# Sources of Volatiles for a Subduction Zone Volcano: Mutnovsky Volcano, Kamchatka

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Abstract—Starting from some assumptions, the fluid balance was calculated for Mutnovsky volcano within simple mixing model by comparison of chemical and isotopic composition of gas emissions with compositions of main geochemical reservoirs in subduction zones. The main deep component (up to 70-73% of the highest temperature fumaroles) is represented by slab fluid released during dehydration of the Pacific plate. The mantle component does not exceed 2.1%. The fraction of gases of continental crust varies from 0.5 to 5% depending on the composition of final component used in calculations. In terms of the gas composition, Mutnovsky volcano is ascribed to the typical subduction volcanoes, but its fluid system is characterized by a complex structure of. Observed chemical variations in volcanic fumaroles are explained by degassing of two magmatic bodies.

Keywords: Kamchatka, Mutnovsky volcano, volcanic gases, fluid balance, slab, mantle, continental crust. DOI: 10.1134/S001670291204009X

# **INTRODUCTION**

Fluid flows in the subduction-related zones of continental margins and island arcs play the key role in the Earth's degassing. Volatiles escaping from subducting oceanic plate (slab) contribute in the generation of island-arc magmas, while volcanic arcs mark the fluid discharge zones at the Earth's surface. The total amount of volatiles that are released from volcanoes and during formation of intrusions in the island-arc zones is compensated by volatiles that are fluxed into magma generation zone from mantle (mantle wedge), oceanic crust, and continental crust [1-3]. However, existing massbalance estimates are few in number and rather approximate ( $\pm$  half an order of magnitude). Volcanoes that discharge high-temperature fumaroles in a state of long-lasting degassing (Satsuma-Iwojima, Momotombo, Kudryavy, and Mutnovsky) provide insight into fluid regime of subduction zone. The behavior of inert and weakly active components (He, Ar, N<sub>2</sub>, CO<sub>2</sub>) and the isotopic composition of light elements (H/ED,  ${}^{3}\text{He}/{}^{4}\text{He}$ ,  ${}^{12}\text{C}/{}^{13}\text{C}$ ,  ${}^{14}\text{N}/{}^{15}\text{N}$ ,  ${}^{16}\text{O}/{}^{18}\text{O}$ ) in gases are used to estimate the substance sources. The proportions of these components in volcanic gases depend on the input of main five geochemical reservoirs of subduction zones: mantle, altered oceanic crust, oceanic sediments, continental crust, and meteoric waters. Each of the reservoirs is characterized by a unique combination of components (geochemical signature). The signatures of the reservoirs could be found in volcanic gases after mixing of fluids and dilution by meteoric waters. For these purposes, different techniques are applied: determination of He, Ar, N<sub>2</sub>, and CO<sub>2</sub> concentrations [4], measurement of mantle helium <sup>3</sup>He flux and helium ratios [5, 6], the study of isotopic composition of nitrogen  $\delta^{15}$ N [7, 8] or carbon  $\delta^{13}$ C [9], SO<sub>2</sub> emission [10], melt inclusions [11], as well as the combination of all these methods [1, 3, 12].

Mutnovsky volcano (South Kamchatka) demonstrates intense and steady gas discharge during at least several dozens of years. The volcano contains three fumarolic fields with gas temperatures from 98 to 620°C (in 2006). Steam vents and Mutnovsky geothermal field were found north of the volcano (Fig. 1). The paper presents the original data on the composition of gases of the volcano and adjacent thermal fields based on sampling in 2006–2007. The whole data massif includes information on major components (H<sub>2</sub>O, CO<sub>2</sub>, S, HCl, HF), trace gases (H<sub>2</sub>, CO, CH<sub>4</sub>, N<sub>2</sub>, Ar, and He) and isotopic ratios (H/D,  ${}^{3}\text{He}/{}^{4}\text{He}$ ,  ${}^{16}\text{O}/{}^{18}\text{O}$ ). Using these data with allowance for the modern concepts on the processes proceeding in the subduction zone, we calculated the contributions of main reservoirs (crust, mantle, and



Fig. 1. Digital topographic model of Mutnovsky volcano.

atmosphere) in the formation of fluids of Mutnovsky volcano.

# GEOLOGICAL DESCRIPTION OF THE REGION

The volcano belongs to the northern segment of the Kurile–Kamchatka volcanic arc and the Eastern (frontal) volcanic belt of Kamchatka. It is situated at a distance 20 km from the Pacific coast and 200 km from the deep-water trench axis. The Moho depth beneath the volcano is estimated as 22 km [13]. The depth to the Benioff zone according to seismological studies is 90–110 km, which is typical of the island-arc frontal belts [14]. The Pacific plates moves relative to Kamchatka with a rate of 8-9 cm/yr [1, 15].

Mutnovsky volcano represents the short volcanic ridge consisting of three merged stratocones M2-M4

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(Fig. 2). Cone M1 is strongly eroded and has no a clear topographic expression. The cones were formed during four subsequent stages of activity in the Late Pleis-tocene–Holocene. During former three stages, the eruption products evolved from basalts to rhyodacites. The last cycle has not been completed yet [16]. All last eruptions of the volcano were phreatic explosions, except for 1848-year eruption, which provided a moderate ejection of juvenile material [17].

An absolute altitude of the volcano is 2323 m, and relative height is 1400 m. Two large craters, Northeastern  $(1.5 \times 2 \text{ km}^2)$  and Southwestern  $(1.3 \times 1.3 \text{ km}^2)$ , are situated west of the main peak of the volcano and partially overlap each other (Fig. 2). The most part of both the craters is covered by glacier, but the lowermost part of the Northeastern crater contains two fumarolic field with moderate emissions and temperatures of 98–280°C. Aktivnaya funnel, the active young crater,  $0.35 \times$ 

The base of the volcano is interpreted as a complex of Upper Cretaceous and Pliocene volcanogenic—sedimentary rocks, with the predominance of volcanogenic component varying in composition from basalts to rhyolites. All these rocks were partially metamorphosed to the greenschist facies and subjected to hydrothermal alterations, mainly propylitization. The Miocene Akhomten granodiorite intrusion  $15 \times 15 \text{ km}^2$  in size is located immediately east of Mutnovsky volcano [18].

The extinct Skalistyi and Dvugorbaya stratovolcanoes and strongly eroded Zhirovsky volcano are located north and northeast of Mutnovsky volcano, respectively (Fig. 1). These volcanoes together with the latter surround the plateau containing the Mutnovsky geothermal field and thermal fields with the low-temperature (98–120°C) steam vents. 16 productive boreholes of the 1 field (2007) feed two geothermal power plants with total capacity of 60 MW.

The nearest active Gorely volcano is located 15 km northwest of Mutnovsky volcano. The modern eruption products of Gorely volcano are basalts and basaltic andesites. However, the volcano is located in the central part of caldera ( $9 \times 13 \text{ km}^2$ ) formed during strong eruption of dacitic ignimbrites [18]. Based on the detailed geochemical study of the lavas of Mutnovsky volcano, Duggen et al. [19] showed that magma beneath this volcano was generated by partial melting of mantle triggered by ascending flow of aqueous fluid dehydrated from slab minerals.

## PREVIOUS STUDIES OF FLUID REGIME OF THE VOLCANO

Mutnovsky volcano is one of the best studied volcanoes of Kamchatka. Soon after 1961 eruption, several papers were published on the thermal power of fumaroles and gas composition [20-22]. Serafimova [21] presented the detailed map of fumarolic fields with temperatures and velocities of gases, as well as analyses of the hottest fumaroles. Polyak et al. [23] and Murav'ev et al. [24] estimated the thermal power of the volcano. Taran et al. [25, 26] studied the compositions of hydrothermal fluids from natural thermal occurrences and boreholes. Conceptual geochemical model of Mut-1 novsky volcano was developed for the first time by Taran et al [27], but fumaroles of Aktivnaya funnel practically were not sampled at that time. The mineralogy of lowtemperature fumarolic incrustations was described in the work of Serafimova [22]. The compositions of gases of high-temperature fumaroles of Aktivnaya funnel, including the concentrations of metals, were reported in the work of Zelenski and Bortnikova [28].

#### SAMPLING AND ANALYTICAL METHODS

Gases were collected in the 100–250 ml Giggenbach ampoules with teflon valve filled with 50 ml 4N KOH and pressurized [29]. In order to take 50 ml of condensate in each sampling point, gas was passed through two





**Fig. 2.** (a) Mutnovsky volcano, view from the south. Volcanic ridge consists of several merged cones. (b) view from the east. Cones M3 and M4 are characterized by peaked craters of significant size. (c) Scheme of volcano with position of fumarolic fields. The plume area approximately corresponds to the intensities of emissions. Photo by M. Zelenski.

 $0.45 \text{ km}^2$  in size, with the most powerful fumaroles is located in the rim of the Southwestern crater. The rocks of the northern and central parts of the volcano experienced intense hydrothermal alterations.

successive bubbler flasks, which were cooled with a snow-water mixture. Gas temperature was measured by CA thermocouple. Gases from geothermal borehole were taken from cyclone separators on the well head with pressure of vapor-water mixture separation of 8 kbar.

In addition to gas, we also sampled meteoric waters: both rain and snow, and waters of local channels, including volcanic lake. In relation with a limited volume of the paper, the compositions of meteoric waters are not listed in tables, but were used in calculations and shown in plots.

