

SURFACE AND GROUND WATERS
IN TERRESTRIAL PERMAFROST REGIONTHERMAL SPRING AT THE POLE OF COLD
(EASTERN YAKUTIA)

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The work reports on new data on geochemistry of water of the Sytygan-Sylba Thermal Spring located in the permafrost zone in the northeast of Yakutia. Data on the content of rare and trace elements, elements of a rare-earth group, oxygen and hydrogen isotopes in the studied waters have been obtained for the first time. Groundwaters of the spring are classified as low-mineralized siliceous thermal waters of the deep origin, which are seasonally fed due to the inflow of more mineralized suprapermfrost waters. The year-round activity of the thermal spring in the zone of continuous permafrost 300–500 m thick is associated with the significant heat flow in the anomalous mantle uplift zone. Geochemical signs of the thermal water of the spring involve an increased concentration of sulfates, anomalous contents of Ge, Mo, W, As and other elements, which may be indicators of halo waters and proximity of ore accumulations.

Key words: *hydrogeochemistry, isotopes, Sytygan-Sylba Spring, permafrost, trace elements, rare earth elements, Northeast of Yakutia, thermal waters.*

INTRODUCTION

Thermal waters in the area of the distribution of thick permafrost in the Northeast of Russia have engaged attention of scientists for a long time [Obruchev, 1927, 1954; Shvetsov, 1951]. However, these waters remain poorly studied due to remoteness and inaccessibility. The Sytygan-Sylba Spring is the only warm spring in Eastern Yakutia. The spring is famous for its location near the Pole of Cold, 80 kilometers south of the Oymyakon village.

The toponym *Sytygan-Sylba* is translated from Yakut as “rotten, slowly flowing water”. The original name *Khuksichan* (Ev. *Хуксичан*) which is translated from the Even language as “hot”, is almost forgotten. The water here is warm, both in winter and in summer.

The Sytygan-Sylba Spring was discovered in 1926 by geologist S.V. Obruchev, who described it for the first time and made the chemical analysis of mineral water [Obruchev, 1927].

In terms of location, physical nature, and composition, water of the Sytygan-Sylba Spring is close to the Talaya Deposit of thermal waters, which is located 400 kilometers to the east on the territory of the Magadan Oblast. The Talaya balneological resort operates on the basis of this thermal spring [Hydrogeology..., 1972; Shepelev, 1987].

The main purpose of this work was to study geological, hydrogeological, and geocryological conditions in the discharge area of the thermal waters and their chemical composition. Data on the content of

rare and trace elements, oxygen and hydrogen isotopes, and elements of a rare-earth group were obtained in the studied waters for the first time.

METHODS

Water samples were taken from the Sytygan-Sylba Spring on February 17, 2018. Chemical analyses were performed in the analytical departments of the Melnikov Permafrost Institute, Siberian Branch, Russian Academy of Sciences (MPI SB RAS) and Analytical Certification Test Center of the Institute of Microelectronics Technology and High-Purity Materials, Russian Academy of Sciences (ACTC IMT RAS). A complete chemical analysis of water samples was performed by capillary electrophoresis at the MPI SB RAS. Concentrations of microcomponents, trace and rare-earth elements were determined using the inductively coupled plasma mass spectrometry (X-7, Thermo Elemental, USA) and atomic emission methods at the ACTC IMT RAS. The stable reproducible geochemical data have been provided for most chemical elements. These data have been obtained by the analysis of subclark sensitivity, i.e., at the detection limits, which are close to clark of an element in the analyzed medium.

GEOLOGICAL AND HYDROGEOLOGICAL
CONDITIONS

In winter, the spring is a small stream flowing out from under a snow-ice dome, which is formed due to evaporation over the water discharge zone. The

water is cooled at a distance of 15–20 m from the snow dome, and an icing of about 50×200 m in size and 1.0–1.2 m thick is formed. According to V.F. Shishkina, who carried out the geological survey in the spring area in 1960, the volume of the icing was 4000 m^3 , and its area was $10\,000 \text{ m}^2$. Trunks of the trees, surrounding the valley, bear traces of mechanical and chemical impact of the icing.

The Sytygan-Sylba Spring ($62^\circ 45' 39.5'' \text{ N}$, $144^\circ 13' 55.5'' \text{ E}$) is situated in the Oymyakon district of the Sakha Republic (Yakutia) of the Russian Federation, 8 km west of Lake Alysardakh, about 1050 m above the sea level (Fig. 1).

The spring is located at the foot of a gently sloping hill about 2 m high. The water flows out of a small sinkhole (about 0.3 m in diameter and 0.2 m deep) formed in loose sediments. Directly at the discharge zone, the temperature varies from 24.5°C to 26.6°C in different periods of the year, even during the Oymyakon winter, which is coldest in the Northern Hemisphere. A stable flow rate of about 0.25 L/s is typical for the spring. In summer, a creek formed by the spring has a wide, more than 50 m, valley, which is associated with the formation of the icing in the winter period. Below the slope, there is a small pond

about 2×3 m in size, which does not freeze all year round. Further, 30–40 m downhill, a pond about 10 m in diameter was formed. Mineral mud is accumulated in this pond; a color of the mud changes from black to gray with depth [Cherepanova, 1988].

