Chemical component depositions in the microbial mats and travertine in the Khoito-Gol thermal spring (Eastern Sayan)

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Abstract. The results of studies of the chemical composition of water, travertine, and microbial mats in the Khoito-Gol mineral spring (Eastern Sayan) are presented. It was shown that the formation of mineral deposits, travertine, and microbial mat is connected with the active functioning of microorganisms and geological and geodynamic conditions. It has been revealed that the diversity of cyanobacterial and sulfur microbial mats increases as the distance from the springs of the thermal water grows. Microbial mats are hardened with carbonates being converted into solid travertine crusts that are built upon the top of older structures to form multi-meter domes. The concentration function of the microbial mats and thermal water showed higher coefficients of accumulation of nickel and beryllium.

1. Introduction
The Eastern Sayan region of the Baikal rift zone is famous for its numerous thermal waters with their favourable conditions for the existence and development of various microbial communities [1, 2]. Microorganisms take an active part in the chemical processes and migration of microelements, they can form mono-mineral rocks and travertine. Microbial mats contain chemical elements in concentration many times higher than those in mineral water. An important role of bacteria in the deposition of many minerals and rocks due to the various metabolism forms of microorganisms is known [3-5]. However, the role of microorganisms in the hydrothermal processes of ore formation has hardly been studied, especially for the young rift systems. It is not quite clear how microelements are distributed in the deposits and mats, and how microbial communities accumulate particular elements depending on hydro-chemical and physicochemical conditions. The high temperatures of water together with reductive environment is accompanied by intensive migration of many metals. For instance, dissolved hydrogen sulphide in the reduced medium is known to react with many metals causing their precipitation from the solution. Such a medium causes formation of organic substances, which concentration can be high enough and lead to decrease of redox potential [6, 7].

The purpose of the research was to study the concentration of the chemical elements in travertine and microbial mats in the Khoito-Gol thermal spring and to determine morphological patterns of mineral formation.
2. Materials and methods

Site description. The Khoito-Gol thermal spring is located in the region of the Baikal rift zone in the Eastern Sayan spurs at a height higher than 1500 m (52°37'255'' N, 99°00'875'' E).

Sampling sites. Physicochemical characteristics of water were determined by common methods [8]. Temperature, \( pH \), redox potential (\( Eh \)), total dissolved solids (\( TDS \)) were measured by portable devices. Sulphide concentration was defined by the colorimetric method; carbonic acid and oxygen – by titration. Chemical elements were determined by the atomic-emission spectroscopy method with inductively fixed plasma, ICP-MS, and atomic absorption at the Institute of Geochemistry SB RAS, Irkutsk city.

Microbial mat samples were taken with the structure saved, were further fixed with 4% formalin, dried out, and separated into layers. The content of total organic carbon (TOC) was determined in the dried mat by Tyurin’s method modified by B A Nikitin [9]. Mineralized fragments of microbial mats were analysed with a field scanning electron microscope HITACHI TM-1000 (Japan). The elemental composition of the minerals was determined with a field scanning electron microscope LEO-1430 VP. To identify the minerals, an X-ray diffraction analysis (B-8 Advance diffractometer with Cu–K\( \alpha \) radiation and a graphite monochromator) was also performed.

3. Results and Discussions

The Khoito-Gol mineral spring has five outflows distributed along the Arshan river (a tributary of the Khoito-Gol river). Waters had neutral or slightly alkaline \( pH \) values and \( TDS \) higher than 500 mg/dm\(^3\). The \( pH \) values were from 7.32 – 7.84. The water temperature ranges from 32.5°C to 33.6°C (table 1).

