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## GEOCHEMISTRY

# Hydrogeochemical Composition of Springs at the Donnoe Fumarole Field, Mutnovsky Volcano (Southern Kamchatka) and Problems of Their Relation with Supercritical Magmatic Fluids

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The Mutnovsky Volcano (main summit at 52°21′ N, 158°16′ E; absolute altitude 2323 m) is located 75 km south of the town of Petropavlovsk-Kamchatsky. In terms of explosive activity and heat discharge, this volcano is presently among the most active volcanoes of the Kamchatka volcanic belt. Two merged craters are located to the northwest and west of the summit. Among several known historical eruptions, the last two eruptions (in 1960–1961 [1, 2] and on March 17, 2000 [3]) were described in detail. Between eruptions, the volcano is characterized by intense fumarole activity. Three fumarole fields are located in the eastern crater (Fig. 1): (1) Verkhnee (i.e., Upper) field with vent temperatures of more than 300°C; (2) Donnoe (i.e., Bottom) field consisting of two relatively separate vents with temperatures up to 150°C; (3) Aktivnaya (i.e., Active) 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 [1–4]. The high seismicity and constant "seismic vibration" of the Earth's crust [5] provoke changes in the position and activity of fumaroles and hot springs at the Donnoe field. These processes could promote the formation of compositionally anomalous springs, whose study provides insight into the hydrodynamics and composition of supercritical magmatic fluids in highly permeable fluid-conductive systems. This paper reports the most interesting data on the composition of some hot springs of the Donnoe field and results of numerical physicochemical modeling of the dynamics of the modern magmatic fluid system of Mutnovsky Volcano.

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## METHODS

In 2003 and 2005, we sampled springs, basins, and mud pot of the Donnoe fumarolic field. Sampling of aqueous solutions was accompanied by in situ measurement of pH, *Eh*, and $Cl^-$ and $F^-$ contents with an Ekspert 001 ion meter. Water aliquots for laboratory analysis during sampling were filtered through a membrane filter 0.45 μm and then transported in a plastic

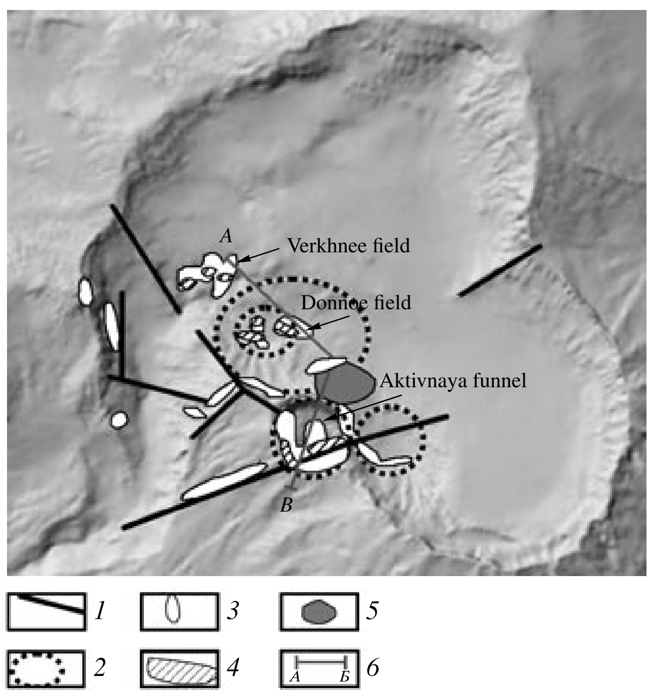


**Fig. 1.** Structure of the Mutnovsky Volcano crater. (*1*) Dikes; (*2*) within-caldera craters and explosive funnels; (*3*) thermal anomaly zones (TIMS data); (*4*) fumaroles, mud pots, and vents; (*5*) contour of Activnaya funnel; (*6*) profile *A–B* (see Fig. 3).

