



SO₂ AND CO₂ EMISSION RATES AT KILAUEA VOLCANO, 1979-1984

By Thomas J. Casadevall, J. Barry Stokes, L. Paul Greenland, Lawrence L. Malinconico, John R. Casadevall,
and Bruce T. Furukawa

ABSTRACT

Quiescent outgassing of the summit region of Kilauea Volcano produces a plume of gas and particles that contains sulfur dioxide and carbon dioxide as principal constituents. The SO₂ and CO₂ are derived from outgassing of magma temporarily stored in the shallow reservoir at a depth of 2-6 km beneath the summit.

Since June 1979 we have made regular measurements of SO₂ emission rates from Kilauea. In 1983 and 1984, measurements of CO₂ emission rates were also made for Kilauea. The average daily SO₂ emission rate from 1979 through 1982 was 170 ± 50 t/d; from 1983-1984, the average daily emission rate had increased to 260 ± 90 t/d. The 1979-1982 rate occurred during a time when no major eruptive activity occurred at Kilauea summit. The increase in 1983 is coincidental with the start of major eruptive activity at the Puu Oo vent on the east rift zone and probably reflects an increase in the rate of magma supply.

The total SO₂ production in 1979-1982 is calculated at approximately 63,000 tonnes annually. In 1983-1984, this annual production is calculated at 95,000 tonnes annually. The SO₂ from quiescent outgassing of Kilauea Volcano contributes less than 1 percent of the total annual global contribution from volcanoes. The 1983-1984 episodes of the Puu Oo eruption produced about 370,000 tonnes of SO₂, or as much as 3 percent of the annual volcanic contribution.

INTRODUCTION

A plume of gas and microscopic particles continuously enters the atmosphere from fumaroles in the southern half of Kilauea caldera. The plume is generally transparent with a light-bluish-gray color due to scattering of light by tiny particles. It contains H₂O, CO₂, and SO₂ as the major gaseous constituents (Cadle and others, 1969, 1971; Darzi, 1981; Darzi and Winchester, 1982c).

In this paper we describe the techniques used to measure SO₂ and CO₂ emission rates at Kilauea, the results from June 1979 through December 1984, and the interpretation of the data. These measurements form a part of the program to monitor Kilauea Volcano from the Hawaiian Volcano Observatory. Their purpose is to determine the long-term emission rates for SO₂ from Kilauea; to evaluate the usefulness of the measurements for forecasting eruptions; and to integrate geochemical observations with geophysical and geologic observations of activity to refine our understanding of how Kilauea Volcano works.

We will show that (1) during periods of relative quiescence, Kilauea emitted a nearly constant flux of SO₂; (2) during the 1983-1984 eruptions at Puu Oo on Kilauea's east rift zone, the rate

of SO₂ release at the summit doubled and has remained at an elevated level; and (3) eruption plumes from Kilauea are characterized by increases in SO₂ of about two orders of magnitude over rates of non-eruptive or quiescent degassing.

BACKGROUND AND PREVIOUS STUDIES

The principal gases released from fumaroles at Kilauea are H₂O, CO₂, and SO₂ (Heald and others, 1963; Cadle and others, 1969, 1971; Gerlach, 1980; Greenland, 1984; Gerlach and Graeber, 1985; Greenland and others, 1985). The SO₂ is interpreted to be of magmatic origin (Sakai and others, 1982). The summit fumaroles at Halemaumau Crater and along the 1971 and 1974 eruptive fissures are the most notable sources of SO₂ in the summit region (Casadevall and Hazlett, 1983) and overly a shallow magma reservoir, envisioned as a plexus of sills and dikes, at a depth of 2 to 6 km (Fiske and Kinoshita, 1969; Ryan and others, 1981). Magma is fed into this shallow reservoir from a zone of generation at a minimum depth of 60 km (Eaton and Murata, 1960; Wright, 1984). Pre-eruptive degassing of magma while enroute to and temporarily stored in the shallow reservoir produces a CO₂-rich gas phase (atomic C/S ratio greater than 10); eruptive degassing produces a CO₂-rich gas phase during summit eruptions (atomic C/S is 5 or less) (Gerlach and Graeber, 1985; Greenland and others, 1985). An SO₂-rich gas phase (atomic C/S less than 1) is produced during rift eruptions from a magma which had already lost much of its CO₂ during equilibration at the pressure conditions of the shallow reservoir (Greenland, 1984; Gerlach and Graeber, 1985).

The preeruption content of sulfur in Hawaiian magma has been determined by Harris and Anderson (1983) to be about 1,300 ppm based on examination of melt inclusions in olivine phenocrysts. Basalt erupted on the sea floor under high confining pressure has lost some sulfur, but still contains between 700 and 1,000 ppm (Moore and Fabbri, 1971; Fornari and others, 1979) and surface flows contain from 50 to 200 ppm (Moore and Fabbri, 1971; Swanson and Fabbri, 1973; Sakai and others, 1982).

The continuous loss of sulfur during noneruptive periods to produce the volcanic plume is due largely to distillation of gas from magma as it reequilibrates to the pressure conditions of the shallow summit reservoir (Harris and Anderson, 1983; Greenland and others, 1985). Greenland and others (1985) suggest this mechanism results in about 150 ppm sulfur loss, while Gerlach and Graeber (1985) suggest a loss of between 300 and 600 ppm from the magma prior to eruption. Magma intruded to shallower depths in the

summit or rift zones may lose additional volatiles including SO₂. Further SO₂ loss occurs through effervescence of the basaltic magma (Swanson and Fabbri, 1973; Naughton and others, 1974; Harris and Anderson, 1983) during eruptions, a process which decreases the concentration of sulfur by approximately 600 ppm (Moore and Fabbri, 1971).

ACKNOWLEDGMENTS

Early support and encouragement for this program came from G. Eaton, Scientist-in-Charge at the Hawaiian Volcano Observatory from 1977–1979, and from R. Christiansen, Coordinator for the U.S. Geological Survey Geothermal Program which funded the purchase of the COSPEC. Continued support from the staff of the Hawaiian Volcano Observatory, in particular R. Decker, R. Okamura, and J. Forbes, is appreciated and gratefully acknowledged. Measurements during July and August 1982 were made by J.T. Prosser of Dartmouth College. The airborne measurements of SO₂ emission rates at Kilauea in July 1983 were made with the assistance of R. Symonds. W.I. Rose, Jr. (Michigan Technological University) and T.M. Gerlach (Sandia Laboratory) provided helpful reviews of earlier drafts of this paper. We dedicate this paper to our friend and teacher Richard E. Stoiber.

ACTIVITY OF KILAUEA, 1979–1984

Since June 1979, Kilauea has experienced two short-lived eruptions in the summit caldera (April and September 1982), a brief eruption at Pauahi Crater on the upper east rift zone (November 1979), a long-lived eruption in the middle east rift zone (January 1983–March 1985), and 13 intrusions (table 29.1). Each intrusion was accompanied by ground deformation and intense seismic activity that included discrete earthquakes and harmonic tremor (Dvorak and others, 1986). Five intrusions were also accompanied by the release of heat and (or) gases at the ground surface in the area of the intrusion.

