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Geochemistry of magmatic gases from Kudryavy volcano, Iturup, Kuril Islands

Yu. A. Taran,[1,*] J. W. Hedenquist,[2,†] M. A. Korzhinsky,[3] S. I. Tkachenko,[3] and K. I. Shmulovich[3]

[1]Institute of Volcanic Geology and Geochemistry, Petropavlovsk-Kamchatsky 683006, Russia
[2]Mineral Resources Department, Geological Survey of Japan, 1-1-3 Higashi, Tsukuba 305, Japan
[3]Institute of Experimental Mineralogy, Chernogolovka, Moscow District 142452, Russia

Abstract—Volcanic vapors were collected during 1990–1993 from the summit crater of Kudryavy, a basaltic andesite volcano on Iturup island in the Kuril arc. The highest temperature (700–940°C) fumarolic discharges are water rich (94–98 mole% H_2O) and have δD values of -20 to -12‰. The chemical and water isotope compositions of the vapors (temperature of thirteen samples, 940 to 130°C) show a simple trend of mixing between hot magmatic fluid and meteoric water; the magmatic parent vapor is similar in composition to altered seawater. The origin of this endmember is not known; it may be connate seawater, or possibly caused by the shallow incorporation of seawater into the magmatic-hydrothermal system. Samples of condensed vapor from 535 to 940°C fumaroles have major element trends indicating contamination by wall-rock particles. However, the enrichment factors (relative to the host rock) of many of the trace elements indicate another source; these elements likely derive from a degassing magma. The strongest temperature dependence is for Re, Mo, W, Cu, and Co; highly volatile elements such as Cl, I, F, Bi, Cd, B, and Br show little temperature dependence. The Re abundance in high-temperature condensates is 2–10 ppb, sufficient to form the pure Re sulfide recently discovered in sublimates of Kudryavy. Anomalously high I concentrations (1–12 ppm) may be caused by magma-marine sediment interaction, as Br/I ratios are similar to those in marine sediments.

The high-temperature (>700°C) fumaroles have a relatively constant composition (~2 mol% each C and S species, with SO_2/H_2S ratio of about 3:1, and 0.5 mol% HCl); as temperature decreases, both S_t and Cl are depleted, most likely due to formation of native S and HCl absorption by condensed liquid, in addition to the dilution by meteoric water. Thermochemical evaluation of the high-temperature gas compositions indicates they are close to equilibrium mixtures, apart from minor loss of H_2O and oxidation of CO and H_2 during sampling. Calculation to an assumed equilibrium state indicates temperatures from 705 to 987°C. At high temperature (≈900°C), the redox states are close to the overlap of mineral (quartz-fayalite-magnetite and nickel-nickel oxide) and gas ($H_2O-H_2-SO_2-H_2S$) buffer curves, due to heterogeneous reaction between the melt and gas species. At lower temperatures (<800°C), the trend of the redox state is similar to the gas buffer curve, probably caused by homogeneous reaction among gas species in a closed system during vapor ascent.

INTRODUCTION

High-temperature fumaroles associated with quiescently outgassing volcanoes provide the best opportunity to collect samples of aqueous fluids exsolving from magmas. However, relatively few volcanoes have had their high-temperature vapors reliably and extensively characterized in terms of major and trace elements and isotopic composition. Since 1990 we repeatedly sampled gases and condensates from high-temperature (≤940°C) fumaroles at Kudryavy volcano, located at the northern end of Iturup island, in the southern portion of the Kuril volcanic arc (Fig. 1; Tkachenko et al., 1992). The maximum temperature of 940°C measured in 1992 is likely the highest ever recorded for a steady-state fumarole at a non-erupting volcano.

Data from high-temperature volcanic fumaroles provide an initial source of information to assess the variation in volatile composition of magmas in terms of tectonic setting, magma composition, depth of degassing, etc. The composition of these vapors also provides information on the factors con-

trolling the oxidation state of magmatic systems (Giggenbach, 1987; Gerlach, 1993a). After presenting our results, we address several questions, including: (1) How may we differentiate the sources contributing major and trace species to fumarole samples (i.e., magma, wallrock erosion, shallow and deep hydrothermal fluids, meteoric water and/or seawater)? (2) How may we distinguish the processes controlling the composition of a volcanic-gas sample (heterogeneous reaction between gas-melt-rock or homogeneous gas phase reactions; mixing and/or oxidation during ascent; reaction with sampling equipment and other artifacts)? (3) What is the main source of water in island arc volcanic gases and their parent magmas; does the isotopic composition of volcanic vapor represent its parent magma?

Previous Studies

In addition to Kudryavy, high-quality samples from high-temperature volcanic fumaroles (following the general principles in Giggenbach and Matsuo, 1991) from around the world allow an assessment of the variables affecting magma degassing. Analyses of major gases plus condensates (for trace elements and water isotopes) are available from high-temperature volcanic fumaroles on Tolbachik, Kamchatka
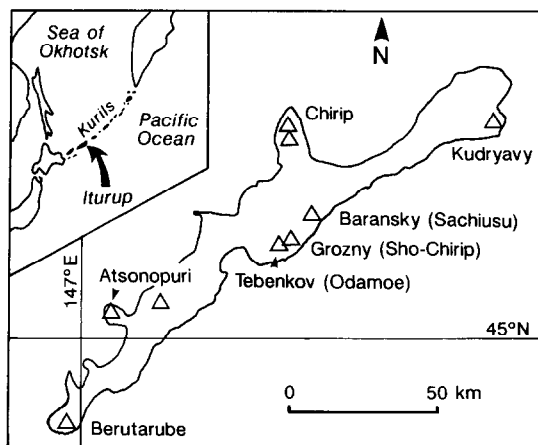
Fig. 1. Location of Kudryavy volcano in northeastern Iturup island, Kuril volcanic arc. The names of the volcanoes are in Ainu, the language of the native inhabitants. Where a Russian name is also in use, the Ainu name is listed in parentheses. Moyoro is the Ainu name for the whole volcanic complex that includes Kudryavy; we are not aware of an Ainu name for the Kudryavy cone.

(basalt, 1010°C; Menyailov and Nikitina, 1980), Momotombo, Nicaragua (basaltic andesite, 886°C; Menyailov et al., 1986; Quisefit et al., 1989), Kilauea, Hawaii, USA (basalt, 950°C; Crowe et al., 1987; Gerlach, 1993a), Merapi, Indonesia (andesite, 915°C; Le Guern et al., 1982; Symonds et al., 1987), Mt. Etna, Italy (basalt, 928°C; Le Guern, 1988), Mt. St. Helens, USA (dacite, 710°C; Le Guern, 1988), Mt. Augustine, Alaska, USA (andesite, 870°C; Symonds et al., 1990), Showashinzan and Usu, Japan (both dacite, 800° and 649°C, respectively; Matsuo, 1961; Mizutani, 1978; Symonds, 1992, and references therein), and Satsuma Iwojima, Japan (rhyolite, 880°C; Matsuo et al., 1974; Matsubaya et al., 1975; Shinohara et al., 1993; Hedenquist et al., 1994). The well-studied gases discharging from Vulcano (Martini, 1993; Bolognesi and D'Amore, 1993) do not have many trace element data for condensates available. White Island, New Zealand, is perhaps the most extensively studied arc volcano in terms of the variation of fumarole gas composition with time (Giggenbach, 1987; Giggenbach and Sheppard, 1989), though the trace element composition of condensates has not yet been systematically studied (LeCloarec et al., 1992).

GEOLOGICAL SETTING

Kudryavy volcano is a small cone (996 m elevation) of basaltic andesite composition which last erupted in 1883 (Gorshkov, 1970). The volcano is part of the post-caldera eruptive complex of the Medvezhya caldera (Fig. 2). The age of caldera formation is unknown, but is unlikely to be greater than 40 Ka (I.V. Melekestsev, pers. commun., 1993). Subsequently, rhyolite domes were extruded inside the caldera margin, followed by a dacite cone (Medvezhy volcano) accompanied by pyroclastic deposits. Next, the andesite cone of Seredni volcano formed, just west of Medvezhy, followed by eruptions of Kudryavy basaltic andesite flows further to the west. Fresh basalt flows of unknown age surround the small composite cone of Men'shoi Brat.

