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REVIEWS

Geological Microbiology

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In the jubilee year of the Institute of Microbiology, Russian Academy of Sciences, it is appropriate to recall that the first publication in the world scientific literature entitled *Microorganisms as Geological Agents* [1] was published in 1903 by the future organizer and director of the institute G.A. Nadson. That work, performed at Slavyanskie Lakes, considered the involvement of microorganisms in the formation of hydrogen sulfide and calcium carbonates; undoubtedly, it greatly influenced the early works of another famous Russian microbiologist, B.L. Isachenko, who investigated the role of microorganisms in the cycles of elements in seas and lakes [2, 3].

In the second half of his life, when Isachenko headed the Institute of Microbiology after the tragic death of Nadson, the scope of his interests also included microbial processes in oil fields and sulfur deposits [4, 5].

1. THE HISTORY OF GEOLOGICAL MICROBIOLOGY

In the history of geological microbiology as an independent science, three main directions can be distinguished, each of which dominated in a certain period and will to some extent have its continuation.

The first direction is the description of functional diversity of the microbial world. The founder of this direction was S.N. Winogradsky [6]. Appraising the contribution of Winogradsky in the development of the new methodology, S.I. Kuznetsov emphasized that “as distinct from the classical methods for the isolation of bacterial cultures on rich nutrient media, Winogradsky put forward the principle of selective media, which immediately allowed him to isolate a number of new microbial species and to study, if necessary, their physiology” [7].

The method of selective media received due appreciation from Winogradsky’s contemporaries and followers. Virtually immediately after the description of anaerobic nitrogen fixers and nitrifiers by Winogradsky, many other specialized microbial groups were discovered; by the middle of the 20th century, all major groups of microorganisms involved in the cycles of biogenic elements and metals were already known to microbiologists.

This physiological–biochemical inventory of the microbial world was continued in the second half of the 20th century, and this resulted in the discovery of new geochemically important microbial processes, primarily, anaerobic ones. Important examples are unraveling of the processes of microbial reduction of iron and manganese, coupled to anaerobic consumption of organic matter or hydrogen; of autotrophic and heterotrophic sulfur reduction; and of anaerobic oxidation of ferrous iron in the process of bacterial photosynthesis.

However, in spite of the hundred-years-long efforts of the world microbiological community, the study of the physiological–biochemical properties of microorganisms is far from completion. According to the most optimistic estimates, we can cultivate no more than 10% of the microorganisms inhabiting the biosphere. Therefore, the search for microorganisms performing novel functions undoubtedly is one of the key tasks of the microbiology of the 21st century.

The second direction of the development of geological microbiology, the ecological–geographical direction, was actively advanced by Soviet microbiologists beginning with the second quarter of the 20th century. As long ago as immediately before World War II, ubiquitous occurrence of microorganisms in all terrestrial, aquatic, and subsurface ecosystems was shown. Moreover, in such specific natural environments as subsurface waters and anaerobic ecosystems, microorganisms proved to be the only living organisms. In the best works performed in this direction, researchers did not confine themselves to using only microbiological methods. Simultaneously with taking samples for isolation of microbial cultures, they performed thorough investigation of the physicochemical parameters of the habitat and attempted quantitative estimation of the microbial activity in situ.

Thus, in the very first book by S.I. Kuznetsov, *Role of Microorganisms in the Cycles of Elements in Lakes* [8], published in 1952, the first attempts were made to use the system approach to microbial activity in lakes. I mean numerous quantitative estimates of microbial activity based on monitoring of the chemical composition of lake water, particularly, seasonal changes of the content of dissolved oxygen.

The main conclusion from the works performed along the ecological–geographical direction of geological microbiology was that, among all living beings inhabiting our planet, microorganisms are the most

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adaptable to environmental conditions, including those adverse for humans, animals, and plants (extremely high and low temperature and pH values, high pressure, etc.).

Thus, already by the middle of the 1950s, it became evident that microorganisms, which possess diverse enzymatic systems and easily adapt to changing environmental conditions, should play an important role in the biosphere cycles of both organic and inorganic compounds. However, most of the experiments were performed with the use of laboratory nutrient media, which, as a rule, were very different in their composition from the natural media in which "wild" microorganisms function.

In the mid-1950s, critically minded microbiologists and geologists began to realize the insufficiency of using only microbiological methods for understanding of the biosphere processes driven by microorganisms.

The search for methods for quantitative estimates of natural processes was motivated in the mid-1950s by a considerable deterioration of the quality of air and water, especially in big cities and industrial regions. The first calculations of the scale of pollution showed that combustion of fossil fuel annually results in the emission into the atmosphere of about 20 billion tons of carbon dioxide, which is a so-called greenhouse gas, and more than 200 million tons of sulfur oxides, which are transformed into sulfuric acid and return to the Earth's surface with acidic rains [9].

These enormous values produced shocking impression on ordinary people; however, to the scientific community it was clear that sober assessment of the danger required development of a complete quantitative model of global cycles of major elements, which would make it possible to estimate the contribution of technogenic components to the global fluxes.

S.I. Kuznetsov was among the leading Soviet scientists who recognized the necessity of development and wide application of quantitative methods for the assessment of the rates of biological processes. He was the first in the world to use, in 1953, radioactively labeled bicarbonate to evaluate the rate of chemosynthesis under conditions as close to the in situ ones as possible [10]. Over the following five years, Kuznetsov's pupils developed quantitative methods for assessment of the rates of the microbial processes of the sulfur cycle, and these methods immediately found wide application in the studies of the sulfur cycle in fresh and marine basins [11, 12]. In the same years, quantitative investigations of the microbial processes of the sulfur cycle in the subsurface waters of oil fields and sulfur deposits were started [13, 14].

Somewhat later, in the early 1970s, the radioisotopic technology of determination in situ rates of microbial processes was used for quantitative assessments of the rates of the methane cycle processes [15].

Before completing the review of methodological approaches used in modern geomicrobiological investigations, we consider it necessary to briefly discuss the possibilities offered by the analysis of the results of studies on the distribution of stable isotopes of biogenic elements in natural compounds of biological and abiogenic genesis. It was established that virtually all natural carbon and sulfur compounds formed with the participation of living organisms are notably enriched with the light ^{12}C and ^{32}S isotopes. Experimental studies of photosynthesis and of the metabolism of a number of pure microbial cultures showed that, during these processes, fractionation of stable isotopes occurs: the metabolic products are enriched with light isotopes, and the heavier ^{13}C and ^{34}S isotopes accumulate in the residual substrate [16].

It is important to stress that the isotopic composition of minerals of biogenic origin does not change with time, and this makes it possible to study the processes of element cycles that occurred in the biosphere of the past geological epochs [9].

2. MICROBIAL PROCESSES OF THE CARBON CYCLE

The driving force of the biosphere processes is the carbon cycle.

Most of the methods discussed above make it possible to assess the geochemical activity of individual functional groups of microorganisms. However, with the accumulation of data, it becomes more and more clear that, under natural conditions, microbial communities with complicated organization operate, in which the functioning of the participants is mutually dependent. In a generalized form, the interaction of functional groups of microorganisms involved in the carbon and sulfur cycles is shown in Fig. 1 [17].

Under aerobic conditions, which dominate in both the continental and oceanic parts of our planet, the major portion of the organic matter produced in the course of photosynthesis is mineralized with the involvement of bacteria, microscopic fungi, and actinomycetes to final products: carbon dioxide and water, which return to the global cycle (Fig. 2) [18].

Anaerobic mineralization of organic matter proceeds via several stages, each of which involves specialized microorganisms (Fig. 1). The final products of anaerobic mineralization include, along with carbon dioxide, reduced compounds: hydrogen, methane, ammonia, and hydrogen sulfide; at the expense of the oxidation of these reduced compounds, chemosynthetic production of organic matter occurs at the interface of the aerobic and anaerobic zones.