Composition of gas–hydrothermal springs, basins, and mud pots in the Donnoe fumarole field (Mutnovsky Volcano), mg/l

| Parameter | Background solutions, $n = 6$ | *Red* basins, $n = 3$ | Lakes in the DFF | | Otkrytyi Hole | Solutions from sublimates |
|---|---|---|---|---|---|---|
| pH | 3.2 | 2.4 | 2.2 | 2.7 | 0.03 | 0.23 |
| *Eh* | 392 | 673 | 690 | 670 | 716 | – |
| $Cl^-$, g/l | 0.1 | 0.1 | 0.064 | 0.021 | **>100** | – |
| $SO_4^{2-}$, g/l | 1.7 | 13 | 2.1 | 1.9 | 11 | – |
| $F^-$ | 0.019 | 11 | 2.2 | 6.6 | 0.01 | – |
| $PO_4^{2-}$ | n.d. | 3.5 | n.d. | 4.4 | 36 | 920 |
| $Na^+$ | 2.1 | 30 | 12 | 7.6 | 130 | 1450 |
| $K^+$ | 3.6 | 1.60 | 3.9 | 0.84 | 200 | 120 |
| $Ca^{2+}$ | 55 | 450 | 349 | 340 | 110 | 53 |
| $Mg^{2+}$ | 2.5 | 62 | 21 | 36 | 29 | 1850 |
| $SiO_2$ | 34 | 170 | 22 | 34 | 99 | 8.52 |
| Al | 5.6 | 410 | 110 | 95 | **720** | **6020** |
| Fe | 7.8 | 2300 | 160 | 260 | 330 | 1120 |
| Mn | 0.086 | 4.5 | 0.47 | 1.0 | 5.5 | 30 |
| B | 0.091 | 0.25 | n.d. | n.d. | **52** | **90** |
| Ba | 0.052 | 0.012 | 0.010 | 0.0016 | 0.24 | n.d. |
| Li | n.d. | 0.019 | n.d. | n.d. | 0.037 | 2.5 |
| Sr | 0.15 | 1.1 | 0.57 | 0.73 | **5.6** | **3.7** |
| As | n.d. | 1.9 | n.d. | 0.25 | 0.39 | **21** |
| Zn | 0.091 | 1.2 | 0.11 | 0.33 | 0.45 | 39 |
| Cu | 0.033 | 3.7 | 0.18 | 1.12 | 0.62 | 5.4 |
| Pb | n.d. | n.d. | n.d. | n.d. | 0.29 | n.d. |
| Ti | 0.031 | ″ | 0.20 | 0.036 | **4.2** | **114** |
| V | 0.022 | ″ | 0.30 | 0.23 | **2.4** | **140** |
| Co | 0.0017 | 1.2 | n.d. | 0.20 | 0.48 | 3.4 |
| Cr | n.d. | 0.15 | ″ | 0.045 | **60** | **11** |
| Ni | 0.0029 | 0.86 | ″ | 0.080 | **33** | **3.5** |
| Nb | n.d. | n.d. | 0.037 | 0.03 | n.d. | 17 |
| Mo | ″ | ″ | n.d. | n.d. | **0.39** | n.d. |
| Sn | ″ | ″ | ″ | ″ | n.d. | **3.7** |
| Zr | ″ | ″ | ″ | ″ | ″ | 0.26 |
| Ga | ″ | ″ | ″ | ″ | ″ | 3.5 |

Note: (–) Not analyzed; (n.d.) below detection limit.

containers. We analyzed the liquid phase squeezed out from a sample of the crust of newly formed minerals in the thermal field.

Cation and trace element composition of the solutions was determined by ICP-AES on an IRIS Advantage device at the Analytical Center of the Institute of Geology and Mineralogy, Novosibirsk. The sulfate contents in aqueous solutions were determined by conventional colorimetric method. Data on metal contents obtained for aqueous solutions from thermal potholes were checked by atomic absorption.

