

# Biogeochemistry of Lake Baikal Stony Littoral

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## Abstract

The problem of biogenic income from rocks into a water ecosystem and of their use by hydrobionts is considered by the example of Lake Baikal biogeocenoses. A complex interreaction of stony material and Baikal water occurs on the stony littoral of Lake Baikal with an active participation of benthic and planktonic hydrobionts. Biogeochemical processes enable income of biophile elements providing productivity of stony littoral and hydrobionts biodiversity. A particular role in the littoral zone belongs to symbiotic organisms: lichens and sponges. They extract from the rocks a wide spectrum of macro- and microelements including phosphorus, fixe nitrogen and consume carbon. Biodiversity and bioproductivity of stony littoral depend on the diversity of petrographic composition of the rocks and on their geochemical peculiarities. Increase of anthropogenic impact onto the stony littoral manifested by income of biogenic elements and alien microbial cenosis flow results in degradation of primary aquatic biogeocenoses.

## Keywords

Stony Littoral, Lake Baikal, Biogeochemistry, Hydrobionts, Biodiversity, Bioproductivity, Anthropogenic Pollution

## 1. Introduction

Riftogenic Lake Baikal is a very good object for studies of biochemical peculiarities of interreaction of fresh waters with rocks. Main agents of this interreaction are endemic plants and organisms in the littoral, which disappeared in major part of the lakes worldwide. Lake Baikal remains a unique object of studies of protobiogeochemical processes.

Chemical state of the Earth crust and biosphere is completely determined by the life of organisms, water influence and chemicals migration (Vernadsky, 1962). A particular role in this system belongs to interreaction between water and rocks with biota participation as only due to this interreaction, the elements

necessary for functioning of aquatic cenosis are supplied permanently (Shvartsev, 2007).

Besides organogens C, H, O, N, P, S, basis of any living system includes nutrients K, Na, C, Mg, Mn, Fe, Co, Cu, Zn, Mo, biogenic non-metallic elements Cl, Br, Si, As and metals Li, Sn, Ti, V, Cr. Metals, thanks to their high catalytic ability, provide a high activity of metalloenzymes and of other metalliferous biomolecules (Haraguchi, 2004). The most important role of metals as primary catalysts in formation and evolution of metabolic systems and metals mineral sources are presented in the papers by M. A. Fedonkin (Fedonkin, 2003). He believes that during the Earth evolutionary process, the geochemical basis of life is narrowing. Burying of chemicals on stable continents supposes their excision from the geochemical turnover. In rift zones and on continents tectonic margins, one can observe primary processes of biogeochemical interreactions of water and biota with ancient magmatic and metamorphic rocks. The accessibility of biophile macro- and microelements determines the productivity and biodiversity in the shore zone of the interreaction between water and rocks. The stony littoral of Lake Baikal represents a unique object for study of protobiogeochemical processes and for revealing of the role of biota in the involving of macro- and microelements into biogeochemical turnover and into re-distribution of chemicals between rocks, benthic and planktonic organisms and water (Suturin et al., 2003) (Figure 1).

Almost the half of Lake Baikal shore is represented by hoes consisting of bedrocks. Tectonic genesis of Lake Baikal and seismic activity provide permanent income of clastogene material and its deposition in the bench zone. Shores abrasion and landslides bring each year into the lake basin more than 1550 thousands m<sup>3</sup> of stony material. The bench stony material under the conditions of a freshwater body may serve as a source of biophile elements diversity for benthic organisms.

