HYDROGEOCHEMISTRY OF THERMAL SOURCES, MUTNOVSKY VOLCANO, SOUTH KAMCHATKA (RUSSIA)

Bortnikova S.B.[a], Bessonova E.P.[b], Gavrilenko G.M.[c], Vernikovskaya I.V.[a], Bortnikova S.P.[a], Palchik N.A. [b]

[a] Trofimuk Institute of Petroleum Geology and Geophysics, Siberian Branch of RAS
[b] Institute of Geology and Mineralogy, Siberian Branch of RAS
Novosibirsk, 630090, pr. acad. Koptug, 3, Russia
[c] Institute of Volcanology and Seismology, Far East Branch of RAS
Petropavlovs-Kamchatsky, 683006, blv. Piip, 9, Russia
e-mail: bortnikovasb@ipgg.nsc.ru

ABSTRACT

In this paper the investigation results of thermal springs of the Mutnovsky Volcano (Kamchatka, Russia) are provided. Mud pots in the Donnoe Field of this volcano have a unique solution composition. High concentrations of a wide spectrum of chemical elements such as Al, Ti, V, Cr, Ni, Co, REE and PGE were discovered there. To explain the mechanisms of solution formation it was made an attempt to describe the fluid evolution and the resulting mixing waters by physical and mathematical modeling. A model illustrates fluid migration from magma chamber to the surface. It is shown that formation of brines corresponding to mud pots composition is possible under the secondary boiling border.

THE SUBJECT OF STUDY

The Mutnovsky Volcano is one the largest and the most active South Kamchatka volcanoes. It is 2323 m high. Two merged craters are located to the northwest and west of the summit (*Fig. 1*). The volcano holds multiple cones of neighboring explosions (Selyangin, 1993).
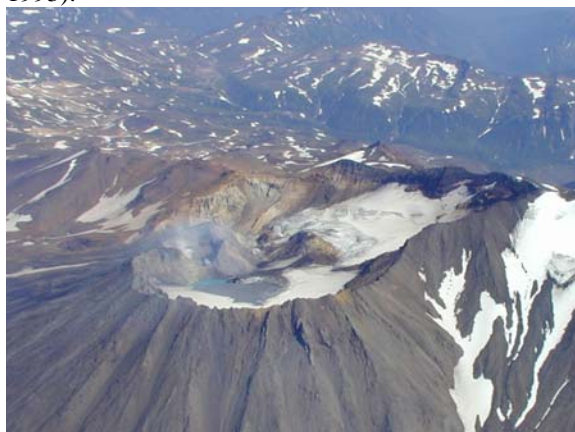

Figure 1. Overview of the Mutnovsky volcano. Foto by N.I. Seliverstov from helicopter

It has passed in the stage of fumarolic and hydrothermal activities characterized by extremely high energy: 1800-1900 MW in the quite long period of non-active times between 1961 and 2000. Some authors suggest this period as "passive explosion" (Melekescev et al., 1987; Polyak, 1966).

Three fumarole fields are located in the eastern crater (1) Verkhnee field with vent temperatures of more than 300°C; (2) Donnoe field consisting of two relatively separate vents with temperatures up to 150°C; (3) Aktive funnel, where powerful gas jets have temperatures up to 570°C. The compositions of gases and hydrothermal solutions of this volcano have been studied sporadically since 1961 (Vakin et al., 1966; Taran et al., 1992; Zelenskii, 2003; Bortnikova et al., 2007 and others). The high seismicity and constant "seismic vibration" of the Earth's crust provoke changes in the position and activity of fumaroles and hot springs at the Donnoe field (*Fig. 2*).

Figure 2. Overview of the anomalous mud pots in the Donnoe Field

A spring study let us understand the hydrodynamics and the features of supercritical magma fluids in the highly permeable zones. In this paper the most interesting analytical data of the Mutnovsky springs composition and the results of physical and chemical modeling of the element species is provided. That allows us to get closer the dynamics of the modern magmatic fluid system of the Mutnovsky Volcano.

