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Y. A. Taran · C. B. Connor · V. N. Shapar  
A. A. Ovsyannikov · A. A. Bilichenko

## Fumarolic activity of Avachinsky and Koryaksky volcanoes, Kamchatka, from 1993 to 1994

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**Abstract** Volcanic gas and condensate samples were collected in 1993–1994 from fumaroles of Koryaksky and Avachinsky, basaltic andesite volcanoes on the Kamchatka Peninsula near Petropavlovsk–Kamchatsky. The highest-temperature fumarolic discharges, 220 °C at Koryaksky and 473 °C at Avachinsky, are water-rich (940–985 mmol/mol of H<sub>2</sub>O) and have chemical and isotopic characteristics typical of Kamchatka–Kurile, high- and medium-temperature volcanic gases. The temperature and chemical and water isotopic compositions of the Koryaksky gases have not changed during the past 11 years. They represent an approximate 2:1 mixture of magmatic and meteoric end members. Low-temperature, near-boiling-point discharges of Avachinsky Volcano are water poor ( $\approx$  880 mmol/mol); Their compositions have not changed since the 1991 eruption, and are suggested to be derived from partially condensed magmatic gases at shallow depth. Based on a simple model involving mixing and single-step steam separation, low water and high CO<sub>2</sub> contents, as well as the observed Cl concentration and water isotopic composition in low-temperature discharges, are the result of near-surface boiling of a brine composed of the almost pure condensed magmatic gas. High methane content in low-temperature Avachinsky gases and the 220 °C Koryaksky fumarole, low C isotopic ratio in CO<sub>2</sub> at Koryaksky (–11.8‰), and water isotope data suggest

that the “meteoric” end member contains considerable amounts of the regional methane-rich thermal water discovered in the vicinity of both volcanoes.

**Key words** Volcanic gases · Vapor-liquid separation · Avachinsky and Koryaksky volcanoes · Kamchatka

### Introduction

Avachinsky (Avacha, 2741 m, 53.26 N, 158.83 E) and Koryaksky (Koryak, 3456 m, 53.32 N, 158.69 E) are two adjacent large stratovolcanoes located 20–30 km north of the most populated Kamchatkan towns Petropavlovsk–Kamchatsky and Elizovo. Both volcanoes are active. They belong to the so-called Avachinsky group of volcanoes, a volcanic ridge crossing the modern volcanic front. The last eruption of Avacha Volcano occurred in January 1991 after a break of 46 years (Ivanov et al. 1995). Weak phreatic explosions at Koryak Volcano were recorded in 1957 (Marenina et al. 1962).

The purpose of this paper is to present first results on the chemistry and isotopic composition of Avacha and Koryak gas discharges. A simple mixing model for the boiling-point-temperature fumaroles is also presented with applications to low-temperature Avacha fumaroles.

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Yuri A. Taran (✉)<sup>1</sup> · Vyacheslav N. Shapar  
Alexandre A. Ovsyannikov · Arthur A. Bilichenko  
Institute of Volcanic Geology and Geochemistry,  
Petropavlovsk-Kamchatsky, 683006, Russia  
Fax: +7 41500 59195  
e-mail: taran@volgeo.kamchatka.su

Charles B. Connor  
Southwest Research Institute, 6220 Culebra Road, San Antonio,  
Texas

*Present address:*

<sup>1</sup>Institute of Geophysics, UNAM, 04510, Mexico D.F., Mexico  
e-mail: taran@tonatiuh.igeofcu.unam.mx

### General setting

#### Avachinsky Volcano

Avachinsky Volcano has a typical Vesuvius–Somma structure and is composed of lava and pyroclastics of basaltic to andesitic composition (Zavaritsky 1977). Lavas of the last 1991 eruption are represented by two-pyroxene andesites with SiO<sub>2</sub> content of 56–58 wt% (Ivanov et al. 1995). Many fumaroles were recorded at the bottom and walls of the 500-m-wide and 200-m-

deep crater. They were practically inaccessible before the 1991 eruption, and only low-temperature gases from the rim were collected and analyzed in 1962 (Kirsanov et al. 1964). Since the 1991 eruption, the main gas activity has been concentrated in a narrow moat between the lava plug and the crater rim. Figure 1a shows sketch maps of the Avacha crater before and after the 1991 eruption. High-temperature fumaroles (up to 500°C) are located now on the SW contact between fresh lava and the crater wall. These fumaroles trace the position of the former most active fumarolic field on the wall, 100 m below the crater rim before the 1991 eruption.

## Koryaksky Volcano

Koryaksky Volcano is a well-shaped cone composed of lava and pyroclastic deposits of basaltic to andesitic composition with basalts predominating (Marenina et

al. 1962). Fumaroles of the volcano are located on the northwest slope at an elevation near 3000 m (Fig. 1b). The main gas jets discharge from the fissure that formed as a result of the 1957 phreatic eruption. A few weak low-temperature fumaroles discharge permanently in a flat summit crater, covered by a glacier. A maximum temperature of 213°C in the fissure fumarole was recorded in 1983 (Taran 1985). The same fumarole in 1994 became significantly less powerful, but the temperature during 11 years remained unchanged (220°C).