METHODS, UNCERTAINTIES, AND ASSUMPTIONS

SO₂ emission rates have been measured at volcanoes since 1972 (Casadevall and others, 1981, 1984; Stoiber and others, 1983) including Kilauea in February 1975 (Stoiber and Malone, 1975) and in October 1978 (Stoiber and others, 1979). Regular ground-based measurements of SO₂ emission rates at Kilauea began in June 1979. Airborne measurements of SO₂ and CO₂ emission rates of the non-eruptive plume at Kilauea caldera and the eruption plume at the Puu Oo began in December 1983.

The emission rates of SO₂ and CO₂ are calculated by multiplying the plume velocity and the gas concentration in a cross-sectional profile of the plume. In this section we describe the methods and uncertainties for the measurements of wind speed, SO₂, and CO₂.

TABLE 29.1.—Summary of activity, Kilauea Volcano: 1979–1984

[S, summit; ERZ, east rift zone; SWRZ, southwest rift zone; I, intrusion; E, eruption; *, gas and (or) heat detected at ground surface above intrusion; n.d., not determined. Intruded volume calculated from Uwekahuna summit tilt ($0.33 \times 10^6 \text{ m}^3 = 1$ microradian). Modified from Dzurisin and others (1984)]

Date	Duration (days)	Location			Erupted volume (in million cubic meters)	Intruded volume
		S	ERZ	SWRZ		
1979						
May 29	1		I			1.0
Aug 12	1		I			.6
Nov 16	1		E		0.4	
1980						
Mar 2	1		I			0.6–1.0
Mar 10	2–3		I*			5.3
Aug 27	1		I*			2.3
Oct 22	1		I*			.6
Nov 2	1		I			2.0
1981						
Jan 19	2	I				n.d.
Jan 24	16			I		>8.0
Jun 25	1	I				1.6
Aug 10	2			I*		35.0
1982						
Apr 30	1	E			0.5	
Jun 22	3			I*		14.1
Sept 25	2	E			3.0	
Dec 9	1		I			1.0
1983						
Jan 3	800+		E		360+	

WIND SPEED MEASUREMENTS

On the east side of the Island of Hawaii northeasterly trade-winds travel from 3 to 20 m/s. These winds carry the plume of gas from the fumaroles on the caldera floor out into the southwest rift zone of Kilauea (fig. 29.1). During winter months this wind pattern is frequently reversed as Kona winds blow from the southwest. We usually assume that the wind speed stays constant during the period of measurement.

For ground measurements of SO₂, the plume velocity is measured at Uwekahuna Bluff on the west side of Kilauea caldera (fig. 29.1) using a hand-held anemometer. Five 1-minute measurements of wind velocity are taken before and after the SO₂ measurements. The average of the before and after wind measurements is used to calculate the SO₂ emission rate.

For airborne measurements of SO₂ and CO₂, we rely primarily on wind direction and speed determinations made twice daily at Hilo Airport by the NOAA radiosonde. These are checked during flight. When possible, we compare true air speed of the aircraft determined while flying in the plume with true ground speed measured by flying a fixed distance (usually 10 miles) both with (tailwind) and against (headwind) the wind. The difference between the true ground speed and true air speed gives the wind speed.

The uncertainty in the measurement of wind speed is typically between 10 and 30 percent. This measurement is the largest single source of uncertainty in measuring the rates of SO₂ and CO₂ emission.

SO₂ MEASUREMENTS

The emission rates of SO₂ are measured using the Correlation Spectrometer (COSPEC; Barringer Research Ltd. of Canada) originally designed for use in pollution studies (Millan and others, 1976; Millan and Hoff, 1978) and adapted to the study of volcanoes (Stoiber and others, 1983). Correlation spectrometry is a remote-sensing technique that uses solar ultraviolet light scattered by the Earth's atmosphere as a source. The spectrally tuned instrument measures the amount of uv absorption by SO₂ present along the optical path through the plume in units of concentration-pathlength (ppm·m) at one atmosphere. Calibration is performed using an internal standard with a known concentration-pathlength of SO₂. A cross-section profile of the plume is determined by multiplying the plume width (m) with the concentration-pathlength. The product of this profile (ppm·m²) and the wind speed (m/s) is the mass flux (ppm·m³/s) and is usually expressed as tonnes per day (t/d).

Most measurements reported here were made with the COSPEC mounted in an automobile that is driven at a constant velocity of 40 km/h beneath the plume as it passes over a road that encircles Kilauea caldera (fig. 29.1B). An SO₂ cross section of the plume is continuously recorded on a chart recorder, and the changes in SO₂ pathlength concentration and geographic position are recorded. Four to six traverses can be made beneath the plume in about one hour. The techniques for airborne measurements are the same as those used at Mount St. Helens (Casadevall and others, 1981).

The large amounts of SO₂ and the enormous size of the eruption plumes at Kilauea presented added problems for airborne measurements. During eruptions in 1979, 1982, 1983, and 1984, the concentrations of SO₂ in the eruption plumes exceeded the measurable capacity using the COSPEC technique and caused saturation of the signal. In April 1984, we installed a high concentration SO₂ disc and calibration cells into the COSPEC to permit measurement of higher concentrations of SO₂. An additional problem is that the large plumes produced during eruptions of Kilauea often remain close to the ground, thereby preventing the aircraft from flying completely beneath the plume. Thus, many of the airborne measurements of SO₂ emission rates of eruption plumes are minimum values.

UNCERTAINTIES

The reported emission rate of SO₂ incorporates uncertainties due to both instrumental factors and variations from natural causes (Casadevall and others, 1981; Stoiber and others, 1983). The latter include real-time variation in gas emission, short-term (minutes to hours) variation in wind speed, and changes in cloud cover. Estimated uncertainties arising from operator and instrumental factors include uncertainty in the instrument calibration (± 5 percent); variation in speed of vehicle used to measure the plume (± 10 percent); uncertainty in data processing (± 5 percent); and uncertainty in the measurement of wind speed (± 10 -30 percent). The effect of these uncertainties and variations on the reported SO₂ emission rate can be minimized by averaging the results of from 4 to

20 traverses each day. In practice, the average of these traverses, that is the average daily emission rate, usually has an uncertainty of ± 10 to ± 30 percent of the reported value.

CO₂ MEASUREMENTS

The emission rates of CO₂ have been measured within the non-eruptive summit plume and at the Puu Oo eruption site (Greenland and others, 1985) beginning in 1983. The technique uses an infrared spectrometer that is flown through the plume at successively higher altitudes while the concentration of CO₂ is continuously measured (Harris and others, 1981). The concentration of CO₂ in excess of the background atmospheric CO₂ content is inferred to be from the volcano. This excess CO₂ generally ranges from 1 to 15 ppm (by volume), compared to an average atmospheric concentration of approximately 320 ± 20 ppm. The altitude-concentration data are used to make a map of excess CO₂ concentration in a cross section of the plume. The product of the cross section-concentration (ppm·m²) and the plume velocity (m/s) gives the emission rate of CO₂ (ppm·m³/s) and is reported as tonnes per day. Each daily value represents a single cross section of the plume requiring between 90 and 120 minutes of continuous in-flight measurement.

The utility of the CO₂ method is limited by the practicality of flying repeatedly through a plume that is usually not visible, as well as by the threshold emission rate. We are aided in tracking the plume by simultaneously using the COSPEC to measure SO₂. Experience at Mount St. Helens (Casadevall and others, 1981; Harris and others, 1981) has shown that SO₂ and CO₂ are usually well mixed in the plume and that maximum CO₂ concentration is typically coincident with maximum SO₂ concentration.

