Volcano–hydrothermal system of Ebeko volcano, Paramushir, Kuril Islands: Geochemistry and solute fluxes of magmatic chlorine and sulfur

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A B S T R A C T

Ebeko volcano at the northern part of Paramushir Island in the Kuril island arc produces frequent phreatic eruptions and relatively strong fumarolic activity at the summit area ~1000 m above sea level (asl). The fumaroles are characterized by low-temperature, HCl- and S-rich gas and numerous hyper-acid pools (pH < 1) without drains. At ~550 m asl, in the Yurieva stream canyon, many hot (up to 87 °C) springs discharge ultra-acidic (pH 1–2) SO_4–Cl water into the stream and finally into the Sea of Okhotsk. During quiescent stages of degassing, these fumaroles emit 1000–2000 t/d of water vapor, <20 t/d of SO_2 and <5 t/d of HCl. The measurement of acidic hot Yurieva springs shows that the flux of Cl and S, 60–80 t/d each, is independent on the volcanic activity in the last two decades. Such high flux of Cl is among the highest ever measured in a volcano–hydrothermal system. Oxygen and hydrogen isotopic composition of water and Cl concentration for Yurieva springs show an excellent positive correlation, indicating a mixing between meteoric water and magmatic vapor. In contrast, volcanic gas condensates of Ebeko fumaroles do not show a simple mixing trend but rather a complicated data suggesting evaporation of the acidic brine. Temperatures calculated from gas compositions and isotope data are similar, ranging from 150 to 250 °C, which is consistent with the presence of a liquid aquifer below the Ebeko fumarolic fields. Saturation indices of non-silicate minerals suggest temperatures ranging from 150 to 200 °C for Yurieva springs. Trace elements (including REE) and Sr isotope composition suggest congruent dissolution of the Ebeko volcanic rocks by acidic waters. Waters of Yurieva springs and waters of the summit thermal fields (including volcanic gas condensates) are different in Cl/SO_4 ratios and isotopic compositions, suggesting complicated boiling–condensation–mixing processes.

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1. Introduction

Ebeko volcano on Paramushir Island is one of the best studied active volcanoes of the Kurilian Island Arc. Its eruptive history in details has been traced by Melekestsev et al. (1993). Geological structure as well as petrology and geochemistry of the eruptive products of Ebeko has been studied by many authors (Markhinin, 1967; Gorshkov, 1970; Fedorchenko et al., 1989; Avdeiko et al., 1992, and references therein). There were several attempts for measuring the heat output by fumaroles and hydrothermal system of the volcano (Nekhoroshev, 1960; Menyailov et al., 1988; Kotenko and Kotenko, 2006). Menyailov et al. (1985, 1988) and Kotenko et al. (2007) reported chemical composition of fumarolic gases during different stages of the volcanic activity. Menyailov et al. (1985, 1988) have measured isotopic composition of the volcanic gas condensates and isotopic ratios of noble gases in two Ebeko fumaroles. Geochemistry of thermal waters has

been studies in Nikitina (1978), Markhinin and Stratula (1977), Fazlullin (1999), Bortnikova et al. (2006) and Kalacheva and Kotenko (2013). Solute discharge by acidic thermal waters of the volcano–hydrothermal system has been measured by Zelenov (1972) and Fazlullin (1999). One of the two deep wells drilled in the vicinity of the volcano found hot water (90 °C). Rychagov et al. (2002) have used core and cuttings from these wells for a detailed mineralogical description of the geological cross-section near Ebeko.

The volcano is attractive for volcanologists and geochemists for several reasons. Frequent phreatic eruptions are hazards to several thousand people living in a small town of Severo-Kurilsk in the vicinity of the volcano (10–12 km from the crater). Secondly, the volcano is characterized by strong fumarolic and hydrothermal activity with abundant manifestations which are easily accessible. A geochemical monitoring program, including systematic sampling of fumarolic gases, was conducted by Igor Menyailov's group in 1960–1980 (e.g., Menyailov et al., 1985, 1988) and the program was partially re-started after almost a 20 year break (Kotenko et al., 2007, 2012; Bortnikova et al., 2006; Kalacheva and Kotenko, 2013; Kotenko and

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Kotenko, 2006). And finally, since the very early stage of the studies of the volcano, it was discovered that unprecedent amounts of solutes are discharged by ultra-acid thermal waters on the western slope of the volcano to the Sea of Okhotsk (Zelenov, 1972; Nikitina, 1978; Fazlullin, 1999). According to Zelenov (1972) and Markhinin and Stratula (1977), the fluxes of chloride(>200 t/d) and sulfate (>600 t/d) measured in 1960 are comparable with or even higher than those from high-temperature fumaroles in some quiescently degassing volcanoes in Kamchatka and Kuril Islands, including the Kudryavy, Mutnovsky and many others (e.g., Taran, 2009 and references therein).

Despite close monitoring of the volcanic activity and many publications, the structure, mechanisms and evolution of the volcano–hydrothermal system of Ebeko remain to be resolved. Main feature of the hydrothermal activity of Ebeko is the existence of two thermal fields separated in the space, both of which discharge ultra-acid Cl–SO_4 and SO_4–Cl hot waters (Fig. 1). The summit field (ca. 1000 m asl) consists of several thermal grounds, low-temperature fumaroles (<120 °C) and near-boiling hyper-acid pools with no or weak outflow rates (Fig. 1). The second thermal field, Yurievsloue springs, is 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 (Fig. 1b). These Yurievskiye springs transport a very high amount of dissolved matter into the sea. It is not understood how these two thermal fields are connected and interacted although there were attempts to build a general conceptual model of the entire system (Nikitina, 1978; Kalacheva and Kotenko, 2013). A part of this question lies the origin of high to very high HCl (up to 0.3 mol%) in low-temperature fumarolic gases of Ebeko because high HCl is a common feature of high-temperature fumarolic gases of arc volcanoes.
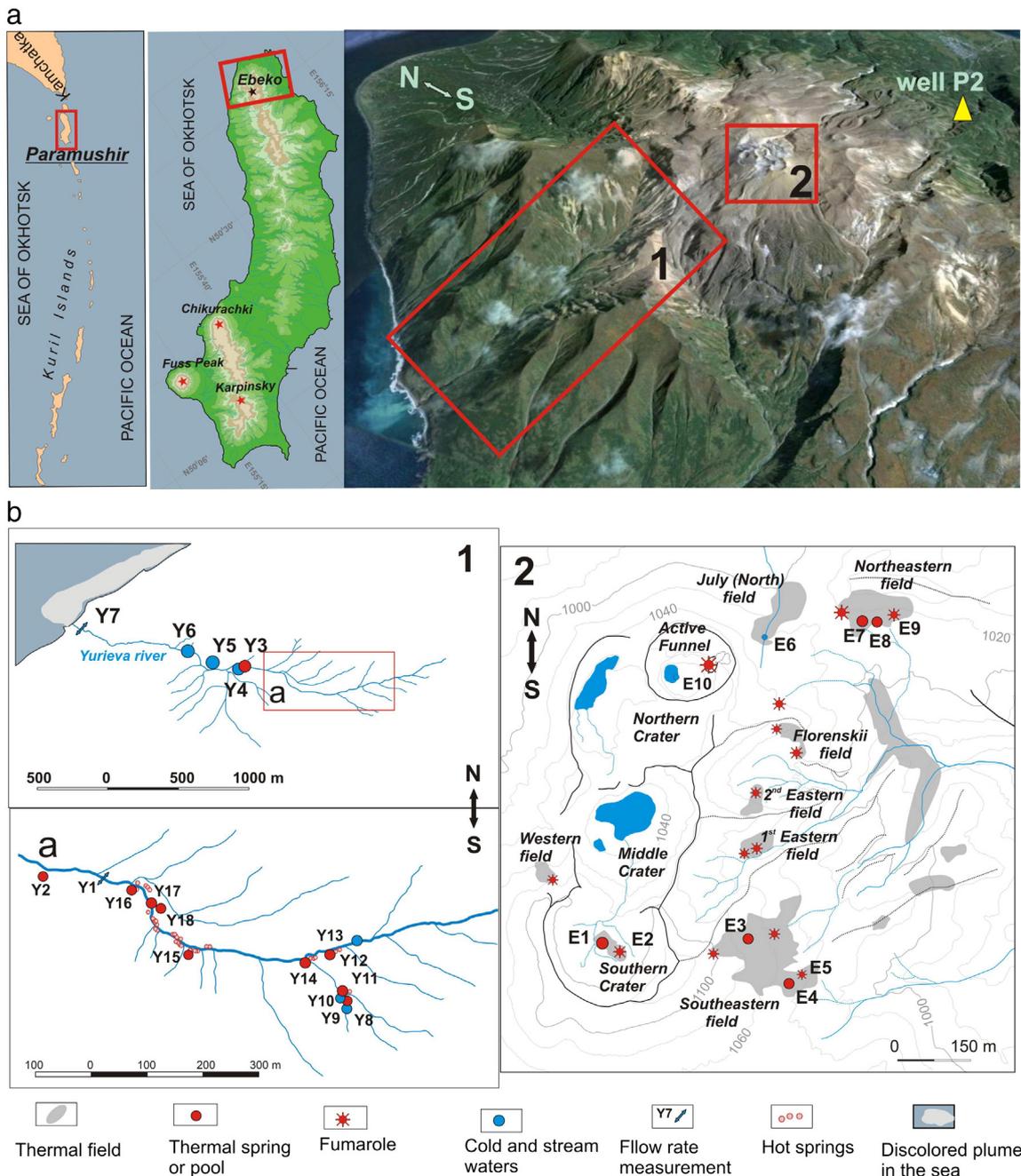

Fig. 1. (a) Location of Ebeko volcano and Google Earth map showing two thermal fields: 1 Yurieva River canyon and 2 summit fumarolic fields of Ebeko. (b) Sketch maps of two thermal fields: 1 Yurieva River canyon and 2 Ebeko thermal field.

In this paper we report data on water and gas compositions of samples obtained during the 2014 field season and compare partially published data from 2005, 2010 and 2012 field campaigns. Our results include major and trace elements in waters, the first documentation of the water isotopic composition of Yurievskie springs and Ebeko pools. A limited data set includes the first report of sulfur and oxygen isotopic composition of dissolved sulfate and $^{87}Sr/^{86}Sr$ for dissolved Sr for Yurievskie springs. We have also measured outflow rates for fumarolic gases and the hydrothermal flux of solutes at the mouth of Yurieva River. The data allowed the re-evaluation of the thermal capacity of the system as well as the solute fluxes. We compare our results with the data of previous studies and discuss the evolution of the system and a possible temporal relationship of water chemistry with volcanic eruptions. Geothermometry based on gas compositions and saturation indices for non-silicate minerals allowed to estimate deep aquifer temperatures and the existence of the two-phase aquifer. We propose that a shallow boiling "brine" is the source for the Cl-rich fumaroles and, possibly, for the ultra-acid Yurievskie springs. The high Cl and S fluxes from volcano–hydrothermal systems are discussed in terms of the volatile recycling in subduction zones (Taran, 2009; Shinohara, 2013).

