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BIOGENIC — ABIOGENIC INTERACTIONS

in natural and anthropogenic systems

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The book of abstracts contains materials of VII International Symposium “Biogenic - abiogenic interactions in natural and anthropogenic systems” (September 26-29, 2022) devoted to the discussion of fundamental and applied aspects of interactions between biogenic and abiogenic components in lithosphere, biosphere and technosphere. The Symposium is traditionally interdisciplinary and is attended by experts in the fields of Earth sciences, biology, soil science, materials science, chemistry, environmental protection and the preservation of cultural heritage. Organizers of the symposium are Saint-Petersburg State University, Saint Petersburg Society of Naturalists and Russian Mineralogical Society.

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Content

The **Russian Mineralogical Society**,

being a part of the International Mineralogical Association, celebrates **2022 – the Year of Mineralogy**. 2022 is the bicentennial of the death of René Just Haüy (born 1743) who is a father of modern crystallography and mineralogy. 1822 is also when Haüy's *Traité de minéralogy* and *Traité de cristallographie* were published. Mineralogy is one of the oldest branches of science, and it plays a key role in our everyday lives.

VII International Symposium "Biogenic - abiogenic interactions in natural and anthropogenic systems" joins the worldwide celebration highlighting an importance of interactions between biogenic and abiogenic components in a lithosphere, biosphere and technosphere in the development of modern science and technology.

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Plenary Session

TRANSFORMATION PROCESSES OF MINERALOGICAL COMPOSITION OF EAST EUROPEAN PLAIN STEPPE SOILS CAUSED BY BIOCLIMATIC INTERACTION IN THE CONTEXT OF GLOBAL CLIMATE CHANGE

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The study of changes in soil properties depending on the dynamics of bioclimatic conditions is one of the main tasks of modern soil science. Modern landscapes of the steppe zone of the European part of Russia reflect a long history of natural evolution, which was characterized by complexity and dynamism due to changes in natural conditions and the increasing impact of anthropogenic factors. Detailed mineralogical and geochemical analyses of East European plain steppe soils and Holocene paleosols were carried out in order to carry out paleoclimatic reconstructions, as well as to expand knowledge about solid-phase residual products of the soil system formed as a result of the evolutionary development of soils. The bulk samples and clay fractions of modern soils were analyzed by XRD, XRF, Mossbauer spectroscopy. The clay-organic-complexes by FTIR and solid-state ^{13}C NMR spectroscopy. The clay mineralogy of soils demonstrates the relationship to climate conditions (illite/chlorite and illite/smectite ratios). The state of iron in the clay fraction stores an information about the intensity of mineralogical transformations by the soil-forming process in connection with the climatic gradient – (Fe^{2+} /Fe $^{3+}$) in the structure of silicates, as well as the ratio of goethite/hematite. Ultrafine ferrimagnets (magnetite and maghemite) determined in buried soils by a complex of magnetic measurements were formed by in situ precipitation in a course of soil formation. To compare the intensity of transformation of parent material for soils under study in a course of pedogenesis the (Fe^{2+}_C – Fe^{2+}_A) / Fe^{2+}_C ratio was used. The analysis of valent state of iron in silicates of the studied modern soils of a steppe zone and changes in their magnetic properties testify the in-situ transformations of iron in a course of soil formation. The magnetism/climate and geochemistry/climate functions gained from the modern soils may be applied to the archaeological buried soils, to obtain climate reconstructions for the time at which buried soils were formed. Considerable changes in the clay and iron oxide mineralogy, molar chemical ratios of the soils permit us to assess the rates of the mineralogical transformations caused by the bioclimatic dynamics in the interval of the last 5000 years. Clay mineralogy of buried soils sensibly reflects the intensity and trends of soil formation. Being also the source of information about the preservation of soil profile (denudation, other types of disturbance like ploughing of the mound or rodents` activity), it allows to contribute to the correct reconstructions of paleoenvironment. Significant changes in the pedogenic magnetic properties, clay mineralogy of the A and B horizons

suggest a mineralogical response time of < ~100 yr. with regard to changes in soil-forming climate. A change in soil mineralogy and as a consequence the transformation of the chemical composition of the buried soils testifies the primary importance of climate factors in comparison with the total duration of the weathering process. The reaction of steppe ecosystems in the south of the European part of Russia to multi-scale climate changes in the past can be used as a basis for assessing the trend of upcoming restructuring in the state of natural and agro-landscapes of the steppe zone.

Acknowledgments: This study was supported by the RFBR (Grant No. 19-29-05178).

PATTERNS OF MINERAL ORGANIZATION IN EPS-HYDROGEL-CALCITE COMPOSITE AGGREGATES: BIOSIGNATURES OF AEROBIC AND ANAEROBIC BACTERIAL AND ALGAL EXTRACELLULAR POLYMERIC SUBSTANCE (EPS)

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Biologically secreted structural materials, such as shells, teeth and bones, are composites of biopolymers and minerals. The incorporated biopolymers exert a strong influence on mineral organization of these structural materials. The effect of biopolymers can be mimicked to some extent by hydrogels. Structural and chemical characteristics of hydrogels can be tailored such that some resemble characteristics of biopolymer matrices within the biologically secreted structural composites. However, commercially available hydrogels are denaturalized, synthetic, compounds and lack many attributes of native biopolymers. In contrast, extracellular-polymeric-substance (EPS) biopolymers are actively secreted by bacteria and algae. EPS protects bacterial/algal cells and enhances the physiological activities of the organisms.

Bacteria and algae inhabit almost every environment within the upper parts of the Earth's crust. When associated with surfaces, the microorganisms secrete a mucilaginous matrix and form a biofilm. Biofilms consist of communities of bacterial/algal cells and the surrounding extracellular

polymeric substance (EPS). The latter is a pliant matrix that structures, stabilizes and protects the biofilm community. EPS occurs in many physical states, as a cohesive gel or/and a dissolved, colloidal, substance. The gel state is present when the EPS encases the bacterial/algal cell. Dissolved, colloidal, states prevail in outer, hydrated, layers of the EPS matrix.

For testing the influence of native biopolymers (EPS) on mineralization and mineral organization, we synthesized EPS-agarose-calcite composites with aerobic and anaerobic bacterial and algal EPS. Crystallization experiments were carried out in a single-diffusion hydrogel system. We investigated the influence of the polymeric substance on (i) EPS-mineral composite formation, (ii) aggregate shape and size generation and (iii) mineral organization in the composite material. We explored the effect of the EPS of (i) aerobic bacteria: *Bacillus subtilis*, *Mycobacterium phley*, *Mycobacterium smagmatis*, *Pseudomonas putida*, as well as of (ii) anaerobic bacteria: *Methanocaldococcus jannaschii* and the influence of the EPS of the (iii) microalgae, the diatom, *Chaetoceros socialis*.

Composite aggregate formation was conducted for two conditions: (i) with bacteria/alga living and actively producing EPS at composite growth and (ii) bacteria/alga cells being killed prior to growth experiments. Hence, in the latter state not producing EPS during composite growth. Composite aggregate characterization occured with with FTIR, FE-SEM-imaging of variously prepared aggregate surfaces and electron backscatter diffraction (EBSD).

We observe:

(i) a difference in influence for composite aggregate formation and mineral organization between bacterial and algal EPS.

(ii) For bacteria we see differences in mineral assembly for the different bacterial communities.

(iii) We observe a difference in aggregate shape, size and calcite organization for experiments carried out with bacteria and alga living or being dead in the course of the growth experiments. Accordingly, bacterial and algal EPSs not only exert a major influence on crystal nucleation and mineral growth; there is also diversity in their influence on composite aggregate formation.

Our study documents that the influence of bacterial/algal EPS on mineralization and mineral organization is not at all as small as so far thought (Yin et al. 2020a, 2020b). In addition, bacterial/algal EPS changes mineral-microstructure/texture in a manner specific to the biologic species forming the EPS. This is a characteristic that, when developed further, can be used as an identification tool for bacterial-calcification in present/past environments (Yin et al. 2020a, 2020b).

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AN INTEGRATED APPROACH TO THE STUDY OF BIOMINERAL INTERACTIONS IN BIOFILMS ON THE STONE SURFACE

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In recent decades, the world scientific community has shown significant interest in the mechanisms of biomineralization with the participation of microorganisms (microscopic fungi, bacteria, lichens). In addition to the fundamental interest associated with the study of the role of bioinert interactions in modern mineral formation at the nano- and microlevels, these studies are stimulate t the development of modern nature-like biotechnologies, such as the detoxification of heavy metals in various media, oil refining, and the healing of microcracks in concrete building structures and cultural heritage sites. The experience of many years of creative collaboration between crystallographers and biologists of St. Petersburg State University alloed propose a comprehensive interdisciplinary approach to the study of biomineral interactions in biofilms on the stone surface and to make a significant breakthrough in the study of microbial biomineralization**.**

The work was carried out in field and laboratory conditionsıo Syntheses of biofilm mineral analogs with the participation of monocultures of fungi and bacteria, as well as their associations (bioinspired syntheses) were carried out in liquid nutrient media (Chapek-Doksa and others) with different glucose content and under oligotrophic conditions of a humid chamber. In the humid chamber, the biomineralization conditions were close to natural, but the process was very slow. In a liquid medium, crystallization occurred much faster than in nature, but it was possible to reproduce it at later stages. Microorganisms were planted on pieces of rocks and minerals of various compositions and densities (carbonates, silicates, phosphates, oxides, sulfides, etc.). The selection of strains of fungi and bacteria was carried out according to the results of a preliminary study of the products of their metabolism by chromato-mass spectrometry. Preference was given to oxalic acid-producing fungi and EPS-producing bacteria, and their associations. In addition, to identify the effect of organic and inorganic components of biofouling on the formation of biominerals and their morphology, model experiments were carried out in

systems with organic and inorganic additives typical of biofilms containing fungi (classical syntheses). The results of these syntheses in many cases made it possible to explain the morphogenetic regularities of biomineralization , revealed on the basis of the study of minerals in biofilms and products of bioinspired syntheses.

The results obtained using the proposed approach [1-3] allowed significant progress in the study of the mechanisms of oxalate and carbonate biomineralization and also contributed to the creation of a scientific basis for the development of effective environmentally friendly and economical biotechnologies.

The work was supported by the Russian Science Foundation grant 19-17-00141 on the basis of St. Petersburg State University resource centers: RDMI, MIM, Geomodel, RMCT, Nanotechnologies, OLMIV.

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ION BEAM IRRADIATION/IMPLANTATION ON POLYMER-BIOCERAMIC COMPOSITES

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Hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$, HAp] the most stable phase of calcium phosphate is structurally similar to the mineral component of bones. HAp exhibits good biocompatibility, bioactivity and osteoconductivity, rendering it ideal for bone and dental replacement applications. It is used in various forms like powders, foam, granules, dense and porous blocks, coating on metallic substrates, composite, cement etc. HAp coated on metal substrates is used for load bearing application enhancing its biocompatibility, bioactivity and osteoconductivity. It has very good mechanical properties and low binding ability with living cell. The surface properties of implant materials, such as

surface roughness, chemical composition, electrical charge, porosity and wettability play an important role in binding with living cells. To tolerate the corrosive environment of the human body and to control the dissolution rate, surface modifications of the implant materials is being employed. The ion implantation and irradiation of the implant can change the properties of the surface in a controllable way without impairing the bulk characteristics. The nano-scale changes in surface like grain size distribution, charge distribution is known to influence the biological performance of the biomaterial. Further, the porosities produced would help in the flow body fluids, bone tissue growth coupled with good biocompatibility.

Here a discussion on the irradiation studies using swift heavy oxygen, gold, silver ions and silicon ions, low energy nitrogen ion implantation and gamma irradiation on HAp -biopolymer composites will be presented. HAp synthesized (powders, films and scaffolds) by various routes such as microwave, hydrothermal, sol-gel was subjected to irradiation/implantation at different fluences. It was seen that the method of preparation of the samples influenced the surface modification in a significant way. The surface was modified with the formation of the nano particles and pores along with enhanced surface roughness. The irradiated surface turned hydrophobic at lower fluence and at higher fluence it became hydrophilic. The irradiation significantly enhanced the surface stiffness of the composites. The irradiation drastically increased the intensity of photoluminescence on irradiation in the samples. The Au ion irradiation tailors surface roughness, contact angle, antibacterial activity and cell proliferation. Low energy nitrogen ions were implanted on composite coatings. At the higher fluence, core/shell morphology was observed whereas, at the lower fluence, plates-like structures were noticed. The porosity of the samples could be engineered by implantation of nitrogen ions. The implantation of the bioceramics with low energy ions could be used to modify the surface and tailor the properties such as electrical, photoluminescence, protein absorption and bioactivity of the biomedical implants. Superhydrophilic surface turned hydrophobic on implantation. The corrosion potential significantly enhanced at higher fluence. The samples exhibited enhanced drug delivering and bioactive properties. The gamma-irradiated magnetic composite films revealed enhanced magnetic properties. Moreover, the contact angle was increased rendering them hydrophobic. Antimicrobial properties of drug loaded irradiated samples were increased. Further, cytocompatibility tests revealed enhanced cell proliferation. The irradiated/implanted composite films possessed multifunctional properties which could be made use of in various biomedical applications.

CRYSTAL CHEMICAL SYSTEMATICS OF DISCRETE COMPOUNDS FORMED IN CHIRAL SYSTEMS OF ORGANIC ACIDS

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The molecules of many organic substances are chiral, i.e. they exist in the form of left L and right D enantiomers. In the literature, one can find many different designations of discrete phases formed in binary systems of organic substances with chiral molecules: racemates, true racemates, false conglomerates, pseudoracemates, quasiracemates, anomalous racemates, anomalous quasiracemates, anomalous conglomerates, anticonglomerates, cocrystals, complexes 1:1 and etc. These designations are not self-sufficient, since they do not give an idea of what compounds are meant by each of the listed designations. Due to the multitude of non-obvious terms and the absence in the literature of a unified approach to the systematics and terminology of discrete compounds with chiral molecules, we have proposed a systematics of equimolar and non-equimolar discrete organic compounds formed in chiral binary systems of one substance (homomolecular compounds, or homocompounds) and in binary systems of different substances (heteromolecular compounds, or heterocompounds).

Systematics is presented in the form of a table. In the case of equimolar homocompounds, rubrics are introduced: symmetrically bound molecules and symmetrically unbound molecules, and in the case of non-equimolar homocompounds, rubrics are introduced: disordered positions of molecules and ordered positions of molecules. In turn, in the case of equimolar heterocompounds, rubrics are introduced: molecules of different substances of different chirality and molecules of different substances of the same chirality, and in the case of non-equimolar heterocompounds, rubrics are introduced: different chirality for molecules of different substances and the same chirality for molecules of different substances. Each section of the table is accompanied by examples. The features of the crystal structure of chiral compounds are considered on the example of the amino acids studied by us. In this regard, the concepts of eponymous and dissimilar molecular dimers of amino acid heterounits are also introduced and the relationship between the type of dimer and the structure of the radical and the conformation of the heterounit molecule is established.

The experimental part was performed in the Research Center of X-ray diffraction Studies of Saint-Petersburg State University. This work was supported by the President of Russian Federation Grant to leading scientific schools NSh-1462.2022.1.5.

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GEOCHEMISTRY OF CULTURAL LAYER AT THE ARCHAEOLOGICAL SITES IN THE CONTEXT OF BIOGENIC-ABIOGENIC SYSTEM.

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The cultural layer development at the archaeological sites is processed in the framework of a biogenic-abiogenic system of the Earth, including natural and historical formations, that occurred in certain geochemical conditions as a result of an evolution of the physical and geographical environment in participants of living organisms. Such a natural-anthropogenic system combining natural components and components of life-activity of prehistorical people possesses homeostatic properties and mechanisms, self-regulating capacities that provide the formation of a substrate of the cultural layer as a result of biogenic system functioning. According to Kamenezky (1970), the cultural layer includes both an anthropogenic component – artefacts, constructions, prints, specific features of chemical composition and natural components inherited from soils and deposits of different genesis or "filler" in the terms of archaeology. Thus, the cultural layer is the product of a biogenic process and could be characterized by a certain geochemical composition including anthropogenic compounds. This composition has differences as well in lithological deposits (abiogenic) as soils (biogenic) systems which were formed outside of the archaeological site.

The geochemical characteristics of the cultural layers were studied for the archaeological sites from the Paleolithic to the Medieval Ages (Eliseevichi, Yudinovo, Serteya, Okhta, Podolye, Tarkhankhut, Niemelyankhovi, Arzhan 2 sites etc.), located in the different landscape zones at Eastern Europe and Southern Siberia. There have been determined the main geochemical characteristics of the cultural layer.

Abnormal concentrations of such association of components (P_2O_{5antr}, CaO_{antr} and Sr_{anthr}) in sediments are attributed to zones of accumulation of bone remains. Such kind functional zones can be connected with animal dressing zone, burial, ritual zone, waste pits etc. Anomalous concentrations of a group of elements (K_2O_{anthr}, Rb_{anthr}) at archaeological sites in the cultural layers are associated with wood ash residues and fireplaces, ash residues from ritual activities, and fires. The group of elements (Ba, MnO, C_{org}) reflects the

accumulation of humus, and organic residues and can characterize areas with food residues, remains of skins, and rotten wood. Combinations of the main groups of elements may also indicate various other types of functional zones, both living zones, household areas, and places of ritual purposes. Thus, it is possible to note the main associations of anthropogenic elements in sediments at archaeological sites that characterize certain functional zones in the framework of the biogenic-abiogenic system of the cultural layer.

This research was funded by RSF, project No. 22-18-00065 "*Cultural and historical processes and paleoenvironment in the Late Bronze-Early Iron Age of the North-Western Black Sea region: interdisciplinary approach"* and the project with financial support from the Ministry of Education of the Russian Federation under program No. FSZN-2020-0016.

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ROTALIID FORAMINIFERAL CALCITE: MESOCRYSTAL ARCHITECTURE, DENDRITIC MICROSTRUCTURE, AND TEXTURE

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Foraminifera belong to the main producers of calcium carbonate in the oceans. Their shells consist of subsequent chambers with mineralized walls. We investigate the crystal architectures and microstructures of all foraminiferal groups by scanning electron microscopy (SEM) and electron back scatter diffraction (EBSD). Compared to other marine organisms, foraminiferal shell mineralization is unique. The mineralization of a new chamber begins with the formation of the primary organic sheet membrane (POS), which is a rhizopodial network of organic matrix. The mineral nucleates within the POS and crystal growth occurs in both perpendicular directions relative to the POS within a lamellipodial organic matrix[1]. Crystal morphology and microstructure are different for the layers formed inside and outside of the POS. The resulting microstructure are diverse for the different groups of foraminifera.

In rotaliid foraminiferal shells the crystals units (calcium carbonate solid matter through which the crystallographic lattice is coherent or semicoherent) are mesocrystals composed of sheaf-like bundles of nanoscale calcite fibers[2] (Fig. 1). The calcite nanofibrils grow perpendicular to the POS towards the outside of the shell. They are crystallographically co-oriented (Fig. 2) within the sheaf-like bundles3. The 200 to 500nm long fibrils have a thickness between 30 and 100 nm. The sheaf-like fiber-bundles form microscale crystal units with dendritic-fractal morphologies. The dendrites interdigitate strongly with abutting dendritic crystal units3 (Figs. 2, 3).

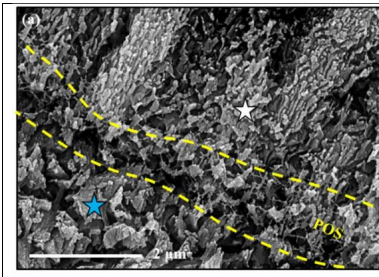

Fig. 1 SEM micrographs of polished and slightly etched shell of the rotaliid foraminifera *Amphistegina lessonii*. (a) Fibrous (white star) and blocky (blue star) calcite layers near the primary organic sheet (POS). (b) Detail showing the calcite nanofibers.

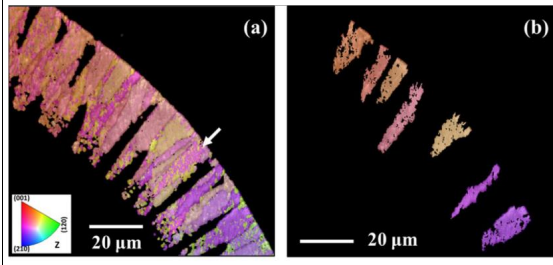

Fig. 2 (a) EBSD orientation map of a shell wall. Color codes for crystallographic orientation. In (b) some individual sheaf-like crystal units composed of fibers as in Fig. 1 are highlighted. The white arrow points to a twinned crystal unit.

The microstructure of the assembly of abutting dendritic crystal units shows an axial texture, i.e. the c-axes are co-aligned and perpendicular to the POS (or the shell vault) within ca. 15-20° orientational spread, while the a-axis directions scatter much more strongly between neighboring units. Based on overall size of the crystal units we differentiate several layers of material. Crystal units in the septa show different nanoscale architecture relative to those in the shell walls.

The most striking and unique feature of the calcite of the order foraminiferal order Rotaliida is extensive formation of growth twins (Fig. 3) with a typical spatial density of about one twin wall every two micrometers; there are regions with up to 2 twin walls per micrometer. We find two twinning

modes: (i) the 60°roation around [001], i.e. the (001) reflection twin that is also known for inorganic calcite, and (ii) the irregular but frequently reoccurring 77° rotation around ~[6 –6 1] orientation relationship (indexing refers to the hexagonal setting of calcite unit cell.). To our present knowledge the latter can only be explained by a regular array of dislocations giving a small-angle deviation from a rational twin relationship.

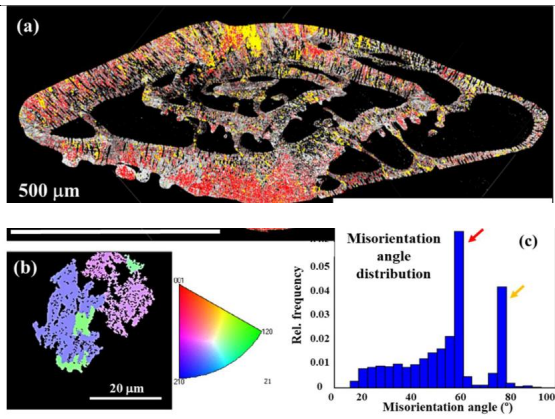

Fig. 3 (a) Distribution of 60° (red) and 77° (yellow) twin walls *over the shell of species P. obliquiloculata*. (b) highlights three fractal crystal units, where color codes for crystal orientation, blue/green are 60° twinned, green/purple are 77° twinned. (c) shows the overall misorientation distribution highlighting the preference for the two twinning modes.

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EXPLORING PRINCIPLES OF AGGREGATION BETWEEN ORGANIC AND MINERAL PHASES ON ICE: INSIGHTS FROM CRYOCONITE GRANULES OF TWO MOUNTAIN GLACIERS

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The glaciological history of Earth spans at least 2.9 billion years as evidenced by diamictites of the Kaapvaal craton in South Africa. Assemblages of mineral and organic species might have been already in place on ice, when subaerial surfaces massively turned into supraglacial during major cooling events

like the Huronian glaciation (2.4-2.2 Ga) or the Cryogenian (0.72-0.64 Ga). Microbe-dominated cryoconite granules (Takeuchi et al., 2010) largely studied today are among the best available analogues to approximate early principles of aggregation between minerals and living organisms on ice. Their aggregates could have synergized dark-colored matter affecting energy balance and biogeochemistry of glaciers in ancient times, as it is now. Recent fine-scale measurements revealed a functional heterogeneity of microbial communities inside cryoconite granules including redox stratification linked to the complex internal structure of granular aggregates (Segawa et al., 2020). Here we employ light microscopy, X-ray microtomography, SEM-EDS with MAPS Mineralogy and Raman spectroscopy to explore physical structure and distribution of mineral and organic phases within cryoconite granules from two mountain glaciers: Leviy Aktru (LA), Altay and Garabashi (GB), Caucasus. Despite different size of LA mesogranules (2-6 mm) and GB microgranules (0.1-1 mm) their void space had similar structure and total porosity in the range of 15-16%. The share of connected pores in both types of granules was high and stable (88-89%). LA pore sizes were within 10-220 μm (30-110 μm most frequent) and GB pore sizes – 10-60 μm (14-38 μm most frequent), with larger pores attributed to the granules core in both cases. Granules often had an embryonic grain represented by a single mineral or a rock fragment and a compacted layer at the periphery. LA mesogranules comprised smaller subgranules. Our dataset suggests phyllosilicates (smectite, kaolinite, chlorite, micas) as an important component of granules physical stability along with the previously widely acknowledged role of extracellular polymeric substances (EPS) and filamentous cyanobacteria. The highest concentration of silty and clay particles (up to 31.6% smectites in GB) occurred at the periphery of granules. They were densely packed in the granule wall subparallel to its outer surface. SEM suggests fine multilayer structure of phyllosilicate clusters within granules wall: up to 18 layers in GB microgranules and >50 layers in LA mesogranules. Phyllosilicate clusters were always interlayered with amorphous C-rich cement originating from EPS. According to the multispectral Raman imaging, the clusters of methyl functional groups ($–CH_3$) were confined to the walls of granules suggesting hydrophobic properties on the surface important for stability of cryoconite microecosystem in meltwater. Consistent outer shell was crucial and complex component of the whole granular microecosystem that sustained inner core and created temporally stable environment for transformation of organic matter instantly inside the aggregate. Combination of physical and chemical stabilization mechanisms in cryoconite granules was reminiscent of microaggregates in complex colloidal systems, e.g., soils. Basic principles of biota-to-mineral aggregation exhibited in modern cryoconite granules of microbial origin suggest similar assemblages could have existed on glaciers earlier in Earth history. If true, environment inside granules provided specific soil-like conditions for biogeochemical cycling alternative to the rest of supraglacial area, especially when ice was a dominant and long-living setting on Earth.

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NON-EQUILIBRIUM CHARGE DISTRIBUTION, ENERGY CONVERSION AND SPATIOTEMPORAL CHANGES IN THE NANOSTRUCTURE OF BONE TISSUE

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Bone is the most complex nanostructured and hierarchically organized matter in nature. We show that bone is also an efficient energy material. Energy storage and accumulation occurs in the nanostructure of mineralized bone. The mineral matrix is composed from coplanar and/or mosaic conglomerates of hydroxyl apatite (HAP) nanocrystallites. HAP (Ca10(PO4)6(OH)2) is the wide-band-gap insulator with strong ionic conductivity associated with the high mobility of hydroxyl ions. The HAP crystallites are separated by hydrated nanolayers with saturated aqueous solution.

The systematic X-ray diffraction, X-ray photoemission, Raman and IR spectroscopic studies of (i) cortical bone of healthy newborn, adult and mature rats and (ii) human femur and tibia in intact and osteoarthritis damaged areas in knee department were carried out. Comparison of the experimental data makes evident the systematic spatiotemporal changes in the atomic-molecular architecture of bone structures. Our main attention is on the distinct deviations in core-electron binding energies, lattice constants of HAP crystal cells, degrees of crystallinity, linear size of crystallites, and Ca-to-P ratios. Their systematic analysis leads to the conclusion that (i) HAP crystallites are negatively charged fractions and intercrystallite water is a positively charged medium and (ii) the mineral matrix is a kind of electric battery, composed from a huge number of nanometric cells. They are most strongly charged in a young bone and discharge with age. The electrostatic energy density is about ≈0.7 eV per cell (≈120 nm3) in young bone and ≈0.1eV per cell (≈170 nm3) in mature bone. The origin of the electric charge is due to the low stoichiometry of HAP crystallites. The counter currents of Ca2+ and OH- ions are responsible for charge dissipation in bone.

New physical insight on nanoenergy and age-related changes in the nanostructure of bone is discussed. We believe that these results will contribute to the further development of (i) the concept of active longevity and improving the quality of life, (ii) new methods of medical imaging at the subcellular level, and (iii) novel fusion technologies for assembling environmentally friendly materials for the accumulation and conversion of electrical energy.

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INFLUENCE OF IRON OXIDE NANOPARTICLES ON VEGETABLE CROPS

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Nanoparticles (NPs) including magnetic FeO_x NPs draw much attention from researchers lately. One of the promising research directions is their use in agriculture. In comparison with traditional microfertilizers, NPs can be used in lesser quantities to achieve the same agronomic effect with reduced environmental stress. The present study was devoted to the synthesis of magnetic NPs of iron oxides with the certain phase composition (magnetite, maghemite) and the assessment of their impact on the growth and development of important vegetable crops (cucumber, lettuce, watercress, tomato).

NPs of the maghemite-magnetite series, differing in their phase composition, textural characteristics, size, and shape owing to the use of various synthesis procedures have been prepared [1-3]. The resulting NPs were magnetite-maghemite solid solutions with different contents of Fe(II) and Fe(III), with a particle size of 5–40 nm [2,3]. The synthesis procedure influenced both on the size and shape of the NPs (spherical or plate-like). They were prone to aggregation, regardless of the synthesis procedure, and formed nanopowders with a specific surface area in the range of 52-92 m^2/g, with cylindrical or slit-like pores. For use in agriculture, nanopowders were mixed with water. Water suspensions of these NPs were stable enough and could last up to 4 months. Iron oxide micelles in water had diameter ~140-650 nm [3].

In a series of lab- and vegetation's experiments under controlled conditions of intensive light culture, it was found that aqueous suspensions of this NPs at concentrations of 0.01 and 0.001 mg/l have the most pronounced stimulating effect on plant growth rates, both after treatment of plants seeds on the example of watercress and with plants foliar treatment on the example of cucumber, lettuce and tomato plants during the vegetative period of their development [1,3,4]. So, for example the revealed significant effect of the ratio of Fe(II) and Fe(III) atoms in solid solutions of the maghemite-magnetite series and modifier (oleic acid) on the increase in the leaf area, length, weight and number of fruits on cucumber plant as a result of foliar treatment. Stimulation of the growth of abovementioned plants under the influence of the FeO_x NPs was mainly due to an increase in the processes of metabolism and the supply of nutrients necessary for plants to the aerial part, as well as due to the activation of the synthesis of photosynthetic pigments - chlorophylls. Ultimately, these positive changes in the indicators of the plants physiological state, treated with aqueous suspensions of this NPs, lead to the formation of higher yields of high quality plant production compared to those in the control. So, in the composition of tomatoes and cucumbers production the increase in the content

of sugars, vitamin C, the content of macro- and microelements, and a predominant decrease in the content of nitrates was noted. The obtained data indicate the prospects for further studies of the mechanisms of the iron oxide nanoparticles effect on plants in order to create highly effective nanopreparations and technologies for their use in crop production.

