Proceedings World Geothermal Congress 2005
Antalya, Turkey, 24-29 April 2005

Hydrogeochemistry of Thermal Springs at Ebeco Volcano (Kuril Islands)

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Keywords: thermal springs, volcano Ebeco, REE patterns, geochemical model.

ABSTRACT

Five contrasting types of waters were distinguished at Ebeco volcano, Paramushir Island, northern Kuriles. All these waters have different mineralization, macro- and microcomponent compositions. Solutions at fumarolic fields have the largest part of magmatic component; crater lakes consist mainly of meteoric waters. The REE content in boiling pots and springs of the Yurieva River is one order higher than in crater lakes or cold streams. The difference between REE distribution (Eu-minimum in crater lakes and cold springs and no Eu-minimum in waters of hot springs) witnesses to significant portion of hypogene fluids in hot hydrothermal manifestations. Solid phases precipitated in and around boiling pots and hot springs are mainly silica group minerals, hydrous silicates and hydroxyl-silicates of aluminium. Significant amount of precipitates may form in cold crater lakes, and this process causes gradual decrease of water mineralization.

INTRODUCTION

Ebeco is an andesitic stratovolcano in the northern part of Paramushir Island, northern Kuriles (Fig.1). Its recent activity is characterized by weak vulcanian eruptions and a variety of permanent fumaroles and hot springs. The volcano attracts attention of volcanologists at least for fifty years on account of its hazard for the town of Severo-Kurilsk, especially after the eruption in 1987 (Melekescev et al., 1993). The geological position of the volcano and hydrogeochemistry of thermal springs was thoroughly researched during last four decades (Belousov et al., 2002; and others). Additionally, I.A Menyailov et al (1988, 1991, 1992) studied composition of fumarolic gases and thermal waters, including trace elements. Several models describing the internal structure and origin of gases and waters were developed.

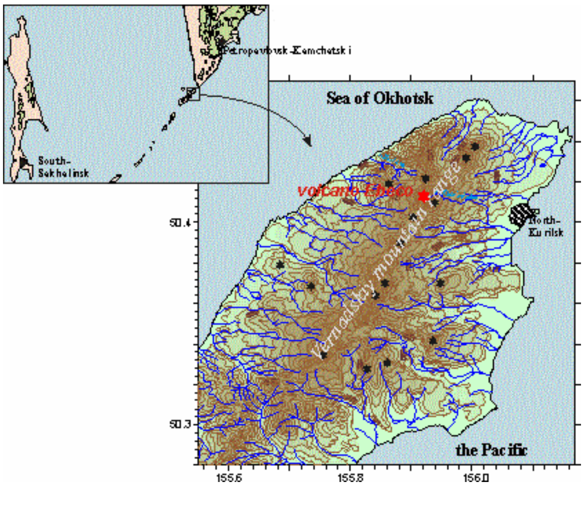

Figure 1. Location of the volcano Ebeco

Thermal springs of the Yurieva River, which is believed to be the most plentiful acid rivers all over the world, are among the most interesting hydrothermal manifestations of the volcano. Springs are located at the western foothill of Ebeco, 2 km along the stream of the river. No fumaroles are associated with the springs. The waters are Al-H-Cl-SO_4 type (S. M. Fazlullin, 1999; 2000).

Five fumarolic fields are situated in the crater zone of Ebeco: the Northeast fumarolic field (the largest one), the field on an outer slope of the northern crater, the field inside the southern crater and on an outer slope of the southern cone, and the field at the headwaters of the Lagerny springs. Main component of fumarolic gases at the all fields is water vapour. Nevertheless the hot springs are not associated with fumaroles everywhere: the thermal manifestations of the southern crater are presented only by gas discharges.

This article concerns geochemistry of thermal waters connected with the hydrothermal system of Ebeco. The study had following objectives: i) to reveal genetic constraints between elements; ii) to determine the hydrogeochemical features of the different water types; to estimate the depth of element origin; iv) to ascertain conditions of element precipitation at sites of water discharges and downstream.

SAMPLING AND ANALYTICAL METHODS

The detailed sampling was performed during 2001 and 2003 field seasons. Water samples were collected from almost all boiling pots and hot water (>90°C) discharges at the Northeast fumarolic field and from headwaters of the Yrieva river. Springs with low-to-moderate temperatures (from 7-15°C to 40-50°C) were also sampled to compare their compositions with that of hot springs. Also samples of incrustations around boiling pots and samples of bottom sediments from water discharges and streams were collected. During sampling procedure we paid special attention at precipitates formed obviously from supersaturated solutions. All samples of sediments or incrustations were dried up and packed in polyethylene bags.