In laboratory, some part of nonabsorbed gases from the Giggenbach ampoules was extracted for  ${}^{3}\text{He}/{}^{4}\text{He}$ isotopic analysis. Remaining gases were analyzed by gas chromatography at the Institute of Volcanology and Seismology of the Russian Academy of Sciences in Petropavlovsk Kamchatskii. The contents of N<sub>2</sub> and Ar in samples were corrected for oxygen: N<sub>2</sub> (corr) = N<sub>2</sub> (samples)-O<sub>2</sub> · 2.3; Ar(corr) = Ar (sample)-O<sub>2</sub>/23. Such a correction is insufficient (some oxygen in samples interacts with H<sub>2</sub>S and CO), but nevertheless improves the measurement accuracy.

Liquid part of sample was oxidized by  $H_2O_2$  during heating up to 80°C in order to transform all sulfur species into  $SO_4^{2-}$  [29]. The CO<sub>2</sub> concentrations in liquid were determined using volumetric method by replacing CO<sub>2</sub> with excess 50%  $H_2SO_4$  in a vacuum chamber at heating. The volume of CO<sub>2</sub> was determined from pressure change in camera (Institute of Experimental Mineralogy, Russian Academy of Sciences, Chernogolovka). The contents of  $SO_4^{2-}$ , F<sup>-</sup>, and Cl<sup>-</sup> were measured in the oxidized alkaline solution on ion chromatograph at the Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences in Moscow.

The isotopic ratios of D/H ( $\delta D \pm 1\%$ ) and  ${}^{18}O/{}^{16}O$ ( $\delta^{18}O \pm 0.1\%$ ) in aqueous solutions of condensates were measured by IRMS method on a Finnigan DELTA<sup>plus</sup>. The oxygen isotopic composition was measured by isotopic equilibration with CO<sub>2</sub> at 25°C, with recalculations using  $\alpha(CO_2-H_2O) = 1.0412$ . The hydrogen isotopic composition was studied by water reduction (1 µl) on a metallic chromium at 800°C. All data are presented relative to SMOW, their linearity and accuracy were controlled using standard IAEA samples OH-1, OH-2, OH-3, and OH-4 (IGEM RAS). Some samples were analyzed using CF-IRMS at the Geological Institute of the Russian Academy of Sciences in Moscow and Instituto de Geofisica UNAM in Mexico.

The <sup>3</sup>He/<sup>4</sup>He ratios were analyzed on a gas static VG Isotopes VG-5400TFT mass spectrometer modified for simultaneous measurement of <sup>3</sup>He and <sup>4</sup>He ions in order to diminish the measurement error in <sup>3</sup>He/<sup>4</sup>He isotopic ratio in <sup>3</sup>He-rich gases. Correction for possible air contamination was made using <sup>4</sup>He/<sup>20</sup>Ne ratio (Instituto Nazionale di Geofisica e Vulcanologia, Palermo).

In the text and tables, the concentrations of components, if not noted otherwise, are given in volume or molar % (%, mmol/mol) ratio.

## GENERAL CHARACTERISTICS OF THE THERMAL OCCURRENCES OF THE AREA

The fumarolic gases usually consist of three main components: "primary" magmatic component releasing directly from magma, "secondary" hydrothermal component separating mainly from two-phase hydrothermal system [30], as well as meteoric vapor. In the magmatic component,  $fO_2$  and speciations of elements with variable valence (H<sub>2</sub>/H<sub>2</sub>O, CH<sub>4</sub>/CO/CO<sub>2</sub>, NH<sub>3</sub>/N<sub>2</sub>, H<sub>2</sub>S/SO<sub>2</sub>) are determined by SO<sub>2</sub>-H<sub>2</sub>S internal gas buffer. Magmatic gases are disequilibrium with rocks. Hydrothermal gases are formed during evo-

lution of meteoric waters  $ASW^1$  with some admixture of magmatic component and enriched in H<sub>2</sub>S, CH<sub>4</sub>, and NH<sub>3</sub>. The oxygen fugacity  $fO_2$  in the hydrothermal component is controlled by equilibrium with rocks, which is close to HM buffer (Fe<sub>2</sub>O<sub>3</sub>/Fe<sub>3</sub>O<sub>4</sub>). Both magmatic and hydrothermal components and their mixture could be diluted by evaporated subsurface meteoric waters, which did not attain equilibrium with rocks and compositionally correspond to ASW.

In this paper, we consider only thermal occurrences with temperature above water boiling at given altitude, i.e. gas vents. The main parameters of the thermal occurrences are shown in Table 1, while the chemical and isotopic compositions of gases are listed in Table 2. Three fumarolic fields are situated within the volcano (Figs. 1, 2). Numerous thermal sites on the outer slopes of the volcano could be united by term "steam jets." Mutnovsky geothermal field represents the independent thermal occurrence.

*Aktivnaya funnel* is the small but most active crater of the volcano with steep walls up to 200 m high and flat bottom. This crater ejects the most powerful (up to 80% of total emission of the volcano) and hottest (620°C in 2006) fumaroles, which have the highest contents of magmatic components in the area.

*The Donnoe field* is located in the lowermost part of the Northeastern crater, on the floor of former lake, which gave him its name. Gases are 3–4 times more diluted by meteoric waters as compared to those of the Aktivnaya funnel, but have the highest HCl/S ratio.

The *Verkhnee field* is located higher than the Donnoe field, beneath the glacier. Though the distance

<sup>&</sup>lt;sup>1</sup> (ASW) Air-saturated water, the meteoric water saturated in air. Calculations were based on composition of water that is in equilibrium with air at 5°C).

Parameters	Aktivnaya funnel	Donnoe field	Verkhnee field	Steam jets	Geothermal fluid
Localization	Aktivnaya funnel crater	NE crater	NE crater	5–10 km north of the volcano	6–8 km north of the volcano
Discharge, kg/s	80*	5**	15**	10-20 (estimate)	560
<i>T</i> , °C***	200-620	98–265	98-280	98	160–170 (borehole head)
Sum of gas components without water, $\%$	1.9–4.2	0.48-1.5	0.24-0.67	0.03-0.3	0.002-0.15
$SO_2/H_2S$	$5\pm3$	0.2 - 2.0	$0.2 \pm 0.1$	~0	~0
R/Ra****	5.29-5.99	7.59-7.67	6.59-6.98	4.11-6.66	3.99-5.89
CH <sub>4</sub> , ppm	0.05-0.73	0.9–2.9	12-24	3–15	0.3–3

 Table 1. Thermal occurrences of the area and their characteristics

Notes: \* Based on measurements of SO<sub>2</sub> emission [31] with allowance for weight-average concentrations of 3.5 wt % SO<sub>2</sub>

\*\* Determined by comparison of the visible area of fumarolic plumes in the photos [32].

\*\*\* 2006

\*\*\*\* R/Ra ratios denotes the He isotope composition, where  $R = {}^{3}He/{}^{4}He$  in sample and  $Ra = {}^{3}He/{}^{4}He = 1.39 \times 10^{-6}$  in atmosphere.

between them is as small as 200 m, their gases sharply differ in composition. The gases of the Verkhnee field are typical hydrothermal gases ( $SO_2/H_2S = 0.2$ ) with high concentrations of methane and temperatures up to 280°C.

Several *thermal sites* with boilers, steam jets, and hot springs are situated on the northern slopes of volcano and further northward. All gas vents have temperature close to the boiling point, extremely low concentrations



Fig. 3. Classification of thermal occurrences of the area in the diagram  $N_2$ -Ar-CH<sub>4</sub>. Gases are subdivided into magmatic, hydrothermal and consisting mainly of meteoric component [4].

of chlorides, but significant amounts of  $CO_2$ ,  $H_2S$ , and  $CH_4$ .

The geothermal fluid from the productive boreholes 1 of the Mutnovsky thermal field contains ~ 0.01-0.05% CO<sub>2</sub>, H<sub>2</sub>S, and other gases of non-atmospheric origin, which is an order of magnitude lower than that in the nearest natural vents. The temperature of  $165 \pm 5^{\circ}$ C in the well head is determined by technological parameters of vapor separation.

Following abbreviations were used for thermal occurrences: Aktivnaya funnel—AF, Donnoe filed—DF, Verkhnee Field—VF, thermal sites with steam jets (SJ), geothermal fluid—GF.

Triple  $N_2$  –Ar–CH<sub>4</sub> diagram (Fig. 3) divides the fumarolic gases into mainly magmatic, hydrothermal, and meteoric types. It is believed that methane is formed in hydrothermal gases owing to the gas-rock interaction, while argon is mainly atmospheric in origin and incorporated in gases with meteoric water [4, 30, 33]. Gases with a great fraction of magmatic fluid in the subduction zone are characterized by high  $N_2/Ar$  ratios. CH<sub>4</sub> and Ar-rich hydrothermal gases are plotted in the lower part of the diagram, with mixing trend observed between high- and low-methane gases. In the geothermal fluid and gases of steam jets, the  $N_2/Ar$  ratio varies from 39 (ASW) to 84 (air). In the gases of Aktivnaya funnel, the  $N_2/Ar$  ratio reaches 800–1500, which is typical of the island-arc volcanoes [4]. The distribution of major components  $CO_2$ -S-HCl is shown in Fig. 4. Mainly hydrothermal gases (Verkhnee field, steam jets, and boreholes) are enriched in  $CO_2$ , while the gases of 1 the Donnoe field have the highest relative HCl contents. The hottest gases of the Aktivnaya funnel have the following proportions of major components  $CO_2$ :S:HCl = 10:5:1, which is close to the average com-

position of volcanic gases of subduction zone  $CO_2$ :S:HCl = 10:5:2 [34]. At the same time, even these

gases are diluted by meteoric waters by  $40\%^2$  as compared to the average island-arc gas. The gases of the Donnoe field are characterized by sharply distinct proportions of CO<sub>2</sub>:S:HCl = 10:10:5, which is presumably caused by high degassing of magmatic body feeding this field. Hydrothermal gases are sharply depleted in chloride due to the gas exsolution from two-phase system.

