

# The Hydrogeochemistry of Thermal Springs on Mutnovskii Volcano, Southern Kamchatka

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**Abstract**—This paper reports results from a hydrogeochemical study of thermal springs on Mutnovskii Volcano. The solutions of boiling pots and the pore water of thermal localities in the Donnoe Field were found to have an anomalous composition over a wide range of chemical elements, including rare earth elements (REE) and platinum metals (PGMs). The solutions of different springs exhibit considerable variations in their major and minor element compositions, indicating differences in the generation and upward transport of solutions. Physicochemical modeling showed that the mud pots studied could have been formed when the separate was ascending along an open fissure channel from the secondary zone of mixed boiling fluids. The high concentrations of titanium, vanadium, chromium, nickel, cobalt, REEs, and PGMs suggest a deep-seated source for these. The chemical forms of the elements in the solutions (primarily free aquaions) and the acidic environment favor high mobility of these elements. Deposition and concentration of these elements under near-surface conditions is unlikely.

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## INTRODUCTION

The hydrogeochemical features of thermal springs that discharge on the flanks and in the craters of active volcanoes depend on several exogenous and endogenous factors that affect magmatic fluids, which are separated from the melt during pneumatolytic differentiation (boiling) of near-surface magma bodies in the interior of volcanic edifices. It is the degree of dilution of the original fluid with ground (vadose) water, i.e., the fluid/meteoric water ratio that is the leading factor that controls the concentrations of chemical elements, as well as the physicochemical characteristics of the thermal solutions that reach the surface. The ratio may be higher or lower depending on the weather and hydrological conditions prevailing on the volcano in question, as well as on the geostructural features of fluid migration paths. Another important factor influencing the formation of volcanic thermal waters is the composition of the host volcanogenic rock masses through which the waters are circulating. The greatest effect in the extraction of chemical elements from host rocks is achieved by those thermal solutions that have less meteoric water [30].

The data published in the volcanological literature during the last decade on a wide range of trace elements and their specific associations in the thermal waters of active volcanoes [2, 29, 30, 32, etc.] enable one to quantitatively estimate the contributions of various endogenous and exogenous sources to the concentrations of chemical elements in order to produce the resulting surface solutions.

All of the hydrogeochemical data and the results of physicochemical modeling of the forms in which elements are found in solutions for actual conditions enable one to get an approximate idea of the structure of the volcanohydrothermal system for an object under study, as well as to understand the processes that are occurring during fluid migration, from the time the fluid was separated from the magma melt to its appearance at the ground surface.

The solutions of several gas-containing hydrothermal springs on Mutnovskii Volcano have chemical compositions that are strongly different from those of similar thermal occurrences on other known active volcanoes of the world where hydrogeochemical studies are being conducted at present [3]. This fact suggests that we may try to answer the question of the origin and possible sources of chemical elements in the thermal waters of Mutnovskii Volcano. With this end in view, the present paper contains a summary and an analysis of the data on the hydrogeochemistry of thermal solutions on Mutnovskii Volcano, suggesting an origin of these solutions based on thermodynamical modeling.

## THE OBJECT OF STUDY

Mutnovskii Volcano is one of the most active volcanoes in southern Kamchatka. Its edifice has a maximum height of 2323 m above sea level and consists of four proximate, successively evolving stratified cones with summit calderas and daughter intracaldera structures, and the

entire Mutnovskii massif involves numerous cones due to parasitic eruptions [25].

The study of Mutnovskii Volcano's past activity shows that the volcano went through its growth phase as far back as during Late Pleistocene time. Its Holocene activity was moderately explosive, being dominated by weak and moderate (mostly phreatic) eruptions without any lava effusion. Along with phreatic eruptions, those discharging juvenile basaltic material occurred during historical time. The material of the recent eruptions starting from 1904 was resurgent; this has been found to be the case for the eruptions of 1927–1929, 1960–1961, 2000, and 2007 [4, 7, 12, 18].

Mutnovskii Volcano was in a phase of fumarole hydrothermal activity with unusually high energy parameters (1800–1900 MW) during a rather long time interval, 1961 to 2000, and during the quiet periods between active phases in the early 2000s; this kind of activity is treated by several investigators as “passive eruption” [18, 22].

During these “quiescent” periods, the volcano's activity finds its way via an extensive network of thermal occurrences in active craters and on the volcano's flanks. It is from this volcano's craters that we know of the existence and constantly observe the high-temperature fumaroles of the Active Crater and the moderate- and low-temperature steam–gas discharges and thermal occurrences in the volcano's Northeast (NE) crater [3, 11, 26, 27, etc.].

The Active Crater is a young explosion crater that originated during the last phase in the activity of Mutnovskii Volcano (Fig. 1). The time of its generation is estimated to be 1200–1300 years ago [25]. At present the crater concentrates the most vigorous and hot steam–gas (fumarole) discharges of the volcano. Accordingly, it is there that the volcano has its maximum mass–energy. B.G. Polyak [22] and Yu.A. Taran et al. [27] estimate that the Active Crater discharges 200 t/day of SO<sub>2</sub> and 1600 MW of thermal energy.

The activity of the Northeast Crater is characterized by the presence of three main sets of gas and hydrothermal vents: two isolated areas (the Northern and the Southern) in the Donnoe fumarole field with temperatures of over 100°C, as well as vents in the Verkhnee fumarole field at temperatures above 300°C.

Owing to the high seismic activity and a practically continuous, spasmodic volcanic tremor in the area of the volcanic edifice [16], the fumaroles and thermal springs in the Donnoe field change their locations and intensity. Probably for this reason, the field produces springs with anomalous compositions; the study of these allows insights into the hydrodynamics and composition of overcritical magmatic fluids in highly permeable fluid conductors. This paper provides analytical data on the composition of springs on Mutnovskii Volcano and the results of physicochemical modeling in order to investigate the forms in which elements are found in solutions; this throws some light on the dynamics of the volcano's present-day magmatogenic fluid system.

## METHODS OF STUDY

In 2003–2006 we sampled springs, water reservoirs, and mud pots in the Donnoe field, water reservoirs in the bottom of the Active Crater (AC) and water from the lake in the Kirsanova Crater; this lake formed after the March 2000 eruption near the AC (Fig. 1).

This sampling was performed as follows: (1) In the Donnoe field on small boiling pots with transparent or semitransparent water; small stagnant reservoirs mostly formed of thawed water, including three reservoirs whose water has a dark red color; and boiling mud pots with color varying between yellowish white to intensely black.

(2) In the offshore part of the lake in the Kirsanova Crater (2003), when its water mass showed vigorous gas and hydrothermal activity; on the surface this involved intensive water turbulence and the discharge of great amounts of volcanic gases into the atmosphere.

(3) In two small lakes in the bottom of the Active Crater and several small temporary “pools” produced by atmospheric precipitation that is not present during dry weather periods.

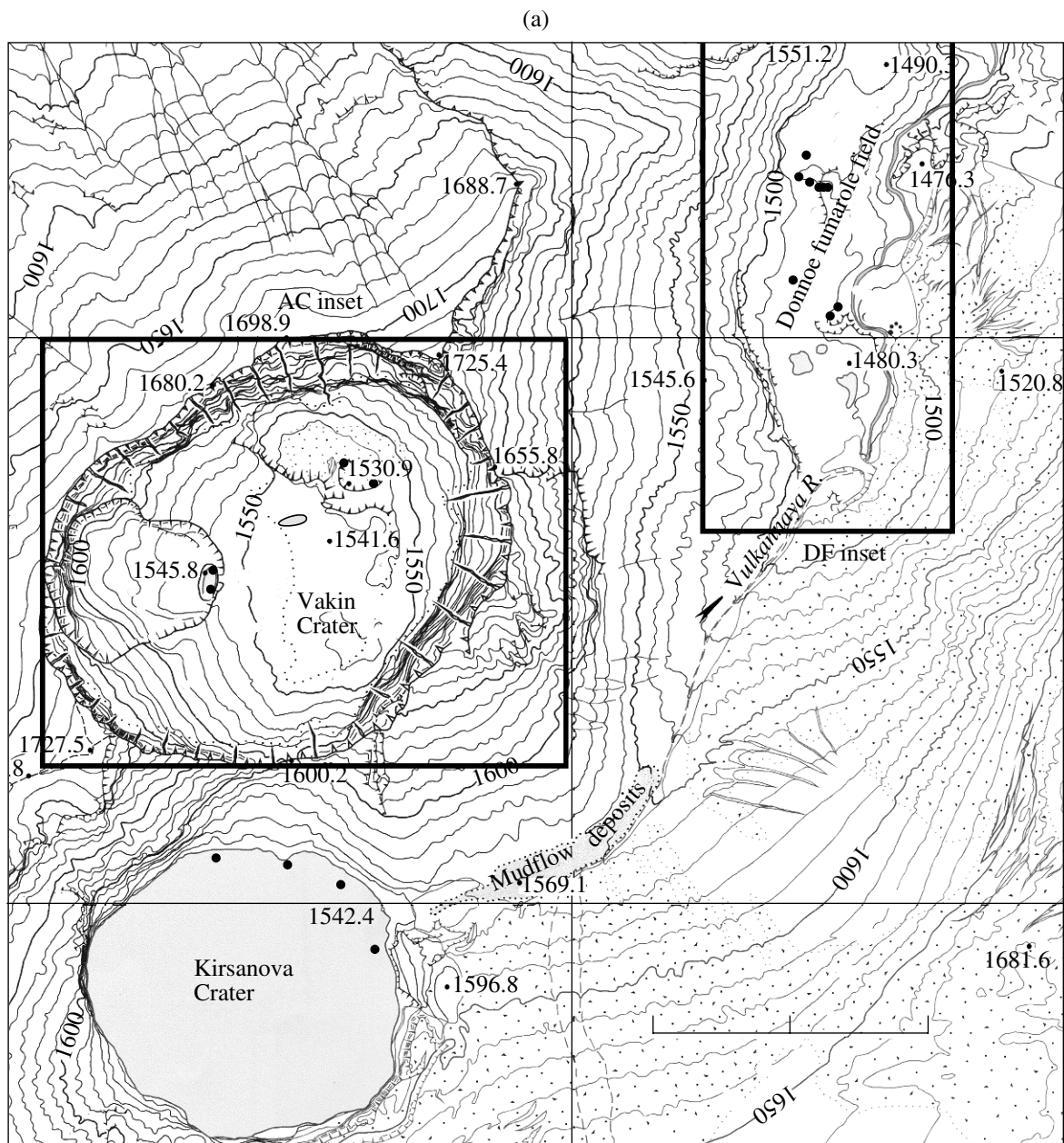
The samples were taken by a fluoroplastic probe; any contact with metals was precluded. When the water was sampled, we measured its pH, Eh, and  $T^{\circ}\text{C}$  at the site after allowing the suspended material to settle. The water samples were filtered during sampling through membrane filters with pore diameters of 0.45  $\mu\text{m}$  for laboratory analysis. The sampled solutions were stored in plastic containers for transportation.

