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REVIEW PAPER

Microbial Geochemical Calcium Cycle

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Abstract—The participation of microorganisms in the geochemical calcium cycle is the most important factor maintaining neutral conditions on the Earth. This cycle has profound influence on the fate of inorganic carbon, and, thereby, on the removal of CO_2 from the primitive atmosphere. Most calcium deposits were formed in the Precambrian, when the prokaryotic biosphere predominated. After that, calcium recycling based on biogenic deposition by skeletal organisms became the main process. Among prokaryotes, only a few representatives, e.g. cyanobacteria, exhibit a special calcium function. The geochemical calcium cycle is made possible by the universal features of bacteria involved in biologically mediated reactions and is determined by the activities of microbial communities. In the prokaryotic system, the calcium cycle begins with the leaching of igneous rocks, predominantly through the action of the community of organotrophic organisms. The release of carbon dioxide to the soil air by organotrophic aerobes leads to leaching with carbonic acid and soda salinization. Under anoxic conditions, of major importance is the organic acid production by primary anaerobes (fermentative microorganisms). Calcium carbonate is precipitated by secondary anaerobes (sulfate reducers) and to a smaller degree by methanogens. The role of the cyanobacterial community in carbonate deposition is recorded by stromatolites, which are the most common organo–sedimentary Precambrian structures. Deposition of carbonates in cyanobacterial mats as a consequence of photoassimilation of CO_2 does not appear to be a significant process. It is argued that carbonates were deposited at the boundary between the “soda continent”, which emerged as a result of subaerial leaching with carbonic acid, and the ocean containing Ca^{2+}. Such ecotones provided favorable conditions for the development of the benthic cyanobacterial communities, which were the precursors of stromatolites.

Key words: calcium, carbonate, inorganic carbon cycle, cyanobacterial mats, Precambrian, stromatolites, microbial communities.

FORMULATING THE PROBLEM

The role of prokaryotes in the calcium cycle is not considered in most microbiology textbooks. Although no bacteria with a special calcium function are known, this function is quite prominent in various eukaryotes ranging from protists (coccolithophorides and foraminifers) to metazoans (e.g., molluscs forming their skeletons from calcium minerals). Coral communities are an example of contemporary reef-builders. In the Precambrian time, however, there were no eukaryotic organisms, and yet vast deposits of calcium carbonate were formed in the Late Archean to Proterozoic. Therefore, either chemical precipitation under physical and chemical conditions differing from present or the involvement of prokaryotes is to be admitted. The latter is well illustrated by the massive development of stromatolites as major Proterozoic reef-builders, the emergence of which was conditioned by the activities of cyanobacterial communities similar to contemporary benthic mats.

Another reason for paying particular attention to the calcium cycle is its intrinsic coupling with the inorganic carbon cycle (C_{inorg}). Dissolved oceanic C_{inorg} and atmospheric CO_2, which are in equilibrium, represent small-scale dynamic pools that, nevertheless, have profound influence on the Earth’s climate through the greenhouse effect. The major part of lithospheric Ca is accumulated in oceanic carbonate sediments, which gave rise to calcareous rock (Fig. 1).

A close connection between the cycle of Ca and cycles of other biogenic elements makes possible the formation of gypsum and phosphorite deposits. Sulfates of the ocean and gypsum deposits in evaporates owe their origin to the oxidative activities of microorganisms of the sulfur cycle. The formation of phosphorites and the conversion of calcium phosphate to a utilizable form were the most likely factors limiting the development of biota in the Proterozoic, given that the limitation by bound nitrogen, characteristic of algae and plant cover, was not critical because of nitrogen-fixing activities of bacterial communities.

Calcium and its carbonates preserve the bicarbonate equilibrium by restraining the decrease of pH by carbonate dissolution and the increase by $CaCO_3$ precipitation. As a consequence, neutral conditions with pH varying from 5.5 to 8.5 are produced in the presence of Ca, under which most organisms thrive. The rest that occur beyond these normal conditions are known as acidophiles and alkaliphiles. These organisms can also be designated as “calciophobs”, in contrast to neutrophilic

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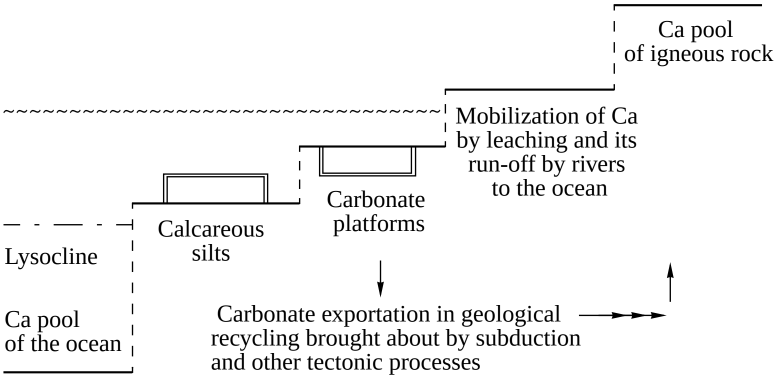

Fig. 1. Calcium pathway in the lithosphere.

ones, which are "calciophilic" with regard to the typomorphic element of landscapes of their environment.

Cycles of Ca and C_{inorg} can be viewed as two sides of one process. At the same time, the cycle of C_{inorg}, through its labile forms CO_2 and HCO_3^-, is linked with the biotic C_{org} cycle. The latter involves autotrophic assimilation of CO_2 in the course of primary production and CO_2 release in the course of decomposition. This proceeds concurrently with the accumulation of stable C_{org} in geopolymers, mainly as dispersed kerogen, accompanied by the release of equivalent amounts of O_2 in the atmosphere. Therefore, the biota indirectly determines the acid-base conditions on the Earth's surface via the Ca cycle and the redox conditions via the O_2 cycle. The biogeochemical succession through the Earth's history altered the thermodynamic conditions and caused the transformation of originally unoxidized igneous rock minerals into minerals of the sedimentary cover.

The outlined arguments warrant a close examination of the scale and forms of participation of prokaryotes in the biogeochemical Ca cycle. The immense literature devoted to calcium carbonates can hardly be reviewed in this paper, and so references are given only to general works dealing with the issues in hand. A vast list of references can be found in [1]. (The physiological significance of calcium as a trace element [2] is not considered in this review.)

Calcium is an element with a constant valence and its chemical reactions cannot serve as an energy source for lithotrophic microorganisms. The dissolution and precipitation of Ca compounds are governed by the pH of the medium, rather than by Eh, despite the fact that carbonates are deposited in the oxygenated zone. The major mechanism of microorganisms' action on Ca compounds is, admittedly, the alteration of the pH of the medium and the formation of the acid-base geochemical barrier (the *D*-barrier, according to the classification by Perel'man and Kasimov [3]). To understand the precipitation of calcium at any particular scale, ranging from cells (tens of microns) to geological formations (tens of kilometers), one needs to examine how this alkaline barrier is formed and maintained.

In this regard, the capacities of prokaryotes and eukaryotes are different. Eukaryotes and, in particular, tissue-forming multicellular organisms are able to create locally in cell compartments or in the intercellular space the conditions needed for depositing Ca-containing skeleton components. With the singular exception of *Achromatium oxaliferum*, prokaryotes lack this capability and, therefore, act upon Ca compounds in the extracellular space via the so-called *biologically mediated reactions.* This differs them from protists and metazoans, which can accomplish *direct biomineralization reactions.* There are, therefore, three channels of calcium circulation to be considered: (1) chemical precipitation of calcium carbonate caused by distortion of chemical and physical equilibrium, as in CO_2 degassing of groundwater emerging onto the surface, or when CO_2 solubility falls down as the temperature increases, or in the course of evaporation; (2) biologically mediated precipitation caused by the alkaline barrier formed as a result of activities of microorganisms; and (3) direct precipitation in skeleton construction involving mechanisms of intracellular mineralization. The dissolution of carbonates is caused by the reverse processes: the increase of the CO_2 concentration due to respiration in the oxygenated zone or anaerobic generation of organic acids.

The necessary condition for a mineral to precipitate is that the source solution becomes supersaturated with respect to the insoluble compound. This state can be calculated from thermodynamic considerations, also for multicomponent systems, as a function of such affecting factors as temperature, pressure, and the presence of competing ions [4]. Most geochemical studies stick to such estimates, rightfully assuming that, in doing so, they get the likely final state of the system. In practice, however, gross supersaturation is not at all infrequent even in homogeneous systems, for example, in solutions in soil due to the formation of colloids and complex compounds, not to mention heterogeneous conditions. Under such circumstances, it is often hard to tell what the actual local conditions are.