The cone of Kudryavy rises about 800 m from its surroundings, is covered by fresh lava flows, and is completely devoid of vegetation. Numerous fumaroles occur at the top of the cone in an elongate crater (approximately 300 × 70 m). Vent temperatures increase along the

crater from the southwest to the northeast, to a maximum of 940°C (Fig. 2, inset); the highest temperature vents also have the strongest discharge, and glow red even in the daytime.

Groundwaters discharge on the floor of the caldera (Fig. 2), where many small lakes are located. Only one thermal spring is known in the area; neutral pH, dilute water discharges at 39°C from the base of lava flows of the Men'shoi Brat cone.

SAMPLING AND ANALYSIS

We collected samples from numerous fumaroles with temperatures ranging from 130 to 940°C; temperatures were measured before collection with a chromel-alumel thermocouple (with an accuracy of ±5°C). Gases were collected separately from condensate samples, with the latter analyzed for more than fifty elements. The isotopic compositions of H, O, S, and C were also determined for some of the samples.

The fumarole samples were collected through 1-m-long quartz tubes, and connected with silicon rubber tubing to evacuated "Giggenbach bottles" (Giggenbach, 1975) filled with 4N alkaline solution (NaOH or KOH). The length of the rubber tubing depended on the accessibility of the sample site, and varied from 15 to 150 cm. In 1990 and 1991 we added 3 g of $Cd(OH)$ to 50 ml of 4N alkaline solution in order to directly absorb H_2S in the bottle. In 1992, $Cd(OH)$ was not added; H_2S and SO_2 concentrations were calculated following the method described by Giggenbach and Goguel (1989). Collection continued until the pressure in the sample bottle was nearly at atmospheric pressure. Condensates were collected into plastic bottles using a glass condenser refrigerated with cold water and snow. We also used a 200 mL glass syringe as a pump to increase the flow through the condenser.

Chemical analyses of the gas samples were performed by several techniques. The composition of the noncondensible gases in the headspace was determined by gas chromatography. The alkaline solutions were analyzed by wet chemistry according to the methods outlined by Giggenbach and Goguel (1989). Major species (Cl, F, SO_4) in the condensate samples were determined by wet chemistry; B and trace elements were analyzed by inductively coupled plasma (ICP) spectrometry techniques (including mass spectrometry, MS, and atomic emission spectrometry, AES).

The condensate samples were also analyzed for the hydrogen and oxygen isotopic composition of water. The CO_2 for carbon isotopic analysis was extracted from the oxidized alkaline solutions with H_2SO_4, and was purified by standard methods on a vacuum line. The SO_2 for total S (S_t) isotopic analysis was extracted by precipitating $BaSO_4$ from the oxidized alkaline samples, using standard methods (e.g., Grinenko and Grinenko, 1974).

COMPOSITION OF FUMAROLIC VAPORS

Isotopic Composition of Fumarolic Water

The isotopic compositions (δD-$\delta^{18}O$) of fumarole condensates (Table 1) are plotted on Fig. 3a, and the δD-Cl relationship is shown in Fig. 3b. The highest temperature samples (>700°C) have an isotopic composition typical of magmatic water associated with subduction-related arc volcanism (Sakai and Matsubaya, 1977; Kusakabe and Matsubaya, 1986; Taran et al., 1989; Giggenbach, 1992a). Sample TK1391 (Table 1; #6) is slightly enriched in D and ^{18}O compared to the other high-temperature samples. This isotopic enrichment may be caused by evaporation of water condensed in the sampling tube. Alternatively, this sample may be the most primitive (least diluted) magmatic vapor collected at Kudryavy (see below); if so, then our endmember magmatic composition (Fig. 3a) must be extended.

Both plots of data (Fig. 3a and b) show apparent mixing trends from the high-temperature group of samples to the low-temperature (<200°C) group of samples, the latter approaching the meteoric water line. The samples from <200°C fu-
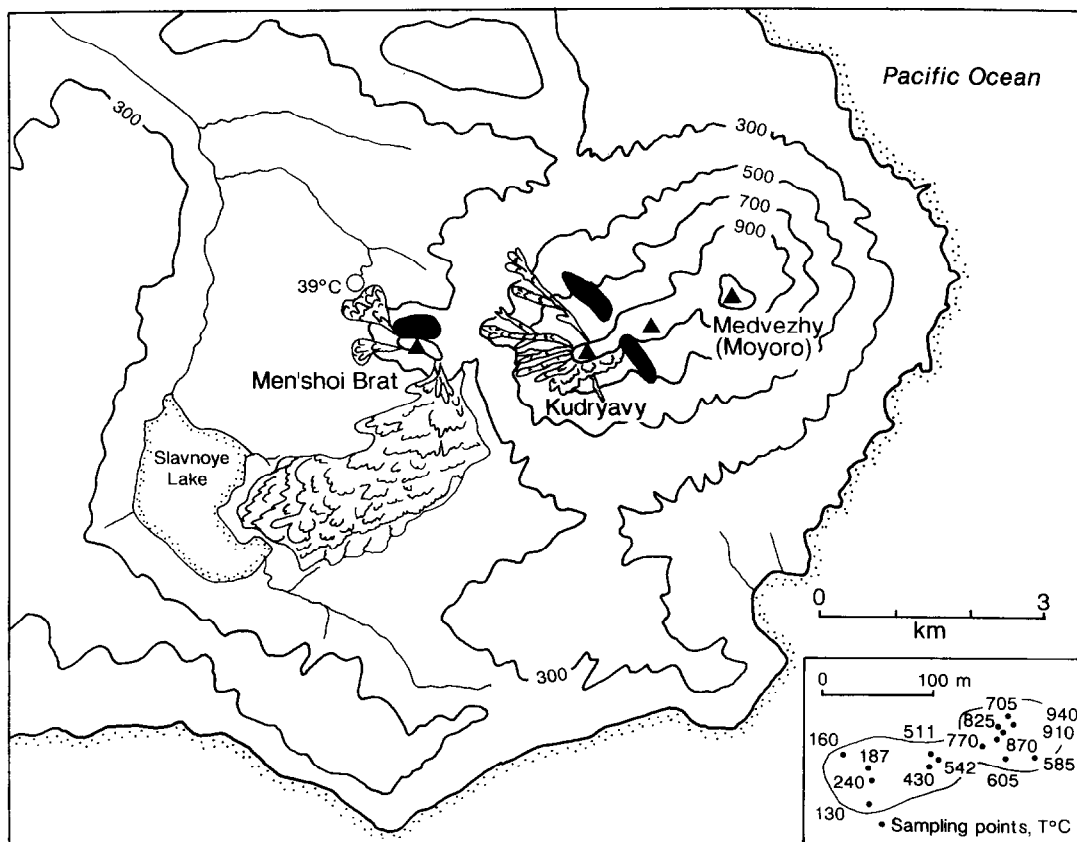
Fig. 2. Sketch map of the area around Kudryavy volcano. The western topographic margin of the Medvezhya caldera is reflected in the arcuate ridge at 300 m elevation. Rhyolite domes (black) erupted within the caldera, followed by the dacite cone of Medvezhy (Moyoro) and an andesite cone (Seredni) about 1 km west of Medvezhy. Subsequent eruptions at Kudryavy and Men'shoi Brat surrounded these cones with fresh basaltic andesite and basaltic lava flows, respectively. The inset shows the locations and temperatures (°C) of fumaroles within the summit depression of Kudryavy. Contours every 200 m starting at 300 m elevation.

maroles (#5, 9, 10, 20) have low Cl concentrations, and indicate that the nil Cl endmember has a δD value of about $-57\%o$ (Fig. 3b). This is similar to the isotopic composition of a 39°C warm spring discharging from beneath the Men'shoi Brat lava flow (Table 2), which plots on the local meteoric water line for the Kuril Islands (Esikov, 1992). However, the corresponding $\delta^{18}O$ value indicated for the Kudryavy endmember diluent is about $-5\%o$, a shift of $5\%o$ from the meteoric water line (Fig. 3a). The difference in δD of the nil chloride endmember ($-57\%o$) and the apparent local meteoric source ($-63\%o$) may be caused by evaporation during heating of the meteoric water.