## Sampling procedure

We used a 1-m-long titanium tube and Giggenbach flasks with 40–50 ml of 4N NaOH for the general gas analysis as well as for the sulfur- and carbon-isotope determination. Condensates were collected in two glass traps in series cooled by snow, using a hand pump. After the collection, the condensates from the two traps were combined for the water-isotope analysis.

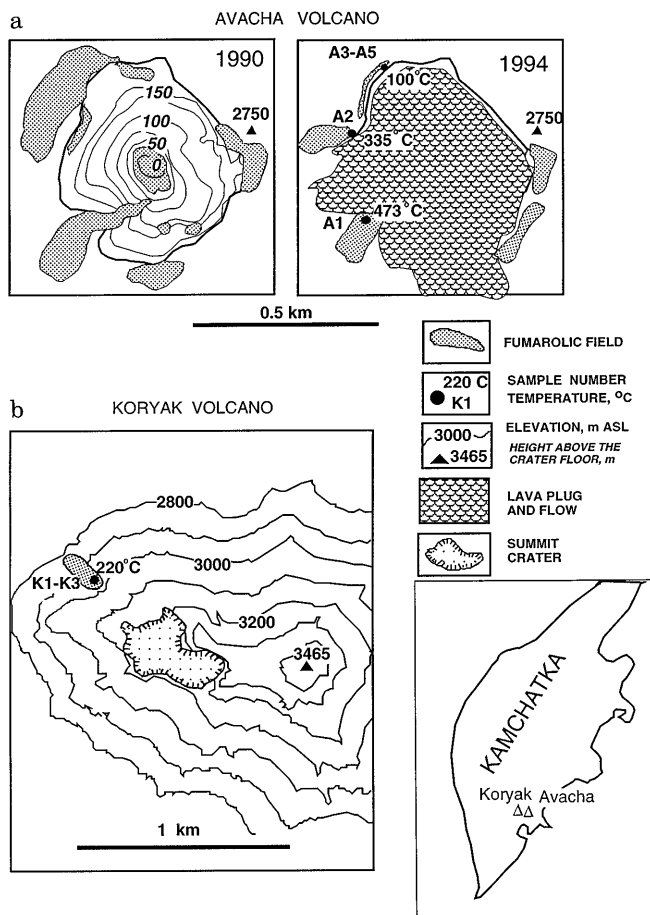
## Results and discussion

### Chemical composition

The chemical and isotopic compositions of gases collected from Avacha and Koryak Volcanoes are presented in Table 1. Two previously published analyses are added to Table 1 for comparison: the 1983 Koryak sample (Taran 1985) and the 1991 sample from a low-temperature fumarole of Avacha Volcano collected just after the eruption in February 1991 (Ivanov et al. 1995).

Water concentrations of the fumarolic gas vary from 878 mmol/mol in low-temperature Avacha fumaroles to 983 mmol/mol in the Koryak fumarole. The highest-temperature Avacha fumarole contains 945 mmol/mol of water, and concentrations of other species are typical for high-temperature “andesitic” gases of the Kamchatka–Kurile arc (Taran 1992; Taran et al. 1995). Excess water in fumarole A2 is caused probably by the entrainment of excess condensate from the sampling tube. Unusually dry, low-temperature Avacha fumaroles contain high CH<sub>4</sub> concentrations and low, but noticeable, amounts of Cl (0.01 mmol/mol of Cl corresponds approximately to 20 mg/kg of Cl in the condensate).