The Sytygan-Sylba Spring is located in the southern part of the Oymyakon highlands, which is part of the long (about 1200 km) and wide (about 300 km) belt of relatively leveled low relief. This part of the highlands can be called the Yana-Indigirka intermountain region. The morphostructure of the intermountain region is characterized by predomination of plateaus and tablelands, that occupy the central part of the Verkhoyansk-Kolyma mountain system between its high-mountain structures – the Chersky and Verkhoyansk ranges. The top surface within the intermountain region is located at the elevation about 1000 m on average. However, on the framing ridges, the top surface rises to the heights of 2000–2500 m, sometimes reaching the heights of about 3000 m. It is likely that the most significant amount of water penetrates into the subsurface within this part of the ridges, and the geological, geomorphological, and, partially, climatic conditions of these areas determine the volume of water resources, isoto-

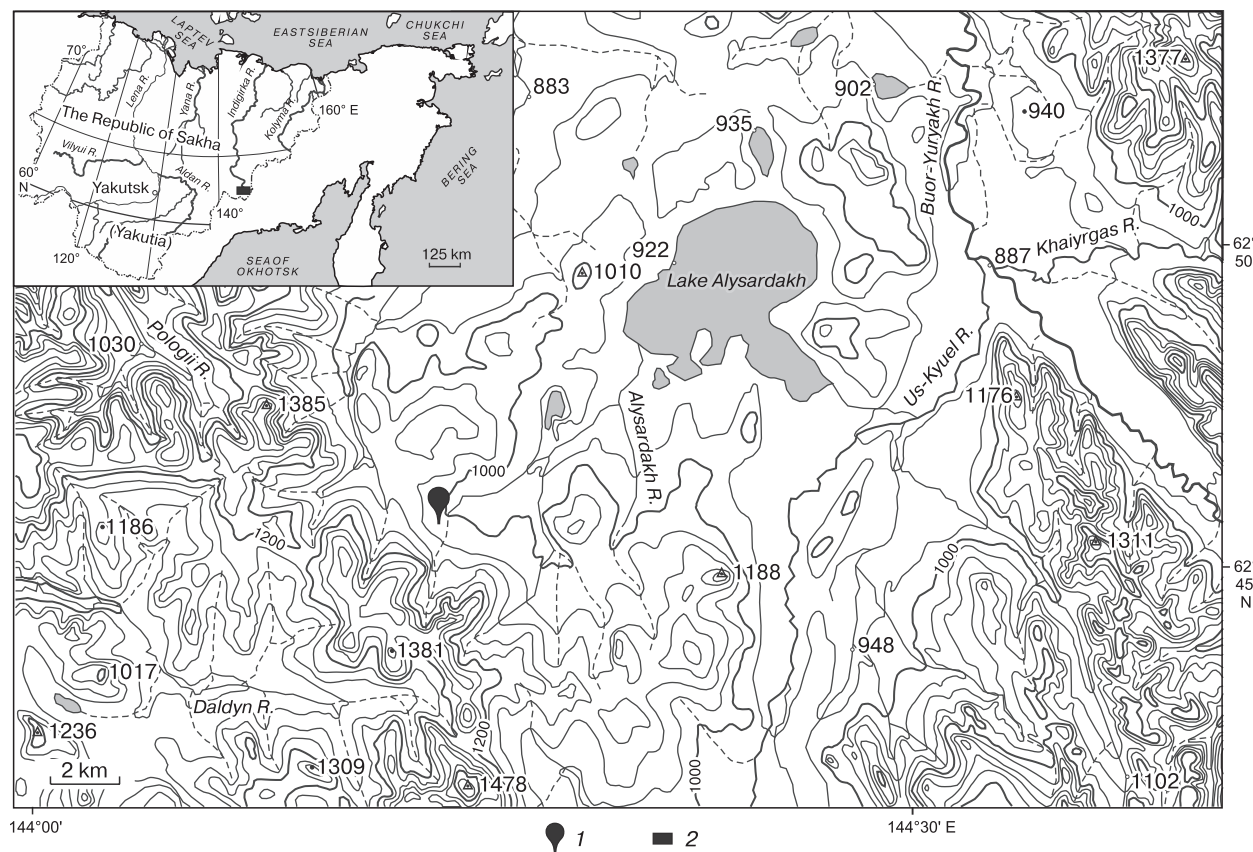


Fig. 1. The overview map of the Sytygan-Sylba Spring.

1 – location of the Sytygan-Sylba Spring; 2 – the studied area in the inset-map.

pic and, to some extent, chemical composition of thermal waters.

The current relief was formed during the Late Cenozoic (Pliocene–Quaternary) after the prolonged (Paleogene–Miocene) stable (quasi-plate) stage, during which the relief was levelled and low-thick continental coal-bearing deposits were accumulated [Zonenshayn, Savostin, 1979; Spektor, 1987].

The river network of the Oymyakon area belongs to the basins of the rivers of the Indigirka River upstream that originate in the Suntar-Khayata Ridge. Icings, the origin of which is associated with river waters and confined subpermafrost waters, are widespread in river valleys. The icings play a great role in the ice regime of the rivers and in the runoff redistribution. The geological structure of the area, where the spring is located [Matveenko, 1972], points to its long and multistage history, which is partially manifested in outcrops of the structural-material complexes (Fig. 2). The most ancient of them is the Verkhoysk Complex, which is composed of the Permian and Triassic marine terrigenous rocks dislocated into northwest-striking linear folds in the Late Mesozoic. The poorly dislocated Cretaceous volcanic rocks of the intermediate and felsic composition, which belong to the marginal continental Okhotsk-Chukotka volcanic belt, occupy the higher stratigraphic position. Large granite massifs, the outcrops of which are located at a distance of 5–10 km from the spring, were formed in the same time. The Quaternary deposits, represented by pebbles, boulders, sands, and silts of the glacial, alluvial, and slope origin complete the section. The spring is confined to the slope of the hill, which is composed of the Cretaceous volcanics and the Verkhoysk Complex.