METHODOLOGY

Various water springs, reservoirs and mud pots in the Donnoe field, the Active funnel and the Verkhnee Lake were sampled in 2003-2006. The Donnoe field contains: i) small semi-transparent water boiling pots; ii) stable shallow water reservoirs, mainly fed by snow melting; iii) three dark red water reservoirs; iv) mud pots colored from slightly yellow to black. Water samples were taken by a Teflon sampler and transported in plastic boxes. Any contacts with metals were excluded. In situ pH, Eh and T were measured after some sedimentation. The samples were filtered using a 0.45 µm membrane filter.

Another group of samples consists of: i) humid solids of hydrothermal altered rocks from hot sites of the Donnoe field; ii) bottom sediments of every reservoir; iii) moist native sulfur from inner parts of fumaroles. Just after sampling each sample was immediately locked in a plastic waterproof bag. Later, in a laboratory, pore waters were pressed out from the samples at 100 atm pressure.

Cations and trace elements were measured by an ICP-AS method using IRIS Advantage instrument at the Analytical Center, IGM SB RAS. A content of REE, PGE, Au, Tl and some other elements were derived using ICP-MS.

RESULTS

Physical and chemical parameters and main ionic composition

The compositions of thermal springs, pots and water reservoirs located in the Mutnovsky area are greatly various. All solutions correspond to acid and ultra-acid waters (pH changes from -0.56 to 3.5) with high red-ox potential which however alters from 160 (in light pots) up to 750 mV (in pore solutions of the hot site). The great varieties are revealed in cation and anion as well as in trace elements composition (Table 1, 2). Anions are mainly presented by chloride and sulfate. In different solutions a ratio between chlorides and sulfates varies essentially. In the transparent ones chlorides prevail over sulfates (Table 1). This prevailing is even more in the mud pots and in the pore waters of sulfur fumaroles. The anion part is composed of 90% of chloride ions (that is up to 56 g/L in the mud pots and up to 24 g/L in the sulfur fumarole pore waters). In contrary, sulfates prevail in other types of water (red reservoirs, Verkhnee Lake, Active funnel reservoirs, Active funnel pore waters). The most sulfate waters are presented in the red reservoirs, where a SO_4 percentage is up to 99% (in average 15 g/L). A path of magmatic HCl might be higher in pots solutions and during sulfur fumaroles formation than that in the other water types.

Furthermore, F-ion is contained in the red waters (up to 11 ppm), the Verkhnee Lake (up to 110 ppm), the Active funnel reservoirs (up to 10 ppm) and in the mud pot solutions (up to 290 ppm). Besides, phosphates are common. The hot site pore waters show a maximum PO_4 quantity (6600 ppm) and the mud pots contain up to 130 ppm of it.

Cation compositions are also very various: i) calcium is a prevailing cation in the transparent springs and water reservoirs of the Active funnel and the Verkhnee Lake; ii) iron takes the first place (as its quota reach up to 66%) in the red reservoirs and the pore waters; iii) Al is a prevailing element in the mud pot solutions.

Table 1. Contents of main ions in solutions of Mutnovsky volcano, ppm

Objects	n		pH	Eh, mV	Cl⁻*	F⁻	SO₄*	PO₄	Na⁺	K⁺	Ca²⁺	Mg²⁺	Fe_total	NH₄⁺
TP	4	mean	3.18	396	0.11	ld.	1.7	ld.	2.1	3.6	55	2.5	7.8	ld.
RR	4	mean	1.60	700	0.15	10	15	6.7	36	1.7	470	120	4300	3.1
VL	4	mean	1.46	550	0.54	91	4.0	9.4	51	6.6	650	205	250	ld.
RAF	5	mean	2.25	526	0.19	35	1.9	ld.	9.4	0.87	520	18	130	0.14
PWAF	10	mean	2.10	540	0.15	ld.	7.1	9.9	110	35	710	63	2000	ld.
MP	14	mean	0.44	466	23	52	3.34	40	150	180	300	91	450	21
		min	-0.56	240	1.1	0.009	0.59	0.28	5.5	6.8	40	1.4	6.3	0.25
		max	2.1	715	56	290	11	130	500	740	1600	510	4300	110
PWHS	8	mean	0.76	684	11		12	2900	4400	295	92	5500	17400	
		min	0.22	619	9.6		8.7	11	93	110	53	71.3	820	
		max	1.8	750	16	ld.	14	6600	7400	410	180	10300	53000	ld.
SF		S-1/06	0.5	660	21	ld.	0.66	15	110	80	220	110	310	4020
		S-3/06	0.35	680	24	ld.	2.56	23	71	30	370	84	400	10500

Commentary (to all tables): n – number of analyses, * in g/L, TP - transparent springs and pots; RR - red reservoirs; VL - Verkhnee Lake; RAC - reservoirs of the Active funnel; PWAC - pore waters of Active funnel; MP - mud pots; PWHS - pore waters of hot sites; SF - sulfur fumaroles; S-1/06 and S-3/06 are sample names; "ld" – element is lower detection limit.