The dissolving of a mineral involves a surface exchange reaction, e.g., with the H^+ ion. The solution near the surface needs to be replenished. In the case of molecular diffusion in the interstitial space, it is a slow process limiting the rate of dissolution. Therefore, groundwaters are most often undersaturated with respect to the host rock [5]. The transition into a stable crystalline state from a supersaturated solution requires the participation of seed particles or nuclei. Nonequilibrium conditions arise from kinetic factors.

BIOGEOCHEMISTRY AND THE BIOLOGICAL CALCIUM CYCLE

The geochemical cycle of calcium consists of the primary cycle, which refers to the extraction of calcium from igneous rock followed by carbonate deposition, and the recycle, consisting of carbonate rock dissolution and subsequent precipitation. The Phanerozoic period was dominated by the recycle, which, in addition, proceeded under an oxygenated atmosphere.

The primary cycle is represented primarily by calcium leaching with carbonic acid from igneous rock via the atmospheric hydrological cycle. On the one hand, this cycle produces carbonates and, on the other, forms residual aluminosilicates or clay. The reaction can be conventionally represented as silicate hydrolysis with carbonic acid, formed by dissolution of carbon dioxide, and the production of carbonate alkalinity

$$CaSiO_3 + 2CO_2 + H_2O = SiO_2 + Ca^{2+} + 2HCO_3^-.$$

The igneous rock is exposed to physical weathering, yielding disintegrated material—marl, gravel, and sand—characterized by a large surface/volume ratio and high permeability. Leaching is active in groundwaters in the oxygenated zone unaffected by evaporation and gives rise to alkaline waters and calcified weathering crust. The seafloor region (subaquatic conditions) and continental plains (subaerial conditions) covered with clay, the terminal weathering product, are protected against the loss of calcium.

In the C_{org} cycle, the CO_2 carbon is concentrated by autotrophic assimilation and then released in the course of mortbiomass decomposition by microorganisms. As a result, the mobilization of calcium is accelerated by the action of decomposers.

On the geological time-scale, the subaerial leaching of silicate and carbonate deposits is the most important mechanism determining the concentration of CO_2 in the atmosphere, and, therefore, the greenhouse effect.

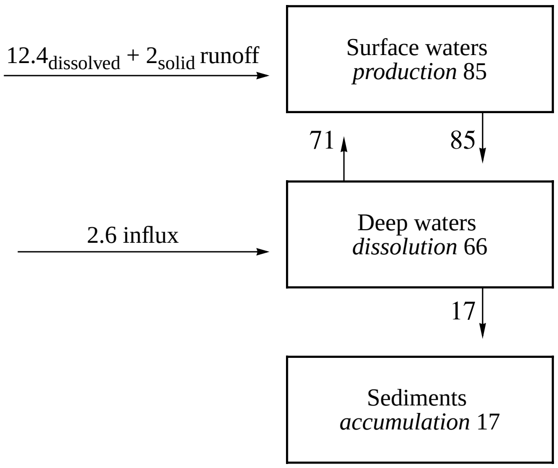

Fig. 2. Biogeochemical calcium cycle (in 10^{12} g-atoms/year) [9].

The accumulation of calcareous sedimentary rock through the Earth's history points to the trapping of carbon dioxide and the openness of its cycle. On the geological scale, the CO_2 cycle depends primarily on the shallow ocean areas, where carbonates form, and their exchange both with the deeper ocean and the mainland. Carbonate silts form from precipitating plankton during diagenesis of bottom sediments. The age of silts does not exceed that of the seafloor bed. Carbonate platforms and reef structures in offshore areas form with the involvement of benthic organisms. In the Precambrian, stromatolitic reefs were formed by cyanobacterial communities. Under subaerial continental conditions, leaching with carbonic acid eventually results in the formation of calcified weathering crust and pedogenic carbonates.

The general model of the geological cycle of calcium must take into consideration the regions of calcium mobilization on the mainland and its deposition in the ocean (Fig. 2) [9].

Contemporary biogenic leaching of calcium can be estimated from the calcium content of the river runoff to the ocean, serving as a terminal sink for Ca. To a very gross approximation, the calcium cycle is determined by the atmospheric hydrological cycle. The oceanic water evaporates and the dissolved CO_2 comes in equilibrium with the atmospheric CO_2. Part of the water precipitates over the mainland as rainfall and becomes enriched with CO_2 produced by the respiration of organotrophs. As the last step the precipitated water leaches calcium and reenters the ocean, which serves as an accumulator for salts delivered by runoff. The balance of calcium in the ocean is determined by its inflow from the mainland and by deposition. Less significant sources of calcium are hydrothermal changes of basalts, porous water, and Ca^{2+} desorption from clay. The average calcium concentration of river water is 0.34 mM, the concentration of HCO_3^- is 0.85 mM; and, in the ocean, the calcium content is 8.98–10 mM [6]. The arid climate, resulting in soda mineralization, limits the mobilization of calcium, and its content in soda lakes at pH > 9 is as low as 0.015–0.07 mM [7]. Locations of Ca accumulation were studied by Ronov and Yaroshevskii and are clearly revealed by clarke concentrations of this element (CaO, %): the overall crust, 8.12; continental crust, 6.98; and subcontinental crust, 7.14. The oceanic crust shell: sedimentary, 22.50; and basaltic, 11.69; the continental shell: sedimentary, 9.94; and granitic, 3.79. Terrigenous rocks typically have low concentrations of calcium; thus pelagic clays contain around 0.93%; meanwhile, the Ca content of calcareous abyssal sediments is 25.5% [8]. Under terrigenous conditions, calcite accumulates in the weathering crust and, in the arid zone, regions of calcite formation are readily identifiable. With a total runoff of 37400 km^3/year, the annual influx to the ocean includes 32.4×10^{12} mol of HCO_3^- as well as 12.4×10^{12} g-atom of dissolved and 2×10^{12} g-atom of suspended calcium. Under modern conditions, assuming that the calcium content of river water is 0.34 mM, it would take merely 1 million years for the concentration of calcium in the ocean to reach 10 mM. The ocean serves as an accumulator for calcium, which is buried in carbonate sediments. The removal of Ca^{2+} from the modern ocean occurs predominantly through the biological formation of calcite on the continental shelf. The net yield of this process is estimated at 17×10^{12} g-atom Ca. The exchange with ocean bottom sediments amounts to $19–24 \times 10^{12}$ g-atom Ca. The resulting carbonate exchange fluxes in the modern ocean are diagrammed in Fig. 2 (in 10^{12} moles/year) [9].

Berner [10] estimated the continental weathering of silicates in the Phanerozoic from their concentration in river runoff, determined by paleoclimatic conditions. As indicated by experimental data for the Alps, silicate weathering increases sevenfold in the presence of plant cover. As a result, in Berner's *3Geocarb II* model, the concentration of CO_2 in the atmosphere as a function of different factors showed an abrupt break and decline some 300 million years ago in the Devonian, with the introduction of plant cover formation into the model. However, there is no geological evidence of such a break. Therefore, it is reasonable to hypothesize the presence, in the Proterozoic time, of a land cover formed by nonvascular plants and algae, which, together with the accompanying organotrophic decomposers, drived the process of igneous rock leaching, playing a role similar to that of modern plants and fungi.

NONBIOLOGICAL REACTIONS OF CARBONATE EQUILIBRIUM

From the geochemical standpoint, the key part in the circulation of calcium and C_{inorg}, is played by the carbonate–bicarbonate equilibrium:

$$\begin{tikzcd}
CO_{2(gas)} \arrow[d, shift left] & & & & \\
CO_{2(dissolved)} \arrow[u, shift left] \arrow[r, leftrightharpoons] \arrow[d] & H_2CO_3 \arrow[r, leftrightharpoons] & H^+ + HCO_3^- \arrow[r, leftrightharpoons] & CO_3^{2-} + Ca^{2+} \arrow[r, leftrightharpoons] & CaCO_3 \\
C_{org} & & & &
\end{tikzcd}$$

The actual state of the system depends on which of its constituent compounds is removed; and, in the above scheme, it is C_{org}. A distinction should be drawn here between the pH, depending on the concentration of the H^+-ion, and the alkalinity A, determined, mainly, by the total of dissolved labile forms of C_{inorg}. The inorganic carbon is determined by the total moles of $CO_2 + H_2CO_3 + HCO_3^- + CO_3^{2-}$; while the alkalinity A is equal to $HCO_3^- + 2CO_3^{2-}$ in mg-equiv. The physicochemical conditions for carbonate equilibrium in aquatic media are determined by the equilibrium constants. The carbonate system determines the pH and, thus, the chemical behavior of minerals, and above all that of carbonates, in most natural waters. The highest buffering capacity is shown at pH 6.4. In soda lakes, the carbonate system is buffered with the HCO_3^-/CO_3^{2-} system at pH near 10.3. Waters in equilibrium with calcite have their pH values in the range 7.3 to 8.4.