The Verkhoysk Complex and the Late Mesozoic volcanic and magmatic rocks were frozen epigenetically, while the Quaternary deposits were frozen syngenetically. The permafrost within the Yana-Indigirka intermountain area and the framing ridges were formed at the end of the Pliocene–the beginning of the Quaternary.

Location of the spring is unique. The structural position of the study area has determined the significant modern tectonic activity and seismicity. Horizontally oriented compressive stresses have been reconstructed in the earthquake sources at the depths of the first tens of kilometers.

According to the model, proposed by V.T. Balobaev [1991], the Verkhoysk-Kolyma system is characterized by the weighted average value of geothermal heat flux of 65 mW/m², which is twice higher than the flux within the Siberian Platform. In view of a small thickness of the continental lithosphere and the granitic layer of the crust in this area, V.T. Balobaev [1991] concludes that the background flux increases due to the significant heat flux from mantle. The highest values of the heat flux, ranging from 80

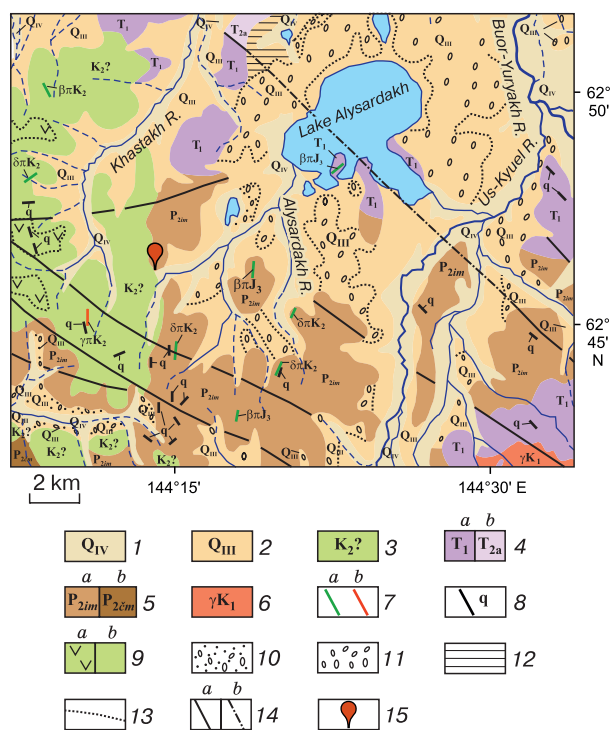


Fig. 2. The overview geological map of the spring location (Scale 1:200 000. Sheet P55-VII).

1, 2 – the complex of the Quaternary deposits: 1 – Holocene, alluvial deposits, 2 – Late Neopleistocene, alluvial deposits; 3 – Late Cretaceous marginal continental volcanogenic complex; 4, 5 – Late Paleozoic–Mesozoic Verkhoysk terrigenous complex of the passive continental margin: 4 – Triassic deposits: *a* – Lower Triassic deposits, *b* – Middle Triassic deposits, Anisian; 5 – Upper Permian deposits: *a* – Imtchan Formation, *b* – Chamba Formation; 6 – Early Cretaceous granite batholites, proto-orogenic complex; 7 – dikes: *a* – porphyry dikes of mafic and intermediate composition, *b* – granitoid dikes; 8 – hydrothermal quartz veins (*q*); 9 – the composition of the Late Cretaceous volcanogenic complex: *a* – rocks of intermediate composition, *b* – rocks of felsic composition; 10–12 – genetic types of the Late Neopleistocene deposits: 10 – water-glacial, 11 – glacial, 12 – lacustrine; 13 – facies boundaries; 14 – faults: *a* – established, *b* – assumed; 15 – location of the Sytygan-Sylba Spring.

to 100 mW/m², are common in the territory of the Yana-Oymyakon intermountain area. According to V.T. Balobaev it “...may be an anomalous mantle of asthenospheric type, the appearance of which leads to partial melting of the Earth crust, transformation of its mineralogical composition, formation of depressions and filling them with sediments” [Balobaev, 1991, p. 135].

The spring belongs to an increased type of thermal regime of thermal waters with a heat flux density of 80–100 mW/m². Such heat flux provides the temperature, which exceeds 1000 °C at a depth of 40 km [Balobaev, 1991, p. 137]. A geothermal gradient (an increase in temperature with depth, usually per 1 km

or 100 m of depth) is 40–50 °C/km. We consider that the location of the spring over the central part of the anomalous mantle ledge and the high heat flow accompanying this ledge explain the very existence of the thermal spring, the relatively high temperature of water (+26.6 °C), and year-round activity of the spring in the field of continuous permafrost 300–500 m thick with the mean annual ground temperature of –3 to –5 °C or lower [Ershov, 1991]. This geothermal anomaly should have formed an extensive hydrogeogenic talik zone. The existence of this zone can be indirectly evidenced by the presence of relatively mineralized water in the Lake Alysardakh, which is located near the area of thermal water discharge. The mineralized water of the lake is unusual for surface waters of the region.