The threshold value for detecting excess CO₂ in the plume depends on the wind speed and dispersion of the plume and the distance from the source at which measurements are made (that is, degree of air dilution). Excess CO₂ of less than 2 ppm is difficult to determine accurately. This concentration effectively becomes our threshold value for detecting excess CO₂ in the plume; in practical terms, emission rates of less than 1,000 t/d are difficult to measure. We estimate a maximum uncertainty in these measurements of ± 40 percent of the reported value.

DATA QUALITY

In addition to real changes in the emission rates of gases, other factors, both natural and operator related, affect the quality of the data. These factors include changes in cloud cover, variation in wind speed and direction, experience of the operators, and instrumentation. Operator experience is important both in making the measurements of SO₂ and wind speed, as well as in reduction of data. Judgment must be used to evaluate the quality of a given day's measurement conditions and in interpreting the chart records. Judgment improves with practice and becomes more uniform with experience. Measurements made daily or at least several times each

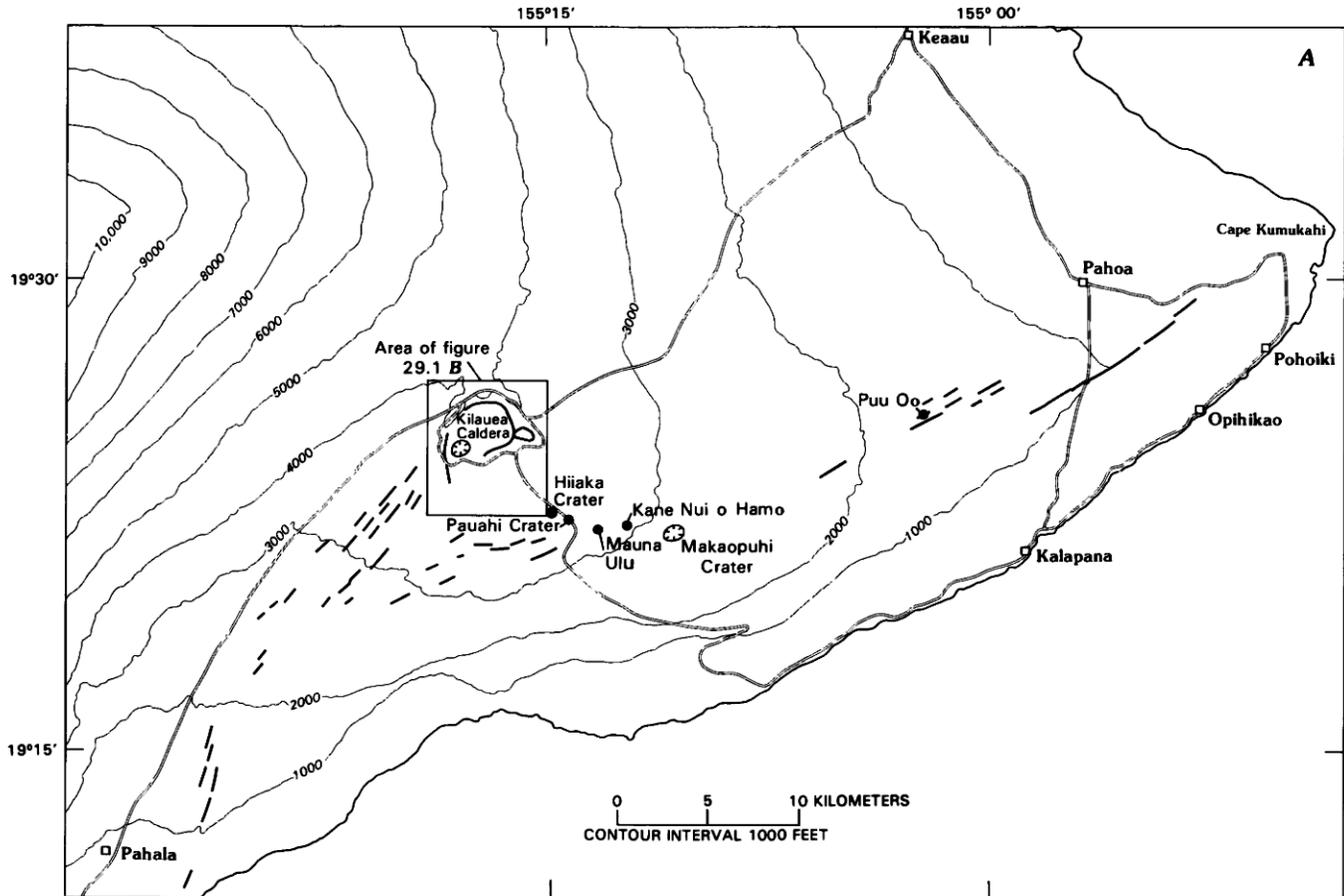


FIGURE 29.1.—Index map of Kilauea Volcano. *A*, Summit area and rift zones. *B*, Kilauea caldera area.

week provide a more reliable indication of background values than measurements made only weekly or less frequently. We have designated data quality as good if the frequency of measurement was weekly or better and if the measurements were made by the same experienced operator. Data of good quality include the summit measurements from June 1979 to June 1980, and from November 1981 through December 1984. Data of poor quality are those which have been collected infrequently by one or more inexperienced operators. The data collected from September 1980 through October 1981 are generally considered to be of poor quality. In addition, during many of the airborne measurements, the concentration of SO_2 exceeded that measurable by the COSPEC. These data should be treated with caution since they likely represent minimum rates for SO_2 emission.

REMOVAL OF SO_2 FROM THE PLUME

We have assumed that the SO_2 measured in the plume accurately represents the mass of sulfur released from the summit fumaroles. We recognize that while enroute to the surface, the SO_2 -bearing gas mixture may be affected by a variety of conditions and

processes that reduce the amount of sulfur reaching the fumaroles (Gerlach and Graeber, 1985). Measurements made during the season of heavy rainfall (December through March) show no significant change in SO_2 emission rate, suggesting that removal of SO_2 , at least by the shallow ground-water table, is probably minimal. Eruption plumes do not appear to be affected by subsurface removal of SO_2 as there is little evidence for magma-ground water interaction during eruption (Greenland, 1984).

SO_2 in the plume may be removed through rainout and through dry deposition. Dry deposition occurs onto soil and vegetation as well as onto atmospheric particles such as sea spray and tropospheric dust (Darzi and Winchester, 1982a, 1982b). Direct deposition of SO_2 may damage vegetation (Winner and Mooney, 1980) and acidify rainfall ($\text{pH} = 3.0\text{--}4.0$), owing to scavenging of SO_2 by rain droplets (Harding and Miller, 1982; Russell, 1982). Salt and dust particles have been detected at the summit of Kilauea (Woodcock, 1960; Darzi and Winchester, 1982b), but their efficiency as scavengers of SO_2 and other gases is unknown. In eruption plumes, where the concentration of particles is higher than in non-eruptive plumes, scavenging of SO_2 by tephra particles may be significant (Naughton and others, 1974; Rose, 1977).

