THERMAL SPRINGS HYDROGEOCHEMISTRY AND STRUCTURE AT NORTH-MUTNOVSKOE FUMAROLE FIELD (SOUTH KAMCHATKA, RUSSIA)

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ABSTRACT

North-Mutnovskoe fumarolic field is the compact group of thermal springs. It locates in the volcano-tectonic zone of the Mutnovsky volcano in an oval deepening with low borders and flat bottom. About 20 strong vapor jets with the charge more than 0.03 kg/sec and temperature 96 – 110 °C are situated there. Hot small lake and tens of mud pots locate on the lowered sites. The thermal field area is $5.5 \bullet 10^3$ m^2.

Whole variety of mud pots was sampled in 2006-2007. In situ pH, Eh, T, and anions Cl^-, F^-, NO_3^-, NO_2^- were measured after some sedimentation of suspension. The samples were filtered using a 0.45 μm membrane filter. Humid solids from mud pot sides were sampled by special sampler on the long handle in thermal proof plastic containers. In laboratory pore waters were pressed out from the samples at 100 atm pressure. Cations and trace elements were measured by an ICP-AES method using IRIS Advantage instrument at the Analytical Center, IGM SB RAS. Content of REE and some other elements were derived using ICP-MS.

The electromagnetic frequency induction soundings were effected at this site at 2007 with NEMFIS (Near surface EM Frequency Induction Sounding) technique, developed in IPGG SB RAS. The geoelectric cross-sections are made along the 5 observation lines. Each cross-section reflects apparent resistivity distribution in the ground.

The compositions of mud pot solutions are various. All solutions correspond to acid and semi-acid waters. Prevailing cations in different pots are Fe^{2+}, Fe^{3+}, Al^{3+}, NH_4^+, in one of the pots – Ca. In the majority of pots concentration of Fe(II) more than Fe(III). High level of Fe(II) in combination with low redox conditions indicates reducing media in the underground reservoir. Among trace elements the main quota is made with Mn, then Zn, V, Sr, Ba, Ti, Cu, B, Co, Cr, Ni, Li, Be. The main features of solutions are the elevated concentrations V, Ti, Co, Cr, Ni in comparison with other volcanic areas. High concentrations of these elements were determined in mud pots of the Donnoe fumarolic field (Mutnovsky volcano). Uniform geochemical association specifies to uniform deep source of the whole volcanic system. Difference in element concentration can be consequence of structural features.

By geophysical prospection vertical shape of subsurface thermal water springs is recognized. Hydrogeochemical zoning of thermal field interior determines variety of mud pots and springs composition.

INTRODUCTION

Boiling mud pots of some volcanoes are very interesting phenomena. Their colors, water-solids ratio (consistence), physical - chemical conditions of their solutions, content of major and trace elements can vary in wide range. High contrasts of the mentioned parameters are usually featured for mud pots, 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), South-East fumarolic field of the Ebeko volcano (Bortnikova et al., 2005), thermal field of the Uzon volcano. Since the parameters are variable at very limited areas, their variability is difficult to explain only by different sources of thermal waters. North-Mutnovskoe fumarolic field is the bright example of the phenomena: numerous mud pots of various colors, consistence, boiling intensity can be found at the small area. It is supposed that large-scale fluid-magma hydrothermal systems and mud pots are driven by the same mechanisms and the scale is the only difference. Thus, the mud pots contrast study can give the understanding of nature and structure of large-scale fluid-magmatic systems of active volcanoes. The aim of the work is to explain the reasons of various thermal occurrences of the North-Mutnovskoe fumarolic field and to determine the

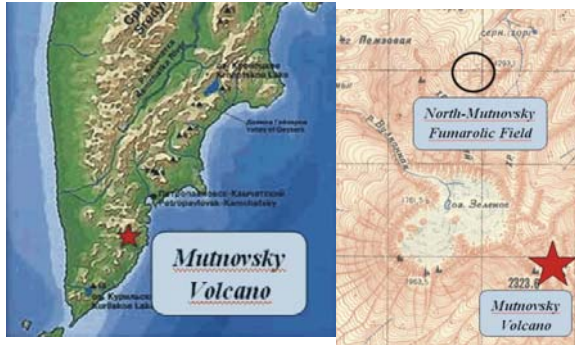possible sources of chemical elements in their solutions.

Figure 1: Location of the North-Mutnovskoe fumarolic field

OBJECT OF STUDY

North-Mutnovskoe fumarolic field is the compact group of thermal springs. It locates in the limit of volcano-tectonic zone of the Mutnovsky volcano in a few km from the main crater (Fig. 1) to northeast.

