

Seawater-rock interaction at Ushishir volcano-hydrothermal system, Kuril Islands

Yuri Taran^{1,2,*}, and Elena Kalacheva¹

¹Institute of Volcanology and Seismology, FEB RAS, Petropavlovsk-Kamchatsky 683006, Russia

²Institute of Geophysics, UNAM, Mexico, 04510, Mexico

Abstract. Ushishir volcano is located in the middle of the Kuril Arc. The Ushishir crater, a closed bay connected with the ocean by a narrow and shallow strait is characterized by a strong hydrothermal activity. Boiling springs, hot pools, fumaroles and shallow submarine vents are manifestations of a magmatic-seawater hydrothermal system with the discharging solution similar in chemical and isotopic composition to the seafloor hydrothermal fluids. The main features of the Ushishir fluids are: (1) water has close to zero δD and a large oxygen isotopic shift (6 - 7‰); (2) high boron concentration (~70 ppm); (3) a significant uptake of Ca and Sr from the rock and Ca/Sr higher than that for seawater with $^{87}\text{Sr}/^{86}\text{Sr}$ ~0.7037, a bit higher than the rock value (0.7032). The measured onshore discharge of boiling water is ~ 5 kg/s; however, a large plume of the discoloured seawater releasing from the outer submarine slope of the volcano indicates a much higher total mass and heat output.

1 Introduction

Kuril Island arc between Kamchatka Peninsula and Hokkaido Island in the NW Pacific (Fig. 1a) is a ~1200 km long chain that consists of about 30 islands, each one with one or more active volcanoes. Almost each island hosts a volcano-hydrothermal system the most of them are of the acidic Cl-SO₄ type. In the middle of the arc there is a small Ushishir archipelago consisting of two islands, Yankich and Ryponkich. The Yankich Island is the upper 400 m of a volcano named Ushishir rising from ~2000 m depth. The island is a small closed bay separated from the ocean by a shallow strait (Fig. 1) and known as hosting an unusual hydrothermal system, more similar to the seafloor magmatic-seawater hydrothermal systems. The system has been preliminary studied in 1980th [1,2]. Here we report new data obtained during the fieldwork in 2016, which include some trace elements, composition of fumarolic gases, isotopic composition of gases (including $^3\text{He}/^4\text{He}$) and isotopic composition of the dissolved SO₄ and Sr.

* Corresponding author: yuri.taran@gmail.com

2 General settings

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 (Fig. 1). Hydrothermal activity is concentrated at the SE corner of the bay (site 1 on Fig. 1). Here, within an area of ~100x100 m², several large pools discharge boiling water to a small hot creek with the measured outflow rate ~ 5 kg/s.

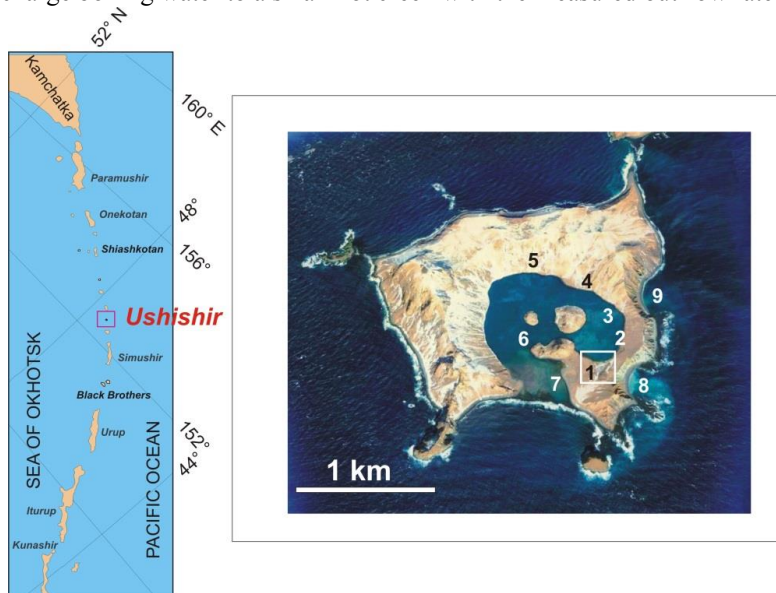


Fig. 1. The Kuril Island arc with location of the Ushishir Islands and a map of the Yankich Island with numbers corresponding to thermal grounds on the shoreline or at shallow depths. Note a large “white” water plume at the eastern coast of the island.

There are also several drainless pools and a small steaming hill to the north of the main thermal water manifestations composed of altered rocks mixed with elemental sulfur. Within this steaming ground there are several weak fumaroles encrusted by sulfur. Other thermal manifestations are open at low tide (sites 2-7 in Fig.1) and discharge diluted warm waters. Gas bubbling from the floor can be seen near the shoreline at sites 2-5. At sites 8 and 9 at the oceanic coast of the island there are no visible vents but an intense underwater discharge in the small bay of the site 8 is marked by the large plume of discolored water.