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A MATTER OF DIET: CRACKING THE STRUCTURAL, MORPHOGENETIC AND FUNCTIONAL BASIS OF DENTAL HARD TISSUES IN CICHLID FISHES

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The formation of hierarchical apatite-organic based hard tissues of vertebrates is evolutionary optimized and exhibits high structural complexity on various length scales and amazing mechanical performance. In my presentation I will focus on the detailed characterization of morphology-structure-composition-property relationships of hard tissues of feeding apparatus of Cichlid fishes. We elaborate and combine an exciting evolutionary model system with cutting-edge spectroscopy, microscopy, diffraction and mechanical testing techniques to analyze structural, chemical and genetic basis of biomineralization process of dental hard tissues of cichlid fishes with different diet specialization (so called “insect eaters” and “snail-crushers”, “soft” and “hard” food specialist, respectively). Multiscale structural characterization and mechanical testing reveal that exceptionally robust teeth of “snail-crushers” have evolved several strategies to co-optimize the composition and structure of enameloid on different hierarchical levels. We foresee, that our new understanding of tooth structure and morphogenesis in cichlids could also advance strategies for synthesizing bioinsipred materials for biomedical application.

BIOMINERAL INTERACTIONS ON THE SURFACE OF ROCK ART MONUMENTS ALONG THE BANKS OF THE TOM RIVER

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There are many unique monuments of rock art in Southern Siberia. They reflect the ancient history of the peoples inhabiting this territory. The preservation of archaeological sites is an important task and requires an interaction of scientists. A significant number of ancient drawings are found on rocky outcrops along the banks of the Tom river (Kemerovo region). The most famous archaeological sites are located on the territory of the Museum-Reserve "Tomskaya Pisanitsa", where we have been conducting stationary observations of the processes of biofouling of petroglyphs since 2014.

Cyanobacteria, algae, fungi, and lichens form the complicated lithobiont communities (biofilms) on the surface of rock surface with petroglyphs. They can cause a noticeable change in the stone material due to the biophysical and biochemical effects on the substrate. In many cases, the development of biofilms is accompanied by damage to petroglyphs. At the same time, the degree of destructive impact of biofilms depends on the composition of the lithobiont community, the state of the rock with petroglyphs, the features of applying the petroglyphs themselves, as well as environmental conditions. In this work, the task was to study the composition and structure of lithobiont communities and their influence on the archaeological sites of the "Tomskaya Pisanitsa".

The complex of research methods included mycological and bacteriological analyzes, gas chromatography-mass spectrometry, X-ray phase analysis, petrographic analysis, light and scanning electron microscopy, as well as modeling of lithobiont systems.

As a result, the composition of bacteria, lichens, and microscopic fungi was studied in the places of ancient drawings at the archaeological site of "Tomskaya Pisanitsa". The confinement of biological objects to certain zones of damage to the stone material, as well as to crust-like formations, is shown. It is revealed that the development of microorganisms is associated with the formation of carbonates and oxalates on the stone surface. In the thalli of lichens, calcium oxalates (wavellite and weddellite) were found. Biofilms dominated by cyanobacteria were found in places of carbonate layers. Studies of calcified crusts using scanning electron microscopy have shown that some of them are formed by filamentous and coccoid forms of cyanobacteria and are covered with calcite crystals. Their cultivation under laboratory conditions

showed a tendency to redeposit calcite.

Thus, biofouling of petroglyphs is characterized by a significant diversity and different mechanisms of impact on stone material, which must be taken into account when deciding on the preservation of rock art monuments.

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MEDICAL GEOLOGY:STATUS AND PROSPECTS OF THE SCIENCE

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In the year 1996 the International Union of Geological Sciences approved formation of an “International Working Group on Medical Geology” (IWGMG), under its Commission on Geosciences for Environmental Planning (COGEOENVIRONMENT). IWGMG was led by the Geological Survey of Sweden. This was followed by UNESCO, which in the year 2000 approved a new project–IGCP # 454 Medical Geology – to emphasize the importance of geological factors that affect human and animal health.

Considerable discussions have taken place on naming the new specialty. Arguments have been made for using ecohealth, geomedicine, medical geology and geomedicine. While all these terms have some merits, none describes the scope better than medical geology, which was adopted by the IWGMG in 1997.

Medical Geology is defined as the science dealing with the relationship between geological factors and health problems in humans, animals and plants. The field of study is complex and requires a multidisciplinary approach using a wide variety of specialists from geologists, geochemists and medical doctors to veterinarians and biologists.

Medical geology covers a wide range of issues from planetary to microscopic – Global warming with its related health impact to how toxic heavy metals may cause cancer.

Since time immemorial, territories where endemic diseases associated with both deficiency and excess of various chemical elements and compounds in natural environments have been known in various regions of our Planet. Examples of such diseases are endemic goiter,

which occurs with iodine deficiency in natural environments, the Urov and the Keshan diseases, the occurrence of which is associated with selenium deficiency in water and soil, dental and skeletal fluorosis due to an excess of fluoride in drinking water, and other diseases that are also known in Russia. Today, the causes of a number of diseases have been reliably established in connection with the use of substandard water contaminated with arsenic in a number of Southeast Asian states, Bangladesh, India.

Exposure to natural and technological dust causes various respiratory diseases, damage to the organs of vision, etc. Its health effects are aggravated by the spores of various fungi and pathogens contained in the composition of dust.

Ash and other products of volcanic activity aggressively affect biota, polluting the atmosphere, water and soil. The danger to humans consists in the morphology and chemical composition of mineral matter particles, the degree of concentration of volcanic gases, etc.

Another area of research is the health of the population in connection with the production activities of mining and metallurgy enterprises. For example, silicosis, asbestos, anthracosis are diseases caused by quartz, asbestos and coal dust. The problem of natural radioactivity and radon safety has also been included in this list and also seems to be very important in this context. The potential danger of chemical elements depends on their physical state and valence index.

Understanding the mechanisms of the impact of chemical elements on the environment and public health allows us to ensure a safe extraction and processing of mineral raw materials, minimizing the impact of toxic chemical elements and compounds on human and environmental health. Thus, medical geology is a strategically significant socially oriented discipline. The study of the conditions, factors and mechanisms of the impact of geological objects and processes on human health and the state of biota, allows us to develop preventive measures necessary for the successful solution of current and planning of long-term tasks of the economic management as well as to implement various social projects based on the interests of all segments of the population.

Philosophical and historical aspects of interdisciplinary research

THE CONCEPT OF SPECIES IN BIOLOGY AND MINERALOGY: A COMPARATIVE STUDY

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Throughout the whole history of science, the difference between living and non-living was a subject of extensive and considerable debates, due to the relevance of this issue to various concepts in philosophy, theology, sociology, and natural sciences sensu stricto. Aristotle was probably the first who raised the problem in his classification of beings, resulting in the formulation of 'the Great Chain of Being' that was at the core of scientific development till the end of the XIXth century. The history of the views on the similarities and differences between living and non-living is well beyond the scope of this contribution, but it is noteworthy that the serious modern analysis of the problem is rarely done on the purely scientific level (with the exception of seminal works by Vladimir Vernadsky in the middle of the XXth century), without specific prejudices external to science.

In this contribution, we would like to abstract ourselves from any external philosophical or theological influences and put the analysis of the problem onto a scientific basis. Our approach is multidisciplinary and is based upon the comparative analysis of basic phenomena that are of high relevance to the fields dealing with living and non-living matter. We shall concentrate on the concept of species, which is at the core of descriptive mineralogy (considering mineral as a basic unit of the solid Earth) and biology (where the concept of species is at the center of any scientific exploration). We are well aware that, in biology, the concept of species is tightly linked to the principle of evolution, since any biological specie is the result of an evolutionary development.

We adopt a rather pragmatic view on the concept of species, the one at use by a practical mineralogist or biologist willing to establish a new natural specie, be it a new mineral from volcanic fumaroles or a new genus of liverworts. Our analysis is intended to reveal similarities and differences in the concept of species employed in descriptive mineralogy and biology viewed from the eyes of practitioners involved in the studies of mineralogical (S.V.K.) or biological (E.A.B.) diversity. First, we provide the definitions of species existing in current mineralogy and descriptive biology, with all its limitations and borders that outline a separate mineralogical or biological entity. Next, general formal procedures are described for the establishment of new species in modern mineralogy and biology, including listing of the necessary data; the concept of cryptic species is considered as well. Then we consider mineralogical and biological diversity, their current state and different

approaches to their estimation and prediction. The problem of classification of species is touched upon in the fourth part of the contribution, though we do not go deep into its philosophical implications; rather we concentrate upon the current methodology used in both fields of scientific enquiry. In conclusion, we try to summarize basic findings of our analysis and to outline similarities and differences in mineralogical and biological concepts of species that are upheld in modern science.

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G. FISCHER VON WALDHEIM, THE EMINENT NATURALIST AND ORGANIZER OF EDUCATION: BIOGRAPHY, SCIENTIFIC HERITAGE AND MEMORY.

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Last year we celebrated the 250th anniversary of Johann Gotthelf (Grigory Ivanovich – in Russia) Fischer von Waldheim (1771 – 1853), the eminent naturalist, professor of natural history at Moscow University and director of the Moscow University's Natural History Museum, founder of the Moscow Society of Naturalists, author of more than 250 scientific publications in the field geology, paleontology, biology, museology, history of science, etc.

Johann Gotthelf Fischer was born in Waldheim, Saxony. He graduated (1792) the Freiberg Mining Academy, being student of the famous geologist A. Werner. He also studied medicine at the University of Leipzig. The first investigations of the young scientist were linked with animal physiology: he published a work on the functions of the fish swim bladder (1795) and on animal respiration (1797), for the last one he was awarded a doctorate in medicine. In 1797 Fischer went to Paris where he studied comparative anatomy, worked at the National Natural History Museum and wrote an immense catalogue of Museum collections. Here he estimated the importance of the systematic principle in the organization of the museum exposition, and later, in Russia, used this principle at Moscow University's Natural History Museum. In1798 – 1804 Fischer lived in Mainz (homeland of the inventor of printing, J. Gutenberg), working at the University as professor of natural history and at the Central School as librarian. He became interested in the history of printing and wrote a fundamental book on this question.

In 1803 Fischer accepted the invitation to take up the Chair of Natural History (the so-called Demidov chair) at Moscow University. In 1804 he arrived in Russia to become professor of this chair and director of the Moscow University's Natural History Museum. In 1805 the Museum was opened to public after the reorganization and became one of the best in Europe. Fischer's activities in Russia were many-sided, it is necessary to notice among them the

organization of the Moscow Society of Naturalists (1805), one of the first scientific societies in Russia. Fischer was the president of this Society until his death. The Society played an important role in the development of natural science in our country, its activity was highly estimated abroad. Fischer participated in the organization and work of the first expeditions of the Society, prepared the descriptions of the geology, mineralogy, paleontology of Moscow region (Gouvernement de Moscou).

Fischer introduced the term "paleontology" in Russia. Being the author of a fundamental work in 5 volumes "Entomographia Imperii Rossici" (1820 – 1851), he made an important contribution in the development entomology.

For many years Fischer was president and professor of the Moscow Medical-Surgical Academy, where he also created a Natural History Museum. Among his pupils we can name professors A. Lovetsky, C. Rouiller, G. Shchurovsky. His son (A.G. Fischer von Waldheim) and grandson (A.A. Fischer von Waldheim) became well-known botanists.

Fischer was member of 70 scientific societies and academies in Russia and abroad, received numerous awards. In 1833 he was elevated to the nobility and from that time was titled Fischer von Waldheim. In his honor one of the minerals received the name "fisherite". After the death of the scientist (1853) an obelisk of red granite was erected on his tomb (at Vvedenskoe cemetery in Moscow) due to the initiative of the Moscow Society of Naturalists.

In 2021 an exposition dedicated to the 250th anniversary of Fischer von Waldheim was organized in the Earth Science Museum of Moscow University. A medal with his portrait was coined, several articles were published in the "Life of the Earth" and other journals.

COMPLICATION: DOES THE COMPLEX COME FROM THE SIMPLE?

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The complication of matter as a whole and its individual objects is an observable fact. Simplification/destruction is subordinated to this process and included in it. From this observation, it seems, an unambiguous conclusion follows that the origin of the simple from the complex is a universal law of development, in fact, development itself. Further research can only concern the concretization of the mechanisms of this process.

The emergence of the complexity of objects of each next level of organization is most often considered as a process of "self-organization" of simpler elements that is enclosed in it itself. For this reason, their influence on the formation of the complexity of system properties can be neglected. At the same time, the environment is not able to be the source of the emerging

complexity of the object, since it is easier organized. Thus, the emerging complexity of the object in such a formulation of the question has neither sources of complexity nor sources of energy, which is another expression of this process.

The development of means of observation leads more and more away from ideas about the simplicity of elements in comparison with their system. Moreover, they turned out to be an erroneous transfer of the simplicity of the means of observation and the observer's thinking to the properties of the object.

In biology, the systematic name “protozoa” has even been assigned to unicellular animals (Protozoa to be translated as the first living creatures). However, in the series "cells - multicellular organisms" the property of being an organism and having its main functions remains constant. At origin, this property is communicated to the system by its elements, which are much more complex than the system itself. All attempts to find internal patterns of morphogenesis of multicellular organisms have been unsuccessful. Biological morphogenesis has sources external to this hierarchical level in the form of complex cell behavior. Cells communicate their complexity not only to the organisms themselves, but also to the communities consisting of them, if any. Organisms and social systems themselves are not capable of achieving results arising from the activity of the cells that form them.

When social systems arise, their complexity is also communicated to them by individuals - in human society, for example, all achievements have personal authorship. The classic example of the development of tools from a "digging stick" to a satellite proves the opposite - these objects do not develop on their own - it is the person who gives them his immeasurably greater complexity.

The complexity and energy of the bonds of atoms and molecules that make up crystals is much higher than the complexity of the crystals themselves, and the complexity of rocks is less than the complexity of their constituent minerals.

Thus, the general complication of matter occurs as a result of the spread of complexity and energy from deeper, ancient levels of its structure to younger ones. Development as such is the origin of the simple from the complex, which corresponds to the principle of energy propagation along a gradient.

ON THE POLYGONAL AND POLYHEDRAL FORMS COMPATIBLE WITH MINERAL AND ORGANIC NATURE: PHILOSOPHICAL INSIGHT

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Biology and mineralogy are united by Linnaeus' definitions of species and individuals and general principles of development. This is the Curie principle, which allows us to reconstruct the material flows and field gradients of the physical environment by the dissymmetry of the individual, i. e. by the deviation of its symmetry from the ideal dictated by the internal imperative. The normal form of a mineral individual is a convex polyhedron. Each of its facets is a flat atomic grid. There is a strict mathematical connection between the structure and the shape of the crystal. Among organisms, there are also many quasi-polygonal and quasi-polyhedral structures formed by meshes, membranes, and shells. Their analysis reveals invariants caused not even by the nature of the physical environment, but by the geometry of space. A number of conclusions follow from the considered examples and mathematical theorems of Euler, Eberhardt, Delaunay, Voronoy and Dirichlet.

1) In nature, there are less or more complex principles of expediency, manifested with varying clarity in mineral and biological structures. Polyhedricity is a fundamental property of mineral individuals, manifested in conditions of free growth. Not so totally, but polygonality and polyhedricity are realized in biological (plant and animal) structures in the range from microns (brochosomes, radiolaria, pollens) to cm (fungi-fullerenes), covering 5 dimensional orders.

2) Mineral and biological individuals are subject to environmental influences that have a material (flows of matter) or field (flows of heat, light, and gravity) nature. For both individuals, the distortion of the external form is determined by the Curie dissymmetry principle. With colonial growth on the substrate, biological and mineral individuals struggle for space, which leads to polygonal partitions of the envelope surfaces.

3) Another fundamental influence is due to the fact that mineral and biological individuals originate and evolve in 3D space regardless of its physical content. This influence is always masked by the influence of the physical environment, merges with it and, as a rule, is not isolated during the study of the object.

4) Nature creates mineral and biological structures, testing all possible possibilities. Generating polyhedral and polygonal structures, it falls into the trap of relations grasped by the Euler and Eberhardt theorems. In the sense of their inevitable subordination to strict relations, their evolution can be called nomotetic. At the same time, the theorems admit an unlimited variety of structures, allowing their wide adaptive (age, environmental) variations.

Polygonal and polyhedral biological structures dialectically combine the features of two styles of evolution.

5) A number of biological polyhedral structures reveal geometric dualism by triangulating the surface according to Delaunay and dual construction according to Voronoy and Dirichlet. This abstract geometric theory underlies modern crystallography. Its applicability in biology indicates the unity of the world.

This leads us to the conclusion that not only a special mineralogical and biological consideration of the objects of nature is necessary, but a more extensive and deep philosophical understanding of the laws of its organization and evolution, and turns us to the names of Descartes, Spinoza, Kant, Hegel etc.

Geochemistry of biogenic-abiogenic systems

INSIGHT TO SPHEROIDAL WEATHERING OF GRANITE (PROTEROZOIC BASEMENT, VORONEZH HIGH).

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Investigated granite corestones were collected in Pavlovsk quarry (Voronezh region). The study area occurs on the eastern slope of the Voronezh Massif, one of the major highs in the Precambrian crystalline basement of the East European Craton. The top of the granite basement is irregularly weathered. The uneven surface of the weathered basement is covered by sedimentary deposits: Devonian, Upper Cretaceous and Pleistocene with total thickness upto 50 m. Locally granitic saprolite has inclusions of boulders – corestones. Their size varies from 10 cm till several meters in diameter. As a rule, corestones are present within the whole saprolite zone upto the contact with Devonian. The upper part of saprolite as well as the pre-Devonian deposits were most probably denudated. The corestones are surrounded by concentric typically multilayered sheets - rindlets (or crusts). The question - underwent the studied crusted corestones the subaerial exposure at the stage of denudation or not is open for discussion. Upto 30 specimens of crusts have been collected and analyzed in details in order to investigate the processes of granite transformations. The crusts are hard (sometimes very hard) and sharply stand apart from the surrounding almost unconsolidated saprolite mass. Typically, they consist from three layers, some – from two or four. Their whole thickness is between 4 and 10 cm. The inner part is solid, ferruginous, middle (the main part) is loose, light grey, the outer part is thin and solid, dark- or greenish grey with the pink spots of preserved microcline. XRD and FTIR data showed that crust material consists from quartz, microcline, biotite and kaolinite. Outer parts of crusts have larger proportion of quartz. Saprolite as well preserves microcline but lost almost all biotite. When studied crusts and their constituents have not shown significant mineralogical differences, magnetic characteristics (MS) demonstrated larger sensitivity. MS values of inner ferruginous parts of crusts are 360-430 $*10^{-8}$ SI, which is comparable to granite. The MS values of the outer parts of crusts are between 10 and 35 $*10^{-8}$ SI. In surrounding saprolite the values are very small, below $2*10^{-8}$ SI. The obtained data show that crusts contain some organic C (~0.1%) and larger phosphorous content in a comparison with saprolite. The more impressive is the behavior of sulphur. In outer crusts its concentration reached 1.1 to 2.5 %; in the inner parts – less than 0.3%. Samples the most enriched in S, have large concentration of Fe as well. Their relatively small MS values presume the presence of pyrite. Outer parts of crusts often contain less Al, but more Si and K. The sensitive parameter reflecting the weathering intensity is Ba/Sr ratio. The results of sub-microscopy observations of crust material showed that a big part of findings is biotic in

nature: spores, bacterial cells, diatoms, acritarches, thalloid structures (probably liverworts) and modern biotic impurities – mycelium and fungi spores *(Basidiospore)*. The most impressive mineral transformations are dissolution of plagioclase and quartz grains and neosynthesis of kaolinite, K-feldspars, Fe-oxides, amorphous silicates with variable composition, framboidal pyrite, Ca-oxalates. Mössbauer spectroscopy data show the neoformation of magnetite. The complex of data allows to presume that processes of saprolitization and crust formation were not synchronous. Development of crusts is the bright example of biotic-abiotic interactions. Crust could be regarded as analogues of soils of extreme environments on the Earth or extraterrestrial.

Acknowledgements

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HEAVY METALS IN NATURAL-ANTHROPOGENIC AND AGRICULTURAL LANDSCAPES OF URBANIZED TERRITORIES

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Private plots and gardens inside the urban territory providing crop production for local population are common in many small and medium-size Russian cities. These lands are often located inside the impact zones of industrial plants. Anthropogenic load on urbanized landscapes provokes changes in the chemical composition of soils, entails a transformation of forms of metal compounds and affects the chemical composition of crop products.

The objectives of this work are:

1) investigation of the forms of bound of metals with soil components in landscapes located in the zone of influence of industrial plants,

2) assessment of the quality of soils and crops.

Geochemical survey of urbanized landscapes of the impact zones of the Tulachermet combine, the Kosogorsky Metallurgical Plant and the Kursk Battery Plant was carried out. An assessment of the ecological and geochemical state of soils of the surveyed regions is given. High concentrations of manganese (reaching in some cases 6000-10000 mg/kg) were recorded in the soils of agricultural landscapes adjacent to the Kosogorsky Metallurgical Plant. Manganese in the soils of agricultural landscapes adjacent to the Kosogorsky metallurgical plant is mainly associated with iron oxides and hydroxides. When redox conditions change (when the territory is waterlogged), high concentrations of manganese may cause negative development of physiological processes in plants.

The increased zinc content in the soils of urbanized agricultural landscapes of Tula was revealed. The iron content in the soils of urban

agricultural landscapes of the impact zone of Tula metallurgical plants is 21000-37000 mg/kg. In the soils of lawns the content of iron reaches 55000 mg/kg. The results of chemical fractionation showed that the main part of iron in polluted soils is in the form of strongly bounded compounds not available to plants. Sparingly soluble iron compounds accounted for 88-96% of the total content. Pollution of vegetation is mainly foliar in nature. The content of heavy metals after washing the fruits of apple trees decreased.

It is shown that the soils of agricultural and natural-anthropogenic landscapes in the impact zone of the Kursk Battery Plant are significantly contaminated with Cd, Pb, Ni, Zn. Accumulation horizon and soil profile are polluted of heavy metals. Contamination by heavy metals of crop products in this zone has been revealed. The pollution by cadmium is the most dangerous one, as it is the most mobile element. A significant amount of total cadmium (30-50 %) is bounded to the fraction of easily replaced and unstable compounds which determines the element high migration activity.

The role of granulometric fractions of different dimensions in the accumulation of heavy metals by contaminated soils has been studied. Studies have established that the maximum concentration of Fe in the soil of the natural-anthropogenic landscape contains in the fraction of 1.0-0.25 mm, which is explained by the deposition of large amounts of iron in the impact zone of the Tulachermet mainly with a coarse fraction.

Studies have revealed that the maximum proportion of heavy metals (in % of the gross content) on polluted light loamy, sandy loam and sandy soils of the surveyed region contains in the fraction of fine sand and dust, that plays a dominant role in the lateral migration of elements due to wind transfer and movement with meltwater.

PECULIARITIES OF SOME BIOGENIC ELEMENTS MIGRATION IN PYROGENIC SOIL SYSTEM IN NOVGOROD REGION (RUSSIAN NORTH-WEST)

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The impact of various natural (windfall, outbreaks of pests), natural-anthropogenic (widfires) and anthropogenic (logging) phenomena causes demutational changes in natural ecosystems. An important factor that disrupts the course of natural processes in biogeocenoses is forest fires, the consequences of which are difficult to predict. Pyrogenesis processes are a widespread phenomenon that has a huge impact on soil formation processes, and it makes us pay special attention to them in the study of natural ecosystems.

It is forest fires that are currently recognized as one of the most significant factors determining the active migration of chemical elements on the earth's surface. Its annual dust and aerosol emission is quantitatively

comparable to the emissions of volcanoes. A high role among pyrogenic emissions belongs to various organic and inorganic compounds, chemical elements, including heavy metals, polycyclic aromatic hydrocarbons (PAHs) and radionuclides, which were in the soil, litter, bark and colk of trees. Their deposition at new places certainly should change the geochemical background of the soil and vegetation cover - these substances together with aerosol particles can be transported through thousands of kilometers. The constantly detected presence of heavy metals in all components of the forest biogeocenosis and their participation in various biogeochemical processes cannot but affect the transformation of their presence forms under the influence of high temperatures because of a forest fire. Therefore, the aim of this work was the geochemical assessment of heavy metals content and peculiarities of their migration in soils of pyrogenic landscapes using the forest ecosystems of the Novgorod region in the North-West of Russia as an example.

The authors conducted studies of postpyrogenic soils in the southern taiga zone in 2022 using the example of the Borovichi forestry territory (quarter 44 of the Pereluchsky district forestry) in the Novgorod region. The top layer of the moss litter was affected by fires of 2021. Three soil pits along the catena (a top of the kame terrace, a slope, and an accumulative position) were put in the postpyrogenic area and one pit – for control, in the non-burnt area. A similar area of the forest ecosystem with the same type of soil, but not subjected to forest fire was used as a control The soil at pyrogenic area is represented by illuvial-ferruginous postpyrogenic podzol on kame sandy loams (Podzol - WRB) with the profile structure Qpyr-E-BF-BC-C. It should be noted that postpyrogenic soils poorly fit into the framework of existing soil classifications. Soils of postpyrogenic succession are represented by surface organogenic horizons that retain traces of pyrogenic impact - burnt moss tirr. The presence of charcoal particles is visually diagnosed at the boundary of organic and podzolic horizons. The lower part of the soil profile has the structure which is typical of podzols.

The morphological organization of postpyrogenic soils profile, their macro-, meso- and micromorphological features, the effect of fire on heavy metals content in soils and temporal dynamics of soil properties changes after fires will be assessed.

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RESPONSE OF PLANTS TO EXPOSURE TO ALUMINUM SMELTERS AS A CHARACTERISTIC OF AIR POLLUTION

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The aluminum industry makes a significant contribution to environmental pollution. In Russia, most aluminum is produced using outdated technology. They are inferior to more modern ones in terms of environmental performance and produce a load on the environment due to the emission of gaseous (CO, CO_2, HF, SO_2, etc.), dusty (Al_2O_3, AlF_3, NaF, etc.) and other compounds.

The aim of the study is to analyze the response of balsamic poplar leaves (*Populus balsamifera* L.) to the effects of emissions from aluminum smelters and to determine the indicator forms of the elements in the components of emissions on their surface.

Biological materials of study are poplar leaves (*Populus Balsamifera* L.). Samples of poplar leaves were collected in September 2014-2017 in the influence areas of the Krasnoyarsk (KrAZ), Bratsk (BrAZ), Sayanogorsk (SAZ), Shelekhovo (IrkAZ) and Novokuznetsk (NkAZ) aluminum smelters. Plant material was dried and was researched in the L. P. Rikhvanov International Scientific and Educational Center "Uranium Geology" at the School of Earth Sciences and Engineering at the Tomsk Polytechnic University by scanning electron microscopy Bruker XFlash 4010. Samples were inspected in back-scattered electrons mode (low vacuum) by X-ray spectral analysis. The F concentration in leaf biomass was determined by the potentiometric method at the Institute of Soil Science and Agrochemistry, Siberian Branch of RAS.

The reaction of balsamic poplar leaves to exposure to emissions from aluminum smelters has been established. It included the appearance of chlorosis and point necrotic spots. Gaseous emissions of HF and SO_2 in interaction with atmospheric and/or transpiration moisture form an aqueous solution of hydrofluoric and sulfuric acids, which cause leaf blade burns in plants.

In the zone of influence of NkAZ the size of the zone of negative impact of aluminum production on the environment is 2 km. The priority indicator elements of the influence of the aluminum industry are Al, Na, Ca and F and their mineral associations. Specific mineral phases were detected on the surface of poplar leaves by SEM-EDS analysis. They reflect the specifics of Soderberg anode production technology used at the KrAZ, BrAZ, IrkAZ and NkAZ. There are Ca-F-containing particles; Al-F-containing particles; Na-Al-F-containing mineral phases, composition close to cryolite; secondary calcium fluoride in poplar leaf stomata, composition close to fluorite. NkAZ also works according to Soderberg's anode technology. However, Ca-F-containing particles, Al-F-containing particles and stomata with calcium fluoride and calcium sulfate were

found on the surface of poplar leaves in the NkAZ influence zone. Differences in the composition of emissions at the same technology depend on the quality and type of raw materials, the method of purification of electrolysis gases. For example, irregularities in the purification technology or their poor performance and low efficiency. SAZ uses a more environmentally friendly and more expensive technology for aluminum production – burnt anodes. This is reflected in the mineral phases on the surface of poplar leaves. A smaller number and variety of specific mineral phases were recorded here. There are Ca-F-containing particles and Na-Al-F-containing mineral phase in a single case.

Newly formed minerals similar in composition to fluorite and gypsum were found in leaf stomata. Calcite crystals are found in the conductive system of leaves in large quantities.

We propose mechanisms of formation of these minerals under the influence of aluminum emissions. It was found that there is a biogeochemical calcium barrier in the stomata of poplar leaves. It neutralizes toxic releases of fluorine and sulfur compounds into inert minerals.

SOIL CONTAMINATION WITH MOBILE FORMS OF CHEMICAL ELEMENTS IN THE ZONE OF IMPACT OF PHOSPHATE FERTILIZER PRODUCTION

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Phosphogypsum is generated during the production of phosphoric acid and during the processing of mined phosphate rock. It can be used in construction, in agriculture as fertilizer, and for the extraction of rare earth elements. However, phosphogypsum contains toxic compounds. Long-term research and monitoring strategies are needed to assess the effects of phosphogypsum storage and use. The purpose of this work is to investigate the mobility of chemical elements in southern taiga soils in the area affected by phosphogypsum dumps. To achieve the goal, the gross content and mobile forms of a wide group (19) of chemical elements in soils in the area of the Kingisepp phosphorite deposit at a distance of up to 5 km were investigated. The field work was carried out from 2019 to 2021. The position in the relief, the wind rose, the geological structure, the type of economic use of the lands were taken into account when setting 8 geo-ecological profiles and 29 reference areas, According to the degree of anthropogenic impact three types of territories were allocated – relatively background areas (forest and bog ecosystems), recultivated overburden rock dumps and large technogenic objects (phosphogypsum dumps and tailings pond). The content of mobile forms of chemical elements in the soil depends on many factors, including the amount of precipitation, and varies from year to year more actively than the gross content. The mobile forms migrate along trophic chains, their content is

regulated by law and is an important indicator of the ecological state of soils. We compared the results obtained with Maximum Allowable Concentration (MAC) (Main State..., 2021) and the median content of mobile forms of elements in soils of the southern taiga of the Barents region (Salminen et al., 2004). It was found that exceedance of MAC in the conditional-background area were detected only for Cu. The reclaimed overburden dumps have Mn (by a factor of three), Cu (by a factor of two) and Pb (by a factor of one and a half) in excess of MAC. In the soils at the phosphogypsum dump and the tailings dump, MACs for Mn (by a factor of two), Cu (by a factor of four), Pb (by a factor of five), Ni (by a factor of five), and Zn (by a factor of one and a half) were exceeded.