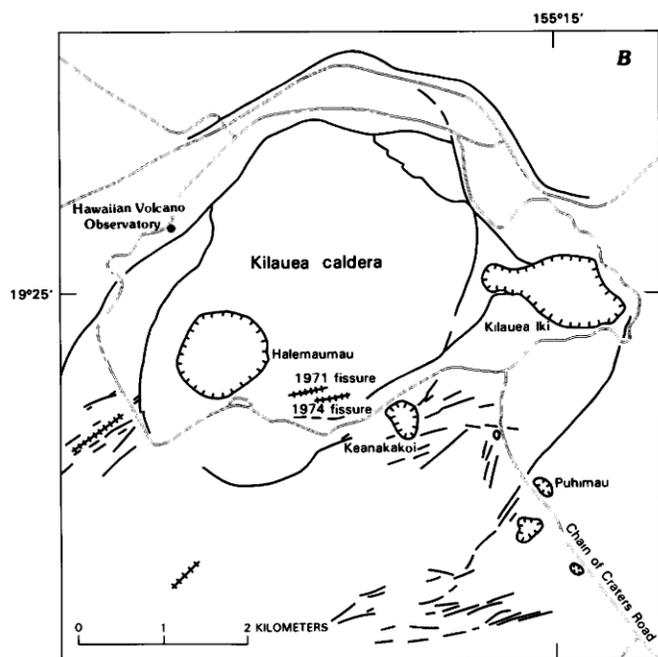


FIGURE 29.1.—Continued.

Some SO₂ in the plume is eventually converted to sulfate; however, studies of Kilauea fume by Cadle and others (1971) indicate that SO₂ dominates over other oxidized forms of sulfur. When the plumes at Kilauea summit and at Puu Oo were measured, they had usually been in the atmosphere for less than a few minutes; some measurements of the larger Puu Oo eruptive plumes require flying farther downwind where plumes may be as much as 1 hour old. This time is short as compared to the removal rates calculated from study of industrial plumes (Roberts and Williams, 1979; Williams and others, 1981) and estimated (Graedel, 1977; Maahs, 1983a; Martin, 1983; Barrie, 1985) as being on the order of less than about 1 percent SO₂ per hour. Removal rates increase only slightly with humidity and with acidity of the water droplets (Maahs, 1983b). The short-lived (usually tens of seconds) condensation cloud at Halemaumau may temporarily absorb some SO₂, but as the condensate evaporates the sulfur is probably released to the atmosphere as SO₂ (Hegg and Hobbs, 1978).

RESULTS

QUIESCENT SUMMIT EMISSIONS OF SO₂

The average daily emission rates of SO₂ from June 1979 through December 1984 are tabulated in table 29.2 and all data are plotted in figure 29.2. To examine these data for trends and changes, we have applied several statistical methods, including analysis of variance, multiple range test (Duncan), and regression analysis with step-wise selection of data to determine the timing and magnitude of changes in SO₂ emission rates. We have applied these

TABLE 29.2.—Summary of SO₂ emission rates for the quiescent plume, Kilauea: 1979–1984

[Values given in tonnes per day; *b*, the slope coefficient of the model; B estimate of *b*; R², percent of the SO₂ emission rate explained by the model; N, number of measurements]

Period	Dates	Daily rate (mean)	95 percent confidence interval for mean	B	<i>b</i> =0	R ²
1A	June 1979 to Mar 15, 1980	160 (N=120)	151–169	0	yes	--
1B	Mar 15 to Jun 1980(?)	100 (N=23)	75–120	0	yes	--
2	Sept 1980 to Aug 11, 1981	190 (N=43)	162–210	0	yes	--
3	Aug 11 to Dec 1981	300 (N=13)	265–326	0	yes	--
4	Feb 1982 to Jan 1983	160 (N=34)	100–220	0	yes	--
5	Jan 1983 to Dec 30, 1984	260 (N=172)	250–265	+0.04	no	2.8

tests to address the following questions: (1) Is it possible to identify periods during which SO₂ emission rates remained relatively constant? (2) If yes, what are the mean SO₂ emission rates during those periods and are there statistically significant differences between means for the different periods? (3) Which means are different and by how much? (4) Are there significant variations within periods which might not be apparent from visual inspection of the data? We have not weighted the data for instrument-related uncertainty, owing mainly to the difficulty in distinguishing between variation due to instrumental or operator errors and variation due to natural causes.

To begin, we visually inspected the data of figure 29.2 and selected 5 periods during which emission data appeared to have remained constant and calculated the mean SO₂ emission rate for each period. These periods include: (1) June 1979–June 1980, (2) September 1980–mid-August 1981, (3) mid-August 1981–December 1981, (4) February 1982–January 1983, and (5) late-January 1983–December 1984. Using the analysis of variance, we tested the null hypothesis (H₀) that the means for periods 1, 2, 3, 4, and 5 are the same (H₀ = u₁ = u₂ = u₃ = u₄ = u₅ versus H₁ such that at least one pair u_i is not equal to u_j) where u_i is the mean SO₂ flux for period *j*. The test statistic (F-ratio) is highly significant (50.48), and we may conclude that the means are not all identical. Table 29.2 contains a summary of the analysis of variance for the five phases including the means of the data and the 95 percent confidence intervals.

To examine if the data within each period are constant within the 95 percent confidence limits, we performed a regression analysis using the least-squares method to test the regression model:

$$Y_i = a + bx_i$$

where *Y_i* is the SO₂ flux and *x_i* is the number of days since December 31, 1978. The coefficient *a* is of no particular use in this application since the origin is arbitrary. The important test statistics are B (the estimate of *b*, the slope coefficient of the model) and R² (the proportion of the SO₂ flux explained by the model). The analysis of variance (table 29.2) for each period tests the hypothesis that *b*=0, which indicates that the slope of a least-squares line is flat. In the initial test for periods 1 and 5, *b* was not equal to 0, indicating that there are trends to the data for these periods.