3 Results and discussion

Our data are shown in Tables 1 and 2. Both sets of data – gas and water – are compared with the data collected in 1986 [2]. The new data include isotopic composition of C, S, He, Sr and concentrations of trace elements (Li, Rb, Cs, Ba and Sr).

3.1 Gas composition

Boiling-point steam vents (Table 1) discharge a typical hydrothermal gas but with a measureable HCl content, probably due to acidity of the boiling water producing this steam. Only H₂S was analyzed, no SO₂ was detected. Concentrations of CH₄ are low. Gases are reduced with $R_H = \log (H_2/H_2O) \sim -3$, which is unusual taking into account a water-

dominated character of the system. All samples contain a significant proportion of the non-atmospheric nitrogen, which is a common characteristic of volcanic gases of the Kuril Arc [3]. He isotopic composition and ratios $\text{CO}_2/{}^3\text{He}$ and $\text{N}_{2,\text{ex}}/{}^3\text{He}$ in the Ushishir gases are typical for subduction zones. Isotopic composition of the vapor corresponds to the equilibrium steam separation at $\sim 100^\circ\text{C}$ (see below the water isotopic composition, Table 2)

Table 1. Chemical and isotopic composition of hydrothermal vapors of Ushishir volcano and some important ratios. Blank cells mean “no data”. $\text{N}_{2,\text{ex}}$ is the non-atmospheric nitrogen ($\text{N}_{2,\text{ex}} = \text{N}_{2,\text{meas}} - \text{N}_{2,\text{atm}}$). The 1993 column shows data from [2]. Analyses are shown on the air-free basis.

Sample	2016		1993
	KEG-3	KEG-4	U-2
H ₂ O	95.34	98.05	97.92
H ₂	0.15	0.051	0.045
CO ₂	3.92	1.76	1.77
HCl	0.019	0.004	
H ₂ S	0.44	0.09	0.12
HF	0.02	0.01	
N ₂	0.129	0.045	0.15
Ar	0.00058	0.00020	0.00074
He	0.00004	0.00002	0.000023
CH ₄	0.00008	0.00006	0.00014
δD	-29.8	-37.1	-30.1
$\delta^{18}\text{O}$	-2.37	-1.84	-4.4
$\delta^{13}\text{C-CO}_2$	-4.5		
$\delta^{34}\text{S-H}_2\text{S}$	-2.1		
${}^3\text{He}/{}^4\text{He}$	6.7Ra	7.3Ra	
He/Ne	2.5	35	
N ₂ /Ar	223	233	206
CO ₂ / ³ He	9.3×10^9	7.5×10^9	
N _{2,ex} / ³ He	2.2×10^8	2.2×10^8	

3.2 Water composition

Water composition is shown in Table 2. Also are shown the representative analysis of a sample collected in 1986 [2], the Pacific Ocean water collected ~ 50 m from the shore, the standard seawater composition according to [4] and the composition of a sample from a seafloor vent at one of the thermal fields of the Lau back-arc spreading center published by Mottle et al. (2011) [5]. It can be seen that our Pacific water is almost identical in composition to the accepted composition of seawater. The Cl and Na concentrations in the Ushishir water are partially depleted comparing to seawater but, similar to the seafloor thermal water, are much higher in K, Ca and Sr, uptaken from the rock. The Ushishir water is also significantly depleted in Mg and SO₄. A general view on the Ushishir thermal solutions can be seen in Fig. 2 as extrapolations to zero Mg and SO₄. We can see here three mixing lines that include meteoric water, seawater and the hydrothermal endmember with non-zero Mg and SO₄. Isotopic composition of thermal water in δD is close to the local seawater composition but significantly positively shifted in $\delta^{18}\text{O}$, much higher than the seafloor fluid discharging at 308°C [5]. This should indicate a low water-rock ratio, rock-dominated regime at the depth of the formation of thermal water. This suggestion is supported by the isotopic composition of dissolved Sr (Table 2). It is almost identical to the average rock value (0.7037 vs 0.7034 [6]) in contrast to the seafloor ${}^{87}\text{Sr}/{}^{86}\text{Sr}$ from the Lau field (0.7043 vs 0.7032). Another evidence of the low water/rock ratio is a high boron concentration (> 70 ppm). In seafloor fluids the concentration of boron as a rule is almost similar to the seawater content of 4.5 ppm with some higher values at sedimentary hosted seafloor systems or due to a secondary enrichment under phase separation conditions (e.g., [7]).

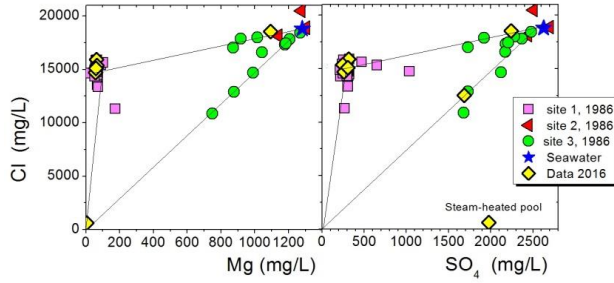


Fig. 2. Chloride vs Mg and SO₄ in thermal waters of the Ushishir volcano. All existing data are plotted. See text for details.

