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Carbonyl Sulfide and Carbon Disulfide from the Eruptions of Mount St. Helens

Abstract. *Ash from the massive 18 May 1980 eruption of Mount St. Helens readily gave off large amounts of carbonyl sulfide and carbon disulfide gases at room temperature. These findings suggest that the sulfur that enhances the Junge sulfate layer in the stratosphere after volcanic eruptions could be carried directly to the upper atmosphere as carbonyl sulfide and carbon disulfide adsorbed on ash particles from major volcanic eruptions.*

The eruptions of Mount St. Helens have provided a unique opportunity to study the sequence of volcanic events that precede and follow the massive dacitic explosions of volcanoes. We report here our studies of gases emitted directly by the volcano and those adsorbed on the ash particles. It has been demonstrated that the Junge sulfate layer in the stratosphere is enhanced after volcanic eruptions (*1*). It has been suggested that the SO_2 from volcanic eruptions is the source of sulfur for this sulfate layer (*2, 3*); however, we have found that volcanic ash releases COS and CS_2 but no SO_2 or H_2S at room temperatures, which may be another significant mechanism for the transport of sulfur from volcanoes to the stratosphere. The idea that the nonvolcanic COS and CS_2 might be a source of the sulfate layer has been suggested by several investigators (*4, 5*). Hobbs *et al.* (*6*) observed that H_2S [~ 1 part per million (ppm)] was the dominant sulfur gas close to the ash plume of the major 18 May and 25 May 1980 eruptions at 3 to 5 km. Small amounts of COS and CS_2 were also observed. The flux of SO_2 increased dramatically only after 25 May, and SO_2 became the dominant gas after the 13 June eruption. These results, together with ours, suggest that SO_2 may not be the major sulfur-containing gas emitted from the volcano until after the major explosive eruption. Thus COS and CS_2, adsorbed on ash, may be more important contributors of volcanic sulfur to the stratosphere.

We collected volcanic ash both before and after the major eruption of Mount St. Helens on 18 May 1980, and from a light aircraft we collected air samples of the volcanic emissions. The air was collected in stainless steel flasks, with inert internal surfaces (rendered inert by the SUMMA process), reaching pressures of 1.35 to 2.0 atm. The trace gases studied were found to be stable in the containers and were analyzed within a few hours after collection. The gases emitted by the volcano underwent great dilution by ambient air before we could collect them, and so we measured $CFCl_3$ (F-11) and CF_2Cl_2 (F-12) in all the samples to obtain an estimate of the dilution factor. If we assume that F-11 and F-12 are entirely man-made, the dilution factor D is equal to $(1 - r)^{-1}$, where r is the ratio of the F-11 concentration in the plume sample to that in ambient air.

The ash samples, collected at several distances from the mountain, were sealed in the field in airtight 2- and 4-liter stainless steel cylinders fitted with Nupro SS-4-H-4 bellow valves. We used this arrangement of valves to first desorb trace gases from the walls of the containers under vacuum and then to purge the containers with a synthetic contaminant-free zero air at 150° to 200°C in the laboratory before filling them in the field with volcanic ash. Samples processed in this way have proven to be free of contaminants as compared to samples casually collected in plastic bags or glass jars. In addition to the direct analysis of the gases in the headspace above the ash in the field samplers, 100-g samples were removed and transferred to similarly cleaned 1.5-liter Pyrex flasks fitted with graded seals to Nupro SS-4-H-4 valves. All the samples were pressurized to 1.0 atm with dry synthetic air and were allowed to stand for at least 4 days before being analyzed. The COS and CS_2 were measured by gas chromatography–mass spectrometry (GC-MS) isothermally at 0° and 100°C, respectively, on a glass column (0.64 cm by 2.7 m) packed with 10 percent OV-101 on Chromosorb W. We made quantitative measurements on 5-ml samples, using single-ion monitoring at mass-to-charge ratio (m/e) 60 for COS and m/e 76 for CS_2. Additional GC-MS scans were made on larger air samples (~ 500 ml) concentrated by a cryotrap. In this case the samples were injected onto the column at 20°C, and then the temperature was raised at 8°C per minute to 150°C. The COS and CS_2 were measured independently with a flame photometric detector (FPD-GC), which was also capable of measuring H_2S, SO_2, and dimethyl sulfide. The CS_2 was measured with an electron-capture detector (EC-GC) in the analysis of the halocarbons present in the samples.

