

Boiling Mud Pots: Origin and Hydrogeochemistry (Donnoe and North-Mutnovsky Fumarolic Fields, Mutnovsky Volcano; South Kamchatka, Russia)

Sofia P. Bortnikova, Svetlana B. Bortnikova, Marina P. Gora, Artem Ya. Shevko, Felix P. Lesnov, Alexei V. Kiryuhin

630090 Novosibirsk, pr. acad. Koptug, 3

bortnikovasb@ipgg.nsc.ru

Keywords: boiling mud pots, hydrogeochemistry, trace elements, rare earth elements, sources of elements

ABSTRACT

The boiling mud pots of some volcanoes are very interesting phenomena. Their color, their water-solids ratio (consistency), the physical - chemical conditions of their solutions, and their contents of major and trace elements can vary widely. These parameters usually vary greatly between mud pots, while transparent thermal springs are the same chemically at one thermal field. Such a phenomenon can be seen at the thermal spring group of the Karymskoe lake (Karpov et al., 2003), the South-East fumarolic field of the Ebeko volcano (Bortnikova et al., 2005), and the thermal field of the Uzon volcano. Since the parameters are variable within very limited areas, their variability is difficult to explain only by different sources of thermal waters. The Donnoe and North-Mutnovskoe fumarolic fields are examples of such phenomena. Mud pots located within small areas are different in size, color, solid-to-liquid ratio, and boiling activity. Study and explanation of such contrast between mud pots parameters can reveal the origin and structure of large magmatic fluid systems under active volcanoes, because we believe that mud pots are little analogues of large hydrothermal systems. In this work, we want to account for causes of formation of various mud pots at Donnoe and North-Mutnovskoe fumarolic fields, and to define possible sources of the elements in their solutions.

1. INTRODUCTION

The boiling mud pots of some volcanoes are very interesting phenomena. Their color, water-solids ratio (consistency), physical - chemical conditions of their solutions, and content of major and trace elements can vary in a wide range. Mud pots usually have high contrasts of these parameters, while transparent thermal springs are the same chemically at one thermal field. Such a phenomena can be seen at the thermal spring group of the Karymskoe lake (Karpov et al., 2003), the South-East fumarolic field of the Ebeko volcano (Bortnikova et al., 2005), and the thermal field of the Uzon volcano. Since the parameters are variable in very limited areas, their variability is difficult to explain using only different sources of thermal waters. Donnoe and North-Mutnovskoe fumarolic fields are good examples of such phenomena. Mud pots located within small areas are different in size, color, solid-to-liquid ratio, boiling activity. Study and explanation of such contrast between mud pots parameters can reveal the origin and structure of large magmatic fluid systems under active volcanoes, because we believe that mud pots are little analogues of large hydrothermal systems. In this work, we want to account for causes of formation of various mud pots at Donnoe and North-Mutnovskoe fumarolic fields, and to define possible sources of elements.

2. SUBJECT OF RESEARCHES

The Mutnovsky Volcano is one of the largest and most active of the 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).

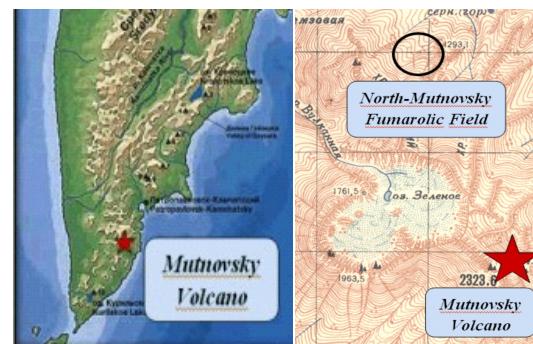


Figure 1: Location of Mutnovsky volcano and the North-Mutnovskoe fumarolic field

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

Three fumarole fields are located in the eastern crater: (1) the Verkhnee field with vent temperatures of more than 300°C; (2) the Donnoe field consisting of two relatively separate vents with temperatures up to 150°C; and (3) the 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).

2.1. Donnoe fumarolic field

The Donnoe field of the volcano (in the northeastern crater) is in an old lakebed. The lake existed up to the 1950s. Later, it disappeared and a fumarole field with varying shape appeared in its place. Three sulfur fumaroles, a large mud pot, and a multitude of small thermal springs and mud pots are active in the field more or less continually. The temperature, color, and their consistency (water/rock ratio) vary widely from small transparent outcrops of boiling water to black mud pots (the proportion of suspended matter in them is as high as 10%). There are mud pots with a yellowish, whitish, or greenish color of the boiling mixture there. A snowfield is located on the slope of the field, which supplies water into the stream during the

melting period. The stream flows in the field, and part of its water mixes with the solutions in the mud pots.

