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Abstract. The article presents the results of researches of thermal waters of South-Eastern solfataric field of Ushishir volcano (Yankicha Island, Central Kurile Islands) in 2007 and 2015. Detailed studies of the physicochemical properties of the hydrothermal springs of the volcano were begun in 1950-60 years. Modern studies have confirmed the stability of physical and chemical parameters of hydrotherms. Modern thermal waters (temperature up to 100 °C), as before, can be attributed to acidic (pH 2.8–3.6), highly mineralized (TDS 23-36 g/l), sodium chloride. The chemical composition and ratio of the main macroelements of hydrotherms are close to the sea waters of the region. The uniqueness of these waters distinguishing them from other coastal hydrotherms of the Kuril Islands is their high acidity. The increased content of balneological elements (Br – 107 mg/l; B – 36 mg/l; I – 0.5 mg/l) in hydrotherms determines their high therapeutic value, which allows them to be used in the treatment and prevention of a wide range of diseases.

1. Introduction

Ushishir volcano (Yankicha Island) is located in the Central Kuril Islands (figure 1a). The terrestrial caldera of the volcano is a circular ridge 250-400 meters of height and 2.5×3 km in diameter at the base, broken on the south and filled with sea waters of Kraternaya Bay. In the centre of the bay two small extrusive domes are located; there are two extrusive domes on the southern shore, 300 meters to the east of these domes the South-Eastern solfataric field is located (figure 1b). A shallow channel connects Kraternaya Bay with the Pacific Ocean. The first descriptions of the Ushishir volcano were given by Ivan Chyorny in 1796 [9]. He described in details Ushishir Islands (Yankicha Island and the Ryponkicha Island), noted 2 kekurs (extrusive domes) in the center of the bay, described the thermal springs, the outputs of the gases and deposition of sulfur on the shore of the bay. The following description was held by the captain Henry James Snow [14]. Detailed scientific studies of an active Ushishir volcano were began in the 1950s. The famous explorer of the Kuril Islands – G. S. Gorshkov suggested [7] that in July, 1884, a phreatic explosion took place in the area of solfataric fields. In the 1960s, E. K. Markhinin investigated the thermal springs of the volcano [11]. Later studies of thermal waters and solfataric gases was continued by L. N. Barabanov [1], V. I. Maltseva [10], V. G. Tarasov [18], G. M. Gavrilenko, [4, 5, 6, 13], Yu. A. Taran [16] and many others. In the 2000s, the author continued the research [8, 19, 20]. The aim of the author's researches was to clarify the current physical and chemical features of the thermal waters of the volcano and evaluation of the prospects of their use as therapeutic hydrotherms. In recent years, interest in the Ushishir volcano increased, complex studies and processing of previously data obtained on the volcano and in coastal waters were carried out [2, 12, 15, 17].

2. Methodology

The author since 2007 has conducted the studies of thermal waters and solfataric outputs of Yankicha Island. Each large spring was recorded on a photo and video camera, its exact coordinates were determined with using of the GPS device, the water temperature and pH were measured. Thermal water samples were taken for analytical studies. Macroelements of 2007 samples were determined by classical chemical analysis, which was carried out by standard methods in the testing laboratory of the FE branch of the FSU "Rosgeolfond" (Yuzhno-Sakhalinsk). The main cations and microelements of the thermal waters sampled in 2015 was done by the accredited laboratory of JSC "Primorgeology" (Vladivostok).

