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UPPER YURYEV THERMAL SPRINGS: EVOLUTION OF CHEMICAL AND ISOTOPIC COMPOSITION (1952–2022) IN CONNECTION WITH PERIODS OF ACTIVATION OF EBEKO VOLCANO (PARAMUSHIR ISLAND)

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Abstract. This paper examines the chemical composition of thermal waters discharged on the northwestern slope of the active Ebeko volcano in the valley of the Yuryeva River. Based on long-term regime observations of the evolution of the chemical and isotopic composition, an assessment is made of the response of volcanic events to the state of the hydrothermal system. It has been shown that phreatic-magmatic volcanic eruptions are preceded by a change in the chemical and isotopic composition of thermal waters due to an increase in the flow of magmatic volatiles entering the system. In the springs there is an increase in the concentrations of anionic components (chloride, sulfate, and fluorine ions), a simultaneous increase in the weight of oxygen and hydrogen isotopes (deuterium) in the direction of "andesitic" waters. Since changes were detected several months before the eruption, such geochemical effects can serve as predictive markers when monitoring the state of the volcano.

Keywords: *Yuryeva River, Paramushir Island, hydrogeochemistry, thermal waters*

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INTRODUCTION

One of the most active volcanoes of the Kuril Islands is Ebeko volcano, located in the northern part of Paramushir Island. A local hydrothermal system is associated with its edifice. The main geothermal reservoir is located at a depth of ~300 Paramushir. A local hydrothermal system is associated with its construction. The main geothermal reservoir is located at a depth of ~300 m from the crater zone and contains a boiling ultra-acidic chloride-sulfate solution with a temperature >200–210°C [Kalacheva et al., 2016]. Lateral flow occurs predominantly in the northwestern direction. Water discharge occurs 2.5 km from the active crater of the volcano in the Yuryeva River valley as a series of descending high-yield Upper Yuryev springs.

Upper Yuriev springs are one of the prominent representatives of ultra-acidic thermal waters (ASC-waters (**A**cid **S**ulfate **C**hloride) [Taran, Kalacheva, 2020]), the main formation mechanism of which comes down to the condensation of volcanic vapors in near-surface conditions and/or dissolution of "acidic" magmatic volatiles (SO_4, Cl, HF) in aerated groundwater with the formation of acid mixtures [Giggenbach, 1997; et al.]. Most ASC-waters have been discovered and described in Japan [Kimbara, Sakaguchi, 1989; Sasaki, 2018] and on the Kuril Islands [Markhinin, Stratula, 1977; Kalacheva, Kotenko, 2013; Kalacheva, Voloshina, 2022; Kalacheva et al., 2021, 2022, 2023; Kalacheva et al., 2016; et al.], similar waters are found in Indonesia [Delmelle et al., 2000; Mazot et al., 2008; Caudron et al., 2018; et al.], Argentina [Varekamp et al., 2009], Colombia [Sturchio et al., 1988; Torres-Ceron et al., 2019] and other countries located along the Pacific coast. The most comprehensive review of ultra-acidic volcanic waters of the world, discharging as thermal springs, was made in the work [Taran, Kalacheva, 2020].

The chemical and isotopic compositions and temperature of ultra-acidic waters are extremely variable. In addition to seasonal and short-term variations caused by changes in precipitation and snow melting, i.e., different degrees of dilution, these waters experience significant changes in the ratios between components associated with activity periods of volcanoes whose edifices host hydrothermal systems. As shown in several cases, the SO_4/Cl ratio and the isotopic composition of dissolved sulfate can serve as activity indicators (see review [Taran, Kalacheva, 2020] and references therein). For example, an increase in the SO_4/Cl ratio was observed in the springs of Copahue volcano simultaneously with the 2000 eruption [Varekamp et al., 2009], which was associated with the intrusion of new magma into the system with deep fluid degassing during ascent. The increase in sulfate and chloride ion concentrations, along with other factors, recorded in 2018 in the crater lake of Maly Semyachik volcano, indicated the onset of a new period of its activation after a long period of quiescence, expressed in increased input of magmatic volatiles (primarily HCl and SO_2) into the volcano's hydrothermal system [Taran et al., 2021]. However, using the example of the boiling Obuki springs, which have been geochemically monitored for 70 years, it has been shown that the hydrothermal system's response can occur not only before or during periods of increased volcanic activity but also many years after the event Ueda et al., 2021].

Due to their difficult accessibility, regular monitoring observations of the Upper-Yuryev springs are not conducted. The authors, when possible, have been conducting research in the Yuryeva River valley since 2003, resulting in a significant accumulation of data, partially used in publications of different years [Kalacheva, Kotenko, 2013; Kalacheva, Voloshina, 2022; Kalacheva et al., 2016].

In 2016 the eruption of Ebeko volcano began, which continues in 2024 as well. There is currently no published data on how the hydrothermal system responded to the events occurring on the volcano. Only in the work of [Kalacheva, Taran, 2019] is the change in isotopic composition (δD, $\delta^{18}O$) of the Upper Yuryev springs that occurred during the period 2016–2017 compared to 2014 reflected. Additionally, in September 2017 a mudflow descended along the valley of the Yuryeva River, changing the riverbed [Kotenko, Kotenko, 2018]. The changes also affected the thermal water discharge area [Kotenko et al., 2020].

Considering the above, the purpose of this work is to study the evolution of the chemical composition of water in the Upper Yuryev springs in connection with changes in the state of Ebeko volcano, using data from long-term monitoring observations. The main tasks include: a) describing the location and discharge conditions of thermal waters as of August 2022; b) detailed study of changes in the chemical and isotopic compositions of spring waters, both across the distribution area and over time; c) identifying possible causes of fluctuations in macrocomponent concentrations and their ratios over time; d) searching for geochemical indicators of the hydrothermal system's response to Ebeko volcano eruptions.

This work is based on the results of the authors' own long-term observations (from 2003 to 2022), as well as all available published data and archival materials for the entire period of observation of the volcano (since 1952).

BRIEF CHARACTERISTICS OF EBEKO VOLCANO

Ebeko volcano, located in the northern part of the Vernadsky Ridge (Fig. 1), has a complex structure. The main morphological elements are several volcanic cones of different ages and states of preservation merged into a single volcanic ridge with large craters at the top [Melekestsev et al.,

