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► **To cite this version:**

D Martin, I B Ardouin, G. Bergametti, J Carbonnelle, R Faivre-Pierret, et al.. Geochemistry of Sulfur in Mount Etna Plume. *Journal of Geophysical Research*, 1986, 91, pp.249 - 261. hal-02326728

**HAL Id: hal-02326728**

**<https://hal.science/hal-02326728v1>**

Submitted on 22 Oct 2019

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## Geochemistry of Sulfur in Mount Etna Plume

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Aircraft measurements of sulfur compounds and trace elements including Po<sup>210</sup> were carried out in the plume of the Mount Etna volcano, at distances 10 to 260 km from the crater. The experiment was performed in September 1983 following the large lava emission of March–August 1983. Trace elements, particularly Po<sup>210</sup> and Si, were measured with the aim of calculating their atmospheric dilution and evaluating their outputs. This study enabled us to determine the SO<sub>2</sub> to SO<sub>4</sub> conversion rates to be between  $2.2 \times 10^{-6}$  and  $4.0 \times 10^{-5} \text{ s}^{-1}$  in a cloud free anticyclonic situation. The main process of SO<sub>2</sub> removal in a volcanic plume should be a heterogeneous process of adsorption of this gas onto large particles. Emission fluxes of SO<sub>2</sub> were found to vary between 27 and 38 kg s<sup>-1</sup>, leading to a mean Po<sup>210</sup> output of 0.4 Ci/d.

### 1. INTRODUCTION

SO<sub>2</sub> is one of the most important constituents of the dry gases emitted by active volcanoes. Understanding of the output of this gas is therefore an important step to characterize their magmatic activity [Friend *et al.*, 1982; Rose *et al.*, 1982; Casadevall *et al.*, 1983]. The climatological impact of SO<sub>2</sub> is mainly due to its subsequent transformation into sulfate aerosols, which are able to modify the radiative balance of the atmosphere. Moreover the flux of trace elements injected into the atmosphere from volcanoes is frequently evaluated by reference to the SO<sub>2</sub> flux [Carbonnelle *et al.*, 1978; Buat Menard and Arnold, 1978; Quisefit *et al.*, 1982; Bandy *et al.*, 1982]. In such a calculation it is obviously necessary to take into account the rate of SO<sub>2</sub> loss by any process and, more particularly, by oxidation. Therefore the kinetic constant of SO<sub>2</sub> oxidation is a fundamental figure for evaluating the influence of volcanoes in the physicochemistry of the atmosphere.

In a previous work by Jaeschke *et al.* [1982] the dilution of the Etna plume was evaluated by comparing the concentration of CO<sub>2</sub> (considered as chemically inert) to its initial value, after deduction of the mean background atmospheric concentration. However, it may be pointed out that a small variation of this background figure leads to significant errors in determining the dilution. In addition, it was shown by Carbonnelle *et al.* [1981] that CO<sub>2</sub> is injected into the atmosphere not only from the Etna crater, but from a large part of the nearby mountain mass. For both these reasons, during the experiments further described, we preferred to evaluate the dilution of the Etna plume by two very different methods. Besides gases such as SO<sub>2</sub> and CO<sub>2</sub>, volcanic plumes are rich in trace metals present as aerosols. These aerosols are either emitted as ashes and magma spray, the composition of which

is similar to that of magma, or arise from gas to particle conversion of volatile materials emitted as vapors and are characterized by high enrichment factors [Vie Le Sage, 1983; Phelan *et al.*, 1982]. The abundance of a given element in different parts of the plume enables us to evaluate its dilution, since its possible chemical transformations do not interfere. Such a method is based upon the assumption that the aerosol residence time is very long compared with the transit time between the crater and the sampling point [Horst, 1977; Lambert *et al.*, 1983]. This hypothesis will be discussed later (see section 3). Two different elements were used simultaneously: silicon, which is abundant in volcanic emissions [Vie Le Sage, 1983], and polonium 210, since this nuclide is considerably more concentrated in a volcanic plume than in the ambient air, according to Lambert *et al.* [1979].

During a series of measurements performed by aircraft in the Etna plume in 1983, a set of data on the plume dilution and its SO<sub>2</sub> concentration was obtained. These data enabled us to calculate the oxidation rate of SO<sub>2</sub> and to evaluate the output of this gas and of several trace elements by comparing the element concentrations to that of SO<sub>2</sub>.

