

## Trace Elements in Native Sulfur as Indicator of Substance Sources in Fumaroles of Active Volcanic Regions (Ebeco Volcano, Paramushir Island)

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### ABSTRACT

Information about trace elements in native sulfur is hardly accessible in scientific literature because of complexity of sulfur preparation analysis. Few available data are relied on semiquantitative spectral analyses. At the same time, composition of native sulfur on volcanoes is an important indicator of volatile transport of elements and can serve as a basis for modeling of volcanic system.

Ebeco is an active andesitic volcano located in the northern part of Paramushir Island, Northern Kuriles. Its activity comprises rare vulcanian eruptions as well as a plenty of permanent fumaroles and thermal springs. During the 2002-2003 field works, a representative collection of native sulfur was picked up from Ebeco fumaroles located at Northwest and South fumarolic fields and on the slope of the Northern crater.

To estimate concentrations of elements a method of "external standard sample" was used. Due to the fact that no certified standards exist for native sulfur, we used our own standard made from superpure native sulfur specification 6-09-2546-77 with added mixture of chemical elements KS-1. The standard was prepared by addition to sulfur of 2.5% HCl solution with set of elements (As, Sb, Se, Te, Cd, Zn, Cu etc) in specified concentrations (1 – 10%). KS-1 was added to sulfur in specified amounts, then standard was dried at 85°C in air until constant weight. After drying standard was ground to 200 mesh and 30 mg pellets 6 mm diameter were made.

With Synchrotron XRF method and standards described above, a wide spectrum of elements was detected in native sulfur. All these elements according to correlation analysis can be divided into two groups. The first group comprises elements that are transported by volcanic gas as aerosol particles: K, Ca, Fe, Ga, Ge, Y, Zr, Nb, Th, U, Cu, Zn. The second group includes volatile elements transported from depth of magmatic system. Obtained results together with available published data allow us to develop a physico-chemical transport model of elements in volcanic gases released from magmatic body.

### 1. INTRODUCTION

Information about trace elements in native sulphur is very limited in scientific literature due to complexities of chemical decomposition and analysis of sulphur. Few existing data about geochemical composition of sulphur are based on spectral semi-quantitative analyses. As, Se, Te were determined by A.S. Uklonsky (1940) in a volcanic sulphur from Japan; only Al, Si, Mg, traces of Fe and B were discovered in sulphur from Ebeco volcano (Surnina, 1961). Sulfur from exogenous deposits contains a wide

spectrum of elements (Yushkin, 1968), but all of them are oxides of silicates group and are obviously contained in sulfur in forms of minerals and rocks particles. At the same time composition of native sulphur is an important indicator of elements source in a gas phase and it can serve as a basis for model construction of a volcanic system functioning. Native sulphur is rarely chemically pure even in the well-formed crystals. It usually contains structural and non structural impurity whose amount makes up tenths of percent to several percent (Yushkin, 1968). G.M.Vlasov (1971) referring to A.P. Zajtseva showed results of detection of trace elements in sulphur from the Medvezhia (Bear's) deposit (Iturup Island) using spectral analysis. Rock-forming elements are the most abundant impurity and are present in the sulphur, probably, in the forms of microinclusions of minerals containing: Si, Al, Mg, Ca, Ga, Fe, Ti, Na, Mn, Cu, Zr are evaluated in significant quantities. V, Pb, Ag, Bi, As, Zn, Ba, Be, F were present in the some samples. Goff et al. (2000) showed results of analysis of sulphur from Mina Azufral and Alcedo. Sulfur samples from Sierra Negra tend to be relatively high in As, Hg, Se, Te, and Sb, and contain detectable amounts of Ag. Two samples of sulphur from Alcedo fumaroles are chemically distinct from Mina Azufral sulfur because these have relatively low concentration of all analyzed metals. The differences in content of metal in the sulfurs between the two areas allow authors to suggest that gases at Sierra Negra originate from degassing magma, whereas gases at Alcedo originate from boiling of hydrothermal fluids (Goff et al., 2000).

The main objectives of the present study were:

(1) to constitute and to adjust of analysis methodology for estimation content of trace elements in native sulphur; (2) to evaluate mechanisms of transport and deposition of trace elements in different types of gas-hydrothermal discharge of volcanic activity: efflorescents onto thermal sites, boiling pots, activity of fumaroles.

### 2. SUBJECT OF THE STUDY

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, 1992) studied composition of fumarolic gases and thermal waters, including trace elements. A gas medium in which the fumaroles are unloaded on Ebeco volcano consists mainly of the following components: H<sub>2</sub>O (has a higher

concentration) CO<sub>2</sub>, SO<sub>3</sub>, HCl, H<sub>2</sub>S, N<sub>2</sub>, Ar, HF, H<sub>2</sub>, CH<sub>4</sub>, CO. Regardless of temperature of fumaroles and activity of the volcano gases of Ebeco volcano are mainly enriched with volatile and chalcophile elements (Hg, Cs, Sb, Cd, Zn, Pb, Cu). Several models describing the internal structure and origin of gases and waters were developed.

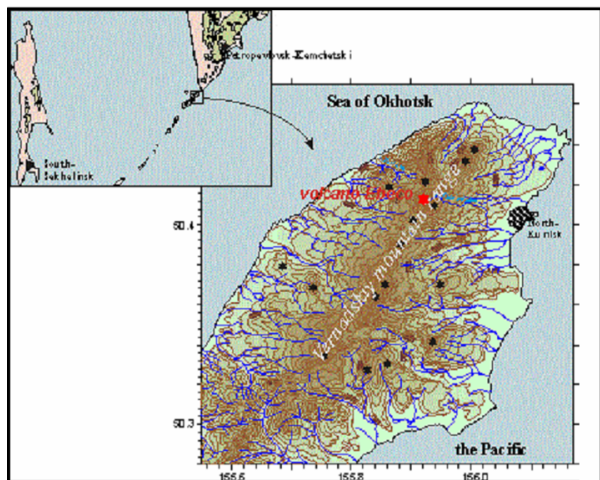


Figure 1: Location of the Ebeco volcano.