In closed systems, like soil and silts, the dissolving of calcite is directly related to the concentration of carbon dioxide in the gas phase. In open systems, where pCO_2 is constant and maintained, for example, by respiration, the process of calcite dissolution never stops. Given that the term entering the equation is the partial pressure of CO_2 assimilated in photosynthesis and released in respiration, the dissolution of calcium carbonates turns out to depend upon aerobic biological processes. The release of carbon dioxide in respiration increases the dissolution of calcite and this explains why sites of carbonate redeposition are confined to the oxygenated zone, where the exchange with the atmosphere is possible. The leaching of calcium is markedly stepped in the presence of mineral acids: nitric acid formed by nitrifiers and sulfuric acid formed by thionic bacteria. In the latter case, the calcium concentration of the solution is determined by the solubility of gypsum.

In anaerobic processes, such as sulfate reduction, the reaction is

$$SO_4^{2-} + 2C_{org} + H_2O = H_2S + + 2HCO_3^-$$

and gives rise to increased alkalinity. In the presence of organic acids, the carbonate equilibrium is determined by the stronger acids. In groundwater, pCO_2 is maintained primarily by respiration in the feeding zone. For water percolating through dolomite, the ratio $Mg^{2+}/Ca^{2+} = 0.6$ but the equilibrium takes a long time to reach.

With the partial pressure of carbon dioxide in the ocean water column increasing with pressure and decreasing temperature, the dissolution of carbonates occurs at a depth of 3.5 km in the Pacific and 5 km in the Atlantic Ocean. This zone is called lysocline, and here the dissolution is faster than burial in bottom sediments. The undersaturation with respect to calcium carbonate begins from a 0.5-km depth. Magnesia calcite penetrates to greater depths.

The carbonate–calcium equilibrium in soils is determined by the state of the soil solution, which, in contrast to water systems, is liable to rapid change with weather conditions. Carbonate systems in soil consist of calcite, Ca^{2+} ions of the exchange complex, Ca^{2+}, $CaHCO_3^+$, $CaCO_3^0$, HCO_3^-, CO_3^{2+}, H^+, OH^-, H_2CO_3, $CO_{2(dissolved)}$, and $CO_{2\ (gas)}$. A thermodynamic calculation of calcite solubility for multicomponent soil solution systems is fairly complicated, but for a long time there were computer programs to do that [11]. Experimental data show significant variation because of so many factors contributing to the equilibrium. The sedimentation of carbonates in soil is to a large degree determined by the three physical processes that increase the concentration of the soil solution: (1) evaporation from the soil surface; (2) transpiration of plants and withering; and (3) seasonal freezing. Each of these processes affects the carbon isotopic ratio of carbonates.

The chemical reactions of the calcium cycle are accelerated manifold by the biota. The most common communities causing primary subaerial leaching are lithophilic lichens and fungi. The rock surface moistened by dew condensation is coated by a thin film of different organisms starting a characteristic rock colonization succession, readily recognized on intrusive rock in the arid areas of Tuva [12] and on granite in Fennoscandia. Tombstones are a suitable model to study leaching because they had a smooth surface when erected, can be readily dated, and are relatively free from excessive man-made pollution. According to different estimates and under various conditions, the biogenic acceleration of limestone leaching can be as high as 10 to 10000 times [13, 14].

The role of the biogenic component of the calcium cycle can be estimated from the isotopic composition of soil carbonates, which was recently analyzed in a study of the CO_2 dynamics for Russia [15, 16]. Soil carbonates are represented by : (1) the lithogenic constituent derived from soil-forming rock; and (2) pedogenic carbonates formed as a result of $CaCO_3$ sedimentation from soil solution. The isotopic ratio $^{13}C/^{12}C$ for marine lithogenic carbonates, e.g., ancient shell rock, varies between +2 and –2‰. Owing to CO_2 diffusion, pedogenic carbonates become enriched with the ^{13}C isotope by +14.4‰ at 0°C; +11.8‰ at 15°C; and +10‰ at 25°C. The concentration of carbon by plants gives rise to increased abundance of the lighter isotope: in C-3 plants, it averages –27‰ and in C-4 plants, –13‰ [17]. Therefore, the origin of carbonates can be inferred from their isotopic composition. Ryskov *et al.* [16] concluded that pedogenic carbonates of Russian soils do not preserve the isotopic composition of the dissolved lithogenic material and originated from organic matter of plants. It follows that the prevailing process of carbonate generation in the pedosphere is microbial decomposition of the dead biomass of primary producers, resulting in the enrichment of soil solution with light CO_2 and in Ca leaching. Regarding the carbon isotopy of carbonates, it should be noted that the isotopic composition of some of the most ancient carbonates from Isua, aged 3.4 billion years, is enriched in ^{12}C and corresponds to that of C_{org} of photoautotrophs [18]. A markedly lighter isotopic composition was found in marine carbonates formed in methane oxidation [19–21]. By contrast, a global increase in $^{13}C/^{12}C$ of carbonates up to +9‰ about 2 billion years ago in the Jatulian is interpreted as a change of the isotopic composition caused by the assimilating activities of cyanobacteria, which became widespread at that time [22].

BIOLOGICAL MECHANISMS OF CARBONATE EQUILIBRIUM

The reactions of reversible carbonate equilibrium in living organisms are catalyzed by carbonic anhydrase, an enzyme of key importance for the problem in hand. Carbonic anhydrase is a Zn-containing enzyme widespread both in organotrophs and in autotrophs. In the former organisms, it is responsible for removing CO_2 from the cell; and, in the latter, for its supply to the cell. In autotrophs, carbonic anhydrase is coupled with the mechanism concentrating the utilizable form of inorganic carbon, which is the CO_2 that reacts with ribulose bisphosphate carboxylase (Rubisco) in the pentose phosphate cycle.

The general reaction of carbonic anhydrase can be expressed as

$$H_2O + CO_2 + E = \underset{\overset{|}{H_2O}}{E} - CO_2 = E + H^+ + HCO_3^-.$$

The activity of carbonic anhydrase can be determined from the rate of pH increases in the presence of dissolved CO_2. Similarly to Rubisco, which is the key enzyme operating at the entry point of the organic carbon cycle, carbonic anhydrase accomplishes the same key function for the C_{inorg} cycle.

Acting in conjunction with Rubisco, carbonic anhydrase concentrates CO_2. The role of Rubisco in plants is well known [23]. A high activity of carbonic anhydrase was shown in calcareous algae *Halimeda* inhabiting coral reefs. Carbonic anhydrase in unicellular algae *Chlorella* and *Scenedesmus* was studied in detail [24]. In eukaryotic algae, various forms of inorganic carbon

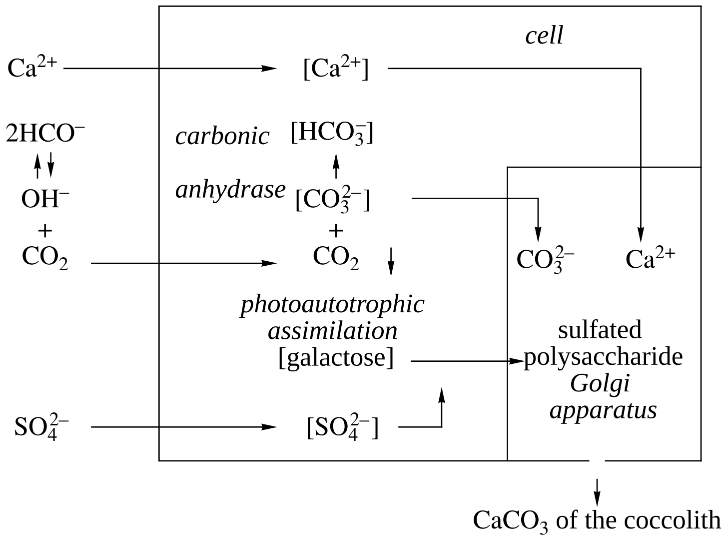

Fig. 3. Deposition of calcium carbonate in cells of coccolithophorides.

are transferred through numerous membrane barriers of the cell by means of their conversion to carbon dioxide, able to diffuse through membranes. By causing rapid attainment of equilibrium between the two forms of carbon dioxide, carbonic anhydrase enables gas to pass through the membrane to sites of its assimilation in autotrophic organisms where CO_2 reacts with Rubisco. The reverse process of carbon dioxide removal occurs in respiration. Therefore, this enzyme is needed by both autotrophs and organotrophs. In cyanobacteria, the coupling of carbonic anhydrase with Rubisco is made possible by their occurrence within a common structure—the carboxysome. In eukaryotic microalgae, a similar conjunction occurs in the pyrenoid.

