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Geochemical Characteristics of Volcanogenic Deposits and Exhalation Mineralization in the Crater Part of the Active Kudryavy Volcano (Iturup Island of the Kuril Arc)

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Abstract—Exhalation ore mineralization is developing in the crater part of the active Kudryavy volcano. Lithogeochemical sampling results have revealed that Re, Au, Ag, As, Bi, Cd, Cu, Ge, In, Mo, Pb, S, Sb, Se, Sn, Te, Tl, W, Zn, Rb, and Cs accumulate in solid fumarole formations. These elements are transported by high-temperature volcanic gases and are deposited in mineral phases in the near-surface horizons of fumarole fields under decreasing temperature conditions. The contents of rhenium and other metals in volcanic deposits of fumarole fields locally reach values characteristic of ore deposits. Zoning of lithogeochemical anomalies in ore element associations has been revealed, expressed by the series Re, Mo, W, Au, Cu, Ag, Zn, Cs, Ge → In → Bi, Cd, Pb, Sn, Tl → As, Sb, Se, Te, (Cu, Ag, Au) in the direction from the highest-temperature fumarole fields to less hot, reflecting their temperature zoning. It is demonstrated that lateral geochemical zoning is caused both by the ore element contents in fumarole gases, which depend on temperature, and by differences in the optimal temperature ranges in which various elements precipitate from gases. Signatures for similar exhalation mineral formation processes have been revealed that occurred in the recent geological past at the neighboring extinct Sredny volcano. This suggests the occurrence of similar processes within other volcanic systems of Iturup Island, which increases the prospects for detecting complex exhalation-related manifestations of rare, base, and noble metals.

Keywords: fumarole gases, volcanic deposits, temperature surveys, lithogeochemical sampling, geochemical zoning, rhenium, rare, base, and noble metals, modern exhalation mineralization, Kudryavy volcano, Iturup Island

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INTRODUCTION

Kudryavy volcano, located on northeastern Iturup Island of the Greater Kuril Archipelago, has attracted the particular attention of researchers for two and a half decades owing to the discovery of high concentrations of rhenium, indium, and other rare, base, and noble metals in fumarole gases and solid products. A number of rare element sulfides have been discovered in the composition of fumarole ore formations, some of them immediately on Kudryavy: rheniite ReS_2, approved as a new mineral species in 2005; kudryavite $(Cd,Pb)Bi_2S_4$; cadmoindite $CdIn_2S_4$; abramovite $Pb_2BiSnInS_7$; and znamenskiite $Pb_4Bi_4In_2S_{13}$. It was found that the formation of rheniite and other ore minerals in the crater part of the volcano derives from high-temperature volcanic gases (Tkachenko et al., 1992, 1999; Znamensky et al., 1993, 2005; Korzhinsky et al., 1993; Korzhinsky et al., 1994; Dobrovolskaya et al., 1996; Yudovskaya et al., 2008; Chaplygin, 2009, 2016). According to some researchers (Shaderman and Kremenetsky, 1996; Shaderman et al., 1996; Kremenetsky and Chaplygin, 2010), fumarole gases containing significant amounts of rhenium and

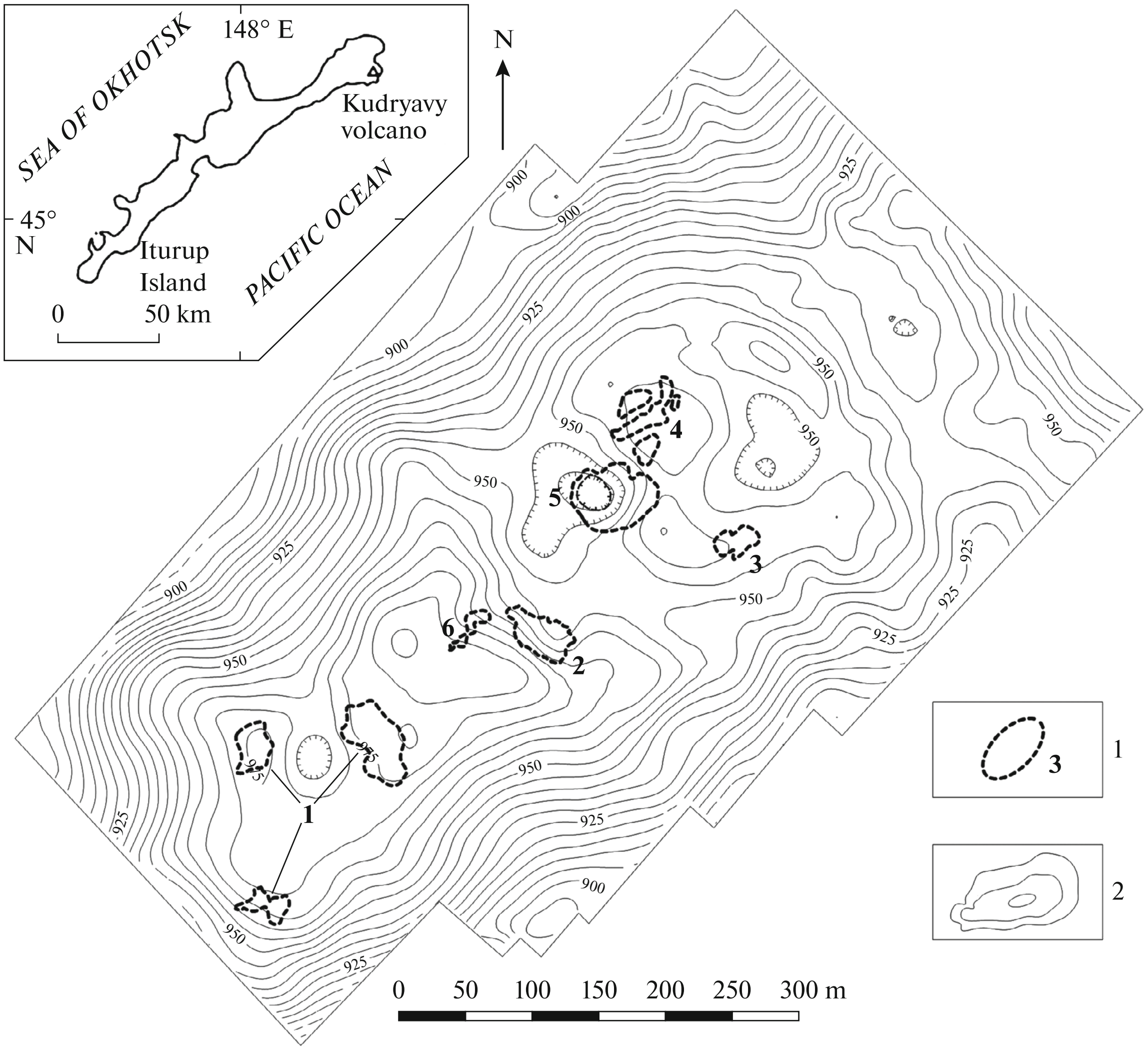

Fig. 1. Relief and main fumarole fields of the crater part of Kudryavy volcano. (1) fumarole fields and their numbers ((1) low-temperature fields of Southern crater; (2) Rhenium; (3) Field 605 (Molybdenum); (4) Kupol; (5) Main; (6) Anhydrite); (2) isohypses of relief.

related elements may be a new, unconventional source of mineral raw materials. Kudryavy volcano—a unique natural ore-producing factory in which magma degassing processes and interactions in the gas–rock–air system occur with subsequent ore mineralization in solid fumarole bodies—is of great interest for studying the geochemistry of volcanic processes and exhalation ore formation, as well as the formation and evolution of porphyry-epithermal systems.

This article is mainly based on new data on the temperatures and elemental composition of fumarole deposits, obtained from studies in 2015 as part of thermal (temperature) and lithogeochemical surveys of the crater part of Kudryavy volcano on a of scale 1 : 2500, as well as detailed thermal imaging of the Rhenium and Molybdenum (Field 605) fumarole fields (Fig. 1). In preparing the article, data from earlier studies on the composition of fumarole gases and solid fumarole formations were also used.[1]

GEOLOGY OF THE VOLCANO

The Kudryavy andesite–basalt stratovolcano is located within the Medvezhya caldera and is part of the Medvezhy volcanic ridge that arose along a NE-trending fault (Ermakov and Steinberg, 1999). The ridge includes the Medvezhy (peak 1125 m), Sredny (1116 m), Kudryavy (986 m), and Menshy Brat (563 m)

[1] In addition to published materials, the article involves data obtained from prospecting and evaluation works by a team from the Institute of Volcanology and Geodynamics (IVG) of the Russian Academy of Natural Sciences in 1993–2001 under the supervision of G.S. Steinberg, which assessed rhenium reserves at the Kudryavy volcano ore occurrence (Iturup Island), reflected in the IVG report under state contract no. 17–98.

volcanoes. Only Kudryavy volcano, the youngest, is active. Since its last volcanic eruptions in 1778–1779 and 1883 (Gorshkov, 1967; Ermakov and Steinberg, 1999), Kudryavy volcano is characterized by intense fumarole activity. Against a background of degassing, quasistationary in nature, phreatic eruptions occur in the crater zone: the last occured on October 7–11, 1999 (Korzhinsky et al., 2002), during which a rounded vent formed with a diameter of 45–50 m and a depth of about 50 m. The temperatures of the hottest fumarole on Kudryavy volcano reached 930–940°C in 1992–1993, the highest ever measured in stationary vapor-gas vents of the volcanoes (Korzhinsky et al., 1993; Taran et al., 1995). Kudryavy is the only volcano in the world where rhenium sulfide has been detected in macro amounts in fumarole incrustations (Znamensky et al., 1993; Korzhinsky et al., 1993; Korzhinsky et al., 1994).