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.

There were described in details previously thermal waters discharged in fumarolic fields of Ebeco volcano as a springs, streams and boiling pots (Bortnikova et al., 2005). The solutions are acid and ultra-acid (minimal pH value = 0.36). The high concentration of numerous chemical elements (Table 1) shows primarily the significant hydrothermal alteration of the host rocks and a wide range of rock-forming and trace elements leaching, and, secondly, of a huge magmatic gases percentage in some boiling pots and springs.

Table 1. Maximal concentration of major and trace elements in thermal solutions discharging at the Ebeco's fumarolic fields, mg/l.

Element	Concentration	Element	Concentration
Cl <sup>-</sup>	9500	Ba	0.13
SO <sub>4</sub> <sup>2-</sup>	9310	Li	0.034
PO <sub>4</sub> <sup>2-</sup>	8.7	Cr	3.6
Mg <sup>2+</sup>	83	Ti	0.89
Ca <sup>2+</sup>	180	V	1.1
Na <sup>+</sup>	70	Zn	0.13
K <sup>+</sup>	55	Cu	0.17
SiO <sub>2</sub>	420	Co	0.025
Al	280	Ni	2.0
Fe	170	Mo	0.0026
Mn	4.1	As	0.039
Sr	1.6	Se	0.0046
Rb	0.61	Be	0.0022
Zr	0.086	Sn	0.01

3. METHODS

While field works of 2001-2003 the representative collection of native sulfur from volcano Ebeco fumaroles located on different thermal fields was gathered: North-East, South and North (Fig. 2).

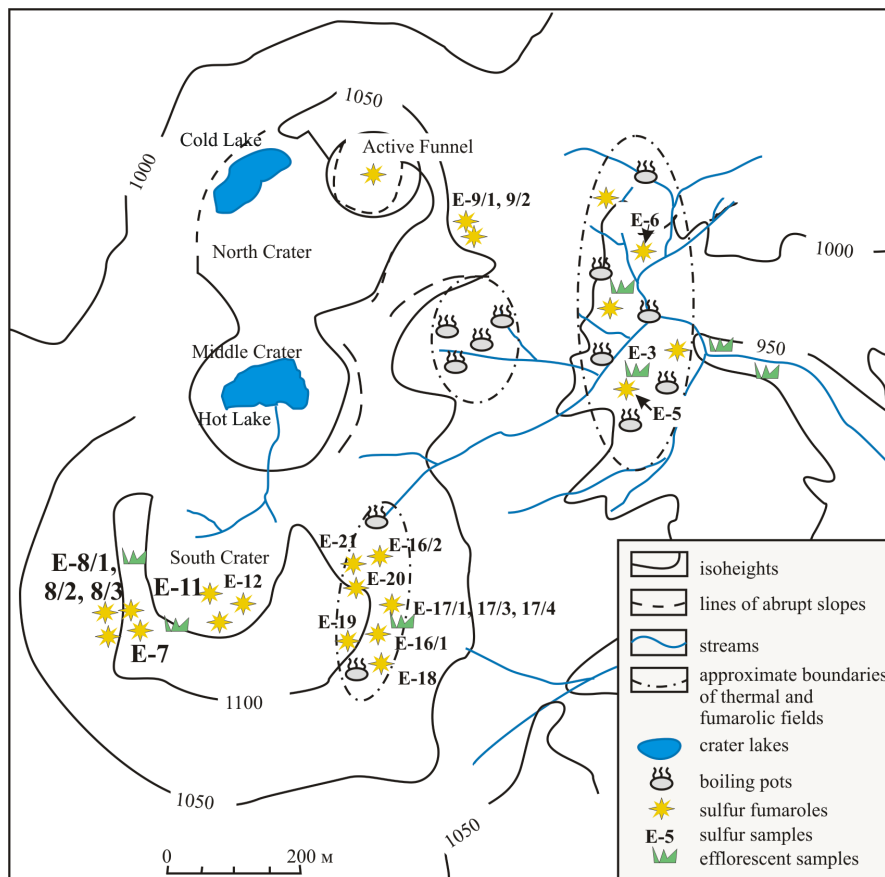


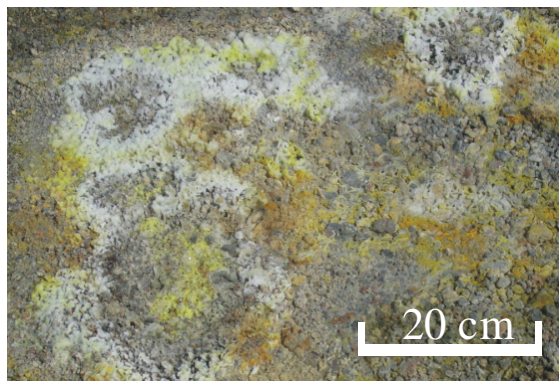
Figure 2: Sampling scheme of fumarolic fields at Ebeco volcano.

Fumarolic structures are constructed from native sulfur of different colors from dirty-grey to pink. Fumaroles reach up to 2 m of height. The main samples are of bright-yellow color. Samples were collected from inner parts of the structures by Teflon sampler and stored in plastic boxes.



**Figure 3: Sulfur fumaroles at Ebeco volcano.**

There were collected samples of efflorescences – modern minerals occurred onto the thermal sites. They look like a crusts and crystals of different colors – white, yellow, green and orange (Fig. 4). They formed onto warm and hot-wet surfaces while gradual evaporation of water-steam separating. The efflorescences were sampled by woody spatule and stored in plastic boxes.



**Figure 4: The efflorescences onto thermal surface at the fumarolic fields.**

Sediments from boiling pots and thermal springs have been sampled in detail. These also composed of various materials: in some springs sediments consists of whitish or grey material (mainly sulfates) alternated with remnants of andesites, in others springs red crusts are formed. They consist of Fe-oxides and hydroxides precipitated from thermal solutions. The collected sediments were dried up on site and stored in plastic boxes.