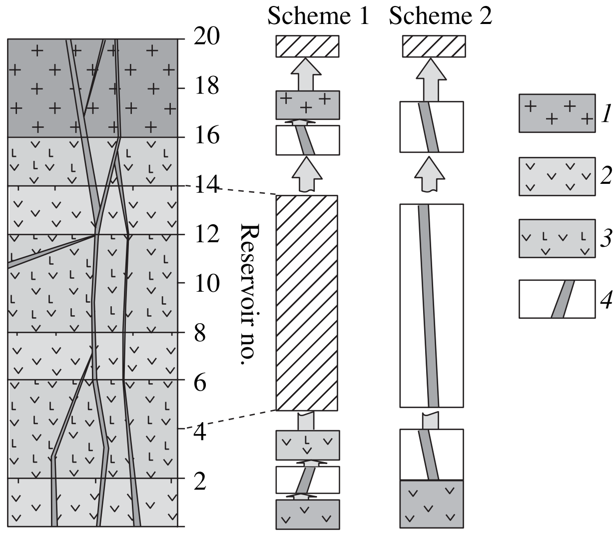


**Fig. 2.** Scheme of model columns. (*1*) Andesidacite; (*2*) basalt; (*3*) basaltic andesite; (*4*) fissure zone.

## RESULTS AND DISCUSSION

The springs studied in the Mutnovsky Volcano crater have diverse composition, but most of them belong to acid waters (pH ~ 2.5–3.5). For the sake of convenience in comparisons, the solutions of springs related to thawed water were taken as the background level (table). Another type of solutions occurs in small "lakes" with negligible subwater emanation and semitransparent water. They are similar to the background solutions in pH value, but differ in higher contents of Al, Ca, Mg, Na, Mn, Fe, As, Cu, Ti, Co, Cr, and P. Three small basins located near the lakes are filled with transparent dark brown or brown-red water. As compared to the background springs, solutions in the basins are more acid and saline (high concentration of Fe, Ca, and Al). The average Fe content is 2.3 g/l (maximum 6 g/l). The solutions have high contents of Cu, Zn, and As.

At the Donnoe field, several mud pots with dark gray to black dense "gurgling" (boiling) mass (*T* ~ 90–94°C, pH 0.33–0.45) occur among springs with semitransparent water, basins, and streams. The solution in one of the holes (Otkrytyi, i.e., Open) is characterized by a unique composition. Anions are mainly represented by $Cl^-$ and $SO_4^{2-}$. Phosphates and fluorides occur in significant amounts.

Cations are dominated by Al and Fe. The solution in this mud pot is marked not only by extremely high contents of chlorides, but also by high contents of Cr, Ni, Co, Ti, and V (two orders of magnitude higher than those in background solutions). The highest contents of these elements previously known from the Kuril–Kamchatka volcanic arc at Kunashir Island [6] are one to three orders of magnitude lower. The solution is also characterized by high concentrations of Au, Mo, and Zr, which are atypical of hydrothermal springs in areas of basaltic andesite volcanoes, and extremely high contents of B and Sr. The compositions of solutions squeezed from sublimates even more emphasize the unique composition of the Donnoe field spring, though significantly differing from solutions of the pot. They have higher contents of Al, B, Ti, V, As, Zn, Cu, and Co and significant amounts of Ga, Nb, Zr, and Sn. In addition to predominant pickeringite and alunogen, oxides and hydrous sulfates of Cr, Ni, Co, and V also occur in sublimates.

The composition of solutions in the boiling potholes of the Donnoe field supports the hypothesis [4] of the existence of brines beneath its surface and requires explanation of the formation of such an unusual composition.

## NUMERICAL PHYSICOCHEMICAL MODELING OF COMPOSITIONAL VARIATIONS IN SUPERCRITICAL MAGMATIC FLUID

It is difficult to determine directly the composition of supercritical magmatic gases [4]. The composition of magmatic gas can only be estimated by numerical physicochemical modeling of equilibrium dynamics of the orthomagmatic fluid system. Modeling was conducted with the method of [7] using a Selector Win program in continuous reactor modification [8]. We considered two approximations for the transportation of magmatic fluid from the fluid separation boundary of a crystallizing basic melt (Fig. 2): (1) filtration of a gas mixture through heterogeneous (compositionally layered) fractured rock of volcanic edifice; (2) 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 [9–11] were used in calculations.

Virtual inspection of all scenarios showed that the C/H ratio should be 0.2 or less in the hypothetic initial gas mixture. If equilibrium is not shifted at temperatures of its mixing with surface water vapors, gas can contain 30% magmatic water vapor, $CO/CO_2 < 10^{-2}$ and $CH_4 < 10\%$. The problem of extraction of major and trace components by magmatic gas from rocks located in a shallow chamber was solved by the second structural scheme (Fig. 2). Under reducing conditions (initial $pO_2$ <14), major and trace elements are weakly