2. Ebeko volcano, phreatic and fumarolic activity

The Ebeko volcano (50°41′N, 156°01′E) is located at the northern part of Paramushir Island, at the north of Vernadsky Ridge (Fig. 1a, b) and composed of several Quaternary volcanic cones. The Neogene volcano-clastic basement occurs below ~200 m asl (Sergeev, 1966; Gorshkov, 1970; Melekestsev et al., 1993). The post-glacial cone of Ebeko is composed by lava flows and pyroclastics of andesitic composition. The summit is represented by three craters: Northern, Middle and Southern (Fig. 1). The modern phreatic and fumarolic activity of Ebeko started after a strong explosive phreatic–magmatic eruption from the Middle crater in 1934–1935 (Gorshkov, 1970; Melekestsev et al., 1993) which ejected about 10^6 t of andesitic ash and bombs. Three phreatic eruptions in 1967–1971 in the Northern crater were preceded by a short episode of increasing temperature of fumaroles (Menyailov et al., 1985). In October 1987, after 16 years of moderate low-temperature fumarolic activity, a new phreatic eruption started in the Northern crater lasting 3 months involving 5–6 daily gas-ash explosions (Menyailov et al., 1988). In February 1989, a longest historic phreatic activity started at a funnel formed in 1967 in the Northern crater and produced a new vent on the eastern slope. The activity ceased in April 1989, but in January 1991 several episodes of gas emission combined with ash ejecta were observed (Menyailov et al., 1992). A week lasting event in March 1998 involved a series of gas-ash explosions accompanied by the formation of new fumaroles and increasing fumarolic temperature at the SE field reaching 460 °C (Fazlullin, 1999). The most recent phreatic activity with many evens took place in 2005–2011 (Kotenko et al., 2007, 2012).

Menyailov et al. (1985, 1988) monitored the fumarolic activity of Ebeko in 1960–1980 and noted changes in the activities of different groups of fumaroles before and after phreatic eruptions. They reported that the gas composition was stable, "steady state", between eruptions within a group, but differs between groups. According to Menyailov et al. (1985, 1988), fumarolic activity in Ebeko is stable at low temperatures (usually, <120 °C) between eruptions, but sharp changes occur shortly before and after phreatic events. They also noted significant a SO_2 proportion in gases with SO_2/H_2S between 1 and 10, and high concentrations of HCl (up to 0.3 mol%). Another notable feature of the thermal fields is the presence of numerous drainless pools or low-discharge springs, and many of them are boiling with concentrated hyper-acid Cl–SO_4-type water. Among them there was a near boiling spring Belyi Klyuch with a low discharge and variable salinity from several to 100 g/L of water with pH ~0 and Cl to 80 g/L (Markhinin and Stratula, 1977). The spring is no longer present.

3. Yurievskie springs

The Yurievskie hot springs have been described in detail by Fazlullin (1999). He has mapped 50 thermal manifestations along the Yurieva River canyon and reported the chemical compositions of these thermal waters obtained during the 1984, 1987 and 1988 field campaigns. The Yurieva River canyonlies ~1 km from the Ebeko craters on the NE slope of Ebeko (Fig. 1a and b). The hydrothermal activity along the canyon begins at 580 m asl and continuous down to 280 m asl. Many vents discharge acidic hot water (with the highest temperature up to 87 °C) into the river. The total river length is about 5 km, it flows into the Sea of Okhotsk and forms a 3 km long discolored plume in the sea (Fig. 1b). The composition of Yurievskie springs was first reported by Ivanov (1961) and subsequently studies on different aspects of the hydrochemistry and the solute fluxes of the springs and the river were carried out by Sidorov (1965), Zelenov (1972), Markhinin and Stratula (1977), Nikitina (1978), Fazlullin (1999), Bortnikova et al. (2006) and Kalacheva and Kotenko (2013).

4. Methods

Volcanic gas samples were collected using a Ti sampling tube and Giggenbach bottles filled with 4 N NaOH solution. Condensates of volcanic vapor were collected using bubblers cooled with snow. Gas samples from Giggenbach bottles were analyzed following the method described by Giggenbach and Goguel (1989). Condensate samples were used for hydrogen and oxygen isotope analysis.

Water samples were filtrated through 0.45 μm filters and collected in plastic bottles. Temperature (±0.1 °C), pH (±0.05 units) and conductivity (±2%) were measured on site by an Orion multimeter. Samples for cation 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. Total SiO_2 and B were determined by colorimetric method using ammonium molybdate (Giggenbach and Goguel, 1989) and carminic acid, respectively. The analytical errors are usually less than 5%.

Concentrations of trace cations were determined by ICP-MS (Agilent 7500 CE). All determinations were performed with the external standard calibration method, using Re and In as internal standards. The accuracy of the results (±5%) was obtained by analyzing certified reference materials (NRCSLR-4, SPS-SW1 and NIST-1643e). The water samples were analyzed for their oxygen and hydrogen isotopic composition, using "Los Gatos" IR spectrometer. The isotope ratios are expressed in permil vs V-SMOW. The uncertainties are ±0.2‰ for $\delta^{18}O$ and ±1‰ for δD (one standard deviation).

For determination of $\delta^{18}O$ for dissolved sulfate, barite was precipitated in the field from thermal waters. The sample barite and a reference barite, NBS-127, were weighed into pure Ag capsule, and placed in Rapid OXY Cube elemental analyzer, manufactured by Elementar, Germany. The air in the sample was purged and filled by He, and the sample was heated at 1450 °C in a graphite crucible in the pyrolysis reactor. CO gas released from the sample was carried by He gas to Thermo-Finnigan Delta Plus XP gas-source mass spectrometer for isotope ratio measurements. 87Sr/86Sr in waters was analyzed in LUGIS-UNAM. Details of the Sr isotope determination can be find in Schaaf et al. (2005).

The stream flow rate of the Yurieva River was measured after choosing an appropriate gauging-station site by the float method with two cross-sections of the measured depth with a distance of 5 m. We estimate the accuracy of the flow rate determination for the Yurieva River as ~20% using 5 independent flow rate measurements. The flow rate of fumaroles was measured by the Pitot tube method with the accuracy ~20%.

5. Results and discussion

5.1. Gas geochemistry and equilibria

The gas analyses from Ebeko fumaroles and the P2 well are shown in Table 2 together with averaged compositions of fumaroles reported by Menyailov et al. (1985, 1988). Gases from different parts of the summit thermal field are all water-rich (97–99 mol%) and show varying contents of HCl and total sulfur and ratios of C/S and H_2S/SO_2 in time and space. Generally, the NE fumaroles are lower in HCl than fumaroles from the SE field. A common feature for all fumarolic gases of Ebeko is low concentrations of H_2 and CO and correspondingly, very low ratios H_2/H_2O and CO/CO_2 (on average, 10^{-6} and 10^{-7}, respectively). Methane concentrations are also low, several ppmV in dry gas.

Menyailov et al. (1985) reported ~5 ppm He in dry gas (recalculated from He/Ar and N_2/Ar) and ^3He/^4He = 6.1Ra in a fumarole from the NE field with He/Ne = 12 (Ra is air ratio of 1.39×10^{-6}). It gives C/$^3He \approx 2.4 \times 10^{10}$—a typical arc value (Hilton et al., 2002). Well P2 contains high He concentration (70 ppm) with ^3He/^4He = 6.4 Ra with He/Ne = 66 (Rozhkov and Verkhovsky, 1990; Taran, 2009). Since P2 water contains high bicarbonate concentration (~2800 ppm, Table 2) and low gas content (~1 mmol/mol, Table 1),C/^3He ratio using the total C (CO_2(gas) + HCO_3^- (aq) + CO_2(aq) (Taran, 2005, 2009) is calculated to be 2×10^{10}, which is similar to the ratios of other fumarolic gases.

The N_2–Ar–He systematics for Ebeko gases is shown in Fig. 2. Almost all data points are plotted between ASW (air saturated water) and Air lines, indicating that gases are contaminated by either air during the sampling and/or analysis. Some samples after "extracting air" still have N_2/Ar ratios close to that of air. The main reason may be the consuming of the air oxygen for oxidation of H2S during sampling and storing. It is also possible that air dissolved in meteoric water may have mixed with the deep vapor with an excess on N_2. Only two fumaroles show excess N_2, as well as the gas from well P2 (N_2/Ar = 150).

All fumaroles of Ebeko have record low temperatures at present (<120 °C), but the temperatures varied from 100 °C to 147°Cin July after the 2005 phreatic eruption (Kotenko et al., 2007). Nevertheless, all fumaroles discharge high in SO_2 compared to H_2S and fumaroles from the SE field are also enriched in HCl. This relatively high SO_2 concentrations were also observed in samples collected by Menyailov et al (1985, 1988) in 1979–1985 (Table 1). A ternary diagram in Fig. 3 shows relative concentrations of CO_2, S_t (total sulfur, SO_2 + H_2S) and HCl for Ebeko fumarolic gases and compares those with the composition of high HCl gases (>97 °C) at Poas volcano (Costa Rica) based on the data reported at the Volcanic Gas workshop in 2003 (Newsletter, 2006. See also Fischer et al., 2015). Relatively high concentrations of HCl in low-temperature volcanic vapors suggest the presence of boiling acidic brine beneath the fumarolic fields. High concentration of HCl in fumaroles (up to 0.2 mol% of HCl in fumaroles, ~4 g/kg or >0.1 mole/kg of vapor) require partitioning of HCl from a high-temperature brine with very low pH and a high-temperature (Simonson and Palmer, 1993; Palmer et al., 2004). The relationship of the concentration of HCl between vapor and brine is expressed by the equation below:

$$K_p = m_v/(m_{H+} m_{Cl-} \gamma^2) \qquad (1)$$

where K_p is the partitioning constant, m_v is molality of HCl in the vapor phase, m_{H+} and m_{Cl-} are molalities of H^+ and Cl^- in solution and γ is activity coefficient (Simonson and Palmer, 1993; Alvarez et al., 1994). Eq. (1) can be re-written as:

$$m_v = K_p 10^{-pH} m_{Cl-} \gamma. \qquad (2)$$

Table 1
Coordinates and field data on thermal and cold waters of Paramushir Island sampled in 2014.

Sample site	№α	Latitude N	Longitude E	T, °C	pH$_{field}$	Eh, mV	Ω, μS/cm	Q, l/s
Yurievskie springs								
Yurievabelow springs	Y1	50° 42.42′	155° 59.10′	32.0	1.81	313	11,670	630
Thermal spring	Y2	50° 42.42′	155° 58.89′	17.6	4.27	158	1501	–
Thermal spring	Y3	50° 42.46′	155° 58.70′	18.0	2.33	264	7230	~0.15
Cold stream	Y4	50° 42.44′	155° 58.67′	7.2	3.67	185	575	~5
Cold stream	Y5	50° 42.44′	155° 58.62′	9.1	3.48	197	841	~10
Cold stream	Y6	50° 42.12′	155° 58.22′	5.3	5.70	70	69	~5
Yurieva mouth	Y7	50° 42.92′	155° 56.77′	20.0	2.18	280	7870	1280
Thermal spring (spring №1)	Y8	50° 42.10′	155° 59.87′	80.8	1.42	390	20,300	~2.5
Goryachiy stream upper springs	Y9	50° 42.10′	155° 59.87′	3.7	4.05	161	173	~1.5
Goryachiy stream	Y10	50° 41.99′	155° 59.93′	60.0	1.48	357	17,960	~6
Thermal spring	Y11	50° 42.12′	155° 59.88′	68.4	1.42	375	19,050	~0.1
Thermal spring	Y12	50° 42.21′	155° 59.86′	34.0	2.04	302	8820	~4
Yurieva upper springs	Y13	50° 42.22′	155° 59.87′	6.7	3.81	178	201	15
Thermal spring	Y14	50° 42.22′	155° 59.50′	45.1	1.73	329	14,500	~3
Thermal spring	Y15	50° 42.23′	155° 59.43′	71.2	1.51	384	18,240	~2
Thermal spring	Y16	50° 42.38′	155° 59.22′	47.5	1.89	322	11,500	~5
Thermal spring	Y17	50° 42.33′	155° 59.28′	31.8	2.23	288	7510	~0.4
Thermal spring	Y18	50° 42.32′	155° 59.31′	41.4	1.93	316	11,170	~5
Ebeko volcano								
Pool	E1	50° 41.20 ′	156° 00.83′	75.2	1.81	355	6060	
Fumarolic condensate	E2	50° 41.12′	156° 00.88′	106.0	0.60	409	186,400	
Pool	E3	50° 41.20′	156° 01.10′	85.1	0.25	484	198,900	
Pool	E4	50° 41.15′	156° 01.16′	89.0	0.61	422	59,900	
Fumarolic condensate	E5	50° 41.16 ′	156° 01.18′	105.0				
Stream	E6	50° 41.55′	156° 01.15′	13.4	3.28	210	1132	
Pool	E7	50° 41.55′	156° 01.29′	72.5	1.25	380	22,300	
Pool	E8	50° 41.54′	156° 01.32′	80.0	1.66	361	7800	
Fumarolic condensate	E9	50° 41.54′	156° 01.35′	109.0	1.86	345	8480	
Crater lake	E10	50° 41.48′	156° 00.97′	16	2.72	252	1663	
Well	P2	50° 39.63′	156° 05.03′	70.9	7.60	−40	10,350	

α: Numbers correspond to those used in Figures. Ω—conductivity; Q—flow rate.