### 2. SAMPLING AND MEASUREMENT TECHNIQUES

The aircraft utilized was a twin engine Piper Seneca II, flying at a speed of about 100 knots (50 m s<sup>-1</sup>) during the experiment. A good determination of altitude and geographical position was possible with instruments on board.

Sampling was completed using three types of equipment: (1) a meteorological probe fixed under the right wing, making continuous measurements of wet and dry temperatures, (2) a correlation spectrometer (Cospec IV) for remote sensing of the integrated concentration path length of SO<sub>2</sub>, and (3) an isokinetic probe shown in Figure 1 for sampling gases and particles.

Wind and temperature data were obtained from radiosoundings at Trapani (West Sicily).

#### Sampling Line

The sampling line is a 20-mm ID Teflon (PTFE) tube, the aperture of which consists of an isokinetic probe of 10 mm diameter, made of chemically treated stainless steel and situated 1.5 m in front of the nose of the aircraft, outside of the boundary layer. The probe is, according to our calculation, in isokinetic conditions at a velocity of 50 m s<sup>-1</sup>, with a flow rate of 15 m<sup>3</sup> h<sup>-1</sup>. A schematic diagram of the installation is shown in Figure 1.

Laboratory experiments have been performed to measure the rate of collection of neutral and charged aerosols through

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Paper number 5B5712.  
0148-0227/86/005B-5712\$05.00

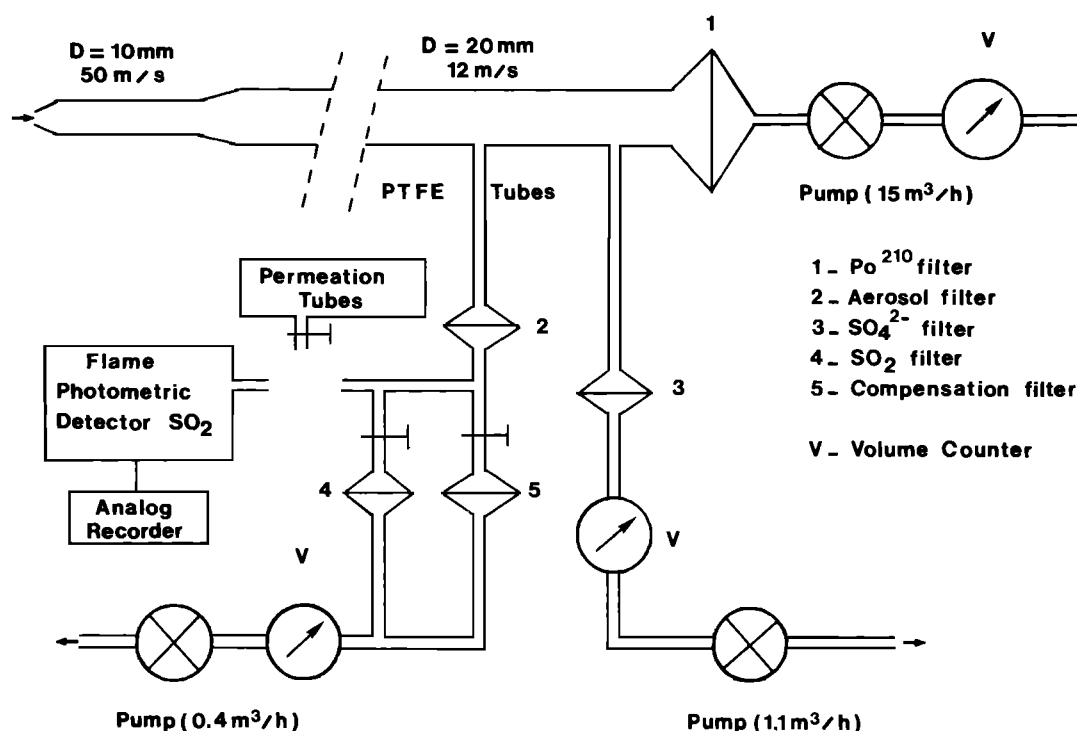


Fig. 1. Schematic diagram of the onboard instrumentation.

