankton (Partensky et al., 1999) .

Cyanobacteria which are most abundant and widespread living organisms on Earth demonstrate a self-sufficient lifestyle due to the ability of oxygenic photosynthesis and nitrogen fixation. Because of effective adaptation to environmental stresses they are nearly omnipresent and thus can be found in all permissive niches except for aphotic, extremely hydrothermal (>80 °C) and highly acidic (pH<5) ones. In particular, the picocyanobacteria Synechococcus and Prochlorococcus occupy the oceanic euphotic zone across the globe and amount a population density

105 cells/mL (Scanlan, 2012) while at the same time Prochlorococcus has not been detected in freshwater bacterial plankton. Moreover, the geographic distribution of marine Prochlorococcus, which avoids latitudes above 60°N (Partensky et al., 1999), is distinct from that of Synechococcus. In fact, low temperature is a permissive environmental factor for the genus Synechococcus, whereas the marine Prochlorococcus should not develop in these conditions (Moore et al., 1995; Johnson et al., 2006) .

The genetic diversity and geographic distribution of picocyanobacteria can be best traced by environmental DNA analysis employing PCR with group-specific primers targeted at the 16S rRNA gene or the cpcBA-IGS part of the phycocyanin operon (Robertson et al., 2001; Crosbie et al., 2003; Ernst et al., 2003). Using this approach, marine Synechococcus were shown to be phylogenetically distant from their freshwater counterparts (Urbach et al., 1998; Crosbie et al., 2003). To address gaps in our knowledge of picocyanobacterial plankton diversity, especially that of Synechococcus picocyanobacteria, high-throughput 454 pyrosequencing of the 16S rRNA gene is applied, which allows for high-scale molecular sampling while sidestepping the need for clone library construction.

Synechococcus picocyanobacteria 16S rRNA sequences deposited in GenBank belong to widely distributed assemblages It should be also pointed out that the Synechococcus genus contains several globally distributed marine, brackish and freshwater lineages (Crosbie et al., 2003): Groups A, B, Cz, E, F, H, I, LBB3 and M; Clusters A, G, LB03, LSI, LSII, MH301, MH305 and PDI; Clade II together with a novel clade described by C. Callieri in 2013. At the same time, there are quasi-endemic clusters showing a limited eco-geographic distribution, e.g. Clusters LSI and LSII from Lake Superior, North America (Ivanikova et al., 2007) .

Except for the assemblages containing numerous Synechococcus picocyanobacteria 16S rRNA gene sequences, there are low-abundance phylotypes which can be assigned to the rare biosphere and represent evolutionary disadvantageous and ineffectively adapted environmental strains (Sogin et al., 2006; Pedrós-Alió, 2012). In conclusion, metagenomic analysis helps understand the diversity and distribution of picocyanobacteria. At the same time, both the real-time PCR and free-flow cytofluorimetric counting should help evaluate their population size as well as their contribution to primary productivity.

COMPLEX RESEARCH OF BIOMINERALISATION IN ANCIENT SEDIMENTARY ROCKS AND MODERN MARINE SEDIMENTS

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In sedimentary rocks biomineralization takes place at different levels of organization of matter that requires a systematic approach and high-tech equipment in its study. Biomineralization (the formation or accumulation of minerals by living organisms) can be “biologically induced” (BIM) and “biologically controlled” (BCM) (Lowenstam, 1981; Mann, 1983). To determine the role of biomineralization in the litho- and ore genesis comprehensive studies of Cimmerian oolitic iron ore (N_{22}, Kerch iron pool) and modern silty-clay marine sediments (Q^{IV}, White Sea) were carried out. The studies were conducted at the Department of Lithology and Marine Geology, Geological Faculty of Moscow State University and in the laboratories of the Institute of Oceanology RAS. Objective: to develop an optimal technique for detection of biological minerals and to study the different types of biomineralization in ancient rocks and the modern marine sediments. To study of biomineral formation at the micro- and ultra-micro level comprehensive laboratory tests were performed: a) light microscopy of samples in thin sections; b) Scanning electron microscopy (SEM); ñ) electron-probe microanalysis (EPMA); d) X-ray diffraction analysis.

Different types of biomineralization were found in the oolitic iron ores of Cimmerian age and modern sediments. BCM in Cimmerian oolitic iron ores may be detected already at the macro level. It is represented by carbonate biominerals made of large (5–7 cm) shells of mollusks and detritus. Light microscopy showed that calcite-siderite detritus has microfibre structure. X-ray diffraction analysis revealed the presence of carbonate biological minerals such as calcite and siderite in ores. SEM-images show that the shell detritus consists of alternating layers of calcite with different ultramicrostructures. In marine sediments BCM is presented by opal. It was discovered as a result of light microscopy of thin sections. It was confirmed by SEM and EPMA. Opal composes fragments of flint shells of diatoms, silicoflagellate skeletons and the spicules of siliceous sponges. BIM in oolitic- and pisolitic iron ores resulted in the formation of various oxides and hydroxides of iron. Microscopic and X-ray analysis of the ores reported presence of such iron biominerals as hematite, goethite, hydrogoethite, lepidocrocite and akaganeite, which compose the basic structural elements of ore — oolites, oolite-like formations and cement. Iron biomorphic formations of different shapes found by SEM and X-ray analysis in the oolitic iron ores and within pisolits, may be an indirect proof of iron bacteria involvement in iron ore process. Silicate biomorphic formations with complex shapes found in cements of oolitic and pisolitic iron ores are likely to point to the involvement of silicate bacteria in the formation of oolites and pisolites — large (up to 5 cm in diameter) round shape iron-clay aggregates with a concentric internal structure. These assumptions need to be clarified in further studies. In marine sediments BIM is found in the form of framboidal pyrite aggregates. Pyrite framboids are recorded in samples of sediment already in the light microscopy of thin sections. SEM help to visualize framboidstructure and different shape of individual crystallites — globular shape, pentagonal dodecahedron, octahedral and pseudocubic shape. Pyrite framboids often formed on the diatom shells surface residues or inside them. The results of these studies are necessary not only for understanding of biogenic substances role in the formation of sedimentary rocks and ores, but also for the reconstruction of paleoenvironment of sedimentary deposits.

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GEOGRAPHICAL COVER AND BIOSPHERE — CONCEPTS, RELATIONSHIPS, EVOLUTION

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A unique planet Earth, as it is life. On Earth there are inherent in all planets of the outer shell, called on the planet geographic. It is within this shell was developing, acquiring all large in size, the bearer of life, the biosphere. The upper border of geographic shell should be at the upper boundary of the troposphere. The troposphere is actively interacts with the earth's surface and all part of her bear the traces of its influence. The main regularities observed directly on the surface of the Earth zone, zoning, the differences between the continents and oceans, and others, is manifest in the troposphere. This is done in particular through the differences in temperature and humidity, dustiness. All the moisture of the atmosphere, in essence, is in the troposphere. The border of geographic shell in the lithosphere, at any stage of its existence, must match the depth of the manifestations of exogenous processes. So, geographical cover is a complicated outer shell of the Earth within which occur under the influence of cosmic phenomena and, first of all, solar energy intensive interaction of mineral, water and gas media, and after the occurrence of the biosphere, and living matter. When did she? Seems most reasonable to associate the appearance of her with the formation of the earth's crust, atmosphere, hydrosphere, climate and climatic types of lithogenesis. And before that was the geographical surface. We can assume that the crust is embodied part of the geographic shell. Obviously, the amount of this shell is little changed over time. He always took the zone of hypergenesis, water and the troposphere. Stability is obvious. This cannot be said about the biosphere. Under it we will understand the shell of the Earth, inhabited by the organisms. The size of her had changed considerably over time. When her uncertain. Judging by the remains of organisms clear that the 3.8–3.5 billion years ago life on our planet already existed. Because these traces of ancient life is not quite primitive, they suggest that life on earth appeared much earlier. With the advent of photosynthetic organisms living matter began to exercise their planetary function. It turned into a force that transforms the atmosphere and the Earth surface due to the radiant energy of the Sun. From this stage began a significant evolution of the geographical shell in the functioning of the biosphere. The main stages of its development were the following. Began with the emergence of photosynthetic organisms at the turn of 4–3.5 billion years ago. The biosphere, because of the ultraviolet radiation, existed only in water mass of water bodies with a depth of 10 m. The environment in the geographical cover was restorative. Only in the area of photosynthesis she was with the "spots" of oxidation. At the turn of 2.2–2 billion years ago atmosphere and conditions on land become oxidation. The environment in the water oxidation, but deeper than 10 m oxidation and restoration. Life exists as early only in reservoirs at a depth of approximately 10 m. In the Cambrian (0.54 billion years ago) the occurrence of the ozone layer, check fatal ultraviolet radiation at the Earth's surface. This occurred, as shown by studies of L. V. Berkner and L. C. Marshall, thanks to the achievement of the oxygen content in the atmosphere from about 0.01 his contemporary. The biosphere could spread throughout the volume of water bodies. Other parameters in the geographical cover remained in General still. It is the appearance of the ozone layer approximately 0.4 billion years ago at a distance from the surface of the Earth led to the spread of the biosphere as modern. Was an intensive evolution of life, accompanied by a growing closer modern. Finally, we can speak about the beginning of the aged (?) the stage of the biosphere development-related impacts on the biosphere and geographic shell intensive human activities, which began may, at the turn of the VII–XIX centuries. It is essential that all these changes occurred as a result of evolution of the biosphere. It has identified many geographic features shell.

BIRTH, LIFE AND DEATH OF ORGANISMS IS THE BASIS OF EXISTENCE OF THE EARTH

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The Earth is a planet of life. Life could appear on it due to the development of geographic shell and the emergence of organic chemical substances further transformed into biogenic result of long evolution. But life could have arisen on Earth and because of bring it from space. In either case, life was on Earth appear in the beginning of development of the planet. After all, sediment age of 3.8–3.5 billion years ago traces of life already. Because they are not quite primitive, it is believed that life on Earth appeared visibly before. Often people believe that the Earth is huge, compared to a paltry film of the biosphere, the planet, and, therefore, life cannot significantly influence it. However, it is worth remembering that the oxygen in our atmosphere, accounting for about 21 % of its composition, created by living organisms, and even more enormous mass of nitrogen, and the paramount importance of biosphere evolution of Land is very bright. The composition of the atmosphere is entirely due to the activity of organisms. The evolution of the atmosphere and first of all a change in the content of free oxygen created ozone screen and led to changes in its position. In the result over time in radical changes in the boundaries of the possible existence of life and its structure. Therefore gradually organisms won the entire surface of the Earth. So, we can talk about integral and permanent co-evolution of the organic world and the environment. Moreover, coevolution manifested outside the biosphere. Today, the atmosphere only in their rank and file belongs to the biosphere, and before the emergence of life on land in the surface of the Earth contact between them was not even. It is believed that solar energy is absorbed by the atmosphere and earth's surface is about 230 $J/m^2 \cdot s$. A significant part of it is used by living organisms and eventually absorbed their remnants and mineral substance in the form of potential energy. This process is demonstrated not only by the accumulation of dispersed organic matter and concentrations, in particular in the form of deposits of fossil fuels, but also on a large scale in the formation of clay minerals from feldspars. At last in the middle of the last century drew attention V.I. Lebedev. About the primary role in the transfer of energy generated by the solar rays, living and mineral substance and says colossal weight of her, manifested in the oxidation of organic matter. It is rated as 0.4 to 0.6 $J/m^2 \cdot s$. Essentially, what this energy is almost outweighs all the energy coming from the bowels of the Earth. This is an indication that the Earth is a planet of life. Energy role of the permanent functioning of birth, life and death of organisms is clearly seen in the annual emerging mass of organic matter. She is now about 233 billion tons. Thus, even if to consider, that the biosphere is there such a capacity of about 3.5 billion years, during this time could be produced (dry weight!) a total of about $8 \cdot 10^{20}$ tons of organic substances. It is almost 30 times throughout the earth's crust and 300 times the mass of sediment shell. Therefore, in parallel with the formation of sedimentary rocks, destroyed about 300 times the mass of organic matter. This conclusion for the biosphere on the assumption of constancy in time the mass of the formed organic matter. If you take even that primary production of the biosphere about the time of its formation grew relatively slowly from 0 to 233 billion tons, the above assessment should be reduced in two times. Fundamentally it changes nothing. It turns out that destroyed organic matter on average, 150 times more than the accumulated abiogenic geological sediments. So perpetually, inextricably birth, life and death of organisms, the unity which ensured the continuity of existence of organisms and thus the biosphere, determined as the evolution of life itself, and the evolution of the planet Earth.

MODERN PROBLEMS OF GEOBIOLOGY

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Geobiology holds a special place among the interdisciplinary sciences because it considers the fundamental questions of Earth life. Its main objective is the study of the interactions between the biosphere and the geosphere. Special attention is given to the role of microorganisms in these processes. For this reason, geobiology is very close to geomicrobiology which study the role of microorganisms as well as their metabolic activity in the geological and geochemical processes. Our report is attempt to highlight the most promising and rapidly developing areas of research in the field of geobiology.

One of the important tasks of geobiology is the study of biodiversity (composition and structure of living organism communities) inhabiting on the rocks in different environment. Currently, there are many rock inhabiting organisms which are able to settle on various rocks and minerals and cause their transformation. Most important and complicated question is the mechanisms of interaction between living organisms and rock substrate. It is known that the microorganisms take part in the processes of dissolution and leaching of rocks, biogenic transport of metal ions, formation and accumulation of various minerals as well as oxidation of iron, manganese, sulfur, phosphorus and other elements. In practical terms these processes can play a significant role in the destruction of buildings and historical monuments which are created from stone materials. New facts about the role of individual groups of living organisms in these processes appear every year. For example, some recent studies show that microscopic fungi (micromycetes) can play a significant role in biogeochemical processes and can be reason of stone building and historical monuments damage. As result it was formed the special direction of science — Geomycology. It studies the role of fungi in geological processes.

One of the important fields of geobiology is connected with the study of biomineralization processes. The formation of minerals more often occurs in the biofilms. This process is result of biochemical activity of living organisms and can reach significant scale. An example is the calcification of alga-bacterial mats. Currently the study of biomineralization processes are conducted both in natural and simulated conditions. Special place in model experiments takes the observation of crystals formation processes under influence of micromycetes and bacteria.

Very interesting and specific field of geobiology is the study of living organisms in extreme habitats (polar regions, hot springs, habitats with hypersalinity, underground space). These organisms are called extremophiles. These studies allow us to understand the adaptive capabilities of modern extremophiles and to interpret their possible role in previous periods of Earth's history. Studies in this area are intertwined with issues of astrobiology connected with the search and study of living organisms that might exist on other planets.

Thus geobiology seems highly interdisciplinary science, closely related to biogeochemistry, mineralogy, astrobiology, microbiology and other areas of scientific knowledge. The development of this area has a great fundamental and practical importance and should be based on the combined use of the newest methods of biological and geological studies.

SOME WORDS ABOUT APPLIED MEDICAL GEOLOGY

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The authors would like to preface by detailing the contributions made by the Russian Geological Society (ROSGEO) Medical Geology

Department in cooperation with ROSGEO regional divisions. Together, they have significantly increased the understanding of applied research in medical geology in order to both affect decision makers and also highlight the significance of initiatives and activities in the field of medical geology.

We have found that social and medical questionnaires in territories affected by unfavourable geogenic and technological processes are one of the most effective instruments used to present the close association between economics, aspects of environmental degradation affecting welfare, and the health of the regional population to decision makers. Comparative studies of recent environmental research performed in such territories are characterized by relatively lower levels and increased levels of environmental and health effects on the population. Studies were also carried out on human well-being from industrial enterprises, mining, oil and gas production, metallurgy enterprises and tectonic and volcano activity.

The chemical composition of hair as well as other tissues of persons from different age groups living permanently in industrial centers and mining areas of Russia and the CIS, as well as those exposed to volcano emissions in the Azores and Chile was quantified by using High Resolution Inductively Coupled Plasma Mass Spectrometry. For example, on average, men exposed to volcanic emissions in the Azores had higher concentrations of Cd (96.9 ppb), Cu (16.2 ppm), Pb (3417.6 ppb), Rb (216.3 ppb), and Zn (242.8 ppm), but not Se (469.6 ppb) in hair. The obtained results demonstrate that humans chronically exposed to volcanic emissions, show high concentrations of essential and non-essential trace metals such as zinc, lead, cadmium, and copper in scalp hair. It is suggested that this type of exposure may be as harmful as living close to industrial facilities.

The results became the scientific foundation for preliminary baseline medical and social assessments performed in mining as well as the oil and gas production territories determined by governmental strategies of economic development in Siberia and the Far East. A social and medical questionnaires was carried out among the populations of mining, oil and gas production and volcano activity territories (Transbaikalia, Tyumen region, and the Kamchatka Peninsula respectively) as well as among populations of territories of lower level of environmental and health effects on the population. The Ivanovo region, for example, was used for further explanations and clarifications of a baseline data. The total amount of respondents in four regions of Russia is numbered more than one thousand people. It was proved that the main environmental factors affecting human health in the territories of Siberia and the Far East are drinking water and air pollution. These factors have been worsened as a result of climatic change.

Finally, it was revealed that the most defenceless category to the environmental impacts is professionals who do field research and geological prospecting works. Their rate of gastrointestinal tract diseases is increased to 15–20 % among geologists who explore oil and gas deposits in the West Siberia. Surveys detected a social depression behind the incidence rate of dis-adaptation and cordial diseases in populations living in the mining areas of Transbaikalia.

The results have shown that there exists an apparent underestimation of geological factors that effect human health by community decision makers. Reports were compiled on the impact that optimization of technological and natural geological factors could have human health.

Section 1

Methods for studying the interactions between biogenic and abiogenic components

SPIN LABELING EPR ANALYSES OF SOIL: A NEW METHOD TO INVESTIGATE BIOGENIC AND ABIOGENIC INTERACTIONS OF AMINES IN THE SOIL ENVIRONMENT AND THEIR ENVIRONMENTAL FATE

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In recent years, spin labeling EPR has successfully been applied for investigating the structure and dynamics of biological macromolecules, particularly nucleic acids and proteins. In 2011 at the university of Osnabrueck, we began to apply spin probes and spin labels to soil samples for the first time and proved that spin labeling and spin probing EPR investigation is a powerful method to study different molecular processes in the soil environment, including not only the interaction of soil constituents with organic chemical contaminants but also structural peculiarities of the soil environment and a change of organic matter in soil.

Spin labeling EPR analyses includes a synthesis of specific label molecules, e.g. stable nitroxide radicals, and an addition of them to soil samples. Analyses of EPR spectra of spin labels interacting with soil allows for observing putative microdomains and pores in the soil environment according to their different hydrophobicity, viscosity and electrochemical properties, as well as a change in the molecular environment of soil influenced by contamination.

In my work, the applicability of spin labeling EPR was extended to introduce a functionalized spin probe approach for the characterization of the interaction of xenobiotic model compounds with soil organic matter influenced by enzymes. A wide variety of emerging environmental xenobiotics includes the aromatic amines, e.g. sulfonamides, as well as the aliphatic amines, e.g. betablockers (atenolol). Also, the aromatic amines can enter the soil environment from the reduction of azo dyes, polynitro aromatic munitions, and dinitro herbicides, whereas the aliphatic amines are released into the soil environment with some illicit drugs (e.g., amphetamines) and biocides (e.g., benzalkonium structure). As shown by many investigators, an application of some xenobiotics with the amine functional group to soil often resulted in a clear reduction of microbial biomass in soil, a change in the soil bacterial community structure, persistent inhibitory effects on the growth rate of soil microorganisms, etc.

The current study focused on the binding affinity of the aliphatic and aromatic amines in soils and an effect of enzymes in soil. For this purpose, stable nitroxide radicals 4-Amino Tempo and Aniline spin labels, which have the aliphatic and aromatic amines, were used to label and probe natural soil and soil slightly enriched in laccase. The investigations showed that only the aromatic amine became immediately bound to soil independent on laccase. In both cases, amine rapidly bound to humic acids as a part of soil organic matter. Then, the process promoted polymerization of humic particles binding amine. The investigation showed that an effect of laccase in soil consisted in binding sites. Laccase oxidized humic substances of soil and changed the distribution of redox potential between microdomains in the soil environment that resulted in segregation of binding sites, which posed a strongly hydrophobic area with the high positive redox potential and can be characterized as lifeless areas in soil. A crucial property of the aliphatic and aromatic amines to become distributed in the soil environment according to their water-octanol coefficient and the distribution of the soil redox potential, defined a binding process. Because of peculiarities of binding sites measured at experiment, they were not accessible for soil biota but polymerization of humic particles led to extension of lifeless areas that resulted in a decrease in microbial biomass in soil. This finding showed that the incorporation of xenobiotics by soil organic mater excluded their toxicity for soil biota. However, accumulated xenobiotics can be further distributed over the food-web.

EHABILITATION OF THE DAMAGED ENVIRONMENT OF OIL-PRODUCING AREAS

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An integrated approach that includes physicochemical and microbiological methods has been proposed to form the basis for improvement of environmental conditions. The feasibility of assessing environmental risk by mapping the effects of air pollution on vegetation has been considered. The environmental risk has been assessed with allowance for the sensitivity of various plant communities to atmospheric pollution.

According to experts, about 840 thousand hectares of soil in Western Siberia is currently polluted with crude oil and oil sludge accumulates in large volumes at oil production sites. Another hazardous factor of the adverse impact of the oil-producing complex on the environment in Western Siberia is the chemical pollution of the atmosphere as a result of associated gas flaring. In connection with this, it is of interest to evaluate the environmental risks of the effect of oil production on the vegetation cover of oil-producing areas.

Oil sludge was sampled from sludge storage pits in the Sovetskoe, Vakhskoye, and Krapivinskoye oil fields in Western Siberia. The organic carbon content of the samples ranged from 44.8 to 195 g/kg of sludge. The reclamation process was run in two steps. The first was washing the sludge with a solution of a surfactant composition in a 1:1 ratio followed by doubly repeated washing with water in the same ratio. The second step, the bioremediation of residual oil pollution of the aqueous phase, was performed in a special container into which the waste solution of the surfactant composition diluted with water was pumped after sludge washing. The oil-contaminated aqueous waste solution was remediated by natural hydrocarbon-oxidizing microflora, which is desorbed and passes into the solution during sludge washing. The average decrement in the amount of polluting petroleum products was 90 %. Oil sludge after washing with the composition and water does not require additional treatment and can be directly used as a road fill material and for other engineering applications. The IR spectrometric study also confirmed the profound destructive changes that result not only in utilization of hydrocarbons, but also the appearance of new functional groups.

The degree of air pollution was calculated with allowance for the factor by which the average annual MPC of substances is exceeded, the hazard class, and the permissible repeatability of a given level of concentration and mass of substances present simultaneously in the air. It is known that the main chemical substances emitted into the atmosphere by burning associated gas in oilfield flares are carbon black, carbon monoxide, and nitrogen dioxide.

The developed procedure of mapping the risks of environmental impact by oil production involves the assessment and cartographic mapping of environmental risk with allowance for the susceptibility of various plant communities to atmospheric pollution. Air Research In our study, the sensitivity of plant groups was determined on the basis of analysis of the environmental regulations recommended by the Atmospheric Institute. The map was obtained by interpretation of the satellite image of the area in the impact zone of the Priobskoe field, one of the major fields of the Khanty-Mansi autonomous district, in which up to 2–3 billion cubic meters of associated gas is annually burned in flares. The images used were obtained by the Landsat-7 satellite.

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PHYTOTOXICITY OF THE WASTES OF ORE PROCESSING, THE DZHIDINSKY TUNGSTEN-MOLIBDENUM COMBINE (BURYATIA)

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Mining plays a significant role in the formation of technogenic landscapes and the extreme ecological situation in a surrounding area. For example, the wastes of ore processing of the Dzhidinsky tungsten-molybdenum combine in the Zakamensky region of Buryatia contain a high amount of heavy metals and toxic elements. Sands of technogenic deposit from delta of Modonkul River formed during emergency gap of tailings dam have concentrations (ppm) of Cu — 38, Zn — 58, Pb — 230, Co — 41, As — 10, whereas ones from Barun-Naryn tailings dum contain Cu — 66, Zn — 275, Pb — 320, Co — 40, As — 20.

The aim of this study was to investigate the effect of toxic contaminants on the higher plants by method of sprouts. The method is based on a test cultures reaction; it allows to determine the toxic effects of any pollutants [1]. Seeds of oats (*Avena sativa*) have been planted out in vegetation vessels filled by different substrates: technogenic sands of deltaic deposit of the Modonkul River and the Barun-Naryn tailings dam, and Baikal sand (as a control sample). Substrates were moistened by distilled water to the total water capacity of 60 %. We determined and monitored, soil moisture by the gravimetric method, germinating ability and energy during the experiment. Duration of germination was 8 days. The results of biotesting are shown in Table.

Table. Indicators of technogenic objects phytotoxicity.

Test function	Control	The Modonkul deltaic deposit	The Barun-Naryn tailings
Germinating energy, B, %	100	100	35
Phytotoxic effect,PhE, %	0	27,4	96,1
Toxicity index		1,0	0,35

Germinating energy was determined by the formula (1):

$$B = a / b \times 100\,\% \qquad (1)$$

where: *a* — amount of germinated seeds; *b* — total amount of seeds taken for experiment.

The length of sprouts was a parameter for determining of the phytotoxic effect (PhE), took was (2):

$$PhE = Dc / Dsp \times 100\,\% \qquad (2)$$

where: Dc the average length of the sprouts in the control sample; Dsp the average length of the sprouts in the test sample.

Reducing germinating energy of oats (*Avena sativa*) up to 50 % is the criterion of dangerous pollution of sands from the Barun-Naryn tailings; its phytotoxic effect was amounted up to 96,1 %. At the same time, the samples of technogenic sands from the Modonkul deltaic deposit showed a level of germinating energy within of control and minor (<30 %) phytotoxic effect. In accordance to the scale of toxicity [2], the last samples can be fits to norm V class of toxicity, whereas the technogenic sands of the Barun-Naryn tailings — to high II toxicity class.

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RADON AS AN AGENT OF INTERGEOSPHERIC INTERACTIONS

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Many properties of tectonic zones can be explained by the unloading of endogenous fluids in them that spread from the external core boundaries across the lithosphere, change the properties of the atmosphere, hydrosphere and ionosphere and affect the biosphere. The radioactive gas radon is of interest from the point of view of intergeospheric interactions. UN experts have estimated the danger of radon irradiation for the population at 43 %.

The goal of the present project was to study volumetric radon activity in the geological structures of the Fennoscandian Shield and to estimate the effect of radon on biological objects. Subsurface radon concentrations in Karelia and Finland were measured using a SRS-05 radon station and Sirad MR 106 N radon indicator-detectors. A site for installing of station and detectors was chosen using the readings of the hydrogen sensor of a Drager X — am 5000 gas analyzer. Surface gamma background was measured by a SRP-68 radiometer. The highest volumetric activity of radon, 14 kBq/m^3, was observed in Late Archean structures that consist of microcline granite. Volumetric radon activity was in Late Proterozoic rocks was 2–4 kBq/m^3 in Proterozoic rocks and 1 kBq/m^3 in Early Archean rock types.

Giant anthills are an example of the effect of radon on biota. In Kostomuksha Reserve, 36 anthills, 1.7–2.0 m in height and 2.3–2.6 m in diameter, are concentrated over an area of 0.15 sq. km and confined to faults in the crust. The radon concentration at this site was estimated at 1300 Bq/l in a spring, and a maximum subsurface radon concentration of 450 Bq/m^3 was recorded on the anthill line. We assume that ants build giant hills because they use radon for parasite control. Our assumption is supported by the results of mathematical modelling.

Plants, too, are sensitive to tectonic zone factors, as shown by satellite images on which fault zones can be seen to induce changes in the composition of vegetation. Radiation load on plants is formed by radon which is supplied to them with water through the roots. Internal irradiation induces radiation stimulation, morphological and genetic changes, radiation disease, aging and death. Irradiation risk is especially high in perennial plants. The typical anomalies of trees in tectonic zones are a variety of shapes, a multi-stem pattern, dichotomy, gnarls, curly grains and rolled stems and branches. Additional small nuclei appear in plant cells in radon unloading zones with a volumetric activity of 200–400 Bq/m^3.

INTERACTION OF MICROBIAL COMMUNITIES AND MINERALS BY USING OF X-RAY DIFFRACTION METHOD

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X-ray structure analysis is successfully used for study of biotic-abiotic interactions in recent years, which allows identifying (i) mineral associations in rocks and soils as well as crystal-chemical parameters of components from the soil solid phase, (ii) the proportion of minerals in the particle-size fractions, (iii) mixed-layer clay minerals with different proportions and trends of layers interstratifying and structural ordering — disordering, (iv) amorphization of minerals affected by microbial communities and plants; (v) processes of congruous and incongruous dissolving minerals, (vi) formation of new minerals (salts) from the products of destruction / dissolution of primary minerals, (vii) degradation and agradation types of layered silicates' transformation.

The objects of the present research are minerals characterized by different structural perfection, crystal-chemical parameters, and sensitivity to exposure. The interaction of the minerals and microbial communities were studied by X-ray diffraction method. Summarizing results, the most informative were individual minerals as well as interstratified minerals, the structure of which is the most sensitive to the influence of the products of microbial community activity. From another side, such a structure of minerals creates the favorable conditions for the microbial activities. The conclusions were illustrated by a few examples.

(1) Oglanlinskaya bentonite clay, which is composed by of individual smectite and zeolite of clinoptilolite type, was affected by metabolic products of Mycobacteria. After the experiment zeolite was totally collapsed that was concluded as based on XRD patterns, where this mineral was not identified illustrating the significantly change in the clay. So, in zeolite a more favorable habitat for microbial communities was created, which is explained by the frame structure of zeolite. Additionally the structure of zeolites is characterized by important property such as exchange of freely associated cations, and high content of nutritional elements for microbial livelihoods.

(2) Fine size fractions separated from biotite and muscovite were used as a growth medium for associations of actinomycete and cyanobacteriae. The growth of the associations on the biotite caused to disintegration of its particles and transformation of biotite into vermiculite through mixed-layer minerals with different tendencies of layers interstratifying in crystallites. Whereas, any changes did not detect in muscovite using X-ray diffraction method which illustrates the differences in crystal-chemical parameters of the minerals determined their resistance to biochemical weathering.

(3) The associations of actinomycete and cyanobacteriae were also grown on kaolinite clay composed of kaolinite and traces of chlorite and mica, which led to amorphization of kaolinite and transformation of chlorite into mixed-layer phases.

FT-IR SPECTROSCOPY AS ADVANCED TOOL FOR THE IDENTIFICATION OF BIODETERIORATION

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Identification of micromycetes, which caused biodeterioration of objects of Art is time-consuming due to cultivation and microscopic examination of culture morphology and can be relatively expensive due to application of molecular techniques. Therefore, direct, accurate and robust detection of fungi and their specific metabolic biomarkers is very essential. To this end, Fourier-transform infrared (FT-IR) spectroscopy appears very promising as a perfect tool to detect and characterize the main components of such chemically very complex probes as micromycetes.

The aim of this study was to find species-specific metabolic biomarkers of some micromycetes using FT-IR spectroscopy. For this purpose, the chemical composition of biomass from five species of micromycetes — *Pichia pastoris, Ulocladium chartarum*, *Saccharomyces cerevisiae, Trichoderma viride and Penicillium sp*.— was characterized.

The infrared analysis was performed using Nicolet 8700 FT-IR spectrometer (Thermo Scientific). All the spectra were acquired in the range of 4000–400 cm^{-1} at a resolution of 4 cm^{-1} and analyzed using OriginLab 9 (OriginLab Corporation) and MatLab 7.12.0 (The MathWorks) software. This study was carried out in the Centre for optical and laser materials research of St. Petersburg State University.

The FT-IR analysis enabled us to identify differences and similarities for all five fungal species in the spectral regions known to be characteristic for certain chemical structures and groups. All the examined fungi show the characteristic infrared absorbance of C—H region dominated by fatty acids (3050–2800 cm^{-1}), polypeptide bonds (amide I at 1600–1700 and amide II at 1540 cm^{-1}) and polysaccharide groups (1200–900 cm^{-1}). Another small band appears at 1587 cm^{-1}, possibly due to deacetylated chitin. Bands at 550–900 cm^{-1} region are typical for low-molecular-weight organic compounds. Of particular interest are regions 1200–1500 cm–1 and 1700–2700 cm^{-1}, which are different for the examined micromycetes and can be considered as fingerprint regions for their identification. FT-IR profile of strong bands at these regions rules out the presence of short aliphatic structures and suggests the occurrence of acid and/or conjugated groups, compatible with fungal metabolites and other aromatic structures. The remarkable thing that application of batch wavelet analysis procedure to obtained spectra enhance the recognition of specific features in spectra.