Table 2
Gas composition (mol%) of Ebeko fumaroles and well P2 (recalculated without air).

Sampling site	Year of sampling	T°C	H_2O	H_2	CO_2	CO	SO_2	H_2S	HCl	HF	N_2	Ar	He	CH_4
This work														
NE Field	2003	110	98.0	0.00001	1.72	1.1E − 06	0.21	0.008	0.018	na	0.0053	1.3E − 04	1.8E − 05	5.0E − 05
NE Field	2004	110	98.7	0.000013	0.79	3.2E − 06	0.29	0.022	0.008	na	0.0055	7.3E − 05	1.5E − 06	6.2E − 06
NE Field	2005	125	97.8	0.000009	1.22	9.0E − 07	0.65	0.033	0.047	na	na	na	1.5E − 05	1.3E − 06
NE Field	2012	115	99.2	0.00001	0.69	na	0.054	0.017	0.001	na	0.024	0.0003	3.5E − 6	1.1E − 5
July Field	2005	147	90.5	0.000015	2.27	4.2E − 06	3.35	0.25	2.75	na	0.132	0.0022	na	4.5E − 06
July Field	2011	106	99.33	0.007	0.58	na	0.034	0.025	0.005	na	0.021	0.0002	7.4E − 6	1.5E − 6
Active Funnel	2008	105	89.59	0.00005	4.71	na	0.41	0.14	0.38	na	3.70	na	na	na
Florensky	2010	117	98.32	0.00001	1.44	na	0.018	0.19	0.03	na	0.014	2.5E − 05	2.35E − 5	6.2E − 7
South Crater	2011	116	95.96	0.0078	3.44	na	0.24	0.005	0.21	na	0.030	0.0004	3.7E − 05	8.7E − 6
SE Field	2009	123	90.07	0.0040	8.40	na	0.89	0.15	0.33	na	0.0076	1.3E − 04	9E − 05	0.0003
SE Field	2010	135	81.22	0.00021	15.2	na	4.08	0.20	0.04	na	0.10	0.0017	1.8E − 04	2.4E − 05
SE Field	2012	120	94.56	0.09	4.80	na	0.16	0.16	0.08	na	0.11	0.003	3.1E − 04	2.5E − 05
Menyailov et al., 1988														
NE Field (4)	1985	93	97.30	0.00091	2.35	5.2E − 07	0.25	0.065	0.0064	5.0E − 05	0.025	0.00013	na	3.9E − 06
Gremuchaya (18)	1984	120	98.46	0.00012	1.28	5.0E − 07	0.17	0.059	0.0054	0.5E − 05	0.0081	0.00018	na	3.2E − 06
Florenskii (4)	1979 − 83	105	97.97	8.2E − 05	1.73	2.3E − 07	0.08	0.08	0.090	0.3E − 05	0.030	na	na	1.1E − 04
E Field (13)	1979 − 85	106	97.80	5.9E − 05	1.86	6.0E − 06	0.066	0.066	0.161	0.7E − 05	0.021	0.00026	na	7.2E − 05
SE Field (8)	1979 − 84	106	97.38	0.00165	1.96	1.8E − 06	0.19	0.15	0.192	1.6E − 05	0.043	0.00066	na	3.5E − 05
Bessonova et al., 2006														
NE Field	1998	130	95.50	1.2E − 05	3.64	5E − 06	0.51	0.15	0.13	0.0005	0.023	na	na	2.4E − 05
This work														
Well P2	1995	80	1.9[a]	0.010	97.6	na	–	–	–	–	2.1	0.014	0.007	0.10

[a]) The gas content for Well P2 (mmol/mol) was calculated using Ar concentration following the method described in Taran (2005).

In acidic solutions with low cation concentrations where [Cl$_{tot}$] is ~[Cl$^-$] + [HCl(aq)]. In turn, concentration of HCl(aq) depends on [Cl$^-$] as

$$m_{HCl(aq)} = \gamma K_d^{-1} 10^{-pH} m_{Cl^-} \qquad (3)$$

where K_d is the dissociation constant for HCl.
Then

$$m_{Cl^-} = m_{Cltot}\left(1 + \gamma K_d^{-1} 10^{-pH}\right)^{-1} \qquad (4)$$

and

$$m_v = K_p K_d 10^{-pH} m_{Cltot} \gamma \left(K_d + \gamma 10^{-pH}\right)^{-1}. \qquad (5)$$

The dissociation constant for HCl under saturation pressure of water vapor varies from $10^{0.81}$ at 100 °C to $10^{-2.33}$ at 350 °C (Tagirov et al., 1997). According to Simonson and Palmer (1993), the partitioning constant K_p can be interpolated at ≤300 °C as:

$$\log K_p = -3.34 + 0.0163t \qquad (6)$$

where t in °C. The activity coefficient for Cl$^-$ is estimated for a solution with 1 M of the total chloride and 1 M of the total sulfate at pH = 0, using a thermochemical computer code, The SOLVEQ code (Reed and Spycher, 1984) yields γ values varying from 0.67 at 100^{0}C to 0.29 at 300 °C using the extended Debye–Hückel equation. Using these data, a relationship between the concentration of HCl in steam vs temperature for the solution containing 1 M of the total chloride and 1 M of the total SO_4 is illustrated at different pH in Fig. 4. The diagram shows that vapor separated from acidic chloride solution contains high HCl and the concentration of HCl becomes similar to that of high-temperature volcanic (magmatic) vapors (e.g., Taran and Zelenski, 2014). We believe that this is the case for Ebeko, as well as for the Poas low-temperature fumaroles (Rowe et al., 1992; Vaselli et al., 2003; Fischer et al., 2015). The presence
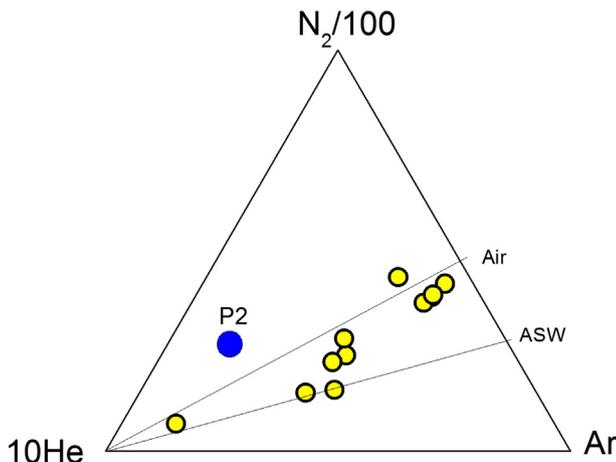

Fig. 2. The N_2–Ar–He ternary plot for fumarolic gases of Ebeko and gas from P2 well. ASW = air-saturated water.
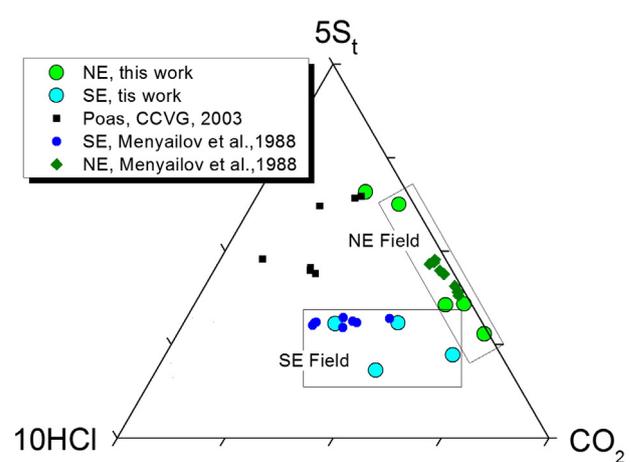

Fig. 3. Ternary diagram CO_2–S_t (total S)–HCl for fumarolic gases of Ebeko. For comparison, the compositions of low-temperature, HCl-enriched gases of Poas volcano are also shown.
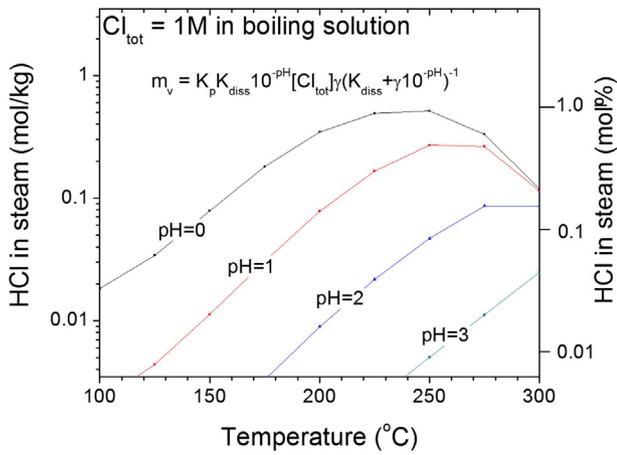
Fig. 4. Concentration of HCl in steam in equilibrium with boiling solution containing 1 M of the total chloride and 1 M of the total sulfate. See text for details.

of acidic brine beneath the Ebeko fumarolic fields is further supported by an unusual combination of H_2/H_2O and CO/CO_2 ratios in fumarolic gases (Fig. 5). The diagram shows the relationship between R_{CO} and R_H and between R_{CH4} and R_H, where R_{CO}, R_{CH4} and R_H stand for log (CO/CO_2), log (CH_4/CO_2), and $R_H = $ log (H_2/H_2O), respectively. It also
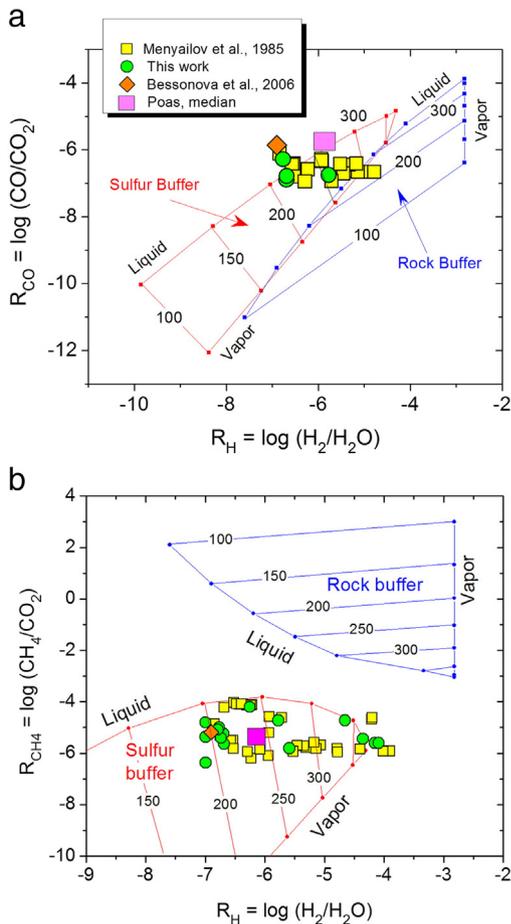

