Only sample 2 (1.8 km) had a significant quantity of ash or detectable elements above the blank values, whereas other samples yielded data only for elements of marine origin. The relative composition of both the 1.8-km and the 1.5- to 5.5-km filter samples is the same for all of the elements measured except for some rare-earth elements, which have relatively large analytical errors. So that we might better interpret these data, we calculated enrichment factors with respect to Al, relative to Taylor's (*5*) crustal values, as follows:

$$EF_{\text{crust}} = \frac{(\text{X/Al})_{\text{air}}}{(\text{X/Al})_{\text{crust}}}$$

where X and Al refer to the concentrations of the trace element of interest and of Al, respectively. Elements with enrichment factors close to unity are not strongly enriched relative to the earth's crust. Enrichment factors up to about 5 are probably due only to variations in the mineral makeup of the source material, in this case, the volcanic ejecta. Figure 1 shows the enrichment factors for the elements determined in the plume samples. Very few elements are enriched, and a few appear to be depleted. The lack of enrichment for the heavy elements may reflect the depletion of these elements in the magma of this volcano.

In contrast, studies of other volcanoes show that eruption plumes and fumaroles have very large enrichments (*6*), as much as 10^5 for the volatile elements Se, As, Sb, Cl, and Br. For Soufriere, the highest enrichments are factors of only 20 to 40 for Sb and Cl, with only detection limits for Se and As. These results indicate that the aerosols sampled by the aircraft were predominantly of ash dispersed into the atmosphere, with little or no chemical fractionation taking place. This same result was observed for the plume from the eruption of Mount St. Helens on 18 May 1980 (*7*). Plumes formed by phreatic or magmatic-phreatic eruption may be expected to have major contributions of airborne ash and only minor amounts of volatile materials. On the other hand, plumes formed by truly magmatic eruptions, with little or no involvement of steam, might be expected to have a much larger quantity of volatile elements and therefore higher enrichments.

When one calculates the mass of ash from the trace-element measurements in the plume and the ash composition, the results are not totally in agreement with those obtained by ashing the filters and weighing the residue. This inconsistency is due either to inhomogeneities in the filter portions used or to a loss of material during the ashing procedure. In general, the composition of the plume-particulate sample is similar to that of the ash that fell on the island, but chemical differences due to some fractionation in the settling process changed the relative elemental composition slightly.

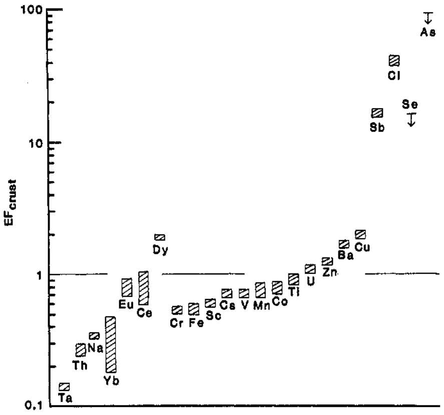

Fig. 1. Crustal enrichment factors for plume samples from the 17 April 1979 eruption of Soufriere, St. Vincent.

Analysis for the radioactive mother/daughter pair ^{210}Po and ^{210}Pb also failed to reveal an enrichment in the more volatile Po (^{210}Po/^{210}Pb = 0.25). Secular equilibrium would dictate a ratio of 1.0, and earlier measurements of magmatic gases in volcano plumes revealed ratios much greater than 1.0 (*8*). For Soufriere, we must conclude that the eruption plume is depleted in volatile elements.

