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The Role of Cyanobacteria in Crystallization of Magnesium Calcites

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Abstract—Laboratory experiments showed the effect of the cyanobacterium *Microcoleus chthonoplastes* on the formation of magnesium calcites, using model solutions (2.14M $MgCl_2$–0.05M $CaCl_2$–0.6M NaCl–0.18M $NaHCO_3$). The conditions of existence of cyanobacteria in such solutions in light or darkness significantly alter the structure of the sediment and the shape and size of the carbonate crystals. Cyanobacteria slow down crystallization due to the formation of exometabolites with a chelating effect, which leads to the precipitation of high-magnesium calcites. In the photosynthetic environment the presence of huntite ($CaMg_3(CO_3)_4$), possible forerunner of dolomite, is prominent.

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Key words: Cyanobacteria, high magnesium calcite, precipitation, huntite.

INTRODUCTION

Recent studies have shown an enormous role to have been played by bacteria, including cyanobacteria, in the processes of sedimentogenesis of the past (*Bacterial Paleontology*, 2002; Rozanov, 2003). The earliest sedimentary rocks were found to contain fossilized remains of microorganisms, which suggests that their communities were very important in the sedimentary processes on the Earth's surface, beginning from the Archean. Our previous study showed a definitive role of microorganisms in the accumulation of phosphorites (Rozanov and Zhegallo, 1989; Gerasimenko *et al.*, 1996, 1999; Zhegallo *et al.*, 2000). Karavaiko *et al.* (1972) and Zavarzina (2004) published information on the effect of bacteria on the formation and transformation of iron minerals. Bacteriomorphic structures were found in bauxites of various age (*Bacterial Paleontology*, 2002; Shkol'nik *et al.*, 2000). Carbonate rocks (limestones and dolomites) are also promising objects in studying the role of the biogenic factor in the sedimentation. Although the remains of fossilized bacteria in these rocks are uncommon, there is evidence suggesting the active participation of bacteria in the accumulation of these rocks in the epicontinental seas of the past (Kazmierczak *et al.*, 1996; Rozanov, 2003). Among the earliest carbonates dated ca. 3.5 Ga, there are carbonate-siliceous stromatolites, which were products of the metabolism of benthic cyanobacterial communities (Walsh, 1992; Schopf, 1993). Thick series of dolomitic stromatolites are described from many horizons in the Proterozoic (Krylov, 1975; Semikhatov and Raaben, 1996). Hence, as early as the earliest stages of the Earth's history, cyanobacteria actively participated in carbonate sedimentation. Based on experiments with various conditions of cultivation of cyanobacteria, we attempted to clarify their role in the precipitation of dolomitic rocks.

Dolomitic rocks, depending on the quantitative proportions of Ca and Mg, include dolomite, protodolomite, high- and low-magnesium calcites. The formula of dolomite is $CaMg(CO_3)_2$. It has a calcite structure, in which the atoms of Ca in every second layer of cations are replaced by atoms of Mg. Protodolomite differs from true dolomite in the increased content of $CaCO_3$ (up to 10 mol %) and in its structural imperfection (*Carbonate Rocks*, 1970). High- and low-magnesium calcites are intermediates between calcite and dolomite. These are normally hard solutions of $MgCO_3$ and $CaCO_3$, representing a continuous row of compounds containing from 1–2 to 50 mol % of $MgCO_3$. Calcite containing less than 4 mol % $MgCO_3$ is low in magnesium, whereas calcite with $MgCO_3$ ranging from 4 to 50 mol % is high in magnesium. Both high- and low-magnesium calcites are widespread in marine sediments, where they form skeletal remains and cement. The most widespread organisms that build their skeleton from magnesium calcite include calcareous red algae, benthic foraminifers, bryozoans, echinoderms, and some crustaceans. The $MgCO_3$ content of their skeletons may reach 20 mol %.

These organisms are main contributors of high-magnesium calcite to shallow-water marine sediments (Chave, 1981). High-magnesium calcites, crystallizing at low temperatures, are metastable. Eventually they are transformed into a stable association of low-magnesium calcite and dolomite (*Carbonates*, 1987). Calcar-

Table 1. Changes in pH in the experiment

	Duration of the experiment		
	3 hours	2 weeks	10 months
Solution with cyanobacteria in the light	8.10	8.30	8.35
Solution with cyanobacteria in the darkness	7.75	8.35	8.40
Control solution	7.50	8.25	8.30

eous skeletons of pelagic coccoliths and foraminifers, which contain small amounts of Mg (1–2 mol % $MgCO_3$), are built from low-magnesium calcite.