Kudryavy volcano consists of a series of lava flows of a Late Holocene andesite–basalt complex overprinted on an extrusive andesite–dacite–rhyolite dome (*Gosudarstvennaya geologicheskaya karta* ..., 2002). In the crater part of the volcano, 900–986 m above sea level, three Late Holocene craters are distinguished: from northeast to southwest, the Tukap, Rhenium, and Southern craters, formed on a NE-trending feeder extensional fault, to the southwest from the Early Holocene Sredny volcano (Fig. 2). The first two craters host four high-temperature fumarole fields with gas temperatures reaching 300–940°C. In the northeast, the Tukap crater hosts the Kupol field, which consists of several adjacent fumarole sites; the Main field, which contains the crater of the last phreatic eruption; and Field 605 (Molybdenum). Further to the southwest, the Rhenium crater hosts the Rhenium and Anhydrite fumarole fields. In the southwest, in Southern Crater, there are low-temperature fumarole fields with gas temperatures of 50–200°C (see Fig. 1). The small-sized Anhydrite field, located west of the adjacent Rhenium field, has intermediate thermal characteristics between the high- and low-temperature fields. According to seismic studies (Zhigulev and Argentov, 2000; Zhigulev, 2010), the presence of a peripheral magma chamber responsible for the volcano's modern activity can be assumed under the Tukap and Rhenium craters at depths of 400–500 m from the surface, inside the general conical structure of Kudryavy volcano, towering above the bottom of the Medvezhya caldera. In addition, at a depth of about 70 m, seismograms have revealed the presence of a porous–fissured gas-saturated isometric body 100–150 m in diameter.

FUMAROLE GAS TEMPERATURE AND COMPOSITION DATA

The gas temperatures of the studied fumarole fields increase from southwest to northeast, from the low-temperature fields of Southern crater (≈50–200°C) to the following high-temperature fields: Rhenium (≈300–600°C) in the crater of the same name, Field 605 (≈400–650°C), Kupol (≈500–850°C), and Main (≈600–940°C) in the Tukap crater. According to the data from (Taran et al., 1995; Chaplygin, 2009), the composition of gases is sharply dominated by water (H_2O ≈ 92.1–98.5 mol %); the characteristic macrocomponents are CO_2, SO_2, H_2S, HCl, and H_2, the typical contents of which range from units to tenths of a mol %; the atmospheric gas content—N_2 and O_2—is extremely small (tenths or hundredths of a mol %). CO, HF, CH_4, and Ar are present in hundredths to thousandths of a mol % or less.

A review of the data on the macrocomposition of fumarole gases taken from (Taran et al., 1995; Chaplygin, 2009) shows that the distribution of gas temperatures and contents of H_2O, CO_2, SO_2, H_2S, and HCl are better approximated by a normal law, while H_2, CO, HF, N_2, O_2, Ar, and CH_4, by a logarithmic-normal law; therefore, the temperature correlation coefficients for the last group of gases were calculated from the logarithms of their contents. $\log H_2$ (correlation coefficient +0.95) is most closely correlated with temperature; the following also show a significant positive correlation: SO_2 (+0.56), H_2S (+0.49), HCl (+0.62), lgCO (+0.79), lgHF (+0.69). There is a negative correlation with temperature for H_2O (–0.67) and a weaker negative correlation for $\lg CH_4$ (–0.39). A direct dependence of the hydrogen content on temperature is manifested both as a whole in the total set of fields with different temperatures, and in individual fields (Fig. 3a); the CO content demonstrates a similar dependence. For acidic gases (SO_2, H_2S, HCl, HF), the direct dependence of the content on temperature is less close and does not occur within individual fields, but as differences in the average contents in fields with different gas temperatures, as can be seen with the example of HCl (Fig. 3b).

Thus, the macrostructure of fumarole gases is determined mainly by their temperature. Hotter fumaroles have higher levels of H_2, SO_2, H_2S, HCl, HF, CO; an increase in their quantities decreases the percentage of H_2O, while also reducing the CH_4. In turn, the CO_2, N_2, O_2, and Ar contents in fumarole gases show no statistically significant relationship with their temperatures.

Most of the available data on the trace element composition of fumarole gases represent the contents of elements in condensates obtained using a ball condenser or a Giggenbach flask with NH_4OH, with the addition of amounts of elements that account for the precipitate when there is significant amounts of it in the condensate (Chaplygin, 2009; Kremenetsky and Chaplygin, 2010). Assuming that trace elements are not lost as they are transported by the gas flow from a fumarole to the sampling device and are completely transferred to the condensate and precipitate, the