The content of mobile Fe in the relatively background area is higher than in the anthropogenic-disturbed areas. The average content of Fe in anthropogenic sites is 34 - 41 mg/kg, and in natural areas five times more - 207 mg/kg. Ba content is on average 36 mg/kg, the maximum content is observed in the soils of large man-made objects and reaches 147 mg/kg. The increased content of mobile Cd is typical for the studied area. The average content of mobile forms of Cd in the soils formed on man-made objects is 2 - 5 mg/kg and reaches 32 mg/kg. At the same time, the local background for Cd is on average 0.06 mg/kg. The exceedance of the content of mobile forms of Cd in anthropogenically disturbed soils over the natural is observed in hundreds of times. Mobile Co and Cr is detected only in the soils of large anthropogenic objects. Cr content is insignificant, Co content is below maximum allowable concentration, but exceeds background values in the Barents region. Search of regularities of transition of heavy metals from labile state to easily accessible for plants and microorganisms forms is one of the urgent tasks. In this case percentage of labile forms increases with increase of gross content. Low-mobile (0-1 %) elements are absent, medium mobility (1-10 %) is typical for Ba, increased mobility (10-20 %) for Pb and Ni, high mobility (more than 20 %) is distinguished by Mn, Cu and Zn. For most elements, mobility increases with increasing of anthropogenic load (Pb, Mn, Cu, Ni, Zn).

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IRON BACTERIA AND THEIR ROLE IN REE CYCLE AND RED BED'S HEMATITE PIGMENT FORMATION

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Deposition of iron hydroxides in bacterial mats from iron-rich springs (Fe^{2+} >3mg/l) of the North-Eastern part of the East European platform is mainly led by so-called iron bacteria (such as *Arthrobacter russicus, Arthrobacter nicotinovorans, Rhodococcus erythropolis, Arthrobacter chlorophenolicus, Gallionella ferruginea, Leptothrix ochracea, Thiobacillus ferrooxidans).*

The study of Q-R iron hydroxides of various origins from the area showed that:

-REE spectra, trace element's content, and isotopic composition of Nd and Sr in iron hydroxides are matching those characteristics of the spring waters, where the oxides were precipitated from;

-iron hydroxides of bacterial origin are accumulating REEs (up to 0.12 wt.%) due to the high sorption capacity of ferryhydrite – the precursor of iron oxides and hydroxides in bacterial communities;

- iron hydroxides from natural environments without iron bacteria contain up to10 times fewer REEs, than those with iron bacteria;

The study of hematite pigment from Paleozoic and Proterozoic sediments from the area (Givetian D2 red beds near riv.Oredezh, arkose sandstones of Terskaya fm (1.2 MA, Kola peninsula), Shoksha quartzites of 1.8 MA, secondary quartzites of B.Tjuters island in the Gulf of Finland) showed that:

-hematite pigment with the remnants of iron bacteria, similar to modern-day bacteria (PIN RAS data) contains elevated REE concentrations (up to 0.15 wt.%), samples without iron bacteria show twice lower REE concentrations than the first ones;

-all studied samples of Paleozoic and Proterozoic hematite pigments have a negative Y anomaly, which witnesses for fresh\slightly salty, rather than truly salty water, they were deposited from.

Summarizing the obtained data we can conclude:

1. Iron hydroxides of bacterial origin play a significant role in the REEs cycle when they are transported from the continents to the sedimentation basins. As red beds are traditionally believed to be deposited in a near continental sedimentation environment, fast deposition of the clastic material with bacterial pigment might have led to the extraction of a significant amount of soluted REEs from the cycle.

2. Geochemical and paleontological study of Paleozoic and Proterozoic hematite pigment allows proposing that large red bed's provinces had been deposited when the environments there were suitable for iron bacteria proliferation.

CALCULATION OF MEAN SR ISOTOPE RATIO FOR THE MODERN CASPIAN AND AZOV SEAS BASED ON THEIR CATCHMENT BASINS

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Mollusks are a natural biomineral system that produces solid minerals during the life of organisms. Mollusks living in the aquatic environment build solid shell by using the special glands. The shell is an external protective skeleton for the body of the mollusk. The mollusk takes the material to build up the shell by feeding from the water during the filtration process. Most mollusks build their shell from calcium carbonate by absorbing the Ca2+ ion and the carbon dioxide anion HCO_3^- from the water. Simultaneously with calcium, the mollusk captures many dissolved elements and accumulates them in the shell in the form of isomorphic impurity. Therefore, the analysis of isotope-geochemical characteristics of carbonate shells allows us to reconstruct the composition of water, which in turn contains elements obtained during the drainage of rocks of the catchement area. Thus, knowledge of the isotope-geochemical composition of carbonate shells of mollusks allows us to reconstruct the composition of eroded rocks within the limits of modern and paleobasins.

One of the most informative elements about the petrographic composition of the catchment area is strontium. Strontium is released as a result of weathering from bedrock. It is transferred to soils, ground and surface waters. Thus, the $^{87}Sr/^{86}Sr$ ratio in water varies depending on different geological composition of eroded rocks. Dissolved strontium is absorbed by plants, mollusks and animals and settles in bones, teeth, chitinous shell cover by replacing calcium. The $^{87}Sr/^{86}Sr$ ratio in biomineral systems reflects this ratio for the aquatic environment in which specific organisms developed.

The object of the study was 15 samples of shells of modern freshwater mollusks (Unio) from the Volga, Belaya, Ural, Don and Kuban rivers. The areas of which are eroded by rocks of various lithotypes, and their catchment basins are the Caspian and Azov Seas. The Sr isotopic composition was determined in crushed samples.

The highest $^{87}Sr/^{86}Sr$ ratio was found in clay-carbonate (0.7124-0.7350) and terrigenous (0.7098-0.7119) lithotypes, the lowest ratio in carbonate (0.7082-0.7083) and halogen-sulfate (0.7075-0.7078) lithotypes.

In addition to the direct measurement of the $^{87}Sr/^{86}Sr$ ratio in mollusk shells, model calculations of the $^{87}Sr/^{86}Sr$ values were carried out, which can supply the studied lithotypes. It is worth saying that the $^{87}Sr/^{86}Sr$ values

obtained by calculation strictly correspond to the empirical data obtained as a result of direct measurement.

The new data obtained in the course of the work are of great importance for various paleogeographic reconstructions and assessment of changes in the composition of feeding provinces in the catchment basins of the Caspian and Azov Seas in the Late Cenozoic.

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BIOGEOCHEMICAL PROCESSES IN SEMIARID SOILS OF THE RUSSIAN PLAIN

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Steppe landscapes are inferior to many other natural zones in terms of self-organisation and stability due to the small level of accumulated biomass; therefore, when environmental conditions change, their stationary state tends to be disturbed, with a slow subsequent restoration (Bazilevich 1993). However, the responses of landscape components are very complex, which is a challenge in predicting the response of ecosystems to environmental change. The soils of the semiarid regions are quite conservative formations. During the Holocene, climatic changes did not directly change soil types (Borisov et al. 2020). With the exception of anthropogenic impact and associated desertification, climate change can affect the properties of steppe soils only through changes in vegetation and weathering.

The aim of the study was to determine the features of weathering and biogeochemical interactions in Kastanozems and Calcisols. For this, a soil transect with a length of more than 700 km was studied in the territory of the southeast of the Russian Plain. The study area is a zone of dry and desert steppes, which is located in various natural regions of the Lower Volga region (Volga and Ergeninskaya uplands, Caspian lowland).

The results of the study showed that the intensity of chemical weathering processes in the soils of the dry steppe zone is quite low. The alkaline environment not only prevents the destruction of primary minerals under the influence of the hydrolysis process, but also hinders the migration of chemical elements in ionic form. Only in the upper soil horizons, where the zone of influence of plant root systems and lower pH values, conditions for chemical weathering can be created. It was revealed that, in more humid true steppes,

where the grass-wormwood association is widespread, plants accumulate a wide range of elements: Ti, Fe, Al, V, Rb, Ba, Mn, Cr, Mg, Sr, Ni, Zn, K, P, Ca, thereby increasing their entry into the upper layers of soils. The possible per year contribution to soil chemical composition of plants of these association for Ti, Fe, Al, V, Rb, Ba, Mn, Cr, Mg and Sr ranged from 0.005–0.07% from the total content in the soil, whereas for Ni, Zn, K, P and Ca, it was an order of magnitude higher (0.03–1.2%). Plants of dry steppes (family Asteraceae and Amaranthaceae) are able to extract Ca, K, PO4, SO4 and Cl from the soil solution contributes to capillary rise of salt cations and anions with soil solutions into the upper soil horizons occurs. They are deposited on the evaporative barrier and react, forming carbonates, gypsum and highly soluble salts and thereby causing soil degradation. The accumulation of Ca, Mg, and Sr by Asteraceae and Amaranthaceae and their pulling into the upper soil horizons activate the process of salinization and alkalinization.

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TRANSFORMATION OF THE TRACE ELEMENT COMPOSITION OF DANDELION (Taraxacum officinale) IN URBAN LANDSCAPES (CASE STUDY OF THE CITY OF SERPUKHOV)

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Technogenic pressure in cities, along with complex interactions between pollutants in the growth environment, are traced in the accumulation and dispersal of chemical elements by plant organs. Such transformations often lead to an imbalance in the chemical composition, which reduces the viability of organisms. The aim of this work is to evaluate changes in the concentrations of essential and toxic elements in the leaves of dandelion (*Taraxacum officinale*) using the data for the city of Serpukhov, which is characterized not only by a high traffic load, but also by a significant number of industrial enterprises of various branches (147 objects) in a relatively small area (32.1 km^2). Plant samples (n=68) were taken using a semi-regular grid with a step of 500 m in the industrial, traffic, residential areas of the city at the beginning of July 2016. Plants of the territory adjacent to the city served as the reference background

for comparison. Sixteen priority pollutant elements were identified by ICP/MS and ICP/AES methods in pre-washed and dried plant material.

The greatest changes in the leaves of urban plants were observed in the accumulation of Bi, Pb, W, V, Cr and As present in emissions from mechanical engineering, metalworking, chemical, textile enterprises and motor transport. The maximum excess over the background for Bi (by 19.6 times) was found in the industrial zone, for Pb, V, Cr and As (by 5.5–2.8 times) − in the traffic zone, which is associated with a high amount of those forms of these elements in the soil which are available to plants. In all land use zones, Fe, Ni, Co, Mo, Sr and Sc also accumulated in dandelion leaves. Along with the active bioaccumulation of toxic elements, a decrease of 1.2–2.6 times compared with the ambient concentrations of essential Mn and Cu was noted.

The leading factor determining the accumulation of Bi, Cr, and Cu in plant leaves is the type of land use. Plant uptake of Fe, Mn, Cr, Ni, W, V, Bi largely depends on the physicochemical properties of urban soils. The association Sc–Fe–V–Cr–Ni–Co formed in dandelion leaves is similar in composition to the soil association Fe–Co–V–As–Ni which indicates the predominant absorption of these elements by the roots (Kuzminskaya 2016). The association Cu–Zn is formed by biophilic elements with similar mechanisms of transfer in the plant.

The Fe/Mn, Pb/Mn, and Cu/Zn ratios in dandelion leaves revealed early disturbances in the processes of photosynthesis, respiration, and enzyme synthesis in most of the plants studied. The greatest imbalance of elements exceeding the physiological optimum by more than 7 times was observed in the industrial and traffic zones, the smallest − in the recreational one.

Changes in the chemical composition of dandelion leaves under the influence of technogenic load were assessed using the index of biogeochemical transformation Zv (Kasimov et al. 2016). Almost half (47%) of the examined plants are characterized by a high and very high level of the index (Zv=30−60). The share with extremely high Zv >60 accounts for 9% of urban plants. An abnormally high content of elements (Zv>80) was found in the industrial and traffic zones. The most balanced relationships between elements (Zv<20) are observed among plants of residential areas.

BEHAVIOR OF IRON COMPOUNDS IN FRACTIONS OF VARIOUS GRANULOMETRIC SIZES IN STEPPE SOILS

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The geochemical behavior of iron in soils determine wide distribution, the ability to change valence and form stable compounds in both the divalent and trivalent states. Soils in the steppes have an oxidizing environment, so iron

in them is an inactive and fairly stable element. In such soil conditions, the trivalent form of iron predominates. The influence of biogenic and climatic factors leads to an increase in the magnetic parameters of the upper layers of soils in comparison with the rock and a decrease in the content of Fe_{2+}, which is due to the greater weathering of silicates. The latter is of great interest for the study of iron as an informative indicator of the action of natural processes in steppe soils. The division of soil into fractions contributes to the differentiation and relative enrichment of the sample with individual components, which makes it possible to study in detail the behavior of iron compounds in the soil.

The aims of this research are studying changes in the states of iron compounds in fractions of various granulometric sizes in steppe soils. The object of the study was selected chernozems and kastanozems (n=10). To do this, on the territory of the southeast of the Russian plain, an average sample was taken every 10 cm from three wells to the parent rock using a soil drill. Isolation of the clay fraction of soils and parent rocks was carried out by washing with separating the sediment into fractions of different particle sizes (2–5, 5–10, 10–50, 50–250, >250 μm). The forms of iron compounds in the obtained samples were determined by Mössbauer spectroscopy (MS-1104 Em). Soil magnetic susceptibility (MS) was measured in the laboratory with the KAPPABRIDGE KLY-2 and in the field with the KT-20 3F-32.

We have determined that the clay fraction (<2 μm) and fine silt fraction (2–5 μm) make the main contribution to the total magnetic susceptibility of the upper layers of the studied soils. Perhaps this is determined by the higher amount of free forms of iron in the soil, which, in the form of dispersed particles of ferrimagnetic iron minerals (magnetite, maghemite), are associated with the clay matrix. An increase in MS in the silt of the parent rock can occur for a number of reasons: the release of iron from aluminosilicates and the transition to oxide and hydroxide forms, the susceptibility to which exceeds the MS of sedimentary rocks; the entry of micro-inclusions of a highly magnetic mineral into the composition of the clay fraction during crushing of large-block soil material; introduction of magnetic material from the upper layers by increasing the total iron content in small soil particles. The Mossbauer spectra of the studied soil samples obtained at room temperature represent a superposition of the Fe^{3+} and Fe^{2+} doublet lines. In some samples, a weak sextet is observed, indicating the presence of a magnetically ordered phase of iron in the form of hematite and goethite. The study of iron phases in the composition of the silty fraction showed that iron ions are in the composition of layered aluminosilicates, Fe^{2+} are in the octahedral environment of chlorite, and Fe^{3+} are in the structure of illite and smectite. Iron can also be present in the form of amorphous impurities, oxidized ferruginous films covering a clay minerals.

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BIOSORPTION OF LANTHANUM

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The unique properties of individual rare earth elements (REE) and their compounds predetermine a wide range of areas of their application in the national economy. For example, La-containing preparations and wastes are widely used as fertilizers, which in turn causes the possibility of pollution by these elements of the environment. REE can accumulate in soil, vegetation, groundwater, rivers, groundwater. All rare earth elements form complexes of various strengths with organic substrates, which makes it possible to use them for the immobilization of elements from technological solutions. The main advantages of biosorbents are their low cost, high efficiency of sorption, and easy disposal. In addition, microorganisms can reduce dissolved metals to form nanoparticles using their metabolic products. The transformation of ionic forms of REE into nanoparticles (mineral phases) leads to a decrease in water migration of ionic forms of REE. The biosynthesis of metal nanoparticles is a promising solution to the problem of remediation of industrial solutions.

The aim of the study was to compare the sorption activity of fungal biomass and humic acids in relation to La.

For experiments on the sorption of La from aqueous solutions, we used a physiologically active biomass of microscopic fungi of two species: *Penicillum canescens* (strain P9(6), previously isolated from a brown coal deposit, and *Talaromyces funiculosus* (strain Tal), previously isolated from the mineral substrate of a gold deposit, as well as for comparison, a preparation of humic acids (HA) isolated from brown coal was used.

The sorption equilibrium of the process of extracting La from a monoelement solution with a concentration of 1 mmol L^{-1} in a slightly acidic medium (pH 5.56-5.72) was established in the process of 24 hours with a maximum capacity of 2.67 and 3.07 mg g^{-1} for P9(6) and Tal, respectively, in contrast to HA, for which the equilibrium occurred after 48 hours. As the initial concentration of La increases to 5 mmol L^{-1} in a weakly acidic solution, the degree of extraction of the element by the studied organic sorbents decreases from 55 to 14%. It is known that the mobility of REE increases in an acidic environment. The maximum sorption capacity, as well as the degree of extraction of La by the fungal biomass for the studied species, was observed at pH 3–4, while for HA these indicators were maximum in the pH range of 5–6.

For a polyelemental solution (from 14 lanthanides) in variants with low initial concentrations (0.01-0.4 mmol L^{-1}) of REE, the quantitative indicators of La extraction by fungal biomass are similar to those indicated above. At a high initial REE concentration (0.5 mg L^{-1}), the extraction of La by the studied organic substrates decreases by an order of magnitude, apparently due to interionic competition for functional groups.

SEM-analysis of fungal biomass showed the presence of phosphorus-containing mineral phases of various morphologies with La content from 40 to 70% and P from 11 to 16%. Accumulation of REE by the cell surface can be carried out due to ion exchange, complexation with carboxyl, phosphate, amino groups, as well as due to the processes of adsorption, microprecipitation, and aggregation. Thus, the fungal biomass of micromycetes, along with humic acids, can be used to extract lanthanum from acidic technological solutions.

MINERALIZATION OF WOOD AND BONE REMAINS OF THE X CENTURY CULTURAL LAYER. STARAYA LADOGA

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In recent years, interdisciplinary research has become increasingly important. The importance of which was noted by V.V. Dokuchaev. Currently, such work carried out within the framework of the archaeological geochemistry. This allows, on the one hand, to clarify the geochemical conditions of vital activity, and, on the other hand, to obtain new information about the processes of fossilization of wood and bone residues.
The area of the Volkhov River is known for archaeological monuments dating from the Neolithic era and up to modern times. The central monument of the Lower Volga region is the Ladoga settlement, which existed since the middle of I millennium AD. The most ancient layers of the Middle Ages were identified in the central part of modern Ladoga on an Earthen settlement. The lower part of the cultural deposits of the settlement represents by an anaerobic layer. It perfectly preserves products made of organic materials: wood, leather, bone, textiles. In the IX-X centuries. In the IX-X centuries. Ladoga was a large multi-ethnic trade and craft settlement on the territory of which traces of the industrial activity of the population associated with the manufacture of glass, metal, bone and ceramics clearly recorded.
Archaeological research in Staraya Ladoga on an Earthen settlement has been going on since the end of the XIX century to the present. The work is carried out by the Old Ladoga archaeological expedition of the IIMC RAS.
The tasks of this joint work of archaeologists and geochemists included: to identify the structural characteristics of the soil; to study the mineral and chemical composition; to determine the features of fossilization of wood and bone remains, to compare with modern wood and ancient (Devonian) samples. The research material was samples of the cultural layer of the X century. Methods of analysis: macroscopic description, granulometric analysis,

petrographic analysis, confocal microscopy, scanning electron microscopy and microrentgenospectral analysis.
Wood and bone remains have a porous structure and contain a large number of mineral mechanical inclusions. The processes of dissolution and recrystallization of phosphate residues are visible in the sections. Scanning electron microscopy and microrentgenospectral analysis made it possible to approach the research most correctly and obtain reliable results.
Among the newly formed mineral phases, pyrite, chalcopyrite, gypsum, barite, iron oxides and hydroxides and organic biofilms were identified. During the fossilization of bone residues in their composition, the Ca/P ratio changes.

The research was carried out in the Resource Centers of St. Petersburg State University (Geomodel, Microscopy and Microanalysis, X-ray Diffraction research Methods, Methods of Substance Composition Analysis) and the VSEGEI Central Laboratory.

GEOCHEMICAL FEATURES OF THE LANDFILL SOIL OF A WASTE PROCESSING PLANT

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The problem of processing, neutralization and storage of municipal solid waste (MSW) is relevant due to the constant growth of their accumulation. When MSW is stored in the open air, as a result of weathering processes under the influence of mechanical, chemical and biological decomposition, chemical elements and compounds can turn into mobile forms and migrate to the surrounding areas, creating soil, hydrochemical and biological anomalies.

The purpose of the study is to identify the geochemical, physicochemical and biological features of landfill soils (LS) of different time burial zones for storing solid waste processing products of one of the waste processing plants (WPP) of St. Petersburg. Research objectives: 1) determination of the component composition of landfill soils; 2) identification of their chemical composition; 3) establishment of physical and chemical properties; 4) establishment of the biological composition; 5) determination of mobile forms of chemical elements; 6) the composition of water drainage channels. Among the soils, two zones are distinguished: a) old burials (2000-2008); b) new burials (2019-2020).

The studies included: analysis of literary sources; macroscopic description and photo documentation, scanning electron microscopy, granulometric analysis, determination of organic C (550 ^{o}C) and CNH analysis for LS. The clay component was studied using X-ray phase and differential thermal analysis. Geochemical features were revealed using X-ray spectral

analysis (complete silicate and microelement analyses), X-ray microspectral and ICP MS analyzes, and mercurymetry; the isotopic composition of hydrogen and oxygen was determined. The physicochemical properties of soil water extracts and water from drainage channels included potentiometric titration, conductometric determination of electrical conductivity, pH measurement, permanganate oxidizability, iodometric titration, determination of chemical oxygen demand, and photometric determination of color. Experiments on the dynamics of washout of mobile forms of chemical elements lasted 1.5 months while recording pH, nanoparticle size, and chemical composition by ICP MS. Biotesting on watercress was carried out, aerobic and anaerobic communities of microorganisms were identified . Chemical weathering indices, total toxicity index, and factor toxicity index were calculated.

The studies were carried out at the Resource Centers of St. Petersburg State University (Geomodel , Microscopy and Microanalysis, X-ray Diffraction Research Methods, Methods for Analyzing the Composition of Matter, Optical and Laser Methods for Studying Matter) and the Central Laboratory of VSEGEI.

BIOLOGICAL WEATHERING OF LOWER PALEOZOIC BLACK SHALES OF SOUTH SWEDEN

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According to V.I. Vernadsky, living organisms are an extremely important agent of the migration of chemical elements in the zone of hypergenesis, which is associated with the biological cycle of atoms in the earth's crust, which consists in the formation and destruction of organic matter. Biological weathering begins with the attachment of microorganisms, lichens, and mosses to rock surface defects. Living matter actively affects the mineral, both by producing chemically active compounds (organic acids), and by extracting elements and mineral compounds from the rock with its destruction.

Black shales are widespread in paleobasins of different ages. These rocks are enriched in a carbon substance (up to 25%) and characterized by the significant content of uranium, molybdenum, copper, zinc and lead.

On the surface of black shales, in microcracks, recesses and intergranular space of the rock, microorganisms actively develop, forming biofilms - communities attached to the substrate and consisting of one or different species of them. One of them is micromycetes - heterotrophic microorganisms that use various organic substances from the substrate or the environment as energy sources for growth and development.

For their identification in biofilms on the shale surface, traditional methods of mycology and microbiology were used. When conducting a

bacteriological study, the isolation of microorganisms was carried out on solid nutrient media: enzymatic meat hydrolyzate to detect heterotrophic bacteria and determine the total microbial number, Aleksandrov's medium with sand to isolate silicate bacteria, potato-ammonia agar to isolate actinomycetes, and liquid nutrient media to isolate chemolithotrophic bacteria. Quantification of bacteria was carried out using the dilution method according to Tepper et al., 2005.

Nutrient media were used for primary isolation, maintenance in culture and identification of micromycetes: classical Czapek-Dox and in various modifications in terms of the content of glucose and some salts, agarized oatmeal broth with the addition of glucose, Sabouraud agar, potato-glucose agar, DRBC medium, water agar, 2% Malt Extract Agar, Wort Agar.

To isolate fungi in culture from black shale samples, the following methods were used: scattering crumbs and small fragments of the substrate onto the surface of the nutrient medium; method of flushing from the substrate surface, subsequent dilution of the resulting suspension and sowing on a nutrient medium; method of selective isolation of fungi from the substrate surface to the nutrient medium using an injection needle.

Depends on differences in growth rate, relation to food sources, the species division of micromycetes occurs. As the result of the experiment, 29 species of micromycetes were isolated.

Mycelial fungi tend to accumulate in places of moss growth, which enhances the destruction of the rock surface, contributing to the formation of primitive soils and aggravating the impact of other weathering agents.

Analytical work was carried out in resources centers of SPBU («Geomodel», «Centre for Microscopy and Microanalysis», «Centre for X-ray Diffraction Studies», «Centre for Optical and Laser Materials Research») and Central laboratory of Russian Geological Research Institute (VSEGEI).

EXPERIMENTAL SIMULATION OF THE PROCESS OF BIOCHEMICAL WEATHERING OF ROCKS OF THE ALBYNSKOE GOLD FIELD (AMUR REGION)

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Microscopic fungi are considered the most active destructors of minerals, which, due to the release of various organic acids into the environment, contribute to the dissolution of the lithogenic base. The goal is experimental modeling of the process of extracting elements from rocks as a result of bioleaching by micromycetes. The work used micromycetes with different adaptation strategies. Fungi were isolated from the soils of the Albynskoe gold deposit: Trichoderma aureoviride Rifai and *Penicillium simplicissimum* (Oudem.) Thom., from the soils of the city of Blagoveshchensk – *Penicillium*

canescens Sopp. The growth of fungal biomass for model experiments was carried out in Czapek's nutrient liquid medium at a temperature of 20° C for 10 days. The duration of experiments on rock leaching under the influence of micromycetes was 10 days. Each variant of the experiment was carried out in duplicate. Destruction was subjected: ore-bearing rock – epidote-mica-quartz metasomatite after micaceous schist (metamorphite) with dissemination of pyrite and arsenopyrite; carbonaceous shale and oxidized, weathered ore. The contents of basic cations and trace elements in the samples were determined by atomic emission (iCAP-6500, Thermo Scientific, USA) and mass spectral (X-7, Thermo Elemental, USA) methods.

During bioleaching, there was a trend of quantitative extraction of elements: with concentrations in leaching solutions of tens and hundreds of mg/l, such macroelements as Si, Ca, Na, K, Fe, Al, Mn end Mg are released, basically, these are rock-forming elements. The group of elements with medium concentrations in solutions (from 10 to 1 mg/l) includes Sr, As, Pb – from coal shale. The remaining elements belong to the group with concentrations in the leaching solution <1 mg/l. It has been established that micromycetes, especially of the genus *Penicillium*, are able to dissolve the mineral substrate of the rocks of the Albynskoe deposit, converting into mobile forms rock-forming elements (Si, Ca, Na, K, Fe, Al, Mn, Mg) and trace elements (Sr, As, Pb) in significant quantities.

For a more complete assessment of the role of the biotic component in the weathering of rocks at the Albynskoe deposit, a calculation was made of the proportion of elements extracted from rocks by microscopic fungi. *P. simplicissimum*, isolated from the soils of the Albynskoe gold deposit, most actively extracted Mg, Ca, Mn, K, Co, Ni, Sr, Y, Cd, Ba, Tl, As, and U from the rocks into solution. The degree of extraction of Mg from different rocks for 10 days of leaching ranged from 0 to 30.93%; Ca - from 9.68 to 37.57%; Tl - 0.1 to 8%. As for the elements that have high environmental hazard indicators for this deposit, the largest share of As extraction was noted from metasomatites (17.7-19.3%), and only Sb - from oxidized ore (0.73-4.79%), while W was practically not leached by fungi from any of the rocks. Under the influence of *P. simplicissimum*, 0.12-0.16% Be and 1.4-5.92% Cd were leached. The highest share of Mo extraction (1.08-16.09%) was observed when the rocks were treated with *Trichoderma aureoviride*. When using culture liquid with *P. simplicissimum* as a "solvent", from 0 to 6.08% U was leached, and when using *T. aureoviride*, the share of U extraction was 1.69-10.34%. An assessment of the degree of extraction of elements from rocks during biogenic leaching showed that the largest share (from 6 to 29%) of the extraction of a number of toxic elements (Sb, Ba, Cd, Tl, Co, Ni, U, Mo, Cr, As, Sr) is observed , mainly from metasomatites and oxidized ore, to a small extent - from carbonaceous shale. W, Ga, Sc are practically not leached by micromycetes from these rocks.

SHORT-TERM VARIATIONS OF ORGANIC COMPOUNDS, STABLE ISOTOPES OF CARBON AND NITROGEN, MACRO- AND TRACE ELEMENTS IN PLANTS AND RHIZOSPHERE SOIL

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Elemental composition of different plants can vary depending on various environmental conditions. Among others, temporal variations are of special interest. Until now, more attention has been paid to long-term (seasonal and annual) changes. However, information on short-term variations of various organic compounds as well as many elements in plants and in the rhizosphere soil is limited. Plants have developed special mechanisms to predict the changes in the environment caused by the Earth's rotation. The mechanisms of short-term (within several hours) variations in the concentrations of mineral elements in different plants and in the rhizosphere soil of the plants are still not clearly understood. Meanwhile, it is reasonable to expect that the concentrations of elements in plants can also change over a relatively short time. The variations in the plant element composition under stable conditions have a cyclic nature due to regular rhythms of different biochemical processes. Because photosynthesis is a dominant metabolic process in the primary metabolism of green cells, other plant activities, in particular, nutrient mobilization, are often synchronized with the rhythms of photosynthesis.

The aim of the research was to study diurnal changes in the concentrations of organic compounds and different macro- and trace elements in widely distributed plant species and in the rhizosphere soil. During last years several experiments were conducted. The plant and soil samples were collected in a field in the course of the vegetation season over a daytime.