The role of chemoautotrophic bacteria in the production of organic matter in the biosphere has been studied in detail in the regions of emanation of overheated hydrothermal solutions in the rift zones of the ocean. These solutions, which at the site of emanation have a temperature of up to 380°C, contain reduced forms of metals, as well as H_2S, CH_4, CO, H_2, and NH_4 formed in the high-temperature reactions under the

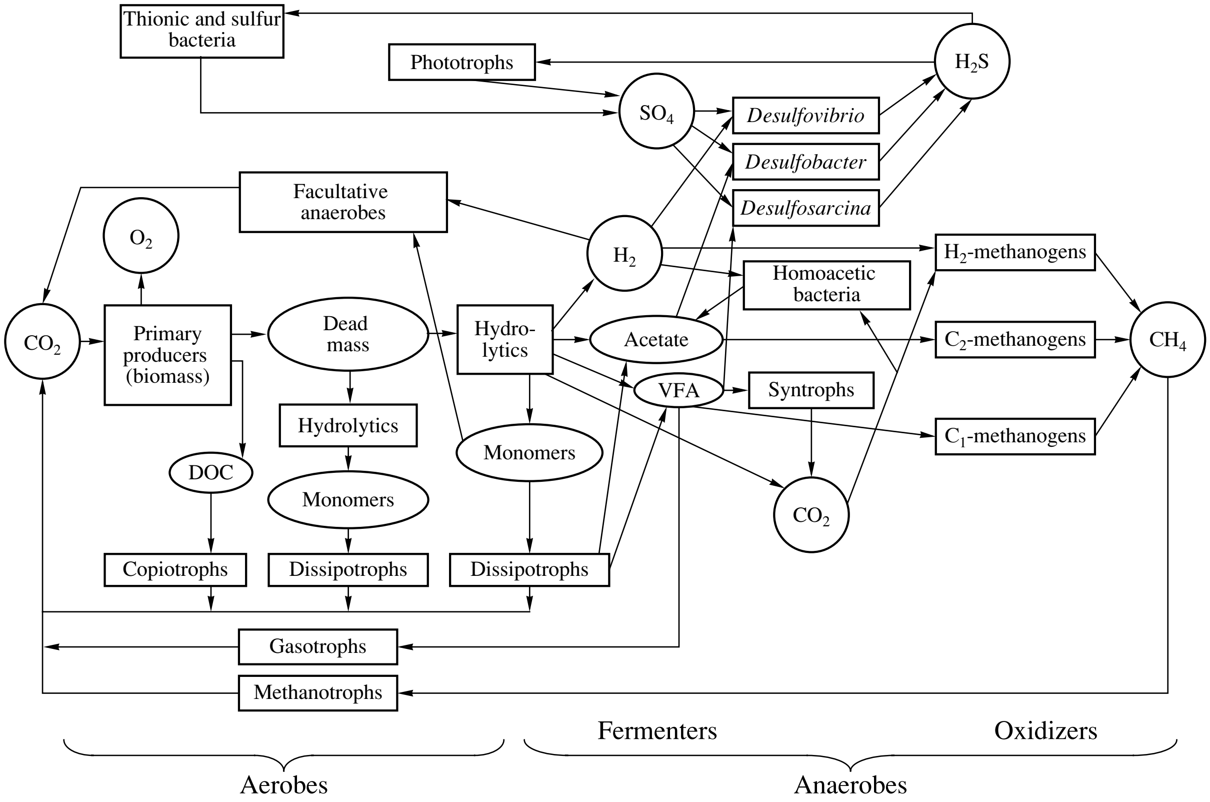


Fig. 1. Scheme of trophic relations of the bacteria of the carbon and sulfur cycles. Microbial groups are outlined with rectangles; substrates and products of microbial activity are outlined with ovals; DOC, dissolved organic carbon; VFA, volatile fatty acids and alcohols [17].

ocean floor. In the zone where the hydrothermal solutions mix with the oxygen-containing ocean water, intense processes of chemosynthesis and methanotrophy take place and biomass of autotrophic microorganisms accumulates [19]. Interestingly, the development of chemoautotrophs and methanotrophs occurs not only in the water but also in specialized tissues (trophosomes) of a number of invertebrates inhabiting the hydrothermal fields [20].

Thus, in the ecosystems of deep-sea hydrothermal fields (*black smokers*), autotrophic and methanotrophic bacteria are the main producers of organic matter for all the heterotrophic components of the ecosystem, from organotrophic bacteria to fish and crabs [20].

Chemolithoautotrophic production of organic matter at the expense of hydrogen having high-temperature genesis is carried out by anaerobic chemosynthesizing microorganisms. During tunnelling of basalts in the region of the Columbia River (Canada), an active community of chemoautotrophic bacteria was found, which included methanogens, sulfate reducers, iron reducers, and acetogens. Chemical analyses of gas and subsurface water, as well as the analysis of the distribution of ^{12}C and ^{13}C, showed that all these microbial groups are geochemically active in the ecosystem under consideration [21].

An important part of the global biogeochemical cycle of carbon is the methane cycle, all reactions of which in the biosphere are driven by specialized groups of microorganisms: methanogens and methanotrophs. Increased interest in the methane cycle is due to two reasons. First, methane, like carbon dioxide, is a greenhouse gas, and, although its concentration in the atmosphere is 150-fold lower than that of CO_2, the greenhouse effect of methane molecules is 26-fold stronger than the effect of the same number of CO_2 molecules. In addition, the rate of annual increase of the methane concentration in the atmosphere is three times higher than that of the CO_2 concentration.

The methane flux to the atmosphere is estimated by different authors as 350–870 million tons per year; all of these authors believe that the main portion (70–85%) of this methane is produced by methanogens inhabiting bogs, waterlogged soils, and digestive tracts of termites and ruminants [22].

The second reason for the increased interest in the methane cycle is the discovery of methane crystal hydrates, which are formed at low temperatures and increased pressures in marine sediments and permafrost soils and grounds. The predicted stores of crystal hydrates are great enough to believe in the possibility of their use as a new industrial energy source.

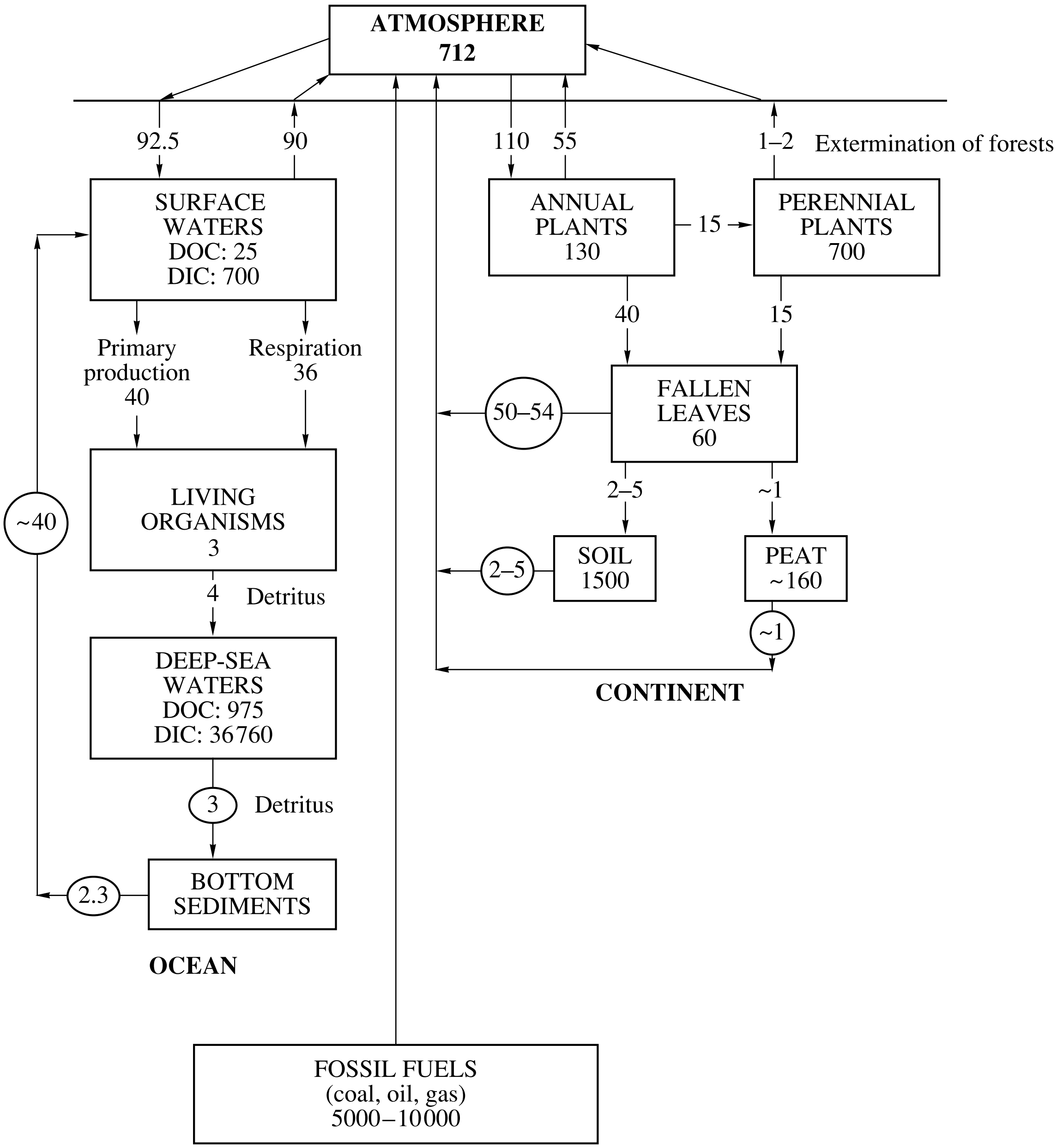


Fig. 2. Reservoirs (rectangles) and annual fluxes (arrows) of the global biogeochemical cycle of carbon. Numerals in the rectangles and at the arrows are megatons of carbon. Numerals in the ovals are the fluxes due to microbial activity [18]. DOC, dissolved organic carbon; DIC, dissolved inorganic carbon.