The results of the air analyses are shown in Table 1. The absence of any CS_2 in the majority of these events and in

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Table 1. Concentrations of COS, CS_2, and CO_2 in the plumes of Mount St. Helens eruptions.

Date (1980)	COS (ppbv)	CS_2 (ppbv)	CO_2 (ppmv)	r (× 100)	D	Comments
30 March	17		392	72	3.6	Eruption, mostly ash
30 March	22		378	69	3.2	Plume edge, mostly ash
30 March	3.3		370	99	100	Mostly steam
30 March	2.1		370	98	50	Residual plume
1 April	7		382	09	50	Eruption, mostly ash
1 April	2.3		350	99	100	In steam plume
8 May	1.2	6.1	374	99	100	Small ash plume
18 May	1.2	0.7	368	99+	100+	Samples collected at periphery of main ash plume only because of danger of flying into the ash cloud
18 May	0.9	1.3	356	99+	100+	
18 May	1.3	0.6	363	99+	100+	
4 June	0.67		362	99+	100+	Remnant plume at 2800 m
17 September	0.85		345	99+	100+	Remnant plume at 2500 m
Ambient background						
	0.50 ± 0.08	0.05 ± 0.01	340 ± 5			General measured values, this work

the two remnant plumes sampled on 4 June and 17 September is noteworthy. It is only in the samples from the major eruption of 18 May that large concentrations of CS_2 are consistently observed. When dilution is considered, the reconstructed concentrations of COS are equivalent to those observed in the phreatic eruptions. Hobbs *et al.* (*6*) observed almost exclusively H_2S (at 0.5 to 1 ppm) and no SO_2 in the in situ analyses of the gases in the plume of 18 May. It thus appears that the eruption of 18 May had a high concentration of reduced sulfur gases. These observations are consistent with the low temperature of the eruptive events sampled, the strong role ground water played in Mount St. Helens' activity, and the fact that the formation of reduced sulfur gases would be favored under these conditions. The anomalous presence of excessive amounts of H_2S in the eruption is consistent with the recent recognition that H_2S is the most stable sulfur gas in the magma melt (*7*). It seems that the major landslide on the morning of 18 May that triggered the eruption did so prematurely before any appreciable conversion of H_2S to SO_2 had occurred in the melt. This conclusion is also consistent with the fact that significant amounts of SO_2 in the Mount St. Helens eruption plumes were not measured until after 25 May eruption (*6*).

In the second phase of our work we studied the gases that desorbed from the ash. The results of the measurements of desorbed COS and CS_2 are shown in Fig. 1 as a function of distance from the mountain. We found that a large number of species desorbed from the ash at room temperature under pressures of 0.5 to 1.0 atm, but COS and CS_2 were by far the most abundant (GC-MS data). The methyl halogens CH_3Cl, CH_3Br, and CH_3I and other halocarbons of higher molecular weight were also observed at concentrations of a few parts per billion by volume (ppbv) except CH_3Cl, which occurred at up to 1000 ppbv. Samples 2, 7, 9, and 12 (Fig. 1A) represent ashfall material collected from the phreatic eruptions. Therefore, the high concentrations of COS, CS_2, and methyl halogens observed reflect the stage when reduced sulfur gases would predominate. The absence of H_2S and SO_2 is believed to be due to their reaction with the ash material to form sulfuric acid or nonvolatile sulfate under appropriate conditions of heat and moisture. When SO_2 and H_2S were injected into the air over a 100-g bed of ash in a sealed flask, the concentrations of SO_2 and H_2S dropped to undetectable levels within a few minutes. This experiment was repeated more than a dozen times with the same result. When the volcanic ash was replaced with sands from various deserts and beaches, the SO_2 and H_2S were also removed but it took several hours. However, COS and CS_2 did not show any such affinity for reaction in the presence of ash or sand.