Favorable conditions for precipitation of high-magnesium calcites and protodolomite exist in environments with high Mg/Ca ratios, increased salinity, and high carbonate alkalinity. The Mg/Ca ratio in the sediment depends on the Mg^{2+}/Ca^{2+} ratio in the solution. In environments with modified seawater (mud, lagoons, sebkhas, and micropores in organic structures), the absolute value of this ratio may determine the composition of the sediment (Nechiporenko and Bondarenko, 1983).

Factors controlling the processes of formation of dolomitic rocks have been repeatedly studied in experiments (Medlin, 1959; Ohde and Kitano, 1978; Sozinov *et al.*, 1982; Nechiporenko and Bondarenko, 1983; Sibley *et al.*, 1994; Fernandes-Diaz, 1996; Pokrovskii, 1996). Among these, the most important is the presence of organic matter as a source of CO_2 and high pH values. Some papers show that organic compounds may catalyze the accumulation of dolomites (Sozinov *et al.*, 1982; Nechiporenko and Bondarenko, 1983). The role of microorganisms, cyanobacteria and their metabolites in particular, in the process of the accumulation of dolomitic rocks is poorly studied. A series of experiments in the Institute of Microbiology, Russian Academy of Sciences, was conducted to extend the knowledge of this role. Precipitates were studied at the Paleontological Institute, Russian Academy of Sciences, using SEM (Camscan) and microanalyzer; at the Geology Department, Moscow State University, using a diffractometer and IK spectrophotometer; and at the Institute of Crystallography, Russian Academy of Sciences, on a diffractometer.

MATERIALS AND METHODS

Chloride-magnesium-calcium solution with added sodium bicarbonate was used in the experiment following the method of Ohde and Kitano (1978). The solution had the following proportions of components: 2.14M $MgCl_2$–0.05M $CaCl_2$–0.6M NaCl. For precipitation an $NaHCO_3$ solution was used with an initial given concentration of 0.18 M.

The alkalophilic strain of *Microcoleus chthonoplastes* from the working collection of cyanobacteria in the laboratory of relict microbial communities at the Institute of Microbiology, Russian Academy of Sciences, was used as the test object. The cyanobacteria with accompanying microflora were cultivated in the light, while they actively photosynthesized, and in the dark in the conditions favorable only for the bacterial growth. In the 100 ml phials containing 50 ml of the calcium chloride and sodium chloride solutions 5 g of culture was placed, after which it was supplemented by the sodium bicarbonate solution, while continuously stirring the content. Carbonate solutions obtained in this way were placed in the shaker for over a long period (up to ten months). At the same time control bottles with a solution prepared using the above method, but without cyanobacteria, were placed on the shaker. The pH of solutions was measured throughout the experiment. The data obtained are shown in Table 1. Measurements showed that in all solutions pH was 8.3–8.4. This may suggest that the ions present in the solution form a buffer solution holding pH in the range of near values. Precipitates from these solutions were washed by the distilled waster, dried, and studied by various methods.

Features of each of the techniques used are briefly summarized below.

An SEM microprobe allows a determination of the elemental composition of the mineral phases present in the sediment. An X-ray allows the determination of the mineral phases present in the precipitate. An X-ray microprobe (Link-860) was used. The results are shown in Pls. 1 and 2.

The crystallographic analysis shows whether mineral phases are present in a sample studied and allows their identification. The analyses were performed by the powder diffractometer (Rigaku D max 3C) and by (DRON-3) (Tables 2–4). The interlayer distances for the most intense lines of the magnesium carbonates are shown in the footnote.[1]

The infrared spectroscopy (IK) allows the diagnostics of a mineral and determination of the degree of its crystallization. The IK absorption spectra of the carbonate precipitates studied were received using infrared spectrophotometers (UR-20) and (Specord). IK spectra depend on the structural features of the matter. The diagnostics of the carbonate precipitates obtained was conducted by the comparison of the IK absorption spectrum of the substance studied with the IK-spectra