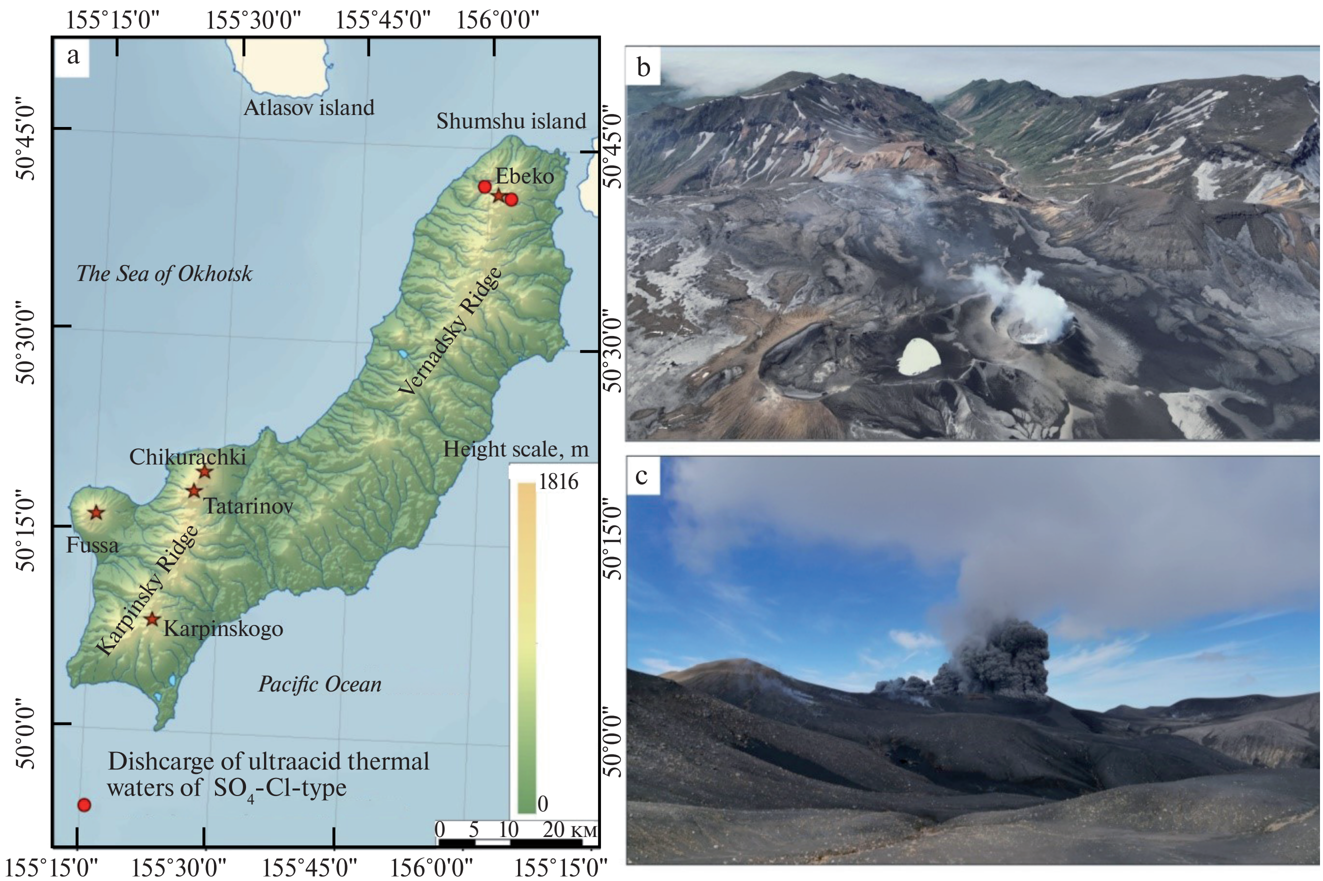


Fig. 1. Paramushir Island (a) and Ebeko volcano: view of the volcano craters and Yurieva River valley (b). Photo by T. Kotenko. Summit area of the volcano, beginning of ash emission from Korbut crater and fumaroles of the eastern slope (c). Photo by E. Kalacheva. Kalacheva.

1993]. According to the cited article, the formation of the volcanic edifice began ~2400 years ago. The first stage involved lava flows and pyroclastic material deposition, which later gave way to explosive eruptions (phreatic/phreatomagmatic). The modern stage of volcanic activity began with a strong phreatomagmatic eruption in 1934–1935. Explosions occurred from a meridional fissure at the bottom of the Middle crater, ejecting ash and large bombs of andesitic composition [Gorshkov, 1954]. The next major periods of activation occurred in 1963–1967, 1987–1989, 2005–2011 [Belousov et al., 2021]. The current eruption began in autumn 2016 and continues to the present day [Kotenko et al., 2018, 2019, 2022, 2023; Belousov et al., 2021; Walter et al., 2020]. The eruption products are represented by ashes and bombs of andesitic composition [Kotenko et al., 2023].

GENERAL CHARACTERISTICS OF THE UPPER YURYEV THERMAL SPRINGS

The springs are located in the upper reaches of the Yuryev River, which drains a large (up to 2 km in diameter) erosional caldera, formed during the glaciation period at the site of the Pleistocene Vlodavets volcano [Rodionova et al., 1966] (Fig. 2). Currently, the caldera is an amphitheater open to the west, dissected by deep barrancos. The height of the caldera cliffs is about 300 m. The preserved parts of the volcanic structure, exposed in the sides, are composed of a sequence of hydrothermally altered opalized agglomerates, interlayered with lava flows represented by two-pyroxene andesite-basalts [Opyt..., 1966]. The total area of altered rocks is more than 15 km^2 with a visible thickness of 200–250 m [Zelenov et al., 1965].

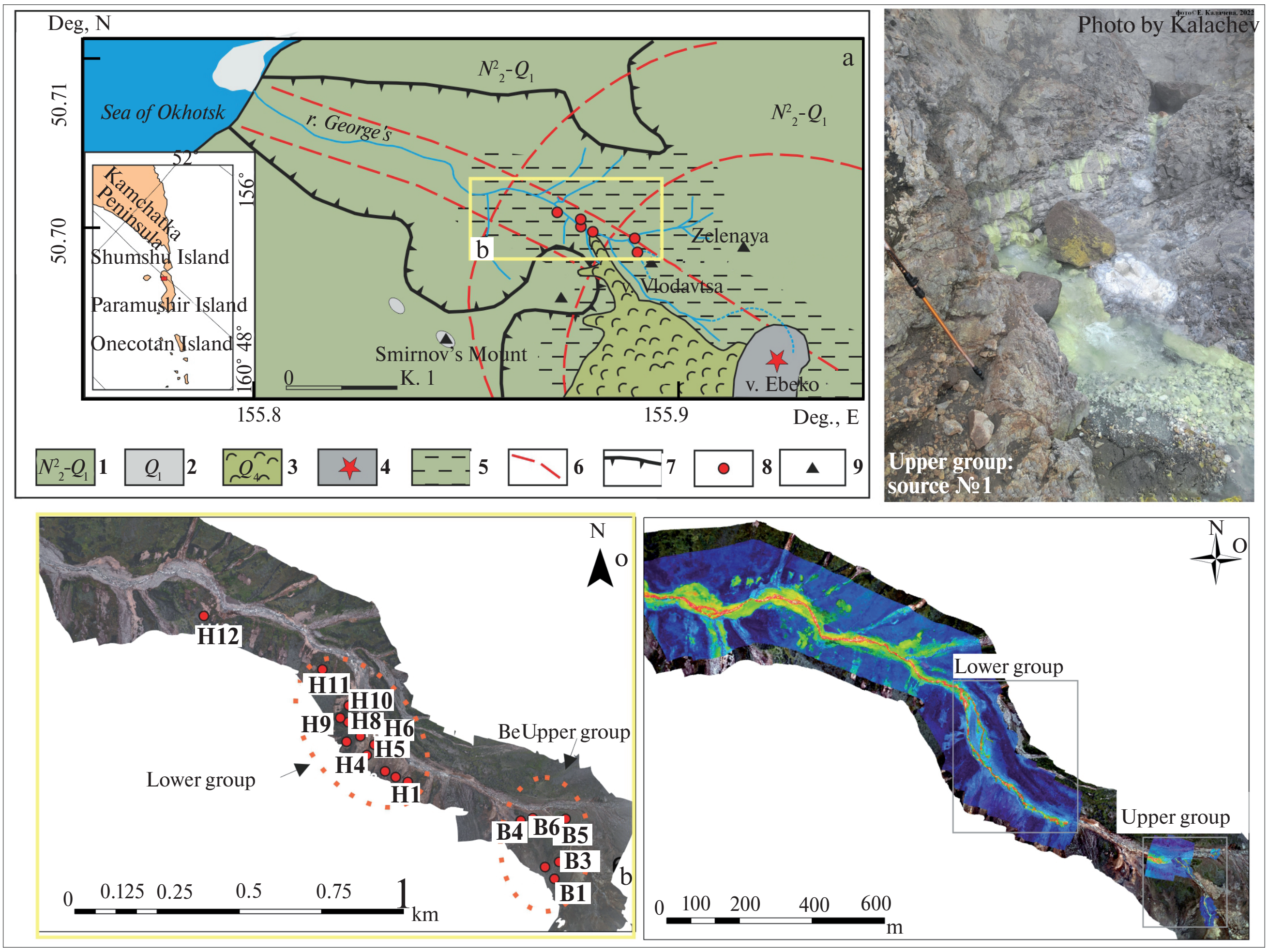


Fig. 2. Geological structure scheme of the Yurieva River valley [Kalacheva, Kotenko, 2013] (a). The inset shows the location of Paramushir Island. Orthophotomap of the upper Yurieva River with water sampling points (b) and infrared imaging of the Yurieva River valley (c). Yuryeva [Kalacheva, Kotenko, 2013] (a). The inset shows the location of the island. Paramushir. Orthophotomap of the upper reaches of the River Yuryeva with water sampling points (b) and infrared photography of the Yuryeva River valley (c).

The beginning of research on the Upper-Yuryev springs dates back to the mid-20th century. They were discovered during geological exploration works in 1952, with the first mention and initial data on the chemical composition of the waters presented in the Geological Report[1]. The springs were annually visited by researchers during the period from 1955 to 1961, and the sampling results from this period are presented in works [Ivanov, 1957; Sidorov, 1966; Rodionova et al., 1966; et al.]. V.V. Ivanov (1957) was the first to determine the formation conditions of the Upper-Yuryev springs as "fumarolic thermal waters of deep formation" due to the interaction of groundwater circulating in the volcanic edifice with volcanic gases. Their geochemical role in the transport of rock-forming elements to the Sea of Okhotsk was examined in works [Zelenov et al., 1965; Nikitina, 1978; Fazlullin, 1999; Kalacheva, Kotenko, 2013], and the volumes of magmatic volatile discharge are presented in [Kalacheva et al., 2016]. Works from recent decades [Bortnikova et al., 2006; Kalacheva, Kotenko, 2013; Kalacheva et al., 2016] provide data on a wide range of microelements and examine the formation conditions of these thermal waters.

[1] *Vlasov G.M.* Main features of geological structure and sulfur deposits of Paramushir Island (Greater Kuril Arc) // Report on exploration works of Paramushir party No. 17 in 1952. Petropavlovsk-Kamchatsky, 1953. 281 p.