(4) We also sampled soil and sublimates in thermal localities and from reservoir bottoms to squeeze the pore water from these:

- wet material from hydrothermally altered host rocks in thermal localities in the northern Donnoe field;
- bottom sediments of reservoirs in the Active Crater;
- and native sulfur from the inner parts of fumarole edifices (from fumaroles in the northern Donnoe field).

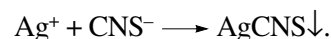
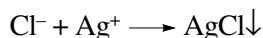
The samples were at once put in sealed plastic packages and the liquid phase was squeezed from these in the laboratory by a press at 100 atm.

The cation composition and the concentrations of trace elements in the solutions were determined by the ISP-AES method using an IRIS Advantage instrument at the Analytical Center of the Institute of Geology and Mineralogy at the Siberian Branch of the Russian Academy of Sciences (AC IGM SB RAS, Chemical Analyst L.B. Trofimova). The concentrations of REEs, as well as of Rb, Sr, Ba, Pb, Th, U in the solutions were determined by the ISP-AES method after dilution and acidulation using external calibration in combination with an inner standard; this was indium at a concentration of 1 ppb. The calibration was based on solutions of standard geological samples. The concentrations of platinum group elements, as well as of Hg, Tl, and Bi were estimated by a semi-quantitative method using an inner standard. All measurements were made by a high precision mass spectrometer (ELEMENT Finnigan Mat) by Chemical Analyst I.V. Nikolaeva.



**Fig. 1.** Sampling scheme for active craters on Mutnovskii Volcano: (a) map of Mutnovskii active craters (made by V.N. Dvigalo in 2003), (b) detailed sampling schemes for Mutnovskii active craters: in Donnoe field (DF) of the Northeast Crater and in the Active Crater (AC) (see insets in Fig. 1a). Small filled circles mark sampling sites.

The anion composition was determined by Analyst S.V. Sergeeva at the Institute of Volcanology and Seismology (IV&S) of the Far East Division (FED) of the Russian Academy of Sciences (RAS). The chloride ion was determined by the volumetric argentometric method with potassium or ammonium thiocyanogen [24]. Chloride ion was allowed to settle in a nitrogen acid environment by excess silver nitrate. This latter was filtered out by sulfocyanate of ammonium or potassium in the presence of an indicator, which was ferric ammonium sulfate:



The samples that were analyzed contained hydrogen sulfide, organic matter, iron (II and III), and aluminum, which hampered the determination of chloride ion. Their effect was removed by oxidizing the samples using hydrogen peroxide or potassium permanganate with subsequent settling of iron and aluminum. The samples were then filtered and analyzed using the procedure outlined above. Sulfate and fluoride ions were determined by specialized techniques that have been developed and tested at the IV&S FED RAS for appli-

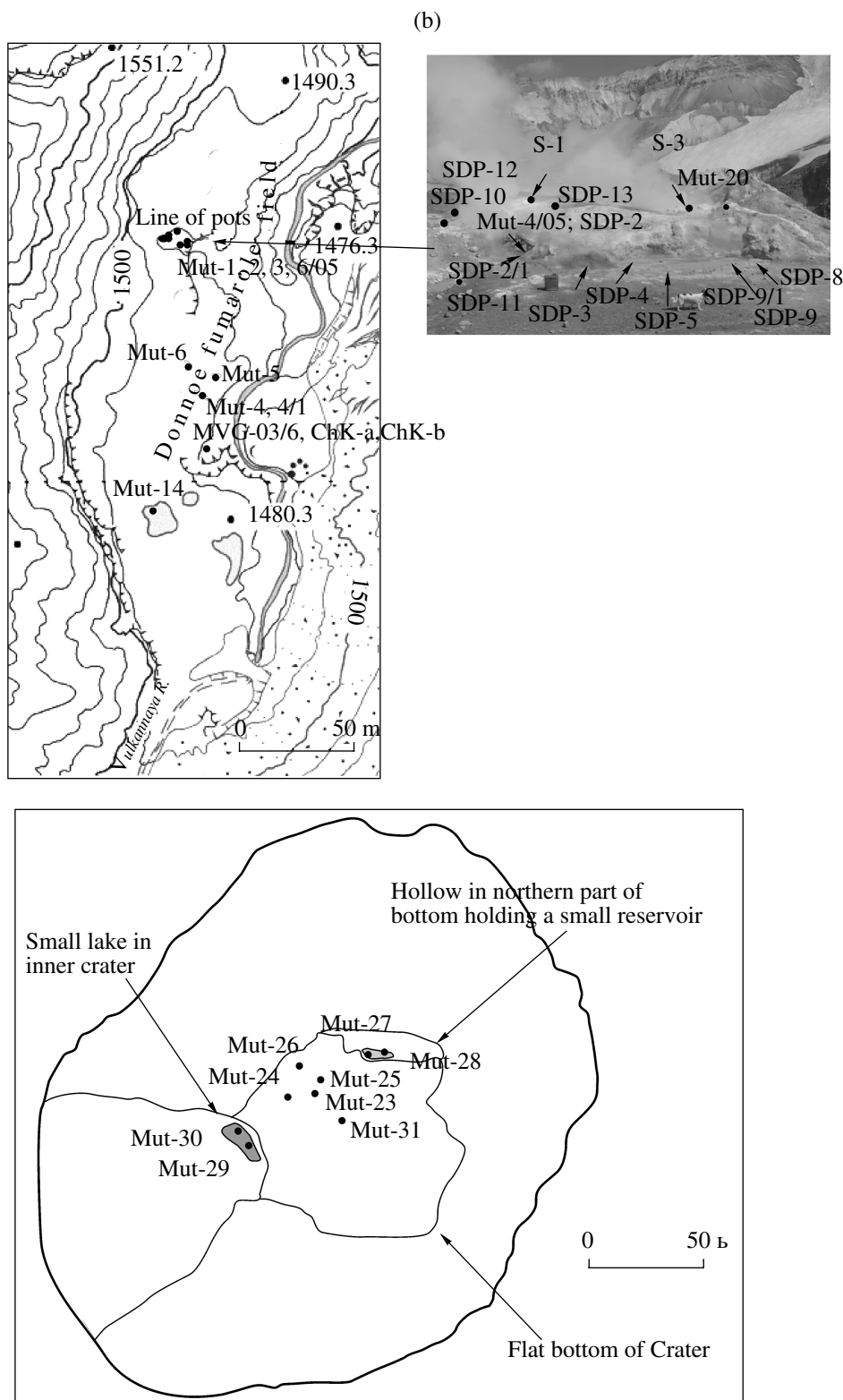
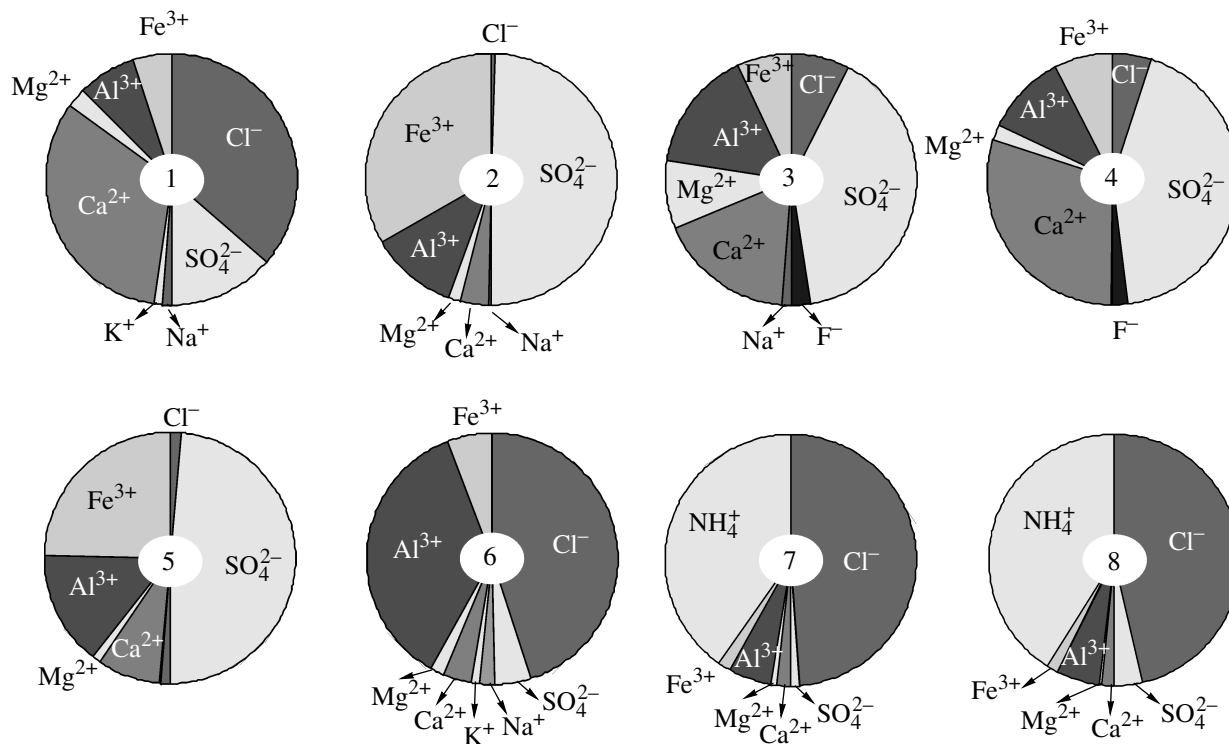