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[1] The interlayer distances for magnesium carbonates are as follows: dolomite $CaMg(CO_3)_2$ 2.89, 2.19, and 1.79; huntite $CaMg_3(CO_3)_4$ 2.82, 1.99, and 1.97; hydromagnesite $Mg_2(OH)_2CO_3 \cdot 3H_2O$ 5.79, 2.90, and 9.2; calcite 3.04, 2.29, and 2.10; aragonite $CaCO_3$ 3.40, 3.27, and 1.98; monohydrocalcite $CaCO_3 \cdot H_2O$ 4.31, 3.06, and 1.93; magnesite $MgCO_3$ 2.74, 2.10, and 1.7 (ICSD Collection Code); protodolomite $(CO_3)_2$ 2.88, 2.19, and 1.78 (in contrast to dolomite showing a diffusion character of basal reflexes and no superreflexes: 4.02, 2.54, and 2.06); magnesium calcite: 3.01 for 5% $MgCO_3$, 2.97 for 20% $MgCO_3$, 2.93 for 37% $MgCO_3$, and 2.89 for 47% $MgCO_3$ (Nechiporenko and Bondarenko, 1983).

Table 2. Data from the X-ray phase analysis of the carbonate sediment formed in the control solution after two weeks of experiment

No.	2-theta	*I*	*d* (A)	I/I_0
1	19.350	27.7	5.326	22
2	23.600	49.8	4.377	40
3	23.746	125.3	4.351	100
4	33.806	115.9	3.079	92
5	33.827	87.7	2.834	70
6	42.000	16.4	2.498	13
7	44.203	39.0	2.379	31
8	46.276	8.9	2.278	7
9	48.805	76.7	2.167	61
10	53.226	38.8	1.998	31
11	54.902	61.1	1.942	49
12	55.200	104.6	1.932	84
13	58.788	12.6	1.824	10
14	60.350	22.0	1.781	18
15	61.049	11.9	1.762	10

Table 3. Data from the X-ray phase analysis of the carbonate sediment formed in the presence of cyanobacteria in the light after ten months

No.	2-theta	*I*	*d* (A)	I/I_0
1	23.380	35	3.8018	17
2	24.580	35	3.6188	17
3	26.220	69	3.3961	33
4	27.160	46	3.2806	22
5	30.160	44	2.9608	21
6	30.340	55	2.9436	27
7	30.720	54	2.9081	26
8	31.240	55	2.8608	27
9	31.420	50	2.8449	24
10	31.700	207	2.8204	99
11	33.160	41	2.6995	20
12	36.080	38	2.4874	18
13	37.860	35	2.3744	17
14	41.520	32	2.1732	16
15	45.460	95	1.9936	46
16	45.880	40	1.9763	19

Table 4. Data from the X-ray phase analysis of the carbonate sediment formed in the presence of cyanobacteria in the dark after ten months

No.	2-theta	*I*	*d* (A)	I/I_0
1	26.040	41	3.4191	44
2	26.180	93	3.4012	99
3	27.200	49	3.2759	52
4	30.440	41	2.9342	44
5	30.740	53	2.9062	56
6	30.900	43	2.8615	46
7	31.700	70	2.8204	75
8	33.120	53	2.7026	57
9	42.860	31	2.1083	33
10	45.460	33	1.9936	35
11	45.820	43	1.9788	46

of etalons published in relevant atlases and in the literature (Giller, 1966). The following spectral regions were used: in the range 706–710 cm^{-1} (calcite), 727–730 cm^{-1} (dolomite $CaMg(CO_3)_2$), and an absorption band covering the range with the maximum of 1080 cm^{-1} in the presence of all carbonate absorption bands (aragonite $CaCO_3$–rhomboid), band of 735 cm^{-1} (magnesite $MgCO_3$), 600 cm^{-1} and 1430–1500 cm^{-1} (two maxima) for hydromagnesite $Mg_2(OH)_2CO_3 \cdot 3H_2O$, double band 867 and 888 cm^{-1}, band 1108 cm^{-1} and a band with two maxima of 1454 and 1470 cm^{-1} (huntite $CaMg_3(CO_3)_4$) (*Modern Methods …*, 1969).

Precipitates obtained were examined after two weeks and ten months after the beginning of the experiment.