For ultraoligotrophic lakes such as Lake Baikal, the income of biophile elements only from aquatic environment is limited. The processes of rocks decomposition occur under the impact of Baikal water, and its aggressiveness towards the majority of materials is determined by undersaturation by majority of ions

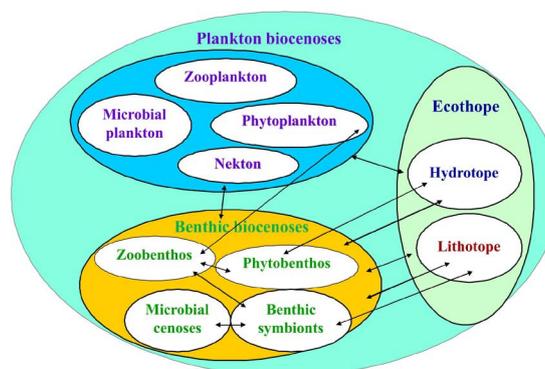


Figure 1. Littoral biogeocenoses.

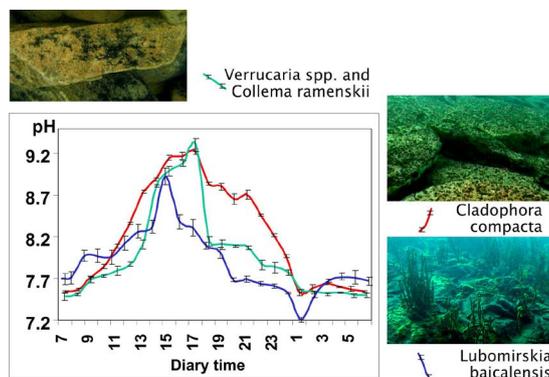
and cations, presence of dissolved oxygen, carbon dioxide and nitrogen, concentrations of which vary during 24 hours (pH 7.4 up to 8.5, oxygen from 87% to 117% of saturation) (Figure 2). One of the causes of minerals degradation in the littoral rocks is variation of physical and chemical parameters during 24 hours. Algae, sponges and water lichens emit during the nighttime  $\text{CO}_2$ , resulting in pH decrease, and during the daytime on the background of absorption of  $\text{CO}_2$  and emission of oxygen, the pH increases from 3 p.m. to 6 p.m. Day and night experiments with each hydrobiont confirmed this hypothesis. Under stony littoral conditions, rocks decomposition is more intensive than on the surface. Under the conditions of littoral with permanent transport of dissolved elements via aquatic environment and of regular variations of carbon dioxide and oxygen concentrations in the water, the leaching process considerably accelerates.

## 2. Objects and Methods

Petrographic analysis of horn and bench rocks from different sites of Lake Baikal was performed. The rocks of stony littoral were studied additionally for grain degree, character of surface sculpture, minerals resistance to processes of aquatic hydrolysis. Stones from the depths of 3 - 15 m were provided by divers. For each sample, species composition of hydrobionts was described, links between hydrobionts amount and diversity and rocks composition and their variety degree were determined.

Samples of hydrobionts (lichens, caddis flies, molluscs, ostracods, amphipods, sponges) collected from stones were subsequently washed in bidistilled water. Washed samples were placed in plastic cups with deionized water and subjected to ultrasound impact. Samples of sponges of branchy shape were divided into parts differing by density, color, amount of mechanical admixtures. Sponges of ball and crust shapes were divided into samples of outer and inner layer, anchoring sole and skeleton.

Samples washed from the admixtures were rinsed with bidistilled water and brought to airy-dry state. Then they were pounded in an agate mortar, and mean samples were composed. Using quartering method, an analytical sample was



**Figure 2.** Diary dynamics of pH parameters in the water layer above different Baikalian hydrobionts.

taken from each sample, it was pounded up to powder concentration in an agate mortar and brought to a constant weight at the temperature of 105°C. Then analytical samples were decomposed in fluoroplastic crucibles at ultrasound impact with mixture of nitric, hydrofluoric and perchloric acids.

Elemental composition of samples was determined using ICP-MS method. The analysis was performed at quadrupole mass-spectrometer "PlasmaQuad PQ2" of British company "VG Instruments". All samples and elements standard solutions represented solutions in 2% HNO<sub>3</sub>. The character of interreaction between rocks and biota was determined using electronic microscopy.