The samples of the host rocks have been collected from contemporary lava flows (fresh andesites) and hydrothermally-altered parts of fumarolic fields. That was done for comparison of geochemical composition of the rocks with modern neogenic minerals.

Samples of native sulfur, efflorescences and sediments were studied with synchrotron radiation X-ray fluorescent (SRXRF) analysis. The method of “external standard sample” was used to estimate concentrations of elements. Due to the fact that no certified standards exist for native sulfur, our standard was made from superpure native sulfur

specification 6-09-2546-77 with added mixture of chemical elements KS-1. This one was prepared by addition of 2.5% HCl solution with set of elements (As, Sb, Se, Te, Cd, Zn, Cu etc) in specified concentrations from 10 to 100 mg/g into the sulfur. KS-1 was added to native sulphur in specified amounts, then it was dried at 85°C in air environment until constant weight was reached. After drying the standard was ground to 200 mesh and 30 mg pellets 6 mm in diameter were made for synchrotron radiation X-ray fluorescent (SR-XRF) analysis.

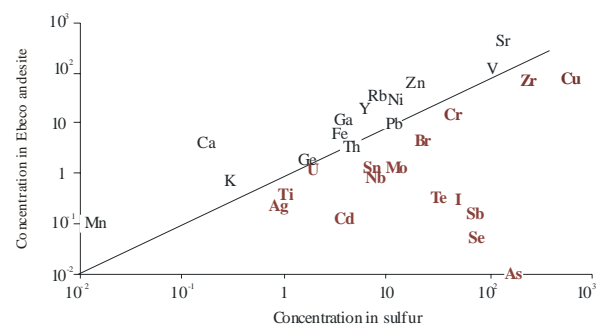
Determination of mineral composition had been done with the help of (using, by employing) X-Ray structural method by diffractometer DRON-4 (CuK $\alpha$  radiation).

Chemical analysis data of the samples were processed using Statistica 6.0 software with such multi-dimensional methods of cluster analysis as the method of Ward (1963) and K-method. The Ward’s method allows to effectively create small size clusters via minimization the sum of squares of any two hypothetical clusters which can be generated during each step, and consecutive estimation of distances among them.

To explain the mechanisms of solution formation it was made an attempt to describe a fluid evolution and the resulting mixing waters by physical and mathematical modeling. A model illustrates fluid migration from magma chamber to the surface. Modeling was conducted with the method of V. Sharapov (2005) using a Selector Win program in continuous reactor modification (Karpov et al., 1995). We considered nonisothermal flow of fluid through a vertical fissured channel from the intrusion base to the surface.

## RESULTS

For the first time a wide spectrum of elements in native sulphur was determined (Table 2). Concentration comparison of elements in sulfur and andesites from volcanic mounting allows to divide them on 2 groups: 1) elements with significant elevation in sulfur then in andesites (Fig. 5); 2) elements with significant elevation in andesites then in sulfur. The first group is composed of elements having properties similar to sulphur (As, Sb, Se, Te), volatile elements (Br, I, Hg) and metals (Ag, Cu, Cr, Sn, Mo). Fluctuations in their content are considerable (tens and hundreds times), however their maximum quantities confined to sulphur from Southern field which is one of the fumaroles fields (see Fig. 2).



**Figure 5: Maximal element concentrations in native sulfur versus their concentrations in andesite at Ebeco volcano, ppm; K, Ca, Fe, Mn, Ti – in %.**

**Table 2. Concentration of main and trace rock-forming elements in samples of native sulfur of the Ebeco volcano, ppm.**

	K	Ca	Ti	Mn	Fe	Ga	Ge	Y	Zr	Sr	Rb	Nb	Th	U	Ni
E-3	0.29	0.080	0.27	0.005	0.21	2.9	0.85	3.4	78	130	7.4	2.2	2.1	1.8	2.3
E-6	0.23	0.078	0.26	0.008	0.32	3.8	1.0	2.2	100	19	3.4	2.5	1.6	0.97	4.3
E-5	0.18	0.035	0.058	0.001	0.044	2.1	0.054	0.58	15	3.0	1.6	0.60	1.5	0.89	1.7
E-9/1	0.20	0.041	ld	ld	0.011	3.0	0.92	0.19	0.65	1.5	1.3	0.15	1.3	1.2	4.3
E-9/2	0.18	0.073	ld	0.003	0.09	2.7	ld	1.1	3.8	5.7	2.7	0.24	1.3	1.3	5.5
E-11	0.13	0.047	0.038	0.002	0.34	2.1	0.16	0.43	14	1.3	1.1	0.72	1.3	0.97	5.8
E-12	0.26	0.17	0.039	0.011	0.57	2.2	1.1	3.8	36	21	8.5	0.80	1.3	0.88	6.6
E-16/1	0.18	0.054	ld	ld	0.014	2.2	1.3	ld	0.25	0.83	1.3	0.10	1.3	0.92	2.8
E-16/2	0.22	0.04	ld	ld	0.004	1.8	0.11	ld	ld	0.77	0.9	0.13	1.2	0.88	2.4
E-17/1	0.20	0.057	ld	ld	0.011	1.9	0.25	0.16	1.1	1.1	1.4	0.13	1.2	1.1	5.6
E-17/3	0.21	0.037	ld	ld	0.007	2.1	0.63	0.25	0.21	0.80	1.1	0.16	1.2	1.2	4.9
E-17/4	0.2	0.047	ld	0.002	0.058	1.8	0.71	0.55	4.0	5.0	2.1	0.21	1.2	1.1	1.3
E-18	0.16	0.028	ld	0.001	0.012	1.9	0.37	0.24	0.34	0.86	0.95	0.21	1.3	1.2	4.3
E-19	0.18	0.033	ld	ld	0.004	2.0	0.72	ld	ld	0.82	1.0	0.16	1.3	1.2	1.9
E-20	0.20	0.067	ld	0.003	0.50	2.3	0.66	0.47	5.9	1.3	1.4	0.17	1.4	0.77	6.6
E-21	0.18	0.050	ld	ld	0.10	1.8	0.62	0.27	10	0.30	1.1	0.32	1.3	0.95	3.4
E-7	0.18	0.036	0.16	0.005	0.55	2.7	0.44	0.76	47	7.3	2.2	2.8	1.3	0.89	4.4
E-8/1	0.20	0.046	0.067	0.001	0.08	1.5	0.86	0.49	19	4.9	2.2	0.69	2.0	1.0	2.9
E-8/2	0.21	0.069	0.18	0.004	0.76	2.7	0.31	1.7	50	18	5.0	3.1	1.2	1.2	6.9
E-8/3	0.17	0.078	1.0	0.006	3.4	1.3	1.8	6.1	240	8.7	4.7	7.8	4.6	0.76	13