the Teflon line. It has been shown [Burghoffer and Charuau, 1985] that 75% ( $\pm 5\%$ ) of the 1.4- $\mu\text{m}$  monodispersed neutral aerosol and only 50% of the 1.4- $\mu\text{m}$  electrically charged aerosol are collected on the filter. The collection rates decrease to 15% for 5- $\mu\text{m}$ -diameter particles. The isokinetic probe was controlled qualitatively by two aerosol electric mobility analyzers, one on the top of a water tank in a rural area and the other in the aircraft flying at the same altitude, by low wind velocity. For aerosol diameters of 0.01 to 1  $\mu\text{m}$ , we found good agreement between both measurements. Assuming that mineral aerosols ( $\text{SO}_4$ , Si, Fe, etc.) are neutral and of appropriate size and that the  $\text{Po}^{210}$  aerosols are positively charged (J. Charuau, personal communication, 1984), the measured aerosol concentrations reported here are then minimum values, 75% and 50%, respectively, of the true concentrations.

#### Aerosol Sampling and Analysis Techniques

Two types of filters were used for aerosol collection. The samples devoted to elemental and ionic analysis were collected by filtration on 0.4- $\mu\text{m}$  Nucleopore filters, which have an efficiency of 90% for particle diameters as small as 0.04  $\mu\text{m}$ . The sampling time was about 1 hour, at a flow rate of about 1  $\text{m}^3 \text{h}^{-1}$ .

The elemental analyses have been performed by wavelength dispersive X ray fluorescence spectrometry (Compagnie Générale de Radiologie  $\alpha 10$ ) according to the method described by Elichegaray *et al.* [1981]. Afterwards, the samples were washed for 1 day in deionized water in a mechanical stirrer. Complementary analyses have been made by ion chromatography (Cunow C403), consisting of an anionic

TABLE 1. Results of Etna Aircraft Measurements in 1983

Date	Sample	Sampling Level, m	Sampling Distance From Etna, km	$\text{SO}_2$ Filter Measurement, $\text{mg m}^{-3}$	$\text{SO}_2$ Meloy Measurement, $\text{mg m}^{-3}$	$\text{SO}_4$ , $\mu\text{g m}^{-3}$	Total Particulate Sulfur, $\mu\text{g m}^{-3}$	$\text{Po}^{210}$ , dph $\text{m}^{-3}$	Si, $\mu\text{g m}^{-3}$
Sept. 22, 1983	blank	2900	9 to 150	N.D.	0.02	1.2	0.2		0.89
	4	2900	155	N.D.	0.22	N.D.	N.D.	5.3	N.D.
	5	2835	257	N.D.	0.08	3.7	1.5	2.3	2.1
Sept. 23, 1983	6	3230	9	0.53	0.55	6.8	3.2	8.1	1.39
	7	3050	276	0.35	0.26	5.4	2.1	4.4	0.49
	blank	3500	10 to 150	0.01	0.02	0.5	0.1	0.3	2.48
Sept. 25, 1983	8	3500	11	1.86	1.26	9.1	4.1	27.5	17.22
	10	3780	164	0.36	0.39	4.8	2.1	12.1	5.97

Concentrations are given for local  $\text{m}^3$  (without P or T corrections). N.D., not determined; dph, disintegration per hour.

TABLE 2. SO<sub>2</sub> Loss Rates (s<sup>-1</sup>)

Date	Dilution Coefficient	Transfer Time, hours	k Mean Value, s <sup>-1</sup>
Sept. 22, 1983	0.44	4.9	8 × 10 <sup>-6</sup> (M)
Sept. 23, 1983	0.54	14.8	3.7 × 10 <sup>-6</sup> (F) 2.2 × 10 <sup>-6</sup> (M)
Sept. 25, 1983	0.44	5.6	4.0 × 10 <sup>-5</sup> (F) 1.8 × 10 <sup>-5</sup> (M)

F, from SO<sub>2</sub> filter measurements; M, from SO<sub>2</sub> Meloy measurements.

column (Vidal 302IC4.6) for the determination of sulfates and chlorides.

The aerosols collected for Po<sup>210</sup> measurements were sampled on Poellman-Schneider cellulose filters, with a flow rate of 15 m<sup>3</sup> h<sup>-1</sup> for about 1 hour. The Po<sup>210</sup> analysis by gross α counting has been described elsewhere [Polian and Lambert, 1979]. The uncertainties in the analytical and volumetric determinations are less than 15%. Pressure and temperature corrections (less than 3%) have not been performed.

