
EXPERIMENTAL ARTICLES

Transformation of Carbonate Minerals in a Cyano-Bacterial Mat in the Course of Laboratory Modeling

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Abstract—A laboratory model of a cyano-bacterial mat with mineral layers of carbonates was used to examine the dynamics of the transformation of calcium–magnesium carbonate under the conditions of a soda lake. The activity of various organisms of the cyanobacterial community results in conditions under which the Ca–Mg carbonate precipitate undergoes changes. The crystal lattice of the initial carbonate is restructured; its mineralogical composition changes depending on the conditions of the mat. In magnesium calcites, which are formed under such low-temperature conditions, a rudimentary cation adjustment can occur with the formation of dolomite domains. These experiments confirm the hypothesis that the dolomite found in stromatolites is of a secondary origin and can be formed in the course of transformation of Ca–Mg carbonates under alkaline conditions in an alkaliphilic cyanobacterial community.

Keywords: cyanobacteria, cyanobacterial mats, carbonates, magnesium calcites, dolomites.

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Different views exist in contemporary literature concerning the nature of Precambrian carbonate sediments and the processes of formation of the dolomite stromatolites [1, 2].

The evolution of dolomite formation in the course of geological history has been revealed. Dolomites, $\text{CaMg}[\text{CO}_3]_2$, were formed predominately in Archean and Proterozoic eras, while during the Phanerozoic time, dolomite accumulation decreased and the portion of limestone increased accordingly. The precise agreement of the temporal distribution of cyanobacteria and dolomite formation, as well as their facial contingency, indicate the possible important role of cyanobacteria in dolomite development [3].

Dolomite sediments and rocks can be formed in reservoirs of varying mineralization. At present, the majority of dolomites are formed in reservoirs with elevated salinity, where cyanobacterial associations develop. Contemporary dolomites have been found, for instance, in the sediments underlying the algal mats of the Gulf of Aqaba in the Red Sea [4]; there, partially

decomposed algal material is the site of carbonate precipitation.

Different opinions exist concerning the role of microorganisms, including cyanobacteria, in the process of dolomite formation. One of them assumes that the significant masses of organic matter produced by cyanobacteria determined the specific geochemical conditions of diagenesis which were favorable for the precipitation of magnesium compounds [3]. Experimental evidence of the role of cyanobacteria *Synechococcus* sp. in calcite and magnesite precipitation in the alkaline Faytleville Green Lake has been presented [5]. According to Friedman and coworkers [4], cyanobacteria participate in the formation of magnesium calcite in cyano-bacterial mats in the Gulf of Aqaba in the Red Sea; they create a microenvironment within the mat which is favorable for the precipitation of magnesium calcites with Mg content up to 40%. Such a significant magnesium concentration can explain the high level of dolomitization of stromatolites in the geological past.

Other authors maintain that the formation of marine peloids of high-magnesium calcites around bacterial colonies is the result of the activity of a number of bacteria, including sulfate reducers [6]. Since the role of

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the latter group in the process of dolomite formation has been experimentally proven, special attention has recently been paid to these organisms [7]. The activity of sulfidogenic bacteria is aimed at the consumption of sulfate oxygen; the resultant hydrogen sulfide is either removed from the system or bound in the form of insoluble sulfides. A deficiency of anions and a surplus of cations and magnesium resulted [3]. Under these conditions, magnesium is more prone to the formation of relatively insoluble carbonates, hydroxyhydrates, or organometal complexes.

Methanogenic bacteria possibly also participate in the formation of dolomites [8], since with their growth results in pH increase, which generally contributes to the precipitation of calcium and magnesium compounds.

However, a number of researchers believe [3, 4, 9] that dolomite, including that found in stromatolites, is of a secondary origin and results from the Ca–Mg transformation of carbonates. There are many indications of the fact that primary precipitation of dolomite proper does not occur. “Most likely, at the stage of sedimentogenesis, calcium and magnesium carbonates precipitate or, at best, protodolomite, and in the course of diagenesis they are converted into real dolomite with its inherent crystal structure and the shape of crystals” [3].

Nevertheless, in spite of this intense interest in the problem of dolomite formation, no specific answer has been obtained to the question concerning the role of cyano-bacterial mats in the formation of dolomites.

Our previous experiments on the simulation of the cyanobacterial community under the conditions of a soda reservoir have demonstrated that no perceptible dolomitization occurred under the conditions of active cyanobacterial photosynthesis [9]. However, alkaliphilic cyanobacteria can influence the formation of various Ca–Mg carbonates; their mineralogy depends on the cultivation conditions [10].

The purpose of this work was the study of the transformation of Ca–Mg carbonates in the laboratory model of an alkaliphilic cyano-bacterial mat under varied conditions in order to improve the understanding of the process of dolomite stromatolite formation.

MATERIALS AND METHODS

An algologically pure culture of the alkaliphilic *Microcoleus chthonoplastes* strain was used to construct the cyano-bacterial mat; the strain was isolated by us from the cyano-bacterial mat of the Khilganta soda lake, Buryat Republic, Russia (although the taxonomic position of this organism is presently questionable due to the newly obtained data on 16S rRNA sequencing, the old name has been retained for the present work). The culture was grown on the S medium at pH 9.05 (i.e., under conditions close to those of the

soda lake), at the temperature of 20°C and under illumination by fluorescent lamps. The S medium contained (g/l): NaHCO₃, 16.8; KCl, 1.0; NaNO₃, 2.5; K₂SO₄, 1.0; MgSO₄ · 7H₂O, 0.02; CaCl₂, 0.04; FeSO₄, 0.01; K₂HPO₄, 0.2; Na EDTA, 0.08.

The Ca–Mg carbonate precipitate for the laboratory simulation was prepared according to Ohde and Kitano [11]; this procedure makes it possible to obtain carbonates from solutions with a broad range of Ca–Mg concentrations. We used the following ratio of components: 2.14 MgCl₂–0.05 M CaCl₂–0.6 M NaCl–0.18 M NaHCO₃, which results in formation of Ca–Mg carbonates with a high Mg content. The presence of NaCl in the solution facilitates incorporation of Mg into the resultant carbonates [11]. Therefore, sodium bicarbonate solution was added drop by drop to the solution of chlorides at the above-mentioned concentrations under constant mixing; the solution was then left on the shaker for two days. After the elutriation of the precipitate, the mineral fraction was obtained; it contained globules of carbonate of the binary series: CaCO₃–MgCO₃ (1–6 μm) with disordered structure. Its composition, according to [12], is defined as approximately 65% MgCO₃ and 35% CaCO₃. Apart from these globules, globules of monohydrocalcite (over 6 μm) were present in the elutriated fraction; the overall chemical composition of the precipitate was therefore shifted to the Ca : Mg ratio close to 1 : 1. The advantage of this globular precipitate is in the fact that the globules are well-identified and their conversion in the experiment can be easily monitored by electron microscopy (Fig. 1).

In order to build a laminar stratified mat, 0.3 g of the carbonate sediment, which was obtained by chemical means, was applied upon the surface of a cyanobacterial film (the initial amount of cyanobacteria was 1 g of damp biomass) grown in 50-ml glass weighing bottles. As a result of phototaxis, the living motile cyanobacterial filaments crept to the illuminated surface and formed a new layer, while the dead filaments remained on the spot, forming the buried layer. The next mineral layer (0.3 g) was added after four days. In the process of building of the laminar mat, the carbonate precipitate became embedded between the layers of cyanobacteria. In order to avoid the spreading of cyanobacterial filaments along the walls of the vessel, the bottles were wound with black paper. More favorable conditions were therefore created for the formation of destruction layers of the mat.

