Geochemical Study of Fumarolic Condensates from Kilauea Volcano, Hawaii[1]

WALTHER M. BARNARD,[2] JOSEPH B. HALBIG,[3] AND JOHN C. FOUNTAIN[4]

ABSTRACT: Results of a geochemical study based on 20 samples of condensates obtained between late December 1987 and early January 1989 at five fumarole sites on or near the summit of Kilauea Volcano, island of Hawaii, are presented. Fumarole chemistry may be explicable in terms of the currently accepted model of Kilauea and its mechanisms of magma replenishment and storage, degassing, and eruptive activity; it may have potential for forecasting eruptions. Fumaroles emit magmatic and recycled gases and aerosols that enter into Earth's exchangeable reservoirs and which have a potentially harmful impact on health and the environment through release of toxic materials and creation of precipitation and vog of acidic character. Condensates from fumaroles were analyzed by neutron activation/gamma-ray spectroscopy. Concentrations of 28 elements are tabulated and statistically analyzed. Seven elements (As, Ba, K, Sc, Se, U, and W) were in concentrations less than their detection limits; 10 elements (Br, Cr, Cu, Eu, Fe, Hf, Mg, Sb, Sr, and Ti) were below their detection limits in 75% or more of the samples; and 11 elements (Al, Ca, Cl, Co, I, La, Mn, Na, S, V, and Zn) exhibited significant variation. Individual fumaroles with distinctive ratios of elements and a high degree of correlation between element pairs are identified.

ALTHOUGH KILAUEA IS one of the most active volcanoes in the world and is probably the most thoroughly studied (the U.S. Geological Survey's Hawaiian Volcano Observatory is located on Kilauea's caldera rim), the chemistry of its fumaroles has never been extensively characterized. Our present knowledge of many aspects of this chemistry (e.g., the variability, controls, and potential applications) is scant, especially with respect to minor and trace elements.

Many fundamental questions remain to be answered regarding the chemistry of volcanic emissions. What elements are emitted and in what abundance? Can a comparison of the amounts and ratios of various constituents differentiate between fumaroles in which the gases and aerosols are, at least in part, of magmatic origin and those in which the exhalations are predominantly of meteoric origin? Can data analysis quantify the relative contributions from magmatic and recycled sources? Do absolute and relative concentrations of components change and possibly presage the onset of eruptions? Do they give any indication of the mechanisms of volcanic degassing and eruption or time of magma storage before eruption? Are changes synchronous at all or most associated vents? Do variations in metal concentrations correlate with those of the halogens, suggesting transport as metal halides? How does Kilauea's fumarole chemistry compare to that of other basaltic volcanoes or other types of volcanoes? What is the fumarolic contribution of metals and semimetals, many of which are toxic, to the atmosphere? What impact do these gases have on air quality, on soils, and on vegetation? What is the estimated con-

[2] Department of Geosciences, State University of New York College at Fredonia, Fredonia, New York 14063.
[3] Department of Geology, University of Hawaii at Hilo, Hilo, Hawaii 96720-4091.
[4] Department of Geological Sciences, State University of New York at Buffalo, Buffalo, New York 14226.

tribution of this source of chemical components to geochemical cycles of elements? To what extent do observations and conclusions reached for Kilauea have general validity, especially for volcanoes of the "hot spot" variety?

Fumaroles consist of magmatic gas mixed with ground water or air or both: during the ascent of magma through the feeding channels of a volcano, small quantities of gas escape (when the quantity of exsolved gas and its own pressure are high enough) and reach the surface, more or less mixed with underground water or air or both enroute, through overlying rock fissures. Logically, the temperature, output (volume and mass), and chemical composition of these gaseous mixtures should evolve as the magma body gets nearer to the surface and as, accordingly, the thickness of the cold, air- or water-saturated "roof" through which the hot magmatic gases have to travel diminishes. Insofar as these modifications can be evaluated or interpreted, particularly through examination of elemental ratios, the results of fumarole monitoring may have potential for revealing mechanisms of magma evolution and for eruption forecasting (Tazieff, 1983a,b).

Ratios of concentrations of constitutents in the condensates may be characteristic and explicable in terms of the currently accepted model of Kilauea and its mechanisms of magma replenishment and storage, degassing, and eruptive activity (Heliker et al. 1986, Tilling et al. 1987). Greenland (1987) summarized the present understanding of how variations in the major Hawaiian eruptive gases, CO_2 and SO_2, relate to the current models of intrusion, storage, and degassing at Kilauea. Analogously, it is possible that condensate samples collected during either repose periods or eruptive periods at the summit and along its rifts contain a record of these conditions. It is not unreasonable to expect that ratios of volatile constituents (other than C/S) will also vary, being controlled, at least in part, by the relative fractionation between a magma and an escaping CO_2-rich fluid.