Fig. 5. Redox-diagrams for H- and C-bearing gases at various temperatures in °C. Data from Ebeko fumarolic fields plot within the two-phase area of sulfur buffer. A blue star is the composition of gas from the P2 well (only for R_{CH4}–R_H). For comparison, it shows the composition of Poas fumaroles reported by Fischer et al. (2015). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

shows the compositions of gases in two buffer systems are plotted: for the so-called "rock buffer FeO-FeO$_{1.5}$" (Giggenbach, 1987) and for "sulfur buffer" defined by Giggenbach (1987):

$$SO_2 + 3H_2 = H_2S + 2H_2O. \tag{7}$$

For the liquid phase the following equilibrium is chosen:

$$H_2SO_3 + 3H_2(aq) = H_2S(aq) + 3H_2O \tag{8}$$
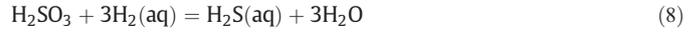
with the equilibrium constant logK(8) $=$ 0.11 $+$ 14,892/T (HSC-7, Roine, 2009). The diagram in Fig. 5 shows that almost all data are plotted within the two-phase region of the S redox-buffer, supporting the presence of acidic liquid beneath the fumarolic field of Ebeko. The majority of the data points are plotted between 200 °C and 300 °C on both diagrams despite a much slower kinetics of the reactions involving methane (e.g., Giggenbach, 1987).

5.2. Geochemistry of waters

The field data and locations of thermal springs and stream waters are shown in Table 2. The chemical compositions of waters from well P2, Ebeko thermal fields and Yurievskie springs (major components) are listed in Table 3. For the 2014 samples for the first time the oxygen and hydrogen isotopic composition of waters was analyzed.

5.2.1. Isotopic composition of waters

Isotopic compositions of Yurievskie springs plot close to the meteoric water line with a clear positive shifts in both $\delta^{18}O$ and δD (Fig. 6a). These shifts are most likely due to mixing with magmatic vapor because there is a very good correlation between chloride concentration and both $\delta^{18}O$ and δD (Fig. 6b). Note that Spring 1, the hottest springs among Yurievskie (sample Y8) is the most enriched in heavy isotopes. Interestingly, the isotopic composition of water from Well P2 is also plotted within the same trend, but with an additional ^{18}O shift due to water–rock interaction (Fig. 6a, b). The extrapolation of the trend observed in the water samples approaches the composition of "andesitic" (or arc-magmatic) water as it was defined by Taran et al. (1989) and Giggenbach (1992) (see also Taran and Zelenski (2014) for the Cl content in arc-volcanic fluids) (Fig. 6b).

Condensates of Ebeko fumaroles are significantly enriched in deuterium compared to the Yurievskie waters but almost all with negative values of $\delta^{18}O$, indicating a large proportion of meteoric water in the acidic boiling brine beneath the fumarolic fields. The δD values for fumarolic vapors ($-40 \pm 10‰$) are quite unusual considering the value of $-80‰$ for local meteoric water. For many volcanoes in the world there is a good correlation between δD and vent temperature or HCl concentration in vapors (Taran and Zelenski, 2014). Low-temperature fumarolic vapor usually contains low HCl and δD close to the local meteoric water values (if there is no seawater contribution). Exceptions from this rule to the authors' knowledge are low temperature (104 °C) fumaroles of Satsuma Iwojima (Shinohara et al., 1993), which formed from magmatic vapors through conductive cooling without contribution of meteoric water. The relationship between the isotopic composition of fumarolic vapors and chloride content in condensates and pools (Fig. 6b) does not clarify the situation. There is no correlation between Cl and δD because δD of condensates are all $\sim -40 \pm 10‰$ independent on Cl contents. Similar δD values were reported by Menyailov et al. (1988) for Ebeko fumaroles sampled in 1979–1983 (Fig. 6a). The isotopic composition of water from drainless pools of Ebeko also does not show a correlation with the chloride concentrations (Table 3, Fig. 6b) and widely varies at low Cl concentrations. The data may suggest that fumarolic vapors and pool waters undergo different degrees of equilibrium and/or kinetic isotopic fractionation associated with evaporation and different proportions of magmatic (volcanic) and meteoric waters. The composition of fumarolic condensates

Table 3
Chemical (mg/L) and isotopic (‰ VSMOW) composition of thermal and cold waters of Paramushir Island. na—not analyzed.

Sample	date	$t°C$	pH_{lab}	Na^+	K^+	Ca^{2+}	Mg^{2+}	Al^{3+}	Fe	HCO_3^-	Cl^-	F^-	SO_4^{2-}	B	SiO_2	δD	$\delta^{18}O$	Sr	$^{87}Sr/^{86}Sr$
Yurievskie springs																			
Y1	12.08.2014	32	1.6	86	54	74	65	252	112	0	1118	1.9	2990	na	274	−78.5	−11.1	1.56	0.70317
Y2	12.08.2014	17.6	3.2	44	22	97	33	73	4.5	0	211	0.1	614	na	241	−81.9	−12.0		
Y3	12.08.2014	18	2.0	53	37	91	41	162	59	0	628	1.7	1541	na	238	−82.9	−12.0	0.98	0.70316
Y4	12.08.2014	7.2	3.3	9.4	3.8	13.3	7.2	16.7	0.5	0	36	1.3	134	1.1	84	−84.0	−12.3		
Y5	12.08.2014	9.1	3.1	11.8	5.4	14	9.4	22	4.7	0	36	0.6	221	na	87	−83.3	−12.2		
Y6	12.08.2014	5.3	7.2	4.8	1.4	4.9	1.4	0.0	0.1	8	5.7	0.3	19.3	na	56	−84.5	−12.4		
Y7	12.08.2014	20	1.8	51	37	87	39	146	66	0	632	2	1715	1.7	196	−81.7	−11.8		
Y8	13.08.2014	80.8	1.2	187	128	230	151	527	28	0	2734	15	6861	4.9	502	−75.2	−9.4	1.98	0.70315
Y10	13.08.2014	60	1.4	139	94	139	109	356	181	0	1811	0.4	5176	2.5	376	−77.2	−10.6	2.17	
Y11	13.08.2014	68.4	1.3	167	116	198	133	438	216	0	2325	13.3	6182	3.5	419	−77.3	−10.5	2.5	0.70316
Y12	13.08.2014	80	1.8	86	66	7	57	257	98	0	799	1.7	2410	na	265	−80.6	−11.5	1.2	0.70315
Y13	13.08.2014	6.7	3.5	4.3	1.4	7.6	2.4	0.9	0.0	0	7.1	0.4	39.1	na	49	−81.1	−12.0		
Y14	13.08.2014	45.1	1.5	111	80	133	85	311	160	0	1349	9.4	4053	na	334	−78.5	−10.8	1.7	0.70316
Y15	13.08.2014	71.2	1.3	169	134	226	132	468	81	0	2308	13.6	6277	3.5	418	−78.4	−10.7	2.99	0.70316
Y16	13.08.2014	47.5	1.7	115	92	105	90	431	148	0	1367	0.4	3662	2.5	358	−78.6	−10.9		
Y17	13.08.2014	31.8	1.5	130	68	212	85	226	112	0	1312	2.2	3355	1.5	135	−80.6	−11.2		
Y18	13.08.2014	41.4	1.4	130	37	200	83	227	142	0	1383	2.4	3622	1.5	125	−79.7	−11.2		
Ebeko volcano																			
E1	16.08.2014																	0.49	0.70319
E2	16.08.2014	106	0.5	0.4	1.1		0.1	738	2	0	25,276	0.2	94	na	0.3	−35.9	−3.5	0.05	0.70426
E4	16.08.2014	82	0.8	9.2	9.7	0.4	1.3	63	12.3	0	5148	<0.2	4450	na	227	−28.7	−0.6	0.27	0.70320
E5	16.08.2014	105	0.6	3.8	3.3	1.5	4.5	25	4.3	0	16,152	22	688	na	3.9	−28.7	−0.6	0.06	
E6	20.08.2014	13.4	2.4	8.1	2.6	58.7	7.3	23	6.2	0	25.6	0.7	345	na	74	−43.5	−4.2		
E7	20.08.2014	72.5	1.1	28	47	0.6	3.5	231	32	0	192	<0.2	8566	na	256	−22.0	3.6	1.74	
E8	20.08.2014	80	1.5	13	17	0.5	3.6	110	17.2	0	11	<0.2	3270	na	304	−45.5	−1.5		
E9	20.08.2014	109	1.7	0.3	0.6	0.1	0.05	2.9	0.6	0	909	<0.2	14	na	3.4	−47.0	−4.8		
E10	20.08.2014	16	2.3	2.5	1.8	66	1.2	12.2	7.9	0	106	0.7	291	na	20	−78.6	−10.8		
Well P2																			
P2	10.08.2014	70.9	7.9	2516	152	23	16	10.3	0.1	1928	2716	0.6	192	5.4	125	−73.7	−7.6	2.05	

derived from the boiling of concentrated acidic brine (see discussion above) may also indicate that the original brine is isotopically lighter in δD and heavier in $\delta^{18}O$. This suggestion is based on the experimental studies of the isotopic fractionation of water between vapor and concentrated NaCl and KCl brines (Schmulovich et al., 1999; Driesner and Seward, 2000). Water vapor has lower deuterium than liquid water at low temperatures, but vapor is enriched in deuterium compared to liquid water above ~220 °C with a maximum fractionation of ~5 ‰ at ~280⁰C (Horita and Wesolowski, 1994). Concentrated aqueous solutions (2–4 M) display this inversion temperature for isotopic fractionation at lower temperatures, <200 °C, and vapor is enriched in deuterium relatively brine by ~10 ‰ at >250 °C (Driesner and Seward, 2000). Therefore, it is conceivable that the acidic boiling brine beneath the fumarolic fields of Ebeko has low δD values in a range of −50 ± 5 ‰ if the temperature is greater than 250 °C. The positive shift in ^{18}O for the concentrated NaCl solutions is near 1 ‰ at >250C. The estimated isotopic composition of the Ebeko brine therefore can be near $\delta D = -50$ ‰ and $\delta^{18}O = -3$ ‰, which is close to the mixing line between local meteoric water of Ebeko and the postulated arc-magmatic water (Fig. 6a).