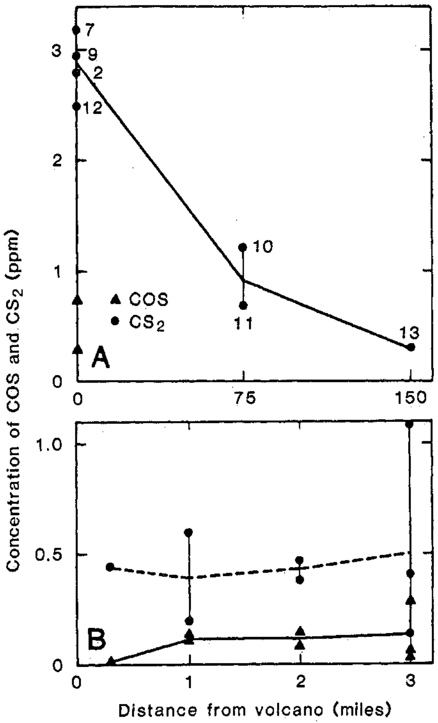

Fig. 1. Concentrations of COS and CS_2 desorbed from volcanic ash samples at room temperature. (A) Concentrations in ashfall material from phreatic eruptions: sample 2, summit (2900 m), collected 2 May 1980; samples 7, 9, and 12, summit, collected 7 May 1980; samples 10 and 11, Tampico, Washington, collected 18 May 1980; sample 13, Warden, Washington, collected 19 May 1980. (B) Concentrations in pyroclastic flow material from May to August 1980.

Momot (*8*) has shown that sulfur in the presence of CO under fumarolic conditions readily forms COS and CS_2. The CS_2, COS, and methyl halogen data show that less material is desorbed from ash samples collected farther away from the volcano, an indication that the more volatile species disappear with the distance the ash travels. It was also observed that SO_2 desorbed from only one heated sample, but its concentration was less by a factor of 5 than that of COS shown in Fig. 1; this result implies that SO_2 may be less abundant than COS and CS_2, but more research is needed on the desorption properties of SO_2 before any firm conclusion can be reached. There was no evidence for the presence of H_2S or dimethyl sulfide in these samples when analyzed with the FPD-GC. The GC-MS scans on all samples showed that CS_2 was the dominant species apart from such major components as water and CO_2, which were not measured at this time. Mild heating, 50° to 60°C, of the ash while flushing the vessel with zero air completely removed all the CS_2, COS, and methyl halogens within a few hours. Although temperatures in the upper troposphere and the lower stratosphere are much lower than 50°C, the fine ash remains in the stratosphere for a long time and is also exposed to intense sunlight. Both processes would lead to significant photodesorption of COS and CS_2. We therefore conclude that volcanic ash may provide a mechanism by which large amounts of COS, CS_2, and other trace gases are transported and eventually released into the upper atmosphere.

It is still very difficult to estimate the quantities of sulfur gases that are injected into the stratosphere by these natural explosive volcanic events. Lazrus *et al.* (*3*) estimated that the sulfur burden in the form of sulfate in the lower stratosphere increased by approximately 0.5×10^9 kg after the Fuego eruption in October 1974. If the total COS and CS_2 concentration at the center of the plume was about 5 parts per million by volume (ppmv), then a 30-km^3 volumetric gas flow into the stratosphere would carry the 0.5×10^9 kg of sulfur. This magnitude of transport into the stratosphere is possible, especially from the major eruption of Mount St. Helens on 18 May 1980. This mechanism would carry COS and CS_2 as well as SO_2, which could be converted to sulfate aerosol by photochemical processes (*4*), enhancing the Junge layer.

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Radium-226 and Radon-222 in the Coastal Waters of West Florida: High Concentrations and Atmospheric Degassing

Abstract. *On the central portion of the west Florida continental shelf, radionuclide activities show unusually wide variations: radium-226 activities up to 350 disintegrations per minute per 100 liters, radon-222 activities up to 1300 disintegrations per minute per 100 liters, and deficiencies of radon-222 as low as −10 disintegrations per minute per 100 liters. Florida's phosphate-rich strata seem to be the principal source of the radionuclides, with the transfer occurring directly from sediments or indirectly in streams, ground-water flow, and geothermal springs. Winter storm fronts may enhance radon degassing in the shelf waters.*