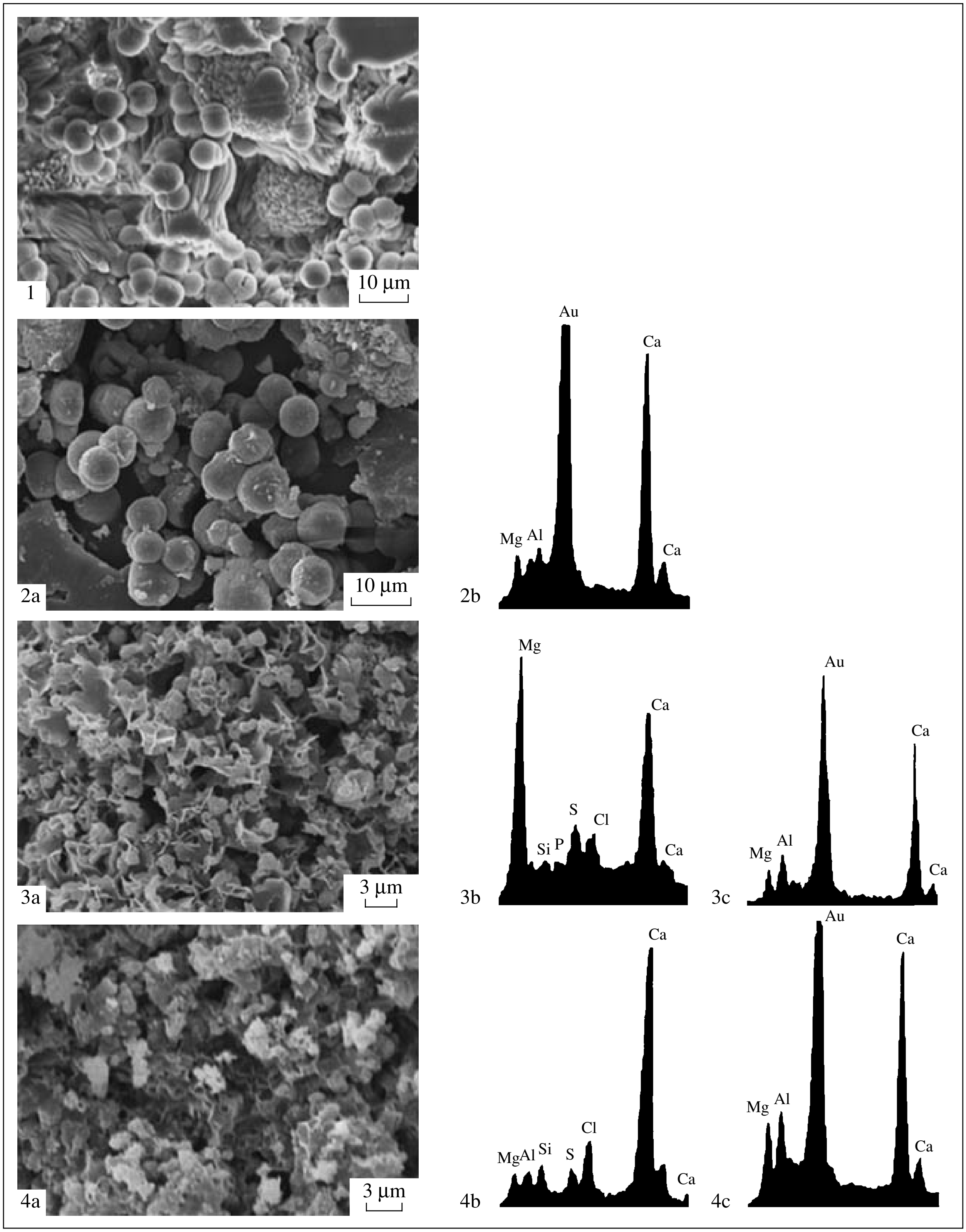
RESULTS AND DISCUSSION

After two weeks the control solution (lacking cyanobacteria) contained a crystallite precipitate composed of monohydrocalcite, magnesium calcite, aragonite, and magnesium calcite (Table 2). The magnesium calcite globules varied in size from 1 to 6 µm (Pl. 1, figs. 1, 2). Supposedly, these globules are represented by magnesium calcite with varying ratios of Ca/Mg, suggesting from d = 2.83 and 3.07A, and from the presence of weakly resolved strips in the region 703–715 cm^{-1} in the IK spectrum (Pl. 2, fig. 1a). Magnesium carbonates that precipitated at the beginning of the control experiment at constant temperature and pressure in closed vessels remained stable for over a long time.

The study of sediment formed in the presence of cyanobacteria over the same length of time (Pl. 1, figs. 3, 4, Fig. 1b) showed that they are clearly different from the control samples (see Pl. 1, figs. 1, 2 and Fig. 1a) both in crystal shape and in mineralogy. Precipitates accumulated in the light and in darkness were similar in composition but different in structure (Pl. 1, figs. 3, 4). The precipitate formed in the light was composed of crystal aggregates of larger size than that formed in darkness and contained areas with globules. Accumulations of fine-grained precipitates were formed in the darkness. A cryptocrystalline carbonate mass with isolated carbonized scales, apparently resulting from the metabolism of cyanobacteria, was present.