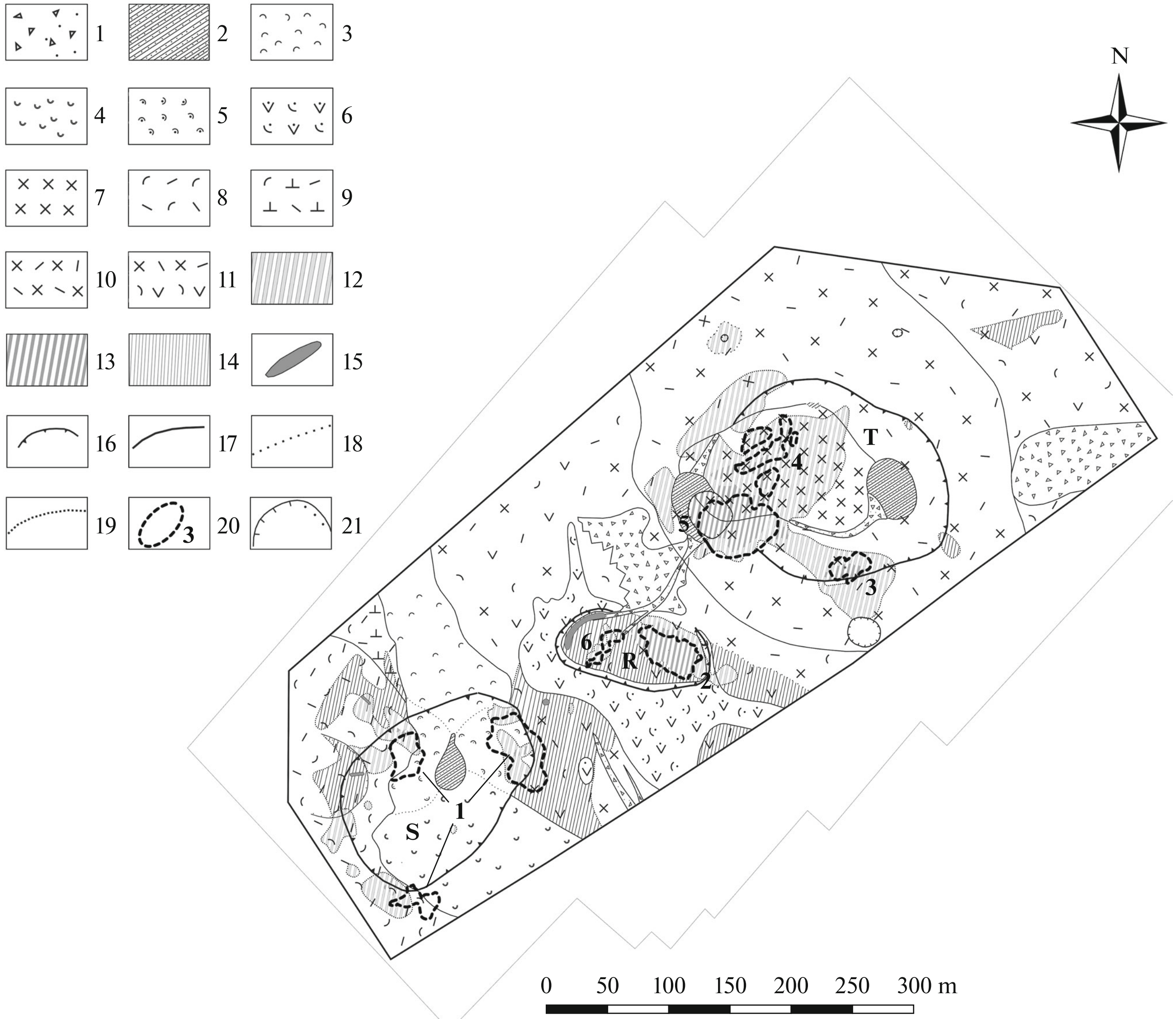

Fig. 2. Geological sketch map of the crater part of Kudryavy volcano. According to geological map compiled by V.A. Ermakov, A.V. Soloviev, and G.S. Steinberg (2001) with changes by P.Yu. Kovtunovich (2016). (1) lahar deposits; (2) crater lacustrine sediments; (3) Chernysh andesibasalt flow; (4) Zevok andesibasalt flow; (5) andesibasalt tephra; (6) andesibasalt tephra and tuffs; (7) andesites; (8) andesibasalt lava; (9) basalt and andesibasalt lavas; (10) andesite lava; (11) andesibasalt and andesite lavas and tuffs; (12) sulfur quartzites, opalites; (13) fumarole hydrothermal deposits; (14) argillizites, secondary quartzites, alunitized and anhydrititized rocks; (15) sheets and veins of anhydrite; (16) craters (T, Tukap; R, Rhenium; S, Southern); (17) contacts of different age rocks; (18) facies contacts; (19) contours of hydrothermal–metasomatic rocks; (20) fumarole fields and their numbers ((1) low-temperature fields of Southern crater; (2) Rhenium; (3) Field 605 (Molybdenum); (4) Kupol; (5) Main; (6) Anhydrite); (21) explosion craters, including eroded ones.

resulting contents (mass fractions) are equivalent to those in the fumarole gas. The results show rather high concentrations of a number of elements, including rare and rarest, in high temperature fumarole gases: Re, up to 22 ppb; In, up to 42 ppb; Ge, up to 306 ppb; Te, up to 260 ppb; etc. Taking into account all possible losses of elements due to partial deposition in the gas sampling tubes, hoses, and on the walls of the condenser, as well as due to contact with atmospheric air at the condenser outlet, the obtained levels of trace elements should be acknowledged as minimal, since the method used to obtain and analyze condensates can only yield understated, never overstated, estimations of contents (Chaplygin, 2009; Kremenetsky and Chaplygin, 2010).

Meanwhile, when the content of elements in fumarole gases was determined via sampling of aerosols using adsorbents and analysis of adsorbents (IVG studies under the supervision of G.S. Steinberg 1993–

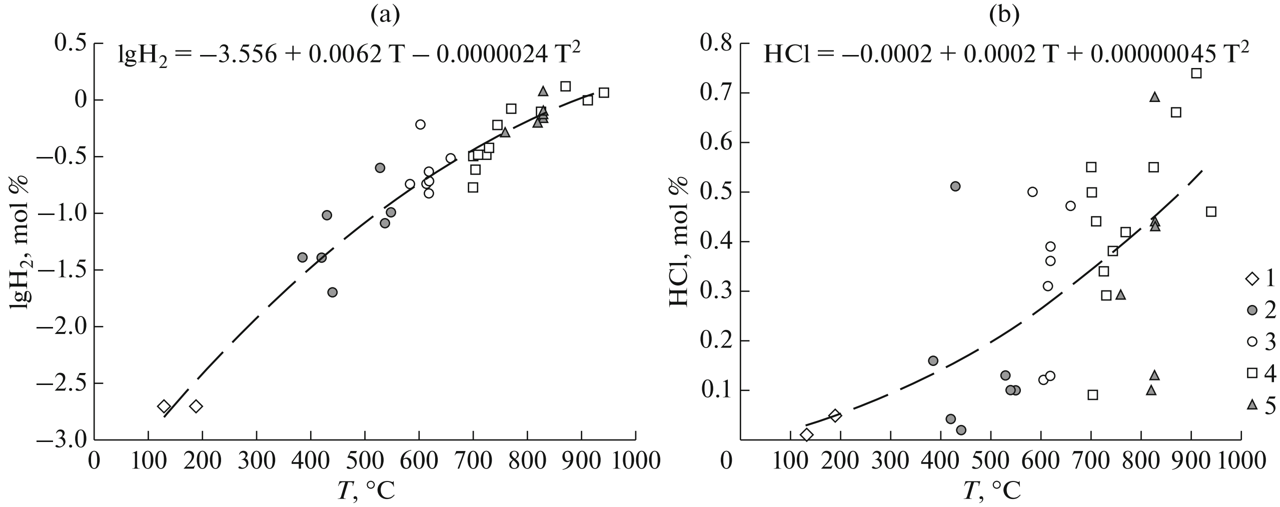

Fig. 3. Dependence of H_2 (a) and HCl (b) contents on temperature of fumarole gases at Kudryavy volcano. According to data from (Taran et al., 1995; Chaplygin, 2009). Fumarole fields: (1) low-temperature fields of Southern crater; (2) Rhenium; (3) Field 605; (4) Kupol; (5) Main.

2001), rhenium and related elements reached values two to three orders of magnitude higher. Perhaps this was due both to the imperfection of the sampling and analytical procedures, and that the sorbent filters used trapped rhenium and other elements not only from the gas-vapor component, but also from the flux of solid particles of the dust fraction carried by fumarole gas flows. Therefore, if we are considering the trace element composition of the gas phase, the data obtained by fumarole gas condensation should be considered more reliable.

A review of the data obtained by the condensation method and presented in (Taran et al., 1995; Chaplygin, 2009; Kremenetsky and Chaplygin, 2010) allows us to conclude that the highest contents of Re and a number of related elements, such as Mo, In , Sn, Zn, Bi, Cd, Pb, Tl, Cs, Rb, Sb, Ge, Cu, are observed, as a rule, in the hottest gases of high-temperature fumarole fields, most often in the hottest gases of the Kupol and Main fields. Therefore, we can talk about a direct, although not necessarily linear, statistical dependence of these element contents on the fumarole gas temperature.

RESEARCH METHOD

During areal lithogeochemical sampling of volcanic deposits of the crater part of Kudryavy volcano in 2015, samples were collected on a 25 × 25 m grid from test pits dug with a titanium shovel at a depth of 20–40 cm from the exposed surface. We sampled modern loose volcanic formations (volcanogenic soil), including deposits within existing and extinct fumaroles. The mass of samples was 0.5–1.0 kg to ensure that during sieving the yield of the analyzed <1 mm fraction was no less than 150–200 g. Geochemical sampling routes were established by GPS. In case particular formations were detected (e.g., individual fumaroles) between the planned points on the route, additional sampling points were set up with the corresponding GPS reference. Sampling at each point was accompanied by soil temperature measurement at the sampling site (in the test pit) using GM-900, CEN-TECH Item 60725 and Testo 835-T2 pyrometers; i.e., a thermal survey was conducted on the same grid simultaneously with lithogeochemical surveys. At the site of detailed works, approximately 750 × 400 m in area, the actual area of which was 0.32 km^2, 500 lithogeochemical samples of loose volcanic deposits were collected. In addition, 70 grab samples of rock material were collected, some of which characterize metasomatites of fumarole fields, including those with disseminated sulfide mineralization; the rest were typical volcanic rocks. Detailed temperature measurements of the Rhenium field and Field 605 were also carried out on a denser observation grid: in the Rhenium field, the average grid density was 6 × 6 m; in the southern half of Field 605, it was 2.5 × 2 m (no survey was conducted in the northern half). On the routes, using a DRG-01T dosimeter, selective measurements of the gamma exposure rate (GER) were taken; all obtained GER values were in the range of 7–15 μR/h, which corresponds to the normal natural background.