It is believed that autotrophic assimilation in some cyanobacteria might incorporate the active transport of the HCO_3^- ion, and this, presumably, enhances their calcite precipitation capacity. The supporting evidence comes from the assimilation of C_{inorg} in alkaline media. Of special interest is the organization of carboxysomes in prokaryotic organisms and pyrenoids in eukaryotes and the existence of membrane mechanisms of C_{inorg} transport, which are believed to be of key importance for the CO_2-concentrating mechanism in autotrophs [25].

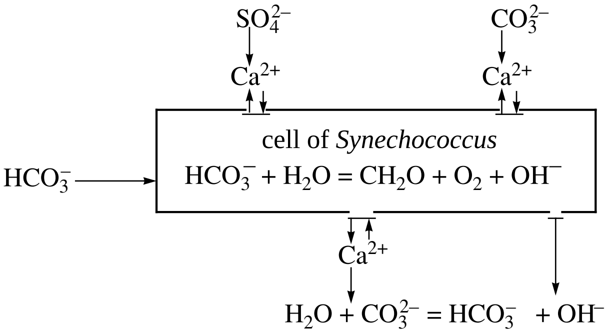

Fig. 4. Participation of cyanobacteria in precipitation of calcium minerals.

Three possible membrane mechanisms of HCO_3^- transport into the cell are hypothesized: (1) symport with Na^+ followed by antiport with Na^+/H^+; (2) ATP-dependent direct transport; and (3) transport by means of an unknown transporter operating at high concentrations of HCO_3^-. The latter mechanism might occur in species inhabiting soda lakes. The interconversion of CO_2 and HCO_3^- inside the cell is sustained by a carbonic anhydrase-like enzyme, but it is HCO_3^- that gets into the carboxysome and, under the action of carbonic-anhydrase, is converted into CO_2 that combines with ribulose bisphosphate and produces phosphoglycerate. All further reactions of the Calvin cycle proceed outside the carboxysome.

The mechanism discussed above does not tell much about the balance in the outer layer surrounding the cell and in the glycocalyx layer. The interaction of such mechanisms with the Ca^{2+} transport specific to cyanobacteria remains unclear. The role of carbonic anhydrase in chemotrophic prokaryotes, and especially in connection with the reactions of calcium compounds, has not been studied in detail. Therefore, the problem of how bacteria catalyze the attainment of carbonate equilibrium in the space close to the cell cannot be regarded as resolved or reduced to the attainment of the physical and chemical equilibrium.

Carbonic anhydrase plays a key part in the formation of skeletal structures in protists. Among contemporary protists, the most important calcification agent is believed to be coccolithophorides, which are unicellular marine plankton algae. Carbonates are deposited in this organism as coccoliths, being structural elements of the skeleton formed within the Golgi apparatus on the organic basal elliptic plate consisting of sulfated polysaccharide. Upon formation, coccoliths migrate out of their cisterns and settle as part of protist's outer carbonate skeleton. The process of calcification is fully controlled by the cell. Calcification and photosynthesis proceed in a one-to-one ratio. A necessary condition for the calcification to proceed is that CO_2 be eliminated from the reaction space. The general course of the process in *Emiliana huxlei* is sketched in Fig. 3.

This diagram reveals the key role of carbonic anhydrase in carbonate transport. The transfer across membranes occurs supposedly in the form of nondissociated carbon dioxide. The crystal develops in the open part of the cell separated by a membrane from the cytoplasm. This calcification mechanism is, obviously, impossible for noncompartmentalized cells of prokaryotes. In coccolithophorides, coccoliths form on elliptical plates consisting of sulfated polysaccharides and made visible by treatment with hypocloride. Similar plates were found in cyanobacteria [26]. Sulfogroups are believed to serve as binding centers for calcium.

The involvement of cyanobacteria in precipitating calcium minerals from lake water with pH 7.9 and Ca^{2+} concentration of 11 mM in the course of photosynthesis was demonstrated in model experiments with *Synechococcus* [27]. Calcite, gypsum, and magnesite were observed to deposit on the cell surface serving as the nucleation center. The sedimentation was caused by a small shift in the pH value induced by photosynthesis. The early stage of gypsum crystal deposition onto the cell surface can be readily seen in electron micrographs. The diagram of the process proposed by the authors of [27] is based on the idea of active transport of bicarbonate during photoassimilation by way of antiport of HCO_3^-/OH^- (Fig. 4).

A presumably chemical sedimentation of calcite was studied using, as an example, calcareous sediments within the water column, the so-called "whitings", which are calcareous cloudings above carbonate shoals in warm climate regions, occurring, for example, within the Bahama carbonate platform and in the Persian Gulf. It was found that 25% of carbonate suspension was constituted by organic matter, with the solid phase attached to picoplankton or decomposed remnants of planktonic algae. The supposed mechanism includes the removal of CO_2 during photosynthesis. Upon dying, the organisms turn into negatively charged surfaces binding cations. The ammonifiers can play a certain part in this process by creating local conditions for precipitation [28].

The kinetics of biological mineralization is regulated not only by attaining the mineral's solubility product but also by crystallization processes with the corresponding biological mechanisms of their initiation and inhibition. These mechanisms include [29]: (1) nucleation and nucleation suppression by organic polyanions and acids; (2) crystal development and its suppression by inhibitors depositing on the crystal surface, e.g., anticalcifying proteins; and (3) epytaxy, i.e., matrix growth of the crystal upon a structured surface. The onset of mineralization, therefore, hinges on the presence of nucleation centers on extracellular heteropolysaccharides—capsules, slime, and sheaths of trichomes. Their emergence depends on the medium conditions and constitutes an adaptive response of the organism quite often observed in the environment and community but rarely found in laboratory cultures. This fact is a source of considerable ambiguity in the interpretation and reproduction of the results.

Calcification in the intercellular space is determined by the rate of diffusion, which, at 20°C, for CO_2 is equal to (in $cm^{-2}s^{-1}$) 1.5×10^{-5}; for HCO_3^- 10.2×10^{-6}; and for Ca^{2+} 8.3×10^{-6}. As a result, the calcification threshold is determined by the rate of C_{org} production and estimated to be 100–200 nmol/(g min). This mechanism was proposed for a calcareous alga *Halimedia* inhabiting coral reefs. A calcification mechanism involving ejection of the OH^- ion by a cell upon utilizing HCO_3^- was put forward for Charales [30]. Similar processes are possible in dense cyanobacterial communities, especially benthic ones, forming pseudotissue. Photosynthesis is unable to significantly shift equilibrium from that observed in seawater with 10 mM Ca^{2+}, and the effect of calcification on alkalinity is weak.

In contrast to skeleton-forming eukaryotes, with prokaryotes, the supply of calcium to their cells is not very important, except when it is required as a trace element in several significant physiological processes, such as nitrogen fixation, photosynthesis, sporogenesis, and other functions that are not considered here and for which special transport mechanisms were evolved by organisms [2].

CALCIUM CARBONATE FORMATION IN CYANOBACTERIAL MATS

The production of calcium minerals by contemporary cyanobacterial communities in both natural samples and laboratory cultures is well documented. In detail, this process was studied for calcium phosphate, which is an important constituent of the biogenic formation of phosphorite deposits [31]. The major issue here is the natural mechanism of phosphate concentration, based on phosphorus accumulation by cyanobacteria. Calcium can be derived from seawater, in which the concentration of Ca^{2+} is close to 10 mM.

