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Geochemistry and Origin of Thermal Waters of the Kuril Islands (Russia)

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ABSTRACT

The Kuril Islands stretch for more than 1200 km from the Kamchatka Peninsula to Hokkaido Island. This area hosts active Pleistocene to Quaternary volcanism with more 30 active volcanoes. At least one hydrothermal system associated with volcanic structures can be found on each island. Differences in volcanic evolution, hydrological and geological conditions have led to differences in the conditions of formation and discharge of hydrothermal systems of the region. There are several hydrochemical types of thermal waters discharging on the islands. Acid sulfate waters (steam-heated waters) with temperatures up to 95°C and TDS up to 5 g/L generated at near-surface levels of thermal fields of most activity volcanoes. At Paramushir, Shiashkotan, Urup, Iturup and Kunashir most of thermal manifestations are acid (pH<4) Cl-SO_4 (SO_4-Cl) waters showing temperatures of 30-90°C with TDS up to 14 g/L. These waters are associated with hydrothermal aquifers inside volcano edifices and formed as the result of absorption of magmatic gases (SO_2 and HCl) by ground waters. Another type of hydrothermal activity are the wide spread coastal hot and neutral springs situated as a rule within the tide zone and formed by mixing of the conductively heated groundwater with seawater. It has Na-Cl composition with temperatures 50-80°C and TDS up to 15 g/L. Coastal neutral springs are on Shiashkotan, Russhua, Uturup and Kunashir islands. Thermal manifestations of Ushishir Island are formed by the absorption of magmatic gases by seawater. Ketoy volcano on the same island hosts a high temperature hydrothermal system with unusual boiling Ca-Na-SO_4 neutral springs and steam vents. Deep Na-Cl waters are tapped by the geothermal wells drilled at thermal fields of big islands (Paramushir, Iturup, Kunashir).

1. INTRODUCTION

The Kuril Island arc stretches over a distance of ~1200 km (Fig. 1) from the south tip of the Kamchatka peninsula to the island of Hokkaido, marking the boundary between the Sea of Okhotsk and the Pacific Ocean. The arc is a region of the contemporary active volcanism, which governs the terrain structure and its prevailing landforms. The islands are built up by volcanic, volcano-sedimentary and intrusive Miocene-Quaternary rocks. Marine, alluvial, deluvial-proluvial loose sediments have played a minor role in building the islands. The bases of volcanic edifices on the larger islands are merged thus forming volcanic ridges extended along the islands. The smaller islands are variably-eroded standalone volcanoes or volcanic complexes. By various estimates the arc area includes 70 to 150 Quaternary volcanoes, ~40 of which are active. Some of them exhibit very active solfatara and hydrothermal processes. These are the Ebeko (the Paramushir Island), Sinarka (the Shiashkotan Island), Pallas and Ketoy (the Ketoy Island), Ushishir (the Yankich Island), Berg (the Urup Island), Baranskiy (the Iturup Island), Mendeleyev and Golovnin (the Kunashir Island) and some other volcanoes.

Differences in volcanic evolution, hydrological and geological conditions have led to differences in the conditions of formation and discharge of hydrothermal systems of the region. This paper reports original data on the chemical and isotope compositions of thermal waters of seven Kuril Islands (Paramushir, Shiashkotan, Rasshua, Ushishir, Ketoy, Urup and Kunashir; **Figure 1 and Table 1**) acquired during the 2015-2017 field campaigns.

2. GENERAL SETTINGS

Paramushir Island is one of the largest among the Kuril Islands (Fig. 1). It extends for more than 100 km from southwest to northeast, its average width is 20–25 km. Over 10 quaternary volcanoes are on the island, five of which (Ebeko, Chikurachki, Tatarinov, Karpinsky, and Fuss Peak) are active ones. The hydrothermal activity is largely concentrated in the near-summit part of Ebeko volcano and on its northwestern slope. The craters and outer slopes contain numerous fumaroles whose temperatures at the vents are between 100–160°C and 480°C, as well as ultra-acid boiling water–mud pots. The thermal Verkthne-Yurievskie springs, are located at low elevations, ~ 550 m asl down to 280 m asl, on the western slope of Ebeko volcano in the canyon of Yurieva River. The acid (pH<2) thermal waters with temperatures ranging from 42 to 85.5 ºC, salinity up to 14 g/L discharge in the river. The springs extend for 600-700 m along the riverbed and include about 30 major vents yielding in total ~200 L/s rates of individual springs ranging from 0.5 to 10 L/s. The composition and geochemical activity of thermal waters were reported in many publications. The latest data on the geochemistry of thermal waters and volcanic gases of the Ebeko volcano are described in paper (Kalacheva et al. 2016).

Shiashkotan Island belongs to the Northern Kuril Islands and consists of two joined volcanoes Sinarka and Kuntomintar with about 18 km of the distance between the summits. Both volcanoes are active, with historic eruptions, and both are characterized by fumarolic and hydrothermal activity. Sinarka volcano is degassing through the extrusive dome with inaccessible strong and hot (> 400°C) fumaroles. The volcanic edifice contains a hydrothermal system whose surface manifestations are concentrated in two thermal fields, the Central Extrusive Dome (CEK) and the Northeast Fumarolic Field (SWTF). Nearly neutral hot springs are discharging along the western shore of the island; their mineral content reaches 12–16 g/L and their temperatures reach 90°C. A total of five discrete groups of springs are situated on the island: Northern Bashmachnye (Bn), Southern Bashmachnye (Bs), Vodopadnye (V), Drobnye (D), and Zakatnye (Z). A large fumarolic field of Kuntomintar volcano in a wide eroded crater hosts many fumarolic vents from boiling point to 240°C. Where fumaroles are on the way of surface water streams, acid (pH 2.3) hot (T occasionally reaching 80°C) springs emerge. Frequent landslide processes in the crater cause relocation of creek channels thus changing the quantity and positions of the hot springs at the field. A detailed description of all groups of the hot springs and thermal fields of Shiashkotan Island as of 1964 is contained in paper (Markhinin, Stratula 1977). The current state and questions about the conditions for creation of the hot springs are addressed in paper (Kalacheva et al. 2015).