Mizutani (1978) noted a similar, though larger, oxygen isotope shift in the meteoric water endmember of magmatic-meteoric water mixtures discharging from high-temperature fumaroles on Showashinzan volcano, in nearby Hokkaido. He attributed this shift, as we do, to meteoric water interaction and oxygen isotopic exchange with hot rock of the volcanic edifice as the meteoric water becomes entrained in the discharge of high-temperature volcanic vapors. At Kudryavy there is a simple pattern of decreasing temperature and Cl concentration with increasing meteoric water component, whereas Showashinzan and most other volcanic fumaroles do not show such regular trends.

Few if any other volcanoes have such a wide range of temperature and Cl concentrations that show a simple relationship to isotopic composition. One reason for the Kudryavy excep-

Table 1. Isotopic composition of fumarolic condensates

#	Sample	Date	Temp. (°C)	Cl (mole %)	δD (‰)	$\delta^{18}O$ (‰)	$\delta^{13}C$ (‰)	$\delta^{34}S$ (‰)
1.	K1290	1990	770	0.42	na	na	-4.7	2.9
2.	K790	1990	511	0.16	-38	2.7	-4.5	5.9
3.	K1190	1990	430	0.54	-26	4.5	-5.2	na
4.	K990	1990	240	0.19	-32	3.9	na	3.6
5.	K690	1990	160	0.002	-49	-2.7	-6.2	6.4
6.	TK1391	1991	910	0.74	-12	8.9	na	na
7.	TK291	1991	585	0.50	-23	6.0	na	na
8.	TK391	1991	542	0.46	-23	5.8	na	na
9.	TK2591	1991	187	0.18	-45	-1.4	na	na
10.	TK1791	1991	130	0.10	-45	-0.2	na	na
11.	ZN1000	1993	932	0.63	-17	5.2	na	na
12.	T926	1993	926	0.70	-21	5.8	na	na
13.	T810	1993	810	0.70	-21	5.7	na	na
14.	ZN800	1993	800	0.66	-19	4.2	na	na
15.	T735	1993	735	0.66	-20	5.8	na	na
16.	T630	1993	630	0.33	-41	2.4	na	na
17.	T538	1993	538	0.33	-29	2.7	na	na
18.	T465	1993	465	0.62	-23	4.5	na	na
19.	ZN300	1993	300	0.67	-27	4.1	na	na
20.	T170	1993	170	0.04	-54	-3.4	na	na
	Warm spring	1993	39	0.00002	-63	-10.5	na	na

Reference numbers 1-20 correspond to data on figures
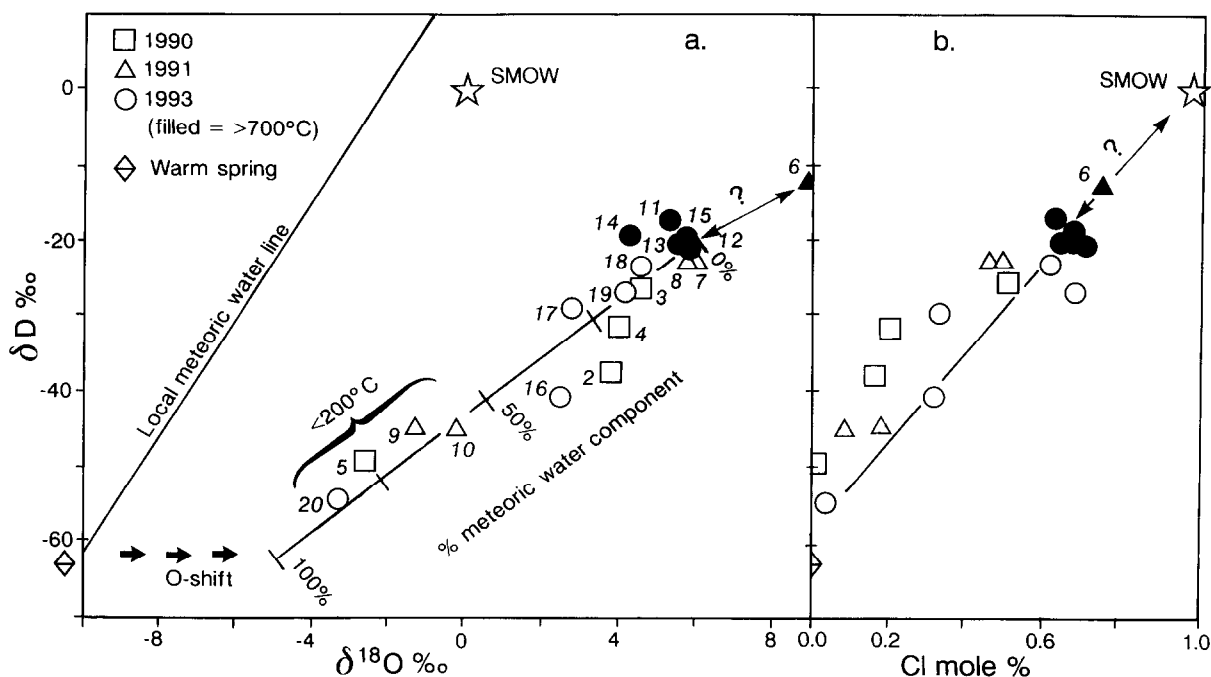na = not analyzed; ZN = sampled by V.S. Znamensky

FIG. 3. Variation of δD with $\delta^{18}O$ (a) and Cl content (b) for Kudryavy fumarole condensates collected in 1990, 1991, and 1993; the local meteoric water line for the Kuril islands ($\delta D = 8\delta^{18}O + 17$) is from Esikov (1992). The filled symbols indicate measured temperatures $> 700°C$. The mixing line (a) is labelled with the percentage of meteoric water component, from 0% (high-temperature magmatic vapor only) to 100% (heated and O-shifted local meteoric water). The 39°C warm spring is dilute and has an isotopic composition close to the local meteoric water line. Sample numbers refer to analyses in Table 1.

tion may be the large difference between the isotopic composition of the magmatic endmember and local meteoric water, which highlights the δD-Cl relation. In addition, the δD-Cl trend projects through the high-temperature fumarolic values to the composition of seawater (Fig. 3b), though accompanied by a $+12‰$ shift in the $\delta^{18}O$ value of the projected seawater endmember. One explanation for this extrapolation to the composition of seawater might be a large component of heated and O-shifted seawater, or connate (sedimentary or subducted) seawater contributing to the high-temperature discharges, as suggested elsewhere (Giggenbach and Matsuo, 1991; Giggenbach, 1992a; Bolegnesi and D'Amore, 1993).

Chemical Composition of Gases

The water concentrations of the fumarolic vapors vary from 92.1 to 98.5 mol% (Table 2), and have a general inverse correlation with fumarole temperature. There is also a nega-

tive correlation between H_2O and Cl, suggesting a simple mixing relationship, as also noted above from the isotopic data. The high-temperature samples collected in 1992 have a slightly higher water content than those collected in 1990 and 1991, with consequently lower C, S, and Cl concentrations. The high-temperature samples have a narrow range of composition on a H_2O-CO_2-S_t diagram (Fig. 4a), with H_2O/CO_2 and H_2O/S_t ratios close to 40 and 50, respectively (except for two samples collected at 187 and 430°C). The C/S ratio averages about 1 for most samples.

Four of the five $<700°C$ samples have compositions indicating S and/or Cl depletion (Fig. 4b), with the 187°C sample (#9) showing the largest depletion in both S and Cl. These depletions may be caused by deposition of native S and absorption of HCl and SO_2 by condensates in the sample tubes, as noted elsewhere (Shinohara et al., 1993). However, mixing with Cl- and S-poor meteoric water, also indicated by the isotopic data, may also contribute to the scatter in the data.