In terms of hydrogeology, the area of groundwater discharge belongs to the Alysardakh geocryological intermountain artesian basin of the Yana-Kolyma cryo-pressure basin. This area is attributed to the zone of continuous permafrost, a thickness of which exceeds a thickness of the sedimentary cover. The significant tectonic fragmentation of rocks and the presence of large tectonic faults determined the wide distribution of subpermafrost fracture-vein waters and icings, associated with local discharges of groundwater in the area.

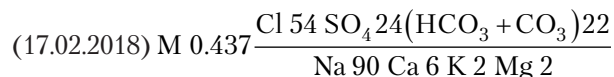
Geological and structural features of the area determine the specific character of the hydrogeological conditions of the area of thermal water discharge. In accordance with the conditions of occurrence and circulation, these waters are fracture-vein thermal waters, which are attributed to the zone of active latitude-striking faults at the place of their junction with the north-northwest-striking faults [Parfenov, 2001].

The Sytygan-Sylba Spring is a unique thermal mineral spring in the studied area. However, it is possible that, in the Indigirka River upstream, discharges of thermal waters are more widely distributed, and Sytygan-Sylba is not the only spring of thermal waters within the Yana-Oymyakon intermountain area [Shvetsov, 1951]. We consider that there are “warm lakes” to the north of this area, in the same morphostructural zone, and further north, beyond the Arctic Circle, there are discharges of subthermal water in the Kular Ridge area.

RESULTS AND DISCUSSION

Results of chemical analyses of water of the spring, which were obtained by different researchers from 1926 to 2018, are given in Table 1. The data demonstrate that the chemical composition of waters of the Sytygan-Sylba Spring has remained stable during almost a century of observations. These waters are mixed in their anion composition with the strong predominance of sodium: sodium bicarbonate-sulfate-

chloride, weakly alkaline (pH 8.2–8.48), with a high silica content of 21–81 mg/L (about 10 % of the total dissolved solids) and low mineralization (0.40–0.51 g/L):



pH 8.48 Eh 0.386 SiO₂ 30 F 19.6.

The geochemical conditions are oxidizing (Eh = 0.25–0.38 V). Water is slightly carbonaceous, CO₂ content is 48.4, and H₂S is 0.45 mg/L. A specific feature of the springs is a relatively constant water temperature (24.5–26.6 °C) in cold and warm seasons. Low mineralization of thermal waters of the Sytygan-Sylba Spring is explained by their formation in terrigenous rocks, which are well washed off water-soluble salts by intensive groundwater circulation.

The basic components, providing mineralization of waters of the spring, are sodium, silica, fluorine, chlorides, sulfates, and bicarbonates. Cl predominates (48–61 %-eq.) among anions. Besides chloride ions, sulfates (up to 110 mg/L) and bicarbonates (up to 109 mg/L) are present in rather high amounts. Among cations, Na⁺ predominates (92–95 %-eq.) with the concentration up to 195 mg/L. The content of other cations is low: K⁺ content is no more than 8.0 mg/L, Ca²⁺ content is up to 5.8 mg/L and Mg²⁺ is up to 3.0 mg/L.

The studied thermal waters are rich in fluorine with the concentration of 19.6 mg/L. The fluorine content is similar to that in the thermal waters of the Talaya Spring (15–20 mg/L) in the Magadan region [Hydrogeology..., 1972]. Low activity of calcium also creates the favorable conditions for the increased activity of fluorine and its accumulation in water.

There are certain variations in the chemical composition of water of the spring in different months: July, November, February, April (Fig. 3). Data obtained in different years have been compared, because no single annual cycle of observations has been carried out. In April, at the end of winter (when the active layer freezes to the maximum), the chemical composition of water of the spring should completely correspond to the composition of deep thermal waters. During this period, as thermal waters of the Sytygan-Sylba Spring move toward the surface through permafrost, they are not supplied by surface waters and not diluted by frozen suprapermfrost waters. In winter time, the temperature of water in the spring remains positive at the discharge zone; however, mineralization of water steadily decreases due to reduction of Na⁺ and SO₄²⁻ concentration (Fig. 3).

In the warm season, when the spring water should be desalinated, mineralization should be decreased, and a role of bicarbonates in the chemical composition of the waters should be increased due to input of less mineralized waters from the free ex-