Despite the significant interest in the Upper-Yuryev springs, a detailed description of them has not been made until now, with all publications providing only brief information. The most complete layout of spring outlets as of the 1980s is shown in [Fazlullin, 1999]. Based on the authors' own long-term observations, accounting for aerial photography and infrared imagery data, this work presents a detailed characterization of thermal water outlets in the Yuryev River valley as of 2022 Yuryeva as of 2022.

The thermal water outlets are localized in two separate groups at the intersection of a latitudinal fault along the river valley with northwest-trending fault disruptions, which represent part of the ring fault disruptions[2]. The first group is concentrated in a small area along the left tributary of the Yuryev River – Goryachiy Stream. The second group begins downstream of the Yuryev River near the front of a young lava flow from Ebeko volcano that descended into the river valley (see Fig. 2).

The first group includes six main outflows and a series of small springs with insignificant flow rates. The uppermost is “Spring No. 1” (see Fig. 2b, p. B1), located at an altitude of 560 m above sea level in the ledge of the streambed (which is “dry” during the summer-autumn low-water period) of the small Goryachiy stream. The discharge of hot (T >80°C) water occurs from a fracture in hydrothermally altered rocks and is accompanied by the deposition of colloidal sulfur, which forms a yellow coating on the stones downstream. Until recently, the main outlet of thermal waters was located at the water's edge on the sloping streambed, which created certain difficulties for sampling during the summer period. During the spring-summer flood of 2022, part of the stream bank collapsed, forming a ledge in the area where the spring is located. As aresult, the thermal-conducting fracture expanded, and the spring shifted to the right, beyond the influence of surface waters. Near the spring, the rock is covered with a network of small cracks from which thermal water also seeps (see Fig. 2). “Spring No. 1” was chosen as a regular monitoring site due to: 1) its location (the highest hypsometrically positioned outlet); 2) maximum physicochemical parameters in the upper group of springs (highest temperature and mineralization, lowest pH) and concentrations of a number of elements. The discharge zone can be traced by a series of springs with low flow rates, flowing from cracks on both sides of the stream. The next major outlets are already in the estuary zone of the stream. Here, at various distances from the channel, there are several springs with mineralization lower than the one that Spring No. 1 has (4–6 g/l), lower temperature (35–40°C), and higher pH (1.6–1.8). One of them is located in a stone heap directly near the mouth (Spring “Ustyevoy”, see Fig. 2b, p. B4). The “Dalniy” spring (see Fig. 2b, p. B5) consists of two adjacent outlets in the frontal part of talus deposits, forming a single stream that flows directly into the Yuryeva River. Another one (spring “Blizhniy”, see Fig. 2b, p. B6) flows out from under the cemented deposits of an old mudflow alluvial fan. Green thermophilic algae develop in the channels formed by the “Dalniy” and “Blizhniy” springs. The absolute altitude of the outlets is 500–517 m.

The second, more powerful and extensive group of springs begins at the end of the lava flow of Ebeko volcano (see Fig. 2b, 2c), descending to the riverbed of the Yuryeva River. The distance between the mouth of the Goryachiy stream and the first spring “At the lava flow” (see Fig. 2b, p. H1) is 350–360 m. The elevation mark of this outlet is 430 m. Discharge occurs from cracks in altered rocks, partially covered by fresh scree. Downstream, there are more than 20 similar local outlets with flow rates from 1–2 to 5 l/s at the water's edge or directly in the riverbed of the Yuryeva River. All of them are high-temperature (T <75°C), highly mineralized (M up to 14 g/l) with low pH values (<1.2). Discharge occurs on both sides of the river from hydrothermally processed lavas that form its banks and bed. The discharge of thermal waters is accompanied by the deposition of water-soluble, predominantly sulfur-containing minerals, which appear on steamed areas along the edges of formed streams

[2] *Leonov V.L.* Assessment of prospects for thermal waters in the area of Severo-Kurilsk // Report. Petropavlovsk-Kamchatsky, 1990. 33 p.

and on nearby stones. During periods of rain and floods, these deposits are washed into the riverbed of the Yuryeva River. The length of the outlets of this group is 400 m, the elevation difference from the upper spring to the lower one reaches 70 m. The Yuryeva River, which collects all thermal runoff, gets heated. The elevated temperature of the river can be traced for a long distance downstream of the springs (see Fig. 2c).

Until autumn 2017 the lower springs of the second group, including Table H11, were located at a distance of ~30 m from the water's edge. They were characterized by lower temperature (<50°C), higher pH (up to 1.6), and lower mineralization (7–9 g/l) compared to springs located near the water's edge. After a mudflow descended down the river valley in 2017, "plowing" the valley all the way to the mouth [Kotenko, Kotenko, 2018], part of the loose material from the banks was carried downstream. In some areas, the riverbed deepened by more than 1 m, in others – it shifted by several meters. As a result, some springs that were previously underwater and could only be detected by elevated water temperature were exposed. The removal of the sedimentary cover on the left side of the river in the area of the lower springs made it possible to determine the true outlets of some springs. It was discovered that they also discharge from cracks in hydrothermally altered rocks upstream (up to 100 m) from their previous outlet location. That is, some springs were covered by alluvial deposits, and the decrease in their temperature and mineralization was determined by water cooling during drainage under the sedimentary cover and possible mixing with groundwater flow. The largest such spring (spring "U uvala", see Fig. 2b, Table H10) with a flow rate of 8–10 l/s discharges on the right bank of the river from under a ridge composed of deposits from old mudflows. Throughout our observation period, this spring demonstrated the greatest variation in temperature and mineralization values, which will be discussed in more detail below.

INITIAL DATA AND METHODOLOGY

Sampling of the waters of the River Yuryeva and Upper-Yuryev thermal springs (hereinafter referred to as UY-springs) was conducted during the summer-autumn low water period over the past 20 years (in 2003, 2005, 2010, 2013, 2014, 2016, 2017, 2019, 2020, 2022). The results from 2010 and 2014 were partially used in the works [Kalacheva, Kotenko, 2013; Kalacheva et al., 2016]. At the sampling points, physical and chemical parameters of water (pH, Eh and temperature, °C) were measured using portable multiparameter analyzers. To separate the dissolved part and fine colloids from suspension, water samples were filtered at the sampling site through a 0.45 μ membrane filter. For subsequent general chemical analysis, water samples were placed in special plastic containers with a volume of 0.5 l, and for microcomponent analysis – in separate containers with a volume of 15 ml. Since the natural pH of the spring water has a value less than 2, no additional acidification was carried out.

Aerial photography of the River Yureva valley was conducted on 05.08.2022 using the DJI Mavic 2 Enterprise Advanced UAV. This device is equipped with a dual camera (model FC2403), which allows taking pictures in visible and thermal infrared ranges. Based on the survey, two orthophotoplans (in visible and infrared range) of the river valley were created for the section where the springs are located.

Analysis of macrocomponents in water samples was performed by the authors in the Laboratory of Postmagmatic Processes at the IVS FEB RAS. Determination of concentrations of Na^+, K^+, Ca^{2+}, Mg^{2+}, F^-, Cl^-, SO_4^{2-} was performed on a Metrohm 883 ion chromatograph. The content of SiO_2 and boron was determined by photocolorimetric method, Al, Fe – by atomic adsorption method. The OriginPro 2024 software package was used for graphical display of geochemical data and interpretation of results.

RESEARCH RESULTS AND DISCUSSION

Chemical composition of thermal waters

Table 1 shows the macrocomponent composition of waters from UYsprings as of 2022. Among the anions of both groups of UYsprings, sulfur-containing ions predominate

Table 1. Chemical composition of the Upper-Yuryev springs according to sampling data from 2022 (mg/l)