Note: hereinafter K, Ca, Ti, Mn, Fe – in %

**Table 3. Concentration of trace elements in native sulfur, ppm.**

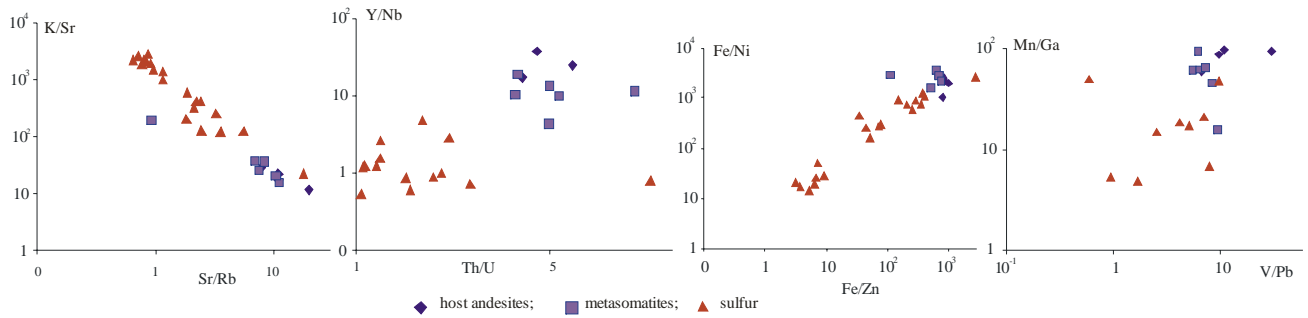
Samples	Cu	Zn	Ag	Cd	Pb	Cr	V	Mo	Sn	As	Se	Sb	Te	Br	I	Hg
E-3	46	14	0.079	0.065	5.6	ld	28	1.7	1.6	3.2	1.4	2.1	0.84	ld	2.3	0.16
E-6	68	15	ld	0.15	4.5	42	31	7.6	1.6	2.0	2.8	0.71	0.7	1	2	ld
E-5	9.3	9.7	0.18	0.082	2.4	ld	4	0.55	0.28	0.67	2.1	1.9	0.8	3.5	1.9	0.16
E-9/1	11	16	0.35	0.22	3.2	ld	ld	0.12	0.1	3.0	13	0.45	1.2	0.5	2.5	0.3
E-9/2	11	17	0.16	0.14	3.3	7	ld	ld	0.13	1.1	7.1	0.16	0.78	0.94	2	0.7
E-11	81	13	0.16	0.072	4.0	15	ld	1.1	1.1	13	42	0.4	15	0.67	1.5	0.41
E-12	21	19	0.11	0.13	6.3	23	3.6	1.3	0.98	12	58	5	0.99	3.7	5.6	ld
E-16/1	8.3	19	0.16	0.12	5.8	ld	ld	0.41	0.11	49	47	0.4	5.2	22	3.6	0.15
E-16/2	7.5	11	0.11	0.13	3.6	ld	ld	ld	0.18	180	41	10	3.5	2.5	3.9	2.2
E-17/1	9.7	17	0.24	0.27	4.6	ld	ld	0.19	0.18	8.7	54	0.29	0.58	14	13	0.19
E-17/3	9.3	13	0.14	3.9	4.2	3.9	7.2	0.15	0.17	2.6	26	0.12	0.34	2.7	3.7	0.15
E-17/4	10	17	0.33	0.18	3.5	16	ld	0.54	0.24	68	21	68	0.56	3.0	13	2.1
E-18	11	13	0.16	0.064	5	12	4.7	0.17	0.11	22	64	0.35	5.7	1.6	48	0.48
E-19	7.9	13	0.13	0.28	5.2	ld	ld	ld	0.08	16	70	0.15	8.5	1.9	46	ld
E-20	15	14	0.19	0.13	4.6	11	ld	0.94	0.5	73	45	1.5	11	0.52	2.0	0.22
E-21	14	13	0.063	0.18	5.3	10	4.5	1.1	0.56	5.1	61	0.15	28	0.64	2.2	0.20
E-7	50	14	0.19	0.14	4.2	9	17	1.1	1.1	1.4	18	0.37	0.88	0.6	1.7	ld
E-8/1	73	11	0.21	0.17	3.0	ld	24	1.4	0.51	7.1	35	0.6	9.5	7.5	6.0	0.13
E-8/2	66	18	0.12	0.16	4.7	ld	12	0.94	1.0	1.7	7.5	0.13	0.84	ld	2.1	ld
E-8/3	600	12	0.85	0.099	11	3.5	110	8.9	7.9	19	20	5.1	33	9.4	7.7	ld

Giff et al. (2000) with reference to thermodynamic model by Symonds and Reed (1993) considered that As, Hg, Se, Te are transported as pure elements, hydrides and sulphides in low-temperature magmatic gases. The second group consists of major and trace rock-forming elements: Ca, K, Mn, Fe, Y, Ga, Rb, Sr and some metals: Ni, V, Zn. Even the maximum concentrations of these elements in sulphur are considerably lower than those in andesites (Ca – in 26 times, Mn – in 10 times, Y, Sr, Zn, Ga – in three times). It is seemingly possible to draw a simple conclusion that these elements are present in composition of aerosols (particles of the host rocks) which are transported by gas streams. In this case the ratios of the elements which are typical for andesites should have remained, but it is not so. Double diagrams of relation between geochemically related elements whose concentration is higher in the andesites than in sulphur or close to them (Fig. 6) have been constructed. It has been taken into account that the aerosols can be particles not only of fresh andesites, but also of hydrothermally-altered rocks. Therefore the metasomatites composition data have additionally been involved. On the

