

# Reports

## Sulfur Dioxide Contributions to the Atmosphere by Volcanoes

**Abstract.** *The first extensive measurements by remote-sensing correlation spectrometry of the sulfur dioxide emitted by volcanic plumes indicate that on the order of  $10^3$  metric tons of sulfur dioxide gas enter the atmosphere daily from Central American volcanoes. Extrapolation gives a minimum estimate of the annual amount of sulfur dioxide emitted from the world's volcanoes of about  $10^7$  metric tons.*

The  $\text{SO}_2$  gas in the plumes of the volcanoes in Nicaragua, El Salvador, and Guatemala emitting plumes of water vapor and gas was measured during the fall of 1972. Two of the nine volcanoes, Santiaguito and Pacaya in Guatemala, were erupting lava; Pacaya was also erupting a small amount of ash. Gas emission appeared to be very strong at San Cristobal, Nicaragua, a volcano which had been dormant from 1635 until May 1971 when the period of strong gas emission began. At Masaya, Nicaragua, the prominent plume was rising from a hole in the frozen surface of the lava lake. The Momotombo, Nicaragua, plume was small. The plumes of Telica, Nicaragua, and Fuego, Guatemala, were small and intermittent.

Measurements of  $\text{SO}_2$  were made with a remote-sensing correlation spectrometer which monitors the absorption of selected wavelengths of the  $\text{SO}_2$  spectra in the ultraviolet regions. The gas from two Japanese volcanoes has been examined with this instrument: Mt. Mihara by T. Okita (1) and Mt. Asama by A. J. Moffat, T. Kakara, T.

Akitomo, and L. Langan (2). Estimates quoted in company literature are 345 metric tons per day at Mt. Mihara (one traverse) and 142 tons per day at Mt. Asama (three traverses).

The principles of correlation spectrometry as exemplified by the  $\text{SO}_2$  correlation spectrometer have been described by Moffat and Millan (3). The instrument consists of telescopes to collect light, a grating spectrometer, an exit mask or correlator, and an electronics system. The correlator is a rotating disk containing two separate reference spectra which are matched against the incoming spectrum. The modulated light signal so produced is monitored by a photomultiplier tube. The amplitude of this modulated signal, when processed by the electronics, is proportional to the number of  $\text{SO}_2$  molecules in the gas cloud, and has the dimensions parts per million multiplied by meters (ppm-m). The data are usually read to the nearest 10 ppm-m. A cell with a known  $\text{SO}_2$  concentration is used as a standard to calibrate the instrumental response. The clear daytime sky is used as the radiation source. Variations which occur in the ultraviolet light level while measurements are being made are compensated for by an automatic gain control.

Measurements were made from distances up to 3 km. The plumes were observed just above the crater and as far as 9 km downwind from the crater.

Measurements were recorded on a strip chart while the optical telescope was moved through the total width of the plume containing the  $\text{SO}_2$  gas to give the concentration of  $\text{SO}_2$  in parts per million multiplied by the cross sec-

tion of the plume in square meters ( $\text{ppm-m}^2$ ). The wind velocity of a horizontal plume or the velocity of a vertically rising plume was multiplied by the  $\text{ppm-m}^2$  value and by the density of  $\text{SO}_2$  gas to give the mass of  $\text{SO}_2$  emitted per unit of time.

Transects of the volcano plumes can be made in three ways:

1) *Traverse.* The correlation spectrometer may be transported by car under the plume so that a continuous record is obtained. The area under the voltage-distance curve thus generated is proportional to the  $\text{ppm-m}^2$   $\text{SO}_2$  value.

2) *Horizontal transect.* After a vertical plume has been sighted just above a crater, the telescope is moved through a horizontal angle across the plume.

3) *Vertical transect.* A plume that is being blown horizontally from the crater can be measured by a sweep through a vertical angle.

The traverse method was used in making the measurements of  $\text{SO}_2$  in volcanic gas in Japan. This method is also used in power plant monitoring, but in Central America the other methods are used most often—because roads either are nonexistent or are too far from the base of the volcano. The correlation spectrometer together with auxiliary equipment is frequently packed into the measurement sites in three packages of 20 kg each. The equipment is reasonably rugged, but under the rigors of field use the electronics require adjustment by trained personnel as well as spare parts not locally available.