# OXYGEN AND HYDROGEN ISOTOPIC COMPOSITION OF WATER AND ESTIMATES OF CONTRIBUTION OF THE METEORIC AND MAGMATIC COMPONENTS

Diagram  $\delta D - \delta^{18}O$  (Fig. 5), in addition to the data points of studied gases, demonstrates the compositions of atmospheric precipitates of this area. These compositions define the Local Meteoric Water Line (LMWL). Twenty seven data points define a regression line with equation  $\delta D = 8.2 \times \delta^{18}O + 16.5$ , which shows the higher deuterium excess than in the equation of the Global Meteoric Water Line of Craig ( $\delta D = 8 \times \delta^{18}O +$ 10). In general, obtained equation of LMWL may be used for further calculations. This is confirmed by the position of data point of the crater lake that was formed after 2000 eruption ( $\delta D = -112\%$  and  $\delta^{18}O = -15.7\%$ ) in the LMWL. The lake originated owing to thawing of multiyear snow covers and glaciers. Since the sample was taken soon after lake formation, the surface evaporation cannot significantly affect the isotopic composition of water. Hence, this composition can be considered as the averaged composition of meteoric water for volcanic crater.

The isotopic compositions of the gases of the Donnoe field and Aktivnaya funnel define a mixing trend between magmatic and meteoric components, which is typical of island-arc volcanoes [35, 36]. The composition of meteoric diluent can be determined from relations HCl–  $\delta D$  and HCl–  $\delta^{18}O$  by extrapolating isotopic parameters to zero HCl concentration (Fig. 6). Obtained values of the meteoric component  $\delta D_{met} =$  $-102 \pm 4\%$  and  $\delta^{18}O_{met} = -9.8 \pm 0.6\%$  reveal a significant oxygen-isotopic shift (+4.5‰) in response to the isotopic exchange with rocks [37]. The value of  $\delta^{18}O = +5.9 \pm 0.5\%$  can be taken as initial composition of water in equilibrium with magmas and should correspond to the oxygen isotopic composition of the Mutnovsky basalts [38] due to the low coefficient of isotope fractionation at melt temperature. Extrapolation of mixing trend to  $\delta^{18}O = 5.9 \pm 0.5\%$  yields  $\delta D =$  $-19 \pm 3\%$ , which plots in the field of so-called "andesitic water" [35, 36]. The fraction of magmatic water  $f_{MAGM}$  in samples corresponds to the projections of data points in mixing trend and can be calculated from equations:

$$f_{\text{MAGM}} = (\delta^{18}\text{O} - \delta^{18}\text{O}_{\text{met}}) / (\delta^{18}\text{O}_{\text{MAGM}} - \delta^{18}\text{O}_{\text{met}}), (1)$$
$$f_{\text{MAGM}} = (\delta\text{D} - \delta\text{D}_{\text{met}}) / (\delta\text{D}_{\text{MAGM}} - \delta\text{D}_{\text{met}}). (2)$$

The fraction of meteoric waters is calculated from balance equation:

$$f_{\rm ASW} = 1 - f_{\rm MAGM}.$$
 (3)

Assuming ideal mixing between two components, equations (1) and (2) should yield similar results. Actually, the difference reaches 10-15% due to the non-ideal sampling and measurements, as well as contribution in the mixture of additional components of unusual isotopic composition.

According to equations (1)–(3), the gases of the Aktivnaya funnel define a scatter of  $f_{MAGM} \sim 28-73\%$ , however, most of the high temperature fumaroles (up to 70% of total volcanic emission) fall in a narrow compositional range of  $61 \pm 3\%$   $f_{MAGM}$ . In the gases of the Donnoe field,  $f_{MAGM}$  varies from 2 to 30%. Similarly, most of the fumaroles of the DF (up to 70% of total field emission) fall in a narrow range of  $25 \pm 3\%$   $f_{MAGM}$  (Fig. 5).

The isotopic compositions of hydrothermal gases do not define mixing trends in the diagram  $\delta D - \delta^{18}O$ , but are grouped into three separate clusters close to LMWL. The Verkhnee field discharges the hydrothermal steam with  $\delta D = -106 \pm 2\%$  and  $\delta^{18}O = -11.5 \pm 0.5\%$ , which significantly differs it from the meteoric component of the Aktivnaya funnel and the Donnoe field. The steam jets on the outer slopes of the volcano are characterized by small (<1%) negative shift in  $\delta^{18}O$  relative to LMWL, which could be caused by the water-steam fractionation at 120-140°C with subsequent steam separation [25, 26, 39]. The fluid from geothermal bore-1 holes reveals a positive 1%  $\delta^{18}O$  shift relative to LMWL, which could be caused by water-rock exchange processes.

The absence of mixing trends in the diagram  $\delta D$ - $\delta^{18}$ O for the thermal occurrences with the predominance of meteoric component requires involvement of additional parameters, for instance, the contents of helium and sulfur in gases, for estimating  $f_{MAGM}$ . Ignoring the outlying values within each of the thermal fields, the S/He ratio ~ const ( $8 \times 10^4$ ) for entire area (Fig. 7). The sulfur and helium contents vary within three orders of magnitude, which corresponds to the dilution of deep-seated component by meteoric waters. Mixing lines in Fig. 7 ties  $f_{MAGM}$  and data point of meteoric waters (4.7  $\times$  10^{-8} mmol/mol He and 1  $\times$  $10^{-5}$  mmol/mol SO<sub>2</sub>). In turn, He<sub>MAGM</sub> = 2.6 ×  $10^{-4}$  mmol/mol and S<sub>MAGM</sub> = 21 mmol/mol were calculated using previously calculated fraction  $f_{\rm MAGM} = 61\%$  for gases of the Aktivnaya funnel:

<sup>&</sup>lt;sup>2</sup> This estimate is based on the water isotopic analysis.

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2.3E-05 0.000487.1E-05 5.3E-05 6.6E-05 0.000496.7E-05 0.00022 0.00068 0.00015 0.00021 0.00086 0.00034 0.00015 0.0018 0.0026 0.0019 0.0028 0.0030 0.0032 0.0033 0.0031  $CH_4$ 0.015 0.0200.0200.0220.0240.0033 0.0139 0.0135 0.0016 0.0016 0.0017 0.0015 0.00160.0025 0.0152 0.0037 0.0053 0.0036 0.0029 0.0027 0.0076 0.0008 0.0022 0.00080.0011 0.00040.0024 0.0021 0.0031 0.0011 0.0041 0.013  $^{\circ}$ 0.075 0.0400.055 0.052 0.037 0.0400.082 0.039 0.051 0.066 0.054 0.086 0.087 0.085 0.083 $z^{2}$ 0.35 0.19 0.240.340.29 0.370.15 0.480.460.420.27 0.36 0.00045 7.3E-05 0.00016 0.00025 0.00032 0.00034 0.000480.00032 0.00026 0.000800.00036 0.00059 0.00056 0.00092 0.00035 0.00027 0.00020 0.00022 0.00019 0.00021 0.00018 0.00016 0.00042 0.00087 0.00023 0.00021 0.0013 År 0.00110.00300.0013 0.00140.0056 0.00440.0057 0.0053 0.00410.0032 0.0020 0.0052 0.00200.0087 0.0390.056 0.0060.0300.011 0.35 $\mathrm{H}_2$ 0.03 0.72 0.78 0.66 0.53 0.316.4E-06 nmol/mol 2.3E-05 2.6E-05 0.00016 9.3E-06 7.0E-06 0.00015 4.9E-05 4.8E-05 4.6E-05 8.3E-06 0.000146.6E-05 8.2E-05 4.9E-05 2.8E-05 5.2E-05 5.2E-05 1.4E-05 2.0E-05 0.00016 0.00018 8.7E-05 0.00012 0.00014 0.00012 0.00013 He 993.7 993.2 997.6 965.9 970.6 965.6 993.7 991.9 984.8 992.5 995.2 996.7 997.4 993.9 962.2 968.7 956.8 958.2 966.3 980.9 961.4 971.7 991.7 Н,О 960.3 967.1 994.1 966.1 Aktivnaya funne 0.26 1.7 0.31 2.3 Donnoe field 0.45 0.13 HCI 0.78 0.030.030.91 0.22 0.01 0.06 0.07 Verkhnee field 2.4 1.8 2.4 2.5 2.5 2.01.3 2.8 1.2 1.9 2.6 1.2 2.1 0.011 0.013 0.013 0.0920.067 0.310.99 0.240.940.36 0.740.22 0.310.870.31lp><br/>dl<br/>> lb≻ ΗF lb> lb> 1.1 <dl lb≻ 2dl <sup>2</sup>dl 0.48 0.85 0.880.812.9 3.8 6.7 6.7 2.1 1.6 3.3 0.71 20.2 17.6 14.1 8.1 15.2 17.6 24.5 22.8 12.1 13.2 13.2 14.1 S 13.6 10.3  $CO_2$ 23.7 26.0 1.8 21.1 24.6 11.3 12.6 23.6 2.8 16.6 2.6 5.7 5.3 1.7 3.1 2.1 5.8 1.6 2.4 1.6 5.0 19.7 2.8 3.1 20.4 16.1 6.1 R/Ra 5.29 5.52 -6.58 5.57 5.99 -7.59 --Ι -53.5 -54.5 -45.3 -58.9-86.4-77.4 -102.8-107.4-103.5-106.9-49.5 -46.5 -55.2-42.7 -72.6 -57.4-73.4-97.6 -82.2 -58.4 -79.0-86.7-76.3 -76.6-41.1 -82.1 δD -104.1% -0.65 $\delta^{18}O$ +0.5-1.0+1.3-2.5 -4.2 -4.3 +1.5-5.9 -8.8 -4.9 -6.8-9.5 -11.2 -11.4-10.9-11.6-0.7 -1.4-1.1 -0.4-5.2 -4.7 -5.0-5.4 -5.2 -2.1  $T, ^{\circ}C$ 380 543 594 5590 5590 5580 315 543 357 205 543 357 543 330 543 330 380 1111 137 263 263 120 98 98 98 98 105 138 98 186 149 212 425 Sample 1-11 1-12 1-13 1-13 2-7 1-14 3-13 1-10 2-12 2-13 3-12 2-10 2-11 1-4 1-5 1-6 1-7 1-7 1-8 2-8 1-9 2-4 2-5 3-2 3-6 3-7 3-1 3-4 1-1