Main ion composition of water samples was analyzed with standard methods: colorimetry (SiO_2); conventional emission spectroscopy (Mg^{2+}, Ca^{2+}); volume titration (Cl^-, SO_4^{2-}) (Na, K, Al, Fe). Analytical errors for main ions are not more than 5%. Trace elements were determined via ICP-AES technique with an average error of 10%.

XRF-SR method with external standards AGV-1, W-2, G-2 was used to analyze a wide spectrum of elements in bottom sediments and precipitates. The limit of detection for most elements was 0.1 ppm with an average error of 15%. Phase composition of sediments and precipitates was analyzed with conventional diffractometer.

The tendency of a mineral to precipitate from the solution or to dissolve in it was computed using the WATEQ4F code (Nordstrom & Ball, 1984).

RESULTS

The hydrochemical zonality of Ebeco thermal fields appears in a contrast changing of macro- and microcomponent compositions of hot and cold springs, boiling pots and streams. Ratios between main cations (Na, K, Mg, Ca, Al, Fe) reflect the probable origin of thermal waters, and intensity of leaching during their ascent. On the basis of composition we distinguish five groups of waters (Table 1).

Table 1. Main parameters of thermal springs

	T, °C	pH	Type	M, g/l	Number
Yrieva river	85-95	1.1	Al-Ca /SO_4-Cl	12.7	8
NE field	95	1.0	Al-Fe/ SO_4-Cl	8	8
South field	88-90	1.3	Al-Ca/ Cl-SO_4	6.7	2
Kuzminka river	50-85	2.5	Ca-Mg/ SO_4-Cl	1.3	5
Crater lakes	5-10	3.5	Ca-Al/ SO_4-Cl	0.12	7

Cl^-/SO_4^{2-} ratio in studied samples varies within wide range while concentrations of other anions are rather small. There is almost a linear dependence between concentrations of Cl^- and SO_4^{2-} in water from crater lakes and from the thermal field at the headwaters of the Kusminka River. Large variations of chloride on the background of stable sulphate concentrations were determined in all boiling pots and from thermal springs of the Yrieva River. We suggest that anions in hot springs and boiling pots are added to surface waters from fluids of deep origin.

Li, Ba, Rb, Sr, P, V, Zn, Cu are established in most samples with moderate variances. Concentrations of Be, Cr, Co, Ni, As vary from the limit of detection till "hurricane" values in some samples. In general, water of springs at headwaters of the Yrieva River has the highest mineralization. However, Mn, Cu, Ti, Cr, V are more abundant in boiling pots of Ebeco. Correlation analysis has revealed dependences between some of elements caused by different temperature and acidity of solutions as well as different geochemical behavior of elements. Fe, Al, Sr, Ti, V, SO_4^{2-} and PO_4^{2-} are well-correlated with pH and between each other (Table 2). These elements form the first typomorphic association (Fig. 2, the left figure). Close dependences of the listed cations with pH and SO_4^{2-} as well as mafic character suggest their predominantly deep origin.

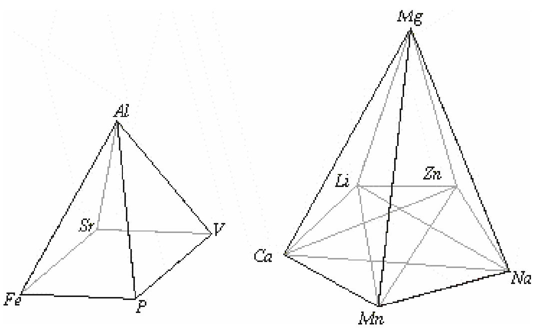

Figure 2: Typomophic associations of elements in solutions

The second typomorphic association (also with high intercorrelations) includes elements easy leaching from wallrocks: Ca, Mg, Na, Li, Mn, Zn (Fig. 2, the right figure). Potassium has moderate-to-high correlations with elements of the first and the second typomorphic associations and may be derived both from deep fluids and subsurface wallrocks.