2.2. North-Mutnovskoe field

The North-Mutnovskoe fumarole field is a compact and attractive group of gas-hydrothermal manifestations. It is located 6 km northward of the Mutnovsky summit within Mutnovsky volcano-tectonic zone (Fig. 1). The area of the thermal field that is confined by the 20°C isothermal line at 50 cm depth is 5500 sq. meters. It looks like as an oval depression with low slopes and flat bottom composed of hydrothermally altered basalts. Within the Field there are about 20 strong steam vents with a output of more than 0.03 kg/s of water vapor and temperature 96-110°C. The hottest places are dotted with small steaming holes (Fig. 2). A small hot pool and several dozen mud and water pots are situated at the lowest parts of the depression. Mud pots are different in their color, temperature and solid-to-liquid ratios. Most pots have different tints of gray, from very light gray to black, but some pots have greenish-gray, brown and blue-gray colors.



Figure 2: Overview of the North-Mutnovskoe fumarolic field

The majority of pots lack outlets or have very little drainage. Stream beds are impregnated with rusty iron hydroxides. “Hydrochemical breccias” typical of hydrothermally altered rocks are forming in the fumarole field.

3. METHODS

3.1. Field sampling

Various mud pots at the Donnoe and the North-Mutnovskoe fields were sampled during 2003-2007. 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; and iv) mud pots colored from slightly yellow to black. Detailed research of hydrogeochemical features of Mutnovsky volcano had been done previously (Bortnikova et al., 2008). The location and features of the mud pots at the Donnoe field are shown on a sketch map of the sampling points (Fig. 3). The mud pots are located very near to two small sulfur fumaroles and are represented by 10 – 15 measurements of discharges of boiling mixtures, which consist of thermal waters and solid suspensions. The distances between the mud pots does not exceed 2 – 3 meters.

At the North-Mutnovskoe field all varieties of mud pots were sampled (Fig. 4). Water samples were taken by a

Teflon sampler and transported in plastic boxes. Any contact with metal was avoided. Also, we measured in situ pH-Eh with HANNA pH-meter and the concentrations of Cl⁻, F⁻, NO³⁻, NO²⁻ ions by a “Econics Expert” ionometer. Iron concentration was measured by a portable HACH colorimeter. The samples were filtered using a 0.45 µm membrane filter.

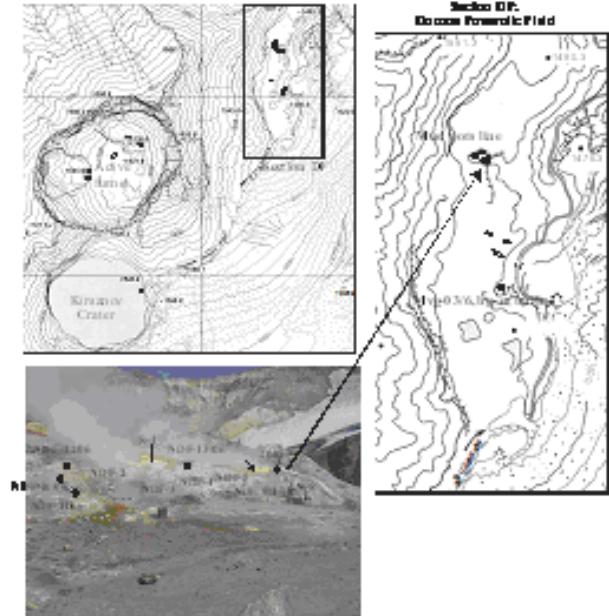


Figure 3: Sampling scheme of mud pots at Donnoe fumarolic field

Another group of samples consists of: i) humid solids of hydrothermal altered rocks from hot sites at studied fields and ii) a wet substance from the inside of pots. Samples were taken by a special instrument with elongated handle and put into polypropylene containers that were packed hermetically for further study of pore waters and solid residue.

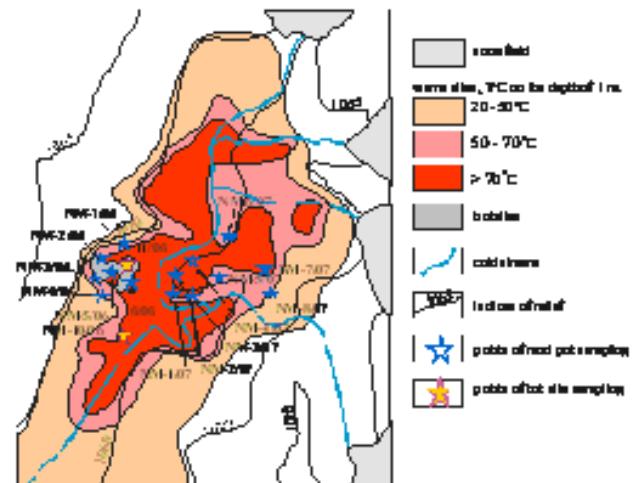


Figure 4: Sampling scheme of mud pots at North-Mutnovskoe fumarolic field

3.2. Laboratory analyses

In the laboratory, pore waters were forced out of samples under 100 bars of pressure. After pore water extraction, water extracts were done on solid remains in the ratio deionized water: solid of 4:1. Solutions were filtered in

one day through a 0.45 μm membrane filter. All obtained solutions were analyzed by ICP-AES (IRIS Advantage) at the Analytical Center, IGM SB RAS (analyst L.B. Trofimova). The content of REE and PGE and some other elements were measured using ICP-MS (analyst I.V. Nikolaeva).