The use of a combination of microbiological, radioisotopic, and stable-isotopic data made it possible, in a number of cases, to quantitatively estimate the portions of methane formed microbially and abiogenically (as a result of thermal catalysis). Thus, in the great anaerobic system of the Black Sea, annual microbial production of methane makes up 10.06×10^9 tons and the contribution of thermogenic methane is 2.37×10^9 tons [23]. As in the case of the Black Sea hydrogen sulfide [15], the major part of methane is formed in the water column and not in the modern bottom sediments.

An important finding, also made with the use of radioisotopic and stable-isotopic methods, was the discovery of the process of anaerobic methane oxidation, driven by an association of methanogenic archaea and sulfate-reducing bacteria [24, 25]. This process occurs in many anaerobic ecosystems; in the Black Sea, 12.3×10^9 tons of methane is oxidized annually [23].

The modern processes of methanogenesis and methanotrophy play an important role in the carbon cycle in municipal rubbish dumps, waterlogged soils, and subsurface waters, as well as in exploited oil fields [26, 27], where microbial methanogenesis promotes enhancement of oil recovery. At coal fields, aerobic methanotrophs may be used to decrease the methane content in the atmosphere of coal mines [28].

Striking the global balance of carbon, one cannot but infer a significant difference between natural and technogenic fluxes. As can be seen from Fig. 2, the geochemical activity of soil microorganisms taken alone, namely, decomposition of leaf litter, peat, and organic matter of soil, results in a carbon flux to the atmosphere that is ten times greater than the flux caused by fossil fuel combustion. In the degradative part of the carbon cycle in the ocean, an additional 40 billion tons of organic carbon is processed (Fig. 2).

Microbial processes of the carbon cycle exert considerable influence on the calcium cycle. In weathering crusts and in soils, leaching of calcium and magnesium occurs under the influence of the carbon dioxide produced during microbial oxidation of organic matter [29].

In the zones of surface bedding of carbonate rocks, microbial CO_2 produced in soil dissolves the carbonate minerals, causing karst formation.

In brackish water bodies and in saline soils, where calcium content is considerably higher than in freshwater ecosystems, microbial CO_2 production due to consumption of organic matter results in sedimentation of carbonate minerals. This process is especially intense under anaerobic conditions, when the process of sulfate reduction is developed; since the hydrogen ion is removed to form H_2S, it results in noticeable alkalization of the medium:

$$SO_4^{2-} + C_{org} \longrightarrow S^{2-} + CO_2;$$
$$S^{2-} + H^+ + OH^- \longrightarrow H_2S + OH^-.$$

In the reduced sediments of seas and brackish lakes, the isotopically light diagenetic calcite, magnesian calcite, and protodolomite precipitate, while anaerobic oxidation of methane from the cold seeps results in the formation of large carbonate constructions consisting mostly of aragonite with extremely light carbon [30]. Formation of isotopically light carbonates also occurs during anaerobic oxidation of the organic matter of subsurface waters by sulfate-reducing bacteria. These processes can be presently observed in the oil fields with carbonate collectors and in the regions of the formation of epigenetic deposits of native sulfur [13]. In the geological past, especially in the Permian and Miocene epochs, thick strata of isotopically light sedimentary carbonates were formed in paragenesis with native sulfur [13].

To conclude the chapter on the microbiological processes of the carbon cycle, it is necessary to remind the reader that organic compounds serve as electron donors in the biological destruction of silicate minerals and in the reduction of oxidized compounds of many elements with variable valence. The processes of reduction of sulfate to hydrogen sulfide (heterotrophic sulfate reduction) and of nitrates and nitrites to dinitrogen have been studied in the most detailed fashion. The processes of reduction of trivalent iron, tetravalent manganese, and hexavalent uranium fall into the same group, as well as the processes of reduction of the salts of chromic, vanadic, and technetic acids, performed by many anaerobic and facultatively anaerobic bacteria. These processes are discussed below.

3. MICROBIAL DESTRUCTION OF SILICATE MINERALS

While the carbon cycle is the motive force of the biospheric processes, rocks are a vast field for microbial activity.

Rocks built of silicate and aluminosilicate minerals comprise the main mass (ca. 95%) of the Earth's crust. In the hypergenesis zone, weathering occurs, caused by physical, chemical, and biological processes. This results in destruction of minerals; migration and redeposition of the constituent elements; and formation of weathering crusts, ore deposits, and soils.

From the microbiologist's point of view, weathering crusts are mostly the zone of destructive processes. Geologists assign the highest priority to the abiotic weathering processes, including those caused by dissolved CO_2 and other chemical reagents. However, already B.B. Polynov stated that "formation of the residual weathering crust (eluvium) cannot be conceived as an abiotic process."

As V.I. Vernadsky justly stated, "decomposition of the kaolin nucleus in the biosphere cannot occur without the action of a specific energy source, without living matter; within the biosphere, it must be a biological process."

Microbiological research has demonstrated that bacteria, yeasts, microscopic fungi, algae, and their communities, as well as symbiotic associations, the lichens, all participate in the destruction of rock minerals. The organisms producing mineral or organic acids, surface-active substances, etc., are the most active in these processes. The developing microbial communities can obtain the required organic and mineral nutrients from the rocks. Relevant research works have been summarized in a number of books and reviews [31, 32]. However, the mechanisms and the mineralogical pathways of microbial destruction of silicates and aluminosilicates are scarcely studied. At the Institute of Microbiology, Russian Academy of Sciences, microbial degradation of the silicate and aluminosilicate minerals of the industrially important rocks and ores has been investigated.

SiO_2 destruction. Quartz is one of the most widespread rock-forming minerals in the Earth's crust. It is highly resistant to weathering and belongs to those silicates in which three-dimensional structures are formed by the silicon–oxygen tetrahedrons connected via the oxygen atoms. Organotrophic and autotrophic bacteria can break down SiO_2; the breaking of the quartz siloxane bond (=Si–O–Si=) depends solely on organic bacterial exometabolites and ambient pH. Destruction of

SiO_2 occurred in the presence of autotrophic bacteria *Thiobacillus thioparus* grown on thiosulfate and of organotrophic bacteria and their exometabolites at pH above 5.0. Three forms of silicon were revealed, monomeric, polymeric, and bound:

$$SiO_2 \xrightarrow{\text{bacteria}} Si_{mon} + Si_{poly} + Si_{bound}.$$

Development of *Acidithiobacillus thiooxidans* on sulfur at pH 1.2–3.6 resulted in very weak destruction of SiO_2. Since silicic acid in solutions is a product of SiO_2 degradation, its binding in a stable, nonhydrolyzable compound by bacteria and their exometabolites shifts the reaction equilibrium and thus facilitates further destruction of quartz [33, 34]. The direct effect of microbial enzymes and exometabolites on the SiO_2 crystal structure must also be taken into consideration: it causes changes in the rigidity of the crystal lattice. Under natural conditions, binding of monomeric silicon by bacteria and their exometabolites may be a process most important in both degradation of silicate minerals and formation of amorphous silica.