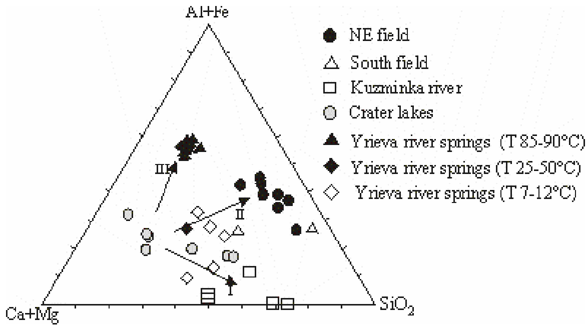

Figure 3. Ratio of main cations in solutions

On the basis of correlation analysis we suggest that ratios between the following components Ca+Mg, Al+Fe and SiO_2 can show proportion of deep and meteoric water in thermal solutions. Water in crater lakes of Ebeco and in cold springs of the Yrieva river are mainly of meteoric origin with minimal portion of deep constituent: all composition points form a compact field on the ternary plot (Fig. 3); some high SiO_2 content in water of crater lake cam be easily explained by more intensive water-rock interaction in the vicinity of Active crater of Ebeco. Composition of crater lakes may be considered as initial one with three trends of further transformation. The first trend reflects small addition of deep fluid and intense interaction with ambient wallrocks. Hot springs and pots at the headwaters of the Lagerny Springs are formed just in such a way. The second trend from crater lakes to pots at northeast fumarolic field shows a greater portion of deep fluid, low pH and high discharge temperatures. Solutions in pots of NE field arise from strata of metasomatically changed rocks of alunite-argillization phase with entirely substituted mafic minerals. The third trend leads from crater lakes to thermal springs of the Yrieva river is determined by the highest deep fluid content; points of their compositions are situated close to each other that suggests weak leaching from wallrocks during water ascent due to the low content of leachable components in deeply metasomatized rocks. Evolution of water composition shown at the ternary plot may be expressed in a different way (dash thick line): from thermal springs of the Yrieva river solution, along a decrease of deep fluid portion, solutions are transformed in pots of NE field, then in the headwaters of the Kislaya Kusminka river, the least portion of deep components show compositions of crater lakes and cold springs. High content of such typically mafic elements as Cr, Ti, V, Co, Ni in solutions of pots comparatively with that in water of crater lakes and the headwaters of the Kislaya Kusminka River confirms these suggestions.

Table 2. Composition of spring solutions

	North-East fumarolic field, n=8				Kuzminka River, n = 5				South fumarolic field	
	mean	min	max	deviation.	mean	min	max	deviation	E-15	E-16
					mg/L					
pH	1.01	0.39	1.47	0.35	2.56	1.85	3.04	0.63	1.32	0.51
Cl	2300	10.6	9510	3840	95.8	10.6	259	140	1500	5540
SO42-	4840	2500	9310	2315	520	235	749	260	1410	3600
SiO2	340	240	410	65.0	330	229	437	85.9	350	360
Ca	54.5	37.7	75.3	13.7	144	95.2	184	34.1	145	20
Mg	29.6	13.4	50.0	14.4	64.0	37.2	82.7	16.5	70.1	9.03
Na	33.0	17.4	50.7	10.4	55.9	47.1	67.7	7.5	70	19
K	34.2	15.0	55.0	13.5	25.1	13.35	46.8	13.2	27.1	33.2
Al	180	94.4	281	53.7	12.5	0.41	43.3	17.9	130	97
Fe	88.0	56.8	165	34.7	8.66	0.005	32.2	13.6	66	45
Mn	1.83	0.80	3.20	0.82	3.05	1.45	4.13	1.1	4.1	0.57
P	1.70	0.80	2.77	0.73	0.072	lld	0.28	0.12	0.6	1.5
Ba	0.055	0.0052	0.13	0.039	0.0067	0.0037	0.0093	0.0025	0.085	0.013
Li	0.009	0.001	0.02	0.0057	0.015	0.0071	0.024	0.0068	0.034	0.005
Sr	1.12	0.32	1.56	0.39	0.027	lld	0.058	0.021	0.5	0.45
Rb	0.35	н.о.	0.59	0.23	0.39	0.20	0.61	0.15	0.51	0.31
Zn	0.037	н.о.	0.12	0.039	0.045	lld	0.10	0.041	0.13	0.012
Cu	0.047	н.о.	0.17	0.057	0.0048	lld	0.018	0.0073	0.0011	0.04
Ti	0.25	н.о.	0.89	0.29		0.0081	0.072		0.073	0.36
V	0.55	0.27	1.06	0.23	0.076	lld	0.17	0.082	0.3	0.23
Be	lld				0.0006	lld	0.0014	0.0005	0.002	0.0004
Zr	0.014	н.о.	0.09	0.029	lld				0.0015	0.012
Co	0.0073	н.о.	0.02	0.0097	0.001	lld	0.0038	0.002	0.01	0.022
Cr	0.64	н.о.	3.57	1.3	lld				lld	lld
Ni	0.32	н.о.	2.0	0.70	lld				lld	lld
					mkg/L					
Pb	14.0	1.8	55.2	23.1	lld				lld	lld
As	2.35	0.01	10.1	4.36	lld				lld	lld
Sb	0.52	0.001	2	0.86	lld				lld	lld
Cs	0.76	0.005	2	1.03	lld				no data	no data
U	2.15	0.008	6.52	3.02	no data				no data	no data
Th	6.5	0.006	25.8	11.2	no data				no data	no data
Tl	0.59	0.032	2.15	0.89	no data				no data	no data
Y	18.5	0.4	68	29.2	no data				no data	no data
Ga	57.8	0.014	200	95.9	no data				no data	no data
Ge	0.58	0.008	2.13	0.92	no data				no data	no data