Negative and low positive \( Eh \) values were measured at the springs, that might be caused by the carbonic acid in the water coming along with the volcanic exhalations as well as from the bottom sediments during sulphate reduction. The physicochemical parameters change downstream, formed by the mineral waters with a decrease in temperature and \( Eh \), and an increase in \( pH \) values and oxygen concentration.

| No. | \( t \), \(^\circ\)C | \( pH \) | \( Eh \) | \( TDS \), mg/dm\(^3\) | \( O_2 \), mg/dm\(^3\) | \( H_2S \), mg/dm\(^3\) |
|-----|----------------|---------|--------|----------------|----------------|----------------|
| 1   | 33.5           | 7.32    | -28    | 592            | 0.4            | 6.69           |
| 2   | 32.9           | 7.62    | -32    | 586            | 0.4            | 7.03           |
| 3   | 33.6           | 7.53    | 8      | 578            | 0.8            | –              |
| 4   | 33.4           | 7.45    | 16     | 535            | 1.2            | –              |
| 5   | 32.6           | 7.55    | 32     | 525            | 1.6            | –              |
| 6   | 32.5           | 7.65    | 28     | 529            | 1.4            | –              |
| 7   | 32.7           | 7.84    | -2     | 482            | 0.4            | 0.52           |

* dash means the absence of data

The field of the travertine sediments that spreads over the springs area demonstrates the substantial concentration of carbon dioxide and rather high concentration of hydrocarbonates. The content of bicarbonate ions varied from 435.5 to 518 mg/dm\(^3\), the concentration of other anions was an order of magnitude less (table 2). The concentration of sulphate ions reached 332.5 mg/dm\(^3\), chloride ions – 28.9 mg/dm\(^3\). The results also show that the value obtained for the concentration of Na\(^+\) is higher than the concentration of Ca\(^{2+}\) in the water samples. This proves that the major element composition of the hot water is dominated by Na\(^+\) meanwhile Ca\(^{2+}\) is a minor component. Lithium, iron, strontium, and boron prevailed among microelements. The concentrations of some metals such as uranium, molybdenum, beryllium, silver, and others are low or very low and were below the limit of quantification.
Table 2. Chemical composition of the water.

| Element, mg/dm$^3$ | No. 1 | No. 7 | Element, ug/dm$^3$ | No. 1 | No. 7 |
|--------------------|-------|-------|--------------------|-------|-------|
| Na$^+$             | 143.0 | 149.0 | Ba                 | 54.74 | 54.75 |
| K$^+$              | 16.0  | 16.3  | Mn                 | 29.23 | 34.32 |
| Ca$^{2+}$          | 11.6  | 12.4  | W                  | 31.02 | 31.00 |
| Mg$^{2+}$          | 4.6   | 4.6   | As                 | 9.26  | 8.81  |
| NH$_4^+$           | 0.08  | 0.15  | Zn                 | 11.90 | 1.72  |
| SiO$_2$            | 9.21  | 21.47 | Ti                 | 5.11  | 5.03  |
| HCO$_3^-$          | 517.95| 435.45| Al                 | 3.02  | 4.56  |
| SO$_4^{2-}$        | 25.92 | 21.76 | V                  | 2.92  | 3.01  |
| Cl$^-$             | 24.15 | 23.91 | Cr                 | 2.67  | 3.36  |
| PO$_4^{3-}$        | 0.044 | 0.085 | Cu                 | 2.56  | 2.50  |
| NO$_3^-$           | 0.005 | 0.006 | U                  | 1.54  | 1.30  |
| NO$_2^-$           | 0.002 | 0.003 | Mo                 | 1.14  | 1.02  |
| Li                 | 0.531 | 516.35| Be                 | 0.94  | 0.81  |
| Fe                 | 0.409 | 412.30| Ni                 | 0.73  | 0.91  |
| Sr                 | 0.393 | 394.67| Ag                 | 0.26  | 0.52  |
| B                  | 0.254 | 245.29| Au                 | 0.14  | 0.03  |

Microbial mats of different types have developed in the outflow area and warm-water zone of the thermal springs. Microbial mats are represented by horizontally stratified microbial communities, exhibiting a structure defined by physiochemical gradients, which models microbial diversity, physiological activities, and their dynamics as a whole system [10, 11].

The Khoito-Gol springs were characterized by two-layer microbial mats up to 2 cm thick. At the upper outlet (Hg1), green microbial mats were found. Mat-forming species of cyanobacteria were from the genus of *Phormidium*. Depending on the physicochemical conditions of the water habitat, the change of microbial communities takes place [12]. Down the stream (Hg2, Hg3, Hg4, Hg5) microbial mats were observed, consisting of cyanobacteria, filamentous sulfur-oxidizing bacteria *Thiothrix* sp., and purple anoxygenic phototrophic bacteria. Down the stream as the temperature lows and the medium acidity changes mainly cyanobacteria *Phormidium* sp. and *Oscillatoria* sp. were dominated.