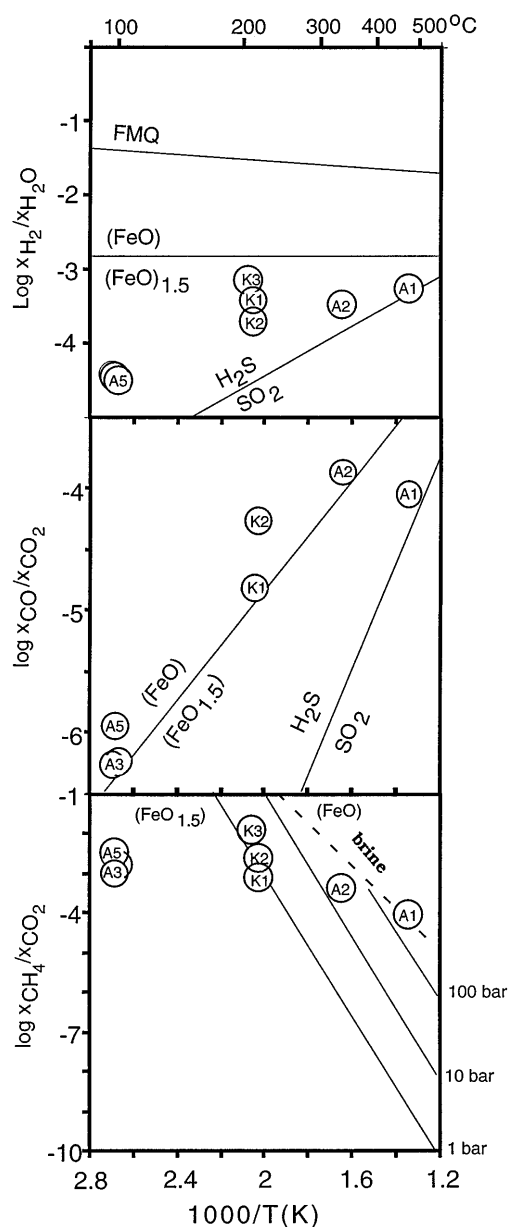
Three redox diagrams for analytical data in terms of  $\log(x_{\text{H}_2}/x_{\text{H}_2\text{O}})$ ,  $\log(x_{\text{CO}}/x_{\text{CO}_2})$ , and  $\log(x_{\text{CH}_4}/x_{\text{CO}_2})$  vs  $1/T(\text{K})$  are shown in Fig. 2. The H<sub>2</sub>/H<sub>2</sub>O ratios relative to some common buffer curves show a trend from typical “hydrothermal” values (Giggenbach 1987; Taran 1988) for low-temperature Avacha gases and the 220°C fumarole of Koryak Volcano, to the “gas buffer” line (SO<sub>2</sub>–H<sub>2</sub>S equilibrium in gas phase at 1 bar total pressure; Giggenbach 1987) for the A1 Avacha fumarole. The CO/CO<sub>2</sub> ratios plot along the (FeO)–(FeO<sub>1.5</sub>) “hydro-



**Fig. 1a, b** Sketch maps of the **a** Avacha crater and **b** summit part of the Koryak volcano. The Avacha crater before the 1991 eruption was more than 150 m deep with numerous fumarolic fields on the bottom, walls and the crater rim (Kirsanov et al. 1964). After the 1991 eruption, the crater was completely filled by lava (more than  $10^7 \text{ m}^3$ ). An excess of lava formed a flow approximately 1.5 km long on the southern slope of the volcano (Ivanov et al. 1995)

**Table 1** Chemical (in mmol/mol) and isotopic (‰) composition of volcanic gases from Avacha and Koryak volcanoes. Concentrations of N<sub>2</sub>, Ar and He are corrected for air contamination; nd – not determined

Sample	Date	T (°C)	H <sub>2</sub> O	H <sub>2</sub>	CO <sub>2</sub>	CO	SO <sub>2</sub>	H <sub>2</sub> S	HCl	HF	CH <sub>4</sub>	N <sub>2</sub>	Ar	He	δD H <sub>2</sub> O	δ <sup>18</sup> O H <sub>2</sub> O	δ <sup>13</sup> C CO <sub>2</sub>	δ <sup>34</sup> S Stot
A1	940912	473	944.9	0.5	22.6	0.0024	23.7	3.4	3.6	0.03	0.003	1.36	0.0087	0.00005	-30	+7.0	-5.2	+5.4
A2	940802	335	972.3	0.32	7.5	0.0011	13.5	2.4	1.7	0.05	0.002	0.85	0.0011	0.00072	-36	+6.7	n.d.	n.d.
A3	940410	102	888.2	0.027	87.8	0.00005	18.0	5.4	0.012	0.03	0.13	0.48	0.00043	0.00010	n.d.	n.d.	n.d.	n.d.
A4	930320	98	878.1	0.033	95.1	0.00005	18.2	9.0	0.06	0.02	0.12	0.10	0.00007	0.00003	n.d.	n.d.	n.d.	n.d.
A5	910223	101	880.1	0.03	89.5	0.00011	26.0	1.3	0.013	0.04	0.30	2.1	0.0014	0.00006	-52	+2.3	-6.1	+7.3
K1	940920	220	982.5	0.21	13.5	0.0002	0.63	0.71	1.1	0.04	0.01	1.3	0.014	0.00002	-58	-0.1	n.d.	n.d.
K2	940920	220	981.1	0.36	13.0	0.0007	5.0	1.9	1.0	0.03	0.03	2.0	0.011	0.00003	-54	+0.6	n.d.	n.d.
K3	830520	213	940.3	0.73	49.7	n.d.	1.5	1.8	0.8	0.03	0.6	1.3	0.01	0.00018	-58	+0.1	-11.8	n.d.



**Fig. 2a-c** Redox diagrams for the Avacha and Koryak volcanic gases with buffer lines and the brine boundaries from Giggenbach (1987; see text for details)

thermal” rock buffer, except for the highest -emperature fumarole A1, where equilibrium appears to be attained in the gas phase.