Table 2. Contents of trace elements in solutions of Mutnovsky, ppm

Objects		Al	Mn	Sr	As	Zn	Cu	Ti	V	Co	Cr	Ni	Be	B
TP	mean	5.6	0.086	0.15	ld.	0.091	0.033	0.03	0.021	ld.	ld.	Ld.	ld.	0.09
RR	mean	670	4	1	2.9	1.2	3.1	0.0085	0.44	1.1	0.14	0.8	0.008	0.49
VL	mean	260	7.1	0.81	0.67	1.2	0.012	0.44	1.2	0.045	0.21	0.052	0.0053	1.2
RAF	mean	84	0.65	0.65	ld.	0.088	0.85	0.066	0.19	0.028	0.0008	Ld.	ld.	ld.
PWAF	mean	570	2.2	2.7	3	3.4	9.8	0.28	1.3	1.2	1.2	0.37	0.0022	2.9
MP	mean	1330	3.5	6.1	0.32	0.55	0.1	3.8	2.7	0.076	6.3	3.1	0.0059	41
	min	47	0.07	0.17	0.06	0.09	0.01	0.01	0.04	0.002	0.14	0.06	0.0016	0.53
	max	3020	8.1	20	0.61	1.9	0.62	15	13	0.48	60	33	0.014	160
PWHS	mean	8800	150	4.3	33	49	29	170	260	2.5	11	3.1	0.57	185
	min	400	3.7	1.7	0.95	2.8	5.4	5.1	1.1	1.1	0.33	0.47	ld.	29
	max	14800	400	7.2	82	110	120	360	430	5.2	18	7.1	0.99	450
SF	S-1/06	490	5.3	1.8	26	2.4	0.85	5.7	1.4	0.12	0.19	0.11	0.003	330
	S-3/06	680	4.3	2.8	150	1.6	2.3	7.2	1.9	0.2	0.36	0.19	0.0035	290

The particular place is taken by the pore water of sulfur fumaroles. Their major cation is NH_4^+ which is considerably prevails over all the others ones (approx. 80 % that is 10.5 g/L). Al is the next wide spread cation in this solutions (11%, up to 680 ppm).

Trace elements

The trace elements contents change in the different solutions. Total concentrations vary from 0.52 ppm in the transparent springs up to 920 ppm in the pore waters of the hot sites (Table 2). In the red reservoirs trace elements we suggest to divide into several groups according to their prevalence. These are: i) Mn and Cu forming equal amounts (23% of total trace element concentration or 3.4 ppm); ii) As and Zn (14 and 12% respectively); iii) Cd and Sr (6% each); iv) Cr, Ni, Co, V and B giving the total percentage less than 15 %. The elements Li, Ti, Ba and Be compose 0.n ppm that is less than 0.5% of the trace element composition.

Copper takes the first place in the Active funnel solutions. Its content reaches almost 10 ppm in the pore waters what is about 30%. The Mn, Sr and As contents are quite high.

The mud pots solutions differ drastically because of high concentration of Cr, Ti, Ni, V. The maximal quota in the trace element set of these solutions belongs to B (58% which is 41 ppm). In the significant concentrations (more than 1 ppm) the following elements are presented: Cr, Sr, Ti, Mn, Ni, V, Nb. The maximum Cr content is found in the pot Otkrytiy solutions where it reaches 60 ppm (Table 2) (Bortnikova et al., 2007). Due to analysis of the solutions in the Volcano Island published by Auippa et al. (2000[2]) the Cr content in the Vasco waters is 45 ppm (unfortunately, the discussion of this phenomena is not given). In the mud pots solutions the significant concentrations of Ga, Ba and Mo present.