Fig. 1. Contd.

cation to specific acid and hyperacid samples. For sulfate ion analysis, the samples were first cleared of unwanted cations by passing the samples through sec-

tions with KU-2 cation-exchange resin. The sulfate ion was then determined by direct titration in an environment that contained acetone using the standard salt of



**Fig. 2.** Percentages of main ions in the solutions of Mutnovskii Volcano: (1), transparent pots and reservoirs in Donnoe field; (2), rust-colored reservoirs; (3), lake in Kirsanova crater; (4), reservoirs in Active Crater; (5), pore water in Active Crater; (6), mud pots in Donnoe field; (7), pore water of fumarole edifice (big fumarole no. S-1 in Donnoe field); and (8), pore water of fumarole edifice (small fumarole no. S-2 in Donnoe field).

barium in the presence of a nitchromaso indicator. The indicator interacts with barium in an acidic environment (pH 2.0), producing a contrasting reaction and a clear-cut violet-to-blue transition of the color of the solution under titration [21]. The fluoride ion was determined by potentiometric titration using a fluoride electrode and an I-130 pH meter. The unwanted influence of iron and aluminum cations was blocked by adding fluoride of sodium to the solutions with concentrations of 0.001N, 0.01N, and 0.1N.

## RESULTS

The solutions in gas-containing hydrothermal springs, pots, and reservoirs situated within Mutnovskii Volcano have very diverse compositions. All of them discharge acidic and superacidic waters (pH between – 0.52 and 3.62) with a high reduction–oxidation potential, which varies within a wide range, from 160 mV in light-colored pots to 750 mV in the pore solutions of thermal localities. Both the main ions and microelements show wide concentration variations. The anion composition mostly includes chloride and sulfate ions (Table 1, Fig. 2). Fluoride ions were found in the waters of rust-colored reservoirs (up to 11 mg/l), in the Kirsanova Crater lake (up to 110 mg/l), in the reservoirs of the Active Crater (up to 10 mg/l), and in the solutions of mud pots (up to 290 mg/l). Significant amounts of

phosphates were found in the solutions of all types. The highest amounts of  $\text{PO}_4^{2-}$  were found in the pore solutions of a thermal locality in the northern Donnoe field (6600 mg/l); the concentration reached 130 mg/l in the water of the pots. Substantial fluctuations in the relationship between chlorides and sulfates were detected in solutions of different origins: the transparent and semitransparent springs have approximately equal concentrations of chlorides and sulfates, while the solutions of mud pots and the pore waters of solfataras contain much greater amounts of chlorides in comparison with sulfates. The anion part (~90%) consists of chloride ions (up to 56 g/l in the mud pots and 24 g/l in the solfataras solutions). Conversely, sulfates have higher concentrations in all the other types of solution (the rust-colored reservoirs of the Donnoe field, the Kirsanova Crater lake, the Active Crater reservoirs, and the AC pore waters). The highest concentrations of sulfates were found in rust-colored reservoirs where the percentage of  $\text{SO}_4^{2-}$  is 99% (an average of 15 g/l). V.V. Ivanov [13] has classified the acid thermal springs by the main anion composition into sulfate–chloride (occasionally chloride) waters of “deep-seated” origin and sulfate waters of “surficial” origin. This approach was subsequently developed by G.M. Gavrilenko in the monitoring of Mutnovskii Volcano based on changes in

**Table 1.** Physicochemical parameters and the main ion composition of gas–hydrothermal springs in the Donnoe field, mg/l

Sample no.	T °C	pH	Eh	Cl <sup>-*</sup>	F <sup>-</sup>	SO <sub>4</sub> <sup>2-*</sup>	PO <sub>4</sub> <sup>2-</sup>	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	NH <sub>4</sub> <sup>+</sup>	Fe	Al <sup>3+</sup>
Transparent pots and reservoirs in the Donnoe fumarole field														
Mut-3/05	57	2.74	350	0.055	n.d.	0.12	n.a.	2.9	5.9	90	4.1	n.d.	9.6	14
Mut-6/05	28	2.88	510	0.070	n.d.	0.25	n.a.	2.6	5.6	120	3.7	n.d.	8.5	7.5
Mut-7/05	16	3.00	690	0.064	n.d.	0.05	n.a.	3.5	5.5	33	2.6	n.d.	17	7.1
Mut-14	14	3.30	550	0.085	n.d.	0.035	n.a.	0.96	0.34	23	1.5	n.d.	9.3	4.3
Mut-1/05	14	3.62	270	0.11	n.d.	0.27	n.a.	1.2	3.5	32	1.5	n.d.	0.67	0.49
Mut-2/05	14	3.51	160	0.26	n.d.	0.18	n.a.	1.7	0.77	32	1.5	n.d.	1.2	0.46
Lake in Kirsanova Crater														
Mut-9	32	1.37	490	0.53	88	6.5	8.6	71	7.4	690	220	n.d.	340	270
Mut-10	32	1.45	510	0.54	90	2.9	9.2	46	7.4	750	240	n.d.	200	280
MVG-03/1	32.5	1.59	n.d.	0.53	75	3.6	9.8	42	5.2	550	160	n.d.	210	240
MVG-03/7	32.5	1.41	n.d.	0.55	112	3.1	10	46	6.5	600	200	n.d.	230	250
Reservoirs in Active Crater (Vakin Crater)														
Mut-27	14	2.32	470	0.16	32	2.2	n.a.	17	1.5	500	20	0.1	160	110
Mut-28	14	2.70	500	0.18	34	2.0	n.a.	7.7	1.1	590	24	0.12	130	99
Mut-29	14	1.82	510	0.21	43	2.0	n.a.	6.5	0.45	650	18	0.15	140	66
Mut-30	14	2.41	520	0.22	39	1.8	n.a.	6.8	0.46	520	14	0.22	100	65
Mut-31	14	2.00	630	0.17	25	1.7	n.a.	8.9	0.85	360	12	0.1	120	80
Rust-colored reservoirs														
Mut-4	14	2.37	660	0.11	9.1	11	n.a.	41.5	2.9	522	107	1.6	2500	490
Mut-5	14	1.90	720	0.18	14.1	28	n.a.	14	1.9	558	200	2.4	7800	850
Mut-6	14	1.60	680	0.14	10	15	10.5	33.7	1.0	280	145	n.d.	5800	780
Mut-4/1	14	0.55	710	0.15	7.0	7.6	2.8	55	0.42	530	45	5.2	1000	580
Mud pots														
Mut-4/05	87	0.03	715	56	1.9	2.2	37	133	200	110	29	n.d.	330	720
SDP-2	87	-0.24	612	34	2.03	1.6	33	190	190	270	110	n.d.	330	1670
SDP-2/1	72	-0.52	500	27	3.7	0.59	27	160	240	230	100	110	310	800
SDP-3	87	-0.31	590	31	0.38	3.3	40	150	200	150	53	30	170	1860
SDP-4	83	0.18	510	13	30	2.7	15	67	120	53	17	10	64	1100
SDP-5	84	-0.03	530	32	115	8.5	120	500	740	170	46	18	190	2700
SDP-6	60	1.76	240	2.5	0.009	0.65	0.68	5.5	7.3	40	1.4	0.25	7.6	170
SDP-7	75	0.46	550	18	25	2.7	45	160	41	700	160	5.4	390	2300
SDP-8	76	0.05	310	3.2	0.12	0.7	21	100	130	62	19	12	56	750
SDP-9	75	-0.11	300	15	0.25	2.2	65	270	380	120	39	30	140	1870
ChK-a	76	2.00	310	1.1	7.4	1.7	0.34	62	8.8	400	94	10	6.3	710
ChK-b	76	2.10	250	1.3	0.41	1.5	0.28	47	6.8	280	72	1.9	6.4	47
MVG-03/6	76	0.46	270	36	290	11	130	200	160	1600	510	11	4300	3000
Pore water of thermal locality														
Mut-20		0.23	750	6.8	n.d.	8.7	920	1450	120	53	1850	n.d.	1120	6020
SDP-10		0.50	726	7.3	n.d.	11	6600	5500	350	96	10300	n.d.	52900	14800
SDP-11		0.46	619	1.9	n.d.	14	1240	5400	400	70	5300	n.d.	9500	9900
SDP-12		1.80	669	8.4	n.d.	9.2	4300	7400	410	70	7300	n.d.	23300	7300
SDP-13		0.22	659	15	n.d.	12	4200	6400	380	84	8100	n.d.	16500	14300
SDP-14		1.34	682	6.0	n.d.	9.0	11	93	110	180	71	n.d.	820	400
Pore water of sulfuric fumaroles														
S-1		0.50	660	21	n.a.	0.66	15	110	80	220	110	4020	310	490
S-3		0.35	680	24	n.a.	2.6	23	71	30	370	84	10500	400	680

Note: \* Cl and SO<sub>4</sub><sup>2-</sup> are in g/l; here and below, n.a. means “the element was not analyzed for presence” and n.d. means “not detected.”

the  $\text{Cl}/\text{SO}_4^{2-}$  ratio in the Vulkannaya River [6, 7]. The fraction of the magmatic HCl seems to be much greater in pot water and during the generation of solfataras than was the case for the generation of other types of spring.