Chemical analyses performed at the laboratory of SGS Vostok Limited JSC (SGS group) included pulverization of samples, determination of Au, as well as Pt and Pd (only in rock material) by fire assay analysis with ICP-AES finish (technique codes: FAI505 and FAI515) and determination of 51 elements—Ag, Al, As, Ba, Be, Bi, Ca, Cd, Ce, Cs, Co, Cr, Cu, Fe, Ga, Ge, Hf, In, K, La, Li, Lu, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, Rb, Re, S, Sb, Sc, Se, Sn, Sr, Ta, Tb, Te, Th,

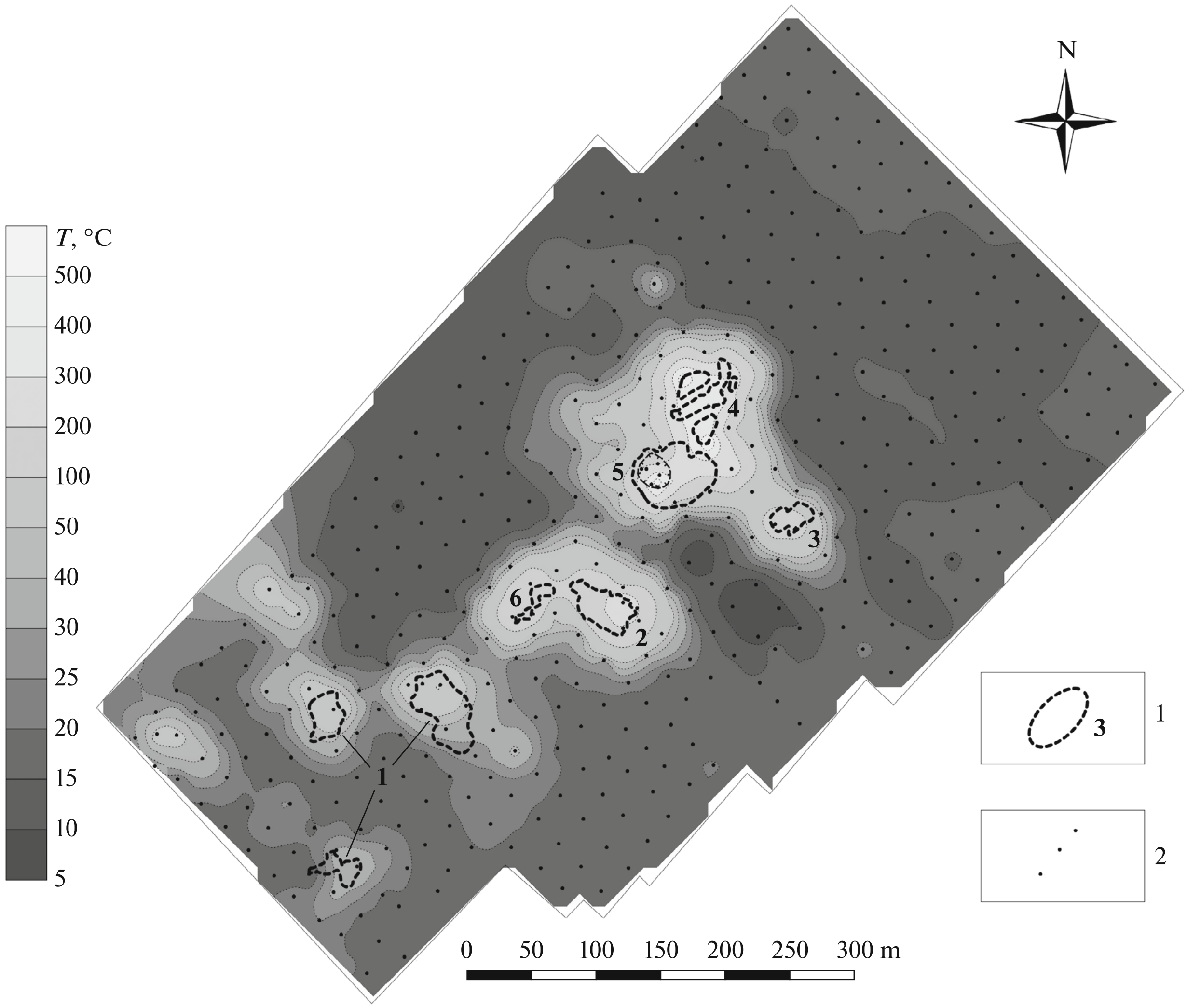

Fig. 4. Map of temperature of near-surface layer of volcanic soils of the crater part of Kudryavy volcano. (1) fumarole fields and their numbers ((1) low-temperature fields of Southern crater; (2) Rhenium; (3) Field 605 (Molybdenum); (4) Kupol; (5) Main; (6) Anhydrite); (2) points of measuring temperature and sampling loose deposits.

Ti, Tl, U, V, W, Y, Yb, Zn, Zr—by the ICP-AES/MS method with microwave autoclave digestion of samples using a mixture of perchloric, hydrochloric, nitric, and hydrofluoric acids (technique code: ICM40B).

When processing the obtained data, statistical analysis methods were used and maps were compiled based on the results of areal geochemical and temperature surveys.

The mineral composition of fumarole-altered volcanic rocks was studied by optical microscopy in transmitted and reflected light and by scanning electron microscopy (SEM) combined with electron probe microanalysis (EPMA) of individual mineral grains on a Jeol JSM 6510LA electron microscope equipped with an energy dispersion attachment (analyst O.L. Galankina, IPGG RAS).

TEMPERATURE SURVEY RESULTS

On the temperature map of the near-surface layer of the volcanic soils (20–40 cm from the exposed surface), all known fumarole fields were identified (Fig. 4), of which the Kupol is the hottest, merging in its southern part with the Main, within which the crater of the last phreatic eruption developed in 1999. The maximum temperature of the volcanic deposits in 2015 was recorded in the Kupol: ~600°C. Note that the temperature was measured in test pits intended for sampling volcanic sediments and open from the surface. This led to a decrease in temperature compared with unopened soils; therefore, the true temperature of the untapped near-surface soil layer at depths of 20–40 cm should be higher. New low-temperature fumarole fields were also identified, of which three fields on the northern and western slopes of the low-temperature

Table 1. Statistical parameters of distribution of element contents in tested crystalline rocks and loose volcanic deposits of Kudryavy volcano

Chem. element	Units	Crystalline rocks (70 samples)			Loose deposits (500 samples)		
		C_{min}	C_{me}	C_{max}	C_{min}	C_{me}	C_{max}
Au	ppm	<0.005	<0.005	0.216	<0.005	<0.005	1.17
Ag	″	<0.02	0.05	20	<0.02	0.23	23.4
Al	wt %	0.07	7.685	14.4	0.12	2.86	14.5
As	ppm	<1	11.5	4080	2	46	2120
Ba	″	<5	148	833	6	153	1240
Be	″	<0.1	0.35	3.7	<0.1	0.2	0.4
Bi	″	<0.04	1.125	3160	<0.04	4.41	744
Ca	wt %	0.01	4.08	13.1	0.03	1.09	>15
Cd	ppm	<0.02	0.24	4060	<0.02	0.14	269
Ce	″	0.07	8.9	48.3	0.1	5.62	50.6
Cs	″	<0.05	0.775	104	<0.05	1.08	38.6
Cr	″	2	64.5	315	2	21	225
Co	″	0.3	18.3	98.9	0.1	9.9	116
Cu	″	1.8	45.4	652	3.7	50.2	2660
Fe	wt %	0.06	5.935	13.6	0.12	3.67	>15
Ga	ppm	0.2	14.85	116	0.4	75	64.8
Ge	″	<0.1	<0.1	2	<0.1	0.1	8.3
Hf	″	0.1	1.615	4.82	0.18	2.19	5.16
In	″	<0.02	0.155	>500	<0.02	0.365	108
K	wt %	<0.01	0.48	5	<0.01	0.39	1.66
La	ppm	<0.1	3.2	18	<0.1	2.25	17.6
Li	″	<1	5	133	<1	4	14
Lu	″	<0.01	0.355	0.92	<0.01	0.2	1.12
Mg	wt %	<0.01	1.865	5.47	<0.01	0.945	4.2
Mn	ppm	2.5	831	2270	12	480.5	1860
Mo	″	0.56	3.03	>10000	0.74	14.5	8870
Na	wt %	0.02	1.425	3.9	0.03	0.6	2.5
Nb	ppm	<0.1	0.6	1.5	<0.1	1	4.6
Ni	″	<0.5	8.9	123	<0.5	5.3	82.1
P	″	<50	370	930	<50	250	1120
Pb	″	0.6	10.15	8840	<0.5	22.8	>10000
Rb	″	<0.2	8.4	490	0.3	7.9	118
S	wt %	<0.01	0.94	>5	0.05	0.675	>5
Sb	ppm	0.08	0.415	51.2	0.2	1.39	24.1
Sc	″	<0.5	36.85	57.4	<0.5	19.1	251
Se	″	<2	2	293	<2	11	205
Sn	″	0.3	1.35	338	0.6	4.3	889
Sr	″	1.4	213	1430	2	66.75	1500
Ta	ppm	<0.05	0.09	0.64	<0.05	0.2	0.96
Tb	″	<0.05	0.505	1.71	<0.05	0.28	2.09
Te	″	<0.05	0.675	163	0.11	2.485	108

Table 1. (Contd.)

