

Biogeochemical Characteristics of Dominant Gastropod Species from the Stony Littoral of Southern Baikal

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Abstract—The trace element composition of dominant gastropod species from the littoral of southern Baikal was investigated. Both different mollusk species and their parts (shells and soft tissues) show specific trace element characteristics. The highest Sr and Ba contents were observed in *Maackia herderiana*. The highest Zn, Cu, and Cd and lowest Pb contents were detected in *Megalovalvata baicalensis*. *Choanomphalus* sp. shows high Mn and Ti and very low Sr, Cu, and Cd contents. Most of Cu, Zn, and Cd and a considerable fraction of Rb, Pb, Mo, Sc, Ce, W, Ga, Y, and Th are incorporated in the gastropod bodies. The maximum concentration of U is also characteristic of the body tissues. The foot tissues of *Maackia herderiana* and *Megalovalvata baicalensis* are depleted in the majority of elements compared with their bodies. Sr and Ba are prevalent in the mollusk shells, where high Mn contents were also detected. A close relationship was observed between the chemical compositions of the gastropods, stony substrate, and bottom water. Group concentration of trace elements is common in the species investigated. Relative to the bottom water layer, the gastropod species concentrate Ti, Mn, La, Co, Y, and V and show similarly low extraction of U, W, Mo, and Cs. Compared with the bottom sediments, the mollusks accumulate Sr. In addition, *Maackia herderiana* and *Megalovalvata baicalensis* accumulate Cd and Zn. *Megalovalvata baicalensis* is distinguished by the ability to concentrate Cu. The following sequence is formed by the gastropods with respect to their capacity to accumulate Cd, Zn, and Cu: *Megalovalvata baicalensis* > *Maackia herderiana* > *Choanomphalus* sp.

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INTRODUCTION

“In any organism, in its elemental chemical composition, we observe the expression of its geochemical role. Organisms do not exist beyond the geochemical processes occurring in the biosphere. In this context, the geochemical role of a particular organism may be distinguished only quantitatively” [1].

Species of living organisms differ not only in appearance, anatomic features, and physiologic characteristics but also in chemical composition, which is controlled by the taxonomic status of living organisms and geochemical features of the landscape [2]. Living organisms selectively absorb almost all the elements of Mendeleev’s Periodic Table to varying degree in accordance with their physiological demands. Of special importance are C, H, O, N (comprising more than 98% of the mass of living matter), P, K, S, Ca, Mg, Si, Fe, and other elements necessary to all organisms for the construction of structural organs, growth, and reproduction. The same elements form the basis of the hydrosphere, atmosphere, and rocks [3].

The littoral zone of southern Baikal, which is an ultraoligotrophic lake, hosts peculiar aquatic biogeocenoses with very high populations (10–44 thousands of individuals per square meter) and biodiversity

(more than 250 invertebrate species). The chemical elements necessary for zoo- and phyto-benthos are acquired from the stony substrate. The supply of components into the benthos biocenosis occurs at the expense of both leaching of chemical elements from the rocks by water and the living activity of organisms [4].

Aquatic invertebrates, including gastropods, are a necessary element in the chain of biogeochemical processes contributing to the fluxes of chemical elements.

The malacofauna of Lake Baikal includes 179 species, 79% of which are gastropods. With respect to the number of species, gastropods are fourth among the invertebrates of Baikal inferior only to amphipods, infusorians, and oligochaetes [5]. Endemic gastropod species account for a considerable fraction (98%) of the biomass of macrobenthic animals in Baikal [6] and are indicators of the habitat [7].

The investigations of the average contents of chemical elements in the biota of Lake Baikal in the context of ecological geochemistry and for the determination of bioindicators of the hydrogeochemical state of the bottom water layer and bottom sediments in the shore zone were launched in the early 1970s by the researchers of the Institute of Applied Geophysics of Gosko-

mgidromet of the USSR, Vinogradov Institute of Geochemistry, and the Institute of Limnology, Siberian Division, Russian Academy of Sciences, and had continued for about two decades. During that period, the elemental chemical composition of soft tissues (body, muscles, liver, and gills) was determined in some gastropods and bivalves, including *Benedictia baicalensis* (southern Baikal, B. Koty Bay) [8, 9] and *Anodonta piscinalis* (coastal zone near the town of Baikalsk; Maloe More, Zagli-Nur Bay) [10–12]. Gastropods show the highest capacity to accumulate chemical elements. According to [8], their tissue concentrate Sc, V, Cr, Mn, Fe, Co, Cu, Zn, Se, Rb, Ag, Cs, La, and Th is relative to seawater.

Gastropods are dominant in the stony littoral of southern Baikal at depths from 2 to 5 m. Their population and biomass show only minor seasonal variations. Among the most abundant species are *Maackia herderiana* (family Baicaliidae), *Megalovalvata baicalensis* (family Valvatidae), *Choanomphalus maacki*, and *Choanomphalus amaaronius* (family Planorbidae) [13].

The goal of this study is to provide biogeochemical characteristics and elucidate the geochemical role of the dominant gastropod species from the coastal zone of southern Baikal.

MATERIALS AND METHODS

The dominant species from the littoral of southern Baikal were used for the investigation of the elemental chemical composition of gastropods. They were collected from various depths (1.5, 3, and 5–10 m) over two years (2003 and 2004) in about the same periods: February, March, April, May, June, October, and November.

Gastropod mollusks were collected into plastic containers with Baikal water from rock fragments and raised by a diver (5 to 10 fragments at each sampling site depending on their sizes). Individuals of each species were kept in distilled water without food for a week and then divided into two parts: samples of whole individuals and samples consisting of separate bodies, feet, opercula, and shells of mollusks. The thickness of the shells was measured at the palatal rim of their aperture with an accuracy of 0.01 mm under a stereoscopic microscope. The masses of bodies and shells (before drying) were determined using a torsion balance with an accuracy of 0.5 mg.

The collected material was carefully washed with distilled water and purged by rotation in a magnetic mixer in a glass with distilled water; the remnants of various admixtures were removed under a binocular microscope, after which the samples were washed with double-distilled water. The samples were allowed to air dry at 30°C and then ground in an agate mortar with the addition of several drops of rectified ethyl alcohol. Each ground sample was loaded into a glass flask and dried to a constant weight at a temperature of 105°C for

5–6 h. The samples were prepared for analysis using the method of acid mineralization with a mixture of nitric, hydrofluoric, and chloric acids in Teflon beakers.

Bottom water was sampled by a diver using plastic syringes at a distance of 10–15 cm from the bottom. Immediately after the uplift, the water samples were filtered through a membrane filter with a pore size of 0.4 µm and acidified with 2% HNO₃. The water samples were stored in a refrigerator before analysis.