Table 1. The chemical composition of thermal waters of the Sytygan-Sylba Spring

Parameters	Date of sampling				
	10–16.11.1926 [Obruchev, 1927]	02.04.1948 [Shvetsov, 1951]	28.07.1984 [Cherepanova, 1988]	14.04.2013 [Trofimova, 2013]	17.02.2018 (authors' data: V.N. Makarov, V.B. Spektor, R.N. Ivanova)
Rate, L/s	0.20	0.25	–	0.25–0.30	–
Water temperature, °C	+26.0	+25.6	+26.6	+25.1	+24.5
Air temperature, °C	–40.0	–11.5	–	–	–
pH	–	–	8.2	9.5	8.48
Eh, mV	–	–	250	–	386
Mineralization, mg/L	483.1	396.6	513	439	436.8
Content*					
Ca ²⁺	7.7/0.38	1.0/0.03	4.0/0.20	8.0/0.8	7.76/0.39
Mg ²⁺	0.2/0.02	6.0/0.47	3.0/0.25	2.24/0.2	1.43/0.12
Na ⁺	186.4/7.90	140.0/6.10	195.5/8.50	179.4/7.8	158.2/6.09
K ⁺	186.4/7.90	140.0/6.10	8.0/0.20	179.4/7.8	4.20/0.13
CO ₃ ^{2–}	–	–	–	–	4.65/0.15
HCO ₃ [–]	108.6/1.78	57.2/0.95	85.0/1.39	103.7/1.7	86.22/1.41
Cl [–]	142.5/4.02	141.0/4.00	150.0/4.23	149.1/1.7	134.99/3.81
SO ₄ ^{2–}	94.0/1.96	80.0/1.65	110.0/2.29	48.0/1.0	82.32/1.71
SiO ₂ ^{2–}	20.6	–	81.0	–	65.3
NO ₃ [–]	–	–	–	–	0.10
NO ₂ [–]	–	–	2.0	–	0.12
NH ₄ ⁺	–	–	–	–	0.05
HPO ₄ [–]	–	–	–	–	0.12
CO ₂	–	48.4	–	66.0	–
H ₂ S	–	0.45	–	9.22	–
Fe ³⁺	–	0.24	–	0.12 (Fe)	0.056 (Fe)

* In a numerator – mg/L, in a denominator – mg-eq.

change zone, the opposite events are observed. In summer, in the water of the Sytygan-Sylba Spring, mineralization significantly increases (by 50–100 mg/L) due to sulfates and sodium chlorides (Fig. 3). The content of Na⁺ and SO₄^{2–} ions increases by about 30 % in July compared to April, when supra-permafrost waters is affected by the maximum winter freezing. Obviously, during the warm season, supra-permafrost waters with higher mineralization inflow to the spring. The very fresh surface bicarbonate waters do not influence the chemical composition of waters of the spring.

In 2018, we obtained new data on the chemical composition of thermal waters of the spring. High concentrations in the thermal spring are typical for strontium – 0.16 mg/L, lithium – 1.39 mg/L, and fluorine – 19.6 mg/L.

Of siderophile elements, only iron and molybdenum have significant concentration in the waters. Fe_{tot} content in thermal waters of the Sytygan-Sylba Spring varies from 56 to 240 µg/L, Mo content is 0.443 µg/L. The concentration of other siderophiles is below the detection limit: Co, Ni < 0. n; Pd, Rh, Au < 0.0 n; Re, Os, Ir, Pt, Ru < 0.00 n (n = 1–9), in

particular: Co and Ni is <0.2 µg/L; Pd is <0.014 µg/L, Rh is <0.012 µg/L, Au is <0.014 µg/L; Re is <0.001 µg/L, Os <0.001 µg/L, Ir is <0.001 µg/L, Pt is <0.002 µg/L, Ru is <0.008 µg/L. The concentra-

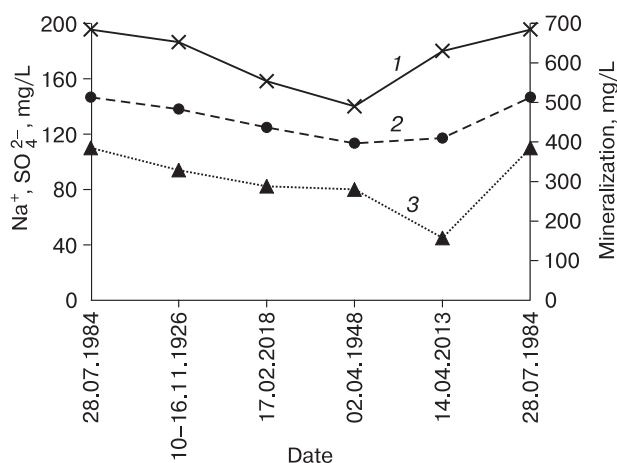


Fig. 3. Variations in mineralization (2) and Na⁺ (1) and SO₄^{2–} (3) content in water of the Sytygan-Sylba Spring on months in different years.

Table 2. Concentration of REEs in thermal waters of the Sytygan-Sylba Spring

Element	REE content		Element	REE content	
	µg/L	Normalized to NASC		µg/L	Normalized to NASC
La	0.0165	$5.3 \cdot 10^{-7}$	Tb	0.00086	$1.0 \cdot 10^{-6}$
Ce	0.0501	$7.5 \cdot 10^{-7}$	Dy	0.006	$1.2 \cdot 10^{-6}$
Pr	0.004	$5.4 \cdot 10^{-7}$	Ho	<0.0008	–
Nd	0.0215	$7.8 \cdot 10^{-7}$	Er	0.0019	$5.3 \cdot 10^{-7}$
Sm	0.0049	$8.8 \cdot 10^{-7}$	Tm	<0.0008	–
Eu	0.0023	$1.9 \cdot 10^{-6}$	Yb	<0.0008	–
Gd	0.0086	$1.7 \cdot 10^{-6}$	Lu	<0.0008	–

Note. Mass-spectral and atomic-emission analyses have been performed at the Analytical Certification Test Center of the Institute of Microelectronics Technology and High-Purity Materials, Russian Academy of Sciences (ACTC IMT RAS, Chernogolovka).

tion of silicon is 30.48 µg/L, the concentration of phosphorus is less than 30 µg/L.