Table 2. Composition of fumarolic gases (mole %)

#	Sample	Date	T (°C)	H₂O	H₂	CO₂	CO	SO₂	H₂S	HCl	HF	N₂	O₂	Ar	CH₄
1.	K1290	1990	770	94.6	0.84	2.23	0.0021	1.07	0.54	0.42	0.0054	0.214	0.09	na	<0.0002
3.	K1190	1990	430	98.1	0.095	0.50	0.0007	0.10	0.33	0.51	0.018	0.340	0.05	na	0.00008
6.	TK1391	1991	910	93.1	1.00	2.36	0.036	1.53	0.50	0.74	0.083	0.547	0.15	0.0050	<0.0002
7.	TK291	1991	585	95.1	0.18	2.49	0.0034	1.18	0.39	0.50	0.057	0.128	0.016	0.0009	0.0047
9.	TK2591	1991	187	98.5	0.002	0.96	<0.00001	0.35	0.11	0.05	0.0082	0.056	0.002	na	0.0081
10.	TK1791	1991	130	95.0	0.002	2.25	<0.00002	2.30	0.26	0.011	0.0005	0.148	0.02	na	0.00036
21.	TK791	1991	870	92.1	1.30	2.70	0.019	2.33	0.58	0.66	0.061	0.261	0.02	0.0016	<0.0002
22.	F1292	1992	940	94.4	1.18	1.80	0.00065	1.80	0.18	0.46	0.025	0.133	0.02	0.0010	<0.0001
23.	F292	1992	825	94.6	0.79	1.81	0.0052	1.69	0.36	0.55	0.029	0.123	0.002	0.0005	0.0013
24.	F1592	1992	705	95.6	0.24	2.11	0.0026	1.20	0.68	0.09	0.013	0.098	0.004	0.0006	0.00063
25.	F1392	1992	605	94.0	0.61	2.80	0.23	1.07	0.66	0.12	0.030	0.280	0.02	0.0025	0.21

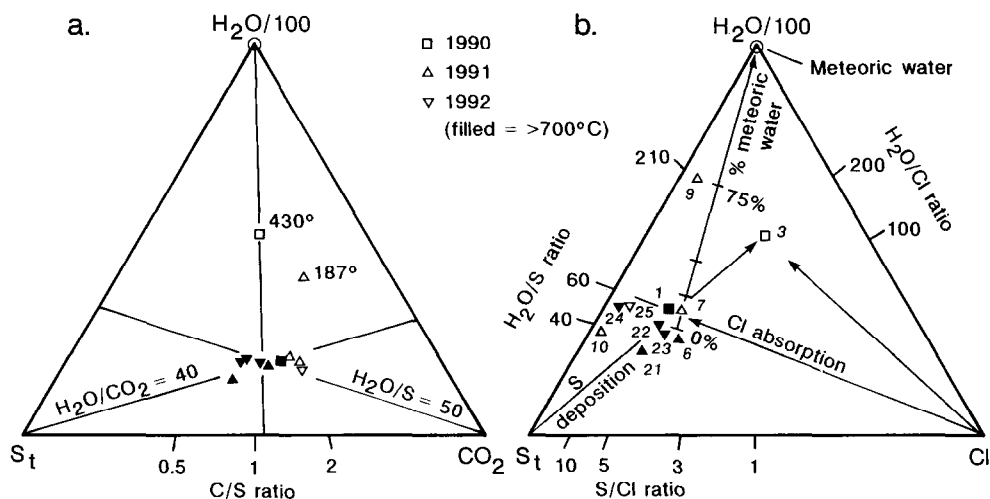Samples #1 to 10 correspond to those in Table 1; na = not analyzed

FIG. 4. Relative H_2O, S_t (total S) and CO_2 (a) and H_2O, S_t and Cl (b) molal contents in the fumarolic vapors for samples collected in 1990, 1991, and 1992 (sample numbers refer to analyses in Tables 1 and 2); filled symbols indicate measured temperatures > 700°C. The arrows indicate the shift of the volcanic gas endmember due to S loss caused by the disproportionation of SO_2 and subsequent deposition of native S, as well as Cl loss due to HCl absorption by condensates (Shinohara et al., 1993). The labelled line (b) indicates the percentage of meteoric water mixed with the magmatic vapor, from 0, 25, 50, to 75%.

For three of the five samples that have both isotopic and chemical data (#3, 6, 7, 9, and 10; Table 2), there is agreement in the percentage component of meteoric water diluent estimated from isotopic (Fig. 3a) and chemical (Fig. 4b) compositions. Most of the shift in chemical composition of sample 9 from that of the high-temperature vapors can be explained by meteoric-water dilution (accompanied by some Cl absorption). The isotopic and chemical composition of sample 6 could be explained by water loss, or alternatively as suggested above, this sample may contain the largest magmatic component. The two inconsistencies between these two sets of data are samples 3 and 10. The high H_2O/S_t ratio of sample 3 may simply be caused by S deposition (Fig. 4b). The low H_2O/S_t and high S_t/Cl ratios of sample 10 are inconsistent with the 60–70% meteoric water component indicated by its isotopic composition (Fig. 3a); this may have been caused by Cl loss (absorption) and S gain (from entrained native S) during sampling of this 130°C fumarole.

The SO_2 concentration exceeds that of H_2S in all but one sample, with SO_2/H_2S ratios averaging ≈3:1 (Table 2). There is no significant difference between SO_2 and H_2S concentrations in the 1990–1991 samples, which contained $Cd(OH)_2$ to absorb H_2S, and the 1992 samples, where SO_2/H_2S ratios were determined using the alkaline iodide titration technique (Giggenbach and Goguel, 1989).

The H_2/H_2O ratios of samples relative to some common buffer curves are shown in Fig. 5. Included is the equimolar coexistance curve for the SO_2-H_2S redox pair at 1 atmosphere pressure. Sulfur species tend to dominate the gases discharged from many volcanoes. For this reason, and because the reaction $3H_2 + SO_2 = 2 H_2O + H_2O$ equilibrates relatively fast at temperatures > 350°C, the SO_2-H_2S pair appears to control the redox state of many volcanic systems; thus, this pair has been called a gas buffer (Giggenbach, 1987), with equimolar coexistance being the optimum buffer ratio. The H_2/H_2O ratios, indicating the redox potential of the high temperature

vapors, lie between the fayalite-magnetite-quartz (FMQ) and nickel-nickel oxide (NNO) mineral buffers curves and parallel to the SO_2-H_2S gas buffer curve. The lowest temperature samples deviate from these gas and mineral buffer curves (Fig. 5, inset), but lie near the magnetite-hematite buffer. This behavior, from high to low temperature, is similar to that noted at other similar volcanoes, such as White Island (Giggenbach, 1987), Mutnovsky (Taran et al., 1992), and Satsuma Iwojima (Shinohara et al., 1993).

The redox potential of three fumaroles was measured using a solid-state sensor (Rosen et al., 1993). Their reported $\log f_{O_2}$ values (and measured temperatures) are -12.32 (890°C), -12.73 (870°C), and -15.32 (720°C); these are plotted as stars on Fig. 5, converted to $\log H_2/H_2O$ (assuming the isomolar ratios of activity coefficients are close to unity; Giggenbach, 1987). These values are similar to those determined from the gas analyses.

The CO/CO_2 ratios (not plotted) parallel the CO/CO_2 isomolar coexistence curve but at higher pressures; with decreasing temperature there is a trend in CO/CO_2 ratios toward that of the rock buffer (FeO-$FeO_{1.5}$; Giggenbach, 1987), also similar to behavior elsewhere (White Island, Satsuma Iwojima). Shinohara et al. (1993) suggest the C gases may equilibrate at higher pressures, but offer no explanation as to why. One other possibility is that CO is lost after sampling, since it is slowly converted to formate by hydroxide in the sample bottles (Giggenbach and Matsuo, 1991).