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Volcanic Gases in the April 1979 Soufriere Eruption

Abstract. *Six gas samples from the 17 April 1979 Soufriere eruption plume were analyzed for carbonyl sulfide, carbon disulfide, carbon monoxide, carbon dioxide, methane, nitrous oxide, fluorocarbon-11, fluorocarbon-12, methyl chloroform, and carbon tetrachloride. Only carbon monoxide, carbon dioxide, carbonyl sulfide, and carbon disulfide were found to have increased mixing ratios as compared with those in clean tropospheric air, but the increases were not sufficient to contribute greatly to the global budgets of these four components.*

Whole-air samples were collected on a KC-135 aircraft mission near Soufriere, St. Vincent, on 18 April 1979, less than 24 hours after the 17 April eruption, which had been preceded by eruptions on 13 and 14 April. These samples have been analyzed by several gas chromatography techniques for carbonyl sulfide (COS), carbon disulfide (CS_2), carbon monoxide (CO), carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), fluorocarbon-12 (F-12 or CF_2Cl_2), fluorocarbon-11 (F-11 or $CFCl_3$), methyl chloroform (CH_3CCl_3), and carbon tetrachloride (CCl_4).

Two simultaneous samples were collected at each of three altitudes: 1800, 7300, and 9450 m. Methods of sample collection have been described in (*1*). Table 1 gives the flight times, latitudes, longitudes, and altitudes for each sample, as well as the results of the analyses of the gases. The amount of each component is reported as a dimensionless mixing ratio. Samples 1 and 2 were collected in the densest part of the plume, whereas sample pairs 3, 4 and 5, 6 were collected at higher altitudes, not necessarily entirely within the plume.

A gas chromatograph–flame photometric detector system (*2*) was used in analyzing for COS and CS_2. A 0.8-liter aliquot was transferred cryogenically for each sulfur-compound analysis. The samples were analyzed for CO, CO_2, and CH_4 with a gas chromatograph–flame ionization detector system and for N_2O, CF_2Cl_2, $CFCl_3$, CH_3CCl_3, and CCl_4 with a gas chromatograph–electron capture detector system (*3*).

To determine which of the measured species are of volcanic or partly volcanic

Table 1. Chemical composition of gases from the April 1979 Soufriere eruption plume; N.R., not reported (*9*).

Sample	F-12 (ppt)	F-11 (ppt)	CH_3CCl_3 (ppt)	CCl_4 (ppt)	N_2O (ppb)	CH_4 (ppm)	CO_2 (ppm)	CO (ppm)	COS (ppb)		CS_2 (ppb)	
									Analyzed August 1979	Analyzed November 1979	Analyzed August 1979	Analyzed November 1979
Altitude, 1800 m; 1650 to 1720 LCT; 13°N to 14°N, 61°W												
1	270	193	106	120	330	1.62	397	0.76	0.9	3.3	0.2	0.4
2	269	194	N.R.	132	333	1.59	378	0.77	1.0	0.8	0.2	0.3
Altitude, 7300 m; 1740 to 1810 LCT; 13°N to 11°N, 63°W to 58°W												
3	284	176	102	149	N.R.	1.57	361	0.68	N.R.	1.9	N.R.	0.5
4	293	194	114	142	N.R.	1.57	365	0.69	N.R.	3.0	N.R.	1.2
Altitude, 9450 m; 1810 to 1840 LCT; 11°N to 14°N, 58°W to 62°W												
5	283	163	115	137	N.R.	1.61	371	1.50	N.R.	1.8	N.R.	0.8
6	273	166	108	131	N.R.	1.60	406	1.65	N.R.	1.4	N.R.	0.4

Table 2. A comparison between the background mixing ratios and those of the volcanic plume.

Mixing ratio	F-12 (ppt)	F-11 (ppt)	CH_3CCl_3 (ppt)	CCl_4 (ppt)	N_2O (ppb)	CH_4 (ppm)	CO_2 (ppm)	CO (ppm)	COS (ppb)	CS_2 (ppb)
Expected background	279 ± 5	178 ± 5	110 ± 6	140 ± 7	331 ± 1	1.55 ± 0.02	340 ± 7	0.2 ± 0.1	0.5 ± 0.2	0.2 ± 0.1
Observed plume	279 ± 10	181 ± 5	109 ± 5	135 ± 10	332 ± 1	1.57 ± 0.02	380 ± 18	0.7 to 1.7	0.2 to 3.3	0.2 to 1.2