Three examples of the potential use of chemical composition of gases as precursors to volcanic eruption are cited here. At Ki-

lauea, Naughton et al. (1975) found that the Cl/F ratio in fume showed an abnormal increase in samples taken at Halemaumau 1 month before the fissure eruption on the floor of the caldera in August 1971. Thomas and Naughton (1978, 1979) showed that, during periods of magma release from Kilauea's summit reservoir, the ratio of helium to carbon dioxide in the fumarole gases decreased substantially from that observed during periods of quiescence. At Mt. Asama, Japan, Noguchi and Kamiya (1963) found increases in fluorine, chlorine, and sulphur preceding an eruption.

Study of the constituents of Kilauean fumaroles is important because (in addition to contributions of recycled ground water of meteoric origin) the fumaroles emit gases and aerosols that are believed to be magmatic and entering, for the first time, into the exchangeable reservoirs (atmosphere, oceans, upper layer of marine sediments, and inorganic and biological materials of the Earth's land areas), where the material may be transferred from one region to another relatively rapidly. Additionally, among the gases and aerosols emitted, many potentially pose a health risk through inhalation or absorption, or by the concentration of toxic chemicals in the food chain of animals and man. Many individual constituents have harmful effects on vegetation (Faivre-Pierret and Le Guern, 1983).

The fumaroles and other sources of volcanic gases at Kilauea emit large concentrations of sulphur-containing species (Casadevall et al. 1987), which result in acid rain (Harding and Miller 1982). Locally, the acid precipitation is suspected to have contributed to the creation of the Kau Desert to the leeward of Kilauea caldera and is thought to have promoted the release of lead in roof-catchment water systems, which are the principal sources of drinking water in many areas on the island of Hawaii. Especially during times of volcanic eruptions, downwind areas on the island are often impacted by "vog," hazy fumes of volcanic origin that affect respiration and reduce visibility.

Since 1920, when samples of volcanic gases were collected from the circulating lava lake in Halemaumau, the principal summit crater,

by T. A. Jaggar, E. S. Shepherd, E. T. Allen, and A. L. Day, scores of papers and abstracts relating to the chemistry of Kilauean gases (especially the major species), particulates, aerosols, fumes, sublimates, incrustations, and soil gases—too numerous to be reviewed here—have been published.

To begin to provide a basis for answers to those questions set forth at the beginning of this introduction and to further our insight on the concentrations of a variety of metals, semimetals, halogens, and other constituents in Kilauean fumaroles, we collected 20 samples of fumarolic condensates between late December 1987 and early January 1989 at five sites on Kilauea's summit and along its upper east rift zone. Concentrations of 28 chemical elements in these samples were quantified by neutron activation analysis and statistically analyzed. The data, however, are far from sufficient to permit answers to many of the foregoing questions, which would require extensive research over a prolonged period.

MATERIALS AND METHODS

Sampling Sites

Figure 1 shows mapped locations of thermal areas at and near the summit of Kilauea Volcano. Five sites, shown as nos. 1, 3, 4, 7, and 20, were selected for sampling of fumarolic condensates, based on ease of accessibility, diversity of age, and a history of gas sampling and analysis by others. Site 3 was selected principally to serve as a control for determining abundances and ratios of constituents in a fumarole that is generally considered to derive its water solely from meteoric origin that has infiltrated the ground.

Site 1 is just south of Halemaumau pit crater, the principal summit crater. The area is characterized by steam vents and cracks, hot air, sulfur gas, and active deposition of sulfur sublimates. Numerous eruptions have occurred in Halemaumau and on the adjacent caldera floor in the present century. Temperature of the sampling vents is usually near 91.7°C.

Site 3 (Steaming Flats/Bluff), on the north rim of Kilauea caldera, contains more than 80 steam vents over an area 1.5 × 0.5 km and is characterized by steam cracks, steaming ground, and vigorous fuming, including gases other than H_2O. It is controlled by caldera faults of pre-1790 age. The temperature of the exhalations is near 91°C.

Site 4 (Sulfur Bank) is controlled by a caldera rim fault and is of prehistoric (pre-1778) age. Thermal activity is characterized by steam cracks, sulfur gas, and active sulfur sublimates. Condensate samples were taken from a well from which gases issue at about 95°C.

Site 7 (1971 fissure) is an eruptive fissure that developed in mid-August 1971 and is characterized by steam vents, hot gas, sulfur gas, and active deposition of sulfur and other sublimates. Its temperature in late December 1987 was 91.5°C (down from the 128° cited by Casadevall and Hazlett 1983).