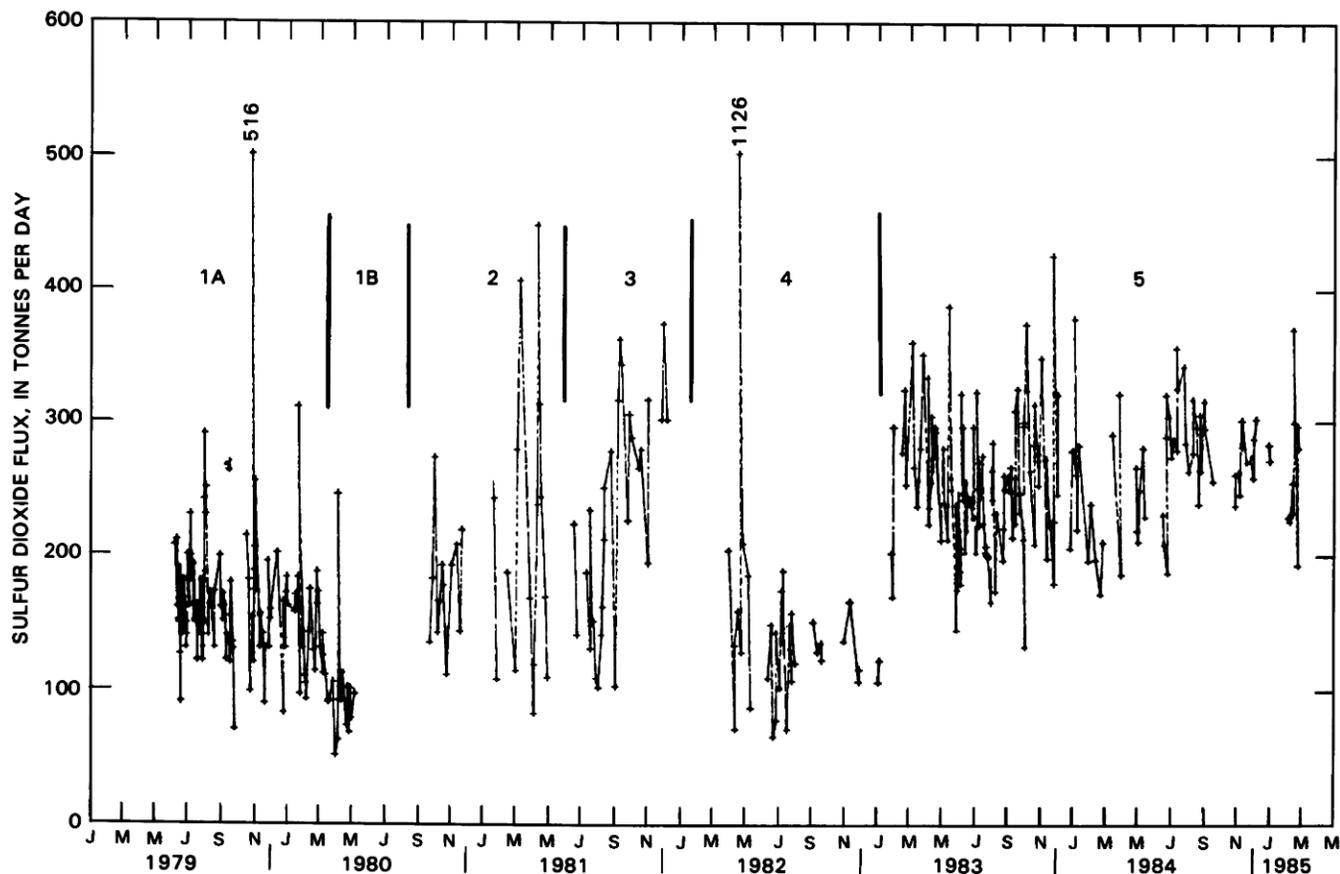


FIGURE 29.2.—SO₂ emission rate data obtained from COSPEC for Kilauea summit area, 1979–1984. Periods 1A–5 separated by heavy black lines.

However, the high R^2 value and negative sign for B (-0.17) for period 1 indicates that the trends in the data for this period are not smooth, but may be due instead to an abrupt decrease in the SO₂ emission rate.

By applying an iterative procedure using step-wise selection of data, we find that a significant decrease in SO₂ emission rates in period 1 occurred in mid-March 1980. On the basis of this test we have subdivided period 1 into 1A and 1B with the break occurring in mid-March 1980. The mean for period 1A (to mid-March 1980) is 160 t/d; the mean for period 1B (after mid-March 1980) is only 100 t/d. Regression analyses show that b for periods 1A and 1B equals 0, indicating that the trends for these two subsets of the data are flat.

We used the multiple range test (Duncan) to identify if the mean emission rates are significantly different from one another. Period 1B has the lowest mean and is significantly different from means for all the other periods at the 0.05 level. Periods 1A, 2, and 4 are not significantly different from each other at the 0.05 level. Periods 3 and 5 have the highest means, but are not significantly different from one another at the 0.05 level.

Lack of measurements for part of the second half of 1980 prevent us from determining whether the transition from period 1B

to period 2 is abrupt or gradual. For period 5, the slope of the regression equation is slightly positive with a low value of B indicating that the data fit a trend of slight increase in SO₂, equivalent to about 0.05 t/d.

SO₂ EMISSION RATES DURING SUMMIT AND UPPER EAST RIFT ZONE ERUPTIONS

On April 30, 1982, a summit eruption lasted for 19 hours and produced about 0.5×10^6 m³ of lava from an eruption fissure located northeast of Halemaumau Crater on the floor of Kilauea caldera. A peak emission rate of 1,150 t/d was measured during the middle of the eruption, and rates dropped to pre-eruption values quickly after activity ceased. On September 25, 1982, another summit eruption began at about 1900 (H.s.t.) and was over by the next morning after the eruption of about 3.0×10^6 m³ of lava. The September eruption took place at night from vents located south of the Crater Rim Road, so COSPEC measurements were not possible. In contrast to the August 1971 and the July 1974 eruption fissures, which host prominent solfataras within the caldera, both 1982 eruptive fissures quickly cooled to ambient temperature and ceased emitting sulfur gases at the end of eruptive activity.

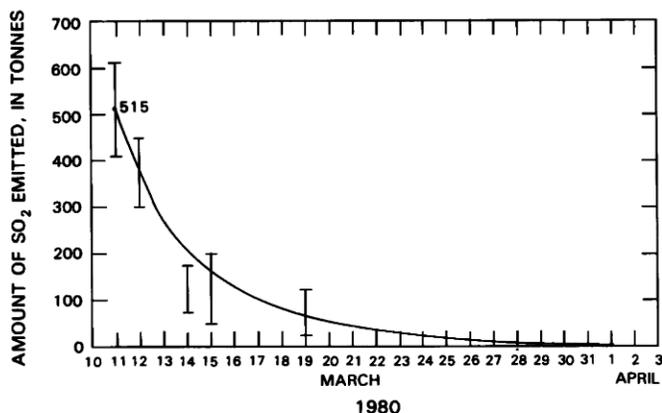


FIGURE 29.3.—SO₂ emission rates following Mauna Ulu intrusion, March–April 1980.

In November 1979, a 22-hour-long eruption occurred from vents east and west of, as well as within Pauahi Crater (fig. 29.1A) and approximately 3.5×10^6 m³ of lava was erupted. COSPEC measurements were possible only during the first several hours of the eruption, before the Chain of Craters Road was closed by a lava flow, and an emission rate of 700 t/d of SO₂ was measured for the vent within Pauahi Crater. The 1979 fissures ceased emitting sulfur gases at the end of eruptive activity.

THE MARCH 10–12, 1980, INTRUSION

On March 2 and 10–12, 1980, two intrusions into the upper east rift zone of Kilauea (fig. 29.1A) between Pauahi Crater and Mauna Ulu were followed within minutes by deflation of the summit region. No lava was observed during these events; however, field studies in 1982 discovered a small volume (about 1 m³) of fresh lava at 770 m elevation along the southeast end of the March 12 fracture (R. Moore, oral commun., 1982).

The March 10–12 intrusion released large amounts of CO₂ and SO₂ from the summit crater of the Mauna Ulu shield and from a 300-m-long N. 60° E. fracture set located between Mauna Ulu and Kane Nui o Hamo (fig. 29.1A). The fractures were quickly coated by elemental sulfur and fumed heavily for several days. The maximum temperature of the gas coming from the cracks was 98 °C. SO₂ emission rates from March 11 to 19 decreased from approximately 520 to 100 t/d, and within 30 days emission rates were less than 3 t/d (fig. 29.3). Approximately 3,000 tonnes of SO₂ was produced from March 11 through April.