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Table 2. ((	Contd.)														
Samole	$J \circ L$	$\delta^{18}O$	δD	R /Ra	$CO_2$	S	ΗF	HCI	$H_2O$	He	$H_2$	Ar	$N_2$	$O_2$	$CH_4$
Audinac	), ( ,	6	00	IN NG						mmol/mol					
3-5	285	-11.6	-104.8	6.98	1.7	0.79	lb>	0.09	997.4	9.7E-06	0.0072	0.00023	0.041	0.001	0.023
3-8	148	-11.7	-106.6	Ι	2.3	0.87	 dl	0.12	9.966	1.1E-05	0.0012	0.00030	0.050	0.0036	0.025
3-9	231	-11.6	-107.8	Ι	2.1	0.82	<dl< td=""><td>0.08</td><td>996.9</td><td>1.3E-05</td><td>0.0050</td><td>0.00020</td><td>0.041</td><td>0.0012</td><td>0.027</td></dl<>	0.08	996.9	1.3E-05	0.0050	0.00020	0.041	0.0012	0.027
3-10	248	-11.2	-106.5	6:59	3.9	0.80	<dl< td=""><td>0.08</td><td>995.2</td><td>1.0E-05</td><td>0.0071</td><td>0.00024</td><td>0.043</td><td>0.001</td><td>0.020</td></dl<>	0.08	995.2	1.0E-05	0.0071	0.00024	0.043	0.001	0.020
3-11	172	-11.8	-107.0	I	2.4	0.77	 dl	0.07	996.7	1.2E-05	0.0045	0.00018	0.039	0.001	0.022
_		_	_	_	_	_	Stear	n jets	_	_	-	-	_	-	
6-1	96	-16.6	-108.2	4.11	0.29	0.93	 dl	0.006	999.1	7.1E-06	0.44	0.0017	0.109	0.0017	0.016
6-12	96	-15.4	-106.8	6.06	1.7	0.44	<dl< td=""><td>0.003</td><td>998.0</td><td>9.8E-06</td><td>0.14</td><td>0.0013</td><td>0.073</td><td>0.0013</td><td>0.0035</td></dl<>	0.003	998.0	9.8E-06	0.14	0.0013	0.073	0.0013	0.0035
6-7	96	I	Ι	I	Ι	Ι	 dl	0.003	9.666	₹Ï	0.28	0.0019	0.10	0.0019	0.011
6-10	96	-14.5	-102.4	99.9	0.89	0.097	<dl< td=""><td>0.016</td><td>0.666</td><td>1.9E-06</td><td>0.043</td><td>0.00023</td><td>0.016</td><td>0.0004</td><td>0.0039</td></dl<>	0.016	0.666	1.9E-06	0.043	0.00023	0.016	0.0004	0.0039
6-11	96	I	Ι	I	1.76	lb>	 dl	0.002	998.0	Ë	0.16	0.00035	0.024	0.0001	0.014
_		_	_	_	_	_	Geotherm	al fluid**	_	_	-	-	_	-	
1-049	163	1	1	I	0.13	0.013	Ι	<dl< td=""><td>6.666</td><td>3.0E-07</td><td>0.0042</td><td>0.00067</td><td>0.049</td><td>0.0030</td><td>0.0011</td></dl<>	6.666	3.0E-07	0.0042	0.00067	0.049	0.0030	0.0011
1-GK-1	166	I	Ι	I	0.12	0.024	I	 dl	9.99.9	1.3E-07	0.0150	0.00019	0.010	0.0019	0.0006
1-037	175	I	Ι	I	0.26	0.037	I	 dl	7.666	4.8E-07	0.0060	0.00040	0.025	0.0052	0.0033
2-049	175	I	I	I	0.11	0.015	I	<dl< td=""><td>9.99.9</td><td>3.1E-07</td><td>0.0027</td><td>0.00036</td><td>0.022</td><td>0.0037</td><td>0.0022</td></dl<>	9.99.9	3.1E-07	0.0027	0.00036	0.022	0.0037	0.0022
2-GK-1	167	I	Ι	I	0.10	0.022	I	<dl< td=""><td>9.99.9</td><td>9.3E-08</td><td>0.0270</td><td>0.00037</td><td>0.017</td><td>0.0063</td><td>0.0013</td></dl<>	9.99.9	9.3E-08	0.0270	0.00037	0.017	0.0063	0.0013
3-049	163	-13.1	-104.2	3.99	0.13	0.011	I	 cdl	9.99.9	2.9E-07	0.0041	0.00066	0.050	0.0029	0.0011
3-013	163	-13.4	-104.6	3.51	0.28	0.006	I	 cdl	7.666	6.5E-07	0.0085	0.00015	0.0055	0.0020	0.0006
3-GK-1	166	-14.1	-107.4	I	0.11	0.034	I	 dl	8.666	1.3E-07	0.0140	0.00019	0.010	0.0018	0.0005
3-037	175	-13.2	-102.9	3.97	0.28	0.034	I	 lp>	7.666	4.7E-07	0.0060	0.00040	0.025	0.0051	0.0033
4-GK-1	164	-14.0	-105.6	I	0.12	0.030	I	<dl< td=""><td>8.666</td><td>1.8E-07</td><td>0.0150</td><td>0.00019</td><td>0.011</td><td>0.0019</td><td>0.0006</td></dl<>	8.666	1.8E-07	0.0150	0.00019	0.011	0.0019	0.0006
4-042	167	-14.1	-109.2	5.89	0.08	0.016	Ι	<dl< td=""><td>6.666</td><td>2.1E-07</td><td>0.0014</td><td>0.00058</td><td>0.035</td><td>0.0037</td><td>0.0001</td></dl<>	6.666	2.1E-07	0.0014	0.00058	0.035	0.0037	0.0001
5-049	163	I	Ι	I	0.15	0.013	Ι	 dl	998.8	3.1E-07	0.0049	0.00069	0.049	0.0028	0.0013
5-GK-1	166	I	Ι	I	0.12	0.029	I	 cdl	6.666	9.1E-08	0.0100	0.00013	0.007	0.0013	0.0005
6-037	164	I	Ι	I	0.24	0.035	I	 dl	7.666	3.5E-07	0.0055	0.00035	0.020	0.0037	0.0022
6-042	167	Ι	Ι	Ι	0.09	0.015	Ι	<dl< td=""><td>6.666</td><td>2.8E-07</td><td>0.0035</td><td>0.00062</td><td>0.044</td><td>0.0049</td><td>0.0009</td></dl<>	6.666	2.8E-07	0.0035	0.00062	0.044	0.0049	0.0009
Notes: * Ta 1 ** O1	ble does n uly boreho	ot include ( les with hig	data on mete <sub>5</sub> h helium co	soric waters ncentration	s. ns are given;	; dashes den	lote the abso	ence of mea	asurements	< dl denote	s below det	ection limit			

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**Fig. 4.**  $CO_2$ -S-HCl diagram for the thermal occurrences of the area. The HCl/S and HCl/CO<sub>2</sub> ratios in the gases of the Donnoe field are 2–4 times higher than those in other fumarolic fields. For designations see Fig. 3.

$$f_{\text{MAGM}} = (S - S_{\text{met}}) / (S_{\text{MAGM}} - S_{\text{met}})$$
  
 
$$\approx S / S_{\text{MAGM}}, \qquad (4)$$

$$f_{\text{MAGM}} = (\text{He} - \text{He}_{\text{met}})/(\text{He}_{\text{MAGM}} - \text{He}_{\text{met}})$$
  

$$\cong (\text{He} - \text{He}_{\text{met}})/(\text{He}_{\text{MAGM}}).$$
(5)

Using the Donnoe field as an example, we may compare the results of calculations with these methods, which allows us to estimate accuracy. Thus,  $f_{MAGM}$ equals 2–30% on the basis of isotopic calculations and 9–25% as deduced from S/He ratio. It is seen that obtained values are sufficiently close.