Site 20 (Puhimau thermal area), on the upper east rift, is controlled thermally by a 1938 intrusive event. This area is characterized by steam cracks, steaming ground, hot air, and vigorous fuming. Temperature of the sampling vent in late December 1987 was 91.7°C (compared to 95° reported by Casadevall and Hazlett 1983).

Sampling Of Condensates

Fumarolic condensates were sampled by drawing the gases into a train of filter flasks (with partial vacuum created by a hand pump) through a Teflon tube that was placed into a fumarole vent. The filter flask assembly consisted of four flasks of 1-liter capacity joined in series with Teflon tubing. (The first set of samples, excluding the first sample at Steaming Bluff, was collected in a train of flasks of 125-, 250-, 500-, and 1000-ml capacity.) This provided for efficient condensation in a flow-through system at ambient temperature. Combining the contents of each flask into a composite sample reduced effects of fractionation of elements caused by differential condensation. The condensates were not artificially acidified (they are naturally acidified with sulfuric acid) or filtered (which would have fractionated the condensates by removing
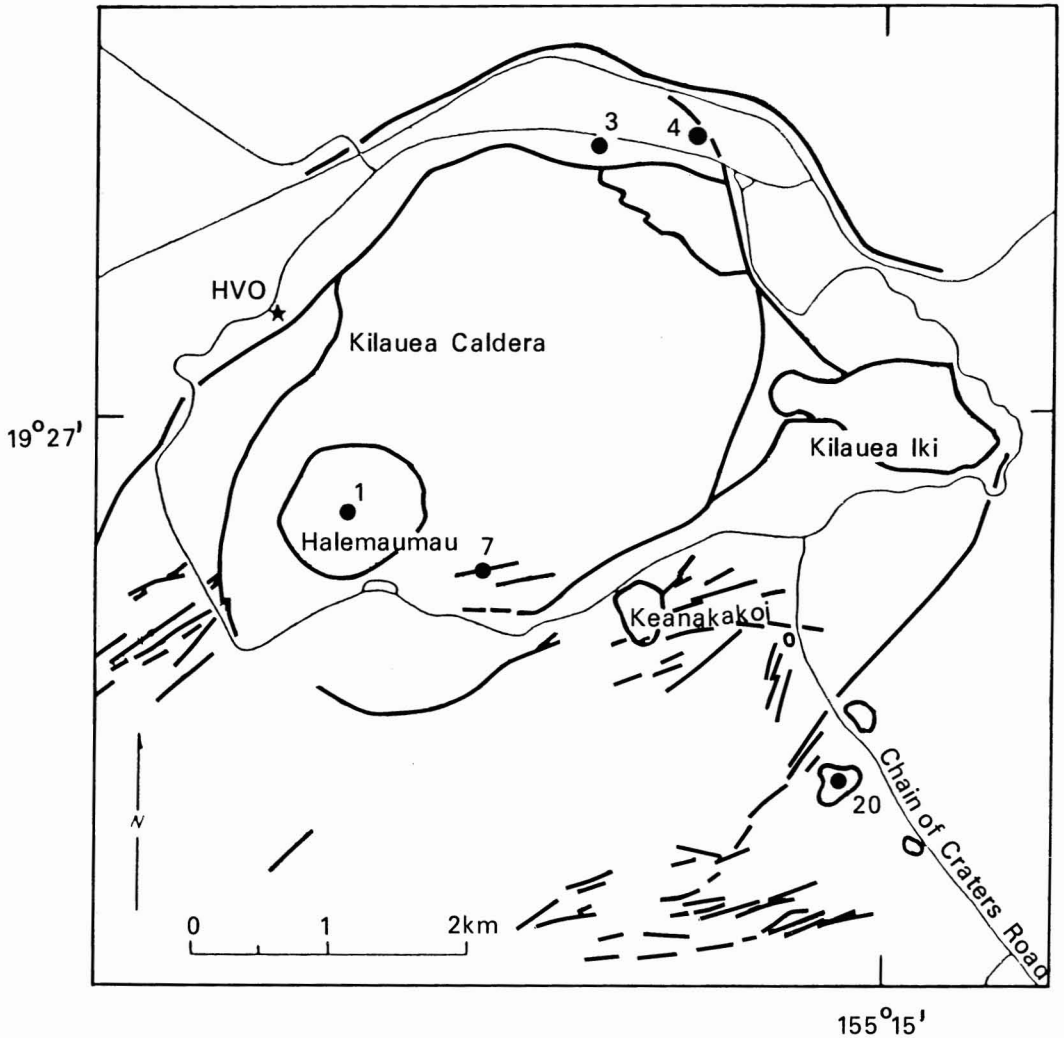
FIGURE 1. Location map of five fumaroles at and near the summit of Kilauea Volcano from which condensate samples were obtained. Heavy lines indicate the principal topographic and structural features of the Kilauea summit area. (Adapted from Casadevall and Hazlett 1983). See text for identification of sites.

the aerosols). The condensates were stored in FEP Teflon bottles until they were analyzed.