Three zones are known to exist in the mat: those of photosynthesis and of aerobic and anaerobic destruction. In order to achieve better understanding of the relationship between the mat layers and the mineral transformations occurring therein, experiments were performed in the following versions: (1), under aerobic

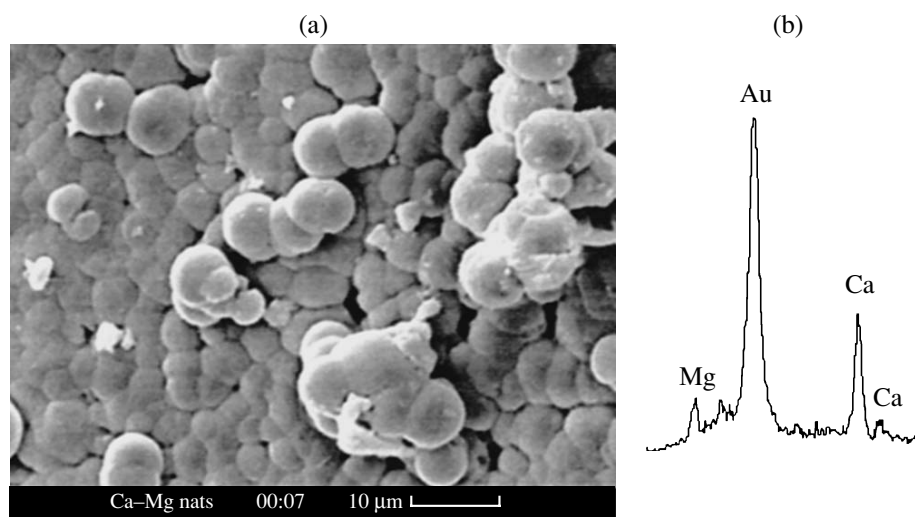


Fig. 1. Original globular carbonate precipitate (a). Scale bar, 10 μ m; elemental composition of the original precipitate (b).

conditions in the light; (2), under aerobic conditions in the dark; (3), under microaerophilic conditions in the dark; and (4), under conditions of natural drying. The mineral sediment without cyanobacteria was used as control.

In experimental variants 1 and 2, the medium was renewed every three–four days, since its quantity in the vessel was minimized in order to prevent the mat from floating due to the active formation of oxygen by cyanobacteria. In the experimental variant 3, the vessel with the mat was filled to capacity with the S medium and covered (the cover was sealed with molten paraffin); it was stored sealed in the dark throughout the experiment. In the experimental variant 4, fresh solution was not added; the mat was kept in an open vessel. The aerobic variants were sampled after two weeks and after nine months and the anaerobic one, after nine months.

The content of dissolved oxygen in the media was determined in a 1-ml cell for biochemical purposes; the cell was equipped with an amperometric sensor with the thermoelectric converter DKTP-02 (Econix-Expert Ltd, Moscow, Russia). The results were processed using the enclosed PC software package.

The experimental material was diagnosed with the CamScan scanning electron microscope equipped with the X-ray microprobe (Link-860) of the Paleontological Institute, Russian Academy of Sciences. Infrared spectroscopy of the samples was performed in the Department of Mineralogy, Moscow State University, on a UR20 IR-spectrophotometer and a FSM-12-01 Fourier spectrophotometer. X-ray powder diffractometry was carried out on a DRON diffractometer in the Institute of Physicochemical and Biological Problems of Soil Science, Russian Academy of Sciences, Puschino, Russia.

RESULTS AND DISCUSSION

1. Changes in the mineral phase of the mat under aerobic conditions in the light

The microscopic and mineralogical analyses of the mat formed after two weeks revealed the following layers: (1), a surface layer with growing cyanobacteria (5 mm); (2), with cyanobacteria in threads, surrounded by minerals (2–3 mm); (3), a mineral layer (2 mm); (4), an underlying colorless mucous layer (2–3 mm); and (5), a lower layer with lysed cyanobacterial filaments and minerals (2 mm).

The results of microscopic and mineralogical analysis of the layers revealed that changes in the initial minerals occurred as early as after two weeks; new mineral phases appeared (Figs. 2a, 2b). In the upper mat layers (1, 2), among unchanged (6 μ m) globules of Ca–Mg of carbonates (Fig. 2a, 1), globules of a larger size appeared (Figs. 2a, 2) on the surface of the slimy film with cyanobacteria. The same globules were revealed in the lower (5) mat layer (Figs. 2a, 6). Minerals similar in habitus and composition have been obtained under laboratory conditions involving bacteria [13]. Small, elongated crystals (carbonates with lower Mg content) (Figs. 2a, 2b, 3, 7) were formed in cyanobacterial (2) and lower layers (5). On the mucus of the intermediate layer (4), large needle-shaped crystals with high Mg content were discovered (Figs. 2a, 5; 2b, 5).

In the mineral layer (3), the cementation of individual globules by calcium carbonate occurs; it forms a united monolith (Figs. 2a, 4) with rough surfaces above and below the layer.

The microscopic data revealed changes in the mineral composition after two weeks of aerobic incubation under light: apart from 6 μ m globules, larger ones appeared, as well as small and large needle-shaped