#### SO<sub>2</sub> Sampling and Analysis

SO<sub>2</sub> was measured by two methods. First, a zinc acetate filter was used to collect SO<sub>2</sub> gas, and a colorimetric method was used for SO<sub>2</sub> chemical analysis [Faivre-Pierret, 1983]. Next, a continuous analysis of SO<sub>2</sub> using a flame photometric detector (FPD) was made. The sampled air was prefiltered. The detector, being nonspecific, indicated the concentration of sulfur in the gaseous state, which is assumed to be essentially SO<sub>2</sub> [Berresheim and Jaeschke, 1983; Bandy et al., 1982; Jaeschke et al., 1982].

The range of concentrations measured was from 0.01 to 4 mg m<sup>-3</sup>. A calibration was made before each flight using three permeation tubes, which generated known concentrations of SO<sub>2</sub>. Previous tests showed a good stability of the measurements. We also tested the influence of altitude and compensated for the decay of the baseline due to pressure decrease with altitude during the flight. The pressure was found to have no influence on the SO<sub>2</sub> measurements. A filter was put in parallel with the SO<sub>2</sub> filter for pressure balancing because of the high sensitivity of the FPD to pressure. In both devices the measurement accuracy is about ±15%.

### 3. EXPERIMENTS AND RESULTS

The field experiments were made during the daytime on September 21, 23, and 25, 1983, following an important period of lava flow in March–August 1983 [Romano, 1983]. On September 25 an “ash deposit” was observed as far away as the city of Catania.

During the experiment, Sicily was under the influence of an anticyclonic center situated to the west of the Mediterranean Basin, giving N and NE sector winds. A subsidence inversion at 2300 m altitude prevented convective exchanges between the boundary layer and the free troposphere. Consequently, there was no interaction between the Etna plume and the industrial emissions from Catania and Syracuse. The sky was clear and cloud free. The relative humidity of ambient air was very low (less than 20%), implying a relative humidity inside the plume of about 45–60% (see Table 1).

Two complete sets of SO<sub>2</sub> and aerosol concentrations were measured on September 23 and 25; they are shown in Table 1, together with data recorded on September 22.

#### Dilution Coefficients

Under the assumption that aerosol removal is negligible during the short atmospheric travel time (0.4 to 15.3 hours, compared with residence times of 5 to 35 days evaluated by Slinn [1983] for particles of less than 10 μm diameter), the dilution coefficient *D* can be directly deduced from the concentration ratios of a trace element at two different sampling sites.

On September 23 the dilution between 9 and 276 km from the crater is found to be 0.49/1.39 = 0.35 for silicon and 4.4/8.1 = 0.54 for Po<sup>210</sup>. The dilution on September 25 between 11 and 164 km is 5.97/17.22 = 0.35 for silicon and 12.1/27.5 = 0.44 for Po<sup>210</sup>. The value on September 22 for Po<sup>210</sup> between 155 and 257 km is 2.3/5.3 = 0.44.

The values deduced for both elements are comparable, although the silicon values are systematically smaller. This difference is attributed to the fact that silicon is mainly a terrigenous element in volcanic plumes and that the presence of large silicon particles cannot be ruled out. By contrast, Po<sup>210</sup> aerosols are certainly mostly produced by gas-to-particle conversion and are therefore preferentially fixed on the finest aerosol component, as indicated by measurements of the size distribution of volcanic Po<sup>210</sup> using cascade impactor (G. Lambert, unpublished results, 1983).

Thus in the following discussion, we use the dilution coefficients given by Po<sup>210</sup>. It is worthwhile to point out that these dilution coefficients should not be compared with one another.

TABLE 3. Measured and Corrected Fluxes of SO<sub>2</sub>

Date	Distance From the Crater, km	Transit Time, hours	Wind Velocity, m s <sup>-1</sup>	<i>k</i> , s <sup>-1</sup>	SO <sub>2</sub> Measured Fluxes, kg s <sup>-1</sup>	SO <sub>2</sub> Corrected Fluxes, kg s <sup>-1</sup>
Sept. 22, 1983	9	0.35	7	8 × 10 <sup>-6</sup>	31	31
Sept. 23, 1983	9	0.50	5	3 × 10 <sup>-6</sup>	26	26
Sept. 25, 1983	11	0.40	7.5	30 × 10 <sup>-6</sup>	38	39
	164	6	7.5	30 × 10 <sup>-6</sup>	31	58

The corrected fluxes are calculated using the formula  $F_{\text{SO}_2}^c = F_{\text{SO}_2}^{\text{mea}} \exp(kt)$ . SO<sub>2</sub> fluxes are given ±20% except the measurement made at 164 km, which is calculated from only one flight traverse, and for which the accuracy is lower, of the order of ±40%.