In the pore waters of the hot sites the major trace elements are V, B, Ti, and Mn. Their contents exceed 150 ppm. The concentrations of the other elements (As, Zn, Cu, Cr, Li, Zr, Sr, Ni, Co) are also very high. The main trace element in the pore waters of the sulfur fumaroles is also B (290-330 ppm what is 61-86 %). The second major element is As (150 ppm). A Sb content is much lower. Another significant element is Ti which volatility is lower comparatively to As and Sb. The concentrations of such elements as Pb, Cr, Co and Ni are higher comparatively to their concentrations in the thermal springs, pots and even in the pore waters of the hot sites though they are not as great as the previous ones. Mn, Zn, Zr and V contents are only few ppm.

All the discussed elements are not the particular features of a separate group of sources. They are found in certain quotas in every kind of solutions. For example, the Cr contents in the pore waters of the Active funnel and Donnoe field, in the red reservoirs and Verkhnee Lake reach up few ppm. The Co and Ni concentrations in the sources are up to 0.n ppm and for the pore waters they are about few ppm. The B content in the pore waters of the Active Crater is 8 ppm. A high contrast of elements content should be noted. It is the evidence of two facts: i) a releasing is very active on the way of fluid to the hot springs and ii) their transportation paths vary in a distinct small area of the surface outflow.

REE composition

The concentrations and distributions of REE should be discussed separately. Its high concentrations are one of particularities of the pots and the hot site solutions (Table 3). These contents in the Mutnovsky solutions are 14 times higher than that in the acid chlorite-sulfate waters of Yellowstone hydrothermal system (Lewis et al., 1997). The total concentrations of REE reach 2 ppm in the pots and in the hot sites solutions they vary from 3.6 to 12 ppm. Similar contents of REE were found in the pot Bolshoi of the

Table 3. Contents of some trace elements, REE, PGE in mud pots and pore waters, ppb

	Solutions from mud pots								Pore waters of hot sites			
	SDP-2	SDP-2/1	SDP-3	SDP-4	SDP-5	SDP-7	SDP-9	SDP-9'	SDP-10	SDP-11	SDP-12	SDP-13
Th	14	11	11	3.9	25	2.4	13	11	217	116	223	208
U	4.3	3.3	2.6	1.1	6.8	1.4	3.3	3.3	81	64	72	64
Tl	360	120	45	2.9	29	8.2	6.9	82	350	278	119	232
Hg	1.6	0.40	0.30	0.40	0.10	0.20	1.0	0.6	ld	nd.	nd.	nd.
Au	0.53	0.34	0.22	0.16	0.25	0.29	0.11	0.27	ld	ld	ld	ld
Ru	0.01	0.032	0.018	0.015	0.028	0.034	0.015	0.022	ld	ld	ld	ld
Rh	0.044	0.038	0.044	0.015	0.13	0.066	0.061	0.057	ld	ld	ld	ld
Pd	2.2	1.8	1.2	0.2	1.4	0.5	0.2	1.1	19	34	30	12
Re	0.017	0.019	0.018	0.04	0.043	0.033	0.01	0.026	62	ld	2.0	3.2
Ir	0.0062	0.0046	0.004	ld	0.0024	0.0031	0.00018	0.003	ld	ld	ld	ld
Pt	1.8	0.9	0.32	0.062	0.45	0.79	0.04	0.62	100	64	39	52
La	170	130	140	55	340	110	170	160	200	10	89	150
Ce	380	300	350	130	920	300	490	410	650	50	350	500
Pr	56	45	55	23	140	54	82	65	150	20	90	120
Nd	220	170	200	92	540	260	310	260	750	160	540	680
Sm	44	37	36	17	90	74	52	50	350	100	280	340
Eu	12	11	8.8	3.6	21	26	11	13	200	72	150	160
Gd	41	36	28	12	58	88	34	42	1000	360	830	1000
Tb	6.6	6.1	4.1	1.6	7.2	14	4.5	6.3	200	80	190	210
Dy	44	38	23	8.4	35	85	23	37	2350	810	1940	2200
Ho	9.1	7.9	4.3	1.6	6	18	4.2	7.3	600	202	500	560
Er	26	23	12	4.3	16	53	11	21	2150	680	1700	1940
Tm	4.1	3.6	1.9	0.7	2.5	8.5	1.7	3.3	350	120	300	340
Yb	27	23	12	4.6	16	51	11	21	2550	860	2100	2300
Lu	3.9	3.4	1.7	0.7	2.2	7.2	1.6	3.0	400	140	340	370