An excess of methane in volcanic gases relative to the gas-buffer equilibrium is usually attributed to fluid-rock equilibrium in high-pressure zones occupied by hydrothermal “brines” surrounding the central column of rising magmatic gases (Giggenbach 1987). CH<sub>4</sub>/CO<sub>2</sub> ratios shown in Fig. 2c are some orders of magnitude higher than the equilibrium values for gas buffer control, but may be projected onto the brine curve calculated for the (FeO)–(FeO<sub>1.5</sub>) rock buffer at temperatures in the range 350–450 °C and pressures of 100 to

200 bar. The points for Koryak Volcano, although close to the rock buffer line at 1 bar pressure and measured temperatures, should also be projected on the brine boundary because of very slow equilibration kinetics below at least 350 °C (Giggenbach 1982; Taran 1988). However, all of these constructions seem to be arbitrary. Why is the temperature indicated for the brine in equilibrium with CH<sub>4</sub> for high-temperature Avacha fumaroles close to the measured temperature? It suggests that the fumaroles are fed exclusively by a 500 °C magmatic brine at a considerable depth, and that the fumarolic vapors rise isothermally; otherwise, we should have an excess of CO<sub>2</sub> from the “dry” magmatic gas. If we have such excess, and CH<sub>4</sub> is contributed only from a brine “envelope,” the actual equilibrium temperature should be lower. If the main source of CH<sub>4</sub> is magmatic gas with very low initial CH<sub>4</sub> concentration, the excess of methane, necessary for the equilibrium in a “hydrothermal” environment, would be supplied through synthesis of CH<sub>4</sub> from CO<sub>2</sub>. But this is impossible in the short time available without special catalysts, which work, as a rule, under very highly reduced conditions (pure metals, hydrides; e.g., Taran 1980). In contrast, the oxidation of an excess of CH<sub>4</sub>, i.e., in opposite direction of the equilibration, is much easier in a volcanic environment. A general discussion about geothermal and magmatic CH<sub>4</sub> beyond the scope of this paper, but on the basis of the previously mentioned considerations we suggest that an additional source of CH<sub>4</sub> required for the volcano–hydrothermal systems underlying Avacha and Koryak Volcanoes, as was suggested previously for the Mutnovsky Volcano fumaroles (Taran et al. 1992).

A possible source of excess CH<sub>4</sub> Avacha and Koryak fumarolic gases is the CH<sub>4</sub>-rich hydrothermal aquifer in Cretaceous basement rocks, discovered in 1986 by deep (3 km) and shallow drilling at the southern base of Avacha and Koryak volcanoes within the so-called Avacha–Koryak depression. This aquifer (Ketkino–Pinachevo geothermal system) extends from the Pacific coast westward for more than 30 km to and contains (Y. A. Taran et al., unpublished data) methane-rich (>80% in dry gas), gas-enriched (up to 0.25 dm<sup>3</sup> NTP gas per kilogram water) saline water (~10 g/kg NaCl) with an average temperature of 80 °C at 1 km depth. These waters contain CO<sub>2</sub> (0.5 vol.% in dry gas) depleted in <sup>13</sup>C (δ<sup>13</sup>C = -21‰), possibly derived from CH<sub>4</sub> as a result of sulfate reduction; CH<sub>4</sub>, some more depleted in <sup>13</sup>C, than common “geothermal” methane (δ<sup>13</sup>C = -35‰); and isotopically light H<sub>2</sub>S (δ<sup>34</sup>S = -28‰) due to the organogenic (methane) or microbial sulfate reduction (e.g., Machel et al. 1995).

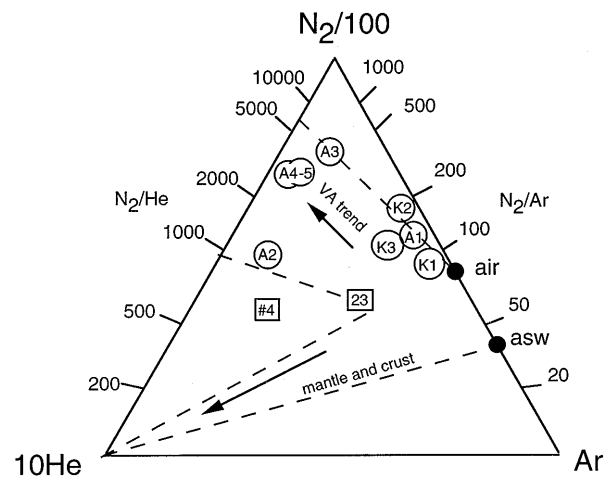
Thus, an at least three end-member mixing model for Avacha and Koryak fumaroles is suggested: a magmatic fluid, meteoric water, and a regional CH<sub>4</sub>-rich thermal water. Such a model appears to be common in many volcanic systems. A well-studied example is Vulcano, Italy, where several models involve a number of sources: magma, hydrothermal water of meteoric ori-

gin, altered and connate seawater, and fresh seawater (Bolognesi and D’Amore 1993; Chiodini et al. 1993, 1995; Tedesco 1995).