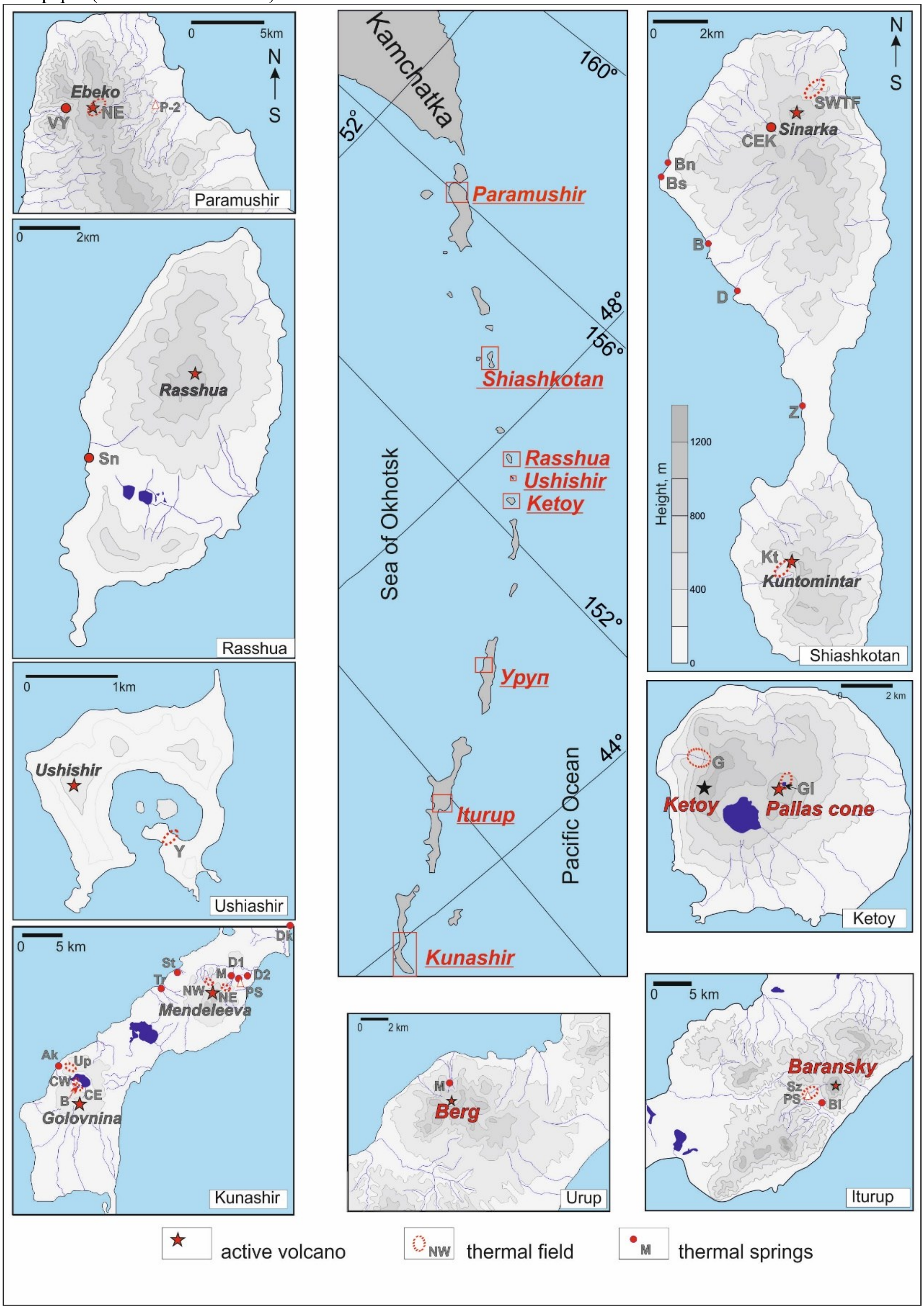

Figure 1: A map of the Kuril Islands. The codes for the thermal fields and springs are in correspondence with Table 1.

Rasshua Island has the shape of an oval that is elongate north–south. The island is composed of deposits discharged by the volcano of the same name. The volcano shows continuous fumarolic activity. Low-temperature fumaroles (below 160°C) are situated in the crater that is open eastward (Taran, 1992). There is a group of near-neutral (pH 6.8–7.4) low-discharge springs in the tidal zone on the western coast of the island. The springs have a mineral content of 3–4 g/L, they are known as "Baths of Snow" (Sn) (See Fig. 1, Table 1). The maximum water temperature measured in 2016 was 35°C. The springs come out as low-flow spouts of water from lava cracks, partially covered by large pebbles cemented by siliceous and ferrous formations. Springs are completely flooded with seawater during high tides.