Neritic waters undergo important processes affecting radium and radon. Rivers carry ^{226}Ra to the sea in dissolved or adsorbed form (*1–3*). Interaction with seawater desorbs particulate radium and increases the effective delivery of dissolved radium by some rivers (*1*, *4*) through a mechanism resembling the desorption of barium (*5*). Waters of the continental shelf off southern California are enriched in ^{226}Ra resulting from either upwelling or release from sediments

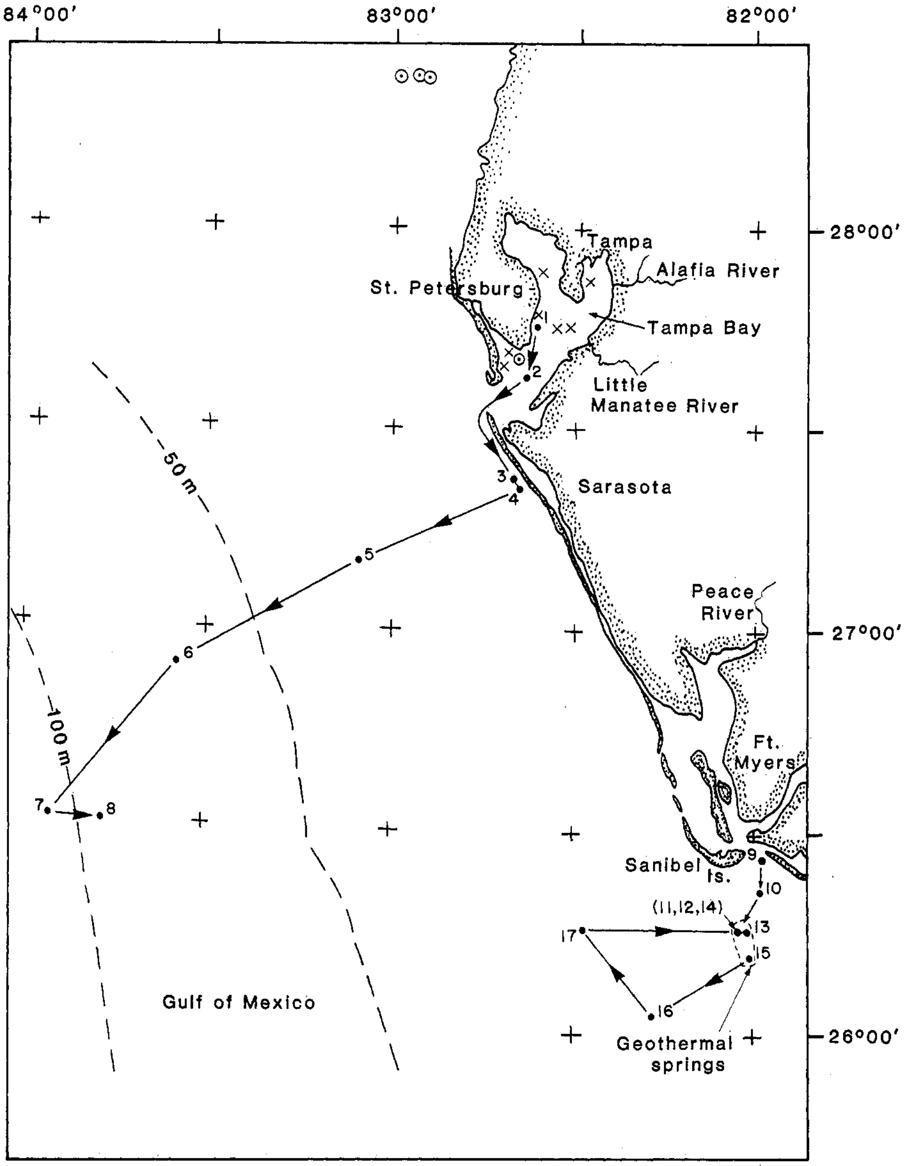

Fig. 1. Stations occupied during the 14-month investigation of radium and radon on the west-central Florida shelf: ●, stations for the cruise in March 1980, with arrows showing the cruise track; ⊙, stations for the cruise in September 1980; x, Tampa Bay stations sampled in February 1981.

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