The rare alkalis are also enriched in the hydrothermal solution comparing to seawater, with concentrations similar to those in the seafloor fluids, except Cs. Differences in the enrichment of solutions with trace elements are caused by the differences in the element abundances in the host rocks. In our case these are tholeiitic basalts of the Lau seafloor and calc-alkaline andesites to dacites of Ushishir.

Table 2. Chemical (mg/l) and isotopic composition of springs and the draining stream (KE21) at the Ushishir thermal field. Also are shown a representative sample from [2] (<1993>), the composition of the Pacific Ocean water near the shoreline (U-2) and the composition of the standard seawater [4]. For the comparison, the composition of a deep seafloor thermal fluid from a vent at the Lau back-arc spreading center [5] is also shown.

	KE20	KE21	KE22	KE23	<1993>	Lau	U-2	SMOW
T°C	95.7	83.4	87.0	97	92.5	308	11	
pH	4.03	5.92	3.56	4.07	3.5	4.1	7.9	8.3
Eh, mV	192	70	222	192			-54	
SiO ₂	392	415	190	86	241	1158	10	5.5
Na	8091	8036	7452	7644	8456	9775	10692	10800
K	816	811	753	771	808	577	386	390
Ca	1189	1186	1081	1114	1134	1768	436	448
Mg	63	66	57	60	54	1.5	1282	1290
Cl	15898	15364	14716	15100	14893	18815	20318	18800
F	2.13					0.15		
SO ₄	318	247	263	307	217		2712	2694
HCO ₃		21					143	142
B	70	74	71	73	75	5.9	4.2	4.5
Li	3.0	2.9	3.0	3.0		3.5	0.19	0.18
Rb	1.37	1.44	1.29	1.39		0.74	0.11	0.12
Cs	0.39	0.38	0.36	0.37		0.02	0.009	0.0003
Ba	0.54	0.53	0.51	0.56			0.019	0.015
Sr	9.88	10.2	9.24	9.82		12.5	5.0	7.8
Ca/Sr	120	112	117	113		141	88	57
Sr/Ba	18	19	18	18			260	520
δD	-1.6	-4.2	3.8	-2.6	-3.7	-0.9	-5.6	0
δ ¹⁸ O	+7.9	+6.3	+9.1	+7.5	+5.6	+1.0	-0.58	0
δ ³⁴ S	+13.7							
⁸⁷ Sr/ ⁸⁶ Sr	0.70368	0.70373		0.70394		0.7043	0.70892	0.7091
⁸⁷ Sr/ ⁸⁶ Sr rock	0.7033-0.7035					0.7032		

4 Concluding remark

The water/rock mass ratio for the Ushishir hydrothermal system can be estimated from the Sr isotopic composition using an approximation derived by Albarede (1995) [8] for closed system fluid-rock equilibrium:

$$W/R = [(R_{HW}-R_r)/(R_{SW}-R_{HW})]x(Sr_r/Sr_{SW}), \tag{1}$$

where R_{HW} is $^{87}\text{Sr}/^{86}\text{Sr}$ of the dissolved Sr in hydrothermal solution, R_r is $^{87}\text{Sr}/^{86}\text{Sr}$ in rocks, R_{SW} is the seawater value and Sr_r and Sr_{SW} are concentrations of Sr in the rock and seawater, respectively. With data from Table 2 and the concentration of Sr in the Ushishir dacite of 359 ppm (author's data) it gives $W/R \sim 2.5$. This is a quite high ratio, in contradiction to the observed both strong oxygen isotopic shift and a high boron concentrations. It can be taken only as a first approximation, and the closed system model is not correct in the Ushishir case. A flow-through multi-step modeling (as for example in [9]) is planned for explanation of the Ushishir fluid composition.

Acknowledgements. The authors thank the crew of the Afina boat for their assistance during the fieldworks. This study was supported by a grant from the Russian Science Foundation # 15-17-20011.

References

1. V.I. Maltseva, *Okeanologia*, **25** (4), 616-622 (1985) (In Russian)
2. Y. Taran, G.M. Gavrilenko, L.V. Chertkova and D.V. Grichuk. *Volc. Seis.*, **15**, 63-79 (1993)
3. Y. Taran, M. Zelenski, I. Chaplygin, et al. *Geochemistry, Geophysics and Geosystems*, **19** (2018)
4. Y. Li, *Geochim. Cosmochim. Acta*, **55**, 3223-3240 (1991)
5. M.J. Mottle, J.S. Seewald, C.G. Wheat et al., *Geochim. Cosmochim. Acta*, **75**, 103-1038 (2011)
6. O.N. Volynets, *Int. Geol. Rev.*, **36**, 373-405 (1994)
7. D.V. Grichuk, *Thermodynamic models of the seafloor hydrothermal systems*. Moscow, ScientificWorld (2000) 304
8. F. Albarede, *Introduction to Geochemical Modeling*. Cambridge University Press, (1995), 543
9. D.V. Gruchuk, *Geochemistry Int.*, **50**(13), 1069-1100 (2012)