5.2.2. Water chemistry: major components

All waters from the Yurievskie springs and Ebeko pools are ultra-acidic, with pH < 2. The Yurievskie waters are of the SO_4–Cl type (by weight), whereas the SO_4/Cl ratio in Ebeko pools show low (<1) and varying SO_4/Cl ratios (Table 3, Fig. 7c). The data plotted in Fig. 7a–c are from this work (2005 and after) and are taken from Zelenov (1972), Nikitina (1978) and Fazlullin (1999). Similar SO_4/Cl ratios in Yurievskie springs (~1:1 molar and 3:1 by weight, Fig. 7c) indicate a simple mixing between meteoric water and one endmember component with high Cl and SO_4. The mixing likely occurs at shallow levels based on the chloride vs temperature plot of all available data (Fig. 8). Spring 1 has been the most concentrated and hottest since the first sampling in 1955 (Zelenov, 1972), but both salinity

and temperature gradually decreased from almost boiling (95 °C) with Cl content >5000 mg/L in 1954 to 78 °C and ~2500 mg/L of Cl in 2014 (Fig. 7a). The concentrations of chloride and sulfate in the Yurievskie springs are decreasing over time with a constant SO_4/Cl ratio (note that the "Cl vs Date" diagram is a semi-log plot). The chemical composition of the Ebeko pools is highly variable both in salinities and SO_4/Cl. Chloride concentrations in pools from the South (E1, E2) and SE fields (E3–E5) of Ebeko are always significantly higher (E3 sample, Table 3) than those in the NE field (E7–E9, Table 3). This is in accordance with the low HCl contents in the NE fumaroles compared to fumaroles of the SE field (Table 1). A ternary plot for cations in waters of the Ebeko pools and Yurievskie springs (Fig. 9) demonstrates notable difference between these two thermal manifestations. Waters from Yurievskie springs are similar in (Na + K)/Mg ratio and vary in Ca. This varying content of Ca is likely due to the precipitation and dissolution of anhydrite. Waters from Ebeko pools are plotted close to the main trend but compositions significantly scatter around this trend. Such a composition of cations is common for waters from ultra-acidic lakes in craters of andesitic volcanoes where strong acidity of water is capable to leach bulk of cations. Indeed, the average composition of the unaltered Ebeko andesitic rock (Martynov et al., 2010) plots within the area of water compositions. Such a composition of cations is common for waters from ultra-acidic lakes in craters of andesitic volcanoes. An inserted ternary plot in Fig. 9 compares the data points for Poas, Ruapehu and Copahue crater lakes (Rowe et al., 1992; Christenson and Wood, 1993; Varekamp et al., 2001) with the data for the Ebeko + Yurieva composition.

It has been suggested that an increase in Mg in acidic waters precedes volcanic eruptions as it was first shown by Giggenbach (1974) for Ruapehu crater lake and this phenomenon was repeated later at Ruapehu and Copahue volcanoes (Christenson and Wood, 1993; Varekamp et al., 2001). Giggenbach (1974) suggested that this is a response on the intrusion of new magma into the acidic aquifer. All available data from the Yurievskie springs since 1955 are plotted in
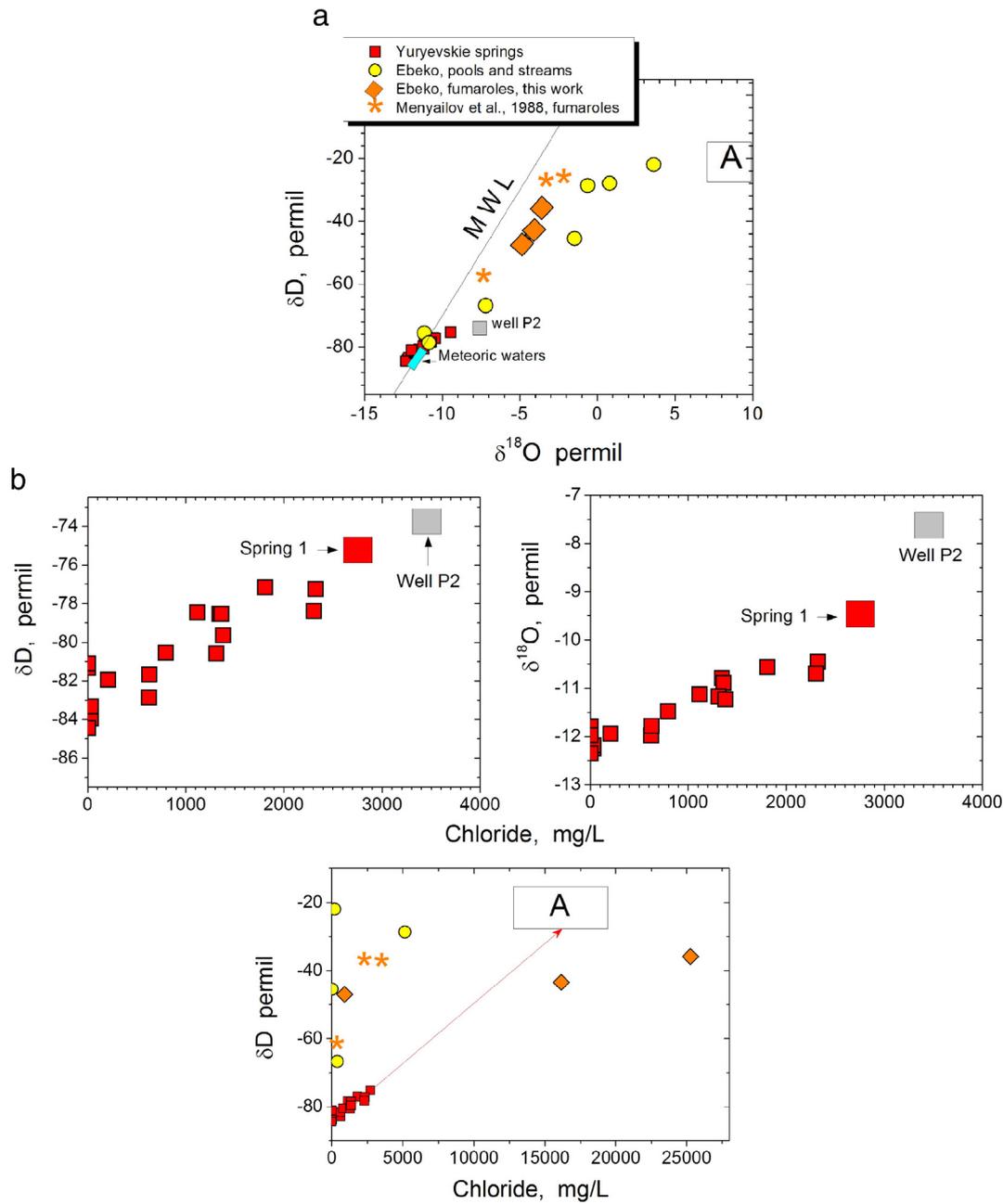
Fig. 6. (a) δD vs δ¹⁸O plot for waters from Spring 1 and Well P2 and volcanic gas condensate in the Ebeko thermal fields. MWL—meteoric water line ($\delta D = 8\delta^{18}O + 10$); rectangular field A shows composition of "Arc-Magmatic" or "Andesitic" water as defined by Taran et al. (1989) and Giggenbach (1992). (b) Correlation between water isotopic composition and chloride content for waters from Yurievskie springs and Ebeko pools. Rectangular field A shows the compositions of arc-magmatic gases (Taran and Zelenski, 2014).

Fig. 10(a, b), where each data set contains from 5 to 30 analyses. A positive correlation is observed between Mg and Cl in Fig. 10a with a mean Mg/Cl of 0.059 and a standard deviation for the slope of 0.014. The only statistically significant increase of the relative Mg concentration occurred in 2010 during the 2005–2011 cycle of eruptions and enhanced fumarolic activity of Ebeko (Fig. 10a, b). The data confirms that the acidic aquifer feeding Yurievskie springs and fumarolic fields of Ebeko may represent a common volcano–hydrothermal system, and therefore, the chemical monitoring of Yurievskie springs may be an effective geochemical tool for predicting eruptive activity of Ebeko volcano.

5.2.3. Water chemistry: trace elements, REE and ⁸⁷Sr/⁸⁶Sr

More than 40 trace elements and a full set of REE were analyzed in waters of the Yurievskie springs and pools from fumarolic fields of

Ebeko (Table 4). Enrichment factor of element i, F_i, were obtained by normalizing the concentration of element, E_i, to Mg, $F_i = (E_i/Mg)_w/(E_i/Mg)_r$, where subscripts w and r correspond to water and rock, respectively, the ultra-acidic waters of Yurievskie springs show a pattern similar to other volcano–hydrothermal systems and crater lakes, such as Keli Mutu and Kawa Ijen crater lakes in Indonesia (Pasternack and Varekamp, 1994; Delmelle et al., 2000), El Chichon acid springs in Mexico (Taran et al., 2008; Peiffer et al., 2011) and Shiashkotan volcanic field, Russia (Kalacheva et al., 2015). The composition of rocks is a mean value of andesitic rocks of Paramushir Island (Avdeiko et al, 1992; Martynov et al., 2010). Several elements are not available in the data set of Paramushir andesites and for them it was used the mean value of arc andesite from Kelemen et al. (2007). Elements showing $F_i \sim 1$ are those completely dissolved from host rocks and they include rare earth elements (REE). Elements that have high F_i, >1 include B, Br, I,
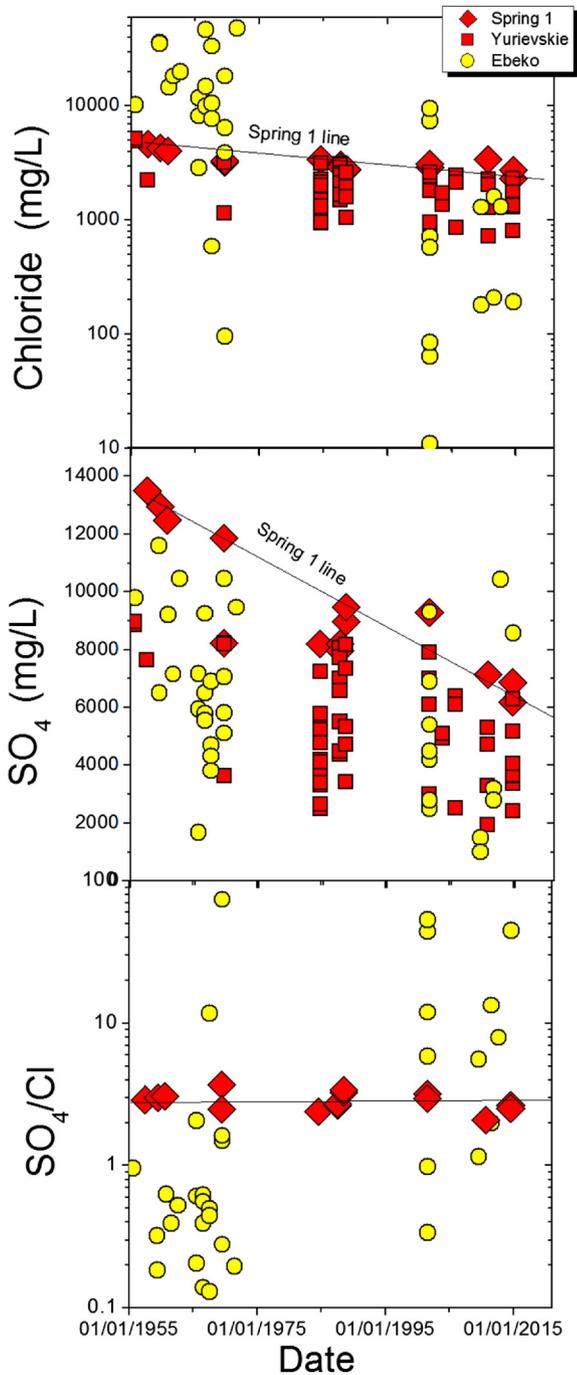
Fig. 7. Chloride, sulfate and SO_4/Cl in thermal waters of Yurievskie and Ebeko over time during the entire period of observation from 1955 to 2015. See text for details and sources of the data.
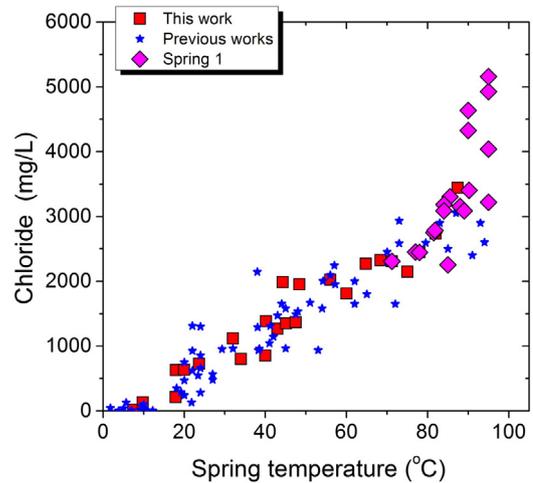

Fig. 8. Chloride vs temperature for Yurievskie spring waters. Data for Spring 1 are from this work (2003–2014) and previous works (see text).