Methane was detected in several high-temperature Kudryavy samples, and, in a few, the CH_4 concentrations are significant. Methane in low-temperature fumaroles generally has a hydrothermal origin (Giggenbach, 1987; Taran et al., 1992), possibly with some organic contamination from the rock, whereas in high-temperature magmatic gas, CH_4 concentrations should be exceedingly low at equilibrium (Gerlach and Casadevall, 1986; Giggenbach, 1987). The high CH_4 (and CO) concentrations in sample F1392 are likely due to
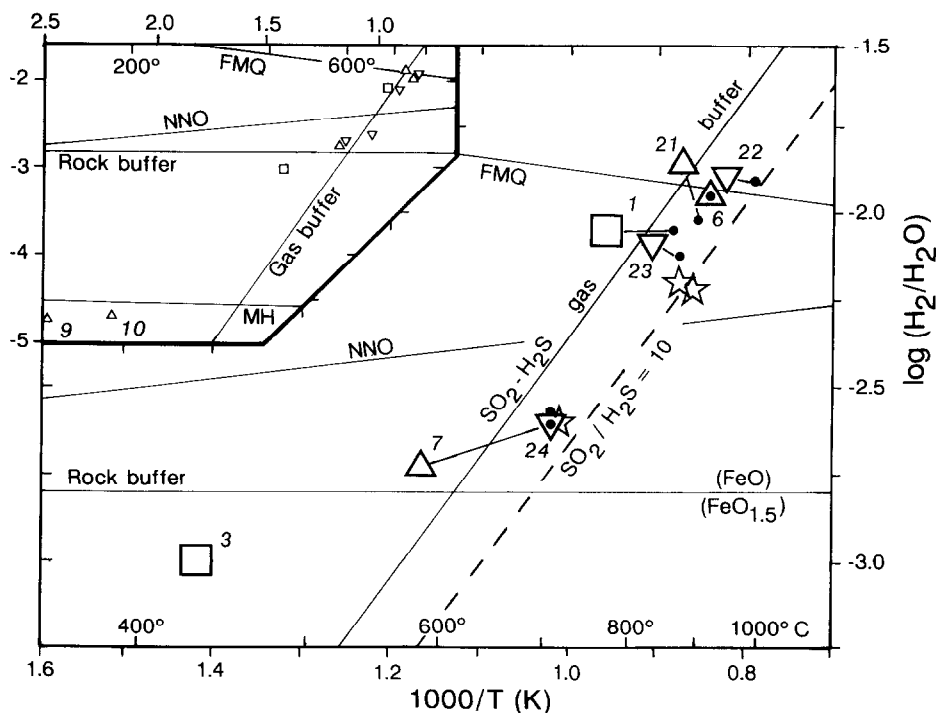
FIG. 5. Variation of the H_2/H_2O molal ratio of fumarolic vapor versus measured temperature (Table 2; symbols from Fig. 4, with no distinction for temperature). Inset shows the same data on a different scale in order to include the two <200°C samples. The mineral buffer curves include fayalite-magnetite-quartz (FMQ), nickel-nickel oxide (NNO) and magnetite-hematite (MH); the altered rock buffer (FeO-FeO$_{1.5}$) and gas buffer (SO_2-H_2S) curves are also shown (Gig-genbach, 1987). Measured redox state (Rosen et al., 1993) vs. measured temperatures are shown as open stars. Equilibrium calculations of ratios and temperatures for the seven samples amenable for calculation (Table 6) are shown as solid dots, connected to the corresponding original analytical data points.

reaction with the long length of rubber tubing used (150 cm), and this observation suggests that much of the CH_4 in the high-temperature gases (>700°C) reported here may have the same origin. Therefore, we do not use the C and H of CH_4 for later mass balance thermodynamic calculations.

All the samples are contaminated to a variable degree by air, which likely occurred before or after collection due to leakage of the Teflon stopcocks. The N_2/O_2 ratios in all the samples are much greater than the atmospheric ratio of 3.72, though this may be in part due oxidation of reduced species. A better indicator of the air contamination is the N_2/Ar ratio; in air this ratio is about 83.6, whereas in "andesitic" gases it may exceed 1000 (Giggenbach, 1987, 1992b; Margo and Pennisi, 1992). The measured N_2/Ar ratios of the samples ($\approx 100–300$) are slightly greater than that of air. For a first approximation of the "magmatic" Ar and N_2 contents, we correct the values based on the O_2 concentrations:

$$N_{2,\,magmatic} = N_{2,\,meas} - 3.72\,O_2 \quad \text{and}$$

$$Ar_{magmatic} = Ar_{meas} - 0.0444\,O_2.$$

The N_2/Ar ratios increase after these corrections for atmospheric contamination, and for the F1292 sample (940°C) reach a value of 650, similar to the maximum value for Usu volcano, Japan (Giggenbach and Matsuo, 1991). Although it is likely that portions of the N_2 and Ar have a magmatic origin, it is not possible to determine the exact concentration. Therefore, N_2 and Ar are neglected in the following calculations.

Isotopic Composition of Gases

The isotopic composition of sulfur (3 to 6‰, Table 1) is typical of island arc values for high-temperature fumarolic discharges (Allard, 1983; Taylor, 1986). The carbon isotope ratios range from −4 to −6‰, close to "primary-magmatic" values, considering that the carbon isotope fractionation between silicate melt and aqueous fluid is about 4‰ (based on experimental data; Javoy et al., 1978; Belomestnykh and Shilobreeva, 1989).

Chemical Composition of Condensates

The aqueous fluid degassing from a calc-alkaline magma at a pressure greater than several hundred bars may contain several wt% or more NaCl (Burnham, 1979; Lowenstern, 1994). However, the NaCl content of high-temperature magmatic vapors quiescently discharging from volcanic fumaroles is generally ≤100 mg/kg (Hedenquist and Lowenstern, 1994). This discrepancy can be explained by the formation of a small amount of hypersaline liquid that separates from the vapor phase and remains at depth (e.g., as observed in fluid inclusions associated with porphyry metal deposits; Roedder, 1984); this is consistent with the immiscibility relations in the system H_2O-NaCl (Sourirajan and Kennedy, 1962). The critical pressure at 800°C is about 1400 bars for the binary system, but may increase to 5 kbar with the addition of SO_2 and CO_2 (Bodnar and Sterner, 1987); thus, an aqueous

fluid exsolved from a magma will generally be affected by immiscibility during ascent and depressurization (Shinohara, 1994). This is supported by the low concentration of NaCl in volcanic vapor, which is similar to that predicted from the solubility of NaCl in vapor at atmospheric pressure (Pitzer and Pabalan, 1986). Upon inception of immiscibility, the hypersaline liquid (or salt at low pressures) will sequester a portion of the chloride-complexed metals (Hemley et al., 1992) exsolved from the magma, leaving the buoyant gas-rich vapor to ascend and discharge at the surface. Nevertheless, condensate samples of high-temperature fumaroles provide a first approximation of the species and concentrations of metals released from a magma during degassing.

The Kudryavy condensate samples (Table 3) were collected in 1991 and 1992 from fumaroles with temperature ranging from 535 to 940°C, in order to estimate the concentrations of elements exsolving from the degassing magma. Symonds et al. (1990, 1992) noted some of the problems associated with interpreting condensates, separate from the effect of immiscibility. The possible sources of trace elements in condensates include ascending magmatic fluid, hydrothermal solutions, rock particles from the conduits walls, products of high temperature gas-rock reactions, and the sampling apparatus (e.g., from Ti or stainless steel sample tubes; Gemmel, 1987). Minor contamination of the magmatic fluid from such sources does not greatly affect thermodynamic calculations based on the concentrations of major components (e.g., the effect of the addition of a small amount of H_2O on redox calculations; Gerlach, 1993a), though the breakdown of rubber tubing through reaction with halogen gases may contaminate the sample with C and H. By contrast, any contamination of the magmatic component makes the interpretation of the trace element abundance in volcanic vapors very difficult.

For example, the δD-Cl correlation (Fig. 3b) indicates that meteoric water is entrained to a varying degree by the Kudryavy volcanic vapors. The meteoric water component circulates to a depth sufficient to be heated, and for water-rock interaction to occur, as indicated by the oxygen isotopic shift. This water is completely vaporized once it is entrained by the high-temperature vapors; the solutes in this meteoric water component may also be incorporated into the vapor and discharged from the fumarole. For this reason, we focus on high-temperature samples because they have the least apparent meteoric-water component (Fig. 3); we examine here the four samples which have trace element data available and which have been little affected by Cl or S loss (Fig. 4b; i.e., samples 7, 21, 22, 23).