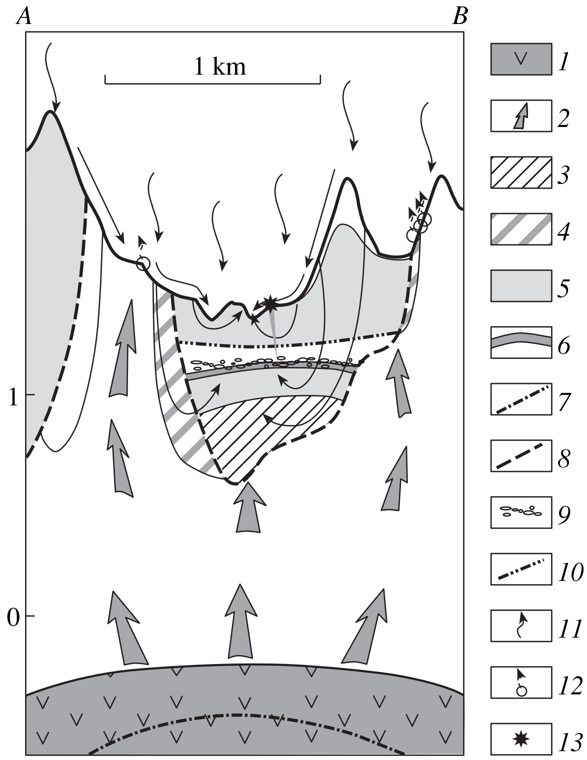


**Fig. 3.** Schematic model of fluid dynamics in the Mutnovsky Volcano section. (*1*) Basaltic body, (source of heat and gases); (*2*) magmatic fluid; (*3*) inferred zone of magmatic gas condensates; (*4*) zone of mixed gases, (*5*) zone of mixed solutions; (*6*) brine formation area; (*7*) retrograde boiling boundary; (*8*) condensation boundary; (*9*) secondary boiling boundary; (*10*) secondary condensation boundary; (*11*) meteoric waters; (*12*) fumaroles; (*13*) Otkrytyi Hole.

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 significant 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 [12]. We propose a qualitative scheme of a mixed (fluid magmatic) system for the present-day morphology of the Mutnovsky Volcano crater (Fig. 3). In this model, the position of the magmatic gas condensation boundary is estimated from dynamics of retrograde boiling of magma in a shallow intrusion [13]. The condensation boundary can be located beneath a zone of magmatogenic 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.

## CONCLUSIONS

Hydrothermal springs of Mutnovsky Volcano with anomalous contents of ore and petrogenic components can be regarded as a local area of brine discharge from the concentration zone of components of magmatic fluids located beneath a phase barrier in the largest meltwater pools in the central part of the crater. Magmatic and supercritical fluids variably diluted by surface water vapors are discharged symmetrically along the central part of the sublatitudinal fault, which controls the position of thermal vents. The higher the position of the fissure zone, the more heated and less metamorphosed fluids reach the volcanic edifice surface. The composition of the ore-forming fluid suggests that the brine formation area can include a modern ore generation zone with specific mineralization.

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## REFERENCES

1. E. A. Vakin, I. T. Kirsanov, and T. P. Kirsanova, Byull. Volcanol. Stantsii, No. 40, 25 (1966).

2. M. E. Zelenskii, A. A. Ovsyannikov, G. M. Gavrilenko, and S. L. Senyukov, Vulcanol. Seismol., No. 5, 25 (2002).
3. M. E. Zelenskii, Candidate's Dissertation in Geology and Mineralogy (Petropavlovsk-Kamchatskii, 2003).
4. Yu. A. Taran, E. A. Vakin, V. P. Pilipenko, and A. M. Rozhkov, Vulcanol. Seismol., No. 5, 37 (1991).
5. A. V. Kiryukhin, V. L. Leonov, I. B. Slovtsov, et al., Vulcanol. Seismol., No. 5, 19 (2005).
6. V. A. Chudaeva, O. V. Chudaev, K. Sugimori, et al., *Chemical Composition of Some Hydrothermally Active Areas in the Kuril Islands: Biogeochemical and Geoecological Processes in Ecosystems* (Dal'nauka, Vladivostok, 2005), Issue 15, pp. 155–200 [in Russian].
7. V. N. Sharapov, Geol. Geofiz. **46**, 459 (2005).
8. I. K. Karpov, K. V. Chudnenko, D. A. Bychinskii, et al., Geol. Geofiz. **39**, 1 (1995).
9. H. Yokokawa, J. Nat. Chem. Lab. Industry **83**, 27 (1988).
10. R. Reid, J. Prausnitz, and T. Sherwood, *The Properties of Gases and Liquids* (McGraw-Hill, New York, 1977).
11. T. L. Woods and R. M. Garrels, *Thermodynamic Values at Low Temperature for Natural Inorganic Materials: An Uncritical Summary* (Oxford Univ., New York, 1987).
12. E. P. Bessonova, Candidate's Dissertation in Geology and Mineralogy (Inst. Geol. Sib. Otd. Ross. Akad. Nauk, Novosibirsk, 2004).
13. V. N. Sharapov, V. A. Akimtsev, V. N. Dorovskii, et al., *Dynamics of the Evolution of Ore-Magmatic Systems in the Spreading Zones* (NITs OIGGM, Novosibirsk, 2000) [in Russian].