Destruction of layered silicates. Destruction of layered silicates was studied with Yakut kimberlites. The main rock-forming minerals of intact Yakut kimberlites are serpentine $(Mg_{5.4}Fe_{0.6})_6(OH)_8(Si_4O_{10})$ and the cement consisting of chlorite $(MgFe^{2+})_3 \cdot [(OH)_2AlSi_3O_{10}]\{(Mg, Fe)_3(OH)_6\}$ and calcite ($CaCO_3$). In a slightly changed rock, the serpentine grains are chloritized at the edges and the cement consists of calcite, dolomite ($CaMg(CO_3)_2$), and chlorite. In strongly changed kimberlite, the serpentine grains have a smectite crust (chlorite transformed to smectite) and the cement consists of calcite and smectite—$(MgCaKNa)[Si]_4(Al_2O_{10})(OH)_2$.

The cultures of *Bacillus stearothermophilus* (60°C) and *Bacillus mucilaginosus* (28°C) grown on organic media selectively dissolved silicate minerals. *B. stearothermophilus* caused mostly dissolution of the serpentine material, resulting in solubilization of magnesium, much more intense than that of calcium and silicon. Under the action of *B. mucilaginosus*, calcite and dolomite were mostly destructed with preferential washout of calcium. Thus, the action of microorganisms on this type of silicates is selective and is possibly dependent on the exometabolite type. A correlation was observed between the secondary changes in the kimberlite minerals in the experiment and in nature. Serpentine is chloritized with subsequent transformation of chlorite to smectite, and the rock is dolomitized due to incorporation of magnesium into the $CaCO_3$ structure. Under the action of microorganisms, changes occur that lead to the final stable state of the rock [35, 36].

For the kimberlites of the southwestern shore of the White Sea, the following types are characteristic: saponitic, serpentine–saponitic, and carbonatized [37]. Under the action of sulfur-grown *Acidithiobacillus thiooxidans* at pH 3.0–6.0, in the serpentine–saponitic kimberlite, saponite, serpentine, and chlorite were completely dissolved, and in the saponitic kimberlite, only calcite and chlorite; saponite was partially dissolved. Gypsum and silica amorphous in X rays were found among the newly formed compounds.

Deep disintegration of kimberlites of this type also occurred, which was practically not noticed in the absence of bacteria. It may be to a large degree caused by such exometabolites as organic acids, lipids, and phospholipids. Sulfuric acid does not cause such deep changes in the kimberlite silicate minerals in this pH range.

Nitrifying bacteria are less effective in the destruction of this type of minerals. Only calcite and dolomite were completely dissolved.

Microbial destruction of insular, sheet, and wireframe silicate beryllium-containing minerals. Beryllium-containing silicate minerals—beryl (insular silicate, $Be_3Al_2Si_6O_{18}$), margarite (sheet silicate, $(Ca, Na)(Li, Mg)\ Al_2 \cdot [(Be, Al)_2Si_2O_{10}] \cdot (OH)_2$), genthelvine (skeletal silicate, $Zn_8S_2\ [BeSiO_6]_6$), and chrysoberyl (oxide, Al_2BeO_4)—are among the most resistant. Under natural conditions, however, their destruction and migration of the elements comprising their crystal lattice occurs. The rate of the destruction of these minerals by *B. mucilaginosus* and exopolysaccharides decreased in the following order: beryl > margarite > chrysoberyl [38]. Be, Al, and Si were solubilized. Their solubilization rates depended on pH and temperature, and the conditions for extraction of Be, Al, and Si were different for different minerals. This finding implies different pathways of destruction of these minerals under different ambient conditions.

Genthelvine contains sulfides of Zn, Mn, and Fe bound to the silicate framework. *Acidithiobacillus ferrooxidans* is capable of genthelvine oxidation at low pH. Extraction of BeO, MnO, ZnO, and SiO_2 increased 22-, 20.5-, 234.6-, and 19.6-fold, respectively, compared to chemical leaching.

In the drainage solutions of mineral deposits, the Be concentration can reach 5–10 mg/l. The idea of microbial participation in the destruction of these minerals in nature is well founded.

Synnerites also belong to wireframe silicates; kalsilite ($KAlSiO_4$) and microcline ($KAlSi_3O_8$) are rock-forming minerals. They contain 22% Al_2O_3; 19% K_2O; and such elements as Pb, Cs, Sr.

For the study of microbial destruction of synnerites, 66 strains of organotrophic microorganisms belonging to 19 genera were used [39]. However, only certain micromycetes were effective in synnerite destruction and liberation of Al, K, and Si. The most active synnerite destructors were *Aspergillus niger* INMI 8, *Rhizopus arrhizus* VKM F-489, *Penicillium chrysogenum* INMI 16, and some others. Pseudomonads were less active in element washout from synnerite. Removal of Si, Al, and K by yeast cultures, excluding *Yarrowia lipolytica*, was insignificant. Thiobacilli and nitrifying bacteria, which produce mineral acids, as well as

B. mucilaginosus, practically did not disrupt the structure of synnerite.

Synnerite destruction occurs due to the dissolution of kalsilite. Both chemical analysis and X-ray phase analysis of the residue demonstrated that it is close in its composition to potassium feldspar ($KAlSi_3O_8$)—microcline.

Microbial destruction of chain and layered silicate minerals. Spodumene (α-spodumene, $LiAlSi_2O_6$) is a low-temperature lithium and aluminum silicate, a mineral with chain and layered structural motifs. In industry, it is considered a highly resistant mineral. Its destruction and lithium recovery require a large expense of energy (heat) and reagents. In nature, however, it is not stable. Microbiological research performed in a spodumene deposit revealed a broad spectrum of organotrophic and lithotrophic microorganisms in the zones of spodumene destruction and in the surrounding rocks, pegmatites and slates; lithium in the contact zone of the surrounding pegmatites with slates was removed to a depth of 200 m [40].

The most active spodumene destructors are certain fungi (*Penicillium notatum, A. niger*), *A. thiooxidans,* and slime-producing bacteria (*B. mucilaginosus*).

Other bacteria characteristic of the spodumene deposit (sulfate-reducing and nitrifying) practically did not disrupt the structure of spodumene.

Our data from X-ray analysis of spodumene samples after treatment with *B. mucilaginosus* exopolysaccharides can serve as an example. At pH 10, the characteristic interplanar distances were the same as in the original sample or after treatment with water (Figs. 3, 4a, 4b). Treating spodumene with the same exopolysaccharides at pH 2.0 (Fig. 4c) disrupted its structure, as evidenced by the disappearance of the following reflexes (in Å): 1.649, 1.734, 1.814, 1.858, 1.923, 1.973, 2.024, 2.054, 2.103, 2.131, 2.218, 2.344, 2.542, 2.665, 3.03, 3.40, 3.42, 3.71, 4.40, and 4.35.

The reflexes with d at 4.27, 4.21, 3.66, 2.92, 2.79, 2.443, and 1.596 broadened, while the reflex at $d = 6.07$ Å weakened.

Active removal of Li, Al, and Si was observed. The intensity of the reflex at $d = 3.34$ Å, characteristic of quartz, was also changed. No changes of the spodumene structure occurred in the control at pH 2.0 without exopolysaccharides (Fig. 4d). The disappearance of the reflex at $d = 3.34$ Å signifies predominant dissolution of the quartz associated with spodumene.

Destruction of bauxite minerals. Bauxites are rocks of complex mineral composition. Their main minerals are boehmite, γ-AlOOH; gibbsite, γ-$Al(OH)_3$; diaspore, α-AlOOH; alumogoethite, (Al,Fe)OOH; alumohematite, $(Al,Fe)_2O_3$; hematite, α-Fe_2O_3; goethite, α-FeOOH; siderite, $FeCO_3$; kaolinite, $Al_2Si_2O_5$; quartz, SiO_2; and chamosite, $(Fe^{2+},Fe^{3+})_3[(OH)_2AlSi_3O_{10}]\{(Fe,Mg)_3(O, OH)_6\}$.

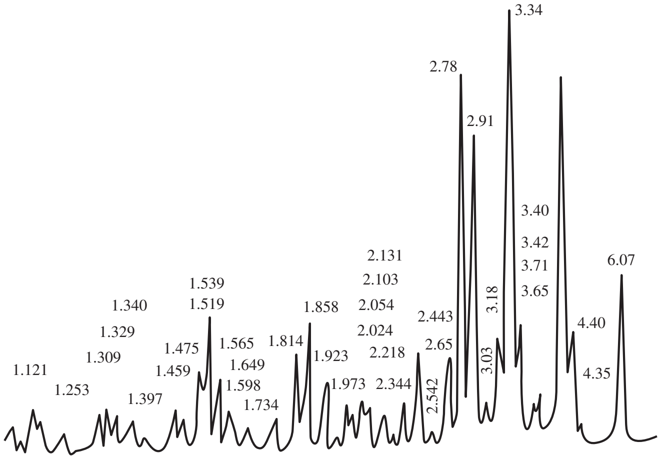
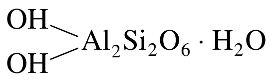


Fig. 3. Diffractometric curves (d values are given in Å) for the original spodumene sample.