The standard approach to represent variations in the composition of volcanic condensates is calculation of enrichment factors (EF):

$$EF_i = (E_i/R)_{vapor}/(E_i/R)_{rock},$$

where E_i is an element in both the vapor condensate and the rock hosting the fumaroles, and R is a nonvolatile reference element chosen for normalization (Zoller et al., 1983; Symonds et al., 1987). Magnesium is used here as the reference element, following the method of Symonds et al. (1990), for sake of comparison. For the rock source we use the major element composition of the Kudryavy basaltic andesite lava

Table 3. Chemical composition of fumarolic condensates

Sample	TK291	TK791	F1292	F292	F1392	F592
#	7.	21.	22.	23.	25.	26.
Date	1991	1991	1992	1992	1992	1992
T (°C)	585	870	940	825	605	535
pH	0.81	0.59	1.01	0.67	1.38	0.78
Cl (ppm)	12210	15380	8580	12850	2070	13580
F	562	503	164	510	105	460
Si	184	197	79.1	98.8	11.3	97.9
Na (ppb)	22500	41200	6100	5000	2560	2440
B	38500	36600	33000	42000	17540	35300
K	12800	28660	5620	9530	20500	15500
Al	9650	13000	3900	7100	8900	4800
I	6700	11600	5400	6100	1400	800
Br	9400	10400	750	750	240	360
Fe	3700	6800	7300	3620	17650	2280
Ca	5000	5500	2000	1730	14300	2300
P	na	na	30800	2000	4000	22700
Mg	1700	1760	500	880	4300	120
As	730	1550	1200	1250	540	630
Zn	580	1000	3100	1000	13500	250
Ti	700	620	140	130	640	160
Cd	230	580	230	880	700	90
Pb	1840	580	1250	110	9700	6400
Zr	380	460	980	1280	650	1200
Mo	4	270	200	110	160	2
Mn	120	210	90	55	180	17
Sr	23	130	10	15	55	10
Cu	32	130	270	90	910	76
Sn	380	130	140	140	210	100
Bi	135	110	40	70	220	45
Se	na	na	170	200	100	na
Rb	38	75	45	50	10	10
Ba	380	74	150	420	140	50
Tl	60	65	160	140	3700	200
Ni	50	55	410	320	50	50
Sc	na	na	60	60	50	56
Cr	24	45	130	115	70	15
W	2	40	30	20	60	3
Ge	37	38	27	10	30	90
Li	24	29	30	15	7	2
Sb	240	20	79	100	510	120
Co	1	16	6	3	5	<1
Te	<5	<5	10	5	15	80
Hg	75	15	28	25	340	35
Cs	na	10	na	na	na	na
Hf	na	na	10	16	7	15
Ce	na	na	2	3	5	4
Re	<1	<1	8	10	2	<0.1
Th	<3	<3	<1	<1	4	15

Samples # 7 to 25 correspond to those in Table 2
Not detected by ICP-MS: Be, Co, La, Ta, U, Re, Os, Ir, Au, I
(<1 ppb); W, Ag (<2 ppb); Th, Pt (<3 ppb); Mo, Hg (<4 ppb).

(Ostapenko, 1970), while mean values of trace element concentrations are from Avdeiko et al. (1992), for Quaternary basaltic andesites of the southern Kurils. For a few elements which are absent from the Avdeiko et al. (1992) database, we have used the mean values for island arc basaltic andesites from the database of Popolitov and Volynets (1981). The composition of our "average" reference rock is given in Table 4.

The calculated EF values for condensate samples with no evidence for a meteoric water component or S and/or Cl loss are plotted on Fig. 6; they were collected from 940 to 585°C fumaroles. Elements with log EF values from 0 to 1, i.e., with normalized abundances in the vapor similar to those of the rock, most likely derive from rock particles eroded from the conduit wall and entrained by the high-temperature vapor. These particles dissolve in the acidic condensate and distort the primary "magmatic" fluid composition. At Kudryavy, Al, Ti, Mn, Ca, and, for some of the samples, Fe and Sr, are largely derived from rock contamination. These are the principal major rock-forming elements, with the exception of Na and K (Si is partially contaminated from the quartz sample

Table 4. Composition of reference rock

Oxides, wt %		Trace elements, ppm			
SiO$_2$	54.52	Ni	16	Ba	365
TiO$_2$	0.88	Cu	54	Sr	608
Al$_2$O$_3$	17.96	Zn	106	V	361
Fe$_2$O$_3$	3.22	Pb	3.2	Cr	117
FeO	6.18	Sn	1.4	Co	29
MnO	0.18	W	0.26	Hf	2.7
MgO	4.00	Mo	1.2	Ce	7.5
CaO	8.78	Be	0.43	Cl	100
Na$_2$O	2.76	B	22.5	Br	4.5
K$_2$O	0.57	F	314	I	0.5
P$_2$O$_5$	0.13	Th	1.1	As	2.4
H$_2$O+	0.31	Nb	1.5	Cd	0.5
H$_2$O-	0.13	Zr	82.5	Bi	0.01
Total	99.62	Li	3.8	Se	0.05
		Rb	27.8	Te	0.001
		Tl	0.3	Sc	7.5
		Ge	1.5	Sb	0.6
		Hg	0.1	Cs	1.5
		Re	0.001		

tubes). The rock contaminants noted here are similar to those determined by Symonds et al. (1992) for the condensates of Mt. Augustine volcano, Alaska, USA.

The EF values for volatile elements such as Cl, I, Bi, F, Cd, B, and Br vary by less than an order of magnitude, despite the 350°C range in vent temperature. By contrast, there is a larger variation (up to two orders of magnitude) and consistent temperature dependence for elements such as Re, Mo, W, Cu, and Co. The stronger temperature dependence of these

EF values agrees with the common observation of sublimates containing these metals around high-temperature fumaroles, such as Re-rich molybdenite (Bernard et al., 1990) and molybdenum "blue," a Mo oxide (Kavalieris, 1994). In particular, pure Re sulfides have been noted at Kudryavy forming at the surface at about 600°C, while molybdenite occurs nearby in sublimates formed above 700°C (Znamensky et al., 1993; Korzhinsky et al., 1994). The high fugacity of Re here is similar to the finding of Crowe et al. (1987) for the Kilauea basalts.

For many other elements there is a smaller temperature dependence, with the EF values for the 940°C condensate generally about half an order of magnitude above the EF values for the 870°C sample, while the EF values for the 585°C condensate are similar to or slightly lower than the EF values for the 870°C sample. The large EF values for many elements suggest a large proportion of most of the trace and some of the major elements are not contributed by rock contamination, but derive largely from a deep source, most likely an aqueous fluid exsolving from a shallow magma.

The Cl/Br ratio of Kudryavy condensates (Table 3) is 5–10 times greater than the marine ratio of 290. The Cl/I ratio is very low due to relatively high I concentrations, exceeding those in Mt. St. Helens condensates (Le Guern, 1988) by more than four orders of magnitude (1–12 ppm vs. 0.5 ppb, respectively). The Kudryavy Br/I ratios are close to the values observed in some marine sediments (Kennedy and Elderfield, 1987; Bölhke and Irwin, 1992), possibly caused by a component of connate water from marine sediments in the high-temperature discharges.

THERMOCHEMICAL EVALUATION OF GAS ANALYSES

Chemical equilibrium among volcanic gas species (Ellis, 1957; Gerlach and Nordlie, 1975; Gerlach, 1980a,b) may be
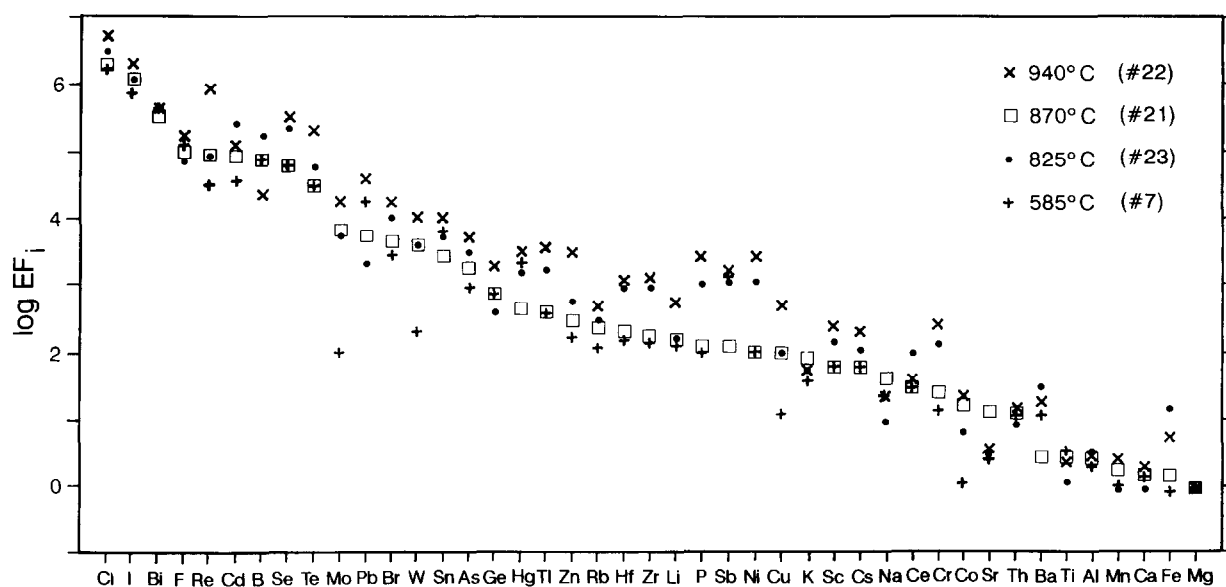

FIG. 6. Calculated enrichment factors (log EF$_i$) for forty-three elements in condensates from four fumaroles (Table 3; #7, 21, 22, and 23). EF$_i$ = $(E_i/R)_{vapor}/(E_i/R)_{rock}$, where E_i is an element in both the vapor condensate and the rock (Table 4), and R is a reference element for normalization (Mg in this case, hence the log EF$_{Mg}$ = 0). The elements are listed in order of decreasing concentrations in the reference 870°C sample.