The calcification by cyanobacterial communities is of particular interest because of the scale of the process they carry out and its primary role in the history of the Earth. Contemporary lagoons with the salinity sufficiently high to cause the precipitation of $CaCO_3$ provide habitat to cyanobacterial mats with a characteristic community structure. In such mats, however, as we showed by the example of Sivash mats, gypsum and calcite undergo sedimentation at a depth of 1–2 mm under the layer of oxygenic photosynthesis in the development zone of purple bacteria [32]. The course of calcification in a cyanobacterial culture of *Microcoleus* was followed in a scanning electron microscope. First, small lumps of calcite appear on sheaths of some cyanobacteria, characterized, apparently, by decreased physiological activity. Then, these lumps start to grow in number and they cover the sheaths by an uneven mineral cover. Quite often, live trichomes creep out of the sheaths, leaving behind empty tubes. Next, the intercellular space starts to be filled with calcite lumps that, eventually, come to form continuous sediment mass. We see, therefore, that sheaths of cyanobacteria and dead cells act as centers of postmortem nucleation. It is worth noting that carbonaceous stromatolites are constituted by grainy carbonate sediment and contain no lithified bacteria. Microfossils occur in stromatolites in dark silicious inclusions. A notable feature of modern cyanobacterial mats with carbonate deposits is that cyanobacteria reside outside the layer of carbonaceous globules. One inconsistency in such a portrayal of this process is that minerals settle predominantly on dead cells, which, naturally, lack any photosynthetic activity, whereas the sedimentation of $CaCO_3$ might be expected to correlate with such an activity. Therefore, it should be concluded that live cells must possess some mechanism that prevents the deposition of calcite. A likely mechanism would be a positive surface charge of a metabolizing cell, e.g. due to H^+, preventing the sorption of Ca^{2+} on the membrane but not on sulfur groups of polysaccharides in sheaths or glycocalix.

The idea that photosynthesis plays a major part in carbonate depositing by markedly increasing the pH in the intercellular space has an inconsistency related to diffusion: for the pH to increase, the exchange with the outer space must be hindered and, at the same time the deposition of calcium requires its inflow from the outside. Therefore, sedimentation may be confined to the pseudotissue of the cyanobacterial community. In spite of the advantages of coupling calcification with photosynthesis, there are few species among cyanobacteria inclined to calcification. Under contemporary conditions, liming proceeds in *Scytonema*, *Calothrix*, *Rivularia*, *Phormidium*, *Lyngbya*, and *Plectonema* at sites of travertine deposition. Such habitats are incommensurable with a wide spatial distribution of stromatolites and calcareous algae in the past.

The next stage consists in formation by cyanobacterial communities of mineral macrostructures similar to stromatolites. As suggested by Krylov, this process was simulated in our laboratory by Orleanskii [33, 34]. The idea consists in depositing on the surface of a cyanobacterial film of $CaCO_3$ either chemically precipitated from the solution covering the film or simply as powder. Some part of mobile cyanobacteria creep out to the light on top of the sediment, while the rest remain in place as a dark layer. Repetition of this process produces a lamellar column. Our attempts to simulate the formation of stromatolites at the expense of physiological processes so far failed. An interesting example of such a lamellar organo-sedimentary structure was found in the Zavarzin Pond in the Uzon caldera [35]. Fine suspension of sulfur washed out by hot spring water was carried into the pond, where thermophilic *Phormidium laminosum* developed. Under daily growth dynamics, a sandwich column was formed in which layers of fine-grade sulfur were interlaced with layers of phormidium.

As indicated by laboratory experiments, the conditions for stromatolite formation and lithification of the cyanobacterial mat are likely to be related with the buoyancy given to the mat by O_2 bubbles, produced in photosynthesis, which tear up and float the mat to the liquid phase. Torn mat pieces are carried away. If the medium is still, the mat can be loose. Formation of calcareous sediments in mats decreases their buoyancy. For this reason, it is only portions of mat made heavy by calcification that rest in places of stromatolite formation and accrete into solid crusts. The mobility of the medium turns out to have several important implications: (1) gas is removed as the liquid flows over the surface and this prevents bubble formation; (2) lightweight pieces of mat are carried away; and (3) the heavy fraction is selected as a result of sedimentation of mineral matter and its cementation.

It follows that facies analysis is needed when considering stromatolite formation. A detailed analysis not only of sections of the stromatolite mass but also and in the first place of the paleosurface can yield additional information on the physical conditions of the sedimentation environment.

PRECIPITATION OF CALCITE BY ORGANOTROPHIC BACTERIA

As previously mentioned, no chemotrophic organism with a definite calcite-producing function was discovered, although characteristic species of cyanobacteria and other bacteria are often found in travertines. A general description of calcite formation based on a model experiment and outlining the key stages of the process was given in 1948 by Issatchenko [36]. In his study he used ammonifiers on a solid peptone-rich medium containing water from sources depositing travertines. Among the emerged colonies, only those of certain species showed calcite sedimentation. Issatchenko concluded that "the carbonate sedimentation, apparently, follows the same pathway in every live species: first, amorphous carbonate is formed, colloid calcite appears next, and then it undergoes crystallization." Issatchenko concludes with a thesis: *omne calx e vivo* [36].

Hence, the following steps of bacteriogenic precipitation of calcite could be identified: (1) formation of an alkaline geochemical barrier; (2) formation of a solution supersaturated with respect to $CaCO_3$; (3) formation of calcite colloids; (4) nucleation of $CaCO_3$ on bacterial slime hosting immobilized Ca^{2+}; (5) diagenetic transformations as such, leading to crystallization of calcium minerals; and (6) transformation of sediments into rock by cementation and consolidation. Essentially the same pathway is considered in present-day studies [37].

Issatchenko's idea concerning the existence of definite species able to precipitate $CaCO_3$ was put in doubt, although, in fact, the important issue here is the occurrence of extracellular structures that could act as preferred nucleation centers. Given that the slime-forming capacity is species and even strain specific and, in addition, depends on the physiological state of the cell, the existence of certain species, indeed, can be questioned. One factor that determines the role of bacteria as sedimentation surface is the chemical structure of the capsule with an, apparently, dominant role of sulfur groups in heteropolysaccharides. As a result, after the precipitation conditions for calcium carbonate are attained in the community the order of precipitation is determined by the selective features of different organisms as nucleation centers.

The role of bacteria in calcium precipitation was bluntly denied by Strakhov, who claimed that "the significance of bacterial calcite forming is negligent" and "of major importance is the chemical settling of calcium carbonate and its introduction in the suspended form" [38]. His viewpoint found wide recognition but currently is not accepted in such a general form. Meanwhile, the notion that the role of aerobic organotrophic bacteria consists merely in generating the needed carbonate alkalinity conditions, which can also be created by the addition of $NaHCO_3$ in amounts equivalent to the decomposed organic matter, was experimentally substantiated by one research team [39]. The specific role of bacteria was defended by another team [37]. At the same time, direct examinations of natural samples reveal that bacterial aggregates quite often occur inside carbonate particles and are encased by bacteria-free crystalline shells [40]. We see, therefore, that direct initiating function of bacterial microcolonies and aggregates in carbonate precipitation is superposed by a chemical process of sediment crystallization made possibly by biologically induced changes in the medium parameters. Sediment crystallization may well be preceded by the formation of amorphous colloids studied by Chukhrov [41], which transform into crystalline minerals only in the course of diagenesis.

The role of chemotrophic organisms in the calcium cycle will be seen from a different perspective if, rather than considering individual species, we focus on the function of their physiological groups and communities. In this case, the role of chemotrophic organisms in the calcium cycles comes out manifestly. The alkaline barrier generated by communities of microorganisms is due mostly to anion decomposition than to alkali production. Therefore, it is the activities of communities of organisms that need to be considered rather than those of individual species. The first step consists in the mobilization of calcium by organisms producing acids, while the second step is precipitation of carbonates by organisms decomposing acids. The contraposition of primary and secondary anaerobes and of microaerophiles oxidizing salts of organic acids is very distinct in the calcium cycle. Groups of organisms increasing the medium pH by eliminating anions set the scene ready for Ca precipitation. At the same time, the process of crystallization depends upon specific conditions determined by the chemical (and stereochemical) properties of surface structures.

Calcium leaching from rock proceeds under the action of dissolved carbonic acid. Initially, carbon is concentrated by primary autotrophs, utilizing atmospheric CO_2 and producing C_{org}. The utilization of CO_2 upsets the carbonate balance and creates conditions for $CaCO_3$ sedimentation. The production of CO_2 takes place in aerobic and anaerobic decomposition of carbon-rich dead biomass. The fact that $CaCO_3$ sediments occur in the oxygenated zone is explained by biologically mediated C_{org} oxidation. Organic matter decomposition by microaerophilic aerobes under limited exchange with the atmosphere gives rise to elevated concentrations of CO_2 in soil air and groundwater of the oxygenated zone. Free exchange with the air makes degassing possible, and this links carbonate formation with oxidative conditions.

A tentative generalization can be made that autotrophs contribute to $CaCO_3$ precipitation and organotrophs to its dissolving. This is not quite true, and the connection, so popular among geologists, between the formation of carbonates and photosynthesis is not universal, although the main underlying factor is still the alkalization of the medium giving rise to the alkaline barrier. In more detail, the acting groups of microorganisms are listed below.