Before use, all tubing, flasks, and containers employed in sampling and storing the condensates were soaked in a HNO_3 acid bath and thoroughly rinsed with deionized water.

The number of samples taken from each site was as follows: Halemaumau, seven (one was fractionated); Steaming Bluff, three (two were combined for analysis); Sulfur Bank, four;

1971 fissure, three; and Puhimau thermal area, three.

On-site Measurement of Unstable Parameters

The only on-site measurement was for temperature, using a Yellow Springs Instrument (YSI) Model 33 salinity-conductivity-temperature (SCT) meter. The temperature probe

was inserted about 0.6 m into the fumarolic vent, where temperature gradient is minimal.

Measurements of specific electrical conductance and pH in the field are not practical because of the rapidly changing temperature and other conditions of the samples during collection.

Analysis Of Samples

Samples were instrumentally analyzed for 28 elements using the technique of neutron activation/gamma-ray spectroscopy under contract to McMaster University's Centre for Neutron Activation Analysis.

The University's 5-megawatt reactor, capable of producing a neutron flux of 5×10^{13} neutrons cm^{-2} sec^{-1}, was operated at 2 megawatts, and samples were irradiated in positions with a flux of 5×10^{12} cm^{-2} sec^{-1}.

All samples were irradiated and analyzed using three schemes. For determination of elements with short-lived radioisotopes, which include Al, Ca, Cl, Cu, I, Mg, Mn, Na, Ti, V, As, Ba, Br, Co, K, and Sr (the first 10 have only short-lived isotopes), 6 to 7 ml of the samples were decanted into polyethylene vials (previously washed in dilute HNO_3 and rinsed with a small amount of sample) and individually irradiated for 300 sec. (The neutron flux is constant and monitored every 4 hr to verify stability.) Once retrieved from the "rabbit" transport system, samples were transferred to nonirradiated precleaned and preweighed polyethylene vials for gamma-ray spectral analysis. These vials were weighed after counting to determine the actual sample weights, which were used in subsequent computations.

Samples were counted on an APTEC 19.8% efficient hyperpure germanium (Ge) detector coupled to a CANBERRA Series 90 4096-channel pulse height analyzer.

The irradiated samples were counted for 600 sec after a delay of 100 to 150 sec, which includes the time necessary to transfer a sample to a nonirradiated poly vial.

For determination of elements with longer-lived radioisotopes, 15 to 25 ml of the samples were weighed, freeze-dried in polyethylene bags, and irradiated for 6 hr in the core of the reactor. Before spectral analysis, the irradiated poly bags were put into nonirradiated poly vials.

These samples were counted on an ORTEC 12% efficient hyperpure Ge detector possessing a resolution of 1.75 KeV at the 1332 KeV ^{60}Co peak; the detector was coupled to the same multichannel pulse height analyzer used for the short-lived isotopes.

The irradiated samples were counted twice: first, for 3000 sec after a delay of 4 days for quantification of Nd, Sm, Eu, Lu, Yb, Th, Hf, As, Sb, W, Br, Sc, Fe, Co, Na, K, and La, and second, for 4000 sec after a delay of 14 days for quantification of Ce, Lu, Se, Th, Cr, Sb, Cs, Fe, Zn, Co, and U.

Empty polyethylene bags were also irradiated and their trace element contents determined for blank correction.

Se (which has a 17-sec half-life isotope) was also determined using a "fast rabbit" (short transfer) system, in which the sample was irradiated for 5 sec and counted for 30 sec after a 4-sec delay. The analytical system included an APTEC high purity Ge detector and CANBERRA Series 85 4096-channel pulse height analyzer.

Standards included National Bureau of Standards No. 1643b (Water), No. 1632b (Bituminous Coal), No. 1633a (Coal Fly Ash), the International Atomic Energy Agency's No. SL-1 (lake sediment), and in-house standards.

Concentrations of each selected element in the samples were determined by comparison of activity per unit weight with the standards, using corrections for Compton scattering and decay.

Statistical analysis of data was performed on line with the Burroughs 7900 mainframe computer at State University of New York College at Fredonia, using the statistical package Minitab, a computing system of Minitab, Inc., State College, Pennsylvania.