Ebeko pools are shown in Fig. 12. Rocks show a pattern common in arc andesite, high LREE without low Eu. The REE for waters normalized to rock (average of 3 samples, Martynov et al., 2010) is essentially flat indicating a congruent dissolution of REE from the rock matrix in the ultra-acidic water. Waters from the two thermal fields (Yurieva and Ebeko) generally cannot be distinguished using these plots except of one 2005 sample (Fig. 12) from a pool at Ebeko with a pattern similar to that for some other acidic water (e.g., Tamagawa springs, Japan, Sanada et al., 2006). The difference between the total REE concentrations in waters can be related to the differences in the $Al + Fe$ content for spring waters and differences in pH. Positive correlation between total REE concentration and $Al + Fe$ has been shown by Kikawada et al. (1993) in acid waters of the Kusatsu-Shirane area in Japan. Data for Yurievskie and Ebeko waters fall near the same trend on the log–log plot of the total REE vs molar $Fe + Al$ concentration (Fig. 13) as the acid crater lake waters in Japan and acidic waters from Shiashkotan volcanic island (Kalacheva et al., 2015). The evidence suggests that the $Al + Fe$ concentration is a good proxy for the total REE concentration in very acidic thermal waters.

Isotopic composition of dissolved Sr dissolved in thermal waters is a good tracer of the origin of the aquifer rocks. For example, Peiffer et al. (2011) used $^{87}Sr/^{86}Sr$ and Ca/Sr ratios of El Chichon volcano–hydrothermal system to distinguish two main aquifers; one composed of volcanic rocks and another deeper one representing sedimentary rocks. In our study, both Yurievskie spring waters and Ebeko pool waters show
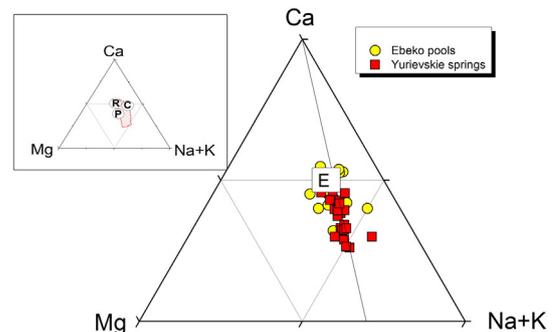
As, Se, Sb, Cs, Rb. They are fluid-mobile elements and may originate from external sources, such as magmatic vapors or sedimentary rocks. The third group of elements are those with $F_i < 1$. They may have been lost as precipitates and co-precipitate as sulfides (Mo, Cu, Ni, Co), sulfates (Ba, Sr) or adsorbed on secondary phases. For example, highly charged cations, such as Sb, Zr, and Nb are easily adsorbed on the surface of secondary minerals. Data points for the Ebeko pools, though generally follow the Yurievskie trend, scatter significantly and on average are plotted higher than the Yurievskie points (Fig. 11).

The REE patterns normalized to chondrite for the Ebeko andesites (Martynov et al., 2010) and acidic waters of Yurieva springs and

Fig. 9. Relative concentrations of $Na + K$, Ca and Mg in waters from Yurievskie springs and Ebeko pools with a square E corresponding to average composition of Ebeko andesites (Martynov et al., 2010). Inserted a diagram showing average composition of Ruapehu (R), Poas (P) and Copahue (C) crater lakes (see text for details).
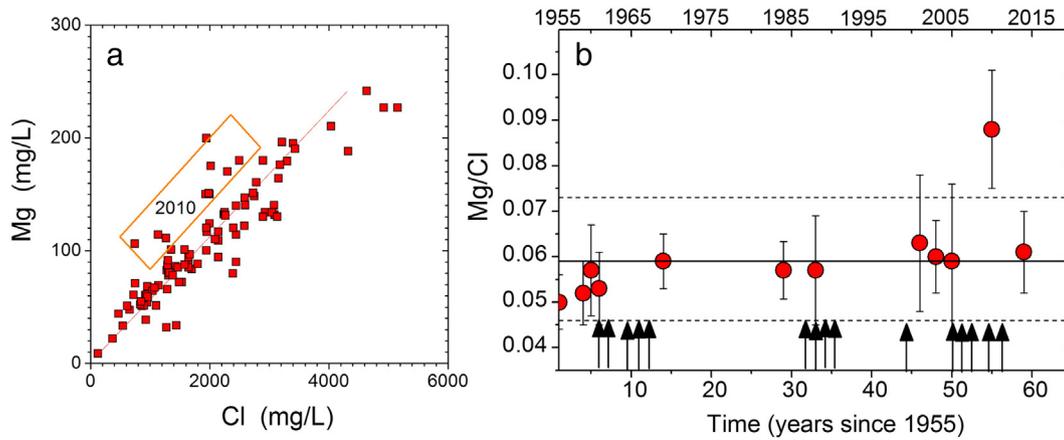
Fig. 10. (a) Mg vs Cl plot for Yurievskie waters. The most of the points above the main trend are from the 2010 samples; (b) Mg/Cl ratio in Yurievskie waters over all time of observation (data of 2003–2014 from this work). Average value and a standard deviation (1σ) are shown for each set of data and the overall 1 sigma range is shown by dashed lines. Only 2010 samples are statistically above the mean value. Black arrows approximately mark periods of phreatic events.

very similar $^{87}Sr/^{86}Sr$ values of ~0.7032 (Table 3), very similar to the Sr isotopic composition of andesites of Ebeko (Martynov et al., 2010). One value of 0.70426 is obtained for a Cl-rich condensate of a fumarole with a low Sr concentration of 0.05 ppm. A slightly high value may suggest a contribution of sea spray since the site is close to the ocean and sea water contains Sr with high $^{87}Sr/^{86}Sr$, 0.7092.

Table 4
Trace element abundances (µg/L) in thermal waters of Paramushir island.
REE are highlighted by bold italic font, <dl—below detection limit.

| Element	Y1	Y3	Y10	Y11	Y12	Y14	Y15	E1	E2	E3	E4	E5	E7	P2
pH	1.6	2.0	1.4	1.3	1.8	1.5	1.3		0.50	0.3	0.8	0.6	1.1	7.9
Cl mg/L	1118	628	1811	2325	799	1349	2308		25,276	nd	5148	16,152	192	2716
Li	48	26	45	48	34	33	67	8.8	<dl	28	<dl	<dl	<dl	624
Be	4.2	3.9	1.5	1.5	3.7	4.1	2.1	3.3	<dl	0.91	<dl	<dl	<dl	2.9
Sc	87	72	103	112	66	86	144	125	<dl	116	<dl	<dl	<dl	33
Ti	50	29	68	78	38	58	92	28	1384	3702	166	1634	12	
V	542	282	688	52	422	603	966	158	24	1311	92	22	493	1.7
Cr	101	58	135	156	75	115	184	11.4	692	1851	83	817	6.1	104
Mn	5981	4058	8922	10,290	4400	7012	11,532	930.5	2470	9023	253	283	649	99
Co	7.9	9.3	7.8	17.0	3.8	27	10.5	2.0	<dl	119	25	1.4	19.3	0.5
Ni	24	17.4	32	39	13.7	34	40	8.0	<dl	45	<dl	369	<dl	2.2
Cu	18.0	23	<dl	15.6	9.8	60	4.9	13.9	<dl	499	<dl	<dl	<dl	73
Zn	588	380	866	994	399	686	1123	69	1398	1188	<dl	101	11.3	1.6
As	555	162	1063	1212	309	623	1325	201	132	2792	89	2171	114	530
Se	11.6	8.4	21	25	7.5	16.9	29	<dl	13	<dl	<dl	281	<dl	50
Rb	168	108	275	320	129	203	350	<dl	3.9	194	35	5.4	41	49
Y	33	24	51	59	23	40	65	<dl	0.04	128	8.6	2.2	14.2	0.17
Zr	0.29	<dl	8.3	8.0	<dl	0.46	7.1	2.1	14.1	146	56	44	54	<dl
Mo	<dl	<dl	0.04	1.1	<dl	<dl	0.24	<dl	<dl	13.5	<dl	<dl	<dl	<dl
Ag	<dl	<dl	<dl	<dl	<dl	<dl	0.26	<dl	<dl	7.7	<dl	<dl	<dl	<dl
Cd	5.0	2.8	8.7	9.6	2.5	6.7	9.6	3.5	0.95	32.9	<dl	0.13	2.4	21.6
Sn	3.5	3.3	0.04	<dl	2.6	2.4	0.17	2.8	8.8	108	<dl	10.9	<dl	3.1
Sb	4.3	3.8	1.7	0.85	3.6	3.4	2.6	3.3	<dl	70	<dl	35	<dl	4.9
Cs	14.6	9.0	27	32	10.9	18.9	33	3.2	<dl	3.8	<dl	<dl	<dl	44
Ba	75	44	132	119	36	49	129	67	36	1133	76	1037	89	1140
La	*30*	*20.0*	*49*	*60*	*23*	*38*	*66*	*13.0*	*<dl*	*90*	*6.0*	*0.44*	*33*	*0.09*
Ce	*73*	*50*	*122*	*148*	*58*	*94*	*166*	*31*	*1.9*	*190*	*17.8*	*2.3*	*71*	*0.11*
Pr	*9.4*	*6.8*	*15.5*	*18.9*	*7.5*	*12.2*	*21*	*4.1*	*<dl*	*22*	*0.99*	*<dl*	*6.4*	*0.05*
Nd	*41*	*29*	*68*	*82*	*32*	*52*	*89*	*17.5*	*0.36*	*102*	*9.7*	*0.53*	*28*	*0.14*
Sm	*8.9*	*6.5*	*14.9*	*18.3*	*6.8*	*11.4*	*19.4*	*4.1*	*<dl*	*22.6*	*0.42*	*<dl*	*3.1*	*0.08*
Eu	*2.7*	*2.1*	*4.5*	*5.5*	*2.0*	*3.5*	*5.9*	*1.4*	*<dl*	*6.8*	*<dl*	*<dl*	*<dl*	*0.35*
Gd	*8.5*	*6.3*	*14.4*	*17.6*	*6.3*	*11.0*	*18.6*	*4.0*	*<dl*	*25*	*0.66*	*<dl*	*3.6*	*0.03*
Tb	*1.3*	*1.04*	*2.0*	*2.5*	*0.92*	*1.7*	*2.6*	*0.68*	*<dl*	*2.8*	*dl*	*<dl*	*dl*	*0.03*
Dy	*6.7*	*5.1*	*11.8*	*14.4*	*4.7*	*8.8*	*15*	*3.9*	*<dl*	*24*	*0.37*	*<dl*	*1.9*	*0.02*
Ho	*1.4*	*1.1*	*2.2*	*2.8*	*0.98*	*1.8*	*2.9*	*0.84*	*<dl*	*4.0*	*<dl*	*<dl*	*dl*	*0.04*
Er	*4.2*	*3.1*	*7.3*	*8.8*	*2.9*	*5.5*	*9.1*	*2.5*	*<dl*	*15.9*	*<dl*	*<dl*	*0.82*	*0.04*
Tm	*0.62*	*0.58*	*0.91*	*1.1*	*0.45*	*0.81*	*1.2*	*0.41*	*<dl*	*1.04*	*<dl*	*<dl*	*dl*	*0.04*
Yb	*4.0*	*3.0*	*7.3*	*9.0*	*2.8*	*5.2*	*9.1*	*2.5*	*<dl*	*16.7*	*0.08*	*<dl*	*0.87*	*0.01*
Lu	*0.64*	*0.57*	*0.9*	*1.2*	*0.45*	*0.83*	*1.2*	*0.41*	*<dl*	*1.3*	*<dl*	*<dl*	*<dl*	*0.03*
Hf	0.09	0.07	<dl	<dl	0.07	0.1	<dl	0.18	<dl	2.5	<dl	<dl	<dl	0.05
Ta	0.33	0.36	<dl	<dl	0.33	0.33	<dl	0.33	<dl	<dl	<dl	<dl	<dl	0.32
Tl	21	14.1	63	76	11.3	30	55	3.1	045	2.2	0.16	<dl	<dl	0.46
Pb	173	7.1	455	554	110	148	497	31	24	159	4.71	<dl	24	0.67
Th	7.4	3.6	15.2	19.1	5.7	10.2	18.9	4.8	<dl	29	2.4	<dl	6.5	0.04
U	2.5	1.6	4.9	6	1.3	3.0	6.4	1.7	<dl	6.8	<dl	<dl	0.33	0.04
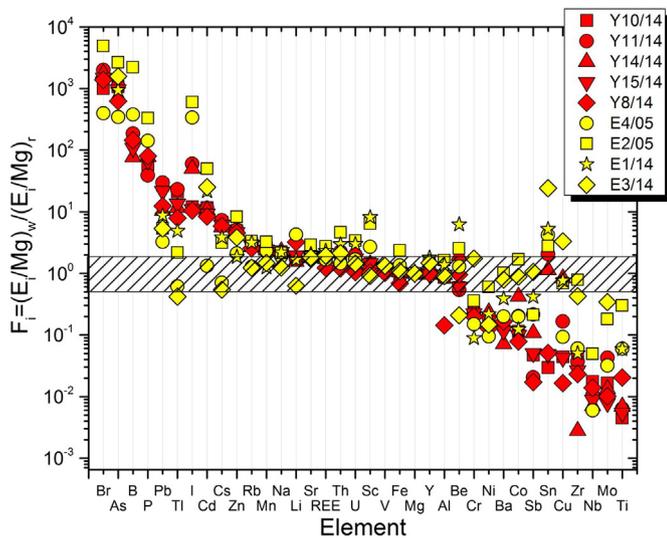
Fig. 11. Enrichment coefficients normalized to Mg for waters of Yurievskie springs and Ebeko pools. Elements within the hatched area ($logF_i$ ~0) were leached from rock by congruent dissolution. See text for discussion.