The cation composition of the solutions investigated here is also variable: calcium is the dominant element in the background springs and reservoirs of the Active Crater, and in the lake in Kirsanova Crater (Fig. 2). The rust-colored reservoirs and pore water are dominated by iron (up to 66%), with aluminum prevailing in the mud pot solutions. The pore solutions from solfatara sublimates hold a special place. The main ion there is ammonium, which evidently prevails over all the other cations (~80%, up to 10.5 g/l). Aluminum is the next by percentage in these solutions (11%, up to 680 mg/l).

The fraction of microelements (this group as the elements called "trace elements" in the western literature) in the overall mineral content of the solutions is a few tenths of a percent in background springs, mud pots and pore water of the Active Crater. It is substantially lower in rust-colored reservoirs and small lakes in the Active Crater (between 0.06 and 0.08%) and is substantially higher in the pore solutions of thermal localities and solfataras, making up 1.5 and 1.2% of the total mineralization, respectively (Table 2). The composition of the dominant microelements also differs. Those in the rust-colored reservoirs can be divided into several sets by abundance: the leading microelements are Mn and Cu (amounting to equal percentages among the microelements, with each at 23% or 3.4 mg/l), the next in abundance are As and Zn (14 and 12%, respectively), the contributions of Cd and Sr are 6% each; the last set of microelements includes Cr, Ni, Co, V, and B; these total nearly 15%. The elements Li, Ti, Ba, and Be, which are present at 0.*n* mg/l, do not exceed 0.5% in the microelement composition. The lake in the Kirsanova Crater has over 50% of Mn the total microelement amount. The solutions of the Active Crater (reservoirs and pore waters) are dominated by copper; its concentration reaches nearly 10 mg/l in the pore waters and the total relative amount is of the order of 30%, with rather high concentrations being also found for Mn, Sr, and As. The mud pots stand out upon the background of the compositions found in springs and reservoirs. The mud pot solutions differ from the thermal solutions known for volcanic regions in having anomalously high concentrations of Cr, Ti, Ni, and V. The majority of the microelement composition of these solutions consists of boron (41 mg/l, corresponding to 58%); Cr, Sr, Ti, Mn, Ni, V, Nb are also found in considerable amounts (greater than 1 mg/l). The highest concentration of chromium in the solutions of the Otkrytyi Pot (SDP-2) reached 60 mg/l [3] (Table 2). Auippa et al. [29] analyzed solutions found on Mount Vulcano (Vulcano Island, Liparian Is.) where chromium was found in a concentration of 45 mg/l in the Vasco Spring (unfortunately, without any discussion of this phenomenon). In addition, significant concentrations of Ga, Ba, and Mo were detected in the solutions of the mud pots. The leading microelements in the pore waters of the thermal localities

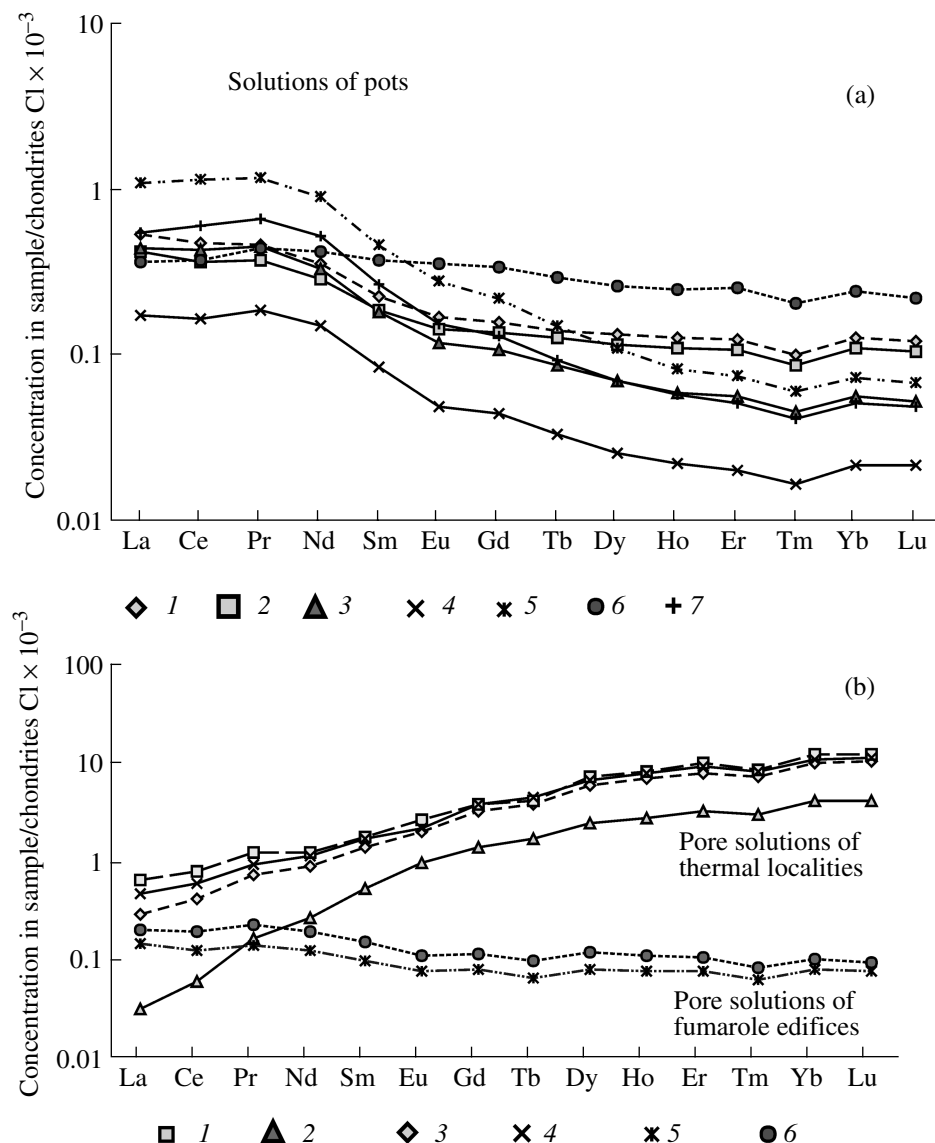
are V, B, Ti, and Mn; the concentrations of these are in excess of 150 mg/l. There are very high concentrations of As, Zn, Cu, Cr, Li, Zr, Sr, Ni, and Co. The dominant microelement in the pore solutions of solfataras is boron, whose concentrations are 290–330 mg/l, or 86 and 61% in the microelement composition. The second element in order of significance in these solutions is As, with concentrations reaching 150 mg/l; antimony is found in substantially lower amounts. The next element by abundance in these solutions is titanium, whose fugacity is not nearly as high as that of As and Sb. Manganese, zinc, zirconium, and vanadium have concentrations of a few mg/l. One should also pay attention to lead, chromium, cobalt, and nickel, which do not have concentrations as high as those of the above-mentioned microelements, but seem to be considerable when compared with those in thermal springs, pots, and even in the pore solutions of the thermal localities. All these elements do not constitute a characteristic feature of any individual set of springs. To a greater or less degree they are present in different types, as, e.g., Cr; the concentrations of this element in the pore waters of the Active Crater and the Donnoe field and in its rust-colored reservoirs, as well as in the water of the Kirsanova Crater lake, have low values between 0.*n* and *n* mg/l. The concentrations of Co and Ni are 0.*n* mg/l in the springs and reach a few mg/l in the pore solutions. The boron concentration in the pore waters of the Active Crater is equal to 8 mg/l.