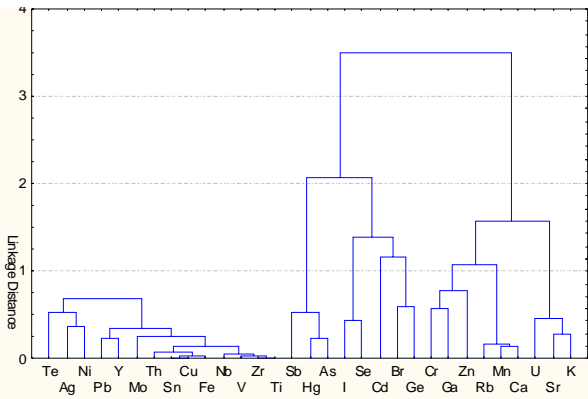
diagrams the fields of points of the elements ratios in sulphur turned out to be considerably isolated from the fields of andesites and metasomatites except for several samples in which impurity of the host rocks is possible. The obtained relation data testify that the elements ratios of the sulfuric constructions significantly differ from those in andesites and metasomatites. Therefore, besides the aerosol transporting, discussed elements could get to sulphur by transport in a gas phase. This assumption demanded further consideration and analysis whereas most of the discussed elements are traditionally considered inert enough and are difficult to leach from rocks, especially by a gas phase.

The cluster analysis allowed to detect the following features in the elements correlations. The elements are divided into two clusters on correlation diagram (Fig. 7).

The left cluster unites two geochemical associations of elements: 1a – Ag-Te-Ni; 1b – Pb-Y, Th-Sn-Cu-Fe, Nb-V-Zr-Ti, Mo. The right cluster consists of following groups: 2a – Sb-Hg-As; I-Se, Cd-Br-Ge and 2b – Cr-Ga-Zn, Rb-Mn-Ca, U-Sr-K.



**Figure 6: Comparison of relations of some rock-forming elements in host rocks and sulfur.**

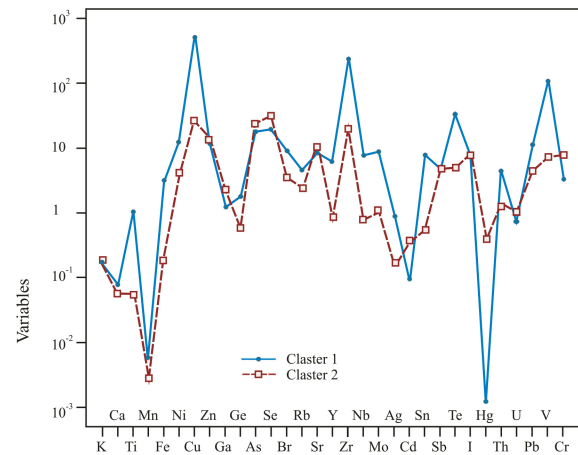


**Figure 7: Tree diagrams for variables Ward's methods. 1 Pearson r.**

Cluster 1 and cluster 2 showing concentration distribution peculiarity are clearly isolated on the diagram of average values which were obtained using K-method (Fig. 8). Consider the two groups of elements as divided by this analysis. 1. An unimodal distribution is typical for K, Ca, Mn, As, Se, Y, Sb, I, U. At the same time coefficient of variations is low for K, Ca, Mn, U, that is, the elements are distributed quite uniformly but As, Se, Sb, I have high coefficient of variations, which shows their non-uniform distribution. These parameters indicate active processes of redistribution and migration of the above elements at formation of sulfuric fumaroles.

Transport of metals is enhanced by acidic conditions. 2. Elements (Ti, Cu, Y, Zr, Nb, Mo, Sn, Te, Hg, Th, V) with obvious bimodal distribution of concentration can be attributed to the second group. Zr, Cu, V, Te has the greatest coefficient of variations among the elements. As can be seen along with such geochemically close to sulphur elements as As-Se-Sb elements Sr-Zr-Cu-Cr-V are mostly non-uniformly distributed, which proves cogently their high activity as well as oxo-hydroxo anion forming elements and consequently their capability to be transported in a gas phase. By the way, secondary zircons have earlier been found using electronic microscopy methods in micropores of potash feldspars from metasomatites of Asachinsky deposit (Southern Kamchatka). The established facts refer to high migration ability of Zr in a gas phase. The established correlation links along with the arrangement of the concentration points of elements on the diagram (see Fig. 5) show a complex way of migration and redistribution of elements during formation of sulfuric fumaroles.

Probably, in certain cases high concentrations of major and trace rock-forming elements (for example, Zr, Cr, Ag, Ti, Nb) could be defined not only by aerosol impurity.