Square of the thermal field is 5.5×10^3 m^2 (isotherm + 20 °C, depth 50 cm). It looks as an oval deepening with low boards and the flat bottom of hydrothermally altered basalts. There are approximately 20 strong steam-and-water mixed jets with the charge more than 0.03 kg/sec and temperature 96 - 110 °C located on the fumarolic field. The set of thin steaming jets appears on the most heated places. On the lowered sites of the field hot lake and some tens mud and water pots are located. Mud pots differ in color, temperature, a consistence. Color of the majority of pots changes in grey scale - from white-grey up to black; there are green-grey, brown, bluish-gray pots. Pots are zero-discharge or have an insignificant drain. Coast and channels of streams on the thermal field are covered by brown hydrooxides of iron. "Hydrochemical breccia" is taking place there. It is the characteristic for zones of hydrothermally altered rocks.

METHODOLOGY

Field sampling

Whole variety of mud pots was sampled in 2006-2007 (Fig. 2). Water samples were taken by a Teflon sampler and transported in plastic boxes. Any contacts with metals were excluded. In situ pH, Eh, T, and anions Cl$^-$, F$^-$, NO$_3^-$, NO$_2^-$ were measured after some sedimentation of suspension. The samples were filtered using a 0.45 µm membrane filter. Humid solids from mud pot sides were sampled by special sampler on the long handle in thermal proof plastic containers. Containers were hermetically locked with the purpose of the subsequent extraction of the pore solutions in lab conditions. Moreover, rocks of

different hydrothermal alteration stage were sampled as well. The hosted basalts were sampled on the field side with no signs of hydrothermal altering. Cross section of metasomatites was mapped in the small stream board (it feeds from thawing snowfield). Upper parts of hot sites were sampled too. The steam and gas jets release continuously there. The rocks there are significantly altered up to soft hot humid substance.
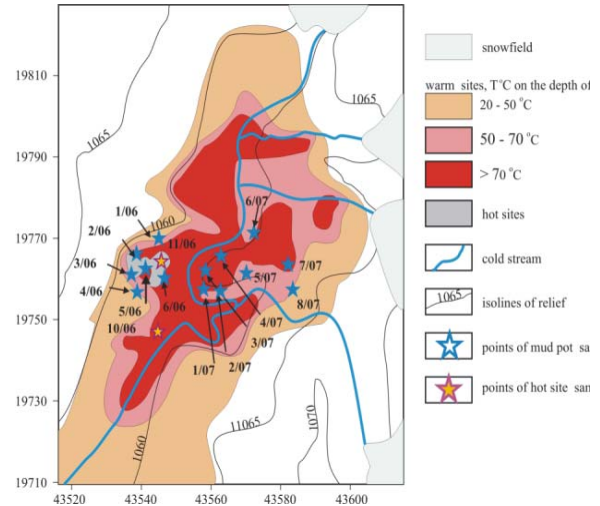

Figure 2: Sampling scheme of the North-Mutnovskoe fumarolic field

Laboratory investigation

Pore waters were squeezed out from the samples of humid solids at pressure of 100atm. Cations and trace elements in solutions were measured by an ICP-AES method using IRIS Advantage instrument at the Analytical Center, IGM SB RAS. A content of REE, and some other elements were derived using ICP-MS. Rocks of the field were studied under optical microscopy. Major components (oxides of silicate groups) were determined by XRF method and trace element composition was determined by XRF-SR method.

Geophysical prospection

Geophysical study in 2007 was provided by using surface electromagnetic frequency induction sounding (NEMFIS) technique. NEMFIS was developed by IPGG SB RAS. The soundings were performed at 14 frequencies in the range between 2.5 and 250 kHz. The obtained data were processed by ISystem software that is the part of NEMFIS. Geoelectrical cross-sections were created along 7 observation lines. Apparent specific resistance (ρ) 2D distribution was plotted on the cross-sections. The final quazi-3D visualization was performed by using the original software.

RESULTS

Hydrogeochemistry of mud pot solutions

Physico-chemical features

The compositions of mud pot solutions are varying in a wide range. Values of pH change in the range of 1.57 - 7.35 (Table 1, Fig. 3). Need to be mentioned,
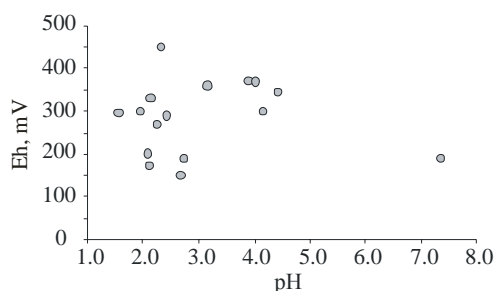

Figure 3: pH-Eh conditions in mud pot solutions

pH values of the majority of pots lay in a gamut 1.95 - 4.20. Extreme values pH = 1.57 are found out only

in one transparent pot (N 2/07), and pH = 7.35 - only in one of the pots as well, having the small size (~ 30 cm in diameter) with a light bluish-gray suspension. The redox potential also shows different values, changing in range 150 - 450 mV (see Fig. 3). Any particular dependency between acidity of solutions and redox-potential is not present.