Conditions for $CaCO_3$ precipitation	Conditions for $CaCO_3$ dissolution
Oxygenic photoautotrophs	Primary anaerobes producing volatile fatty acids; aerobic organotrophs producing acids (e.g., fungi); lithotrophs producing acids: nitrifiers, thionic bacteria, sulfur bacteria
Secondary anaerobes: denitrifying sulfate reducers, methanogens	Homoacetic bacteria
Aerobes utilizing volatile fatty acids Ammonifying decomposers	Aerobic organotrophs, especially microaerophiles, causing elevated concentration of CO_2

It is clear from the above list that groups of microorganisms play very definite roles in the calcium and inorganic carbon cycles and, therefore, the batch effect can be studied without trying to assign any particular species a role beyond that of edifier. It should be recognized with reference to the calcium cycle that it is not particular organisms but rather the environmental conditions for the community that are specific. This point can be readily illustrated by laboratory experiments relating, for example, to chalk dissolution during carbohydrates fermentation and to carbonates production in acetate decomposition by methanogens and sulfate reducers.

All cycles of major biogenic elements turn out to be coupled with the calcium cycle. In the nitrogen cycle, ammonifiers produce high pH contributing to carbonate precipitation. By forming nitrate, nitrifiers dissolve limestone, and this, by the way, is an important factor in the erosion of building surfaces, particularly, in polluted urban air. Denitrifiers, by decomposing nitrates, contribute to carbonate precipitation. The oxidation of reduced sulfur compounds by thionic bacteria leads to carbonate decomposition and gypsum formation. On the mass scale, this process is effective under evaporitic conditions in formations of reefs. The dissolution of carbonates present in the stone facing of buildings by sulfuric acid is intensified by the formation of gypsum, which causes exfoliation, as a result of its large specific volume. Sulfate reducers, as previously mentioned, precipitate calcium carbonate. In the phosphorus cycle, the dissolution of calcium phosphates is caused by numerous acid-producing organisms. The precipitation of phosphates in cyanobacterial mats leads to the formation of phosphorite deposits. The association between the cycles of biogenic calcium and iron is negative because iron becomes mobile under the conditions at which the calcium content is low but ferrugeneous limestones are formed.

Most significant for the calcium cycle is the cycle of organic carbon (Fig. 5). Given that the main suppliers of CO_2 to soil (pedospheric) waters are microorganisms decomposing concentrated organic matter of the dead biomass, it is easy to see that, under the oxygen atmosphere, this function is accomplished by aerobic organotrophs, sustaining the calcium cycle by dissolving and eventual precipitation of calcium in the course of CO_2 degassing into the atmosphere. Under anaerobic conditions, the relations are basically different. Physiological groups of microorganisms are coupled by trophic relations in communities. The distribution of groups of organisms within the trophic network of the community suggests the likely sequence of precipitation and dissolution of $CaCO_3$. Calcium precipitated by photoautotrophs—the primary producers—is dissolved by primary organic-acid-forming anaerobes, to be once again precipitated by secondary acid-decomposing anaerobes, e.g., methanogens and sulfate reducers, as shown in the diagram of community trophic interactions.

The role of secondary anaerobes in calcium precipitation and, especially, in the cementation of porous rock space, is well know. Above all, this function was shown in sulfate-reducing bacteria, converting dissolved sulfates or gypsum into hydrogen sulfide with concurrent precipitation of calcium carbonate. The formation of carbonate is very spectacular in cultures of aceticlastic methane-producing bacteria. Owing to calcite formation, the specific weight of methanosarcinas aggregates increases and they start to settle to the bottom as if their density were 2 g/cm^3 [42]. Granules of methanogenic consortia from wastewater treatment plants are often covered with carbonate minerals, dominated by $CaCO_3$ [43]. A vivid example of the role of anaerobes in calcite sedimentation is the formation of calcareous crusts with isotopically light carbonate in methane seepage areas on the seafloor, e.g., at hydrogen sulfide zone of the Black Sea [18].

Decomposition in a closed space by microorganisms of C_{org} concentrated by biota produces CO_2 and is the major route of accelerated Ca extraction from igneous rock. The second most significant route is the formation of organic acids, shown for some aerobic fungi but more typical of the group of *primary anaerobes* (fermentative microorganisms). The third most significant route is the formation of mineral acids by *aerobic chemolithotrophs*, e.g., by nitrifying or thionic bacteria. The latter give rise to gypsum formation and this links the carbonate cycle with the sulfur cycle. Calcium salts of organic acids are decomposed by *secondary anaerobes*, above all by sulfate reducers and aceticlastic methanogens, leading to calcium sedimentation and porous space cementation. Cementation in the oxygenated zone might be associated with decomposition of calcium salts of organic acids by aerobes. Anaerobic chemotrophic organisms that precipitate $CaCO_2$ and above all primarily sulfate reducers developing in the porous space precipitate calcite and cause cementation, which decreases rock permeability. The formation process of the carbonate horizon in soils, where organic matter undergoes decomposition, was analyzed in detail by soil scientists. A minimal autonomous community sufficing for rock degradation is constituted by lithophilic lichens, which comprise both producers concentrating CO_2 into C_{org} and decomposers [13].

A comparison of the capacity of different extremely anaerobic organisms to dissolve carbonate breccias showed the strongest process to occur in a culture of a psychrophilic anaerobic fermenting organism *Ruminococcus* (=*Lactosphaera*) *palustris*, isolated from an outlet of a spring in a forest near Moscow [44]. It is usually thought that the formation of calcite eliminates gaseous CO_2. In fact, this is not quite true. In accordance with the equation $2HCO_3^- + Ca^{2+} \rightleftarrows CaCO_3 + H_2O + CO_2$, the dissolution of calcite leads to the *take up* of carbon dioxide, while its sedimentation to evolvement of CO_2, concealed by a relatively high pH. Microflora of decomposers developing in the cold climate can create an additional sink for CO_2 at the expense of carbonate dissolution.

This leads to a paradoxical conclusion that regions of cold humid climate, where carbonates are continually dissolved and carried out into the ocean, constitute a sink for atmospheric CO_2, and warm ocean regions, where carbonates are deposited, serve as a source of CO_2. Actually, in the final analysis, carbon dioxide is eliminated by this cycle.

CALCIFIED MICROBIAL COMMUNITIES OF THE PAST

The leaching by carbon dioxide could be very active in the Archean in the period following the degassing of Earth and, therefore, the mobilization of Ca could have occurred very early. The ratio between sediments of marine and continental origin can be estimated from the Sr isotopic ratio. The possibility to distinguish between basalt and granite as primary sources is based on the $^{87}Sr/^{86}Sr$ isotopic ratio, given that basalts are rich in ^{86}Sr and continental granites in ^{87}Sr. As a result, the isotopic ratio of weathered carbonates is reflected by the seawater $^{87}Sr/^{86}Sr$ ratio. The later figure fails to identify the continent as the predominant source of Ca.

Stromatolites, as the most important fossil of the Precambrian, were the subject of detailed investigations for dozens of years [21]. Stromatolites are lithified remnants of microbial communities, which, in addition to cyanobacterial edificators, included a variety of microorganisms that in most cases were able to completely decompose organic matter, most often replacing it by carbonates. Stromatolites are for the most part strongly dolomitized. Calcareous algae differ from stromatolites in that their thalli are enclosed in homogeneous fine-grained calcium carbonate. “Blue-green calcareous algae, dating back to the Cambrian time, reached their fullest flower in the Lower Paleozoic and only in small quantities stepped over the Mesozoic boundary. No data relating to the calcareous algae of the Cenozoic are available. Sparse populations of this algoflora are still found in mostly continental bodies of water” [45].

A clear enough distinction can be drawn between an older epoch of predominantly dolomite formation and the later one, which was predominantly calcareous [46]. A major part of sedimentary carbonate rock was formed in the Proterozoic, when only physicochemical reactions and biogenic ones mediated by prokaryotes were effective [47]. Most of dolomites emerged in this epoch, while the Phanerozoic is characterized by the accumulation of limestone and decreased formation of dolomite. Dolomitization proceeds by the reaction $Ca^{2+} + Mg^{2+} + 2CO_3^{2-} = CaMg(CO_3)_2$, which produces dolomite with the solubility product of 10^{-15}. Dolomite has an alternating arrangement of Ca and Mg layers. Under normal conditions, magnesian calcite with interlaced layers of Ca and Mg is produced. Direct production of either dolomite or protodolomite by biological mineralization is not known, and they are assumed to form in diagenesis, although high-magnesium calcite can be deposited by bacterial communities. The available evidence of dolomite depositing in a sulfidogenic community does not necessarily point to the leading role of bacteria. The problem of ancient dolomite formation is not yet solved [48].