Of lithophile elements, the high content ($>n$, µg/L) was established for Li (1390–2050), Br (275), Sr (160–212), Al (24.9), Mn (3.1), B (1.68), and Ba (1.1). The content of other lithophile elements ranged from $0.n$ to $0.00n$ µg/L: W (0.715), V (0.17), Cs (0.088), Rb (0.085), Be (0.048), Zr (0.038), Th and U (0.008), Hf (0.007). B/Cl ratio = $1.24 \cdot 10^{-5}$, which is almost 4 orders of magnitude lower than in seawater, and close to this parameter (<0.007) in thermal springs in the areas of active volcanism.

Gallium, zinc, arsenic, germanium, lead, and antimony should be highlighted in a group of chalcophile elements. Their concentrations range from $n - 0.n$ µg/L: Ga (1.8), Zn (1.2), As (0.85), Ge (0.762), Pb (0.14), Sb (0.105). Cu content in the studied thermal waters is less than 0.7 µg/L, Ti content is less than 1 µg/L. The following elements have concentrations below the detection limit: Se <5 µg/L; Hg <0.7 ; Sc <0.3 ; Sn <0.022 ; Te <0.018 ; Ag <0.01 ; Cd <0.009 ; Nb <0.008 ; In <0.005 ; Ta <0.003 ; Te <0.001 ; Bi <0.001 µg/L*.

The geochemical characteristics of thermal spring waters, which contain sulfates and anomalous amounts of ore elements (germanium, molybdenum, tungsten, arsenic and others) may be indicators of the halo waters suggesting close proximity to ore bodies [Makarov, 1998].

We have obtained the first data on the content of rare-earth elements (REE) in the studied thermal waters (Table 2). The concentration of REE is generally low: $\geq 0.0n$ µg/L. The spectrum of the REE distribution, normalized to North American Shale Composite (NASC), is characterized by a high content of light REEs (more than 80 %), which are moderately enriched in medium REEs and depleted in

heavy REEs. Low concentration of REEs in the waters may be caused by alkaline values of pH in thermal waters, controlling the REE content and determining decrease in the REE content [Sholkovitz, 1995].

A poor cerium anomaly and an apparent europium anomaly are indicated. The tetrad effect is insignificant. This pattern of the REE distribution with the well-manifested Eu anomaly is typical for hydrothermal solutions [Haas *et al.*, 1995; Dubinin, 2006]. The high positive Eu anomaly may be an indirect indicator of the thermal impact during the formation of a liquid phase. Although, we cannot exclude the possibility that the enrichment by europium occurred during diagenesis of marine sediments under anaerobic conditions [Ivanova, 2020].

The similarity of the composition of REE in the spring water with sandstones and siltstones of the Verkhoysk Complex points to inheritance of their composition, particularly, in terms of the significant amount of light REEs and the europium anomaly. The lack of heavy REEs may be associated with a geochemical barrier (influence of supraperafrost waters, chemisorption on clayey minerals) during discharge.

Such characteristics of the REE spectrum as well as the anionic composition and low content of macro-components, indicate the location of the spring in the zone of discharge of fracture waters.

The relationship between the thermal spring and the supraperafrost and surface waters can be established on the basis of the comparison of the REE spectra of the spring waters and the samples from wedge ice, massive ground ice, and river water, which were obtained in Eastern Yakutia [Ivanova, 2020] and normalized to the NASC standard (Fig. 4) [Gromet *et al.*, 1984].

* Mass-spectral and atomic-emission analyses have been performed at the Analytical Certification Test Center of the Institute of Microelectronics Technology and High-Purity Materials, Russian Academy of Sciences (ACTC IMT RAS, Chernogolovka).

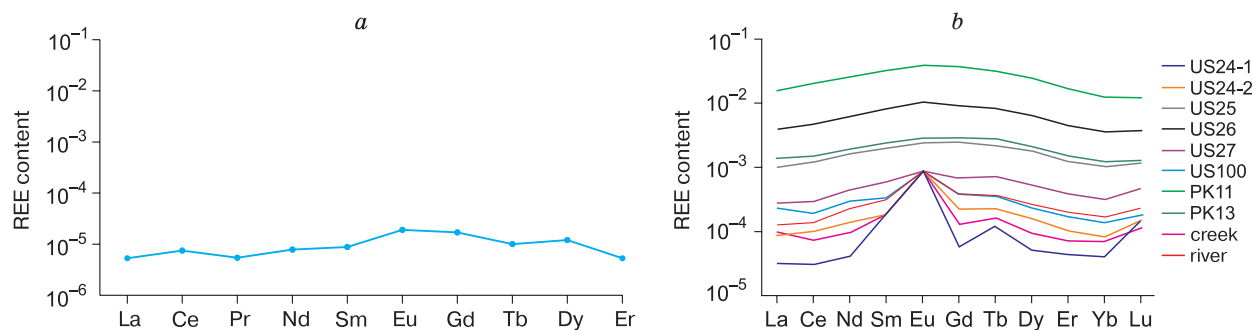


Fig. 4. REE content, normalized to NASC:

a – in water of the Sytygan-Sylba Spring; *b* – in ground ice (US: 24–27, 100; PK: 11, 13) and surface waters (creek, Adycha River).