The elemental composition of the samples was determined by the ICP MS method using a Plasma Quad PQ2+ (Thermo Elemental) quadrupole mass spectrometer. The instrument was calibrated on the basis of the GSORM State Standard Solutions. The samples were diluted with deionized water. All the samples and element standards were 2% HNO₃ solutions. In order to correct for the instrumental drift and matrix effect, an internal standard (In) was introduced into the solutions. The assessment of the accuracy of elemental determination was performed using candidate reference materials: the dry residue of Baikal water, perch tissue from Lake Baikal, and an aquatic plant from Lake Baikal (*Elodea canadensis*) [14].

The difference between the trace element compositions of bodies, feet, opercula, and shells was characterized by the biogeochemical parameter CRPO, which was proposed for plants by Kovalevskii [15] as the ratio of element contents in various organs of plants. CRPO is the ratio $C_o/C_{t.o}$, where C_o is the content of the element in the organ, and $C_{t.o}$ is the content in a reference object (usually in old branches, wood, and roots), in our case, a gastropod shell.

The degree of the biologic accumulation of elements in gastropods was estimated relative to water and bottom sediments by means of the coefficient of biologic absorption [16, 8] calculated for dry matter: $K_a(K_d) = C_{ig}/C_{is}$, where K_a is the coefficient of biological absorption relative to the trace element composition of water, K_d is the coefficient relative to the composition of bottom sediments, C_{ig} is the concentration of the i th element in the dry gastropod biomass in ppm, and C_{is} is the concentration of the same element in the dry mineral residue of Baikal water or bottom sediments (habitat). In order to calculate K_d and construct trace element distribution patterns for the objects studied, the arithmetic mean contents of trace elements in the coastal and deep-water sands of Lake Baikal were used. According to Pampura et al. [17], they can be considered as the first average estimates of the abundances of elements in Baikal sediments. In our opinion, the average elemental composition of the coastal and deep-water sands adequately reflects the average compositions of rocks from the bottom of the Listvennichnyi Bay.

The coastal rocky exposures in the region of the Listvennichnyi Bay in southern Baikal are composed of Precambrian metamorphic rocks, which experienced extensive cataclasis and weathering. Most of the rocks

are gneissose plagiogranites. They host zones of microcline granitoids and stringers and veins of microcline and albite rocks. Zones of plagioclase rocks with veinlets and aggregates of almandine garnet were also documented. The plagiogranites contain amphibolite layers and clots. Some zones of plagioclase rocks are cut by calcite veins and stringers. A lake-facing abrasion terrace is built up of the same rocks as the cliff, but they are strongly altered by the hydrolysis processes. The incrustations of iron and manganese hydroxides are completely desorbed; the rocks are affected by extensive aquatic weathering, including primarily the congruent decomposition of carbonate veinlets [4].

ELEMENTAL COMPOSITION OF MOLLUSKS

The chemical compositions of the gastropod species are dominated by the elements characteristic of living matter, including Ba, Sr, Mn, Ti, Zn, Cu, Ni, and Co. On the other hand, the average trace-element contents (Table 1) form the following sequence of trace element concentration for each species.

Maackia herderiana: Sr > Ba > Mn > Ti > Zn > Cu > Ni > V > Co > Pb > Rb > Cd > Zr > Ce > La > Mo > U > Sc > Nb > Y > Ga > Ge > W > Th > Cs;

Megalovalvata baicalensis: Sr > Mn > Zn > Cu > Ti > Ba > V > Ni > Cd > Rb > Co > Zr > U > Mo > La > Ce = Pb > Sc > Y > Nb > Ga > W = Ge > Cs > Th;

Choanomphalus sp.: Sr > Mn > Ti > Zn > Ba > Ni > V > Cu > Rb > Co > Pb > Zr > Ce > La > U > Sc > Mo > Y > Cd > Ga > Nb > Th > W > Ge > Cs.

The maximum Sr and Ba and high Ti concentrations were found in the slow-moving Baicaliidea *Maackia herderiana* the stomach of which contains mainly plankton diatoms [18]. The maximum Zn, Cu, and Cd and the minimum Pb contents are characteristic of the Valvata *Megalovalvata baicalensis* which "pastures" on the surface of stones often covered by sponges of the genera *Lubomirskia* and *Baicalospongia*. The chyme of *M. baicalensis* contains considerable amounts of sponge spicules and symbiont green algae [18], which show high contents of Cu (280–530 µg/g dry material), Zn (85–170), and Cd (7.5–10.0). The species *Choanomphalus* sp. consumes benthic diatoms [18] and shows high contents of Mn and Ti and extremely low contents of Sr, Cu, and Cd.

The contents of Sr, Ba, Ti, Mn, Ni, Co, V, Cd, Nb, and U in the gastropods from the littoral of southern Baikal are several times higher than the levels of these elements in the average composition of mollusks [19] or average concentrations conventionally accepted as background values for the hydrobionts of freshwater ecosystems [2] (Table 2).

ELEMENTAL COMPOSITION OF MOLLUSK SHELLS

Gastropods perform tremendous work to accumulate Ca in their shells. It is known that the content of CaCO₃ in shells is usually higher than 97%, and the remaining fraction is represented by the organic substance conchiolin [1]. The shell of Baikal gastropods is thin, its thickness is no greater than 0.2 mm and accounts for 36–49% of the mass of *Megalovalvata baicalensis* 68–75 wt % of *Choanomphalus* sp., and 61–80 wt % of *Maackia herderiana*. The dry mass of the shells of the species studied contains 34–37% Ca. The cold and low mineralized water of Baikal [20] is not favorable for more extensive precipitation of calcium carbonate in the shell of Baikal gastropods.

Sr and Ba are the most abundant trace elements in the shells of the gastropod species. High content of Mn (Table 1) and similarly low Cd (0.02–0.04 µg/g of dry mass) and Cu (1.34–2.66) were detected. The presence of Mn, from traces to 0.023%, in the shells of freshwater mollusks was reported as early as 1872 by Döring [1]. It is notable that the shells of *Maackia herderiana*, *Megalovalvata baicalensis*, and *Choanomphalus* sp. contain significant amounts of a number of elements typical of the bone and epithelium tissues of mammals (Sr, Ba, Mn, V, and Ti) [21]. The shells of *Maackia herderiana* show the maximum contents of Sr and Ba and differ from the shells of *Megalovalvata baicalensis* and *Choanomphalus* sp. in lower Mn contents. The concentrations of U in the shells are similar and lower than in the bodies of the gastropods. This difference is especially distinct in the movable species *Megalovalvata baicalensis* and *Choanomphalus* sp. (Table 1), which scrape food from rock fragments. The content of U in marine gastropods is usually within 0.0001–0.01 µg/g of dry mass, which is significantly lower than in the Baikal mollusks. Gastropod shells with elevated U contents (0.433 µg/g of dry mass) were found in offshore California [22].