Table 1: The coordinates of thermal fields and springs

Sumple code	Date mo/yr	Sampling site	Island	Coordinates N	Coordinates E	T, °C	pH	S, mS/sm
acid SO_4- water								
NE(E)	08/2014	Ebeko, thermal field	Paramushir	50°41'28"	156° 1'19"	80.0	1.50	7.80
NETF	08/2016	Sinarka, thermal field	Shiashkotan	48°52'28"	154°11'53"	77.8	2.64	3.32
G	08/2017	Ketoy, thermal field	Ketoy	47°21'11"	152°26'07"	30.8	3.19	2.54
Gl	08/2016	Pallas Cone, crater lake Glazok		47°20'39"	152°28'48"	16.0	2.40	3.28
Stz	07/2016	Baransky, thermal field	Iturup	45°05'37"	147°59'19"	-	2.86	1.53
CW	08/2017	Golovnin, thermal field 1	Kunashir	43°52'19"	145°29'44"	72.0	1.83	9.94
Up	09/2015	Golovnin, thermal field 3		43°54'05"	145°29'31"	96.0	2.58	3.84
CE	09/2015	Golovnin, thermal field 2		43°51'55"	145°29'53"	75.0	2.15	3.31
NE(M)	09/2015	Mendeleev, thermal field 1		43°59'24"	145°45'21"	99.6	2.35	2.16
NW	09/2015	Mendeleev, thermal field 2		43°59'15"	145°43'41"	56.6	2.09	1.99
acid Cl-SO_4 (SO_4-Cl) water								
VY	08/2014	Ebeko, V-Yurievskie springs	Paramushir	50°42'06"	155°59'52"	80.8	1.20	20.30
	08/2016			50°42'06"	155°59'52"	84.0	1.32	35.30
	07/2017			50°42'06"	155°59'52"	86.3	0.99	49.20
CEK	08/2017	Sinarka, springs near extrusive dome	Siashkotan	48°52'29"	154°10'12"	43.9	3.41	8.09
Kt	08/2016	Kuntomintar, crater		48°45'32"	154° 0'46"	96.1	1.73	19.61
M	08/2017	Berg, springs near extrusive dome	Urup	46° 4'16"	150° 3'48"	31.0	3.15	3.95
Gl	07/2015	Baransky, springs 'Blue lakes"	Iturup	45°05'00"	147°59'25"	-	1.50	24.90
B	09/2015	Golovnin, Kipayschee lake,	Kunashir	43°51'50"	145°30'04"	44.0	1.86	3.01
D1	09/2015	Mendeleev, N-Doctorskie springs		44° 0'06"	145°47'18"	47.7	3.50	3.50
M	09/2015	Mendeleev, Mendellevskie springs		43°59'58"	145°46'05"	81.8	2.28	8.00
D2	09/2015	Mendeleev, V-Doctorskie springs		43°59'59"	145°46'25"	87.3	2.13	7.97
Na-Cl –water								
Sn	08/2016	Springs Snoy	Rasshua	47°44'19"	152°58'25"	35.3	7.39	6.31
V	08/2016	Vodopadnye springs	Shiashkotan	48°51'41"	154° 5'58"	91.1	7.50	20.70
D	08/2016	Drobnye springs		48°50'46"	154° 5'35"	55.7	6.33	18.28
Z	08/2016	Zakatnye springs		48°47'38"	154° 4'33"	73.3	6.30	4.10
Bs	08/2016	Bashmachnye (South) springs		48°53'21"	154° 6'28"	75.2	6,95	6.22
Bn	08/2016	Bashmachnye (North) springs		48°53'37"	154° 7'9"	62.0	6.63	9.95
Ak	09/2015	Alyokhinskie (K) springs	Kunashir	43°54'18"	145°29'11"	100	8.46	6.40
Tr	09/2015	Tretyakovskie springs		43°59'06"	145°39'21"	95.7	7.24	3.76
St	09/2015	Stolbovskie springs		44° 00'26"	145°41'00"	78.0	6.90	3.39
Dk	09/2015	Dobryi kluch		44°10'21"	145°59'32"	58.0	6.40	2.26
W1	08/2017	well		43°59'39"	145°46'23"	99.1	6.70	6.50
W2	09/2015	well "Goryachy Plyazh" (GP)		44°00'07"	145°47'28"	66.0	7.29	5.20
P2	08/2014	well	Paramushir	50°39'42"	156° 5'26"	70.9	7.90	10.35
PS	07/1990	well	Iturup	45° 05'35"	147°59'16"	190.0	6.30	
Y	08/2016	Ushishir, thermal field	Ushishir	47°30'29"	152°49'10"	95.7	4.03	33.60

In the middle of the Kuril Islands there is a small Ushishir archipelago consisting of only two islands, Yankich and Ryponkich. The Yankich Island is the upper 400 m of a volcano named Ushishir rising from the ~2000 m depth. The island is a small closed bay separated from the ocean by a shallow strait and known as hosting an unusual hydrothermal system, more similar to the seafloor magmatic-seawater hydrothermal systems. The crater bay is about 60 m deep, 1 km wide and is separated from the ocean by a strait, which is < 1 m deep at low tide. The maximum elevation of the crater rim is about 350 m asl. The exposed summit of the volcano is composed of andesite, and there are three small dacitic domes inside the crater. Hydrothermal activity is concentrated at the SE corner of the bay. Here, within an area of ~100x100 m^2, several large pools discharge boiling water to a small hot creek with the measured outflow rate ~ 5 L/s.

Ketoy Island consists of several volcanic edifices ranging in age between Upper Pleistocene and the present that were destroyed by large landfalls. Pallas Peak is an active volcano; its last eruption took place in 1924 (Gorshkov, 1967). At present the volcano shows vigorous fumarolic activity concentrated on the eastern outer slope of the cone just below the summit. The maximum temperatures of the fumaroles as measured in July 2016 exceeded 700°C (Taran et al., 2018). The crater of the volcano is filled with the cold acid Lake Glazok, whose diameter is approximately 300 m. The large solfataric field of Ketoi Volcano (in the upper reaches of Gorchichnyi Brook) contains steam-and-gas vents and thermal springs with temperatures between 20 and 100°C, pH between 2 and 7.5, and a mineral content reaching 2–3 g/L. Geochemistry and a detailed description of the thermal fields of the Ketoy island are provided in paper (Kalacheva et al. 2018).