Ebeco Volcano and in the Verhne-Urevsky springs (Paramushir Island, one of the Kuril Islands) where they are 690 and 360 ppb respectively (Bortnikova et al., 2005). However, in the Mutnovsky volcano pots REE concentrations are much higher. The REE patterns in different pots are similar except the pot SDP-7 (*Fig. 3*). In pots LREE considerably prevail over HREE, whereas in the pot SDP-7 a REE pattern is a gentle line due to HREE enrichment. It should be noted an absent of Eu- minimum in all solutions despite of rather high re-dox potential. It can be connected with fast transport of deep fluid having reduced media and purchase of oxidative conditions just near surface.
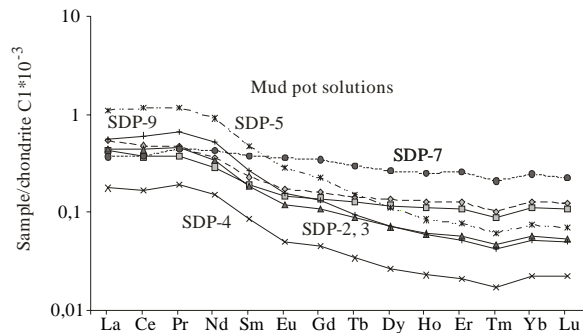

Figure 3. REE patterns in the solutions of mud pots

As for hot sites solutions the REE pattern is completely different that is the HREE are essentially

prevail over LREE (*Fig. 4*). In the pore water of sulfur fumaroles the REE patterns are similar to that of pot SDP-7, though the concentrations are slightly lower. Since all the solutions discharge on the local area it is difficult to understand this significant difference in REE patterns.
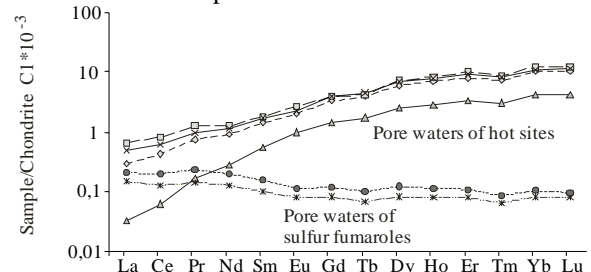

Figure 4. REE patterns in the pore waters of the hot sites and sulfur fumaroles.

The REE presents in waters can be explained as leaching from the host rocks under subsurface conditions (Lewis et al., 1997; Shennon et al., 1991). Stability in solutions depends on pH-conditions and red-ox potentials (Marcos, 2002). There is direct correlation between the REE distributions in the thermal waters and their acidity (Bau, 1991; Lewis, 1997). Nevertheless this correlation is not very strong. It is supposed that some other factors may influence on releasing and presence of these elements in solutions. According to S. Krainov (1973) the high REE concentrations in ground waters were connected

with the alkaline nepheline syenites. They reach in total 8.7-664 ppb. We should paid attention that these waters interact with the rocks containing elevated REE concentrations. Mutnovsky volcano is composed of andesites, basalts and ryolites only (Selyangin, 1993). These rocks can not supply high REE concentrations in the solutions. Evidently there are two main reasons of this phenomenon: i) ultra-acid media and high temperatures of fluids that may force to dissolve these elements; ii) features of fluid transport to the surface. Since the rocks building the volcano contain a few REE concentrations the obtained data must indicate on deep sources of fluids and on their multiple enrichment at geochemical barriers inside the volcano.