However, there are almost no data on the distribution of REEs in the components of the hypergenesis zone in the region. Therefore, when interpreting the obtained data, we have used the results of the studies of V.V. Ivanova in the basin of the Adycha River [Ivanova, 2020]. Terrigenous sediments and granitoids are widespread in this area, as well as in the area of the spring. These regions are characterized by the similar chemical composition of atmospheric precipitation [Makarov, 2014]. These data suggest that the chemical composition of natural waters of the hypergenesis zone was formed under similar conditions in both regions.

The REE spectrum of wedge ice and massive ground ice reflects the chemical composition of soil solutions penetrating into ice from the suprapermafrost perched aquifer. The positive Europium anomaly of ice is associated with the groundwater composition and the increasing of the concentrations of chemical elements due to cryogenic or ore concentrating. REE content in water of the Sytygan-Sylba Spring is significantly lower than their content in river water and wedge ice (Fig. 4). This indicates that the spring is located in the groundwater discharge zone, which is poorly associated with the background surface waters and ground ice.

Mineralization and Na^+ and SO_4^{2-} content in the spring water significantly increase in the summertime. This points to the very weak (almost zero) dilution of water of the Sytygan-Sylba Spring by surface and suprapermafrost waters (Fig. 3).

Data on oxygen and hydrogen isotopes in water of the spring have been obtained for the first time. Isotope analysis has been carried out at the MPI SB RAS on the Picarro L2140-i Isotope and Gas Concentration Analyzer (analysts N.I. Lykhota and G.T. Maksimov). This allowed us to measure simultaneously $\delta^{18}\text{O}$, $\delta^{17}\text{O}$ and δD in solids, liquids, and vapor. Table 3 demonstrates characteristics of the oxygen and hydrogen isotopic composition of atmospheric precipitation and water of the thermal spring. The calculated value of meteoric waters

$\delta\text{D} = a \cdot \delta^{18}\text{O} + 10 \text{ ‰}$. Substituting the value $\delta^{18}\text{O} = -21 \text{ ‰}$ for rainwater (Table 3), we obtain $\delta\text{D} = -178 \text{ ‰}$, the real, current value of -169 ‰ . Some enrichment of the modern meteoric waters in heavy hydrogen may result from the increased role of precipitation due to the sources of evaporation located nearby (Pacific Ocean).

In water of the spring, $\delta\text{D} = -179.31 \text{ ‰}$, which is very close to the calculated parameters of atmospheric precipitation. They reflect the composition of atmospheric precipitation for a long period of time preceding the modern one, when the Atlantic transfer prevailed. This is evidenced by the lowering of deuterium in water of the spring, which has been lost during the long-distance transfer of atmospheric moisture. The small amount of precipitation, enriched in heavy hydrogen, falls during the summer. This precipitation is consumed generally by accelerated evaporation.

In terms of balneology, warm (subthermal) waters of the spring can be used as therapeutic, anion mixed, sodium waters in a similar way to thermal waters of the Talaya Deposit. The presence of such balneological components as fluorine, metasilicic acid, rare elements, many of which are biologically active components, allows us to recommend the waters of

Table 3. The isotopic composition of oxygen and hydrogen of atmospheric precipitation and water of the thermal spring

Natural waters	$\delta^{18}\text{O}$	δD
Atmospheric precipitation, March–June	–21...–23	–160...–169
Spring	–20.89	–179.31
Snow, March (Oimyakon Area)	–37.44	–
	–38.08	–
Standard Mean Ocean Water (SMOW), ‰	–0.1985	–0.01985

Note. Isotope analysis has been carried out at the MPI SB RAS (analyser Picarro L2140-i Isotope and Gas Concentration Analyze).

the Sytygan-Sylba Spring for external therapeutic and prophylactic use in the form of baths.

CONCLUSIONS

Almost a lapse of a hundred years of observations reveals that waters, heated up to 26 °C in the Triassic terrigenous fractured sediments, are not subjected to significant temperature fluctuations and variations in the chemical composition. Specific features of nitrogen thermal waters of the Sytygan-Sylba Spring are low mineralization (0.4–0.5 g/L), complex anionic composition, predomination of sodium in the cation composition, weakly alkaline reaction, predomination of nitrogen in the gas composition, significant concentrations of silicic acid, fluorine, tungsten, molybdenum, germanium, arsenic and others. A distinctive feature of thermal waters of the Sytygan-Sylba Spring is the presence of sulfates in the ionic composition.

Very low (ng/L) REE contents were established in the water of the Sytygan-Sylba Spring. In terms of REE contents and correlation with spectra of river water and ground ice, these waters are thermal waters of the groundwater discharge zone, poorly related to the background regional surface waters and ice.

The isotopic composition of the thermal waters may indicate a certain role of snow recharge in the formation of a hydrogenous component of the Sytygan-Sylba Spring waters.

There is the significant increase in mineralization (by 50–100 mg/L) due to the concentration of sulfates and sodium chlorides in the water of the Sytygan-Sylba Spring in summertime. It can be assumed that during the warm period, when thermal waters enter the active layer, groundwater mixes with mineralized permafrost waters. Subsequently, since mid-November, as the active layer freezes and the inflow of groundwater decreases, mineralization of the spring water has decreased (by 15–20 % by the end of the winter period as compared to the summer period of time).

Stability of the hydrogeothermal parameters of the spring points to the relatively deep propagation of fracture systems, which serve as the regulating reservoirs and make their long-term regimes consistent. A crucial role of deep factors in the stable hydrogeochemical character of the thermal spring is clearly in evidence.