RESULTS AND DISCUSSION

The analytical data for 28 elements in 19 samples (including two that were combined 1:1, thus giving 18 analyzed samples) are given in Table 1. A single abnormally high

TABLE 1

CONCENTRATIONS* OF ELEMENTS IN KILAUEAN FUMAROLES

	HALEMAUMAU						STEAMING BLUFF		SULFUR BANK				1971 FISSURE			PUHIMAU THERMAL AREA		
NAA no.	5	9	14	20	13	23	17	24	7	21	12	22	6	18	15	8	11	26
Date†	871229	880111	880409	880430	880719	890104	880430 and 880731 combined 1:1	890104	871231	880430	880712	890104	871230	880409	880727	871231	880727	890104
ELEMENT																		
Al	150	35	55	55	55	36	55	130	50	20	35	30	45	40	65	270	360	210
As	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
Ba	<30	<30	<30	<30	<30	<30	<30	<30	<30	<30	<30	<30	<30	<30	<30	<30	<30	<30
Br	3	<3	<3	<3	<3	<3	<3	<3	5	<3	<3	<3	<3	<3	3	<3	<3	<3
Ca	1250	450	880	2000	1010	<100	320	140	500	840	1590	<100	1150	690	1470	350	2630	380
Cl	400	720	240	240	150	130	140	90	380	450	170	270	490	2500	—	310	180	140
Co	2.2	0.7	4.3	1.2	0.7	<0.7	1.8	<0.7	1.1	1.2	1.4	<0.7	0.9	<0.7	1.2	<0.7	1.4	<0.7
Cr	<10	16	<10	<10	<10	15	<10	<10	<10	<10	<10	<10	<10	14	<10	<10	<10	<10
Cu	<15	20	<15	<15	<15	<15	<15	20	40	<15	<15	15	<15	<15	<15	<15	<15	<15
Eu	0.1	<0.1	0.1	<0.1	0.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.1	<0.1	0.1	<0.1	<0.1	<0.1
Fe	100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	150	<100	<100
Hf	<3	<3	<3	<3	<3	3	<3	<3	<3	<3	<3	<3	<3	<3	<3	<3	<3	<3
I	12	8	19	15	13	5	12	<3	14	35	30	8	8	<3	<3	10	17	12
K	<1000	<1000	<1000	<1000	<1000	<1000	<1000	<1000	<1000	<1000	<1000	<1000	<1000	<1000	<1000	<1000	<1000	<1000
La	1	3	1	2	2	<1	<1	<1	<1	1	<1	<1	4	1	2	<1	<1	<1
Mg	<250	<250	<250	<250	<250	<250	<250	<250	<250	<250	<250	300	<250	<250	300	270	1000	<250
Mn	2	<1	3	2.5	1.5	<1	1.5	1	1	2.5	1.5	<1	1.5	<1	3	4.5	18	3
Na	740	930	880	1050	300	550	1000	460	320	1440	780	600	880	760	920	550	1060	540
S (ppm)	170	290	80	50	40	70	<10	<10	30	10	<10	<10	1670	180	100	<10	10	<10
Sb	<20	<20	<10	<10	<10	<7	<10	<7	<20	<10	<10	8	<20	<10	<10	<20	<10	<7
Sc	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Se	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Sr	<30	<30	<30	30	<30	<30	<30	<30	<30	<30	<30	<30	<30	<30	<30	<30	<30	<30
Ti	<30	<30	<30	<30	<30	<30	<30	<30	<30	<30	<30	<30	<30	<30	50	<30	<30	<30
U	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
V	0.5	<0.2	<0.2	0.4	<0.2	<0.2	<0.2	0.2	<0.2	0.6	0.2	<0.2	<0.2	<0.2	<0.2	0.5	<0.2	0.6
W	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
Zn	520	1300	440	560	310	290	250	<100	580	1730	570	330	220	160	120	170	530	260

* All concentrations, except for S, are in ppb.
† Interpret first two digits as year, second two as month, last two as day (e.g., 871229 is 29 December 1987).

TABLE 2

FRACTIONATION OF ELEMENTS IN SAMPLING

NAA NO. ELEMENT	1 125 ml	2 250 ml	3 500 ml	4 1000 ml
Al	80	100	25	35
As	<10	<10	<10	<10
Ba	<30	<30	<30	<30
Br	11	4	2	4
Ca	2800	800	250	450
Cl	720	850	200	630
Co	1.7	1.2	1.5	2.9
Cr	<10	<10	<10	<10
Cu	<15	<15	<15	<15
Eu	<0.1	<0.1	<0.1	0.2
Fe	<100	<100	<100	<100
Hf	<3	3	<3	<3
I	17	30	30	5
K	<1000	<1000	<1000	<1000
La	3	2	<1	1
Mg	<250	<250	<250	<250
Mn	3	5.5	1.5	1.5
Na	340	920	1100	1740
S (ppm)	250	190	260	220
Sb	<20	<20	<20	<20
Sc	<5	<5	<5	<5
Se	<5	<5	<5	<5
Sr	<30	<30	<30	<30
Ti	<30	<30	<30	<30
U	<2	<2	<2	<2
V	<0.2	0.3	<0.2	0.4
W	<10	<10	<10	<10
Zn	1000	670	430	150

NOTE: All concentrations, except for S, are in ppb. Samples no. 1–4 (Halemaumau, 29 December 1987) were collected in a train of filter flasks as follows: 1, 125-ml flask, first in train, 21 ml collected; 2, 250-ml flask, second in train, 23.5 ml collected; 3, 500-ml flask, third in train, 30 ml collected; 4, 1000-ml flask, fourth in train, 35.5 ml collected.

determination of chloride in the sample collected on 27 July 1988 at the 1971 fissure apparently was invalid (there was no correspondingly high cationic component) and was deleted.