The concentrations and distribution of rare earth elements calls for a special discussion. High REE concentrations constitute another distinguishing feature of the solutions of the pots and thermal localities. Compared with the highest concentrations for acid sulfate and chloride sulfate waters of the Yellowstone hydrothermal system as reported in [34], the REE concentrations in the thermal solutions of Mutnovskii Volcano are several times greater, while one of the thermal pots (SDP-5) showed an increase by a factor of 14. The total concentrations of REEs reach 2 mg/l in the pots and vary between 3.6 and 12 mg/l in the solutions of the thermal localities (Table 3). A similar concentration value was found in the Bol'shoi Pot on Ebeko Volcano [2] and in the Verkhne-Yur'evskie springs, where  $\Sigma\text{REE}$  reached 690 and 360  $\mu\text{g/l}$ , respectively. However, the Mutnovskii pots have appreciably higher REE concentrations. The REE concentration in the solutions of the pots is similar, with the exception of the SDP-7 thermal pot, where the spectral curve is a flat line, which means that there is a depletion in light REEs and an appreciable enrichment with heavy REEs (Fig. 3a). The solutions of the thermal localities show a completely different REE distribution; the heavy part is considerably greater than the light part (Fig. 3b). The REE distributions for the pore solutions of the Donnoe solfataras are practically replicas of the configuration shown by the curve of the SDP-7 pot. Considering that all these solutions were found in a comparatively restricted area, it is difficult to find an explanation of this considerable difference in the redistribution of the REEs.

**Table 2.** Concentrations of some chemical elements in the solutions of gas-hydrothermal springs on Mutnovskii Volcano, mg/l

Sample no.	SiO <sub>2</sub>	Mn	Ba	Sr	As	Zn	Cu	Ti	V	Co	Cr	Ni	Be	B
Transparent pots and reservoirs in the Donnoe fumarole field														
Mut-3/05	110	0.13	0.056	0.19	<0.05	0.088	0.029	0.006	0.052	<0.002	0.01	<0.003	<0.001	0.22
Mut-6/05	54	0.13	0.13	0.26	<0.05	0.089	0.034	0.17	0.064	<0.002	<0.003	<0.003	<0.001	0.16
Mut-7/05	24	0.089	0.05	0.24	<0.05	0.088	0.047	<0.005	<0.005	<0.002	<0.003	<0.003	<0.001	0.15
Mut-14	7.0	0.098	0.017	0.06	<0.05	0.12	0.028	0.0041	0.0072	0.0037	<0.003	<0.003	<0.001	<0.003
Mut-1/05	1.6	0.035	0.023	0.073	<0.05	0.072	0.022	<0.005	<0.005	<0.002	<0.003	0.007	<0.001	0.01
Mut-2/05	3.2	0.036	0.039	0.082	<0.05	0.087	0.04	<0.005	<0.005	<0.002	<0.003	<0.003	<0.001	<0.003
Lake in Kirsanova Crater														
Mut-9	190	7.2	0.061	0.88	0.75	1.2	0.012	0.43	1.1	0.0475	0.42	0.13	0.0053	0.9
Mut-10	190	7.3	0.061	0.87	0.76	1.3	0.011	0.44	1.2	0.047	0.095	0.0093	0.0054	1.5
MVG-03/1	190	6.9	0.34	0.70	0.46	1.2	<0.002	0.38	1.3	0.037	0.22	0.032	<0.001	1.0
MVG-03/7	210	6.8	0.48	0.80	0.71	1.2	<0.002	0.53	1.3	0.048	0.099	0.034	0.0051	1.2
Reservoirs in Active Crater (Vakin Crater)														
Mut-27	37	0.90	0.0091	0.71	<0.05	0.14	1.3	0.045	0.20	0.026	<0.003	<0.003	<0.001	<0.003
Mut-28	34	0.88	0.0065	0.65	<0.05	0.12	1.2	0.041	0.20	0.039	<0.003	<0.003	<0.001	<0.003
Mut-29	29	0.54	0.0054	0.44	<0.05	0.086	0.33	0.037	0.18	0.029	<0.003	<0.003	<0.001	<0.003
Mut-30	28	0.52	0.0057	0.46	<0.05	0.057	0.33	0.035	0.17	0.0087	<0.003	<0.003	<0.001	<0.003
Mut-31	13	0.39	0.014	0.96	<0.05	0.026	1.0	0.17	<0.005	0.037	<0.003	<0.003	<0.001	<0.003
Pore water in sediment for reservoirs in Active Crater														
Mut-25	150	1.3	0.022	1.8	<0.05	1.6	1.1	0.014	0.31	0.15	2.6	0.15	<0.001	<0.003
Mut-26	260	3.9	0.058	3.7	5.1	15	24	0.84	3.2	1.7	0.84	1.3	0.0048	7.5
Mut-27	190	3.1	0.045	1.3	<0.05	3.0	1.1	<0.005	0.14	0.23	2.7	0.29	0.0021	<0.003
Mut-25	200	1.1	0.017	1.9	<0.05	0.94	1.6	<0.005	0.37	0.17	0.89	0.11	<0.001	2.2
Mut-27'	190	2.1	0.015	1.1	<0.05	2.6	2.1	0.0085	<0.005	0.18	0.83	0.084	<0.001	<0.003
Mut-29	200	1.1	0.013	1.9	10	0.94	39	<0.005	0.37	7.3	1.3	0.11	0.0055	2.0
Mut-29	270	1.2	0.014	1.3	1.5	1.4	1.2	<0.005	1.2	0.63	1.2	0.35	<0.001	0.81
Mut-31	220	1.1	0.032	2.8	4.8	1.3	5.9	0.12	0.9	0.45	0.5	0.28	<0.001	1.7
Rust-colored reservoirs														
Mut-4	190	1.7	0.018	1.0	<0.05	0.88	0.71	<0.005	<0.005	0.65	0.053	0.49	0.006	0.48
Mut-5	150	0.63	0.017	0.86	<0.05	0.32	0.34	<0.005	<0.005	0.23	0.065	0.18	0.0014	0.28
Mut-6	170	11	<0.001	1.3	5.7	2.3	10	0.013	0.82	2.7	0.34	1.9	0.017	<0.003
Mut-4/1	170	2.5	0.012	0.89	0.2	1.4	1.5	0.004	0.06	0.66	0.11	0.61	0.0074	0.72
Mud pots														
Mut-4 /05	100	5.5	0.24	5.6	0.39	0.45	0.62	4.2	2.4	0.48	60	33	<0.001	52
SDP-2	190	5.9	1.8	5.5	0.36	0.69	0.06	15	2.6	0.08	0.39	0.11	0.003	160
SDP-2/1	87	5.5	1.5	4.3	0.06	0.67	0.02	10	2.2	0.08	4.6	1.9	<0.001	130
SDP-3	220	2.8	1.9	6.5	0.12	0.43	0.06	7.9	2.3	0.03	0.38	0.12	<0.001	33
SDP-4	270	1.1	1.02	2.1	0.23	0.18	0.01	0.78	0.92	0.02	2.3	0.93	<0.001	9.1
SDP-5	240	3.0	0.63	20	0.61	0.39	0.050	3.2	4.5	0.05	5.0	1.8	0.0063	32
SDP-6	7.9	0.07	0.05	0.17	<0.05	0.09	0.02	0.02	0.040	0.002	0.14	0.080	<0.001	0.53
SDP-7	400	5.3	0.36	12	0.50	1.3	0.25	1.2	5.4	0.05	4.4	1.6	0.0047	30
SDP-8	250	1.0	0.38	2.7	<0.05	0.40	0.04	0.88	1.0	0.010	0.92	0.38	0.0016	9.0
SDP-9	320	2.0	0.29	11	<0.05	0.58	0.09	5.1	2.8	0.030	0.57	0.07	<0.001	17
ChK-a	130	4.0	0.04	0.2	<0.05	0.10	0.01	0.01	0.08	<0.002	<0.003	<0.003	<0.001	3.8
ChK-b	100	3.1	0.04	0.2	<0.05	0.12	0.02	0.01	0.06	<0.002	0.26	0.12	<0.001	2.9
MVG-03/6	1100	8.1	0.27	13	<0.05	1.9	<0.002	4.4	13	0.066	2.1	0.55	0.014	92
Pore water of thermal localities														
Mut-20	8.4	30	<0.001	3.7	21	38	5.4	114	140	3.4	11	3.5	<0.001	90
SDP-10	20	400	0.21	4.6	82	110	120	180	430	5.2	18	7.1	0.99	450
SDP-11	5.9	91	0.13	3.5	67	33	14	270	280	1.5	8.5	1.4	0.70	110
SDP-12	8.6	140	0.13	5.2	12	36	13	360	370	2.5	11	3.5	0.81	89
SDP-13	13	230	0.06	7.2	17	73	15	100	350	1.4	18	2.7	0.89	340
SDP-14	50	3.7	0.47	1.7	0.95	2.8	6.1	5.1	1.1	1.1	0.33	0.47	<0.001	29
Pore water of sulfuric fumaroles														
S-/06	36	5.3	0.61	1.8	26	2.4	0.85	5.7	1.4	0.12	0.19	0.11	0.0030	330
S-3/06	59	4.3	0.39	2.8	150	1.6	2.3	7.2	1.9	0.20	0.36	0.19	0.0035	290