Certain strains of *A. niger* were the most active in the destruction of the minerals of the kaolinite–boehmite bauxite. The extraction of Si, Al, and Fe, as compared to the control, increased by 96- to 164-, 327- to 472-, and 26- to 48-fold, respectively. Both yeasts and organotrophic bacteria of the genus *Pseudomonas* caused weak destruction of bauxite.

Kaolin destruction. Kaolins are argillaceous rocks consisting of at least 50% of the kaolin-group minerals. Kaolin in all its varieties has the formula



$$\left.\begin{matrix}OH\\OH\end{matrix}\right\rangle Al_2Si_2O_6\cdot H_2O$$

and is the main component of all kaolin clays.

The iron-containing minerals of the original kaolin studied were hematite, α-Fe_2O_3; goethite, α-FeOOH; magnetite, Fe_3O_4; anatase; and kaolinite.

Treating this kaolin sample with a community of organotrophic aerobic and anaerobic bacteria, including iron reducers, resulted in pronounced transformation of iron-containing minerals, apart from the destruction of kaolin. For example, the portion of the magnetic iron fraction increased from 12 to 52%. Ferrihydrite ($5Fe_2O_3\cdot 9H_2O$) of biogenic origin, the rare hydroxide akaganeite (β-FeOOH), and pyrite were found; crystallization of the thermodynamically unstable weakly ordered protolepidocrocite increased to the level characteristic for the typical lepidocrocite (γ-FeOOH); and kaolin microaggregates were destroyed and the contact between kaolin particles and iron-containing minerals disrupted. These events led to increased removal of quartz, mica, and hydromica with the magnetic fractions [41, 42].

These studies demonstrated that microbial destruction of silicate minerals is an indirect process dependent on microbial exometabolites and occurring under specific physicochemical conditions. It is associated with microbial production of specific organic and min-

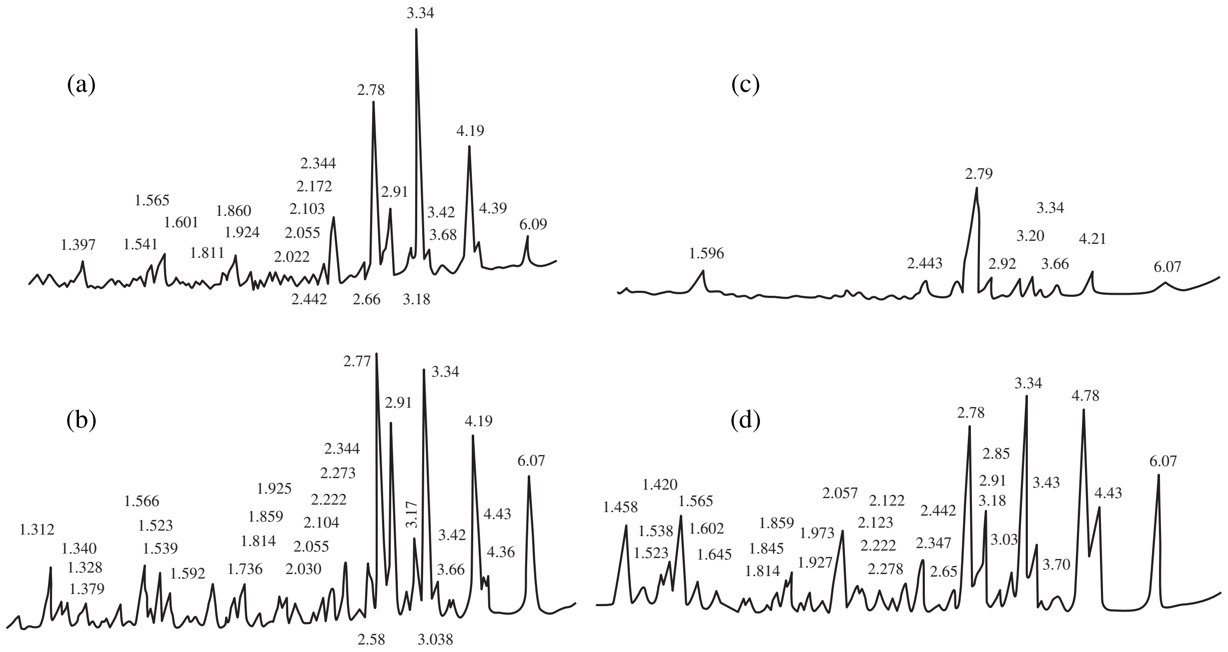


Fig. 4. Diffractometric curves for spodumene samples treated with (a) *B. mucilaginosus* exopolysaccharides at pH 10, (b) sterile water at pH 10 (control), (c) *B. mucilaginosus* exopolysaccharides at pH 2.0, and (d) sterile water at pH 2.0 (control).

eral acids, alkali, and polymers, whose effect depends on the silicate crystallochemical characteristics and mineral composition, pH, temperature, and other factors.

Diatomic algae, which deposit siliceous material in vesicles, are an exception; the biochemistry of their silicon assimilation is not clear. A chemolithotrophic destruction pathway is possible for silicate minerals in the presence of elements with variable valence.

4. MICROBIAL PROCESSES OF THE SULFUR CYCLE

About 99.99% of the world sulfur reserves is concentrated in the lithosphere in the form of metal sulfides, mostly pyrite (FeS_2), and evaporite sulfates and in the seas and oceans in the form of dissolved sulfate. Like most of the elements with variable valence, sulfur is constantly changing its chemical state.

In the lithosphere, dissimilatory reduction of sulfur and sulfates and oxidation of reduced compounds are the two main processes responsible for the transformation of sulfur compounds.

Presently, about 30 genera of sulfate-reducing bacteria are known, which use sulfate instead of oxygen as the electron acceptor and oxidize anaerobically H_2 or organic compounds to gain energy for growth:

$$C_{org} + SO_4^{2-} \longrightarrow S^{2-} + CO_2.$$

A number of new genera and species of these bacteria were described at the Institute of Microbiology, Russian Academy of Sciences, by E.P. Rozanova, T.N. Nazina, and other researchers, e.g., *Desulfomicrobium baculatum, Desulfomicrobium apsheronum*, *Thermodesulfotomaculum mobili*, *Desulfotomaculum salinus*, *Desulfobacterium cetonicum*, *Desulfotomaculum kuznetsovii*, and others.

Zhilina has also described the first representative of alkaliphilic anaerobic sulfate-reducing bacteria, *Desulfonatronovibrio hydrogenovorans* gen. nov. sp. nov., which utilizes only H_2 and formate as electron donors and grows at pH 8–10 (optimum at pH 9.7). Bacteria reducing thiosulfate or sulfite are facultative anaerobes. Sulfur respiration is characteristic of a wide range of anaerobic thermophilic microorganisms, both bacteria and archaea.

Thermophilic bacteria with true sulfur respiration are represented by a number of genera and species: *Desulfurella acetivorans, D. multipoteus, D. kamchatkensis, D. propionica, Hippea maritime* [43, 44], and *Desulfurobacterium thermolithotrophum* [45]. They grow at temperatures of 40–110°C, using H_2 and organic acids as electron donors.

The ability to reduce sulfur at the expense of H_2 oxidation was found among the acidophilic (pH 1–3) hyperthermophiles of the genera *Pyrodictium* (80–110°C), *Stigiolobus* (57–89°C), and *Acidianus* (65–96°C) [46, 47], as well as in the mesophilic bacterium *A. ferrooxidans* [69, 74].

The contribution of sulfate- and sulfur-reducing bacteria to the formation of H_2S in broad ranges of temperature and pH is enormous.

Their geochemical activity results in the formation of such sulfide minerals as pyrite (FeS_2), pyrrhotine (FeS), cuprite (CuS), chalcosine (Cu_2S), sphalerite

(ZnS), etc., in the zones of secondary enrichment of sulfide ores and in bottom sediments of aquatic ecosystems and even in the formation of sulfur and carbonate deposits.