It was found that changes in the total amounts of C, N and stable isotopes of the elements in the rhizosphere soil during day can be significant and differ in the soils taken from roots of different plants if though the plants grow at the same place and under the same conditions. The concentrations of some other elements in the rhizosphere soil of the plants varied in a similar way. The daily fluctuations of element concentrations in roots and leaves of the plants were also large. In many cases, a decrease of element concentration in roots correlated with an increase of its concentration in leaves.

The concentrations of many elements and organic compounds in different plant species growing at the same place were often statistically significantly different. This can be explained by the fact that the plants belong to different classes. It can also be assumed that the plants were capable of giving different reactions on the varying environmental conditions. Considering such short-term variability of element concentrations in plants and in the rhizosphere soil, it is necessary to carefully choose the timing of sampling to ensure the correct interpretation of experimental data.

ECOLOGICAL AND GEOCHEMICAL ASSESSMENT OF SOIL SALINIZATION IN THE TERRITORY ADJACENT TO LAKE KUCHUK (ALTAI KRAI)

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According to the soil-geochemical zoning of the south of Western Siberia, the Kulunda Plain belongs to the province of active water-salt exchange with the predominance of salt inflow over their removal. A distinctive feature of the plain climate is the excess of evaporation over precipitation, which, under conditions of poor drainage, contributes to salt accumulation in all landscape components: surface water and groundwater, ground, soil and plants. The main area of the Kulunda Plain is characterized by a flat relief rich in lakes. Lake Kuchuk is the largest salt deposit in Western Siberia, the main reserves of which are concentrated in its brine. The extraction of sodium sulfate at the deposit is carried out by the company OJSC "Kuchuksulfate". Development is carried out in an open way. The possibility of dust removal from such industrial facilities as a salt evaporation pond and a salt storage creates a threat of soil salinization in the adjacent territories.

Soil studies were carried out in 2020 and 2021 in areas adjacent to the boundaries of the enterprise, as well as in the background area.

The result of the wide development of salinization phenomena is the complexity of the soil cover of the plains with the inclusion of Solonetz and other soil types with Sodic supplementary qualifier and progressive salt accumulation in low lacustrine landscapes. Thus, Solonetz and Solonchaks in the study area account for more than 20% of the soil cover. The presence of natural salinization significantly complicates the assessment of the anthropogenic contribution.

According to the results of the morphological analysis of the studied soils, no significant differences were found within the same classification type between the soils of the background area and the impact zone of the enterprise. The soils of the sanitary protection zone of the enterprise were saline Solonetz, in which salinization was manifested deeper than 30 cm. Compared to the background soils, they have a higher salt content (including in the topsoil layer). The salt composition of these soils was almost completely dominated by Na^+ and SO_4^{2-} ions, while the background soils were characterized by a greater variety of cationic and anionic compositions with a noticeable content of soda.

The most saline ones were located in the former lake basin, in the center of which the enterprise's salt evaporation pond is now located. The slopes of the basin are a mechanical screen that prevents the transfer of salt particles over long distances.

The difference at the low level of soil taxonomic designation, both in the background area and in the impact zone of the enterprise, was determined by

the influence of the position of the soil in the relief (catenary differentiation) and vegetation. Thus, the depth of saline and carbonate horizons, the thickness of the surface layer above the natric horizon depended on the slope position of Solonetz. The presence of trees and shrubs compared to the steppe areas contributed to the change in the salt and carbonate profiles of soils, an increase in the thickness of the humus horizon and the content of organic matter.

VERTICAL-TRANSVERSE BIOGEOCHEMICAL STRUCTURE OF POPLAR CROWN (*POPULUS BALSAMIFERA* L.) UNDER TECHNOGENIC LOAD

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We have studied the distribution of the content of chemical elements in the leaves of the crown of a free-standing poplar (*Populus balsamifera* L.) in a residential area near the industrial site of a large nuclear fuel cycle plant in Novosibirsk. Leaf sampling was carried out at the end of the growing season using an aerial platform at a height of 2 to 15 meters (in increments of 1 meter) from the western and eastern sides of the crown, taking into account the direction of the prevailing winds.

To preserve information about the aerosol component, the leaf samples were not washed with water, they were dried in open kraft bags at room temperature in a well-ventilated room. Then the dry leaves were subjected to two-stage dry mineralization (GOST 26929-94) at a temperature of 450 °C under standard conditions.

The content of 28 elements was determined by instrumental neutron activation analysis: Na, Ca, Sc, Cr, Fe, Co, Zn, As, Br, Rb, Sr, Ag, Sb, Cs, Ba, La, Ce, Nd, Sm, Eu, Tb, Yb, Lu, Hf, Ta, Au, Th, U. The analysis was carried out in an accredited nuclear geochemical laboratory at the research nuclear reactor at the National Research Tomsk Polytechnic University according to certified methods.

The following features were revealed in the distribution of chemical elements along the vertical profile of the poplar crown:

1) relatively uniform distribution in height (Ca, Cr, Co, Zn, As, Br, Rb, Sr, Ag, Sb, Ba);

2) content of chemical elements decreases from bottom to top (Na, Sc, Fe, Cs, REE, Hf, Th);

3) content of chemical elements on the windward side is on average 1.5–6 times higher than on the leeward side (Hg, U).

Analysis of the results of the experiment showed that mainly biophilic elements are evenly distributed along the vertical profile of the poplar crown. Their entry into the leaves is probably due to the bark mineral nutrition. The elements whose content decreases from the bottom up along the vertical profile

of the poplar crown reflect the composition of mineral dust deposited on the surface of the leaves from the air. Naturally, the dust content is higher in the surface layer of air.

The transverse (lateral) distribution of Hg concentrations in the leaves of the poplar crown relative to the emission source showed that in the lower tier on both sides of the crown at a height of 2-3 m, the concentration of Hg in the leaves is approximately equally high. The distribution of U concentrations in the leaves of the poplar crown relative to the emission source showed that on the windward side of the crown, the U content in the leaves is on average 6 times higher than its content on the side of the "wind shadow". The maximum concentrations of U were observed at a height of 4-6 m from the earth's surface. The transverse (lateral) nature of the distribution of Hg and U in the leaves indicates that the poplar retains the technogenic flow of these chemical elements dangerous to the environment and humans, the source of emission of which is a nuclear fuel cycle enterprise.

Biomineralization and nature-like materials and technologies

MORPHOLOGICAL DIVERSITY OF FRAMBOIDAL PYRITES FROM THE KUCHUGURY MUD VOLCANO

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The active mud volcano Kuchugury ("Plevak") is popular as an object of free therapeutic mud. It is a small lake with liquid mud substrate located in a 5 km from the village of the same name. Its eruptions can be accompanied by gas, water and oil release. Mineral composition of the substrate and neomineralization formed under exogenic conditions are of great interest.

Composition of clay fraction was determined by X-ray diffraction analysis of oriented and unoriented samples under standard diagnostic treatments (Shimadzu XRD-6000 diffractometer, CuK_{α}, Ni-filter). Mud consists of a mixture of clay minerals: illite, kaolinite, chlorite, smectite and illite/smectite. Their main components are swelling minerals – Na-smectite and interstratified poor-ordered illite/smectite with with relatively small content of illite part. The presence of quartz, halite, feldspar and a small amount of pyrite is also noted.

Thin fraction was removed from the mud and minerals remaining after panning were studied in bulk sample s by scanning electron microscopy (SEM) (TESCAN MIRA LMS (S6123) with an INCA Energy 450 X-max 80 EMF spectrometer, carbon deposition).

Framboidal pyrites are very diverse morphologically: they compose thin crusts, nodules. Cubic and octahedral pyrite is formed on them; they replace foraminifer's shells (Fig. 1).

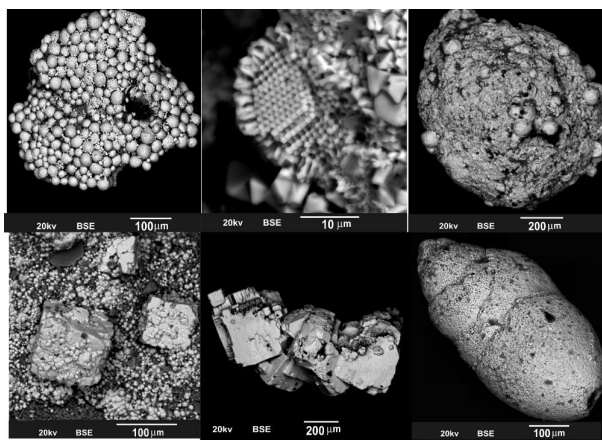

Fig.1. Pyrite morphological types.

Several morphological types of pyrite were identified using SEM (Fig. 1):

- small framboids (diameter 5–10 μm) consists of sub-micron cubic pyrite crystals 0.5–1 μm in size;

- so called pyrite “sunflowers” - rims surrounding a framboidal core resulting in a regular sub-spherical morphology in low pyrite saturation conditions;

- large euhedral crystals – octahedrons, cuboctahedrons which in turn can form even larger cubic forms. It is believed that different shapes and sizes of framboidal pyrite correspond to different environmental conditions including the presence or absence of organic matter.

SYNTHESIS OF COMPLEX COMPOUND OF MAGNESIUM (II) IONS WITH GLUTAMIC ACID

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Keywords: Synthesis, amino acids, complexes of magnesium, metal complexes, glutamic acid.

In this work, the synthesis of magnesium (II) complexes with glutamic acid from an aqueous solution of magnesium hexahydrochlodide salt and a glutamic acid solution was carried out by the following method:

In a beaker with distilled water, electrolysis is carried out on graphite electrodes, the essence of which is to bring the pH to ~ 10 in the presence of a small amount of $MgCl_2$ to increase the electrical conductivity of the solution. After that, we dissolve the Glu suspension in 2 ml of an aqueous solution (pH ~ 10). Then we add the $MgCl_2*6H_2O$ suspension. Evaporation of the solution at room temperature was used, during which a chemical reaction of Glu with Mg^{2+} and crystallization of the resulting compound took place. After a few days, a crystalline precipitate was obtained. The precipitate was filtered and washed with a small amount of water, dried at a temperature of 50-60 ° C to remove excess moisture.

The data of spectroscopic characteristics of the compounds obtained by the method of infrared Fourier spectroscopy are presented, the spectra of the studied samples were recorded in the range from 500 to 4000 cm^{-1}.

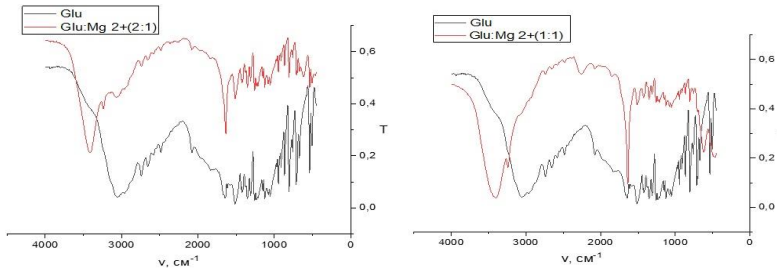

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Figure. IR spectra: 1- Mg^{2+}: Glu ratio 2:1; 2- Mg^{2+}: Glu ratio 1:1;

The morphology and shape of the solid phase particles were studied by optical microscopy using an XSP-140 series electron microscope, solid phases of magnesium with glutamic acid were used as the material for the study. The formation of complex compounds of the type “magnesium ion (II) – glutamic acid” in molar ratios of metal - amino acid - 1:1; 1:2 is proved. The presence of a covalent bond formed by a donor-acceptor mechanism with an unshielded electron pair of a nitrogen atom of an amino group of amino acids and a magnesium (II) ion, and also a magnesium (II) ion with a carboxyl ionic group of glutamic acid. Prepared compounds they will find application in production of drugs, where they can be used as the main component. The data obtained on the specific types of amino acid coordination will be able to increase the prediction reliability for structure of compounds, which are poorly studied and to provide new opportunities for improving directed synthesis methods for complexes of a specific structure and composition. Also it can fundamentally contribute to studies areas of biochemistry that consider bioprocesses regulation using metal ions.

EXPERIENCE OF USING THE EYE AS AN OPTICAL SYSTEMS FOR OBSERVING MICRO-OBJECTS

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As is known, a magnifying glass is often used to study small-sized objects [1]. With its help, an enlarged image of the surface of the object, which is facing the observer's eye, is obtained. The surface must be illuminated, for example, by the sun. This is a variant of studying objects in reflected light. To study objects in transmitted light (“transmission”), the visual axis of the eye,

the magnifying glass and the object must be oriented to the light source. If it is the sun, then there is a danger of damage to the eye by direct light radiation passing by the edges of the object.

To exclude damage to the eye, the following method for observing a microobject is proposed. The eye itself is used as a magnifying glass. Near the eye, at a distance equal to or less than its front focal length (it is approximately taken equal to 17 mm, counting from the cornea of the eye), a small flat mirror is placed, for example, several centimeters in diameter for comfortable holding in the hand). An object of observation is placed between the mirror and the eye. The radiation that shines through this object is formed due to its reflection between the cornea of the eye and the mirror. The impact of direct (not re-reflected) light radiation on the retina of the eye is excluded due to the inclination of the propagation axis of this direct radiation relative to the visual axis by an angle exceeding the angular field of view of the eye.

Due to the fact that the image quality when using the eye as a magnifying glass fully depends on the physiology of vision and the optical properties of the eye, the discussed method of observation can also be used for research in ophthalmology.

COMPOSITION OF THE IMPREGNATING SOLUTION FOR BACTERIAL BIOMINERALIZATION AND FEATURES OF ITS INTERACTION WITH CEMENT SYSTEM COMPONENTS

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Building materials and products are subjected to various types of corrosion, the development of which is associated with a large number of variable factors occurring in a complex relationship. The speed and nature of corrosion processes depends on the permeability of concrete products. The migration of aggressive substances in the body of the concrete matrix as a result of transport mechanisms (filtration, capillary transfer, diffusion) leads to a change in porosity and, as a consequence, the physical and mechanical properties of materials. The intensity of transport processes is determined on the one hand by internal parameters (the nature and composition of the binder and other components of the cement and concrete system, the size of aggregates and pores), on the other – by external parameters (the condition and degree of uniformity of the surface of the product, the presence of protective coatings, impregnations, insulation, etc.). In turn, it was found that microbial-induced calcite deposition contributes to an increase and/or prolongation of the resistance of materials to external aggressive factors.

Within the performed studies, rational compositions of the inoculate with four different types of bacteria (*B. pumilus, S. pasteurii, B. megaterium, L.*

sphaericus) were developed, the degree of restoration of the continuity of the surface of cement stone samples using these compositions was assessed.

In view of the fact that the cement stone system is a multiphase polystructural system, attention is paid to studies of the effect of the composition of individual components of the concrete mixture and impregnating hydrophobic solutions on the intensity of biocementation. The following aggregates were analyzed: quartz sand, marble chips, ground cement stone and carbonized ground cement stone of various fractional compositions. The dependences of lithification and the depth of impregnation of microcracks in cement stone on the type of filler and its fractional composition are established.

In order to optimize the process of applying an impregnating biocementitious composition, a hypothesis has been proposed about the possibility of introducing bacterial inoculate and precursors into the composition of the emulsion. The use of a polysiloxane emulsion based on a water-soluble polymer intended for the hydrophobization of the surface of cement concrete products, due to its biopositivity due to the absence of volatile organic substances in its composition as a solvent of hydrophobizing resin, is proposed as a base composition. To establish the influence of individual components and technological features of emulsion production on the producing ability of bacteria, an assessment of the effect of organosilicon liquid GKZH-94, polyvinyl alcohol (PVA), temperature and intensity of dispersion (emulsification) on them was carried out. The absence of harmful effects of both PVA and GKZH on B. pumilus bacteria was recorded. Heating the PVA solution with a bacterial inoculum to 60° C led to sporulation of more than 80% of bacteria. It has been established that high-speed dispersion causes cell damage, there is a sporulation of bacteria up to $1{,}3\times10^6$ CFU/ml against the initial value of 2×10^8 CFU/ml. The analysis of the influence of individual components and technological operations of obtaining an emulsion on the preservation of the viability of bacterial cells confirmed the prospects of the expressed hypothesis.

ADSORPTION OF CONGO RED USING HYDROXYAPATITE NANOPARTICLES ENGINEERED BY CATIONIC INCORPORATION HAP:X (X = FE, NI, ZN, CO, AND AG)

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Every year, 7x105 tonnes of dye are produced in various industries around the world, and their dyes are improperly disposed of into bodies of water. Even a very low concentration of dye pollution is harmful to humans, animals, and the aquatic environment. The removal of Congo red (CR) dye using nano-hydroxyapatite (nano-HAp, HAp:X (X = Fe, Ni, Zn, Co, Ag) by batch adsorption process will be presented. The samples were synthesised by co-precipitation and ultrasonication techniques. The dopants were used to engineer the crystallinity, crystallite size, particle size and shape, and colloidal stability of the adsorbent. The adsorption equilibrium of CR is obtained (98%) rapidly in 1 min. Sustained adsorption was observed in a wide range of pH (3–11). In addition, the final pH of water is maintained at 7 0.3 after the completion of the adsorption process. Removal of CR by monolayer and chemisorption processes was confirmed by the Langmuir and second-order kinetics, respectively. The adsorption of CR as revealed by the DKR isotherm was found to be dominated by chemisorption rather than the ion-exchange process. Furthermore, the adsorption of CR is spontaneous and exothermic in nature. The regeneration efficiency is 98–40% up to 7 cycles without any chemical treatment. These results reveal HAp as a potential adsorbent for the removal of CR without any secondary byproducts.

Keywords: Congo red adsorption, Regeneration, isotherm, Gibbs free energy

STRUCTURAL AND MORPHOLOGIGAL PROPERTIES OF HYDROXYAPATITE-HYALURONIC ACID COMPOSITES

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The production of hybrid organo-inorganic phosphate materials is a promising area of research in the development of biopolymer composites for medicine. The structure-forming glycosaminoglycan of biological fluids, hyaluronic acid, can be used as an organic matrix. The aim of the work is to study the structural and surface characteristics of hydroxyapatite and high-molecular hyaluronic acid composites obtained from model solutions of human synovial fluid.

The composites were synthesized from a prototype synovial fluid of a healthy adult average person. Sodium hyaluronate (high molecular weight) was used as a source of high molecular hyaluronic acid (HHA, high molecular weight sodium hyaluronate, qualification "h"). Precipitation crystallization time was 7 days. The composition and surface of the obtained sediments were studied using X-ray phase analysis, SEM, single-point nitrogen adsorption by the BET method (S, m^2/g). The crystal chemical parameters are determined by the least squares method. The values of the coherent scattering regions (D, the

minimum sizes of crystallites) are calculated using the Debye-Scherrer formula by reflex (002).

Results and discussion. It was found that the main phase of all samples is calcium-deficient carbonate-containing hydroxyapatite (CHA, table 1). CHA-HHA composites are amorphized due to the presence of calcium phosphate and polysaccharide in their composition. In the crystal lattice of samples № 4 and № 5, there is a narrowing of the unit cell along the *a* axis, as a consequence, a decrease in its volume to values characteristic of biogenic apatite. It is possible that a B-type CHA is formed (B-type: $Ca^{2+} + 2PO_4^{3-} = VCa + 2CO_3^{2-}$).

Table 1. Crystal chemical lattice parameters, crystallite sizes and specific surface area of composites

№ sample	HHA, wt. %	Axis *a*, Å	Axis *c*, Å	*c*/*a*	V, Å	D, nm	S, m^2/g
1	0	9.459±0.002	6.874±0.002	0,726	532,6	22,09	130±7
2	0,15	9.455±0.002	6.870±0.002	0,727	531,9	18,12	125±6
3	0,1	9.475±0.002	6.871±0.002	0,725	534,2	18,12	110±6
4	0,15	9.446±0.002	6.869±0.002	0,727	530,8	13,72	110±6
5	0,2	9.433±0.002	6.861±0.002	0,727	528,7	15,62	116±6

CHA polysaccharide powders, compared with the pure phase, have smaller crystallite sizes (*D*, table 1). It is likely that their growth is inhibited by reducing the rate of diffusion processes in viscous media. The minimum size of the coherent scattering regions is characteristic of sample № 4 (HHA 0.15 wt. %). From model solutions with a higher concentration of HHA (0.2 wt. %, sample № 5) precipitates with larger crystallites were obtained. Perhaps due to the formation of three-dimensional structures of "grids" between the polysaccharide molecules, providing selective diffusion of dissolved particles. In general, powders with a developed specific surface area are formed in the presence of HHA (table 1). Despite the viscosity of the model media, due to the presence of a large number of carboxyl groups, Na^+, K^+, Mg^{2+} and Ca^{2+} cations are actively concentrated from the solution on the surface of the samples. With a content of 0.2 wt. % in the model medium, samples with a more developed surface were obtained.

Thus, CHA-HHA composites have a developed specific surface area, are close in composition to bone apatite, which indicates their promising use as materials that stimulate osseointegration in the replacement of bone defects.

SYNTHESIS OF COMPOSITE MATERIALS ON HYDROXYLAPATITE AND POLYMERS OF CHITOSAN AND CHITIN

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Keywords: crystallization, hydroxyapatite, chitosan, chitin, composite, morphology, thermal properties, dissolution

Due to biocompatibility with human tissues, as well as the ability to enhance regenerative processes during wound healing, bacteriostatic/bactericidal properties, chitin and chitosan are of great interest for use as matrices in the creation of biocomposites based on inorganic substances.

Of greatest interest as an inorganic component in the composition of composite materials are calcium phosphates, namely hydroxyapatite (HA). Hydroxylapatite is the least soluble of all calcium orthophosphates. Pure HA is never found in biological systems, however, due to the similar chemical composition of bone and dental mineral, hydroxylapatite is widely used in orthopedics and traumatology.

Composite materials synthesized on HA and natural polymers of chitosan and chitin can have high biocompatibility and bioactivity, osteoinductivity, and resorption.

The synthesis of HA (Ca/P = 1.70) in the presence of chitin was carried out similarly to the synthesis of the DCPD–chitosan composite, but the pH of the system was maintained at a level of 12.0 ± 0.5 by adding a concentrated ammonia solution. In the synthesis of HA, a solution of calcium nitrate was added to a solution of ammonium hydrogen phosphate with a concentration of 0.040 mol/l in such a concentration that the ratio nix = $Ca(NO_3)_2$ / $(NH4)_2HPO_4$ was 1.70.

When mixing solutions containing a solid suspension of the polymer, white precipitates formed. After keeping each solution for 72 hours, the precipitate was filtered off, washed from the ammonium nitrate formed in the course of the reaction, and dried in a chamber at t = 80°C until complete removal of water.

Synthesis of the HA-chitin composite was carried out similarly to the synthesis of the HA-chitosan composite, but the polymer chitin was used instead of chitosan. In a flask with ammonium hydrogen phosphate, chitin was added with a mass of 0.02; 0.08 or 0.16g.

When mixing solutions containing a solid suspension of the polymer, white precipitates formed. After keeping each solution for 72 hours, the precipitate was filtered off, washed from the ammonium nitrate formed during

the reaction, and dried in a chamber at t = 800C until the water was completely removed.

The resulting powders were studied by physicochemical methods

The composition of the synthesized samples based on HA, chitin and chitosan is constant, the presence is confirmed by IR-Fourier spectroscopy, the presence of HA phases is confirmed by XRF. All composites are deposited in the form of crystallites of a certain shape, and their size increases with an increase in the biopolymer content in the initial solution. With an increase in the calcination temperature, the mass of all composites decreases. The rate of dissolution of samples based on chitin in an isotonic solution is less than for composites based on chitosan.

Thus, HA-based samples synthesized in the presence of chitin and chitosan exhibit similar properties when dissolved in an isotonic solution.

INFLUENCE OF A SERIES OF AMINO ACIDS ON THE PROPERTIES OF CALCIUM CARBONATE SYNTHESIZED IN BILE

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Keywords: calcium carbonate, vaterite, aragonite, calcite, synthesis, phase composition, dispersion, crystallization, gallstones, human bile

Polymorphic in nature calcium carbonate is characterized by the existence of six different modifications: crystalline - calcite (stable), aragonite and vaterite (metastable); hydrates – monohydrocalcite, amorphous $CaCO_3 \bullet H_2O$ and ikaite (hexahydrate).

Mathematical modeling that the amino acids histidine (His), arginine (Arg), methionine (Met) and tryptophan (Trp) in the composition of the peptide have strong Ca-O interfacial bonds, as well as O ••• H hydrogen bonds with the (001) surface of aragonite , that is, theoretically, they can stabilize the formation of this crystalline modification during the precipitation of $CaCO_3$ from solution. Of interest is the effect of these amino acids on calcium carbonate precipitated from bile, because vaterite formation usually occurs under these conditions. The transfer of $CaCO_3$ to another phase during its crystallization under natural conditions of the human body can reduce the stability of the resulting microparticles and lead to inhibition of cholesterol crystallization. The study of the effect of amino acids on the $CaCO_3$ crystallization process is carried out by varying the model concentrations of AA at constant model concentrations of Ca^{2+} and HCO_3^- ions and pH in the reaction mixture. Synthesis of two samples of $CaCO_3$ was carried out in the absence of amino acids, other conditions being equal.

Holding the resulting solution in a BIOTRON-4 thermostatic cabinet for 7 days at a temperature of 310 K. Vacuum filtration, the filter cake is washed with distilled water twice with 50 ml. Sludge drying for 24 hours in a BIOTRON-4 thermostatic cabinet at 310 K, then for 24 hours in a desiccator at room temperature to constant weight (to remove all chemically unbound water). Dry dehydrated powder is sent for weighing to determine the yield, and then for physical and chemical studies. The content of $CaCO_3$ in the composition of the solid phase of all synthesized samples was determined by complexometric titration. The samples obtained with Arg have the maximum yield with respect to $CaCO_3$, while the minimum yield is with Met. An increase in the amino acid concentration leads to an increase in the mass fraction of calcium carbonate in the case of His and Arg and to its decrease in syntheses with Met and Trp. It is important to note that the inhibitory effect of Met on the crystallization of $CaCO_3$ and on precipitation in bile in general.

For the amino acids Met and Arg, their stabilizing effect with respect to metastable aragonite has been proven: with an increase in their concentration in bile, an increase in the mass fraction of aragonite in the composition of the solid phase occurs. This may have an inhibitory effect on further growth and aggregation of gallstones, as aragonite differs from vaterite in its morphology, zeta potential, and consequent adhesion to cholesterol. IRFS results correlate with XRF data. Optical microscopy showed the presence of vaterite spherulites in all obtained powders. It was established by the PCS method that calcium carbonate microparticles with a radius of less than 10 μm are represented by three fractions. Of greatest interest are syntheses with His and Trp, in which, with increasing amino acid concentrations, an increase in the proportion of the small fraction and a decrease in the proportion of the large fraction are observed. The radii of particles of all fractions increase in this case. The obtained results indicate the need for further study of mineral formation in human bile using model systems in order to identify mechanisms, establish functional dependencies, and determine the causes of the formation of gallstone embryos.consider bioprocesses regulation using metal ions.

DEVELOPMENT OF TECHNOLOGY FOR IMPROVING ORGANIC SOIL BY MICROORGANISMS IN CIVIL ENGINEERING

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Civil construction implies the creation of civil facilities, which include highways and railways, industrial enterprises, residential buildings, bank protection structures, etc. Most often, the mechanical properties of natural soils are insufficient to meet the growing requirements in this area. The solution to

the problems of civil engineering is provided by the arrangement of a homogeneous, well-compacted subgrade.

Currently, this problem is solved by chemical cementation, where bentonite and silicates are mixed into the soil. This approach can have a negative impact on the environment. An alternative to this method, which has a minimal impact on the soil ecosystem, is soil stabilization using mineral-forming microorganisms or soil biocementation [1]. The most well-known methods of biocementation are enzyme-induced precipitation and microbiological precipitation of $CaCO_3$ where the processes are caused by ureolysis. In the process of ureolysis, urea hydrolysis occurs due to the metabolic reactions of microorganisms inducing the precipitation of calcium carbonate minerals deposited in the voids of the soil, thereby increasing its strength [2].

The purpose of this work was to develop a technology for increasing the strength of organic soil by its treatment with suspensions of microorganisms. In the course of the work, microorganisms were evaluated for their ability to precipitate calcium carbonate crystals, and the parameters of pH, biomass accumulation, and changes in urease activity during the growth of selected bacteria were determined. In our work, the optimal medium for soil compaction was selected. The irrigation method was chosen as a method of introducing the working solution as well as the method of bioincreasing soil microflora. Selected strains of bacteria were tested for their ability to increase the strength characteristics of organic soil. Three types of soil, taken from different areas of the Leningrad region, were studied for their ability to withstand the load and for the amount of calcium carbonate formed. The leader in the selected parameters was the bacterial mixture, which contained the previously reported bacteria [3]. At the moment, work is underway to scale the experiment into the field.

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COPPER OXALATE, MOOLOOITE: FINDINGS IN NATURE AND SYNTHESIS PATHWAYS

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The work focuses on the mineral moolooite, $Cu(C_2O_4)\cdot nH_2O$, in biofilms and contributes to the essential questions on microbial oxalate biomineralization. Moolooite was found in lichen thalli on surfaces of weathered copper ore in the dumps of the Voronov Bor deposit (Central Karelia, Russia) for the first time and was investigated using set of methods (X-ray powder diffraction, scanning electron microscopy, Raman and EDX spectroscopy). The species of microorganisms (lichens and fungi) that accumulate copper oxalate were determined. The morphogenetic patterns of biomineral formation using results of model experiments are discussed.

The results obtained and the analysis of the literature data allow us to confidently assume that moolooite and other copper oxalates (middlebackite, fiemmeit, wheatleyite and antipinite) form in Nature, most likely, as the result of metabolic products of living organisms (birds, lichens, fungi and other) reaction with associated (primarily, underlying) rocks and minerals, i.e. are biominerals. It has been confirmed that the likelihood of moolooite finding in saxicolous lichen L.inops (well-known inhabitant of communities developing on copper-bearing minerals) is very high.

Single findings of wheatleyite in nature are well explained by the fact that it is water-soluble and can be stored for a long time only under special conditions. Probably, this can also explain the rare occurrence of other copper oxalates (middlebackite, fiemmeit, antipinite), but there still no data on their solubility.