SO₂ AND CO₂ EMISSIONS: AIRBORNE MEASUREMENTS: 1983–1984

Airborne measurements of SO₂ and CO₂ emission rates were made for eruption and intra-eruptive plumes at Puu Oo and for non-eruptive plumes at Kilauea caldera beginning in 1983 (table 29.3). The plumes from the eruptive episodes of Puu Oo are enormous in terms of SO₂ burden and physical size. The high concentration of

TABLE 29.3.—Emission rates of SO₂ and CO₂ during Puu Oo eruption episodes: 1983–1984

[—, no data; n.d., not determined]

Phase	Duration (hr)	Date	SO ₂	CO ₂	Lava volume (m ³ × 10 ⁶)	Rate (m ³ /hr)
			(tonnes/day)			
1983						
6	73	Jul 24	24,000 ± 4,700	--	9.4	0.13
7	56	Aug 15	15,700 ± 4,200	--	10.2	.18
7	56	Aug 17	17,500 ± 5,500	--	n.d.	n.d.
8	24	Sept 6	6,700 ± 1,800	--	7.0	.29
9	52	Sept 16	17,600 ± 10,300	--	8.7	.17
1984						
14	19	Jan 31	11,800 ± 4,300	--	5.9	³ 0.31
15	19	Feb 15	² 27,000	14,700	8.6	.42
16	31	Mar 4	² 18,000	³ 3,200	11.8	.37
17	22	Mar 30	5,100 ± 3,100	--	9.6	³ .46
21	8	Jun 30	28,000 ± 6,200	--	5.7	³ .71
28	15	Dec 4	32,000 ± 10,400	--	n.d.	³ .85

¹From Greenland and others (1985).

²Calculated values (see Greenland and others, 1985).

³Calculated from HVO monthly reports.

SO₂ saturated the COSPEC signal, and plume widths often exceeded 50 km.

The episodes of the Puu Oo eruption have been well documented (Wolfe and others, chapter 17), including accurate measurements of erupted volumes and rates of lava production (table 29.3). Emission rates of SO₂ were measured during 8 eruptive episodes (6, 7, 8, 9, 14, 17, 21, and 28) of Puu Oo in 1983–1984; these rates range from 5,100 to 32,000 t/d (table 29.3). Rates for episodes 15 and 16 have been calculated from CO₂ flux measurements and fumarole gas composition (Greenland and others, 1985). The uncertainty in these measurements ranges from 15 to 40 percent of the reported values.

Between eruptive episodes at Puu Oo, gas is emitted continuously. On December 2, 1983, 24 hours after the end of phase 12, the SO₂ emission rates averaged 260 t/d; a week later the emission rates were 20 t/d. The CO₂ emission rates at Puu Oo were below the level of detection (less than 800–1,000 t/d) on both December 2 and 9. These data are consistent with gas sampling from the Puu Oo vent and with airborne measurements of eruptive plumes that indicate the CO₂/SO₂ ratio has been less than 1 (Greenland, 1984; Greenland and others, 1985).

On December 9, 1983, the emission rate of SO₂ in the summit region was 300 ± 30 t/d; the emission rate for CO₂ was 3,600 t/d. On February 13, 1984 the emission rates for SO₂ and CO₂ were 220 and 1,600 t/d, respectively (Greenland and others, 1985). These airborne measurements indicate a CO₂/SO₂ ratio greater than 5, in general agreement with measurements of fumaroles in the summit region.

DISCUSSION AND INTERPRETATION

RATES OF SO₂ EMISSION: NON-ERUPTIVE PLUME

The statistical analysis of the COSPEC data for 1979–1984 reveals that levels of SO₂ release remain relatively constant for

periods of months to years. Changes in the SO₂ flux generally correlate with other events at Kilauea such as eruptions or intrusions. We suggest that rates of SO₂ emissions, and changes in those rates, closely reflect magmatic processes at Kilauea. The relatively constant rates of SO₂ emission during periods 1A (before mid-March 1980), 3 (from August through December 1981), and 4 (February 1982 through January 1983) reflect the steady supply of magma to the shallow reservoir. The intrusions of magma into the upper east rift zone in March 1980 apparently diverted some magma out of the shallow reservoir and caused a 35 percent decrease in the rate of SO₂ emission from the summit region. In contrast, the southwest rift zone intrusion of August 1981 was followed by an increase in SO₂ emission rates (period 3), reflecting a temporary increase in the rate of magma supply as indicated by rapid reinflation of the summit chamber (Dvorak and others, 1986). Another rapid increase in the emission rate starting in January 1983 (period 5) occurred coincidentally with an increase in magma supply rate that began with the Puu Oo eruption (Wolfe and others, chapter 17; Greenland and others, 1985).

For the period 1976–1982, magma was supplied to the shallow reservoir at about 5.6×10^6 m³/mo (Dzurisin and others, 1984), and at 12×10^6 m³/mo for the period 1983–1984 (chapter 17). From the mean rate of SO₂ emission from 1979–1982, we calculate that between 150 and 400 ppm sulfur were released by the magma stored in the shallow reservoir. A similar amount of sulfur was released during 1983–1984 using the higher rates of magma supply (Wolfe and others, chapter 17) and higher rates of SO₂ emission. This calculation suggests that about 10 to 30 percent of the 1,300 ppm sulfur (Harris and Anderson, 1983) initially dissolved in the parental melt is released to provide the daily rates of SO₂ measured in the non-eruptive plumes.

We noted earlier that distillation of magma as it re-equilibrates in the shallow reservoir may account for a sulfur loss of between 150 ppm (Greenland and others, 1985) and from 300 to 600 ppm (Gerlach and Graeber, 1985) prior to eruption. Thus, though some overlap exists in the amount of sulfur lost as determined from magma supply rates and SO₂ emission rates (150–400 ppm) as compared to the range of sulfur expected, the quantity of sulfur detected at the surface is apparently less than the amount of sulfur actually released from the magma. Gerlach and Graeber (1985) suggest that some SO₂ may be prevented from reaching the surface due to removal in the hydrothermal alteration of the volcanic pile or reaction with the deep hydrothermal brine, or it may be lost by separation of an immiscible sulfide melt during summit storage.

To discuss this problem more thoroughly, we need (1) to know more about the nature of the hydrothermal system postulated to overly the shallow magma reservoir, (2) more careful study of the volatile contents of intrusive bodies, and (3) additional study of melt inclusions to determine more precisely the primary sulfur content in Hawaiian basaltic magmas.

MAUNA ULU INTRUSION, MARCH 10–12, 1980

The fate of the sulfur remaining in the magma after its partial

distillation in the shallow reservoir depends on its subsequent history. For the period 1956–1983, Dzurisin and others (1984) have shown that approximately 65 percent of the magma supplied to the shallow reservoir was stored through intrusion into the summit and rift zones of the volcano; approximately 35 percent was erupted. Only the extruded volume is largely outgassed of sulfur, whereas the intruded magma is less completely outgassed.

If intrusion is sufficiently shallow, further gas loss may be quite efficient. The initially large flux and subsequent rapid decrease in SO₂ emission rates which followed the intrusion near Mauna Ulu in mid-March 1980 is interpreted to reflect the pattern of outgassing of a portion of magma following its intrusion to a shallow depth. The SO₂ emission rates at the summit decreased significantly after this intrusion and remained low for at least three months. The volume of intruded magma estimated from the net summit deflation (16 microradians) during the event is approximately 5.2×10^6 m³ (that is 0.33 million m³ per microradian; Dzurisin and others, 1984). Assuming efficient degassing of 2.2 kg/m³ of sulfur (loss of 800 ppm S; $\rho = 2.8$ g/cm³), the 3,000 tonnes of SO₂ released during this event require a magma volume of 1.4×10^6 m³. However, overburden pressures require greater solubility of sulfur in the melt, thus only about 30 percent of the dissolved sulfur in the reservoir-equilibrated magma would have had to escape to produce the SO₂ emissions of this event.