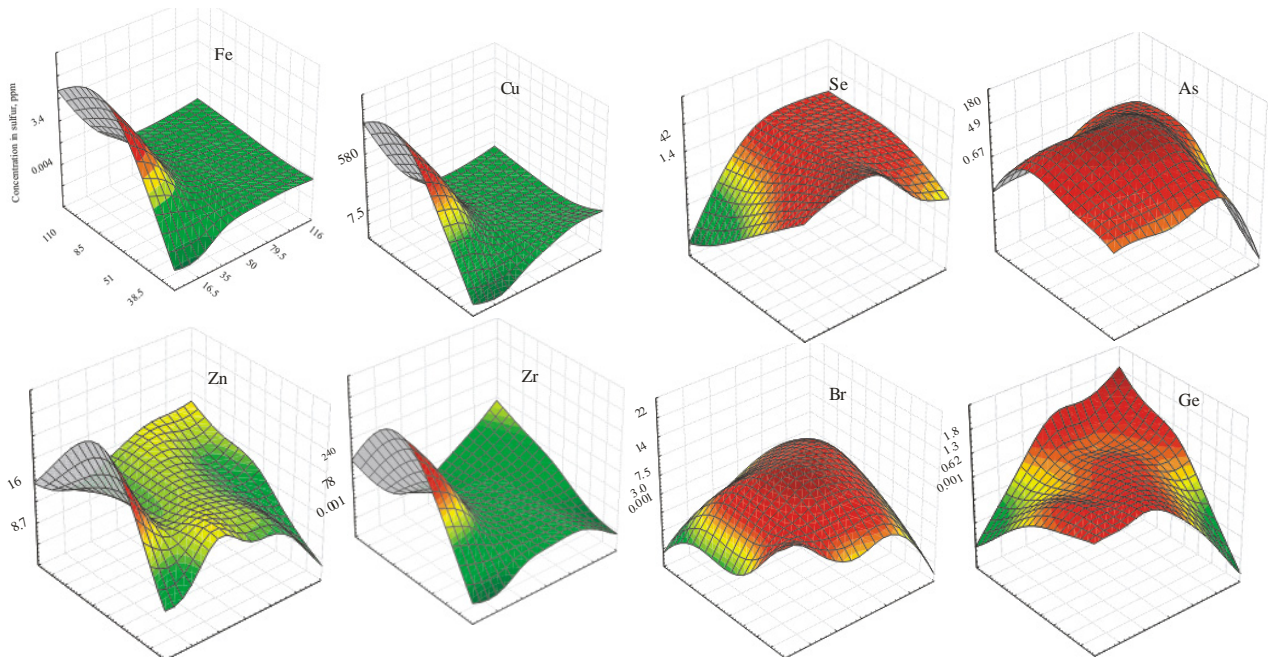


**Figure 8: Plot of means of each cluster.**

Chemical properties of the elements define their possibility of leaching by high-temperature acid gases from rocks followed by transportation of the elements in form of various compounds. Nb-V-Zr-Ti cluster reflects the close connection of these elements in the rocks. But at the same time, higher concentrations of Nb, Zr, Ti in sulphurs in comparison with andesites allowed to assume their chemical transport. Chemical and geochemical properties of the given elements at high-temperature conditions and in gas medium which are characteristic for fumaroles at Ebeco volcano (Menyalov et al., 1988) confirm this assumption. Zr at temperatures  $> 300^{\circ}\text{C}$  can form dioxide  $\text{ZrO}_2$  and hydride  $\text{ZrH}_2$  with water steams (Ivanov, 1997). Nb forms easily soluble and volatile compounds with haloids (F, Cl, B, I) which boil at low temperatures ( $254 - 400^{\circ}\text{C}$ ). Niobium fluoride compounds show ability to complexation. Complexes compounds of niobium fluorides are volatile and are easily soluble. The properties of niobium complexes are apparently of great importance during migration of this element in geochemical processes (Geochemistry, 1964).

Constructed distance weighted least surfaces for each element simultaneously with their distributions show different ways of the elements transport (Fig. 9). Such elements as As, Se, Br, Ge have maximal concentration in the Northeast fumarolic field, while Fe, Cu, Zn, Zr have maximal concentration in sulphur from the Southern fumarolic field.

A great amount of Hg, Sb, I were supplied to the flanks of the fumarolic fields. Obtained features of volume element correlations indicate complexity of structure of supply channels and element differentiation during gases ascent.



**Figure 9: 3D Surface Plots (Distance Weighted Least Squares) for two groups of elements.**

Let's compare elements concentrations in three types of surface new-forming substances: sulfur, efflorescences and sediments at boiling pots via host andesites. Oxo-hydroxo anion forming elements As, Sb, Se, Te, I have the highest concentrations in sulphur as compared to andesites of volcanic construction (on 2 – 4 order, Fig. 10). Elements Cu, Mo, Br, Zr, Ag, Cr also have increased concentration in sulphur, but in a less degree (by 3 – 8 times).

In sediments and efflorescences concentration of oxo-hydroxo anion forming elements also substantially exceeds that in andesites, although it is considerably lower there than in sulphur (Table 4, 5; Fig. 10). Metals (Cr, V, Fe, Pb, Rb and Sr) are mostly concentrated in sediments. It testifies to the more active migration of the metals with solutions of the given composition which are deposited at an exit of boiling waters to the surface. Cr and V are easily transported in water solutions under acid conditions and are accumulated in sediments of boiling pots in essentially higher concentration, than in the efflorescences and sulphur. When comparing such geochemically related elements as

Pb and Ag, Zn and Cd higher mobility of elements-impurity (Ag and Cd) compared to the mobility of most abundant Pb and Zn can be seen and these are accumulated in sulphur. Sn and Mo which also have maximum concentration in native sulphur can be found in sediments of boiling pots in comparable quantities. Efflorescences forming from vapor phase which is apparently a condensate after secondary boiling of the mixed solutions contain rather low concentration of the elements in question. Only Ca, Ga, Zn have been detected to have higher concentration in efflorescences, it is most probably the result of leaching from rocks and reprecipitation as secondary mineral phases. In the mineral composition of efflorescences are detected various sulphates, sulphates dihydrate and hydroxo-sulphate of metals (Table 6). Considerable quantity of minerals which are formed on thermal sites testify to the complex composition of thermal solutions from which these are deposited, and fluctuations of physicochemical parameters.