### 3. Results and Discussion

Near-shore outcrops are represented by pre-Cambrian metamorphic rocks subject to an intensive cataclasis and weathering processes.

An intensive rocks hydrolysis and congruent decomposition of carbonate strings. Favorable conditions for formation of original aquatic biogeocenoses are formed on the bench: the abundance of bottom invertebrates is 10 - 44 thousands of specimens per 1 m<sup>2</sup>. There are here at a limited territory more than 250 invertebrates species. The biodiversity of benthic organisms is due to combination of several factors: non-grained debris, presence on them of fragments of rocks subject to surface weathering, diversity of rocks petrographic and geochemical composition. The last factor determines the biodiversity of stony littoral.

Non-grained blocks with a complex surface structure are inhabited mainly by algae, lichens, sponges, molluscs, ostracods and caddis flies.

Rocks hydrolysis results from manifold renewal of waters composition. Under subaquatic conditions, there are two factors—elimination of hydrolysis products from the active zone and variation of ratio of oxygen and carbon dioxide in the water during 24 hours. Variation of waters pH towards alkaline composition results in elimination of aluminum and silicon released at aluminosilicates decomposition.

Under the impact of water with high content of carbon dioxide and low content of calcium hydrocarbonate in the solution, the reaction:  $\text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{Ca}(\text{HCO}_3)_2$  will be shifted towards alkaline composition. Hydrolysis results in replacement of cations of alkaline and alkaline-earth elements in the crystal lattice by hydrogen ions from dissociated water molecules.

Hydration is also due to the water activity. Ferric iron coagulates and falls out, ferrous one also falls out after a rapid acidification. Ferruginous silicates are subjected to acidification among first ones.

Biological weathering supposes physical and chemical changes in rocks and minerals under the impact of hydrobionts and their byproducts. The organisms extract from a rock minerals and accumulate them transforming the excess into a solution. Phytobenthic organisms form organic acids (oxalic, citric, malic, succinic ones), which destroy minerals. Nitrifiers compose nitric acid, sulfur bacte-

ria and thionic ones—sulfuric acid. Lichens emit carbon dioxide and specific acids and destroy the rocks both in chemical and in mechanical way due to hyphae penetration into cleavage surfaces of primary minerals. Sponges develop after lichens using their composition for building of their organisms as well as borrowing initially prepared by lichens stones surface (Figure 3).

Rocks weathering degree is important for the development of benthic algae, epilithic crustose lichens and sponges. Great porosity of stones outer frame, preliminary decomposition of primary rocks provide better anchoring of hydrobionts and simplifies getting of minerals from the rocks (Figure 4).

Even within one stone, one can see difference in minerals resistance to chemical and biological decomposition. Quartz grains, garnet strings and albite contractions remain fresh, not subjected to weathering and not occupied by lichens, algae and crust sponges (Table 1). The degree of minerals resistance to interaction of Baikal water was determined using petrography and electronic microscopy of the rock surfaces, to which benthic organisms attached themselves. Only quartz remained non-variable among all the minerals.



Figure 3. A stone “corroded” by a sponge.