Urup Island stretches from north to south for 120 km and has a maximum width of ~20 km. Berg (Fig.1) is the island 's active volcano whose caldera is breached on the NW, measuring ~ 2 km in diameter with a ridge height of up to 1200 m. The caldera is filled by an extrusive dome composed of coarse pyroclastic sediments with interlayers of short lava flows. The modern solfatara activity is localized on the steep walls of the crater located in the north-eastern part of the flat summit of the dome. Numerous acid (pH = 3-3.3) warm (T up to 39°C) springs are spaced from the extrusion dome along two streams that carry water away from the caldera (M, see Fig. 1). When thermal waters reach the surface, iron hydroxides precipitate in the form of long blankets covering the beds of thermal streams. The streams that carry the thermal waters away flow into the Sea of Okhotsk with a distance of about 1 km between them. When the acid waters meet the sea water, they produce trails of different colours, measuring 20 to 50 m in width subject to tidal and wind currents.

Iturup is the largest island in the Kuril arc; its length is approximately 200 km. It consists of several volcanic chains connected by low necks of the Neogene basement. Eight volcanoes on the island are active. The hydrothermal activity is largely concentrated in the middle of the island, near the edifice of Baransky Volcano. More than ten groups of thermal springs are discharging at its base and on the slopes, with the largest being an ultra-acid (pH 1.5) spring called Golubye Ozera (GO) whose water has temperatures that can reach 100°C. Its discharge is, according to various estimates (Znamensky and Nikitina, 1985; Taran et al., 1995a), between 50 and 60 L/s. The Okeanskoe geothermal field has been drilled near one of the solfataric fields (Starozavodskoe field, Stz) and the eponymous geothermal power plant has been in operation until 2016. The thermal fields and springs of the volcano were intensively studied in the latter half of the 20th century. A detailed description and the chemical composition can be found in (Markhinin and Stratula, 1977; Taran et al., 1995b, among others). More recent research on thermal water geochemistry was reported in (Chudaev et al., 2017).

Kunashir is the southernmost island of the Kuril archipelago. Two dormant volcanoes at the south of the island, Golovnin (543 m als) and Mendeleev (888 m als) are characterized by a strong hydrothermal activity. Thermal fields of both volcanoes discharge vapors at boiling point temperature and acid to neutral hot waters. Mendeleev volcano is a complex stratovolcano located in the central part of Kunashir Island. It is named after Russian great scientist Dmitry Mendeleev. The volcano is composed by andesitic-dacitic eruption products with 3 nestled calderas (6-7, 3.-3.5, 1-1.5 km in diameter). An extrusive dome was formed inside the youngest caldera. The historical eruption was a small phreatic explosion in 1880. Four thermal fields are known at the eastern and northern flanks of the volcano, and several groups of thermal springs are located at its slopes and close to the eastern and western coasts of the island (see Fig. 1). Golovnin volcano forms the southern end of Kunashir Island. It is named after Russian explorer Vasily Golovnin. It has a 4.2x4 km wide caldera with two acid lakes and numerous thermal vents around and on the bottom of the lakes. Goraychee (Hot) Lake, 1.1x2.6 km^2, and Kipayschee (Boliling) Lake of 0.1x0.3 km^2. The lake Goraychee is drained by a stream through a narrow gap in the western caldera wall. The only known historical eruption of Golovnin volcano was a minor phreatic explosion in 1848. The andesitic-dacitic Golovnin volcano in the past had mainly explosive eruptions and there are no exposed lava flows. Caldera forming eruptions occurred about 43,000 years ago. Several lava domes grew later on the caldera floor. The results from recent research in the geochemistry of thermal water and gases on the volcanoes can be found in Kalacheva et al. (2017a, b).

3. METODS

Water samples were filtered in the field through 0.45μm filters and collected in plastic bottles. Temperature (±0.1 °C), pH (±0.05 units) and conductivity (±2%) were measured on site by an WTW multimeter. Samples for cations analyses were acidified with ultra-pure nitric acid. Concentrations of major dissolved species (Na, K, Ca, Mg, Cl, SO_4) were determined using ionic chromatography. Alkalinity as HCO3 was measured by titration using a 0.1 M HCl solution. The analytical errors are usually less than 5%. The water samples were analyzed for their oxygen and hydrogen isotopic composition, using "Los Gatos" IR spectrometer in the Institute of Volcanology and Seismology, Kamchatka, Russia. The isotope ratios are expressed in permil vs V-SMOW. The uncertainties are ±0.2‰ for δ18O and ±1‰ for δD (one standard deviation).

4. RESULTS AND DISCUSSION

4.1 Hydrochemistry of major species and classification of thermal waters

Representative analyses of major species and some important micro-components (Al, Fe) in thermal waters of the Kuril Islands are shown in **Table 2**. Three main types of thermal waters can be distinguished here (**Figure 2**):

The first type includes acid (pH < 4) sulfate waters with temperatures below 100°C. These waters were formed by the process where low-temperature volcanic vapors whose gas phase is dominated by CO2 and H2S were absorbed by surface or ground water in the thermal fields themselves (Steam-heated waters). The discharges mostly consist of water or water–mud pots, and drainless or low-discharge occurrences. The waters with low pH leach the rock-forming elements and microelements from the host rocks in proportions similar to that in the rock (isochemical dissolution), with the total amount of dissolved salts in boiling pools with transparent water being below that in the water–mud pots. The average mineral content is 2–5 g/L. The main cation is Ca^{2+} (up to 100–150 mg/L), Fe and Al are always present in concentrations that can reach 100 mg/L. This type of water is present on nearly all islands that contain solfataric fields in craters and on the slopes of volcanoes (see **Table 2**). It should be noted that a single field can contain other types of water besides the acid sulfate type; this depends on definite hydrogeological and morphostructural conditions, on the path and length that meteoric waters percolate, and on the depth of steam condensation. As an example, the eroded crater of Ketoy Volcano on the eponymous island was found to contain (Kalacheva et al., 2018) boiling springs whose water is of the low alkaline (pH reaching 7.6) Na–Ca–SO_4 type with a low mineral content (below 1.5 g/L). This paper is only concerned with acid sulfate waters.