Sample	Sampling location	Code	T, °C	pH_{lab}	F^-	Cl^-	SO_4^{2-}	Na^+	K^+	Ca^{2+}	Mg^{2+}	Fe_{total}	Al^{3+}	SiO_2	Mineralization, g/l
Upper group															
Oc-75/22	"Spring No. 1" (l/b)	V1	88	1.25	54.3	2232	6517	168	75.5	307	127	180	329	315	10.32
Oc-76/22	spring below "Spring No. 1" (l/b)	V2	84	1.28	50.2	2061	5798	162	74.6	302	125	180	334	316	9.42
Oc-78/22	Spring (l/b)	V3	56	1.64	32.1	1123	3554	134	63.3	245	93.2	177	300	222	5.96
Oc-80/22	spring "Estuarine" (l/b)	V4	65	1.40	41.1	1535	4703	131	64.8	246	100	162	302	264	7.56
Oc-74/22	spring "Distant" (l/b)	V5	38	1.76	24.2	796	2560	84.1	53.6	147	51.7	76.6	219	162	4.18
Oc-79/22	spring "Near" (l/b)	V6	43	1.76	23.4	775	2429	81.1	49.5	141	55.8	77.6	214	172	4.03
Lower group															
Oc-82/22	spring "At lava flow 1" (l/b)	N1	85	1.25	53.3	1988	5850	164	80.9	302	126	188	343	319	9.43
Oc-81/22	spring "At lava flow 2" (l/b)	N2	85	1.26	51.9	1954	5832	161	82.4	296	123	194	356	312	9.38
Oc-83/22	Spring (l/b)	N3	77	1.34	48.6	1737	5153	151	80.0	275	115	185	358	275	8.39
Oc-84/22	Spring (l/b)	N4	74	1.38	51.4	1873	5688	166	82.6	313	122	234	431	404	9.38
Oc-85/22	Spring (r/b)	N5	88	1.29	56.4	1903	5592	165	83.4	303	125	186	374	282	9.08
Oc-86/22	Spring (r/b)	N6	81	1.38	54.5	1819	5512	168	83.7	303	126	183	425	320	9.01
Oc-87/22	Spring (l/b)	N7	67	1.58	38.6	1375	3853	134	64.3	266	107	132	366	253	6.60
Oc-88/22	Spring (r/b)	N8	71	1.47	44.3	1590	4634	154	77.7	286	117	157	388	294	7.76
Oc-89/22	Spring (l/b)	N9	75	1.56	43.6	1636	4818	150	73.6	297	119	144	388	305	7.99
Oc-90/22	spring "At the ridge" (r/b)	N10	48	1.64	22.9	1104	3237	120	64.4	200	83.7	116	299	209	5.44
Oc-91/22	spring "Extreme" (l/b)	N11	53	1.76	32.0	1153	3287	133	64.1	261	96.7	139	339	239	5.75
Oc-92/22	Spring "Limonite wall" (l/b)	N12	19	3.33	4.3	183	669	48.9	17.3	96.0	30.4	1.61	61.5	131	1.25

Note. r/b – right bank of Yuryev river, l/b – left bank of Yuryev river.

(SO_4^{2-} + HSO_4^-) and Cl^-. The main components of the cationic part are Al^{3+}, Fe^{2+}, Ca^{2+}. Both in the Upper and Lower groups, there are two types of thermal water outlets that differ in their physicochemical parameters and mineralization. Springs associated with fractured altered lavas are characterized by high temperatures, greater mineralization, and the lowest pH value (1.2–1.4). The average temperature range of such outlets is 80–90°C, mineralization ranges from 9–10 g/l. Concentrations of SO_4^{2-} and Cl^- reach 6.5 g/l and 2.2 g/l respectively. Maximum contents of Al^{3+} (425 mg/l), Ca^{2+} (312 mg/l) and Fe_{total} (234 mg/l), as well as SiO_2 (404 mg/l) were found in the springs of the Lower group. All springs are characterized by elevated levels of boron (2–5.3 mg/l) and manganese (3–7 mg/l). Springs flowing among stone heaps or from under deposits of old mudflows have lower temperatures, less mineralization, and higher pH (see table 1).

As we have previously noted [Kalacheva, Kotenko, 2013; Kalacheva et al., 2016], the content of anions and the total mineralization of UYsprings are directly related to their temperature. The hottest springs show the highest concentrations of Cl^- and SO_4^{2-} as well as the maximum amount of dissolved salts in general (Fig. 3). In the distribution of points by groups, there are no differences; all points fall into one field and form a single trend reflecting a positive correlation between the components. Such a distribution indicates a significant influence of dilution processes of thermal waters by cold groundwater in the discharge zone without changing the original hydrochemical type of water. It should be noted that the points representing water compositions from 2003–2020, while within the boundaries of the general trend, are mostly located on the graphs above the data from 2022, which is associated with higher concentrations of anions and greater mineralization during this period.

In the relationships between cations and anions in both groups of VY-springs, a high correlation is also observed (Fig. 4). Additionally, the distribution of points indicates that the Lower group springs are not derivatives of the Upper group, but represent an individual outlet of thermal waters. In addition to the observed temperature dependence on the degree of dilution by groundwater, within each group, the influence of groundwater on reducing element concentrations is also well defined. The ratios of macrocomponents remain constant in all springs, indicating uniform formation conditions.

As shown in the review [Taran, Kalacheva, 2020], many ASC waters have high fluorine concentrations and low Cl/F ratios, which serves as one of the indicative markers of direct magmatic contribution to their formation (Fig. 5a, “magmatic waters” zone). Near this zone is the area of compositions of high-temperature volcanic gases (relative concentrations of HCl, SO_2+ H_2S and HF). The compositions of the Upper-Yuryev springs occupy a single compact area in the “magmatic waters” zone with an average molar ratio of SO_4/Cl = 1 and F^- = 50–60 mg/l. The location of points along a single line SO_4 /Cl = 1 (see Fig. 5b) indicates a simple mixing of meteoric waters with a single spring water fluid with high contents of sulfate and chloride ions.

The Upper Yuryev springs are characterized by a total distribution of cations (Al + Fe/Ca + + Mg/Na + K) close to that of the rock (see Fig. 5c). Recently published [Kotenko et al., 2023] compositions of different-aged andesites of Ebeko volcano were used as the spring rock. It is clearly visible that the points reflecting the compositions of Upper Yuryev springs are concentrated near the older rocks of Pleistocene age.

Changes in chemical and isotopic composition of thermal waters over time

Upper Yuryev springs have a long history of research dating back to the early 1950s. Comparative analysis of hydrochemical data over an extended observation period can help identify patterns in the overall variability of the springs' component composition and determine the response to the eruptive activity of Ebeko volcano. The main processes controlling changes in the chemical composition of ultra-acidic thermal waters over time may be: a) seasonal fluctuations caused by changes in meteoric recharge; b) transformation of water formation conditions in the feeding reservoir in response to changes in the state of the host volcano.

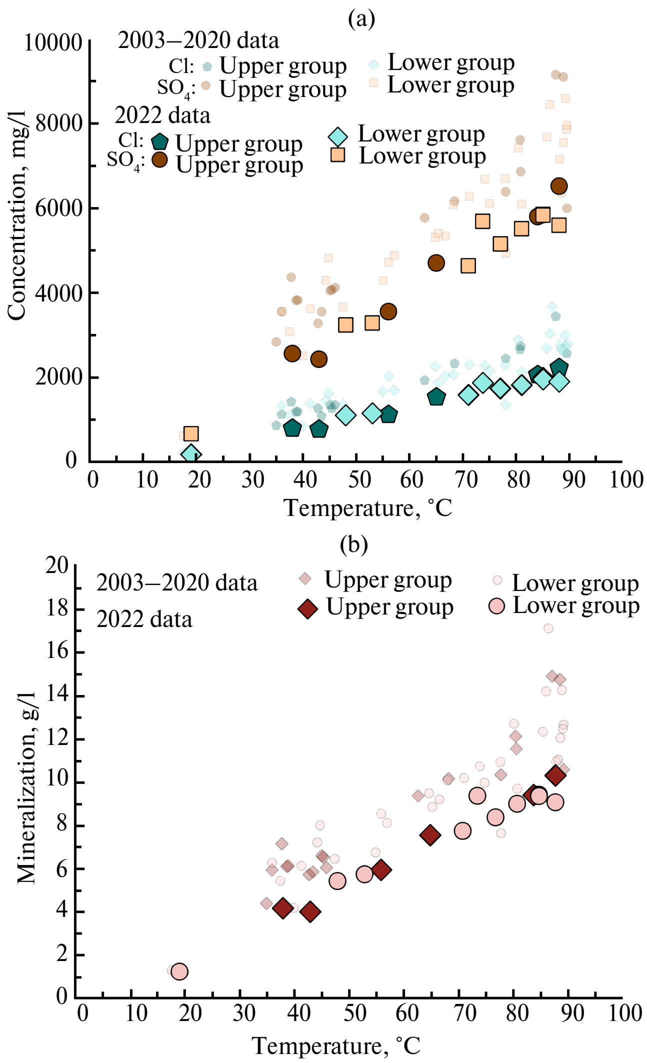
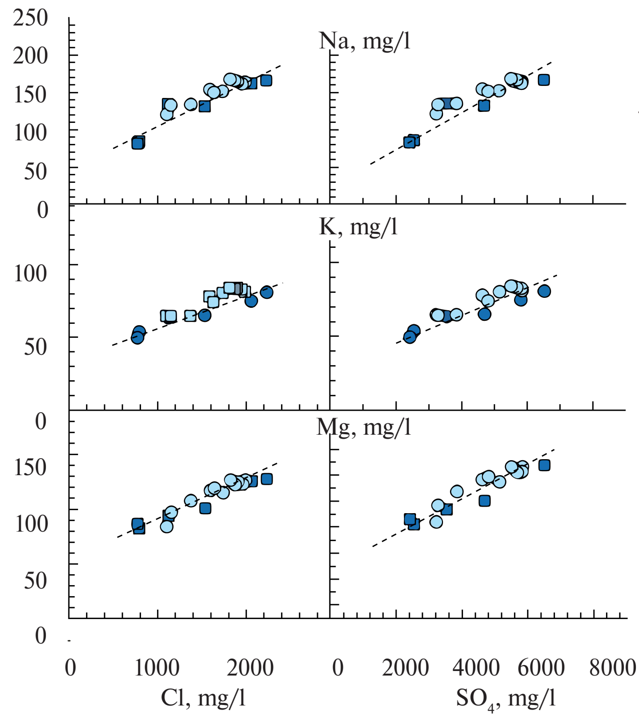


Fig. 3. Correlation of Cl^- and SO_4^{2-} content (a), mineralization (b) with water temperature of springs.