The results of the 20th sample, in which the individual flask contents were preserved and analyzed separately to assess element fractionation by differential condensation, are given in Table 2. The data affirm the desirability of changing to four 1-liter sampling flasks, which effected more efficient condensation of the gases and aerosols, and the need to composite the contents of the individual flasks.

In all samples (including the fractionated portions), the following seven elements were present in concentrations below their detection limits (given in ppb): As (10), Ba (30), K (1000), Sc (5), Se (5), U (2), and W (10).

In addition, in 75% or more of the determinations (in both composited and fractionated samples), 10 elements were present in concentrations below their detection limits (all in ppb): Br (3), Cr (10), Cu (15), Eu (0.1), Fe (100), Hf (3), Mg (250), Sb (7 to 20), Sr (30), and Ti (30).

Of the 28 elements quantified, only the following 11 showed significant variation: Al, Ca, Cl, Co, I, La, Mn, Na, S, V, and Zn. Discussion of statistical analysis, ratios, and correlations will be limited to these 11 elements.

Statistical analysis of the concentrations of these 11 elements in the entire set of individual samples (in which the contents of the individual filter flasks used in collecting the sample were combined) is given in Table 3.

Because of the small number (two to six) of samples analyzed from each fumarole, statistical analysis of data for each fumarole is not particularly meaningful, except perhaps for Halemaumau (Table 4). However, to provide a summary of the range of element composition, Table 5 lists the extremes of the means and the corresponding fumarole source for 11 elements.

The foregoing data suggest the following tentative comparisons among individual fumaroles with respect to absolute concentrations of elements:

1. The condensates of Steaming Bluff (the "reference fumarole") contained the least mean Ca, Cl, La, Mn, S, and V (or shared this distinction with one or more other fumaroles) and had next to the least mean I and Zn.

2. Halemaumau's fumarole chemistry was not particularly distinctive.

3. The fumarolic condensates of Sulfur Bank had the highest mean I and Zn, but also showed the greatest variation in these elements; its sulfur content is much less than that of Halemaumau or the 1971 fissure, both of which, like Sulfur Bank, also deposit sulfur sublimates.

4. The 1971 fissure condensates were characterized by greatest mean concentrations of Cl, La, Na, and S, least mean concentrations

TABLE 3

STATISTICAL ANALYSIS OF 19 SAMPLES*

ELEMENT	MIN	Q1	MEDIAN	Q3	MAX	MEAN
Al	20	35.8	55	135	360	94.2
Ca	< 100	343	765	1305	2630	< 881
Cl	90	145	240	425	2500	411
Co	< 0.7	< 0.7	1	1.4	4.3	< 1.2
I	< 3	7.2	12	15.5	35	< 12.7
La	< 1	< 1	< 1	2	4	< 1.4
Mn	< 1	1	1.5	3	18	< 2.8
Na	300	548	770	948	1440	764
S (ppm)	< 10	< 10	35	118	1670	< 153
V	< 0.2	< 0.2	< 0.2	0.4	0.6	< 0.3
Zn	< 100	208	320	562	1730	< 469

NOTE: All concentrations, except for S, are in ppb. Min, minimum; Q1, first quartile (25%); Q3, third quartile (75%); Max, maximum.
* 17 individual and two composited (Steaming Bluff 880430 and 880731 were combined 1:1) samples.

TABLE 4

STATISTICAL ANALYSIS OF SIX HALEMAUMAU SAMPLES

ELEMENT	MIN	Q1	MEDIAN	Q3	MAX	MEAN
Al	35	35.8	55	78.8	150	64.3
Ca	< 100	363	945	1438	2000	< 948
Cl	130	145	240	480	720	313
Co	< 0.7	0.7	1	2.7	4.3	< 1.6
I	5	8	12.5	16	19	12.2
La	< 1	1	1.5	2.2	3	< 1.7
Mn	< 1	< 1	1.8	2.6	3	< 1.8
Na	300	488	810	960	1050	742
S (ppm)	40	48	75	200	290	117
V	< 0.2	< 0.2	< 0.2	0.4	0.5	< 0.3
Zn	290	305	480	745	1300	570

NOTE: All concentrations, except for S, are in pbb. Min, minimum; Q1, first quartile (25%); Q3, third quartile (75%); Max, maximum.

of Zn and I, and they were among the lowest in Co and V.