Major components

Chloride- and sulfate-ions in a different ratios and different concentrations determine an anionic composition of solutions (Table 1, Fig. 4). Sulfate prevails in the majority of pots; however in three black pots chloride makes a major percentage 68 - 95 % among anions. Phosphate- and nitrate-ions are found in rather small amount in some pots (maximal concentrations are 5.2 and 6.4 mg/l accordingly). Cationic composition of mud pot solutions is rather various. Iron (Fe^{2+} and Fe^{3+}) is a main cation in major of pots, in others, located beside the leading part belongs to Al^{3+}. Normally, the content Fe^{2+} is much higher than Fe^{3+}. There are a few pots where major cation is NH_4^+. Only in one of the pots the dominant cation is Ca^{2+}.

Table 1. Concentration of elements in mud pot solutions, mg/L

Pot N	1/06	2/06	3/06	4/06	5/06	6/06	7/06	8/06	1/07	2/07	3/07	4/07	5/07	8/07	7/07
T	79	87	82	92	85	67	82	85	72	92	87	89	75	67	65
pH	2.12	1.95	2.08	2.25	2.33	4.15	2.43	2.14	3.9	1.57	2.68	3.16	2.74	4.02	7.35
Eh	174	300	200	270	450	300	290	330	370	297	150	360	190	368	192
Cl	680	900	25*	82	14	160	1.4*	4.8*	28	13	29	10	3.7	2.9	9.1
SO_4^{2-}	1.9*	2.2*	1900	980	1200	470	880	2.1*	1500	2800	530	1600	1500	480	72
PO_4^{2-}	ld	1.96	2.36	5.20	0.46	0.43	0.55	0.37	ld	ld	ld	ld	1.20	ld	0.45
NO_3^-	0.5	2	1.6	ld	ld	ld	1.4	0.8	4.4	3.3	6.4	3.4	2.6	6.3	5.1
Ca^{2+}	55	28	34	14	18	6.2	15	2.9	21	14	19	35	40	17	16
Mg^{2+}	39	13	21	8.9	7.6	3	15	5	18	7.5	7.9	57	30	8	4.1
Na^+	13	8	7.4	5.4	6.5	4.3	14	3.5	4.3	3.6	5.2	6	3.9	1.8	3.6
K^+	38	5.4	2.7	6.6	2.5	2.1	9.2	1.3	2.5	1.7	2.3	2.3	0.6	3.6	1.2
NH_4^+	130	23	19	ld	ld	ld	68	14	9.8	53	39	27	0.48	86	21
SiO_2	94	170	120	250	120	65	250	190	130	130	120	140	210	130	32
Fe	220	480	290	82	93	110	33	170	14	280	26	330	47	12	0.1
Fe^{2+}	220	360	260	1.24	80	55	25	140	25	235	40	0	50	23	0
Al	27	200	70	3.4	23	3.1	4.6	53	55	36	17	97	140	7.1	0.17
B	ld	0.21	ld	0.01	0.02	0.02	0.03	0.01	0.06	0.03	0.06	0.06	0.05	0.04	0.04
Mn	2.3	0.97	0.98	0.67	0.75	0.18	0.76	0.32	0.84	0.51	0.44	2.9	1.6	0.64	0.1
Zn	0.75	0.33	0.71	0.1	1	0.12	0.09	0.1	0.3	0.18	0.67	1	0.43	0.44	0.02
Cu	0.07	0.03	0.01	ld	0.02	ld	ld	ld	0.07	0.01	0.02	0.29	0.08	0.19	0.01
Cr	0.01	0.12	0.02	ld	0.005	ld	ld	0.01	ld	ld	ld	ld	ld	ld	ld
Ni	ld	0.04	ld	ld	0.02	ld	ld	ld	ld	0.01	ld	0.09	0.04	0.01	0.03
Co	ld	0.1	ld	ld	0.03	ld	ld	0.02	ld	ld	ld	0.19	0.02	ld	ld
Ti	0.02	0.02	0.06	0.02	0.07	0.05	0.02	0.03	ld	0.06	ld	0.06	0.008	ld	0.01
V	0.56	0.64	0.34	0.26	0.03	ld	0.1	0.25	0.15	0.15	0.06	0.53	0.82	ld	ld
Sr	0.28	0.18	0.24	0.1	0.18	0.05	0.12	0.04	0.07	0.15	0.13	0.16	0.16	0.52	0.08
Ba	0.01	0.87	0.06	0.06	0.06	0.06	0.06	0.06	0.03	0.07	0.04	0.04	0.03	0.07	0.04
Li	0.01	0.007	0.01	0.01	0.007	ld	0.01	0.005	ld	ld	ld	0.006	0.005	ld	0.004