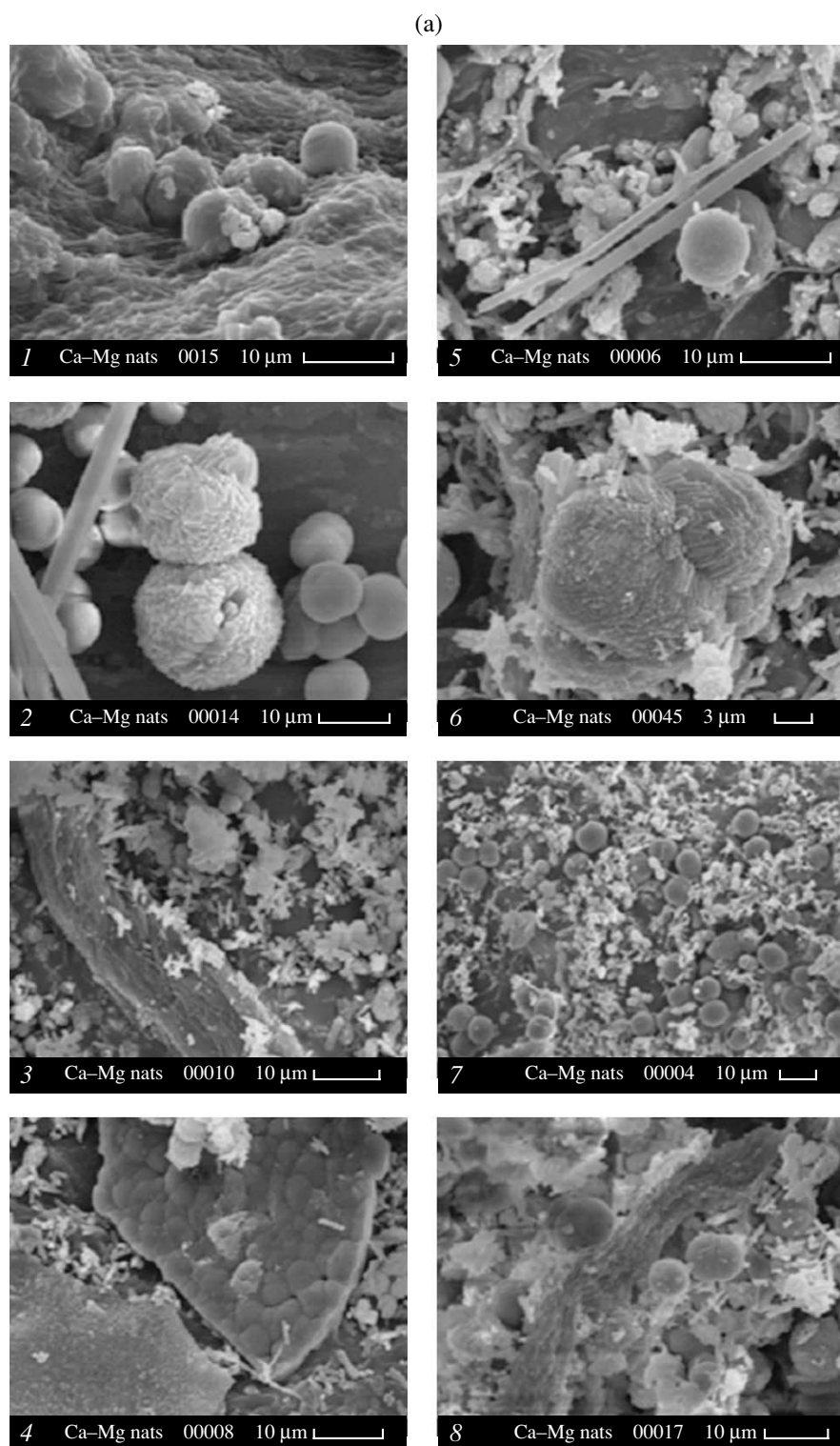


Fig. 2. Transformation of the mineral precipitate (a) in the light (1–7) and in the darkness (8). Experiment duration, two weeks. Scale bar, 10 μm. Upper mat layer with cyanobacteria covered in mucus encrusted with carbonate globules (1); upper mat layer; formation of new mineral phases (2); medium mat layer; cyanobacterial filaments surrounded by small elongated crystals (3); layer of carbonate precipitate, upper surface (4); mineral phase on a mucous film; twin crystals, calcite, long needle-shaped crystals, magnesium carbonate (5); bottom layer; newly formed mineral phase, sequential growth of differently oriented layers of low-magnesium calcite (6); mineral phase on the mucous film, bottom layer; globules of Ca-Mg carbonate with low Mg content (7); mineralization of the decomposing cyanobacterial filaments and cementation of the mat cavities by the carbonate of a calcium composition (8). Elemental composition of the mat layers (b): globules (1, 5, 6, 7–1); needle-shaped crystals (7–2).

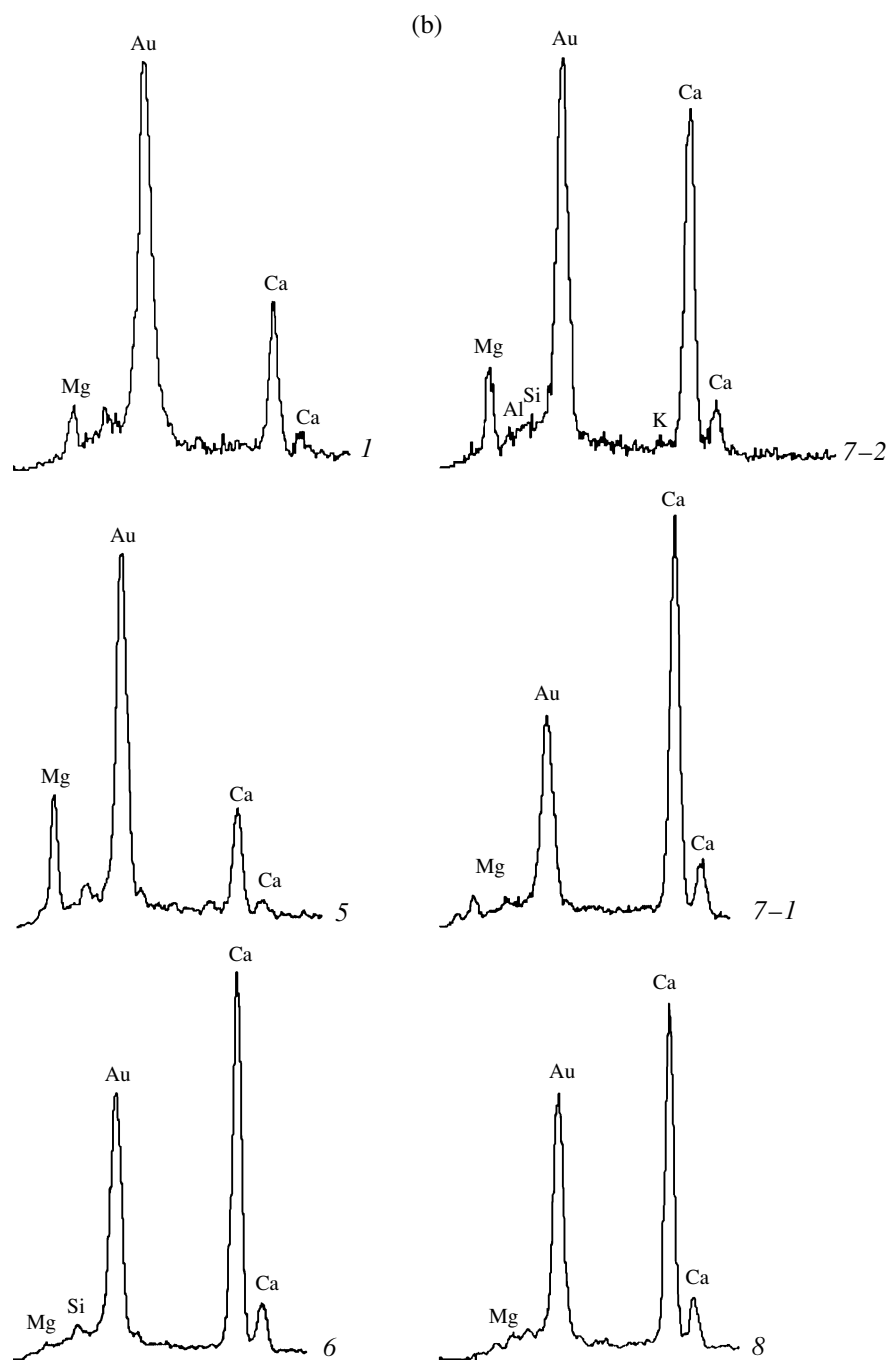


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crystals. X-ray microprobe analysis revealed that they all belonged to Ca–Mg carbonates. X-ray powder diffractometry confirmed the change in the initial carbonate sediment after two weeks of incubation in the light (Fig. 3a). A new Ca–Mg carbonate phase appeared: $d_{104} = 2.940\text{--}2.950$ (high-magnesium calcite with MgCO_3 content of about 30%). Since the zone of anaerobic destruction in the lower layers of the mat has not

yet been formed after two weeks of incubation, cyanobacteria and aerobic destructors were responsible for these transformations of carbonates. In the control version without microorganisms, the change in the precipitate included the formation of a phase of hydrated hydromagnesite (dypingite, $\text{Mg}_4(\text{CO}_3)(\text{OH}) \cdot 5\text{H}_2\text{O}$; interplanar spacing, 10.6, 5.86; and 6.34 Å) and aragonite (Fig. 3b).