5. Puhimau had the greatest means for Al (which was strikingly distinctive), Ca, Mn, and V, while those for Co, La, Na, and S were (or were among) the lowest.

Element concentration ratios were calculated to assess their usefulness in comparing and distinguishing among fumaroles. Unfortunately, this was impeded by the fact that many concentration values were less than their detection limits, resulting in imprecise ratios. Many ratios exhibited a wide range of values, and overlapping of values among the fumaroles was frequent. Nonetheless, several regularities emerged:

1. For all samples from Steaming Bluff and Puhimau, Ca/Al was < 8, Cl/Al was < 3, and S/Al was < 0.2; the mean ratios were greater than these respective values for the other fumaroles, which also exhibited considerable ranges of values.

2. Puhimau condensates had the minimum Na/Al (all values < 3), Cl/Mn (all values < 69), and Na/Mn (all values ≤ 180); for all samples of other fumaroles, these ratios were greater than the respective values.

3. The 1971 fissure samples had the least Zn/S (≤ 1.2) and Zn/Cl (< 0.5); Zn/Cl for other samples typically ranged from 1 to 4.

4. Zn/Al was < 5 for all samples from Steaming Bluff, Puhimau, and the 1971 fissure, and ≥ 11 for Sulfur Bank; Halemaumau's values overlapped the intermediate range.

TABLE 5

EXTREMES OF MEANS AND FUMAROLE SOURCE

ELEMENT	MAXIMUM		MINIMUM	
Al	Puhimau	280	Sulfur Bank	34
Ca	Puhimau	1120	Steaming Bluff	230
Cl	1971 fissure	1495	Steaming Bluff	115
Co	Halemaumau	< 1.6	1971 fissure, Puhimau	0.9
I	Sulfur Bank	22	1971 fissure	< 5
La	1971 fissure	2	Steaming Bluff, Sulfur Bank, Puhimau	≤ 1
Mn	Puhimau	8.5	Steaming Bluff	1.2
Na	1971 fissure	853	Puhimau	717
S (ppm)	1971 fissure	650	Steaming Bluff, Puhimau	≤ 10
V	Puhimau	0.4	Steaming Bluff, 1971 fissure	≤ 0.2
Zn	Sulfur Bank	803	1971 fissure	167

NOTE: All concentrations, except for S, are in pbb.

5. Mean Na/Cl was least for the 1971 fissure (0.7) and greatest for Steaming Bluff (6.1); only Steaming Bluff and Puhimau had Na/Cl > 5 for individual samples.

6. Na/S was < 10 for the 1971 fissure and ≥ 46 for all samples from Steaming Bluff and Puhimau; values for Halemaumau ranged from 3.2 to 21.

7. All values of Na/Zn were ≥ 4 for Steaming Bluff and the 1971 fissure and ≤ 2 for Halemaumau and Sulfur Bank; Puhimau had intermediate values ranging from 2 to 3.2.

8. Ca/Zn was > 4 in all samples from the 1971 fissure and < 4 in all others, except for one Puhimau sample.

9. All Ca/Na values were < 4; no fumarole exhibited distinctive values.

Pearson product moment correlation coefficients were calculated to examine correlations between pairs of individual elements. Imprecise values (those listed as "$<$") were excluded.

In the set of 18 analyzed samples the only correlation coefficients that were $\pm > 0.7$ were La:S (0.785, 9 pairs), Al:Mn (0.777, 14 pairs), and La:V (-0.866, 3 pairs); the last is the least meaningful because of the small number of pairings. The low incidence of correlation between paired elements in the complete set of samples confirms the observation that specific element ratios vary for individual fumaroles.

(If a given element ratio had the same value for all samples, the coefficient would be 1.)

In an individual fumarole, a significant degree of correlation may be expected if the only source of variation is in water content: the absolute concentrations of elements change, but the ratios of elements remain constant.

For the six Halemaumau samples, correlation coefficients of $\pm > 0.7$ were exhibited for Cl:S (0.972, 6 pairs), Cl:Zn (0.961, 6 pairs), S:Zn (0.898, 6 pairs), Co:I (0.771, 5 pairs), La:Zn (0.743, 5 pairs), Co:La (-0.785, 5 pairs), I:La (-0.711, 5 pairs), Mn:I (0.876, 4 pairs), Mn:Na (0.824, 4 pairs), and Co:Mn (0.794, 4 pairs).