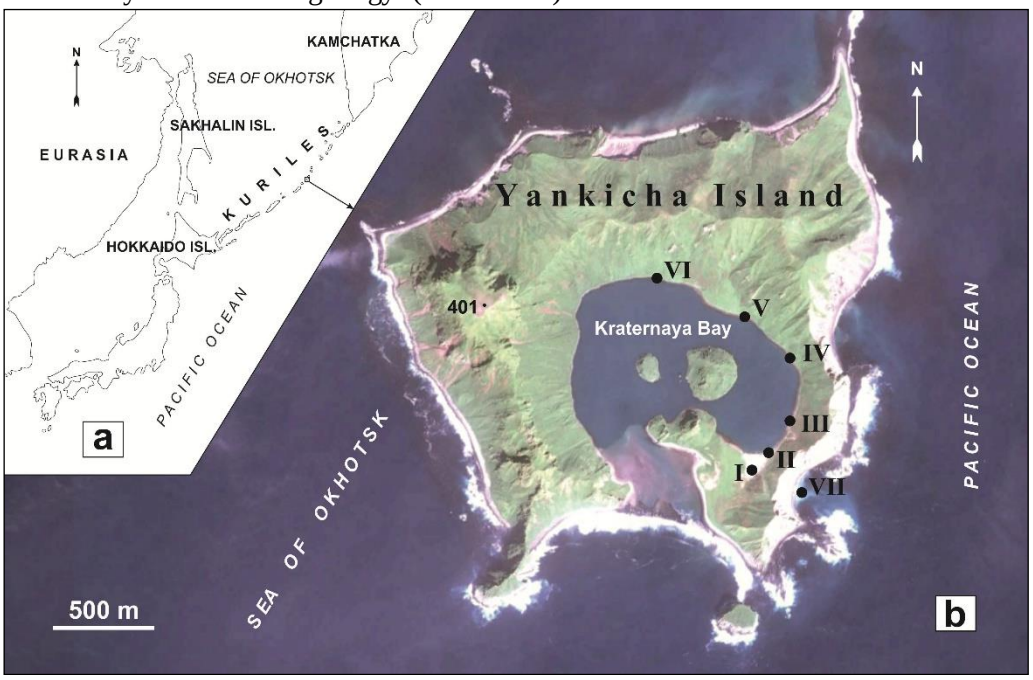

Figure 1. The geographical position of the Yankicha Island (a), and thermal areas (b) of the Ushishir volcano [1, 10, 16] (Google Earth)

3. Results

Ushishir volcano now shows high hydrothermal and solfataric activity. The previous researchers [1, 10, 16] distinguished several surface and underwater thermal sites inside the caldera (figure 1b). On the south-eastern outer slope of the caldera, a powerful plume is seen in the ocean, characteristic for the outputs of acidic thermal waters [15], but hydrotherms on the shore could not be detected. Perhaps, the unloading of acidic thermal waters is carried out here only on the bottom, close to the shore.

The main land outputs of thermal waters and solfataric gases are concentrated in the South-Eastern solfataric field. Significant changes in solfataric-hydrothermal activity of South-East of the field in comparison with the data of previous researchers [7, 1, 11, 6, 16], were not observed. Two thermal sites can be distinguished on the solfataric field (I and II in figure 1b). In the Northern part (thermal area II) solfataric outputs are observed at the foot and on the slope of the 3-4 meter high terrace (figure 2). The temperature of emanated gases reaches 100 °C. Carbon dioxide (49-78 %), nitrogen (12-33 %), and hydrogen sulfide (4.6–8.6 %) dominate in gas composition of solfataras [16]. At the foot of the terrace there are small thermal springs with acidic waters (pH 2.8) and temperatures up to 98 °C. According to [1, 10], their mineralization reaches 32-36 g/l, their sodium chloride composition is similar to the sea waters of the bay. The southern section (thermal area I) occupies the area about 1000 m^2 (figure 3).Both solfataras with a temperature of 100-103 °C and numerous of boiling thermal springs of sodium chloride composition are located here. The temperature of the springs reaches 101°C, pH 3.4. The composition of emanated gases of thermal springs [16] does not differ from solfataras of the northern section, also carbon

dioxide (87-91 %), nitrogen (3.2–3.8 %), hydrogen sulfide (2.0–6.5 %) prevail here. In the central part of the southern site of hydrothermal several boiling springs interflow and form a spring with a length of 80 m, which falls into Kraternaya Bay. Physico-chemical features of thermal waters of South-Eastern solfataric field for the period of their studies have not changed (table 1). If we compare the results of the analysis from 1962 till 2015, we can see that the content of the main components and their ratio are the same. Hydrothermals have high mineralization (23-27 g/l), low pH (3.4–3.6), the temperature in different years reached 86-100 °C.