The second type includes acid (pH < 4) chloride–sulfate (sulfate–chloride) waters with temperatures of 30–100°C and a mineral content reaching 14 mg/L. This type of water is generally formed within the upper parts of volcanic edifices. These special conditions favor the generation of shallow restricted water-bearing horizons that absorb easily dissolved volcanic gases such as SO_2 and HCl. They are largely discharged at intermediate heights in volcanic edifices as individual or distributed vents that emit nonartesian waters (or water under local pressure) at considerable discharges reaching 5 L/s at some vents. All known springs in this set are listed in

Table 2. It should be noted that each set of springs has its own characteristic weight relationships among the basic anions. As is shown in **Figure 3**, the thermal waters that are discharged on the slope of Ebeko, Berg, and Baransky volcanoes make a single trend with Cl/SO_4 ~ 0.3. The waters of Kuntomintar volcano are typically dominated by rather than Cl^-, but the ratio is different, Cl/SO_4 ~ 0.1. The ultra-acid waters of Sinarka, Mendeleev, and Golovnin volcanoes are dominated by the Cl^- ion with the weight ratio Cl/SO_4 ~ 1.7. All waters in this set exhibit a great diversity of cations with high concentrations of Ca^{2+}, Mg^{2+}, Na^+, Fe, and Al (see **Table 2**).

Table 2: The chemical (mg/L) and isotope (‰) composition of thermal waters

Code	Cl-	SO_4^{2-}	HCO_3^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	Al^{3+}	$Fe_{общ}$	δD	$\delta^{18}O$
acid SO_4- water											
NE(E)	11.0	3270	0	13	17	0.5	3.6	110	17.2	-45.5	-1.5
NETF	17	1868	0	46	11	65	17	213	86	-40.7	-0.6
G	9	1101	0	64	6	420	46	17.3	0.85	-58.2	-5.5
Gl	33	1311	0	16.5	3.4	181	7.5	96	33	-71.7	-10.7
Stz	12	715	0	42	17	98	27	18.6	8.4	-58.1	-8.2
CW	35	4105	0	12	4	5	3	113	56	-30.2	-1.0
Up	14	2875	0	34	0	196	76	95	162	-42.6	-5.0
CE	52	1556	0	112	10	108	16	33	4.1	-17.9	3.7
NE(M)	10	689	0	17	2	16	10	34	16.6	-57.7	-8.4
NW	10.5	965	0	45	5	70	23	20	4.8	-59.5	-8.4
acid $Cl-SO_4$ (SO_4-Cl) - water											
VY (2014)	2734	6861	0	187	128	230	151	527	28	-75.3	-9.4
VY (2017)	2839	8404	0	255	159	405	159	572	524	-72.4	-9.4
VY (2019)	3045	8442	0	258	178	393	171	632	339	-71.0	-9.0
CEK	2234	1612	0	290	23	459	481	3.8	246	-54.6	-6.0
Kt	2659	4450	0	79	17	524	58	395	38.5	-43.6	-3.1
M	527	1097	0	179	22	320	145	16.6	1.8	-69.2	-9.9
Gl	1692	3739	0	176	44	155	39	134	70	-58.2	-7.4
B	649	485	0	209	24	66	26	н.о.	н.о.	-49.7	-6.7
D1	738	368	0	921	26	92	27	31	34	-54.8	-8.0
M	1230	1085	0	398	39	142	52	26	54	-54.9	-7.5
D2	1512	975	0	577	58	149	62	21.6	52	-54.6	-7.5
Na-Cl – water											
Sn	2714	372	92	704	35	156	44	<0.04	<0.5	-59.0	-8.5
V	8699	952	174	4593	212	324	407	<0.04	<0.5	-42.6	-5.0
D	7309	932	210	4013	171	270	394	<0.04	<0.5	-45.6	-5.9
Z	3586	197	287	1742	149	166	107	<0.04	<0.5	-53.7	-7.1
Bs	2378	76	116	1224	93	248	4	<0.04	<0.5	-63.3	-8.4
Bn	5974	632	191	3054	155	320	209	<0.04	0.77	-52.7	-6.9
Ak	2077	108	79	1198	77	25	0.03	<0.04	<0.5	-55.0	-6.3
Tr	1430	59	120	823	83	59	1.5	<0.04	<0.5	-67.7	-9.5
St	1023	431	240	684	46	112	10	<0.04	<0.5	-68.0	-9.4
Dk	502	358	31	346	7	90	1	<0.04	<0.5	-67.6	-9.9
W1	3008	31	46	2277	326	124	3	<0.04	<0.5	-51.9	-6.5
W2	1200	309	107	877	70	156	14	<0.04	0.9	-52.0	-7.4
P2	2716	192	1928	2516	152	23	16	10.3	0.1	-73.7	-7.6
PS	3192	66	34	1840	452	56	0	н.о.	н.о.	-60.0	-5.2
Y	15898	318	0	8091	816	1189	63	0.38	<0.5	-1.6	7.9

The third type of thermal waters is distinguished by its near-neutral pH (6.2–7.4) and chloride potassium compositions. The mineral content varies between 3–4 and 8–10 g/L and the temperature varies between 30 and 100°C. The conditions of generation and those of discharge are different for these waters. The present set includes all foreshore springs on Shiashkotan, Rasshua and Kunashir Islands. The Na-Cl type also includes the deep waters reached by drilled wells on Paramushir, Iturup, and Kunashir islands. The Cl/SO_4 ratio for the thermal waters exhibits several trends. The compositional points for the springs on Shiashkotan and Rasshua extend along the line of mixing with seawater and their average weight ratio is ~9 (**Figure 4a**). The foreshore springs on Kunashir and the waters that were reached by wells can be divided into two sets. The Stolbovskie (St) and the Dobryi Klyuch (Dk) lie considerably above the line of mixing with seawater (**Figure 4b**). The same part of the diagram also contains data points for the shallow wells drilled in the area of the Goryachy Plyazh (Gp) sanatorium on Kunashir Island. The other set includes all the boiling springs (Tr, Ak) and deep geothermal wells. They typically have very low concentrations of ions (see **Figure 4b**).