4. RESULTS

4.1. Physical and chemical parameters of solutions

The compositions of pots located in the Donnoe field vary greatly. All solutions correspond to acid and ultra-acid waters (pH changes from -0.56 in mud pots to 2.97 in pore solutions, Fig. 5) with high redox potential which varies from 310 to 640 mV (in pore solutions of the hot site). The North-Mutnovskoe pots are characterized by wider variations in pH values from 1.57 to 7.35. It should be mentioned that the pH values of the majority of pots are in the interval from 1.95 to 4.20. Extreme pH values are rare: pH = 1.57 occurs only in one transparent pot (NM-2/07) and pH = 7.35 occurs only in a small sized pot (~ 30 cm in diameter) with a light bluish-gray suspension (NM-7/07). The redox potential also varies from 150 to 450 mV. No particular dependency between the acidity of solutions and their redox-potential is present. The groups of springs are separated on the diagram despite great variations in pH-Eh parameters in different groups of solutions.

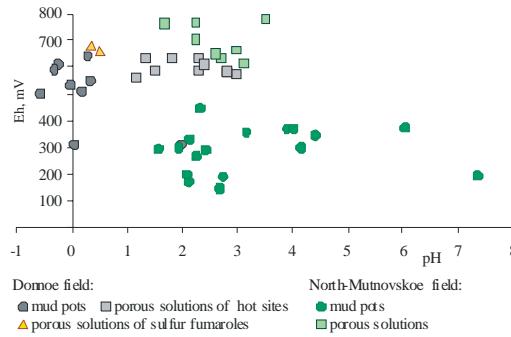


Figure 5: pH-Eh diagram for different solutions of the Donnoe and the North-Mutnovskoe fumarolic fields

4.2. Major ionic composition

4.2.1. Donnoe fumarolic field

The cation and anion compositions of solutions vary greatly. Sulfate and chlorides are the main anions; they make up 83 – 98 % of the anions (that is up to 56 g/l in the mud pots, Fig. 6).

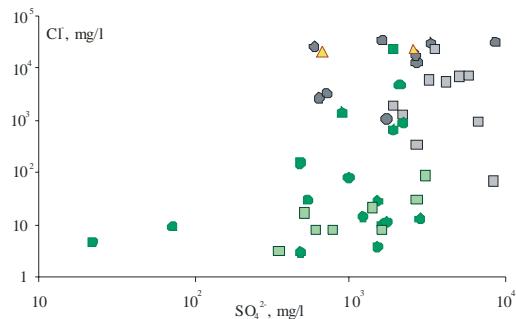


Figure 6: Major anion concentrations in solutions. Symbols are the same as in Fig. 5

Furthermore, fluoride is found in mud pot solutions (up to 290 ppm), but in North-Mutnovsky pots fluoride is below

the detection limit. Additionally, phosphates are common. The hot site pore solutions have the maximum PO₄ quantity (6600 ppm), while the mud pots contain up to 130 ppm PO₄.

The dominant cation is Al. The second main element is Fe. As a rule, bivalent iron ions dominate over trivalent ones, despite the oxidizing conditions in solutions.

4.2.2. North-Mutnovskoe field

The major anions of the pore solutions are chloride and sulphate, which have different concentrations. Sulphate dominates in the solutions of most pots. In only 3 pots does chloride amount to 68 – 95 % of the total anions. Phosphates (up to 5.2 ppm) and nitrates (up to 6.4 ppm) were measured in some pots. Cation composition is also different. Iron ions (bivalent or trivalent) are usually the most abundant, but in some pots the most abundant cation is Al. In some pots, ammonium NH₄⁺ dominates, and there was the only pot with Ca as a major cation. Potassium, Na, and Mn can be considered as secondary cations. Potassium and Na concentrations do not exceed several ppm and have mole fractions less than 1%. Only one pot, NM-1/06, contains 38 ppm K and 13 ppm Na. Concentrations of Mn range from 0.1 to 7.6 ppm, which exceeds the concentrations of K in three pots.

4.3. Trace elements

4.3.1. Donnoe fumarolic field

The main feature of mud pot solutions is high concentrations of Cr, Ni, Co, Ti, and V (Fig. 7). The maximum Cr content is in the pot N NDF-2, which was sampled in 2005, and is 60 ppm (Bortnikova et al., 2007). High concentrations of Co and Ni were also measured in this pot (33 and 0.48 mg/l, respectively). According to analyses of solutions from the Volcano Island published by Auippa et al. (2000), the Cr content in the Vasco waters is 45 ppm (unfortunately, the discussion of this phenomena is not given). The maximum measured concentrations of Ti and V are in pore solutions (more than 100 mg/l).