DISCUSSION

Mutnovsky volcano thermal springs has the particular composition, very different from other, worldwide known volcanic areas, as we can see from publications. The data on maximal element concentrations in the thermal waters of Ethna (Auippa et al., 2000[1]), Vulcano (Auippa et al., 2000[2]), El Chichon (Taran et al., 2003), Ebeko (Bortnikova et al., 2005) are shown at *Fig. 5* together with maximal concentrations measured at Mutnovsky mud pots and pore waters of hot sites.
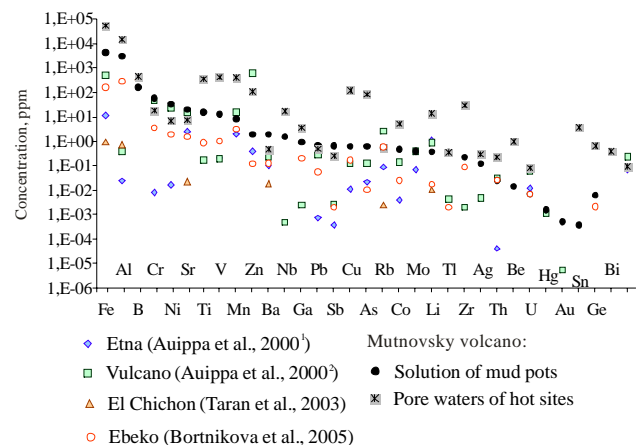

Figure 5. Maximal concentrations of trace elements in solutions of the Mutnovsky thermal springs in comparison with others volcano waters

The association of Ti-V-Cr-Co-Ni is especially notable. Ti and V concentrations in the Mutnovsky waters are two orders higher than that in Vulcano waters. In the pore waters of the hot sites the Ti and V concentrations are extremely high (even more than 100 ppm). Ti concentration in a crater lake of Kawa Indjen volcano (Indonesia) described by K. Zelenov (1965) is 23.42 ppm though it is higher in the Banjipati river creek because of the river forming brooks evaporation. The Co, Cr and Ni concentrations do not vary so much as Ti in the solutions. However this association can be an

evidence of an unusual source. The high contents of "exotic" elements, such as Nb, Ga, Zr and Tl seem to be surprising.

Besides, in the pots and the hot sites solutions the elements of a Pt group (PGE) were found: the total concentration of Ru, Rh, Re, Ir and Pd in the pots is up to 4 ppb and in the pore waters is 180 ppb (see Table 3). It was mentioned (Hanley, 2005) that in high temperature hydrothermal magma systems, high chloride fluids may control primal concentrations and redistributions of the elements of Pt group because of HCl making complexes $PtCl_3H$. Dissolubility of Pt may be high under elevated temperatures (800-900 ºC) and high salty solutions. The theoretical thoughts make these elements dissolubility noticeably lower than that in reality. The complexes with HS^- are more probable in low temperature mediums (Wood, 2002). The stable association Cr-Ni-Ti-V in the solutions and an important correlation of the Pt group elements with Co (0.965), V (0.915), Cu (0.888), Ni (0.863) and Cr (0.845) corroborates that a combined transport of these elements was linked with magma fluids. In the Mutnovsky solutions this association of chemical elements (Cr-V-Ti-Co-Ni-PGE-REE) is completely different to any known in this region epithermal Au-Ag deposits (Asachinsky, Rodnikovy, Mutnovsky) which typomorphic elements are Zn, Pb, Cu, Ag, Sb, Te and Au (Takahashi, 2005).

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

Calculations were based on the following assumptions: intrusion is located at a depth of 10–1 km from the surface; fluid accounts for about 3 wt % of the crystallizing solution; and pO_2 of fluid corresponds to the interval between IW and QHem buffers. In modeling, we took into account the alternation of basalts, basaltic andesites, and dacites in the section. The presence of high-porosity rocks (tuffs) and fracture zones was also considered. From the "source" to reactor N 20, the pressure varied from 3000 to 500–300 bar; temperature from 1000 to 300°C. The independent components of the source were 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; N/F = 1. Thermodynamic databases were used in calculations (Reid, 1997; Woods and Garrels, 1987; Yokokawa, 1988).

Under reducing conditions (initial pO_2 <14), major and trace elements are weakly leached from basalts. These processes are most expressed for Mn, Mo, and Co, the contents of which in gas can be as much as several ppm. Condensation of such gases is accompanied by the formation of acid reduced solutions (pH 4.5, *Eh* –0.2) with metal contents (mg/L): Co 0.0005, Mo 0.000001, and Mn 2. Increase in contents of Cl, Fe, and S by an order of magnitude leads to increase of the mobility of components by several orders of magnitude. The gas phase in the last reservoir shows gradual accumulation of Co, Cr, Mo, Ni, V, Al, Mn, and Ti. However, the contents of most components in the magmatic gas condensate are no more than several ppm.

