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Russian Geology and Geophysics 58 (2017) 47–58

RUSSIAN GEOLOGY AND GEOPHYSICS

www.elsevier.com/locate/rgg

Mineralogical and geochemical features of bacterial mats and travertines of the Khoito-Gol thermal spring (*East Sayan*)

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Received 27 July 2015; accepted 24 April 2016

Abstract

The mineralogical and geochemical features of the Khoito-Gol ecosystem (fresh thermal waters–microorganisms–travertines) of the Baikal Rift Zone and the aspects of the interaction among its components were studied. The research has shown that the behavior, distribution, and accumulation of trace elements are determined mostly by the geochemical barriers of geologic and biologic genesis in the flowing-water habitat of bacteria of the Khoito-Gol spring. Formation of biominerals by different functional groups of its bacterial community is considered.

Keywords: trace elements; bacteria; mats; geochemical barriers; concentration processes; travertines

Introduction

The problem of study of natural mineral formation processes and geochemical concentration of chemical elements, related to microorganism activity, is widely discussed in the world literature on geological microbiology, bacterial paleontology, biogeochemistry, and biomineralogy. On the one hand, the interest to this problem is triggered by the need for the solution of topical tasks of ecology (purification of sewage, industrial, and domestic waters from toxic elements), medicine, and biotechnology (Gadd, 2009; Gadd and Raven, 2010; Konhauser, 2007; Pümpel and Paknikar, 2001). On the other hand, the results of this study favor the development of fundamental fields of geoscience, such as the evolution of the geosphere–biosphere system, reconstruction of past biogeochemical cycles (Yushkin, 2002; Zavarzin, 2002, 2003, 2011), and ecosystems and their interactions (Grudev and Yakhontova, 1996; Perel'man, 1977; Yakhontova et al., 1994).

This paper presents results of mineralogical and geochemical research into the Khoito-Gol ecosystem (thermal waters–microorganisms–travertines) of the Baikal Rift Zone (Fig. 1). The goal of the performed studies was to elucidate the interaction among the system components and their role in the behavior, distribution, and accumulation of chemical elements, including transition metals Cr, V, Ni, Co, Pb, Zn, Cu, Mo, and Sn, and to assess the role of different functional groups of bacteria in mineral formation.

In addition to the most vital elements, i.e., C, H, N, O, S, P, and Cl, there is also a group of elements essential to life, including ions of Na, K, Ca, Mg, and transition metals, both light (Mn, Fe, Cr, V, Co, Ni, Cu, and Zn) and heavy (Mo and W) (Marakushev and Marakushev, 2004; Marakushev et al., 2003). Based on analysis and generalization of data on microbial interaction with chemical elements, Toeniskoetter et al. (2004, 2016) compiled a Biochemical Periodic Table, in which not only the above transition metals but also lanthanides and other elements of Mendeleev's Periodic Table are referred to as biophilic elements. The ecosystems of thermal springs with bacterial communities and travertines in the Baikal Rift Zone contain many elements of the Biochemical Periodic Table (Lazareva et al., 2012; Plyusnin et al., 2000; Tatarinov et al., 2011), actively participating in mineral formation and petrogenesis of travertines and geyserites of this zone (Lazareva et al., 2010; Namsaraev et al., 2006; Plyusnin et al., 2000, 2011; Sorokovikova, 2008; Tatarinov et al., 2005, 2006, 2010, 2011; Zamana and Pinneker, 1999).

It was also established that bacterial biomass accumulates noble metals over a broad temperature range (up to 55 ºC)

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1068-7971/$ - see front matter
http://dx.doi.org/10.1016/j.rgg.2016.04.013

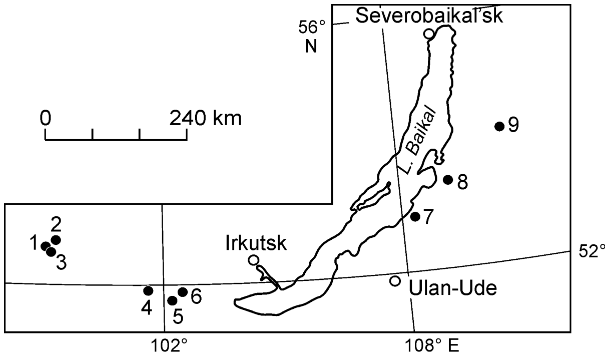

Fig. 1. Schematic map of location of thermal springs with travertines in the Baikal Rift Zone, after Borisenko et al. (1976) and Plyusnin et al. (2000). *1–9*, thermal springs with travertines: *1*, Khoito-Gol; *2*, Kholon-Ugun; *3*, Ara-Shutkhulai; *4*, Shumakskii; *5*, Zhemchug; *6*, Arshan; *7*, Goryachinsk; *8*, Gusikha; *9*, Garga.

independently of the pH and qualitative macro- and micro-component compositions of thermal spring waters (Tatarinov et al., 2011).