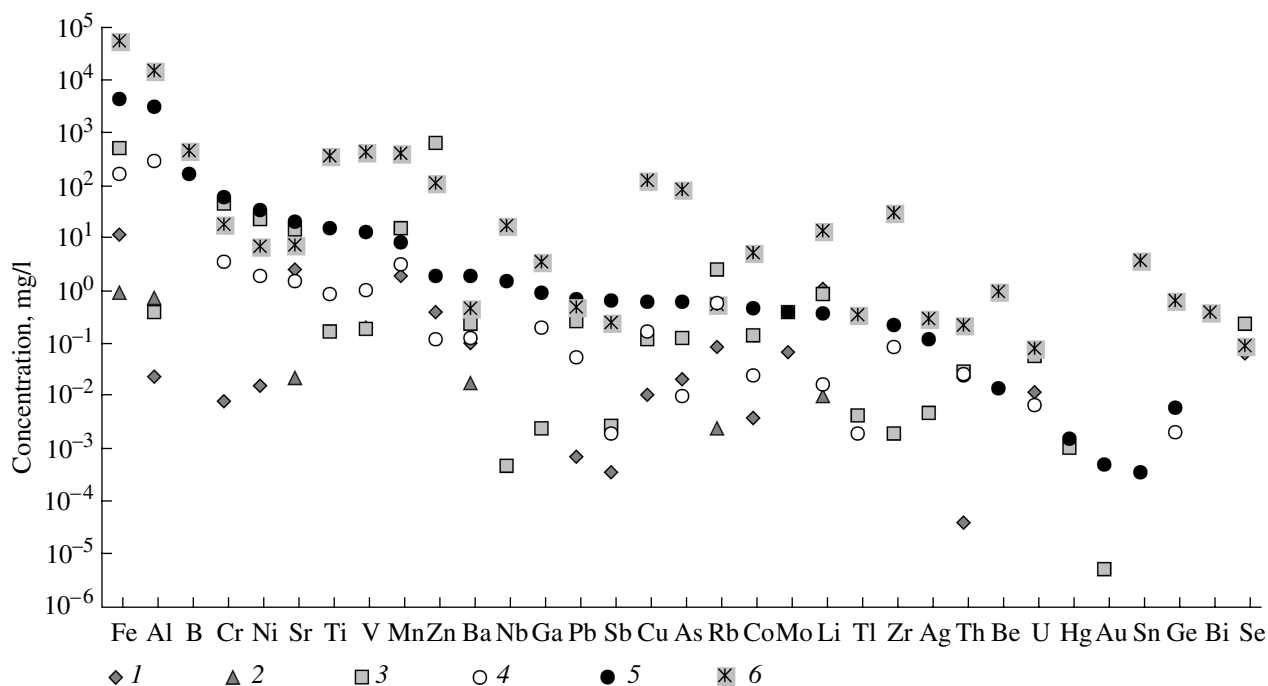


**Fig. 3.** The REE distribution in the solutions of mud pots (a), pore waters of thermal localities and fumarole edifices (b). For fragment (a): (1), SDP-2; (2), SDP-2/1; (3), SDP-3; (4), SDP-4; (5), SDP-5; (6), SDP-7; (7), SDP-9. For fragment (b): (1), SDP-10; (2), SDP-11; (3), SDP-12; (4), SDP-13; (5), S-1; and (6), S-3.

## DISCUSSION

The Mutnovskii solutions are unique in composition compared with the thermal springs in other volcanic regions worldwide as reported in the literature. Figure 4 shows published data showing the highest concentrations of elements in the thermal waters of Mount Etna, Sicily [30], Mt. Vulcano, Vulcano I., Liparian Is., [29], El Chichon Volcano, southern Mexico [41], and Ebeko Volcano, Paramushir I., Kuril Is. [2] juxtaposed with the highest concentrations found in the solutions of boiling mud pots and pore waters of Mutnovskii. One especially notices the T—V—Cr—Co—Ni association. The elements of this group behave very similarly, as shown by the high correlation coefficients of their mutual relationships (Table 4). The concentrations of Ti and V in the Mutnovskii pots are two

orders of magnitudes greater than those in the Vulcano solutions, while the pore solutions of the thermal localities contain Ti and V in extremely high concentrations (greater than 100 mg/l). K.K. Zelenov [8] reports titanium concentrations in the crater lake of Kawah Ijen Volcano, Indonesia (23.42 mg/l); the concentration is much higher at the source of the Banjipati River flowing from the lake and in its upper reaches due to evaporation from the small rivulets that contribute to that river. The difference in the concentrations of Co, Cr, and Ni in the Mutnovskii pots is not so glaring, but when considered in association with Ti and V, these elements may provide evidence of an unusual source that supplies them into the solutions we have investigated. In addition, one may well wonder at the high concentrations of such "exotic" elements as Nb, Ga, Zr, and



**Fig. 4.** Highest concentrations of chemical elements in the solutions of gas-hydrothermal springs in some volcanic regions: (1) Etna [28], (2) El Chichon [41], (3) Vulcano [27], (4) Ebeko [2], (5) mud pots on Mutnovskii Volcano, (6) pore solutions of thermal localities.

Ti. Considering the sources of elements, it is of interest to study the balance between major elements and minor elements in the rocks of the volcano's edifice (Table 5). The rocks analyzed have compositions similar to those of low potassium andesites and basalts typical of eastern and southern Kamchatka [23]. The concentrations of nearly all microelements analyzed in the andesite are below the clarke values [5, 38], except for V, Co, and Cu (these are at near-clarke levels) (Table 5). The basalts present a similar pattern. Some slight excess was only recorded for V, Ge, Ag, Cd, and Pb. It follows from this that the volcano's rocks do not contain high concentrations of the elements for which increased amounts have been found in the thermal solutions. Explanations of the anomalies discussed are thus to be sought in the composition of the magma fluid and in the specific structural pathways of its transport.

The presence of REEs in water is unambiguously considered as leaching from the host rocks in surficial conditions [34, 39, 43], and the stability of these elements in solutions is directly controlled by the pH conditions and the redox potential (Eh) [36]. Studies on the abundance of REEs in thermal water showed that the concentrations of these elements is in direct correlation with the acidity of the respective solutions [31, 35], but the correlation is not strict. It has been hypothesized that there are some other factors that can strongly affect the supply and presence of these elements in solutions. Krainov [17] reports the concentration of REEs in the ground water of an agpaite nephelinitic syenite massif to be  $\Sigma\text{REE} = 8.7\text{--}664 \mu\text{g/l}$ , in

spite of the fact that the water is interacting with rocks with increased REE concentrations. We can probably state two main causes of high REE concentrations in the solutions: (1) the physicochemical parameters of the fluids (a superacidic environment and high temperature), which possess a high capacity for dissolving these elements [14], (2) features peculiar to the upward transport of the REEs. Since the rocks that compose the edifice of Mutnovskii Volcano have insignificant concentrations of REEs, it follows that the anomalously high concentrations of these in volcanic water must be related to a deep-seated source of the fluid, as well as to a high degree of enrichment occurring at geochemical barriers in the volcano's interior that we have no knowledge of as yet.

Apart from the data quoted above, platinum group elements were detected in the solutions of the pots and thermal localities,  $\Sigma(\text{Pd, Re, Pt})$ , being as high as  $4 \mu\text{g/l}$  in the pots and up to  $180 \mu\text{g/l}$  in the pore solutions (Table 3). Hanley [33] remarks that high chloride fluids in high temperature hydrothermal magmatic systems may be responsible for an initial concentration and redistribution of PGEs, which is controlled by complexing with HCl ( $\text{PtCl}_3\text{H}$ ). The solubility of Pt can be very high at increased temperatures ( $800\text{--}900^\circ\text{C}$ ) and in solutions of high salinity. The theoretical predictions of PGE solubility are substantially below the actual solubility. Bisulfide complexes with  $\text{HS}^-$  are likely to occur in colder environments [44]. A stable Co-Cr-Ni-Ti-V association in the solutions and a significant correlation of the PGE distribution with Co (0.965), V (0.915), Cu (0.888), Ni (0.863), and Cr (0.845)

**Table 3.** Concentrations of some trace elements, REEs, and PGEs in solutions of boiling pots and in pore water, µg/l

Sample no.	Th	U	Tl	Hg	Au	Pd	Re	Pt	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Solutions of mud pots																						
SDP-2	14	4.3	360	1.6	0.53	2.2	<0.1	1.8	170	380	56	220	44	12	41	6.6	44	9.1	26	4.1	27	3.9
SDP-2/1	11	3.3	120	0.40	0.34	1.8	<0.1	0.9	130	300	45	170	37	11	36	6.1	38	7.9	23	3.6	23	3.4
SDP-3	11	2.6	45	0.30	0.22	1.2	<0.1	0.32	140	350	55	200	36	8.8	28	4.1	23	4.3	12	1.9	12	1.7
SDP-4	3.9	1.1	2.9	0.40	0.16	0.2	<0.1	0.062	55	130	23	92	17	3.6	12	1.6	8.4	1.6	4.3	0.7	4.6	0.7
SDP-5	25	6.8	29	0.10	0.25	1.4	<0.1	0.45	340	920	140	540	90	21	58	7.2	35	6.0	16	2.5	16	2.2
SDP-7	2.4	1.4	8.2	0.20	0.29	0.5	<0.1	0.79	110	300	54	260	74	26	88	14	85	18	53	8.5	51	7.2
SDP-9	13	3.3	6.9	1.0	0.11	0.2	<0.1	0.04	170	490	82	310	52	11	34	4.5	23	4.2	11	1.7	11	1.6
SDP-9'	11	3.3	82	0.6	0.27	1.1	<0.1	0.62	160	410	65	256	50	13	42	6.3	37	7.3	21	3.3	21	3.0
Pore water of thermal localities																						
SDP-10	220	81	350	n.d.	<0.1	19	62	100	200	650	150	750	350	200	1000	200	2350	600	2150	350	2550	400
SDP-11	120	64	280	n.d.	<0.1	34	<0.1	64	10	50	20	164	104	72	360	80	806	202	678	124	860	136
SDP-12	220	72	120	n.d.	<0.1	30	2.0	39	89	350	90	540	280	150	830	190	1940	500	1700	300	2100	340
SDP-13	210	64	230	n.d.	<0.1	12	3.2	52	150	500	120	680	340	160	1000	210	2200	560	1940	340	2300	370

supports simultaneous transport of these elements by magmatic fluids.