Fig. 13. Correlation between the total REE concentration and Al + Fe molar concentration in acidic waters of Yurievskie springs and Ebeko pools. Points for Ebeko pools with lower REE concentrations are from the 2005 samples, not shown in Table 4.

5.2.4. Solute geothermometry of Yurievskie springs

5.2.4.1. Saturation index approach.
The major cations in ultra-acidic waters of the Ebeko are present through congruent dissolution of the host rock, and thus, any cation geothermometers using Na, K, Mg and Ca are not applicable. On the other hand, water from Yurievskie springs, as many other ultra-acidic waters, are close to saturation with respect to amorphous silica (Fig. 14). Therefore, estimation of temperatures of precipitation of alumino-silicate secondary minerals using the saturation indices (SI) approach is not correct taking into account that as a rule

the most of the SI of alumino-silicate secondary minerals show temperatures of saturation close to that of quartz. Using the SOLVEQ code (Reed and Spycher, 1984) with the updated SOLTHERM thermodynamic data base we estimated temperature of saturation for non-silicate minerals, common for the advanced argillic alteration, including diaspore, gibbsite, alunite, anhydrite, celestine and barite. Results are shown in Fig. 15 for the hottest and most mineralized Y8 (Spring 1) water. The estimated SI-temperatures (at log SI = 0) for anhydrite, alunite and diaspore are between 130 °C and 200 °C. Other sulfates, celestine and barite, are undersaturated in the range of temperatures. Barite approaches the saturation level at the sampling temperature.

5.2.4.2. SO4–H2O oxygen isotope equilibrium and sulfur isotopic composition.
Kinetics of the isotopic exchange between oxygen in water and dissolved sulfate (bisulfate) depends on temperature and pH. It is fast (days-hours) in water with pH < 2 and very slow at neutral pH (Lloyd, 1968; Chiba and Sakai, 1985). Therefore, the isotopic equilibrium may be attained for acidic waters of Yurievskie springs with pH < 2 and the isotopic equilibrium temperature may be used to evaluate the aquifer temperatures. The hottest Spring 1 yields the isotopic equilibrium temperature of 188 °C, and other two springs 166 °C using Mizutani and Rafter (1969) (Table 5). The real temperature could be higher considering a possible re-equilibration in low pH water during its ascent to the surface and dilution with groundwater.
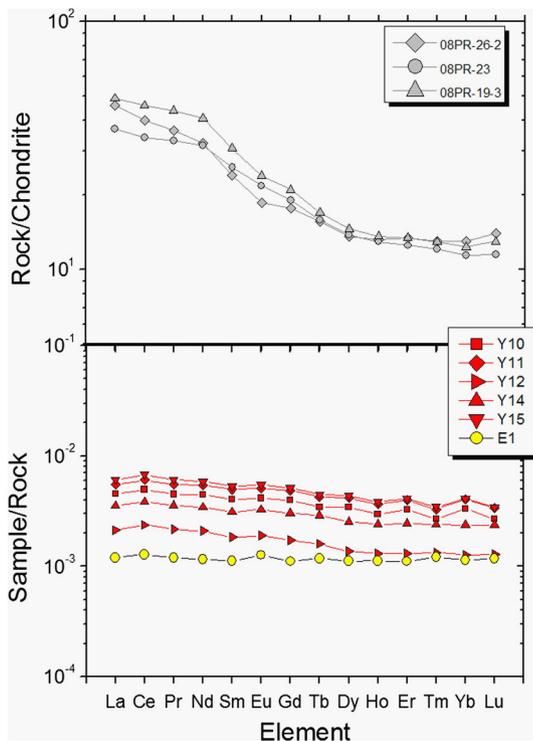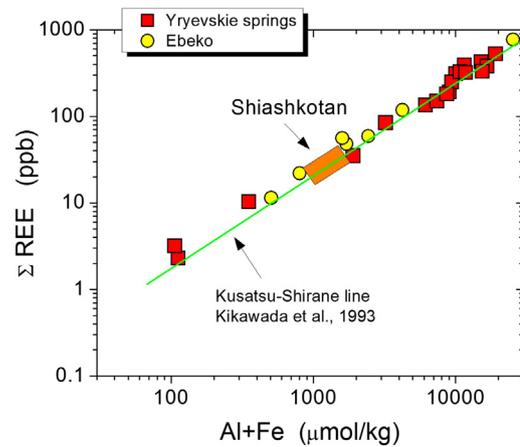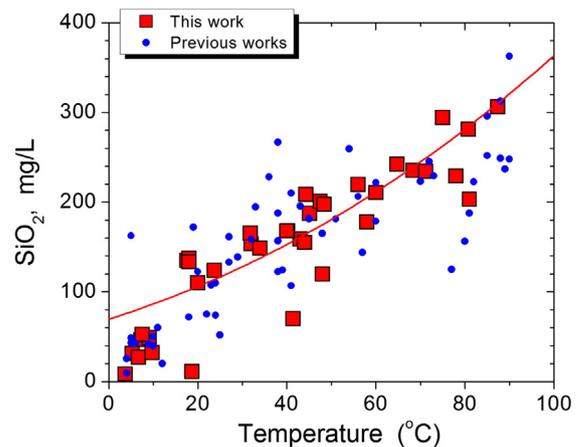

Fig. 12. REE abundance in unaltered Ebeko rocks reported by Martynov et al. (2010) normalized to chondrite (McDonough and Sun, 1995) and in Yurieva and Ebeko. All waters are normalized to the average Ebeko rock.

Fig. 14. Concentrations of dissolved Si expressed as SiO_2 in Yurievskie waters vs outflow temperature. All data plot close to the solubility of amorphous SiO_2 (log SiO_2 = 4.52–731/TK; Fournier, 1977).
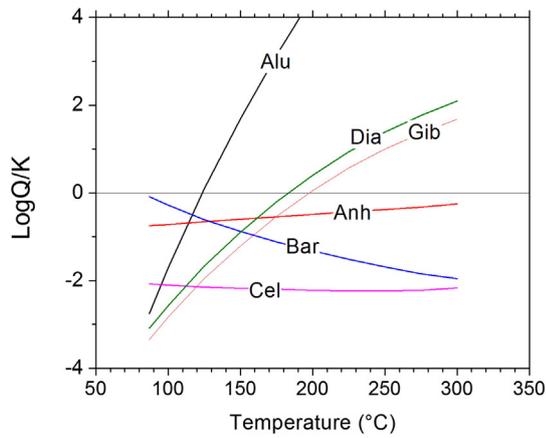
Fig. 15. Saturation indices (SI = log Q/K, where Q is measured and K is calculated solubility product) for non-silicate minerals for the Spring 1 water. Alu–Alunite; Anh–Anhydrite; Bar–Barite; Cel–Celestine; Dia–Diaspore; Gib–Gibbsite. Computed using SOLVEQ computer code (Reed and Spycher, 1984).