ELEMENTAL COMPOSITION OF MOLLUSK TISSUES

The bulk chemical composition of mollusks is sharply different from the compositions of their particular parts. Table 3 shows the ratios of trace element contents in the soft tissues of the gastropod species to the contents of the same elements in the shells. It can be seen from Table 3 that the body is depleted relative to the shell in Sr, Ba, Ti (*M. herderiana* and *M. baicalensis*), Mn, Ni, and V, whereas the main portion of Cu, Zn, and Cd and significant fractions of Rb, Pb, Mo, Sc, Ce, W, Ga, Th, and Y occur in the body. With respect to Cd and Cu contents in soft tissues, the gastropod species form the following sequence: *Megalovalvata baicalensis* > *Maackia herderiana* > *Choanomphalus* sp. The maximum concentration of U was detected in the body tissues of gastropods. With respect to U content in bod-

Table 1. Average contents of trace elements in the gastropods of southern Baikal, µg/g of dry mass

Element	<i>Maackia herderiana</i>					<i>Megalovalvata baicalensis</i>				<i>Choanophthalus</i> sp.		
	Individual	Shell	Body	Foot	Operculum	Individual	Shell	Body	Foot	Individual	Shell	Body
	*402 (8)	1069 (16)	1017 (13)	678 (6)	490 (1)	37 (1)	37 (5)	56 (5)	16 (1)	318 (7)	230 (7)	137 (5)
Sc	0.19 ± 0.03	0.18 ± 0.03	0.42 ± 0.11	0.35 ± 0.10	0.47	0.18	0.18 ± 0.04	0.24 ± 0.15	0.39	0.42 ± 0.24	0.17 ± 0.02	0.47 ± 0.19
Ti	80.1 ± 31.0	44.1 ± 10.9	37.8 ± 14.9	22.8 ± 7.1	13.05	42.59	15.8 ± 5.8	13.98 ± 1.14	5.27	91.2 ± 27.2	39.7 ± 30.2	51.3 ± 15.5
V	11.3 ± 4.8	13.6 ± 5.6	4.83 ± 0.06	1.35 ± 0.91	n.d.	11.28	9.99 ± 6.82	1.90 ± 0.24	10.56	10.1 ± 5.7	10.9 ± 6.4	6.71 ± 3.22
Mn	134.5 ± 25.6	132.6 ± 37.1	106.1 ± 22.4	16.5 ± 3.5	72.86	148.36	205.0 ± 80.9	99.4 ± 20.4	39.91	201.2 ± 69.4	221.7 ± 92.0	69.2 ± 21.9
Co	1.03 ± 0.10	1.01 ± 0.07	0.53 ± 0.21	0.23 ± 0.14	n.d.	1.00	0.93 ± 0.33	1.31 ± 0.14	0.20	1.28 ± 0.54	0.84 ± 0.34	0.65 ± 0.29
Ni	11.3 ± 0.8	11.5 ± 0.8	1.76 ± 0.45	1.93 ± 0.81	3.95	9.79	11.5 ± 3.9	3.60 ± 0.31	1.04	12.2 ± 0.7	9.9 ± 3.7	3.08 ± 1.46
Cu	27.6 ± 10.2	1.34 ± 0.65	71.2 ± 15.0	10.37 ± 1.96	2.31	81.45	2.66 ± 1.21	210.1 ± 67.4	23.61	6.44 ± 1.22	1.71 ± 0.61	19.2 ± 10.4
Zn	40.3 ± 11.1	9.15 ± 2.16	84.0 ± 10.9	51.2 ± 9.0	17.55	102.71	7.4 ± 3.6	253.8 ± 22.5	51.05	38.5 ± 12.7	12.0 ± 6.4	51.8 ± 22.9
Ga	0.07 ± 0.01	0.07 ± 0.02	0.08 ± 0.03	0.03 ± 0.01	0.03	0.06	0.06 ± 0.03	0.05 ± 0.01	0.03	0.22 ± 0.11	0.09 ± 0.04	0.18 ± 0.09
Ge	0.04 ± 0.01	0.08 ± 0.03	n.d.	0.002 ± 0.001	n.d.	0.04	0.05 ± 0.03	n.d.	0.02	0.03 ± 0.02	0.06 ± 0.02	0.02 ± 0.01
Rb	0.67 ± 0.18	0.47 ± 0.15	0.59 ± 0.30	0.47 ± 0.30	0.06	1.22	0.21 ± 0.10	2.43 ± 0.96	4.02	1.63 ± 0.66	0.39 ± 0.18	0.76 ± 0.35
Sr	425.3 ± 14.9	462.8 ± 32.8	64.6 ± 18.4	81.4 ± 17.9	10.32	329.11	208.3 ± 39.9	18.8 ± 5.0	23.83	267.2 ± 13.8	255.2 ± 86.9	43.7 ± 14.6
Y	0.11 ± 0.04	0.09 ± 0.02	0.08 ± 0.05	0.02 ± 0.008	0.05	0.17	0.05 ± 0.02	0.06 ± 0.03	0.01	0.27 ± 0.10	0.11 ± 0.09	0.54 ± 0.19
Zr	0.54 ± 0.07	0.45 ± 0.15	0.49 ± 0.34	0.13 ± 0.09	n.d.	0.52	0.21 ± 0.17	0.15 ± 0.10	H.o.	1.08 ± 0.56	0.70 ± 0.39	0.60 ± 0.35
Nb	0.18 ± 0.12	0.10 ± 0.02	0.04 ± 0.038	0.04 ± 0.02	0.06	0.13	0.07 ± 0.03	0.02 ± 0.01	0.01	0.16 ± 0.06	0.11 ± 0.06	0.15 ± 0.03
Mo	0.34 ± 0.04	0.25 ± 0.02	0.70 ± 0.16	0.24 ± 0.09	0.10	0.30	0.09 ± 0.04	0.70 ± 0.06	0.16	0.35 ± 0.10	0.18 ± 0.06	0.49 ± 0.14
Cd	0.66 ± 0.11	0.03 ± 0.01	1.67 ± 1.06	0.15 ± 0.03	0.13	1.70	0.02 ± 0.014	7.39 ± 1.23	0.61	0.24 ± 0.06	0.04 ± 0.01	0.23 ± 0.16
Cs	0.02 ± 0.01	0.01 ± 0.003	0.01 ± 0.004	0.02 ± 0.006	0.01	0.01	0.01 ± 0.003	0.01 ± 0.006	0.01	0.02 ± 0.01	0.01 ± 0.005	0.01 ± 0.02
Ba	143.0 ± 75.0	136.0 ± 23.5	56.2 ± 18.3	33.0 ± 8.1	4.32	19.34	18.1 ± 1.6	7.71 ± 2.21	6.27	35.2 ± 7.8	32.2 ± 7.0	22.8 ± 7.8
La	0.37 ± 0.09	0.39 ± 0.12	0.15 ± 0.07	0.05 ± 0.03	0.09	0.28	0.36 ± 0.04	0.15 ± 0.05	0.03	0.64 ± 0.35	0.47 ± 0.25	0.62 ± 0.30
Ce	0.39 ± 0.18	0.29 ± 0.11	0.24 ± 0.15	0.03 ± 0.01	0.17	0.19	0.09 ± 0.02	0.16 ± 0.02	0.03	0.74 ± 0.31	0.51 ± 0.29	1.21 ± 0.56
W	0.04 ± 0.01	0.04 ± 0.01	0.04 ± 0.03	0.06 ± 0.04	0.06	0.02	0.03 ± 0.01	0.05 ± 0.03	0.01	0.04 ± 0.03	0.02 ± 0.006	0.05 ± 0.02
Pb	0.80 ± 0.38	0.69 ± 0.10	1.25 ± 0.69	0.67 ± 0.48	0.38	0.19	0.26 ± 0.18	1.28 ± 0.31	0.49	1.15 ± 0.63	0.99 ± 0.75	2.97 ± 0.86
Th	0.03 ± 0.01	0.01 ± 0.006	0.03 ± 0.01	0.01 ± 0.003	0.01	0.01	0.01 ± 0.005	0.02 ± 0.007	H.o.	0.05 ± 0.02	0.05 ± 0.01	0.19 ± 0.32
U	0.32 ± 0.05	0.31 ± 0.05	0.41 ± 0.14	0.06 ± 0.03	0.29	0.48	0.21 ± 0.12	1.31 ± 0.15	0.05	0.55 ± 0.13	0.25 ± 0.14	0.80 ± 0.36