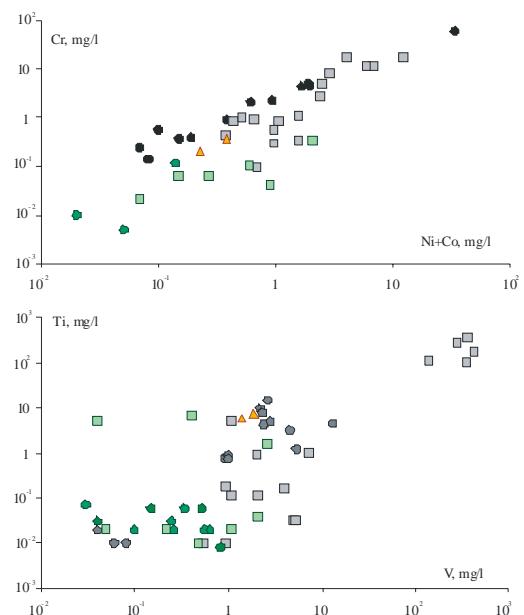


Figure 7: Concentrations of some trace elements in solutions.

4.3.2. North-Mutnovskoe field

Concentrations of the previously discussed elements in pot solutions at the North-Mutnovskoe field are lower than those in the Donnoe pots. However, the following elements have high concentrations: Cr -0.12, Ni - 0.09, Co - 0.19 (see Fig. 7).

Pore waters squeezed out from samples taken from pots' walls differ from free solutions taken inside the pots. It is important to note that V and Ti reach maximum concentrations in pore solution of mud pot NM-2/06 (2.6 and 1.5 mg/l respectively).

Association of elements Cr-Ni-Co-Ti-V is characteristic of the mud pot and pore solutions as at the Donnoe, and North-Mutnovskoe fields. Close correlation between these elements testifies to the similar behavior of these elements during hydrothermal transport.

4.4. REE concentration and patterns

4.4.1. Donnoe fumarolic field

The concentrations and distributions of REE should be discussed separately. Having high REE concentrations is one of particularities of the pots and the hot site solutions at the Donnoe field (Table 1). Total REE concentrations in solutions from mud pots range from 10^{-2} to 7×10^{-2} chondrite (Boynton, 1984). These contents in the Mutnovsky solutions are 14 times higher than those in the acid chlorite-sulfate waters of the Yellowstone hydrothermal system (Lewis et al., 1997). The total concentrations of REE reach up to 2000 ppb in the pots. In the hot sites solutions, they vary from 3600 to 12000 ppb (4 chondrite). Similar contents of REE are found in the pot Bolshoi at Ebeko Volcano and at the Verhne-Urevsky springs (Paramushir Island, one of the Kuril Islands) and 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 four pots (SDP - 3, 4, 5, 9) are similar (Fig. 8). The curves have negative slopes with significant enrichment in LREEs relative to HREEs. Solutions of the pots SDP - 2, 2/1 differ from the solution of the pot 7 in that they have comparatively elevated concentrations of HREEs. The solutions of the pots (especially solutions of the pot N

7) show flatter REE patterns. It should be noted that a negative Eu anomaly is lacking in all the solutions in spite of having high redox potential. This can be related to rapid transportation of deep fluid, which has reduced host media, to oxidative conditions just near surface.

As for hot sites solutions, the REE pattern is completely different, that is the HREEs essentially prevail over the LREEs (Fig. 8). Since all the solutions discharge into the local area, it is difficult to understand this significant difference in REE patterns.

So, the wide variations in REE concentrations and patterns found in thermal solutions indicate that very complex processes control the leaching, migration, and distribution of REEs. Water extracts from the solid substance of Donnoe hot sites contain comparatively high REE levels, although lower than those in pore solutions by more than three orders of magnitude (Fig. 8). This means that some part of the REEs is present in the solid as easily soluble compounds. Nevertheless, REEs behave differently under subsurface conditions. LREEs form more soluble compounds than HREEs. The ratio of pore solution: water extract for LREE varies 2 – 11. At the same time, this ratio is 40 – 130 for HREE. Consequently, HREEs are enriched in solutions, but they form more stable phases than LREEs in solids.

4.4.2. North-Mutnovskoe field

In free solutions from inside the pots, total REE contents vary two orders of magnitude from 0.9 to 95 ppb. In pore solutions taken from mud pots, total REE content is significantly higher: 18 – 160 ppb (Table 2). In pore solutions taken from thermal sites, total REE content averages 20 ppb.

According to REE patterns, the mud pots can be divided into three groups (Fig. 9). The first group (pots NM 1, 3, 8) has a smooth pattern with HREE enrichment. The second group (pots NM 2, 7) has slight LREE enrichment. The third group (pots NN 4, 5, 6) has noticeable HREE enrichment. In pore solutions taken from these mud pots, REE patterns are almost the same but at higher concentrations level (Fig. 9). Pore solutions from thermal sites have LREE enrichment that distinguishes them from all other types of solutions.