The formation of filamentous sulfur-oxidizing bacteria *Thiothrix* sp. facilitated alkalization of the environment and an increase in the content of sulphide. Sulfur-oxidizing bacteria are involved in the accumulation and crystallization of sulfur [2]. Further downstream cyanobacterial mats became more loosened with air bubbles and homogeneous in composition. Over time and in the absence of nutrient media microbial mats dried out in thin layers.

X-ray diffraction and scanning electron microscopy were used to characterize the crystal phase and morphology of minerals precipitation in microbial mats and travertines. The use of a scanning electron microscope clearly shows typical fragments of the structural and textured patterns of mineral cuts. As shown in figure 1, well-developed mineral sediments that form globules and dense clusters were observed in the microbial mats. As a result of elemental analysis of globules using a scanning electron microscope, calcium (up to 82%), silicon, sulfur, and copper were detected. Aluminium (up to 44%), calcium (up to 42%), as well as nickel, iron, copper, silicon, and magnesium were found in the crystals.

X-ray diffraction (XRD) identified the crystalline phases of the microbial mats and travertines. Based on the results of X-ray phase analysis, carbonate minerals (calcite) and silicate minerals (quartz, aluminosilicates) were found in the microbial mats and travertines of the springs. Studies showed that calcite is the most abundant mineral forming in the mats and travertines. The calcite crystals had an oval shape with cyanobacterial filament impressions or rhombic shape. Calcite grains were seen in the
globule bound with cyanobacteria filaments, this allows us to conclude that the formation takes place with the direct participation of microbial communities. Structural peculiarities of crystals give evidence of the mineral deposition that occurred due to the hydrothermal waters [13-14].

Depositions of silica were observed in the microbial mats and travertines of the springs. The microbial mats contained siliceous formations of biogenic origin in the form of siliceous covers on cyanobacteria filaments and the valves of diatom algae. Depositions of silica were represented by hexagonal quartz.

The mineral composition of sediments correlates well with the chemical composition of water. Calcium concentration in the sediments is explained by the formation of calcite crystals large enough. Siliceous formations in the mode of the opal sediments were noticed in microfossils, in the bags on the filaments of cyanobacteria and diatom algae. High concentrations of strontium and iron enable mineral crystallization of these elements. Aluminium participation explains the formation of aluminosilicates crystals.

Microelemental analysis of the travertine and mat samples revealed a high concentration of strontium (400-750 g/t), as in the water (table 3). Relatively high proportions of barium (45-250 g/t) might indicate the formation of strontium-bearing barite minerals. High concentration of strontium was confirmed by earlier studies that indicate high isotope ratio $^{87}\text{Sr}/^{86}\text{Sr}$ (0.7106) in the travertine of the Khoito-Gol mineral spring in comparison with travertines of other Eastern Sayan’ springs (0.7085-0.7086) and Zhoigan (0.7091) [14].

It is important to mention the prevalence of alkaline earth metals: Sr (400-750 g/t) and Ba (45-250 g/t). The accumulation of such elements as boron (up to 110 g/t), zinc, copper, beryllium, germanium, nickel, and others was explained by various lithological and petrographic kinds of rocks [15]. Thallium, molybdenum, and silver were detected as minor components.

The increase of microelements’ concentrations in cyanobacteria mats is caused by their ability to be deposited with certain elements [16]. Cyanobacteria are effective biological sorbents of metals in an aqueous medium [17].