TABLE 4. Elemental Aerosol Concentrations ( $\mu\text{g m}^{-3}$ )

Date	Sample	Distance From Source, km	Po <sup>210</sup> , dph m <sup>-3</sup>	Si	Al	P	Cl	Cl <sup>-</sup>	K	Ca	Ti	Fe
Sept. 22, 1983	blank			0.89	0.19	0.04	0.15	0.20	0.05	0.04	0.05	0.3
Sept. 25, 1983	blank		0.3	2.48	0.17	0.03	0.13	0.17	0.05	0.03	0.04	0.3
Sept. 23, 1983	6	9	8.1	1.39	0.25	0.05	1.25	1.20	2.55	0.24	0.02	0.23
Sept. 25, 1983	8	11	27.5	17.22	7.63	0.32	0.33	0.2	2.01	4.04	0.47	3.53
Sept. 25, 1983	10	164	12.1	5.97	2.73	0.12	0.08	0.2	0.66	1.34	0.17	1.28

Here, dph is disintegration per hour.

In effect, the gaseous emissions from an active volcano are essentially discontinuous, and even after long-range transport the plume could be heterogeneous, depending on atmospheric stability.

#### SO<sub>2</sub> Loss Rate

Most of the physical and chemical processes described for explaining the removal of atmospheric SO<sub>2</sub> assume first-order reactions [Moller, 1980; Turco et al., 1979]. The variation of SO<sub>2</sub> concentration with time can be written as follows:

$$(\text{SO}_2)_t = D(\text{SO}_2)_{t_0} \exp(-kt)$$

where  $D$  is the dilution coefficient and  $k$  the loss rate. The five sets of data given in Table 1 lead to the values of  $k$  shown in Table 2.

It is clear that the SO<sub>2</sub> loss rate is not at all constant from one day to another. For instance, the values found on September 23 are extremely low, of the order of  $1 \times 10^{-6} \text{ s}^{-1}$ , which is comparable to the value indicated in the case of homogeneous gas phase conversion [Moller, 1980; Turco et al., 1979; McKeen et al., 1984]. The higher values on the other 2 days may correspond to the existence of heterogeneous processes working in addition to the homogeneous reactions. In effect, on September 25, the plume was particularly rich in particles, as shown by analysis of its elemental composition.

It is noteworthy that Jaeschke et al. [1982] found values of  $1.7 \times 10^{-4}$  and  $5 \times 10^{-4} \text{ s}^{-1}$ , which are about 1 order of magnitude larger than ours. This discrepancy could be accounted for either by the fact that our measurements were performed farther from the crater than theirs (0–20 km), where coarse particles were possibly present, or by the low accuracy

of measurements due to their use of CO<sub>2</sub> as a dilution tracer [Carbonnelle et al., 1981].

At this stage we must emphasize that we have poor knowledge of the actual SO<sub>2</sub> removal processes. However, there is a general agreement that the final product of SO<sub>2</sub> transformation is SO<sub>4</sub>. Therefore a significant loss of SO<sub>2</sub> should result in a corresponding increase of SO<sub>4</sub> concentration in order to balance the sulfur budget, an important topic to be examined in an later section.

#### SO<sub>2</sub> Flux

The principle of the Cospec method, described by Stoiber et al. [1983] and classically utilized for evaluating volcanic outputs [Zettwoog and Haulet, 1978; Malinconico, 1979; Friend et al., 1982; Casadevall et al., 1983; Stoiber et al., 1983], consists of simultaneous measurement of the SO<sub>2</sub> concentration path length integrated along a vertical plume section and the wind velocity at the same place. The results of our study are shown in Table 3, in which the SO<sub>2</sub> values were corrected for losses by using the values of  $k$  indicated in Table 2. It is clear that, due to the low values of  $k$ , the corrections are generally small at distances from the crater of the order of 10 km. On the contrary, in the range of 100–200 km, it is necessary to make this correction. The observed variations of the flux are due to discontinuous emissions from the volcano. In previous studies, Zettwoog and Haulet [1978], Malinconico [1979], and Faurie-Pierret et al. [1980] found mean values of the order of 2000 to 6000 tons per day, which are comparable to our findings.