Isotopic composition of S in SO$_4$ is similar for all three springs and in the range of that in other ultra-acidic volcanic waters. Delmelle et al. (2000) reported values near +22‰ for the Kawah Ijen crater lake, whereas Rowe (1994) showed δ^{34}S value of +14 ‰ for an average of dissolved sulfate in Poas crater lake water. Sulfate in acidic volcanic waters can be produced by recombination of the volcanic SO$_2$ at condensation and mixing with groundwater:

$$4SO_2(aq) + 4H_2O = 3H_2SO_4 + H_2S(aq) \qquad (9)$$

or

$$3SO_2(aq) + 2H_2O = 2H_2SO_4 + S_o. \qquad (10)$$
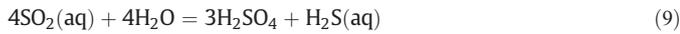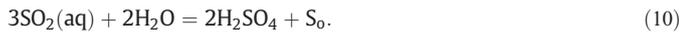
Assuming that these reactions are the main source of SO$_4$ in acidic volcanic waters, the molar ratio of (H$_2$S/SO$_2$), r$_s$, in the condensing vapor can be estimated suggesting isotopic equilibrium between all four sulfur species: SO$_4$, SO$_2$(aq), H$_2$S(aq) and S$_o$ and using isotopic balance (Taran et al.,1996: Kusakabe et al., 2000):

$$\delta^{34}S_{SO4} = \delta^{34}S_{tot} + \Delta_{SO4-H2S}r_s(1 + r_s)^{-1} + 1/3\Delta_{SO4-So}(1 + r_s)^{-1} \qquad (11)$$

where δ^{34}S$_{tot}$ is the isotopic composition of the total dissolved sulfur and ∆ are equilibrium isotope fractionation factor for the pairs of SO$_4$–H$_2$S and SO$_4$–S$_o$. If one aquifer feeds low-temperature fumaroles of Ebeko and Yurievskie hot springs, we can estimate the r$_s$ ratio for the resulting gas after magmatic gas condensation in this aquifer assuming the equilibrium temperature of 200 °C (a bit higher than the temperature of the SO$_4$–H$_2$O oxygen isotopic equilibrium) using ∆$_{SO4-H2S}$ = 31‰ and ∆$_{SO4-So}$ = 30‰ (Ohmoto and Rye, 1979). For arc magmatic gases the isotopic composition of the total sulfur usually close to +6‰ (e.g., De Hoog et al., 2001). The isotopic composition of dissolved sulfate in Yurieva waters is +18.8‰. With these values the solution of the Eq. (11) is r$_s$ = 0.2, or the concentration of H$_2$S is significantly lower than that of SO$_2$ in a gas at isotopic and chemical equilibrium

among main sulfur species at 200 °C. This is in agreement with the composition of the Ebeko fumaroles (Table 2) where H$_2$S/SO$_2$ as a rule is ≪1. Thus, the temperature of Yurievskie springs, both using the saturation indices approach and the oxygen isotope composition of SO$_4$and H$_2$O, is calculated in the range of 150–190 °C for the aquifer feeding the springs. It can be intermediate temperature, quenched at some level between the aquifer and discharge. If the same aquifer feeds low-temperature HCl-rich fumaroles of Ebeko, its temperature should be in the range 200–300 °C as it is shown above using gas equilibria (Fig. 5).

6. Gas and solute fluxes

Nekhoroshev (1960) first estimated the heat flux from the Ebeko fumaroles and reported a value of 28 MW of the fumarolic heat output based on the measured ≈11 kg/s of the output of steam emission (assuming enthalpy of 2500 kJ/kg of steam). Menyailov et al. (1988) have measured the fumarolic flux in 1979 and 1983 and reported two similar values of ≈24 kg/s of the steam output (≈60 MW). Our measurements in 2003 (see also Kotenko and Kotenko, 2006) yielded the steam output of ≈11 kg/s, which is the same as the value obtained by Nekhoroshev in 1960. Recalculation to weight percent gives an average composition of fumarolic steam for the most powerful vent of the SE field: 88.1 wt% H$_2$O, 9.6 wt% CO$_2$, 2.0 wt% total S (H$_2$S + SO$_2$) and 0.24 wt% HCl. Assuming that these values are representative for the total volcanic vapor output from Ebeko, daily fluxes are ≈840 t/d of H$_2$O, 95 t/d of CO$_2$, 19 t/d of SO$_2$ + H$_2$S and 2.2 t/d of HCl. Taking into account the uncertainty in the measured flow rates and scatters in the gas composition, the uncertainty in the estimate is probably not less than 100%. Selected data on fumarolic fluxes over time are shown in Table 6.

The 2005 measurements have been conducted after a series of phreatic explosion and the formation of a new short-lived "July Field" with fumarolic temperatures up to 460 °C with a high SO$_2$ and HCl content (Kotenko and Kotenko, 2006). The estimated fluxes in April, 2009 within the last phreatic cycle, based on the comparison method (areas of the fumarolic plumes on photo images) and the average composition of fumaroles of the SE field, were similar to those measured in 2005. Finally, the last 2012 measurements during a period of the steady-state passive degassing, gave estimations close to the data of Menyailov et al. (1988). Therefore, the main gas flux during this long passive degassing period is lower than 20 t/d for (SO$_2$ + H$_2$S) and 5 t/d for HCl, although this period includes short phreatic activity.

The Yurieva River collects all Yurievskie thermal waters and flows into the Sea of Okhotsk with a measured flow rate of 1.5 ± 0.3 m^3/sand contains 632 mg/L of chloride and 1715 mg/L of sulfate at the mouth of the river. The data provides the fluxes of the dissolved chloride and sulfate 82 t/d and 222 t/d, respectively. The amount of sulfate is equivalent to 148 t/d of the SO$_2$ flux. Comparing to the gas fluxes from Ebeko fumaroles (<5 t/d of HCl and <20 t/d of SO$_2$ + H$_2$S) the hydrothermal flux from thermal springs is much greater. The estimated hydrothermal flux (we believe that the uncertainty is not higher than 30%), is similar to the measured gas fluxes using remote techniques volcanic gas fluxes from many passively degassing volcanoes hosting high-temperature fumarolic fields

Table 5

Isotopic composition of oxygen in water and dissolved sulfate (‰ V-SMOW) and sulfur of the sulfate (‰ CD), pH and SO$_4$ concentration in three samples from Yurievskie springs (isotopic equilibrium temperatures are calculated using calibration by Mizutani and Rafter, 1969).

Sample	δ^{18}O-SO$_4$	δ^{18}O-H$_2$O	t°C-isot	δ^{34}S-SO$_4$	pH	SO$_4$ ppm
Y8	−0.06	−9.4	187	18.9	1.2	6861
Y11	−0.27	−10.5	166	18.4	1.3	6182
Y14	0.01	−10.8	166	18.3	1.5	4053

Table 6

Fumarolic output of H$_2$O, CO$_2$, SO$_2$ + H$_2$S and HCl (t/d) and heat output (MW) from Ebeko fumarolic fields. nd—not determined.

Year	1960[a]	1983[b]	2003[c]	2005[c]	2009[c]	2012[c]
H$_2$O	864	1804	840	7593	6767	1864
CO$_2$	nd	79	95	448	219	185
SO$_2$ + H$_2$S	nd	13.3	19	933	71	19
HCl	nd	3.8	2.2	418	13	5

[a] Nekhoroshev (1960).
[b] Menyailov et al. (1988).
[c] Kotenko et al. (2012) and this work.

(Vulcano, Kudryavy, Mutnovsky, etc., see Taran, 2009, and references therein). Even greater fluxes from Yurievske springs have been reported by Zelenov in 1957 (Zelenov, 1972) and Shilov in 1960 (cited by Markhinin and Stratula, 1977). At those times the vent temperature of Spring 1 was near boiling. During the period from 1984 to 2014 the Spring 1 temperature varied between 78 and 87 °C and the flux of Cl ranged from 62 to 98 t/d for chlorine. These fluxes (Cl and SO_4) from Ebeko-Yurieva are much greater than those from other hydrothermal systems of the Kamchatka-Kuril subduction zone (Taran, 2009). The fluxes are even much greater than that from other acidic volcano–hydrothermal systems in the world (Table 7) and comparable with those of giant meteoric-hydrothermal system at Yellowstone and Domuyo (Hurwitz et al., 2007, 2010; Chiodini et al., 2014).

7. Conceptual model of the Ebeko-Yurievskie volcano–hydrothermal system

High HCl concentrations in low-temperature fumaroles and low relative concentrations of H_2 and CO in volcanic gases are attributed for the presence of a boiling aquifer beneath the summit area of Ebeko. This aqueous solution should be highly saline and hyper-acidic. Gas and solute equilibria suggest that the aquifer temperature is probably not less than 200 °C (~ 250 °C from the fumarolic gas geothermometry and ≤200 °C from solute and isotope geothermometry of Yurievskie waters). The curve of boiling-points at various depths by Ellis and Mahon (1977) shows that water at 250 °C boils at ~ 300 m. This aquifer appears to be in "steady-state" balanced by the in-flux of magmatic fluid from depth and meteoric water from the surface and an outflow as fumarolic vapors and drainage to Yurievskie springs. The system is similar to other areas where acidic water represents crater lakes and associated shallow aquifers. Examples include those at Poas, Copahue, Kawah Ijen (Rowe et al., 1992; Varekamp et al., 2001; Delmelle et al., 2000). In the case of Ebeko, the acidic water is concealed at a considerable depth. Temperature of fumaroles of Ebeko is controlled by the two-phase steam-water mixture above the aquifer. The temperature is higher than the boiling point of pure water at the elevation of the fumarolic field due to high concentration of solutes. The mechanism causing phreatic eruptions at Ebeko is probably similar to that at Poas volcano where hot gases suddenly ascend through ruptured seals (Fischer et al., 2015; Rouwet and Morrissey, 2015). When the pressure of hot gases drops and the fractures are filled again by the two-phase boiling fluid, temperature of fumaroles re-establish at the stationary level.

Assuming that one aquifer feeds Cl and sulfur to fumaroles, an equivalent amount of CO_2 for the Cl flux from Yurievskie springs should come out through the volcano edifice. With the CO_2/S weight ratio in Ebeko

fumaroles close to 6 the diffusive and advective flux of CO_2 through the edifice should be 600–800 t/d.

8. Conclusions

Ultra-acidic volcano–hydrothermal system of the Ebeko volcanic massive discharges both fumarolic gases and hyper-acid waters near the summit of Ebeko volcano and ultra-acid hot waters of the Yurievskie springs on the western slope. The spring waters are drained by Yurieva River which flows to the Sea of Okhotsk.

Ebeko low-temperature fumaroles are enriched in HCl (up to 0.3 mol%) which is attributed to boiling of a hyper-acid brine at ~250–300 m depth below the summit at temperature of 250–300 °C. The existence of a two-phase, liquid-water aquifer is also supported by redox-equilibria in the H_2O–H_2–CO–CO_2–CH_4 system, temperature estimates based on saturation indices of Yurieva spring waters for some non-silicate minerals, and the oxygen isotope equilibrium temperatures of water and sulfate.

Major and trace element composition (including REE) of Ebeko-Yurievskie acidic waters is similar to compositions of other ultra-acidic volcanic waters (crater lakes) elsewhere in the world suggesting congruent dissolution of volcanic rocks. The ^{86}Sr/^{87}Sr values of 0.70315–0.70316 for dissolved Sr are similar to those for Ebeko andesites.

The fluxes of chlorine and sulfur (as SO_2) from the fumaroles in the summit area (<5 t/d and <20 t/d, respectively) are almost one order of magnitude lower than the fluxes from the Yurievskie springs along the Yurieva River. The total outputs from thermal fields of Ebeko volcano are among the highest ever measured in the world.

The Ebeko-Yurievskie volcano–hydrothermal system is similar to those for ultra-acidic crater lakes such as Poas and Copahue. Unlike crater lakes, the thermal manifestations at Ebeko-Yurievskie is fed by a shallow aquifer below the surface.

Table 7
Chloride and sulfur fluxes (t/d) from Ebeko-Yurieva and other volcano–hydrothermal systems.

Volcano–hydrothermal system, year	Chloride	Sulfur (as SO_2)	Reference
Yurieva, Ebeko volcano			
1957	222	448	Markhinin and Stratula (1977)
1960	264	443	-"-
1984	62	106	Fazlullin (1999)
1987	76	127	-"-
2013	98	120	Bortnikova et al. (2006)
2014	82	148	This work
Other volcano–hydrothermal systems			
Shiashkotan (Kurils), 2011	27	70	Kalacheva et al. (2015)
Poas, 1990	35	60	Rowe et al. (1992)
El Chichon, 2008	42	5	Taran and Peiffer (2009)
Copahue, 2001–2004	38	135	Varekamp et al. (2001)
Domuyo, 2010	160		Chiodini et al. (2014)
Yellowstone, 1986–2007	140	150	Fournier (1989), Hurwitz et al. (2007)

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