In conclusion, as FT–IR spectroscopy is less time-consuming and less expensive method compared to microscopic and molecular methods, it can be successfully applied for the routine identification of fungal species damaged different art objects.

CALCIUM CARBONATE BIOMINERALIZATION: BIOCHEMICAL STUDIES OF PEPTIDES AND PROTEINS. THE CASE OF BRACHIOPOD SHELL MATRICES

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Biocalcification represents the process by which living organisms develop mineralized structures from calcium salts: carbonates, phosphates, oxalates or sulphates. Among them, calcium carbonate-based biominerals are the most abundant structures, including the mollusc shell, one of the best examples of a biologically-controlled mineralization. This control is performed by an extracellular organic matrix, secreted by specialized tissues, *i.e.*, the mantle epithelium in the case of molluscs: together, they contribute to sculpt the final mineral architecture. Some components of the matrix that are secreted in the extrapallial space interact with precursor mineral ions, mainly calcium and bicarbonate, before being subsequently occluded in the growing shell [1]. This multifunctional matrix is complex and contains proteins, polysaccharides, mucopolysaccharides and lipids. According to current models, it plays an essential role in crystal nucleation, polymorph selection, growth orientation and extent of growth [2]. In addition, it is supposed to interact with the mantle epithelial tissue. The precise mechanism of shell formation is still not understood in detail. However, the identification of structure-function of many extracellular matrix proteins should open fascinating applied perspectives like the development of biomaterials with improved mechanical properties [3] or the development of bone substitute materials [4]. One of the questions of interest for our team is to identify, describe and characterize the larger number of proteins as possible in different extracellular organic matrices. Many qualitative results have been collected by the use of different biochemical approaches such as monodimensional SDS-PAGE. In addition, various proteomic investigations — coupled or not with transcriptomics — were carried out on diverse organic matrices. In this manner, our team has identified the primary structures of a large number of new proteins in several mollusc models: edible mussels, oysters, nautilus, clams, or freshwater mussels [1] [5] [6] [7]. So far, the sequences of approximately 150 proteins from different shells have been inventoried. Finally, despite increasing the number of identified proteins, we should be aware of the limitations of the different techniques [8] [9] [10] and the difficulty to study non-model organisms, for which genomic/transcriptomic data are not yet available [11] [12].

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DISTRIBUTION OF ORGANIC COMPOUNDS IN THE SYSTEM OF THE GEOCHEMICALLY LINKED MIRES

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Mires accumulate some 4.3 thousand km 3 of water, which is typically enriched in organic matter (OM) of humus nature. Our research was centered on the characterization of the biochemical processes of peat deposits in the system of oligotrophic mires.This research was conducted in the watershed mire ecosystem (MES) on the northeastern periphery of the Vasyugan Mire. This territory are represented by the following biogeocenoses (BGC): shrub–sphagnum–pine (high ryam, transitional–accumulative part of the profile), shrub–sphagnum–pine (low ryam, transitional–accumulative part of the profile), and a sedge–sphagnum swamp (autonomous part of the profile) .

In evaluating the contents of organic matter (OM), it can be seen that the botanical composition of a peat notably affects its chemistry. For example, the presence of cotton grass in the botanical composition of a peat definitely causes an increase in the bitumen contents. Comparing the OM compositions of the acrotelm and katotelm, one can readily note, first of all, the remarkable difference in the concentrations of humic acids (HA) and compounds hydrolyzed easily and with difficulty (easily hydrolyzed (EH) and hydrolyzed difficulty (DH)). At the same time, higher EH contents in the water discharge zone testifies for their probable inflow from the eluvial part of the geochemically linked mires. The redistribution of water-soluble compounds in the acrotelm occurs throughout the profile, with the highest contents typical of the transitional- accumulative part of the mires, a fact providing additional evidence of the occurrence of material migration.

It should be mentioned that microflora is quite active if the medium is acid. The content of microbial biomass in the BGC of the catena varies from 0.18 to 1.42 kg/m^2 in 1-m layer and is just a little bit lower than that in the European part of Russia, a fact also highlighting the high microbiological activity of oligotrophic peat deposits. At the same time, the content of microbial biomass in the peat deposit of the sedge–sphagnum swamp is four times higher than in the peat deposit of the low ryam. These are differences between the major components of the microbial biomass in the acrotelm and katotelm, but the character of these processes differs. Bog waters have a yellowish color. The FA contents in bog waters are greater than the HA concentrations by factors of 5–20 which is consistent with the concentrations of these elements in the peats. The high concentrations of mobile organic compounds in the peats and the relatively high microbiological activity throughout the whole peat deposit also confirm that the chemical composition of the runoff from the swamped catchment area is controlled not only by atmospheric precipitation, but also by biochemical processes in the peat deposit itself. The removal of soluble organic carbon with the runoff was equal to 6945 kg/km^2 or 6.9 g m^{-2} yr^{-1}. Our results demonstrate the importance of determining not only the type of peat in a peat deposit but also the botanical composition of this peat. Consequently, their OM should also show different degrees of polymerization, causing the great compositional diversity of bog waters. This should be taken into account in studying mires.

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SOME ASPECTS OF GEOLOGICAL MICROBIOLOGY IN THE SCIENTIFIC HERITAGE OF V. O. TAUSON (ON THE OCCASION OF THE 125TH ANNIVERSARY OF THE BIRTH)

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The name of Vladimir Ottovitch Tauson (W. O. Tausson in German transcription) occupies an important place in the history of Russian school of microbiology and the development of natural sciences in Moscow State University. V. O. Tauson (1894–1946) was born in Ryazan. Having finished (1912) the real school in Moscow he entered the Moscow State University, but his studies were interrupted by the 1st World War, followed by the Great October Socialist Revolution and the Civil War. He could return to Moscow only in 1922 and finished the University in 1924. In his diploma work Tauson dealt with the destruction of the paraffin by the mould *Aspergillus flavus*, this topic was proposed by his teacher, professor E. E. Uspensky, who detected this hydrocarbon-degrading organism on the wall of the paraffin vessel during his early investigations of the role of Si for plants (so he could not utilize for plants vessels of glass). E. E. Uspensky (1889–1938) was the founder of the Department of microbiology at Moscow University (1924), and V. O. Tausson became one of the first graduate-students of this department. The study of the destruction of paraffins by *A.flavus* opened a new branch in microbiology, linked with the investigations of the utilization of hydrocarbons by microorganisms, their physiological, ecological and biotechnological aspects.

Next works of Tauson were related with the microbial oxidation of phenantrene (1925, thesis), naphthalene, aromatic, saturated and non-saturated hydrocarbons, wax, oils, etc. They opened a new direction in the geological microbiology linked with the microbial destruction of caustobiolithes.

V. O. Tauson paid much attention to the role of microorganisms in geological processes, such as weathering of rocks, role of microorganisms in the formation, transformation and destruction of several caustobiolithes (peat, coal, petroleum). These works were of great practical importance. At the same time V. O. Tauson investigated the mechanisms of the oxidation of hydrocarbons, the physiology and metabolism of hydrocarbon-oxidizing microorganisms. These works gave rise to an original bioenergetic conception of the exothermic character of microbial biosynthesis.

V. O. Tauson headed the division of bioenergetics and geological activity of microorganisms in the Microbiological Institute of Moscow University. He also took an interest in some problems of the evolution of microorganisms. In 1934 he participated to the expedition on Pamir, where he studied the microbiota of highlands and posed the question about their endemism, isolation and evolution.

In 1930s V. O. Tauson taught to the students of the Department of microbiology of Moscow University the new discipline called "The geological activity of microorganisms". In 1935 he received the title of doctor of biological sciences and professor. Most materials of his course were included in his books “The great works of little beings” and “The heritage of microbes”, which were published in 1948, after the death of their author. Most problems posed and investigated by V. O. Tauson keep today their importance.

BIOGENIC AND ABIOGENIC MICROBIOMORPHS IN GEOLOGICAL ENVIRONMENTS

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Geological specimens of different composition and age including phytogenic buildup *Gemmaphyton* (Geyser valley, Kamchatka), Carboniferous tabulata *Syringopora* (Podmoskovye) and Precambrian shungite rocks (Republic of Karelia) were studied using scanning electron microscopy (SEM) with energy-dispersive X-ray spectroscopy (EDX) and transmission electron microscopy (TEM) with selected area electron diffraction (SAED) .

Some specimens were purposely contaminated by filter paper fibers to study sample preparation artifacts and reveal any criteria of difference between organic objects and fossils. Filter paper fibers are characterized by different diameter, variable morphology in a fiber length, indirect connection with a host rock. Chemical composition of those are similar to the composition of underlying minerals with carbon-enriched content resulted from carbohydrate constitution of the fibers.

Both biogenic (diatoms, microbial buildups) and abiogenic microbiomorphs have been found in the *Gemmaphyton*. Biogenic microbiomorphs occur into a surrounding rock and are remarkable for similar generic sizes. Some of those had an influence upon condensation of an ambient substance and marks of subsequent transformation during fossilization. On the contrary, abiogenic microbiomorphs are characterized by different sizes and found into pores where aqueous fluids may travel. TEM and SAED study revealed those consisting of amorphous silica. Chemical composition of biogenic microbiomorphs is more complicated than that of abiogenic ones and involves additionally calcium, phosphorus and other elements.

Micro- and nano-sized Ca-bearing fibers were identified in internal pores of corallite fossils in the tabulata *Syringopora*. Traces of an ancient microbiological activity accompanied transformations of corallites were also found, namely, nanosized spherical fossils with shells and complicated internal structure, possibly viruses. Some of fibers consist of amorphous external casing and internal monocrystalline matter. Single-crystal analysis of SAED patterns leads to conclusion that the matter is ikaite ($CaCO_3 6H_2O$) used as the sure paleothermometer of a cold water environment. The relict of ikaite unstable at elevated temperatures occurs into the fibers possibly owing to a stability growth of it in closed volume.

Obvious biogenic microbiomorphs (*Cyanophyta* and *Chroococcales*) and presumably abiogenic objects, that are similar in morphology and structure to synthesized carbon fibers and particles, were revealed in different shungite rocks. Those are mineralized and carbonaceous microfossils respectively with different structural ordering. The former type occurs in brecciated rocks and the latter links with shungite carbon.

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IDENTIFICATION OF PEDOGENIC PROCESSES IN THE SOILS OF ULTRA-CONTINENTAL CLIMATE BASED ON CLAY MINERALOGY

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Wide spread in Central Yakutia permafrost-affected soils forming under the cold ultra-continental climatic conditions are named “Palevye (Pale)” following the Russian Classification, or Cryosols (WRB, 2006). The studied profiles have been forming on the calcareous loess-like parent substrate. The clay size fraction (<1 μm) was studied by X-ray diffraction and FTIR spectroscopy methods to determine clay minerals' transformations initiated by pedogenesis.

Smectitic minerals (most likely random mixed-layer illite-smectite and probably chlorite-smectite where the proportion of smectite layers is e"50%) are predominant in clay size fraction with subordinate chlorite and illite as well as the products of their transformation with smectite (vermiculite) layers < 50% in the upper horizons. Besides that traces of kaolinite were also identified. The important note underlining uniqueness of the soils is their mineral composition inherited from the parent substrate. Based on the data obtained, the loess-like substrate of Central Yakutia is enriched by chlorite in comparison with that of the loess-like parent material of European Russia.

Pedogenesis has brought about change in the upper horizons, including a marked reduction in the expandability of the smectitic phase accounted for by partial or completely decomposed of smectitic phase, together with a relative reduction in the contents of both illite and chlorite. Illite has been at least partially transformed to a mixed-layer illite-vermiculite (smectite), whereas chlorite has either been completely decomposed or has transformed to a mixed-layer expandable component. Thus distribution of clay minerals in soil profiles assigned by acidification has been illustrated by a study is similar with in "acidic" soils from forest zone of humid climate. That is confirmed by the fact that pH values in the soils profiles change from alkaline in the bottom horizons to acid in the upper part despite the calcareous parent substrate, ultra-continental climate, and as consequence a low level of precipitation. Acidification of the upper horizons is most probably initiated by vegetation community, especially moss. Besides that change of pH values in the profiles is determined by seasonal migration of dissolved carbonates.

REGULARITIES OF HUMIFICATION THE RESIDUES OF CORN IN DIFFERENT MINERAL SUBSTRATES

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Humus plays very important role in soils. It provides major physical and chemical properties and functions of soils and such important function as fertility. At the same time the regularities and mechanisms of processes of humus formation are studied insufficiently. Till today we have only the hypothesis of humification of plant residues, but do not have the theory of this process. The role of mineral components of soil in processes of humus formation is studied especially poorly. The aim of our investigation is to study the influence of composition and properties of mineral matrix on the transformation of plant residues (on the example of corn residues). The substrate (silica sand, loam, silica sand + 15 % of bentonite and silica sand + 30 % of kaolin) was mixed with 10 % corn residues (milled to 3–5 mm) and incubated in stationary conditions from 6 to 19 months. Sampling for the analysis was performed every month, and two times in the first month. The dynamics of mineralization and humification of plant residues (PRs), was studied applying elemental and bulk analyses of neogenic organic matter (OM), densitometric fractionation of substrates; FTIR, solid-phase ^{13}C NMR spectroscopy and scanning electron microscopy with electron microprobe. It was shown that the mineralization and humification processes had a wave-like character. We explained this by the transformation of microorganisms population together with the change of amount and quality of the OM in the system. The main mechanism for stabilization of neogenic OM was adsorption on mineral matrix with formation of relatively resistant compounds. This is selective adsorption depending on the composition and properties of mineral matrix. The FTIR and ^{13}C NMR analyses of OM distribution in different substrates and densitometric fractions showed that sand and fraction > 2.2 g/cm^3 are enriched with the compounds of aromatic nature and polypeptides. Fractions 1.4–2.2 g/cm$_3$ accumulate compounds containing alkyl and carboxyl group as well. The heavy fraction (> 2.2 g/cm^3) have higher aromaticity indexes than light fraction (1.4–2.2 g/cm^3).

Thus the humification of PRs is of wavy character, which is most manifested in the loamy substrate. This related to the changes in the total abundance, activity of the microorganisms and the structure of the microbial cenoses during the experiment because of the varying quality of the organic material in the systems. The stabilization of humic substances in the substrates is related to the formation of stable mineral–organic compounds with finely dispersed components or fractions of substrates. The light fraction (1.4–2.2 g/cm^3) accumulates, along with aromatic compounds, substances containing alkyl and carboxyl groups to a higher extent than the heavy fraction (> 2.2 g/cm^3). The higher values of the aromaticity index of the humic substances in the heavy fraction of the loamy substrate compared to that in the light fraction indicate the formation of the most stable aromatic compounds, which can form the basis of the humic acids (HA) nucleus. These compounds are poorly accessible for microorganisms and ensure the preservation of not only humic acids but also many fulvic acids. We also do not exclude the possibility of the matrix synthesis of the HA-like substances.

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LEIFMAN-VASSOEVICH COEFFICIENT AS ONE OF THE FUNDAMENTAL CHARACTERISTICS OF COALIFICATION FLUID GENERATION

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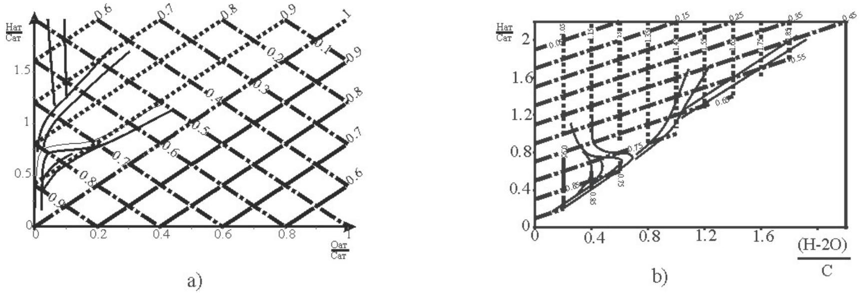
The problem of assessing gas-generating potential of coals has a long and complicated history. It is a combination of important and fundamental principles of geology — temperature, pressure and geological time. To find the solution, we approach this problem with experimental and theoretical methods. As far as the most theoretical methods are concerned, they are characterized by a logical error: authors consider the process of coalification as the conversion, and the authors of these methods are completely assured that they know this process — which is not the case. The most advanced experimental technique was proposed by Saxby J. D., Bennet A. J.R. [3]. But it is far from perfect — it misses, in my opinion, one of the important elements of coalification: time. To compromise between these two methods (experimental and theoretical) they were trying to explore the evolution of nitrogen during the coalification [1, 3]. The French researchers applied this method only to the study of a limited area, Russian authors apply it to all grades of metamorphism from peat through the stone and brown coal to anthracite and metatrait (but the authors overlooked that they only used vitrinite reflection index, ignoring the main coal-generating (carbon-generating) elements: carbon, hydrogen and oxygen). We will consider only theoretical point of view, ignoring experimental methods for evaluating fluid generation during catagenesis of coals. The value of gas-generating potential of coal is calculated not as arithmetic average (or arithmetically proportional) between two extreme values (on the one side we have consequence by which generation of water is getting into null, on the other side — consequence by which either methane (or its homologues) or carbon dioxide is getting into null), but by geometric average (or geometric proportional). Thus Van Krevlen and Leifman-Vassoevich diagrams show direct dependence between the location of the line of equal values of matter losses (by metamorphosis of coals) at the null generating of water (dash-dot), of methane (dot) and dioxide carbon (dash) (fig.) .



a) b)

Fig. Position on the chart of Van Krevelen (a) Leifman-Vassoevich (b) lines equal values (null) of generation of water (dash-dotted), dioxide carbon (dashed) and methane (dashed line) and the values for each line.

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MISUNDERSTANDINGS DURING THE SOLUTION OF THE EQUATIONS OF MATERIAL BALANCE

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We will use the portion of the table shown in [5], but with important clarifications. In accordance with the data of [5] we consider four variants of calculating loss of organic matter in coal. First two options will take into account all the data on the elemental composition of the coal, only the second option will not count on the average, and the average harmonic. This alternative calculation is purely abstracted and not connected with the assessment of the potential scale of coalification fluid generation, as accepted in the literature, but this variant of possible solutions is very essential for the analysis.

Now we analyze the situation for a traditional method, when the solution was found on average (or arithmetically proportional) and average harmonic (or harmonically proportional). All is clear for arithmetically average or arithmetically proportional; however it should be explained for harmonically medium or harmonically proportional. As it follows from [3] the harmonic mean of n positive numbers A1, A2,…, AP (n> = 2) — a number equal to. Harmonically average the numbers A1, A2,…, AP is the inverse value with the average of the values back to A1, A2, … AP …”. There is an expression for geometric average = and for the harmonic mean.

As can be seen from the written formulas, the harmonic mean is the inverse value of the arithmetic mean and including and therefore this value will be used in our calculations. For the analysis we will use the data given in the work [6], but for the same interval we will conduct two ways of computing — first, as it is shown in [6], and second — we will exclude the intermediate stage, as if it did not exist, and compare the results. We do it specifically, in order by mathematical induction [1] to come to the unequivocal conclusion that only by calculation of the geometric average it is possible to calculate the loss of organic matter and consequently the possible volumes of generated fluids and primarily methane (and/or its homologues).

The lack of space does not allow you to present a complete calculation, so we will restrict ourselves to the fact that when comparing on the one hand — an arithmetic average, and on the other, with an average harmonic — on the one hand decreases (with an average arithmetic when calculating the three indicator against two), but on the contrary increases (with an average harmonic measured at three indicator against two) [1].

If we analyze all of this, we have to admit — it is the geometric average (or in a broader sense geometrically proportional) [4] that is the desired value, what we wanted to prove. Unfortunately the author didn't think that everything was so simple and original.

When calculating the carrying side of the process according to the geometric average (or in a broader sense, geometric proportional) eventually meets the principle known as the law of Hess, according to which " … the thermal effect of the reaction depends only on the initial and final States reacting substances, but does not depend on intermediate stages of the process …" [2] — only in this case we can talk about carrying side of the process.

Thus, when solving the equations of material balance, only geometric average (or in a broader sense geometrically proportional) should be used!

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AMINO ACID COMPOSITION OF CLAY-ORGANIC–MATTER COMPLEXES RESISTANT TO OXIDATION BY PEROXIDE

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With the use of modern methods it was shown, that fixation of organic substance in forms resistant to H_2O_2 treatment is related to change of actual structure of clay aggregates. Formation of organic–smectite complexes with a disordered c*-axis structure is a universal and usual way for the kinetic stabilization of the system during pedogenesis under forest-steppe conditions.

The main source of smectites are beds of the transformed volcanic ashes, however deposits of similar type practically are not present within the Central Russia region. As alternative sources, bentonites of fresh-water and sea basins are used. These bentonites were accumulated in the continental basins as the products of secondary micas biogenic degradation on the paleo catchments areas. Here zones with the most intensive interactions between clay minerals and organic matter are soils. Since Devonian the formation, degradation, transport and redeposition of a soil material is constant stages of sedimentary process. Most of the sediment carried in rivers is likely to have been part of a soil profile at some stage. Continental depositional environments are also sites of soil formation. Therefore actual structure of clay minerals in specific deposit may be has a soil history. The main aim of the study was to experimentally substantiate this phenomenon.

We *investigated the* amino acid composition of organic matter (OM) fixed in the labile spaces between the layers in the forms resistant to H_2O_2 treatment. In this work, bentonite-like clay samples of Upper Pliocene Akchagylic Stage were used. The <2.5-µm fraction was separated by the elutriation of a stable suspension after the treatment of the samples with 1 mol/l CH_3COOH and their washing with distilled water. Then, they were multiply treated with 30 % H_2O_2 at room temperature for 30–40 days. *Acid hydrolysis* was performed using 1 mol/l HCl at 110 °C for 24 h. Amino acids were determined by HPLC (Flexar, Perkin Elmer).

In the acid hydrolysis products of the stable OM typical albuminous amino acids are presented. As well as for clay fraction of soils, we could see that the grouping of amino acids in acidic, basic and neutral groups show that in the composition of stable ÎM there are no acidic amino acids practically. The main part of their is presented by neutral amino acids. In the neutral amino acids composition amino acids not bearing partial charges and not solvated water prevail.

Distinctions between amino acids group composition of stable OM <2.5-µm soil fraction soils and Pliocene clays in some cases can practically be absent. In other cases Pliocene clays contain a little smaller relative quantity of neutral hydrophobic amino acids. However the general mechanism remain.

At the heart of mechanism which define amino acid composition features of OM bounding fine-dispersed Pliocene clays and forest-steppe soils mineral phases in resistant to H_2O_2 treatment forms the selective binding of neutral, hydrophobic and basic amino acids by fine-dispersed phases which is caused by the physical and chemical reasons lays.

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BIOLOGICAL CONTAMINANTS IN SEDIMENTARY ROCKS

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Microbial paleontology is a discipline focused on the study of fossil prokaryotic organisms. This field, which has emerged during the 1980s, is of importance for understanding the genesis of sedimentary rocks, including mineral products such as oil. The principal technique of this research is scanning electron microscopy.

Our long-term study of Earth rocks and meteorites in a scanning electron microscope has yielded a very extensive and unique body of data on biogenic structures occurring in those objects. These data helped clarify conditions and mechanisms of genesis of various rocks and ores, while discovery of biomorphic structures in meteorites allowed to confirm the existence of extra-terrestrial life. It turned out, however, that besides the in-situ biomorphic structures, which form an inherent part of the rock, these objects may also contain extraneous biomorphic structures of various origin. We refer to such structures as biological contaminants. Recognition of such contaminants among biogenic structures is important in reconstructing the conditions of genesis and the age of various sedimentary rocks and ores.

Analysis of our data has shown that biological contaminants in rock samples can be classified into two groups according to their genesis.

The first group includes those contaminants that result from the already formed rock becoming colonized by various organisms, not only spreading on the surface but also penetrating inside the rock through cracks, interlayer spaces, cavities, etc. Such contaminants are encountered most frequently. This type of contamination may occur in natural environments, under certain conditions even repeatedly, as well as during preservation of rock samples in laboratories, collections, and museums. This group includes hyphae of lower fungi, actinomycetes, cyanobacteria, and various other bacteria. Under favorable conditions these contaminants may, with time, become mineralized.

The second group of contaminants includes those organisms or their remains which end up in rocks as a result of their being transported there, mechanically, by wind or water. In natural environments these are predominantly diatoms, plant spores or pollen, testate amoebae, small insects and other organisms in the millimeter size range. Such contamination may even occur in laboratories, for example, when the samples are washed with unfiltered tap water containing diatoms or ostracod shells, or — very commonly — when plant pollen and spores enter through open windows during the spring time.

The most frequently encountered contaminants are actinomycetes and hyphae of lower fungi, which some researchers mistake for in-situ filamentous bacteria who participated in the genesis of the rock. During scanning electron microscopic studies it is very important to carefully observe spatial relationships between the rock matrix and the biogenic objects. One has to keep in mind that the in-situ filamentous organisms cannot cross layers and are always oriented parallel to stratification planes.

The study was supported by the Russian Foundation for Basic Research grants 13–4–00933a and 14–04–00260a.

Section 2
Biomineralization in geosystems

BIOMINERALIZATION AND MODIFICATION OF CLAYS DUE TO ACTIVITY OF CYANOBACTERIA

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Microbial weathering and biomineralization are the wide spread processes which occurs in different geochemical environments and are important in sediments and soils formation. The residues of fossilized microorganisms, including cyanobacteria, are an evidence of their communities being the most important factor of sedimentation on the Earth surface from the Archaean time. Ancient microbial communities were involved in both formation and transformation of many minerals. Cyanobacteria or blue- green algae are oxygenic photoautotrophic organism. Silicified microfossils of cyanobacteria (stromatolites) are found in deposits beginning from the age of 2.7Ga years. In our days, cyanobacteria create the relict communities in the extreme ecological conditions — regions with the hydrothermal activity, hyper saline reservoirs and alkaline lakes.

The goal of this work was to study the changes in mineral compositions of different clays under the action of productive and destructive processes (growth and fossilization) of alkalophilic cyanobacterial communities. The last study particularly was connected with possible transformations of palygorskite at the laboratory experiments under the growth and fossilization of cyanobacteria *Microcoleus Chthonoplastes* and *Oscillatoria terebriformis (*collection of the Institute of Microbiology, RAS). The palygorskite was separated from Late Carboniferous deposits in Moscow region (Russia). The experiments with Cyanobacteria and clays have been done with light and in the darkness. Cyanobacteria were incubated for 7, 15, 30 and 60 days at 28 °C. Control bottles without cyanobacteria were incubated at the same conditions. The fossilization processes were studied by scanning electron microscope (SEM). Mineralogical investigations included X-ray diffraction, FTIR, XRF and magnetic measurements. Biological activity parameters of cyanobacteria in the presence of clays were determined too. The peaks of chlorophyll concentration and oxygen were observed for the first 7 days of the experiments. After it the gradual decreases of biological activity take place.

The largest chlorophyll concentration was observed for the experiments with bentonite and kaolinite, palygorskite and the smallest — with illite. Ńyanobacteria affects the properties of studied clay. The observed processes were fast; obtain data show that biochemical transformations we observed have the multi-step nature. Process of dissolution and transformation is influenced most strongly by the live cyanobacteria in the conditions of their photosynthesis. It has no visible influence on the structure of palygorskite (XRD). By the influence of Cyanobacteria we observed by FTIR the decrease of silanol group (SiOH outer surface), more intensive congruent dissolution and dispersion of palygorskite particles. Formation of Mg- carbonates was found. The results of the interaction *Microcoleus chthonoplastes* with palygorskite were compared with our previous laboratory experiments including bentonite, illite and kaolinite. It has no visible influence on the mineralogy of bentonite. Whereas the development of more smectitic layers within the illite matrices in case of illite was found. Cyanobacteria influence the properties of iron compounds, which are present in all studied clays as impurities.

MINERALOGICAL AND GEOCHEMICAL ANOMALIES IN THE SILICEOUS-FERRUGINOUS SEDIMENTARY ROCKS OF URALS VMS DEPOSITS: EVIDENCE OF BIOGENIC ACTIVITY

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The siliceous-ferruginous sedimentary rocks at the top and the flanks of the Urals VMS ore bodies host the mineralized tube worms. In spite of their small diameter, some of them may be compared with the near vent tube worms discovered in the modern and ancient black smoker systems (Little et al., 1999). The tubes are hollow-centered or incrusted by concentric layers of microcrystalline hematite or hematite-quartz aggregates. The central parts of the tubes are locally filled with hematite of gel-like, lumpy, inequigranular, and cellular microtextures. The hematitic biomorphs are associated with abundant silica-hematitĺ filaments and spherules, which are comparable with some hemoautotrophic bacteria found in the modern vent sites (Juniper and Fouquet, 1988). Recent work on the ancient VMS deposits indicates an important role of similar biogenic processes during formation of the red hematitic cherts (Greene and Slack, 2003) .

The bacterial origin of the studied filaments and spherules is also indicated by extremely light carbon isotopic composition ($\delta^{13}C$ from –4.5 to –8 ‰) relative to the supra-ore limestones (from –0.67 to +2.2 ‰) .

The high Fe, Mn, P, Ti, K, and REE contents in siliceous-ferruginous rocks reflect the considerable amount of authigenic minerals of these elements, which are localized both inside the tubes and in the rock (Mn-bearing calcite, Fe-bearing chlorite, sulfides, leucoxene aggregates, apatite, barite, monazite, and lanthanite). The LA-ISP-MS analysis of biomorphic hematite revealed the high contents of Mn (up to 9393 ppm), As (up to 1872 ppm), V (up to 779 ppm), W (up to 1091 ppm), Mo (40 ppm), and U (up to 8.7 ppm). The elevated concentrations of these elements are also typical of the fossil fauna found at some Urals VMS deposits (Maslennikov, 2006).

The distribution of biogenic elements depends on the species of the tube worms, physico-chemical habitat conditions, and the concentration of elements in the fluids during sedimentogenesis. The variation in textural, mineralogical, and geochemical features of the studied rocks shows that, during postdiagenetic processes, the biomorphs are destroyed and become similar to abiogenic textures that leads to dissolution of authigenic minerals and significant changes in the distribution of biogenic elements.

The work is supported by the Program of Uralian and Siberian Division of Russian Academy of Science (project no. 12–C–5–1010). Execution of microprobe and LA–ICP–MS analyses was supported by Russian Scientific Foundation (project no. 14–17–00691) .

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ON THE FORMATION OF CARBONATE STRUCTURES (BIOHERMS) ON THE SEABED ROCK MATERIAL OF THE RUSSIAN PROSPECTION AREA ON THE MAR*

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During the cruise 36 of the R.V. Professor Logatchev, organized by the FGUNPP “Polar Marine Geological Prospecting Expedition” we studied loose biogenous high-carbonate sediments (measured carbonate content over 75%), built mostly of phoraminifera shells and lying over serpentized peridotites. Here we have uplifted tubes of white smokers built of carbonate (visually identified as aragonite) less than 10 cm high, similar to those described in the hydrothermal vent field Lost City. In the studied region at depths less than 3 km (over the lysocline** level) two young volcanos were found; they had burst through the sediments of Holocene-Late Pleistocene age.

When viewing schlichs of the samples collected in the layers of these

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*MAR — Mid-Atlantic Ridge;

**Lysocline is a term used in marine lithology and geology to denote the border separating in marine sediments different complexes of carbonate microfossiles both of good and poor integrity. The term is directly related to the concept of calcium carbonate compensation depth (CCD), the level below which calcite dissolution rate grows very rapidly, and the carbonate content in the marine sediments drops. In the North Atlantic it corresponds to 4300 m.

sediments (their thickness rarely exceeded 1m), we noticed a dissolution of calcite phoraminifera shells, their replacement by aragonite and accretion with redeposited carbonate. It is interesting that pH measurements in the section of loose biogenous water-saturated sediments have shown that their acidity increases with depth to the figure of 5.6 even in the first centimeters. When the samples were dried in smal cotton bags at a temperature of 90°Ń, the fabric desintegrated as if under the influence of acid. This means that the sediments were impregnated with hydrothermal solutions and/or volcanic gases.

The seafloor rock material was examined alongside with the sediments. In the dredged samples of basalts, less often of serpentized peridotites and lithified carbonate biogenous sediments we found carbonate structures (bioherms?) less than 15 cm high, normally about 1 cm in diameter, rarely up to 4 cm; they resembled coral branches, though different in their inner structure. Outside they are covered with a thin film of manganese minerals. The base, often isometric, may be either solid or porous. The pores are multiple diffuser channels. These structures may have sealed tops. In the section they are represented by solid carbonate formations, or they may have a concentric-zonal structure with necessary one or several through channels. The channels are often filled with biogenous sediments. It is clearly seen that the phoraminiphera shells in the sediments filling the channels, are dissolved and absorbed by the structure walls. Though the carbonate structures (bioherms?) have a through channels, they differ from the tubes of white smokers in form and structure. Possibly, these carbonate formations were built by colonies of microorganisms and may be regarded as bioherms.