Notes: Numbers in parentheses denote the number of analyzed samples. n.d. means not detected. Analyst L.F. Paradina.

* Total number of individuals or their parts.

Table 2. Comparison of (1) the trace element compositions of the Baikal gastropods *Maackia herderiana*, *Megalovalvata baicalensis*, and *Choanomphalus* sp. with (2) the average trace-element composition of mollusks [19] and (3) the abundances of chemical elements in freshwater hydrobionts, which are regarded as the background level [2]

Element	Ratios of trace element concentrations					
	<i>Maackia herderiana</i>		<i>Megalovalvata baicalensis</i>		<i>Choanomphalus</i> sp.	
	1 : 2	1 : 3	1 : 2	1 : 3	1 : 2	1 : 3
Sc	–	0.90	–	0.86	–	1.99
Ti	4.00	3.20	2.13	1.70	4.56	3.65
V	16.07	5.00	16.11	5.01	14.36	4.47
Mn	13.45	2.06	14.84	2.28	20.12	3.09
Co	0.51	4.68	0.50	4.55	0.64	5.82
Ni	2.83	0.89	2.45	0.77	3.06	0.96
Cu	1.38	0.88	4.07	2.61	0.32	0.21
Zn	0.20	0.26	0.51	0.66	0.19	0.25
Ga	–	0.38	–	0.34	–	1.26
Rb	0.03	0.08	0.06	0.16	0.08	0.21
Sr	7.09	56.70	5.49	43.88	4.45	35.63
Zr	–	0.60	–	0.58	–	1.20
Nb	–	7.32	–	5.42	–	6.49
Mo	0.17	0.30	0.15	0.26	0.18	0.31
Cd	0.22	2.21	0.57	5.67	0.08	0.81
Cs	–	0.03	–	0.02	–	0.03
Ba	47.67	27.50	6.45	3.72	11.75	6.78
La	–	0.29	–	0.22	–	0.51
Ce	–	0.22	–	0.11	–	0.42
W	0.80	6.67	0.40	3.33	0.89	7.38
Pb	1.14	0.76	0.27	0.18	1.64	1.09
Th	–	0.06	–	0.02	–	0.10
U	–	2.01	–	3.00	–	3.41

Note: Dashes mean no data.

ies, the mollusks form the following sequence: *Megalovalvata baicalensis* > *Choanomphalus* sp. > *Maackia herderiana* (Table 1).

The foot tissues of *Maackia herderiana* and *Megalovalvata baicalensis* are depleted in most trace elements compared with their bodies. The concentrations of trace elements in the feet form the following sequences: Sr > Zn > Ba > Ti > Mn > Cu > Ni > V for *M. herderiana* and Zn > Mn > Sr > Cu > V > Ba > Ti > Rb > Ni for *M. baicalensis*. The foot tissues of these species are enriched relative to the shells in Cs, Cu, Zn, Cd, and W (*M. herderiana*), and Pb and Mo (*M. baicalensis*). The concentrations of Rb in the samples of the body and, especially, foot tissue of *baicalensis* are much higher than in their shells (Table 3).

Gastropods of the prosobranch group have an operculum, which serves to close the shell aperture. It is dominated by organic matter, and its inorganic constituent is usually composed of CaCO₃ [1]. Among other

elements, the operculum of *Maackia herderiana* contains relatively large amounts of Mn > Zn > Ti > Sr > Ba > Ni > Cu (Table 1).

The bodies of the gastropod species are enriched in Cu, Zn, Cd, Mo, Rb, and U and depleted in Mn, Sr, Ba, Ti, Co, Ni, V, Y, La, Ce, and W (from 0.02 to $n \times 10^{-6}\%$) relative to their shells. All these elements participate to a varying degree in important living processes. There are no specific biogenic chemical elements for living organisms. All the elements of the biosphere are captured by them [23]. The presence of particular concentrations of chemical elements in living organisms suggests by itself their definite biological role [21]. The pronounced influence of trace elements on physiological processes is explained by the fact that they occur in the composition of respiration pigments, vitamins, hormones, enzymes, coenzymes, etc.