Lamellar crystals were formed on the surface of the scales. Because of very small size of the crystals, it was difficult to diagnose their composition using the microprobe. It was, however, visible that different areas of the precipitate are different in the composition of the elements present (Pl. 1, figs. 3b, 3c, 4b, 4c). Based on the

Plate 1



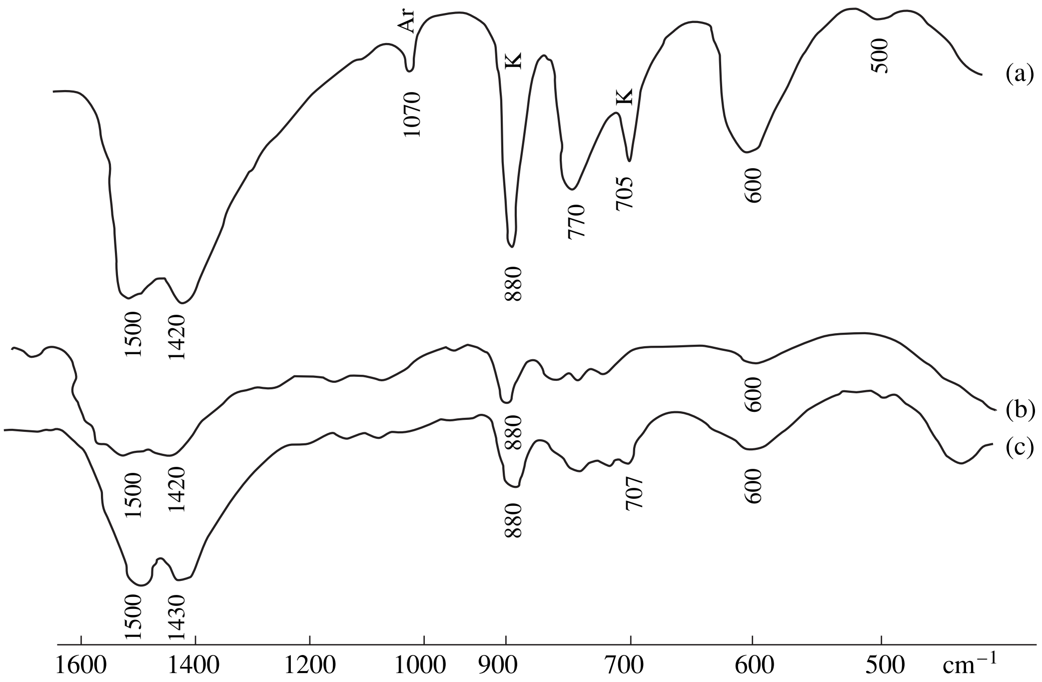


Fig. 1. Infrared spectra of the carbonate sediments after two weeks of experiment: (a) from the control solution; (b) from the solution with cyanobacteria in the light; (c) from the solution with cyanobacteria in the dark.

results of the IK-spectroscopy (Figs. 1b, 1c), the presence of magnesium calcite and the low content of the crystalline calcite were observed.

In the next ten months of the interactions between the solution, precipitate, and culture, the carbonate component of the precipitate obtained underwent further crystallization (Pl. 2, figs. 2, 3) showing the presence of magnesium calcite with a varying content of $MgCO_3$, aragonite, huntite $CaMg_3(CO_3)_4$ and perhaps some protodolomite (Tables 3, 4). As in the 2-week-long experiment, precipitates formed in the course of the 10-month-long experiment in the light and in darkness were similar in the composition of carbonates, but with different shape and size of crystals.

The experiment held in the light, after ten months a carbonate precipitate with varying size and composition was accumulated. The precipitate contains crystals different in mineral composition and shape (globular, lamellar, and scaly) (Pl. 2, figs. 1, 2). Their size varied from a few micrometers to a few tens of micrometers. The X-ray analysis (Table 3) showed the presence of aragonite, magnesite, and huntite. Especially interesting are crystals in the shape of rosettes (Pl. 2, fig. 1a), microprobe analysis of which showed the predominance of Mg over Ca, whereas the X-ray phase analysis and infrared spectroscopy supported the presence of huntite $CaMg_3(CO_3)_4$ (Pl. 3, fig. 2a). The structure of this mineral is similar to that of dolomite and is interesting as a possible predecessor in a sedimentary environment. The unit cell of huntite is equivalent to the cleaved calcite rhombohedron. Each atom of Ca corresponds to three atoms of Mg. However, atoms of Mg are displaced in relation to the ideal positions corresponding to the vertices of a calcite-like cell (Lippmann, 1973).