The thermal waters that are discharged in the crater of Ushishir Volcano do not fit any of the types above. They typically show the highest mineral content (up to 26 g/L), a temperature close to the boiling point (95–97°C), and an acidity of pH ~ 4. The waters of the low discharge water–mud pots have chloride sodium compositions with chlorine-ion concentrations close to those typical of seawater (see **Table 2**). The sulfate-ion concentrations are considerably below those in sea water. The cation component contains Ca^{2+} and K^+, in addition to sodium ions. The concentration of Mg^{2+} is very low.

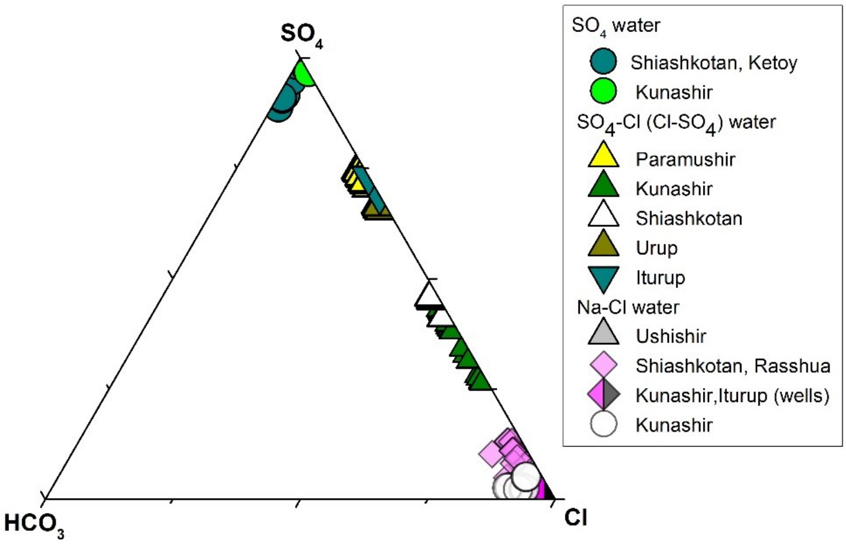

Figure 2: Anions composition of thermal waters

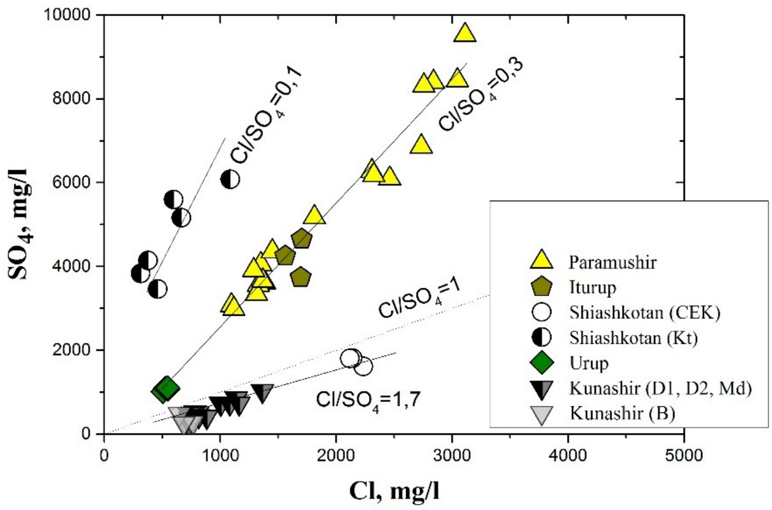

Figure 3: The SO_4 vs Cl relationship in acid SO_4–Cl (Cl–SO_4) waters of the Kuril Islands.

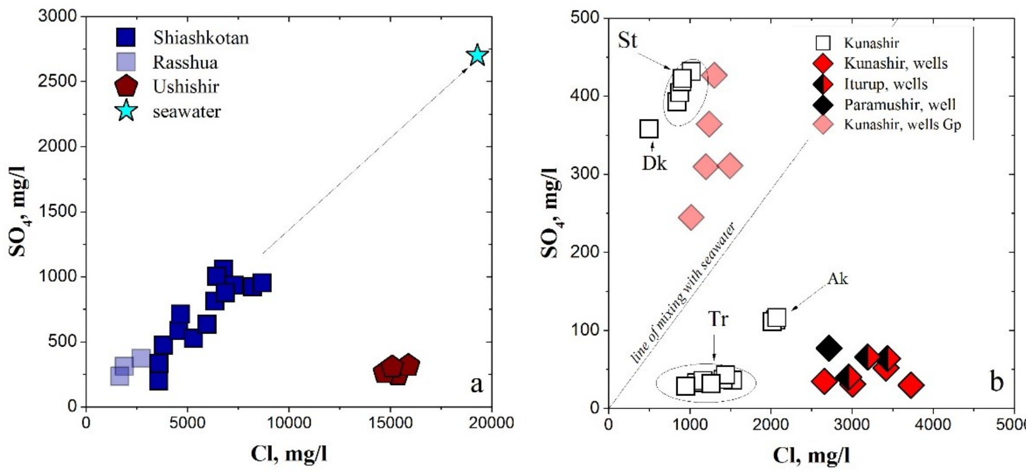

Figure 4: The SO_4 vs Cl relationship in Na–Cl waters of the Kuril Islands. The codes for thermal fields and springs are in correspondence with Table 1 and Fig. 1.