The other fumaroles had four or less samples, and with some imprecise determinations, the number of pairings is reduced to a level where correlation analysis becomes almost meaningless. However, for the record, the following lists correlation coefficients for element pairs where the coefficient was > 0.9 with three pairings:

Sulfur Bank—Al:Mn (-0.982), Ca:Co (1.0), Mn:Na (0.996), and Mn:Zn (0.942).

1971 fissure—Al:Ca (0.906), Ca:Na (0.984), La:S (0.929), and S:Zn (0.935).

Puhimau—Al:Ca (0.913), Al:Mn (0.950),

Al:Na (0.924), Ca:I (0.964), Ca:Mn (0.995), Ca:Na (1.0), Ca:Zn (0.973), I:Mn (0.932), I:Na (0.956), I:Zn (0.999), Mn:Na (0.997), Mn:Zn (0.945), and Na:Zn (0.967).

Correlations based on only three pairings must be recognized as being very tentative.

The foregoing results are based on only 20 samples, all of which were collected during a period of relative quiescence at or near Kilauea's summit (eruptive activity was, however, taking place lower down on the east rift). Because of this inactivity (since late September 1982), it has not been possible to date to observe possible changes of chemistry that may accompany renewal of activity. The data do support the conclusions that (1) four of the five fumaroles (Halemaumau excepted) individually exhibit distinctive mean absolute concentrations of elements, and (2) individual fumaroles are also characterized by distinctive ratios of element pairs, with Steaming Bluff and Puhimau having the greatest similarities.

Future work should include determination of both K and Mg by a technique (e.g., atomic absorption or plasma emission spectrophotometry) that is more sensitive to these elements than that employed in this study.

LITERATURE CITED

CASADEVALL, T. J., and R. W. HAZLETT. 1983. Thermal areas on Kilauea and Mauna Loa Volcanoes, Hawaii. J. Volcanol. Geothermal Res. 16:173–188.

CASADEVALL, T. J., J. B. STOKES, L. P. GREENLAND, L. L. MALINCONICO, J. R. CASADEVALL, and B. T. FURUKAWA. 1987. SO_2 and CO_2 emission rates at Kilauea Volcano, 1979–1984. Pages 771–780 in R.W. Decker, T. L. Wright, and P. H. Stauffer, eds. Volcanism in Hawaii. U.S. Geol. Surv. Prof. Pap. 1350.

FAIVRE-PIERRET, RENE, and FRANCOIS LE GUERN. 1983. Health risks linked with inhalation of volcanic gases and aerosols. Pages 69–81 in Haroun Tazieff and J.-C. Sabroux, eds. Forecasting Volcanic Events. Elsevier, Amsterdam.

GREENLAND, L. P. 1987. Hawaiian eruptive gases. Pages 759–770 in R. W. Decker, T. L. Wright, and P. H. Stauffer, eds. Volcanism in Hawaii. U.S. Geol. Surv. Prof. Pap. 1350.

HARDING, D., and J. M. MILLER. 1982. The influence of rain chemistry of the Hawaiian Volcano Kilauea. J. Geophys. Res. 87(C2): 1225–1230.

HELIKER, CHRISTINA, J. D. GRIGGS, T. J. TAKAHASHI, and T. L. WRIGHT. 1986. Volcano monitoring at the U.S. Geological Survey's Hawaiian Volcano Observatory. Earthquake Volcanoes 18(1): 3–71.

NAUGHTON, J. J., J. B. FINLAYSON, and V. A. LEWIS. 1975. Some results from recent chemical studies at Kilauea Volcano, Hawaii. Bull. Volcanol. 39:64–69.

NOGUCHI, K., and H. KAMIYA. 1963. Prediction of volcanic eruptions by measuring the chemical composition and amounts of gases. Bull. Volcanol. 26:367–378.

TAZIEFF, HAROUN. 1983a. Some general points about volcanism. Pages 9–16 in Haroun Tazieff and J.-C. Sabroux, eds. Forecasting Volcanic Events. Elsevier, Amsterdam.

———. 1983b. Some general points about volcano monitoring and forecasting. Pages 165–171 in Haroun Tazieff and J.-C. Sabroux, eds. Forecasting Volcanic Events. Elsevier, Amsterdam.

THOMAS, D. M., and J. J. NAUGHTON. 1978. Changes in fumarolic gas compositions as precursors to volcanic eruption (abstract). Geol. Soc. Amer., Abstracts to Programs 10(7): 504.

———. 1979. Helium/carbon dioxide ratios as premonitors of volcanic activity. Science 204(4398): 1195–1196.

TILLING, R. I., CHRISTINA HELIKER, and T. L. WRIGHT. 1987. Eruptions of Hawaiian Volcanoes: Past, Present, and Future. U.S. Geol. Surv. Gen. Int. Publ.