This work was supported by Russian Science Foundation (project N 19-17-00141). The laboratory researches were carried out in the Research Park of Saint Petersburg State University, the SEM investigations — in the "Resource Center Microscopy and Microanalysis (RCMM)" and in the Centre for Geo-Environmental Research and Modelling (Geomodel), the XRD measurements — in the X-ray Diffraction Centre.

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CRYSTAL CHEMISTRY, PHASE TRANSFORMATIONS AND MORPHOLOGY OF (Mn, Mg) C_2O_4 SOLID SOLUTIONS

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The minerals lindbergite $MnC_2O_4*2H_2O$ and glushinskite $MgC_2O_4*2H_2O$ are rare biofilm minerals. Manganese oxalate dihydrate was found in the thallus of the lichen *Pertusaria corallina* on manganese ore (Wilson and Jones, 1984) and approved as a new lindbergite mineral in 2003 after a detailed mineralogical description of crystals from Boca Rica mine, Galiléia, Minas Gerais, Brazil. Magnesium oxalate dihydrate was found in thalli of the lichen *Lecanora atra* on serpentinite (Insch, Kincardineshire and Island of Rhum, Inner Hebrides. Scotland) by Wilson et al. (1980) and approved as a new mineral glushinskite in 1987 (named for Petr Ivanovich Glushinskii (1908-), who first found this mineral on the river Lena, Yakutia, Russia). Minerals belong to the humboldtine group, are considered isostructural (sp.gr. C2/c) and are characterized by the general formula (Mn, Mg , Fe)$C_2O_4 \cdot 2H_2O$.

In order to explore the patterns of incorporation of Mg^{2+} - ions into linbergite and Mn^{2+}- ions into glushinskite the solid solutions (Mn, Mg)$[C_2O_4]\cdot 2H_2O$ (sp.gr. C2/c) were synthesized and investigated by a complex of methods: powder X-ray diffraction (PXRD), scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) spectroscopy. Oxalate crystal powder were precipitated into solutions at $Me^{2+}/C_2O_4 \leq 1$ in the presence/absent of citric acid (1 mmol/l). In order to reveal the concentration at which lindbergite - glushinskite chemical equilibrium is achieved thermodynamic modeling was also executed by means of DATABASE & SPANA software (former Hydra & Medusa).

The study has revealed significant differences between lindbergite and glushinskite crystal structures and morphology. Lindbergite forms flattened crystals while glushinkite forms pseudo-octahedral crystals with faces of rhombic prisms. Mg ions intensively enter lindbergite crystal structure, which leads to significant changes of unit cell parameters. On contrary, Mn incorporation into glushinskite crystal structure is relatively slow. It also leads to changes in unit cell parameters but simultaneously leads to breaches in long-range order along [010] direction. At $Me^{2+}/C_2O_4 < 1$ in absence of citric acid Mn incorporation into glushinskite causes formation of 2D periodic structure. At a ratio of Mg/(Mn+Mg) ~50 – 70% both lindbergite and glushinskite phases are precipitated along, forming complex crystal intergrowths. Thermodynamic modeling gives the equilibrium ratio Mg/(Mn+Mg) ~ 60% as well.

The oxalate minerals of lindbergite - glushinskite series can be considered as solid solutions with limited miscibility. The isodimorphic lindbergite–glushinskite transition occurs abruptly at close contents of Mg^{2+} and Mn^{2+} ions in solution. Possible symmetry violations occurring in this case

are planned to be studied in more detail by single crystal X-ray diffraction in the future.

The research was supported by RSF grant 19-17-00141 and SPbU Reseach Park: Centre for X-ray Diffraction Studies and Centre for Geo-Environmental Modelling and Research.

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CRYSTAL CHEMISTRY AND NATURE OF PHOTOCATALYTIC ACTIVITY OF Ti-MODIFIED HYDROXYAPATITES

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Ti-modified hydroxyapatite and its photocatalytic properties are widely studied for more than two decades. Ti-modified hydroxyapatite, along with biocompatibility, has photocatalytic properties, which widens its application areas. The patterns of the interaction of titanium with hydroxyapatite, including the incorporation of titanium ions into hydroxyapatite, and the origin of its photocatalytic properties are yet poorly studied. The goal of our research is to find out how Ti^{4+} ions incorporate into hydroxyapatite and to reveal the nature of photocatalytic activity of Ti-modified hydroxyapatite. Three series of hydroxyapatites were precipitated from Ti-containing solutions (Ti/Ca = 0.01 – 0.60): series 1 and 2 were obtained using $Ca(NO_3)_2$, $(NH_4)_2HPO_4$ and $TiCl_3$ as main components with different order of mixing at T=95 °C and series 3 was obtained using $Ca(OH)_2$, H_3PO_4 and $C_{12}H_{28}O_4Ti$ T=50 °C. The precipitates were annealed at 700 °C for 6 hours. Wide set of diffraction and spectroscopic methods have been applied to study the phase composition of the precipitates and the crystal chemistry of the resulting hydroxyapatites. Their photocatalytic properties were investigated using diffuse reflectance spectroscopy and reaction of acetaldehyde decomposition under UV-visible light.

The results of the study showed, that the use of X-ray powder diffraction alone does not allow to detect the presence of additional titanium phases (list), which (at Ti/Ca rations in solution more than 0.10), along with

hydroxyapatite, are present in impurity amounts in all precipitations. After annealing these phases are transformed into crystalline TiO_2 modifications (rutile and/or anatase).

Comparison of changes in unit cell parameters with increasing titanium content (before and after annealing) revealed incorporation of Ti^{4+} ions into different sites of hydroxyapatite crystal structure: in P-site (up to Ti/Ca ~ 0.07, 3rd series), in P and Ca-sites (up to Ti/Ca = 0.06 – 0.34, 1st and 2nd series).

Band gap of precipitates reduces with increase of Ti content, which indicates Ti-modified hydroxyapatites absorb UV light. However, precipitations demonstrate high photocatalytic activity (comparable to activity of TiO_2-based photocatalysts) only after annealed, when anatase and/or rutile are present in all cases. As shown in the example of series 3, "TiO_2-apatite" core-shell composites are able to form.

Thus, the photocatalytic activity of Ti-modified hydroxyapatite is primarily due to the presence in the synthesis products of crystalline TiO_2 phases, and not to the incorporation of Ti^{4+} ions into the apatite.

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STRATEGY FOR CREATION OF THE UNIVERSAL REUSABLE SUBSTRATE BASED ON NEW GENERATION POLYMERS FOR GROWING PLANTS IN MODERN PROTECTED GROUND STRUCTURES

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The problem for optimizing the composition, properties, structure of the root habitat of plants in a protected ground structures remains unresolved, since this is a multicomponent task with several variables depending on the specified conditions, agrotechnologies the production- and adaptive potential of the cultivated vegetable crop. All greenhouse substrates, due to the peculiarities of their use, are actively influenced by the microclimate and the applied agrotechnical methods. As a result, their quality deteriorates rather quickly, which negatively affects the productivity of plants. In this regard the creation of new materials with the required properties and having a known stable structure, as well as being able, upon contact with water, to pass from a light-weight solid form to a gel-like porous form, resistant to conditions of intensive light culture, is in demand and very promising for wide industrial use. To date, it is known that hydrogels and polymers are used as additives to substrates to

improve their hydrophysical properties, etc.. The creation of a sustainable environmentally friendly gel - a substrate saturated with the necessary food and energy sources for plants, physiologically active substances with protective properties, is a pioneering direction.

In this work, we describe the strategy and ways of creating such gel substrates. namely, through: using as basis the high water absorption polymer hydrogels formed by crosslinking copolymers of 3-sulfopropyl methacrylate and 2-hydroxyethyl methacrylate, as well as 3-sulfopropyl methacrylate and vinyl acetate. In addition, it was shown the route for the synthesis for the first time of hylrogels, constructed from cross-linked star-shaped macromolecules consisting of a nanosized titanium dioxide core as a branching center and rays of hydrophilic polymethacrylic acid. This will make it possible to achieve a synergistic effect in the process of growing plants on such a gel substrate due to the presence of uniformly distributed titanium dioxide nanoparticles in it, which exhibits photocatalytic properties. In this case, the aggregation of titanium dioxide nanoparticles will be suppressed due to their covalent incorporation into the hydrogel structure, and the concentration of nanoparticles in the hydrogel can be controlled by changing the length of polymethacrylic acid chains, which determines the shell thickness around titanium dioxide nanoparticles.

Along with this, the creation of a series of gel substrates containing, in addition to the gel of the indicated composition, salts of macro- and microelements necessary for plants in selected concentration ratios is described.

We are currently running a series of vegetation's experiments with main vegetable crops to evaluate the dynamics of changes in the properties and composition of new gel substrates when growing the plants under controlled conditions of intensive light culture. At the same time, the photosynthetic apparatus, antioxidant systems and biochemical compositions reactions, as well as the growth and productivity indicators are evaluated in plants. The obtained research results will make it possible to give recommendations on the possibility of further direction development of such substrates for crop production in protected ground.

The study was supported by a grant from the Russian Science Foundation No. 22-26-20087, https://rscf.ru/project/22-26-20087/" and a regional grant from the St. Petersburg Science Foundation

MICRO-ADMIXTURE ELEMENTS IN FRAMBOIDAL PYRITES OF THE SULFIDE ORES OF SOME DEPOSITS OF THE URALS

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Framboidal pyrites are found in rocks of different genesis and geological age, indicating hydrothermal influence or hydrothermal-sedimentary origin of deposits. A number of researchers have believed that such pyrites are formed as a result of the vital activity of bacteria. The bacterial cells are not preserved as fossils, but the products of microbial vital activity (extracellular biopolymers, biofilms, some metabolites) are able to mineralize and persist in rocks for a long time. Therefore, it is important to identify signs in ancient sediments that indicate their microbial origin. For example, we present the results of studies of framboidal pyrites from rocks of some deposits of the Urals: Safyanovskoye (Cu-Zn-pyrite), Moskovka (placer gold ore, pyrites are associated with bitumen) and Mikheevskoye (copper porphyry). The samples were studied by scanning electron microscopy (SEM) (JSM-6390LV JEOL) and TESCAN MIRA LMS (S6123) with an INCA Energy 450 X-max 80 EMF spectrometer, carbon sputtering). At the Sayanovskoye deposit in carbon-siliceous (Fig. 1a) rocks and pyrite ores (Fig. 1b) framboidal pyrites with covers preserved on bacterial colonies due to mineralization with silicon dioxide (Fig. 1) are observed. In the SEM photo they look like a translucent film that negatively affects the image quality (Fig. 1a).

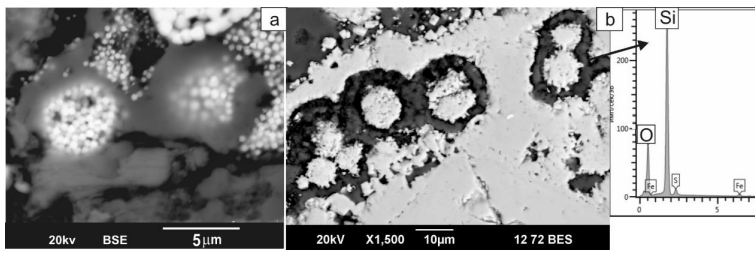

Fig. 1. Framboidal pyrites with mineralized SiO2 covers, Safyanovskoe deposit: a – in carbonaceous-siliceous rock; b – in pyrite ores. The specific conditions during the formation and burial of framboids are indicated by the elements-impurities Ni, As, Co in the sulfide composition of the covers of these biomorphoses (Fig. 2).

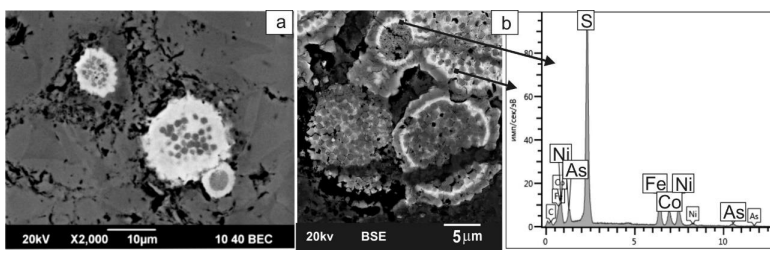

Fig. 2. Framboidal pyrites with micro admixtures of Ni, As, Co in the composition of the covers: a – Moskovka deposit; b– Mikheevskoe deposit. Thus the study of the elemental composition and morphology of framboidal pyrites makes it possible to identify the features of a surrounding environment during their formation and burial.

THERANOSTIC NIOSOMES AS A PROMISING TOOL FOR ANTICANCER THERAPY

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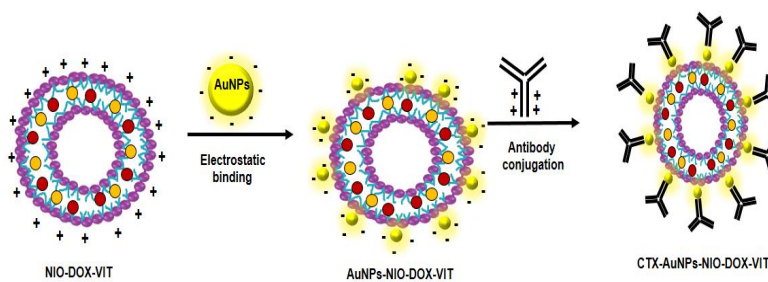
Chemotherapeutic drugs into smart nanocarriers that provides synergistic effects and further surface modification for specifically targeting a tumor site improves their therapeutic effectiveness, reducing their side effects. To achieve this goal, both doxorubicin (DOX) and vitexin (VIT) were encapsulated in niosomes and their surface is modified with gold nanoparticles (AuNPs) as well conjugated with EGFR antibody. This is the first report to use this combination to apply for triple negative breast cancer studies. The interaction between noisome vesicles and AuNPs was studies in the FTIR. The cumulative release profile occurred in two phases, an initial burst release that lasted for 3–9 h, followed by a sustained, slow-release that was maintained at least for 72 h. Release mechanism is dominated by the diffusion mechanism which normally depends on drug concentration between niosome vesicle and dissolution media. The physicochemical parameters such as size, morphology, surface charge, and biological investigation of the noisome vesicles were examined with the triple-negative breast cancer MDMB-231 cell line. Invitro cytotoxicity and cellular uptake of noisome vesicles were compared within the control groups. In vitro anticancer therapy was achieved to evaluate the potential synergic anticancer activity of the optimized multifunctional niosome vesicles.



Schematic representation of antibody conjugation

BIOMINERALIZATION OF CARBONATES BY CYANOBACTERIAL COMMUNITIES IN STREAMS AND RIVERS FEEDING PETERHOF FOUNTAINS (RUSSIA)

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Cyanobacteria take part in the processes of carbonate sedimentation, but the role of cyanobacterial communities in the formation of carbonate sediments (ancient and modern) is not completely clear. We studied the cyanobacterial communities connected with carbonate sediments of the freshwater bodies feeding the historical Peterhof fountains (Saint- Petersburg, Russia) [1]. We were interested in the mineral composition and species diversity of cyanobacteria in carbonate sediments of the water supply system of Peterhof fountains, also we tried to reveal the relationship between the mineral composition of carbonate sediments and inhabiting microorganisms' species. Cyanobacterial communities were studied by metagenome analysis and optical microscopy. Carbonates associated with cyanobacterial communities (both in situ and in vitro) were studied by powder X-ray diffraction analysis, scanning electron microscopy, energy-dispersive X-ray spectroscopy, and Raman spectroscopy. The following minerals were found in the samples from the Peterhof water supply system: calcite, aragonite, dolomite, quartz, feldspar (albite, microcline), and mica. Silicates (quartz, feldspar, and mica) are parts of the underlying substrate material. Calcite and dolomite could be both parts of underlying bedrock (limestone/dolomite) and newly formed biominerals, whereas aragonite could be biomineral only, as no aragonite-bearing rocks are known in the studied region. According to the mineral composition the studied carbonate sediments can be divided into two groups: microorganism related – aragonite, Mg-calcite and abiogenic – dolomite, low-Mg calcite. A number of experiments have been carried out to study the interactions between cyanobacteria and carbonate precipitation. Samples from model experiments were enriched in organic material with minor mineral components. Therefore, no reliable PXRD data were obtained, whereas Raman spectroscopy reveal the presence of calcite.

Cyanobacteria of 24 genera were revealed in sediments composed of calcite and aragonite. The use of metagenomic analysis made it possible to identify cyanobacteria from 17 genera. The most abundant are *Phormidium* (47%), *Tychonema* (27%), *Chamaesiphon* (16%), *Leptolyngbya* (15%), *Calothrix* (20%). The crystallization of carbonates on the surface of 13 species of cyanobacteria was found. Using model experiments, a significant contribution of cyanobacterial species of the Oscillatoriaceae family (*Phormidium* spp., *Lyngbya* sp., *Oscillatoria formosa*) to carbonate biomineralization is demonstrated.

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MODELING THE STAGES OF THE OXALATE-CARBONATE PATHWAY BY FUNGAL-BACTERIAL ASSOCIATIONS IN DIFFERENT NUTRIENT CONDITIONS

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The oxalate carbonate pathway (OCP) is a global biogeochemical process that transfers atmospheric CO_2 into the geological reservoir as $CaCO_3$. OCP is carried out with the active participation of plants, fungi and oxalotrophic bacteria[1]. Their very labile metabolism result in oxalate and/or carbonate biomineralization The influence of the environment on these processes, the conditions under which carbonate crystallization turns into oxalate and vice versa, is not well understood. The aim of this work is to study in vitro the influence of the metabolism of fungi, bacteria and their associations on patterns of oxalate and/or carbonate crystallization in different nutrient conditions

The fungi *Aspergillus niger* and *Penicillium chrysogenum* and also the bacteria *Bacillus subtilis* were chosen for the experiments. These organisms are producers of oxalic acid (OA), the presence of which is necessary for oxalate formation. *P. chrysogenum* and *B. subtilis* produce also extracellular polymer matrix (EPS), which is necessary for carbonate formation. Monocultures and their paired fungus-bacteria associations were grown in liquid Čapek Doks media with different glucose concentration (from 1 to 30 g/l), as well as in oligotrophic conditions of moist chamber. Marble blocks, which were placed on Petri dishes, were used as a source of calcium.

It was shown that the metabolic activity of the studied microorganisms is a multifactorial process, the flow of which significantly depends on the cultivation trophic conditions, including the concentration of sugar in the medium. The composition of the metabolites secreted by fungi and bacteria (the first, the ratio between the EPS and OA concentration) significantly affects pH values of the crystallization medium and, as a result, the phase composition and morphology of the precipitating calcium oxalates and calcium carbonate crystals. On the example of *A. niger-B. subtilis* associations it was shown that the acidification activity of micromycetes may suppress the formation of

bacterial EPS and prevent the formation of calcite[2]. In turn, the pH of the medium significantly affects the metabolism of microorganisms. Under the influence of the fungus Penicillium chrysogenum and investigated bacterial–fungal associations depending on the cultivation conditions crystallization of carbonates can turn into crystallization of oxalates and vice versa. On the example of *P. chrysogenum* as well as *P. chrysogenum-B. subtilis* association, it has been shown that an increase in the concentration of glucose in the nutrient medium can lead to a more intensive OA and EPS production, i.e. promote crystallization of both oxalates and carbonates.

Based on the study, it can be reasonably assumed that the oxalate-carbonate pathway can proceed from oxalates to carbonates and from oxalates to carbonates, depending on trophic conditions.

The research was funded by the Russian Science Foundation (grant 19-17-00141). Some studies have been carried out on the basis of the resource centres of the St. Petersburg State University: Development of cellular and molecular technologies, Microscopy and microanalysis, Geomodel, X-ray diffraction research methods.

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THE ADSORPTION FLUORIDE FROM WATER BY MESOPOROUS HYDROXYAPATITE/CHITOSAN NANOCOMPOSITES

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The presence of F^- ion in water is known to have either a helpful or harmful outcome, contingent upon the concentration level of the pollutant. This work deals with the removal of F^- ion from water using hydroxyapatite with two different weight ratios of chitosan (x = 1% and 4%) synthesized by the co-precipitation method and dried using lyophilization technique without any chemical modification. The adsorbent morphology changes from rod to sphere

with chitosan incorporation. The colloidal stability of the adsorbents and F^- adsorption capacity was significantly enhanced. HAp/CS4 recorded the maximum F^- adsorption capacity of 240 mg/g, 150 mg/g, and 70 mg/g in 30 min at pH 3, 7, and 9 respectively. In addition, the sustainable regeneration efficiency (90% in 30 min) up to the 7^{th} cycle was displayed by HAp/CS4. The kinetic data of adsorbents indicates the monolayer and the strong chemisorption as confirmed by Langmuir and Dubinin- Kaganer- Radushkevich (DKR) isotherms, respectively. After F^- ion adsorption, the structure and surface morphology of the adsorbents reveal the formation of the fluorapatite by the mechanism of ion exchange and electrostatic interaction. The results demonstrate that the chitosan plays a major role in the HAp matrix and has superior F^- ion removal characteristics in addition to being cost-effective.

MAGNETIC STRUCTURES IN FORAMINIFERA

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[3] Far Eastern Federal University

Studies of biogenic composite materials based on the calcite matrix are currently a relevant task, since biogenic frameworks have a number of advantages over their artificially derived equivalents. Foraminifera are one of the major sources of biogenic calcium carbonate. Foraminifera shells can be classified as biogenic porous microparticles of calcium carbonate. Such porous microparticles can be used as a basis for creating composite materials obtained by introducing various fillers into the porous shell structure. The main area of application of these composites is medicine, namely, targeted drug delivery. Another option of creating composite materials based on the mineral skeleton of foraminifera is coating the surface of the shell with nanoparticles of different composition. Such structures can be used as electrodes for water purification by the catalytic oxidation method. Calcium carbonate microparticles, which can be controlled by an external magnetic field, are of particular interest. Magnetic particles are formed in foraminifera during the processes of their mineral substitution. Magnetic structures on foraminifera carcasses may also appear during formation of iron-containing biogenic concretions on the surface of mineral skeletons.

The paper investigated the structural-phase and chemical composition and magnetic properties of iron-containing formations on foraminifera shells from the Russian exploration region of the Mid-Atlantic Ridge (samples were provided by I.G. Dobretsova, mineralogist of the PMGE Ocean Prospecting and Surveying Party). Methods of magnetic separation, optical microscopy, scanning electron microscopy, X-ray spectral microanalysis, and ion etching were used, and hysteresis characteristics were measured.

The strongly magnetic fraction is represented by foraminifera shells on the surface of which pseudomorphoses of cladding minerals of the talc and serpentinite groups with inclusions of crystallites of iron oxides were formed. The medium magnetic and weakly magnetic fractions contain unsubstituted foraminifera shells containing ferromanganese and iron-containing formations. According to the morphology of the aggregates, it is possible to assume their biogenic origin. The skeletal shape of the crystals according to the SEM data is characteristic of minerals of the spinel group, and the nonlinearity of the magnetization curve corresponds to magnetically soft ferrimagnetics. Application of the theoretical model of magnetostatically interacting particles with effective spontaneous magnetization made it possible to calculate the hysteresis characteristics, which agree well with the experimental data. This allowed assuming that the mineral that determines the magnetic properties of the objects is magnetite.

MICROBE WEATHERING AND BIOMINERALIZATION OF VOLCANIC ROCKS OF TOLBACHIK VOLCANO, KAMCHATKA, RUSSIA

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Lichens and cyanobacteria are considered to be the pioneers of the settlement under extreme conditions and take an active part in rocks weathering. We studied the process of weathering of volcanic rocks and biomineralization under the influence of lichen and cyanobacteria in extreme conditions of Tolbachik Volcano area, Kamchatka, Russia. Rock samples with lichen / cyanobacteria biofilms were studied by a complex of methods (optical and scanning electron microscopy, powder X-ray diffraction and energy-dispersive X-ray spectroscopy). We found that the acidic environment of biofilms favor oxalate biomineralization under the action of lichens and suppresses the carbonate biomineralization under the action of cyanobacteria. Calcium (whewellite, $Ca(C_2O_4)\cdot H_2O$, and weddellite, $Ca(C_2O_4)\cdot(2.5\text{-}x)H_2O$ ($0 \leq x \leq 0.25$)) and copper oxalates (moolooite, $Cu(C_2O_4)\cdot 0.4H_2O$) were found only in lichen biofilms on old (> 1000 years) cinder cones. It was shown that lichens extract calcium and heavy metals (Cu, Pb) from the underlying rock and increase their content in biofilm. Obtained results shows high abundancy of biomineralization in terrestrial environment, including extreme and provides some insights into mechanisms of microbe biomineralization. This work was supported by Russian Science Foundation (project No 19-17-00141).

FORMATION OXALATES OF TRANSITION METALS (Fe, Mn) UNDER THE ACTION OF THE FUNGUS ASPERGILLUS NIGER IN EXPERIMENTAL CONDITIONS

Zelenskaya M.S.[1], Izatulina A.R.[1], Frank-Kamenetskaya O.V.[1], Vlasov D.Yu.[1,2], Gurzhiy V.V.[1], Rusakov A.V.[1]
1 - SPbGU, 2 - BIN

Microfungi were able to alterate solid substrate in various environments and play a noticeable role in the formation of insoluble calcium oxalate crystals in subaerial biofilms on rock surfaces. The present work devoted to the studies of biomineralization mechanisms under the influence of lithobiotic microbial community (in particular, microscopic fungi). Oxalate crystallization under the influence of fungus *Aspergillus niger* (one of the most active stone destructors) was studied in vitro conditions on Mn,Ca-bearing minerals of manganese ores: todorokite, kutnohorite and on the surface of two iron- bearing mineral substrates: pyrrhotite and siderite rocks. The obtained results demonstrate a significant effect of the chemical composition of the underlying mineral substrate on the processes of mineralization under the action of fungus *Aspergillus niger* .The mechanisms of humboldtine, lindbergite, falottaite formation were discussed. It was shown that more intense leaching of Ca-ions (compared to Mn and Fe-ions) from todorokite, kutnohorite and siderite leads to an earlier crystallization of calcium oxalates (predominantly whewellite) compared to manganese and iron (lindbergite, falottaite, humboldtine). Formation of manganese oxalates on the surface of Mn,Cabearing minerals under the influence of A. niger fungus occurs via complex redox processes (Mn2+ to Mn3+,4+ and vice versa), which depends on the oxidation state of manganese ions in the underlying mineral substrate and on the pH of crystallization medium. The behavior of the Fe (II) / Fe (III) / oxalate system is extremely complex, as shown by various experimental studies. Possibly microbial oxidation or oxidation in air of Fe (II) to Fe (III), followed by hydrolysis and precipitation of iron oxides, probably, iron (III) is likely to form fundamentally soluble oxalate complexes The in vitro regularities of oxalate crystallization (variations in the phase composition of the obtained products, crystal morphology, the incorporation of isomorphic impurities) on the surface of Ca,Mn-bearing and iron- bearing minerals under the action of the *A. niger* fungus can now be used for describing the crystallization processes occurring in nature with the participation of micromycetes, on surfaces of various minerals, primarily containing ions of transition metals of variable valence (Mn, Fe, and other). The observed patterns are important for understanding the processes occurring when using micromycetes, in particular, A. niger, in the bioleaching of iron, manganese and other metals from processed ores, as well as for cleaning environmental objects of heavy metals.

This work is supported by Russian Science Foundation (project N 19-17-00141). The laboratory researches were carried out in the Research Park of

Saint Petersburg State University, the SEM investigations in the “Resource Center Microscopy and Microanalysis (RCMM)” and in the Centre for Geo-Environmental Research and Modeling (Geomodel), the XRD measurements in the X-ray Diffraction Centre.

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Medical geology

SYNTHESIS OF SILVER IONS DOPED 45S5 BIOACTIVE GLASS WITH HIGHLY INTERCONNECTED PORES FOR BIOMEDICAL APPLICATIONS

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The silver ion doped multifunctional porous 45S5 bioactive glass was synthesized by sol-gel technique and subsequent sintering at 800˚C. The phase of 45S5 bioglass, $[(Na_{0.11}Ca_{0.89})(P_{0.11}Si_{0.89}O_3)]$ which is essential for assisting the self-repair process of enamel was formed along with sodium calcium silicate ($Na_2Ca_2Si_3O_9$) phase. FT-Raman analysis revealed the influence of silver ions in the modification of sodium calcium silicate due to the creation of high defects/vacancies. Further, the pore size of 2AgBG was enhanced by 52% compared to the pristine. In addition, zeta potential, antimicrobial activity, *in vitro* bioactivity, hemolysis, cell viability and proliferation were significantly enhanced by the doping of Ag ions. Very low level of doping of silver ions (0.02 wt%) compared to the reported values (≥0.75 wt%) much below the toxic level (≤0.05mg/L) was employed to achieve the porous interconnected structure. Hence, it could be an outstanding material for tissue engineering, bone and dental applications.

INFLUENCE OF LITHOLOGICAL AND GEOCHEMICAL FEATURES OF THE TERRITORY ON THE FORMATION OF THE MINERALOGY AND GEOCHEMICAL COMPOSITION OF MAMMALIAN TISSUES

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In the 2020 - 2022 years joint work of two groups (the first group is from Tomsk Polytechnic University, the second group consists of representatives from Pacific Geographical Institute and Far Eastern Geological Institute, Far Eastern Branch of Russian Academy of Sciences) let to perform filed investigations and collect samples in three areas: Primorsky Krai, Gorny Altai and Irkutsk region. More than 400 organs and tissues samples from 10 animals were taken (includind Sus scrofa, Sus scrofa domesticus and Corex). Domestic pigs are thought to be a model species for understanding the regularities of

processes that lead to the formation of the human body chemical composition that lives in specific geochemical environmental conditions. All biological samples were studied with the use of ICP-MS ("Water" Center of TPU and INAA (nuclear reactor of TPU). Individual organs and tissues of animals were studied using scanning electron microscopy (IISEC "Uranium Geology" of TPU). The results obtained suggest that there is a specific feature in the animal's body, which represented with the concentration of rare-earth elements of middle and heavy subgroups and the presence of micromineral phases of these elements in bones, wool and brain. At the same time, the migration of rare-earth elements in the body of herbivores and omnivores has differences and leads to greater concentration in the brain of herbivores and the digestive system of omnivores. Overall, the performed studies allowed to reveal the features of the mammals' elemental composition (more than 60 chemical elements) on the territory of Primorsky Krai. The next result is establishing the trophic chains specifics from the rocks to the mammals' organism. Data obtained allowed us to formulate the hypothesis about the possible causes of the animals' geophagia. It was suggested that the geophagia reason in the Sikhote-Alin mountains and others territory may be related to the input of heavy REE with plant feed and water and following toxic effect on animals. It is likely that the replacement of light REE, which could play an important role in the body, with heavy analogs, that are unable to perform these functions, can lead to serious violations of metabolic processes. These violations may be the reason for the instinctive consumption of mineral (e.g., clay-zeolite) sorbents enriched with sodium and light REE. Obviously, this issue requires further study with the expansion of the regions where geophagia is common, as well as research methods.