Table 5. Calculated correspondence temperatures (°C)

#	Sample	T°C (meas)	H2O	H2	CO2	CO	SO2	H2S
1.	K1290	770	862	861	739	617	871	834
6.	TK1391	910	916	906	920	915	915	901
7.	TK291	585	722	720	773	761	720	684
21.	TK791	870	977	958	877	855	964	923
22.	F1292	940	1008	998	810	780	995	996
23.	F292	825	893	875	830	740	882	870
24.	F1592	705	712	696	669	665	718	704
25.	F1392	605	801	814	>1200	>1200	870	835

meas = measured temperature

tested by calculating the "correspondence temperatures" (CT values), i.e., temperatures at which the analytical concentration of major species (H_2, H_2O, CO, CO_2, H_2S, and SO_2) are equal to their calculated equilibrium concentrations. If the CT values for all species agree by ±10°C (the typical uncertainty in volcanic gas analyses; Gerlach, 1993a), then the gas composition was probably an equilibrium mixture. When the CT values disagree, the causes for the disequilibrium may be discerned, assuming that equilibrium prevailed among the fumarole gases. This assessment serves as a basis for the restoration of disequilibrium mixtures by removing disequilibrium effects caused by mixing with another fluid, oxidation, correction for water loss or gain during sampling, and other collection or analytical artifacts (Gerlach, 1980a,b, 1993b; Gerlach and Casadevall, 1986).

In order to examine our analytical results (Table 2) and the subsequent conclusions regarding buffer mechanisms (Fig. 5), we used the computer program SOLVGAS with thermodynamic database GASTHERM (Symonds and Reed, 1993) to determine the chemical equilibria among the major gas species. We computed CT values for Kudryavy gas analyses (Table 5), using the H_2, H_2O, CO, CO_2, H_2S, and SO_2 analytical data. All samples represent nonequilibrium compositions except for TK1391 (measured temperature 910°C), which has an average calculated equilibrium temperature of 912°C, within the ±10°C limit used to define equilibrium conditions.

The criteria for selecting the appropriate calculation procedure are discussed by Symonds et al. (1994), though this is based to a degree on experience. Most gas samples were calculated to an equilibrium state by incrementally extracting from the CO–CO_2 system the amount of O_2 corresponding to the air contamination (determined from the measured N_2/O_2 ratios). The success with this approach suggests that the lower CO and CO_2 CT values (Table 5) are due principally to the oxidation of CO during or after collection. The nearly constant H_2O content (Table 2) and C/S ratio (Fig. 4a) of these samples also support this suggestion. The calculated CT values for TK291 (585°C) suggest oxidation of H_2 occurred due

to contamination by air or water (Gerlach and Casadevall, 1986); since the water content of TK291 is similar to other high-temperature samples, oxidation by air is the most likely explanation. The CT equilibrium value for this sample, 710°C, was obtained by incrementally removing 0.43 mmole O_2 from the sample, and converting H_2O to H_2. Sample F1392 (605°C) will not approach equilibrium because of the large excess of C species, likely due to contamination by the rubber tubing used for sampling.

After these calculations, the CT values converge to the equilibrium temperatures reported in Table 6, within ±5°C, except for sample TK791 (870°C), which may have lost some water by condensation (Fig. 4b; #21). For this gas sample, which has a measured CO/CO_2 ratio close to equilibrium at the measured temperature (Table 5), we incrementally added H_2O to the analysed composition until the measured redox state (Rosen et al., 1993) at 870°C was obtained (equivalent to log f_{O_2} = −12.73 ± 0.12). All the CT values of this sample converged to a final equilibrium temperature of 880°C, after the incremental addition of up to 270 mmole H_2O to the analytical amount. The calculated equilibrium compositions are also given in Table 6.

The equilibrium temperatures and redox values for the seven samples that have CT values which converge (Table 6) are plotted as log H_2/H_2O vs. $1/T$ (Fig. 5). These values have an average SO_2/H_2S ratio of ≈3, and show less scatter than analytical data.

Of fundamental interest are the mechanisms for controlling redox reactions in high-temperature volcanic gases. Is the process related to heterogeneous reactions between gas species and melt, or to homogeneous reactions in the vapor phase? One possible mechanism, based on study of high-temperature gases from Kilaeua volcano (Gerlach, 1993a), could be the exchange of oxygen between gas and the rock. In other words, the gas phase is open with respect to a rock matrix in the sense of redox processes; this heterogeneous process is likely to be faster than any homogeneous gas-gas reaction (Gerlach, 1993a). On the other hand, Giggenbach (1987) suggested that during cooling in a volcanic system the vapor phase may be considered as a closed system, where the redox capacity is being consumed at the expense of "internal" reserves, namely, due to reactions among S species (hence the term gas buffer). Giggenbach (1987) and Taran et al. (1992) have shown this latter effect occurs in moderate temperature (350–700°C) fumarolic gases.

In the melt-buffering case, the redox values for calculated equilibrium compositions should have a temperature dependence close to the buffer curve for a natural mineral assemblage. The curves of the NNO and FMQ mineral buffers, as

Table 6. Calculated equilibrium temperatures, redox values and gas compositions (mole %)

#	Sample	T°C (meas)	T°C (equil)	log fO2 (equil)	H2O	H2	CO2	CO	SO2	H2S	COS	S2	HCl
1.	K1290	770	855	-13.07	94.91	0.84	2.22	0.021	1.06	0.51	0.0006	0.021	0.42
6.	TK1391	910	912	-12.17	93.82	1.05	2.37	0.034	1.50	0.46	0.0006	0.027	0.74
7.	TK291	585	710	-15.31	95.22	0.25	2.49	0.003	1.17	0.37	0.0003	0.009	0.50
21.	TK791	870	888	-12.46	94.81	0.88	1.85	0.021	1.53	0.43	0.0004	0.023	0.46
22.	F1292	940	987	-10.93	94.61	1.15	1.78	0.034	1.79	0.18	0.0002	0.010	0.46
23.	F292	825	869	-12.66	94.87	0.72	1.80	0.015	1.65	0.38	0.0003	0.020	0.55
24.	F1592	705	705	-15.58	95.67	0.26	2.11	0.004	1.18	0.68	0.0004	0.019	0.094

meas = measured temperature; equil = calculated temperature at equilibrium composition

well as the FeO-$FeO_{1.5}$ buffer for altered (oxidized) rocks (Giggenbach, 1987), differ mainly in absolute magnitude, but have nearly the same slope in terms of redox state versus $1/T$ coordinates. However, the slopes of the gas buffers, particularly the SO_2-H_2S curve, differ markedly from the mineral and rock buffer curves.

Based on our observations at Kudryavy, above 900°C (near the solidus temperature), a heterogeneous set of reactions between gas and rock (melt) likely control the redox state (Gerlach, 1993a). However, it is impossible to distinguish at high temperatures, on the basis of our data, the actual mineral and gas buffer reactions, due to the overlap of buffer curves and our data (both the analytical data and the equilibrium calculations, plus the redox state measurements). Below $\approx 800°C$, the sample points have a trend similar to that of the SO_2-H_2S gas buffer, with SO_2/H_2S ratios near 3 for the calculated equilibrium compositions. Thus, it appears that homogeneous reactions of species in a closed gas system dominate during cooling from ≈ 800 to 600°C. As temperatures decrease further (to <500°C), the oxidized rock buffer may begin to affect the gas composition (Giggenbach, 1987), though our lowest temperature samples (Fig. 5, inset) are even more oxidized than that expected for equilibrium with the FeO-$FeO_{1.5}$ in the rock (possibly an artifact of sampling).