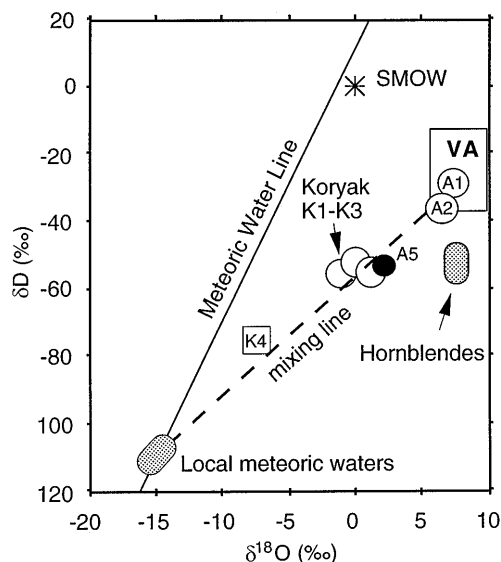
Figure 3 shows relative N<sub>2</sub>, Ar, and He concentration in volcanic gas samples and CH<sub>4</sub>-rich waters. Also shown are compositional areas delineating mixtures of meteoric components, air, and air-saturated water, and arc- and mantle-type magmatic volatiles, according to Giggenbach (1992b). Samples from Koryak Volcano and the A1 Avacha fumarole are strongly contaminated by air, but gases from low-temperature Avacha fumaroles occupy positions suggesting a volcanic arc-type magmatic source (VA). However, an excess of N<sub>2</sub> can also be provided by a crustal source, organic-rich sediments such as those responsible for high N<sub>2</sub>/Ar ratios in natural gases (Jenden et al. 1988) and in our case a main source of CH<sub>4</sub> in regional thermal water. Therefore, the low N<sub>2</sub>/He ratio in the A2 discharge, similar to those in the Ketkino thermal water, may be additional evidence for a contribution from this aquifer to the volcanic gas discharges. It is also significant that the <sup>3</sup>He/<sup>4</sup>He ratio in the Ketkino CH<sub>4</sub>-rich gas is 3.7 times that in air (Rozhkov and Verkhovsky 1990) suggests mixing of magmatic (VA) and crustal helium.

#### Isotopic composition of fumarolic gases

Isotopic compositions (δD-δ<sup>18</sup>O) of fumarolic condensates (Table 1) are plotted in Fig. 4 together with the composition of local meteoric water (Taran 1985; Cheshko 1994) and the isotopic composition of water from well no. K4 (800 m depth, 80 °C, NaCl = 9.8 g/kg). We also added δD-δ<sup>18</sup>O values measured on “green” hornblende from the tephra of the 1945 Avacha eruption (Taran et al., submitted). The higher-temperature



**Fig. 3** Relative N<sub>2</sub>, He, and Ar contents in fumarolic gases from Avacha and Koryak volcanoes and CH<sub>4</sub>-rich gases (well nos. 4 and 23) from Ketkino geothermal system located at the southern base of both volcanoes. Also the trends of volcanic arc (VA) and mantle-derived fluid compositions are shown. (From Giggenbach 1992a)



**Fig. 4** Craig plot for water-isotope composition of volcanic gases. Average meteoric water composition and a value for thermal water from well no. 4 of Ketkino are from Cheshko (1994). VA is area for the “volcanic arc” (subduction-type) gases. Also shown is area of hydrogen and oxygen isotopic compositions of hornblendes from pyroclastic rocks of the 1945 Avacha eruption (Taran et al., submitted)

samples from Avacha Volcano have an isotopic composition close to that of magmatic water associated with subduction-related arc volcanism (VA area on the plot, Sakai and Matsubaya 1977; Taran et al. 1989; Giggenbach 1992b). The hydrogen-isotopic shift between the hornblende and volcanic vapor composition corresponds to the fractionation factor between hornblende and an aqueous fluid at magmatic temperature (Suzuki and Epstein 1976). The points for the Koryak condensates indicate approximately two thirds of magmatic water. The isotopic composition of the Ketkino thermal water (point K4) is shifted from the meteoric water line and falls close to the mixing line. The point A5 for the low-temperature fumarolic vapor also lies close to, but somewhat below, the mixing line.

The isotopic compositions of total sulfur and CO<sub>2</sub>-carbon for Avacha Volcano (Table 1) do not differ from those of common “subduction”-type volcanic gases (Taylor 1986). However, carbon of CO<sub>2</sub> from the Koryak fumarole is depleted considerably in the heavy isotope (−11.8‰). This, in combination with relatively high CH<sub>4</sub> concentrations, also suggests some mixing of the Koryak magmatic gases with regional CH<sub>4</sub>-rich waters.

#### A simple mixing model for boiling-point temperature fumaroles

In addition to mixing of magmatic with thermal water in the formation of the Avacha–Koryak volcanic gases, there is a problem to explain both the chemical and iso-

topic composition of the low-temperature, near-the-boiling point gases at Avacha Volcano (A5 fumarole). For 4 years it had a nearly constant chemical composition with high CO<sub>2</sub> contents; water isotopic compositions corresponding to mixing of magmatic and meteoric end members; CO<sub>2</sub>/S<sub>tot</sub> ratios much higher than in the high-temperature (parent) gas; and a low, but significant, Cl content.

The lack of Cl and other chemical changes in low-temperature volcanic fumaroles are ascribed to separation of vapor from a liquid solution within the volcanic edifice. These “brines” likely formed through cooling and condensation of magmatic vapor or its mixture with local meteoric water (Ivanov 1960; Giggenbach 1987; Taran et al. 1992) or water from other sources.