Note: lld – lower limit detection

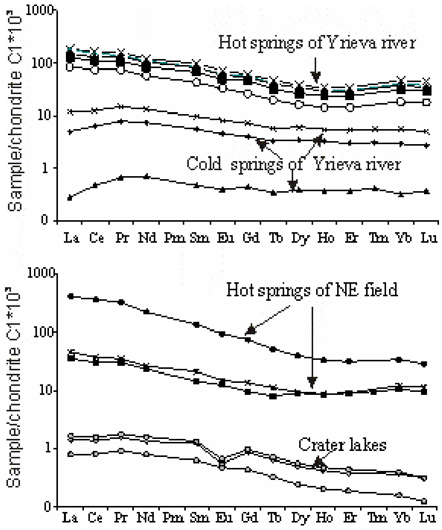

Figure 4. REE patterns in solutions

Distribution of REE in geothermal water discharges of Ebeco is worthy of separate discussion (Fig 4). REE distribution in hot and cold waters have similar slope of patterns both for light and heavy rare elements, but the total REE content in pots of Ebeco and thermal springs of the Yurieva River is one order higher than in crater lakes or cold streams. The obvious reason is high temperature and low pH of water. The only difference is an absence of Eu-minimum in hydrothermal solutions. This may be accounted for the reduction conditions in deep fluids where Eu^{2+} remains stable but it is easily removed from oxidized water in cold lakes.

According to thermochemical modelling, a variety of macrocomponent compounds reach their saturations in hot hydrothermal waters of Ebeco. They are: amorphous silica, iron oxides and hydroxides, aluminium hydroxides, allophane and pyrophyllite (Fig. 5). Some sulphates also have concentrations close to saturation. A list of compounds that may form suspension in cold water of crater lakes is more extensive. Besides Si, Al, Fe phases it contain also Mn carbonate - rhodochrosite. As the temperature of water decreases and pH increases, solid phases are abundantly precipitates, forming crusts and outgrowths along streams from boiling pots at NE fumarolic field. Such crusts consist mainly of hydrous sulphates (halotrichite $FeAl_2(SO_4)_2{\cdot}22H_2O$, tamarugite $NaAl(SO_4)_2{\cdot}6H_2O$, gypsum $CaSO_4{\cdot}2H_2O$, jarosite $KAl_3[(OH)_6(SO_4)_2]$, meta-alunogen $Al_2(SO_4)_3{\cdot}13,5H_2O$) and less of hydrous silicates (revdite - $Na_2(Si_2O_5){\cdot}5H_2O$) and phosphates (sampleite - $NaCaCu_5(PO_4)_4Cl{\cdot}5H_2O$). Tamarugite forms isometric flattened white crystals, which are in close association with acicular crystals of halotrichite (Fig. 6a, 6b). Sampleite also found here as rounded greenish crystals. Revdite forms isolated acicular aggregates (Fig. 6c) or occurs together with tamarugite and halotrichite (Fig. 6d, 6e). Gypsum forms typical dovetail crystals. Copiapite $Fe^{2+}Fe^{3+}{}_4(SO_4)_6(OH)_2{\cdot}20H_2O$ occurs as aggregates of splintered crystals. Natural mineral association is similar to the calculated one.