Figure 2. Solfatars of the thermal area II South–Eastern solfataric field (Ushishir volcano).

Figure 3. Solfatars and boiling thermal springs of the thermal area I South–Eastern solfataric field (Ushishir volcano).

Table 1. Chemical composition (mg/l) and main parameters of thermal water of the thermal area I (South–Eastern solfataric field, Ushishir volcano).

Index	1	2	3	4	5
T, °C	86.0	90.3	92.5	100.0	100.0
pH	3.5	3.60	3.4	3.44	3.38
Na^+	8413.4	7487.9	8928	7050.0	8449.5
K^+	977.1	872.6	795	760.0	705
Ca^{2+}	1117.4	1082.2	1088	1077.0	771.5
Mg^{2+}	59.9	73.0	102	42.5	129
NH_4^+	0.8	n/d	n/a	0.7	<0.5
Fe^{2+}	n/a	<0.05	n/a	0.48	<0.05
Fe^{3+}	n/a	n/d	n/a	<0.05	<0.05
Al^{3+}	n/a	n/d	n/a	n/a	n/a
H^+	n/a	0.2	n/a	0.45	n/a
Cl^-	15822.2	14291.6	15620	13756.0	15096.5
SO_4^{2-}	255.5	223.8	472	206.0	272
NO_3^-	n/a	n/d	n/a	<0.1	<0.2
NO_2^-	n/a	n/d	n/a	<0.01	21.0
CO_3^{2-}	n/a	n/d	n/a	n/d	<6.0
HCO_3^-	n/d	n/d	n/a	n/d	<6.1
SiO_2	208.7	120.1	183	102.0	223.15
TDS	27253.5	24582.1	27188	22995.1	25548.8

Notes. 1 – thermal spring (studied by E. K. Markhinin, 1962 [11]); 2 – thermal spring (studied by L. N. Barabanov, 1970 [1]); 3 – thermal spring [16]; 4 – thermal

spring (studied by the author in 2007); 5 – thermal spring (studied by the author in 2015); *n/d – not detected; n/a – not analyzed*

Complete chemical analysis of hydrothermals conducted in 2015 (table 2), showed higher content of trace elements such as boron (36 mg/l), bromine (107 mg/l), iodine (0.5 mg/l), lithium (7.7 mg/l), manganese (2.7 mg/l), arsenic (1.4 mg/l), strontium (15.5 mg/l).

Table 2. Microcomponents of thermal water of the thermal area I in 2015 (South–Eastern solfataric field, Ushishir volcano).

Elements	Content (mg/l)	Measurement error (±mg/l)	Elements	Content (mg/l)	Measurement error (±mg/l)
Al	0.56	0.07	Cu	0.0054	0.0019
Ba	0.76	0.09	Mo	<0.001	-
Be	<0.0001	-	As	1.44	0.18
B	36.3	4.6	Ni	<0.001	-
Br	107.5	4.5	Hg	0.0037	0.0009
V	<0.001	-	Pb	<0.001	-
Bi	<0.01	-	Se	<0.0001	-
W	<0.01	-	Ag	<0.005	-
Fe^{2+}	<0.05	-	Sr	15.5	1.3
Fe^{3+}	7.3	0.3	Sb	<0.005	-
I	0.54	0.02	U	<0.002	-
Cd	<0.0001	-	PO_4	<0.01	-
Co	<0.001	-	F	<0.10	-
Li	7.7	1.2	Cr	<0.001	-
Mn	2.7	0.4	Zn	<0.005	-