Large-scale extraction of components from basalts requires the presence of oxidized high-temperature gases, which could be formed in the upper part of the volcanic–hydrothermal system via mixing of magmatic fluids with overheated vapors of oxygen-enriched surface water. We propose a qualitative scheme of a mixed (fluid magmatic) system for the present-day morphology of the Mutnovsky Volcano crater. In this model, the position of the magmatic gas condensation boundary is estimated from dynamics of retrograde boiling of magma in a shallow intrusion. The condensation boundary can be located beneath a zone of magmatic fluids, the size of which depends on water-saturation of the host rocks. High-temperature mixed gases (surface water vapor and magmatogenic acid gases) are formed along the external boundary of condensation. The newly formed aggressive gas can leach most elements from host basalts. The gas is partially condensed to mix with magmatic fluid, while solutions are diluted and cooled in the course of their ascent. The next geochemical barrier (the second boiling zone) is characterized by the exsolution of some components (primarily, water vapor and small amount of acid gases) into the gas phase, while the remaining portion is enriched in some elements (Cr, Ni, V, Ti, and others) up to the required level. Thus, we assume that the hydrothermal spring in the Donnoe field is related to the zone of enriched brines arising at the secondary boiling boundary. This assumption is confirmed by thermodynamic calculations.

The composition of the thermal sites pore waters is very significant. High concentrations of a wide range of elements found there make the subsurface phase barrier evident. On this barrier a final partitioning of solutions into condensate and separate take place. During this process the condensate disappears as "refined" water vapor and the separate remains in pore space as high-mineralized solutions.

Thus, we were trying to find out the element species for the all spring types and an equilibrium solid phases taking into account the possible genesis kinds of the studying solutions. In different solutions percentage of three principal species (aqua-ions, sulfate and chloride complexes) is various excluding Al which is present in all type solution as Al^{3+}completely (Table 4). K and Na form aqua-ions mainly but in the red reservoirs quota of their sulfate complexes is high and for Mg and Ca sulfate species prevail there, no chlorides are contained in waters.

Table 4. Element species in solutions, % from total

Species	Transp. springs	Red reserve.	Mud pots
Ca^{2+}	80	32	75
$CaSO_4$	20	68	1
$CaCl^+ + CaCl_2$			24
Mg^{2+}	68	18	72
$MgSO_4$	32	82	2
$MgCl^+$			26
K^+	98	69	98
KSO_4^-	2	31	1
KCl			1
Na^+	98	69	98
$NaSO_4^-$	2	31	1
$NaCl$			1
Fe^{2+}	100	98	
Fe^{3+}		1	17
$FeCl^{2+}$			66
FeF^{2+}		1	16
$HFeO^{2+}$			1
Al^{3+}	100	100	100
Mn^{2+}	90	45	50
$MnSO_4$	10	55	1
$MnCl^+$			49
Co^{2+}	ld	99	50
$CoCl^+$		1	50
Cr^{3+}	ld	100	99
$HCrO_4^-$			1
Cu^+	10		
Cu^{2+}	4	100	54
$CuCl^+ + CuCl_2^-$	86		46
Ni^{2+}	ld	100	96
$NiCl^+$			4
V^{3+}	5		
VO_2^+	90	100	98
HVO^{2+}	5		
H_3VO_4			2

Except aqua-ionic species in the mud pot solutions metals form halogenic complexes. For different metals their parts vary from 18 % (as for Na) up to 82 % for Fe (66 % $FeCl^+$ and 16 % FeF^+). Sulphate complexes produce only 1 % of Ca and 2 % of Mg. As and P form their own acids: H_3EO_4 and $H_2EO_4^-$.

V the same as As and P in such solutions are presented as vanadates as well as it was mentioned (Wehrli and Stumm, 1989) In the oxidized acid waters the dominating V species are the anions H_3VO_4 and VO_2^+ that are similar to phosphates. This element is very stable towards various chemical

effects and may be dissolved in HF only, or in any acid that is also a strong oxidant. Among F and V distribution in the solutions high positive correlation exists (K_{corr} = 0.799, boarder value is equal to 0.549 for β = 1 %), but with NO^{3-} there are no correlation though nitric acid possesses the strongest oxidation properties. Apparently it is HF that plays the main role in V release into solutions. The studying samples contain at least some amount of this acid. Cr except aqua-ions forms a few hydrochromite complexes ($HCrO_4^-$) which may be dissolved in diluted HCl and H_2SO_4. It is obvious that the presence of Cr in the mud pots can be explained by these chemical properties.