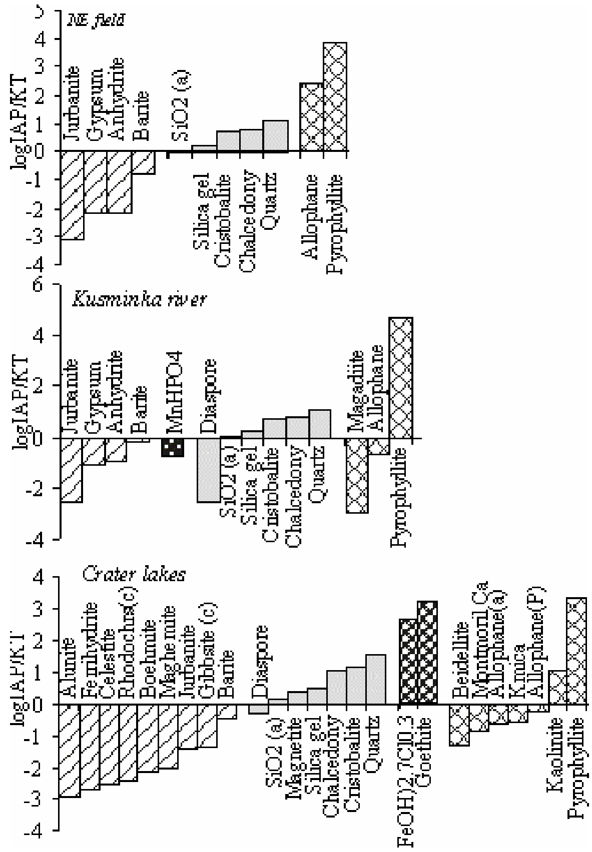

Figure 5: IAP/KT in solutions in relation to possible solid phases.

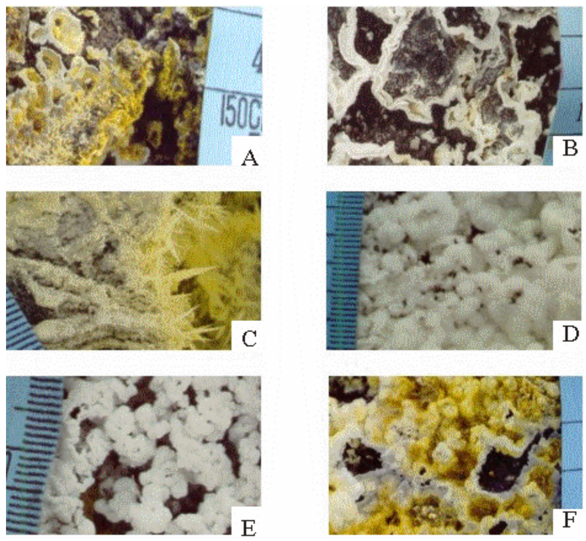

Figure 6: . Photo of minerals formed onto surfaces of fumarolic fields.

CONCLUSION

1. Five contrast types of waters were distinguished. Each type is associated with one group of hot springs or fumarolic field: Yrieva river springs, NE field, south field, crater lakes, Kusminka River field. All these waters have different mineralization, macro- and microcomponent compositions.
2. Correlation analysis marked out three typomorphic associations of elements. The relative portion of the each association shows proportions of meteoric and hypogene water in solutions of hot springs.

Solutions at fumarolic fields have the largest part of magmatic component; crater lakes consist mainly of meteoric waters. The composition of springs at Kusminka River field derived from intensive water-rock interaction.

3. The REE content in boiling pots of Ebeco and thermal springs of the Yurieva River is one order higher than in crater lakes or cold streams. The difference between REE distribution (an evident Eu-minimum in crater lakes and cold springs and no Eu-minimum in waters of hot springs) witnesses to significant portion of hypogene fluids in hot hydrothermal manifestations. This is in accordance with cations and anions trends of these waters.
4. Solid phases precipitated in and around boiling pots and hot springs are mainly silica group minerals, hydrous silicates and hydroxyl-silicates of aluminium. Significant amount of precipitates may form in cold crater lakes, and this process causes gradual decrease of water mineralization.

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