Chem. element	Units	Crystalline rocks (70 samples)			Loose deposits (500 samples)		
		C_{min}	C_{me}	C_{max}	C_{min}	C_{me}	C_{max}
Th	″	<0.2	0.8	2.9	<0.2	0.6	4.4
Ti	wt %	0.01	0.42	0.84	0.09	0.64	2.96
Tl	ppm	<0.02	0.3	125	0.02	2.235	343
U	″	<0.1	0.3	1.2	<0.1	0.2	0.6
V	″	1	262.5	502	2	168	655
W	″	<0.1	0.6	1370	<0.1	1.5	274
Y	″	<0.1	17.6	58.9	0.2	9.55	59.8
Yb	″	<0.1	2.2	6.1	<0.1	1.3	6.8
Zn	″	5	72.5	7220	5	46.5	550
Zr	″	2.9	46.6	140	4.3	58.55	152
Re	″	<0.05	<0.05	82.7	<0.05	0.07	405
Pt	″	<0.01	<0.01	0.01	n.a.	n.a.	n.a.
Pd	″	<0.005	<0.005	<0.005	n.a.	n.a.	n.a.

C_{min}, C_{me}, C_{max}, minimum, median, maximum values of contents, respectively; n.a., no analyses.

Southern crater and north of the Kupol field were rather contrasting.

Based on the results of detailed temperature surveys in the Rhenium field and southern half of Field 605, the following maximum soil temperature values were recorded at individual points: in the former, 516°C; in the second, 687°C.

LITHOGEOCHEMICAL SURVEY RESULTS

The results of the areal lithogeochemical survey of loose sediments carried out in the crater part of Kudryavy volcano and supplemented by selective testing of crystalline rocks show that a number of elements in the solid formations of active fumaroles reach high concentrations comparable to those in economic ore deposits: Re, Au, Ag, As, Bi, Cd, Cu, In, Mo, Pb, S, Sb, Se, Sn, Te, Tl, W, and Zn; Ge, Rb, and Cs also accumulate with them, although not in high concentrations. In all, there are 21 elements accumulated (Table 1). This list includes all elements whose contents in fumarole gases, as noted above, directly depend on gas temperatures. As a result, these elements are transported by ascending vapor-gas fumarole flows and, separating from them at geochemical barriers near the exposed surface and directly on it (primarily, at the temperature drop barrier and contact with atmospheric air), they accumulate in active fumarole deposits, forming lithogeochemical anomalies of exhalation genesis.

Intense areal anomalies of the above elements in volcanic deposits are associated with high-temperature fumarole fields, with the most contrasting anomalies of most metals corresponding to the Kupol, which, along with the Main, is hotter than Field 605 and much hotter than the Rhenium. This is seen, in particular, for rhenium when comparing the map of rhenium contents in solid volcanogenic formations (Fig. 5) with the temperature map of the surface layer of volcanic soils (see Fig. 4). The most intense areal rhenium anomaly corresponds to the Kupol field; the second most intense are those of adjacent Field 605 and the Main. Together they form a rather vast anomalous geochemical rhenium field encompassing the northeastern peak of Kudryavy volcano (Tukap crater). A less intense rhenium anomaly, smaller both in size and concentration, corresponds to the Rhenium field inside the crater of the same name. Several low-contrast anomalies are located on the periphery of the intense anomalous field on the slopes of the northeastern peak of the volcano, as well as in the region of low-temperature fumarole fields on the slopes of the southwestern peak (Southern crater).

Almost all the high contents of ore elements in the tested crystalline rocks, as well as in loose deposits, were recorded in high-temperature fumarole fields. The maximum Re, Au, Ag, Cu, In, Sn, Tl, and Te contents in individual samples (for numerical values, see Table 1) were identified in the hottest fields, the Kupol and Main; Mo, W, Zn, and Ge, in the Field 605; and As, Bi, Cd, In, Pb, Sb, Se, in the Rhenium. It is also noteworthy that abnormally elevated contents of a number of ore elements were also recorded in rock material samples collected on the northeastern slope of the extinct Sredny volcano: Re, up to 0.18 ppm; Au, up to 0.02 ppm; Ag, up to 0.21 ppm; As, up to 50 ppm; Cu, up to 105 ppm; In, up to 0.2 ppm; Mo, up to 54 ppm; Se, up to 13 ppm; Te, up to 4.3 ppm. Even though these contents are significantly lower than at the active

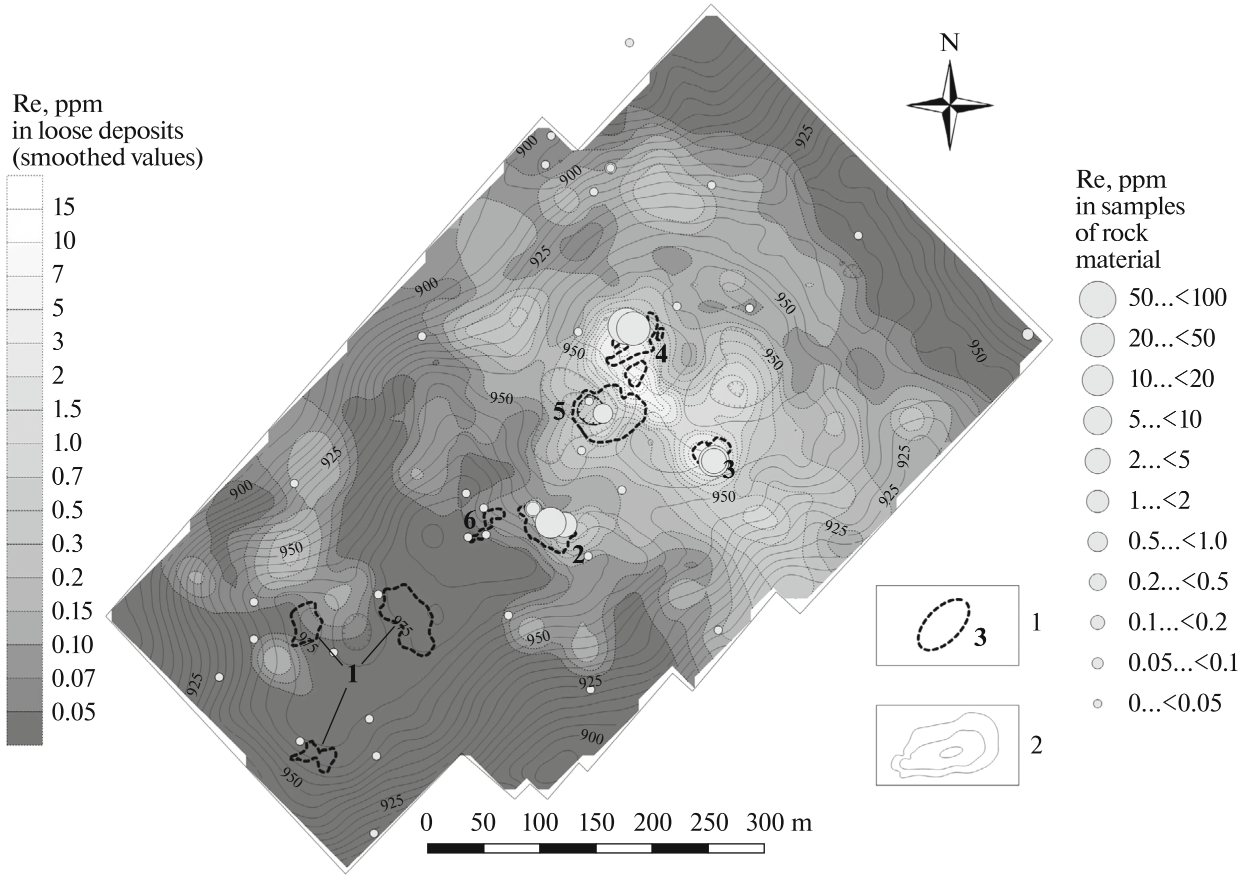

Fig. 5. Map of rhenium contents in solid volcanic formations of the crater part of Kudryavy volcano. (1) fumarole fields and their numbers ((1) low-temperature fields of Southern crater; (2) Rhenium; (3) Field 605 (Molybdenum); (4) Kupol; (5) Main; (6) Anhydrite); (2) isohypses of relief.

Kudryavy volcano, it can be assumed that in the recent geological past, similar exhalation ore mineralization processes took place at Sredny volcano. Taking into account that only eight samples were collected on Sredny volcano, it can be expected that systematic sampling will reveal higher contents of these elements in paleofumarole field deposits.

The results of factor analysis of the geochemical data reveal that, both for crystalline rocks and loose deposits (Table 2), the group of elements intensively accumulating in solid fumarole formations is divided into two associations. In the first (factor 2), the main role is played by In, Cd, Mo, Sn, Re, W, Tl, Au, Bi, Pb, with Ag, Cu and Zn attracted—this association is related to the highest-temperature conditions of exhalation mineralization. In the second association (factor 3), the main role is played by Te, Se, As, Sb, S, this association is related to lower mineralization temperatures. These two associations as a whole positively correlate with each other, primarily due to elements that are simultaneously included in both associations (Sn, Pb, Bi, Tl, As, Sb).