We assume that both hot magmatic gases and groundwater are involved in the formation of a boiling solution, which in turn separates at shallow depth (at atmospheric pressure and corresponding temperature of boiling) into fumarolic vapor and brine. In a steady-state regime the input

$$M_i = M_{ig} + M_{id} \quad (1)$$

is equal to the output

$$M_o = M_{of} + M_{ob}, \quad (2)$$

where  $M_{ig}$  and  $M_{id}$  are mass inflow rates of the groundwater and deep vapor, respectively, and  $M_{of}$  and  $M_{ob}$  are the mass outflow of fumarolic vapor and brine, respectively. Then,  $Y_i = M_{id}/M_i$  the fraction of magmatic water in the total mixture and  $Y_o = M_{of}/M_o$  is the fraction of steam in the total steam–water discharge. The parameter  $Y_i/Y_o = M_{of}/M_{id}$  is the ratio of mass inflow of magmatic vapor to mass outflow of fumarolic vapor. Note that in an ideal “adiabatic” cell there should be one-to-one correspondence between  $Y_o$  and  $Y_i$ , and  $Y_i/Y_o$  must have a unique value. But actually we have a “black box” with unknown intrinsic properties, and therefore,  $Y_o$  and  $Y$  have to be considered as independent variables.

The most important major variables in volcanic gases are the contents of CO<sub>2</sub>, S, and Cl, as well as the isotopic composition of water. Sulfur behavior in a real brine-vapor system is complicated by redox, disproportionation, and mineral deposition reactions. Therefore, we consider a system with known (or unknown) water isotopic composition, and CO<sub>2</sub> and Cl concentrations in end members (magmatic gas and groundwater) and in fumarolic vapor.

#### Concentration of CO<sub>2</sub>

We assume that the groundwater is CO<sub>2</sub>-free. Then the total CO<sub>2</sub> concentration in the steam–water mixture is

$$x_{CO_2} = x_{CO_2,i} Y_i \quad (3)$$

where  $x_{CO_2,i}$  is the concentration of CO<sub>2</sub> in magmatic vapor. After redistribution of CO<sub>2</sub> between vapor and

brine, for the vapor (fumarolic) phase we have:

$$x_{CO_2,o} = x_{CO_2,i} Y_i B_{CO_2} / (1 - Y_i + Y_i B_{CO_2}) \quad (4)$$

where  $B_{CO_2}$  is the distribution coefficient for  $CO_2$  between steam and water and  $x_{CO_2,o}$  is the  $CO_2$  (output) concentration in fumarolic vapor. Since at  $100^\circ C$ ,  $B_{CO_2} \gg 1$  ( $\sim 10^3$ ; Giggenbach 1980) a good approximation at  $Y_i > 0.01$  is:

$$x_{CO_2,o} = x_{CO_2,i} Y_i / Y_o \quad (5)$$

Thus, the  $CO_2$  concentration in fumarolic vapor depends only on the ratio of mass flow rates for the deep magmatic  $CO_2$  and fumarolic steam. Note that the lower the fumarolic output in comparison with a deep input (the major part of the magmatic gas condenses, forming a brine), the higher the  $CO_2$  concentration in the fumarolic steam.

Isotopic composition of waters

The isotopic composition of a mixture of magmatic and groundwater end members in the  $\delta$ -notation can be expressed from the mass balance as

$$\delta_i = (\delta_{id} M_{id} + \delta_{ig} M_{ig}) / M_i \quad (6)$$

or

$$\delta_i = \delta_{id} Y_i + \delta_{ig} (1 - Y_i). \quad (7)$$

If  $\Delta^* = \delta_{id} - \delta_{ig}$  is the difference between  $\delta$ -values of the magmatic and groundwater end members,

$$\delta_i = \delta_{id} - (1 - Y_i) \Delta^*. \quad (8)$$

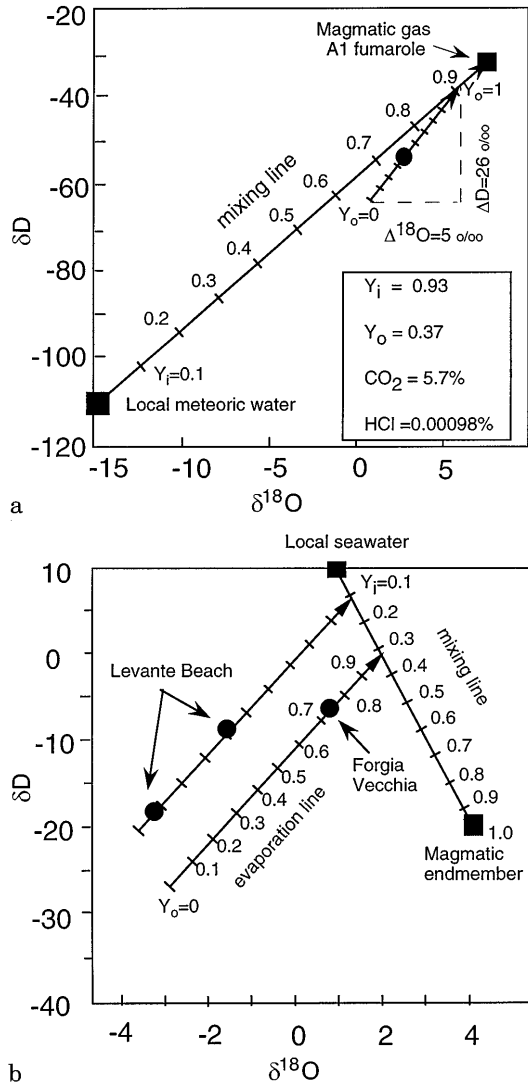
On the other hand, for equilibrium single-step steam separation (Giggenbach and Stewart 1982)