In addition, the forms of biogenic concentration of metals are different: Pt and Pd are concentrated as organometallic compounds (clusters), and Au and Ag, as organometallic compounds (85–90%) and native metals (15–10%) (Tatarinov et al., 2011).

However, the geochemical behavior of most of trace elements (Sr, Ba, B, Cr, V, Ni, Co, Pb, Zn, Cu, Mo, Sn, and Be) and their mineral forms in the ternary ecosystem water–microorganism–travertine remained unstudied.

In this paper we investigate the Khoito-Gol ecosystem and present new data, which partly help to solve the above tasks for such systems of the Baikal region.

Methods

The physicochemical parameters and chemical macrocomponent composition of water sampled from different outlets were determined by common methods. The temperature, pH, redox potential (Eh), mineralization, and oxygen and sulfide contents of water were measured at the sampling localities. Temperature was measured by a Prima sensor electrothermometer; pH, by a pHep2 pH meter (Portugal); and Eh, by an ORP meter (Portugal). Mineralization (M) was determined by a TDS-4 tester (Singapore, and sulfide concentration by the colorimetric method. Analysis was carried out as follows. Cadmium acetate solution (4 ml) was added to a water sample (1 ml); then, 100 μl of the mixture were sampled, and the total volume was made up to 5 ml with distilled water. Next, 1 ml of N,N'-dimethyl-para-phenylenediamine and 50 μl of ferrous ammonium sulfate were added, and the mixture was stirred. After 10 min, the total volume was made up to 10 ml with distilled water. The optical density of the solutions was measured with a photocolorimeter ($\lambda = 670$ nm, cell thickness is 1 cm) relative to the distilled water, with addition of reagents. Sulfide content was determined from the calibration curve. The content of dissolved oxygen was determined with a MAPK 302E analyzer, and the contents of hydrogen carbonates and carbon dioxide, by titration.

The water samples for trace-element analysis were infiltrated through a membrane and conserved with concentrated HNO_3 (special-purity grade). The contents of trace elements were determined by ICP–AES, ICP–MS, and AAS at the Institute of Geochemistry, Irkutsk.

At the Khoito-Gol water outlets, one-, two-, and three-layered bacterial mats composed of different functional groups and microorganism species form in the flowing-out brooks (Barkhutova et al., 2011; Tatarinov et al., 2010). For study of the elemental composition of mats, we sampled a purple mat layer with species similar to *Rhodopseudomonas palustris*, *Rhodobacter capsutatus*, *Thiocapsa* sp., and *Chlorobium* sp. and a green mat layer with predominant cyanobacteria of the genera *Oscillatoria* and *Phormidium*. The samples were dried at room temperature and were then analyzed by SR–XRF for the same trace elements as in the water samples (the analyses were performed at the Institute of Geochemistry, Irkutsk). The content of total organic carbon (TOC) was determined in the dried mat by Tyurin's method modified by B.A. Nikitin (Arinushkina, 1980; Nikitin, 1972). Mineralized fragments of biofilms from the above mat layers and of sulfur bacteria *Thiothrix sp*. and their morphostructural features were revealed and examined with a HITACHI TM-1000 electron microscope. The elemental composition of the minerals was determined with a LEO-1430 VP scanning electron microscope.

The established total elemental composition of the mineral grains in the dried bacterial mass was converted to minerals, based on the stoichiometric relationship. In order to identify the minerals, we also performed an X-ray diffraction analysis (B-8 Advance diffractometer with Cu–K_α radiation and a graphite monochromator).

We sampled and studied travertines of two varieties: (1) highly porous loose rocks with numerous bacterial films and (2) massive and compact geyserite–travertine rocks with scarce bacterial films.

Results

Thermal spring waters

As we reported earlier (Tatarinov et al., 2010), the hydrologic system of the Khoito-Gol spring is nitric-carbonic sodium hydrogen carbonate drainage waters with the following characteristics: $T = 29–36$ °C, pH = 7.0–9.1, and Eh = 32–194. We supplemented these data by the parameters of waters sampled at different outlets (Fig. 2). The temperature of these waters is low and varies over a narrow range of values (32.5–33.6 °C), the pH variations are also insignificant (7.3–7.8), and the Eh values lie in the interval from –32 to +32 mV. Compared with the earlier obtained water characteristics (Tatarinov et al., 2011), the data presented in Tables 1 and 2 show lower mineralization (M) (1.5 times) and contents of Ca^{2+} (nearly twice), SiO_2 (2.7–6.3 times), SO_4^{2-}