4.2 Water isotopes

Globally, variations of isotope composition of atmospheric precipitates and surface waters are distributed quite regularly and can be described by the Craig equation (1961) named as a global meteoric water line (GMWL), $\delta D=8\cdot\delta^{18}O + (10)$. For the Kuril-Kamchatka region, Cheshko (1994) estimated a local meteoric water line (LMWL) described by the equation $\delta D = 8\cdot\delta^{18}O + (15 \pm 1)$. The isotopic composition of the studied cold surface waters show linear trends on the δD *vs.*$\delta^{18}O$ plot and located on the local meteoric water line (**Figure 5**). The latitude effect is controlled by the geographic position of the islands. On the average, surface waters of the northern Paramushir Island show lower values of deuterium (by 20 ‰) and ^{18}O (by 3 ‰) when compared to those reported for the southern Kunashir Island. Surface waters of the central islands (Shiashkotan, Ketoy, Rasshua and Urup) show similar values and their compositions occupy intermediate positions in the **Figure 5**.

Most of the points for the steam-heated waters group close to or located on the local meteoric water line (LMWL; **Figure 5**). Boiling springs and drainless and low-discharge pools show a trend towards isotopically heavier values of δD and $\delta^{18}O$ relative to the LMWL. Such a shift could be caused by a partial contribution of magmatic water. However, increased supply of magmatic water to thermal waters is accompanied by the increase of chloride-ion concentrations (Taran and Selenski, 2014), whereas waters of the studied boiling pools are almost free of chloride-ion. The slope of this trend is between 3 and 3.5, which is likely due to kinetic fractionation during the surface boiling (Giggenbach and Stewart, 1982). It should be noted that in spite of the similar slopes of the isotope shifts reported for different islands, their datapoints form individual trends in the **Figure 5** due to the latitude effect. For example, δD of thermal waters from Ketoy and Shiashkotan Islands are by 10 ‰ lower than those observed in similar waters from Kunashir Island.

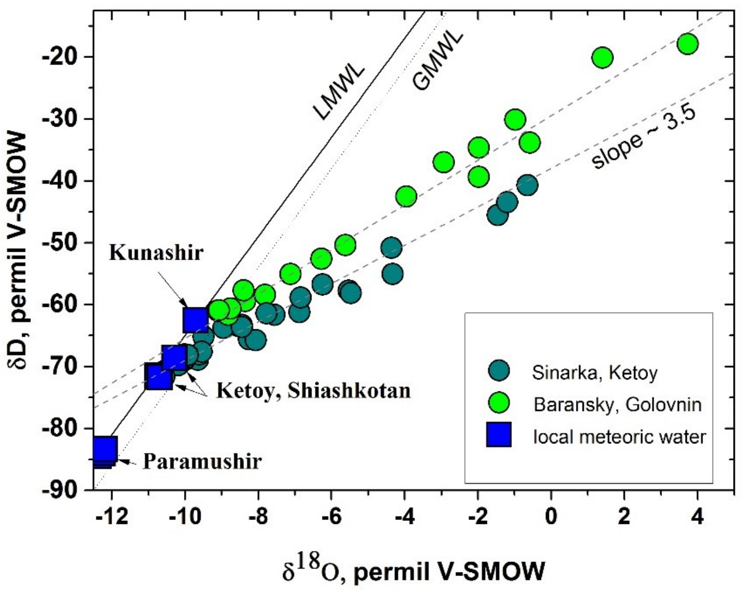

Figure 5: Isotopic composition of the meteoric and steam-heated waters

Along with the data of acid chloride-sulfate thermal waters, the δD *vs.*$\delta^{18}O$ diagram (**Figure 6a**) shows data obtained for the volcanic gas condensates from some Kurilian volcanoes (Taran et al., 2018). Most of the datapoints for springs start from the meteoric water line forming, together with the condensates, a common trend towards the compositions of andesitic waters (A), representing magmatic waters of subduction zones (Taran et al., 1989; Giggenbach, 1992).

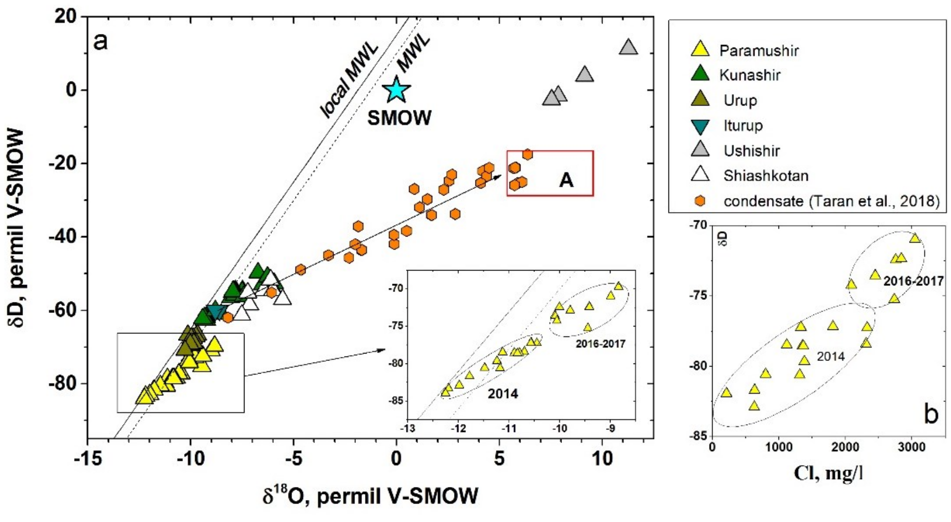

Figure 6: a) Isotopic composition of acid Cl-SO_4 waters from Kuril Islands and volcanic vapours (see text). Inserted is the δD *vs.* $\delta^{18}O$ plot for the Yurievskie springs on Paramushir Island. b) δD *vs.* $\delta^{18}O$ diagram for the Yuryevskie springs