The material used in our studies was aqcuired during the cruises of the R. V. Professor Logatchev, organized by the Polar Marine Geological Prospecting Expedition and financed by the Federal Agency of Subsurface and Natural Resources and ecology of the Russian Federation.

ON BACTERIA PARTICIPATION IN THE FORMATION OF MAGNETITE BALLS AND INTRODUCING MAGNESIUM TO THE COMPOSITION OF HYDROTHERMAL FERRIFEROUS CRUSTS FROM THE MAR[*]*

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In schlichs of the samples of deep-sea sediments taken in the Russian Prospection Area (RPA) we often find small magnetic balls of unclear origin. Similar balls were also noticed in quartz-sulfide ore; one finding was in the hydrothermally modified basalt from the ore field Zenith-Victoria. Their origin remained unclear; some think that it is cosmic dust.

One magnetic ball with shiny smooth surface was extracted from hydrothermally modified basalt. It was examined with scanning transmission electron microscope in transmission and scanning modes. It has shown that the ball surface is covered by many caverns and cracks, has a polygon structure with distinct growth zones around multiple crystallization centers. The scanning has shown that this substance may be definitely related to magnetite only at one probing point at the surface of the ball. In other probing points, in the cracks, they have detected a compound matter mainly consisting of iron, silicon, aluminium (in the descending order) with admixtures of manganese and titanium at concentrations of one percent order.

To understand the origin of a magnetic ball of such uncommon composition, it was examined in transmission mode. As a result it was found out that calcite with different morphology of formation makes the basis of its inner part. Also, the following minerals have been detected: manganite, vernadite, talc, graphite, apatite, carbonous matter and amorphous polycomponent particle. The fact that the inner part of the ball is calcite with different morphology of formation means that the magnetite envelope on the calcite most probably has an organic origin (phoraminiphera). The evidence of this is that the sizes of the magnetite balls correspond to those of phoraminipherae; also the found pseudomorphoses of magnetite on phoraminipherae in sediments confirm this. The multiple crystallization

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* MAR is Mid-Atlantic Ridge;

centers of magnetite on the ball surface may also indicate an involvement of microorganisms in its formation.

The majority of iron hydroxide crusts from the deep-sea hydrothermal vent fields of the MAR are formed as a result of passing hydrothermal fluids through biogenous carbonate sediments, transforming the latter (by metasomatic replacement) into loose ferrous crusts. They show a mass of relict fauna and amorphous or weakly-crystallized glassy veins of aluminium-iron-silicon composition. Using STEM in the scanning mode we analyzed one fragment of the vein with a relict fossilized Ethmodiscus. On the surface of metasomatically replaced Ethmodiscus microfossils on bacteria in the form of dots and lines were noticed. Chemical analysis of the surface of the fossilized Ethmodiscus has shown the following composition: iron, copper, phosphorus, silicon (in the descending order). Also sulphur, aluminum, calcium, chlorine, potassium and titanium were registered. Their content does not exceed 3 %. The chemical base of the microfossils on bacteria is built by the same elements, though silicon content increases noticeably and manganese shows up. Thus we may assume that magnesium is introduced to the crusts by bacteria.

The material used in our studies was acquired during the cruises of the R. V. Professor Logatchev, organized by the Polar Marine Geological Prospecting Expedition and financed by the Federal Agency of Subsurface and Natural Resources and ecology of the Russian Federation. The STEM works were made by Dr. Dobinchouk.

EFFECT OF BIGENOUS CARBONATE SEDIMENTS ON THE FORMATION OF MODERN SULFIDE ORE ON THE MAR

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The article is dedicated to the studies of morphology, structure, mineral and chemical composition of sulfide ore, ore-beaing and metalliferous sediments of the hydrothermal vent fields Semenov, Ashadze-1, Zenith-Victoria and Peterburgskoy on the Mid-Atlantic Ridge. We have measured Eh and Ph of interstitial waters, isotope composition of C and O in calcite of ore-bearing and background sediments.

It was found out that the major part of the sulfide structures occurs in the Holocene — Late Pleistocene sediments; it is a new type of sulfide mineralization, not earier described in the MAR zone. This type of ore is formed as a result of metsomatic replacement of biogenous carbonate sediments by hydrothermal minerals at diffusive infiltration of hydrothermal fluids through the sediments.

Metal- and ore bearing sediments differ from the background ones in their physical and chemical characteristcis, isotope composition of C and O, higher contents of ores (Fe, Cu, Zn and Mn), Si, Mg and metasomatic replacement of the calcite shells of microorganisms by hydrothermal minerals.

We present a formation model of ore-bearing sediments and sulfide ore at the entering of diffuse fluids into biogenous seabed sediments Deposition of hydrothermal minerals at a distance from the focusing sources shfts towards a subsurface zone (following Y. V. Bogdanov) where we meet sea waters together with hydrothermal diffuse waters. The mineralization is taking place at a geochemical barrier in the zone of interaction of metalliferous fluids, saturating them with seawater and bigenous calcite unstable in acidulous media. At the intial stages or at a weak fluid pressure (e.g., at exogenous contact of the existing structures) metalliferous and\ or ore-bearing sediments are formed due to metasomatic replacement of separate sea shells. The long influenceof hydrotherms results in the complete substitutuion of sedimentary biogenous material and final formation of sulfide structutrss at its place. C^{org} of biogenous sedimets participates in the sulfide structure formation. The secondary deposition of dissolved calcite takes place at the seabed sediments in the form of aragonite crust.

We assume that the ore material is coming from beneath directly into the biogenous carbonate sediment, which becomes one of the most important sources of ore-bearing and that metalliferous sediments are much more common in the ocean than it was thought before. We may also think that the large accumulations of sulfide ores, rich in minerals, may be found in the sediments and beneath.

The material used in our studies was aqcuired during the cruises of the R. V. Professor Logatchev, organized by the Polar Marine Geological Prospecting Expedition and financed by the Federal Agency of Subsurface and Natural Resources and ecology of the Russian Federation.

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METASOMATIC MODEL OF FORMATION OF MASSIVE SULFIDE ORES IN BIOGENIC BOTTOM SEDIMENTS ON THE OCEAN FLOOR

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Sulfide ores, carbonate, ore-bearing, and metalliferous sediments were investigated in hydrothermal fields of northern equator-related zone of the Mid-Atlantic Ridge; among them: the Semyonov (13°31’N), Ashadze –1 (13° N), Zenith-Victoria (20°08’ N), Peterburg (19°52’N) fields. Carbonate coccolith–foraminifera bottom sediments are 1.5–3 m thick while metalliferous, 0.25–0.6 m. On the basis of a faunal assemblage, the age of sediments is dated as Holocene-Upper Pleistocene (0–128 ka). Sediments rest on hydrothermally altered basalts and peridotites. The major part of sulfide constructions occur in sediments, representing a new type of sulfide mineralization, unknown earlier in the MAR zone. It is formed by metasomatic replacement of biogenic carbonate sediments with hydrothermal minerals during diffuse percolating of hydrothermal solutions through sediments.

Sulfide constructions show signs of metasomatic replacement of enclosing sediments: they are often tabular-formed; the height of sulfide constructions corresponds to the thickness of layers; ores contain relics of sedimentary (stratified and organic) textures and structures, inclusions of microfauna shells, replaced by sulfides and other hydrothermal minerals; in many cases, the crust of lithified sediments with zones of carbonate leaching and redeposition is observed on the surface of constructions (usually on their roof) .

Metalliferous and ore-bearing sediments, which include sulfide constructions, are widespread in the form of spots, being different from background ones in physical and chemical characteristics, isotope composition of C and O, increased content of ore components (Fe, Cu, Zn, and Mn), Si, Mg, and metasomatic replacement of calcite shells by hydrothermal minerals. All this suggest a direct effect of hydrothermal solutions on sediments. Mineralization occurred on the geochemical barrier, in the zone of interaction among metalliferous fluids, sea water saturating the sediments, and biogenic sedimentary calcite, unstable in the acid environment. Biogenic carbonate bottom mud serve both as geochemical barrier (presence of reactive biogenic carbonate material) and physical, which makes difficult rapid migration of ore-bearing solutions and encourages precipitation and accumulation of useful components. It is proposed that supply of ore substance directly into the biogenic sediment by fluids from below is one of important sources of development of metalliferous sediments and it is more widely spread in the ocean than previously thought.

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BIOMONERALISATION OF GLUCOSE, CELLULOSE AND LIGNIN IN SAND-ILLITE MIXTURES: EFFECT OF MINERAL NITROGEN APPLICATION

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Two long-term incubation experiments (300 and 450 days) were performed to estimate the effect of nitrogen on the mineralization and humification of organic substances. Glucose, cellulose and lignin were mixed with mineral substrate, sand or a mixture of sand and illite (4:1), inoculated with the soil suspension (Mollisol; soil-to-water ratio 1:10), adjusted with NH_4NO_3 solution to C/N ratios ranged from 2 to 300, and incubated at 22°C. Mineralization of organic substances was estimated by CO_2 emission measured by gas chromatography. N and C content in the samples were determined with CN-analyzer. The composition of organic substances before and after long term incubation was determined by solid-state ^{13}C-NMR spectroscopy.

The glucose decomposition was described by a single exponential decay function. Patterns of lignin and cellulose decay were fitted to a double exponential decay function indicating two pools of organic matter, labile and recalcitrant. Nitrogen fertilization enhanced glucose mineralization, but not significantly affected cellulose and lignin mineralization. These results might explain the inconsistency in to date literature the nitrogen effect on SOM mineralization. We suppose that the effect of nitrogen depends on the proportion between labile and recalcitrant compounds in SOM.

In the course of the incubation 3.5 % lignin, 20–40 % cellulose, 60–85 % glucose were mineralized. The fact that glucose was not mineralized by microbes completely indicates that carbon was reutilized by microorganisms and transformed into recalcitrant forms. Values of mean residence time of glucose turnover and the decomposition of labile pool of cellulose and lignin were similar (MRT ~30 days). By contrast, MRT of the recalcitrant pool varied from 6–18 years for cellulose to 75–170 years for lignin.

Nitrogen application affected the composition of organic substances synthesized by microorganisms in the course of glucose decomposition. 100 % of organic substances were identified as O-alkyl at the start of glucose decomposition. After incubation finished the abundance of O-alkyl decreased while the abundance of aromatic fragments as well as alkyl and carbonyl groups increased. The minimal changes in chemical structure of decay products were found at $C/N = 300$ while the most dramatic transformation was observed at $C/N=6$. The presence of illite in the mineral mixture increased the contribution of aromatic fragments to the decay products. Therefore long-term incubation resulted in maximum transformation of glucose in the sand — illite mixture at $C/N = 6$, with 51 % O-alkyl, 14 % aromatic, 21 % alkyl, 3 % carbonyl, and 11 % carboxyl carbon. Approximately a half of organic carbon in this treatment was extractable with 0.1N NaOH, i.e. was identified as a humic acid-like compound.

Unlike glucose, decomposition of cellulose and lignin did not caused NMR — detectable effects on the composition of organic substances.

STROMATOLITIC BUILDUPS AS GEOSYSTEMS AND THEIR MINERALIZATION

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Stromatolites are thin-bedded rocks, which were formed by interaction of blue-green algae and sedimentation. They were formed 3.5 Ga ago, were widely distributed in the Precambrian, occur in the Phaneorozoic, and their formation has continued until now. Their structure and distribution have been studies, and formal classification of stromatolites on the basis of build up morphology and their microstructure has been compiled. However, mechanism of the formation of these rocks can be deciphered only by estimating the contribution of will of stromatolite builders. A new technique with a use of electron microscope made it possible to establish diverse mineralized biogenic ultramicrounits, which were responsible for the formation of definite microtexture of the rock, and to determine their element composition. Obtained results showed that stromatolites are complexly organized geosystem, in which different components interacted to exchange by matter, energy, and information. The thinnest mucous biofilm including diverse green-blue algae was formed on the mineral precipitate. It rapidly grew over an increasingly wide area. The community extracted carbon and other biophile elements from environment, thus providing mutual penetration of components of the geosystem. When generation of organisms in colony reached maximal size, substrate was depleted and the community lost nutrient medium. The concentration of macro and microelements required for cell growth and functioning decreased, and their growth and reproduction terminated. The CO2 extraction by organisms caused an increase of water đH, which accelerated sedimentation. Thus, components show not only direct, but also opposite relations, which intensified cyclicity of the process and initiated self-regulation of the geosystem. A direct relation — vital activity of blue-green algae — disturbed its dynamic equilibrium, while opposite relation in form of sediment precipitation) reduced impact of the organisms on the geosystem and temporally stabilized environment. During sediment precipitation, the viable trichoma rapidly moved to a new feeding substrate and created colony on its surface. Biocenosis evolved by selecting and transformation of organisms, which allowed them to survive under varying external conditions. The blue-green algae community is the self studying and conformable biological system, which flexibly incorporated into climatic, geological, atmospheric, and other natural conditions. A successive change of reproduction of bacterial films and precipitation of mineral sediment led to the formation of thin-bedded rocks. Such stromatolitic reef may extend for several kilometers. The emergence of unfavorable conditions hampered its integration: bacterial film that initially covered the entire surface of mineral sediment becomes incapable of merging. Organisms colonized «islands», which are separated by variable amount of sedimentary material. This process in the sequences manifested itself by a change of stratiform stromatolites by columnar forms. At the retrograde stage of the basin evolution, the volume of build ups significantly diminished, which facilitated the formation of organisms that were not attached to substrate and able to passive dislocation. These organisms later formed oncolites. The development of extreme flexibility of stromatolitic geosystem and its components during evolution led to the relative isolation of boundaries and strengthening inner relations. The unity and interaction of biogenic and abiogenic components defined its independence, formed integrity and resistivity of buildup to the environmental impacts and preserved spatiotemporal organization of components, their ordering, and mutual arrangement. When external impact disturbed vertical and lateral structures of geosystem and interrelations between its components, it gradually lost its ability to regeneration and degraded.

THE BLACK SMOKERS OF STYLSKY GORST OF THE SOUTHWEST DONBASS AS AN EXAMPLE OF ANCIENT BIOMINERALIZATION

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In geological systems the modern and ancient sulphide black smokers of hydrothermal type a known. Modern active black smokers form on the ocean floor the deposits of sulphide ores.

Therefore, it is important to find and explore their ancient analogs and to understand the genesis of these amazing formations.

Modern black smokers — is sulfide building, which have the form of cones or tubes. They have a height of several tens of meters.

Over black smokers rises the black "smoke" — flows of hot hydrothermal fluids, which consists of a gas and the metals sulphides.

Sulfide tubes of smokers are shrouded a bacterial clusters. They can survive the 120 °C and to absorb hydrogen sulfide and methane. They form on the Smokers a growths — bacterial mats. Not far from the sulfide structures in hydrogen sulfide substrate inhabited by many different organisms. They exist in a symbiotic relationship with bacteria. Thus, the biological life outside smokers is determined by the processes of chemosynthesis and methanotrophs (Koronovskiy, 1999). Currently on the ocean floor are about 100 active and relict hydrothermal fields are known.

Ancient smokers of Phanerozoic age not much is known. For the first time in Ukraine by author in the southwest part of the Folded Donbass in Stylsky career in sediments of the Tournasian age black smokers was found. Stylsky quarry located in zone Volnovahsky ancient fault (Machulina et al, 2004, Machulina, 2008). Opening the black smokers and sulphide ores in this area indicate the development in Stylsky career paleohydrothermal field, which was formed in the zone of rising fluid flow in conditions Stylsky horst.

Investigations by electron microscopy show that sulfides (mainly pyrites) consist of numerous framboids which have bacterial origin. Thus, it is evident that the bacterial community of active modern smokers eventually are undergo mineralization, we can observe this in ancient smokers.

The discovery of the black smokers and the large field of the sulfides in the Stila quarry testify to the development of a paleohydrothermal field, which allows us to assume the presence of a deposit of pyrite-polymetallic ores on the depth.

CALCIUM CARBONATE BIOMINERALS: DECIPHERING THE PROTEINS OF THE SKELETAL MATRIX

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In Nature, biocalcifications are among the most abundant biogenic mineralized structures. They contain small amounts of amalgamate of proteins and polysaccharides that are secreted during the calcification process. These macromolecules are thought to control the morphology of the crystallites and to spatially organize them in well-defined microstructures. Collectively defined as the skeletal matrix, the proteins have been the focus of a large number of studies aiming at synthesizing *in vitro* 'biomimetic' materials, according to a bottom-up approach. However, recent proteomic investigations performed on the organic matrices associated to the mollusc shell, to the coral skeleton or to the sea urchin test and spine have quashed our hopes to generate, with only few 'macromolecular ingredients', biomimetic materials with properties approaching to those of natural biominerals. As a mean value, each matrix comprises a minimum of few tens of different proteins that seem to be strictly associated to biocalcifications. Furthermore, these proteins, which constitute the 'skeletal repertoire', are not identical from model to model. Although they can be grouped in families according to their functional domains, they exhibit a tremendous variability in their primary structures, which surpasses all what molecular models show. Among the proteins that are currently detected, one finds RLCDs-containing proteins (Repetitive-Low-Complexity Domains), diverse enzymes, proteins that contain protease inhibitors domains and, at last, proteins, which exhibit a typical ECM (Extra Cellular Matrix) signature. Today, we still do not understand how the skeletal matrix works, and unveiling the complex functioning of its protein elements is one of the challenges of the coming decade, in biomineralization research, both from fundamental and applied viewpoints. Beside fascinating evolutionary aspects, understanding the link between organic and inorganic materials is a key-issue in biomaterials and environmental sciences.

BIOGENIC STRUCTURES IN CARBONATE NODULES OF PERMIAN PALEOSOLS

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We studied the carbonate nodules from the paleosol profiles of Urzhumian and Severodvinian reference sections of Permian in Kazan Volga region. This sections are represented by red-color continental lacustrine-alluvial deposits. Paleosols were identified and described in more than twenty levels of this sections by the paleopedology features: *in situ* roots, slickensides, gleyed zones, carbonate nodules, blocky peds etc. Among the non-carbonate paleosols, the main paleosol orders from studied sections are eluvial-illuvial gleysols and paleoloesses, according to Naugolnykh, S.V. (2004), or calcic gleysols and gleyed vertisols, by Mack, G.H. (1993), host rocks are red-colour siltstones and mudstones.

Paleosols reflect gaps in sedimentation, subaerial exposure of sediments and their intensive interaction with the atmosphere and the biosphere. Paleosol's maturity expressed in thickness of the rocks affected by pedogenic transformation, as well as in complete development of paleosol horizons. However, in many cases, the paleosol horizon A is cut off by subsequent erosion, and horizons Bg, Bk and C preserved in sequences.

In order to reveal a mineralogy and lithogenic features of pedogenic carbonates, we have studied carbonate nodules from Bk horizons of Urzhumian and Severodvinian paleosols. A few carbonate nodules were analyzed by scanning electron microscopy (SEM), d ^{13}C and d ^{18}O isotopic analysis, X-ray diffraction and x-band EPR.

All of nodules are of two types: ovoid, sharp-edged nodules and mottled cementation zones, often formed around *in situ* roots. These two types form the mutual transitions with one another and have size 2–30 mm. Carbonate nodules from Urzhumian paleosols consist mainly of dolomicrite, whereas those from Severodvinian ones consist of calcimicrite, that may indicate a climate changes from arid to semi-arid.

SEM study allowed to detect a widespread presense of fossilized bacteriomorphic filaments on the surface and edges of carbonate and clastic mineral grains in all types of pedonodules. Coarser grains of diagenetic calcite, contain usually not such filaments. The mineral composition of the filaments corresponds to mineral composition of the substrate grains, i.e. calcite/dolomite/silica. A regular facilitation of isotopic composition d 13C in pedogenic carbonates compared with sedimentary ones, confirms the formation of first with the participation of the lighter carbon of biogenic origin.

Thus, carbonate nodules in the Permian paleosols were formed, most likely, by the direct participation of chemolithotrophic aerobic (?) microorganisms, and their activities was stopped after the overlapping of paleosols with new sediments.

BIONANOMINERALS OF IRON OXIDES IN THE WEATHERING BASALTS OF VIETNAM — CRYSTALLOMORPHOLOGICAL, THERMAL AND MAGNETIC PROPERTIES

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At the recent time it was established that the crust of weathering (CW) and the related deposits of ore and nonmetallic useful minerals are a peculiar chemical reactor on synthesis of natural biogenic and nonbiogenic nanoparticles, having the distinctive features of the physical and chemical properties. Authors have been carried out the complex study of ferriferous bauxites samples and concretions from cuirass in CW of Vietnam basalts.

Crystallomorphological properties. Magnetite according to SEM forms the pyramidal colonies having the size in diameter ~ 200 μm in the basis and ~10 μm at the top. They are made by coccoid chains, forming in turn the step layers with area decrease to top of a pyramid. In TEM the mineral is presented by volume dendrite-like formations about 2 μm in size. « Branches» dendrites are combined by microdruzes of clearly expressed cubic crystalline particles of magnetite of 40–60 nm in size. Hematite forms the stratified spherical and fanlike twins in the size from shares to one — one and a half μm, combined mutually sprouting disks with thickness less than 100 nm. As it appears from TEM pictures disks completely consist of a set of nanoparticles in the size of 20–30 nm. Similar formations of hematite were received as a result of synthesis with participation of organic substance (Neiderberger M., et al 2002). Goĺthite is generally presented by the big star-like twins regularly distributed among coccoid bacterial forms. Combination of considered individuals is observed. TEM patterns demonstrated the presence of aggregates (1.2×1.0) μm in size) of the star-like growths corresponding to twins and trillings of this mineral quite often covered by a thin amorphous films of an oval form of alumosilicate structure, and goethite is established only on microdiffraction pictures and magnetic properties. The sizes of star-like crystalline particles and covered with a film crystallites respond to the pictures obtained in SEM (see above).

Thermal properties. STA confirms a biogenic origin of studied minerals with fixing of relicts of the organic substance participating in their formation. High-temperature exothermal effect is explained by the decomposition or a destruction of organomineral phase. Carbon in organic compounds, which transformation catalyzed by a surface of minerals, at high temperatures cooperates with oxygen from air if survey is made in the oxygen atmosphere, and with oxygen which is released from a crystal lattice of a mineral as a result of its destruction when heating, in the argon atmosphere, with formation of CO_2.

Magnetic properties. Unusual magnetic behavior typical for layered synthesized nanostructures was found in these sediments consisting from two Fe-phases-goethite and hematite in variable proportions. This specific magnetic behavior revealed variable shapes of hysteresis loops (mainly constricted) for natural samples and exchange bias after samples cooling in the magnetic field. Both these phenomena improve the biologically induced formation of these intimately connected minerals as natural layered nanostructures with exchange anisotropy in interface.

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BIOMINERALIZATION OF PRECIOUS METALS

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In concoction processes of chemical elements in weathering crust microorganisms have the special value that is stipulate by a huge variety of ecological niches occupied by them and great opportunities of their enzyme activity. In model tests the kinetics and also the possibility of concoction and biogenesis of ultradisperse forms Au, Pd, Pt in different physical and chemical conditions was examined. The maximum rate of extraction of Pd and Pt from solution by Penicillium canescens biomass at different pH values (fig. 1) is observed in sour solutions (pH 1–2) and makes 16 and 47 mg/g of an element respectively, whereas the maximum rate of extraction of Au (to 24 mg/g) by fungic biomass is observed in subacidic solutions (pH 4–5), thus microfungus extracts palladium and platinum from chloride solutions at rate of 87–95 % at optimum acidity of solution, gold to 99 %. Biosorption rate from pH depends on a metal form finding in solution, possibility of ions hydrolysis, ionization of functional groups of biopolymers of a fungi cell wall.

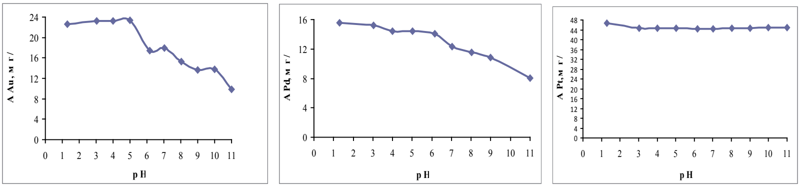

Fig. 1. Curve sorptions of Au, Pd, Pt by fungic biomass at different pH values.

By the method of scanning electronic microscopy the Pd and Pt distribution over all mycelium surface was established (fig. 2). The possible sites of a complex formation of metal with an organic matrix are –S,–N,–O containing functional groups of structural components of a cell wall.

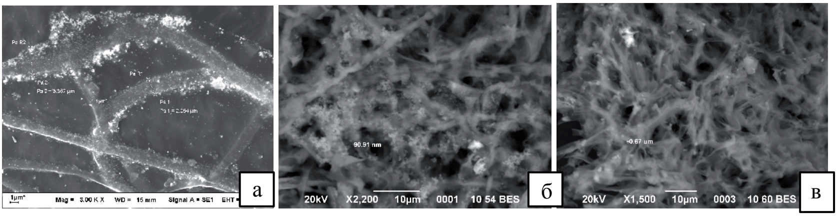

Fig. 2. Surface of hyphas with sorbed particles of Au (a), Pd (b) and Pt (c).

The sorption process of precious metals by a fungic cell wall proceed differently: interaction process of ionic Au with an organic matrix is continuing up to formation of metal nanoparticles, further on which gold units are formed whereas interaction of Pd and Pt stops at a sorption stage. It is supposed that biomineralization mechanisms of precious metals are caused by several reactions — anion exchange, a complex formation and oxidation-restoration.

The sorption process of precious metals by a fungic cell wall proceed differently: interaction process of ionic Au with an organic matrix is continuing up to formation of metal nanoparticles, further on which gold units are formed whereas interaction of Pd and Pt stops at a sorption stage. It is supposed that biomineralization mechanisms of precious metals are caused by several reactions — anion exchange, a complex formation and oxidation-restoration.

INITIAL BIOMINERAL TRANSFORMATION OF SHUNGITE ROCKS

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Shungite rocks of Karelia (Russia) represent a large group of diverse carbonaceous Precambrian rocks in an area more than 9000 square kilometers. Shungite rocks have simple mineral composition, which contain shungite (carbon with traces of N, O, H and S), and may consist quarts, mica, carbonates and traces of other minerals.

The method of scanning electron microscopy (SEM) (VEGA 11 LSH TESCAN with analytical attachment INCA Energy OXFORD Instruments) was used for investigation of change of mineral composition of shungite rocks at interaction with biological objects. The study of morphological and microstructure features of carbon and minerals was carried out by transmission electron microscopy (TEM) (EM-125). Shungite was studied by differential thermal analysis (DTA) and Raman spectroscopy methods.

Terrestrial ecosystems of shungite rocks covered with lichens. Transition layer between the lichens and the shungite rock is well visible. Comparing with the original rock composition of this layer is characterized by lower content of iron and titanium, and by absence of calcium and magnesium. In addition the concentrations of silicon and aluminum accordingly are increased. Floccus of the lichens penetrated into the substratum were usually very thin (the thickness is only 1–3 microns) and with long cells. They are often curved around stable minerals such as quartz and potash feldspar. In the transmission image of the field of floccus distribution, the facet of crystals is well visible.

Samples from a transitional and underlying area with and without floccus of the lichens were selected to identify an influence of lichens on biomineral transformation shungite rocks. DTA study show that peaks of thermal oxidation of carbon from transitional area are shifted in the direction of smaller energy to ~10 °C. It denotes increased structure imperfection of carbon as compared to shungite from underlying rock that leads to the reduction of its temperature destruction. Raman spectroscopy revealed that the intensity ration of D and G bands (the R1 — parameter) of carbon from a transitional layer is considerably less than that of carbon from underlying rock (Table) .

Table. DTA and Raman spectra parameters obtained for initial and biomineralized shungites

Shungite	DTA		Raman spectroscopy				
	T_1 (° C)	T_2 (° C)	G (cm^{-1})		D1 (cm^{-1})		R1
			band position	FWHM	band position	FWHM	
underlying area	448	565	1581	51	1342	74	1.76
transitional layer	430	555	1576	36	1343	52	0.9

Shungite rocks situated in water are a substratum for development of unicellular and multicellular algae. In some cases have been found imprints of destruction of shungite rocks by diatoms. The interaction of multicellural algae with shungite rocks lead to the separation of particles from shungite rocks by a bottom side of thallome. Films appearing on the surface of the shungite rocks as a result functions of algae contain up to 50 % oxides of iron and 40 % oxide of silicon.

Thus, biomineralogical transformations of shungite rocks occur both on air and in water.

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KOLA BAY, RESULTS OF GEOECOLOGICAL STUDIES

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Kola Bay is comparable to the industrial areas of the United States, Canada, Germany, according to the degree of anthropogenic impact. Its ecosystem is exposed to significant anthropogenic impact for several decades and is in a depressed state.

Geochemical characteristics of modern sediments of the Kola Bay — one of the most important indicators of the state of the geological environment and assess the impact on her natural geological and anthropogenic processes, objects and phenomena.

In the Kola Bay allocated 9 geochemical regions, as a result analysis of the systematic component of geochemical field. Spatial position of regions and their geochemical specialization depend on the composition of geological formations of the coastal zone. Analysis of “geochemical spectra” shows that from south to north in the bottom sediments decreases the total number of elements in the surplus relative to the background, and increases the number of items in deficit. Technogenic geochemical association connected with the local sources of some chemical elements. Elevated concentrations of Cu, Zn associated with the bases of the Northern Fleet of Russia (NFR), which are located in Severomorsk and Polyarny. Elevated concentrations of Cd, Hg, in Northern knee may be associated with the base of NFR, deposit of reactor compartments and a plant for recycling, located in Olenya and Sayda bays.

Chemical elements are grouped into four groups depending on their forms of a finding in the modern bottom sediments. 1 — Co and Ni. Forms associated with hydroxides of Fe and Mn, as well as insoluble forms are main for them. The share of other forms is small. 2 — Cu, Pb and Zn. For these elements the most common forms are: associated with hydroxides of Fe and Mn, with of humus organic matter and insoluble forms. 3 — Cr found primarily in an insoluble form. Its other forms are associated with hydroxides of Fe and Mn, with of humus organic matter. 4 — As is significantly different from the other elements. Its most common form is associated with humus organic matter. A significant portion of the arsenic is at water-soluble form.

Increasing the concentration of water-soluble forms of Zn and Cd takes place in the port area of Murmansk. Bottom sediments in this area are contaminated with hydrogen sulfide.

Thus, the study of the forms of chemical elements in modern sediments shows that there is a risk of secondary pollution of the Kola Bay, when physicochemical conditions of sedimentation will vary.

According to long-term observations revealed that modern sediments are characterized by a high concentration of petrochemicals.

BIOMINERALIZATION IN BAUXITIC LATERITES OF MODERN- AND PALEOTROPICS OF EARTH

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20–30 years ago participation of organic substance in processes of supergene ore genesis was a vexing question. Research under electronic microscopes (SEM and TEM) bauxites, the Fe and Mn ores associating with weathering rocks discovered in them a great number of various biomorphes [1]. We undertook more detailed studying of bauxites and laterites of various age and added the previous results with new data. The top part of a lateritic profile including laterites *in sensu stricto*, bauxites and even zones of clay minerals (ęŕîlinite, halloysite, montmorillonite), contains plentiful traces and products of interaction of a substratum with live organic substance and mortmasses. Laterites are broken by cracks and penetrated by roots of trees and bushes on depth more than 10 m that provides deep penetration of microorganisms. The surface of laterites is hidden under the dense feltlike film weaved from filamentous fungus, roots of vegetation and fossilized microorganisms. Dying off, they turned in plant-shaped concretions, replaced with such biominerals, as gibbsite-$Al(OH)_3$, goethite-$HFeO_2$, hematite-α-Fe_2O_3, halloysite-$Al_4(OH)_{10}[Si_4O_8(OH)_2 \cdot 4H_2O$. They formed poorly crystallized masses and idiomorphic crystals in cavities. The top 100 cm of laterites called by a zone of a biological pedoturbation, are completely processed by digging organisms. Earlier it was represented that they make only mechanical impact on rock. By us it is shown that digging organisms, including worms, completely mill all minerals of a substratum, passing it through the digestive path and satiate it with biochemical active substances (Fig. 1). It causes dissolution of all minerals (кaolinite, gibbsite, hematite, quartz, etc.) except rutile — TiO_2 occurring as the thinnest needle

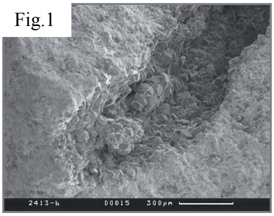
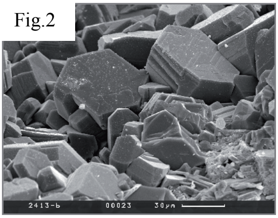


Fig.1

crystals. Possibly, rutile can be used as the indicator of the inferior limit of acidity in biogeochemical reaction (pH more or equal 2). Gibbsite, passed through a digestive path, recrystallizes and forms surprising on beauty and the perfection idiomorfny crystals filling courses of worms and covering their walls (Fig. 2). We managed to find the paradoxical phenomenon: pass of worms through large (2–4 cm) quartz crystals. The entrance is surrounded with a biofilm similar to a saliva and turned into units of crystals of hematite, and the mineralized excrements corresponding to halloysite.