The subdivision of elements into two associations—highest-temperature (Au, Re, Mo, W, Ag, Cu, Bi, Tl, Sn, Cd, In, Pb) and lower-temperature (As, Te, Se, Sb, S) exhalation mineralizations—also demonstrate the results of R-modification of cluster analysis of data on loose deposits (Fig. 6); in this case, Ge tends toward the highest-temperature assemblage. Almost all other elements occupying the left side of the cluster diagram are antagonists of the elements of these two associations resulting from exhalation mineralization.

MINERALOGICAL RESEARCH RESULTS

The results of mineralogical studies of samples recovered in 2015 from the Rhenium, Field 605, and Kupol fumarole fields showed that the ore mineralization of fumarole deposits is unevenly distributed and is represented by: (a) small disseminated crystals and individual grains; (b) thin crusts and aggregates overgrowing clastic grains and pores; (c) thin veinlets in conjunction with other phases. The mineral composition is mainly represented by pyrite; in oxidation zones, by hematite and goethite, as well as magnetite

Table 2. Factor loadings according to results of varimax factor analysis, performed with logarithms of element contents in loose deposits of the crater part of Kudryavy volcano

Chem. element	Factors			Chem. element	Factors		
	1	2	3		1	2	3
logAu	–0.37	**0.74**		logNa	**0.90**		
logAg		0.50		logNb		0.36	
logAl	**0.85**	–0.34		logNi	**0.67**		
logAs		0.46	**0.80**	logP	0.57	–0.30	
logBa				logPb		**0.72**	0.36
logBe	**0.89**			logRb	0.51		
logBi		**0.72**	0.54	logS	–0.41		
logCa	**0.91**			logSb		0.45	**0.66**
logCd		**0.85**		logSc	**0.94**		
logCe	**0.90**			logSe		0.26	**0.79**
logCs		0.58		logSn	–0.31	**0.82**	0.32
logCr	**0.66**			logSr	**0.86**		
logCo	**0.81**			logTa			
logCu		0.50		logTb	**0.92**		
logFe	**0.86**			logTe		0.29	**0.81**
logGa	**0.87**	–0.27		logTh	**0.85**		
logGe		0.28		logTi	–0.30	0.33	
logHf	0.29			logTl		**0.76**	0.49
logIn		**0.91**		logU	**0.82**		
logK	**0.81**			logV	**0.90**		
logLa	**0.89**			logW		**0.77**	
logLi	**0.87**			logY	**0.90**		
logLu	**0.91**			logYb	**0.90**		
logMg	**0.92**			logZn	**0.68**	0.44	
logMn	**0.91**			logZr	0.31		
logMo	–0.28	**0.83**		logRe		**0.77**	
Weight, %	38.7	17.3	6.8	Weight, %	38.7	17.3	6.8

Loadings in excess of 0.60 are shown in bold; loadings whose absolute value is less than 0.25 are not shown in table.

grains. Among the other sulfide minerals, galena, chalcopyrite, sphalerite, pyrrhotite, greenokite, bismuthine, and Cu–In–Cd–Bi phases (bismuth-bearing roquesite; possibly cadmoindite, etc.) were identified. Most of the rare phases were found in the Kupol field, including bismoclite (BiOCl). The crystals and grains of In, Cd, and Bi minerals range from several to ten microns in size (Fig. 7). Rhenium-bearing phases in the studied samples were not detected; however, it should be noted that some phases could not be unambiguously identified, because they are represented by intergrowths no more than a few microns in size. As for rhenium contents of tens of ppm, the presence of intrinsic mineral phases of this metal could be expected, the assumption remains that they were present in the composition of fine disseminations not identified by the method.

DISCUSSION

Nature of Lithogeochemical Anomalies

The lithogeochemical anomalies of exhalation genesis in the loose volcanic deposits of the crater part of Kudryavy volcano revealed from the results of areal lithogeochemical survey are not secondary dispersion patterns typical in practice of geochemical explorarion, but lithogeochemical anomalies with a more complex genesis. They began to form from the onset of volcanic activity and continue to form to this day as a result of exposure to loose formations of ascending fumarole vapor-gas fluids (endogenic source). Their main formation process is not dispersion, but concentration of ore elements, which is the main property of primary, not secondary, lithogeochemical halos.

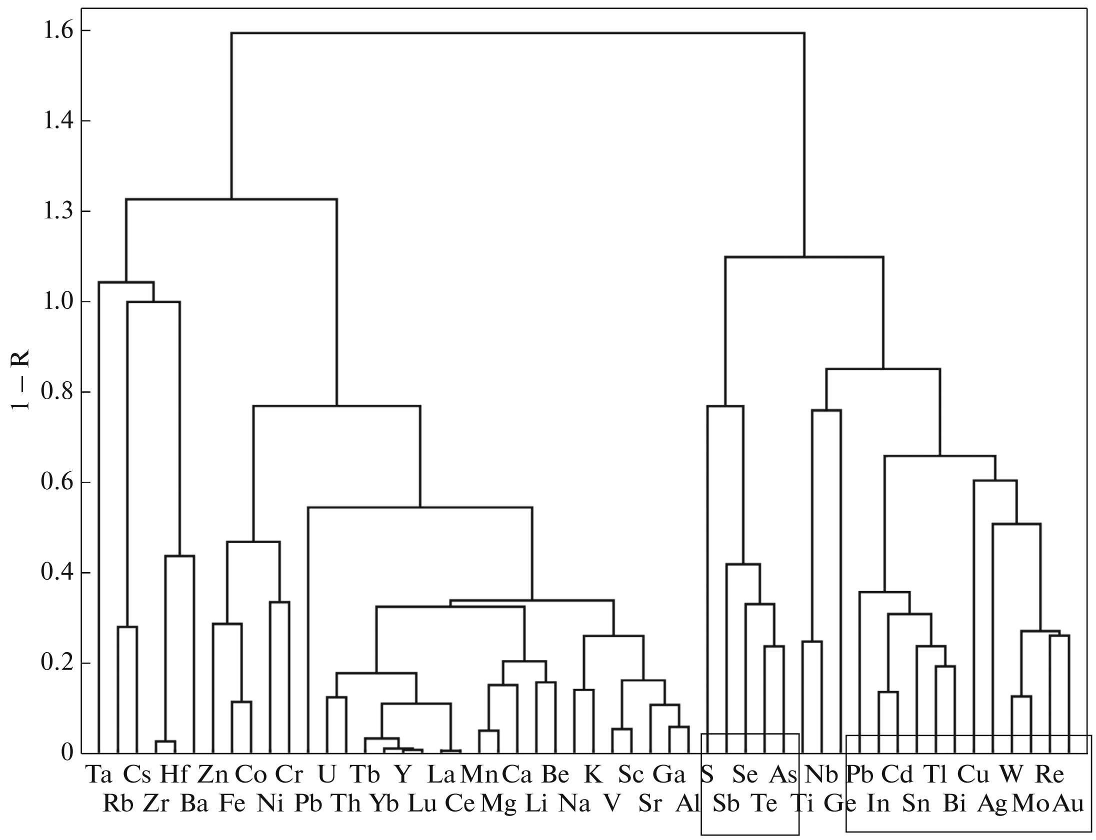

Fig. 6. Cluster analysis dendrogram of geochemical data (logarithms of element contents) for loose volcanogenic deposits of the crater part of Kudryavy volcano. R, correlation coefficient. Framework includes main ore element associations of exhalation mineralization.

Simultaneously with the ongoing transport and accumulation of elements in the loose cover of the crater part of the volcano, accumulated material is also dispersed by two main exogenic processes. The first is ubiquitous mechanical dispersion of solid particles of loose deposits as a result of two types of mechanical migration: quasidiffusion (nondirectional mixing and spontaneous movement of particles) and directed gravitational movement of particles downslope. These are the typical mechanisms by which secondary lithogeochemical dispersion patterns form in the conditions of prevailing mechanical migration of elements. The second process is an aerogenic dispersion. Vapor-gas mixtures with dust-sized particles emitted by fumaroles into the atmosphere deposit ore elements on the exposed surface as solid and liquid precipitation. An additional aerogenic mechanism is aeolian dispersion of surface layers of the loose volcano cover with redeposition of solid particles. Owing to both processes, ore elements are dispersed from their fumarole sources into surrounding loose formations and, ultimately, from the crater part of the volcano to its slopes. Solid-phase mechanical dispersion within loose deposits and aerogenic dispersion are the processes by which secondary lithogeochemical patterns are formed.