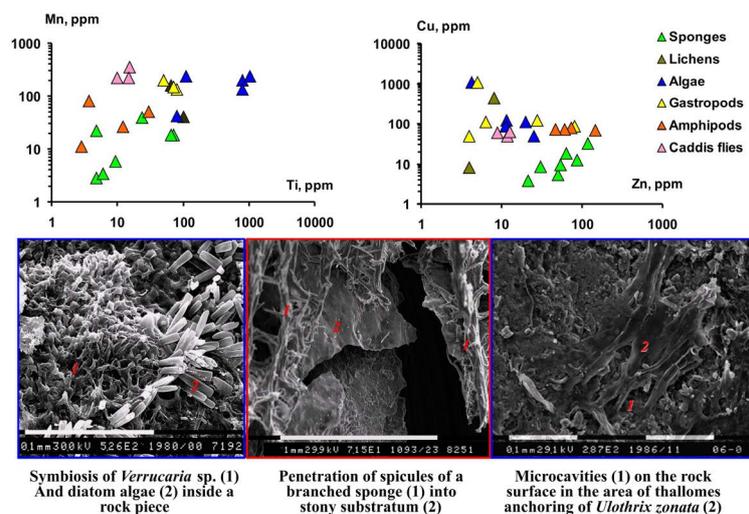


Figure 4. Character of interaction between hydrobionts and a rock and character of microelements accumulation in them.

**Table 1.** Minerals resistance in Lake Baikal littoral.

| Very resistant | Resistant              | Weakly resistant | Non-resistant |
|----------------|------------------------|------------------|---------------|
| Quartz         | Orthoclase             | Muscovite        | Anorthite     |
|                | Albite                 | Muscovite        | Biotite       |
|                | Almandine              | Microcline       | Magnetite     |
|                | Titaniferous magnetite | Hematite         | Pyroxenes     |
|                |                        | Amphiboles       | Olivine       |
|                |                        | Grossular        | Apatite       |
|                |                        | Epidote          | Calcite       |
|                |                        |                  | Dolomite      |
|                |                        |                  | Hydroxides    |

The analysis of stony littoral biogeocenoses showed an important role of hydrobionts in rocks destruction. An especial role in aluminosilicates decomposition belongs to diatom algae. The algae cover first of all weathered, clayed rocks; while destroying clays, they get necessary for them deficit silica.

Such symbiotic organisms as lichens and sponges play an important role in stony littoral biogeocenoses. They provide extraction of phosphorus from rocks and nitrogen fixation. Symbiont cenosis of a fungus with green and blue-green algae includes as well azotobacter. Polysymbiont cenosis get the ability to fixe dissolved in the water nitrogen. Terrestrial crustose lichens form up to 250 acids. Oxalic acid provides calcium extraction. Chelation is basic process of rocks disintegration and extraction of metals, calcium and magnesium by lichens.

Study of biogeochemical role of underwater lichens showed that they inhabit stony littoral selectively according to petrographic and mineralogical composition. Maximal lichens abundance is found in near-shore, shallow-water (up to 3 m) zone. Crustose lichens are mainly found on amphibolites, as well as on mica string in plagiogranites. The intensity row of elements consuming by lichens is specific:

| I        | II            | III                  | IV     |
|----------|---------------|----------------------|--------|
| P, S, Ca | K, Na, Mg, Mn | Fe, SiO <sub>2</sub> | Ti, Al |

Extracting elements of first and second groups for their organisms building, aquatic lichens release elements from groups III and IV, which are actively used by other hydrobionts, first of all, by sponges (**Figure 5**).

Study of macro- and microelemental composition of Baikalian benthic organisms showed the specifics of elements concentration by different groups of hydrobionts.

Anchored forms of symbiotic hydrobionts, first of all, lichens concentrate a considerable amount of elements. A geochemical peculiarity of lichens is accumulation of elements, the transfer of which by water is difficult. These are titanium, gallium and rare-earth elements. Extraction of rare-earth elements from weathered rocks is a specific feature of fungi, which are main lichens' symbionts. This is determined by fungi ability to absorb and adsorb rare-earth elements and to form composition of rare-earth elements with fungi metabolites. In sponges, especially in their top parts, such biophile elements as sodium, potassium, phosphorus and copper are concentrated. There are in sponges bottom part elevated concentrations of manganese, nickel, lanthanum. The sponges accumulate lead, cadmium and thorium (Figure 6). It is seen from Figure 6 that from sole (1) of the sponge to its upper (4), the concentrations of such sparingly soluble elements as Ti, Co, Mo, rare earth elements and Th decrease. Chalcophylic elements (Cu, Cd, Pb) have the same concentrations in the whole sponge. This suggests that the sponges use for their vital activity different sources of chemical elements, i.e., stony substratum and water. Molluscs and ostracods are characterized by an elevated content of alkaline-earth elements. It is characteristic for them as well to accumulate sulfur, selenium and arsenic. Amphipods are characterized by high phosphorus content. Among microelements, they show contrast high values of zinc concentrations. Caddis flies are particular only by magnesium content.