Fig.2



The described phenomena are established on numerous bauxite deposits of India, Guinea and Brazil of the modern tropic and on the ancient deposits of the Chadobets uplift in Siberia, where they remain more than 30 million years after alteration of paleotropic climatic conditions.

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PARTICIPATION OF ALGAE-BACTERIAL COMMUNITY IN FORMATION OF MODERN STROMATOLITES IN COCK SODA LAKE (ALTAI REGION)

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Cock Soda Lake is a hypersaline soda lake with high carbonate alkalinity and pH about 10. It is located in Kulunda Steppe (Altai Region, Russia). This kind of lakes is also characterized by the almost complete absence of Ca^{2+} and Mg^{2+} due to the extremely high total alkalinity. During the 10-year period of observations the salinity of the Cock Soda Lake varied from 50 g/l to 200 g/l (in June-July). Total alkalinity varied from 0.5 M to 2.7 M Na_2CO_3+$NaHCO_3$ during the same period.

We have found microbiolites in this lake, which represent crusts with the alternation of dark-grey, light-brown and very thin white layers. The algae- and cyanobacterial community exists on the surface of the microbiolites. Also, the microfossils of the algae, cyanobacteria and bacteria are found in the structure of the microbiolites. Thus, it is possible to define these laminated organo-sedimentary structures as modern stromatolites.

The modern stromatolite was studied on microtomograph Skyscan 1172. Layers with different rentgen-contrast are well revealed in virtual sections. This allowed to observe the presence and distribution of layers with different composition and structure in space, as well as to identify microporous (cavernous) structure of stromatolite.

The distribution of chemical elements through the stromatolite grinder, which includes all types of layers, was studied by the EDX on Scanning Electron Microscope Zeiss EVO50 with microanalyzer INCA Oxford 350.

The predominant chemical elements in stromatolite are Ca, Mg and Si. The presence of Ca and Mg is caused by chemistry of groundwaters. Mg can also appear in the stromatolites from the phototrophic biomass while its destruction (as it is a component of chlorophyll molecules) .

It was shown that Si and Mg are distributed evenly throughout the grinder. For the distribution of Ca a thin high density layer is characteristic. This Ca-rich layer has a white color and consists of almost pure calcite.

The light-brown layers represent exopolysaccharides (EPS) mineralized predominantly by Mg and Si. The dark-grey and the light-brown layers contain mineralized biota and EPS, but biota is more abundant in the dark-grey layer. The exopolysaccharid sheaths are mineralized first by Mg and then by Ca, that may reflect different stages of dolomite formation. A growth of crystals of Ca-Mg-carbonates occur in this layer in direct connection with EPS: the sheaths of cyanobacteria and slime of other bacteria and also cell envelopes of eukaryotic algae. The study of the stromatolite by methods IR-spectroscopy and X-ray diffraction confirmed the formation of crystals of stoichiometric dolomite and Ca-rich-dolomite. This confirms our statement about the impact of biota in formation of dolomite.

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Section 3
Biomineral interactions in soil

EFFECT OF ORGANIC FERTILIZER ON THE BASIS OF PEAT TO CHANGE THE PROPERTIES OF SODDY-PODZOLIC SANDY SOIL

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A variety of a chemical compound and properties of peat allows to receive highly effective organic and organic- mineral fertilizers which application promotes increase of fertility of soils and manufacture of competitive agricultural production. Return from maintained peat bogs last decades has sharply decreased, nevertheless process of drainage and development of peat deposits proceeds, mainly on purpose торфодобычи on fuel and for manufacture of composts and nutritious grounds. It is known, that most a peat effective utilization on fertilizer is it composting with various organogenic materials: manure, a dung, green manure, etc. Using of peat in the pure state on fertilizer, according to a number of researchers, inefficiently.

In field experience on soddy–podzolic sandy soil as fertilizers used various peat composts, and also peat in the pure state. Organic fertilizers brought under the first culture 4-full grain-row a crop rotation in the doses containing 200 kg of nitrogen on 1 ha. As a result of researches on change of separate agrochemical indicators of soil of arable horizon experimental data are received for crop rotation.

So, peat application has in the pure state led to increase of exchange acidity of soil on 0,2 units, value hydrolytic acidity on 0,5–0,7 meq/ 100 g of soil has raised. In other variants of experience physical and chemical properties of soil remained at former level. The maintenance of mobile phosphorus and exchange potassium at use of organic fertilizers has decreased in comparison with initial on 25–40 %, thus in soil of a control variant the decrease has averaged 60 %.

Use of examinees of organic fertilizers in a combination to the mineral has allowed to raise efficiency of their application. The positive balance of humus and nutritious elements in soil has been thus noted. The greatest gain of mid-annual efficiency of a crop rotation without collateral production has been noted at entering peat-poultry compost and has made 11,2 dt ha^{-1} g.u. On a background of mineral fertilizers efficiency of application of all organic fertilizers applied in experience, including peat in the pure state has increased. Thus the increase in mid-annual efficiency of a crop rotation was authentic, the greatest gain is noted in variants at use peat-poultry and peat-manure composts and has made 16,6–18,8 dt ha^{-1} g.u. Thus, application of organic fertilizers on the basis of peat and others organogenic materials in grain-row crop rotation on soddy-podzolic sandy soil has influenced agrochemical properties of soil. The humus positive balance, mobile phosphorus and exchange potassium in arable horizon of soil is noted. Peat in the pure state as by results of researches of did not realise fertilizer, its acidifying action on soil has been thus noted. Application organic-mineral systems fertilizers was most effective. Mineral fertilizers have raised efficiency of organic fertilizers, including peat in the pure state on 11–25 %. The increase in mid-annual efficiency of a crop rotation was authentic, application peat-poultry compost was most effective.

SPECIFICITIES OF BIOGENIC ELEMENT MIGRATION IN SYSTEM SOIL–INFILTRATION WATERS IN ARAGATS MOUNTAIN MASSIF

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Since recent decades negative man-induced impacts upon the environment have been intensifying dramatically and have already brought to substantial changes in global functions of soil and consequently to its degradation. For this reason studying and assessment of the status and qualitative composition of soils are among urgent issues of today.

Recent findings on composition of water-migration flows of elements in mountain ecosystems show that human intervention and climatic changes trigger disturbance of biogenic elements migration in the ecosystem.

This research was implemented between 2011–2013 in alpine (3250m a.s.l.) and meadow-steppe (2085 m.a.s.l.) belts of the Aragats massif. The research goal was to study a water-migration flow of elements with regard to their inflow with atmospheric precipitation, distribution and leaching into infiltration waters. The stated goal was achieved through studies of migration of elements in system atmospheric precipitation-soil-infiltration waters.

Studies have revealed the mineral composition of atmospheric precipitation. By mean contents cations and anions in composition of atmospheric precipitation are ranged in decreasing order (mg/l) as follows: meadow-steppe belt (at a height of 2085 m a.s.l.) — Ca^{2+} (25.7) >Mg^{2+} (7.1) >K+ (12.8) >Na+ (6.4) and SO_4^{2-} (119.7) >HCO_3^- (28.8) >Cl– (16.3), alpine belt (at a height of 3250m a.s.l.) — Ca^{2+} (15.7) >Mg^{2+} (5.9) >K^+ (9.2) >Na^+ (4.7) and SO_4^{2-} (26.7) >HCO_3^- (19.3) >Cl^- (8.8) .

A study of water migration of chemical elements in the soils has shown that lysimetric waters of the alpine belt have a low pH and relatively low contents of chemical elements at a depth of 0–50 cm. Lysimetric waters of the both belts are characterized not only by high contents of HCO_3^-, Ca^{2+} and SO_4^{2-}, but also by their dominance among cations and anions. Low contents of nitrates in lysimetric waters of alpine belt is explained by low nitrifying potential of soils, and this is caused predominantly by acid reaction and low temperatures of the soils.

For the studied period in alpine and meadow- steppe belts the contents of ammonia nitrogen (NH_4^+) transported with atmospheric precipitation into soils were 4.20 and 6.80 kg/ha respectively, and its removal from the soil to lysimetric waters respective 0.75 and 3.20 kg/ha. Similar data were obtained for the rest elements, too, whereas in the case of nitrates one may observe quite an opposite picture as nitrate removal from soil is higher than its inflow to soil with atmospheric precipitation. Migration activity of HPO_4^{2-} in the studied soils is poor unlike nitrates (NO_3^-) which are not absorbed by soil colloids, do not form hard soluble salts and therefore due to good mobility they leach easily from a root-inhabited layer into ground waters. There they become unavailable for plants and finally may cause pollution of underground waters.

The researches indicate that as compared with nutrients Ca^{2+}, Mg^{2+}, SO_4^{2-} and Cl^- migrate more actively, their contents making respective 23.5; 8.5; 21.5; 10.1 in alpine and 32.8; 19.5; 33.4; 19.6 kg/ha in meadow-steppe belt.

The obtained results prove that the higher absolute altitudes (alpine belt), the higher, but not lower, the contents of organic compounds in lysimetric waters are, and that lysimetric solutions of the soils of alpine vs. meadow-steppe belt are more acid and less mineralized.

So, collation between basic migration flows of biogenic elements in the ecosystem beginning from their inflow (with atmospheric precipitation) to soils up to their loss (the in-soil flow) support a conclusion that the strongest transformation of a migration flow of elements in the system of Aragatsi massif occurs in a meadow-steppe belt.

TRANSFORMATION OF SHUNGITE CARBON IN SOIL

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Shungite rocks of Karelia (Russia) form a large, diverse group of black sedimentary-volcanic Proterozoic (2.0 Ga) rocks with giant elemental carbon reserves. Soils, formed on the shungite rocks, are characterized by high gumus content, poorly differentiated soil profile, and are neutral or slightly acid. Shungite carbon (shungite) from soil and underlaying shungite rock was studied by thermal differential analysis (DTA) and Raman spectroscopy methods. The DTA data show that shungite soil consists of of organic matter (46%) and shungite (6%). The Raman spectra of shungite from soil and underlying shungite rock are consistent with poorly ordered carbonaceous material (CM) [1].

According to the traditional approach for CM structural ordering estimation [1, 2] it is possible to assume that the structural ordering of shungite from soil is higher than that of shungite from underlying rock, due to lower values of Raman parameters R1 and R2 (Table). However, the shungite from soil has significantly larger FWHM (full width of half maximum) of D1 band that corresponds to its lower degree of structural ordering [3]. D1-band has been attributed to in-plane defects of graphene layers, thus its intensity decreases as CM structural ordering increases [2]. But for shungite from soil the decreasing of D1 band intensity is accompanied by increasing of its FWHM, probably, due to the formation of new bonds of various energy during the interaction with impurity atoms or molecules. Additionally the absence of any bands in the second-order region and the presence D3 and D4 bands, specific for poorly ordered carbons, are evidences of the low degree structural ordering of soil shungite. The D3 band was not detected for the shungite from undelying rock.

Model experiments on soil heating were carried out to study the stepwise destruction of soil organic matter. According to the DTA data the thermal oxidation of organic matter occurs at heating to 280 and 400 °Ñ, but the content of shungite does not change as well as its Raman spectra. So the impurity molecules, interacted with shungite, are not the soil gumus molecules. Raman spectra of soil shungite heated at 500 °Ñ become similar to that of shungite from underlying rock with respect to intensity and FWHM of the D1 band. But the bands in the second-order region still were not detected for shungite from soil that indicate lower degree of structural ordering of shungite from soil in comparision with the shungite from underlying rock. Thus the degree of structural ordering of shungite decreases in soil due to the various physical and chemical processes as well as the soil microbial activity.

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PEDOSEDIMENTARY MODEL OF UPPER PERMIAN PALEOSOLS FORMATION AND DURATION OF PEDOGENESIS (THE NORTHEAST OF THE MOSCOW SYNECLISE)

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A vertical sequence of seven Upper Permian paleosols composing the Klimovsk pedocomplex was studied in the basin of the Sukhona River in the Klimovsk section and the Salarevo section (Vologda oblast). The data obtained were discussed and interpreted by using some theoretical concepts: hierarchical soil organization on macro-meso-micro- and submicrolevels in relation to the specific pedogenic processes, the pedosedimentary model of pedogenesis. The pedosedimentary model presumes that pedogenesis (perceived as in situ transformation of parent material) either coincides in time with the deposition of solid particles, or alternates cyclically with sedimentation processes.

The total thickness of the Klimovsk pedocomplex in this section reaches 9.5 m. There were 7 such individual pedo-sedimentary cycles identified within the Klimovsk pedocomplex and though the thicknesses of each of them varies from 30 to 150 cm; their common genetic horizonation remains conformable: sequence of stagnic (eluvial-gley) and cambic horizons developed in the upper parts of the red-colored sediment. Each pedo-sedimentary cycle started from the stage of deposition of weakly- or non-laminated red-colored sediments (thickness — 50–150 cm). It was rather single-stage or short-term deposition act (n×1 year) similar to the catastrophic inundation of the lowlands bringing large volumes of silt and clay sediments. The next stage was a pedogenic one and long-lasting (n×10^2–10^3 years), when sedimentation ceased or became drastically reduced. On this stage, the fresh red-colored sediments were transforming in situ by the climatic and biotic agents, i.e. modified by pedogenesis.

The pedogenetic interpretation of the revealed soil diagnostic features enables us to define the set of specific pedogenic processes (SPP) that formed the studied Upper Permian paleosols. These processes could be divided into the SPP common for all studied paleosols and the SPP special for luvic and calcic subgroups. The common SPP are: stagnation (gleyzation due to surface perched water), stagnic redistribution and segregation of Fe and Mn, both within the solum and in individual horizons, structural metamorphism which is reflected in blocky-prismatic structure formation, vertic features formation. In addition to the common SPP, the lessivage was developed in Luvic (non calcic) Cambisols and carbonate migration and segregation — in Calcic Cambisols.

The analysis of the whole Rovdian sedimentary member and including in it pedocomplexes gives the possibility to assess the number and duration of the soil formation stages, i.e. number and duration of the sedimentation breaks. Without the absolute dates for the studied paleosols the evaluation of the pedogenesis duration for each individual paleosol was done through empirical knowledge about the characteristic times of SPP which formed these paleosols. It should be noted that all these pedogenetic processes belong to the groups of fast (with short characteristic times) processes like stagnation and pedogenic structural metamorphism, or moderately fast processes like migration of carbonates, lessivage, and synthesis of palygorskite.

VARIATIONS OF CHEMICAL COMPOSITION OF LOESS-SOIL COMPLEXES OF THE SOUTHEAST OF RUSSIAN PLAIN AS THE SIGN OF CONDITIONS OF THEIR FORMATION AND DYNAMICS OF THE CLIMATE IN PLEISTOCENE

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Loess — soil complex is a large complex of continental deposits of Pleistocene age mainly arising under the alternation of glacial and interglacial periods. Loess accumulation and soil formation processes are syngenetic. However, it is assumed that formation of loess basically formed in special cryo-arid conditions of glaciations under the influence of a complex sub aerial processes in which sedimentation from of silt material air prevailed. Formation of bedrocks on parent loess occurred interglacial and interstadial stages which differed growth warmly and humidity, and also relative stabilisation of a surface. The climatic changes, occurred in glacial ages, strengthened one of these processes, reduced another. That reflected in change mineralogical and chemical composition of loess and led to formation of bedrocks in the short-term seasons of warming.

The aim this research was the study of chemical composition of loess and soil complexes with a view to identify the characteristics of their formation and evaluation of natural conditions in the steppe zone of the South Russian Plain during the Pleistocene. For this purpose, a comparative analysis of the chemical composition of different ages loess- soil complex (cuts “Otkaznoe”, “Port-Katon”, “Shabelskoe” and “Melekino”, located on the territory of the Terek-Kuma plains and the Azov — Kuban lowlands) was conducted by the X-ray fluorescence spectroscopy.

The geochemical method of research of uneven-aged depositions it one of the most dynamically educing areas in Quaternary geology and paleoclimatology. Geochemical parameters are widely used for the decision of many problems, such as definition of sources formation of loess, intensity eolian transport, definition of a climate and vegetation in regions of sedimentation and many other things.

Thus, our study revealed that loessial depositions of the studied cuts have similar chemical composition with prevalence Si, Al, Fe and Ca. It is positioned that chemical composition of loess of Ciscaucasia (cuts “Otkaznoe”) differs from chemical composition of loess Azov. The first haves heightened Si and Al and lower Ca and Mg in comparison with loess of Azov region that is possibly associated with prevalence in this areas of east conduction of air masses and introduce of a stuff from Caucasus.

Chemical composition of the loess cuts “Melekino”, being in Northeast Sea of Azov differs both from loess of Ciscaucasia, and from loess of Southern Sea of Azov. Bad sorting of quartz grains and high maintenance Zr in loessial horizons cuts “Melekino” concerning loess of southern coast of gulf of Taganrog, shows rather short trajectory of a dust and affinity of its source. It can be associated with difference of a geologo-geomorphological constitution of northern and southern coasts of gulf of Taganrog, also with conduction terrigenous a stuff from the north on the south.

Accumulation Si and Zr and reduction of maintenance Al and K in all studied cuts from more ancient epoch to more modern is marked. This fact means that, eolian transport was rather to more serotinal cold epoch of a Pleistocene, in particular, in the Valdai glaciation. In the activization seasons soil-forming processes in warm interglacial ages in palaeosol in comparison with loessial depositions the augmentation of concentration Fe, Mn which are intensively involved in biological circulation, to 42 and 0,9 mg/g accordingly, and Rb, collecting as a result of increased weathering processes, to 113 mkg/g is marked.

THEORETICAL CONCEPTS ABOUT ORGANIC MATTER, HUMUS, HUMIC SUBSTANCES IN SOILS AND THEIR ADEQUATE EXPERIMENTAL DETERMINATION

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In the development of classical concepts (Vaksman, 1937; Tiurin, 1937, Orlov et.al., 1996), soil organic matter is considered as a many-component, heterogeneous and polyfunctional continuum of organic substances in the conglomerate with mineral particles subdivided into pools and fractions that are different in composition, turnover rate, stability and other structural-functional characteristics. According to Orlov et al. (1996) there is a difference between “humus” and “soil organic matter” concepts, following the statement of Alexandrova (1980) that humus formation is a very specific soil process. In American glossary of soil terms “humus is a more or less stable part of the soil organic matter that remains in soil when the major part of plant or animal residues has been completely decomposed”. In our opinion, the following definition is more appropriate to the present eco-bio-physico-chemical concepts: “humus is a soil subsystem formed from the organic substances and compounds of plant, animal and microbial origin stabilized through the humification and non-humification pathways”. Humification is a (bio) chemical alteration of organic residues with the formation of humic substances, whereas the non-humification stabilization is another process and phenomena which are capable to increase the stability of organic substances to biotic and abiotic effects without their transformation into humic substances. Currently, the procedure of preparing soil samples to determine the humus content in soil includes: 1) careful choice of remains from plants and animals and other organic inclusions under the magnifying glass, 2) homogenization of soil to obtain the particles of <0.25 mm in size, 3) biochromate oxidation by Tiurin's method or dry combustion and 4) C^{org} recalculation to humus, using the coefficient of 1.724. Before measuring soil organic matter by Tiurin's method in modification (GOST 26213–91) "… all the visible non-decomposed roots and plant residues are removed by pincers".

The widely known concept determines humic substances as a biogenic, amorphous, heterogeneous, and chemically active continuum of biomolecules that is recalcitrant under natural conditions and is formed through random chemical transformations and physicochemical interactions of diverse precursors with the formation of supramolecular assemblies from different numbers of individual components of relatively low molecular weight due to nonvalent interactions. Humin should be no longer regarded as the 'mystery component' of SOM (Hayes et al, 2010). Based on the experimental evidences it is clear that most of the humin components do not satisfy the classical definitions for humic substances. These components should be regarded as a mixture of largely identifiable biological molecules derived from plant materials composed predominantly of resistant non-polar moieties in intimate associations with, and protecting some biodegradable biomolecules, all in intimate associations with the soil mineral colloids. It's possible to assume that the humic substances exist in soil but they are not in that kind and in that quantity which is extracted by chemical fractionation after Tiurin's method in modification proposed by Ponomareva, Plotnikova, Kononova, Belchikova or IHSS. Moreover, having the same chemical composition they are very specific in 1) geometric form, 2) ratio between supramolecular and polymer structures and 3) other characteristics in different soil types. Currently, the practical procedures of humic substances extraction are far from perfection. The attempts to study their natural status in soil samples are rather descriptive by nature and should be scientifically grounding and interpreting with the required accuracy.

NEW GEOCHEMICAL BARRIER TO DETOXIFY OF SOIL FROM ARSENIC AND MERCURY

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The given article reveals a problem of weeding soil from heavy metals, in particular from arsenic and mercury. Authors got a new geochemical barrier, consisting of a mixture of the utilized bird's dung, a marble crumb and a peroxide of calcium with the high absorbent activity. The research results allow to eliminate undesirable influence of heavy metals on plants and to get ecological clear products.

The negative impact of hazardous substances on objects of biogeocenoses appears in different ways, especially with respect to the soil, which is the main component and the foundation of operation of all terrestrial ecosystems.

Every year there is an increase of the intensity of soil environment pollution by heavy metals, so the search and development of effective environmental and economic methods of providing access to clean crop production is a challenge for the agricultural sector. The certain scientific and practical interest about the solution to this issue is the creation of geochemical barriers in the soil system to inhibit the translocation of heavy metals in plants.

It is known that the toxic components are adsorbed by organic substances and many mineral components of soils, as a result there is a change in the level of their toxicity and bioavailability. Manifestation of the adverse effects of polluting substances in agro-eco-system depends on the solubility of the pollutants, their mobility in soil and species characteristics of crops.

Analyzing data from the literature [1–3] and the results of our experiments [4] to study the sorption capacity of different materials for the management of migration, the translocation of As and Hg we have selected the geochemical barrier consisting of a mixture of recycled bird droppings, marble chips and calcium peroxide, which have high sorption.

Calcium peroxide is a well-known commercial product which is manufactured on an industrial scale. It is widely used. The main decomposition products are hydrogen peroxide, oxygen, and thus it is used for bleaching, eliminating bad smells, as a local disinfectant. It is also known the use of calcium peroxide for agriculture to improve the growth of various crops at the expense of aeration as a result of the collapse of hydrogen peroxide to oxygen. When you add hydrogen peroxide it accelerates the process of decay. In addition the introduction of calcium peroxide into the soil makes it possible to adjust the pH value in the ecosystem due to the formation of $Ca\,(OH)_2$.

The use of calcium carbonate and hydrogen peroxide, bird droppings reduce significantly the flow of heavy metals into plants due to their adsorption properties.

These obtained experimental dependences can be taken as the theoretical basis for the selection of sorption processes to develop a series of environmental measures.

As it follows from the experimental data presented in Table 3, the number of heavy metals arriving at plants to create geochemical barrier does not exceed regulatory levels (Hg — 0,5 mg / kg, As — 0,3 mg / kg in food). The presence of peroxide calcium in geochemical barrier not only helps to detoxify the soil from heavy metals and to detoxify the bacterial, fungal, parasitic and viral microorganisms.

Thus, the introduction of arsenic and mercury contaminated soil mixture of poultry manure, calcium carbonate and hydrogen peroxide can eliminate the undesirable effects of heavy metals on the plants and grow the environmentally friendly products.

APPLICATION OF RAMAN SPECTROSCOPY AND HIGH-PRECISION GEOCHEMISTRY FOR STUDY OF STROMATOLITES

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Stromatolites are mineralized microbial buildups which vary in morphology, have carbonate composition and characteristic fine lamination [1]. Morphology of the buildups (stratiform, bulbous, bimical or columnar) is defined by microbial comunity as well as environmental conditions:

water depth, currents etc. Stromatolite formation is a result of complex biogenic and abiogenic processes [1]. Taking in account, that stromatolites are microbial buildups, it is necessary to prove their biogenic origin. For this purpose there are a number of criteria, one of them is presence of synsedimentary carbonaceous matter within individual laminae.

Paleoproterozoic (2.0–2.2 Ga) stromatolites from drill cores of the ICDP Project FAR DEEP [2] were studied by Raman spectroscopy (RS) and ICP mass spectroscopy (LA-ICP MS) methods. Carbonaceous material (CM) was identified by Raman spectroscopy within individual stromatolites laminae, and it consists of rare irregular grains with size ca. 30 mm, disseminated through a matrix of dolomite.The Raman spectra for CM in stromatolite samples are consistent with poorly ordered CM [3]. The first-order region of the CM Raman spectra shows two well-resolved bands: D1 at about 1350 cm $^{-1}$ and G band at about 1594 cm $^{-1}$ with similar band width (FWHM=50–55 cm $^{-1}$). The intensity band ratio R1=D1/G is 1.5. In the second-order region, CM stromatolite samples are characterized by bands S1 (2697 cm $^{-1}$) and S2 (2920 cm $^{-1}$). RS study of CM in ancient microfossils can not itself provide deûnitive evidence of biogenicity. However, it can not only conûrm the presence of CM, that is of great importance for ancient stromatolites, but also is used to determine the methamorphic temperatures of CM. According to Raman data the metamorphic alteration temperatures of CM from studied stromatolites would be roughly determined to be around 400 °C. These temperatures are consistent with greenschist facies, and it is in agreement with the metamorphic grade of underlying and overlying basalts [2]. Thus we can assume that the CM of these stromatolites has the syngenetic origin.

Profiling geochemical microsampling of Paleoproterozoic stromatolites has revealed considerable variations in the concentrations of trace elements induced by the internal heterogenecity of the structures. Many elements display multi-order cyclicity indicated by variation in the step length between the peaks on the variation curves. Strong correlations in the group HFSE — Zr, Ti, Y, Nb, La, Th and U and those of zirconium with Ge, Cd, Sb and Bi suggest contamination of chemically precipitated carbonate matter by acid crustal and exhalative material.

Morphological features of the studied Paleoproterozoic stromatolites together with identification of synsedimentary carbonaceous matter by

Raman spectroscopy are strong argument for biogenic origin of these carbonate buildups. Precision geochemical analysis of the stromatolite laminae composition links to sedimentary settings and environmental conditions of the microbialite formation.

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EFFECTS OF LONG-TERM STRAW INCORPORATION ON SOIL BIOLOGICAL PROPERTIES AND CONTENT ORGANIC MATTER FRACTIONS

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The after-harvesting residues, such as straw of cereal and grain legume, are an now one of the most essential annually renewed resource of soil fertility reproduction in the conditions of traditional farmyard manure and composts deficiency and negative balance of organic matter and nutrient in arable soils. Russia annually produces about 100–120 million tons of crop residues. However till this moment this huge resource is used extremely irrationally and impractical. Role of plant residues in preservation and reproduction of arable soils fertility is often underestimated. Not enough experimental data that characterize the changes in biological and humus status at long intensive regular use straw as a fertilizer.

In long-term field experience (in experimental field of our institute) on sod-podzolic sandy loam soil within 15 years spent studying of influence of grain and leguminous straw on dynamics of microbiological parameters, the content and qualitative composition of soil organic matter (SOM). Winter wheat, lupine, barley straw incorporated into the soil in 5-full grain-row crop rotation (a winter wheat, lupine, a potato, barley, annual grasses) one — two-and is triple for rotation (in the sum from 9 to 27 t/ha for 3 rotation) in combination with low doses of mineral NPK-fertilizers.

By results of researches, unitary use of straw (1 times in 5 years) has made insignificant short-term impact on biological parameters and humus content of soil under study.

At 3 multiple during a rotation straw entering steady tendencies of change of biological properties are established: the increase in actual and potential biological activity (cellulolitic activity, emission C–CO_2, nitrifying activity, number of proteolitic, amilolitic, cellulolitic microorganisms). Changes in structure of soil microbial community under the influence of regular incorporation of straw were expressed in relative increase actinomicetal a component and relative reduction of number of representatives autochthonous microflorae.

The basic tendencies in change humus state of sod-podzolic sandy loam soil influenced by repeated application of straw were increase in the content and a share in structure SOM easily decomposable and labile components: hot-water exstractable carbon (C^{hwe}) — on 26–38 mg/kg of soil (15–22 %), labile carbon (0.1 M $Na_4P_2O_7$ exstractable) (C^{lab}) — 85–128 mg/kg (9–14 %), also microbial biomass (C^{mic}) — on 49–80 mg/kg of soil (18–29 %); increase in the content and a share of not hydrolyzed rest in humus structure for the account non hydrolyzed vegetative rests, decrease in optical density humus acids of 1st and 2nd fractions (movable, "free" and bound to the Ca), that as a whole can testify to "rejuvenation" humus fund, accumulation as a part of molecules humus acids neogenic, poorly condensed, aliphatic fragments. While in variants with maximum in experience by straw doses slight increase of the content of total carbon (TOC) on 0,06–0,08 % (the initial content — 0,68 %). The notable changes predetermines increase in biological availability and mineralized of SOM, and also its more active participation in biological circulation of carbon and nutriens, soil-formation processes and productivity of land.

INORGANIC PHOSPHATE SOLUBILIZING BACTERIA ISOLATED FROM AGARICOMYCETE HYPHOSPHERE

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Soil inhabiting agaricomycetes with different ecological strategies — symbiotrophs and litter saprotrophs — are dominants within forest ecosystem mycobiota which biomass in soil takes second place after plants. These fungal groups play principally different roles in ecosystems and vary in nutritional modes, ways of carbon acquisition, limiting factors of their development and their contribution to Ñ and N cycles. Presence of such substantial difference between symbiotrophs and litter saprotrophs allows presuming distinction in their interactions with other groups of soil biota and mycosphere selection favorable for specific groups of organisms too.

Functionally active agaricomycete mycelia provide such zone as hyphosphere and determine its space organization. Hyphosphere arranges specific habitats where soil physical and physicochemical properties change drastically. Numerous organic compounds enter hyphosphere from mycelia. Interactions with mineral and organic soil components and with soil biota as well take place in the hyphosphere. As a result, substantial rearrangement of taxonomic and functional community structure occurs here. Hyphosphere is comparable to rhizosphere in its ecological importance.

Conversion of insoluble phosphorus compounds to soluble forms available for plants considered to be one of the most important functions of symbiotrophic fungi either of arbuscular or ectomycorrhizas. It is well known that symbiotrophs take part in these processes along with numerous bacteria occurring in mycorrhizosphere and hyphosphere of extrametrical mycelia (Lapeyrie et al., 1991, Wallander, 2000, Landeweert et al., 2001, Frey-Klett et al., 2005). The role of litter saprotrophs‘ hyphosphere microorganisms in these processes remains unknown. Thus we carried out a comparative analysis of Ca-orthophosphate-solubilizing bacteria in hyphosphere of 12 dominant and frequent agaricomycete species with different ecological strategies and influence indexes on bacterial CFU numbers more than 1 (symbiotrophs Cantharellus cibarius, Boletus badius, Paxillus involutus, Tricholoma stiparophyllum, Hebeloma crustuliniforme, Russula cyanoxantha, Lactarius aurantiacus; litter saprotrophs Gymnopus dryophilus, G.peronatus, Clitocybe nebularis, C.odora, Lepista nuda; control samples were taken outside the colonies). Soil suspension was planted at mineral selective agar medium TCP containing Ca-orthophosphate (Ramanankierana et al., 2006), Ca-orthophosphate solubilizing activity was detected according to solubilizing zones around the colonies on media. In symbiotrophs‘ hyphosphere notable increase of phosphate solubilizing bacteria was detected (51–83 %). Only in P. involutus hyphosphere twofold decrease of these bacterial group was observed. Considering notable increase in general CFU numbers of bacteria in hyphosphere, the numbers of phosphate solubilizing bacteria have about 2–6.5 fold higher values. Absolutely different pattern is characteristic for litter saprotrophs‘ hyphosphere. There is no statistically significant increase in phosphate solubilizing bacteria, their contribution to total numbers was about 32.34 % in control samples and 36.76 % in hyphosphere.

So the principal distinction between symbiotrophs and litter saprotrophs in selective accumulation of phosphate solubilizing bacteria in mycosphere was determined.