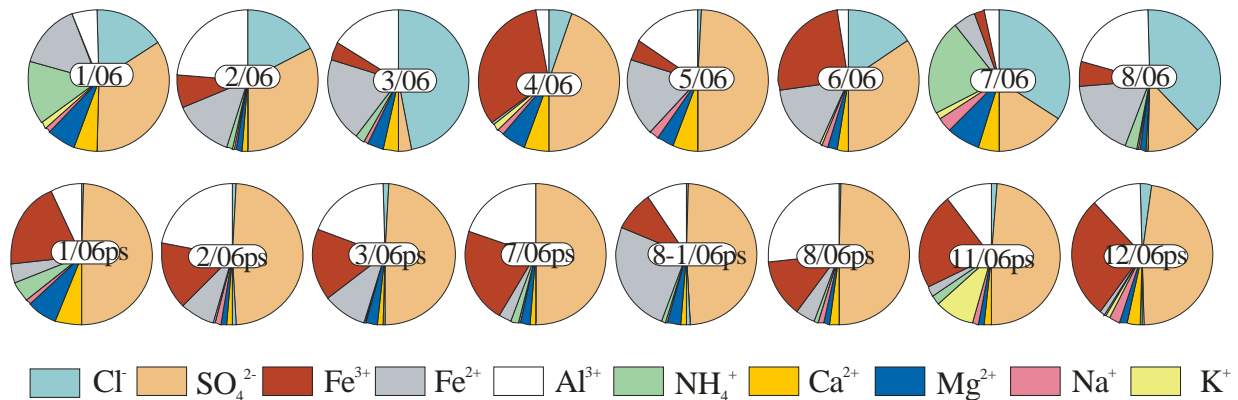Note: * - in g/l; ld – element is lower than limit of detection.

Figure 4: Percentage of major ions (mg-equ %) in mud pots and pore solutions. Sample numbers are shown in the center of the diagrams. "ps" denote pore solutions.

Minor elements

Elements K, Na, Mn are concerned to be the minor elements in mud pot solutions. Contents of K and Na make a few mg/l (only in one N 1/06 they rise up to 38 and 13 mg/l accordingly), in the majority of pots their moll percentage in cation composition is lower than 1 %. Concentration of Mn changes from 0.1 up to 7.6 mg/l; in three pots Mn concentration exceeds K ones.

Trace elements

Trace elements exhibit a wide range of concentrations. Elements Zn, V, Sr are most distributed among them (see Table 1). Their concentrations at average make 0.n mg/l. Elements Zn and Sr normally are present at thermal solutions of similar compositions in rather high concentrations. High concentrations of V are the unusual fact. The association of Cr-Ni-Co is interesting. These three elements are determined not in all samples, but in some solutions reach rather high values (maximum concentrations: Cr - 0.12; Ni - 0.09; Co - 0.19 mg/l).

Hydrogeochemistry of pore solutions

Pore solutions from the substance, taken from internal walls of pots, differ from free solutions of the same pots. Higher values of pH (except for the one pot N 7/06) and much lower contents of chlorides (on one - three orders) are characteristic. The main cations (Fe, Al and Mg) and the majority of trace elements (Mn, Zn, Cu, Cr, Ni, Co) in all cases are higher in pore solutions than in free boiling solutions in pots (Fig. 5).

It is necessary to note, the contents of V and Ti reach the maximum values in pore solution of the mud pot N 2/06 (2.6 and 1.5 mg/l accordingly). Arsenic and antimony, which were not found out in pots, are contained in high concentrations in pore solutions (up to 7.1 mg/l in N 2/06); Al^{3+} is the main cation there,

as in the pot N 8/06). The maximum contents of Fe (including Fe^{2+}), B, Cr, Ba, are in pot N 2/06 also.
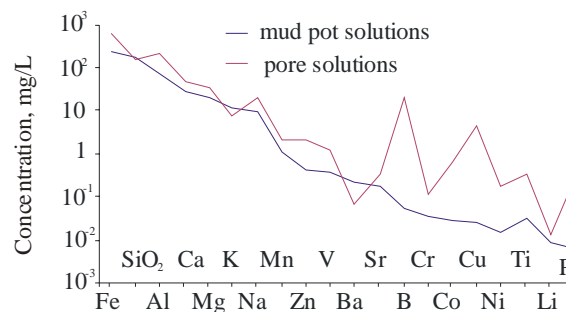

Figure 5: Comparison of element concentrations in mud pots and pore solutions (averages)

REE patterns

The content and REE patterns represent special interest. In solutions of pots total concentrations of REE change within the range of 2 orders - from 0.9 up to 95µg/l. Their contents are appreciably higher in pore solutions of pots: from 18 up to 160µg/l (Table 2). In pore solutions of thermal sites REE concentration is lower - about 20µg/l. By REE patterns pots can be divided into 3 groups (Fig. 6). In the first one (NN 1/06, 3/06, and 8/06) the line of the patterns is smoothed, however, enrichment by heavy REE is distinctly observed. In the second group it is possible to relate pots NN 2/06 and 7/06. In solutions of these pots LREE nevertheless are higher than HREE. The third group is represented by 3 pots (NN 4/06, 5/06, 6/06) where significant enrichment by HREE observed. In pore solutions of the same pots the form of curves is almost the same, but the concentrations are higher. Unfortunately, pore solutions of three pots in which sharp enrichment by a HREE was found out, have not been analyzed. Pore solutions of thermal sites differ from the other types of solutions due to the fact that LREE appreciably exceed a heavy part in them.