This study was financially supported by the Russian Science Foundation (Projects No. 20–67-47005 and 20–64- 47021)

SPECTROSCOPIC METHODS FOR THE STUDY OF BIOSUBSTRATES AND CONCRETIONS

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Spectroscopic methods are indispensable for the study of biosubstrates and concretions. Research requires the study of phase and element analysis. To study solid biosubstrates and concretions, methods are needed to study their morphology – IR spectroscopy, Raman spectroscopy, X-ray diffraction analysis, electron microscopy. These methods make it possible to conduct a phase analysis, and the information obtained together makes it possible to determine the mineral composition of the concretions, or to evaluate changes that have occurred in the structure of the biosubstrate, for example, bone tissue.

To determine the trace elements present in biological objects, various spectral methods are used: atomic absorption (AAS), atomic fluorescence (AFS), atomic emission (AES) spectrometry, inductively coupled plasma mass spectrometry (ICP MS), X-ray fluorescence analysis (XFA). The number of elements determined by these methods depends on their detection limit and on their content in the biosubstrate.

The most promising and widely used element-specific trace element detector is ICP MS. The advantages of this method are well-known: high sensitivity, wide dynamic range, good reproducibility of results, applicability for detecting most chemical elements, the ability to *on-line* work. The ICP MS method usually has no alternative when analyzing biosubstrates, first of all, this applies to objects such as serum and plasma, urine, hair, cerebrospinal and amniotic fluids, low concentrations of trace elements in which limit the use of any other detectors, However, the ICP MS method has its limitations. When using inductively coupled plasma as an ionization source, it is necessary to take into account possible spectral interference – the superposition of signals of polyatomic and double-charged ions, isobaric overlays and the matrix effect. An effective way to correct interference in quadrupole mass spectrometry is the use of reaction or collision cells, or mathematical correction. Optimal separation of the ion signals of the detected elements and polyatomic ions is also achieved using high-resolution mass spectrometry.

The use of the ICP MS method with laser sampling makes it possible to obtain unique information about the biosubstrate by examining it locally in different zones or in layers.

To detect the forms of trace elements present in biological objects, gas and liquid chromatography methods are needed, preferably in combination with mass spectrometry with different ionization methods. When possible, the determination of the shapes of the elements is carried out in online mode. This reduces the analysis time, improves reproducibility of results, reduces the risk of contamination of samples and the likelihood of loss, oxidation, degradation of analytes by bacteria.

THE ELEMENTAL STATUS OF MAN AND THE QUALITY OF THE ENVIRONMENT (KOLA REGION)

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The quality of the environment is assessed based on the detection of man-made pollutants in the atmosphere, water and soil. The population of the Kola region lives in an industrially developed area, which determines the increased

anthropogenic load on the environment and humans. This impact is amplified by the climatic features of the region.

The state of the Kola region, especially its central part, is determined by the enterprises operating on its territory (JSC "Kola MMC", JSC "Olkon", JSC "Kovdorsky GOK", Kirov branch of JSC "Apatit" PhosAgro, JSC NWFC, LLC Lovozersky GOK, etc.), they supply a large volume of dust emissions, which transforms the entire environment.

The biosphere of the region annually receives more than a thousand tons of Cu and Ni per year. Dusts also contain Fe, Pb, Zn, As, Se, Te, Sb, Cd, Sn, Hg. To assess the elemental composition of dust emissions, soils, plants, groundwater, sediments and biosubstrates, a modern precision method was used - inductively coupled plasma mass spectrometry.

Over the years of their activity, polluted zones have formed around large mining and processing enterprises (up to the formation of wastelands), in the soils of which there are increased concentrations of certain elements. Ecotoxicants received with dust releases further migrate in the system of soil and water bodies of the geochemical zone and cannot but affect the elemental composition of organisms located in this territory. The nature of the migration of toxic elements depends on the phase composition of dust and determines the form of their presence in natural objects.

The results of hydrochemical studies indicate a high level of pollution of water sources, including sources of drinking water supply. Anthropogenic pollution of the natural environment causes serious concern for its negative consequences for the health of various groups of the population.

The human body is constantly exposed to the multifactorial effects of the environment, to which a person adapts with permanent residence in this territory. The superposition of natural and man–made factors - the intake of certain elements into the body forms their complex associations in the human body, which can lead to a change in its functional features.

Interdisciplinary research is needed to better understand the relationship between the environment and the health of people living in the Kola region, it is necessary to study not only the chemical composition of various natural environments, but also the elemental composition of the biological environment of the human body.

Elemental analysis of whole blood, gastric juice, etc. allows you to assess the elemental status in real time, while the analysis of hair, nails, bone tissue allows you to identify the accumulation of a number of elements in the body.

Comparison of the elemental composition of drinking water, dust emissions with the elemental composition of biosubstrates, as well as comparison of the content of chemical elements in the biological environments of human inhabitants of relatively "clean" and man–made territories, allows us to identify the levels of accumulation of chemical elements in human biosubstrates depending on the geochemical and geoecological conditions of the territories of his residence.

INVESTIGATION OF GALLSTONES OF RESIDENTS OF THE KOLA REGION BY SPECTRAL METHODS

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Concretions are quite common in the gallbladder, intrahepatic and bile ducts. The elemental composition of gallstones is associated with the geoecological features of the place of residence of patients. The role of elements in stone formation and the severity of the course of cholelithiasis has been little studied. In this regard, the study of the phase and trace element composition of gallstones, depending on their morphological characteristics, is relevant and interesting. The study of the mineral composition of gallstones is focused mainly on calcium and phosphorus, a limited number of elements are determined.

It is known that gallstones contain cholesterol, bile pigments (bilirubin), can be calcified (contain calcium salts and other elements).

The purpose of this work is to analyze the structure and elemental composition of gallstones of residents living in the Kola region using spectral analysis methods.

In the work, 6 samples of stones obtained during cholecystectomy of patients performed in the surgical department were examined. The methods of IR spectroscopy, Raman spectroscopy and X-ray phase analysis, rentgen-fluorescence analysis and inductively coupled plasma mass spectrometry (ICP MS) for elemental analysis after acid decomposition of samples were used for the study.

The studied samples have a color from yellow to black. According to the results of the conducted studies and morphological characteristics, they belong to cholesterol, mixed and pigmented. The assignment of stones to one or another type of bile concretions was carried out according to the totality of the results obtained. The average content of the components in the stone was determined after the complete decomposition of the samples. 74 elements were determined by the ICP MS method, the limit of determination is from 0.01 to 0.0001 ppm, the error is up to 15%, depending on the element being determined. The mass fraction of calcium in the samples ranges from 0.06 to 31.4%, there is a correlation with phosphorus, but the concentration of phosphorus does not exceed 0.1%. The mass fraction of elements is reduced in the range of Na, Mg, Fe, K, Cu, Ti, Mn and ranges from 0.000 n to 0,n %, the proportion of the remaining elements do not exceed tens of ppm.

INFLUENCE OF FLUORINE ON FORMS OF MIGRATION OF LANTHANOIDES IN NATURAL AND POLLUTED WATER OF THE LOVOZERO MASSIF.

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In 2020, the authors examined the influence of the chemical composition of the Lovozero massif rocks on change in the chemical composition of the natural waters formed within the Lovozero massif and its nearest northern framing with considering the rock composition in the catchment area and anthropogenic influence. For these purposes, modern precision methods of analysis (e.g., ICP MS) and physicochemical modeling using the Selector software package were applied. Chemical analyses of water (sampling took place in autumn 2020) and the results of modeling the "water-rock-atmosphere" interaction showed comparable calcium, sodium, magnesium, hydrocarbonates, fluorine, chromium, cobalt, vanadium, lanthanum, cerium, zirconium and barium concentrations and pH values. The study revealed the need to take the water coming from the flooded mines under special control.

For this reason, we examined the streams running down from Alluaive mountain slopes, where the abandoned mine workings are located, and the bowels of the mountain contain a large amount of water-soluble minerals and those easily altered in atmospheric conditions. These minerals are villiomite (NaF), halite (NaCl), natrite, trona, thermonatrite, and several others (Khomyakov, 1990). In 2009, water gushed through the mouth of the shaft of the Umbozero mine due to shutdown of pumping. Mine waters filled the lower horizons of this mine and came to the surface through transport passages. Water began to flow into the Umbozero lake.

During the expedition in November 2021, surface water samples from the Alluaive mountain (the Shomijoki river, Loparitoviy stream) and groundwater samples were sampled for chemical and isotopic study. The results of the comprehensive study showed a fundamental difference in the isotopic and chemical composition of the waters contaminated by the waters of the flooded Umbozero mine.

A thermodynamic study of the weathering processes in the Lovozero massif for the "water-rock-atmosphere" system at a temperature of 5°C showed the influence of the elements from rocks of the studied massif on the formation of the chemical composition of natural waters. An increase in the “water-rock” interaction level leads to an increase in the concentrations of F^-, Cl^-, SO_4^{2-}, HCO_3^-, in the solution. This affects on the mobility of lanthanum, cerium and other elements due to the formation of complexes with them. The relatively high content of fluorine, phosphorus, and $HCO3^-$ in the solution facilitates the dissolution of silicates, which results in releasing Si, Al, P into the solution. Monitoring of waters from a flooded mines with an increase in the water-rock interaction level showed several times higher pH value (9.7) and concentrations, mg/l: Na (52.3), HCO^{3-} (73.77), F^- (3.80), P (0.13), Al (0.13), Si (7.82), V(0.0012), U(0.0008), La (0.00030), Ce (0.00069) than in natural waters.

Also, during sampling, studies of the isotopic composition of these waters were carried out for isotopes $\delta^2$2H and $\delta^2$18O. Owing to these studies, it is possible to visually appreciate the speed and degree of the underground flow influence on the studied water bodies, and the “cleaning factor” due to dilution with meteoric and surface waters.

THE INFLUENCE OF WATER TREATMENT ON THE CHANGE IN THE CHEMICAL COMPOSITION OF DRINKING WATER IN LOVOZERSKY DISTRICT (MURMANSK REGION)

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The chemical composition of underground and surface waters and sources of drinking water supply is the most important geochemical and ecological factor since the geochemical properties of waters have a direct biochemical effect on the human body and its physiological functions. The leading indicators negatively affecting the health of the population of the Kola Peninsula are: pollution of water bodies, insufficient concentration of macronutrients in drinking water sources, changes in the state of elements as a result of process treatment and transportation through water supply networks.

The purpose of this work is to assess changes in the chemical composition of drinking water supply in Lovozero village, Murmansk region,

as a result of water treatment using physico-chemical modeling (PC "Selektor").

According to the chemical composition, water from the intake (Virma River) is characterized by high natural iron content, color and turbidity. According to the water studies carried out by the State Unitary Enterprise "Olenegorskvodokanal" and the Federal State Institution "Center of Hygiene and Epidemiology in the Murmansk Region in Monchegorsk, Olenegorsk and Lovozersky district", the following conclusion has been made from the water intake and distribution network of Lovozero village: "water from the Virma River does not meet the requirements of the Guidelines for ensuring the quality of drinking water [GOST 56237-2014]. Currently, the network wear is 93 %.

The existing water treatment process for the central water supply of Lovozero rural settlement includes chlorination, coagulation and filtration [Water supply process ..., 2014]. Disinfection is carried out with liquid chlorine in accordance with the requirements of GOST (supplier is AOOT "Caustic", Volgograd) and AQUA-AURAT aluminum polyoxychloridecoagulant; water is stabilized with a soda ash solution with a concentration of 50 mg/l.

During the expedition work in November 2021, we took samples of the waters from the Virma River and the central water supply (canteen, village pump). To solve this problem, we used a physico-chemical model of water-rock interaction adapted to the conditions of the Murmansk region and allowing to assess the ecological situation in the presence of natural or man-made influence [Sandimirovetal., 2022]. Adding NaOCl – 0.316; Na_2CO_3 – 0.158; $AlCl_3$– 0.0050 mol to the Virma River model (per 1000 liters of source water), we obtain a change in the concentration of the solution (mg/l): Al – 0.057 to 0.192; Na – 2.62 to 17.2; HCO_3 – 15.7 to 35.7; Cl – 3.3 to 13.8; pH – 6.67 to 7.67, which is comparable to similar concentrations in the village pump water (mg/l): Al – 0.176; Na – 18.64; HCO_3 – 49.19; Cl – 11.3; pH – 7.68. Physico-chemical modeling makes it possible to predict changes in the forms of migration of both macro- and microcomponents of water and, if necessary, optimize the consumption of reagents.

CHEMICAL COMPOSITION OF GASTRIC JUICE AND THE IMPACT OF POTABLE WATER ON IT: MONITORING AND MODELING

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The goal of this study is to collect new data on the chemical composition of gastric juice (GJ) in the residents of Apatity-Kirov District of Russia's Murmansk Region and the effect of medicinal water on the chemical composition of gastric juice using physicochemical modeling.

As part of the RFBR grant approved in 2018, we developed a model describing the environment in the human stomach (using the Selector software) based on existing literature (an idealized model) with the following parameters: pH 1.23, Eh 0.092 B, Na1160, Ca 5.03, K 590, P 3.18, HCl 5000, H_2CO_3 1200, SO_4^{2-} 10, NH_4OH 80 (mg/l), water 993 g, average temperature +38°, pressure 1 10^5 Pa (1 bar). When the concentration of HCl in the system changes (between 5190 and 1580 mg/l), while the concentrations of other elements are constant, the values of pH and Eh change (from 1.199 to 10.48 and from 0.094 V to -0.515 V, respectively) , which indicates the formation of acid-base and redox barriers.

Our study of the chemical composition of the gastric juice in the residents of Apatity-Kirov District (a random sample of 20 patients) showed a match between the chemical elements in the gastric juice and in naturally occurring water (Central water intake). Element concentrations in the GJ were several orders of magnitude higher than in natural water, low average concentrations (relative to the idealized GJ model) of the elements Na, Cl, K were found at a high concentration of phosphorus. The presence of La, Ce, Zr was also found. A number of patients had low HCl acid levels in the stomach (hypochlorhydria), whose functions include break down food, absorbing certain nutrients such as protein and vitamin B12, destructing bacteria and other pathogens in the stomach. Hypochlorhydria can be caused by age (the stomach produces less acid as we age), medications, or bacterial infection (https://medicalinsider.ru/news/gipochlorgidriya-prichiny-simptomy-i-trechenie). Prolonged hypochlorhydria may contribute to gastric juice depletion, weakening the natural protection, and lead to an increased risk of gastric cancer and pathological changes not only in the gastrointestinal tract,

but also in the entire human body(Tannenbaum et al. 1981; Cater, 1992; Senin et al., 2011).

Deviations from the idealized GJ model are associated with the incidence of conditions of different nature and severity in the patients: cancer (25% of the total number of diseases, 99.6<Na<340, 57.2<K<158.7, mg/l), cholecystitis (5%, Na 302.6; Al 7.72; P 94.4; K 36.8; Ca 46.7 mg/l), anemia (5%, Na 298.5, K 72.5 mg/l),TORCH infection (5%, Na 342.9, K 59.7 mg/l); osteoarticular diseases (15%, elevated calcium and phosphorus 12<Ca<32.6, 92.4<P<114), cardiovascular diseases (5%, above average content of boron (11.9 mg/l), lithium (0.024 mg/l), low Na (513.7 mg/l) and K (116.4 mg/l)), gastrointestinal diseases (40%).

Chemical composition of the gastric juice of patient 1 before (pH 1.48 Ca^{2+}12.3; Na^{+} 821.9; K^{+} 275.7; Mg^{2+} 6.95; Cl^{-} 4940; P 46.3 mg/l) and after treatment (pH 6.09 Ca^{2+} 14.8; Na^{+} 223.1; K^{+} 60.2; Mg^{2+} 2.05; Cl^{-} 1930; P 8.13 mg/l) indicates change in the course of the treatment - the concentrations of sodium, potassium, chlorine, magnesium, phosphorus decreased several times.

Using thermodynamic modeling, we showed that the results of treatment with the mineral water from Krasnodar Territory match those of drug treatment. Mineral water should be considered as an effective medical resource for the prevention and treatment of stomach diseases. This approach opens up new prospects for research in the field of ecology and medicine.

MICROELEMENT STATUS OF MINING WORKERS

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At the present stage of development of society, the health of the population is deteriorating. An important reason for this is environmental pollution as a result of anthropogenic impact. According to WHO, environmental risks include undrinkable water, urban air pollution and exposure to heavy metals, which are most often present in the environment in the zone of influence of industrial enterprises. The population living in such areas is at risk of developing so-called environmentally caused diseases. These diseases are not separated into a separate group according to the official classification; their symptoms are similar to those of other pathologies and can be masked by them. Environmentally dependent diseases are rarely diagnosed due to the fact that at the early stages of their development, the system of compensatory reactions of the body is activated, which ensures the preservation of its functions. However, with prolonged exposure to an adverse factor, such protection ceases to work and decompensation occurs, leading to the development of degradation processes of the body. In this case, not only the development of new diseases may occur, but also an exacerbation of the course of existing ones. For the early

diagnosis of environmentally dependent diseases in the population, the trace element composition of biological substrates (hair, blood, etc.) is studied.

The main source of environmental pollution in the city of Sibai (Republic of Bashkortostan) is the Sibay branch of the Uchalinsky Mining and Processing Plant - a city-forming enterprise for the extraction and enrichment of copper ores, which includes quarries, underground mines, dumps, tailings dumps and a processing plant.

The purpose of this work was to study the elemental composition of biosubstrates of workers of this mining and processing plant. The biosubstrates were analyzed in an accredited testing laboratory of the Center for Biotic Medicine (Moscow, Russia).

As a result of the conducted studies, it was found that the average concentrations of most of the studied chemical elements in the blood of workers were within physiological limits. At the same time, cases of increased content of elements such as cobalt and cadmium have been identified. The average thallium content was equal to the upper limit of the norm. The deficiency in the hair was revealed by the content of the following elements: Se (in 52.4% of the examined), I (in 50.0%), Cu (in 28.6%), Si (in 23.8%), Zn (in 14.3%), K (in 26.2%), Co (in 9.5%), Mn (in 7.1%), Ca (in 4.8%), as well as Na, Mg, P, Fe, Cr (in 2.4%). An increased content of P (33.3%), Ca (16.7%), Mg (9.5%), Fe (7.1%), Zn (7.1%), Cd (4.8%), as well as Na, K, Cu, Se (2.4% each) was revealed. The remaining chemical elements were within the control values. With increasing age, a decrease in the content of phosphorus and selenium was noted in the workers' hair. Thus, the study revealed elevated concentrations of toxic metals cadmium, thallium, cobalt and manganese, as well as a deficiency of essential trace elements iodine and selenium in the blood. In the hair of a number of examined persons, a reduced content of iodine, selenium, copper, zinc and cobalt was revealed.

The results obtained indicate that the population of this region is at risk of developing both metal toxicosis and deficiency of vital trace elements. This fact requires the strengthening of control over the level of toxic substances in the atmospheric air, soil, water, food and the implementation of measures to reduce the risk to public health, including the correction of trace element status.

Organic mineralogy

SPHERULITIC CALCITE CLUSTERS AS A MANIFESTATION OF THE RELATIONSHIP BETWEEN ABIOTIC PROCESSES AND BIOLOGICAL MECHANISMS

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Unusual spherulitic calcites combined into various clusters (Figure) were found in the microbial-pelitomorphic matrix of fine clastic breccias during the study of Upper Miocene bryozoan bioherm limestones in the section at the Cape Kazantip on the Kerch Peninsula of Crimea. The microbial-pelitomorphic matrix contains iron hydroxides and dissolution cavities with newly formed quartz crystals, rarely with grains of a sheaf-like celestine, barite. These breccias were found in between bioherm layers in contact with bryozoan bioherms. The formation of spherulitic calcites most likely could take place in the contact zone of carbonate silt and microbial matter characterizing the matrix of lithobioclastic material. A similar process could occur in the presence of elevated concentrations of Na, Ba, Cl^- and SO_4^- ions relative to normal sea water, i.e. in saline waters (Bischoff et al., 2019; Mercedes-Martin et al., 2022). It has been shown that in modern microbial mats of salt lakes and under laboratory experimental conditions, spherulitic calcite is formed from waters with moderate and high calcium/alkalinity ratios $[Ca^{2+}]/[CO_3^{2-}]$. It was previously established that hydrothermal seeps were an additional process during the formation of the Kazantip bryozoan bioherm complex (Antoshkina et al., 2021). These seeps, as established, were due to the activation of an ancient mud volcano (Antoshkina et al., 2020). Electron microscopic studies of the breccia matrix revealed the neoformation of the minerals barite, halite, celestine, high-Mg calcite, as well as dolomite in intergrowths with calcite, which is not typical for carbonate sedimentation. In addition, the presence of accumulations of framboidal iron oxide (after pyrite) was noted. The composition of seep solutions was characterized by the predominance of sulfate-chloride components.

According to many published papers, some elements, such as magnesium, can not only affect the stability of the crystalline CaCO3, but also play important roles in the formation of spherulitic morphology (Wu et al., 2017**)**. Clusters of spherulitic calcites serve as an important indicator of paleoenvironments, since the formation of such structures is a clue to the influence of abiotic processes and the influence of biological mechanisms in the formation and early diagenesis of nonskeletal carbonates (Brasier et al., 2015; Chan et al., 2019; Hodgson et al., 2018).

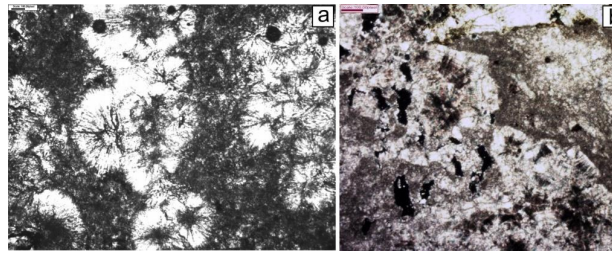

Figure. Microphotographs (a, b) of spherulitic calcite clasters in the microbial (a) and microbial-pelitomophic (b) matrix of interbiohermic fine clastic breccias, Upper Miocene, Kazantip.

MINERALS IN PLANTS: CASE STUDY OF *LITHOSPERMUM ARVENSE* AND *CELTIS* FRUITS

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Biomineralization is common process in plants. Minerals are formed in most plant tissues and organs including fruits. Commonly reported minerals precipitated in plants are calcium carbonates (amorphous or calcite), calcium oxalates and amorphous silica (He et al. 2014). The study focused on the fruits of *Lithospermum arvense* and *Celtis*, which are preserved abundantly in archaeological areas and can be used for paleoenvironmental reconstructions (Pustovoytov et al., 2004).

For fruits of both *L. arvense* and *Celtis*, scanning electron microscopy combined with energy dispersive microanalyzer revealed the presence of two mineral phases in pericarp (fruit wall). The chemical composition of the first mineral phase included calcium, carbon and oxygen, so it can be interpreted as calcium carbonate or oxalate. The second mineral phase was composed of silicon oxide. Raman spectroscopy analysis showed that the first mineral phase composed of calcium and carbon was represented only by calcite for both *L. arvense* and *Celtis*. It was identified by the characteristic bands located at 708 $cm^{-}$and 1088 cm^{-1}. Since the Raman spectra of crystalline phases of silicon oxide or opal were not recorded for the studied fruits, we assumed that the silicon oxide phase corresponded to the amorphous SiO_2.

Though the *L. arvense* and *Celtis* fruits have similar mineral composition, the distribution of mineral phases in fruit pericarps is distinct. The external layer of pericarp of *L. arvense* was presented by closely packed epidermal cells filled by amorphous SiO_2. It had thickness varied from 10 – 20 μm at the wall surface or 50 – 70 μm between the papillas. The middle part of pericarp of *L. arvense* fruits composed of sclerenchyma cells filled by calcite and embedded in a SiO_2 matrix with variable admixture of Ca and presumably

organic matter. The calcite-filled cells had undulated irregular shape, or were elongated and oriented along the inner pericarp wall. Moreover, in the inner area of mesocarp the cells might be filled by calcite as well as amorphous SiO_2.

Contrary to the *L. arvense*, the external layer of the exocarp of *Celtis* fruits was characterized by closely connected cells filled by calcite. In the middle area, the size of these cells decreased and the SiO_2 matrix surrounded the cells might be observed. The inner area of the pericarp was presented by discontinuous layer of closely packed cells filled by amorphous SiO_2. Since in *L. arvense* fruits, unlike to *Celtis* fruits, amorphous SiO_2 is actively precipitated in the cells of external layer of pericarp, that makes it possible to preserve calcite of the inner layers unchanged for a long time, fruits of *L. arvense* might be more useful for paleoenvironmental reconstructions compared to *Celtis* fruits.

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INDUCED CHANGE OF 9,10-DIPHENYLANTHRACENE POLYMORPHES.

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Spatially offset Raman spectra (SORS) were obtained from the surface layer of a 9,10-diphenylanthracene (DPA) single crystal with 785 nm laser. Most of the Raman spectra correspond to the most common crystal structure of DPA - the α-polymorph. On the basis of differences in Raman spectra measured on the surface of a single crystal were found some "Abnormal zones" with the structure of the γ-polymorph. These zones covered only several percent of the full surface.

Spectral studies by the SORS method in the region of anomalous zones showed that in the deeper near-surface layers of the crystal, the γ-polymorph transforms into the α-polymorph structure. The prolonged laser irradiation of the "Abnormal zones" with measuring of Raman spectra showed that a photoinduced transition of the DPA crystal structure from the γ-polymorph to the α-polymorph took place in the focal region of the lens of the Raman spectrometer. The proposed approach can be useful for controlling the photoinduced change in the characteristics of the surface layers of organic semiconductor structures formed by epitaxial growth.

CARBON ISOTOPE COMPOSITION OF THE PAI-KHOI AMBER-LIKE RESIN (NW ASIA)

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The fossil resin localities are known in the Quaternary deposits of the NE Pai-Khoi. The fossil resins of these localities are less studied in contrast to the Baltic and European ambers.

This study is based on the collections of the fossil resins stored in the Geological Museum (Syktyvkar, Russia; collection #160). Totally 13 samples of Pai-Khoi amber-like resin (retinite group) were studied. The samples were collected from the Quarternary placer on the bank of the Peschanaya River (N 69°36'44.91“ E 62°07'17.24”). The material of the placer is supposed to be reworked deposits of the Late Cretaceous - Early Paleogene Sayakha Formation.

The Pai-Khoi amber-like resin is honey-yellow in color and bright. Results of IR spectroscopy and differential thermal analyses suggest that the amber-like resin corresponds to gedanite. The FTIR spectra show a lack of a “Baltic shoulder” at 1247 - 1160 cm^{-1} in association with a series of bands of low intensity at 1247, 1175, 1125, 1037, and 972 cm^{-1}. The differential thermal patterns demonstrate an exothermic peak at 150-160° and weak endothermic peaks near 120 and 170°.

The $\delta^{13}C$ value in the Pai-Khoi samples ranges from -27.6‰ to -22.2‰. The mean value of $\delta^{13}C$ for the measured samples is about -25.2‰ (standard deviation 1.8, n=13). This value differs significantly from those of the Baltic amber (c.a. -23‰) and is similar to the $\delta^{13}C$ values of the Malaysian (late Miocene) and Tadkeshwar (early Eocene) amber-like resins. The wide range of variations of the $\delta^{13}C$ values of gedanite of the Peschanaya River locality suggests diverse sources of the gedanite in this placer. Probably the placer had been formed by the material reworked from different parts of the sequence of the Sayakha Formation.

Biomineral interactions in soil

MICROBIOME OF PRIMARY SOILS OF OPEN-PIT DUMP COMPLEXES

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Studying the dynamics of soil microbiota composition at different stages of ecogenesis is the most important task of modern ecology and soil biology. Ecogenesis is the main process that provides the formation of a favorable (optimal) environment for communities of organisms colonizing solid-phase parent material or soil substrate. At the same time, ecogenesis is one of the models of the primary interaction between vegetation and substrate during the development of new geoenvironments (the actualistic model of land development by plants and modern scenarios of colonization of free substrata). Ecogenesis is also carried out in unfinished scenarios of soil biogeomembrane destruction (pyrogenic, erosion, technogenic scenarios). Since ecogenetic and demutational ecosystems shifts are characterized by the presence of a direct material and energetic connection between the parameters of ecosystem and edapotope development, the study of the microbiome at the boundary of ecosystems interactions is highly demanded. Changes in the parameters of the living part of ecosystem lead to irreversible changes in the organization of the edaphotope, which, in turn, lead to changes in the local conditions of the biotope (living part of terrestrial ecosystem). The indicated process and functional relationship is expressed primarily in the case of primary (ecogenetic) or demutational assimilation of the biota of the lithological substrate. We studied the development by microorganisms of the most ranked lithological substrates, recently exposed on the surfaces of post-technogenic landscapes in various natural zones. Since the intensity of biolithogenic interactions sharply decreases with time, when intra-soil ecological niches are diversified and soils pass a zonal (or close to it) level of development or the next stage of developmental evolution, chronoseries of soil formation were studied. Study of formation of microbiome at initial (recent, primary, initial) stages of soil formation is carried out, that in the future will help to reveal ontological essence of soil formation process at the stage of formation of zonal embryonic profiles in postanthropogenic and postpyrogenic variants of development. It is shown, that at the present stage of development of soil biology, it is necessary to accumulate primary data on taxonomic and functional composition of microbiome, and, also their analysis by means of modern statistical methods. The obtained data on microbial precursors of soil formation in the future will help to identify microbial drivers of soil formation and to develop controlled technologies of reclamation and accelerated natural regeneration.