As a source of carbon, organic matter plays an important role for the microbial community. Investigated microbial mats and travertines contained from 3.24 to 17.93% by dry weight of organic carbon (table 3). The highest concentration of organic matter was noted in the purple mat under the layer of the green mat. The least amount was noted in the travertine under the layer of the green mat.
Table 3. \( \text{C}_{\text{org}} \) (%) concentrations and microelement composition (g/t) of microbial mats and travertines of the Khoito-Gol spring.

| Element | Concentration | Petrified mat of grey colour (No. 2) | Mat of purple colour (No. 3) | Mat of dark-green colour (No. 4) | Travertine of light-green colour (No. 5) |
|---------|---------------|-------------------------------------|----------------------------|----------------------------------|-----------------------------------------|
| C\(_{\text{org}}\) |               | 4.04                                | 17.93                     | 7.22                             | 3.24                                    |
| Sr      |               | 400                                 | 455                       | 750                              | 680                                     |
| Ba      |               | 250                                 | 51                        | 45                               | 170                                     |
| Zn      |               | 16                                  | 12                        | 9.9                              | 19                                      |
| Be      |               | 14                                  | 11                        | 4                                | 18                                      |
| Ge      |               | 11                                  | 9.5                       | 15                               | 9.7                                     |
| Cu      |               | 7.8                                 | 5.7                       | 4.4                              | 33                                      |
| B       |               | 2.5                                 | 58                        | 110                              | 4.4                                     |
| Ni      |               | 3.3                                 | 3                         | 5.1                              | 7.3                                     |
| V       |               | 3.1                                 | 4                         | 3.6                              | 5.1                                     |
| Sn      |               | 1.6                                 | 4.8                       | 4.9                              | 1.6                                     |
| Pb      |               | 2.2                                 | 2.0                       | 2.2                              | 3.2                                     |
| Cr      |               | 2.3                                 | 0.78                      | 0.79                             | 4.1                                     |
| Co      |               | 0.41                                | 6.3                       | 13.0                             | 0.76                                    |
| Tl      |               | 0.12                                | 0.51                      | 0.88                             | 0.54                                    |
| Mo      |               | 0.07                                | 0.24                      | 0.19                             | 0.14                                    |
| Ag      |               | 0.11                                | 0.02                      | 0.01                             | 0.06                                    |

Accumulation factors \( C_a \) were calculated for some chemical elements considering their concentration ratio in the microbial mat and in the spring water [18]. The results show that the concentration of elements with strong accumulation, such as Sr (1.91), B (0.43), Zn (0.83), is not of maximum values (table 4). Cu, Ba, Ni, Mo are the elements with average accumulation. Nickel has the highest coefficient (6.99) among the elements studied. Beryllium, element with weak accumulation, has rather high value of \( C_a = 4.25 \).

Table 4. Accumulation coefficients \( (C_a) \) of the chemical elements of the mineral spring Khoito-Gol.

| Element | Average concentration (ug/g) of dry substance. Dark-green mat No4 | Average concentration (ug/g) in water | Coefficient of accumulation \( (C_a) \) |
|---------|---------------------------------------------------------------|-------------------------------------|--------------------------------------|
| Be      | 4.0                                                          | 0.94                                | 4.25                                 |
| Sr      | 750                                                          | 392.96                              | 1.91                                 |
| Cu      | 4.4                                                          | 2.56                                | 1.72                                 |
| B       | 110.0                                                        | 254.42                              | 0.43                                 |
| Ba      | 45.0                                                         | 54.74                               | 0.82                                 |
| Zn      | 9.9                                                          | 11.90                               | 0.83                                 |
| Ni      | 5.1                                                          | 0.73                                | 6.99                                 |
| Mo      | 0.19                                                         | 1.14                                | 0.17                                 |
4. Conclusion
Thus, it has been shown that the physicochemical conditions influence the formation of travertine and the sedimentation of microbial mats of the Khoito-Gol mineral spring. The formation of minerals is connected with the activity of microorganisms and geological-geodynamic conditions. The research allows tracing the spatial evolution of the concentration and the functional activity of microbial mat community. The species diversity of cyanobacterial and sulfur microbial mats increases downstream. The most active processes of microbial production and destruction take place in the zone of high pH and Eh values in the absence of hydrogen sulphide. Under alkaline and oxidizing conditions, the intensive process of microbial mat lithification takes place, which suppresses the organic substance production and bacterial mats formation. Thin and loose mats were cemented with carbonates transforming into travertine solid crusts. These crusts are layered on top of the older structures that form multi-meter domes near the outlets of thermal waters. The concentration function of accumulation was revealed for several chemical elements. Nickel and beryllium showed a higher ratio.

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