DISCUSSION

The Isotopic Composition of "Andesitic Waters"

Significant hydrogen isotopic shifts from local meteoric water values are common in magmatic waters discharging from island arc volcanoes along plate margins. The value of this shift does not depend on the magma composition (Sakai and Matsubaya, 1977; Allard, 1983; Kusakabe and Matsubaya, 1986; Menyailov et al., 1986; Taylor, 1986; Taran et al., 1989). Most data were obtained for volcanic gases of andesitic and more acid volcanoes; hence, the term "andesitic water" was introduced (Taran et al., 1989; Giggenbach, 1992a); a more appropriate term may be subduction-zone magmatic water. Giggenbach (1992a) argued that the majority of magmatic water discharged from convergent-margin volcanoes is recycled seawater from subducted oceanic sediments, though with some modification due to mineral-water fractionation processes.

Our results for Kudryavy clearly indicate that the low-temperature fumarolic discharges are a mixture of high-temperature magmatic vapor and meteoric water. However, the high-temperature end of this mixing trend suggests that O-shifted seawater in some form may constitute a large component of the parent vapor. This "seawater" could be connate water in subducting sediments that is heated to high temperature by associated magma.

Other island volcanoes beside Kudryavy have isotopic and chemical trends that suggest shallow seawater may mix with high-temperature magmatic discharges; examples include White Island (Stewart and Hulston, 1975; Giggenbach and Matsuo, 1991), Augustine (Kodosky et al., 1991), and Vulcano (Giggenbach and Matsuo, 1991; Bolognesi and D'Amore, 1993). I. Menyailov (unpubl. data) also argued that the high temperature (580°C) waters with high δD values

from the coastal cinder cone and lava flow of Alaid volcano are of marine origin.

These observations raise some doubts that the D enrichment of magmatic water discharged from andesitic volcanoes has a source solely in the zone of slab dehydration and magma generation in the mantle wedge. If this were indeed the case, the water most enriched in D should come from basaltic island arc magmas formed in the upper mantle as a result of partial melting initiated by composite mid-ocean ridge basalts (MORB) + "slab" fluid (Tatsumi, 1989; Stolper and Newman, 1994). The few isotopic data available for basaltic island arc and plate margin volcanoes show a wide spread of δD composition, ranging from $-80\%o$ for Tolbachik gases (Menyailov et al., 1984) to $-44\%o$ for Klyuchevskoy volcano (Taran et al., 1991) to $-7\%o$ for Alaid discharges (I. Menyailov, unpubl. data), all Kamchatka-Kuril volcanoes. Momotombo, Nicaragua, waters are -7 and $-11\%o$ (Allard, 1983; Menyailov et al., 1986). These data are all restricted to samples with $\delta^{18}O$ values with a "rock signature" of $>6\%o$.

To resolve this conundrum, it is necessary to identify both the general mechanisms to allow for the incorporation of connate seawater during magma ascent and ponding, particularly for acid magmas formed in shallow crustal chambers, as well as specific mechanisms that can account for the apparent direct involvement of seawater (e.g., based on apparent mixing trends towards local seawater at Vulcano; Bolognesi and D'Amore, 1993). The problem is hydrological in nature, and may be solved by an integrated set of stable and radiogenic isotope constraints (δD, ^3H, ^{36}Cl, ^{11}B, ^{10}Be, etc.). For andesitic and more acid volcanoes, it is necessary to take into consideration the potential variation in sources of water (Taran, 1992), including a large portion derived from crustal material.

The second side of this problem, though we do not address it with the Kudryavy data, is application of isotopic trends of magma degassing (Taylor, 1986; Matsuhisa, 1992) to determine the endmembers of island arc magmatic waters. For example, there are no observations of degassing trends in δD values of high-temperature vapors of andesitic volcanoes, despite these trends being commonly noted in the presumably corresponding magmas, now crystallized and eroded (Taylor, 1986).

Cause of Long-Term Fumarolic Activity at Kudryavy

An outstanding question arising from this study concerns the reason for the long-term and apparently stable existence of very high temperature fumaroles at Kudryavy volcano. The presence of high-temperature fumaroles at Merapi, Mt. St. Helens, and Augustine volcanoes are coupled with the growth of extrusive domes, and appear to reflect a process of volcano eruption—the extrusion of viscous lava. However, the quiescent, high-temperature (>900°C) fumaroles at Kudryavy, as well as at the basaltic volcano of Momotombo and the rhyolite dome at Satsuma Iwojima, appear to be the consequence of a shallow magmatic process that is not accompanied by lava eruption. Near-solidus fumarole temperatures suggest the presence of near-surface magma.

The regular distribution of the fumarolic temperatures in the Kudryavy crater (Fig. 2, inset) suggests a stable plumbing system in the volcanic edifice. The simplest model is a con-

vecting and degassing magma chamber with a conduit filled by magma in which the gases exsolve, the bubbles coalesce, and upon separating from the magma, the gases ascend to the surface.

The chemical (CO_2/H_2O ratio) and isotopic (δD and $\delta^{13}C$) signatures of the fumarolic vapors indicate that the Kudryavy magma is only slightly degassed. Otherwise, the CO_2/H_2O ratios and the δD and $\delta^{13}C$ values should all be lower, considering the distribution coefficients and isotopic fractionation factors for H_2O and CO_2 between melt and an aqueous fluid (about 20‰ and 4‰ for H and C isotopes, respectively; Taylor, 1986; Gerlach and Taylor, 1990). This indicates the continuous replenishment of the outgassing magma by new batches of fresh, volatile-rich magma (as suggested by Le Cloarec et al., 1992, for White Island), or alternatively, that there is some mechanism by which gas streams from deeper magma to reach the near-surface conduit at a temperature above the magma solidus. Such magma replenishment or gas streaming is required, considering that the last eruption occurred >100 yr ago, and that there is still a large output of volatiles (at least 10^6 t/y of water, based on a heat flow estimate of 150–200 MW, as determined from pitot tube measurements). An even more extreme case is at Satsuma Iwojima, where high-temperature outgassing ($\leq 880°C$) has been occurring for as much as 1000 yrs without eruption, with an annual water flux of $\approx 8 \times 10^6$ t (Hedenquist et al., 1994). Despite the large size of these fluxes, and their requirement for significant volumes of convecting magma, both Kudryavy and Satsuma Iwojima are relatively small edifices, 600–800 m high. These observations for Kudryavy suggest that the magma rose close to the surface ≈ 100 yrs ago, only to remain in a shallow reservoir, convecting from a larger magma chamber at depth. The top of this convection cell could be located directly under the northeast, hottest part of the crater.

CONCLUSIONS

The fumarolic activity of Kudryavy volcano is characterized by quiescent, steady-state outgassing, with very high temperatures (up to 940°C). The chemical composition of the water-rich volcanic gases, which have a high δD value, indicate simple mixing between a magmatic vapor and O-shifted meteoric water; the former appears to be comprised of a large component of altered seawater.

The spectrum of components in high-temperature condensates shows that rock-forming major elements are largely derived from rock particles eroded from the wallrock. In contrast, the enrichments of many trace elements in these condensates indicate that they come from magmatic fluid. The highly volatile trace elements (Cl, S, I, F, Bi, Cd, B, Br) are uniformly enriched for various vents. Exceptions include species such as Re, Mo, W, Cu, and Co, with EF values highly dependent on vent temperature; some of these elements, such as Re and Mo, form sulfide sublimates at the surface as the gases cool. Unusually high I concentrations in the vapors may be due to magma-marine sediment interaction.

Thermochemical evaluation of the gas samples suggests that they were most frequently modified by disequilibrium oxidation of CO to CO_2 and H_2 to H_2O, and by water loss during sampling in some cases. The calculated equilibrium compositions from >700°C vents have equilibrium temperature up to 987°C and contain about 94 mol% water, about 2 mol% each C and S species (with SO_2/H_2S ratios of about 3:1), and 0.5 mol% Cl. In general the redox states of the Kudryavy gases vary in a manner similar to the SO_2-H_2S gas buffer, although at high temperatures (>900°C) the redox state can also be explained by rock (melt) buffering near the FMQ buffer.

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