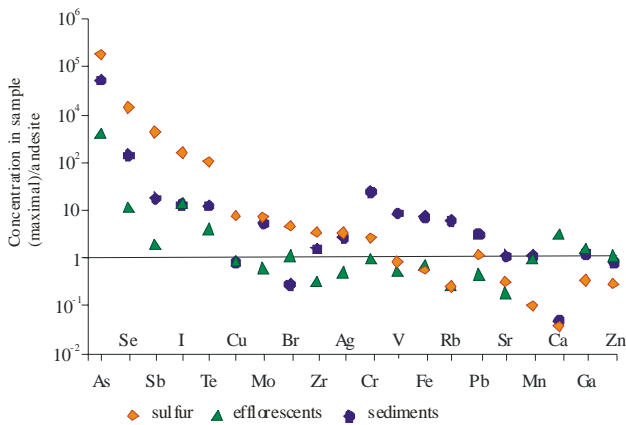
**Table 4. Element concentrations in efflorescences, ppm.**

n = 6	K	Ca	Ti	Mn	Fe	Ga	Ge	Y	Zr	Sr	Rb	Nb	Th	U	Ni
mean	0.35	3.0	0.036	0.049	2.3	8.5	0.51	3.6	9.5	58	7.1	0.14	1.0	1.3	8.7
minimum	0.29	0.19	0.01	0.002	0.11	3.6	0	2.4	2.3	44	5.7	0	0.39	0.90	2.7
maximum	0.44	14	0.056	0.11	4.3	19	1.1	5.4	21	79	8.7	0.41	1.7	1.7	17
	Cu	Zn	Cd	Pb	Cr	V	Mo	Sn	As	Se	Sb	Te	Br	I	Hg
mean	37	48	0.15	3.2	9.6	36	0.38	0.26	1.3	0.22	0.09	1.2	1.2	3.8	0.049
minimum	9.7	13	0	1.3	6.3	3.7	0.16	0	0	0	0	0.97	0	3.5	0
maximum	70	72	0.34	4.5	16	70	0.81	0.49	4.0	0.60	0.30	1.3	5.1	4.2	0.25

Note: hereinafter n – number of samples

**Table 5. Element concentrations in sediments from springs and pots, ppm.**

n = 13	K	Ca	Ti	Mn	Fe	Ga	Ge	Y	Zr	Sr	Rb	Nb	Ni	Cu	Zn
mean	0.39	0.12	0.10	0.05	8.9	4.8	1.0	6.0	50	160	45	1.8	12	34	22
minimum	ld	ld	ld	0.003	0.16	ld	ld	ld	5.3	18	1.5	0.37	5.6	16	1.7
maximum	0.88	0.22	0.21	0.12	43	14	3.1	16	100	500	200	5.1	22	61	53
	Cd	Pb	Cr	V	Mo	Sn	As	Se	Sb	Te	Br	I	Hg	Bi	Ag
mean	0.24	14	85	250	3.0	0.90	13	2.5	1.0	2.3	0.93	1.1	0.37	1.7	0.32
minimum	ld	3.4	ld	ld	1.3	0.25	1.7	ld	0.12	1.1	0.58	ld	ld	ld	0.11
maximum	0.63	31	390	1200	7.2	1.9	53	6.9	2.8	4.0	1.3	3.9	1.5	7.8	0.68



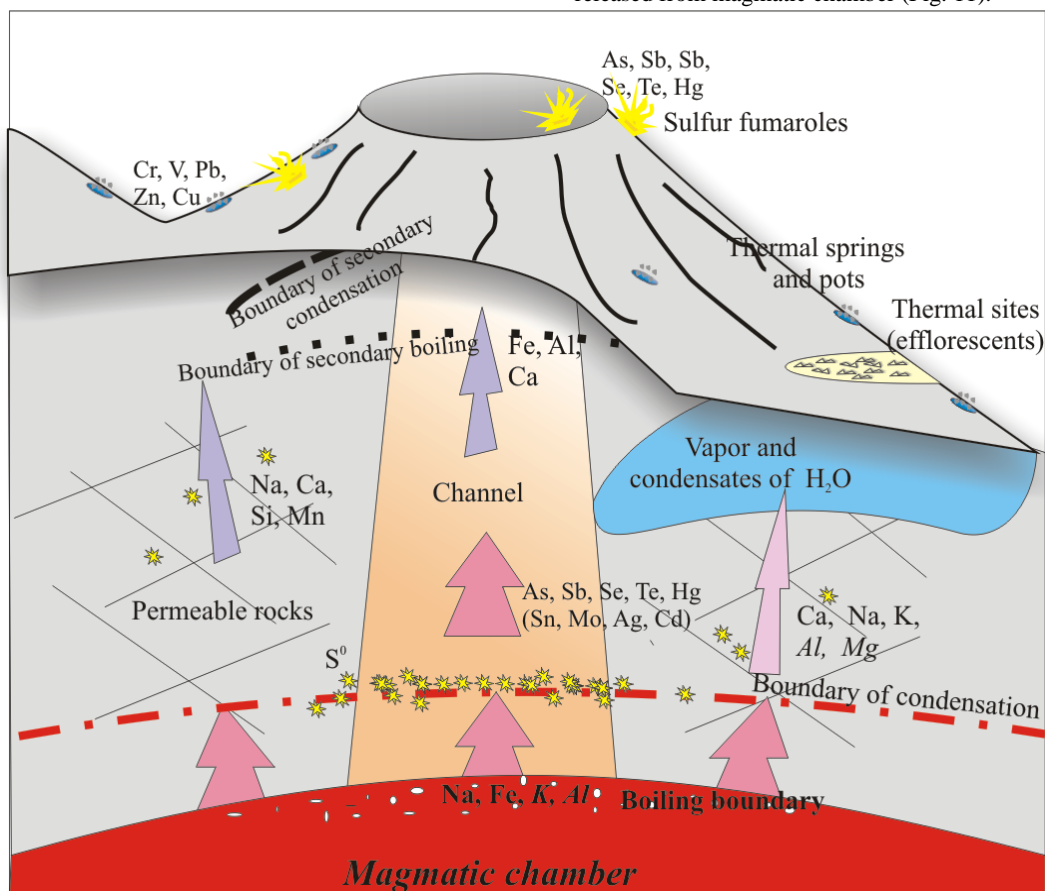
**Figure 10: Comparison of element concentrations in different substances (normalized under the concentration in andesites).**

The main minerals are hydrosulfates of rock forming elements (alunogen, pickeringite, apjohnite, misenite) which are actively leached from the host andesites during interaction with acid solutions. Accessory minerals consist of rare sulphates of both major and trace elements (Zn, Cu, V). A considerable quantity of the minerals forming on thermal sites, additionally testify to the complex composition of thermal solutions from which they are deposited and to fluctuations of physico-chemical parameters. However, despite of the wide list of neogenic phases, effluences are poorer in an element composition than native sulphur and sediments from pots.