Contribution of magmatic water to acid Cl-SO_4 waters is determined by their Cl content and by a difference in the δD between magmatic and meteoric waters and is estimated as 15-20%. Boiling thermal waters of the Ushishir Island form a separate group in the diagram. They are mainly related to the mixing of volcanic emanations with seawater, which is reflected by the locations of their datapoints in the δD *vs.*$\delta^{18}O$ diagram. Changes in the isotopic composition of these waters in the periods of the volcano activity are well expressed in the case of Yuryevskie springs at Ebeko volcano (Paramushir Island) that were sampled in 2014, 2016 and 2017. Eruptive activity of Ebeko volcano began in October 2016 and continues to the present. In the δD *vs.*$\delta^{18}O$ plot (**Figure 6a**), isotope compositions of the Yuryevskie springs (data from 2014) are plotted close to the meteoric water line, showing, however, a distinct positive shift of both $\delta^{18}O$ and δD. The compositions of the 2016 and 2017 samples form an extension of this trend, which is accompanied also by the increasing concentrations of chloride-ions in the composition of thermal waters (**figure 6b**). Thus, the Ebeko volcano eruption triggered changes in the isotope and chemical composition of the Yuryevskie springs.

Positive shifts of δD and $\delta^{18}O$ are typical of the studied sodium-chloride near-neutral thermal waters. Coastal springs of Shiashkotan and Rasshua Islands show a trend extending from the local meteoric water line towards seawater, which is also evidenced by the δD *vs.* Cl trend (**Figure 7 a, b**) showing mixing with seawater. Isotopic composition of waters discharged by the coastal springs at the flanks of the Mendeleev volcano (Kunashir Island) shows much lower values if compared to that of meteoric water at the sea level, which is probably related to the higher altitude of the catchment basin. The water of the boiling Alekhinskie springs (Figure 7a, number 1) is heavier isotopically than that of the other foreshore springs and exhibits a well-pronounced oxygen shift that is due both to heavier isotopes emerging during boiling and loss of steam and to interaction with the host rocks.

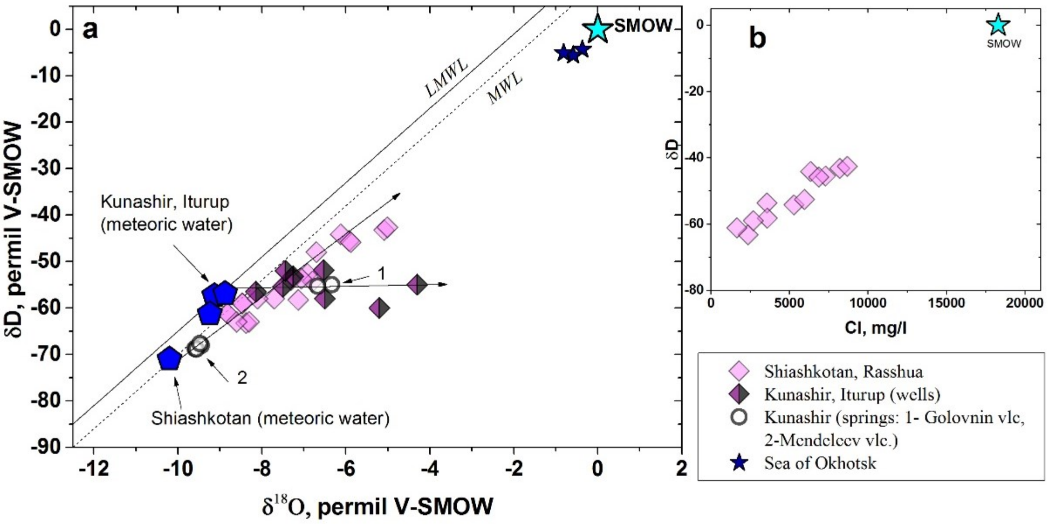

Figure 7: Isotopic composition of sodium-chloride near-neutral waters: a) δD *vs.* $\delta^{18}O$, b) δD *vs.* Cl

A horizontal oxygen shift occurs for the underground thermal waters reached by wells on several islands (see Fig. 7b). The water from wells on the neighboring Kunashir and Iturup islands has similar values of δD. The water in well P2 on Paramushir Island has a lighter isotope composition that is similar to the local meteoric water in δD (see Fig. 4). The intensity of the water–rock interaction (the water/rock relationship) when isotope exchange takes place is reflected in the magnitude of the shift in $\delta^{18}O$.

4. CONCLUSIONS

Differences in volcanic evolution, hydrological and geological conditions have led to differences in the conditions of formation and discharge of hydrothermal systems of the region. Three major hydrochemical types of thermal waters discharging on the islands can be distinguished:

Acid sulfate waters (steam-heated waters) with temperatures up to 95°C and TDS up to 5 g/L generated at near-surface levels of thermal fields. The isotopic composition of the steam-heated SO_4 waters is controlled by the surface boiling and kinetic fractionation with a characteristic slope of 3.5 on the δD *vs.* $\delta^{18}O$ diagram.

Acid ($1<pH<4$) chloride-sulfate (sulfate-chloride) waters showing temperatures of 30-90°C with TDS up to 14 g/L. These waters are formed by absorption of magmatic gases (SO_2 and HCl) by ground waters, and discharge mostly through the weakened zones from beneath extrusive domes. Ebeko volcanic complex (Paramushir Island) hosts the most powerful hydrothermal system with a high discharge rate of hot SO_4-Cl acidic water (Yurievskie springs). The isotopic composition of acid Cl-SO_4 and SO_4-Cl waters is controlled by mixing between meteoric water and magmatic vapor with the maximum magmatic contribution of ~ 20%

Near-neutral (6.2<pH<–7.4) chloride-sodium waters with temperatures up to 100°C and TDS from 3 to 15 g/l. These waters discharge along the shores of the Shiashkotan, Rasshua, Iturup, Kunashir Islands and are also tapped by the wells drilled at thermal fields of big islands (Paramushir, Iturup, Kunashir). Near neutral Cl-Na coastal springs form their isotopic composition by mixing with seawater. Hot water from geothermal wells and some boiling springs show an oxygen shift due to the water-rock isotopic exchange.

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