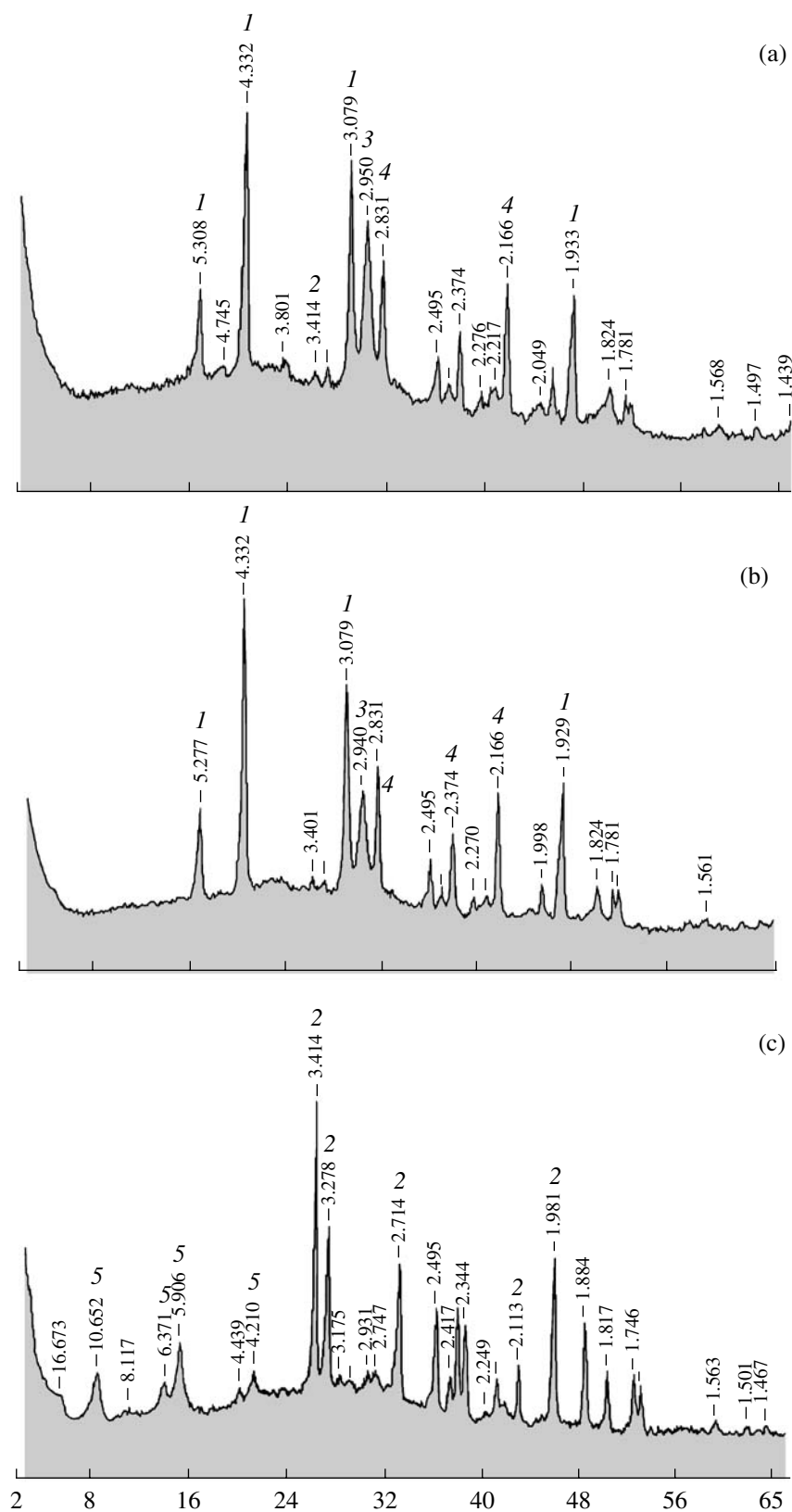


Fig. 3. X-ray powder diffractometry of the carbonates transformed after two weeks of laboratory simulation in the light (a) and in the darkness (b); (c), control experiment without cyanobacteria. Mineral composition: monohydrocalcite (1); aragonite (2); high-magnesium calcite (3); original Ca-Mg carbonate (4); and dypingite (5).

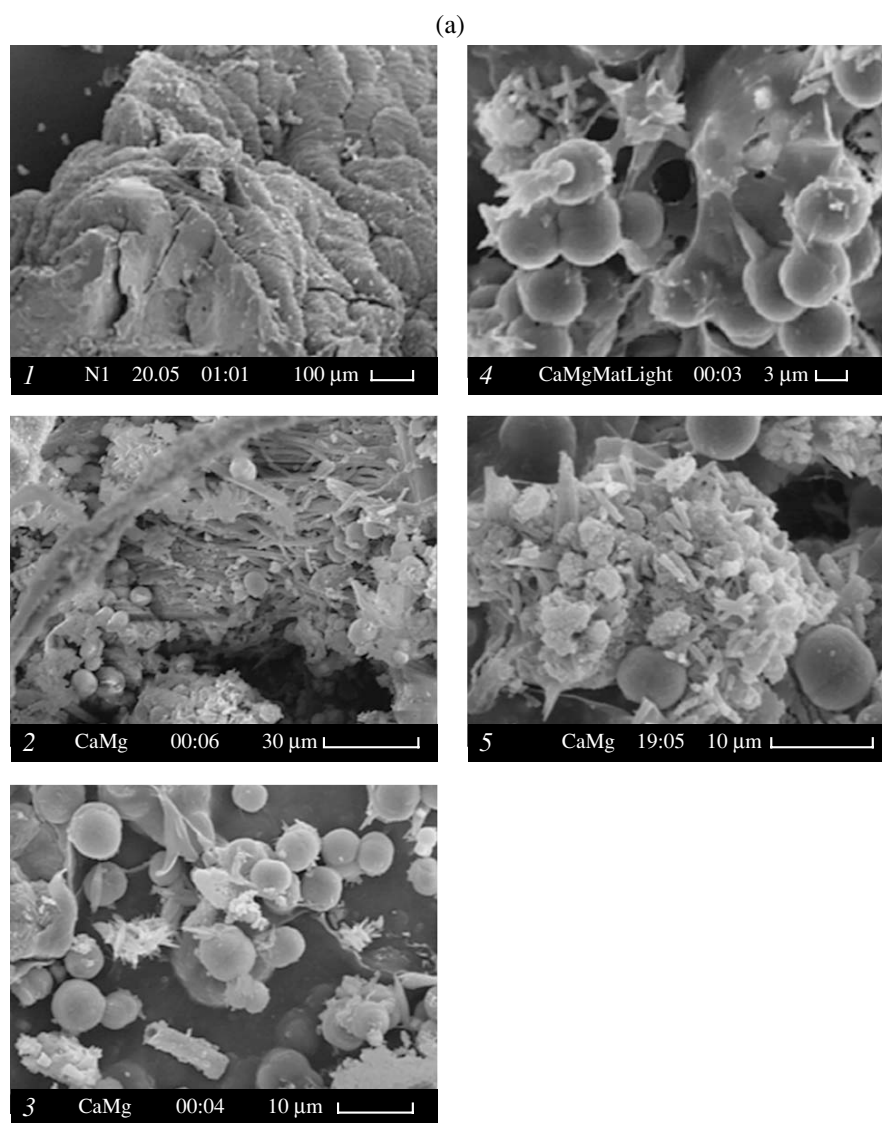


Fig. 4. Transformation of the mineral precipitate (a) in the cyano–bacterial mat in the light. Experiment duration, nine months. Elemental composition of the mat layers (b). Upper layer, threads of cyanobacterial filaments; scale bar, 100 μm (1); filaments in mucus, the mineral layer also covered with mucus; scale bar, 30 μm (2); fragment of a mineralized sheath containing Ca and Mg; scale bar, 10 μm (3); mucous film covering the original globules of Ca–Mg composition; scale bar, 3 μm (4); newly formed mineral phase of the Ca composition cementing the mat; scale bar, 10 μm (5).

After nine months, even more pronounced transformations of the carbonate precipitate occurred. The entire mat became more compact; its layers became denser. The following layers can be distinguished in the section: (1), upper cyanobacterial (1–2 mm); (2), mucous (3–4 mm); (3), mineral (2 mm); (4), whitish, strongly mucous, very thick (up to 8 mm); and (5), grayish thin layer (<0.5 mm). Active cyanobacterial growth and photosynthesis in the light over the course of nine months resulted in increased pH (from 9.05 to 10.45) and dissolved oxygen content (from 6.2 to 22 mg/l). The upper layer consists of interlaced plaits of *Microcoleus* (Fig. 4a, 1). The mineral globules which were revealed in the two-week experiment were not

found. X-ray microprobe analysis revealed accumulation of a number of elements in the mucous layer (4), located below the mineral layer (Fig. 4b, 1). Most of cyanobacteria were not mineralized (Fig. 4a, 2). An individual fragment of a mineralized sheath was found, which had Ca–Mg composition (Figs. 4a, 3, 4b, 3). The entire mineral layer and the individual globules of carbonate precipitate were covered with a mucous polysaccharide film (Fig. 4a, 4).

X-ray analysis revealed significant changes in the mineral phase (Figs. 6a). A new phase of carbonate precipitate of calcium composition was found, which cemented the mat (Figs. 4b, 5). The content of monohydrocalcite decreased compared to the initial precipitate.