Measurements were made of each plume on as many as 5 days and as few as 1 day. One hundred twenty-five transects of these plumes provided data from which the  $\text{SO}_2$  emission was calculated (Table 1). The larger plumes carried about 300 tons of  $\text{SO}_2$  per day, smaller plumes about one order of magnitude less. The plumes which were visibly larger contained more  $\text{SO}_2$ . The precision of measurement was variable owing to variations in several factors including wind measurements, unequally appropriate measurement sites, and short-term changes in the rate of emission of  $\text{SO}_2$ .

Measurements from Pacaya and Santiaguito volcanoes are representative of the standard deviation and standard error of other sets of measurements from other volcanoes. The  $\text{SO}_2$  emission from Pacaya, measured one day from 11 vertical transects across the plume 900 m from the cra-

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*Scoreboard for Reports:* In the past few weeks the editors have received an average of 68 Reports per week and have accepted 12 (17 percent). We plan to accept about 12 reports per week for the next several weeks. In the selection of papers to be published we must deal with several factors: the number of good papers submitted, the number of accepted papers that have not yet been published, the balance of subjects, and length of individual papers.

Authors of Reports published in *Science* find that their results receive good attention from an interdisciplinary audience. Most contributors send us excellent papers that meet high scientific standards. We seek to publish papers on a wide range of subjects, but financial limitations restrict the number of Reports published to about 15 per week. Certain fields are overrepresented. In order to achieve better balance of content, the acceptance rate of items dealing with physical science will be greater than average.

ter, averaged 312 tons per day. The standard deviation as a percentage of the mean is 22 percent. The standard error of the mean is 7 percent. The SO<sub>2</sub> emission data from 16 horizontal transects of the plume from crater Caliente, Santiaguito, on a single day had a standard deviation of 36 percent and a standard error of the mean of 9 percent. On another day the standard deviation of 13 transects of crater Caliente was 35 percent and the standard error of the mean was 10 percent.

The total amount of SO<sub>2</sub> emitted by Central American volcanoes (Table 1) is 1300 tons per day. If the standard errors and the standard deviations involved in the measurements are considered, one concludes that quiescent volcanoes with noticeable vapor plumes emit on the order of 10<sup>2</sup> tons of SO<sub>2</sub> per day, similar to the amount produced by an average coal-burning, power-generating station. Volcanoes with small plumes emit an order of magnitude less. We estimate that 10<sup>3</sup> tons of SO<sub>2</sub> per day was emitted during October through December 1972 in Nicaragua, El Salvador, and Guatemala. This would correspond to between 10<sup>5</sup> and 10<sup>6</sup> tons of SO<sub>2</sub> emitted per year at this rate. The emission of 10<sup>2</sup> tons of SO<sub>2</sub> per day from a volcano would extract the sulfur needed to form a 10<sup>6</sup>-ton sulfide ore body with 50 percent sulfur in 25 years. Emitted under water, the sulfur might have formed a Kuroko type massive sulfide deposit. The economic geologist may not have thought that volcanic submarine ores could form this quickly.

The amount of magma that is being degassed can be estimated from the SO<sub>2</sub> emission as  $1.8 \times 10^5$  tons if we assume that the basaltic magma loses 0.07 percent sulfur during eruption, the estimate of Moore and Fabbri (4), and note that in December 1972 Pacaya emitted 260 tons of SO<sub>2</sub> per day. These measurements of the SO<sub>2</sub> were made while a basaltic lava flow in the flank of the cone was extruding an estimated  $2.6 \times 10^4$  tons of lava per day. This lava would have given off 0.07 percent sulfur or only 36 tons of SO<sub>2</sub>. This suggests that much intrusive magma is degassing.