The elevated Cu content in the gastropod bodies is probably related to the special role of Cu in the blood

Table 3. Trace element contents in the samples of bodies, feet, and opercula of gastropods normalized to the compositions of their shells

Element	<i>Maackia herderiana</i>			<i>Megalovalvata baicalensis</i>		<i>Choanomphalus</i> sp.
	Body/Shell	Foot/Shell	Operculum/Shell	Body/Shell	Foot/Shell	Body/Shell
Rb	1.25	0.99	0.13	11.72	19.37	1.97
Cs	1.05	1.33	0.89	0.75	1.00	1.63
Cu	52.97	7.72	1.72	78.90	8.87	11.23
Sr	0.14	0.18	0.02	0.09	0.11	0.17
Ba	0.41	0.24	0.03	0.42	0.35	0.71
Zn	9.18	5.60	1.92	34.05	6.85	4.31
Cd	54.63	4.79	4.24	369.50	30.50	5.86
Ga	1.14	0.50	0.45	0.72	0.48	1.98
Sc	2.32	1.94	2.58	1.34	2.23	2.70
Y	0.90	0.19	0.57	1.28	0.22	5.06
La	0.38	0.13	0.23	0.41	0.08	1.32
Ce	0.81	0.11	0.59	1.83	0.34	2.36
Th	2.29	1.22	0.92	2.00	n.d.	3.80
U	1.32	0.20	0.95	2.98	0.24	3.24
Ge	n.d.	0.02	n.d.	n.d.	0.38	0.24
Pb	1.81	0.97	0.55	4.90	1.88	3.02
Ti	0.86	0.52	0.30	0.83	0.33	1.29
Zr	1.09	0.29	n.d.	0.71	n.d.	0.86
V	0.35	0.10	n.d.	0.19	1.06	0.61
Nb	0.45	0.43	0.60	0.29	0.14	1.38
Mo	2.80	0.96	0.40	7.59	1.73	2.79
W	1.23	1.78	1.68	1.91	0.36	2.50
Mn	0.80	0.12	0.55	0.49	0.19	0.31
Co	0.52	0.23	n.d.	1.41	0.22	0.77
Ni	0.15	0.17	0.34	0.31	0.09	0.31

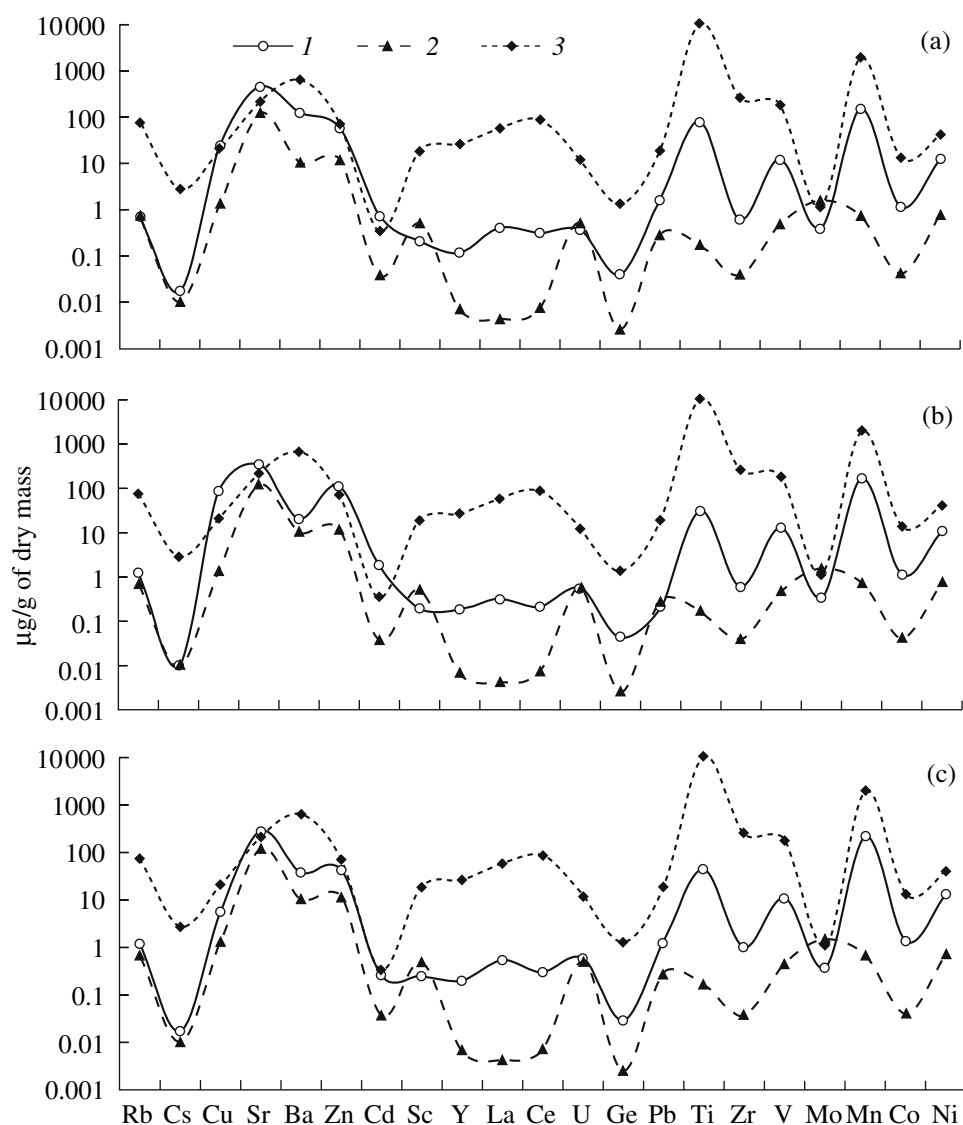
system, which was first noted by Harless, and the presence of copper-bearing proteins, hemocyanins, in blood and muscle tissues [1]. Elevated Cu, Zn, Cd, Pb, and Ni contents in the tissues of gastropods were reported in [24]. According to Martin and Flegel [25], the enrichment of Cu in the liver of *Loligo opalescens* (class Cephalopoda) correlates with high Cd and Zn contents. Among the microconcentrators of Cd are Neritidae, Viviparidae, Lymnaeidae, and Bulinidae gastropods from the background freshwater ecosystems of the European part of Russia, the Caucasus, and Tien Shan [2]. Low-molecular-weight proteins showing the properties of metalloproteins (peculiar proteins containing Zn, Cu, Cd, and Hg) were extracted from the organs of marine bivalves [26, 27].

The chemical composition of benthic invertebrates is formed in accordance with their species characteristics and the biological role of elements and is closely related to their abundances in the habitat (water and

bottom sediments). While the systematic status is of primary importance for major elements (physiological features of organisms were fixed by heredity during the period of species formation, after which animals and plants procured necessary components under any conditions, even from a poor soil and a poor water basin), the geochemical characteristics of the landscape are most important for many trace elements [3].