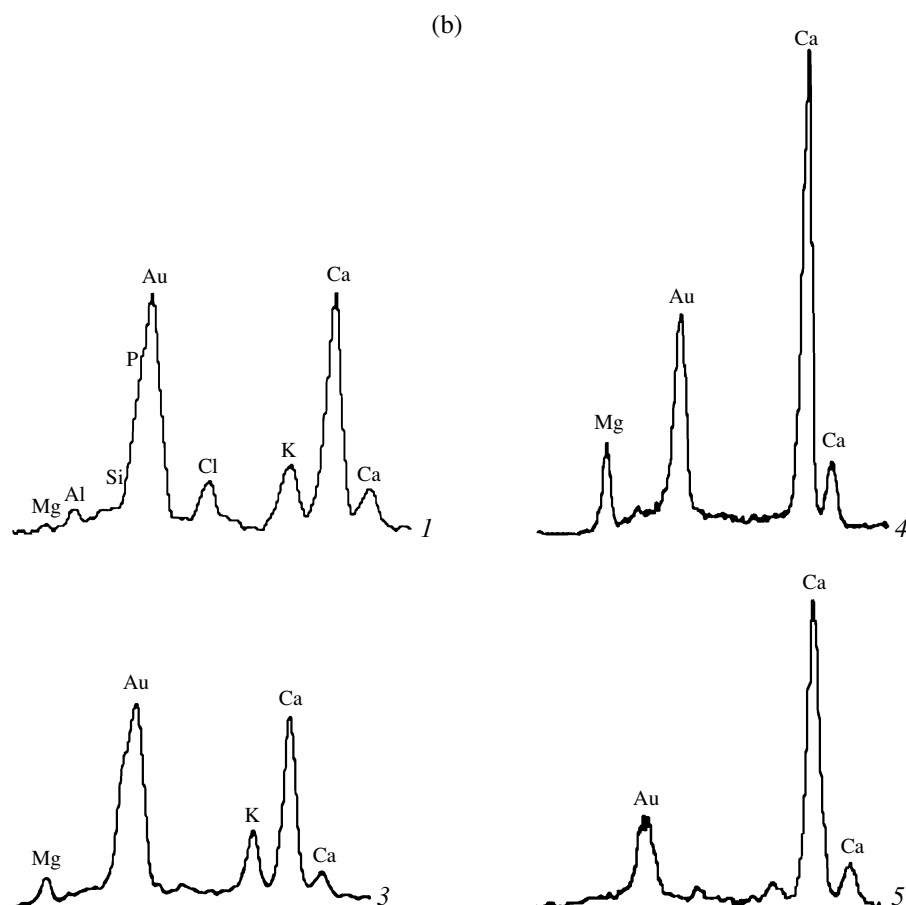


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The monohydrocalcite phase was not present at the interface between the sediment and mucus. High-magnesium calcite ($d_{104} = 2.931$, according to [12] with MgCO_3 content of ca. 40%) was the main mineral. The band at 730 cm^{-1} in the IR spectrum (Fig. 5, 3) indicated the presence of a dolomite phase [14] (over 1%).

Thus, unlike the control, where the transformation of the initial precipitate occurs in the direction of magnesite (Fig. 5, 2; band at 740 cm^{-1} in the IR spectrum), aerobic incubation in the light for nine months in the experiment resulted in the formation of a new phase of calcite (701 cm^{-1}); the mineral phase Ca-Mg carbonates becomes ordered with the formation of dolomite domains.

2. Change in the mineral phase of the mat under aerobic conditions in the darkness

After two weeks of incubation in the dark, mineralization of the decomposed cyanobacterial biomass and noticeable cementation of the mat by carbonate (mostly of calcium composition) occurred (Figs. 2a, 8, 2b, 8). A large quantity of small needle-shaped crystals can probably be of both biogenic and abiogenic origin [16].

Mineralogical analysis (Fig. 3, 2; Fig. 5, 5) has demonstrated insignificant differences between the changes, which occurred after two weeks in the light and in the darkness; thus, the effect of the photosynthetic or bacterial component was therefore not revealed.

After nine months of incubation, three layers were discernible in the mat: an upper layer, consisting of the decomposed cyanobacterial filaments; a medium mineral layer; and the bottom layer, which consists of detritus mass with mineral inclusions. The medium pH was 9.6; the concentration of dissolved O_2 decreased from 6.2 to 2.4 mg/l. For the purposes of mineralogical analysis, the mat could be subdivided only into two parts, mineral and detrital ones. Monohydrocalcite was clearly revealed in the mineral sediment. In Ca-Mg carbonate, two phases were present: the initial disordered Ca-Mg-carbonate ($d_{104} = 2.831$) and high-magnesium calcite ($d_{104} = 2.950$), which corresponds to magnesium calcite with MgCO_3 content of 30% (Fig. 6, 3). This is an indication of the partial recrystallization of the initial carbonates. The abundant mucus, which surrounds the precipitate, possibly seals it up and prevents further

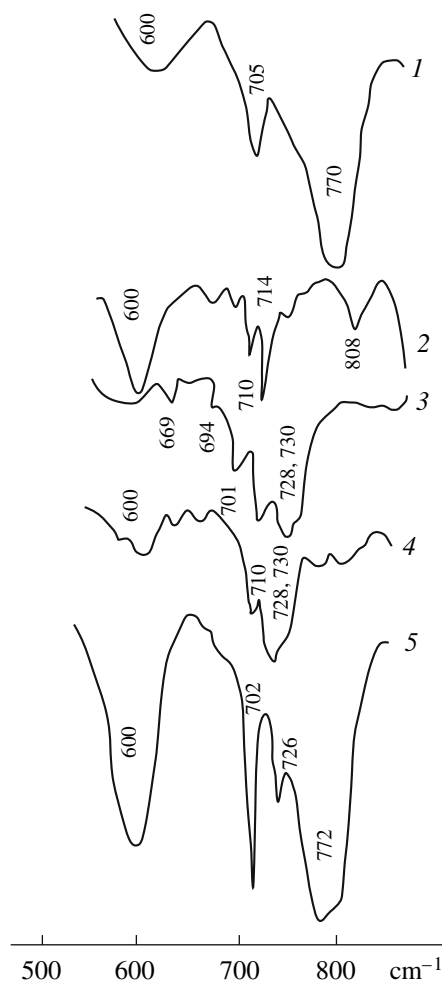


Fig. 5. IR spectroscopy of carbonates: original carbonate (1); (2–5), transformed in the course of nine months of laboratory simulation: control without cyanobacteria (2); light, aerobic conditions (3); dark, microaerophilic conditions (4); dark, aerobic conditions (5).

transformations. However, some secondary mineralization occurs on the mucus (Fig. 7, 1), as is evident with the analysis of the detritus mass, where the globules of carbonate lie singly. The spheres are formed by precipitation of secondary crystals on the surface of the initial carbonate globules (Fig. 7, 2, 3). Thus, the transformation of the carbonate precipitate under aerobic conditions in the darkness (under the conditions of aerobic destruction of the mat) has its special features. In these conditions, the initial precipitate is better preserved than in the previous experiments. Under the conditions of aerobic destruction, CO_2 and organic acids are formed, which shifts the carbonate equilibrium. The small degree of changes in the Ca–Mg carbonates of the initial precipitate is most probably the result of the production of large amounts of mucus, which under these conditions has some specific features; the mucus envelops the precipitate and protects it from transformation. The newly formed phase consists of magnesium calcite

with MgCO_3 content of 30%. Change occurs in the phase of monohydrocalcite. Its presence noticeably increases (Fig. 5, 5, 600 cm^{-1}). Bacterial decomposition of organic matter is known to promote significant accumulation of this mineral [16].