Table 1. Concentration of REE and PGE in mud pot, porous solutions, and water extracts, $\mu\text{g/l}$

Elm	Mud pot solutions							Pore solutions/Water extracts			
	SDP-2	SDP-2/1	SDP-3	SDP-4	SDP-5	SDP-7	SDP-9	SDP-10/06	SDP-11/06	SDP-12/06	SDP-13/06
La	170	130	140	55	340	110	170	200/14	10/17	89/40	150/53
Ce	380	300	350	130	920	300	490	650/62	50/55	350/110	500/130
Pr	56	45	55	23	140	54	82	150/13	20/8.7	90/22	120/25
Nd	220	170	200	92	540	260	310	750/61	164/35	540/110	680/120
Sm	44	37	36	17	90	74	52	350/19	104/10	280/33	340/35
Eu	12	11	8.8	3.6	21	26	11	200/7.5	72/4.9	150/13	160/12
Gd	41	36	28	12	58	88	34	1000/23	360/12	830/47	1000/50
Tb	6.6	6.1	4.1	1.6	7.2	14	4.5	200/4	80/2	190/9.5	210/9.0
Dy	44	38	23	8.4	35	85	23	2400/28	810/15	1940/72	2200/61
Ho	9.1	7.9	4.3	1.6	6	18	4.2	600/5.8	200/2.9	500/15	560/13
Er	26	23	12	4.3	16	53	11	2200/16	680/8.2	1700/46	1900/35
Tm	4.1	3.6	1.9	0.7	2.5	8.5	1.7	350/28	120/1.2	300/7.3	340/5.3
Yb	27	23	12	4.6	16	51	11	2600/20	860/8.0	2100/47	2300/31
Lu	3.9	3.4	1.7	0.7	2.2	7.2	1.6	400/2.8	140/1.0	340/6.7	370/4.4
Pd	2.2	1.8	1.2	0.2	1.4	0.5	0.2	19/0.16	34/0.22	30/0.5	12/0.2
Re	-	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	62/0.91	<0.1/0.015	2/0.1	3.2/0.1
Pt	1.8	0.9	0.32	0.062	0.45	0.79	0.04	100/0.11	64/ld	39/0.45	52/0.2

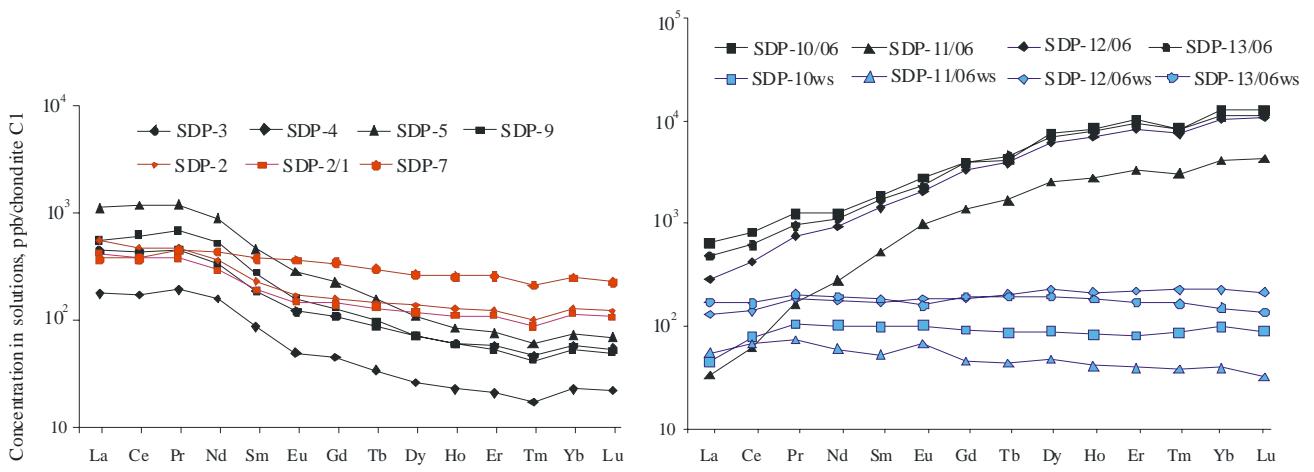


Figure 8: REE patterns in mud pot solutions (SDP-2 ÷ 9), pore solutions (SDP-10 ÷ 13/06) and water extracts (SDP-10 ÷ 13/06ws) at Donnoe field

Table 2. REE concentrations in solutions at North-Mutnovskoe fumarolic field, µg/l