As our research has shown, springs with lower temperature and mineralization are most susceptible to seasonal fluctuations. All of them are confined to loose sedimentary cover, resulting in interaction with groundwater. The most illustrative example of changes in the physicochemical parameters of a spring due to varying degrees of dilution by near-surface waters is the "U uvala" spring (see Fig. 2b, p. H10). During the period from 2005 to 2022, the chloride ion content in the water of this spring varied from 800 to 2250 mg/l, temperature changed from 40 to 63°C, and mineralization – from 4 to 10 mg/l (Table 2). Unfortunately, the spring flow rate was not recorded during sampling periods, but visual assessment



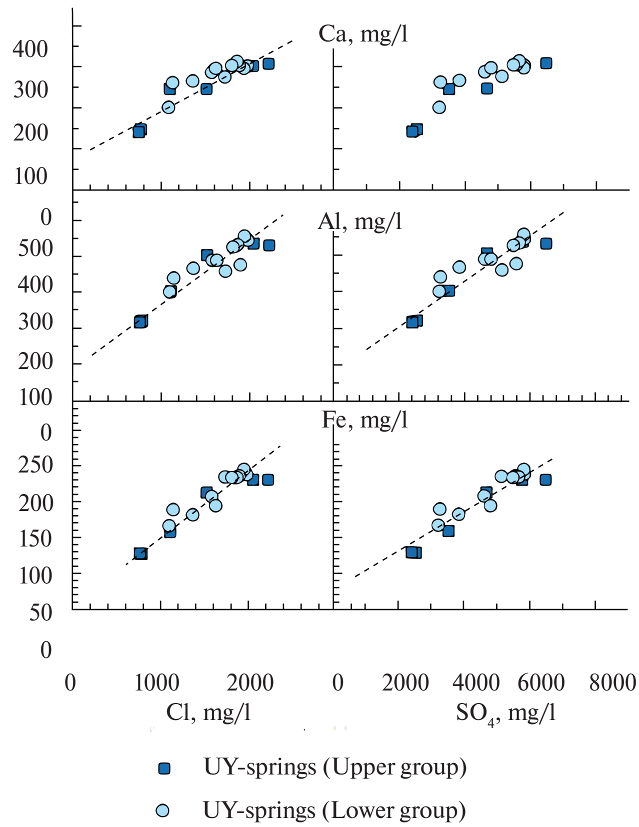


Fig. 4. Ratio of anions and cations in the Upper Yuryev springs.

Table 2. Chemical composition of the "U uvala" spring according to sampling data from 2005–2022

Year	Sampling date	T, °C	pH_{lab}	F^-	Cl^-	SO_4^{2-}	Na^+	K^+	Ca^{2+}	Mg^{2+}	Fe_{total}	Al^{3+}	SiO_2
2005	17.09.2005	40.0	1.57	30.2	851	2509	64	56.6	124	53	148	187	181
2010	18.09.2010	64.8	1.53	n.d.	2269	5307	238	135	417	131	237	508	261
2014	13.08.2014	41.4	1.44	n.d.	1383	3622	130	36.5	200	82.7	142	227	325
2016	31.07.2016	44.8	1.63	34.1	1449	4363	148	105	234	90.2	268	438	234
2017	13.07.2017	36.0	1.67	35.0	1352	4131	131	95.2	199	82.5	142	334	372
2019	13.08.2019	66.7	1.61	57.1	2026	6340	209	134	325	138	249	540	197
2020	07.08.2020	68.2	1.61	58.0	2056	6207	200	115	431	136	223	545	217
2022	05.08.2022	48.0	1.64	22.9	1104	3237	120	64.4	200	83.7	116	299	209

Note. n.d. – no data.

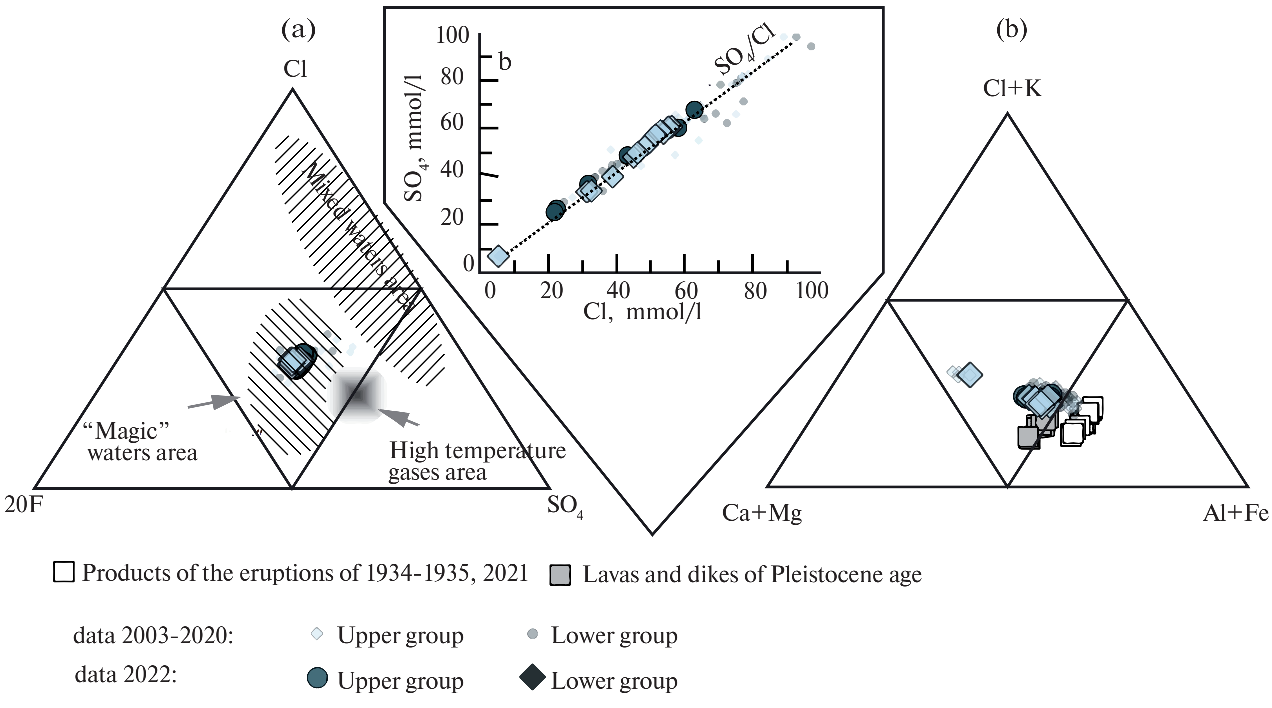


Fig. 5. Diagrams of relative contents of macrocomponents in thermal waters (molar concentrations): anions (a), SO_4/Cl ratio (b), cations (c).
Rock composition – according to data from [Kotenko et al., 2023].

of photo and video materials from previous years indicates an increase in water volume during periods when the lowest temperatures were recorded.

How the water composition of the spring changed in different sampling years is clearly demonstrated in Fig. 6. Chloride ion is used as a normalizing indicator for all comparisons, as it is the most conservative element that does not form secondary mineral complexes during mixing of acidic thermal and surface waters. There is a positive linear correlation between temperature, mineralization, macrocation contents and Cl^- concentration with the same relationship between mineralization and temperature (see Fig. 3b). Some scatter in Ca^{2+} concentrations (see Fig. 6b) may be related both to loss during water mixing due to salt formation along the filtration path in loose deposits, and to re-dissolution when the proportion of thermal waters increases during “drier” years.

In springs with high temperatures (>80°C) at relatively stable temperature and pH, there is variability in anion and some cation concentrations that cannot be explained by simple mixing with groundwater/surface waters (see Fig. 3, 4).