A rough estimate of the world annual contribution of SO<sub>2</sub> from volcanoes to the atmosphere can be made by extrapolating from these Central American data. We estimate that there are 50 volcanoes in the world with prominent vapor plumes (like Masaya,

Table 1. Amounts of SO<sub>2</sub> gas issuing from volcanoes in Guatemala, El Salvador, and Nicaragua.

Volcano	SO <sub>2</sub> (metric tons per day)
<i>Guatemala</i>	
Santiaguito	420
Fuego	40*
Pacaya	260
<i>Nicaragua</i>	
San Cristobal	360
Telica	20*
Momotombo	50*
Masaya	180
Total	1330†

\* Data less reliable. † Very small plumes issued from fumaroles in the craters of the volcanoes Santa Ana and Izalco, El Salvador. Very approximate estimates from field data suggest that these plumes account for no more than a few tons of SO<sub>2</sub> per day.

San Cristobal, and Pacaya) and 50 with smaller ones (like Telica or Fuego in October 1972) and that the SO<sub>2</sub> content of these volcanoes is similar to that of the Central American plumes. The estimate of the number of volcanoes with vapor plumes is based on a count of the volcanoes in the catalog of active volcanoes (5) which in 1 year seem, from the not-too-adequate descriptions, to have been emitting plumes. Taken together, these 100 volcanoes would emit on the order of  $7 \times 10^6$  tons of SO<sub>2</sub> per year. This estimate excludes the contribution of underwater volcanism and excludes the SO<sub>2</sub> degassing from volcanoes during major eruptions of great clouds of ash. This estimate is based on the further assumption that the composition of the world's volcanoes is correctly represented by the spectrum of composition represented by the Central American examples. From analyses of soluble components on volcanic ash, Taylor and Stoiber (6) estimate that  $8 \times 10^6$  tons of SO<sub>2</sub> per year are produced in the form of soluble material on the surface of ejecta from violently erupting volcanoes. Much SO<sub>2</sub> from these eruptions fails to be deposited on the ejecta. Adding this minimum amount to our estimate gives a combined figure of 10<sup>7</sup> tons of SO<sub>2</sub> per year. We emphasize that this is a minimum estimate since we still are not accounting for all the SO<sub>2</sub> from the very active vents, which must be a very large amount. This estimate is an order of magnitude higher than that of Kellogg *et al.* (7) who indirectly estimated the emission of  $1.5 \times 10^6$  tons of SO<sub>2</sub> annually

from the degassing of erupted material only. The difference in the two estimates may represent, at least in part, the amount of SO<sub>2</sub> that is degassed from intrusive magma in the plumes of volcanoes. This difference suggests that the volume of intrusive magma being degassed through volcanic craters may be several times greater than that which is extruded.

If it is assumed that the average rate of sulfur emission over geologic time is the estimated present minimum annual rate, then  $2 \times 10^{16}$  tons of sulfur would have been emitted from volcanoes in  $4.5 \times 10^9$  years. This estimate is an order of magnitude greater than Rubey's estimate (8) of the amount of sulfur in the oceans and sediments not accounted for by rock weathering, and it is not much greater than a similar estimate of Taylor and Stoiber (6) based only on the sulfate content in ash leachates. If other mechanisms of sulfur transfer from the interior to the surface are negligible, then the case is strengthened for the gradual outgassing of the earth as proposed by Rubey (8).

Our estimate of the annual amount of SO<sub>2</sub> emitted from volcanoes (10<sup>7</sup> tons) is an order of magnitude less than the estimate of the annual contribution of SO<sub>2</sub> to the atmosphere as pollution (10<sup>8</sup> tons) [Kellogg *et al.* (7)].

RICHARD E. STOIBER

Department of Earth Sciences,  
Dartmouth College,  
Hanover, New Hampshire 03755

ANDERS JEPSEN

Environmental Measurements, Inc.,  
Annapolis, Maryland 21401

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9. We thank K. Kronmiller of Environmental Measurements, Inc., and geologists from Dartmouth College, especially R. A. Wood and M. J. Carr, for invaluable field assistance. Supported in part by Dartmouth College and Environmental Measurements, Inc. The greater part of the support came from NSF grant GA-26026.

31 May 1973; revised 17 August 1973