Oxidation of sulfur and its reduced compounds. Sulfur compounds are unstable in natural environments and are oxidized both chemically and by microorganisms, including photosynthesizing bacteria, filamentous and unicellular sulfur bacteria, thionic bacteria, moderately thermophilic sulfobacilli, archaea, and many organotrophic bacteria. At the Institute of Microbiology, Russian Academy of Sciences, V.M. Gorlenko and other researchers described many new genera and species of phototrophs; it was established that purple sulfur bacteria are capable, in addition to photosynthesis, of dark anaerobic lithoautotrophic growth at the expense of the oxidation of H_2S and sulfur. R.S. Golovacheva and G.I. Karavaiko [48] described a new genus of moderately thermophilic bacteria, *Sulfobacillus*, whose representatives oxidize Fe^{2+}, S^{2-}/S^0, and sulfide minerals, and a new genus and two species of archaea, the sulfur-oxidizing *Sulfurococcus mirabilis* [49] and *Sulfurococcus yellowstonensis*, which oxidizes Fe^{2+}, S^{2-}/S^0, and sulfide minerals [50]. T.A. Pivovarova, I.A. Tsaplina, and T.F. Kondrat'eva investigated the biodiversity of the strains of chemolithoautotrophic acidophilic bacteria of the genus *Acidithiobacillus*, isolated from various ecological niches and oxidizing Fe^{2+}, $S^{2-}/S, ^0$ and sulfide minerals at pH 0.5–6.0. Kondrat'eva and coworkers developed genetic approaches to the monitoring of these bacteria in natural and technogenic environments. The thermophilic nitrate-reducing bacteria of the genera *Thermothrix, Aquifex*, and *Ammonifex* (57–95°C) and archaea of the genera *Pyrobaculum, Ferroglobus*, and *Pyrolobus* (65–113°C) oxidize sulfur compounds with nitrate as the electron acceptor [51–56]. After the works by Winogradsky and other researchers, colorless sulfur bacteria attracted attention as active geochemical agents involved in the sulfur cycle in water bodies and sulfur springs. G.A. Dubinina developed methods for the cultivation of unicellular sulfur bacteria and described new genera and species of these bacteria; she also described new species of the filamentous sulfur bacteria of the genera *Beggiatoa* and *Thiothrix* and a new species of gliding sulfur bacteria of the genus *Leucothrix.*

Dubinina and her pupils established the functional role of sulfur compounds, which, in the absence of catalase, can serve as exogenous antioxidants involved in the elimination of toxic oxygen species—H_2O_2 and O*—formed during growth on organic substrates. However, under microaerobic conditions, *Beggiatoa* is capable of chemolithoautotrophic growth at the expense of sulfur compounds used as electron donors in the energy metabolism [57]. These bacteria, like purple bacteria and *T. thioparus*, form S^0 and then oxidize it to the final product, SO_4^{2-}.

Sulfide minerals are semiconductive crystals. Upon oxidation, they undergo destructuring due to the breakage of bonds in their crystal structures and loss of electrons. As distinct from silicate minerals, sulfide minerals can be sources of energy for specific acidophilic chemolithotrophic bacteria and archaea.

Among the best known bacteria and archaea that oxidize sulfide minerals are *A. ferrooxidans, A. thiooxidans, Leptospirillum ferrooxidans, Sulfobacillus* species, and archaea of the genera *Acidianus, Metallosphaera*, and *Ferroplasma.*

Oxidation of sulfide minerals by microorganisms can be considered as a corrosive bioelectrochemical process. The study of this process was started at the Moscow Institute of Steel and Alloys and the Institute of Microbiology, Russian Academy of Sciences, as long ago as in the early 1970s with arsenopyrite (FeAsS) and pyrite (FeS_2) as the objects of study [58, 59].

The reactions occurring on the surface of the mineral can be represented as follows:

$$\text{Anode reaction: } FeAsS \longrightarrow Fe^{2+} + As^{3+} + S^0 + 7\bar{e}.$$

$$\text{Cathode reaction: } 3.5O_2 + 14H^+ + 7\bar{e} \longrightarrow 7H_2O.$$

Bacteria accelerate this electrochemical process by influencing the electrode potential of the mineral, its electric charge and conductivity, as well as the redox potential of the medium, and also by oxidizing Fe^{2+} and S^0 to final products:

$$Fe^{2+} \longrightarrow Fe^{3+} + \bar{e},$$

$$4\bar{e} + O_2 + 4H^+ \longrightarrow 2H_2O;$$

$$4Fe^{2+} + O_2 + 4H^+ \longrightarrow 4Fe^{3+} + 2H_2O;$$

$$S^0 + 4H_2O \longrightarrow SO_4^{2-} + 8H^+ + 6\bar{e}.$$

Fe^{3+} is in turn a strong oxidant for many sulfide minerals; e.g.,

$$FeAsS + Fe_2(SO_4)_3 + 1.5H_2O + 0.75O_2 \longrightarrow 3FeSO_4 + S^0 + 7\bar{e}.$$

Fe^{2+} and S^0 are reoxidized by bacteria to Fe^{3+} and H_2SO_4, and the cycle is reiterated.

In a mixture of different sulfide minerals that form galvanic couples, bacteria primarily oxidize the anode.

The role of the above-considered microorganisms in the natural sulfur cycle is enormous. The geological scale of the processes discussed above is determined by both sulfate-reducing bacteria and sulfur- and sulfide-oxidizing microorganisms.

The determinations of the rates of biogeochemical processes in natural environments performed over the last decades made it possible to assess the scale of component processes of the global sulfur cycle. As mentioned above, the main component process is bacterial sulfate reduction. It was shown that the integral production of reduced sulfur in bottom sediments of the ocean reaches 492 Mtons per year [18]. This amount of microbially formed H_2S is almost three times greater than the annual industrial extraction of all kinds of sulfur-containing raw materials (169 Mtons). The major part of the hydrogen sulfide formed by microorganisms in bottom sediments is oxidized in the sediment upper horizons or in the near-bottom water. About 111 Mtons of reduced sulfur annually binds to metals and is thus removed from the global cycle in the form of sulfides, pyrite (FeS_2) first of all. The annual microbial production of hydrogen sulfide in the anaerobic zone of the Black Sea is around 30–50 million tons [60]. A thorough study of the geochemical activity of microorganisms in sulfur deposits provided convincing evidence of their role in the genesis of sedimentary sulfur deposits [13]. Their formation is underlain by the processes of microbial sulfur reduction and microbial and chemical oxidation of H_2S to elemental sulfur under certain geological conditions. The sulfur in these deposits is associated with carbonate rocks (limes); this fact relates the two processes—sulfate reduction and carbonate formation. The emergence of sulfur strata in the zone affected by oxygen and surface waters leads to the development of powerful processes of bacterial oxidation of sulfur [61]. This results in a decrease in the technological value of the sulfur ore or even in disappearance of small sulfur deposits; the oxidation process is accompanied by the formation of sulfuric acid. It was experimentally shown that chemical oxidation of elemental sulfur virtually does not occur. The deposits of sulfide ores are usually of a hydrothermal origin. Upon the emergence of a sulfide ore in the zone affected by oxygen, powerful oxidation processes develop irrespective of the climatic zone of the deposit localization. As distinct from elemental sulfur, sulfide minerals can be oxidized chemically; however, chemolithoautotrophic bacteria accelerate the oxidative processes by one to three orders of magnitude. According to data of American researchers (cited in [62]), in the 1930s, the rivers of the Pittsburgh district received daily about 9000 tons of sulfuric acid as a result of pyrite oxidation in coal mines. In 1932, the annual acidic pollution of the Ohio River was equivalent to 3 million tons of strong sulfuric acid.

During spontaneous oxidation of pyrite and copper sulfide minerals, about 500 tons of copper and 700 tons of sulfuric acid were annually released with the mine waters of the Degtyarskii mine in the 1960s [63].

Due to the natural influx of acidic mine waters, the Tinto River in southwestern Spain is an extremely acidic ecosystem; the water has pH 1.5–3.1 and contains heavy metals in high concentrations (iron, 0.4–20.2 g/l; copper, 0.02–0.70 g/l; zinc, 0.02–0.56 g/l). This ecosystem is inhabited by the chemolithotrophic bacteria *A. ferrooxidans, A. thiooxidans, Leptospirillum* sp., and *Ferroplasma* sp. [64, 65].

Investigation of these processes is of great ecological importance and eventually provides theoretical grounds for the elaboration of measures of sulfur ore preservation and technologies for obtaining of metals from ores and concentrates.