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CHANGING IN SOIL POROUS MEDIA AT PRESENT OF WATER, CRUDE OIL AND MICROORGANISMS

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Soil structure is one of the main parameters forming soil fertility, its buffer properties, bioavailability and mobility of environmental pollutants. This characteristic can be affected by such factors as wetting / drying, present of surfactants, production / destruction of organic matter. Here an attempt to relate impact of water, crude oil and microbial activity on porous space is described. Chernozem leached, gray-forest soil, rendzina soil and sand have been studied. The soils were divided on the following parts: 1) control, 2) soil treated with hot vapor, 3) soil contaminated with 1,5 % of crude oil in weight before the experiments. The soils were packed in the plastic columns with diameter 15 mm and height 70 mm. Then, there moisture of 0,75 of full water capacity was created in the columns. During the interval from 0 to 90 days the soils have been sampling and analyzing. Sizes of aggregates, porosity, soil respiration, total protein, total organic carbon were measured. X-ray microtomography, analysis of gaseous phase and UV-spectrophotometry were conducted. A tomograph General Electric Phoenix V|tome|X S240 was applied. An analyzer iTOC–CRDS OIAnalytical & Picarro equipped with modules Aurora 1030S and Aurora 1030W to analyze gaseous phase were used. UV-spectrophotometry was carried out by an analyzer for liquids LUMEX Flourat-02–3M (light filter with wavelength 240–285 nm, transmission peak 265–270 nm).

Interpretation of tomographic pictures allowed to link gradations on the gray scale with sorts of particles. Dense mineral particles were represented on the pictures in most cases as the gradations 200 and higher, clay-mineral aggregates — as the gradation from 110 to 195 with maximum of distribution — 160–170. Organic matter in friable consistence was reflected as the gradations 50–110. Images of sandy grains overlapped above-mentioned intervals from the gradation 80 to the 170. The part of pictures presented large soil pores had the gray gradations most likely lower than 70. Crude oil added into soil was reflected on the pictures as a part of organic matter phase by the gray gradations about 80 with wide spread. These data were fitted with grain-size analysis by sedimentation. Water and crude oil caused conglomeration of the soil aggregates in all the cases considered. Contamination by crude oil had resulted in increasing of visual porosity of soil, visual pore size that may be interpreted as soil cracking. These results were supported by sedimentology of the samples. On the contrary, water had reduced porosity, thus, water and oil played antagonistic roles in this sense. Simultaneously, quantity of total organic carbon was decreasing during 90 days of the experiments both in the control and in the oil-contaminated soil. This could lead to loosing of the organic glue which stuck aggregates one to another. Dynamics of soil organic matter was shown to be a quasi linear decreasing function of time. The rate of organic matter degradation had achieved the highest mean at the initial moment in the control and by 30 days in the oil-contaminated cases. This rate was twice higher in the oil-contaminated gray forest soil and sevenfold higher in the chernozem than at the controls. The main decline of total organic carbon was occurred due to microbial respiration. At the same time total protein accumulation in the soils was observed. It had rate from 2 to several tens of mg/g of dry soil for 30 days in the oil-contaminated and in the control cases, respectively. Production by living cells and released soil enzymes might contribute to this process. Thus, the parallel processes of aggregation and loosing of organic carbon in the experimental soils had indicated that there is a non-direct link between quantity of organic substances and conglomeration of soil particles.

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Section 4

Geochemistry of biogenic-abiogenic systems

HUMUS FILMS AND HUMUS ACCUMULATIONS IN SOILS OF ANTARCTICA

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Soils of Antarctica are quite diverse and they are known as soils of severe climatic conditions with relatively weak profile and low organic carbon contents. Humus formation provides the accumulation of organic matter in different forms. Meanwhile, the biogenic processes in these soils are active and they results in formation of organic films (stains) on the surface of minerals and rocks. These humic accumulations provide the weathering processes as well as formation of humic like plasma in soil cracks and porous medium. Micro morphological evident o humic films accumulation are discussed in details. Another way for biogenic interactions is formation of microfilms of guano on the soil surface and cutans of guano in soil cracks, even on the 30 cm depth. This way realizes by only under the bird rockeries and nder pinnipedia beaches. The guano cutans are homogenous and forms one layer of organic accumulations. The way of organic films accumulation on the mineral surface is only one aspect of humus formation in Antarctic soils. The opposite process is the accumulation of humified organic colloidal material on the edges of decaying organic remnants. In these case, humic substances formed are less homogenous in their chemical composition and properties than those in organic films on the mineral surface.

Another one process developed in Antarctic soils — is migration of undercomposed detritus humus trough down the soil profile, until it meets the massive rock or permafrost layer. These accumulations form the second peak of soil organic matter in profile, and they most expressed in coarse textured soils with lack of the fine earth.

Thus, the humus forms in soil of Antarctic are very different. Raw humus accumulated not only in uppermost horizons, but migrates even into deep layers by mechanical way. Dissolved humic substances forms the cutans of the mineral surface not only in humus accumulative horizons, but even in middle part of profile. Humus forms differentiations is a main attribute of soils formation which differs the real soil from regolith or ahumic soils of polar deserts.

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QUANTITATIVE ESTIMATIONS OF ENVIRONMENTAL AND GEOCHEMICAL STATE OF SOIL AND ITS CHANGES

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For informed decision making to improve the ecological and geochemical environment in several geochemical and primarily in organomineral (bioinorganic) systems, the quantitative assessment of their conditions and the changes occurring in them is necessary. For such works new indicators put into practice by V.A. Alekseenko are being successfully used in different regions for more than 20 years. There are the Indicators of Absolute (IAA) and Relative Accumulation (IRA). IAA shows the mass of a certain chemical element (or its compounds) accumulated in a particular part of the system as a result of geochemical processes occurring per unit area. Landscapes, soils, all the vegetation of a specific area, plant species, surface or ground water, etc. could be the studied as a part of the system. In case of complete substitution of one geochemical landscape by another (radical change of landscape-geochemical environment) in calculating the amount of IAA the concentrations of elements in the newly formed part of the landscape are compared to the landscape similar to the one that was previously on the site to replace.

During the investigations of soils in the study area it is determined the difference between the background content before the start of these processes and after their completion: $C_1 — C_2$. When after the end of the processes the content has decreased (i.e. it has occurred the takeaway of elements), the IAA value is negative. The study of technogenic changes in the vertical soil profile showed that they usually develop in agricultural and residential landscapes to a depth of 30 cm.

The determination of the average density of soils in Southern Russia allowed to assume after accounts that the increase (decrease) in the concentration of chemical elements in soils by an amount equal to $1 \cdot 10^{-3}$ %, within the upper 30 cm layer corresponds to an increase (decrease) of their weight by 6 tons on an area of 1 km^2.

In some cases, instead of the value of the background content in a certain part of the geochemical system can be used the average concentration in the Earth's crust or a certain normalizing indicator (i.e. threshold limit value, TLV) .

However, such a quantitative measure of how IAA required for many decisions related to environmental issues does not provide sufficient information about the most negative impact of certain chemical elements in each case. Let's consider the following example. An increase of hundreds of tons per 1 km^2 of iron content in the soils is less hazardous for organisms than an increase of 10 tons of mercury and arsenic. It happens due to the different average concentrations of these elements in the Earth's crust. High content of Fe (average 4.64 %) is habitual for organisms over a long period of development and evolution and the high concentrations of Hg ($8.3 \cdot 10^{-3\%}$) or As ($1.7 \cdot 10^{-3\%}$) are unaccustomed. The Indicator of Relative Accumulation (IRA) was proposed by V.A. Alekseenko to overcome this geochemical feature. IRA shows the ratio between the mass of the element accumulated (lost) as a result of the processes occurring in a certain part of the geochemical system (i.e. IAA) and the background content (or the average concentration in the Earth's crust). Thus, we can assume that IRA = IAA/C_1.

SEVERAL GEOCHEMICAL FEATURES OF URBAN SOILS

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Urban soils are being under the greatest technogenic pressure among the bioinorganic (organomineral) systems. Their geochemical features reflect an overall ecological-geochemical state of territories, within which most of the population spends most of their lives. Depending on the technogenic impact we have described seven different groups among the settlements: 1) millionaire cities (> 700 thousand people); 2) half-millionaire cities (300–700 thousand people); 3) cities with a local significance (100–300 thousand people); 4) small towns (< 100 thousand people); 5) small settlements, villages, hamlets; 6) tourist and recreational areas; 7) mining sites settlements. The cities differ by the human-made impact and by the number of inhabitants. This fact has facilitated the division of cities by groups. During studying cities in detail it is expedient to consider the cities of 2nd 3rd and 4th groups depending on their main industries and the cities of 7th group, depending on the extracted material.

The analysis of geochemical characteristics of soils of more than 300 settlements in Europe, Asia, Africa, Australia, America has allowed us to determine the average concentrations of 50 chemical elements in this organomineral system.

The research methodology allows to consider these concentrations as the abundances in urban soils for the period of late XX century — early XXI century.

Based on a comparison between the abundances in the Earth's crust, in the Earth's soils and in urban soils the following conclusions could be done:

1. The accumulation of such elements as Ag (5,3 times), As (9,4), Bi, Mo (2,2), Sn (2,7), W, Yb (in the gaps — the excess over the concentration in the Earth's crust, times) is caused by both natural soil formation processes and technogenic activity.

2. The abundances of B, Ba, Ca, Cl, Hg, Li, P, Pb, Sr, Zn in urban soils have occurred firstly because oà the technogenic impact. Their abundances in urban soils exceed the abundances in the Earth's crust and in the Earth's soils.

3. Soils of each determined groups differ by the association of elements in increased and decreased concentrations.

4. Several cities in these groups distinguish themselves by the critically increased concentrations of the number of elements. The developed industries in these cities could be a reason for this sufficiently rare appearance.

5. The increased concentrations of chemical elements are able to save for decades in urban soils even after the removal of the general sources of pollution input to the soils.

6. The established abundances of chemical elements in urban soils reflect the geochemical (ecological-geochemical) characteristics of the joint impact of natural and technogenic processes in our-days' time period. With the development of science and technology the abundances may gradually change. The rate of these changes is still poorly predictable. The authors hope that the abundances of chemical elements presented for the first time may and will be used during various ecological and geochemical studies.

MIGRATION MODELS OF CU, ZN, CD IN SOILS UNDER IRRIGATION WITH URBAN WASTEWATER

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The wastewater is that released from municipal and industrial production. The urban wastewater containing a great amount of heavy metals (HM) like Cd, Cu, Fe, Mn, Ni, Pb, Zn is utilized for irrigation and fertilization of agricultural fields and may lead to a continuous HM accumulation in soils. It is considered that the heavy metals are accumulated only in the topsoil, however, the irrigated wastewater used for a long period of time contributes to soil contamination at a depth.

The information on mathematical models to show the HM migration in soils is rather scanty in literature. Probably, predominant is the idea that HM being accumulated in topsoil don't migrate downwards the soil or the HM migration is not significant for evaluating the soil contamination. However, it is worth emphasizing that this migration constitutes a risk to contamination of the environment and groundwater and for this reason dynamic mathematical models are an important aspect in scientific research.

The present study is aimed at estimating adequate application of migration models for the HM transport downwards the soil profile in the case of irrigation with natural and urban waste- water for a long period of time. The heavy metals of interest in this study are Cu, Zn and Cd.

The field experiments have been carried out in Egypt (Goma Botkhina Saad near Alexandria). Two test areas were located on alluvial soils of lacustrine origin (light-textured sandy loams). One of them was irrigated with river water for more than 40 years. The other test area was irrigated with mechanically and biologically treated wastewater during 20 years. The other two test areas were located in an oasis of Libyan Desert, being covered by the loam sandy yellow-brown desert soil and irrigated with groundwater during 30–40 years and wastewater for 20 years.

Soil samples were taken from horizons and layers. For modeling the data about all the studied soil layers to the depth of 150cm found an application. The investigation were realise during 3 years. The total HM content in soil was determined by the half-quantitative method of spectral analysis.

To simplify the procedure, we assumed that the parameters of migration models including the initial HM content are invariable both in soil profiles and in the period of long-term irrigation. The diffusional model is a constant substance flow at the surface of the half-continuous medium (in the given case — at the soil surface) and the substance input to soil occurs during the irrigation season of every year. The convective-diffusional model is a mass exchange of the substance at the surface of the half-continuous medium.

Having subtracted the initial HM content, the interval of values for the total HM content was calculated as equaled to ± 10 % from the initial one with account of a possible measurement error. Different combinations of model parameters were used to calculate the HM content at a soil depth for the given period of irrigation. The values of parameters seemed applicable if they were within the above 10 % interval for all the soil layers. Such an approach allowed evaluating the interval of values for every parameter. When comparing the data about the HM input to soil together with irrigation water during the whole irrigation period, the HM accumulation in soil determine experimental and calculated by using the values of model parameters it seemed reasonable to arrive at conclusion about adequate utilization of mathematical models.

THE PROBLEMS OF THE ECOLOGICAL GEOCHEMISTRY OF THE BIG SITIES GEOECOSYSTEMS

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Ecological geochemistry is the most actual field of studies within the Earth sciences because it is connected not only with human life but with life on the Earth in common. Biosphere is not the «environment» for living beings but the system of geochemical and geophysical bio-inert interactions where are presented grandiose processes of chemical and energy exchange on the boundary between different types of a matter: life and «inert existence» may change all of them quite much. That is why traditional for the western science literature term “environmental geochemistry” is not always enough correct.

Ecological geochemistry — direction in the field of geochemical knowledge, exploring the relationship between living and inert matter at the level of the chemical elements as a form of organization of matter.

Natural regional factors associated with confinement of the city to the major regional geological structures and regional geochemical fields, as well as to specific climatic and landscape zones, in particular, natural regional factor for St. Petersburg is its confinement in the boundary between the rocks of the East European Platform and the Baltic crystalline shield. This is reflected in the structure of the Gulf of Finland, the difference between the nature of the erosion of the northern and southern shores, the composition of its sediments, as well as on the difference hydrogeological, paleolandscape conditions between the north and south of the city.

Manmade regional factors caused primarily distant air and water transport of matter and hit the city in areas of its distribution. This is most clearly manifested in the content of radionuclides in soil and water towns, “covered with” fallout after the Chernobyl accident.

Local environmental factors determined manifestation of local hydro, wind, landscape and paleolandscape, geological and geochemical conditions. In particular, the position of the horizon in the Ordovician shales Dictyonema limits of St. Petersburg defines a zone of high radon hazard in its southern regions. Location of buried valleys determines geotechnical risks, such as subway construction. A dominant air circulation system leaves its mark on the distribution of deposition of pollutants in different districts.

Local manmade factors — the most complex and difficult to analyze the factors in the study group geoecosystem big cities. They represent a set of constantly changing sources of harmful substances into the air and the urban drainage system.

Identification of specific factors in the formation of geochemical fields and anomalies are a major problem of ecological geochemistry of cities.

Particular risk from the standpoint of environmental geochemistry allocated dump household and industrial waste. Ecologically safe disposal of such dumps in Russian cities is practically not produced, by subjecting the population of cities to real geoecological risks.

GEOCHEMICAL ELEMENTS IN DEVELOPMENT OF NATURAL BIO-INERT SYSTEMS

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The source of chemical elements for the being developed bio-inert systems is the mineral base in the main. In particular, this concerns the systems localized on land where only fresh water from meteorological precipitation, more often nearly distilled, is present.

We studied the bio-inert systems of the sulfide curative mud, localized in the high and low tide zones of river mouths, and the systems formed by lichens on the dumps of ore deposits in mountains. It was established that in any case the first biostarting autotrophic microorganisms assimilate Fe and S. Contamination with other elements — Mg, Al, Si, Cl, Ca, Na, K — depends on a kind of biota and underlying minerals. On the other hand, organisms influence the mineral base contaminating it with ferments and mucus that is demonstrated by the bioorganic elements appeared in the mineral analyses. Heavy metals (W, As, Zr, Ag, Ir) are not used by the growing organism, they are toxic for it, so scheelite, silver, and some sulfides remain intact even through the processing them with ferments.

The assimilated elements perform their role and then are excreted by the system in the form of biominerals. A part of them form the organism integuments: diatom valves, mollusk shells, and so on. Others are separated as aggregates of some mineral forms: pyrite framboids, rounded segregations of sulfides and iron oxides. These unusual for crystals forms are present also in the sulfide curative mud and inside the lichens bodies and are, most likely, the results of the vital functions of sulfate-reducing bacteria, which appear in the system later as the autotrophic microorganisms accumulate the organics.

The bio-inert systems are the natural mechanism of the redistribution of chemical elements between the inert and alive matter in the biosphere.

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TRACE ELEMENT COMPOSITION OF WOODY VEGETATION IN MONGOLIAN CITIES

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The study aims to evaluate the changes of trace element (TE) content in urban vegetation associated with emissions of industry, heating power complex, traffic and mining of non-ferrous metals. For environmental and geochemical assessment of woody species about 160 samples of poplar leaves and 44 samples of larch needles were collected in Mongolian cities and their suburbs during 2010–2013. The concentrations of Mn, Fe and 20 the most dangerous TEs in the samples were measured using ICP method and compared with the background values to display the anthropogenic disturbance of chemical composition of Populus laurifolia and Larix sibirica. The study areas included two large multi-industrial cities (Ulaanbaatar and Darkhan) and a city with mining and processing copper and molybdenum ore (Erdenet) .

To identify regional geochemical features of background plants their TE composition was compared with the TE concentrations in annual world biomass gain (Dobrovol'sky, 1998). For urban plants growing in different land-use zones enrichment factors (EFs) relative to background values were calculated. Ecological state of trees was diagnosed via ratios Fe/Mn and Pb/Mn. Changes of TE contents in leaves and needles due to the air and soil pollution were assessed using the coefficient of biogeochemical transformation Zv, which reflected the disruption of normal ratio between TEs in plant organs (Kosheleva et al., 2012) .

In Darkhan city poplar leaves accumulated Zn, As, Cd, Sb, Pb, Cu (EF 5.4–1.3) and dissipated Co and Mo. Concentrations of the first association were the highest in the industrial zone (EF 7.6–2). Residential areas were distinguished by Zn, As, Sb, and Cd bioaccumulation, traffic zone — by Zn, recreation area adjacent to roads — by Cd. The ratio of Fe/Mn in the leaves of poplar in urban environment changed significantly, indicating the photosynthesis disturbance, especially in the industrial and transport zones. The ratio Pb/Mn = 0,012 was 3 times higher than the background one, and for the industrial zone this factor was 6.

Within Erdenet city area Cd-W-Ti-U-As-V-Pb-Br-Ga-Zr appeared to be the elements of a strong accumulation in larch needles (EF > 2.0), whereas Ba-Mn-Sr-Cr-Sn were elements of a strong biodispersion (EF < 0.5). In industrial areas the greatest anthropogenic delivery of As, Mo, Cu, Br, Se, Mn (EF 5.1–1.6) was detected, in ger areas — Cd, Pb, Co, Zn, V (EF 9.2–1.8). In multistoried building areas the biodispersion of Mn, Ni, Cd, Mo, Co was observed.

Most of the areas were characterized by the Zv values of 10–20 or less, i.e. referred to the group with the minimum degree of transformation or close to the background. According to Zv values changes in the TE composition of larch needles were almost 2 times more significant than of poplar leaves. Populus laurifolia proved to be tolerant to anthropogenic impact. In contrast, Larix sibirica appeared to be a good indicator of the contamination caused by industrial and traffic emissions.

MOLECULAR-MASS COMPOSITION OF URBAN SOILS FULVIC ACIDS

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The humus factor has a great impact on soil formation under the urban environment conditions. The certain information volume dealing with the urban soil humus content and composition has been received by the present time. The humane acid properties are known to be the most important humus constituents. However they have been studied insufficiently.

The object of our research are various cenosis soils within the North and North-western Moscow districts. The fulvic acids were segregated by Ponomareva's technique from the acid solution. The latter remains after the deposition of humane acids. Sefadeks by G-50 was applied in this ammonium concentration put on to the column constituted 10 mg/ml. The distilled water served as a solvent.

The forestry experimental farm cenosis is changed only a little. This farm is located within the city limits. According to the data obtained the sod-podzolic soil fulvic acids consist of 3 fraction having e" 23 400, 14 000 and 8910 atomic mass units (a.m.u.) molecular mass. Their relative content is 5,2; 86,0 and 8,8 % respectively. The average weight fulvic acid molecular mass constituted 14500 a.m.u. The Urban Timiryazev Street fulvicacigs are subdivided into 3 fractions. The molecular mass fractions are equal to ðàâíû e" 23 400 (6,5 %), 12 300 (71,1 %) and 7350 (14,4 %) a.m.u. The average weight molecular mass is 13 250 a.m.u.

Petrovsky Park, KoptevskyBoulvard and between-the-house area urban soil fulvic acids contain 4 fractions. Their molecular masses are within the certain limits: fraction 1 — e" 23 400 (12,7–14,2 %), fraction 2–13 120–16 980 (21,9–42,4 %), fraction 3–11 530–13 120 (16,7–52,9 %), fraction 4–6050–10 810 (3,7–43,3 %). The average molecular mass is 16100 and 1470 a.m.u.

The 2nd Sandy Street square urban soil fulvic acids comprise 5 fraction that have the following molecular masses: e" 23 400 (23,5 %), 18 100 (13,6 %), 13 120 (44,5 %), 8910 (2,6 %) and 6890 (15,8 %) a.m.u. The average molecular mass is 17170 a.m.u.

We are comparing two kinds of urban soils: urban forest so-podzolic and ordinary urban ones. The human influence predominates over the natural soil formation in the latter. There are the following processes in it. The molecular mass and relative content of some particular change.The fucvic acid dispersion degree and their molecular mass increase.

RARE EARTH ELEMENTS IN QUARTERNARY DEPOSITS — THE MAIN PARENT SOIL-FORMING MATERIALS OF NORTH-WEST RUSSIA

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Properties and chemical composition on the deposits of the North-West Russia and soils they form are fairly well investigated (1); however the data on the content of rare earth elements (REE) are extremely scarce with little research done on their role in soil formation and the production process of plants. This is mostly due to the technical complexity of determining content of REE.

The study presents the results of investigation of REE content in soil-forming parent materials of the North-West of Russia (including the South Karelia) that differ in genesis specifically in moraine loams (both carbonate and non-carbonate), varved clays, lacustrine-glacial sands and sandy loams, fluvioglacial and alluvial sands.The REE (including yttrium) were determined by ICP-MS on the extract of HF.

Lower limit of detection was: for Nd- 25 mg/kg, Ce, Er-0,15 mg/kg, La, Yb-0,1 mg/kg, Tb, Pr, Eu- 0,05 mg/kg, Y-0,01 mg/kg.Compared with the REE composition reported for sedimentary cover of Russian plate (2) concentration of all elements was found to be somewhat lowered with only Ce concentration to be o the same magnitude. The quantitative content in deposits determined the following order of the elements: Ce > La > Nd > Y > Pr > Sm > G g > Dy, Er > Yb > Eu >Tb | Ho > Tm | Lu. Among the parent soil-forming materials varved clays was characterized by a maximum concentration of all the REE, which is due to formation of clays in the deep glacial lakes enriched fine-dispersed materials. The lowest the REE concentrations were in alluvial deposits. Moraine loams had the REE content in-between these two extremes.

Regional backgrounds of the REE concentrations in deposits were found to be for Ce-, 43,8, La-20,8, Nd-19,5, Y-15,2, Dy-2,7, Er-1,5, Gd-3,4, Pr-5,2, Sm-5,7, Yb-1,4, Eu-0,7 mg/kg. The REE concentration above the regional background in varved clays and moraine loams and below the background in all other type of deposits is a distinct characteristic of the REE distribution.

Comparison of the REE content in parent soil –forming materials of different soil — geographic districts of the North-West (1) showed that clays Lovatskaya-Volkov district had the highest the REE contents and interselga depressions Baltic –Ladoga region had lowest. Among non-carbonate moraines of Chudskoy and Luzhsky-Shelonsky districts are distinct in their elevated the REE content. Based on the Ree content, carbonate moraines follow a series districts (in descending order) Luzhsky > Chudskoy > Predvaldaysky > Pskovsky > Izhorsky. In glaciofluvial sands the highest the REE contents was observed in Velikye tårminal moraine district and the lowest — in Lovatskaya- Volkhov and Velikoretskaya districts of glaciolacustrine plains. Lake-glacial sands were generally poor in the REE. Overall the REE content depended on the amount of clay (<0,01 mm) and fine silty and clay particles in deposits especially when comparing deposits of the same origin. Deposits of the North- Eastern part of the region located within the moraine and glaciofluvial plains were found to be poorer in the REE than deposits of the South-Western hilly terrain — elevated part.

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THE ROLE OF BIOINORGANIC INTERACTIONS IN BIOTIC PURIFICATION OF WATER ENVIRONMENT

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Elimination of pollution in various water environments of the Earth's hydrosphere is one of the most pressing problems. We have developed the system of control and regulation of processes of biological wastewater treatment and self-purification of natural water (biotic purification of the water environment) — bioestimation [1, 2] .

The principal novelty of bioestimation lies in the fact that it pays special attention not to the discrete component of the water environment, transformation of quality, but the continuous process of water quality formation.

Long-term observations have shown that biotic purification of water environment is primarily carried out in the process of vital activity of organotrophic bacteria which are considered to be the major decomposers of contaminations. Three critical groups of factors were found to govern continuously the activity of these bacteria: I — dynamic characteristics (flowage, macroturbulence, microturbulence); II — the load (the impact of readily oxidizable substances and difficult oxidizable substances); III — industrial waste (the impact of sugars, toxicants, alcohols, and lipoids). Indicator microorganisms — bioestimators — have been selected for each of these nine factors. The population size of such bioestimators can be used to identify the changes in the vital activity of the major decomposers. The second major distinction of bioestimation: the purpose of bioestimation is not only to establish the impact of the specific disturbing factor based on the results of the process monitoring, but also to instantly develop rehabilitation recommendations which are an integral part of bioestimation. At that each factor is identified and eliminated irrespective of other factors as bioestimators are biotically independent. This has been proved by means of multivariate statistical analysis which also made it possible to establish threshold abundance values for the bioestimators. In each specific case the presence of such bioestimators in amounts exceeding the respective threshold indicates the need for rehabilitative intervention in a water environment. The third aspect distinguishing bioestimation from other methods of biological control is its universal nature. As bioestimators are not species but groups of organotrophic microorganisms showing similar environmental preferences, they can inhabit any water environments, i.e. various hydrosphere objects, whether fresh or saline, natural or artificial, and also soil moisture and tissue fluids of plants [3].

The experience in the wide use of bioestimation revealed that insufficient importance is still taken of the group of dynamic factors governing of the water environment on the vital activity of the main decomposers pollution. This aspect is a bright example of bioinorganic interaction.

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GEOCHEMISTRY OF SOIL NANOPARTICLES

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One of fundamental problems of soil science is studying of natural mechanisms of metals behavior in a pedosphere that has both scientific, and applied value. Thus the most important part is assigned to mobile migratory and capable forms of chemical elements.

It has been shown that soil colloids play an important role in existence and functioning of the soil and participate in migration of chemical elements. Colloidal particles (the size less than 1000 nanometers) play an important role not only by elements transport on a soil profile; they can react with a mineral matrix and control availability of chemical elements (Cances, 2003; Shein, 2007; Wilson, 2008) .

The fact of interaction of organo-mineral colloids with soils microparticles was noted in the middle of the last century, but only at the present time became possible to reveal fractal structure of organo-mineral soil gels to create colloidal and chemical model of the soil (Fedotov, 2009) .

There are some methods for allocation of soil colloids: centrifugation methods, expression and replacement were used; for selective extraction of any components of a soil — a leaching method. However addition of chemical reagents for extraction can lead to emergence of artifacts, there is a lot of reasons for which emergence.

Modern analytical equipment and methods of direct visual supervision nano-objects allowed to distinguish particles up to 0,25 nanometers in size. However definition of a chemical composition of nanoparticles causes certain difficulties. When carrying out electron probe researches because of their ultra small size of particles the probe with a diameter of 1 mkμ burns them through that doesn't allow to estimate their chemical composition separately from a matrix. Thus limits of detection of chemical elements are at the level of 0,01 % that a priori excludes from the analysis sphere the majority of microcells. It is necessary to consider also that the local structure of separate particles of test doesn't reflect geochemical specifics of a sample.

The colloidal fraction (nanofraction) with a particles size less than 1000 nm is taken by water from a soil by water under specially picked up conditions. The nanofraction represents part of test in which chemical elements are in ionic, molecular and colloidal forms, and concluded in soil inter-grain space — water colloidal and salt solution. Thus, the more steam space of a sample, the higher in it a nanofraction share (to the 6th weight.%). Soils and its nanofraction are analyzed by the ICP MS method.

The analysis of nanofractions allows to lower a detection limit for rare and scattered elements and considerably to expand a circle of defined elements, and also to receive reliable information at ultralow levels of their concentration. It creates opportunity significantly to increase informational content of soil and geochemical researches.

Comparison of geochemical features of the soil as a whole and its nanofractions allows to estimate a share of the chemical elements which are in the fixed and mobile forms. It is very important for creation of model of metals colloidal transport in a soil.

TRACE ELEMENTS MOBILITY AND MICROBIOTA ACTIVITY IN TAILINGS DAM (AFTER SULFIDE-TUNGSTEN ORES DRESSING) AND ADJACENT SOILS

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The studies were conducted within tailings dum of Dzhida tungsten-molibdenum plant that was closured in 1997. Composition of tailings sands show processing ores content: sulfides, sulfosalts of iron, lead, zinc, copper, bismuth, molybdenum, as well fuhlore, wolframites, calcium tungstate. Soils of adjacent territory including those inhabitants use for vegetable-growing, also have been studied. Investigation complex included BCR sequential extraction procedure was used to examine trace elements forms of presence (Rauret et al., 1999). The mobile forms of trace elements in tailings and soils were defined by using acetate ammonium buffer. Study of microbiota activity had been carried out by field experiments with using “cotton strip assay” method (Metodi, 1991) .

It was determined that during three years in the top layer of tailings dam the average content of all studied metals had been decreased while the maintenance of the mobile forms of copper, lead and zinc had been increased. BCR fractions proportion in tailings also had been changed: exchangeable and weak acid soluble fraction had been increased for all metals; reducible fraction (carbonate form) had been decreased for copper and zinc; oxidisable fraction had been increased for copper. Mobile form content in tailings is higher than in soils.

By results of tailings samples microbiological analysis were separated chemolithotrophic bacteria *Acidithiobacillus* sp. This microorganism use in response energy sources sulfide minerals, elementary sulfur, its reduction forms. Concentration of culture microorganisms enriches 10^{4-5} cell/ml, this may evidence about theirs considerable contribution in processes of metal sulfides transformation. By microbiological analysis in tailing samples bacteria — sp. *Pseudomonas, Bacillus, Micrococcus, Flavobacterium,* yest *(Rhodotorula),* actinomyces, microscopic funguses (*Penicillium, Aspergillus, Trichoderma, Mucor, Cladosporium*) also are revealed. This heterotrophs may make a contribution in chemical elements migration at complicated landscape-climatic conditions as leaching agents.

Field experiments for study cellulosolytic and proteolytic microbiota activity showed that proteolytic activity in stale tailings is higher than in soils adjacent territories. This is one of evidences that microorganism activity may be factor causes higher metal mobility in tailings in comparison to soils. Microbiota activity in soils of urban territories directly depends on contamination level. It was noted oppression of cellulosolytic and proteolytic activity in soils with maximum contamination level.

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Section 5

The role of living organisms in the destruction of cultural heritage

IMPACT OF MICROORGANISMS ON THE MONUMENTS IN THE SUBTERRANEAN ARCHAELOGY MUSEUM IN MOSCOW

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Today the understanding of the necessity of preservation of the cultural heritage develops all over the world. The most difficult task is to preserve the archaeological monuments in the place where they were found (in situ). The issue of operation of the subterranean archaeology museums is poorly explored and complicated.

The first subterranean museum in Russia was built in Moscow on the territory of the museum “Palaty boyar Romanovykh” (Romavov Palace Chambers) on the archeological excavation site. Its exhibition includes the own archeological remains obtained during the two digs in 1983–85 and 2005 and provides a glimpse of Moscow and Zaryadye of the 12–16th centuries.

The pieces made by blacksmiths, potters, bone-carvers, jewelers representing the handicraft trading quarter indicate that this part of Moscow was occupied as early as during the pre-Mongolian period. The monuments of the 15th century speak for the trading quarter turning into the aristocratic district and appearance of the luxurious town mansions: the chalkstone that decorated the house front and fragments of the chalkstone sarcophagus. The key piece of the exhibition is the ruined cook stove of the Romanov Boyars (16th century). Another unique item is the “window in the past” through which one can see the preserved in situ soil profile of the cultural layer of the 16–17th centuries with a great number of interesting inclusions (bones, pottery, structural stone, etc.).