Accumulations of microorganisms found in this precipitate were mineralized by magnesium calcite (Pl. 2, fig. 3).

In contrast to the experiment held in the light, precipitate accumulated in the darkness has particles of uniform size (1–2 μm) (Pl. 2, fig. 2). Isolated rounded grains were present inside and on the surface of the

Explanation of Plate 1

SEM photographs and elemental composition of carbonate sediments obtained.

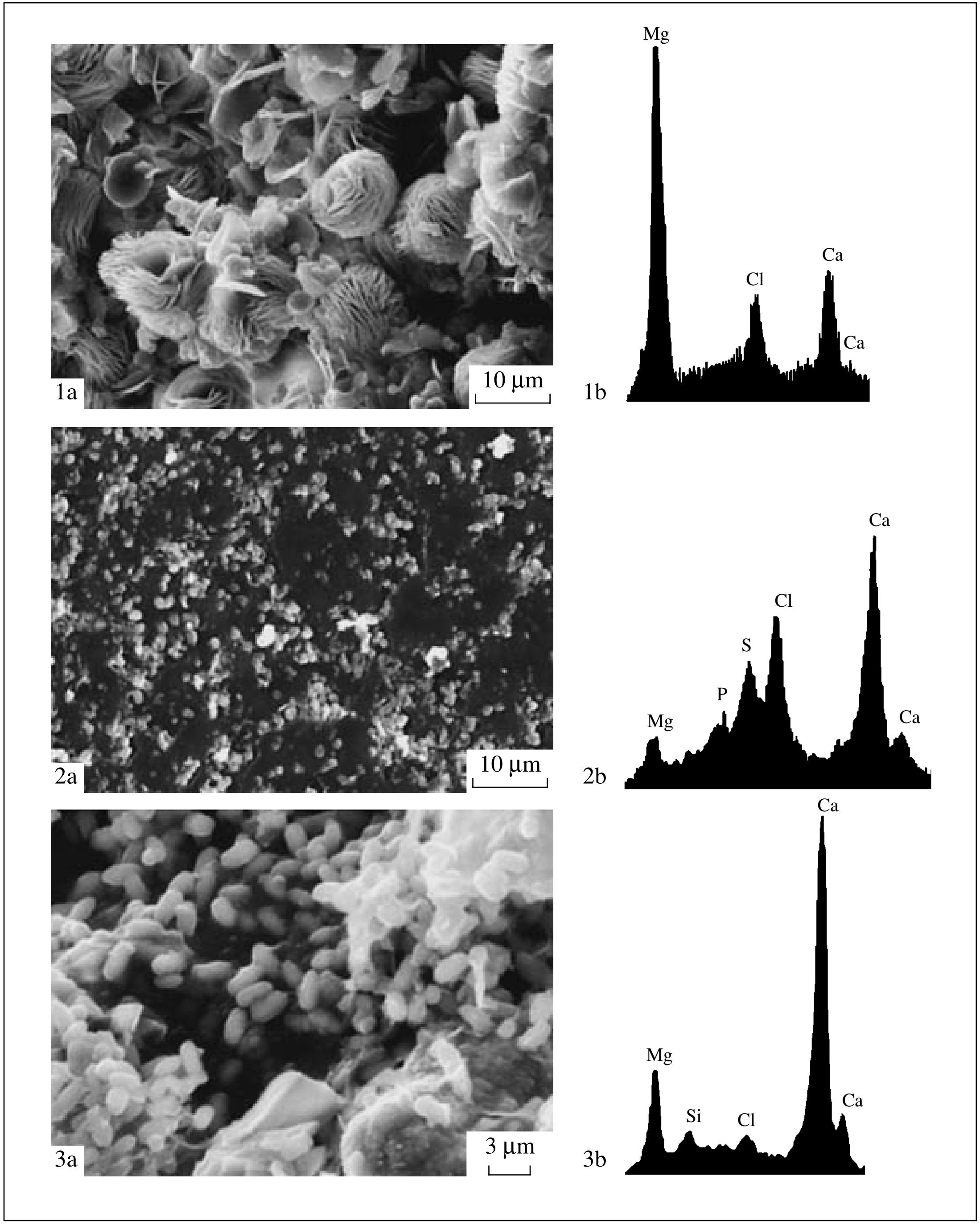
Fig. 1. Carbonate sediment from the control solution (without cyanobacteria) after two weeks of experiment.