## LOCAL INHOMOGENEITY OF GAS DISCHARGE OF MUTNOVSKY VOLCANO

Three fumarolic fields of the volcano have three separate sources, because compositions of gases of these fields are inconsistent with each other. For each field, the concentrations of components or their proportions cannot be derived by mixing or dilution of gases of two other fields. The hydrothermal gases of the Verkhnee field differ from the meteoric component of the adjacent Donnoe field in terms of water isotopic composition (Fig. 5), while their methane content is an order of magnitude higher than that in the adjacent fields (Fig. 3). The gases of the Aktivnaya funnel have the highest concentrations of  $CO_2$ , S, N<sub>2</sub>, and He, and N<sub>2</sub>/Ar ratio. The Donnoe field is characterized by the highest ratios of HCl/S (Fig. 4), He/CO<sub>2</sub> and He/N<sub>2</sub> (Fig. 8e), and the maximum  ${}^{3}\text{He}/{}^{4}\text{He}$  ratio expressed via R/Ra (Fig. 8b).

The HCl predominance in the gases is indicator of the latest degassing stages [40, 41]. The HCl/S = 0.4– 0.5 for most fumaroles of the Donnoe field, which is 2-4 times higher than those for the Aktivnaya funnel (samples with extremely low HCl, which was removed by groundwaters, were omitted from consideration). An increase in magma degassing could be accompanied by the increase in the relative He concentrations. Since the solubility of He in the melt is higher than the solubility of  $CO_2$ ,  $N_2$ , and Ar, the degassing peak will occur later. For instance, Nuccio and Paonita [42] showed that gases with relatively high He contents are exsolved from the melt at the late stages of degassing, whereas  $CO_2$ , N<sub>2</sub>, and Ar contents by that time will progressively decrease. Actually, the He/N<sub>2</sub> (Fig. 8a) and He/CO<sub>2</sub> ratios (similar plot) for main group of the fumaroles of the Donnoe field are 1.5-2 times higher than those in the Aktivnaya funnel.

However, the high helium contents could be caused by not only fractional degassing, but also by the high fraction of mantle component in magma. The light <sup>3</sup>He isotope is regarded as an indicator of mantle fluid. With increasing total helium concentrations, the R/Ra ratio increases and reaches maximum of 7.67 at the Donnoe field (Fig. 8b). It was previously established [27] that the fumaroles of the Donnoe field have  $R/Ra \sim 8$ . However, the gases of the Aktivnaya funnel, at the highest <sup>4</sup>He concentrations, have R/Ra = 5.29-5.57 (Table 2). Since <sup>3</sup>He/<sup>4</sup>He ratio shows no fractionation during separation from silicate melt, the R/Ra ratio remains constant regardless of degassing stage. The high R/Ra ratios at the Donnoe field unambiguously indicate the presence of magma with elevated fraction of mantle component.

While studying the geochemistry of lavas of the Mutnovsky (front arc) and Gorely (back-arc) volcanoes, Duggen with co-authors concluded that some basalts of Mutnovsky were presumably "contaminated" by melts with more significant contribution of mantle component, which are typical of Gorely volcano [19]. The magmatic body<sup>3</sup> of similar composition is capable of providing the elevated R/Ra, He/N<sub>2</sub>, and He/CO<sub>2</sub> ratios in gases. Simultaneously, the high HCl/S, He/N<sub>2</sub>, and He/CO<sub>2</sub> ratios could be interpreted as indicating the later degassing stage of the melt. Hence, the fumarolic gases of the Donnoe field were presumably supplied by independent magmatic body II, which differs in composition from the magmatic body I beneath the Aktivnaya funnel.

<sup>&</sup>lt;sup>3</sup> The study of volcanic gases cannot separate between degassing of the melt and cooling intrusion beneath volcano. We use a term "magmatic body" to designate the volume of liquid (magmatic camera) or hot but cooled magma (intrusion) in a degassing state.



Fig. 5. (a)  $\delta D - \delta^{18}O$  diagram for steam jets, geothermal fluid, and meteoric waters of Mutnovsky volcano. Most of the data points for fumarolic gases are arranged along the main mixing trend between the "andesitic" waters and local meteoric waters that experienced isotopic shift in  $\delta^{18}O$ . (b) Mixing model for Mutnovsky volcano in the  $\delta D - \delta^{18}O$  diagram. There are only one composition of magmatic "andesitic" waters and relative diversity of compositions of meteoric component, which is explained by the water–rock isotopic exchange overprinted by vapor–liquid fractionation. A slope of vapor–liquid fractionation corresponds to the fractionation temperature of 120–140°C. Local Meteoric Water Line.



Fig. 6. Correlation dependence in the coordinates Cl– $\delta D$  (a) and Cl– $\delta^{18}O$  (b). Extrapolation to zero values of HCL yields the composition of meteoric component  $\delta D = -102\%$ ,  $\delta^{18}O = -10\%$ .

## HE, N<sub>2</sub>, AR: KEYS TO THE ORIGIN OF MAGMATIC FLUIDS

According to the modern concepts [1, 2], the fluids from subduction zone are fluxed into magma generation area from four main reservoirs: mantle wedge, altered oceanic crust (AOC), oceanic sediments (SED = Sediments), and continental crust (CC).

Data on the composition of mantle wedge fluids are practically absent, and the use of compositional data on the MORB (Mid-Ocean Ridge Basalts) gases is considered to be the best approximation. Hereinafter, we understand the term MORB as the mantle wedge rocks.

The AOC rocks were formed in the mid-ocean ridge zones. However, unlike MORB, mature AOC consists mainly of hydrothermally altered basalts and gabbros



**Fig. 7.** S/He ratio for the thermal occurrences of Mut-

novsky volcano. Fraction  $f_{MAGM} = 61\%$  for the Aktivnaya funnel was determined from the hydrogen and oxygen isotopic composition of water. Designations are shown in Fig. 4.

5–6 km thick with significant content of water- and carbonate-bearing minerals.

The meteoric waters (ASW = Air Saturated Water) factually represent the individual (fifth) reservoir, but do not contribute directly in the magma generation, mixing with magmatic fluids only near surface.

Calculations were based on the modern concepts on the behavior of volatiles in subduction processes, which could be summarized as following main assumptions.

"Noble-gas subduction barrier." The comparison of concentrations and isotopic composition of noble gases in the upper mantle, oceanic crust, oceanic sediments, and atmosphere led Staudacher and Allegre to conclude that at least 98% of the noble gases in the island-arc processes are not injected into upper mantle with subducted slab, but return back into atmosphere [43]. Authors do not consider nitrogen, though it is close to noble gases in properties. Hilton et al. [1] and Bebout [44] indicate a significant data scatter on nitrogen recycling for different island arcs, but later works demonstrated that nitrogen balance in subduction zones, including Kurile-Kamchatka arc [3], in general is close to one [8, 11]. Let us assume that He,  $N_2$ , and Ar from AOC and SED completely return into atmosphere with volcanic gases.

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 $He/N_2$ ,  $10^{-4}$ 

10

*Water recycling.* The content of pore waters in the water-saturated terrigenous-diatomaceous and diatomaceous muds of SED reaches 40–56% and 66–77%, respectively [45]. It is considered that the pore waters are squeezed at the initial stage of diagenesis at subduction depths up to 5–10 km [2]. Only structurally bound water (3–4 wt %) involved in the minerals in low-grade metamorphic rocks reaches deeper levels [44, 46, 47]. The behavior of structurally bound water during slab subduction is controlled by the corresponding equilibria. Based on experimental data, Schmidt and Poli suggest that only 18–37% of structurally bound water (i.e., 0.8-1.2 wt % of the rock) can reach magma generation zone during dehydration [46].

Fore-arc discharge of volatiles is presumably caused by migration of squeezed pore waters SED to the surface.  $CO_2$  and noble gases are partially released together with pore waters [43, 46]. There are few data on the existence of underwater discharges of volatiles in the oceanic margin zones [43, 48], including Kamchatka shelf [49]. However, in terms of total intensity, the known fore-arc percolations are several orders of magnitudes lower than gas discharges on volcanoes. The model does not take into account the possible fore-arc loss of volatiles, but, however, is well consistent with data on the composition and thickness of AOC and SED in the Kamchatka area.

 $CO_2$  recycling. Significant fraction of  $CO_2$  is released from slab at depths up to 75 km [50], but some part inject mantle in the form of carbonates that are stable under the upper mantle temperatures and pressures [51, 52]. Most of geologists believe that only 40% of CO<sub>2</sub> from AOC and SED reaches island-arc magma generation zone [1, 2, 11]. This value determined for the Kurile–Kamchatka arc was as low as 20% [3].