The characteristics of the REE spectrum as well as the anionic composition and the low content of macrocomponents, suggest that the spring is located in the zone of fracture water discharge. Based on the chemical composition and geological conditions of the discharge area of the Sytygan-Sylba Thermal Spring, the groundwaters belong to the low-mineralized siliceous thermal waters of the deep origin, which are recharged seasonally due to the inflow of more mineralized suprapermfrost waters.

The geochemical features of waters of the thermal spring (the increased concentration of sulfates in the ionic composition, the anomalous content of germanium, molybdenum, tungsten, arsenic and other elements) can be valuable in geochemical exploration of ore accumulations in this region.

In terms of balneology, these waters can be used as therapeutic waters for external treatment and prophylactic in the form of baths, by analogy with the thermal water of the Talaya Deposit.

Acknowledgements. *The authors are grateful to V.V. Ivanova Doctor of Geological-Mineralogical Sciences (post-doctorate degree in Russia) (Gramberg All-Russian Scientific Research Institute for Geology and Mineral Resources of the Ocean – VNIIOknegeologia) and researcher R.N. Ivanova (Melnikov Permafrost Institute, Siberian Branch, the Russian Academy of Sciences) for help in the collection of the factual material and data interpretation.*

References

- Balobaev, V.T., 1991. Geothermy of the frozen zone of the lithosphere in the northern Asia. Publishing House of the SB RAS, Novosibirsk, 193 pp. (in Russian).
- Cherepanova, A.P., 1988. New data on the Sytygan-Sylba Mineral Spring (Yakutia). Research of frozen strata and cryogenic events. IMZ SO AN SSSR, Yakutsk, pp. 90–97 (in Russian).
- Dubinin, A.V., 2006. Geochemistry of rare earth elements in the ocean. Nauka, Moscow, 359 pp. (in Russian).
- Ershov, E.D. (Ed.), 1991. Geocryological Map of the USSR. Izd-vo Mosk. Un-ta, Moscow (in Russian).
- Gromet, L.P., Dymek, R.F., Haskin, L.A., Korotev, R.L., 1984. The North American Shale Composit: Its composition, major, and trace element characteristics. Geochim. et Cosmochim. Acta 48, 2469–2482.
- Haas, J.R., Shock, E.L., Sassani, D.C., 1995. Rare earth elements in hydrothermal systems: estimates of standard partial modal thermodynamic properties of aqueous complexes of the rare earth elements at high pressures and temperatures. Geochim. Cosmochim. Acta 59, 4329–4350.
- Hydrogeology of the USSR. Vol. XXVI. North-East of the USSR, 1972. Nedra, Moscow, 296 pp. (in Russian).
- Ivanova, V.V., 2020. Geochemical features of spectra of rare earth elements in deposits of the Eastern Siberia as a new indicator of the Late Pleistocene climate change in the zone of periglacial lithogenesis—Dissertation for the degree of Doctor of geol.-mineral. sciences, St. Petersburg, 408 pp. (in Russian).
- Makarov, V.N., 1998. Geochemical Fields in Permafrost. IMZ SO RAN, Yakutsk, 116 pp. (in Russian).
- Makarov, V.N., 2014. Geochemistry of the snow cover of the taiga and mountain permafrost landscapes. Led i Sneg (Ice and Snow), No. 1 (125), 73–80.
- Matveenko, V.T. (Ed.), 1972. State Geological Map of Russian Federation at a scale of 1:200 000. List P-55-VII. Izd-vo "Aerogeologiya", Leningrad (in Russian).
- Obruchev, S.V., 1927. The Sytygan-Sylba Spring on the Indigirka River (YaASSR). Kurortnoye Delo, No. 4, p. 8.

- Obruchev, S.V., 1954. Unknown lands. Travels to the North 1917–1930. Molodaya gvardiya, Moscow, 347 pp. (in Russian).
- Parfenov, L.M., 2001. Tectonics, Geodynamics and Metallogeny of the Territory of the Republic of Sakha (Yakutia)/ M.I. Kuz'min (Ed.). MAIK Nauka/Interperiodika, 571 pp. (in Russian).
- Shepelev, V.V., 1987. Spring waters of Yakutia. Knizhnoye izd-vo, Yakutsk, 27 pp. (in Russian).
- Sholkovitz, E.R., 1995. The aquatic chemistry of rare earth elements in rivers and estuaries. *Aquat. Geochem.* 1, 1–34.
- Shvetsov, P.F., 1951. Groundwaters of the Verkhoyansk-Kolyma Fold Area and Features of their Manifestation Associated with Low-temperature Permafrost. Izd-vo AN SSSR, Moscow, 280 pp. (in Russian).
- Spektor, V.B., 1987. Structure and kinematic of the Verkhoyansk–Kolyma folded system. In: *The Formation of Relief of the Siberia*. Nauka, Novosibirsk, pp. 152–156 (in Russian).
- Trofimova, T.P., 2013. The chemical composition of waters of the Sytygan-Sylba Mineral Spring. Collection of scientific articles based on the results of the international scientific-practical conference. Kul'tInformPress, St. Petersburg, pp. 147–149 (in Russian).
- Zonenshayn, L.P., Savostin, L.A., 1979. Introduction to Geodynamics. Nedra, Moscow, 311 pp. (in Russian).

Received August 30, 2020

Revised version received October 22, 2020

Accepted December 18, 2020