#### Particulate Matter Flux

The particulate matter flux may be calculated from the concentration ratio of a given element to that of SO<sub>2</sub>, multiplied by the SO<sub>2</sub> flux at the same place. It is not necessary to take into account the SO<sub>2</sub> losses, as the SO<sub>2</sub> flux and concentration are measured simultaneously. The concentrations of the measured elements are shown in Table 4, and the fluxes in Table 5. These values agree rather well with results reported previously by Vie Le Sage [1983].

It is noteworthy that the flux values determined on September 25 are almost identical at 11 and 164 km from the crater, at least for the elements measured here. It is especially the case for sulfate aerosols and for silicon, which is obviously present as more or less complex silicates. Therefore it is clear that further than a few kilometers from the crater, the removal rate of the aerosols is very low. Consequently, it seems valid to use the small sized Po aerosols as a measurement of plume dilution.

TABLE 5. Atmospheric Particulate Matter Emissions From Etna Volcano

Element	September 23,	September 25	
	9 km	11 km	164 km
Po <sup>210</sup>	0.26	0.43	0.43
SO <sub>4</sub>	29	19.2	22.4
Si	5.9	35.9	28.2
Al	1.1	15.9	12.9
P	0.2	0.7	0.5
K	10.8	4.2	3.1
Ca	0.99	8.4	6.3
Fe	0.97	7.6	6.0
Ti	0.1	1.0	0.8

Values are tons per day, except Po<sup>210</sup>, which is in curies per day.

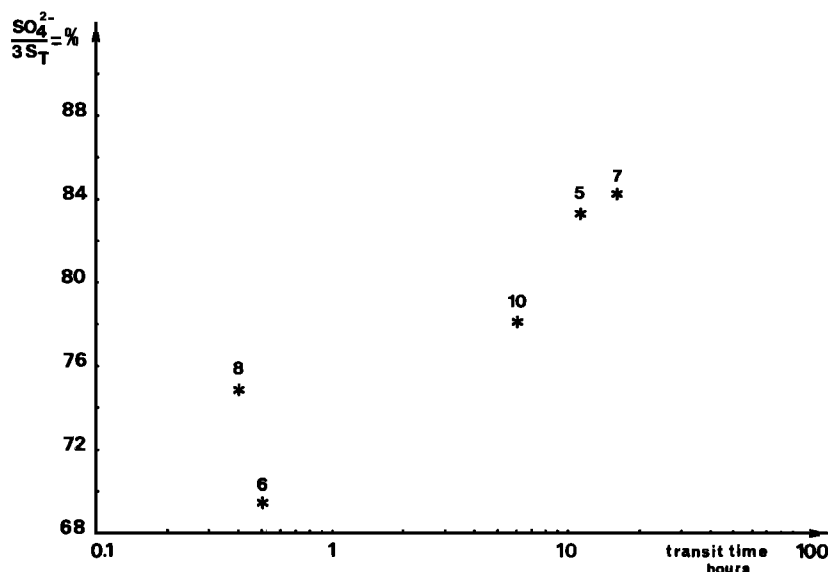


Fig. 2. Percentage of sulfur as  $\text{SO}_4$  relative to the total sulfur as particulates versus atmospheric travel time.

#### 4. CONCLUSION

##### Sulfate Puzzle

As mentioned above, particulate sulfur was measured in each experiment. It may be seen in Figure 2 that about 80% of this sulfur consists of  $\text{SO}_4$ , which is in agreement with the usual observations. In fact it may be observed in Figure 2 that the percentage of sulfur as  $\text{SO}_4$  in particulate sulfur increases with time lag between emission from the crater and sampling. This is consistent with the idea that  $\text{SO}_2$  losses are essentially due to its oxidation into  $\text{SO}_4$ . In such a case the sulfur budget should be balanced, which means that after correction for dilution (measured through the  $\text{Po}^{210}$  concentration) the concentration of total sulfur (gaseous and particulate) should be approximately constant. However, this is not what happened. In Table 6 we compare the loss of sulfur as  $\text{SO}_2$  and its increase as  $\text{SO}_4$ .

It appears that the loss is between 0 and  $230 \mu\text{g m}^{-3}$ , whereas the increase is less than  $1 \mu\text{g m}^{-3}$ . Sulfur losses have been computed by using filters and FDP measurements. On September 23 the low value of  $k$  ( $3 \times 10^{-6} \text{ s}^{-1}$ ) and the low flux emission of solid material are critical for the accuracy of

the  $\text{SO}_2$  filter measurements. On September 25, both measurements show a strong discrepancy between the total loss of sulfur as  $\text{SO}_2$  and its total increase as  $\text{SO}_4$ .