ACCUMULATION OF TRACE ELEMENTS BY MOLLUSKS RELATIVE TO WATER AND BOTTOM SEDIMENTS

The close relations between the elemental chemical compositions of gastropods, bottom sediments dominated by coarse detrital material, and near-bottom water layer are illustrated by the diagrams (figure). It is clearly seen that the lowest contents of the elements, except for Sc, Mo, and U, are characteristic of water,



Distribution of chemical elements in (1) the gastropods (a) *Maackia herderiana*, (b) *Megalovalvata baicalensis*, and (c) *Choa-nomphalus* sp.; (2) bottom water; and (3) bottom sediments of southern Baikal [17].

and the maximum contents, except for Cu, Sr, Cd, and Mo, were detected in the bottom sediments. The chemical compositions of gastropods are mainly intermediate in trace element contents. It can be easily seen that the maximum and minimum contents on the logarithmic curves of trace element concentrations in the bottom sediments and gastropods often coincide and show stronger differences from the curve of water composition. The positive anomalies of Mo and U, which are readily leached from rocks by oxygen-saturated water, and negative anomalies of Y, La, Ti, and Mn, which are relatively immobile in oxidizing environments, in the trace element distribution patterns of water are opposite to those in the trace element diagrams of bottom sediments and gastropods. In contrast, the positive anomaly

of Ba in the logarithmic curve of bottom sediment composition is accompanied by negative Ba anomalies in the compositions of water and gastropods (figure). The similarity of trace element distribution patterns in the gastropods and bottom sediments or in the gastropods and water indicates the existence of common physico-chemical and biological processes responsible for the concentration of elements by living matter, gastropods in the given case.

Among the nine triads that can be formed from the elements analyzed in the gastropods, water, and bottom sediments, Sc-Ti-V, Co-Ni-Cu, Ni-Cu-Zn, Cu-Zn-Ga, Rb-Sr-Y, Sr-Y-Zr, Y-Zr-Nb, Cs-Ba-La, and Ba-La-Ce, there are three triads, Sc-Ti-V, Co-Ni-Cu, and Ni-Cu-Zn, violating the Oddo-Harkins rule (aver-

age Galactic abundance of chemical elements with even atomic numbers is always higher than those of the neighboring elements with odd atomic numbers). The Oddo–Harkins rule is never simultaneously violated in the compositions of water, bottom sediments, and gastropods. The relations of Co–Ni–Cu and Ni–Cu–Zn are disturbed in the trace element compositions of water and gastropods, and the disturbance of the Sc–Ti–V triad is observed in the composition of water only. The regular distributions of chemical elements always hold true for the compositions of bottom rocks. “Life in the biosphere is the only factor disturbing the regular course of chemical element dispersion in the Earth’s crust” [23]. This is probably responsible for the deviation in the distribution of chemical elements in the natural components of freshwater ecosystems from the idealized average galactic distribution of elements in accordance with the Oddo–Harkins rule [2].

Regular relationships between the compositions of internal and external media can be characterized by means of the coefficient of biological absorption. If the concentrations in a biologic object and its environment are defined in the same way, the coefficient of biological absorption characterizes the degree of element concentration in living matter relative to its habitat (in our case, relative to water and bottom sediments). The intensity of element entrainment into the process of biological migration is not uniform. The inspection of this coefficient for various species and various parts of particular gastropods reveals both differences and common features.

Relative to the bottom water layer, the gastropod species of interest extensively concentrate $Ti > Mn > La$ ($K_a > 3.0$). The highest degree of absorption of these elements that is observed in *Choanomphalus* sp. *Maackia herderiana* and *Choanomphalus* show also active Ce absorption, while *Megalovalvata baicalensis* is especially efficient in the accumulation of Cu ($K_a = 3.8$) and Cd ($K_a = 2.91$). All the mollusks accumulate, although to a lesser degree, Co, Y, and V ($K_a \geq 1.0$). In contrast to other species, *Choanomphalus* concentrates also Zr relative to the water. *Maackia herderiana* and *Choanomphalus* sp. are distinguished by Ni accumulation, and *Maackia herderiana* and *Megalovalvata baicalensis* concentrate Ge. The gastropod species show low degrees of U, W, Mn, and Cs absorption relative to the water (Table 4).

Relative to the bottom sediments, the gastropod species concentrate Sr ($K_d > 1.0$) in the order *Maackia herderiana* > *Megalovalvata baicalensis* > *Choanomphalus* sp.

In this case, the degrees of Ti, La, Ce, Y, Cs, and Zr involvement into the biogeochemical cycle are negligibly small ($K_d < 0.01$). In contrast to *Choanomphalus* sp., *Maackia herderiana* and *Megalovalvata baicalensis* have $K_d > 1.0$ for Cd and Cu, and the most active concentra-

tor of Cd and Cu, *Megalovalvata baicalensis* also accumulates Zn (Table 4).

The degree of accumulation of chemical elements varies between both the gastropod species and between parts of particular animals.

The shells of the gastropod species are enriched in Ti, Mn, La, Co, Ni, Ce, and V relative to the bottom water of Baikal. Only Sr is accumulated in the gastropod shells relative to the bottom sediments. This element is most extensively concentrated by the slowly moving species *Maackia herderiana* (Table 4).

With respect to K_a values, the trace elements concentrated in the gastropod body ($K_a > 1.0$) form the following sequences: *Maackia herderiana* $Ti > Mn > Cu > Cd > Nb > La > Ce$; *Megalovalvata baicalensis* $Cd > Cu > Mn > La > Co > Ti > Zn > Ce$; and *Choanomphalus* sp. $Ti > Ce > La > Mn > Y > Zr > Co$. Compared with the bottom sediments, the bodies of *Maackia herderiana* and, especially, *Megalovalvata baicalensis* concentrate Cd, Cu, and Zn. The absorption coefficients of Cu, Zn, and Cd for *Choanomphalus* sp. are 0.96–0.71. The foot tissues show very low degrees of trace element accumulation, and the minimum coefficients of biological accumulation were obtained for the opercula of *Maackia herderiana*. They concentrate $Mn > Ti > Ce > La$ relative to the water (Table 4).

Table 5 shows some important geochemical ratios of trace elements for the compositions of gastropods, bottom water, and bottom sediments. The geochemical pairs of trace elements Rb : Sr, Zn : Cu, Zn : Cd, Ni : Co, and Ti : Zr show similar relationships in the compositions of gastropods, bottom water, and bottom sediments: $Rb < Sr$, $Zn > Cu$, $Zn > Cd$, $Ti > Zr$, and $Ni > Co$. Noteworthy are the low Rb : Sr ratios in the water and gastropods and higher values in the bottom sediments, which are significantly enriched in Rb. The Zn : Cu ratio is low in *Maackia herderiana* and *Megalovalvata baicalensis* which actively accumulate both Zn and Cu. This ratio increases in *Choanomphalus* sp., which weakly absorbs Cu and approaches in the concentration of this element the bottom water layer, where Zn strongly dominates over Cu owing to its higher mobility in oxidizing environments. The Zn : Cd ratio of *Maackia herderiana* and *Megalovalvata baicalensis* is also very low because both these species accumulate Zn and Cd. *Choanomphalus* sp. contains less Cd, and its Zn : Cd value approaches that of the bottom sediments and water. The Ba : Sr ratio is low in the water and gastropods and increases by a factor of 9–50 in the composition of bottom sediments. The behavior of this ratio in the water and gastropods is controlled by the low mobility of Ba, the high intensity of Sr leaching from rocks, and Sr accumulation by gastropods. The Ti : Sc, Ti : Zr, and Mn : Mo ratios are very low in the bottom water owing to the very low mobility of Ti, Zr, and Mn under oxidized conditions and higher mobility of Mo. These ratios are much higher in the gastropods and bottom sediments. *Maackia herderiana*, *Megalovalvata baicalensis*, and,