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MICROMORPHOLOGICAL FEATURES OF ABIOGENIC-BIOGENIC INTERACTIONS IN SUSPENDED SOILS OF SOUTH VIETNAM

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Traditional soils formed on various mineral parent materials are characteristic of classical zonal ecosystems and dominate on the surface of modern land. Nevertheless, in the tropical forests of South Vietnam, the soil-forming process is "detached" from the topsoil surface of the landscape, partly remaining there, and in a substantial mass passing into epiphytic communities of tree ecosystems. Epiphytic communities are characterized by suspended soils, causing interest among many researchers. These soils do not have all the classical attributes of soil formation, in particular, a mineral soil-forming rock. The source of mineral matter for these soils is atmospheric precipitation and aerosols. The rich ash cycle in tropical forests results in most of the mineral elements not returning to the soil or weathering crust surface, but remaining in the cycle as an ash. Because of this, suspended soils are not consist on 100% of organic matter and organo-mineral interactions take place. This study focuses on the micro morphological features and microstructure of suspended soils of South Vietnam. Micro monoliths of suspended soils were sampled by us in the field in 2018-2019 in Vietnam. They were used to make thin sections, which were studied using a Leica MC 170-HD polarizing microscope. Micromorphological studies allowed us to establish the following. The organic material of the studied suspended soils is clearly divided into undisturbed, inherited from litter, which is retained in epiphytic soil formations and well humified, darkly colored in brown and dark gray, indicating a possible intensive transformation of organic matter at different vertical levels of epiphytic communities. In some samples, humification concerns only the marginal parts of plant remains, while in others, it penetrates inside. This is related to the tissue structure of specific plant residues. In other soils, the association of organic-mineral particles with the formation of first- and second-order aggregates typical of the humus horizons of ordinary soils is observed. Thus, on the base of data obtained we can conclude that parent material is not obligatory factor of humification and organo-mineral aggregates formation. Suspended soils have a number of substantive micro morphological features that can be used in the future for their identification and classification.

MICROBIOME STRUCTURE OF THE HYPERHYMIC CHERNOZEM AFFECTED BY THE TYPE OF LAND USE

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The microbiome structure of Hyperhumic Chernozem (WRB, 2014) located in the Kamennaya Steppe nature reserve (the Voronezh Region, Russia) was studied. The soil transects were crossed over: the mown fallow plot, forest plantation, and wheat crops. A distance between soil profiles was about 140 m. The soil samples were collected at the same time from the soils horizons up to a depth of 100 cm (in fallow up to 200 cm). The age of the fallow land and field-protecting plantations is about 100 years; whereas the arable land use of former feather-grass steppe is about 200 years old.

The key plots of soil pit location are characterized by similar parent substrate, climate parameters (mean annual precipitation and temperature), and humus-accumulative type of pedogenesis. The history of land use of this territory is known. That allows us to use these profiles as the possible objects to investigate the specificity of the microbiome structure affected by the type of land use.

The microbiome of different taxonomic levels (phylum, class, order, family, genus, and species) was studied based on the methodological approach (Andronov E.E., 2011). The microbiome structure analysis was performed in different aspects: a) changes in the microbial community along the depth of soil profiles, b) evaluation of the similarity and differences in the microbial community of the surface and middle soil horizons of different lands, and c) comparison of the microbocenoses in parent substrate from soils affected by the different land use systems.

Seven phyla dominate the microbial community structure in all profiles: *Proteobacteria, Actinobacteria, Firmicutes, Verrucomicrobia, Acidobacteria, Gemmatimonadetes*, and *Chloroflexi*. The share of the first three phyla is from 70% to 90% of the whole volume. They are represented by phyla p. *Actinobacteria, p. Verrucomicrobia* and *p. Acidobacteria.* Along the profile the content of the predominant phyla *p. Actinobacteria, p. Verrucomicrobia* and *p. Acidobacteria* are decreased, while the content of *p. Proteobacteria* and *p. Firmicutes* are increased.

The upper horizons of the forest and fallow soils are characterized by the similar taxonomic structure of the microbiome with predominance of phyla *Actinobacteria* (1), *Proteobacteria* (2), and *Firmicutes* (7). They have the same positions in the soils despite the type of land use system.

158 families were identified in the microbial community of soils; their content varies in the range of 0.10–11.10%. Among the families whose share

exceeded 1%, representatives of 19 families of the seven phyla mentioned above were identified.

We have observed that the profile distribution of only 3 families *Gaiellales (Actinobacteria), Rhodoplanes (Proteobacteria),* and *Chthoniobacteraceae (Verrucomicrobia)* was directly relates to land use. Their proportions decreased in the arable horizon compared with fallow and forest soils.

It was revealed that the land use impact is obvious at the phyla and family levels, while it is not pronounced at the genus and species levels. That indicates the existence of multiply relationship between microbiome structure and land use type.

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TRANSFORMATION OF SOILS OF THE LITTORINA TERRACE UNDER THE INFLUENCE OF URBANIZATION (ST. PETERSBURG, RUSSIA)

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St. Petersburg is one of the largest cities in Russia. The city is located at 59º57′N 30º19′E, at the mouth of the river Neva, on the coast of the Gulf of Finland, Baltic Sea. The historical center of the city occupies the lowest part of the Neva lowland - the Littorina terrace (absolute elevations up to 10 m above sea level). The Littorina terrace is composed of alluvial-marine sands and sandy loams. During the period of the city's existence, the territory of the Littorina terrace experienced the highest degree of landscape transformation relative to other parts of the city. However, within the city center itself, the degree of anthropogenic impact on soils is differentiated: the minimum of soil cover transformation is observed in the parks, and the maximum takes place in built-up area and under the road network.

The following series of soils has been established on the Littorina terrace, according to the degree of anthropogenic transformation: 1. Stratified gray-humus-gley soil (Elagin Island). 2. Urbistratified gray-humus ferruginous gleyic soil (Kamenny Island). 3. Urbistratified gray-humus stratozem on buried gray-humus soil (Own Garden, Yelagin Island). 4. Urbostratozem on buried gray-humus-gley post-agrogenic soil (Summer Garden). 5. Technogenic

urbostratozem on buried gray-humus-humus-gley soil (Rumyantsev Square). 6. Technogenic urbostratozem, sealed under asphalt, on buried urbistratified gray-humus-gley soil (Nevsky Prospekt, 11). The following parameters were determined in the soils according to standard techniques: pH_{H2O}, C_{org} content, content of mobile phosphorus compounds, $CaCO_3$ content, and total content of heavy metals (Pb, Cu, Zn). Additionally, the particle size distribution and the presence of soil salinity were selectively determined. The minimum degree of anthropogenic transformation of the profile was observed in gray-humus-gley soils. These soils are closest in structure and properties to natural analogues found outside the city center, on the waterlogged southern coast of the Gulf of Finland. The maximum degree of soil morphological features and chemical properties transformation was observed in technogenic urbostratozems, especially sealed under pavement ones. These soils were characterized by a large number of anthropogenic inclusions, high alkalinity, and even the presence of salinity. The content of heavy metals does not always correlate with the number of anthropogenic inclusions in the soil and varies along the profile depending on the land use history. However, buried natural soils and parent rocks were characterized by a minimum content of heavy metals. Thus, under urban impact in the central part of St. Petersburg, the initial gray-humus-gley soils were buried under anthropogenic (cultural) layers with a total thickness of up to 150–190 cm. Based on the phase analysis, it can be concluded that the main mass of the cultural layer consists of local material.

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ORGANOMINERAL INTERACTIONS IN SOILS OF THE BUNGER HILLS (EAST ANTARCTICA)

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The diversity of the soils of one of the largest ice-free areas of Antarctica after the Dry Valleys - the Bunger Hills or Bunger Oasis (66°17′S 100°47′E, 900 km^2) were studied for the first time over a long field season within the 63 seasonal Russian Antarctic expedition (about 1 month, January 2018). The Bunger Hills are characterized by similar climatic factors and conditions to the coastal and trans-shelf oases of East Antarctica (Larsemann Hills, Thala Hills, Schirmacher, etc.), the maximum thickness of the active permafrost layer is more than 120 cm. The absence of penguin colonies and therefore small populations of the south polar skua and snow petrel leads to an extremely insignificant transfer of organic matter from the sea, which is typical of many

coastal oases of East Antarctica, and the absence of ornithogenic soils. Only in small wind shelters in the stones and rock baths, there is a local ornithogenic introduction of organic matter. The main soil types represented in the Bunger Hills, except for ornithogenic and post-ornithogenic soils, are similar and close to the soils of other previously studied oases of East Antarctica, but the differences are already apparent in the soil cover.

The soil cover of the Bunger Hills has a mosaic structure that is not determined by the breadth and distance from the ocean or glacier but by local conditions (geomorphological position, size of the meso-relief forms, the presence of wind shadow for fixing all-year snow patches, lateral moisture runoff, granulometric composition of parent rocks, the amount of fine earth material, drainage of meltwater of the snow patches in the upper 5 cm). An important geochemical feature of the oasis is the extensive distribution of fine crystalline salt inlays of two groups on the soil surface: carbonate-chloride-sulfate and predominant carbonate compositions. The Bunger Hills oasis is a more arid variant of the Mid-Antarctic snow-patch cryptogamic barrens. Under such extreme conditions, organo-mineral complexes are formed where clay minerals play an important role.

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RESULTS OF THE STUDY OF HUMIC ACIDS IN THE COMPOSITION OF SOILS OF DIFFERENT HORIZONS

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One of the urgent problems in the Omsk region is land pollution. The quality of cultivated soils directly depends on the measures taken to improve their structure and physico-chemical properties through the restoration of the biological cycle of organic matter and gas exchange. The development of measures for the restoration of exploited soils is impossible without understanding the degree of influence of animal organisms on them - representatives of the mesofauna, in particular earthworms. The decisive role of lumbricides in the processes of improving the quality of the soil is due to the dominant participation in structure formation, an increase in the duty cycle and aeration, and the accumulation of easily soluble compounds in the soil that contain elements of mineral nutrition in a form accessible to plants. Factors of the progressive influence of the vital activity of earthworms on the processes of transformation and maintenance of the ecological balance of soils that are not subject to anthropogenic impact are successfully used in vermicultivation and obtaining biohumus. The issues of the possibility of using earthworms as a

subject of biological reclamation of various types of cultivated soils and the issues of processing poultry and livestock waste with the help of lumbricides require additional research in specific conditions. In terms of solving these problems, biological soil reclamation should be considered as a category of biodynamic agriculture.

Among the inhabitants of the soil, earthworms meet the requirements for the choice of bioindicators to the greatest extent, swallowing the soil, they come into contact with pollutants from the inside, and not just from the outside. These animals are numerous, sedentary, with a small individual habitat area. They have a relatively large size, which is convenient for anatomy. Living organisms have the most available energy contained in labile humic acids. The values of these indicators changed irregularly over the years of research and were largely determined by the quality and physical ripeness of the soil during the period of mechanical processing.

Using the method of IR spectroscopy, soil samples of different horizons and after the impact of earthworms on the processes of transformation and maintenance of the ecological balance of soils were studied contribute to studies areas of biochemistry that consider bioprocesses regulation using metal ions.

The content of humus and labile humic substances stabilized at an average level, the values of these indicators did not change, it can be said that the processes of mineralization of organic matter were replenished by the volume of the non-commercial part of the products that were left in the fields. Humic acids prevailed in the composition of soil humus, but the content of the most valuable fraction associated with calcium was insufficient (25%).

SOILS UNDERLAIN BY SOLID ROCKS IN THE COLD ENVIRONMENTS: GENESIS, MINERALOGY, AND SPECIFICITY OF FINE EARTH FORMATION

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One of the topical fundamental soil science issues is the soil fine-earth formation from the solid rocks. That allows to assess: (i) allochthonous/ autochthonous origin of the fine earth, (ii) rock weathering rate affected by time and climate conditions, (iii) group of minerals that are inherited from the rock and their fate in the soil profile affected by pedogenesis, and (iv) trends of soil formation from an initial profile into mature one. The study objects are located in the regions with cold environments of European Russia and Siberia.

The acidic soils (Inceptisols and Spodosols) that have mostly developed from an autochthonous fine earth of silicate solid rocks, were studied in European Russia and Siberia. Their fine earth is mostly a result of silicate rock disintegration and the mineralogy reflects the influence of the subjacent solid geology. It was revealed the initial stage of fine earth formation affected by biofilms. The latter was confirmed by a model experiment: in the autochthonous accumulations the rock fragments remain attached to the solid rock due to the release of extracellular polymeric substances by the biofilms. Weathering of the contribution of inherited minerals can be enhanced by pedogenesis (e.g. chlorite and illite transformation into mixed-layer clays or vermiculite occurred in the soils on meta-gabbro amphibolite). It was also established (e.g. soils on the dolerite – traprocks of the Central Siberia Plateau) that rock weathering led to the formation of iron-clay-organic coatings on the surface of rock fragments retarding its further weathering.

Opposite to the soils on the silicate solid rocks, the red-colored calcareous Inceptisols underlain by limestone of the southern Siberia (the Baikal region) have formed from the allochthonous fine earth. The latter was confirmed by mineralogy data. However, occurrence of disintegrated limestone fragments in the soil profiles is keeping the alkaline environment, in which mineral association is rather stable.

Thus, it was revealed based on mineralogy approaches: (i) the fine earth origin in the soils underlain by two major groups of solid rocks that are distinctly different – silicate ones within different genesis and composition and limestone and (ii) the trends of weathering and alteration of inherited minerals in the soil profiles in the cold environments.

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AGGREGATION AND DISINTEGRATION OF CLAY SOIL PARTICLES UNDER CARBON DIOXIDE AND A CHEMOLITHOTROPHIC COMMUNITY

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The aim of the work presented was to establish the influence of an active chemolithotrophic community on contacts between clay particles under conditions simulating the water-saturated subsurface and deep layers of a clay soil. Carbonate clay was sampled from Quaternary deluvium on Permian variegated clays from a depth of 1.5-2.0 m on the watershed of the Volga and Sviyaga rivers. An experiment was carried out with the soil particles' size distribution detected at two levels of carbon dioxide and a chemolithotrophic biofilm stimulator and two exposures - 2 and 6 months. The soil was stuffed into experimental vessels after grinding and sieving through a 0.25 mm cell.

The vessels had sealed water circulation. For uniform distribution, the soil was treated with the stimulator trough porous ceramic disks - carriers exposed for 14 days in the cultural liquid based on a washout from cave calcite speleothems and a modified R2 medium. The organic matter content introduced into soils in this way was 0.3 and 1.9 mg/g of soil at exposures of 2 and 6 months, respectively, on the zero day of the experiment. The soil particles' and microaggregates' size distributions were estimated on a Beckman Coulter laser particle size analyzer. Surface interactions between particles were characterized using the author's wetting contact angle procedure for soil specimens. The soil organic matter transformation was assayed by the Tyurin method (TsINAO's modification). The carbonate cement content in the soil was estimated by the method of V.E. Sokolovich. After 2 months of experiment in the option under the only hydration influence (control) the fraction of 2-50 μm began to dominate due to the destruction of microaggregates >50 μm. Chemolithotrophs stimulated in the normal atmosphere led to increasing aggregation of particles into microaggregates >50 μm and median size of microaggregates (17 μm versus 13 μm), relative to the initial option. Chemolithotrophs stimulated under a high CO_2 content caused the disintegration of even mechanically strong particles. After 6 months of experiment the median size of microaggregates increased in all experimental options: the largest increase - up to 33 μm - was observed when chemolithotrophs were stimulated under a high CO_2 content. The volume fraction of microaggregates >100 μm in the options under a high CO2 content exceeded one in the initial option (12–16% versus 7%), herewith these microaggregates were less resistant to ultrasound, i.e. they possessed a higher degree of crystallinity than microaggregates at the normal content of CO2. According this, the degree of crystallinity decreased in the control and in the stimulated chemolithotrophs under a high CO2 content options can be concluded. On the contrary, that increased in the stimulated chemolithotrophs in the normal atmosphere and in the high CO2 content control options. The high crystallinity could correspond to the calcite form of carbonates, and an amorphous phase – to organomineral one. The particles' aggregation was accompanied by their hydrophobization, with raising wetting contact angle to 91° in the stimulated chemolithotrophs under a normal atmosphere option after 6 months. The biofilms that developed in the studied soil followed the internal nonlinear dynamics of organic matter accumulation, surface hydrophobicity formation and cement crystallization, as well as contributed to the particles' aggregation inside a period of 2-6 months.

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PALEOSOLS OF THE MIDDLE PERMIAN CONTINENTAL DEPOSITS OF THE SENTYAK SECTION, RUSSIA

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The section of Kazanian stage is situated in the European Russia, on the right bank of Kama river (55°42'06.7"N, 51°44'08.2"E) and it is the reference section for Lower Kama region [1]. The upper part of the Lower Kazanian and the entire Upper Kazanian are represented by red beds containing non-marine fauna and paleosol profiles.

Field description of paleosols and laboratory methods were used including micromorphological analysis of thin sections, scanning electron microscopy (SEM) and others.

Four types of paleosols were identified, 3 types developed on siltstones and 1 type developed on limestones (calcareous paleosols). The first three types of paleosols contain root traces in situ, carbonate nodules, and differ in their degree of maturity. Type 1 paleosols are weakly developed, they dominate the section and classified as Protosols [2] despite the presence of carbonate nodules. Type 2 paleosols are strongly developed and occurred only in the Lower Kazanian deposits. They classified as Calcisols [2] due to well defined Bk horizon (calcrete). Type 3 paleosols are moderately developed and classified as (argillic) Calcisols [2], since the main feature is the presence of carbonate nodules.

A characteristic feature of this section is the occurrence of calcareous paleosols directly on red-colored Type 3 paleosols; this can be traced at several levels in the Upper Kazan deposits. Carbonate paleosols are represented by micrite-ostracod dark gray lumpy limestones with wavy layering and subvertical and subhorizontal root imprints. Microscopically, these limestones exhibit biomorphic structures of two types: a) sedimentary, fibers, coccoids covering micritic grains, and b) diagenetic, rod-shaped, filamentous, forming the surface of large sparite grains of secondary calcite. These sparite grains most often fill the root canals.

Thus, the red-colored paleosols of this section were periodically covered by the waters of shallow lake basins, in which carbonate sediment accumulated simultaneously with soil formation with the direct participation of microbial community. After the lithification of carbonate mud, microbial activity continued and contributed to the formation of secondary calcite crystals in root voids and pores.

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BLACK CARBON STOCKS IN THE SOILS OF PINE FORESTS IN THE LENINGRAD REGION. IS EVERYTHING ACCOUNTED FOR?

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Forest ecosystems are the most important pool of carbon in terrestrial ecosystems. The size and stability of this pool are determined by the texture and gross chemical composition of soils, the relief, the type of forest vegetation, as well as by human activities. Forest fires, modifying the biological cycle, lead, on the one hand, to an impulsive loss of carbon from the ecosystem, on the other hand, form stable compounds, called black carbon (Cpyr). The ratio of carbon loss and stabilization depends on the type of forest fire (crown or surface) and the burning temperature. Now Russia's forests deposit atmospheric carbon. The increasing frequency of anthropogenic fires can turn the forest ecosystems into a source of carbon dioxide and reduce the productivity of forest stands. For the rational use of natural resources, it is important to clarify the carbon pools in forest soils. As of 01.01.2022, the area of forest lands and lands of other categories, where forests are located, is 6041.2 thousand hectares in the Leningrad region. The forest cover of the territory is 57, 6% (https://nature.lenobl.ru). The distribution of forests by predominant tree species (%) is as follows: small-leaved 31, spruce 31, pine 38 (Fedorchuk, Neshataev, Kuznetsova, 2005). Pine forests occupy the most drained, nutrient-poor areas and are the most fire-prone.

Estimates of organic carbon compounds (Corg) pools in soils of drained forests in Leningrad region, according to different authors, are of the same order. For post-pyrogenic forest soils an increase in Corg pools in mineral horizons is noted. There are still unaccounted fractions of soil C. This is carbon of pyrogenic compounds (Cpyr). After fires, a thin layer of charcoal remains, over which forest litter recovers. Usually, when studying the genesis of soils, samples from that thin pyrogenic layers (1-3 cm) are not taken. The same can be said about the podzolic pyrogenic horizon of Epyr, colored in gray tones by charcoal of different size (from large to dusty particles). Charcoal affects the accuracy of Corg determination.

Our study plots were in pine forests of Leningrad Region in the following districts: Kurortny, Lodeynopolsky, Lomonosovsky, Luga, and Priozersky. Taxation characteristics of forest stands, species diversity of ground cover, age and type of forest fires (according to plant species composition of ground cover and thickness of annual rings of pines trunks), morphological and general physical and chemical characteristics of soils, stocks of soil organic matter

(according to losses during ignition and according to Corg by Turin). The forest floor by sub-horizons (L, F, and H) and the underlying pyrogenic layer were sampled at five points near the base soil pit with a 25x25 cm frame. Mineral horizons were sampled in fivefold replications from the base soil pit. The age of crown fires in the studied pine forests ranged from 60 to 140 years. It was found that the C pools in the forest floor varied in the range of 1.2-3.2 kg/m^2 and in the mineral layer of 20 (30) cm 1.5-4.4 kg/m^2, in the 1-3 cm pyrogenic layer, containing charcoal and detritus, the 0.3 to 2.1 kg/m^2. The choice of modifications of methods for determining the content of hygroscopic water (H_2Ohygr, 70 and 105 °C) and losses on ignition (LOI 550 and 900 °C) contributes to the clarification of the obtained values. H_2Ohygr differs by a factor of 1.5-2.0 not only with changes in drying temperature, but also it depends on the season (whether the heating in the room is on). The LOI of the soils studied do not depend on the selected temperatures. The conversion coefficient C to organic matter is more often used 1.724, while it has long been suggested to round this value to 2 (Ponomareva and Plotnikova, 1980; Orlov, 1985).

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THE LITHOLOGICAL DIVERSITY ASSESSNENT AS A FACTOR OF POTENTIAL FIRTILITY: THE CASE OF ARABLE SOILS OF THE YAROSLAV REGION (CENTRAL RUSSIA)

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The arable soils restricted to the three districts of the Yaroslavl oblast (the Upper Volga region) in this report were examined. These soils had been studied in the period 1980–1990; after that, they were gradually eliminated from plow condition, and nowadays, these soil massifs are in a state of abandoned land. The more than 360 soil profiles represented by Retisols Aric having different Podzolization degrees and formed on different parent rocks that predominate within the watershed positions of the investigated area were analyzed.

The lithogenic diversity of the investigated area is widely represented. More than a third of the studied soils (130 profiles) were formed on non-carbonate loess-like (mantle) loams. Almost 16% of the studied arable soils consisted of soils formed on moraine loamy deposits and water-glacial sandy deposits underlain by moraine. The quota of loess-like loams on moraine deposits and lake-glacial sandy deposits is 8%. The lake-glacial sandy deposits on loess-like loams occupied 6% of the territory, the rest being quota of the parent pocks represented by rare variants within them. They are: soils on

carbonate moraine; soils on loess-like loams underlain by carbonate moraine deposits; soils on water-glacial sandy deposits; and soils on inverse bipartite sediments—moraine underlain by water-glacial sandy deposits, a very rare type of parent rock. Depending on the lithological matrix, all the studied soils were subdivided into 10 groups and analyzed for their important agro-ecological features, such as humus content, pH_{KCl}, and exchange forms of phosphorus and potassium.

The analysis of the average and median values for all studied soils together and for each group separately showed that the soils on the loess-like loams in all features had an average position among all groups. Soils on the moraine deposits have analytical data close enough to soils on the loess-like loams. The soils on the carbonate moraine and loess-like loams underlain by moraine deposits are the most profitable in terms of the content of exchangeable phosphorus and potassium. The soils on the carbonate moraine are also characterized by the lowest acidity among all soils, and the soils on the loess-like loams underlain by the moraine have the maximum humus content.

In comparing soils on sandy water-glacial deposits with this parent material underlain by moraine, a significant improvement in the properties of the latter to an above average level was found. The improvement of properties was also noted in Retisols Aric, formed on loess-like loams underlain by moraine. Soils on water-glacial deposits, lake glacial sandy loams and the latter, underlain by loess-like loams, are characterized by analytical data below the average level of values. Bedding with loess-like loams in this case does not lead to an improvement in their properties. The minimum values for all features were demonstrated by soils on water-glacial deposits overlain by a moraine. Thus, all the analyzed features of the studied soils were initially determined by the lithogenic matrix factor. The lithogenic basis proceeds to save its value in arable soils during the process of introducing fertilizers. This is very important for support for water and air regimes and capacity features of soils, which is important for fixation of nutrients and their accessibility to plants.

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MOSSES ARE SIGNIFICANT IN THE TRANSFORMATION OF DEVONIAN SANDSTONES

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Plant-substrate interactions between bryophytes and rocks in early succession stages differ from interactions between vascular plants and soil. The aim of this study is to evaluate the contribution of epilithic bryophyte vegetation in the processes of bioweathering and pedogenesis. The material on

mosses-liverworts communities was collected on natural Devonian sandstone outcrops located in the south part of the Leningrad Region (Russia). Studied Devonian sandstones are mainly made of silica (>80%) and differ in the content of feldspar, kaolinite, hematite, and other minor clay minerals, which leads to different vegetation. Using X-ray fluorescence spectroscopy, we compared the chemical composition of the intact fresh rock and the upper layer of rock under moss cushions. The total carbon content was determined by Tyurin dichromate-oxidation method. The Kononova-Belchikova method helped to reveal the humus fractions composition and allowed to determine the content of humic acids carbon. The humic acids optical density was measured at 465 nm on a photoelectric colorimeter by Ponomareva-Plotnikova method. Received data show changes in the chemical composition of the upper layer of substrate, indicating the weathering processes under bryophytes activity. This is the change in the content of rock-forming elements relative to their content in the intact rock and the formation of primary soil. The content of calcium, sulfur, iron mainly increased in the weathered layer. The change in potassium content largely depends on its content in the intact fresh rock (the increase of its content in the upper layer was noted mainly on the sandstone with low potassium content). The changes in calcium and sulfur contents in the weathered layer are positive correlated. The changes in the concentrations of iron and other metal elements are also positively correlated. In general, the weathering of the substrate under the vegetation activity occurs with different intensity. Apparently, the change in the content of elements depends on their "initial" contents in the fresh rock, however, it is largely determined by ecophysiological features of the bryophyte species. For example, acidophilic species on very pure quartz sandstone contributes to accumulation of elements in the upper layer of sandstone. For primary soil, the humus composition under different bryophyte communities was described. The main part of bryophyte humus consists of chemically aggressive fulvic acids, the humic acids with very low optical density are also present. The formation processes of humus and soil mainly depend on vegetation. The highest concentrations of humic matter are noted under communities with not true-epilithic species (multi-substrate bryophytes, bryophytes of forest litter and soil).

Analytical work was carried out in Resource Centres of SPbU ("Centre for X-ray Diffraction Studies", "Centre for Microscopy and Microanalysis", "Chemical Analysis and Materials Research Centre").

Effect of microorganisms on natural and artificial materials

MICROFOULING OF EXPERIMENTAL ANTI-CORROSION COATINGS

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In winter period 2021 – 2022 in the coastal area near Sevastopol (Black Sea), we studied microorganisms' communities of the periphyton from various coatings.

The polymethylacrylate (PMA) plates were used as a control sized 56,08 x20,20x0,342 mm, and the pates covered with the experimental compounds (xylol solution + acrylic resin (axopol)) with the addition of nanoparticles (NP): ZnO-FeZnO, CuO-FeCuO, $ZnTi_2O_4$-ZnO, $ZnTi_2O_4$-TiO_2 и Ag-TiO_2) and paint bioplast (BP). The final concentration of NP in the coatings was 5% of the mass.

The plates were fixed in metal frames at a 3 cm distance from each other; the structure was placed at a depth of 2 m perpendicular to the water surface. The studies were conducted on 3, 13, 24 and 52 days. Bacteria and micromycetes were isolated by seeding on agar media. Microalgae and cyanobacteria were studied in suspension of flushes or after cultivation on the modified liquid media of Gromov №6, prepared with using the seawater.

Quantity of heterotrophic bacteria changed from $0{,}02 \cdot 10^2$ to $9{,}2 \cdot 10^2$ CFU /cm^2 (colony-forming units/cm^2). On all the substrates maximal count values were observed at 24-th day, and minimal – at 52-d.

During the studies, we determined 55 fungi species of 24 genera, 2 divisions and the group of unidentified Fungi species. Dominated by representatives of the family Aspergillaceae (genera *Aspergillus* –10 species; *Penicillium* – 10; *Talaromyces* – 2; *Paecilomyces* – 1), Pleosporaceae (*Alternaria* – 9, *Stemphylium* – 1) and Cladosporiaceae (*Cladosporium* – 3). Number of the taxons found on the coatings varied from 17 (BP) to 29 (NP ZnO-FeZnO). There was no statistically significant difference identified in the number of fungi on different coating types, their average count varied from 13 (NP ZnO-FeZnO) to 36 (NP Ag-TiO_2) CFU /cm^2, species count changed from 17 (BP) to 29 (control, NP $ZnTi_2O_4$-ZnO). Total average quantity within the exposure time varied from 4 and 5 CFU /cm^2 (24-th and 52-d days) to 17 CFU /cm^2 (13-th day), number of species was from 15 (52-d day) to 42 (13-th day). Low values of bacteria and fungi count in all versions of the experiment evidence of high bacterial and fungal resistance of the materials at the initial stages of plunging the samples into the sea with the decreasing temperature from 13,3°C to 6,3°C.

Within the structure of fouling on the samples 22 microalgae taxon were identified up to the genera level (*Navicula*, *Pinnularia*, *Melosira*, *Nitzschia*, *Amphora*, *Entomoneis*, *Pleurosigma* and others), 6 taxon – to the division level (Cyanobacteria, Dinophyta, Chlorophyta, some Ochrophyta), also the ribbon-like organisms of unclear systematic position were determined. On the coatings the number of forms varied from 9 (BP) to 19 (NP $ZnTi_2O_4$-ZnO). While the exposure time was increasing from 3 to 52 days the total taxonomic diversity of microalgae raised from 2 to 21 forms.

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STRUCTURE AND BIOMINERAL INTERACTIONS OF MICROORGANISM COMMUNITIES ON THE MONUMENTS OF ROCK ART IN MINUSINSK BASIN

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Minusinsk Basin is outstanding regions in Russia according to the concentration of archaeological rock art monuments from the Stone Age to ethnographic modernity. Many planes with petroglyphs are covered with biofouling and crusty formations that have different colors and structure. The study of their composition and mechanisms of formation is of a great importance for solving the problems of dating and preserving rock paintings.