This discrepancy could be accounted for by a very short residence time of sulfate aerosols in the plume. The calculated values of the residence time are of the order of  $6 \times 10^{-2}$  to 1.7 hours. This result is in total disagreement with the values usually admitted, which are of the order of 1 week [Lambert *et al.*, 1983]. Moreover, we have pointed out previously that the aerosol fluxes are approximately constant during time intervals of the order of 10 to 15 hours. Therefore it seems that sulfate removal from the plume cannot account for the discrepancy.

Jaeschke *et al.* [1982] have also discussed this problem and concluded that data suggest aerosol residence times as short as 0.3 to 0.6 hours. Possible explanations could be the dry deposition of  $\text{SO}_4$  aerosols and the sedimentation of these particles. The first possibility is ruled out because the plume stayed at about 2800 m above sea level and above the temperature inversion, which prevented any exchange with the mixing layer; consequently, the plume could not reach ground level.

The sedimentation velocities of particles vary between  $0.014 \text{ cm s}^{-1}$  for  $1\text{-}\mu\text{m}$ -diameter particles and  $1.3 \text{ cm s}^{-1}$  for  $10\text{-}\mu\text{m}$  particles [Kasten, 1968]. This shows to what extent sedimentation could affect particles. Keeping in mind that particles with diameters larger than  $5 \mu\text{m}$  are collected with poor efficiency, it is reasonable to suggest that the missing sulfur was absorbed on larger particles.

This observation supports the idea that homogeneous  $\text{SO}_2$  to  $\text{SO}_4$  conversion, which should lead to sulfur concentration in small particles [Bonsang *et al.*, 1980], is not the dominant process, at least in a volcanic plume. The presence of sulfur in large particles could result from  $\text{SO}_2$  adsorption on these preexisting particles, according to the observations made in industrial desulfuration processes [Kyte, 1981]. This explanation is in agreement with the fact that the higher the particle concentration in the plume, the more important the sulfur losses, as can be seen by comparing the results obtained on September 23 and 25.

TABLE 6.  $\text{SO}_2$ - $\text{SO}_4$  Balance

Date and Distance	Dilution Coefficient	Sulfur Loss as $\text{SO}_2 = X$ , $\text{kg m}^{-3}$	Sulfur Income as $\text{SO}_4 = Y$ , $\text{kg m}^{-3}$
Sept. 23, 1983 $d_2 = 276 \text{ km}$ $d_1 = 9 \text{ km}$	0.54	$32 \times 10^{-3}*$	$0.58 \times 10^{-3}$
Sept. 25, 1983 $d_2 = 164 \text{ km}$ $d_1 = 11 \text{ km}$	0.44	$-18.5 \times 10^{-3}\dagger$ $-230 \times 10^{-3}*$	$0.26 \times 10^{-3}$
		$-82 \times 10^{-3}\dagger$	

$$X = (\text{SO}_2(d_2) - D \times \text{SO}_2(d_1)) \times M_s/M_{\text{SO}_2}; Y = (\text{SO}_4(d_2) - D \times \text{SO}_4(d_1)) \times M_s/M_{\text{SO}_4}, \text{ where } M_s \text{ and } M_{\text{SO}_2} \text{ are molecular weight.}$$

\*Filter measurements.

†FDP measurements.

**Acknowledgments.** The authors wish to thank J. Lebronec, D. Cheymol, and P. Borrel for technical assistance and the pilot, M. Beaulieu, for his understanding during the flights. Several other persons made helpful contributions, and we thank them warmly, particularly J. Dubois (EDF, Direction des Etudes et Recherches), G. Cara (IRV), M. Orlando (SIO), Cl. Daude (Ambassade de France), C. Manoni (Aviation Civile Italienne), R. Patane (Catania Airport), and the staff of the meteorological service of Catania. The authors are particularly grateful to M. Zephoris for many helpful discussions and to C. Regnault for typing the manuscript. The research was partly supported by CNRS/PIREN under grant 83/53 and CNRS/PIRP-SEV. CFR contribution 748.

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(Received July 8, 1985;  
revised January 30, 1986;  
accepted April 1, 1986.)