Regular observations over the museum operation and maintenance during the years 1990–2005 showed the optimum alternative of the exhibits preservation at the annual average humidity not exceeding 60 % and the temperature 10 °C that was affected after the second excavation carried out in 2005 inside of the underground facility and during preparation for the new exhibition.

Rapid changes of temperature (up to 27 °C) and humidity (up to 100 %) and further burst of the microbial contamination of the items resulted in the complete buckling of the ruined brick house cook stove of the 16th century with the exposed earth foundation that has been exhibited in the museum since 1990. Therefore, its chemical preservation in situ was carried out without delay in 2007.

Within the subsequent nine years the countermeasures against increasing humidity and microbiota (fungi and bacteria) of the air in the museum were taken continuously. However, the burst of the microbial contamination of the indoor air in the November 2012 reached the high and extremely high level as compared to the previous observations. This resulted in the destructive action on the museumfied item “window into the past” causing sloughing of the soil and inclusions. Such catastrophic condition in the museum required the urgent efficient disinfection of the entire premises. This could be performed only with the use of the special ultraviolet bactericidal (sterilizing) irradiator. The aero-microbiological analysis conducted in 2013 and 2014 showed that the rate of the microbial contamination in the indoor air significantly decreased to the indicators complying with the permissible level.

The works performed on disinfection of the underground facility made it possible to create the safe conditions for preservation of the archeological items and arranging excursions to the museum.

BIOPHYSICAL AND BIOCHEMICAL DESTRUCTION OF MARBLE IN THE NECROPOLISES OF THE STATE MUSEUM OF URBAN SCULPTURE IN SAINT-PETERSBURG

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There are two ways of natural stones distraction: physical and chemical. Living organisms such as fungi, algae and lichens participate in the destruction of the stone. Physical action on the rock monument is connected with biofilm formation and mechanical penetration, followed by the growth in the rock. Biochemical effects are the production of organic acids and metabolic products, which lead to flaking and coloring material.

The study addresses the problem of preservation of stone monuments in St. Petersburg. One aspect of this problem is to protect the stone material from biofouling with participation of micromycetes. The study examines the processes related to the activity of fungi on the surface of stone, and also evaluated possible causes intense destruction of natural stone in the urban environment. Objective of these study: description of species diversity and the destructive role of micromycetes on the Carrara marble monuments in Necropolis of Alexander Nevsky Monastery.

As result 54 species of micromycetes were isolated from the surface of the marble. Half of them belong to the dark-colored anamorphic fungi. Fungi belonging to Ascomycota and Zygomycota were identified. After comparing the data with data from previous years we can talk about the existence of a group of dominant species micromycetes which can destroy marble sculptures. *Alternaria alternata, Aureobasidium pullulans, Cladosporium cladosporioides, Hormonema dematioides* were more typical species for Necropolis of Alexander Nevsky Monastery. They can form gray-black biofilms on the marble surface. It was observed that the fungal defeat most often connected with the accumulation of dirt, dust and moisture. Fungal structures can penetrate into all possible holes and cracks. Micromycetes can develop between the crystals as well as penetrate into the micro- and macrocracks. It was noted that the fungal structures present in black crust at all stages of enrichment gypsum patina formation. But the role of fungi in this process is still not clear.

It was shown the main source of stone fungal defeat is the soil. A lot of micromycetes are typical representatives of the soil microbiota. Trees are also the source of infection. Natural exudates of trees get to the surface of the stone and serve the source of nutrition for fungal community. Most contaminated areas with black-colored biofilms on the marble monument surface were situated from near the plant and soil. The intensity of chemical and biochemical damage depends on the humidity of the air, and also on the species composition and microbial population density. Dissolution of carbonate rocks may occur as a result of several processes, one of which dissolution of $CaCO_3$ by organic acids.

The laboratory experiments on artificial inoculation of Carrara marble by micromycetes *Alternaria alternata* and *Penicillium brevicompactum* were made. As result it was shown the formation of grey-black biofilm consisting of hyphae, conidiophores and conidia. Also it was noted the formation of calcium oxalate crystals on the surface of the marble under the influence of *Penicillium brevicomapctum*.

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PROTECTING PETROGLYPHS IN KARELIA AGAINST BIODESTRUCTION: NEW FINDINGS

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Acid rocks, such as granites and gneiss-granites prevail in Karelia. Their outcrops are suitable habitats for lichens. Rock outcrops have formed many lakeshores and riverbanks. Granite rock outcrops on the eastern shore of Lake Onega bear the monuments of ancient rock art — petroglyphs, which are part of the world cultural heritage. Like any other rock substrate they are altered by changes in ambient conditions and under the impact of the biota (Fadeeva, 1996; Sonina and Fadeeva, 1998, 1999; Sonina, 2000; Fadeeva and Sonina, 2000, 2001a, b, 2007; Sonina et al., 2008).

The different habitation conditions (rock substrate moisture and structure, primary soil patches with plants) generate a rich variety of lichen microhabitats. The very surface of rock carvings provides additional opportunities for colonization by lichens. A limiting factor for the development and growth of lichens is the waterbody’s hydrological mode, which controls the selection of the colonizing species and further formation of lichen assemblages. Quite extensive rock portions (zones) differing in the substrate and lichen cover characteristics, as well as in the degree of petroglyph destruction by lichens can be distinguished on the rocks at different distances from the water edge (Fadeeva, 1996). Lichens of the crustose, foliose and fruticose life forms (biomorphs) successively contribute to the process of substrate (petroglyphs) transformation. Species with a crustose thallus are most closely attached to the substrate, and alter it the most as they live. In some zones they may be massively abundant. This combination turns them into the dominant petroglyph biodestruction agent. Foliose and fluticose lichens are less closely attached to the substrate, produce less impact on the petroglyph substrate and, hence, pose less risk to the rock carvings. The practical implication is that any 'ecological catastrophe', even of a local scope, be it the consequences of growing uncontrolled recreation (fires) or willful manipulations with petroglyphs themselves (such as lichen removal from the surface by abrasive materials or harsh chemicals), will result in a rapid colonization of the thus 'prepared' petroglyph substrate by the most aggressive biomorphs.

Apparently, the protection measures to be chosen depend on the impact zone in which the petroglyph falls. The option that seems to be most effective in fighting lichens and least damaging for the substrate in zone 2 (medium damage), where most rock carvings are located, is to treat petroglyph surfaces with ethanol or industrial methylated spirits (tested by N. Lobanova's team at Lake Onega petroglyphs in 2008). In zones 3 and 4 (heavy and dramatic damage), where petroglyphs are few and visually indiscernible, treatment can be applied only to the regularly demonstrated images and groups. The carvings rarely used for demonstration purposes should rather be left as they are, since their clean-up may lead to undesired consequences. For instance, a substantial contribution to the lichen cover in zones 3 and 4 is made by *Umbilicaria deusta*. This umbilicate foliose lichen is attached to the substrate by a hyphal strand — gomphus, i.e. the area of impact on the substrate is minimal. Being at the same time rather aggressive towards other species, e.g. towards crustose lichens, this species will easily outgrow them, and then inhibit their further growth and development. If *Umbilicaria deusta* are removed from the rock, which is indeed one of the practices, the cleared surface will eventually be occupied by crustose species, which cause a heavier and more extensive damage to the carvings.

Assessment of protection measures of petroglyphs against biodestruction was carried in 2013 with the support of R&D project of Ministry of Economical development of the Republic of Karelia.

MOULD FUNGI ON MINERAL MATERIALS OF HISTORICAL BUILDINGS

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Microscopic (mould) fungi can grow on mineral-based surfaces causing significant negative effect despite their demand for organic compounds as sources of carbon and energy. Mould fungi attack materials located not only indoors but also outside of building. Mineral building materials situated in the open air are liable to become covered with dust and infiltrated with rain- and groundwater which results in their being saturated with considerable amounts of organic substance sufficient for the development of heterotrophic microflora. Fungi utilizing available organic constituents can decompose mineral materials in a form of biological weathering.

The historical buildings in Belarus are in various state of repair: from romantic ruins to full modern restorations. One of the most famous places in Belarus is Nesvizh Palace. It was rebuilt and restored many times. In Soviet times palace was used as a Sanatorium. Since 2004 to 2012 restoration was carried out in the palace. In many places on plaster and fresco under later layers mould fungi colonies has been revealed. Some of them were seen by the naked eye due to dark pigmentation or discoloration, the others were similar to coat of dust. Unfortunately systematic mycological investigations during restoration were not performed. *Cladosporium* and *Penicillium* spp. were isolated from the dark spots on frescoes. *Penicillium* strains were able to produce significant quantity of oxalic acid. In addition to those fungi from showered plaster *Verticillium* sp. was isolated.

In the crypt of Nesvizh Farny Cathedral that was used as a burial vault from 17 century on marble gravestones mould fungi belonged to genera *Aspergillus* were abundant. On wet crumbling sections of vault walls *Stachybotrys chartarum* was dominant. These fungi are known as active destroyers of building materials due to ability to synthesize acidic metabolites and may be dangerous for human health. Many species of

Aspergillus produce mycotoxins (*aflatoxins, ochratoxins*, and so on) — toxic compounds which can be produced at all times, or only under specific conditions. The inhaled mycotoxins are approximately 40 times more toxic than those which penetrate through the digestive tract. Mycotoxin excreted by *S.chartarum* referred to as stachybotryotoxicosis causes serious symptoms and health problems such as mental and neurological impairment, breathing problems, damage to internal organs etc.

The most widely used paints up until the 20th century was lime wash. Typically it has white colour. But the natural earth pigments were also used on occasion to give these paints attractive colours. These coatings offered a good protection for buildings but required regular maintenance. Biodamage of wet exterior walls covered with mineral paint usually is caused by microscopic alga, mould fungi — much rarer. However, there are cases when fungi colonize modern mineral paint composition extensively. For example, the external walls of Kossovo palace during restoration works became covered with black and pink spots formed by colonies of genera *Alternaria* and *Fusarium.*

In order to investigate the process of colonization of mineral materials by isolated fungi in different conditions of humidity and temperature Convey Diffusion Cells were used. They consists of a shallow circular glass vessel, 40–70 mm in diameter, containing a central well and with a closely fitting lid sealed with grease permitting to save the specified conditions inside.

ANALYSIS OF MICROBIAL COMMUNITIES BY USING HIGH-THROUGHPUT SEQUENCING — A NEW APPROACH APPLIED TO STUDIES OF CONSERVATION STATE MONUMENTS

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Stone monuments (statues, fountains, memorials, buildings, etc.) are apparently indestructible artefacts that were built to last. Depending on the chemical composition and structure, stones may be friendly or hostile to colonization by eukaryotic and/or prokaryotic communities. Biological activity of living colonizers may intensify the weathering processes of stone monuments. This is because cultural artifacts provide a range of elements (calcium, aluminum, silicon, iron and potassium) which are necessary for microbial metabolism. Microbial solubilization of rock material is the leading biochemical mechanism of mineral decay and includes the production of acids and alkalines as well as biosorption and chelating (complex-formation). Moreover, human activity could enhance the bioerosion by providing more nutrients to epilithic and endolithic microbial communities.

Next generation sequencing (NGS-sequencing) is a novel molecular technique providing a quick and comprehensive analysis of microbial community, including microorganisms which are not considered by classical microbiological techniques. Pyrosequencing allows the identification of a large number of microorganisms, confirming some already identified by the cultivation-dependent methods such as fungi of the genera *Penicillium, Aspergillus* and *Cladosporium*, but also provides a great contribution to the identification of not previously identified several genera and species, giving also a detailed overview of contaminants which was not possible with the other approaches. Chemoheterotrophic *Actinobacteria* and *Gammaproteobacteria* are dominant bacterial phyla found in biofilm as well as in endolithic niches of stone samples. To date, there is little information on endolithic archaea and chemolithoautotrophic bacteria. The results obtained on several samples of plaster, ceramic decor element as well as wooden board show a strong relationship between the most deteriorated areas of the architectural elements and higher microbial contamination.

Application of molecular methods in the analysis of microbial communities colonizing the surface of the cultural heritage monuments allows the identification and quantification of individual species as well as the taxonomic groups of various levels, and, so, helps to grapple with different issues, including the restoration-construction expertise. The knowledge about the microbial communities present on monuments surface is of utmost importance to develop effective conservation and mitigation strategies.

DEVELOPMENT OF ROCK-INHABITING MICROFUNGI ON ARTIFICIAL (SYNTHETIC) MARBLE SCULPTURE IN THE SUMMER GARDEN (ST. PETERSBURG)

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Curators and restorers of collection from the Summer Garden has long raised concerns of condition of marble sculpture. This collection includes works of famous masters of the XVIII century, it had been exhibited on the open air for three centuries. As result the collection suffered greatly. Negative impact on the safety of monuments have physical and chemical weathering, numerous restoration intervention and acts of vandalism. Eventually marble sculpture lost polishing and destruction of the surface layer of stone began. This situation created favorable conditions for the development of active microorganisms.

During the reconstruction of the Summer Garden (2009–2011 years) all marble statues, busts, sculptural groups (exception — the sculptural group "Peace and Abundance ") and most of the marble pedestals were moved to the exhibition halls of Russian museum.

Replicas of monuments from artificial marble were installed in the Summer Garden. Artificial marble consist of marble chips and polyester resin. Contents of marble chips in the material reaches 80 %, which create similarity of artificial marble to the natural marble (to artificial marble likeness to the natural marble) they decorative qualities and mineral composition. Such material is less susceptible to weathering than natural marble, because it does not absorb moisture and dirt. It is known that microorganisms can degrade natural marble. Microfungi influence on artificial marble studied much less.

The aim of this work is comparison the dynamics of complexes microfungi on different stone materials (granite, artificial marble and natural marble) in local ecosystems of the Summer Garden. Since 2006 natural marble statues were investigated in the Summer Garden. Since 2012, copies of articles from artificial and natural marble and granite pedestals were investigated.

It is shown that artificial marble covered by microfungi despite the presence of toxic resins in its composition.

During the three spring-summer- autumn round study 39 microfungi species from 17 genera and 3 subdivisions were identified. Among which 15 typical rock-inhabiting species were observed on the surface of the statues and pedestals. More than 50% of the species have dark pigmented mycelium or spores.

Microfungi species composition varies at all rocky substrates. The greatest similarity observed between the artificial and natural marble, and the smallest between the artificial marble and granite. Similarity coefficient ranged from 0.37 to 0.51 (Sorensen coefficient) and from 0.22 to 0.34. (Jaccard's coefficients) Mycobiota have lower species diversity. The highest species diversity was recorded on natural marble (19 species). The smallest species diversity was recorded on granite (12 species). Artificial marble was intermediate (16 species).

Dynamics of microfungi on artificial marble surfaces were study. Increase of species diversity during the spring-summer season were noted. There were no change in the species of dominant complex.

Frequency of occurrence microfungi *Aureobasidium pullulans* increased during the summer period from 65% to 90%. Frequency of occurrence of *Cladosporium herbarum* consistently increased from 50% in spring to 70% in early autumn.

It is shown that in the early spring on the surface of artificial marble statues were not observed visual damage. At the same time (in late September) the initial stages of chemical and biological damage was visually recorded in late September.

MICROFUNGI IN SCREE AND PRELIMINARY SOIL OF COASTAL EAST ANTARCTICA

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Microbial communities are the basis of the Antarctic ecosystem. They represent biosphere habitat which can provide insight into microbial communities which utilize energy sources other than photosynthesis and in the same time live in very poor organic source environment. Fungal community and its role in scree and preliminary soil environment remains small known.

Microorganisms inhabit in scree substrates and primary soil in coastal areas of the mainland and the adjacent islands. Low temperatures are combined there with dry air and high insolation. In such cold deserts life is represented mainly by cryptoendolitic organisms including fungi.

The objectives of our work are: (1) the investigation of microfungi of East Antarctica, (2) the comparison of microfungi complexes from rock and primary soils, (3) a biological study of microorganisms, inhabiting on the surface of rock substrates and primary soils.

Mycological studies were conducted during Antarctic summer of 2012–2013 year (seasonal work of 58 Russian Antarctic Expedition) in the ecosystems of East Antarctica. Samples of rocks, primary soils and cyanobacterial mats were studied. Isolation of micromycetes in pure culture was performed by inoculation of culture medium by small fragments of the substrate as well as soil dilutions, washings from the substrate surface on the such media as Czapek-Dox, Czapek with soil extract, potato glucose agar, potato-carrot agar, Sabouraud agar, mineral medium with cellulose. Microcolonial fungi were collected by the method of selective isolation. Cultivation of microfungi was carried out at temperatures of 4–5° and 20–21 °C.

As result 34 species of fungi which belong to 18 genera from *Zygomycotina, Ascomycotina, Basidiomycotina, Deuteromycotina* were identified. More various fungal communities were revealed in the preliminary soil (28 species). Only 15 species of microfungi were detected in scree.

One of the main characteristics of primary soil mycobiota is the presence of sterile forms of microfungi: filamentous (light- and dark-colored) and yeast (dark-colored). The great number of sterile isolates was isolated from the surface of soil horizon. Microfungi were detected (from 1 to 5 species) in most of investigated samples.

The black-colored micromycetes with the different morphology were predominated on the rocks and minerals. Species of *Acremonium*, *Aureobasidium*, *Cladosporium*, *Phialophora*, *Ulocladium* and anamorphic

Coelomycetes were often found on the surface of the rock. The bulk of dark hyphae were concentrated in the surface layer and cracks under the crust of weathering. Fungi of the genus *Geomyces* were also recorded on rock substrates.

To better understand the mechanisms of microbiota formation on the rock substrates and primary soil habitats in Antarctica it is necessary to apply the ecosystem approach including the analysis of interactions between lower eukaryotes (fungi and algae) and prokaryotes.

THE LICHENS ON CARBONATE STONE SUBSTRATES IN ST. PETERSBURG, RUSSIA

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Monuments of historical and cultural heritage are one of the most valuable elements of the city environment, which has long history of development. Monument’s materials are exposed to weathering and biodestruction. Lichens are one of the most active agents of these processes. So far there were no special investigations of the lichens participating in biodestruction of monuments in Saint-Petersburg. The aim of this work is estimation of lichen diversity on stone carbonate substrates in city and study of relations between lichens and such substrates.

On the base of the published historical data and our published materials we estimated lichen diversity and frequency of occurrence of lichen species on stone carbonate substrates as far as particular substrate preferences of lichens from this group. Literature published from 1922 to 2014 was analyzed (including the author’s papers for the last nine years) .

Altogether 67 species are known from carbonate stone substrates in the limits of St. Petersburg. The most diverse genera are *Verrucaria* (13 species), *Physcia* (5) and *Lecanora* (4). We estimated frequency of occurrence for 54 lichen taxa (all *Verrucaria* species were mentioned as one taxon for identification difficulties, especially in the field). Each record on every substrate in each publication was considered (totally 525 records).

The most common taxa are *Verrucaria* spp. (88 records), *Candelariella aurella* (70), *Lecanora dispersa* (60), *Athallia holocarpa* (36), *Lecanora crenulata* (35), *Phaeophyscia orbicularis* (31) and *Xanthoria parietina* (29) .

There are four main types of carbonate stone substrates in St. Petersburg — limestone, carbonate tufa, marble (natural materials) and concrete (artificial material). All the most common lichen taxa inhabit more than one type of carbonate substrates. All these taxa occurred more than in 50% of cases on concrete. *Athallia holocarpa* and *Xanthoria parietina* prefer concrete more than in 80% of cases. 63% of taxa known from stone carbonate substrates in St. Petersburg occurred on concrete only and were not recorded from natural carbonate materials. Vise versa 9.3% of taxa (5 species) only inhabited natural carbonate materials and were not recorded from concrete. They are *Clauzadea monticola*, *Enchylium limosum*, *Lepraria incana*, *Scytinium lichenoides*, *S. subtile*.

The lichens of stone carbonate substrates insignificantly contribute to the lichen flora of St. Petersburg. Thirteen species inhabit only this type of the substrates what represent about 2% of lichen diversity of the city (about 570 species are known for St. Petersburg now). Most of these species have been recorded from concrete only.

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DETERIORATION OF SAINT — PETERSBURG STONE MONUMENTS CONNECTING WITH THE ACTIVITY OF MICROORGANISMS

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Biodeterioration of nature stone is a biosphere process, which proceeds considerably faster in urban areas (anthropogenic) medium than in nature one. The results of long-term monitoring of St. Petersburg monuments showed that stone deterioration processes of monuments often connect with the active of micro-organisms (bacteria, fungi, algae and lichens). The main way for the mechanical action of microorganisms on rocky substrate is based on their ability to penetrate into the structural space of surface stone layer which leads to fragmentation and loss elements of rock. Their development in the fine stone materials (pore radius 1–2 μm) is observed mainly under the surface stone flakes that give a microbial protection from sun exposure and high temperatures. As a result, stone flaking and exfoliation occur. Such forms of destruction are present on many stone monuments of St. Petersburg. Due to release into the external environment of aggressive organic and inorganic acids, organisms provide a chemical weathering of the stone (especially carbonate stone). Under the influence of acids, produced by bacteria, micromycetes, algae and lichens, dissolution of stone components is accelerated. Also the result of acid active can be bioleaching of particular chemical elements and secondary mineralization. All mentioned processes occur on monument in St. Petersburg. Dissolution of carbonate rock leads to such forms of weathering as microkarst and «bone tissue structure». Microkarst often appears on monuments made of Ruskeala marble, but «bone tissue structure» — on the monuments made of porous limestone, which was mined in the Pudost village not far from St. Petersburg. Secondary minerals as calcium oxalates (weddellite and *whewellite*) and gypsum are presented on the surface of carbonate monuments in St. Petersburg. Metasomatic crystallization of calcium oxalates is initiated by microorganisms which produce the oxalic acid. Transformation of calcite into the gypsum is related to presence of high level concentration of SO2 in the atmosphere of megalopolises. In this situation, microorganisms, mainly micromycetes and bacteria, accelerated the process of gypsum formation. Intensity of gypsum patina formation directly depends on the moisture availability. Hence, the most intensively formation of gypsum patina occurs on the surface of highly porous Pudost limestone and also on the monuments with complex surface relief (often made of Carrara marble) .

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COLONIZATION OF MUSEUM CERAMICS BY MICROSCOPIC FUNGI

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Microscopic fungi play a considerable role in the deterioration of cultural heritage. Due to their enormous metabolic activity and ability to grow at low water activity values fungi are able to inhabit and decay different types of organic and mineral materials used for historical art objects. Mould contamination of ceramics most often is found in exhibition rooms and museum depots with disturbed temperature and humidity regime. Dirt, soot, and other contaminants, accumulating on ceramic surfaces, may represent significant source of nutrients for fungi and accelerate fungal colonization.

Numerous mycological inspections of Belarusian State Museum of Folk Architecture and Rural Lifestyle revealed seasonal mould damages of museum ceramic objects, caused by abrupt changes of temperature and formation of moisture condensation on the surface of objects. Due to this fact in a given period the mould damage of porous ceramics was much less significant than of glazed one. Inside the ceramic tableware also formation of stagnant zones of air was observed, which explains more intense colonization of inner surfaces of the objects. On ceramic objects in heated indoor depositories throughout the year the genus *Aspergillus* dominated, in exposure rooms — the genus *Penicillium*, except for the summer months when the part of *Aspergillus* increased.

At the same time, serious undesirable changes in properties of ceramics can be caused by so-called “salting out effect”, induced by chemical and biological influences. Evaluation of damaging effect of fungi of the genera *Aspergillus* and *Penicillium* has shown that in wet chamber the surface of ceramic samples was covered with white bloom, where with the help of X-ray analysis revealed a high content of silica, silicates and aluminates of calcium, which was not observed in control. Among *Aspergillus* species *A. ustus, A.niger, A.versicolor* and *A.cervinus* were the most active inductors of “salting out effect” on ceramics.

More often mycobiota of bioaffected ceramics is represented only by several aggressive species. Nevertheless, in many cases after restoration and conservation works, mould fungi community on ceramic surfaces becomes more rich and diverse. Basically, it may be associated with biocide treatment of ceramic objects. Treatment of ceramics stored in damp basements without ventilation by 2% aqueous solution of most frequently used in restoration practice quaternary ammonium compounds (QACs) at first protected art objects from mould attack for sufficiently long period of time. But then the ceramics became covered with fungal hyphae. Laboratory study of fungal growth on ceramics, treated with different concentrations of QACs, showed notably high biocide resistance of fungal isolates belonging to the genus *Aspergillus*. Spores of biocide-resistant strain *A.niger K* actively grew with 0,2% of the biocide, whereas the growth of collection culture even at 0,1% content of the biocide was completely inhibited. It is very likely that the leading factor in allowing the fungus to withstand such high concentrations of biocide is its ability to acidify the environment. In liquid medium the final pH in medium with 0.01% biocide was 4.2, with 0.001% — 1.6. The decrease of pH-level led to the decline of biocide activity which is effective only in alkalescent medium.

The experience of mycological practice shows that the desired fungitoxicity could be provided only with the help of microbiological preliminary testing of biocide substances in modeling conditions in vitro. Close collaboration of mycologists and restorers will help to provide appropriate biocide treatment for conservation of museum objects.

GRANITE WEATHERING IN CITY ENVIRONMENT

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Stone is very important building material which was widely applied in city building of Russia (Petersburg, Vyborg, Priozersk, Primorsk) and Finland (Helsinki, Lappeenranta, Kotka, Hamina, Kuopio). It has allowed to keep and inform history up to now. Granite is one of the most widespread types of a stone in architecture of these cities which were under construction near to mining areas of the Vyborg granite‘s rapakivi massif.

Wide use of a natural stone in building of Petersburg has created its majestic shape. The granite is considered as one of stones symbol of the city. Granite was broke out on islands in gulf of Finland, in area Piterlahti and Monrepo quarries. Later granites of area of Sortavala and Karelian isthmus (areas Kuznechnoe and Kamennogorsk) have started to be used actively. Granites rapakivi, granito-gneisses and other granites are widely used in architectural furniture of Finnish cities.

Granite is very heavy stone, but it destroyed under the influence of time, becomes ill, covered by mosses and lichens. Destruction of a natural stone as a result of airing process is global process. Mechanical communications between stone particles collapse under the influence of water, a wind, because of a temperature drop. Rock-forming minerals such as, micas, pyroxenes, amphiboles and field spars transfer to clay minerals and are washed away from soil. Harmful chemical influence is rendered by gases and the substances which are in air and water.

During the dissolution of carbon dioxide of air in rainwater coal acid is formed and acid leaching of rocks is begine. An airs oxygen makes an acidification and transition of chemical elements in oxides forms. Particles of rocks and the minerals, being in aerosols make shock mechanical influence on a granite. It is not surprising that, stone destruction in city environment proceeds much faster, than under natural conditions. Destruction is caused by complex influence of physical, chemical and biological factors which are closely interconnected.

The analysis of mechanisms destruction of natural stones demands the complex approach assuming use of a wide arsenal of modern analytical methods and application of professional efforts of experts of various directions. The knowledge of factors and understanding of the mechanism of destructions processes of a stone will allow to create a methodical basis of a choice of a stone for building and to develop methods of brushing and preservation of a stone in the conditions of accruing technogenesis for preservation of a stone heritage.

The purpose of our research is revealing of physical, chemical and biological features of a granite rapakivi destruction in the city environment in landscape of Fennoskandian for the purpose of creating the methodology of similar researches.

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APPLICATION OF SILVER NANOPARTICLES TO PREVENT BIOCORROSION PALAEOLITHIC PAINTINGS

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Now problems of biodegradation and biodeterioration become more and more relevant. One of the most aggressive agents, which cause biodegradation, is microscopic fungi. Due to the specifics of their vital functions, this group of microorganisms is able to use a variety of materials as power supply, both natural and synthetic. Bacteria creates a lot of problems too. The most complicated cases remain those, where a group of organisms, including bacteria and fungi, causes damages.Special case of biodegradation is the destruction of Paleolithic art. For example, the cave of Shulgan-Tash Burzyan District, Republic of Bashkortostan, Russian Federation, which has the status of natural and archaeological, historical and cultural complex. The cave is known for the rock paintings of prehistoric man Paleolithic period, dated from the late Solutrean period to the middle of the Madeleine.Here is the following problem arising during the process of fighting microflora: it is necessary to protect the paintings from chemical and mechanical effects. In this regard, it becomes urgent to develop the method of influence on the microflora, which would be safe for the picture.

It was proposed to apply the suspension of silver nanoparticles stabilized by covering them with miramistin. After stabilization had been performed dialysis. Antibacterial component miramistin effectively destroys bacteria. Silver possesses indiscriminate toxicity towards many biological objects.Laboratory experiments were conducted regarding the microorganisms isolated from the swab taken from the drawings surface. While testing the samples of the bacteria *Staphylococcus aureus*, *Bacillus cereus*, *Bacillus sp*. and fungi *Botrytis cinerea*, *Penicillium chrysogenum*, *Trichoderma sp*., *Chaetomium globosum* it was shown that contact of microorganisms with the suspension of nanosilver with concentration of Ag 5×10^{-5} g/ml resulted in significant reduction of CFU.Bacterial cultures were grown in meat infusion agar (PCA). For the cultivation of *Chaetomium globosum* had been used wort agar, for the cultivation of micromycetes had been used Czapek-Dox. Microorganisms were treated with a suspension of nanoparticles of silver with concentration of $5 \cdot 10^{-5}$ g / ml. Then they were inoculated into solid medium. Fungi were taken in the form of spores and mycelia. The temperature for culturing bacteria in the incubator was 37°, C for fungi 22 °C. The result of bacterial growth had been evaluated after 24 hours, *Chaetomium globosum* after 2–4–6 days, micromycetes after 7–14 days. Here was estimated the number of colony forming units in the experimental and control samples. Experiments were performed in triplicate. Outcome was assessed as a percentage of control / experience. Within the experiment, the cell suspension of bacteria and fungi spore suspension was made in sterile aqueous solution.

The experiment revealed that the number of bacteria had been reduced by 98%; mycelium micromycetes by 90–92%, the dispute micromycetes by 74%; mycelium hitridy by 80–95% hitridy dispute by 57%.

Thus, it was shown that silver's nanoparticles stabilized by miramistin inhibit the growth not only of the developed mycelium, but also affects the fungi at the time of spore germination. Therefore, single treatment will provide prolonged effect and get rid of bacterial and fungal microflora. The suspension is transparent and acts in low concentrations, it can be applied by spraying, contactless. In addition, processing of limestone around the picture allows to block growth of mycelium and bacterial colonies on the drawing area.

SIGNIFICANCE OF ORGANIC ACIDS PRODUCTION BY FUNGI IN BIODETERIORATION OF STONE AND ADAPTATION TO STRESS

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Organic acids production by fungi has an important role in weathering processes of stone. The ability to excretion of organic acids is determined by species characteristics of fungi as well as environmental factors. The aim of this work was to study of organic acids production by fungi under influence of some stress factors.

The fungi *Aspergillus niger* and *Penicillium citrinum* isolated from surface of marble were cultivated on artificial nutrient media with different composition of carbon and nitrogen sources, presence or absence of calcium carbonate and under stress influence: presence of heavy metals (Zn and Cu); biocides, UV-irradiation.

Oxalic acid was produced during the growth of fungi on various carbon sources (glucose, fructose, sucrose, mannitol, sorbitol, gluconic acid) and even at low concentrations. But oxalic acid was produced in very little amount if NH_4NO_3 or NH_4Cl were used as nitrogen sources. The low amount of oxalic acid on ammonium media may be associated with decrease of pH due to H^+ production on NH_4^+-contained media. Oxalic acid production also controlled by C/N ratio: acidification activity of fungi increased at high concentration of sugars and low concentration of nitrogen salts. Malic, citric, fumaric and succinic acids were produced only with high content of carbohydrates and mainly on liquid media.

The addition of $CaCO_3$ in the media induced the increasing of oxalic acid production and decreasing of citric acid production. The production of oxalic acid in calcium-contained substrates led to formation of calcium oxalates crystals. Insoluble crystals also were detected on Zn^{2+}-containing media. Presence of Zn^{2+} in different concentration (0.025–2.0 mM) had stimulating effect on oxalic acid production by fungi on nitrogen media. Cu^{2+}also stimulated oxalic acid production but only in low concentration (0.025 mM). The oxalic acid production by adapted strains of *P. citrinum* was stimulated by higher copper concentration (Cu^{2+} 1 mM) but no Cu-contained crystals were detected in the media or on mycelium. On ammonium media both heavy metals (Zn and Cu) did not induct the oxalic acid production by fungi. The growth of mycelium on ammonium media under influence of high concentration of Zn and Cu had the atypical morphology with swollen cells, presumably accumulating metals inside the cell. On nitrate liquid media, Zn have less toxic effect on grown rate than on ammonium media presumably due to binding Zn in insoluble salts.

In spite of direct action on organic acid metabolism other physical and chemical factors had influence on acidification activity of fungi.