*Mainly mantle origin of <sup>3</sup>He* Owing to the absence of reliable data on the composition of mantle-wedge fluids, we use the MORB compositions. The R/Ra ratio of  $8.5 \pm 0.79$  established for most MORB samples show no significant variations over the entire Earth's system of mid-ocean ridges [1, 53]. The absolute concentrations of <sup>3</sup>He in the oceanic crust, oceanic sediments, and ASW are 4–6 orders of magnitude lower than those in MORB (Table 3). He-rich dry gases of continental crust have R/Ra < 0.3, which yields low <sup>3</sup>He in recalculation to aqueous fluid. Some researchers [54] indicate the high  ${}^{3}\text{He}/{}^{4}\text{He}$  ratios (up to 30–100 Ra) in the top beds of oceanic sediments, which is explained by uninterrupted, though low (in absolute contents) influx of cosmogenic <sup>3</sup>He with interplanetary dust. However, due to the low concentrations and diffusion losses of helium with pore waters at the early diagenetic stages, the influence of cosmogenic <sup>3</sup>He on a total subduction balance is regarded as insignificant [1]. In first approximation, >99% <sup>3</sup>He in the magmatic fluid are of mantle origin.

Fractionation during gas exsolution from melts [1, 41, 42, 55, 56] affects the  $N_2$ -Ar-He-CO<sub>2</sub> proportions,

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(a) 8 DF ÷ 6 ▲□ 4 A П 2 ASW 0.00004 0.00008 0.00012 0.00016 0 R/Ra (b) DF 8 пР 7 b Δ AF Δ 0 6 5 Mantle fluid o 4 Slab fluid 3 2 1 0 0.00004 0.00008 0.00012 0.00016 <sup>4</sup>He, mmol/mol Fig. 8. Behavior of He/N<sub>2</sub> and R/Ra ratios with variations

**Fig. 8.** Behavior of  $\text{He/N}_2$  and R/Ra ratios with variations of <sup>4</sup>He concentrations. (a)  $\text{He/N}_2$  ratios at the Donnoe field on average is 1.5 times higher than those in all other fumaroles of the volcano. (b) R/Ra ratio increases with increase of He concentration and reaches maximum at the Donnoe field (7.7), which is the closest to the mantle values (8.5). With further increase in He, the R/Ra ratio decreases to 5.29 in the fumaroles of Aktivnaya funnel.

with generally unknown degree of fractionation. Pairs of components  ${}^{3}\text{He}/{}^{4}\text{He}$  and N<sub>2</sub>/Ar reveal minimum fractionation (close solubility in silicate melts), however calculations based on He/CO<sub>2</sub> or He/N<sub>2</sub> ratios should be treated with caution. At the present stage of calculations, fractionation cannot be taken into account during degassing.

## INITIAL CONCENTRATIONS OF COMPONENTS IN GEOCHEMICAL RESERVOIRS

Data on the composition of initial reservoirs are few in number and show wide variations in different works.

MORB samples were mainly obtained by dredging midocean ridges. MORB compositions, regardless of sampling locality, are sufficiently homogenous in terms of  $^{3}$ He/ $^{4}$ He, Ar/He, N<sub>2</sub>/He, and CO<sub>2</sub>/He ratios [56–60]. However, the absolute concentrations of the components could vary depending on the degree of rock degassing. Samples AOC and SED were obtained from the core of borehole drilled in the framework of ODP/DSDP programs, as well as by direct sampling of unconsolidated sediments of the seafloor surface. Helium isotopic data are available only for SED and upper part of AOC. Data on three components  $({}^{3}\text{He},$ <sup>4</sup>He, and Ar) that are suitable for mixing calculations are reported only in the work of Staudacher and Allegre[43]. According to this work, practically all <sup>3</sup>He and most part of <sup>4</sup>He (including radiogenic <sup>4</sup>He) were removed from basalts and gabbros of AOC owing to the diffusion in the course of hydrothermal-metasomatic alterations. In calculations, the values of  ${}^{3}\text{He}/{}^{4}\text{He}$  ratios for the uppermost AOC horizons were extrapolated for the entire layer of oceanic crust. The N2 concentrations for AOC and SED were taken from [44] and [61].

Much more complex situation exists for continental gases. Only analyses containing He, N<sub>2</sub>, and Ar are suitable for modeling SED-AOC-CC system. Original data on the gases of continental crust for Kamchatka are absent, and only few published data on other regions meet this condition. Characteristics of crustal gases CC1 were taken from the borehole in the Permian-Carboniferous sedimentary rocks at the Hugoton-Panhandle gas field, USA [62]. The crustal gases taken from the Ordovician-Devonian metamorphic rocks in the KTB superdeep wells in Germany are the best studied 1 [63, 64]. For these boreholes, data on free fluids and gases entrapped in crystal lattice are available. Free fluids of KTB are designated in the paper as CC2a. Gases bound in KTB minerals are designated as CC2b (depths of 3-7 km) and CC2c (depths 0-3 km). The main components of gases CC1 and CC2 are methane and nitrogen. Carbonic-nitrogen gases CC3 were estab-1 lished in the boreholes of the Colorado Plateau and Rocky Mountain, United States [65]. These provinces are made up of Precambrian to Mesozoic partially metamorphosed sedimentary and intrusive rocks. Gases CC4 of the young continental crust (Cenozoic granitoids overlain by sedimentary rocks) were taken 1 from the boreholes of the Yangbajing geothermal field in Tibet [66]. The gases CC4 are characterized by R/Ra =0.14–0.45 and in terms of  $N_2$ –Ar–He proportions are plotted in the mixing line between gases CC1-CC2 and ASW.

In the diagram log(He/Ar) vs log(N2/He), the compositions CC1–CC2a–CC2b–CC2c–AOC define a single trend, while CC2c and AOC compositions are practically indistinguishable from each other. The latter can be easily explained given the fact that CC2c gases are the gases entrapped by minerals in the rocks of the top 3-km layer of the continental crust; while AOC gases were entrained in the minerals from rocks of the uppermost hundreds of meters of oceanic sequence. Bach et al suggest that the He decrease in KTB minerals with simultaneous enrichment in free fluids is caused by He diffusion to the surface [63]. Similar processes occur also in the oceanic crust [43]. The similarity of the processes (generation of radiogenic Ar and He and advection/diffusion of gases to the surface) presumably provides similar gas compositions, in spite of the differences in rock composition and tectonic settings.

In relation with the diversity of crustal gases the question arises as to which of their compositions should be used in calculations. Additional geochemical and geological data are required to solve correctly this problem, which is beyond the scope of this paper. We performed our calculations for several compositions, which was reflected in the results. In any case, the fraction of continental gases in the crustal fluid is no more than 6-7%.

Table 3 lists the concentrations of  ${}^{3}$ He (R/Ra), He,  $N_2$ , and Ar in the fluids of geochemical reservoirs in the magma generation zone of island-arc volcanoes. It should be emphasized that this table reports data both for rocks (MORB, AOC, SED, CC2b, CC2c) and for free fluids (ASW, CC1, CC2a, CC3). For solid rocks, we took the ratios of concentrations of corresponding components in the rock to the total content of all volatiles in the rock, including H<sub>2</sub>O and CO<sub>2</sub>, but excluding sulfur and halogens. For KTB rocks (amphibolites and paragneisses), direct data on the water content are absent. The water concentration was estimated using published mineral composition of the rocks and the average concentrations of water in the corresponding minerals, as well as the water content in the similar rocks. The value of 1% was taken in calculations.

#### CALUCLATIONS OF MIXING OF COMPONENTS

Calculations are based on the comparison of He, Ar, and N<sub>2</sub> concentrations and H/D,  ${}^{3}\text{He}/{}^{4}\text{He}$ , and  ${}^{16}\text{O}/{}^{18}\text{O}$  isotopic ratios in the volcanic gases and in the initial geochemical reservoirs MORB, AOC, SED, CC, and ASW. The five-reservoir mixing can be expressed by a system of four independent linear mixing equations plus mass balance equation. Subsequent solution of a set of particular systems simplifies calculations.

Meteoric waters and magmatic gases. Fractions  $f_{\text{MAGM}}$  and  $f_{\text{ASW}}$  were previously calculated in the coordinates  $\delta D - \delta^{18}O$  and log(S)-log(He), formulas 1–5, Figs. 5 and 7. Fraction  $f_{\text{MAGM}}$  varies from 73% in the gases of Aktivnaya funnel to 0.07% in the geothermal boreholes, and that of  $f_{\text{ASW}}$  from 27% to 99.93%, 1 respectively (Table 4a).

*Calculation of mantle, non-mantle, and crustal fractions.* The sum of all fractions in a gas equals one:

$$f_{\rm ASW} + f_{\rm MORB} + f_{\rm AOC} + f_{\rm SED} + f_{\rm CC} = 1.$$
 (6)

Reservoir	R/Ra*		Н	He		$N_2$		Ar	
Reservon	mean	σ	mean	σ	mean	σ	mean	σ	
MORB	8.5	0.79	0.011	0.003	0.57	0.17	0.0056	0.02	
AOC	0.15	0.18	3.1E-5	2.9E-5	0.068	0.023	4.4E-5	2.1E-5	
SED	0.12	0.15	3.2E-5	1.2E-5	7.5	5.2	4.1E-4	2.7E-4	
CC1	0.19	0.025	0.0052	0.0018	0.17	0.035	5.9E-4	2.0E-4	
CC2a	0.22	@ н.д.	0.0044	1.4E-4	0.52	0.027	9.4E-4	1.4E-4	
CC2b	0.22	@ н.д.	0.0012	0.001	0.61	0.49	5.7E-4	5.0E-4	
CC2c	0.22	@ н.д.	3.8E-4	1.7E-4	1.5	0.96	9.3E-4	4.4E-4	
CC3	0.76	0.5	0.92	2.1	13.4	24.8	0.23	0.38	
CC4	0.24	0.13	0.025	0.032	8.5	4.1	0.13	0.084	
ASW	1	0.0	1.56E-08	0.0	0.00392	0.0	1.07E-4	0.0	

Table 3. Concentrations of components in geochemical reservoirs, mmol/mol

\* Concentration of <sup>3</sup>He can be calculated using formula: <sup>3</sup>He = <sup>4</sup>He (R/Ra)/745000.