$$\delta_i = \delta_f + (1 - Y_o) \Delta_e, \quad (9)$$

where  $\Delta_e = \delta_l - \delta_v = (1000 + \delta_v) \ln \alpha$ ,  $\alpha$  is the vapor-liquid isotopic fractionation factor, and  $\delta_f$  is isotopic composition of fumarolic vapor. Combining Eqs. (8) and (9) we obtain:

$$\delta_f = \delta_{id} - (1 - Y_o) \Delta - (1 - Y_i) \Delta^*. \quad (10)$$

Using two equations for  $\delta D$  and  $\delta^{18}O$  we can calculate the fractions of magmatic component and of steam in the volcanic-hydrothermal system, if the isotopic ratios for both O and H in groundwater, magmatic steam, and fumarolic steam are known. A simple graph also can be used for these purposes (Fig. 5). Our values for the isotopic fractionation factors at  $100^\circ C$  are obtained by averaging the data of Majoube (1971), Arnason (1977), and Truesdell et al. (1977) for  $1000 \ln \alpha$ . In the  $\Delta$ -notation  $\Delta_e D = 26\text{‰}$  and  $\Delta_e^{18}O = 5\text{‰}$ . The point  $Y_i$  is determined from the intersection of the mixing line linking groundwater and magmatic steam with a segment passing through the point of the isotopic composition of fumarolic vapor with a slope  $\Delta_e D / \Delta_e^{18}O$ . The end point of the segment gives a maximum isotopic fractionation at the single-step steam separation ( $Y_o = 0$ ), and the intersection indicates that there is no



**Fig. 5a, b** Diagrams for calculation of  $Y_i$  (fraction of magmatic gas) and  $Y_o$  (fraction of steam in a shallow boiling aquifer) resulting from mixing of magmatic vapor with groundwater. Fraction of magmatic gas is determined from the intersection point between the mixing line connecting the local groundwater and magmatic end-member compositions and a segment whose length and direction correspond to the water-isotope fractionation at  $100^\circ C$ . The  $Y_o$  value is determined from the position of the measured value of fumarolic vapor on this segment. **a** Avacha A5 fumarole, mixing with local meteoric water. The slope of the mixing line is close to the slope of the evaporation line, causing “poor resolution.” The figure shows calculated fractions and concentrations of  $CO_2$  and Cl; **b** Boiling-point fumaroles at Vulcano Island, Italy. Mixing with local seawater causes “good resolution.” (Selected data for Vulcano from Chiodini et al. 1995)

liquid in the system. It is clear from Fig. 5a that if both the mixing line and fractionation line have the same slope, the  $\delta$ -values of fumarolic steam lie on the mixing line, but actual values of  $Y_i$  depend on values of  $Y_o$  minus the fraction of steam in the aquifer. In this case we need to use an additional equation, which is Eq. (6) for  $CO_2$  concentrations. The best “resolution” is obtained when the fractionation slope ( $\sim 5.2$  at  $100^\circ C$ )

differs strongly from the mixing line slope, such as in tropical areas or, for example, in the case of low-temperature fumaroles at Vulcano Island, Italy (Chiodini et al. 1995), assuming only two end members: magmatic vapor and shallow seawater (Fig. 5b).

### Chlorine concentration

In natural steam–water mixtures, steam is practically Cl-free for nearly neutral pH solutions, but contains some Cl in boiling acidic solutions (Ellis and Mahon 1977; Truesdell et al. 1989). Steam–water distribution coefficients for HCl and NaCl solutions were recently measured by Simonson and Palmer (1993). For practical purposes it is appropriate to use not the true distribution coefficient

$$B_{HCl} = m_{HCl,v} / m_{HCl,l} \quad (11)$$

where  $v$  and  $l$  are related to vapor and liquid solution, respectively, and  $m_{HCl}$  is the concentration of molecular HCl, but the “apparent” distribution coefficient

$$B_{Cl}^* = (m_{Cl,total,v}) / (m_{Cl,total,l}) \quad (12)$$

where  $m_{Cl,total}$  is the sum of concentrations of all dissolved Cl species. It is assumed that the solution under consideration is a mixture of free acids (HCl, H<sub>2</sub>SO<sub>4</sub>) and has not had time to be neutralized due to interaction with wall rocks. For a pure HCl solution at 100 °C,  $B^*$  depends on the total Cl concentration and can be expressed with reasonable accuracy (Table 3; calculated from data of Simonson and Palmer (1993) as:

$$B_{Cl,100}^* \approx 0.1 \sqrt{m_{Cl,f}} \quad (13)$$

where  $m_{Cl,f}$  is the concentration of total Cl in the fumarolic vapor phase in moles per kilogram.