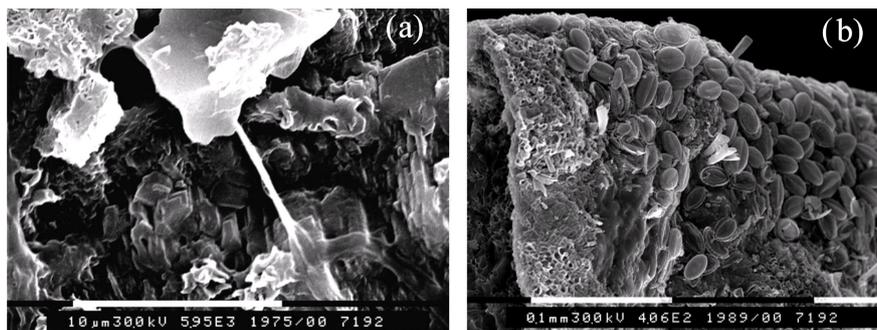


Figure 5. The character of interaction between benthic organisms and rocks: (a) Thalloses and hyphae of *Verrucaria* sp. inside a rock piece; (b) Diatom algae on the thalloses of *Collema ramenskii*.

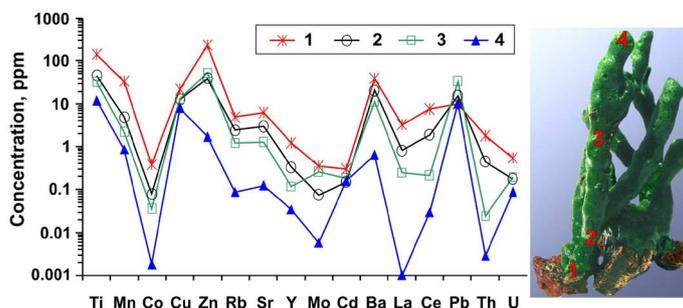


Figure 6. Microelements distribution in Baikalian sponges *Lubomirskia baicalensis*: 1—sole, 2—lower part, 3—middle part, 4—upper (osculum) part.

## 4. Conclusion

Biogeocenoses, in which bedding stone substratum serves as a source of biophile elements for zoo- and phytobenthos, form in Lake Baikal littoral zone. Income of additional components into benthic biocenosis occurs both due to leaching of elements with water from rocks and due to life activity of symbiont organisms. Petrographic and geochemical composition of stony substratum is important for biogeocenoses productivity and biodiversity. Biogeochemical processes on Lake Baikal stony littoral provide biodiversity and bioproductivity of benthic hydrobionts. Process of biogeochemical extraction of macro- and microelements from rocks has similar features for stony littoral of oceans and rift lakes. The biogeocenosis of Lake Baikal stony littoral, which formed during several millions of years, is destroyed due to surface and subaquatic drainage of anthropogenically polluted waters (Kulikova et al., 2017; Sutorin et al., 2016). On one hand, the incoming flows of biophile elements replace complex biogeochemical processes of extraction of necessary elements from rocks. On the other hand, heterotrophs and micromycetes of intestinal flora annihilate symbiotic cenosis of the stony littoral. Such non-characteristics for Lake Baikal littoral biocenoses as Spirogira and Elodea start developing instead of existing endemic benthic belts of algae. Ecological crisis in Lake Baikal littoral is mainly anthropogenic processes resulting in destruction of existing benthic biocenoses.

## Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

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