SO₂ FROM KILAUEA—ANNUAL BUDGET AND GLOBAL IMPACT

From the averaged monthly emission rates for SO₂ (table 29.2) we have calculated the average annual emission rates of SO₂ from quiescent outgassing of Kilauea from 1979–1984. These are: 1979, $58,500 \pm 15,000$ t/yr; 1980, $52,000 \pm 15,000$ t/yr; 1981, $83,000 \pm 30,000$ t/yr; 1982, $58,500 \pm 18,000$ t/yr; 1983, $95,000 \pm 33,000$ t/yr; and 1984, $95,000 \pm 33,000$ t/yr. The global anthropogenic contribution of SO₂ to the atmosphere is estimated at between 100×10^6 t/yr (Likens, 1979; Cadle, 1980) and 150×10^6 t/yr (Berresheim and Jaeschke, 1983). The global volcanic contribution is estimated to be 15×10^6 t/yr (Berresheim and Jaeschke, 1983) with the majority coming from a few large eruptive events. The contribution of SO₂ from quiescent outgassing of Kilauea contributes less than 1 percent of the annual global contribution from volcanoes.

The 1983–1984 eruptions of Puu Oo produced about 0.37×10^6 t/yr of SO₂ (calculated from the 1983–1984 total erupted magma of 307×10^6 m³, corrected to dense rock equivalent, or DRE, using a 20 percent vesicularity correction, and estimated to release 3 kg of SO₂ per cubic meter of DRE lava) and may have contributed as much as 3 percent of the annual volcanic contribution. Though the individual eruptive episodes of Puu Oo contributed large amounts of SO₂ to the atmosphere, these emissions were confined to the lower troposphere, and eruptions seldom continued for longer than 72 hours. The local impact of such emissions on vegetation and rainfall chemistry may be dramatic (Winner and Mooney, 1980); however, their global impact remains small.

ERUPTION PREDICTION USING EMISSION RATE DATA

At Asama Volcano, Japan, Noguchi and Kamiya (1963) demonstrated that the amounts of sulfur gas emitted by the volcano increased prior to explosive eruptions. At Mount Etna, large increases in the rate of SO₂ emission were observed before each of two Strombolian eruptions in 1977 (Malinconico, 1979). At Mount St. Helens, increases in SO₂ emission rates were noted two to four weeks prior to 2 of 12 eruptions between 1981 and 1983 (Casadevall and others, 1983). These studies indicate that increases in SO₂ emission rates precede some, but not necessarily all, types of eruptive activity.

From experience with emission-rate data at Mount St. Helens, Casadevall and others (1983) note that confidence in using the data for prediction of activity increases with the frequency and regularity of measurements. We have scrutinized the present data for Kilauea and find no hindsight indication of pending activity. If such increases happen only days or hours before activity, it is unlikely that we would recognize them using the frequency of measurements made during 1979-1984.

Measurements of SO₂ and CO₂ emission rates require considerable investments of time and effort, and the present techniques simply are not practical for making continuous measurements. Different methods of measurement, as well as more careful integration of geochemical data with other geophysical measurements, are necessary if we hope to use emission rates to improve our abilities to predict impending activity.

REFERENCES

- Barrie, L.A., 1985, Scavenging ratios, wet deposition and in-cloud oxidation: an application to the oxides of sulphur and nitrogen: *Journal of Geophysical Research*, v. 90, p. 5789-5799.
- Berresheim, H., and Jaeschke, W., 1983, The contribution of volcanoes to the global atmospheric sulfur budget: *Journal of Geophysical Research*, v. 88, p. 3732-3740.
- Cadle, R.D., 1980, A comparison of volcanic with other fluxes of atmospheric trace gas constituents: *Reviews of Geophysics and Space Physics*, v. 18, p. 746-752.
- Cadle, R.D., Lazrus, A.L., and Shedlovsky, J.P., 1969, Comparison of particles in the fume from eruptions of Kilauea, Mayon, and Arenal volcanoes: *Journal of Geophysical Research*, v. 74, p. 3372-3378.
- Cadle, R.D., Wartburg, A.F., and Grahek, F.E., 1971, The proportion of sulfate to sulfur dioxide in Kilauea Volcano fume: *Geochimica et Cosmochimica Acta*, v. 35, p. 503-507.
- Casadevall, T.J., and Hazlett, R.W., 1983, Thermal area of Kilauea and Mauna Loa: *Journal of Volcanology and Geothermal Research*, v. 16, p. 173-188.
- Casadevall, T.J., Johnston, D.A., Harris, D.M., Rose, W.I., Jr., Malinconico, L.L., Stoiber, R.E., Bornhorst, T.J., Williams, S.N., Woodruff, Laurel, and Thompson, J.M., 1981, SO₂ emission rates at Mount St. Helens from March 29 through December, 1980, in Lipman, P.W., and Mullineaux, D.L., eds., *The 1980 eruptions of Mount St. Helens*, Washington: U.S. Geological Survey Professional Paper 1250, p. 193-200.
- Casadevall, T.J., Rose, W.I., Jr., Fuller, W.H., Hunt, W., Hart, M., and Moyers, J.L., 1984, SO₂ and particles in quiescent volcanic plumes from Poas, Arenal, and Colima Volcanos, Costa Rica and Mexico: *Journal of Geophysical Research*, v. 89, p. 9633-9641.
- Casadevall, T.J., Rose, W.I., Jr., Gerlach, T.M., Greenland, L.P., Ewert, J., Wunderman, R., and Symonds, R., 1983, Gas emissions and the eruptions of Mount St. Helens through 1982: *Science*, v. 221, p. 1383-1385.
- Darzi, Michael, 1981, Fumarolic aerosols from Kilauea volcano, Hawaii: *Nuclear Instrumentation Methods*, v. 181, p. 359-365.
- Darzi, Michael, and Winchester, J.W., 1982a, Aerosol characteristics at Mauna Loa observatory, Hawaii, after East Asia dust storm: episodes: *Journal of Geophysical Research*, v. 87, p. 1251-1258.
- 1982b, Resolution of basaltic and continental aerosol components during spring and summer within the boundary layer of Hawaii: *Journal of Geophysical Research*, v. 87, p. 7262-7272.
- 1982c, Volcanic aerosol phosphorus, chlorine, and sulfur at Kilauea, Hawaii: *Journal of Geophysical Research*, v. 87, p. 11,095-11,101.
- Dvorak, J.J., Okamura, A.T., English, T.T., Koyanagi, R.Y., Nakata, J.S., Sako, M.K., Tanigawa, W.T., and Yamashita, K.M., 1986, Mechanical response of the south flank of Kilauea Volcano, Hawaii, to intrusive events along the rift systems: *Tectonophysics*, v. 124, p. 193-209.
- Dzurisin, Daniel, Koyanagi, R.Y., and English, T.T., 1984, Magma supply and storage at Kilauea Volcano, Hawaii: *Journal of Geophysical Research*, v. 21, p. 177-206.
- Eaton, J.P., and Murata, K.J., 1960, How volcanoes grow: *Science*, v. 132, p. 925-938.
- Fiske, R.S., and Kinoshita, W.T., 1969, Inflation of Kilauea Volcano prior to its 1967-1968 eruption: *Science*, v. 165, p. 341-349.
- Fornari, D.J., Moore, J.G., and Calk, L., 1979, A large submarine sand-rubble flow on Kilauea Volcano, Hawaii: *Journal of Volcanology and Geothermal Research*, v. 5, p. 239-256.
- Gerlach, T.M., 1980, Evaluation of volcanic gas analyses from Kilauea Volcano: *Journal of Volcanology and Geothermal Research*, v. 7, p. 295-317.
- Gerlach, T.M., and Graeber, E.J., 1985, The volatile budget of Kilauea: *Nature*, v. 313, p. 273-277.
- Graedel, T.E., 1977, The homogeneous chemistry of atmospheric sulfur: *Reviews of Geophysics and Space Physics*, v. 15, p. 421-426.
- Greenland, L.P., 1984, Gas composition of the January 1983 eruption of Kilauea Volcano, Hawaii: *Geochimica et Cosmochimica Acta*, v. 48, p. 193-195.
- Greenland, L.P., Rose, W.I., Jr., and Stokes, J.B., 1985, An estimate of gas emissions and magmatic gas content from Kilauea Volcano: *Geochimica et Cosmochimica Acta*, v. 49, p. 125-129.
- Harding, Duane, and Miller, J.M., 1982, The influence of volcanic outgassing on rain chemistry of the Hawaiian volcano Kilauea: *Journal of Geophysical Research*, v. 87, p. 1225-1230.
- Harris, D.M., and Anderson, A.T., Jr., 1983, Concentrations, sources, and losses of H₂O, CO₂, and S in Kilauean basalt: *Geochimica et Cosmochimica Acta*, v. 47, p. 1139-1150.
- Harris, D.M., Sato, Motoaki, Casadevall, T.J., Rose, W.I., Jr., and Bornhorst, T.J., 1981, Emission rates of CO₂ from plume measurements, in Lipman, P.W., and Mullineaux, D.L., eds., *The 1980 eruptions of Mount St. Helens*, Washington: U.S. Geological Survey Professional Paper 1250, p. 201-207.
- Heald, E.F., Naughton, J.J., and Barnes, I.L., 1963, The chemistry of volcanic gases. 2. Use of equilibrium calculations in the interpretation of volcanic gas samples: *Journal of Geophysical Research*, v. 68, p. 545-557.
- Hegg, D.A., and Hobbs, P.V., 1978, Oxidation of sulfur dioxide in aqueous systems with particular reference to the atmosphere: *Atmospheric Environment*, v. 12, p. 241-253.
- Likens, G.E., 1979, Acid rain: *Scientific American*, v. 241, p. 43-51.
- Maahs, H.G., 1983a, Measurements of the oxidation rate of sulfur (IV) by ozone in aqueous solution and their relevance to SO₂ conversion in nonurban tropospheric clouds: *Atmospheric Environment*, v. 17, p. 341-345.
- 1983b, Kinetics and mechanism of the oxidation of S(IV) by ozone in aqueous solution with particular reference to SO₂ conversion in nonurban tropospheric clouds: *Journal of Geophysical Research*, v. 88, p. 10,721-10,732.
- Malinconico, L.L., 1979, Fluctuations in SO₂ emission during recent eruptions of Etna: *Nature*, v. 278, p. 43-45.
- Martin, L.R., 1983, Kinetic studies of sulfite oxidation in aqueous solution, in