3. Changes in the mineral phase of the mat under microaerophilic conditions in the darkness

After nine months, the mat lost its compactness and became a detrital mass, divided by a loose mineral layer; pH was 9.55; the concentration of dissolved O_2 decreased to 2.2 mg/l. Electron microscopy of the material obtained from various parts of the former mat (Fig. 8a, 1–7) shows that the initial carbonate precipitate was only slightly changed in the upper part of the mat (Figs. 8a, 1, 2, 4; 8b, 1). Significant changes occurred in the lower layers (Fig. 8a, 6, 7). Crystals of Ca–Mg composition were formed on the surface of the globules of the primary precipitate (Figs. 8a, 7; 8b, 7).

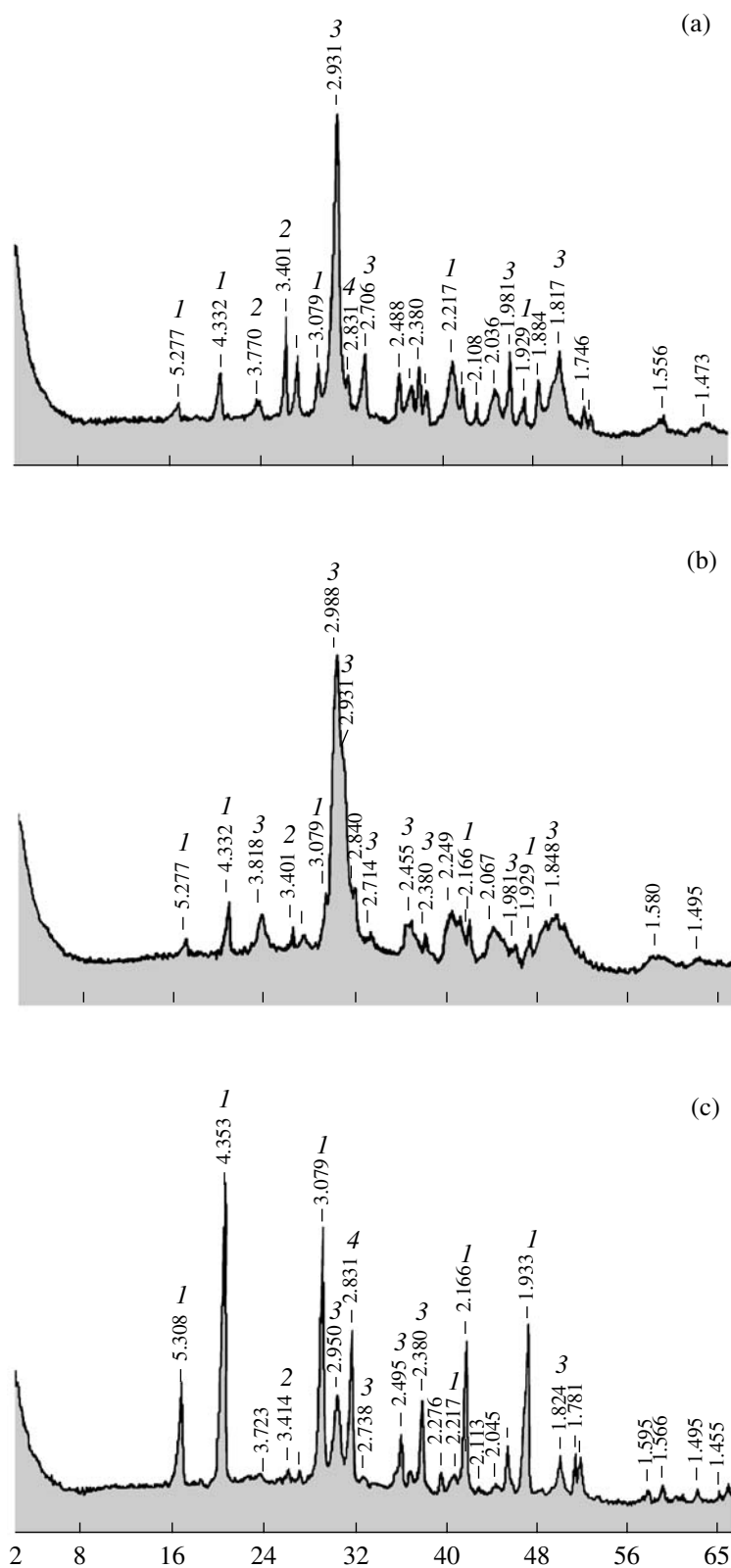


Fig. 6. X-ray powder diffractometry of the carbonates transformed after nine months of laboratory simulation: aerobic conditions in the light (a); microaerophilic conditions in the dark (b); aerobic conditions in the dark (c). Mineral composition: monohydrocalcite (I); aragonite (2); high-magnesium calcite (3); original Ca-Mg carbonate (4).

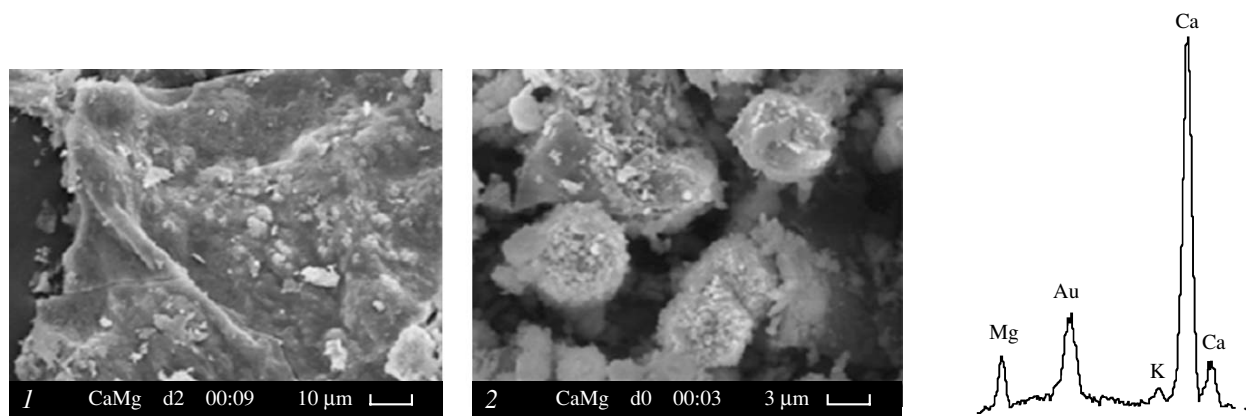


Fig. 7. Transformation of the mineral precipitate in a cyano-bacterial mat in the darkness under aerobic conditions. Experiment duration, nine months. Detritus mass in slime; scale bar, 10 µm (1); spheres formed by precipitation of secondary crystals on the original carbonate globules; scale bar, 3 µm (2); elemental composition of the mat (3).

Among the decomposed filaments of cyanobacteria (Figs. 8a, 3, 8b, 3), mineralized sheaths of Ca composition appeared occasionally (Fig. 8b, 5). Minerals of new form and composition were revealed. Growth of calcium carbonate crystals around the globules of the primary precipitate occurred (Figs. 8a, 4, 7; 8b, 4), as well as formation of giant globules (more than 30 µm) (Fig. 8a, 6); the latter ones were the globules of the initial precipitate cemented together with calcium carbonate.

The general mineralogical analysis of the carbonate composition for the mat as a whole revealed recrystallization of the initial sediment under these conditions with the formation of several mineral phases. A broad peak on the diffractogram (Fig. 6b) with $d_{104} = 2.840\text{--}2.988$ indicated the formation of several phases of magnesium calcite differing in MgCO_3 content: 40 and 18%, monohydrocalcite was also present. IR spectroscopy showed the presence of calcite (710 cm^{-1}) and dolomite (730 cm^{-1}) (Fig. 5, 4).

Our experiences have demonstrated that the transformation of initial carbonates was more intense under microaerophilic conditions in the darkness (Fig. 6b) than under aerobic conditions. In the former case, the initial carbonate was completely transformed, while it was preserved under aerobic conditions (Fig. 6a, c). The transformation rate under microaerophilic conditions was higher than under aerobic conditions. Under microaerophilic conditions, the mat lost its compactness; decomposed cyanobacteria were mixed with mineral particles. This close contact between the mineral and organic components led to the most extensive transformation of the carbonate precipitate.