**Table 6. Mineral composition of effluences at thermal sites of Ebeko volcano.**

Minerals	Formula
Main minerals	
Pickeringite	$MgAl_2(SO_4) \times 22H_2O$
Apjohnite	$MnAl_2(SO_4) \times 22H_2O$
Алуноген	$Al_2(SO_4)_3 \times 17H_2O$
Misenite	$K_8(SO_4)(SO_3OH)_6$
Trace minerals	
Zincovoltaita	$K_2Zn_5AlFe_3^{3+}(SO_4)_{12} \times 18H_2O$
Dolerophanite	$Cu_2OSO_4$
Jurbanite	$Al(OH)SO_4 \times H_2O$
Arhbarite	$Cu_2(AsO_4)(OH)$
Plaggite	$V_2O_2(OH)_3$
Gypsum	$CaSO_4 \times 2H_2O$
Zaherite	$Al_{12}(SO_4)_5(OH)_{26} \times (0-20)H_2O$
Mercallite	$KHSO_4$
Minamiite	$(Na,Ca)Al_3(SO_4)_2(OH)_6$
Semikite	$MgSO_4 \times H_2O$
Ca-longbeinite	$K_2Ca_2(SO_4)_3$
Konyaite	$Na_2Mg(SO_4)_2 \times 5H_2O$
Brochantite	$Cu_4SO_4(OH)_6$
Mooreite	$(Mg,Mn,Zn)_{15}(SO_4)_2(OH)_{26} \times 8H_2O$
Sarmientite	$Fe_2(AsO_4)(SO_4)OH \times 5H_2O$
Picromerite	$K_2Mg(SO_4)_2 \times 6H_2O$
Fibroferrite	$Fe(OH)SO_4 \times 5H_2O$
Minosrargite	$VOSO_4 \times 5H_2O$

Obtained results, together with available published data about gas composition (Menyalov et al., 1988) and hydrogeochemistry researches of Ebeko volcano springs (Bortnikova et al., 2005) allow us to construct a physico-chemical transport model of elements in volcanic gases released from magmatic chamber (Fig. 11).



**Figure 11: Physico-chemical model of volcanic-hydrothermal system of Ebeko volcano.**

Magmatic gases rising from the chamber leach a considerable quantity of rock-forming and trace elements from the lowest parts of volcanic construction. In order for the parameters of magmatic gases to be preserved during uprise of the gases presence of well-permeable zones or fracture channels in volcanic construction is necessary. Oxo-hydroxo anion forming elements As, Sb, Se, Te, some metals and rock-forming elements are supplied on the surface with magmatic gases and sulphur. A part of the gases on the way to a surface can mix with meteoric waters, and further transport of the mixed solutions leads to discharge on the surface in the form of boiling pots which have acidic and highly acidic media and high concentration of many chemical elements.

On the surface secondary compounds and phases are deposited in boiling pot sediments because parameters of solutions change. The part of the gases which minimally interacts with pore waters and rises toward the surface through fracturing zone or an open channel, comes out in the form of sulfuric fumaroles where trace elements are deposited as part of native sulphur. As a result the elements which are transported with a gas phase and in the form of an aerosol are precipitated with sulphur. Se and Te are closest geochemically to sulphur, and the greatest similarity of properties is showed by the raised temperatures and reductive conditions of endogenous processes (Ivanov, 1996). On a structure of molecules  $H_2Se$  and  $H_2Te$  are similar with  $H_2S$ , that is  $H_2Se$  and  $H_2Te$  are quite capable to be transported in a gas phase together with hydrogen sulfide, and their quantity in native sulphur can probably be an indicator of the share contribution of magmatic gas. In the given conditions Sn obviously has the maximum similarity to Sb and As which are closely located in the periodic table with Sn. Mo having highest concentration in native sulphur is probably also capable to be transported with gases from deep parts of volcanic construction. Mo is a strong complexing element, so it can be transported in isocomplexes and heterocomplexes:  $M(Mo_2O_{10})_4^{2-}$  where  $M = Si^{VI}, B^{III}, Sb^{III}, As^{IV}$ , that is in connection with typical elements-impurity of sulphur (Ivanov, 1997).

Zn, Pb, Cr, V are actively transported by solutions. Accumulation of these elements results from repeated weathering of host rocks by mixed fluid on the way to the surface. The similarity of properties of sulphur having absolute valence is stronger with Cr subgroup elements, than with Se and Te, but properties of compounds of lowest valence are similar to the row S-Se-Te whereas Cr subgroup elements lose similarity with sulphur (Nekrasov, 1965). Cr is preferentially leached by solutions because hydrogen compounds  $EH_2$  characteristic of S, Se, Te have no similar ones in Cr group. Precipitation and concentration of elements occurs according to their geochemical properties under existing conditions. Manifestation of thermal solutions on a surface means appearance of a geochemical barrier where the temperature sharply decreases and the redox potential raises, hereupon compounds and minerals of the elements present in solutions are precipitated. For example, samples of sediments, mainly composed of Fe-hydroxides contain a high concentration of a wide spectrum of elements capable of co-precipitation with Fe-hydroxides in adsorbed form (As, Bi, Se, Te, V, Cr), or in the form of own compounds (Pb). Rather low concentration of rock-forming elements (Y, Zr, Ga, Ge) in the samples, point to minimal mechanical contribution of host rocks to composition of precipitation and therefore about the hydrogenous formation mechanism of the given type of a deposit. Other precipitation type is a light substance mainly composed of metal sulphates. This type also contains high quantities of

oxo-hydroxo anion forming elements (Se and Te) and metals (Mo and Cd). Possibly during formation of this precipitation type the elements enter in the form of impurity to the main secondary minerals.

The part of the mixed solutions which reaches the surfaces in the water-saturated area is gradually divided into evaporating water steam and pore solutions, which leads to occurrence of efflorescents on heated-up places. Efflorescents are most "sterile" with respect to trace elements, which can be explained by formation of water steams in near-surface environment on thermal sites and therefore by absence of a source of elements released into this phase.

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