5. MICROBIAL PROCESSES OF THE IRON AND MANGANESE CYCLES

Microbial reduction of iron and manganese oxides. Iron is one of the most abundantly occurring elements in the Earth's crust. Microorganisms can gain energy from both Fe^{3+} reduction and Fe^{2+} oxidation. Most of the Fe^{3+}-reducing bacteria have been isolated and studied over the last several decades [66–68]. These are bacteria of the genus *Pseudomonas*, strains of *Shewanella putrefaciens* and *Geobacter*, and *Desulfitobacterium frappieri* strain G2. Strain G2 can use as electron acceptors crystalline Fe^{3+} oxide, soluble forms of Fe^{3+}, and iron of silicate minerals; the electron donors used are H_2 and a number of organic substrates, such as formate, lactate, malate, pyruvate, ethanol, and butanol.

The amount of Fe^{2+} formed per mole H_2 consumed was 2.12 ± 0.35 ($n = 3$), which agreed with the reaction

$$2Fe^{3+} + H_2 \longrightarrow 2H^+ + 2Fe^{2+}.$$

The thermophilic archaeon *Sulfolobus acidocaldarius* can also reduce Fe^{3+} under microaerobic conditions during S^0 oxidation at a temperature of 70°C and pH 1.6 [69].

An association of thermophilic anaerobic microorganisms that was obtained from hydrothermal vents of Kamchatka was reported to be capable of dissimilatory reduction of amorphous iron oxide during growth on acetate at 55–76°C [70].

The strictly anaerobic bacterium *Bacillus infernus*, isolated from sediments from a depth of 2700 m, can reduce Fe^{3+} with formate and lactate [71]. Microorganisms capable of Fe^{3+} reduction with the use of H_2 as the electron donor are widespread in natural environments. They have been isolated from continental hydrothermal vents (*Thermoterrabacterium ferrireducens*, 50–74°C) and oil fields (*Deferribacter thermophilus*, 50–65°C) [72, 73]. Most of the anaerobic cultures isolated from formation waters of high-temperature oil fields can reduce Fe^{3+} with molecular hydrogen or peptone as the electron donors; among such organisms, *Thermotoga* (50–75°C), *Thermoanaerobacter* (40–80°C), and archaea of the genus *Thermococcus* (41–88°C) [66] should be mentioned.

Fe^{3+} can also be reduced, under mesophilic conditions (<40°C), by the acidophilic chemolithoautotrophs *A. ferrooxidans* and *A. thiooxidans*, which use as electron donors S^0 and certain organic substrates [69, 74], and, at 55°C and pH 2.0, by *Sulfobacillus* representatives (under anaerobic conditions).

Many (but not all) of the microorganisms that reduce Fe^{3+} can also reduce Mn^{4+}.

The reduction of Mn^{4+} can proceed both enzymatically and as a result of the chemical oxidation of such metabolites as organic acids, peroxides, etc. During its enzymatic reduction, Mn^{4+} is used as an electron acceptor, and the reduction involves operation of the electron transport chain. Among metabolites, the most active Mn^{4+}-reducing compounds are formic and oxalic acids.

Microbial oxidation of Fe^{2+} and Mn^{2+}. These processes widely occur in natural environments and are driven by diverse microorganisms. The best known bacterial agents of these processes in neutral media are *Gallionella, Leptothrix, Siderocapsa, Ochrobium, Siderococcus, Pedomicrobium, Metallogenium*, and others. However, many ordinary heterotrophic microorganisms are also able to oxidize Fe^{2+} and Mn^{2+}. In certain freshwater environments, their number reaches 50–90% of the total amount of bacterioplankton; on average, it is about 12%. The final products of the oxidative processes are oxides of trivalent iron and tetravalent manganese, which are deposited on the surface of the cells.

The physiological implications of these processes may be different in different microorganisms. Certain microorganisms isolated from sediments of freshwater wetlands can grow chemolithoautotrophically with Fe^{2+} as the electron donor and O_2 as the electron acceptor.

Unicellular iron bacteria, such as *Gallionella*, are also capable of autotrophic oxidation of Fe^{2+}. Several strictly autotrophic acidophilic microorganisms are known to use Fe^{2+} as the energy source. *A. ferrooxidans* and *L. ferrooxidans* autotrophically oxidize Fe^{2+} under aerobic conditions at temperatures of 2–40°C and pH 0.8–5.0 according to the reaction

$$Fe^{2+} \longrightarrow Fe^{3+} + \bar{e}\,.$$

Bacteria of the genus *Sulfobacillus* oxidize Fe^{2+} under mixotrophic conditions at temperatures of 20–60°C and pH 1.1–5.0. Recently, a new family of strictly autotrophic, mesophilic (35–42°C), acidophilic, Fe^{2+}- and FeS_2-oxidizing archaea, *Ferroplasmaceae,* was described, which includes the genus *Ferroplasma* and the species *F. acidophilum* [75].

The archaeon *Ferrolobus placidus*, isolated from shallow-water marine hydrotherms, oxidizes Fe^{2+} under autotrophic conditions at temperatures of 65–95°C, using NO_3^- as the electron acceptor [53]. The biochemical processes of the oxidation of Fe^{2+} and Mn^{2+} by heterotrophic microorganisms have a peroxide mechanism. Like in the case of some sulfur-oxidizing microorganisms, oxidation of Fe^{2+} and Mn^{2+} by these heterotrophs is not coupled to energy conservation but serves for defense against the peroxides formed by these microorganisms. This is the so-called indirect mechanism of the oxidation of Fe^{2+} and Mn^{2+}. Since the reaction $Mn^{2+} + 1/2O_2 + H_2O \longrightarrow MnO_2 + 2H^+$ is characterized by a standard free energy of 70 kJ (at pH 7), the oxidation of Mn^{2+} can, generally speaking, provide for bacterial growth.

Microbial synthesis of minerals. In the microbial cycles of elements, synthesis of various minerals occurs. Extracellular formation of magnetite (Fe_3O_4) was reported to occur in pure cultures of bacteria [76], including thermophilic ones [77], and in microbial communities [78–80]. During the development of a microbial community that included iron-reducing bacteria, the content of magnetite in kaolin increased from 12 to 52%; ferrihydrite ($5Fe_2O_3 \cdot 9H_2O$) and the rare hydroxide akaganeite (β-FeOOH) were also formed [41, 42]. Magnetotactic bacteria are known that deposit inside their cells magnetite (Fe_3O_4), [80] greigite (Fe_3S_4) [81], or greigite and pyrite [82]. The magnetosomes in cells are surrounded by bilayered membrane structures.

Thus, it is evident that the microorganisms that reduce or oxidize iron and manganese are ubiquitous in natural environments with different temperatures and pH values; they play a geological-scale role in the natural iron and manganese cycles.

Microbiological investigations of iron–manganese ores, bottom sediments of continental and marine water bodies, regions of volcanic activity, deep-sea concretions of the Pacific Ocean, and ores of the Chiaturskoe manganese deposits, together with model laboratory experiments, allowed Kuznetsov and Dubinina to substantiate the leading role of the biogenic factor in the ore-formation processes. This led to radical reconsideration by geologists of the concepts of iron–manganese ore formation.

6. MICROBIAL PROCESSES OF ELEMENT REDUCTION

It has long been known that microorganisms can enzymatically oxidize many of the elements with variable valence, using them as electron donors. Examples are the microbial oxidation of Fe^{2+}, S^{2-}/S^0, Mn^{2+}, U^{4+}, Sb^{3+}, etc. A great advance in geological microbiology was the discovery of the ability of microorganisms to reduce oxidized forms of elements, often using them as terminal electron acceptors, i.e., in dissimilatory processes. Several examples of such processes were already considered above (reduction of S^0, Fe^{3+}, and Mn^{4+}). As electron donors, organic compounds may be used. Directly or indirectly, microorganisms can reduce $U^{6+}(U^{4+})$, $Tc^{7+}(Tc^{5+}, Tc^{4+})$, $Cr^{6+}(Cr^{3+})$, $Co^{3+}(Co^{2+})$, $Au^{3+}(Au^0)$, $Ag^{+1}(Ag^0)$, $Hg^{2+}(Hg^0)$, $Mo^{6+}(Mo^{5+})$, $Pd^{2+}(Pd^0)$, $As^{5+}(As^{3+})$, $Te^{7+}(Te^{4+})$, and a number of other elements [83–88].