Table 3. Chemical composition of water from “Spring No. 1” (1952–1922), mg/l

Year	Sampling date	T, °C	pH_{lab}	F^-	Cl^-	SO_4^{2-}	Na^+	K^+	Ca^{2+}	Mg^{2+}	Fe_{total}	Al^{3+}	SiO_2	Reference
1952		n.d.	n.d.	n.d.	4677	9116	n.d.	n.d.	540	225	500	n.d.	n.d.	Vlasov, 1953 (Report)
1955		95.0	0.86	52.0	4928	8854	287	268	344	267	417	608	n.d.	Ivanov, 1957
1957		90.0	1.32	n.d.	4346	12407	395	190	478	230	595	1023	256	Zelenov, 1972
1959		90.0	1.15	n.d.	4380	12895	385	260	251	204	599	996	326	Zelenov, 1972
1960		94.0	1.08	79.9	4042	12482	351	230	463	210	461	994	273	Rodionova et al., 1966
1961	August 1961	95.0	1.25	n.d.	3220	11861	278	248	404	196	526	989	260	Markhinin, Stratula, 1977
1969		85.5	1.26	11.3	3305	8224	327	156	421	179	392	612	270	Nikitina, 1978
1984	August 1984	85.0	1.48	52.8	2252	5595	166	95	341	134	376	475	284	Fazlullin, 1999
1987	September 1987	84.0	1.14	86.6	3008	8067	220	125	376	140	314	636	242	Fazlullin, 1999
2005	10.09.2005	78.0	1.20	40.0	2446	6386	129	95	192	90	257	474	247	This work
2010	17.09.2010	87.4	1.27	n.d.	3440	7149	297	147	481	190	349	522	330	Kalacheva, Kotenko, 2013
2013	24.08.2013	90.0	1.34	n.d.	2769	6278	276	98	411	173	227	480	286	This work
2014	13.08.2014	80.8	1.20	n.d.	2736	6861	187	128	230	150	228	526	502	Kalacheva et al., 2016
2016	31.07.2016	80.4	1.12	61.0	3284	9454	255	159	305	159	224	572	263	This work
2017	13.07.2017	84.8	1.18	64.0	3461	9101	219	144	332	138	252	466	584	This work
2019	13.08.2019	89.5	1.19	68.5	2561	7995	250	136	379	172	312	520	197	This work
2020	07.08.2020	85.7	1.21	75.0	2661	7610	220	106	317	159	341	472	176	This work
2022	05.08.2022	89.1	1.25	54.3	2232	6517	166	75.5	307	127	180	329	315	This work

Note. n.d. – no data.

Table 4. Chemical composition of the “Near the lava flow” spring (1957–2022), mg/L

Year	Sampling date	T, °C	pH_{lab}	F^-	Cl^-	SO_4^{2-}	Na^+	K^+	Ca^{2+}	Mg^{2+}	Fe_{total}	Al^{3+}	SiO_2	Reference
1957		90.0	1.12	n.d.	4674	13492	328	220	543	241	673	1200	274	[Zelenov, 1972]
1959		90.0	1.19	n.d.	4330	13259	310	295	253	178	591	1079	314	[Zelenov, 1972]
1960	10.09.1960	90.0	1.25	6.0	3284	8245	143	154	248	111	177	453	281	[Sidorov, 1966]
1969		84.0	1.3	12.5	3184	8193	317	162	409	176	383	627	271	[Nikitina, 1978]
1984	August 1984	90.0	1.26	98.0	3404	8206	273	166	421	195	447	769	348	[Fazlullin, 1999]
1987	September 1987	89.0	1.14	86.6	3089	8212	219	112	396	132	324	630	227	[Fazlullin, 1999]
1988	August 1988	81.8	1.1	80.3	2788	9469	191	128	356	160	360	629	214	[Fazlullin, 1999]
2001		87.0	0.98	n.d.	3140	9310	198	198	270	130	250	630	200	[Bessonova et al., 2006]
2003	26.08.2003	81.0	1.41	51.0	2135	6094	119	116	208	114	225	432	219	This work
2013	24.08.2013	84.0	1.16	n.d.	3018	6811	294	104	470	183	246	634	288	This work
2014	13.08.2014	71.2	1.30	n.d.	2308	6277	168	134	226	132	80	468	418	[Kalacheva et al., 2016]
2016	31.07.2016	86.7	1.03	79.1	3659	10670	312	180	436	172	553	580	480	This work
2017	13.07.2017	86.3	0.99	76.4	3153	9465	258	178	393	171	339	632	677	This work
2019	13.08.2019	88.1	1.39	70.1	2725	7849	256	143	394	176	292	520	192	This work
2020	07.08.2020	86.4	1.41	73.2	2787	7957	229	109	384	165	285	494	184	This work
2022	05.08.2022	85.0	1.26	51.9	1954	5832	161	82.4	296	123	194	356	312	This work

Note: n.d. – no data.

Let's examine the changes in macrocomponent content using two springs with the longest geochemical data series as examples: “Spring No. 1” (Upper group) and “Near Lava Flow” spring (Lower group). These springs were first sampled in 1952.[1] Throughout the observation period (see Table 3, 4), the contents of Cl^- and SO_4^{2-}, dissolved aluminum and iron in the 1950s were notably higher than in the subsequent observation period. Fluctuations in other cation contents (Ca^{2+}, Mg^{2+}, Na) are not as significant. In the initial period (1955–1961), the maximum water temperature (94–95°C) and the lowest pH (0.86) were recorded. Mentions of low-temperature fumaroles in the upper reaches of the Yurieva River also relate to this period [Zelenov et al., 1965].

In Fig. 7 shows the change in the content of major anions and their ratios in the monitoring

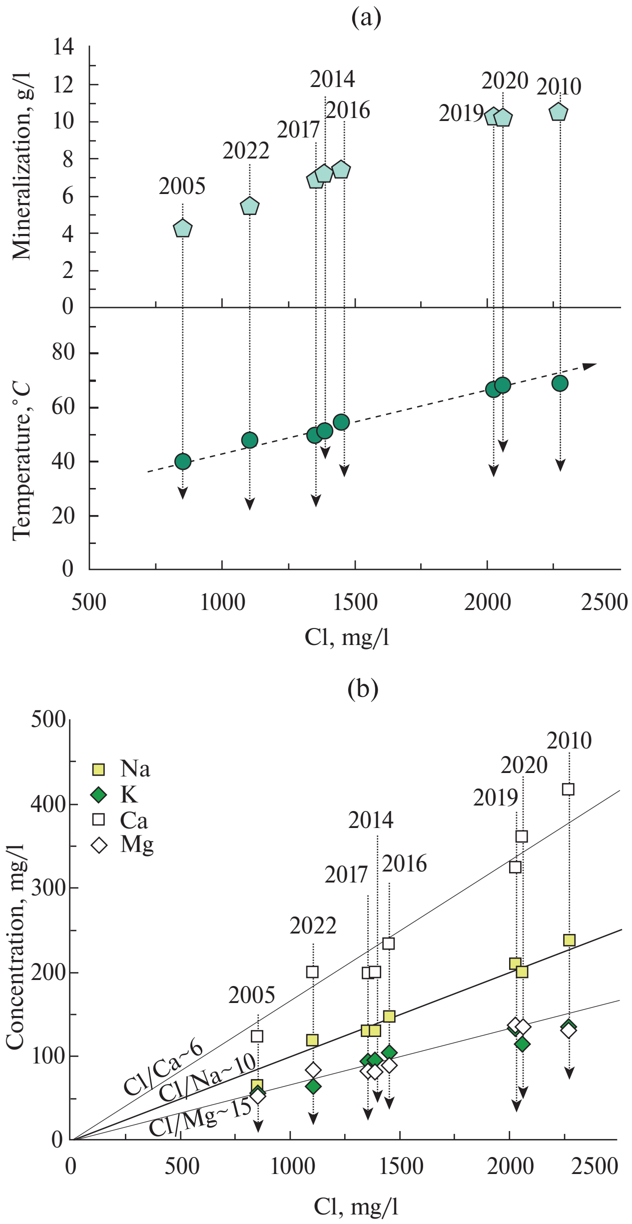


Fig. 6. Correlations of Cl (temperature, mineralization, cations) for the "U uvala" spring.
Numbers on the graphs show the year of sampling.

springs over time and in comparison with the periods of Ebeko volcano activation. Such correlation was studied by us earlier [Kalacheva, Kotenko, 2013; Kalacheva et al., 2016], but it was not possible to make a definitive conclusion, as an incomplete set of data was used, which should have included the period of preparation for the volcano eruption, the time of eruption and the period after it. Over the past eight years (since 2016), we have managed to obtain geochemical information confirming the response of the hydrothermal system to events occurring on Ebeko volcano.

It should be noted that in the initial observation period of the SE springs, the highest contents of major anions were detected, which could be associated with higher hydrothermal activity of Ebeko volcano as a whole. During this period, there was a thermal lake Goryachee in the Middle crater of the volcano with a diameter of up to 200 m and a depth of up to 20 m. The average water temperature was 30–35°C, reaching 90°C in the locations of underwater steam-gas vents. The water in the lake was ultra-acidic with pH up to 1.3, of SO_4–Cl–Na composition with mineralization up to 4.7 g/l. Powerful fumarole and hydrothermal activity was observed around the perimeter of the lake [Gorshkov, 1954; Ivanov, 1957; Zelenov et al., 1965]. On the southern shore of the lake, almost at water level, there was a large intensely gassing spring with pH <1 and a temperature of 77°C [Ivanov, 1957]. Water (Q ~1–2 l/s) flowed from a wide crack (section up to 10 cm) and poured into the lake. From the early 1960s, hydrothermal activity in the Middle crater began to decline [Experience..., 1966] and by the mid-1960s had practically disappeared [Skripko et al., 1966]. At the same time, the activity of other fumarole fields did not cease: the total fumarole discharge of Ebeko volcano, instrumentally measured since 1959 [Kotenko et al., 2022; Menyailov et al., 1988; Nekhoroshev, 1960] was 0.9–2 thousand t/day in inter-eruptive periods. In comparison with these data, the volcanic inflow necessary for the equilibrium state of Lake Goryachee is ~1.4 thousand tons/day, obtained through mass-balance and energy calculations for 1952 [Pasternack, Varekamp, 1997], appears to be very significant. The total gas emission of the volcano, according to the lowest estimate, could exceed 2.3 thousand tons/day.