	Mud pot solutions								Pore solutions of mud pots						Pore solut. of hot sites	
	NM-1/06	NM-2/06	NM-3/06	NM-4/06	NM-5/06	NM-6/06	NM-7/06	NM-8/06	NM-1/06ps	NM-2/06ps	NM-3/06ps	NM-7/06ps	NM-8/06ps	NM-8'/06ps	NM-11/06ps	NM-12/06ps
La	1.1	4.7	0.7	0.6	1.7	0.6	0.20	0.37	4.6	14	6.7	9.2	3.8	0.84	3.8	4.2
Ce	3.0	11	1.8	1.4	4.4	1.6	0.19	0.67	11	33	18	21	6.9	1.8	8.3	6.7
Pr	0.62	1.9	0.39	0.45	0.87	0.42	0.051	0.13	2.1	5.4	3.6	3.4	1.1	0.30	1.3	0.97
Nd	3.1	8.2	2.1	3.4	4.6	2.9	0.15	0.71	11	24	20	19	4.6	1.6	5.1	3.4
Sm	1.3	3.1	0.93	3.9	2.2	2.9	0.035	0.40	3.9	6.7	7.8	7.9	1.4	0.89	1.2	0.92
Eu	0.45	0.91	0.32	2.0	0.82	1.4	0.009	0.17	1.5	2.1	3.4	3.3	0.51	0.44	0.42	0.29
Gd	1.7	3.3	1.3	12	4.0	7.0	0.046	0.85	5.7	7.7	14	12	1.9	2.0	1.1	0.86
Tb	0.28	0.57	0.26	2.4	0.91	1.5	0.009	0.17	0.99	1.2	3.0	2.2	0.47	0.37	0.17	0.15
Dy	2.1	3.7	2.1	23	9.1	12.3	0.072	1.33	8.9	10	27	21	2.9	3.5	1.4	1.0
Ho	0.47	0.77	0.50	5.6	2.6	2.8	0.017	0.29	1.9	2.2	6.3	4.6	0.66	0.80	0.28	0.22
Er	1.4	2.1	1.5	17	8.5	8.4	0.045	0.91	5.6	6.6	20	14	2.0	2.4	0.79	0.62

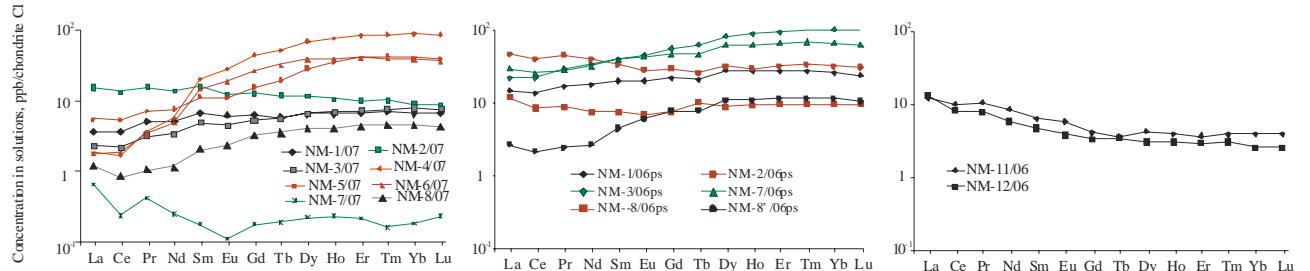


Figure 9: REE patterns in mud pots (left diagram) and pore solutions (middle and right diagrams) at North-Mutnovskoe field.

REEs display high correlation with a large number of elements (Al, V, Mg, Mn, Zn, Ti, Fe, Ni, Co, Cu and PGE) in the solutions (Fig. 10). The HREE group practically repeats the values of correlation coefficients for elements with total REE. As opposed to the HREE group, the LREE group is correlated only with Sr, Al, Ni. The obtained correlation dependences show that HREEs play the main role in the behavior of REEs during leaching and migration with thermal solutions.

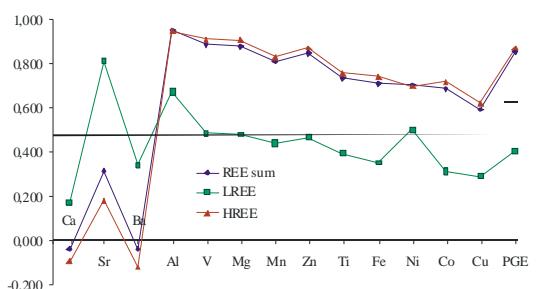


Figure 10: Values of correlation coefficients between REE and some elements

The main question that arises during analysis of concentrations, REE patterns, and correlation dependences is what is the HREEs enrichment process. HREE enrichment could occur as a result of the interaction of magmatic gases with ultrabasic rocks in the deep parts of volcanic structures. The fractionation of REEs and PGEs occurred during the partial melting of mantle ultrabasic rocks. LREEs were removed into the basalt solution (for example with monoclinic pyroxene), but HREEs and PGEs mainly remained in the ultrabasic restite. Light REEs left in the basalt melt (for example, with clinopyroxenes), but HREEs and PGEs mainly remained in ultrabasic restite. No ultrabasic rocks are known to occur in the Mutnovsky volcano. However, on the basis of the obtained data on the composition of solutions, it can be assumed that ultrabasic rocks are present in the composition of the Mutnovsky volcano construction. It is possible that the restites that didn't react with magmatic gases separated from the basalt chamber exist in the way of movement of solutions that supply the fumarolic fields of Mutnovsky volcano. The confirmations for this assumption are detection of high concentrations of PGE (Pt, Pd, Re) in pore solutions of the Donnoe field (Table 1) and significant correlation coefficients of the elements with total content of REEs and HREEs. The second necessary condition for occurrence of solutions of such composition at the surface is their transport through opened fracture channels minimizing influence of host basalts on gas and dissolved phases. Higher correlation coefficients of the LREEs with Ca, Sr, Ba (though for Ca and Ba they are statistically insignificant, but nevertheless we find it necessary to note them), compared to HREE and total REE fit logically to the general picture of REE behavior in the hydrothermal process. Most probably, plagioclases and monoclinic pyroxenes from basalts were a source of the LREE, which indicates an insignificant interaction of rising solutions with the host basalts composing the transport channels walls. It is known from previous studies that the presence of REEs in waters can be explained by leaching of the host rocks under subsurface conditions (Lewis et al., 1997; Shannon et al., 1991). However in our case, interaction obviously occurred in the deep parts of a system and solutions reached the surface with almost unchanged composition.