Table 4. Coefficients of biological accumulation of trace elements by gastropods relative to (1) water and (2) bottom sediments

Element	<i>Maackia herderiana</i>										<i>Megalovalvata baicalensis</i>	
	Individuals		Shell		Body		Foot		Operculum		Individuals	
	1	2	1	2	1	2	1	2	1	2	1	2
Rb	0.06	0.01	0.04	0.01	0.05	0.01	0.04	0.01	0.01	0.001	0.11	0.02
Cs	0.11	0.01	0.07	0.004	0.07	0.004	0.09	0.01	0.06	0.004	0.06	0.004
Cu	1.29	1.38	0.06	0.07	3.33	3.56	0.48	0.52	0.11	0.12	3.81	4.07
Sr	0.23	2.13	0.25	2.31	0.03	0.32	0.04	0.41	0.01	0.05	0.17	1.65
Ba	0.89	0.23	0.84	0.22	0.35	0.09	0.20	0.05	0.03	0.01	0.12	0.03
Zn	0.23	0.61	0.05	0.14	0.47	1.27	0.29	0.78	0.10	0.27	0.58	1.56
Cd	1.14	2.07	0.05	0.10	2.87	5.23	0.25	0.46	0.22	0.41	2.91	5.31
Ge	1.13	0.04	2.04	0.07	n.d.	n.d.	0.04	0.001	n.d.	n.d.	1.03	0.03
Pb	0.19	0.05	0.17	0.04	0.30	0.07	0.16	0.04	0.09	0.02	0.05	0.01
Ti	31.7	0.01	17.4	0.005	15.0	0.004	9.02	0.002	5.16	0.001	28.7	0.01
Zr	0.93	0.002	0.77	0.002	0.84	0.002	0.23	0.001	H.o.	H.o.	0.89	0.02
Mo	0.01	0.34	0.01	0.25	0.03	0.70	0.01	0.24	0.004	0.10	0.01	0.30
W	0.05	0.03	0.04	0.03	0.05	0.03	0.07	0.05	0.07	0.05	0.02	0.02
Mn	12.7	0.07	12.5	0.07	10.0	0.06	1.55	0.01	6.89	0.04	14.0	0.08
Co	1.61	0.09	1.59	0.08	0.82	0.04	0.36	0.02	n.d.	n.d.	1.57	0.08
Ni	1.02	0.31	1.04	0.32	0.16	0.05	0.17	0.05	0.35	0.11	0.88	0.27
Sc	0.02	0.01	0.02	0.01	0.05	0.02	0.05	0.02	0.06	0.03	0.02	0.01
Y	1.02	0.004	0.83	0.004	0.74	0.003	0.16	n.d.	0.47	0.002	1.61	0.01
La	5.5	0.01	5.96	0.01	2.27	0.003	0.78	n.d.	1.36	0.002	4.24	0.01
Ce	3.5	0.005	2.55	0.004	2.08	0.003	0.28	n.d.	1.50	0.002	1.68	0.002
V	1.6	0.07	1.97	0.09	0.70	0.03	0.20	0.01	0.001	0.0001	1.63	0.07
U	0.04	0.03	0.04	0.03	0.05	0.04	0.01	0.01	0.04	0.03	0.06	0.04

Element	<i>Megalovalvata baicalensis</i>						<i>Choanomphalus</i> sp.					
	Shell		Body		Foot		Individuals		Shell		Body	
	1	2	1	2	1	2	1	2	1	2	1	2
Rb	0.02	0.003	0.22	0.03	0.36	0.05	0.15	0.02	0.03	0.01	0.07	0.01
Cs	0.06	0.004	0.05	0.003	0.06	0.004	0.10	0.01	0.05	0.003	0.08	0.01
Cu	0.12	0.13	9.82	10.50	1.10	1.18	0.30	0.32	0.08	0.09	0.90	0.96
Sr	0.11	1.04	0.01	0.09	0.01	0.12	0.14	1.34	0.14	1.28	0.02	0.22
Ba	0.11	0.03	0.05	0.01	0.04	0.01	0.22	0.06	0.20	0.05	0.14	0.04
Zn	0.04	0.11	1.43	3.85	0.29	0.77	0.22	0.58	0.07	0.18	0.29	0.78
Cd	0.03	0.06	12.7	23.09	1.05	1.91	0.42	0.76	0.07	0.12	0.39	0.71
Ge	1.35	0.04	n.d.	n.d.	0.51	0.02	0.73	0.02	1.62	0.05	0.39	0.01
Pb	0.06	0.02	0.31	0.08	0.12	0.03	0.28	0.07	0.24	0.06	0.72	0.17
Ti	6.26	0.002	1.58	0.001	2.08	0.001	36.1	0.01	15.69	0.004	20.2	0.01
Zr	0.36	0.001	0.25	0.001	n.d.	n.d.	1.85	0.005	1.20	0.003	1.03	0.003
Mo	0.004	0.09	0.03	0.70	0.01	0.16	0.02	0.35	0.01	0.18	0.02	0.49
W	0.03	0.02	0.06	0.04	0.01	0.01	0.05	0.03	0.02	0.02	0.06	0.04
Mn	19.4	0.11	9.39	0.06	3.77	0.02	19.0	0.11	20.9	0.12	6.54	0.04
Co	1.46	0.08	2.05	0.11	0.31	0.02	2.00	0.11	1.32	0.07	1.02	0.05
Ni	1.03	0.32	0.32	0.10	0.09	0.03	1.10	0.34	0.89	0.27	0.28	0.09
Sc	0.02	0.01	0.03	0.01	0.05	0.02	0.05	0.02	0.02	0.01	0.06	0.03
Y	0.43	0.002	0.54	0.002	0.09	0.0004	2.57	0.01	1.02	0.004	5.13	0.02
La	5.48	0.01	2.27	0.003	0.45	0.001	9.62	0.01	7.13	0.01	9.38	0.01
Ce	0.77	0.001	1.41	0.002	0.26	0.0004	6.53	0.01	4.53	0.01	10.7	0.02
V	1.44	0.06	0.27	0.01	1.53	0.07	1.45	0.06	1.58	0.07	0.97	0.04
U	0.03	0.02	0.08	0.06	0.01	0.005	0.07	0.05	0.03	0.02	0.10	0.07

Table 5. Key geochemical ratios of trace element pairs in the compositions of gastropods, bottom water, and bottom sediments