These processes occur in wide pH and temperature ranges and can be driven by aerobic, facultatively anaerobic, and anaerobic bacteria. Thus, the anaerobic hyperthermophile *Pyrobaculum islandicum* can reduce, at neutral pH and 100°C with H_2 as the electron donor, such elements as S^0, Fe^{3+}, U^{6+}, Tc^{7+}, Cr^{6+}, Co^{3+}, and Mn^{4+}. Fe^{3+} was reduced to magnetite; U^{6+} was reduced to the insoluble mineral uraninite, which was deposited extracellularly; Tc^{7+} was transformed to the insoluble Tc^{4+} or to Tc^{5+}; Cr^{6+} was transformed to the less soluble

Cr^{3+}; Co^{3+} was reduced to Co^{2+}; and Mn^{4+} was reduced to Mn^{2+} with the formation of manganese carbonate. At pH 2.0–3.0, Tc^{7+} can be reduced, both aerobically and anaerobically, by the acidophilic bacteria of the genus *Acidithiobacillus* (*A. ferrooxidans* and *A. thiooxidans*); at pH 10, it can be reduced by the haloalkaliphilic bacteria of the genus *Halomonas*.

Even such an inert metal as gold can be dissolved and accumulated by various microorganisms [89]. In alkaline medium (pH 9–10), amino acids, proteins, and peroxides produced by bacteria form Au–N bonds via amino groups; this results in the formation of complexes, primarily of an anionic nature:

$$Au^0 \xrightarrow[\text{amino acids}]{H_2O_2} \text{Au–N}.$$

Free ionic and colloidal gold is actively sorbed by various microorganisms. These two processes are related to mobilization, redistribution, and transport of gold in the biosphere. It migrates with surface waters and groundwaters. In biogenic ecosystems, the physicochemical parameters of gold migration change toward greater mobility of gold.

After its migration, gold may crystallize on microorganisms. Formation of crystals of gold was reported to occur on the surface of algal cell walls [90] and in the cell walls of organotrophic bacteria [91, 92]. The crystals of gold are typically hexagonal or triangular plates or are needle-shaped. Their shape and size depend on the microbial species, cultivation conditions, and some other factors.

Microorganisms are involved in the accumulation of gold deposits in zones of volcanic activity. Thus, thermophilic algal–bacterial communities promote the formation of gold concentration fields in these regions.

The data obtained demonstrate the operation in the biosphere of the cycles of virtually all elements with variable valence and the importance of the geochemical activity of microorganisms, including that occurring in subsurface geospheres under conditions of deficiency or absence of oxygen.

7. THE PRACTICAL IMPORTANCE OF GEOLOGICAL MICROBIOLOGY

The complex, large-scale investigations in the field of geological microbiology, which have been carried out for a long time, allowed a number of problems of practical importance to be solved. Methods were developed for the assessment of the rates of photosynthesis; bacterial chemosynthesis; and processes of the cycles of carbon, sulfur, and a number of other elements in various ecotopes; these methods find wide application in ecological studies, including those related to the production rates in water bodies, toxicant degradation, and monitoring of natural environments in connection with the progressive increase of the anthropogenic load.

The investigation of the physiology of microorganisms and their geochemical activity in the deposits of minerals promoted the establishment of biogeotechnology—a science dealing with microbial methods of the extraction of oil and processing of ores and concentrates. The theoretical and practical foundations of biohydrometallurgy were laid in monographs by Kuznetsov, Karavaiko, S.I. Pol'kin, and coauthors [58, 62, 93, 95] and were later developed further in the works of other researchers [96, 97].

Semiindustrial trials were performed of the bacterial–chemical method of copper leaching from waste piles of low-grade ores at several deposits in the Soviet Union. At the Kounradskoe deposit of the Balkhashmed' Enterprise, this technology was used on the industrial scale: 2400 tons of copper per year was produced, without significant investments. The production cost of 1 ton of copper was decreased from 606 to 229 rubles (prices of year 1989).

Together with the Moscow Institute of Steel and Alloys, biohydrometallurgical technologies for processing of complex copper–zinc, copper–arsenic, and copper–tin–arsenic concentrates, tails, and intermediate products were developed and tested under semiindustrial conditions.

In the gold-mining industry, a pressing problem is processing of complex gold–arsenic concentrates obtained from ores by enrichment methods. These ores will be are the main sources of gold in the 21st century. The biohydrometallurgical technology developed by joint efforts of the Institute of Microbiology, the Moscow Institute of Steel and Alloys, and the Central Research Institute of Geological Prospecting allows up to 98% of gold to be extracted from these concentrates. The technology has been tested with concentrates obtained from ores of virtually all large deposits of the Commonwealth of Independent States. Following the recommendations of the above institutes, this technology was successfully introduced into practice at the Olimpiadinskoe deposit of the enterprise Polyus. An industrial plant was launched in 2001. By this moment, the plant has compensated the investments and produces about 1 ton of gold per month. A task for the future is implementation of these technologies with different types of mineral raw materials and development of new generations of the technologies.

A most important problem related to the exploitation of oil fields is the enhancement of oil recovery since natural reserves of oil are limited and nonrenewable. The currently used methods of oil field exploitation allow no more than half of the oil to be extracted from the stratum.

The biotechnology of oil recovery enhancement developed by M.V. Ivanov and his pupils is based on the activation of microbial processes in oil strata, particularly on the stimulation of the production of surfactants, organic acids, and other products of bacterial metabolism of the oil in the near-bottom zones of injection wells [26, 27]. Only during the testing of this technology in Tatarstan, Bashkiria, and West Siberia, about 500000 tons of additional oil were recovered. The technology is also applicable to high-temperature oil fields with carbonate collectors flooded with salt waters.

An extremely important new biogeotechnology is that developed to decrease methane concentration in coal mines with the help of methane-oxidizing bacteria [28].

8. CONCLUSIONS

Over the more than hundred years that have passed after the publication of the works by Ehrenberg and Kramer, who observed deposition of iron oxides on the trichome surface of iron bacteria and sulfur granules in the filaments of *Beggiatoa*, geomicrobiology has become a large division of modern natural science. The use of methods of classical microbiology, ecology, and biogeochemistry presently makes it possible not only to quantitatively estimate the role of microorganisms in the cycles of elements at different levels (from an ecosystem to the biosphere) but also to control the direction and rate of microbially driven processes under in situ conditions with the aim to develop new biotechnologies for bioremediation of the environment and for extraction and processing of minerals.

At the modern stage of geomicrobiology development, attention is paid not only to the roles in the cycles of elements of separate functional groups of microorganisms but also to the cooperation observed in the natural multicomponent microbial communities and to their interactions with plants and animals. These investigations often employ not only microbiological and biogeochemical methods but also methods of molecular ecology.

Further progress of geomicrobiology can be expected to occur along the following directions:

(1) Physiological–biochemical diversity of microorganisms

Detailed investigations of physiological–biochemical and molecular biological peculiarities of microorganisms involved in the key reactions of the global cycles of elements and isolation of new organisms active in these processes.

(2) Microbial mineralogy

Experimental studies of the mechanisms by which microorganisms participate in the formation and destruction of rocks and their component minerals.

(3) Microbial biogeochemistry

Assessment of the results of microbial activity in modern natural ecosystems of various levels of complexity, up to the biosphere level.

(4) Microbial biogeotechnology

Development of a theoretical basis for the control of natural microbial processes of environment bioremediation and of formation and destruction of the deposits of minerals with the aim to minimize the negative effect of industrial and agricultural activities and develop more ecologically safe and less expensive methods for extraction and processing of mineral resources.

It should be emphasized that recognition of the leading role of microorganisms in the global cycles of elements in the modern biosphere led to the origination of a new field of science at the interface of biology and geology, namely, of microbial paleontology [98], which studies the role of microorganisms in the formation and evolution of the biospheres of the past geological epochs of our planet.

It would not be an overstatement to say that it was the Russian scientists S.N. Winogradsky, G.A. Nadson, B.L. Isachenko, V.I. Vernadsky, and then S.I. Kuznetsov and his pupils who made the greatest contribution to the development of the concepts and directions of geomicrobiology that are currently being intensively advanced by many laboratories abroad.

Unfortunately, after the collapse of the Soviet system of financial support of fundamental research, experimental works on geomicrobiology notably decreased in number, although the applied aspects of geomicrobiology, particularly, biogeotechnologies for the recovery and processing of oil and nonferrous and precious metals, are used by enterprises of the extractive and processing industry in modern Russia.

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