So, the main feature of pot solutions is a wide range of concentrations and relatively high level in concentrations of V, Ti, Co, Cr, Ni (in comparison with similar fumarolic fields in other active volcanic regions (for example, Giammanco et al., 1998; Auippa et al., 2000; Taran et al., 2003; Bortnikova et al., 2005). The named elements are present in high concentrations in mud pots in Donnoe fumarolic field of the Mutnovsky volcano (Bortnikova et al., 2007). Their presence in solutions testifies to a uniform deep source of the whole volcanic system. Variations in element contents of certain pots and fumarolic fields indicate various structural ways of superficial outputs.

Geochemistry of host rocks

Hydrothermal alteration
The analysis of elements' behavior during host rock hydrothermal alteration has been done for revealing the possible sources of elements releasing in solutions. Fresh basalts hosting the thermal field are low-potassium, characteristic for East and Southern Kamchatka (Selyangin, 1993). Practically all trace elements in these rocks are on a near-clarke level (Rolingston, 1994). Rocks correspond to typical ones and do not contain elevated concentrations of those elements which high quantities have been found out in thermal solutions. Taking into account the fact that a source of the majority of chemical elements in solutions of pots is a host rock of the volcanic construction, interacted with rising fluids, we see that the revealed anomalies should search for an explanation in composition of a magmatic fluid and in features of structural ways of its transport. Total alteration of basalts occurs due to sulfuric acid leaching. Hydrothermal substitution begins from dissolution of plagioclase and pyroxene, abundant silicifiucation of bulk rocks. Plagioclase relicts are replaced by fine-grained quartz, and Fe-ochers formed on the boundaries of pyroxene grains.

Table 2. Concentration of REE in different solutions, ppb

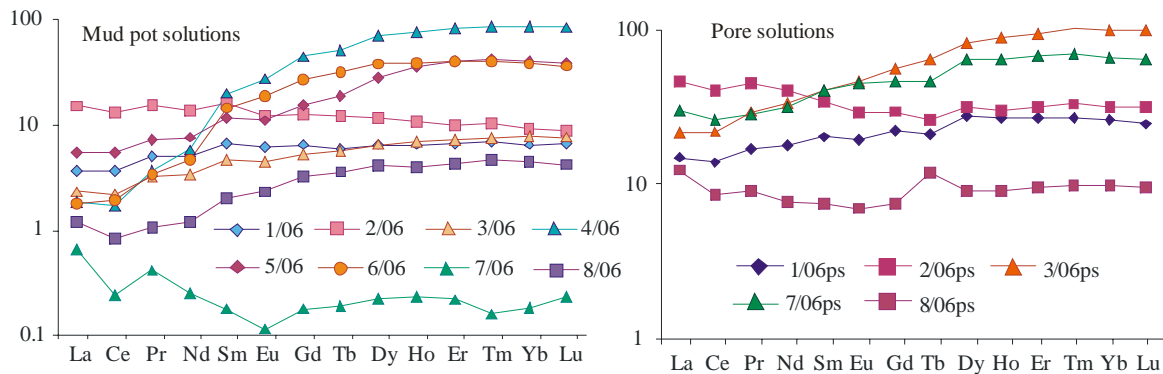|	Mud pot solutions								Pore solution of mud pots						Pore solut. of hot sites	
N	$1/_{06}$	$2/_{06}$	$3/_{06}$	$4/_{06}$	$5/_{06}$	$6/_{06}$	$7/_{06}$	$8/_{06}$	$1/_{06ps}$	$2/_{06ps}$	$3/_{06ps}$	$7/_{06ps}$	$8/_{06ps}$	$8'/_{06ps}$	$11/_{06ps}$	$12/_{06ps}$
La	1.1	4.7	0.7	0.6	1.7	0.6	0.20	0.37	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	0.55	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 6: REE patterns in mud pots and pore solutions. Y-axis is REE concentrations in samples, ppb/chondrite C1

Then residual relics were dissolved totally and substituted by secondary minerals.