Sample	Rb : Sr	Zn : Cu	Zn : Cd	Ba : Sr	Ti : Sc	Ti : Zr	Mn : Mo	Ni : Co	Sc : Y	La : Ce
<i>M. herderiana</i>	0.002	1.46	60.9	0.34	424.3	148.0	394.1	11.02	1.76	0.94
<i>M. baicalensis</i>	0.004	1.26	60.4	0.06	403.3	139.6	494.5	9.79	1.06	1.47
<i>Choanomphalus</i> sp.	0.006	5.98	157.6	0.13	218.2	84.5	572.6	9.56	1.54	0.86
Bottom water	0.01	8.31	304.7	0.09	0.33	4.33	0.46	17.43	72.9	0.58
Bottom sediments	0.37	3.30	206.3	3.05	553.2	40.9	1800.0	3.00	0.71	0.66

especially, *Choanomphalus* sp. intensely absorb Ti and Mn and, to a lesser extent, Zr. The Sc : Y ratio of gastropods varies within a narrow range and is similar to that of the bottom sediments but tens of times lower than that of the water. The Co : Ni ratio is the lowest in the bottom sediments, increases in the trace element composition of gastropods, and reaches the maximum values in the bottom water layer. The La : Ce ratios of the bottom sediments and water are similar. The gastropods actively accumulate these elements relative to the bottom water; the concentrations of La and Ce in them are similar, and the La : Ce ratio approaches 1.0. The concentration of Ce in *Megalovalvata baicalensis* is lower than that of La, which is at odds with the Oddo–Harkins rule.

Thus, the formation of the elemental composition of the gastropod species occurs in a regularly way: many geochemical ratios of trace elements in the gastropods correspond to those of bottom sediments. The maximum discrepancy is observed for the Ti : Sc, Sc : Y, and Mn : Mo values between the compositions of gastropods and water. Despite the low contents of Ti, Mn, Zr, Y, La, and Ce, the gastropod species are capable of accumulating these elements.

CONCLUSIONS

The trace element composition of *Maackia herderiana*, *Megalovalvata baicalensis*, and *Choanomphalus* sp., which are the dominant species of the littoral of southern Baikal, is extremely diverse and controlled by the biologic characteristics of the mollusks and the chemistry of their habitat. The elemental chemical composition of gastropods, as well as any living organism, is formed in the system water $\rightleftharpoons$ rock $\rightleftharpoons$ living matter. The chemical composition of the gastropod species considered here is characterized by the prevalence of Ba, Sr, Mn, Ti, Zn, Cu, Ni, and Co, which are typical of living matter.

In the system considered here, the Oddo–Harkins rule for element triads is never violated simultaneously in the compositions of water, bottom sediments, and gastropods. The relations Co–Ni–Cu and Ni–Cu–Zn are violated in the trace element compositions of water and gastropods, Sc–Ti–V is disturbed in the composi-

tion of water only, and Ba–La–Ce is disturbed in the composition of *Megalovalvata baicalensis*. The regular distribution of chemical elements always holds true for the bottom sediments.

The deviation from the regular distribution of chemical elements observed in the gastropod species is in general not anomalous in the biosphere and probably related to the geochemical function of living matter, which is “the only factor disturbing the regular course of chemical element dispersion in the Earth’s crust” [23].

The processes of trace element concentration by living matter are controlled by common physicochemical and biological processes. In our case, this is suggested by the similarity in many components (Rb, Cs, Cu, Sr, Zn, Cd, Ge, Pb, Zr, V, Co, and Ni) of the trace element distribution patterns of the bottom water, bottom sediments, and gastropods. Direct or indirect relations between the trace element compositions of gastropods and bottom sediments are indicated by the coincidence of positive and negative anomalies in the distribution curves at Y, La, Mo, Ti, and Mn.

The elemental chemical composition of the gastropod species is formed in a regular way, which is suggested by the similar values of most geochemical ratios of elements in the bottom sediments and gastropods. The maximum discrepancy is observed between the Ti : Sc, Sc : Y, and Mn : Mo ratios of gastropods and water. Despite the low contents of Ti, Mn, Zr, Y, La, and Ce in the water, these elements can be accumulated by the gastropod species.

The gastropods studied show group concentration of trace elements. The contents of Ti, Mn, La, Ce, Co, V, and Y in *Maackia herderiana*, *Megalovalvata baicalensis*, and *Choanomphalus* sp. are higher than in the water, whereas these gastropod species show minor absorption of Mo, Cs, W, and U. The most active concentrator of Ti and Mn is the pulmonate mollusk *Choanomphalus* sp. In addition to the aforementioned elements, the prosobranchs *Megalovalvata baicalensis* and, to a lesser extent, *Maackia herderiana* intensely absorb Cu and Cd.

The biogeochemistry of the gastropod species relative to the bottom sediments is controlled by the accumulation of Sr. *Maackia herderiana* is the most active

concentrator of this element. In addition, *M. herderiana* and, especially, *M. baicalensis* concentrate Cd and Zn. *M. baicalensis* is distinguished among the other species by its ability to concentrate Cu. With respect to the concentration capacity of Cd, Zn, and Cu, the gastropods form the following sequence: *Megalovalvata baicalensis* > *Maackia herderiana* > *Choanomphalus* sp.

The gastropod species considered here show elevated U content compared with the average compositions of mollusks or hydrobionts from freshwater ecosystems, which is probably related to the high mobility of U under littoral conditions and its high content in the bottom sediments of southern Baikal.

Specific features were observed not only in particular species but also in separate parts of the gastropods. The shells are enriched in Ti, Mn, La, Ce, and V relative to the water and in Sr relative to the bottom sediments. The maximum Sr content was detected in the shells of *Maackia herderiana*. Relative to the bottom water layer, the bodies of *Choanomphalus* sp. are enriched to the highest degree in Ti, and the bodies of *Megalovalvata baicalensis* accumulate Cd > Cu > Mn. Compared with the bottom sediments, the three species most extensively absorb Cd, Cu, and Zn, while *Megalovalvata baicalensis* and, to a lesser extent, *Maackia herderiana* concentrate these elements in their body tissues.

Thus, the dominant gastropod species from the littoral of southern Baikal play an important role in the migration and accumulation of chemical elements. They serve, first, as a source of trace elements for larger gastropod-eating animals; second, as a source of enrichment of bottom sediments, bottom water, and living benthic organisms in alkali earth metals, Ti, Mn, La, Cu, Zn, Cd, etc. after the sequential (soft tissues, inner layers of shells, and outer layer of shells) mineralization of dead animals.

Information on the elemental chemical composition of living organisms from Lake Baikal is very important and valuable, as providing insight into the evolution of the elemental composition of living matter and its relation to the continuously changing composition of the environment.

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