Ultrabasic rock formations are found in the cretaceous basement of Eastern Kamchatka belt extending along Eastern coast as far as the Avachinskaya group of volcanoes and to the south (Колосков et al., 2001). Xenoliths of ultrabasic rocks are found in volcanic rocks from Eastern Kamchatka volcanic belt. Facial analysis of the xenoliths testifies to their formation at comparatively shallow depth between formations of upper mantle and lower crust. These xenoliths are fragments of restites which may be one of the components of a mantle–crust transition layer in which a majority of Kamchatka volcanoes initial magma chambers are located. All this gives reason to expect that the deep structure of the Mutnovsky volcano also contains ultrabasic rocks that have been moved to the near surface horizon but are not yet found. Their presence is indicated by the obtained data on thermal water composition.

REE stability in solutions depends on pH conditions and redox potentials (Marcos, 2002). There is a 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 other factors may influence the releasing and presence of these elements in solutions. According to S.

Krainov (1973), the high REE concentrations in ground waters are associated with alkaline nepheline syenites. The sum of all REE reaches up to 8.7-664 ppb. We note that these waters interact with the rocks containing elevated REE concentrations. The Mutnovsky volcano is composed only of andesites, basalts, and ryolites (Selyangin, 1993). These rocks can not supply high REE concentrations in the solutions, especially enrichment in HREE. Evidently there are two main reasons for this phenomenon: i) the ultra-acid media and the high temperatures of fluids may make fluids dissolve these elements and ii) features of fluid transport to the surface. Since the rocks building the volcano contain a low REE concentrations, the obtained data must indicate a deep sources for fluids and multiple enrichments at geochemical barriers which exist inside of the volcano.

Besides in the pots and the hot sites solutions, Pt group elements (PGEs) are 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. It has been mentioned that in high temperature hydrothermal magma systems, high chloride fluids may control primary concentrations and redistributions of the elements of the Pt group because HCl makes complexes with PGEs, e.g. PtCl_3H (Hanley, 2005). The solubility of Pt may be high under elevated temperatures (800-900 °C) and in highly salty solutions. The theoretical thoughts make these elements' solubility noticeably lower than in reality. Complexes with HS^- are more probable in low temperature mediums (Wood, 2002). The stable association of following elements 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 magmatic fluids. In the Mutnovsky solutions the association of the chemical elements (Cr-V-Ti-Co-Ni-PGE-REE) is completely different to these from any known epithermal Au-Ag deposits (Asachinsky, Rodnikovy, Mutnovsky) within this region where typomorphic elements are Zn, Pb, Cu, Ag, Sb, Te and Au (Takahashi, 2005).

5. CONCLUSIONS

In the mud pots at the Mutnovsky volcano fumarolic fields, the anomalies in composition of the solutions are discovered. The concentrations of many chemical elements in these solutions are considerably higher than those in any other known volcanic waters. Distinctive features of solutions are three typomorphic associations of chemical elements: Cr-Ti-V-Ni-Co; REE; PGE.

High correlation coefficients specify similar behavior of these element associations in a deep source, in processes of leaching, during migration with magmatic gas ascent, and in solutions.

The positive slope of the REE patterns in pore solutions at the Donnoe field and in solutions at the North-Mutnovskoe field indicate an existence of ultramafic restites in the path of solutions' (or gasses') ascent, although ultramafic rocks at Mutnovsky volcano are yet unknown.

ACKNOWLEDGEMENTS.

We are indebted to G.M. Gavrilenko for support and help during field sampling. This study was performed with financial support from the Russian Fund of Fundamental Researches (grant N 07-05-00910) and IP SB – FEB RAS N 96.

REFERENCES

Auippa, A., Dongara, G., Capasso, G. and Allard, P.: Trace elements in the thermal groundwaters of Vulcano Island (Sicily), *Journal of Volcanology and Geothermal Research*, **98**, (2000), 189-207.

Bau, M.: Rare-earth element mobility during hydrothermal and metamorphic fluid-rock interaction and the significance of the oxidation state of europium, *Chemical Geology*, **93**, (1991), 219 – 230.

Bortnikova, S.B., Bessonova, E.P. and Zelenskii, M.E.: "Hydrogeochemistry of thermal springs at Ebeko volcano (Kuril Islands)", *Proceedings World Geothermal Congress 2005. Antalia, Turkey*, 24-29 April, 2005.