REEFOGENIC FORMATIONS AND LANDSCAPE FORMATION BY MICROBIAL COMMUNITIES

The connection between the carbonate cycle and halogenesis, including the sulfate one, becomes manifest at the landscape and facies levels. The building of reefs and large-scale calcium carbonate sedimentation are both caused by activities of communities of organisms that, in addition to skeletal forms, as we currently know, include carbonate-depositing primary producers—algae and cyanobacteria. The net result of their activities is the accumulation of carbonates, and this creates specific physical conditions for the community. A model of such ecosystems are coral reefs—the most widespread reef builders in modern warm seas. The zonal character of calcium carbonate distribution is closely related with the climatic conditions [38], and so calcareous minerals can be viewed as indicators of paleoclimate [49].

A different aspect of microbial formation of calcium carbonates relates to paleogeographic conditions. It is believed that, in thalassocratic epoches, platforms were covered by epicontinental seas. The depths were insignificant and more or less stable across the whole water space with leveled bottom profile. The sediment layers propagated over large distances. In humid climates, a washing out regime can be supposed in which atmospheric precipitation reaches considerable depths and pushes up groundwater, rich in mineral components, to the surface. The epicontinental sea, or some of its parts, can be regarded in this case as something like a big filtration window enabling interaction between surface and underground waters. This model presumes that the pool of minerals does not reside in ocean waters only but is constituted by the underground hydrosphere, leaching the underlying rock. Emerging to the daylight surface, these waters enter the development region of photoautotrophic communities. This can explain the high concentrations of mineral components in places of development of cyanobacterial mats. The location in thalassocratic epochs of continental platforms under epicontinental seas could contribute to the predominant development of biocenoses associated with the subsurface hydrosphere and to the formation of vast regions populated by cyanobacterial mats [50].

Fossil organogenic geological structures are isolated calcareous bodies owing their origin to the activities of organisms able to accumulate and deposit calcareous material. Such structures can be divided into two large

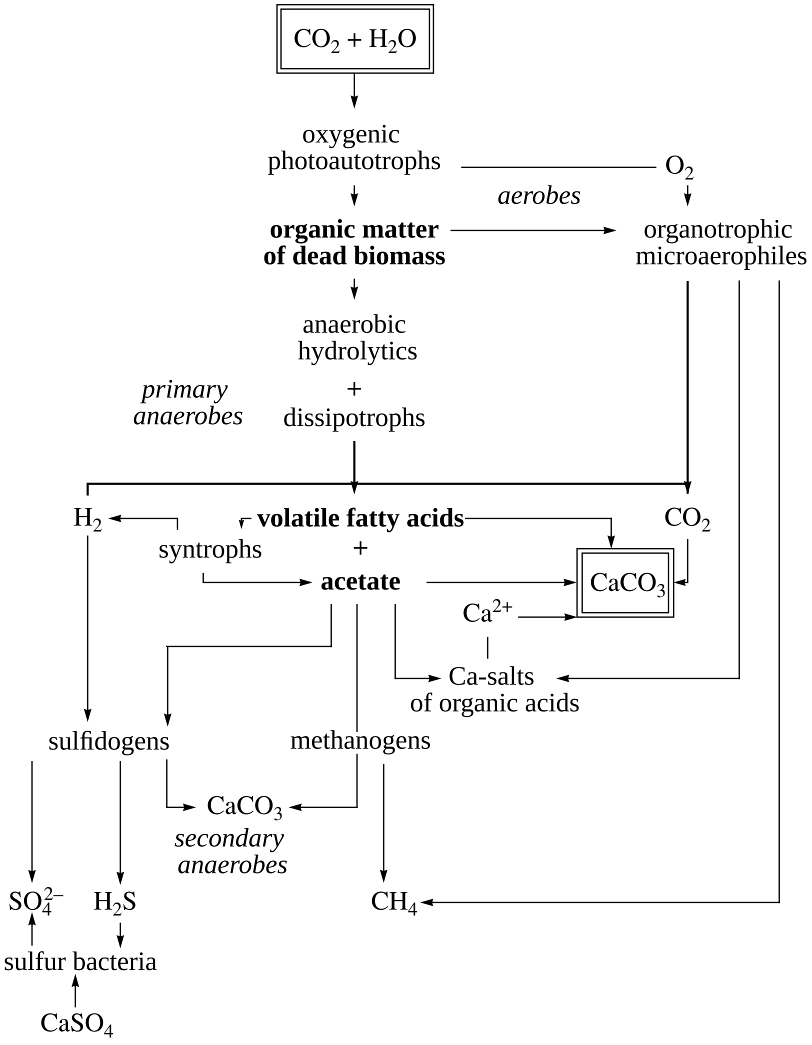

Fig. 5. Involvement of calcium in the trophic network of a microbial community.

groups: Precambrian stromatolites and “coral reefs”. The latter term broadly refers to a variety of multicellular skeletal organisms that evolved in Late Precambrian times and became predominant in the Phanerozoic. “Coral reefs” are given their name by similarity with modern structures but in the past they also were formed by other groups of eukaryotic multicellular colonial organisms, able to form skeletons. These organisms include calcareous algae and multicellular animals with three-dimensional skeletons. Modern coral reefs are highly complex ecosystems characterized by extraordinary biodiversity of species, in which the form-giving role is played by corals. Stromatolites and reef builders coexisted over a relatively short period. They occurred in different circumstances: stromatolites developed a carpet covering of a surfaces—a “mat”,—whereas reefs covered rocks. Both types are referred to as biostromata when represented by bedded structures and as bioherms when they are dome-shaped.

Reefogenic formations in sedimentation basins emerged in certain facies zones: the front slope; reef zone, back-reef flats, and shelf lagoon with free water exchange. These zones occur in marginal zones of continents, intracontinental glacial troughs, microcontinents, and island arcs. On the landscape level, stromatolites formed a sedimentation barrier in the boundary zone between the shallow shelf and the deeper parts of the ocean. This barrier emerged in the process of sediment movement along the shore and was similar to reef barriers or island chains. Stromatolite belts sometimes extend several hundred kilometers in length and measure several hundred meters in thickness. On the facies level, they are similar to tidal flats and sandbars, which also serve as sedimentation traps [51].

Geomorphologically, the formation of carbonate reefs requires that a limited space be formed, e.g., a chain of islands or banks produced by the alongshore movement of sediments. These sediments undergo cementing by calcifying communities, e.g., stromatolites, and enclose lagoons, where halophilic communities of microorganisms thrive, which are very similar for different regions. A few examples of such lagoons are those of Sivash [32], California Bay, and Solar Lake in Sinai [52]. Reefogenic formations encircle shallow waters and restrict water exchange, giving rise under arid conditions to evaporitic circumstances, in which evaporative concentrating of dissolved salts proceeds until precipitation. As a result, evolvement of the halogenous formation occurs. The term halogenous applies here to all readily soluble compounds from calcium sulfate to K, Mg, and Na chlorides and sulfates. In addition to chloride compounds, sulfates also are regarded as belonging to this group, which, by its origin, is connected with the evaporitic group. The lagoons provide a habitat for halophilic microbial communities, characterized by the predominance of cyanobacteria in biogeochemical reaction of organic matter production and organisms of the sulfur cycle in decomposition reactions [32].

At the same time, a suitable morphology of the coastal zone alone is not enough to build reefs. In cold humid climates, reefs do not form, and mats merely fix sediments by the organic matrix, as shown by the example of the North Sea [53], where calcium is carried out into the ocean and redistributed by currents. The Bahamas serve as a model of contemporary carbonate formation in warm humid climates and the Persian Gulf area in arid climates [54].

“SODA CONTINENT”

Igneous rock leaching by carbonic acid is regarded as the primary mechanism of calcium mobilization. Waters of the atmospheric hydrological cycle and groundwaters react with rock and make the pool of alkaline waters. Leaching of alkaline-earth metals with their eventual deposition as carbonates, proceeds under subaerial conditions and is regarded by geochemists as the major mechanism of eliminating CO_2 from the atmosphere. The source of CO_2 is assumed to be degassing that proceeds predominantly outside continental platforms through the seafloor. The conventional concept that immediately follows is that, originally, the ancient ocean was mildly acidic [55].