If groundwater does not contain Cl, the total Cl concentration in a steam–water mixture,  $m_{Cl}$ , can be determined by the mass balance:

$$m_{Cl} = Y_i m_{Cl,i} = m_{Cl,f} Y_o + m_{Cl,b} (1 - Y_o) \quad (14)$$

where  $m_{Cl,i}$  and  $m_{Cl,b}$  are Cl concentrations in the magmatic end member and brine, respectively. We can rewrite this as:

$$Y_i m_{Cl,i} = m_{Cl,f} (1 - Y_o + B_{Cl}^* Y_o) / B_{Cl}^* \quad (15)$$

where  $B_{Cl}^*$  is the apparent distribution coefficient (Eq. (12)). The order of magnitude for  $B^*$  values is  $\sim 10^{-2}$  at  $m_{Cl} = 1$  m to  $\sim 10^{-6}$  at  $m_{Cl} = 0.01$  m in solution. Therefore, we can replace Eq. (15) by

$$Y_i m_{Cl,i} = m_{Cl,f} (1 - Y_o) / B_{Cl}^* \quad (16)$$

Using the empirical expression (Eq. (13)) for  $B^*$  and the Cl concentration in both magmatic and fumarolic gas in mole%, we obtain ( $Y_o \neq 1$ ):

$$x_{Cl,f} = 0.0055 Y_i^2 x_{Cl,i}^2 (1 - Y_o) \quad (14)$$

When  $Y_o = 1$ , there is no brine in the system.

In summary, now we have simple rules for variations in the isotopic composition of water, slightly soluble CO<sub>2</sub>, and highly soluble Cl, which assume: (a) ideal mixing of end members; (b) single-step steam separation from the two-end-member boiling mixture; and (c) equilibrium partitioning of species between solution and vapor. The model does not correspond to reality, but should allow maximum isotopic and chemical effects for a completely open, through-flow system to be obtained.

### Applications

Both the mixing parameter,  $Y_i$ , and steam fraction in the shallow aquifer,  $Y_o$ , may be evaluated at known  $\delta D$  and  $\delta^{18}O$  values. Figure 5 displays calculations for the low-temperature Avacha fumarole A5 (Fig. 5a) and, as an example of “good” resolution, those for Levante Beach and Forgia Vecchia fumaroles at Vulcano Island (Fig. 5b), according to data of Chiodini et al. (1995). Figure 5a shows results of calculations for the A5 Avacha fumarole. The CO<sub>2</sub> concentrations are obtained from Eq. (5), and to calculate Cl concentration in the A5 fumarolic gas we used Eq. (17). The agreement between calculated and observed data is qualitative (see Table 1) but reasonable. If errors of the isotopic analyses ( $\pm 2$ –4‰ for  $\delta D$  and  $\pm 0.1$ –0.3‰ for  $\delta^{18}O$ ) are taken into account, some error is accepted in defining end-member compositions, and the essentially first-order approximation of the model itself is recognized. In the Avacha case, the mixing slope is very close to the fractionation slope, and results are very sensitive to the choice of the end-member isotopic compositions and the accuracy of isotopic analysis. There are some disagreements for the calculated CO<sub>2</sub> concentration in Vulcano fumaroles (not shown in Fig. 5b and not discussed herein). The model can be improved by including a third end member, meteoric water.

According to the model, the reasons for high CO<sub>2</sub> concentrations in the low-temperature gases of Avacha are a high fraction of magmatic gas and low fractions of secondary steam. The lower Cl concentration obtained in the model may be the result of over-estimating the partition coefficient  $B_{Cl}^*$ . The real brine is not a mixture of pure acids, but a partially neutralized solution. The CO<sub>2</sub>/S<sub>tot</sub> ratio may change in the low-temperature environment, due to the precipitation of native sulfur.

### Conclusions

The fumarolic activity of Avacha and Koryak volcanoes in 1993–1994 was characterized by steady-state degassing. The maximum temperature and the chemical and water isotopic compositions of the Koryak fumarole has not changed over the past 11 years. The volcanic vapors represent an approximately 2:1 mixture of magmatic gas and meteoric water.



New fumaroles appeared after the 1991 eruption on the summit of Avacha Volcano with maximum-temperature accessible sites of 473 °C, and they discharge almost pure magmatic gas. According to a simple mixing model, which takes into account single-step steam separation from a partially condensed mixture of magmatic gas and meteoric water, and the partitioning of CO<sub>2</sub> and Cl between steam and water, the low-temperature Avacha fumaroles are derived from the condensed magmatic gas with a low meteoric water fraction. High methane concentrations in the Koryak and low-temperature Avacha gases may be the result of mixing of a methane-rich regional thermal water with magmatic fluid.

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