Thus, lithogeochemical anomalies in the crater part of Kudryavy volcano are mixed endogenic–exogenic anomalies, combining the properties of both primary exhalation ore mineralization halos and secondary dispersion patterns. The closer to the source (modern or former fumarole), the greater the role of the primary concentration process of ore elements; the halo is predominantly primary in nature. Conversely, aside from a modern or paleofumarole source, secondary ore element migration processes are decisive and the lithogeochemical anomaly is typically a secondary dispersion pattern. All of this is important for a correct interpretation of lithogeochemical anomalies in volcanic deposits.

Geochemical Zoning

When comparing single-element geochemical maps based on the contents of different elements, spatial zoning of the location of anomalies of different element associations and its dependence on the temperatures of fumarole fields are clearly manifested. The hottest fumarole fields, the Kupol, 605, and

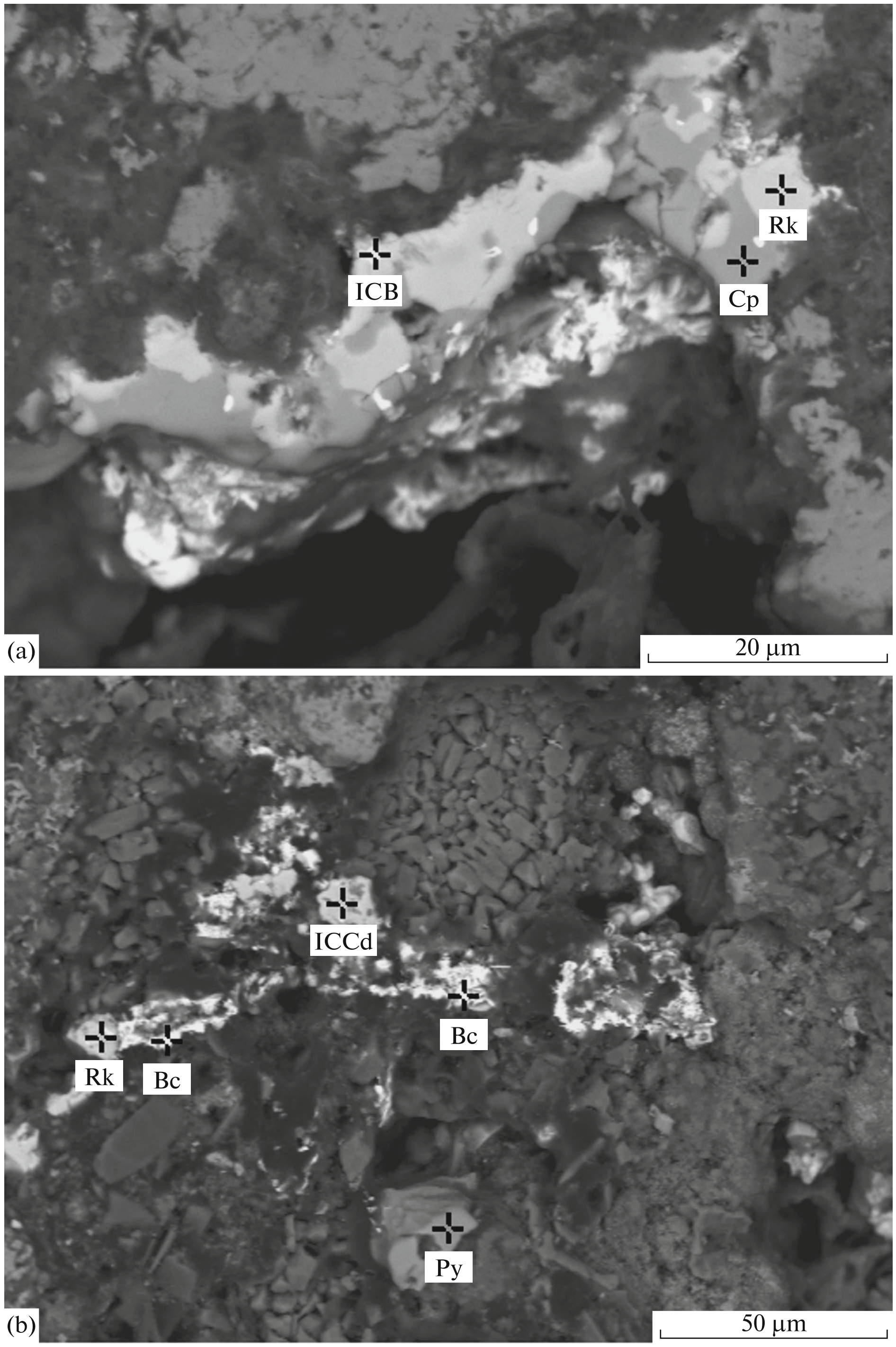

Fig. 7. Ore minerals in rocks of Kupol field (SEM-BSE). (a) chalcopyrite (Cp), roquesite (Rk), In–Cu–Bi sulfide (possibly roquesite intergrown with Bi phase) (ICB); (b) roquesite (Rk), In–Cu–Cd sulfide (presumably, roquesite intergrown with cadmoindite or grinokite) (ICCd), bismoclite (Bc), pyrite (Py).

Main, and to a lesser extent, the Rhenium, are associated with Re, Mo, W, Au, Cu and Ag anomalies (copper, silver, and gold also form weak anomalies in the low-temperature fumarole region). There, contrasting In anomalies, local Zn anomalies, and weak Cs and Ge anomalies are also observed. The Rhenium field, and to a lesser extent the Kupol and 605 fields, are characterized by contrasting Bi, Cd, Pb, Sn, and Tl anomalies. As, Sb, Se, and Te anomalies are associated with the Rhenium and Anhydrite fields, as well as with the 605 and Kupol, but to a much lesser extent. These elements also form weak anomalies in the low-

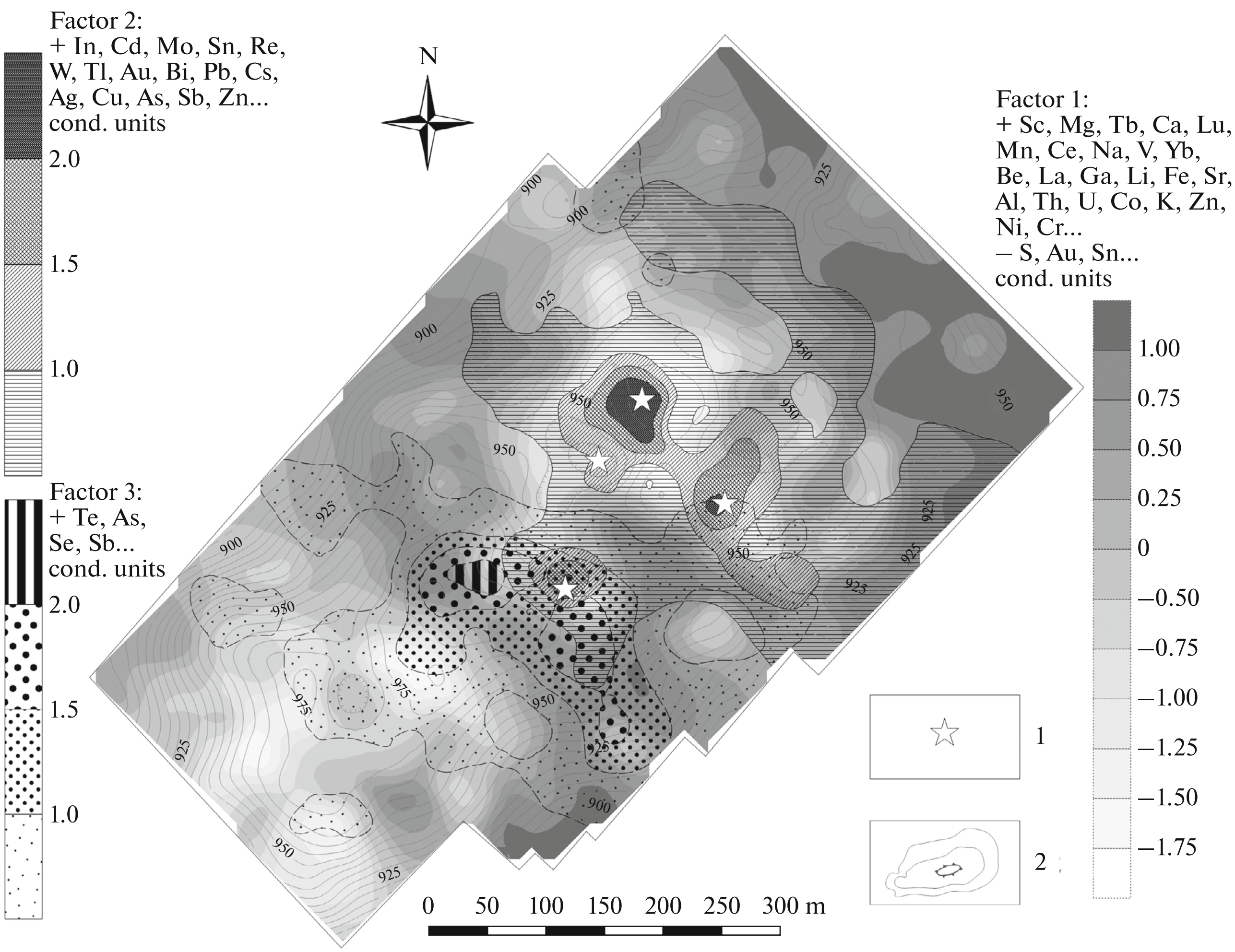

Fig. 8. Map of factor scores as multi-element indexes of composition of loose sediments of the crater part of Kudryavy volcano. (1) centers of high-temperature fumarole fields; (2) isohypses of relief.

temperature fumarole fields in the southwest of the surveyed area. Sulfur is found both in low-temperature fields and in less hot parts of high-temperature fields at their periphery.