The features of physical and chemical properties of hydrothermals of the South-Eastern solfataric field of Ushishir volcano (content and ratio of macro-and microelements, acidic reaction of the environment) depend on the conditions of interaction of sea and fresh groundwater with host rocks and solfataric gases. The ratio of Na/Cl of thermal waters is identical to the sea waters of the Sea of Okhotsk (table 3). The ratio of other macroelements and micro-components differs significantly in thermal waters and seawater. Thermal waters are more enriched, for example, with boron and bromine, than sea waters. Reduced content of magnesium and sulfate ion in hydrothermals (Na/Mg, Ca/Mg, Mg/Cl, Cl/SO_4 in table 3) can be explained by changes in sea water due to high-temperature interaction with the rocks of the volcano [16]. Thus, the chemical composition of hydrothermals indicates a significant participation of marine waters in their genesis.

Table 3. The ratio of some macroelements and microcomponents of water of the Sea of Okhotsk (1) and thermal water (2) of the thermal area I of Ushishir volcano (studied by the author).

Index	Na/Cl	Na/Mg	Na/B	Ca/Mg	Mg/Cl	Cl/SO_4	Cl/Br	Cl/B	Br/B
1	0.548	7.74	2596.08	0.29	0.0708	7.33	307.62	4737.34	15.39
2	0.559	65.49	232.76	5.98	0.0085	55.50	140.43	415.88	2.96

The hydrotherms of the South-Eastern solfataric field of Ushishir volcano have an acidic composition (pH 2.8–3.7), so they are unique among other coastal sodium chloride hydrotherms of the Kuril Islands with pH 7-9. The acidic thermal waters of Ushishir volcano can be explained by the

interaction with the solfataric gases that come out in boiling thermal springs. The hydrogen sulfide, being a part of the solfataric gases, oxidizes in hydrothermals and forms sulfuric acid, which increases the acidity of the water.

It is interesting the composition of deposits at the bottom of the thermal springs of solfataric field, studied in different years [1, 17]. Modern sediment in thermal springs is represented by [17] various minerals (quartz, sulfur and opal with admixture of natroalunite and alunite) and is characterized by relatively high contents of arsenic, strontium and barium. Arsenic in thermal springs can be added from sea water; also it is possible a gaseous migration of arsenic. Strontium and barium may also be leached from andesitic rocks, which are containing rocks for thermal springs. The entire surface of the South-Eastern solfataric field is hydrothermally changed and in some places is covered with a crust of sulfur with a thickness of 5-7 cm. Hydrothermally changed clay rock [17] is represented by a mixture of cristobalite, quartz, opal and alunite with the higher content of barium and strontium. Natural sulfur deposits around the solfataras, it often forms the needle-shaped crystals of yellow color.

The thermal waters of South-East solfataric fields of Ushishir volcano is used by a few tourists and fishermen to swim, diluting thermal springs there on the shore with the sea waters of the bay. Acidic thermal waters due to high temperature, high mineralization and the content of balneological components (boron, bromine, iodine) are therapeutic waters for external use. Hydrotherms can be attributed to the group of bromine (bromine 25-120 mg/l) chloride sodium highly mineralized (15-30 g/l) waters of Starorussky type [3]. Unlike the waters of Starorussky type, the hydrotherms of Ushishir volcano have a greater therapeutic value, as they are acidic and have a high temperature. These waters are recommended for the treatment and prevention of diseases of the blood circulatory system, musculoskeletal system, and skin diseases.

4. Conclusions

Conducted by the author in 2007 and 2015, the studies of thermal waters of South-Eastern solfataric field of Ushishir volcano has shown that their physic-chemical properties have not changed since the 1950-60th years. There are thermal springs with acidic waters (pH 2.8–3.6) and temperatures up to 98-100 °C with mineralization 23-36 g/l, sodium chloride composition is similar to the sea waters of Kraternaya Bay. Higher content of balneological microelements (bromine – 107 mg/l; boron – mg/l; iodine – 0.5 mg/l) in hydrothermals determines their high therapeutic value, which allows them to be used in the treatment and prevention of a wide range of diseases.

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