origin, the measured mixing ratios are compared in Table 2 with the normally expected burdens in clean tropospheric air (background) for the appropriate time and place. For example, F-12 has both a latitudinal gradient and an increasing burden with time (*4*). The mixing ratio of F-12 increased 10.9 percent from December 1977 to December 1979. The regression line for F-12 as a function of time for ground-level measurements at 47°N was

$$y = 266.8 + 0.28x$$

where y is the F-12 mixing ratio in parts per trillion and x is the time in weeks (week 1 starts on 17 December 1977). The latitudinal gradient for this component has also been measured. The regression line calculated from data collected in September 1979 was

$$y = 285.5 + 0.078x$$

where y is the F-12 mixing ratio in parts per trillion and x is the degrees of latitude between the intertropical convergence zone (about 5°N in this case) and 50°N. The expected background value reported for F-12 in Table 2 has been selected on the basis of a comparison of this and other similar data. The expected background values in Table 2 for F-11, CH_3CCl_3, CCl_4, and N_2O have been similarly obtained from the same measurement programs that provided the comparison data for F-12. The mixing ratios of N_2O and CCl_4 have not been observed to change by more than ±2 ppb or ±10 ppt, respectively, over several years time. For CH_3CCl_3, on the other hand, there has been both a significant latitudinal gradient and an increase with time. The behavior of F-11 in the atmosphere has been similar to that of F-12.

Table 2 shows that none of these five components has exhibited significant increases in the mixing ratios in the volcanic plume. This observation is in keeping with the generally accepted fact that most of the emissions of the halocarbons are of anthropogenic origin, whereas N_2O is a predominantly naturally emitted atmospheric constituent resulting from microbial action.

The expected background values of the remaining components listed in Table 2 have been obtained from measurements made by investigators at Washington State University. These measurements are in agreement with values reported in the literature (*5*).

Of the five remaining gaseous atmospheric components measured in these samples (CH_4, CO_2, CO, COS, and CS_2), CH_4 is the only one that does not appear to be present in amounts greater than those expected in the free troposphere (Table 2). However, the degree to which the CO, CO_2, COS, and CS_2 values are increased does not suggest that this volcanic event made any major contributions to the global budgets of these four constituents. The CO_2 mixing ratio is increased by only about 10 percent, and the CO, COS, and CS_2 mixing ratios increased a maximum of six to eight times. These data support earlier indications (*6*) that volcanoes represent a minor source of COS on a global basis. The emissions of CS_2 and COS clearly are orders of magnitude less than that of SO_2 (*6*). This fact is in agreement with recent conclusions about H_2S and COS (*6*). The major interest in this respect centers around whether the sulfur transported to the stratosphere in large explosive events in compounds other than SO_2 need be considered relative to stratospheric aerosol formation (Junge layer). These scanty data do not permit flux measurements to be made, but the conclusion must be that only a small proportion of the sulfur in volcanic emissions is carried by these gaseous compounds.

Although higher altitude aerosol samples had a much lower ash content, comparable mixing ratios for COS, CS_2, CO, and CO_2 were found at all altitudes sampled. This behavior was also observed for the sulfate measured in the aerosol samples (*7*). Insufficient three-dimensional sampling of the volcanic plume prevented a decision on whether the ash and gaseous plume separation is due to (i) vertical fractionation, (ii) horizontal fractionation caused by changes in the nature of ejected material during the course of the eruption coupled with subsequent differing downwind movement, or (iii) depletion of gaseous components in areas of high ash content due to the adsorption of the gases onto the ash. Large amounts of COS and CS_2 have been observed to be desorbed from Mount St. Helens ash on heating (*8*). The sulfur carried in the aerosol as sulfate [the range is 0.5 to 1.5 ppb (by volume) when converted from parts per billion (by mass) as reported in (*7*)] is comparable with the sulfur carried in the plume gases as COS and CS_2.