The major minerals among them are quartz (it different structural species such as opal, chalcedone, tridimite), Fe – hydroxides, gypsum – anhydrite. The minor minerals in metasomatites are Fe-sulfides (pyrite, marcasite), native sulfur. Water-based sulfates apjohnite $MnAl_2(SO_4)_4 \times 22H_2O$, pickeringite $MgAl_2(SO_4)_4 \times 22H_2O$, butlerite $Fe^{3+}(SO_4)(OH) \times 2H_2O$ winebergite $AlSO_4(OH)_{10} \times 7H_2O$, sulfate: anglesite ($PbSO_4$), hydroxile-silicate of Al antophyllite formed in the course of the last stages of hydrothermal alteration are trace minerals. The substance of the upper part of hot sites is completely altered rocks which do not contain any relics of hosted basalts. The substance is continuously altering under action of heating, gas-steam jets, sulfur fumaroles. These rocks are composed by native sulfur and opal as major minerals, the minor one is anhydrite. Rare sulfides were determined in slight quantity kalininite – Cr_2ZnS_4, villamanite – CuS_2 and also bassanite - $CaSO_4 \times H_2O$, clinozoisite $Ca_2Al_3O(SiO_4)(Si_2O_7)OH$. Mud pot suspensions consist of mixture of kaolinite-smectite, pyrite, marcasite. Quartz, alunogene, anhydrite are minor minerals in mud pots. Native sulfur, talk, butlerite are determined in suspension of some mud pots. Mineral composition of mud pots differs in major minerals ratio and occurrence of trace particular minerals which are characteristic of particular pots.

Element behavior

Geochemical features of rock hydrothermal alteration were retraced on the consequence of basalt substitution by secondary minerals. The studied solids were divided into four groups: 1) fresh basalts; 2) metasomatites containing some relics of host basalts (hereafter these rocks will be named as "metasomathites"); 3) completely altered substance from hot sites (hereafter – "hot sites"; 4) suspension of mud pots. We suppose the formation of hot site substance and mud pot suspension occurred under action of a somewhat different processes. Steam-gas mixture ascending through a comparatively dry vapor system releases as jets, fumaroles, and vapor sites. If ascending fluid mixes with more quantity of meteoric (surface) water, it boils as mud pots and the composition of gurgling suspension forms from basalts, interacted with sulfur-acid solutions. From the above reasoning, let us analyze the geochemistry of hydrothermal alteration (metasomatism) on this field.

Almost all petrogen elements (oxides of silicate group) were removed from basalts while hydrothermal alteration. In metasomatites, composing a thermal field, the contents of silica at the average corresponds to the contents one in basalts, though with small fluctuations in a few samples. As it is proved by mineralogical investigations, silica re-deposition goes actively as its various species. Contents of TiO_2 are appreciably higher, than in basalts, due to its passive enrichment probably. On all the rock-forming oxides (excepting SiO_2 and TiO_2) metasomatites are depleted in comparison with fresh basalts (Fig. 7). Rocks of the thermal sites (through which steaming jets of different intensity go) are subjected for warming and steam - gas treatment. Even in the greater degree they are depleted by rock-forming oxides, excepting TiO_2 again (its contents in these samples is 5 times above, than in basalts) and silica.
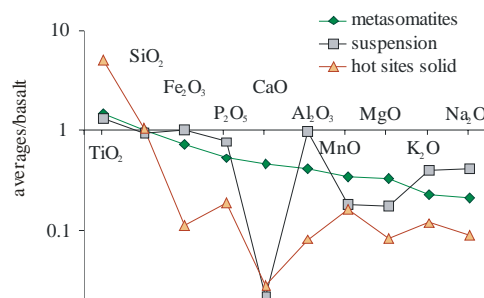

Figure 7: Comparison of basalt and metasomatites composition

In a suspension of pots contents of SiO_2, Al_2O_3, Fe_2O_3 on the average corresponds to the contents in basalts. Components P_2O_5, Na_2O, K_2O, MnO, MgO, CaO leaches actively, CaO - farthest.

Trace elements can be divided into some groups by their behavior in removal-deposit process in system «metasomatits - thermal sites - pots suspension» (Fig.8).

The first group includes oxo-hydroxo forming elements: Te, Se, As, Sb. Their common tendency is the accumulation in the top parts of the thermal sites and in the suspension of pots. Metasomatites are a little enriched with arsenic, but Te, Se and Sb in them are not found. Halogens (I and Br) found out a various behavior. Iodine is leached from metasomatites, enriching thermal sites and a suspension of pots. Bromine collects in metasomatits a little, and even more in thermal sites. In metasomatites it is possible to note light enrichment of Sn comparatively with other metals (Ni, Cu, Zn, Ag, Cd, Pb), they remain at the same level, as in basalts, or are leached. Thermal sites are distinctly enriched with tin, lead, and less – with silver. The suspension of pots even in a small degree is enriched with metals, except for zinc and lead. Elements, which can show amphoteric properties (Cr, V, Mo) in the given conditions, are leached from metasomatits and suspensions of pots. At the same time on thermal sites there is enrichment with vanadium and molybdenum. From trace rock forming elements only Ge appreciably enriches metasomatites, however in thermal sites and suspensions of pots also zirconium and niobium are concentrate.
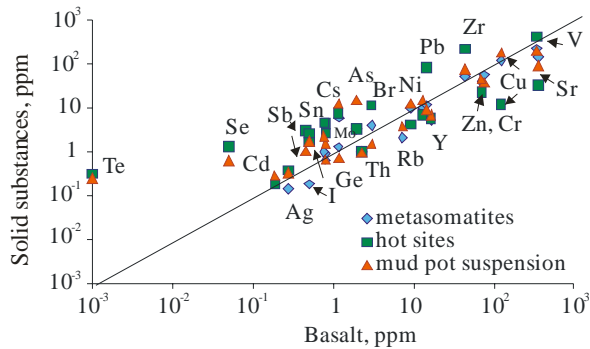
Figure 8: Average metal concentrations in the hosted basalts versus average concentrations in solid substance of the fumarolic field

Gemerally, it is possible to obtain the following picture of elements migration (Fig. 9).