Meanwhile, subaerial leaching by carbonic acid in arid climates unavoidably results in soda mineralization and formation of solods in the pedosphere. The scale of soda water production was estimated within the framework of the “soda ocean” hypothesis [7, 56]. It could be very large in internal parts of supercontinents, such as Pangaea. The location of contemporary soda deposits is indicative of this possibility. Groundwaters resulting from leaching are alkaline [5] and could provide habitats for a relict alkaliphilic microbial community. Alkaliphilic, obviously not oceanic, microflora could be functionally quite diverse [57, 58].

The key condition for carbonate depositing is the setting of a chemical alkaline barrier. This could be formed between the continent with soda waters in arid parts and the ocean with water composition close to its modern state. The interface zone between continental and oceanic waters, in this case, would be the area of carbonate deposition and a biological ecotone. The mixing of waters need not necessarily occur on the continental shelf. It could also take place in epicontinental seas connected with the ocean but having underneath the continental rather than oceanic crust.

Species of microorganisms are regarded as universally occurring, but the development of their communities must be closely correlated with the geographic conditions. It is significant that, being confined to certain geographic circumstances, cyanobacterial stromatolites-forming communities themselves were involved in landscape formation on a very large scale. In our view, reefogenic formations not only give rise to certain physical conditions but also indicate the location of the geochemical barrier between the ocean and the continental slope. Carbonic acid weathering on the continent sets up the conditions for soda salinization and the formation of alkaline calcium-free waters. The warm ocean serves as a terminal sink for calcium originating from humid climate regions and the source of endogenous CO_2. The alkaline geochemical barrier forms in the regions where vadose waters of the continent meet with oceanic waters. Such locations are indicated by the formation of stromatolites containing phosphates because phosphates are mobile in alkaline media free from calcium and iron.

To put the hypothesis of the geochemical to test, it remains to simulate the behavior of cyanobacterial communities in the interface region. The experiment was performed with a culture of *Microcoleus chthonoplastes*, isolated from soda lake Khylgatyn, Chita oblast, far eastern Russia. The culture was placed in a bath with an agar slope that had a hole filled with a medium for alkaliphilic cyanobacteria with pH 10.2. In a different version, the slope was made of potter’s clay the wet surface of which was covered by a thin layer of hot agar (10 ml/100 cm^2) to preclude mudding. The deeper part of the bath was filled with a 20-mM solution of $CaCl_2$ and $MgCl_2$ in 3.5% NaCl. The “continental” component in this experiment was represented by soda waters, in which only anions were mobile, whereas the “seawater” contained a variety of cations. *Microcoleus chthonoplastes* was plated midway between the hole and the “ocean.” The trichomes of the cyanobacterium spread by gliding on the wet surface. The formation of calcium carbonate beneath the shoreline of the “ocean” was apparent in the form of a characteristic strip of white globules in the diffusion area of soda water from the hole. The formation of carbonate was especially abundant in zones of massive growth of

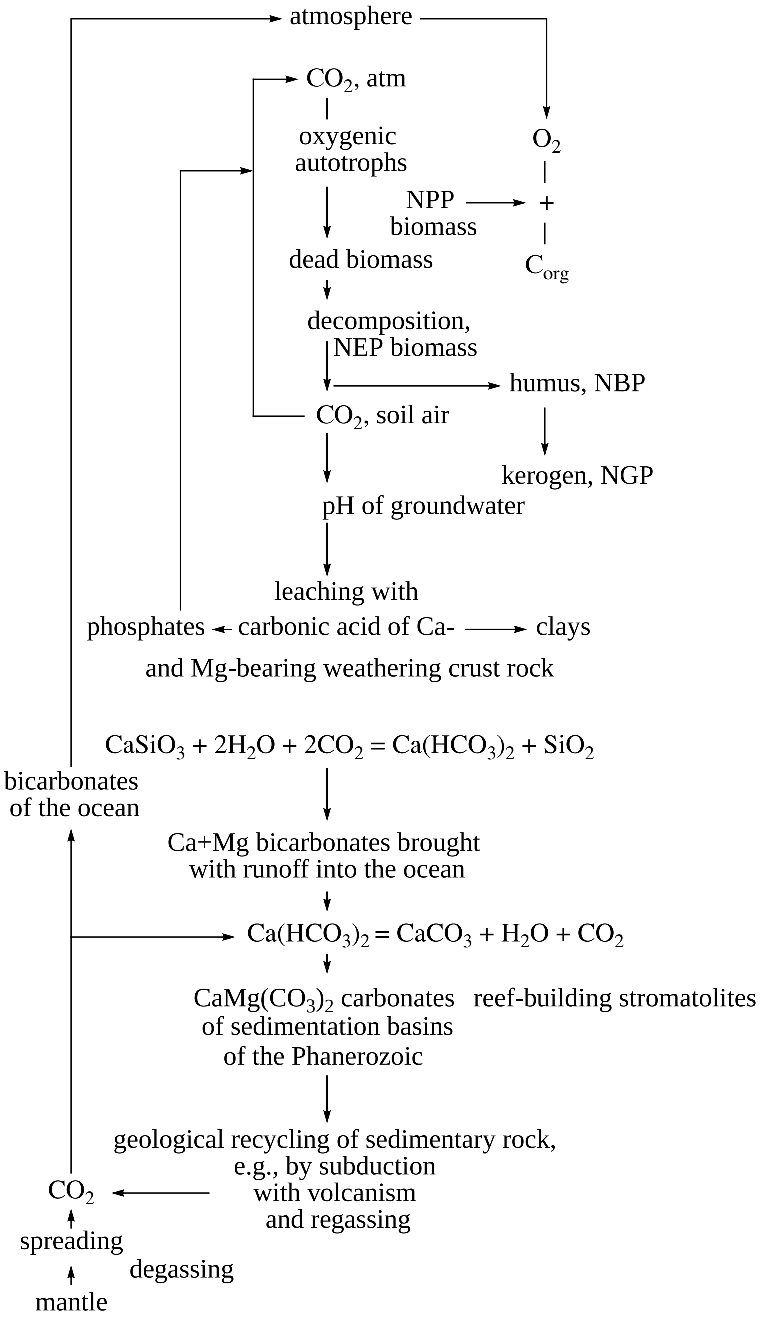

Fig. 6. Participation of biota in the calcium cycle: NPP is the net primary production (photoassimilation minus respiration); NEP is the net ecosystem production (NPP minus annual decomposition by organotrophs) at balance with O_2 utilized by organotrophs; NBP is the net biome production; and NGP is the net geosphere production due to deposition during sedimentation.

the organism. Outside the growth zone of microcoleus, the chemical sedimentation of carbonate was scattered and its density much lower. This model illustrates the correlation between the development of microcoleus and the alkaline barrier, where calcium is deposited. Naturally, this 20-cm model is no more than a school-level illustration of the basic idea.

CONCLUSION

The overall diagram of the coupling between calcium and carbon cycles is shown in Fig. 6.

Having considered the role of microbial communities in the circulation of calcium and inorganic carbon, one can easily see how wrong it is that one of the most important biologically mediated geochemical processes failed to receive the due attention of microbiologists. Here, the most important processes operate not on the level of individual cells or pure cultures but rather on the level of communities that not only develop in particular environments but also change them. The microbial calcium cycle played a key part in the emergence of the biosphere. The major conclusions follow.

Depositing of calcium carbonates was the main route of elimination of CO_2 from the atmosphere and the hydrosphere, which is in equilibrium with the former. The elimination of CO_2 saved the planet from the "runaway greenhouse effect."

The dynamics of calcium carbonates was the main mechanism maintaining the neutral pH by causing sedimentation in response to alkalization and dissolution in response to acidification. Therefore, neutrophiles are at the same time calciophiles.

Biologically mediated circulation of calcium up to the Neoproterozoic revolution with a definite upper limit in the Cambrian proceeded due to the activities of prokaryotes alone. Depositing of dolomites and formation of calcareous platforms is traced to this period. The prokaryotic biota participated and continues to participate in biologically mediated chemical weathering, significantly increasing its rate.

Among prokaryotes, there are no organisms with a specific function to precipitate or dissolve calcium carbonates (except for several cyanobacteria). Prokaryotes are involved in biologically mediated reactions of calcium circulation, and the key role in such a situation is played by communities of microorganisms. The direction of reactions is determined by the physical and chemical conditions, but their kinetics is largely governed by microorganisms.

The calcium cycle has two phases: (1) the extraction and mobilization of calcium from igneous rock by leaching mostly with carbonic acid but also with biologically formed organic acids, in the end leading to clay formation; and (2) the sedimentation of calcium, resulting in the formation of calcareous rock mass. In the Precambrian, this cycle was mediated by prokaryotes. Beginning from the Cambrian, calcium was deposited primarily through the concentrating activities of biotas or, to put it differently, through direct participation of skeleton-forming organisms.

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