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Stratospheric Nitrogen Dioxide in the Vicinity of Soufriere, St. Vincent

Abstract. *In April 1979, measurements of nitrogen dioxide in the upper atmosphere were made near Soufriere Volcano by twilight optical-absorption techniques. The derived value of 5 × 10^{15} molecules per square centimeter column implies an enhancement of 25 percent over earlier abundances measured in the same latitudinal regions. This enhancement may represent the normal stratospheric variability of nitrogen dioxide in the equatorial region but in any case may be considered an upper limit to the volcano's effect on the total nitrogen dioxide abundance.*

On 15 April 1979, a series of flights of a NASA P-3 aircraft, coordinated with the SAGE (Stratospheric Aerosol and Gas Experiment) satellite, was scheduled in the vicinity of Barbados (13.03°N, 59.48°W) in order to investigate the possible stratospheric effect of the 13 to 14 April series of volcanic eruptions of Soufriere. The first flight was on 17 April; the major eruption of the volcano took place while the aircraft was airborne and headed toward St. Vincent. The flight plan consisted of a series of circles taken around the volcano, outside the region of the plume.

During the next 2 days, additional flights were made in an attempt to deduce the drift pattern and altitudinal extent of the volcanic aerosols in the atmosphere at and above the level of the aircraft. Unfortunately, it was quite cloudy during this whole period. As the NO_2 measurements obtained from the visible spectrophotometer required clear skies or at least uniform cloud coverage, subsequent NO_2 measurements were made on the ground in Barbados just before each aircraft flight on 18 and 19 April. The aerosol results from the lidar (light detection and ranging) measurements and the in situ quartz crystal microbalance cascade impactor are reported in (*1*) and (*2*).

The absorption features of the NO_2 molecule cover a large region of the visible spectrum. The most intense absorption bands are in the region from 4250 to 4550 Å and are easily accessible by means of modern spectrophotometric systems. Noxon *et al.* (*3*) made a detailed study of the observed twilight absorption by NO_2. They obtained a series of curves relating the relative absorption (between the maximum absorption near 4395 Å to the minimum absorption near 4420 Å) to the solar zenith angle for different model NO_2 height distributions at a fixed total abundance of 1.1 × 10^{16} molecules per square centimeter column. We scaled the data obtained in our program to the height profile curves taken from Noxon *et al.* (*3*), as corrected by Noxon (*4*), to deduce the NO_2 abundance.

To obtain the amount of absorption at each solar zenith angle, we used essentially the technique of Noxon *et al.* (*3*) and an instrument with 3-Å resolution. The zenith scattered light versus wavelength for the sun at a zenith angle of less than 75°, where there is little NO_2 absorption (less than 0.5 percent) because of the small optical depth, was divided point by point into data obtained at higher solar zenith angles. A smooth line drawn through the resultant curve determines the percent absorption of each of the three absorption maxima of NO_2 in this wavelength region.

The flight data for 5 April near 37°N, for 12 to 14 April south of the equator, and for 17 April near the volcano, as well as the 18 and 19 April ground-based observations in Barbados, show a considerable degree of scatter with respect to any NO_2 height profile. Figure 1 presents the data obtained for the 17, 18, and 19 April evening twilights. The percent absorption scale was varied to make these data points fall within the group of altitude curves given by Noxon *et al.* (*3*). We then used the relative scale factor together with the total abundance of 1.1 × 10^{16} molecules per square centimeter column, used to produce Noxon's curves, to deduce the abundance that would produce the observed data points. Although it is difficult to select a specific representative altitude curve for these data points, the curve should be the same for the three data sets obtained here, because we do not expect much of a latitudinal variation in the height distribution for this time of the year (*5*). The percent absorption obtained in the three latitudinal regions translates into various total amounts of NO_2 at each latitude. We plotted these values as large black dots on the graph of latitudinal variation in NO_2 observed by Noxon (*5*) [corrected by Noxon (*4*)] (Fig. 2). We have also included in Fig. 2 similar NO_2 data obtained on another SAGE-coordinated series of flights at high latitudes in July 1979.

Our data for 5 April and for 12 to 14 April are higher than Noxon's by about a factor of 1.4. This difference could be

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