We tried to describe the evolution of the fluid and the resulting mixed solutions by a physicochemical model in order to explain the mechanism responsible for generating the solutions. The model describes the migration of a fluid from a magma chamber to the surface.

This modeling was carried out by V.N. Sharapov's method [28] using the SelectorWin program with the flow-reaction-vessel modification [15]. The movement of magma fluid from the boundary where it separated from a crystallizing basite melt was treated as a nonisothermal flow along a vertical fissure channel from the intrusion contact to the volcano's surface. Our modeling of the fluid-rock interaction incorporated the fact that the volcanic edifice contains alternating basalts, basaltic andesites, and dacites, as well as highly porous horizons (tuff) and cracked zones (Fig. 5). The intrusion was assumed to lie at depths of 1–10 km from the Earth's surface. The relative weight of the fluid is of the order of 3% of the weight of the crystallizing melt, the fluid  $pO_2$  corresponds to the interval between the WZ and Ohem buffers. The pressure was varied between 3000 and 500–300 bars in the space between the "source" and reaction vessel no. 20,  $T$  was between 1000 °C and 300 °C. The independent components at the "source" included Si, Al, Ti, Fe, Ca, Mg, Na, K, C, H, O, Cl, F, N, and S;  $C/H = 1-0.01$ ;  $S/Cl = 1-0.2$ ;  $F/Cl = 0.3-0.1$ ; and  $N/F = 1$ . We used the thermodynamic data bases from [37, 45, 46].

The extraction of major and trace elements does not proceed vigorously under reduction conditions (with the initial  $pO_2 < 14$ ). The extraction goes on best for Mn, Mo, and Co (their concentrations reach a few mg/l in gases). When the gas is condensed, acid reoxidized solutions are formed (pH 4.5, Eh -0.2) with appreciable concentrations of metals (mg/l): 0.0005 for Co, 0.000001 for Mo, and 2 for Mn. When the concentrations of Cl, F, and S are increased by an order, the components gain several orders in mobility. There is a gradual accumulation of Co, Cr, Mo, Ni, V, Al, Mn, and Ti in the gas phase in the last reservoir. However, the concentrations of most components in the condensate of magmatic gas do not exceed a few mg/l. Substantial extraction of a component from basalt requires the presence of oxidized high temperature gases, which can form in the top of the Mutnovskii volcanic hydrothermal system when magmatogenic fluids mix with the superheated steam of shallow oxygen-rich waters [1]. When the magmatogenic fluid has been separated, it is saturated with (mostly) major components, both when interacting with the chamber rocks and with the rocks in the lower section above the chamber (Fig. 6). Further ascent of the magmatogenic fluid can either produce its condensation and a zone of condensed magmatogenic fluids or lead to interaction with shallow waters, resulting in high temperature gases that are enriched with acidic components and oxygen from the gases. When such gases interact with rocks, they leach many elements, including both essential and trace elements. The mixed gases may be

**Table 4.** Correlation coefficients ( $r_{\beta}$ ) between some elements

$n = 39$	Ti	V	Cr	Ni
V	<b>0.888</b>			
Cr	0.288	<i>0.368</i>		
Ni	0.129	0.164	<b>0.967</b>	
Co	<b>0.666</b>	<b>0.774</b>	<i>0.339</i>	0.233

Note:  $n$  is the number of analyses; the values of  $r_{\beta}$  in bold are for  $\beta = 1\%$ , those in italics are for  $\beta = 5\%$ .

**Table 5.** Composition of basalts and andesites for Mut-21 novskii Volcano and concentrations of some trace elements

Component	Basalt	Andesite
SiO <sub>2</sub>	50.07	59.52
TiO <sub>2</sub>	1.09	0.95
Al <sub>2</sub> O <sub>3</sub>	19.25	17.52
Fe <sub>2</sub> O <sub>3</sub>	11.67	7.69
MnO	0.16	0.12
MgO	4.67	2.21
CaO	9.75	6.98
Na <sub>2</sub> O	2.45	3.35
K <sub>2</sub> O	0.31	1.43
P <sub>2</sub> O <sub>5</sub>	0.17	0.19
V	280	112
Cr	120	11.4
Ni	24	13.6
Co	29	16
Cu	110	63
Zn	87	55

Note: Concentrations of oxides in silicate group are in %, those of trace elements are in g/t.

transported upward to the surface or to the condensation interface. When on the surface, gases of this composition and temperature are discharged in the Active Crater. The next geochemical barrier for mixed condensed fluids will be the boundary of secondary boiling. A brine zone forms under the boundary of secondary boiling. The gas phase absorbs greater amounts of water and some acidic gases, while the major and trace components remain entirely in the separate. It is in these separates that the appropriate concentrations of elements are reached. Further passage of the fluids to the surface can occur unhampered (along open channels); it appears that this is the mechanism whereby the mud pots are generated in the Donnoe field. As well, the processes occurring in the interior of the volcanic edifice may be complicated by interaction with the next-to-come portions of meteor and formation water and by secondary condensation, which causes dilution, thus dramatically reducing the concentrations. This is observed

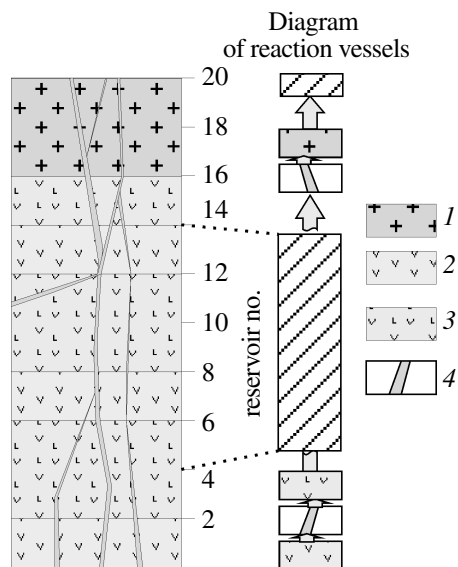


Fig. 5. Structure of the column to be modeled: (1) andesite-dacite, (2) basalt, (3) basaltic andesite, (4) cracked zones.

in nearby thermal springs, whose solutions are substantially less rich in chemical elements.

In order that a solution with an anomalous concentration of trace elements should be generated, the following requirements must be met: (a) magmatogenic gases with concentrations of HCl, HNO<sub>3</sub>, HF, and sulfurous compounds exist; (b) mixing with surficial solutions, which are enriched with oxygen and significantly add to the amount of aggressive fluids occurs; and (c) the concentration of mixed fluids at the boundary of secondary boiling occurs.

Having thus gained some understanding of possible generation of the solutions under study, we tried to ascertain the forms in which the elements are found in all types of springs and the phases in equilibrium with these. We determined the chemical forms of the elements by physicochemical modeling, again with the help of the Selector program.

Most of the metals for which the calculation was carried out (Ca, Mg, K, Na, Fe, Al, Mn) are found in a free, aquaion form (Table 6) in the transparent pots and reservoirs of the Donnoe field, except for copper which forms chloride complexes (86% of the total concentration). The second most significant form is different for different elements, and seems to be important, in our opinion. The Ca, Mg, and Mn found in the transparent and semitransparent pots and springs form an appreciable number of sulfate complexes: 20, 32, and 10%, respectively. Quartz (70% of the total amount of secondary minerals) and pyrite (30%) may be the equilibrium solid phases in these springs, with possible admixtures being native sulfur, barite, covellite, and zinc hydrosulfate.