REE from the high acid solutions may be found either as aqua ions or in chloride and sulphate complexes (Shennon et al., 2001; Sverjensky, 1984).

Through detailed analysis of the Ti behavior in volcanic waters K. Zelenov (1965) came to a conclusion that in an effusive process Ti may come into the surface as it combines with haloid and sulfur gases. High temperatures cause Ti to become a very chemically active metal that easy combines with haloids, oxygen and sulfur. The huge Ti concentrations in the sulfur fumaroles solutions of the Donnoe field become clear taking to account the K. Zelenov's results and the known data about chemistry of this element. In the high acid solutions near the surface Ti is still agile enough to form different valence complexes with Cl, F, sulphate. The high Ti concentrations in the mud pots solutions along with other facts such as big chloride, considerable significance of Al, Fe(II) prevailing over Fe(III) may be evident of an essential contribution of magmatic fluids in the composition of the thermal solutions unloading in the form of muds. M. Zelensky supposes (2003) that the portion of the magma gas in the Donnoe field solutions vary from 0.5 up to 24 %. Obviously the mud pots solutions and the porous waters of the thermal sites contain the maximum portion of it because of solution ascent in the open fracture channels from the second boiling zone.

As modeling shows transparent springs must have sediment consisting of quartz (70 %) and pyrite (30 %) on the whole and also natural sulfur, barite, covelline and hydrosulfate Zn there may be. In red reservoirs the mineral association that is characteristic for oxidation conditions presents in sediment. Besides dominating hematite (95 %) and 4 % of quartz there are also anhydrite and barite as dash. The possible solid phases forming in the pots solutions are pyrite (70 %), chlorite, alunite, diaspore (10 %).

At the same time onto surface of hot sites various secondary minerals were determined by XRF method (Table 5). The major minerals are pickeringite and alunogen. Except for them Co, Ni, Zn, Al hydrosulphates as well as Mn, Fe and Co chromates, acid salts of Na were distinguished. The big variety of mineral phases constituent efflorescence emphasizes once again particular physico-chemical conditions of this barrier.

Table 5. Mineral composition of efflorescence onto hot sites surface

Mineral	Formula
Pickeringite	$MgAl_2(SO_4)_4 22H_2O$
Alunogen	$Al_2(SO_4)_3 17H_2O$
Pyrite	FeS_2
Trace minerals:	
Moorhouseite	$CoSO_4 \times 6H_2O$
Manganochromite	$(Mn,Fe)(Cr,V)_2O_4$,
Cochromite	$CoCr_2O_4$,
Ni-hexahydrite	$NiSO_4 \times 6H_2O$,
Bilinite	$FeFe_2(SO_4)_3 \times 22H_2O$
Ditrichite	$ZnAl_2(SO_4)_4 \times 22H_2O$
Gunningite	$ZnSO_4 \times H_2O$
Matteuccite	$NaHSO_4 \times H_2O$
Moorhouscite	$CoSO_4 \times 6H_2O$
Sanderite	$MgSO_4 \times 2H_2O$
Stanleyte	$VOSO_4 \times 6H_2O$
Ferrohexohydrite	$FeSO_4 \times 6H_2O$

CONCLUSIONS

In the thermal springs of the Mutnovsky Volcano the anomalies in composition of the solutions were discovered. The concentrations of many chemical elements in these solutions are considerably higher than that in any other known volcanic waters.

Anomalous springs can be regarded as a local area of brine discharge from the concentration zone of magmatic fluids located beneath a phase barrier in the largest meltwater pools in the central part of the crater.

Final phase barrier is located just near surface of the Donnoe field. Saturated solutions are generated there. Trace element concentrations in the solutions reach up to extreme values. Numerous secondary minerals (sulfates and hydrosulfates of Mn, Fe, Co, Cr and others) are formed as efflorescence due to evaporation. At water-mineral interaction they can be sources of high-mineralized acid solutions.

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