Bearing strata hydrothermal process goes with significant import of oxo-hydroxo elements and halogens, which are allocated between the secondary altered rocks (metasomatites, new-forming solids on thermal hot sites, a suspension of pots), appreciably enriching them in comparison with fresh local basalts. The metals contained as impurity species in basalts, are actively redistributed due to sulfur-acid leaching. This process goes actively, which is testified by the big variety in metal contents in solutions and suspensions of pots. Minor rock-forming elements also act in thermal solutions, but in a lesser degree.

Relative mobility of elements

The relative mobility (RM) of elements is calculated from their water/rock concentration ratio, normalized to sodium:

$$RM = (X/Na)_w/(X/Na)_r$$

where w and r refer to the solution and the fresh rock (basalts) respectively. This approach was applied to Etna groundwater (Aiuppa et al., 2000) referring to the previous researches (Gislason and Eugster, 1987). Analyses of element relative mobility in the system "thermal solution – host rocks" allow revealing

orders which have good accordance with the main geochemical features of the elements. The most mobile elements releasing in solutions are oxo-hydroxo forming ones: B, As, Sb, Bi, Se. Then there is a group of metals: Cu, Zn, Pb, Ni, Fe, Co, and K. Elements showing amphoteric properties make the third group of mobility (U, Al, V, Cr, Mn). Inert elements in this system are the main ones and trace rock-forming elements are: Mg, Sr, Li, Ca, Th, Zr, Ba, Ti. In the combination with the data on metasomatites geochemical composition and suspensions of mud pots it is possible to assume, the elements of the first group are originated from the deeper source, obviously, with magmatic gases. They are very mobile and concentrate in the top parts of hydrothermally altered rocks, as a reason of anomalies occurrence in solids and solutions. Metals are rather actively leached under action of hydrothermal alteration of host rocks and redistributed in mud pots between dissolved and suspended phases. Inert elements in a small amount nevertheless release in solutions from host rocks which are depleted by these elements in the course of transformation to metasomatites.

The principal reason of the large variability in the physical - chemical conditions of mud pots and a wide range in chemical element concentrations, we believe, is a complicated structure of subsurface geochemical barrier. There is a boiling up of rising solutions which are a mix of magmatic fluids and meteoric waters and their division into a condensate and separation on this barrier. In that case when the barrier is located just near the surface, in solutions of mud pots the separate composition is prevailing (the most mineralized acid solutions with the high contents of trace elements). In a situation when the barrier is shipped downwards, the composition of surface solutions will be made of the greater part of a condensate in a mix with the meteoric waters with different composition and conditions.
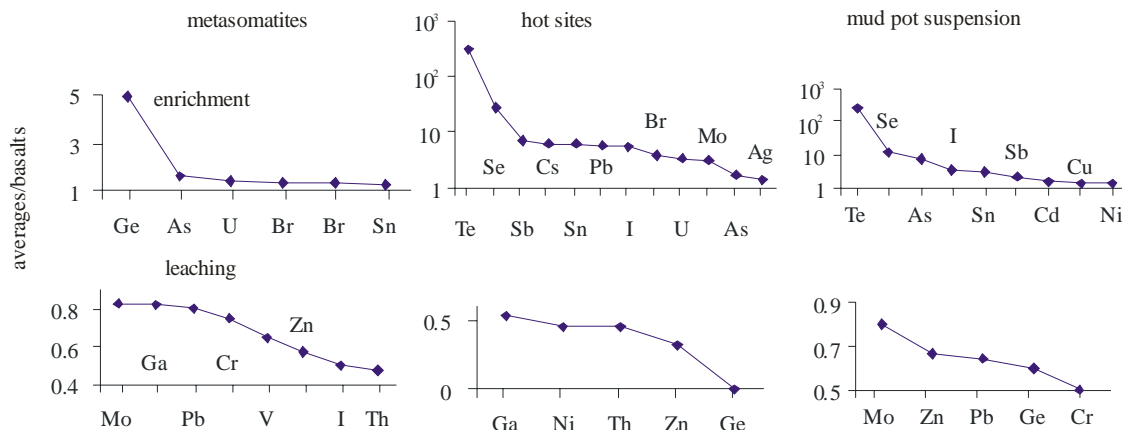

Fiugure 9: Element enrichment-depletion in the course of rock hydrothermal alteration.