4. Changes in the mineral phase in the course of mat drying

In the experiment, which simulated conditions close to the natural ones (those of natural drying of the mat),

at $20\text{--}25^\circ\text{C}$ the inner carbonate layers exhibited significant changes, different from those revealed by previous experiments. First of all, decrystallization of the globules of the initial precipitate occurred, with the formation of lamellar crystals (Fig. 9). X-ray microprobe analysis revealed the presence of only crystals of magnesium composition on the outer surface of the dried film of the mat (Fig. 9, 1a), i.e., Mg was removed from the Ca–Mg carbonate precipitate. Thorough mineralogical study of these crystals by infrared spectroscopy and X-ray powder diffractometry was hindered by their small quantity. X-ray powder diffractometry revealed two mineral phases in the mineral interlayers inside the nesquehonite ($\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$, interplanar spacing, 6.40; 3.84; and 2.62 \AA) and monohydrocalcite ($\text{CaCO}_3 \cdot \text{H}_2\text{O}$, interplanar spacing, 4.31; 3.06; and 1.93 \AA).

Thus, our experiences have demonstrated that the transformation of carbonate precipitate occurs in the course of both productive (light) and destructive (darkness) processes in cyano-bacterial mats under alkaline conditions, i.e., under conditions close to those of soda lakes (Fig. 10); the composition of the precipitate depends on the surrounding microenvironment. These transformations are influenced by the balance of organic and mineral components of microenvironments, oxygen content, and pH. In all cases the crystal lattice of the initial carbonate is restructured. The recrystallization of the precipitate in the mat under varied experimental conditions is characterized by the rate of precipitate changes. The dolomite domains can be formed in the light (under photosynthetic) and in the darkness under microaerophilic conditions. However, since three processes occur in an illuminated mat (photosynthesis, aerobic, and anaerobic decomposition of cyanobacteria), it is likely that the destructive (anaerobic) component of the mat is responsible for dolomite formation, rather than the productive component; the effect of cyanobacteria is only indirect, i.e., by chang-

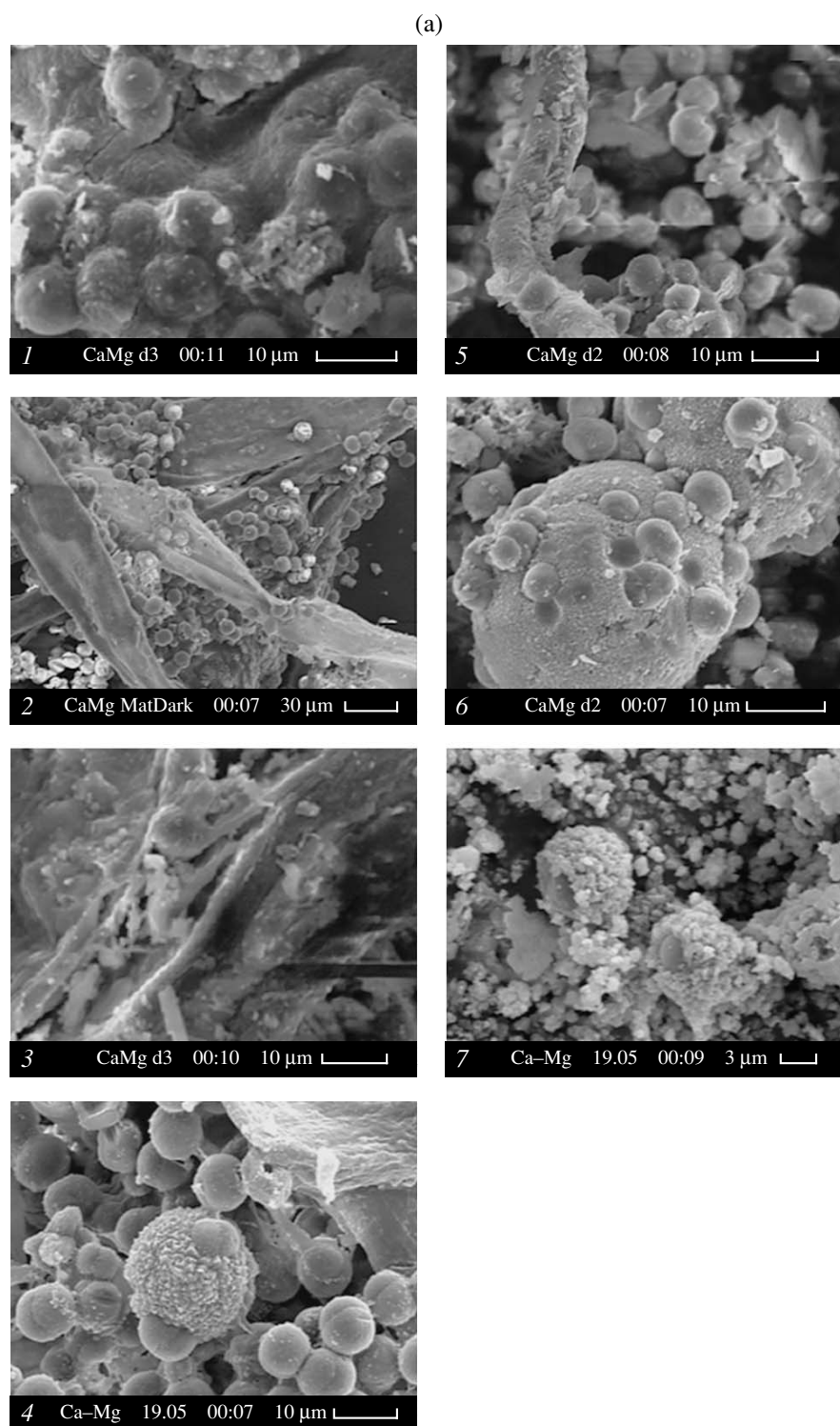


Fig. 8. Transformation of the mineral precipitate (a) in a cyano-bacterial mat in the darkness under microaerophilic conditions. Experiment duration, nine months. Scale bar, 10 μm (1, 3–6); 30 μm (2); 3 μm (7); the mucus covering the globules of the original precipitate is mineralized by Ca–Mg carbonate (1); upper mat layer: mucus formation in the course of decomposition of cyanobacterial filaments; globules slightly changed (2); decomposed cyanobacterial filaments in the mat (3); growth of spherical calcite crystals around the globules of the original precipitate; contact between the mineral and cyanobacterial layers (4); mineralized sheaths of Ca composition (5); globules of the original precipitate embedded in a newly formed globule (ca. 30 μm) of Ca composition (6); growth of the secondary fine crystalline precipitate on the original globules (7). Elemental composition (b).