Assuming that  $f_{CRUST}$  practically lacks <sup>3</sup>He, the fraction of mantle and crustal fractions can be calculated using simple relations:

$$f_{\text{MORB}} = ({}^{3}\text{He}_{\text{gas}} - {}^{3}\text{He}_{\text{ASW}})/{}^{3}\text{He}_{\text{MORB}},$$
 (7)

$$f_{\text{CRUST}} = f_{\text{AOC}} + f_{\text{SED}} + f_{\text{CC}} = 1 - f_{\text{MORB}} - f_{\text{ASW}}.$$
 (8)

Each component of crustal and non-mantle fractions can be also calculated using helium ratios  $X^i/{}^3$ He(ratio of component concentration  $X^i$  to the  ${}^3$ He concentration in mantle fluid),  $X^i = ({}^4$ He, Ar, N<sub>2</sub>):

$$X_{(CRUST)}^{i} = [X_{(Gas)}^{i} - X_{(ASW)}^{i} \cdot f_{ASW} - {}^{3}\text{He}_{(Gas)} \cdot X^{i}/{}^{3}\text{He}]; \qquad (9)$$

$$X_{(1-MORB)}^{i} = [X_{(Gas)}^{i} - {}^{3}He_{(Gas)} \cdot X^{i} / {}^{3}He].$$
 (10)

The following ratios were used:  ${}^{4}\text{He}/{}^{3}\text{He} = 85000$ ; N<sub>2</sub>/ ${}^{3}\text{He} = 2.1 \times 10^{6}$ , Ar/ ${}^{3}\text{He} = 42000$ .

Diagram  $R/Ra - log(he/N_2)$  (Fig. 9) shows the mixing lines between mantle and non-mantle fractions  $f_{\text{MORB}}$  and  $f_{(1-\text{MORB})}$  for gases of all five thermal fields. In turn, each non-mantle fraction consists of a combination of crustal gases and ASW. In Fig. 9, crustal fractions are indistinguishable, since they are plotted closely to each other, practically in single line. The fraction of  $f_{\rm MORB}$  in gases is extremely low and varies from 0.1– 1.1% for the Aktivnaya funnel to 0.003% in the geothermal fluid. Taking into account only magmatic gases  $f_{\rm MAGM}$  and excluding dilution by meteoric waters, the fraction  $f_{\text{MORB}}$  is relatively higher in the gases of the Donnoe field and reaches there 2.1% against 1.5–1.8% for the Aktivnaya funnel. Such a great difference is consistent with hypotheses that the Donnoe field was fed by an independent magmatic body.

*Crustal fractions*. The He–N<sub>2</sub>–Ar system makes it possible to separate the AOC, SED, and CC fractions. Unfortunately, the high uncertainty of data on N<sub>2</sub> and Ar due to dilution by corresponding atmospheric gases introduced with meteoric waters prevents reliable separation of the gases into fractions for all fumarolic fields, except for the Aktivnaya funnel. The molar fractions of He, N<sub>2</sub>, and Ar in the initial AOC, SED, and CC compositions are denoted as  $h_k$ ,  $n_k$ ,  $a_k$ , k = 1, 2, 3; and correspondingly, as H, N, and A in CRUST mixture. Fractions AOC, SED, and CC in the component CRUST are designated as  $f_1$ ,  $f_2$ , and  $f_3$ . These fractions can be determined by solving four equations with three unknowns:

$$f_{1}h_{1} + f_{2}h_{2} + f_{3}h_{3} = H;$$
  

$$f_{1}n_{1} + f_{2}n_{2} + f_{3}n_{3} = N;$$
  

$$f_{1}a_{1} + f_{2}a_{2} + f_{3}a_{3} = A;$$
  

$$f_{1} + f_{2} + f_{3} = 1.$$
(11)

The system (11) is overdetermined and inconsistent. In addition, its equations are significantly disparate: coefficients could be low in three equations and equal 1 in one equation. The disparity can be removed by omitting f3 from the last equation.

$$f_3 = 1 - f_1 - f_2; \tag{12}$$

and substituting (12) in the former three equations of system (11):

$$f_{1}(\mathbf{h}_{1} - \mathbf{h}_{3}) + f_{2}(\mathbf{h}_{2} - \mathbf{h}_{3}) = \mathbf{H} - \mathbf{h}_{3};$$
  

$$f_{1}(\mathbf{n}_{1} - \mathbf{n}_{3}) + f_{2}(\mathbf{n}_{2} - \mathbf{n}_{3}) = \mathbf{N} - \mathbf{n}_{3};$$
  

$$f_{1}(\mathbf{a}_{1} - \mathbf{a}_{3}) + f_{2}(\mathbf{a}_{2} - \mathbf{a}_{3}) = \mathbf{A} - \mathbf{a}_{3}.$$
(13)

The system (13) consisting of three equations with two unknowns is also overdetermined and inconsistent, i.e. yields no unique solution. The approximate solution of system with the minimum norm of discrepancy (for

Fraction	Aktivnaya funnel		Donnoe field		Verkhn	ee field	Stear	m jets	Geother	mal fluid
Traction	mean	σ	mean	σ	mean	σ	mean	σ	mean	σ
MORB	0.94	0.3	0.45	0.16	0.04	0.02	0.03	0.025	0.003	0.002
CRUST	60	5	25	9	3.8	0.8	1.3	1.2	0.15	0.08
ASW	~39	5	~74.5	9	~96.2	0.8	~98.7	1.2	~99.85	0.08
CRUST/MORB	64	—	48	—	95	—	43	—	50	—

Table 4a. Calculated fractions of fluids in the gases of Mutnovsky volcano (vol %)

**Table 4b.** Relative fractions of AOC, SED, and CC in the crustal fraction CRUST for the Aktivnaya funnel using different fluids of continental crust (CC1, CC2a, CC2b, and CC2c) for calculations

	Fractions used in calculations:									
Fraction	C	C1	CC	C2a	CC	C2b	CC	C2c		
	mean	σ	mean	σ	mean	σ	mean	σ		
AOC	0.96	0.009	0.96	0.009	0.93	0.03	0.91	0.03		
SED	0.032	0.008	0.032	0.008	0.03	0.007	0.025	0.01		
CC	0.006	0.005	0.008	0.006	0.04	0.03	0.065	0.035		

instance, least square method) can be determined using any mathematical software package. After solution of system (13) relative to fractions  $f_1$  and  $f_2$ , the fraction  $f_3$ can be found from (12).

Calculations were based on arithmetic mean of data on reservoir compositions. The accuracy of such solution is discussed below. Substitution of four different compositions CC1, CC2a, CC2b, CC2c yields different calculated fractions of AOC, SED, and CC in the fraction CRUST. If free fluids CC1 and CC2a are used in calculations, their fraction in the crustal fluid accounts for tenths of percents. However, the use of compositions CC2b and CC2c (gases in minerals) in calculations results in the increasing role of fluids of continental crust up to 3-4% and 6-7%, respectively, at the expense of AOC (Table 4b).

In the diagram  $\log(\text{He/Ar}) - \log(N_2/\text{He})$ (Fig. 10), the mantle component was excluded from volcanic gases, i.e., all samples are represented by data points of fraction  $f_{(1-\text{MORB})}$ . The composition CRUST corresponds to the magmatic gas of the Aktivnaya funnel minus mantle component, i.e., factually, to the pure crustal fluid. All compositions of volcanic and hydrothermal gases of the volcano are plotted near the CRUST–ASW mixing line. The gases of the Donnoe and Verkhnee fields show a shift to the ASW–SED line, indicating the admixture of gases from sedimentary rocks, which are close to SED fluids.

Calculation in absolute concentrations yields SED/AOC  $\sim$  1/30 for CRUST composition, indicating relatively low content of SED fluids. At the same time, altered oceanic crust AOC supplies fluid with low con-

tents of components, while fluid SED is much more concentrated due to the high content of organic matter in sediments. The mixing of 30 parts of diluted AOC fluid and only one part of SED fluid indicates that  $\sim 70\% N_2$  and  $17\% CO_2$  in slab fluid was derived from sediments SED.

Calculated data can be compared with true thickness of oceanic crust. Component SED in the works [43, 44] is presented for consolidated sediments of the lowest metamorphic grade (3%). For recalculation to watersaturated oceanic sediments (45-54% H<sub>2</sub>O), the concentrations of all components should be decreased with coefficient of 15-18. Recalculation yields AOC:SED = (2.0-2.5):1, which corresponds to the 6-km thick layer of altered oceanic crust with density of 2.6 g/cm<sup>3</sup> and water content of 4%, and 330-400-m thick layer of water-saturated sediments with density of  $1.35 \text{ g/cm}^3$ and the water content of 50%. Calculated data are close to true proportions between AOC and SED. According to seismological studies and deep-water drilling [15, 67], the thickness of sedimentary cover in the northwestern Pacific is 500-600 m at a thickness of altered oceanic crust of 5-6 km.