Fig. 2. Globules of magnesium calcite: (a) photograph and (b) elemental composition of globules.

Fig. 3. Carbonate sediment with cyanobacteria in the light after two weeks of experiment: (a) photograph and (b) and (c) elemental composition of the sediment.

Fig. 4. Carbonate sediment with cyanobacteria in the dark after two weeks of experiment: (a) photograph and (b) and (c) elemental composition of the sediment.

Plate 2



Explanation of Plate 2

SEM photographs and elemental composition of the carbonate sediments obtained.

Fig. 1. Carbonate sediment with cyanobacteria in the light after 10 months of experiment: (a) photograph and (b) elemental composition of the sediment.

Fig. 2. Carbonate sediment with cyanobacteria in the dark after ten months of experiment: (a) photograph and (b) elemental composition of the sediment.

Fig. 3. Accompanying bacteria developed after ten months of experiment: (a) photograph and (b) elemental composition of the sediment.

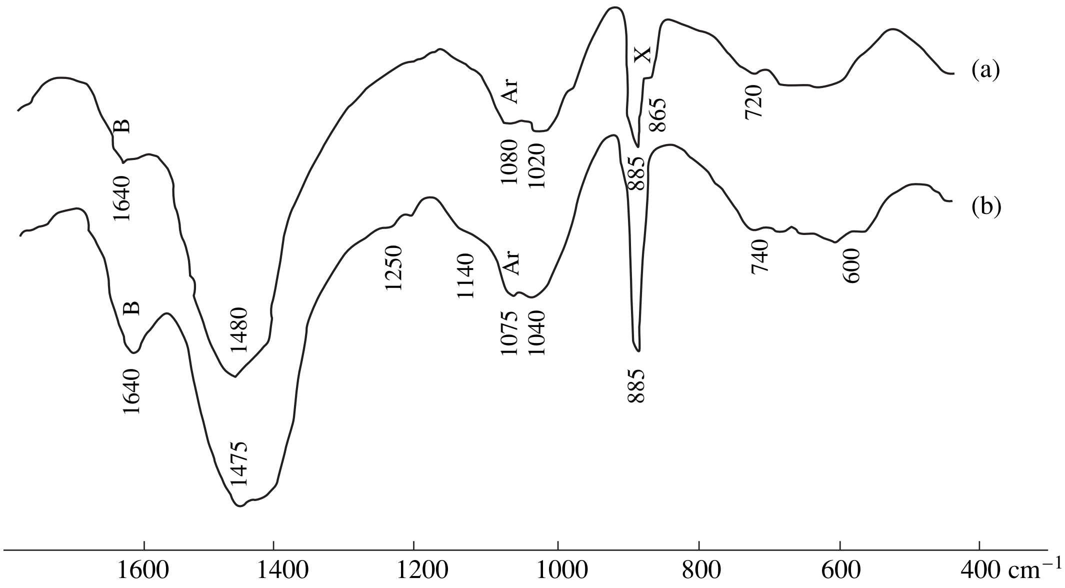


Fig. 2. Infrared spectra of the carbonate sediments with cyanobacteria after 10 months of experiment: (a) in the light and (b) in the dark.

polysaccharide film, as well as small accumulations of fine-grained sediment. The IK-spectrum (Fig. 2b) of this sediment showed that the rounded particles had a regular structure. This is indicated by well-resolved, clear (rather than diffuse) absorption bands, which were observed at the stage of the two-week-long experiment (Fig. 1b). The microprobe data support the presence of magnesium calcite (Pl. 2, fig. 2). The X-ray phase analysis (Table 4) showed that magnesium calcites accumulated in darkness contained a wider range of the high-magnesium phase than the precipitate formed in the light. Supposedly, in this case a protodolomite phase (d = 2.89) was formed.