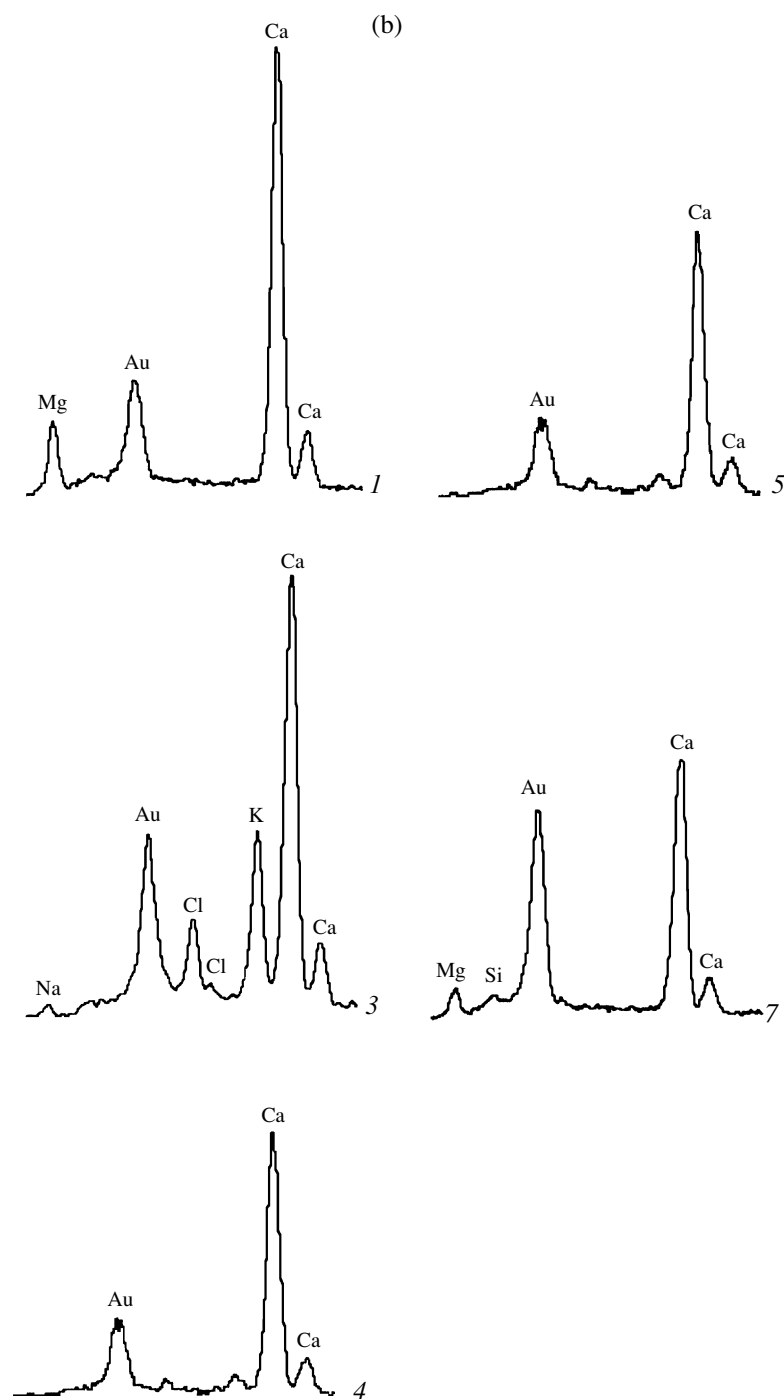


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ing the physical and chemical conditions in the mat. This conclusion is in accordance with the previously published works about the role of sulfate-reducing bacteria in the formation of dolomites [6, 7, 17]. Our studies, however, make it possible to assert that the totality of the reactions, which occur in the entire mat under the conditions of active cyanobacterial photosynthesis, contributing to the process of dolomite formation.

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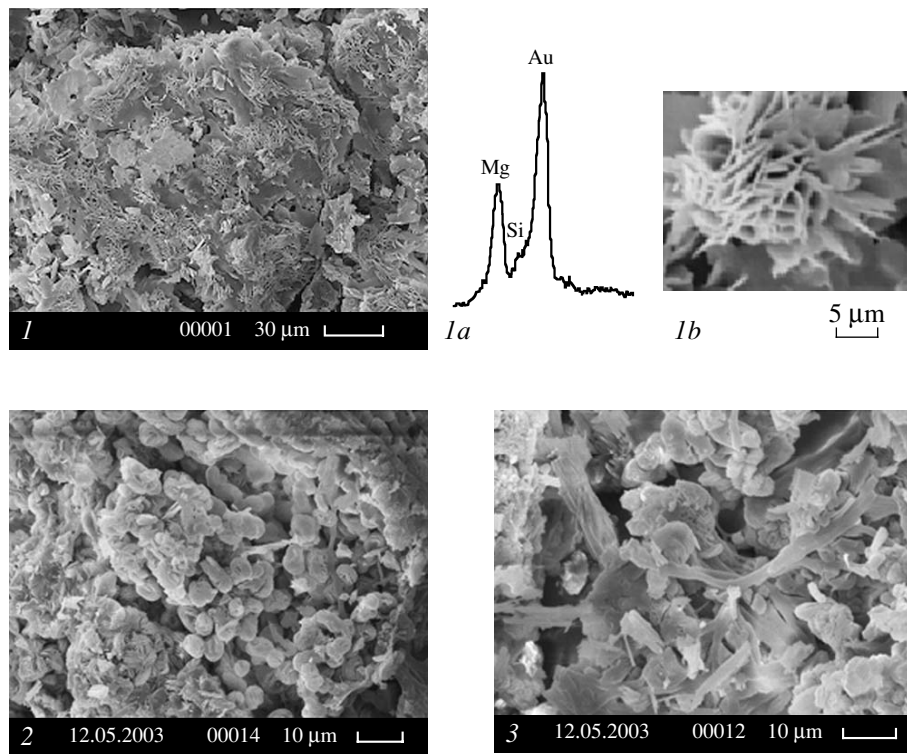


Fig. 9. Transformation of the mineral precipitate in a cyano-bacterial mat under the conditions of natural drying: external surface with magnesium minerals (*I*); elemental composition of the crystals (*Ia*); scale bar, 30 μm ; magnified crystal fragment; scale bar, 5 μm ; (*Ib*); lamellar crystals formed as the result of decrystallization of original carbonate globules; scale bar, 10 μm (*2*); remnants of dried scale bar, 10 μm (*3*).

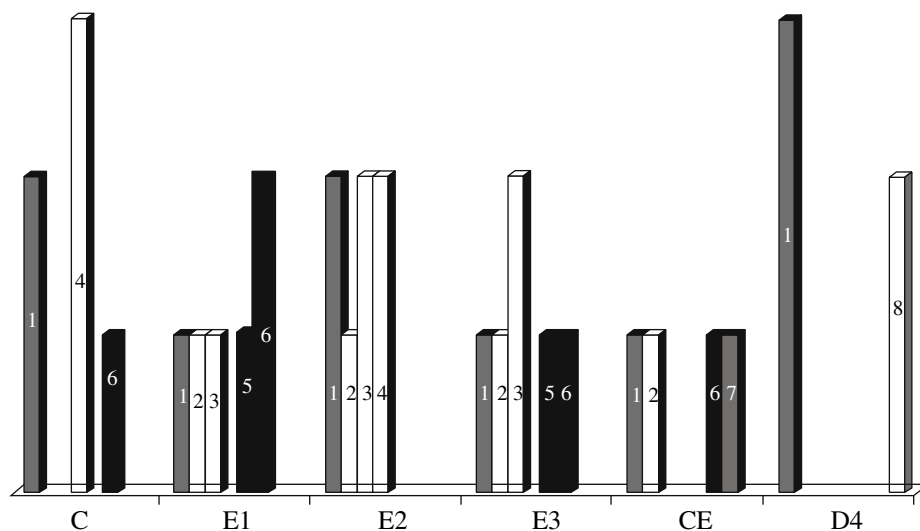


Fig. 10. Bar chart (in arbitrary units) of the presence of minerals in the mat under various conditions: original control (C); control after nine months, without cyanobacteria (CE); illuminated mat, aerobic conditions (E1); mat in the darkness, aerobic conditions (E2); mat in the darkness, microaerophilic conditions (E3); dried mat (D4). Monohydrocalcite, $\text{CaCO}_3 \cdot \text{H}_2\text{O}$; (1); aragonite, CaCO_3 ; (2); high-magnesium calcite, $(\text{Ca}, \text{Mg})\text{CO}_3$ (Mg, 5 to 40%) (3); original Ca-Mg carbonate (4); dolomite, $(\text{Ca}, \text{Mg})\text{CO}_3$ (5); hydromagnesite, $\text{Mg}_2(\text{OH})_2\text{CO}_3 \cdot 3\text{H}_2\text{O}$ (6); magnesite, MgCO_3 (7); nesquegonite, $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ (8).

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