The aim of this study was to analyze microorganisms, biochemical and mineral phase composition in various types of biolayers, as well as to assess their possible contribution to the processes of monuments damage.

The samples were collected from rock art monuments: Sukhanikha Mountain, Georgievskaya Mountain, Caucasian pisanitsa (south of Krasnoyarsk krai), several locations in the Oglakhty Mountains, and on the slabs of the fence of Big Salbyk mound (Republic of Khakassia). A complex of methods for studying the layers included mycological analysis, the identification of cyanobacteria, gas chromatography–mass spectrometry (GC-MS), X-ray phase analysis (XPA), light microscopy, and scanning electron microscopy (SEM) microprobe X-ray spectral analysis.

The surface of sandstone with petroglyphs is covered with various types of biolayers and biomineral crusts. A significant part of open rocky surfaces in conditions of high degree of insolation is covered with a continuous dark-colored fouling. The results of the study indicated that these biolayers are biofilms of cyanobacteria, formed mainly by the *Gloeocapsopsis magma*. This type of layer contain significantly less fungi than communities with the dominance of lichens and primary soils.

Light-colored porous crusts are ubiquitous in Minusinsk Basin. They are mainly formed by calcite, although in some cases they contain a significant amount of quartz, feldspar, and mica. This crusts were rich in organic substances (mainly sugars, polyols, fatty acids, and sterols). Cyanobacteria (mainly coccoid forms) and microscopic fungi were detected in them. Depressions containing microassociations of the organisms are formed in some places.

The gypsum crusts unlike calcite-containing crusts are almost not inhabited by microorganisms. Like on the surface of the desert varnish, trehalose prevailed in the samples of gypsum crusts, that is important for the survival of fungal conidia. The sulphatization of natural stone is one of the most terrible "diseases" for stone monuments in different environmental conditions, their growth itself leads to serious damage to the surface layer of the stone and can be one of the main processes leading to a loss of the rock art.

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INFLUENCE OF IONIZING RADIATION MICROFUNGI OF POLAR LATITUDES

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Microfungi of the polar latitudes are eukaryotes and extremophiles, which makes them one of the best model objects both for research in the field of astrobiology and radiology .

In our experiments, both species of yeast (Rhodotorula, Exophiala, Aureobasidium) and mycelial fungi (Pseudogymnoascus, Cladosporium) with various types of pigments (melanin, carotene) were exposed to irradiation.

Irradiation was carried out with a proton beam with an energy of 1 GeV, gamma radiation with a photon energy of 1.17 and 1.33 MeV in the dose range from 0 to 200 Gy. Parallel to proton irradiation, vacuum ultraviolet (VUV) radiation (173 nm) was irradiated.

The results of proton irradiation showed the presence of stimulation of growth processes: at doses less than 50 Gy, the probability of survival (SP) exceeded 100% at all species of fungi in our studied.

The greatest growth (SP=130%) was achieved in the mycelial species Pseudogymnoascus. To Cladosporium growth stimulation was observed at higher radiation doses of 75 Gy, which may be due to the presence of melanin in the cell wall. Non-pigmented spores of Pseudogymnoascus (SP=30%) had the lowest survival probabilities at doses of 200 Gy, while melanin-pigmented yeast of the Exophiala species had the highest values (SP=90%).

Under gamma irradiation, a similar form of dependence of the probability of survival was revealed to proton irradiation: growth stimulation was present at low doses with a further decline with increasing dose. Under VUV irradiation, a type of DNA destruction similar to radiation was found: as a result of exposure to VUV radiation, double-strand breaks appeared.

Potential applications of the data obtained include the development of effective radioprotective materials for astronauts in manned space flights, the assessment of the habitability of an extraterrestrial orbit, the determination of a way to protect people from the side effects of ionizing radiation treatment, the creation of new radioprotectors for cancer patients undergoing radiation therapy. Further improvement of the experimental methodology will determine a better understanding of the interaction of protons with living organisms, and will serve as a start for new research.

HOW SPECIFIC IS LOCAL BIODIVERSITY ON THE UNIQUE CALCAREOUS MRAMORNY ISLAND IN THE WHITE SEA

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Carbonate rock outcrops are extremely rare in the south-eastern part of the Baltic, or Fennoscandian, Shield. Marble deposits are known from the region's southern fringes – Kovadjarvi, Ruskeala and Tivdia deposits, as well as on islands Kalkkisaari in Lake Ladoga and Yuzhny Olenii in Lake Onega. An item that stands out is marble outcrops discovered recently in the north of the region – on unique Mramorny (Marble) Island in the White Sea. Carbonate rocks of Mramorny Island (65.420921 N, 34.631167 E, area 0.2 ha, elevation 4 m a.s.l.) constitute a ca. 5–40 m thick lens-shaped body thrown into isoclinal folds. They are associated, interbedded and deformed jointly with amphibolites and are cut by granite-aplites. Their major minerals are dolomite (ca. 70–90%), calcite, biotite and hornblende. Isotopic data show that Mramorny Island

carbonate rocks are endogenously igneous carbonatites. Geochronology data date the magmatic stage of carbonatite formation to 2420±20 Ma and metamorphic alterations of this rock to 1845±15 Ma. During the survey in 2018, 82 species of vascular plants, 25 mosses and 44 lichens were recorded from the island. The vascular plant flora was not very specific, but richer in species compared to other White Sea islands of similar size. High frequencies and abundances were noted also for such calciphilous species as *Botrychium lunaria*, *Draba incana*, and *Saxifraga cespitosa*. The moss flora was not rich, but the proportion of calciphilous species was quite high – there occurred *Brachythecium glareosum*, *Brachythecium turgidum*, *Distichium inclinatum*, and *Ditrichum flexicaule*. For *Brachythecium glareosum*, Mramorny Island is the only location among White Sea islands where the species has been found. The calciphilous lichens encountered were *Bilimbia sabuletorum*, *Caloplaca stillicidiorum*, *Candelariella aurella*, *Cladonia pocillum*, *Fuscopannaria praetermissa*, and *Xanthoria elegans*. Five species (vascular plant *Rhodiola rosea*, mosses *Brachythecium glareosum, Brachythecium turgidum, Distichium inclinatum*, and lichen *Ramalina subfarinacea*) are listed in the regional Red Data Book. The unique geological structure of the island has had the most pronounced effect on the bryoflora, less so on the lichen flora, and the weakest effect on the flora of vascular plants. The latter can be attributed to the small size of the island and the peculiarities of its relief, which leads to an almost unhindered transport of carbonatite weathering products into the sea by rainfall and seawater.

The research was carried out by the state assignment of the Department of Multidisciplinary Scientific Research, Forest Research Institute, Institute of Biology and Institute of Geology of the Karelian Research Centre of the RAS.

LABORATORY EXPERIMENT AS ONE OF THE ANALYTICAL TECHNIQUES FOR INVESTIGATION OF MICROMYCETES FROM THE SHULGAN-TASH CAVE

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In the aphotic zone (170 - 350 meters from the entrance) of Shulgan-Tash (Kapova) cave microbiotic settlements consisting of micromycetes, actinomycetes, yeast and bacteria were found on rock surfaces. 97 strains of micromycetes assigned to 26 genera were isolated from microbial foulings. Among them fungi of the genus *Aspergillus*, *Penicillium* and *Fusarium* and sterile forms prevailed. Representatives of *Penicillium implicatum* and

Geomyces pannorum are typical inhabitants of the Shulgan-Tash cave and other caves. Development of fungi on the walls of caves with Paleolithic paintings is especially dangerous for the drawings. Micromycetes are able to form organic acids and dissolve calcite. The purpose of our work is a laboratory experiment on cultivation on different carbon sources of *Penicillium implicatum* IB-G-76 micromycetes isolated from the soils of the Shulgan-Tash cave and investigation of their ability not only to dissolve but also to form mineral phases of $CaCO_3$. For this purpose media with various sources of carbon and energy of natural origin were used: Chapek medium + $CaCO_3$ (calcite); potato-glucose agar medium (CAA) + $CaCl_2$; CAA medium + $CaCO_3$ (calcite); starch medium + $CaCO_3$ (calcite). During the experiment it was found that the growth of the strain of *P. implicatum* IB-G-76 caused the complete dissolution of calcite in the medium and formation of crystal aggregates in the body of the fungal colony and on the media periphery.

The morphology of these aggregates was studied by scanning electron microscopy (SEM) (JSM-6390LV JEOL with an INCA Energy 450 X-max 80 EMF spectrometer, carbon sputtering). The specific morphology of these neoforms determined the name of the sample - "Oduvan" (Fig.1). The phase composition of the samples was determined by X-ray diffraction analysis of the samples (diffractometer Shimadzu XRD-6000, CuKα radiation). The “dandelion” sample consists of well-crystallized calcite with an almost ideal composition of Ca_2CO_3. The unit cell parameters of the mineral are a = 4.985 Å and c = 17.050 Å. An insignificant impurity (1-2%) of sodium bicarbonate hydrate $Na_3H(CO_3)_2*2H_2O$ is determined. A feature of this sample is that the calcite reflection [104] on the diffraction pattern has a relatively high intensity which is often characteristic for biogenic calcites.

Thus organic acids produced by the strain of P. *implicatum* IB-G-76 completely dissolved calcite under the colony of the fungus and contributed to calcite neoformation on the surface of the colony far apart the growth zone of the microorganism.

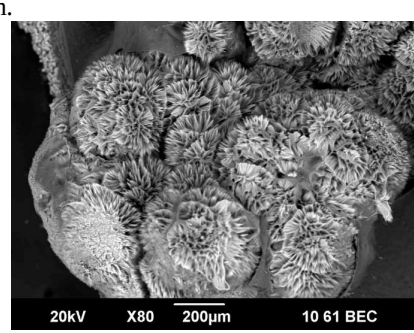

Fig.1. Oduvan - like calcite aggregates.

ON THE QUESTION OF THE FORMATION OF ONCOLITHS.

Litvinova T.V.
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The black oncolites of the Kalanchevo formation in the Venda of the Baikal-Patama Highlands of Yakutia have a rounded shape and a concentric structure, ranging in size from 4-5 to 12 mm in diameter. They contain the following remains of organisms: a) closely contiguous hollow non-segmented tubular formations with a diameter of 0.8 to 2.1 microns, a length of up to 3.5-4 microns, with a circular cross section. They are inclined in one direction, partially flattened and noticeably expand towards the open end. Clusters in the form of inclusions are formed in the rock, separated by a cavity from the host rock. They are confined to the central part of the oncolitis. b) the remains of relatively large (2 x 30 microns) recrystallized filamentous cyanobacteria. Successively envelop the oncolith at each stage of its formation, leveling the surface. The number of filamentous microfossils increases towards the peripheral part of the oncolitis. Comparison of the fossilized microorganisms remains in host rocks and in oncoliths (SEM) showed that bacterial films and coccoid cyanobacteria Myxococcoides sp. with a size of 10-15 microns are present in both. In the host rock, bacterial films form microfoils or accumulate in groups of several closely contiguous formations. Coccoid cyanobacteria have a spherical shape and smooth surface, individual dents are rare. In oncoliths, fragments of bacterial films are much thinner, with a smooth surface, and do not form clusters. Coccoid cyanobacteria ***in the oncoliths*** are crumpled, flattened, with a strongly deformed surface, form clusters. Some of them are enclosed in a carbonate case. There are no filamentous forms of biogenic formations in the host rocks.

Black oncolites should be considered as complex organogenic sedimentary formations. They arose as a result of hydrodynamic bottom processes accompanied by the vital activity of mainly filamentous cyanobacteria of two varieties: relatively large filamentous forms that developed on their surface, and small tubular formations.

As a result of movement along the bottom, a carbonate contraction or a colony of tubular organisms, like a snowball, clung to sedimentary material, part of which was sprinkled. Filamentous Cyanobacteria developed on the surface of the organogenic sedimentary formation, the mucous mass of which (glycocalyx) partially or completely enveloped the oncolith. The subsequent movement of the mucus-covered oncolith was accompanied by the sticking of its surface with carbonate material and the remains of inanimate coccoid microfossils. The recesses resulting from the fallen grains of sand were re-mastered by colonies of tubular cyanobacteria. The most viable trichomes were selected for the new mineral cover and a colony of filamentous microfossils was recreated. Due to the high carbon content in organisms, and especially in the glycocalyx, which was even more concentrated during the dehydration of

mucus, large filamentous cyanobacteria formed a concentric stratification with a high content of organic carbon. During the lithification of the sediment, dehydration and compaction of the material led to the formation of black monolithic concentric interlayers alternating with carbonate sludge. The mineral layer of oncolite was unevenly diluted with organogenic material – colonies of tubular cyanobacteria.

The layering of oncoliths, in comparison with stromatolites, is more complex and less differentiated. The mottled coloration of the mineral layer occurs due to the remains of organisms (tubular formations). The acceptability of rounded shapes and their alignment by the efforts of the bios dominate at each stage of oncolyte growth, which indicates the unity of biotic and abiotic processes during its formation.

In the rock containing oncolites, a small amount of relatively evenly dispersed biogenic material (remnants of coccoid microfossils and bacterial films) gives it a dark gray uneven color, with fragments of layered stromatolite texture.

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MICROORGANISMS AT DIFFERENT STAGES OF FORMATION OF STROMATOLITE STRUCTURES

Litvinova T.V.
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In the rocks of the Phanerozoic, stromatolites have a rather limited distribution and low power, unlike stromatolite reefs of the Precambrian. However, the remains of cyanobacteria in them are preserved much better, and the intensity of secondary processes affects the breed much less. The small size of the buildings allows us to consistently trace the development and change in the composition of organisms and their role in the formation of stromatolites .

In the Solikamsk horizon of the Ufa tier of the Permian system (Urals, Chusovaya River), stromatolite structures have been installed, in which three stages of their formation are clearly recorded: initial, intermediate and final (Naugolnykh, Litvinova, 2021).

1. The initial stage. Uneven clusters of up to six coccoid microfossils identical in parameters in the form of regular balls measuring about 10 microns in diameter. Relatively small fragments of individual thin bacterial films. Filamentous cyanobacteria are very rare, their length does not exceed 1 micron. They occur in groups of 5-8 formations.

2. Intermediate stage. Separate coccoid microfossils do not form clusters. Dense thick fragments of bacterial films with a wrinkled surface form groups of two or three formations. Bundles of filamentous microfossils with a length of 20-23 microns are often included.

3. The final stage. Rare coccoid microfossils up to 5 microns in diameter. Large filamentous microfossils with a length of more than 100 microns and a width of up to 8 microns are widespread. At their end, an oval bud-like growth may occur. Chains of small (1 micron) coccoid formations appear, connected by a thin thread. Bacterial films tightly cover a significant part of the space.

The comparison of the three stages shows the essential role of cyanobacteria in the formation of the morphology of stromatolites. Separate clusters of coccoid microfossils and rare fragments of bacterial films form a gravelite texture at the first stage. The change in the number and composition of the organisms-builders leads to a change in the texture of the rock (Table 1). A noticeable increase in their number and a consistent increase in size at the second and third stages involve the carbonate material in biogenic activity. This leads to the construction of columnar stromatolites. Trichomes are multiplying more and more actively on the surface of the precipitate. Extracellular mucus becomes an obstacle to the penetration of other organisms, as indicated by numerous dense and large fragments of bacterial films. The number of filamentous cyanobacteria reaches their maximum development at the final stage of stromatolite formation (Table 1, III), their size increases significantly again. This leads to a noticeable differentiation of mineral and biogenic materials in the sediment. During the lithification process, a thin layering is formed in the stromatolite columns due to their alternation.

TABLE 1

Stages	containing rock %	remains of cyanobacteria, %			Texture rock
		а) coccoid	б) bacterial films	в) filamentous	
I	89	7,4	1	0, 6	gravelite
II	65	4	20	9	column
III	18	2	43	37	layered column

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EXAMPLES OF TECHNOGENIC MINERAL FORMATION ON THE SURFACE OF ARCHITECTURAL OBGECTS

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The features of the structure, mineral and chemical composition of crystals on various natural and artificial materials of cultural heritage monuments have been studied by methods of optical and electron microscopy,

and petrographic analysis. The samples were studied using an EZ4 D stereomicroscope (Germany), transparent polished sections analyzed using an OLYMPUS - BX-51 polarization microscope, with photography of the most interesting areas of the fragments under study. The scanning electron microscope Hitachi TM 14000 Plus (Japan) with the prefix energodisperse was used to study the features of micromorphology, microstructure and element composition of the selected areas energy dispersive X-ray spectroscopy Quantax 75 (Bruker, Germany).

The objects of research are architectural, memorial, museum monuments, stacked and decorated with natural (limestones, dolomites, marbles, shells, etc.), or artificial (ceramic and cement) materials. Morphology, structure, composition of crusts and layers were studied by us at different objects (theses and article 2018, St. Petersburg). It was shown that despite the different substrate (carbonate or silicate rocks), the mineral composition of neoplasms on natural objects is rather monotonous: carbonate, iron oxide, ferromanganese compounds with a characteristic zonal structure predominate, sometimes containing alumosilicate admixture.

The mineral composition of the surface changes of architectural objects is dominated by gypsum, coloring oxides and hydroxides of iron, less often manganese, and among the efflorescences - sodium sulfates and halite. We found jarosite among the sulfates. At the end of the 1990s, when studying the embedded slab of organogenic detritus limestone, the discolorations of needle-shaped jarosite were collected (according to the X-ray phase analysis of the reference), which turned into yellow powder during long-term storage of the sample. Currently, jarosite has been found in the detachments on the back side in the form of small inclusions of different concentrations, which gives a yellow color to organogenic limestone. Jarosite in association with gypsum, goethite is found in dolomites and sandstones in the form of scattered inclusions or in interlayers enriched with clay substance. The former were removed by washing with water, the latter were preserved, which is due to the technogenic transformation of iron-containing minerals. Melnikovite was found from aqueous iron sulfates, confined to masonry sites under the soil cover. Iron sulfates are easily soluble salts that persist in various climatic conditions from steppe to permafrost. Rare forms of neoplasms in the form of spherical tangled fibrous formations of magnesium hydroxide were found on the contact of a cast-iron plate and a sand filling of the floor of the St. George Cathedral of Yuriev-Polsky.

In urban conditions, on objects in the construction of which mortars and cement materials are used, neoplasms - streaks, spots, crusts - also differ in a micro-layered structure, zoning of mineral composition and micromorphology. The most resistant to biogenic destruction are the surfaces of glazed tiles, as well as archaeological finds of household ceramics. Thin films of carbonate substance often serve as a reinforcing material of the degraded glaze surface. When it is cleared, an optical effect similar to irrigation is detected.

The study of natural calcite, malachite and quartz crystals revealed the deposition of finely dispersed neoplasms on the faces and edges of quartz in calcite burrs, on fibrous malachite accretions and the surface of malachite buds.

PHYSIOLOGICAL CHARACTERS AND METABOLOMIC PROFILE OF LECANICILLIUM GRACILE ISOLATED FROM MINERAL BUILDING MATERIALS

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Fungi are essential members of lithobiont communities playing one of the leading roles in mineral substrates deterioration (Gadd, 2017). During our survey of fungi colonizing mineral building materials (i.e., limestone and plaster) inside the cultural heritage sites in Russia, we have isolated verticillium-like micromycete that we have described as *Lecanicillium gracile* V.B. Ponizovskaya, A.A. Grum-Grzhim., Georgieva & Bilanenko (Cordycipitaceae, Ascomycota). The fungus was obtained in high amounts (10^4–10^5 CFU/g) that reflected its active development on these substrates. The development of fungi over a period of time may be determined by a combination of various factors (Warscheid and Braams, 2000). Among them water availability and external pH are the most important climatic conditions on indoor mineral substrates (Verdier et al., 2014; Li et al., 2020). We have attempted to evaluate mechanisms of functioning of *L. gracile* on mineral materials inside cultural monuments and to reveal its possible participation in biodeterioration process. For this purpose, dependence of the growth rate of *L. gracile* on parameters of water activity (a_w) and pH of substrate were studied. Then, composition of metabolites in the mycelium and in the culture fluid of *L. gracile* was characterized. Finally, quantitative analysis of the extracellular polymer matrix (EPS) excreted by the fungus was performed.

Growth tests at different a_w values have revealed that *L. gracile* grew best at maximum a_w studied (about 0.99 a_w), dramatically reduced growth rate at 0.95 a_w and did not grow at 0.9 a_w. Then, *L. gracile* successfully developed at extremely wide pH range (i.e., pH 4–10) and was alkalitolerant. We believe that this character gives to *L. gracile* an advantage in colonization of limestone and plaster and proliferating there for a long period in the conditions of long-lasted material humidification as pH of these materials inside cultural heritage sites may vary from slightly acidic to alkaline (pH 6–9) (Verdier et al., 2014; Ponizovskaya et al., 2019). While developing on stone materials, mycelium penetration into the substrate causes mechanical destabilization of the mineral structure (Warscheid, Braams, 2000). In the exponential growth phase, the

diversity of metabolites in the mycelium was low. In the stationary growth phase, *L. gracile* possessed high enzymatic activity as the diversity of metabolites in its mycelium was high. It is known that members of *Lecanicillium* genus are entomogenous and fungicolous (Zare & Gams 2001). It is proposed that verticillium-like species could decompose chitin in insect remains and fungi on indoor mineral substrates (Gorbushina & Petersen 2000). Studies of the culture fluid have shown that *L. gracile* excreted EPS and changed pH of the medium to an alkaline. EPS contribute to biofilm formation, can protect from adverse environmental factors (Grum-Grzhimaylo et al., 2016), make biocidal treatment ineffective (Sand, 1997) and destabilize mineral matrix (Gadd, 2007). Moreover, under alkaline conditions EPS excretion leads to secondary calcite precipitation in the case of fungal development on Ca-containing materials (i.e. limestone, marble) (Sazanova et al., 2020).

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BIODETERIORATION AND WEATHERING OF NATURAL STONES IN KIEL, GERMANY

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Kiel is a seaport on the Baltic Sea, located in a temperate maritime climate. It was founded in the 30s of the 13th century. Kiel has a rich stone decoration. A significant part of urban ecosystems is made up of natural stone (carbonate and silicate rocks), which is used for cladding buildings, in the construction of embankments, foundations, pavements, as well as in the creation of sculptural monuments. Monuments of historical and cultural heritage are one of the most valuable elements of the environment of any city with a long history. The stone materials of the monuments are subject to weathering and biodegradation. For example, gypsum crusts can often be seen on stone surfaces in the city. Fungi, cyanobacteria, algae, and lichens can be noted among the biodestructors, which form biofilms on the monument surfaces. Lichens and fungi are able to release acids, which leads to the destruction of the surface and the formation of secondary minerals.

In October 2021 25 samples were taken from various stony substrates (limestone, sandstone, granite) to study the stone biodegradation and the

composition of microorganisms in subaerial biofilms in Kiel. Samples were taken into sterile containers. Identification of cyanobacteria and fungi was carried out by standard methods according to morphological characteristics. In total, 28 taxa of cyanobacteria with a rank below the genus, of 18 genera, 14 families, 4 orders, were identified. Phormidesmis sp. is the most common among all identified taxa (found in 5 samples). It is interesting to note the finding of Chamaesiphon polonicus in fountains located within the city center, since this genus are most often found in mountain rivers and cold springs. Also 38 species of micromycetes and non-spore-bearing light and dark-colored isolates of microscopic fungi were isolated. The most common are the following species: Alternaria alternata, Cladosporium cladosporioides, Scytalidium lignicola, Alrernaria oudemansii, Mucor racemosus, Fusarium oxysporum, Mortierella lignicola, as well as non-spore-bearing dark-colored and light-colored isolates of microscopic fungi.

Scanning electron microscopy and X-ray microanalysis made it possible to reveal the nature of biogenic-abiogenic interactions for carbonate (limestone) and silicate (sandstone and granite) rocks.

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TROPICAL CLIMATE INFLUENCE ON THE COLOR CHARACTERISTICS OF PROTECTIVE ORGANOSILICATE COATINGS

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Organosilicate coatings (OSC) of cold curing are widely used to protect various surfaces from the effects of adverse environmental factors (elevated temperature, high humidity, ultraviolet and radioactive radiation). They perform two functions at once - protective and decorative. In connection with the expansion of the geography of the use of OSC, it became necessary to ensure their high weather resistance in a tropical climate. At the same time coatings must retain their decorative properties (appearance, color and gloss).

OSC based on a polymeric binder (polydimethylphenylsiloxane), fillers (fine mica and talc), but with different pigments (Cr (III, VI), Sr and Mo compounds) were exposed for 11 months in a marine tropical climate. The

place of field tests is the climatic station of the Joint Vietnamese-Russian Tropical Center in the coastal zone of the South China Sea (neighborhood of Nha Trang) [1]. The analysis of the color characteristics of the coatings, illustrated by color charts, made it possible to characterize the change in the color of the coatings, by which to evaluate the color fastness and weather resistance of the coatings. These results made it possible to optimize the composition of the pigment. Chromium(III) oxide turned out to be the pigment providing the highest color stability of the coatings.

To improve the physical and mechanical properties of the OSC and increase their stability in contact with water, the organosilicate compositions were modified with YD-128 epoxy resin. Both OSC and modified OSC were exhibited for 6 months at 2 sites of the Tropical Center. In one case, the samples were placed near the sea (Nha Trang), and in the other, they were exposed to even more intense solar radiation (Ho Chi Minh City). After 6 months of testing, visually both types of coatings did not change color. However, the digitization of the results of observations showed that there were changes in the shades of colors in both types of coatings. These changes are somewhat more pronounced, where more intense solar radiation is observed. Chromium(III) oxide pigment performs best in maritime tropical climates. Pigments based on iron and strontium compounds showed approximately the same results, worse than Cr_2O_3 in a maritime climate, at high humidity, but somewhat better withstood more intense solar radiation. The results obtained also indicate the possibility of using hybrid organosilicate compositions based on polydimethylphenylsiloxane and epoxy resin to expand the functionality of protective and decorative OSC for their operation in the tropics.

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KAMSKOJE USTJE CAVE ROCKS' SURFACES CHANGING UNDER MATURE AND FRESH BIOFILMS

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Biofilms inhabiting cave mineral formations can potentially be used for technologically amending soils and building materials. In the present research we aimed at the estimation of the impact of an active chemolithotrophic community on surface properties of cave mineral formations. Gypsum, dolomite, marble onyx and porous calcite speleothem were sampled from the walls of the Kamskoje Ustje caves, namely Yurjevskaya cave and Sjukeevo

tunnels (Republic of Tatarstan), formed in the deposits of the Permian system at the contact of the dolomite roof with gypsum. The anthropogenic and zoogenic pollutions were maximally excluded while sampling. The samples were stored in two ways: under common museum conditions after surface polishing, as well as under conditions preserved an alive biofilm. The preservation method was realized through storation in a strong aluminum foil at natural humidity and a temperature of +12(±2)°C. A factorial experiment to determine effects of dispersion, roughness, fresh treatment with a chemolithotrophic community, as well as a mature biofilm on the surface was carried out. The surface treatment with a chemolithotrophic community was made by immersing the rock specimens in a cultural liquid based on washout from cave calcium-carbonate speleothem, which were incubated for 14 days in the modified R2 medium. Taxonomic profiling of the community was carried out using metabarcoding for the 16S rRNA gene. V3-V4 16S rDNA sequences were processed using the DADA2 pipeline, functional prediction of microbial community was provided by PICRUSt2 program. After 1 month of the rock specimens' exposition with the microbial community theirs surfaces were studied using the author's device for the contact angle measuring, and routine instrumental methods such as SEM (FEI XL-30ESEM), EDS (EDAX) and RAMAN spectrometer (inVia Qontor). Hydrogeochemical situation was estimated in the washing solution. Biofilms' organic matter was clearly visible on SEM images of the rock specimens' surface. The biofilm composition included 10 genus of bacteria with an abundance of more than 0.1%, among them - uncultivated wb1-P19. The R2 medium stimulated representatives of 9 out of 10 genus: particularly, there were Nitrospira spp. possessing the ability to oxidize ammonium and complete the nitrification cycle and Hyphomicrobium spp. using both organic and inorganic carbon for growth optionally. Reconstruction of the biofilm biochemical pathways suggests the possibility of building up organic matter trough inorganic matter consumption. The contact angle variance can be used as an indicator of the surface properties heterogeneity: it was 80-90% determined by biofilm properties on the mineral surfaces studied. The rock surface wettability proved to relate cations released into washing solution. Green phosphorescence characterized marble onyx had 2 maxima and a total average duration of 1.78 seconds, which clearly indicates the presence of forbidden electronic transitions, which are possible in the presence of aromatic or diene compounds. After fresh treatment with the microbial community, phosphorescence was reduced by about 3 times. The rocks' surface conservation by mature biofilm vice versa freshly attached one was detected. The dynamics of rock surface properties during biochemogenesis managed by both environment as such as intrinsic biofilm factors has been assumed.

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ANTHROPOGENIC INFLUENCE ON COMPLEXES OF MICROFUNGI IN THE SOILS OF ARCTIC (BOLSHEVIK ISLAND, THE ARCHIPELAGO NORTHERN LAND (SEVERNAYA ZEMLYA)).

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Extreme conditions of high latitudes can be considered as models of the primary colonization of terrestrial landscapes and simulated space and martian conditions. The polar desert zone is the most northern zone on the global latitudinal profile, which leaves an imprint on all the characteristics of its living cover.

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

59 species from 33 genus were isolated from the soils of local polar territory by using cultural methods. At the same time, significant differences were noted in the species composition and the number of fungi in areas that differ in the degree of anthropogenic pollution.

The abundance indices (CFU number) in anthropogenic polluted soils were significantly higher (by an order of magnitude), in comparison with natural habitats. These results were confirmed by the use of a metagenomic analysis of soil samples selected in the polluted and "control" soils at areas of island Bolshevik .

In total, 88 taxa of microfungi were identified in soil samples using metagenomic analysis, 52 of which were recorded on anthropogenic polluted soils. It is important that metagenomic analysis confirmed the nucleus of the mycobiota of soil communitiesthe obtained by classical methods.

When the rank of the identified taxa declined, the number of differences in the results obtained by the two different methods increased. Using metagenomic analysis in control (unpolluted soils), a high proportion of fungi of the genus Emericella was noted, while in polluted soils they were not detected. The metagenomic data confirmed the presence of species from the genus Penicillium in anthropogenically polluted soils (with a relatively low

share of participation), whereas in of control soils samples they were not detected at all. Other differences of the compared communities of micromycetes are also noted.

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

Author's Index