The established lateral geochemical zoning from northeast to southwest, from the high-temperature Kupol and Main fields towards the low-temperature fields, can be represented in the following series, which reflects the zoning of the location of exhalation ore mineralization from the highest temperature to mineralization that forms at lower temperatures:

$$\text{Re, Mo, W, Au, Cu, Ag, Zn, Cs, Ge}$$
$$\rightarrow \text{In} \rightarrow \text{Bi, Cd, Pb, Sn, Tl}$$
$$\rightarrow \text{As, Sb, Se, Te, (Cu, Ag, Au)}.$$

This lateral lithogeochemical zoning of the crater part of Kudryavy volcano is reflected in the map of multi-element indicators (Fig. 8), which are the values of the corresponding factors (see Table 2). In the northeastern and southwestern parts of the studied territory, decreased values of factor 1 reveal areas of intensive removal of rock-forming (Mg, Ca, Na, Fe, Al, K) and minor rock-forming (Sc, Tb, Lu, Ce, V, Yb, etc.) elements as a result of acid leaching of elements not transported by gases during fumarole activity. Abnormally high values of factor 2 mark a region of principal accumulation of elements of the highest-temperature mineralization. Anomalies of increased values of factor 3 delineate a region with principal accumulation of exhalation mineralization elements associated with active lower-temperature fumaroles. It is possible that in the southwestern half of the surveyed area mineralization of Re, Mo, W, Au, Cu, Ag, In, Ge, and other elements of the highest-temperature association may have occurred under anomalies of elements of the medium–low temperature association, at a depth closer to the heat source.

Lateral lithogeochemical zoning, which reflects the zoning of exhalation ore mineralization in the crater part of Kudryavy volcano, results primarily from

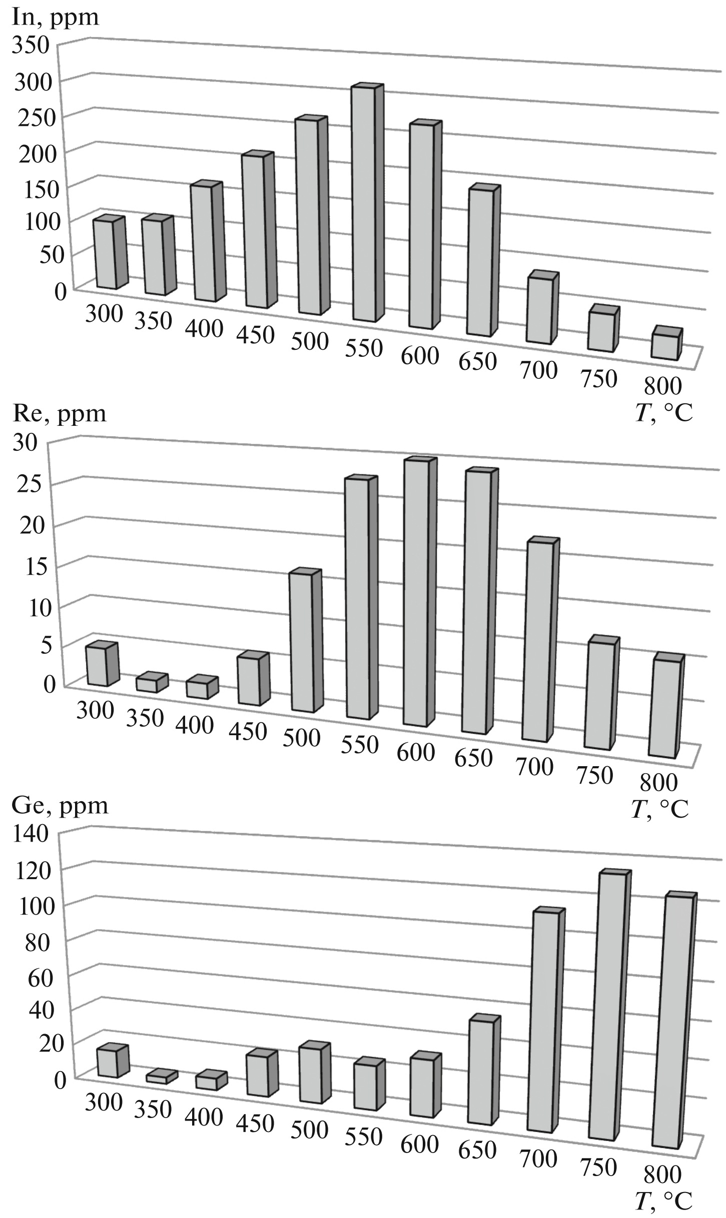

Fig. 9. Average contents of In, Re, and Ge in fumarole crusts of Kudryavy volcano for different temperatures of fumarole gases.

differences in the temperatures of fumarole gases. The contents of elements transported into volcanic soil by fumarole gases have positive correlation coefficients with the soil temperature, and the negative correlations between the contents of major rock-forming (Mg, Al, K, Na, Ca, Fe) and minor rock-forming (Sc, Yb, Ga, REE, Y, V, etc.) elements with the soil temperature are the results of their acid leaching and removal from sediments of the hot fumaroles.

Earlier, in 1994–1995, during IVG prospecting and evaluation works on assessing the rhenium reserves at the Kudryavy volcano ore occurrence in the Rhenium and 605 fields, detailed testing was carried out on fumarole crusts, which are metasomatites with exhalation mineralization, which develop mainly on the surfaces of voids and along fissures. Sampling was accompanied by temperature measurements of discharged gases. Chip, grab, and channel samples were taken, the total number of which amounted to 178 in the Rhenium and 66 in Field 605. All samples were analyzed for Re, In, and Ge. Processing of data from this test showed that the contents of all three elements have significant positive correlation coefficients with temperature, but the dependence deviates significantly from linear. This is because each of these three elements has distinct temperature ranges for maximum deposition from fumarole gases: germanium is most intensively deposited at temperatures of 700–

800°C, rhenium at 550–650°C, and indium at 500–600°C (Fig. 9). Therefore, the temperature range for deposition of these elements from fumarole gases from highest to lower temperatures is as follows:

$$Ge \rightarrow Re \rightarrow In.$$

Thus, the lithogeochemical zoning in the crater part of Kudryavy volcano is due to two main reasons. The first is the ore element contents in hot fumarole gases, which directly depend on temperature. The second is that there are different optimal temperature ranges for deposition of different elements from gases. As a result, from northeast to southwest, from the hottest fumarole fields to less hot, high-temperature associations of elements in solid fumarole formations are replaced by medium- and low-temperature ones. Moreover, the Rhenium field, the temperatures of which, measured in 2015, varied within 220–520°C, is a transition between high- and medium- to low-temperature fields and is characterized by transitional ore element associations.

CONCLUSIONS

The main geochemical feature of the volcanic deposits of the crater part of Kudryavy volcano is that they are now undergoing the formation of exhalation ore mineralization with accumulation in solid volcanic formations of Re, Au, Ag, As, Bi, Cd, Cu, Ge, In, Mo, Pb, S, Sb, Se, Sn, Te, Tl, W, Zn, Rb, and Cs, which are supplied by high-temperature fumarole gases and are deposited when the temperature drops in the surface–atmosphere contact zone. The zonal distribution of lithogeochemical anomalies of associations of these elements reflects the temperature zoning of the fumarole fields and the differences in the temperature ranges for deposition of different elements from fumarole gases. Signatures have been revealed that similar exhalation mineralization processes in the recent geological past occurred on the neighboring extinct Sredny volcano. This suggests that similar processes occurred within other volcanic systems of similar genesis that formed on Iturup and other islands of the Kuril Arc. At the active Kudryavy volcano, the mining development of complex mineralization of rhenium and other metals is hardly possible at present due to continuing hazardous volcanic events. However, in the adjacent territory of Iturup Island and, possibly, on other islands of the Kuril Archipelago, we can expect the discovery of complex ore deposits formed by volcanic processes similar to those occurring now at Kudryavy volcano.

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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