UV-irradiation stimulated excretion of oxalic acid by *Aspergillus niger*. Poliguanidin-based and azole-containing biocides presence in the medium in depending of concentration led to increase or decrease of organic acids production by fungi. During the adaptation for biocides the acidification activity of *A. niger* generally increase.

The results indicate that oxalic acid is a major acid producing by fungi in Ca-containing substrates. Its production induces the stone biodeterioration due to solubilization of some minerals and secondary mineral formation. Oxalic acid production depends on growth condition as well as induced by wide range of different stress factors.

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DEVELOPMENT OF STONE MONUMENTS MONITORING SYSTEM WITH USING OF COMPUTER TECHNOLOGY

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Monitoring of the cultural heritage state is significant factor for their preservation, the timely restoration and conservation. Known approaches to monitoring of monuments in the open air are based on the combination of visual assessments, including the method of qualimetric examination and analysis of damaged materials using complex instrumental methods (Frank-Kamenetskaya, Vlasov, 2014). The aim of this work is to develop a system for monitoring of cultural heritage using new computer technology. For this purpose, the system should consider the original form of the monument, with all its destructions (physico-chemical, biological, anthropogenic). The next step, the system conducts repeated recordings of the monument form with the use of digital technologies. Then, all the images are compared with each other on set of information signs and we can identify some differences from the original image. Analysis of these differences allows us to determine the degree of change and assess the condition of the monument.

The first step in creating of this system is the development of the program CONSOLIDATOR-BIO, which allows to assess the biological fouling of surfaces of stone monuments on the basis of the color characteristics of objects (Shchigorets et al., 2009). Later it was shown that the most informative features of objects (weathering of monuments) are their spectral and spatial characteristics. The proposed method of image comparison is based on the spectral characteristics of the studied monument. Photographing of the objects is carried out in visible and invisible spectra. Most information on the biological objects can be obtained, for example, when shooting is in the infrared range. Primary image processing, recognition of weathering features and assessment of their potential hazards as well as evaluating of the overall state of the monument is made with the using of the complex computer programs, and the results are accumulated in a special database. This system works as the expert one. It has been shown the possibility of classification of the main groups of organisms on monuments and assessment of the biofouling area in time by using this method. This method was tested during the survey of ancient petroglyphs in Republic of Khakassia, Tomsk petroglyphs, as well as on a number of historical monuments in St. Petersburg.

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TRANSFORMATION OF MINERALS UNDER THE INFLUENCE OF MICROSCOPIC FUNGI

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The aim of this work was to research regularities of metasomatic transformation of rock forming minerals (calcite, apatite, mica) associated with the activity of microscopic fungi.

Experimental section

The biomimetic experiments aimed on researching the effects of microfungi Aspergillus niger (active producer of organic acids) on calcite marble, fragment of mammoth tooth (hydroxyapatite-organic composite), piece of single crystal abiogenic fluorapatite (Sludyanka deposit), powder of synthetic precipitation hydroxyapatite and piece of synthetic fluorphlogopite $KMg_3[Si_3AlO_{10}]F_2$ have been carried out. The synthesis products were studied by scanning electron microscopy, microprobe analysis and X-Ray powder diffraction methods.

Discussion of Results

In all experiments with Ca-minerals (calcite, apatite) crystals of calcium oxalates (monoclinic whewellite and / tetragonal weddellite) were obtained.

On a marble surface crystallization of calcium oxalates starts from the formation of almost ideal dipyramidal and dipyramidalprismatic (with dominant {101} pyramidal faces) crystals of metastable weddellite under $pH<5$. The stable calcium oxalate monohydrate whewellite forms as multiple spherulite looking intergrowths of lamellar crystals on hyphae in the fungal mycelium on the surface of culture broth. Tetrahonal biomimetic crystals are very close by their morphology and size to the crystals which we found in the oxalic patina on the surface of marble and limestone monuments in Tauric Chersonesos.

The metasomatic transformation of hydroxyapatite is more intense than fluorapatite, which is well explained by their spective solubility ratio. On the surface of fragments of mammoth tooth and powder of synthetic apatite the numerous lamellar whewellite crystals (from 1 to 70 microns) and spherulite looking intergrowths of them are seen. Besides there are large dipyramidal weddellite crystals up to 100 microns (often shattered). The continuous carpet of lamellar whewellite crystals (from 20 to 60 microns) with traces of their dissolution is seen on the surface of fluorapatite single crystal. The traces of their dissolution are visible. Weddellite crystals are absent.

Experiments with mica showed the dissolution of phlogopite, the leaching of several elements (Mg, K after 1 and 2 months; Al after 6 months) and the precipitation of secondary minerals. The contents of minerals precipitated on the surface of mica plate includes several phases. There are small hexagonal crystals (probably fragile calcium micas), needle shaped crystals, close to the underlying mica in contents as well as the intergrowths of irregular forms and single crystals of Al and Mg minerals.

The results obtained in this work give evidence that microscopic fungi play a significant role in the precipitation of secondary minerals.

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MYCROMYCETES ON STONE MONUMENTS IN NECROPOLISES OF THE STATE MUSEUM OF URBAN SCULPTURE (SAINT-PETERSBURG)

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The sculptures and constructions made of stone have a special position among the unique architecture ensemble of Saint-Petersburg. The deterioration of stone monuments is well-known phenomenon which is not only caused by natural and anthropogenic factors, such as atmospheric humidity and temperature changes, air pollution, salts, but also by microbial activity. The composite communities of microorganisms are found on the surfaces of stone monuments, and the fungi take an important role in that polymicrobial system.

The investigation of damaged stone material was carried out on the monuments in the Necropolis of the State Museum of Urban Sculpture (Saint-Petersburg). The Necropolis contains the unique collection of monuments made of various types of marble, limestone, sandstone and granite. Specimens for analyses were collected from the damaged stones with non-destructive techniques.

During 10 fields seasons the deteriorated stone in monuments was studied and different types of rock damaged were described.

During the period of investigation more than 1 hundred species of microscopic fungi were isolated from different types of damaged stone. More than 80 species of microfungi were found on different types of marble, 68 species were isolated from limestone and more than 50 species of micromycetes were isolated from different granite monuments.

The group of dominated species on different types of stone includes *Alternaria alternata, Aureobasidium pullulans, Cladosporium cladosporioides, Cladosporium herbarum, Cladosporium sphaerospermum, Coniosporium sp., Epicoccum nigrum, Fusarium oxysporum, Hormonema dematioides, Monodyctis levis, Penicillium brevicompactum, Phaeococcomyces exophialae, Phaeosclera sp., Scytalidium lignicola, Ulocladium chartarum*. The absolute domonated species of microfungi on different stone substrate were *Aureobasidium pullulans, Cladosporium cladosporioides, Alternaria alternata*. This spesies of fungi characterized by strong resistance to unfavorable atmosheric influence. The cells of this fungi contain melanin pigments which protected them.

Fungi form small colonies and mycelia in the cracks and in the hollows of stone surfaces. The peculiatities of colonization of rocks by fungi and other microorganisms were studied by the methods of SEM-analysis. The permanent presence of microcolonial fungi specific for surface of stone and the location of this meristematically slow-growing micromycetes in cracks and microcavaties of minerals are revealed.

The destructive processes taken place in stone surface caused by activity of different organisms (bacteria, algae, fungi and lichens). The rate of biodeterioration pricesses on stone monuments mainly depends on quantative and qualitative presence of microorganisms on the monument surface and determined by environmental conditions.

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Section 6
Medical geology

DETERMINATION OF SOME POLYCYCLIC AROMATIC HYDROCARBONS (PAHS) AND SIMPLE STATISTICS OF HEAVY METALS CONTENTS IN THE HONEY SAMPLES FROM NIGDE CITY, TURKEY

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The aim of the present work was to investigate the levels of three important PAHs (Naphthalene, Benzo [a] pyrene (BaP) and Anthracane. Honey samples were collected from 67 different stations, during the 2007–2008 periods from Nigde City. The samples were analysed by using Gas Chromatography – Mass Spectrometry (GC–MS). Naphtalene residues were found in the 24 honey samples (For GC–MS limit of detection is 1 ppb and the upper limit 100 ppb in the Europen Union MRLs). In six samples were found BaP residues (1.51 ng/g ±0.47). However, antracene residues were found in eight examples (1.59 ng/g ±0.85). Heavy metal contents of honey samples collected along the Nigde City are given in Pb, Ni, Cr and Cd concentrations are between 0.20–0.4286, 0.55–0.9987, 0.24–0.9654, 0.11–0.3229 μg/g, respectively. Average concentrations Pb, Ni, Cr and Cd are found as 0.293999, 0.787187, 0.794632, 0.18163 μg/g, respectively.

PROBLEMS OF ENVIRONMENT SAFETY, INCLUDING OF FOOD QUALITY, AND HUMANITY SURVIVING

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Numerous statistical data on the frequencies growth of all possible illnesses and deaths by them, in particular, on the forecast of cancer patients doubling in 2030 have recently appeared on the Internet. Among the reasons for this, well known addictions of the diseased to bad habits or diets, viral infections, environmental degradation, excessive insolation are usually listed. One of the important factors is the quality of food products used by people around the world. Over the past 1.5–2 decades, most food products began being produced with a large variety of different additives; many of them even in very low concentrations are hazardous to health. These include E-additives, artificial citric acid, lecithin, many preservatives, flavour enhancers, gaseous substances, for example, $N^{2,}$ SO^2, and others. Lists of their harmful effects are well known. Cultivation of fruits and vegetables with the use of harmful amounts of chemical fertilizers [1] and treatment with different chemicals should also be added here. One more global factor can be attributed to chemically various pollution, for example the dust and gaseous emanations due to anthropogenic activity and from volcanoes. Some useful recommendations need to be given the people living not only nearby "hot points" but also and in connection with a direction of streams of a wind. Therefore the monitoring of clear and simple advices is actual in different regions of our Earth. The most simple and easy measures can be accepted to make our food safe.

WHAT FOR and WHY many nations have moved to the use of harmful additives in the food industry? WHY? This may be a consequence of creation by non-experts of bad instructions and standards for food production and cultivation and treatment of vegetables, fruits, and berries. Now — WHAT FOR? I think that, apart from the desire to get some monetary gain = profit, there could emerge one of the laws of nature that no one can cancel. This is the law of Malthus, acting somewhat peculiar in the human world and in modern conditions, when overpopulation in some specific regions may cause only local wars and skirmishes, but not a global world war. The latter has still been prevented by bans on the use of nuclear weapons. But how at the present time, in the absence of natural selection, the Nature can fight overpopulation of our human species? After all, there are no creatures stronger than humans on the Earth, and the presence of intraspecific selection remains a question. Therefore, the Nature probably activates a large number of food and beverages of poor quality. Who will survive the battle with the new challenges? Obviously, only smart people who either live preserving the natural state of the Nature, thus preventing their offspring from the negative impact of all this chemistry, or simply stop buying products that are somehow poisoned. There are good reasons why smart managers and owners of restaurants, or simply smart rich people now have learned to use the services of becoming popular food brokers. They find farmers producing environmental friendly products to conclude agreements on delivery with them. Quality monitoring of different products can be made, for example, by nitrate meter — an instrument that determines conductivity in the measured product. Use within 6 years of this device have allowed me to improve essentially the health, in particular, to forget about earlier existed factor of a blood pressure. A careful study of labels allows culling of products with harmful additives. These simple techniques make it possible to provide yourself and your family a real improvement in health. Only domination of reasonable, environmentally competent authorities in the countries can be a reliable guarantee for the survival of humanity.

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THE IMPORTANCE OF QANATS IN EFFECTIVE USAGE OF GROUNDWATER

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Water has a vital important for human like the other living begins. Unfortunately, while the need for fresh water is increasing, the amount of fresh water is decreasing because of some reasons such as population growth, industrialization, global warming etc. Besides, conventional methods, like well and pump, without careful consideration cause to reduce the groundwater level and to dry up the reservoirs. So, the protection of present water becomes much more important than getting water. On the other hand, the horizontal wells system (qanats) has been using for hundreds of years in specific regions. Qanats reduce the evaporation and leakage, keep the natural balance of groundwater without pumping and energy consumption and make it “renewable resources for sustainable development”. The main aim of this study is to find suitable places for qanats in terms of geology and hydrology and to create a model for new water projects in Antalya.

ECOLOGICAL-DEMOGRAPHIC ASPECTS OF AIR POLLUTION IN KARELIA

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From the standpoint of ecological geology, sources of environmental impact (including technical objects) and biota (including humans) are components of natural-technical ecological-geological systems (side by side with the lithosphere). In turn, the atmosphere is considered as a component of the environment, bordering with lithosphere and closely interacting with the ecological-geological systems. It is through the air in the zone of influence of the pollution emissions from industrial, energy and other technical objects the rapid harmful impact on living organisms occurs. This fact applies fully to human.

During ecological-demographic studies in the Republic of Karelia for the first time a statistically significant correlation was set between the emission of pollutants into the atmosphere from industrial and others economic objects, transport, on the one hand, and mortality of the population on the other hand.

So, the reduction in mortality from diseases of the circulatory system is statistically related to decreasing emissions from Manufacturing Industries (except Primary Aluminum Production in the Segezhskiy district), primarily from the pulp and paper industry, as well as from objects of Energy and Housing Communal Services. The coefficient of determination (R2) for the general linear model that combines these types of economic activity, based on data for the period 2002–2012, amounted to 0,93.

The sharp rise in emissions from motor vehicles in 2006–2009, probably, identified an abrupt transition to higher level of mortality from neoplasms in 2008–2011 (Fig.). In the case of such transitions from quantity to quality, the implementation of further procedures for health risks assessment requires consider the presence of the lag between the time of exposure and the appearance of the final effect, in this case the absence of a specific term survival in patients with malignant neoplasms.

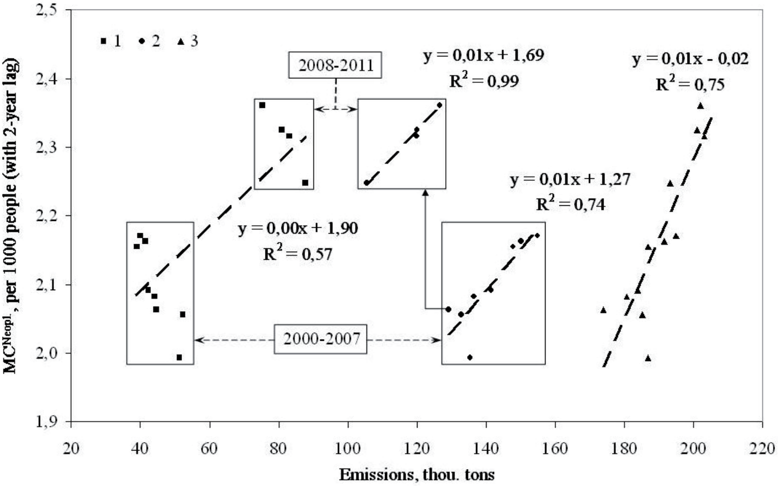

Fig. Emissions of pollutants: 1 — from motor vehicles, 2 — from all stationary sources, 3 — total emissions (1 + 2) in 1998–2009 and mortality from neoplasms in 2000–2011 (MC – mortality coefficient)

In the future, created statistical models will be complemented the newly incoming data to confirm reliability of ones. In case of deviation the new data from these models, the impact of previously absent or weakly manifested factors should be assess.

Similar calculations for Petrozavodsk were conducted using the data on emissions of key pollutants and frequency of wind directions. So, total mortality and mortality from diseases of the circulatory system associated with the presence in the emissions of carbon monoxide and sulfur dioxide, mortality from external causes (accidents, poisoning and injuries) — sulfur dioxide, total mortality excluding deaths from external causes — carbon monoxide and particulate matter. Reduction of the mortality from neoplasms, statistically associated with the emissions of nitrogen oxides, stops, and it has been increasing since 2008, what may be a consequence of the sharp rise in emissions from motor vehicles in 2006 (availability of 2-year lag). Most dangerous for the majority of the population of Petrozavodsk are emissions from objects of Northern Industrial Zone in combination with north-west wind (frequency of 5–10 % in annual course).

REGIONAL PECULIARITIES OF MICROELEMENTS ACCUMULATION IN OBJECTS OF ENVIRONMENT AND THEIR INFLUENCE ON POPULATION HEALTH (ON THE EXAMPLE OF TRANSURAL REGION OF THE REPUBLIC OF BASHKORTOSTAN)

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Enrichment of the South Ural by the complex of mineral resources, especially polymetallic ores, have resulted in increased levels of some chemical elements in soils, water, vegetation and other parts of ecosystem. In addition, intensive and long-term exploitation of complex ores and development of the mining industry both have made a significant additional contribution to the environmental pollution by heavy metals that could negatively influence to the health of people living in the territory. Recent researches have shown a close relation between the content of certain trace elements in the environment and the development of a number of diseases, such as goiter, Graves’ disease, diabetes, multiple sclerosis and other [1–4]. The results indicate significancy of human body microelement profile for the functioning of different organs and systems and the need for research of communication of somatic and thyroid diseases with environment trace element composition, in the formation of which the main role is played by the geological-geomorphological conditions in the area. We conducted researches on studying of the maintenance of a number of heavy metals and trace elements in objects of environment of Transural region of the Republic of Bashkortostan. There is an increased content of Cu, Zn, Cd and in some cases of Pb, in soil, surface water, plants, and in the hair of inhabitants. For instance, hair of the Sibay Ore-dressing Plant workers was characterized by a high content of Cu, Pb, Cd, Zn. It is established that the aggravation of worker's health is correlated with accumulation of the Pb and other metals in the hair. However, the content of some elements in the patients biosubstrates was significantly reduced. So, hair of Sibay teenagers have low levels of such chemical elements as Se and Co. Teenage morbidity has considerably increased for last years. One possible reason for this could be the disbalance of the microelements in the organism. Obtained results prove a perspective research areas at the intersection of medicine, geology and ecology, the aim which is to study the whole range of environmental factors that can adversely affect the health of the population.

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THE OBSERVATION OF GALLBLADDER STONE IN THE NIGDE CITY, CENTRAL TURKEY

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The aim of study is to detect the physical and chemical features of the gallbladder stones taken from patients in the Nigde city of Turkey. The physical classification was done on 42 gallbladder stone samples between the dates of October 2010 and January 2011.

Gallstones properties yellowish, brownish, coffee-and-black colors and opaque and vary between 0.1–3.7 cm. In the chemical studies with FT-IR method, minerals and their chemical formula are as such: Newberyite $MgHPO_4(H_2O)_3$; % 13,94 Mg; % 17,77 P; % 4,05 H; % 64,24 O. Carbonate Apatite $Ca_5(PO_4)_3$ (OH, F, Cl);% 39,36 Ca; % 18,25 P; % 0,07 H; % 2,32 Cl; % 1,24 F; % 38,76 O. Aragonite $CaCO_3$;% 40,04 Ca; % 12,00 C; % 47,96 O. Newberyite + Carbonate Apatite; % 2,79 Mg; % 18,16 P;% 0,86 H;%43,81 O;%31,49 Ca;%1,86 Cl;%0,99 F. Hidroxyl apatite $Ca_5(PO_4)$ 3OH; % 39.89 Ca, % 18.50 P, % 0.20 H, % 41.41 O. Struvite+ammanium urate $MgNH_4PO_4(H_2O)$ 6; % 9.90 Mg, % 12.62 P, % 6.57 H, % 5.71 N, % 65.20 O. In polarizan microscope studies, phosphate minerals, struvit, apatite, aragonite and calcite were detected. Minerals give radial, acicular, twiggy, oolitic (rithmic intercalation), crackle, cavernous, cleaving, recessed and colored appearance.

If the patient is too much cholesterol, bile salts or bilirubin maintains, consists of the liquid harden into stones. The complaints of disease for adults are distension, stomachache, eructation, gas, indigestion.

Section 7

Mineral formation in living organisms and biometric materials

INFLUENCE OF OSTEOTROPIC MATERIALS ONTO THE OSTEOGENESIS IN THE DENTAL PRACTICE

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Osteotropic materials are a type of materials that may cause osteoinduction or ectopic osteogenesis (The formation of bone tissues in the soft structures).

The main components of such materials are complex of non-collagen proteins which are known under the name of "bone morphogenetic proteins".

Hydroxyapatite, tri-calcium phosphate and collagen compositions are the carriers of such proteins. Ability of these materials to cause osteoinduction is widely used in dental practice for treatment of the destructive forms of periodontitis.

These materials are introduced into the bone destruction zones of the jaw bone by either one of conservative, surgical or combined methods. Duration of materials' presence in such zones, frequency of replacement and treatment term depend on the actual clinical situation, size of the zone and the pharmacological characteristics of the material itself.

Since sterility is one of the critical conditions for successful treatment of destructive forms of periodontitis in all cases the materials with not only osteotropic, but also antiseptic properties were used.

This, in turn, contributed to the slowing down of the inflammatory process in the lesion zone.

This method was used for 5 years (2007–2012) for 242 patients aged from 18 to 71 years old, who had various somatic pathologies (diabetes, cancer, diseases of cardiovascular system, bronchial asthma) .

The results of the applied treatment were evaluated as being positive in cases of anatomical and functional restoration of teeth, X-ray diagnosed reduction or complete elimination of bone destruction zone and clinical safety. In all represented cases the long-term results (from one to five years) were evaluated as positive.

Based on the above observations we can conclude that the use of the osteotropic materials in dental practice allows restoration of the destruction zones of the jaw bone effectively even for patients with concomitant somatic pathology when supplemental aseptic methods (physiotherapy, antibiotic therapy etc.) are impossible and to minimize surgical intervention.

DETERMINATION OF NUCLEATION PARAMETERS OF COMPOUNDS FORMED FROM A MODEL SOLUTION OF SALIVA AND PLAQUE LIQUID

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One of the important trends in the field of crystallization from solutions is to study crystallization in biological fluids. Complexity of studying of formation soluble compounds from model solutions of biological fluids consists in their composition. It has a large number of components, and there are many factors influencing on the possibility of crystallization. And because the process occurs under nonequilibrium conditions, the flow is responsible for his kinetic factors.

The aim of this study was to investigate the kinetics of biominerals nucleation in model solutions of the oral cavity.

As a model formulations of oral solutions it was used the values for inorganic basic components and the pH of saliva and plaque liquid. The concentrations of reactants and their initial ratio in the solution was selected so that the ionic composition and ionic strength of the solution were close to the data parameters of the modeled system. Supersaturation is created by a chemical reaction (1), which was carried out by mixing solutions in the mold of soluble compounds of calcium chloride, ammonium hydrogen phosphate and potassium.

XRD results of solid phase synthesized in the simulation showed that the X-ray diffraction pattern obtained by crystallisation at $pH = 6{,}50 \pm 0{,}01$, corresponding mixtures of calcium phosphates with a predominance of brushite. Noting the presence of poorly soluble phosphate impurity $Ca_4H(PO_4)_3 \cdot 2.5H_2O$, $Ca_{10}(PO_4)_6(OH)_2$, the content is slight.

While studying the effects of supersaturation S (S = 5, 10, 15, …, 50) on the parameters of nucleation we found that the dependence of the induction of supersaturation was nonlinear. This behavior is consistent with theoretical concepts: the induction should depend exponentially on the supersaturation. By comparing experimental data for the saliva and plaque liquid, it is noted that the first system is more resistant to S equals 20. In the second phase the mineral system begins to form even at S equals 15, which is associated with a higher initial concentration of Ca^{2+} ions and HPO_4^{2-}. It was graphically determined the order and nucleation constants for the two systems: saliva — n_N= 4.5, k=$2{,}78 \cdot 10^8$ $sec^{-1}l^n mol^{-n}$; plaque liquid — n_N= 6.5, k= $7{,}26 \cdot 10_{10}$ $sec^{-1}l^n mol^{-n}$. Based on the calculated data of the specific surface energy it was determined that both systems are characterized by heterogeneous nucleation of crystallites. According to the theory of Gibbs-Folmer evaluated critical size embryos for simulated systems it has the order of 1 Å and decreases with increasing supersaturation. Studying the effects of organic and inorganic additives on the nucleation stage, it was revealed the accelerating effect of additives: $HCO_3^- > C_6H_{12}O_6 > F^-$, and the retarding effect of additives: protein (casein) > Mg_2^+. Ramer analyzing particles using laser diffraction, it was found that crystallization proceeds faster in plaque liquid and its composition is favorable for the growth of smaller crystallites (52,6–26,1 mm); modeling saliva solution conditions promote the formation of larger crystals (198,4–41,8 microns) .

PHASE COMPOSITION OF KIDNEY STONES DETERMINED BY DIFFERENT PHYSICAL METHODS

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It is well known, that living organisms are containing more than 50 biominerals [1]. The most widely produced biomineral is hydroxyapatite, which is the most important component of vertebrate bones and teeth. At the same time, different minerals (brushite, struvite, etc.) could form in tissues of living organisms due to pathological biomineralization. Thus, there is great interest in studying of properties of pathological minerals and understanding the mechanisms of pathological biomineralization.

The aim of this study was to determine phase composition of kidney stones of human being and dog (14 samples) by the methods of X-Ray Diffraction (XRD), ^{1}H and ^{31}P Nuclear Magnetic Resonance (NMR) and Electron Paramagnetic Resonance (EPR). Joint complex investigation of the properties of physiological and pathological minerals could provide the necessary knowledge for creation of new type of synthetic "bioinspired" nanostructure materials for different medical problems solution.

It was shown by the XRD method that kidney stones comprise mainly by whewellite and whedellite, less frequently by apatite, struvite and brushite. Predominant phase composition of the uroliths depends on the geographic region and samples studied in given work were mainly represented by apatite, struvite and brushite.Sulfate and carbonate EPR-centers were detected in all samples. We could suppose, that sulfate centers indicate presence in the sample of sulfate minerals. Carbonate centers we could correlate with the presence of apatite. Joint applying of XRD, EPR, ^{1}H and ^{31}P NMR methods allows determining both main mineral phases and impurity phases.

Methodic for evaluation of quantity of phosphate minerals and organic minerals in pathological mineral formations by combine usage of ^{1}H and ^{31}P NMR and XRD methods is proposed.

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CRYSTAL GENESIS OF CALCIUM OXALATES FROM RENAL STONES

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Most part of the human urinary system stones consists of calcium oxalates both stable monohydrate (whewellite, $CaC_2O_4{\cdot}H_2O$) and metastable dihydrate (weddellite, $CaC_2O_4{\cdot}(2{+}x)H_2O$) and the amount of calcium oxalate stones is from 45 to 80% depending on the region. Physiological liquid (urine) several times supersaturated for calcium oxalate under the normal conditions, thus the calcium oxalate renal stones could be formed in the organism of any healthy person, but actually does not. Despite the fact that the formation of pathogenic biominerals dicussed in many papers, so far there is no experimental basis for the theory to explain the formation of any pathogenic minerals in the body.

The results of the calcium oxalate renal stones internal structure investigation (whewellite spherulitic aggregates, correlation between whewellite and weddellite, thin rhythmic zoning of whewellite renal stones after the organic substance impurity, weddellite dendrite structures) show the essentially nonstationary processes of calcium oxalate phases crystallization. Repeated nucleation acts of whewellite spherulites, periodic alternation of whewellite and weddellite phases reflect changes in the composition of physiological solution caused by external factors related to the activity of the organism. Fine zoning of the whewellite units — is a consequence of self-oscillation growing processes. This zoning is characterized by periodic and chaotic components, and could be described using fractal statistics from 2 to 5 parameters. Within stone segments with more complex and simpler dynamics of formation are localized. Last ones call for the description of one less parameter. The impurity poisoning of the spherulites surface is proposed as a mechanism of self-oscillations, leading to the hysteresis of growth rates and periodic growth stops with deposition of organic matter.

Features of the stones internal structure are determined by the processes of nucleation, oxalate crystallization kinetics, whewellite and weddellite phase stability that has been studied in model systems in terms of variation of temperature and concentrations of inorganic and organic components of the solution. The results showed that the inhibition of nucleation and crystal growth processes of calcium oxalate monohydrate in physiological solution at its conventional amino acid composition is caused by adsorption of amino acids on the surface of the stone. Crystallization of whewellite starts with the concentration of oxalate ions raises up to the values of oxalatourea desease. Addition of organic substance (ovalbumin, gelatin, protein-containing media) or microorganisms (bacteria and viruses) in the oxalatourea desease conditions facilitates crystallization of whewellite and leads to the simultaneous formation of weddellite with a variable amount of water, that causes the different weddellite stability. Addition of magnesium ions, sodium ions and carbonate ions to a solution leads to the co-crystallization of whewellite and weddellite.

XRD studies were performed at the X-ray Diffraction Centre of St.Petersburg State University.

GRANULAR CARBONATE HYDROXYAPATITE IN AN ORGANIC MATRIX GELATIN

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Millions of people each year suffer from diseases of the locomotor system (coxarthrosis, osteoporosis, etc.). It is known that the mineral component of human tissue is calcium-deficient hydroxyapatite biological (HA) $(Ca, Na, Mg)_{10}(HPO_4, CO_3, PO_4)_6(OH)_2$, which is able to stimulate reparative osteogenesis and restore the injured bone without causing immune rejection reaction. Currently the biocomposites based calcium phosphates (FK) in combination with different polymer binders (gelatin, albumin, chitosan, etc.), reinforcing additives and drugs draw much attention of scientists. The most convenient form for using the biomaterials are granules. Granulation is carried out with the aim of improving the technological properties of the powder (to prevent sticking, delamination of molded articles, etc.). The aim of this work was the synthesis of Carbonate Hydroxylapatite (KGA) from the model synovial fluid solution and forming the granules of KGA in the polymer matrix gelatin. The study developed a method of forming a composite KGA — gelatin. It established that in the entire range of variation of gelatin concentrations occurs pellet formation, characterized by a mesoporous structure with increasing content of protein components from 5% to 10% CHA in the composition of the granules is a sharp decrease in the total pore volume of about 6.5 times that correlate with a decrease of the specific surface (Sud.). It was shown that the pellets of KGA — gelatin represent bidisperse system consisting of spherical particles having a diameter of 1–2 mm. This is caused by the increase in the viscosity of the initial suspension with increasing gelatin concentration, which leads to an increase in surface tension of the droplets and consequently impairing its dispersion when flowing out of the capillary opening. It was found that after the heat treatment of the granules at a temperature T = 400 °C the carbonization of gelatin takes place, as indicated by blackening of the material, the spherical shape is kept completely to 1 mm, and the fraction is reduced by about 25 % for fractions of 2 mm at ùgelatin = 15 %. Annealing composite at T = 600 °C, 800 °C leads to the incomplete and complete burnout gelatin. At T = 800 °C the sintering inorganic matrix biomaterial occurs, due to the partial removal of CO_2 from the structure of Carbonate Hydroxylapatite (KGA), which correlates well with the results of the scanning electron microscopy. Micrographs indicated the presence of aggregates composed of crystallites of round and cubic forms, such morphology characterise the Carbonate Hydroxylapatite (KGA) and the hydroxyapatite (HA). The results of this work can be used for the production of ceramic materials for medicine, namely for traumatology and reconstructive surgery, dentistry and developing drug delivery systems.

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SYNTHESIS AND STUDY OF SR-CONTAINING APATITE PREPARED FROM MODEL SYNOVIAL FLUID OF HUMAN

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Deossification characterized by impaired synthesis of bone matrix protein and excretion of calcium phosphates from the crystal structure of hydroxyapatite. But at the present research questions are relevant to synthesis of biocompatible material. Such materials are needed for disease prevention and treatment of human solid tissues. Over the last decade the study of the nature of strontium injection into the hydroxyapatite structure is a topical issue, because until now it has not been set the exact mechanism of strontium ions embedded in the bone apatite. Thus, the purpose of this work — study of the mineralization processes from the prototype human synovial fluid in the presence of strontium compounds. The synthesis was carried out from the modeling environment to approximate ion electrolyte composition, pH, ionic strength to human synovial fluid. Deposition of the solutions was performed at pH = 7.4. For containing Sr — Carbonate Hydroxylapatite in model experiments strontium and calcium was added, and their concentration was varied in the range from 0 to 100 wt % of the maximum possible concentration of strontium and calcium. Crystallization was carried out for 7 days. When replacing calcium on strontium in solid solutions the materials with homogeneous structure can be obtained, from $Ca_{10}(PO_4)_6(OH)_2$ to $Sr_{10}(PO_4)_6(OH)_2$ (HAP). According to X-ray diffraction results obtained materials are composed mainly of HAP and brushite. Increasing of strontium corresponds to an increasing in the proportion of brushite and declining share of HAP. To determine the quality of the synthesized material it was used IR spectra of HA powders with different content of strontium ions. All spectra are characterized by the presence of OH — groups of bands stretching vibrations in the wavelength region 3570–3730 $cm^{-1,}$ and deformation vibrations at 3000–3600 — OH groups involved in hydrogen bonding. It can be noted: bending vibration ×4 O–P–O in PO_4^{3-} — 640–550 cm^{-1}, asymmetric stretching vibrations of P–O×$3PO_4^{3-}$ — in; 1060–1030 cm^{-1}, deformation vibration of the O–C–O in CO_3^{2-} — 870–879 cm^{-1}. Based on these data we can conclude that the calcium phosphate admixture with carbonate ions was formed. The spectra also show that with increasing concentration of strontium, the content of carbonate ions in powders decreases. When exposed to high temperature, crystalline phases are undergoing phase transitions: 1) In the first stage, there is a reduction of 15 mas.% in the temperature range from 100 to 280. This can be attributed to removal of weakly bound adsorbed water from the solid phase. 2) At temperatures of 280–550 mass loss is negligible and corresponds to the removal of crystallization water. 3) According to the IR results, the samples contain carbonate ions, therefore, reducing the weight of the precipitate during the heat treatment in the temperature range 500–900 associated with removal of carbonate ions.