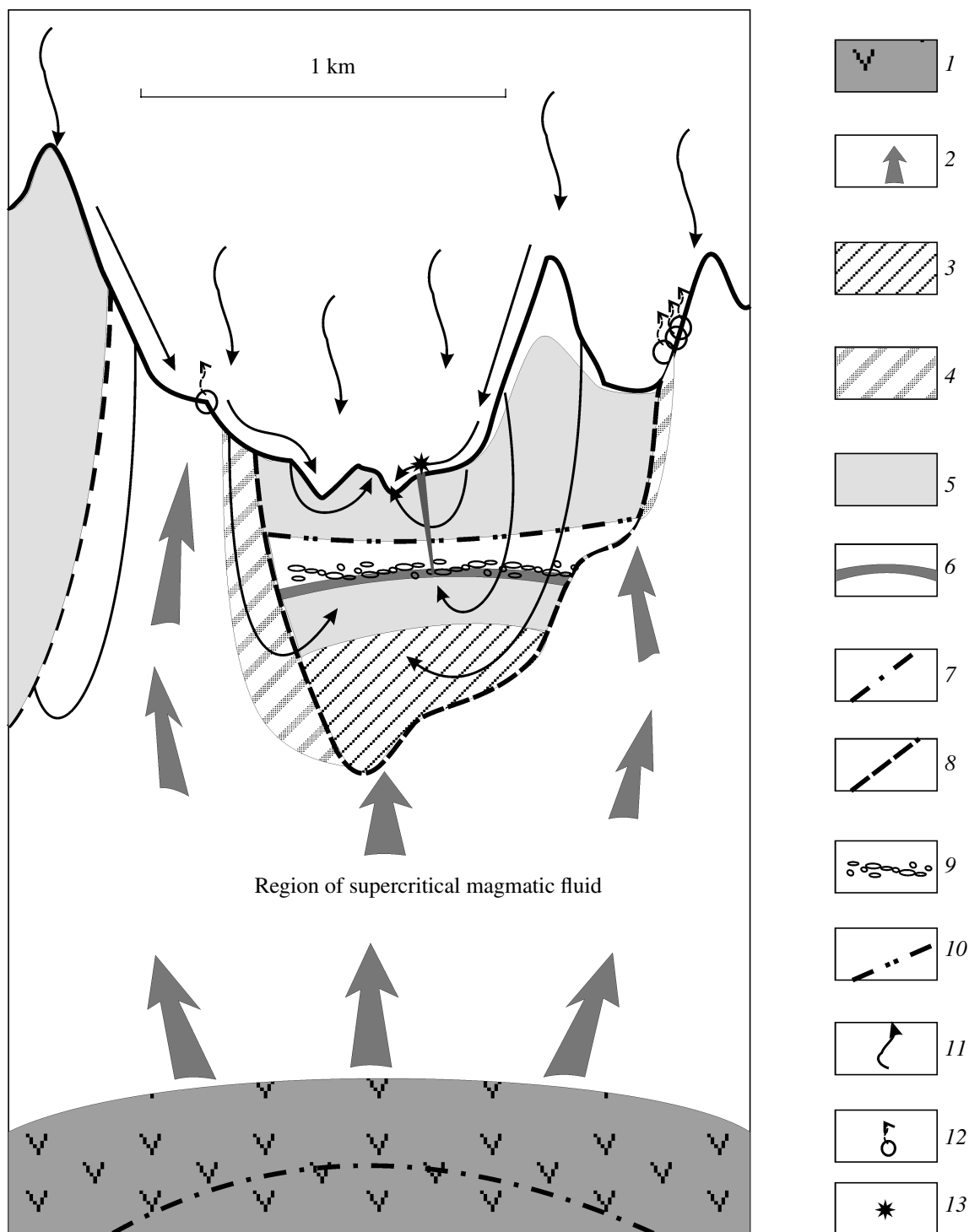
In the solutions of the rust-colored reservoirs, the sulfate form of Ca and Mg is by far the prevailing one compared with the aquaion form, amounting to 68 and

82%, respectively. The percentage of the sulfate form for alkali metals (K and Na) is not as high, reaching 30%, while chloride forms are altogether absent. Antimony and phosphorus form their own acids: H<sub>3</sub>AsO<sub>4</sub> (85%), H<sub>2</sub>AsO<sub>4</sub><sup>-</sup> (15%), H<sub>3</sub>PO<sub>4</sub> (83%), and H<sub>2</sub>PO<sub>4</sub><sup>-</sup> (17%). A mineral association characteristic for oxidation environments may form in the sediment (based on modeling results), with the dominant minerals being hematite (95%) and quartz (4%), while anhydrite and barite may be present as admixtures.

The second most significant chemical form for the elements considered here as found in the solutions of the mud pots consists of chloride complexes; the percentage of these varies for different metals between a few percent (for K and Ni) and 66% (for Fe). Sulfate complexes are formed only by Ca, Mg, K, and Mn in small amounts.

REEs may be found in superacidic solutions both as free ions and in chloride and sulfate complexes [40].

The prevailing form for vanadium is VO<sub>2</sub><sup>+</sup>. It is of interest to note that this element can be present in such solutions in the form of an acid, similarly to antimony and phosphorus, as was shown in [42]; the phosphate-like anions H<sub>2</sub>VO<sub>4</sub><sup>-</sup> and HVO<sub>4</sub><sup>2-</sup>, are the dominant forms of vanadium found in oxidized water. Vanadium is very stable when in contact with various chemical agents; it is soluble only in HF or in acids that are also strong oxidizers [19]. There is a high positive correlation between the distributions of F and V in solutions (K<sub>corr</sub> = 0.799, the limit value at β = 1% is 0.549), but no correlation is observed with NO<sub>3</sub><sup>-</sup> (nitric acid is the strongest oxidizer). It appears that the leading role in extracting vanadium into solutions is that of hydrofluoric acid, which is found in varying amounts in the samples studied. Chromium forms, apart from aquaion, very small amounts of hydrochromate (HCrO<sub>4</sub><sup>-</sup>). This is soluble in diluted HCl and H<sub>2</sub>SO<sub>4</sub> [20]; the appearance of chromium in the solutions of the pots is evidently determined by these chemical properties. Antimony and phosphorus mostly occur in the form of acids, viz., arsenous acid (H<sub>3</sub>AsO<sub>4</sub>) and phosphorous acid (H<sub>3</sub>PO<sub>4</sub>). A detailed analysis of the behavior of titanium in volcanic waters carried out by K.K. Zelenov [9, 10] led him to the conclusion that titanium, when involved in an effusive process, can come to the surface in the form of compounds with halide gas and sulfur dioxide. When at high temperatures, titanium becomes very active chemically and vigorously combines with halides, oxygen, and phosphorus [20]. Recalling Zelenov's results in combination with the well-known chemical properties of this element, one can see why titanium is found in such high concentrations in the solutions of a sulfuric fumarole edifice in the Donnoe field. When shallow superacidic solutions are generated, titanium remains quite mobile and forms diversivalent complexes with chlorine, sulfate, and fluorine. Its increased concentrations in the pot solutions, when considered along with



**Fig. 6.** Schematic diagram of fluid dynamics in the section of Mutnovskii Volcano: (1), basaltic body, the source of heat and gases; (2), magmatic fluid; (3), zone of possible existence of magmatic gas condensates; (4), zone of mixed gases; (5), zone of mixed solutions; (6), zone of brine generation; (7), boundary of retrograde boiling; (8), condensation boundary; (9), boundary of secondary boiling; (10), boundary of secondary condensation; (11), meteor water; (12), fumaroles; and (13), mud pots

other facts, such as the high chlorine content, the leading role of aluminum, and the dominance of Fe(II) over Fe(III), may all point to a considerable contribution of magmatic fluids to the composition of the hydrothermal

solutions that are discharged in the form of thermal water pots and mud pots. M.E. Zelenskii [11] estimates that the percentage of magmatic gas in the Donnoe thermal springs varies in the range 0.5–24%. The solutions of

**Table 6.** Chemical forms of elements found in the solutions of thermal springs, in % of bulk amount

Forms	Transparent pots and reservoirs	Rust-colored reservoirs	Mud pots	Forms	Transparent pots and reservoirs	Rust-colored reservoirs	Mud pots
Ca <sup>2+</sup>	80	32	75	Sr <sup>2+</sup>	100	0	80
CaSO <sub>4</sub>	20	68	1	SrCl <sup>+</sup>	0	0	20
CaCl <sup>+</sup> + CaCl <sub>2</sub>	0	0	24	K <sup>+</sup>	98	69	98
Co <sup>2+</sup>	Ì.Ó.	99	50	KSO <sub>4</sub> <sup>-</sup>	2	31	1
CoCl <sup>+</sup>	0	1	50	KCl	0	0	1
Cr <sup>3+</sup>	Ì.Ó.	100	99	Mn <sup>2+</sup>	90	45	50
HCrO <sub>4</sub> <sup>-</sup>	0	0	1	MnSO <sub>4</sub>	10	55	1
Cu <sup>+</sup>	10	0	0	MnCl <sup>+</sup>	0	0	49
Cu <sup>2+</sup>	4	100	54	Na <sup>+</sup>	98	69	82
CuCl <sup>+</sup> + CuCl <sub>2</sub> <sup>-</sup>	86	0	46	NaSO <sub>4</sub> <sup>-</sup>	2	31	0
Fe <sup>2+</sup>	100	98	0	NaCl	0	0	18
Fe <sup>3+</sup>	0	1	17	V <sup>3+</sup>	5	0	0
FeCl <sup>2+</sup>	0	0	66	VO <sub>2</sub> <sup>+</sup>	90	100	98
FeF <sup>2+</sup>	0	1	16	HVO <sup>2+</sup>	5	0	0
FeOH <sup>2+</sup>	0	0	1	H <sub>3</sub> VO <sub>4</sub>	0	0	2
Mg <sup>2+</sup>	68	18	72	Ni <sup>2+</sup>	0	100	96
MgSO <sub>4</sub>	32	82	2	NiCl <sup>+</sup>	0	0	4
MgCl <sup>+</sup>	0	0	26	Al <sup>3+</sup>	100	100	100

the pots and the pore waters of the thermal localities evidently contain the highest concentration of this gas, because the solution (separate) is rising from the zone of secondary boiling along open fissure channels.

Modeling suggests that pyrite (70%) is a possible solid phase that forms in the pot solutions; as well, chlorite, alunite, and diasporite can be deposited in substantial amounts (10%). X-ray crystal analysis applied to the solid matter at the thermal localities reliably identified alunite, diasporite, pyrite, cobalt and nickel hydrosulfates, as well as manganese, iron, and cobalt chromates.

### CONCLUSIONS

(1) Solutions with anomalous composition have been found in thermal localities of Mutnovskii Volcano with concentrations of many trace elements considerably in excess of those measured in the thermal waters of other active volcanoes of the world.

(2) The thermal springs in the Donnoe field of Mutnovskii Volcano may be viewed as local areas where brine is discharged from a region of concentrated components of mixed fluids under the zone of secondary boiling.

(3) The associations of chemical elements in the solutions of mud pots found in increased concentrations (Cl§Al–Ti–Cr–Ni–Co–REE–PGE) provide evidence of a

deep-seated origin of the fluids with subsequent concentration of the solutions at geochemical barriers.

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SPELL: 1. basalts, 2. andesites, 3. chondrites, 4. supercritical