In analyzing the results of experiments of precipitation of magnesium carbonates in the presence of cyanobacteria, it is noticeable that the accumulation of the sediment was controlled not only by the reaching of the level of oversaturation of carbonates in the solution, the constantly high pH, but also by the presence of the metabolites of cyanobacteria. The amount and quality of the substances extracted to the environment significantly affect the process of carbonization. In the light, cyanobacteria extract carbohydrates, amino acids, organic acids, and vitamins in the free and bonded state. For instance, it is shown that *Microcoleus chthonoplastes* (Zvyagintseva *et al.*, 1995), secretes volatile (butyrate, acetate) and non-volatile (succinate, fumarate, malate, citrate) organic acids. The cyanobacteria *Synechococcus lividus*, depending on environmental conditions, may release into the environment from 12 to 100% of assimilated carbon (Bauld and Brock, 1974), which, certainly, would affect the process of mineralization. The illumination conditions as a factor determining the intensity of photosynthetic processes in cyanobacteria significantly affect the dynamics of the concentration of soluble organic compounds, and the amount of accompanying bacterial flora (Sakevich, 1985).

In darkness, in normal conditions (in the presence of oxygen), cyanobacteria perform respiratory metabolism. The absence of light decreases the growth of cyanobacteria, while advantageous accompanying bacteria absorb exometabolites of cyanobacteria at a great rate. For instance, during simultaneous cultivation of *M. chthonoplastes* and halobacteria, as soon as after five minutes 13% of marked compounds originally contained in the filtrate of the producer was found in the cells of the halobacteria (Zvyagintseva *et al.*, 1995). In addition, the products of decay of cyanobacteria are accumulated in the environment. These can be utilized by bacteria. The medium is affected by the process of decomposition, extraction of acids, including RNA, which degrades in the light (Singer and Doolittle, 1974).

The extracellular polymeric substances (EPS) of polysaccharide nature in large quantities extracted by cyanobacteria are noteworthy. Polysaccharides, constituting the base of EPS, could be subdivided into two groups: polysaccharides of cell walls and extracellular, or glycocalyx. The glycocalyx was subdivided into well-structured polysaccharide sheath, polysaccharide capsule, surrounding a polysaccharide sheath and closely connected to the cell, and mucus forming polysaccharides, which are not in fact connected with the organism. Uronic acids are important functional group of EPS because they contain carboxyl groups responsible for the interactions with other molecules and metals, which is crucial for rock accumulation. EPS may be hydrophilic and hydrophobic. The structure of EPS, depending on chemical composition, presence of functional groups, and temperature, determines whether this be gel or colloid, thus producing a strong effect on the sediment (Stal, 2000).

The main functions of EPS include protection from drying up and from toxic substances and participation in the process of calcification (Stal, 2000). The latter is supported by the experimental data of Kupriyanova *et al.* (2004), who discovered carbonic anhydrase (CA) in the glycocalyx of *Microcoleus chthonoplastes*. This ferment catalyzes the reversible reaction of hydration following the equation ($CO_2 + H_2O = HCO^{3-} + H^+$) and participating in the CO_2-concentrating mechanism. According to Kupriyanova *et al.* (2004), CA facilitates the formation of the calcareous skeleton in corals and deposition of the calcium scales in coccolithophorids. Therefore, the discovery of CA in the glycocalyx of cyanobacteria explains the development of a mineral sheath in these organisms and demonstrates the role of glycocalyx in fossilization.

Metabolites of cyanobacteria also affect crystallization rates. In our experiments, in the solutions containing cyanobacteria, crystallization of the precipitate noticeably slowed down in the first two weeks, apparently due to the formation of soluble complex compounds with organic radicals and to a decreased activity of the Ca^{2+} and Mg^{2+} ions. Many lifetime excretions of cyanobacteria are known to have a high chelating effect (Stal, 2000). The presence of these processes may be supported by the comparison of the precipitate in the control solution and in the experiment in the presence of cyanobacteria in two weeks of interactions (Table 1).

Experimental data obtained show that the differences in the morphology of the sediment deposited in the light and in the darkness are affected by organic compounds, i.e., cyanobacteria and their metabolites, and also as a result of the change in the partial pressure of CO_2, O_2, and other gases taking part in their metabolism. The partial pressure of these gases is different in the light and in darkness and has an effect on the process of carbonate sedimentation.

CONCLUSIONS

The presence of *Microcolius chthonoplastes* in the solution of 2.14M $MgCl_2$–0.05M $CaCl_2$–0.6M NaCl–0.18M $NaHCO_3$ slows down the process of crystallization of magnesium carbonates due to the formation of exometabolites with a chelating effect. The presence of cyanobacteria in the light or in darkness considerably alters the structure of the sediment, size of carbonate crystals, and their shape. Where photosynthesis was present, huntite (possible forerunner of dolomite) was clearly observed. In the dark, protodolomite was formed in association with a broad range of magnesium calcites, as a result of the crystallization of the carbonate sediment.

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