On the other hand, if we pay attention to the increase in the ratio of SO_4^{2-} to Cl^- during the period 1957–1960, which was then followed by a decrease, then by analogy with our observations of the modern eruption (2016–2024) we can assume, following [Belousov et al., 2021],

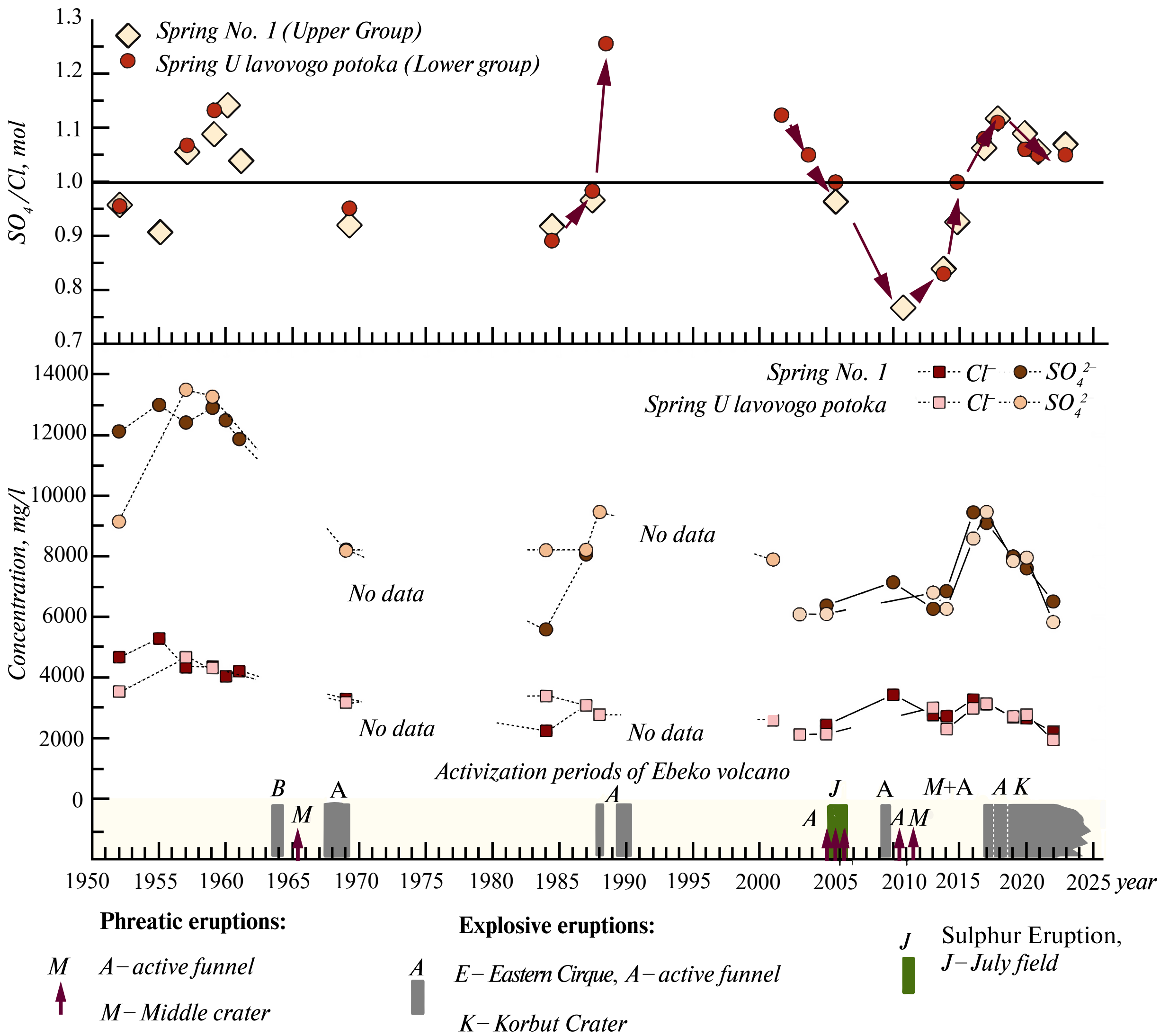


Fig. 7. Temporal changes in SO_4 and Cl contents in the Upper Yuryev springs waters and their ratio (SO_4/Cl) in comparison with periods of Ebeko volcano activation.

that precursors of magma rise existed, but the magma did not reach the surface, the eruption did not occur, and the aureole with anomalous thermal and geochemical properties reached the hydrothermal system. The consequences were expressed in high content of SO_4^{2-} and Cl^- pH decrease and, consequently, increased interaction of the solution with the host rocks and the transition of a larger amount of rock-forming elements, primarily aluminum and iron, into the solution (see Table 2).

The cause of further weakening of hydrothermal activity in the volcano craters could be changes in the system of fumarole feeding channels [Nikitina, 1978] and the shift of the main fluid discharge to other areas. In particular, the overgrowth of fluid-conducting channels and cracks as a result of their captation by minerals of hydrothermal genesis. As evidenced by the observation data from 1950–1960 years [Ivanov, 1957; Sidorov, 1966], the weakening of thermal activity, especially in the Middle Crater, occurred gradually, over a long (more than 10–15 years) period, with an increase in fumarole discharge observed at the North-Eastern field [Menyailov et al., 1988]. The large-scale weakening of hydrothermal discharge on the volcano in the future most likely occurred in response to a decrease in the flow

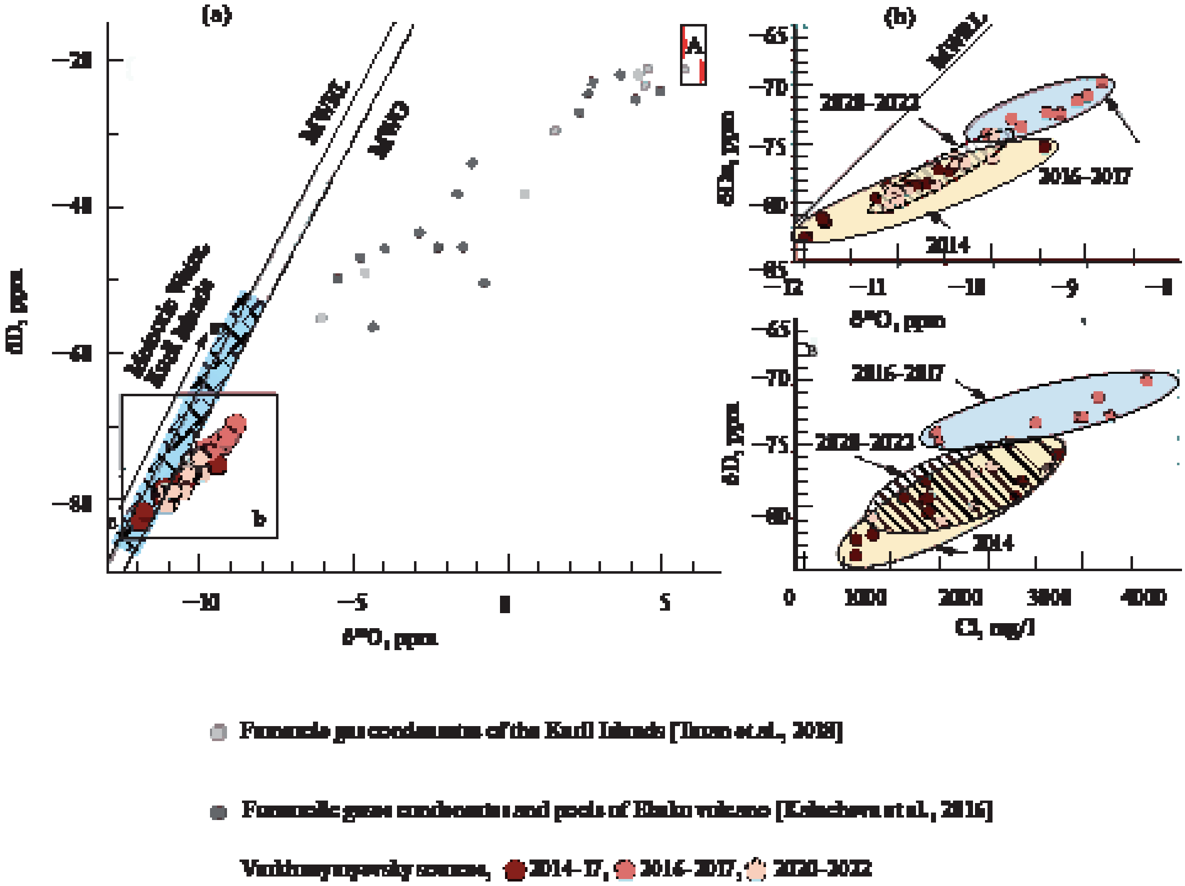


Fig. 8. Isotopic composition of the Upper Yuryev springs (according to 2014–2022 data).
a – correlation of $\delta^{18}O$ to δD (A – distribution area of andesitic waters, according to [Taran et al., 1989]; RLMW – regional line of meteoric waters, according to [Cheshko, 1994], GMW – global meteoric water line, according to [Craig, 1961]; arrow N–S indicates the change in isotopic composition of surface waters from northern to southern islands); b – correlation of $\delta^{18}O$ to δD for the Upper Yuryev springs (enlarged fragment) with highlighting of characteristic data distributions by individual periods; c – correlation of Cl to δD for the Upper Yuryev springs (2014–2022) with highlighting of characteristic data distributions by individual periods.

of magmatic fluid into its hydrothermal system as a whole.