Bortnikova, S.B., Sharapov, V.N. and Bessonova, E.P.: Hydrogeochemical Composition of Springs at the Donnoe Fumarole Field, Mutnovsky Volcano (Southern Kamchatka) and Problems of Their Relation with Supercritical Magmatic Fluids, *Doklady Earth Sciences*, **413A**, N 3, (2007), 410–414.

Bortnikova, S.B., Bessonova, E.P., Gavrilko, G.M. et al.: Hydrogeochemistry of Thermal Sources, Mutnovsky Volcano, South Kamchatka (Russia). *34 Stanford Geothermal Workshop*. Stanford University. January 28 – 30, (2008).

Bortnikova, S.B., Bortnikova, S.P., Manstein, Yu.A. et al.: Thermal Springs Hydrogeochemistry and Structure at North-Mutnovskoe Fumarole Field (South Kamchatka, Russia). *PROCEEDINGS, Thirty-Fourth Workshop on Geothermal Reservoir Engineering*. Stanford University, Stanford, California, February 9-11, (2009), SGP-TR-187.

Boynton, W.V.: Cosmochemistry of the rare earth elements: meteorite studies. *Rare Earth Element Geochemistry*. Ed. P. Henderson. Oxford-Amsterdam: Elsevier, (1984) 63 – 114.

Hanley, J.J.: The aqueous geochemistry of the platinum-group elements (PGE) in surficial, low-T hydrothermal and high-T magmatic-hydrothermal environments *Exploration for Platinum-Group Element Deposits*. Ed. By J.E. Mungall. *Short Course Series*, Canada, **35**, (2005), 35 – 56.

Koloskov, A.V., Pusankov M.Yu., and Piroshkova, E.S.: Inclusions of ultramaphysts in basalts: to the problem of composition and genesis of the layer "crust – mantle". Geodynamics and volcanism of Kurilo-Kamchatka system. Petropavlovsk-Kamchatsky, (2001) 428.

Lewis, A.J., Palmer, M.R., Sturchio, N.C. and Kemp, A.J.: The rare earth element geochemistry of acid-sulfate and acid-sulfate-chloride geothermal system from Yellowstone National Park, Wyoming, USA, *Geochemica et Cosmochimica Acta*, **61**, № 4, (1997), 695-706.

Karpov, G.A., Bortnikova, S.B., Kusmin L.Yu. et al.: Hydrotherm geochemistry of the Academy Nauk Caldera (Kamchatka), *Hydrogeology and Water Geochemistry of Folded Regions of Siberia and Far East (Eds. O.V.Chudaev). Proceedings of Conference 11.09.2003 – 15.09.2003*, (2003). Vladivostok: Dalnauka, 108 – 117.

Marcos, N.: Low-temperature mobility of Rare Earth Elements (REE), K, and Th at the Olkiluoto Site, SW Finland, *Material Research Society. Symposium Proceedings*, **713**, (2002), 825-832.

Melekescev, I.V., Braitseva, O.A. and Ponomareva, V.V.: Activity dynamics of Mutnovsky and Gorely volcanoes in Golicene and volcanic dangerous for surrounding regions, *Volcanology and Seismology*, **3**, (1987), 3 – 18 (in Russian).

Polyak, B.G.: Geothermal features of present volcanism areas on Kamchatka example, Moscow, (1966), 180 (in Russian).

Selyangin, O.B.: New data on Mutnovsky volcano: structure, evolution, development, *Volcanology and Seismology*, **1**, (1993), 17-35 (in Russian).

Takahashi, R., Matsueda, H., Ono S. and Okrugin, V.M. "Sulfidisation state and elemental distribution at the Mutnovskoe polimetallic deposit in South Kamchatka, Russia", *Abstract with Program Volume, The Society of Resource Geology*. June 15 – 17 2005. Tokyo, Japan. (2005), № 0-07.

Taran, Y.A., Pilipenko, V.P., Rozhkov, A.M. and Vakin, E.A.: A geochemical model for fumaroles of the Mutnovsky volcano, Kamchatka, USSR, *Journal of Volcanology and Geothermal Research*, **49**, (1992), 269-283 (in Russian).

Vakin, E.A., Kirsanov, I.T. and Pronin, A.A.: Active funnel of the Mutnovsky Volcano", *Byull. Volcanol. Stantsii*, **40**, (1966), 25-36 (in Russian).

Wood, S.A. "The aqueous geochemistry of the platinum-group elements with applications to ore deposit. The Geology, Geochemistry, Mineralogy and Mineral Beneficiation of Platinum-Group Elements" (Ed. L.J. Cabri), *CIM Special Volume*, Montreal, **54**, (2002), 211 – 249.

Zelenskii, M.E. "Element transport and mineral formation in zones of high temperature fumaroles on Mutnovsky volcano (Kamchatka)", Ph.D. Thesis. Novosibirsk. (2003), 20 (in Russian).