Conclusion

- According to the XRD it was found that by the increasing concentration of strontium ions in a model system increases the proportions of brushite in the solid phase;

- IR spectroscopy established the presence of carbonate anions in the strontium-substituted apatites;
- DTA shown that mass loss increases with increasing concentration of strontium ions in the initial solution as a result of heat treatment samples.

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SYNTHESIS AND CHARACTERIZATIONOF HYDROXYAPATITE AND NANOCOMPOSITES BASED THEREON

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Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, HAP, Ca/P=1.67) is the basic mineral of bone and teeth. Synthetic hydroxyapatite because of it biocompatibility, osteoconductivity and low biodegradability is extensively used as an artificial biomaterial for different biomedical applications, mostly for the recovery of the bone defects. The main HAP disadvantage is its fragility, which significantly limited the possibility of its application. This is why a lot of studies have been focused on improving HAP's properties by incorporating biodegradable synthetic and biopolymers.

HAP/polymer nanocomposites are promising materials for bone tissue engineering because they are very similar to the bone. This method is based on the repair of bone defects using the patient's own cells and scaffold, providing them a three-dimensional growth, differentiation and proliferation. Scaffolds must meet the requirements of biocompatibility and biodegradability, comprise the biologically active molecules to control cell behavior, and exhibit appropriate mechanical properties for different objects of regenerating bone tissue.

Composition and structure of the scaffold must be able to adjust their mechanical properties and introduced the signaling molecules that control the behavior of cells into the material. More studies showed the possibility of changing the mechanical properties of the scaffolds by varying the degree of porosity and mass content of hydroxyapatite, but the influence of particle shape on scaffolds characteristics is almost not studied. Also a number of approaches to bio-functionalization of the scaffolds surface and capacity were proposed. In this regard, a promising approach is the use of functionalized HAP with different morphology for simultaneously solutions both of the problems.

Up to now, many kinds of chemical synthesis methods for the preparation of HAP nanoparticles with different shape and sizes have been introduced. The wet chemical process is the most reported method for preparing HAP particles. This process is simple, low cost, and suitable for industrial production.

It should be noted that formation of HAP nanoparticles is very sensitive to the synthetic conditions (pH, temperature, procedure). In addition the control the characteristics of the product suggested using chelating agents.

The most promising is the use of amino acids as chelating agents because they are physiological substances and can be used for further HAP biofunctionalization. It is known that amino acids can be absorb on HAP surface but previously used high concentrations of amino acids that correspond to the process of biomineralization in the body.

In the present study the hydroxyapatite nanoparticles with different shape have been obtained via wet chemical process using glycine as a chelating agent. The morphology parameters have been determined by a number of methods including XRD, TEM, DLS and specific surface area estimation (the BET model). The influence of pH and temperature on NPs morphology at low level concentration of glycine were studied. The relation between the NPs shape and the acid-base equilibrium of the charged groups of the glycine molecule and zero point of HAP was shown. The 3D scaffold loaded by sphere, spindle- and needle-like HAP were prepared and were characterized by XRD, tomography and SEM measurement. The dependence of elastic coefficient value of scaffolds and the shape of its inorganic component were determined.

STUDY OF CALCIUM OXALATE CRYSTALLIZATION BY OPTICAL MICROSCOPY

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Studying of crystallization of compounds that enter into the composition of physiogenic and pathogenic organic-mineral aggregates (OMA) is important and actual field of modern researches. One of the main components of OMA is calcium oxalate which has a large significance in its formation. It is found in the stones of the urinary system, the salivary stones and in other pathogenic mineralization. High prevalence of oxalate stones in the urinary system explains the increased interest in the study of the crystallization of calcium oxalate in the conditions close to the environment of the human body. However, the causes and mechanisms of pathogenic aggregates are not fully understood and it requires the further study.

The aim of this work is the study of the calcium oxalate crystallization and determination of the size and number of crystals by stereometric metallography.

The process of crystallization has been studied at 37 °C and three values of supersaturation ($\gamma = 40, 50, 60$).

Calcium oxalate supersaturation was produced by a chemical reaction, which has been realized by mixing the stock solutions of the stoichiometric composition of the soluble compounds. All series of experiments were carried out at constant stirring. Samples were taken and placed on a slide at certain time intervals. For samples with supersaturation $\tilde{a} = 40$ calcium oxalate crystallization process was carried out at three values of temperature ($t = 37, 50, 60$ °C) .

Practical method of metallography was used to investigate the parameters of the crystal structure of calcium oxalate. Thus, the method for estimating the size of the linear sections of microparticles (characterizes the particle diameter) and the method for estimating the number of the cutting lines and the sizes of the microparticles sections were implemented on an optical microscope Neophot-2. The lengths of the chords were determined taking into account the increase of the linear structure of the image.

It was found that while increasing initial supersaturation, the fraction of calcium oxalate monohydrate crystals increases. It was shown that the crystals dimensions of calcium oxalate at the same supersaturation of the solution do not change as the temperature of crystallization increases (about 25 microns monohydrate, dihydrate — 7.5 microns). It was found that there is a formation of unsplit crystals of calcium oxalate monohydrate by the increasing of the temperature (Fig.1) .

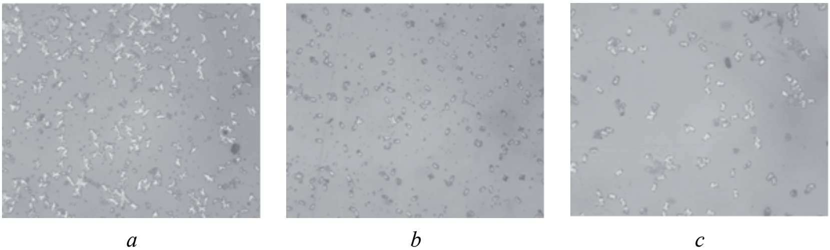

Fig.1. Results of optical microscope at different temperature: a – 37°C; b – 50°C; c – 60°C

Thus, it has been shown that crystals are formed solid and their size decreases about 15–17.5 microns at temperatures 50 °C and 60 °C. Calcium oxalate monohydrate crystallized mainly at the temperature 37 °C, at the same time at 50 °C and 60 °C the amount of monohydrate and dihydrate calcium oxalate is drastically reduced due to the appearance of solid crystals.

SYNTHESIS OF TITANIUM BEARING APATITES AND ANATASE-APATITE COMPOSITES BY PRECIPITATION METHOD

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Apatites, synthesized in the titanium containing medium, are characterized by photocalitic activity, bioactivity and enlarged hardness [1–4]. For this reason such apatites hold much promise for medicine and other fields of science and engineering. These unique properties can be caused either by occurrence of titanium cations in the apatite structure either by adsorption of titanium dioxide at the surface of apatite. Main goal of present paper: to synthesize titanium containing hydroxyapatites and anatase-hydroxyapatite composites.

Apatites and anatase-hydroxyapatite composites were synthesized by precipitation method in ammonium containing medium at the 85–90 ºC (the 100 ml of 0.1 M/l solution of $(NH_4)_2HPO_4$ was mixed with the 200 ml of 0.1 M/l solution of $Ca(NO_3)_2$ during 0.5 hour). Value of solution pH was kept in 8–11 range by adding in $(NH_4)_2HPO_4$ solution of the required amount of NH_4OH solution. Synthesized precipitates were heated up to 90–100 ºC for an 2 hours, then washed by distilled water, and then dried at the 100–110 ºC during twenty-four hours. Besides by synthesis of titanium containing hydroxyapatite the $TiCl_3$ solution was add to crystallization medium and by synthesis of anatase-apatite composites the powder of titanium dioxide (mix of 25–85 nm particles of anatase and rutile in proportion 3:1) was add to solution.

X-ray powder study has demonstrated that increase of Ti^{3+}/Ca^{2+} ratio in solution (from 0.05 to 0.25) leads to getting of monophase apatite samples. Increasing of value of this ratio to 0.50 cause appearance of additional anatase phase, amount of which in precipitation increase with increasing of Ti^{3+} cation concentration in crystallization medium. Microprobe analysis of synthesized monophase apatites has shown that titanium content in precipitation f gradually increase (from 0.88 to 21.24 wt%) with increasing of titan concentration in solution. Values of unit cell parameters of titanium bearing hydroxyapatites change as following: ***a*** — from 9.420 (4) to 9.458 (5) Å, ***c*** — from 6.883 (4) to 6.873 (4) E. X-ray phase analysis of precipitations has also shown that by synthesis of anatase-hydroxyapatite composites the anatase amount increase versus increasing of concentration of titanium dioxide in medium of crystallization. The study of photocatalitic properties of synthesized samples is now in progress.

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SYNTHESIS OF FLUORAPATITE FROM MODEL SOLUTION ORAL FLUID

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Promising direction of modification of hydroxyapatite in terms of obtaining a material with improved properties is the introduction in the structure of hydroxyapatite fluorine atoms. Such transformation will improve the stability of the material in the active medium of the human body and increase bioactivity while maintaining biocompatibility important property of hydroxyapatite.

The aim was to develop a synthesis of fluorapatite from model solutions of oral fluid and study the effect of amino acids on the composition of the precipitate.

The synthesis was carried out from a model solution, approximate on ion electrolyte composition, pH, ionic strength of the human oral fluid. Deposition of the solutions was performed at $pH = 6.93 \pm 0.05$, corresponding to the normal physiological pH value of the oral liquid.

On the prepared samples it has been studied the adsorption of three amino acids: serine, glutamic acid and glycine. The concentration of amino acids in the adsorption experiments varied from 0.003 to 0.0012 mol/l.

According to the results of the experiment built dependence of adsorption on the concentration of amino acids in solution (Fig. 1) and linear forms Langmuir isotherm (Fig. 2) for the three amino acids.

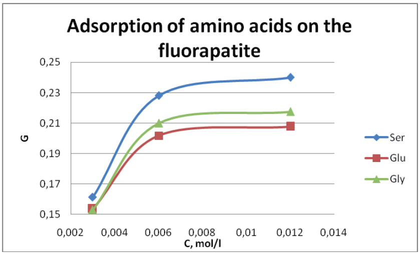

Fig. 1 The dependence adsorption amino acid of the concentration of solution

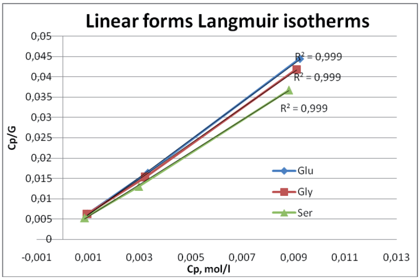

Fig. 2 Linear forms isotherm Langmuir for the various amino acids

It was found that the adsorption obeys the Langmuir theory, because the values obtained adsorption are linear Cp/G = f (Cp) with a high correlation coefficient (R2 = 0.999). From figure 1 it is possible to establish a number of adsorption of amino acids: Ser>Gly>Glu.

Thus, it has been proposed a synthesis fluorapatite of the model solution oral fluid and studied the effect of amino acids on the composition of the precipitate.

BIOMIMETIC APPROACH TOWARD THE GROWTH OF A PATHOLOGIC BIOMINERAL: MORPHOGENESIS OF CALCIUM OXALATE DIHYDRATE IN THE PRESENCE OF POLYACRYLIC ACID

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The morphogenesis of calcium oxalate hydrates in aqueous solutions was investigated by varying the pH, oxalate concentration, and the concentration of the sodium salt of polyacrylate (PAA). With increasing amounts of PAA in solution, the shape of tetragonal calcium oxalate dihydrate (COD) changes from bipyramidal through elongated bipyramidal prisms to dumbbells and finally reverts to rodlike tetragonal bipyramidal prisms. PAA is incorporated into the prismatic zones of the growing COD crystals, thereby reducing the growth rate of the {100} faces along the <100> direction. Dumbbells start to develop through “non-crystallographic” branching from the prism faces and the formation of “multiple head” crystals. The various shapes and structures of the biomimetic COD/PAA crystals and aggregates are closely related to the well-known “pathologic” individuals observed in the urine of patients with urinary disease (including urinary stones) .

CRYSTALLIZATION PARAMETERS OF THE SOLUTIONS SIMULATING THE COMPOSITION OF HUMAN BLOOD PLASMA IN THE PRESENCE OF DIFFERENT ADDITIVES

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The establishment of the kinetic characteristics of crystallization of insoluble compounds formed in biological fluids is a modern direction of science. The interest was aroused by the fact that these compounds are form in the pathogenic minerals. They are diseases the human organism and are also used in the synthesis of advanced biomaterials.

The main difficulty of the study of such systems is their composition. Biological fluids consist of a plurality of components, both inorganic and organic. For example, it is known that the plasma contains 90–92 % of water and 8–10 % of dry matter: low molecular organic compounds (urea, uric acid, amino acids, etc.), very large and complex structure of protein molecules, partially ionized inorganic salts.

The main purpose of this study was to character the crystallization of the prototype human plasma under close to physiological conditions.

Several solutions with different initial supersaturation were used for studying the crystallization of the solution and the modelling the composition of blood plasma. The correction of pH to physiological values was performed by adding 30 % NaOH solution or HCl (conc.). Visual method was used to determine the induction period. The investigation of the the crystallization kinetics was carried out with the use of photometric methods. Residual concentration of calcium ions was detected with the potentiometric method. The type of microcrystallisation in the resulting solutions was defined by optical microscopy. The composition of the solid phase was investigated by X-ray phase analysis and IR spectroscopy.

For the fist time, a study found that the induction time decreases with the degree of supersaturation of the model solution.

We can distinguish three sections on the experimental curves which are characterized by different rate of change of the induction time. It turned out that the calculated overall reaction order was fractional and equal to 1.62. It is well known that a value of the order indicates the number of particles entering into the nucleus, and the constant value describes the total amount of particles formed.

Specific surface energy and critical radius of nuclei was also calculated on the basis of nucleation periods depending on the supersaturation. It was found that with the increase of supersaturation increases the value of the surface energy. This suggests that observed mechanism changes the heterogeneous nucleation to homogeneous. Similar studies were conducted in the presence of additives.

Then the kinetic curves were obtained for the test solutions. The order of the growth process and the rate constants were calculated by the graphical method based on the received data.

It was established that the order is zero, and the constant decreases with increasing supersaturation. A similar experiment was carried out for solutions in the presence of additives. It was found that the main effect of additives have is on the nucleation process.

The kinetic characteristics for changing the calcium ion concentration have also been calculated.

According to the results of X-ray phase analysis and IR spectroscopy the mixture of carbonatehydroxylapatite A-type and whitlockite was identified in the solid phase.

CALCIUM PHOSPHATE MINERALIZATION IN CARDIOVASCULAR TISSUE

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Calcium phosphate mineralization in human and animal organisms retains fundamental importance as a source of constructional material for the formation of bone tissues, teeth and many pathological formations. At present there is no general theory for to explain the formation of calcium phosphates in a living organism. However, many researchers think [1] that the nucleation of calcium phosphate particles on heart valves and in blood vessels occurs as a result of intracellular or cell-related processes similar to bone mineralization. Hydroxyapatite nanocrystals discovered by us in blood plasma of healthy donors allow us to assume that along with cell mechanisms there is a physiological process of extracellular calcium phosphate mineralization [2, 3]. We prove relying on the experimental data that human blood plasma can serve as a primary source of the formation of hydroxyapatite. Results of the investigation of structural and morphological features of calcificates in arteries, cardiac valves and their bioprostheses with the help of scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HREM) confirm our assumptions. Numerous observations of calcificates in heart valves and their bioprostheses and arteries, carried out with the help of SEM, show that deposits do not contain any ordered image similar to bone structure. This can be seen both in the observations of the morphology of calcificates and their cross-section pictures [4].

To explain the results obtained, we carried out modeling *in vitro* of hydroxyapatite formation in blood plasma of a healthy adult person under controlled conditions similar to physiological ones (T=37 °C, pH=7,4). The concentration of physiologically significant fraction — ionized calcium and phosphorus in the aqueous solution corresponded to their concentrations in blood plasma. In addition, we also modeled the process when the concentration of ionized Ñà and P in the aqueous solution exceeds their normal concentration in blood plasma. This condition can correspond to hypercalcinemia and hyperphosphatemia.

It was established that the formation of hydroxyapatite in blood is controlled by the concentration of ionized magnesium and by blood proteins, such as albumin, which is a transport protein. We also substantiate the possibility of subsequent participation of physiological hydroxyapatite, formed in blood plasma, in the construction of bone tissue and in pathological mineralization processes in cardiovascular tissue.

This work was suppoted by RFBR, grant 13–05–00921.

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SYNTHESIS OF SILICON-SUBSTITUTED HYDROXYAPATITE ON TITANIUM SUBSTRATES

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One of the central tasks of implantology is to develop new biomaterials and surface modification implants to ensure their full integration with the relevant body tissues [1]. Currently the leading position of the materials for producing coatings on implants is occupied by calcium phosphate (CP), in particular silicon-substituted hydroxyapatite (Si–HAp), similar in its characteristics to the mineral component of the human bone tissue [2]. It is known that the Si–HAp is a material which has the ability to induce bone growth, namely of inducing the effect of osteoblast differentiation of mesenchymal cells into an osteogenic progenitor direction and angiogenesis. The objective was to study the processes of deposition of Si–HAp synthesized from SBF solution on titanium substrates and the selection of optimal conditions for ceramics based on Si-HAp.

Titan of VT 1–0 was taken as a substrate. Prior to the deposition of Si-Hap on the titanium substrate the substrate was treated in different ways: etching by a mixture of acids HNO_3: HF (1:1); perforated; subjected to laser ablation; without processing. As a medium for Si–HA coating was chosen SBF medium (with a concentration of silicate ions 1.00; 2.50; 5.00 wt.%) .

During the deposition of Si–HAp on titanium substrates it was found that at the beginning, within 3 days, the deposited particles of Si–HAp take the form of titanium rough surfaces (Fig. 1a). Then, after the change of the titanium substrates and the suspension after 3 days of incubation for additional 3 days, the directed crystals grow (Fig. 1b, c), in particular in the form of cylindrical columns, forming the ordered system of crystals above and near the surface of the disordered titanium substrate. After 6 days of the continuous incubation of samples in the slurry Si–HA the crystal growth is observed in the form of dendrites (Fig. 1d) .

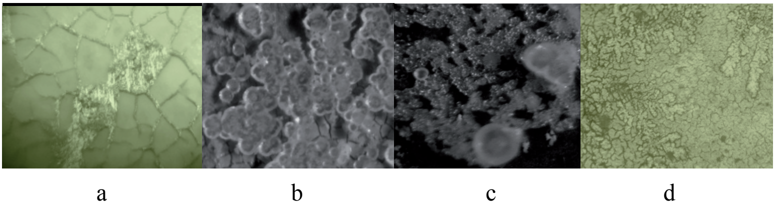

Figure 1 The microstructure of the samples with the addition of silicate ions produced on titanium substrates a, b—is not subjected to the treatment; a, d — etched in a HNO_3: HF

The work was supported by RFBR project (13–05–90432 Ukr_f _à). XRD studies had been performed at the X-ray Diffraction Centre of St.Petersburg State University.

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Section 8
Organic mineralogy

CRYSTAL CHEMISTRY OF NON-EQUIMOLAR DISCRETE COMPOUNDS FORMED IN THE SYSTEM OF MALIC ACID ENANTIOMERS

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Organic compounds composed of enantiomeric molecules (chiral molecules) are abundant in the nature. Being constituents of fossilized remnants, such compounds participate in various geological processes occurring in sedimentation strata. Almost all known amino acids and substantial part of hydroxy acids, enzymes, proteins, etc. are chiral substances.

Singularity of crystal chemistry of such chiral substances consists in specificity of isomorphic miscibility of enantiomeric molecules. In contrast to non-chiral organic compounds, in chiral systems the geometric factor is configuration of a molecule, rather than its shape and dimensions. Detailed crystallochemical study of enantiomers and their mixtures can provide with data useful in understanding the mechanism of a molecule configuration influencing the relationships of solid phases in chiral systems.

A convenient model system for such kind of investigation is one composed of *S*- and *R*-enantiomers of typical dicarboxylic acid, i.e. malic acid, $C_4H_6O_5$. The acid has a chain molecule that contains one asymmetrical carbon atom (chiral center). *S*- and *R*-enantiomers of malic acid in equimolar ratio (1:1) form a binary compound — a true *RS*-racemate, which can take three different polymorph modifications: two known monoclinic RS_{M1} and RS_{M2} and a triclinic modification RS_{Tc}, which was discovered by the present authors [1]. Polymorph diversity of the *RS*-racemate depends upon composition of crystallization medium and crystallization rate [1].

The authors [2] suggested that this system could contain so-called “anomalous racemates” having the enantiomer ratio S: R = 1:3 (3:1). The proposed conclusion was based on the results of DSC study. Later [3] this conclusion was proved to be incorrect.

We have studied molten mixtures formed in the enantiomeric system ($S — R$) and two systems of the enantiomer — racemate type ($S — RS_{M1}$ and

RS_{M2}—R) by means of X-ray diffractometry. In all the systems involved, the ranges of solid solution are rather limited [4]. At the same time, in each one of the systems there were found discrete compounds having the following stoichiometric ratios of the levorotatory and dextrorotatory molecules: S: R = 1:3 and 3:1 [5]. The S — RS_{M1} system was found to form a stable compound of the formula S_3R_1, while the S — R and RS_{M2}—R systems form intermediate metastable phases firstly, which gradually transform themselves into stable compounds of the formulae S_3R_1 and R_3S_1, respectively (designations of the phases are proposed by the authors). Structural model of the S_3R_1 (R_3S_1) compound was also proposed.

The investigations were performed using the equipment of the Saint-Petersburg State University Resource Centers "X-ray diffraction studies" and "Geomodel".

This work is supported by RFBR (projects 10–05–00891 and 10–02–01303) .

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COMPOSITION AND STRUCTURAL FEATURES OF AMBER FROM BEACH PLACERS ON THE EAST COAST OF SAKHALIN, ACCORDING TO IR SPECTROSCOPY

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We studied an extensive collection of amber samples from beach placers, which are located between the estuary of the Najba River and the village of Starodubskoe. Amber originates from erosion of local Paleogene coal deposits. The size of amber pieces ranges from several millimeters to 5–6 cm. Pieces are mostly of irregular form, some pieces are oblate-shaped, disk-shaped or have rounded or drop-like shape. Amber is transparent to opaque, pale yellow to brownish-red or cherry-red, with resino-vitreous or layered texture. Many of the samples are more vivid-colored on the periphery, some pieces are covered with black carbonaceous coatings. IR study have shown that most of amber samples were rumanites while some others were classified as retinite amber. Some samples had zonal structure, with central parts composed of rumanite surrounded by retinite.

The studied amber consisted mainly of saturated hydrocarbons (methyl and methylene groups were detected, which are characteristic for abietic acid). Samples also contained aromatic hydrocarbons and oxygenated compounds. According to prevalence of these minor components, all samples were divided into two classes. In the case of prevalence of aromatic hydrocarbons (absorption peak at 1459 cm^{-1}), IR spectra of the samples also contained intense peaks at 819, 709, and 617 cm^{-1}, which can be accounted for by bending vibrations of C–H bonds in aromatic rings, and a weak absorption band at 1030–1200 cm^{-1}, caused by stretching vibrations of C–O ester groups. Amber from the first class contained cyclohexane (absorption at 1650 cm^{-1}), cyclohexane derivatives (1005 cm^{-1}), and saturated hydrocarbons with a branched chain (1343 cm^{-1}). This amber was also characterized by high content of alcoholic hydroxyl groups (absorption peak at 3460 cm^{-1}) as well as their dimers (absorption peak at 3530 cm^{-1}). Some samples of this class were enriched in ester groups (absorption at 1100–1300 cm^{-1}), and also showed absorption peak at 975 cm^{-1} due to non-planar deformational vibrations of C–H bonds.

Another class of samples was enriched in oxygenated compounds, which prevailed over aromatic hydrocarbons. Samples of this class showed spectra belonging either for ester groups, (absorption peaks at 1722–1725 cm^{-1}) or for carboxyl groups (1698–1705 cm^{-1}). IR spectra of samples with approximately similar contents of ester and carboxyl groups showed low absorption peaks in the range of 1100–1300 cm^{-1} and also in more long-wave region. The second class of samples contained little free hydroxyl groups. Some of the samples, which were enriched in ester groups, in addition to absorption peaks at 1722–1725 cm^{-1} demonstrated an absorption peak at 1230 cm^{-1}. In addition to peaks due to vibrations of ester compounds, absorption peaks were present associated with vibrations of the group $C = C-O-C$ of aromatic ethers (1042 cm^{-1}) and with vibrations of the $C = O$ group, conjugated with a $C = C$ bond in aromatic radical (1635–1648 cm 1). The structure of this type of amber samples showed a significant number of free hydroxyl groups.

SOME FEATURES OF A SULFIDIZATION TRIASSIC AMMONOIDEAS SOUTHERN PRIMORYE

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A study (optical microscopy and the microphotography, scanning electronic microscopy, the X-ray spectral microanalysis, the X-ray diffraction microanalysis and infrared spectroscopy) of fossilized shells of Triassic ammonoideas Ussurijuvenites artyomensis and U. popovi from upper zone Mesohedenstroemia bosphorensis, exposed in the surroundings of Artem (Primorsky Krai), revealed the details of their internal structure and mineral composition, as well as the main features of the skeleton sulfidization of these clams. Walls of covers and septums studied shells are put by dense uniform calcite with aragonite impurity; filling of cameras ammonoideas also from calcit with insignificant impurity of dolomite. Sustainable organic substance contained by the shell wall whorls and septums represent a unique geochemical barrier-membrane, which in the course of sulfatereduced of iron sulfide precipitation occurred. Interaction getting into external and intermediate cameras of shells of cations of iron with, being formed during sulfatreductional process, hydrogen sulfide led to sedimentation on walls of cameras of sulfides of iron. The subsequent partial recrystallization of the formed sulfides of iron led to complication of their morphological variety. The enclosing rocks and external shell's chamber, compounds of Fe^{3+} framboidal form consistently restored to Fe oxide, monoculfide and disulfides of iron. Penetrating into the interior of the shells bivalent iron cations were deposited in the form of xenomorphic discharge of pyrite. Inside siphon, the interior of one of the bowls formed specific pyrite-phosphate mineralization. In shalls of the ammonoideas were established pyrite, mackinawite, greigite, goethite, hydrogoethite, Fe protoxide, Fe–Cu–sulfides, native Fe, Cu, W, Al, cerussite, scheelite and barite. Identified during the research, some regularities in formation of sulfides can be used when reconstructing the conditions in transformation of bottom sediments at the stage of diagenesis recovery.

APPLICATION OF SOME PHYSICAL–CHEMICAL METHODS FOR INVESTIGATION OF BIO-CARBONATIC MATERIAL

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Lithological syngenetic concretions are often found in sedimentary rocks of different geological age formed in various facies conditions. The presence of these formations indicates locally abundant events left their traces at the benthic layer of paleobasins. Now it is demonstrated that this concretions are lithified edifices of bacterial communities that have developed at the area of benthic gas-fluid hydrocarbon seeps. Results of electron paramagnetic resonance analysis (EPR EPR spectrometer PS100.H operating frequency 9.272 GHz) confirmed the fact that microbial activity during their formation was very high. Thus at EPR spectra of dolomite nodules (Upper Permian evaporite deposits P2 kz2, right bank of Volga from Krasnovidovo to Tenishevo, Tatarstan) typical for fossilized protein organic matter (collagen) signals of organic carbon are present. By means of scanning electron microscopy (JSM-6390LV, JEOL; carbon deposition) and energy-dispersive spectrometry (EDS — Inca Energy 450) mineralized fossils of prokaryotes were established in some concretions. Also these specific nodules are characterized by the presence of dolomite crystals morphologically differ of their chemogenic analogues from enclosing rocks with rhombohedral habit. Their shapes may be cubic, spherical and multilobe.

The most impressive evidence of the bacteria involvement in the formation of nodules and specific crystal are our laboratory experiments for bacterial reproduction of secondary calcite analog formations in caves. The experiment was conducted on the basis of the cave Shulgan-Tash (Republic of Bashkortostan). As seed crystals were used needle-fibre calcite, lacustrine calcite aggregates and soil with gypsum crystals. Petri dishes were infected with direct bacterial inoculation. In a month on nutrient solution containing $CaCl_2$–3.3 g/l (with succine acid 3.54 g /l and agar 15 g/l as carbon sources) formation of micronodules and crystals with specific cubic morphology was observed. By XRD diffraction (diffractometer Shimadzu XRD-6000, CuKα) was established that neogenic material is presented by calcite and from nutrient solution containing $MgSO_4$ (0.2 g / l) aggregates of magnesian calcite were formed. For the latter mineral unit cell parameters were calculated: a = 4.9808 Å, c = 17.0295 Å, V = 365.8806 Å3. These values are in good agreement with published data obtained for biogenic magnesian calcite with a low content of Mg [1, 2]. At some SEM images we can see stages of consecutive bacterial overgrowth of a cubic crystal and micronodule formation. Summarizing we can say that with the help of various physical methods and experimental data bacterial genesis of carbonate concretions was proved.

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COMPOSITIONAL AND THERMAL DEFORMATIONS OF CRYSTAL STRUCTURE OF SOLID SOLUTIONS IN THE L-THREONINE — L-ALLO-THREONINE SYSTEM

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Threonine is one of the 20 essential amino acids that are, except for glycine, optically active due to the presence of asymmetric carbon, i.e. a chiral center, in their molecules. Threonine belongs to essential amino acid, since it cannot be produced in a human body. As to its structure, threonine (Thr) has not only one, but two chiral centers, and consequently can form four stereoisomers: L-Thr and D-Thr (one pair of enantiomers), and L-*allo*-Thr and D-*allo*-Thr (another pair of enantiomers). Each representative of the first pair is a diastereomer for each representative of the second pair, and vice versa, each representative of the second pair is a diastereomer for each representative of the first pair. Diastereomeric molecules in the L-Thr — L-*allo*-Thr pair are characterized by *the same* sign of optical activity, while the optical sign of the diastereomers in the D-Thr — D-*allo*-Thr pair does no coincide with that of the above pair, but is *the same* for the latter pair. Similar to the enantiomer molecules, molecules of the diastereomers in the other two pairs, viz. L-Thr — D-*allo*-Thr and D-Thr — L-*allo*-Thr, possess *different* optical signs.

We have studied the influence of a molecule configuration and its optical sign upon the ability of the molecule to form solid solutions in two enantiomeric and four diastereomeric systems of threonine. The present work summarizes the results obtained via investigating the diastereomers and their co-precipitated mixtures of the L-Thr — L-*allo*-Thr system by means of X-ray diffraction, and temperature resolved XRPD, as well as by means of single crystal XRD. The system selected can serve as a model to study features of solid solution formation in chiral organic systems. Understanding of features of solid solutions formation can be helpful in solving two mutually exclusive tasks: one consists in separation of solid solutions, and the other involves preparation or tailored synthesis of such solid solutions. Solving the first-mentioned task is a primary objective of pharmacy and medical science, when some levorotary and dextrorotary enantiomers possess different pharmacological effects. The second mentioned objective is important for creating crystalline materials with tailored properties on the base of chiral substances.

It was found that the diastereomeric system of L-Thr — L-*allo*-Thr is a system containing continuous solid solutions. This makes the L-Thr — L-*allo*-Thr system (and, correspondingly, D-Thr — D-*allo*-Thr system) principally different from eutectic systems (enantiomeric and other diastereomeric systems). Comparing the crystal structures of the L-Thr and L-*allo*-Thr diastereomers and their solid solutions showed that the distances between methyl groups of the neighbor molecules depended to a great extent upon a crystal composition, while the lengths of hydrogen bonds did not differ significantly. The concept of *compositional* and *thermal* deformations was formed based upon the results of analyzing the correlation of the orthorhombic cell parameters with compositions and temperatures of the samples. Comparative analysis of the said deformations was also performed.

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