- Calvert, J.G., ed., SO₂, NO, NO₂ oxidation mechanism: atmospheric considerations, v. 3, of Acid precipitation series: Boston, Butterworth, p. 63-100.
- Millan, M.M., Gallant, A.J., and Turner, H.E., 1976, The application of correlation spectroscopy to the study of dispersion from tall stacks: *Atmospheric Environment*, v. 10, p. 499-511.
- Millan, M.M., and Hoff, R.M., 1978, Remote sensing of air pollutants by correlation spectroscopy—instrumental response characteristics: *Atmospheric Environment*, v. 12, p. 853-864.
- Moore, J.G., and Fabbi, B.P., 1971, An estimate of the juvenile sulfur content of basalt: *Contributions to Mineralogy and Petrology*, v. 33, p. 118-127.
- Naughton, J.J., Lewis, V.A., Hammond, D., and Nishimoto, D., 1974, The chemistry of sublimates collected directly from lava fountains at Kilauea Volcano, Hawaii: *Geochimica et Cosmochimica Acta*, v. 38, p. 1679-1690.
- Noguchi, K., and Kamiya, H., 1963, Prediction of volcanic eruption by measuring the chemical composition and amounts of gases: *Bulletin Volcanologique*, v. 26, p. 367-378.
- Roberts, D.B., and Williams, D.J., 1979, The kinetics of oxidation of sulphur dioxide within the plume from a sulphide smelter in a remote region: *Atmospheric Environment*, v. 13, p. 1485-1499.
- Rose, W.I., Jr., 1977, Scavenging of volcanic aerosol by ash: atmospheric and volcanic implications: *Geology*, v. 5, p. 621-624.
- Russell, C., 1982, The effects of acid environments on metabolic gas exchange in *Usnea australis* Fr.: Honolulu, University of Hawaii, MS thesis, 131 p.
- Ryan, M.P., Koyanagi, R.Y., and Fiske, R.S., 1981, Modeling the three-dimensional structure of magma transport systems: Application to Kilauea Volcano, Hawaii: *Journal of Geophysical Research*, v. 86, p. 7111-7129.
- Sakai, H., Casadevall, T.J. and Moore, J.G., 1982, Chemistry and isotope ratios of sulfur in basalts and volcanic gases at Kilauea Volcano, Hawaii: *Geochimica et Cosmochimica Acta*, v. 46, p. 729-738.
- Stoiber R.E., Malinconico, L.L., and Casadevall, T.J., 1979, SO₂ monitoring by remote sensing at Kilauea Volcano, Hawaii [abs.]: Hawaii Symposium on Intraplate Volcanism and Submarine Volcanism, Hilo, HI, Abstract volume, p. 174.
- Stoiber R.E., Malinconico, L.L., and Williams, S.N., 1983, Use of the correlation spectrometer at volcanoes, in Tazieff, H., and Sabroux, J.C., eds., *Forecasting Volcanic Events*: Amsterdam, Elsevier, p. 425-444.
- Stoiber R.E., and Malone, G.B., 1975, SO₂ emission at the crater of Kilauea, at Mauna Ulu and at Sulfur Banks, HI [abs.]: *Eos*, v. 56, p. 461.
- Swanson, D.A., and Fabbi, B.P., 1973, Loss of volatiles during fountaining and flowage of basaltic lava at Kilauea Volcano, Hawaii; U.S. Geological Survey *Journal of Research*, v. 1, p. 649-658.
- Williams, D.J., Carras, J.N., Milne, J.W., 1981, The oxidation and long-range transport of sulphur dioxide in a remote region: *Atmospheric Environment*, v. 15, p. 2255-2262.
- Winner, W.E., and Mooney, H.A., 1980, Response of Hawaiian plants to volcanic sulfur dioxide: stomatal behavior and foliar injury: *Science*, v. 210, p. 789-791.
- Woodcock, A.H., 1960, The origin of trade-wind orographic shower rains: *Tellus*, v. 12, p. 315-326.
- Wright, T.L., 1984, Origin of Hawaiian tholeiite: a metasomatic model: *Journal of Geophysical Research*, v. 89, p. 3233-3252.