Tables 4a–4b summarize the calculated values of relative inputs (fractions) of geochemical reservoirs of subduction zone for the gases of Mutnovsky volcano. All five fractions can be distinguished in the fumaroles of the Aktivnaya funnel: MORB, AOC, SED, CC, and ASW. Other gases are reliably subdivided only into three fractions: MORB, ASW, and joint fraction CRUST, consisting of fluids of oceanic and continental crust.



**Fig. 9.**  $R/Ra-\log He/N_2$  diagram. Mixing lines connect the compositions of MORB and non-mantle fractions  $f_{(1-MORB)}$  in the gases of the corresponding thermal fields. A scatter in compositions of initial reservoirs is denoted by dashed fields. Ticks in mixing lines denote the fraction of MORB (in %).

#### ACCURACY OF CALCULATIONS

Below we report the estimate of calculation accuracy performed in the paper for three principally different cases: (1) accuracy in determination of composition of final mixing component by extrapolating trend; (2) accuracy in calculations of mixing of two components with one tracer; (3) accuracy in calculations of mixing of three components with three tracers.

(1) First case is implemented by calculating the isotopic composition of meteoric component for mixing trend with magmatic gases (Fig. 6). The chloride concentration in gas is analyzed depending on  $\delta D$  and  $\delta^{18}O$ . Least-square approximation with trend extrapolation to the intersection with y = 0 (HCl = 0) yields (HCl = 0)  $\mu_{aet} \delta D_{met} = -102$ ,  $\sigma (\delta D_{met}) = 4\%_0$ ; and  $\delta^{18}O_{met} = -9.8$ ,  $\sigma (\delta^{18}O_{met}) = 0.6\%_0$ . Standard deviation of meteoric component of mixing in terms of oxygen isotopic composition  $\sigma (\delta^{18}O)$  is significantly less than  $\sigma (\delta D)$ , being comparable with  $\sigma (\delta^{18}O_{magm}) = 0.5\%_0$  for magmatic component.

(2) Calculating the mixing of two components with one tracer (for instance, ASW– $f_{MAGM}$  or  $f_{MORB} - f_{1-MORB}$ ) for fractions of each of final compositions yields:

$$f_{1} = (C_{2}-C_{S})/C_{2}-C_{1});$$

$$f_{2} = (C_{S}-C_{1})/C_{2}-C_{1});$$

$$f_{1} + f_{2} = 1;$$
(14)

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where  $f_1$  and  $f_2$  are fractions,  $C_1$ ,  $C_2$ , and  $C_S$  are concentrations of tracer in the final compositions and in their mixture. Then, applying the error theory, the standard deviation of fraction  $\sigma f_1$  can be expressed via standard deviation of compositions as follows:

$$\sigma f_1 = \sqrt{\left(\frac{df_1}{dC_1}\sigma C_1\right)^2 + \left(\frac{df_1}{dC_2}\sigma C_2\right)^2 + \left(\frac{df_1}{dC_s}\sigma C_s\right)^2}, \quad (15)$$

 $\sigma f_2 = \sigma f_1$ . Differentiating formula (15), we obtain:

$$\sigma f_{1} = \left\{ \left[ \frac{C_{2} - C_{s}}{(C_{2} - C_{1})^{2}} \sigma C_{1} \right]^{2} + \left[ \frac{C_{s} - C_{1}}{(C_{2} - C_{1})^{2}} \sigma C_{2} \right]^{2} + \left[ \frac{-1}{C_{2} - C_{1}} \sigma C_{s} \right]^{2} \right\}^{1/2}.$$
(16)

We can take  $\sigma C_{\rm S} = \sigma C_1 = 0.6\%$ ,  $\sigma C_2 = 0.5\%$ ,  $C_1 = -9.8\%$ ,  $C_2 = 5.9\%$ ,  $C_{\rm S} = -0.5\%$  (groups of the hottest fumaroles AB). After substituting in formulas (14) and (16), we obtain  $f_1 = 0.45 \pm 0.045$ . Thus, at set values of compositions and standard deviations, the calculation accuracy of fraction of magmatic gas from isotopic composition is 10%. It is seen from formula (16) that the calculation error is mainly defined by the measurement error in gas composition  $\sigma C_{\rm S}$ .

(3) Formulas for mixing of three compositions with tracers can be obtained by the same way:



Fig. 10. Log He/Ar–log N<sub>2</sub>/He diagram. Data points are given for non-mantle fractions of volcanic gases  $f_{(1-MORB)}$ . Point CRUST denotes the crustal fraction in the gases of Mutnovsky Volcano. In the He–N<sub>2</sub>–Ar system, the compositions of gases of the Donnoe field correspond to 0.1–0.15 CRUST, which is approximately two times lower than values determined in the  $\delta D - \delta^{18}O$  system. Inconsistence is presumably caused by magma fractionation with depletion of gases in highly volatile components.

$$\sigma(f_i) = \sqrt{\sum \left(\frac{df_1}{dC_{j,k}} \sigma C_{j,k}\right)^2},$$
 (17)

where  $f_i$  are fractions,  $(C_{j,k})$  are the concentrations of tracers (j) in the final compositions (k) and in their mixture. However, the difficulty of the calculations rapidly increases with increasing of system complexity. For analytical calculation of standard deviation, each of three fractions  $f_i$  should be differentiated with respect to 12 arguments  $(C_{j,k})$ , with very intricate formulas for each derivative.

Analytical differentiation of fractions could be substituted by numerical differentiation, which is carried out by the following way. The starting equation system is solved as matrix, where solutions are the fractions of final compositions  $f_i$ . Further, one of 12 arguments in the matrix is substituted and the corresponding value of fraction  $f_i$  is determined. The limit of  $d(f_i)/d(C_{j,k})$  at d approaching zero equals derivative of fraction d for argument  $C_{j,k}$ . Thus, the behavior of fraction  $f_i$  is studied and the value of derivative for each of arguments is determined.

Then, derivatives should be multiplied on standard deviation of the corresponding argument  $[d(f_i)/d(C_{j,k})]\sigma(C_{j,k})$ . At low  $\sigma(C_{j,k})$ , calculations can be simplified by substituting  $[(C_{j,k}) \pm \sigma(C_{j,k}]$  instead of  $(C_{j,k\pm d})$ . The value of the fractions should be changed by approximately  $\Delta = [d(f_1)/d(C_{j,k})\sigma(C_{j,k})]$ . Obtained

12 values of  $\Delta(C_{j,k})$  for each of fractions should be squared, summed up, and rooted :  $\sigma f_i = [\Sigma(\Delta(C_{j,k}))^2]^{1/2}$ . Such an algorithm contains significantly lesser computing operations and does not unitlize intricate formulas, which are usually obtained during analytical search of partial derivatives. Numerical differentiation could be performed in any mathematical software packages.

Standard deviations for fractions of crustal fluid  $\sigma$   $f_{AOC}$ ,  $\sigma f_{SED}$ ,  $\sigma f_{CC}$  calculated using numerical differentiation are shown in Tables 4–6 together with values of fractions. The values of  $\sigma(C_{j,k})$  for calculations were taken from Table 3, uncertainty in determination of volcanic gas composition was taken to be 10%.

#### **CONCLUSIONS**

1. Mutnovsky Volcano is the typical subductionzone volcano, which is in a state of long-term stationary degassing. Volcanic and hydrothermal gases (including geothermal fluid) of different composition and temperature are discharged within the volcano and on its northern slopes. Regardless of temperature, the composition and character of discharge, all thermal fields of the area are characterized by the common sources of substances and the general trends in fluid mixing. These sources are following: (1) mantle fluid; (2) crustal fluid; (3) meteoric waters variably modified due to water rock interaction. For gases with the high content of

deep components, the crustal fluid may be subdivided into fractions AOC (altered oceanic crust), SED (oceanic sediments), and CC (continental crust).

(2) Fraction of meteoric waters accounts for 27% for the Aktivnaya funnel to 99.85% and more in the geo-thermal fluid; the fraction of deep fluid is, respectively, 73-0.15%.

(3) Mantle fraction in a deep fluid is as low as 1.5-1.8% for high-temperature fumaroles of the Aktivnaya funnel and 2.0-2.3% for gases of the Donnoe field, steam jets, and geothermal fluid. The content of continental gases in the deep fluid is estimated between 0.6% and 6.5% depending on final component used in the calculations. The main fraction of deep fluid in all thermal occurrences of the area is formed by dehydration of oceanic crust and oceanic sediments of the Pacific lithospheric plate in the subduction zone of the Kurile–Kamchatka island arc (slab–fluid).

(4) Observed compositional heterogeneity of fumarolic gases of Mutnovsky volcano is explained by degassing of two independent magmatic bodies. The magmatic body I is at the relatively early stage of degassing and provides up to 80% of total discharge of volcano in the Aktivnaya funnel crater. Magmatic body II is characterized by the later degassing stage, the higher content of mantle component, and releases fluids with different proportions of components. These fluids are discharged at the Donnoe field. The existence of two magmatic bodies of different composition at different degassing stages beneath Mutnovsky volcano is consistent with concepts of complex polycyclical evolution of the volcano.

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