Structure of fumaroli field subsurface

Geophysical prospecting (frequency EMI sounding by NEMFIS) shows the inner structure at the depth up to 7 m (Fig. 10), giving additional information for the discussion. The resistive (blue color) and conductive (red color) zones can be seen. The zones describe spring channels and phase barrier structure. The reliance between electric resistance and hydrothermal system parameters is complicated. Low electric resistance is not always an indicator of high mineralization of the pore water. Mineral composition of the dredge, water/rock ratio as well as temperature and mineralization affects to the resistance. Generally, red color describes acidic hot highly mineralized solutions with high water/rock ratio. Upper parts of conductive zones (red vertical plumes on cross-sections) correspond to the last, near surface geochemical barrier, where solutions separate. Steaming and gas-vapor streams at thermal field are the examples of such a separation. Cross-sections of thermal field featured approaching of hot springs up to the surface (red zones) and their boiling. Pore water composition at thermal fields is the result of division into condensate and separate. Condensate goes out as gas-vapor jets, separate stays at pores. Similar process can be seen in the pots, where the fluid boiling in the pot and separate stays at the pot walls. The mutual interaction between boiling fluids of mud pots and pore solutions leads to partial mixing of them, but highly mineralized fluid mainly remains in pores.

CONCLUSIONS

Compositions of mud pots on North-Mutnovskoe Fumarolic Field vary in a wide range of element concentrations as well as in chemical-physical conditions of solutions. The elevated contents of Co-Ni-Cr-V-Ti association specify the unity of the fluid source of the Mutnovsky volcano thermal fields and of the described field.

The REE concentrations and patterns rather various in mud pots of a thermal field testify to active unstable processes of dissolution of a host rocks mineral matrix and releasing of separate REE groups in solutions.

Geophysical prospecting has shown a structure of subsurface spaces of the thermal field and has found out hydrogeochemical zonality. It is caused by a varying level of a phase barrier on which there is a boiling of solutions and their division. We explain variations in mud pot compositions by the distinctions of the mechanism of solution division with the subsequent rise to a surface of their different fractions.
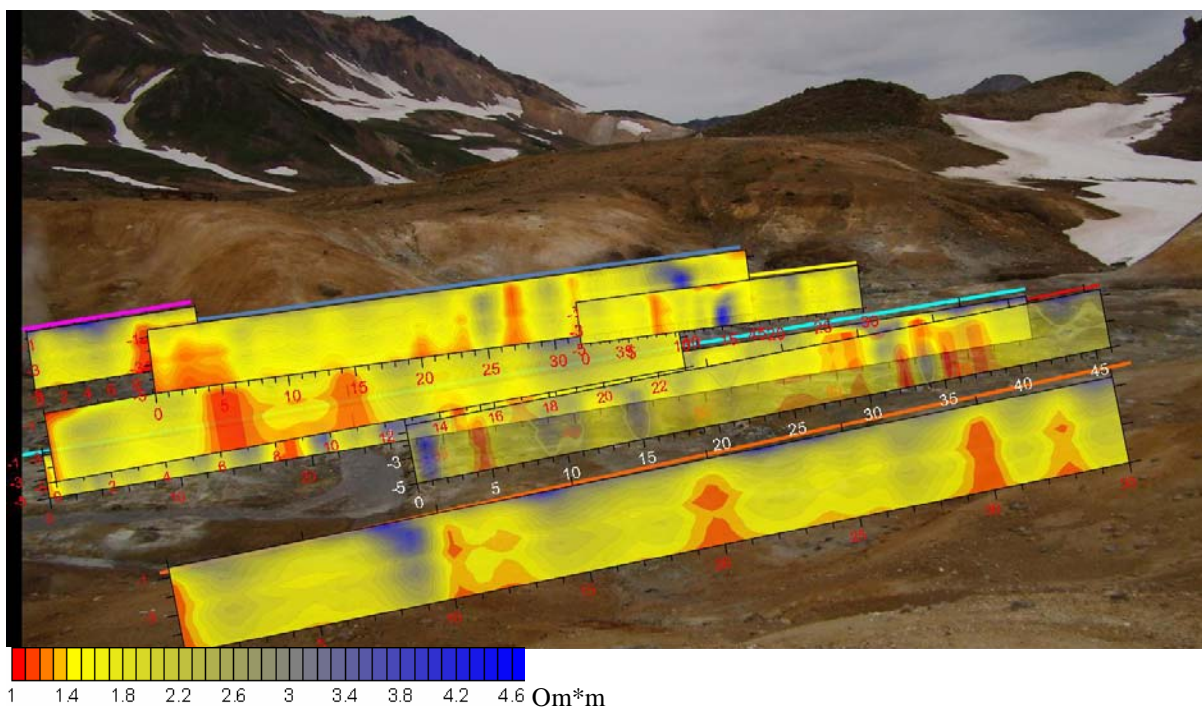
Figure 10: Profiles showing distribution of specific resistance in subsurface inner space on North-Mutnovsky Fumarolic Field.

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