The rare sampling data from the period from 1970 year to 2003 year do not allow us to judge the reaction of the hydrothermal system to the intensification of volcanic activity during this period (see Fig. 7 and Table 3, 4), but a certain tendency of increasing the SO_4/Cl ratio before the explosive events of 1987–1990, described in the work [Melekestsev et al., 1993] is observed. Since 2003, a more or less regular monitoring of the chemical composition of the Upper Yuryev springs has been conducted. In the period from 2003 to 2010, a constant decrease in the SO_4/Cl ratio (from 1.13 to 0.75) is observed. Whether this decrease occurred gradually or stepwise is difficult to assert due to the absence of regular observations in 2006–2009. It is also impossible to make unequivocal conclusions that the preceding decrease in the indicator was caused by the “sulfur” eruption that occurred in 2005–2006 on the northeastern slope of the Northern crater (July fumarole field) [Kotenko et al., 2007] or by preparation for the 2009–2010 activation period, expressed by a series of explosive bursts from the Active funnel [Kotenko et al., 2010, 2012]. No significant fluctuations in the chemical composition of water were detected during this period. With almost annual sampling (2010–2022), it was possible to identify the system's response to volcanic events. In the fall of 2016, a new stage of eruptive activity of the volcano began, which continues at present. Almost 5 years before this event, we observed the beginning of growth in the SO_4/Cl ratio, which continued until 2017. A sharp increase (compared to 2014) in concentrations of Cl^- (by 20–59%) and SO_4^{2-} (38–70%) in water was recorded 2.5 months before the eruption began in 2016, which is a direct consequence of the increased input of magmatic fluid into the hydrothermal system. High values of anions persisted in 2017. Starting from 2019, despite the continuing eruption, there is a decrease in anion concentrations to the pre-eruptive period of 2013–2014. However, the SO_4/Cl ratio, which slightly decreased by 2020, remains consistently high (~1.1).

In parallel with the change in the chemical composition of thermal waters, a heavier isotope composition of $\delta^{18}O$ and δD was detected in the samples from 2016–2017 relative to 2014 [Kalacheva, Taran, 2019]. On the graph (Fig. 8) the published data are supplemented with data points from 2020 and 2022 years. The summary of the obtained results is as follows.

1) The isotopic compositions of the Verkhne-Yuryev springs according to 2014 sampling data are localized near the meteoric water line, but with a noticeable positive shift in δ^{18} O and δD due to mixing of magmatic vapors and meteoric waters (see Fig. 8a), they are also characterized by a high correlation between Cl-ion concentrations and δD and $\delta^{18}O$ values (see Fig. 8c).

2) Data points from 2016 and 2017 years lie on the continuation of the trend noted for 2014 samples (see Fig. 8a, 8b), simultaneously with the isotopic composition becoming heavier in thermal waters, the concentration of chloride ions increased (see Fig. 8c), which, according to [Taran, Zelenski, 2014], is a sign of an increase in the proportion of magmatic water in the supply of thermal waters and volcanic vapors.

3) In the pre-eruptive period from October 2015 to September 2016, an increase in the content of SO_2, CO_2, H_2 in all fumarole gases and HCl in high-temperature gases of Ebeko volcano was also detected, as well as a change in the isotopic composition of water in their condensates [Kotenko et al., 2022]. That is, the increase in concentrations of sulfate and chloride ions and changes in the isotopic composition of thermal waters occurred simultaneously both in the summit part of the volcano and on the northwestern slope. This, in our opinion, confirms the existence of a single feeding hydrothermal system.

4) As of 2020 and 2022, the Verkhne-Yuryev springs showed a restoration of pre-eruptive values of 2014 for isotopic composition and chloride-ion concentration (see Fig. 8).

Thus, a response of the hydrothermal system of Ebeko volcano to its eruption that began in 2016 was identified. The response occurred only during the preparatory period, when there was an increase in degassing of the magmatic system feeding the volcano, and persisted in the initial phase of the eruption. After a certain period of time, we again observe a significant decrease in primarily sulfate and chloride ions. Moreover, in 2022 the lowest values in the entire history of observations of the volcano were recorded. Possibly, while the eruption continues, the hydrothermal system will be further “diluted” with meteoric water. Noticeable changes were also recorded in fumarolic gases around the summit, indicating the unity of the feeding hydrothermal system. Degassing of fresh rhyolitic magma creates a halo with anomalous thermal and geochemical properties in front of its flow, which reaches the hydrothermal system first [Belousov et al., 2021], causing pre-eruptive changes, including in the chemical and isotopic compositions of thermal waters and fumarolic gases due to increased flow of acidic gases (primarily SO_2 and HCl). For the first time, these changes were recorded 3–4 months before the eruption began, but they likely started somewhat earlier, as thermal water sampling was not conducted in 2015. The delayed conditions of water exchange in the volcanic edifice resulted in the persistence of anomalous parameter values during the initial period of the eruption. After the magmatic body breaks through the hydrothermal system, the cooling magma, having already released part of its gases, self-isolates from the system. All eruptive activity occurs through the flow front, while only a small amount of gases enters the hydrothermal system. Possibly, for the Upper Yuryev springs, the response time to changes in the volcano's state, from the preparation stage for eruption to its beginning, and the time to return to a “normal” state has a duration of 1–2 years and depends on the speed of magma ascent and water exchange rate. This assumption requires additional routine observations of the chemical and isotopic composition of the waters.

CONCLUSION

In the northern part of Paramushir Island, in the Yuryeva River valley, a unique type of thermal volcanic waters of sulfate-chloride composition with pH = 1.2, temperature up to 85–90°C, and mineralization up to 10–11 g/l is discharged. The discharge occurs through two groups of Upper-Yuryev springs. High correlation between anions and cations, and physico-chemical parameters indicate a single spring of supply.

Changes in the chemical composition of thermal waters occur due to seasonal fluctuations and in response to changes in the state of the host volcano. Waters of springs confined to loose sedimentary cover are most susceptible to seasonal fluctuations. In the springs of the main thermal discharge zone with high temperatures (>80°C), variability in anion concentrations is observed, associated with periods of volcanic activation. Phreato-magmatic eruptions are preceded by changes in the chemical and isotopic compositions of thermal waters due to an increase in the flow of magmatic volatiles entering the system. The increase in the SO_4/Cl ratio in water began almost 5 years before the start of the eruptive activity stage of the volcano in 2016 and continued until 2017. A sharp increase (compared to 2014) in concentrations of Cl^- (by 20–59%) and SO_4^{2-} (38–70%) in water was recorded 2.5 months before the eruption in 2016, which is a direct consequence of increased input of magmatic fluid into the hydrothermal system. High anion values persisted in 2017 as well. Starting from 2019, despite the ongoing eruption, there is a decrease in anion concentrations to the pre-eruptive period of 2013–2014. However, the SO_4/Cl ratio, which slightly decreased by 2020, remains consistently high (~1.1). Parallel to the change in chemical composition of thermal waters, an enrichment of isotopes $\delta^{18}O$ and δD was detected in samples from 2016–2017 compared to 2014.

The obtained data indicate that for the Upper-Yuryev springs, the response time to changes in the volcano's state from the eruption preparation stage to its beginning and the time to return to a "normal" state has a duration of 1–2 years and depends on the magma ascent rate and water exchange rate.

For further study and detailed elaboration of the aspects of the hydrothermal system response of the volcano to the ongoing eruption, it is necessary to continue a series of observations of the Upper-Yuryev springs. The most productive for monitoring observations are "Spring No. 1" (Upper group of springs) and one of the springs located near the front of the lava flow of Ebeko volcano.

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CONFLICT OF INTEREST

The authors of this work declare that they have no conflict of interest.

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