Lazrus *et al.* (11) addressed the problem of the possible impact of volcanoes on stratospheric ozone concentrations. Volcanic hydrochloric acid vapor injected above the tropopause can react with the hydroxyl radical to yield atomic chlorine, which is capable of catalytically depleting ozone.

Measurements of stratospheric acid chloride before the major eruption of Volcan de Fuego in Guatemala in October 1974 indicated no significant enhancement of chloride (12). On the other hand, measurements of the ratios of HCl to SO_2 in tropospheric explosive eruption plumes of Volcan de Fuego, in conjunction with the observed tenfold enhancement of stratospheric sulfate throughout the Northern Hemisphere after the major Fuego eruption, suggested that a significant increase of HCl should also have occurred. We did not observe any preferential removal of HCl relative to SO_2 as a function of the age of the tropospheric Fuego plumes. The failure to observe significant enhancements of stratospheric acid chloride was attributed to the solubility of HCl, which is 300 times greater than the solubility of SO_2 in water at 0°C. If the copious quantities of water typically condensing from volcanic plumes as they cool become appreciably acidic, the solubility of SO_2 is even further depressed. Most of the ash particles, which are likely to be made more massive by coatings of ice, were found to leave the stratospheric plume of Mount St. Helens within several days (13), probably also causing a selective depletion of chloride relative to sulfur. Though the particulate chloride appears to be consistently enhanced during the earliest stages, the resulting enhancement of stratospheric chloride concentrations after extensive mixing of the plume throughout the stratosphere should be very small. This also applies to the acid chloride vapor concentrations in the plume. We do not know the extent to which the eruption plume was initially enriched in HCl, but observations continue to suggest that major eruptions do not significantly enhance stratospheric acid chloride levels. Measurements of HCl and SO_2 in the tropospheric plumes of Mount St. Helens are under way. Our observations do not preclude the possibility of significant enhancement of stratospheric chlorine by organic halogen compounds enriched in the volcanic plume.

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13. N. Farlow (*ibid.*) reported that the particles sampled on 19 May 1980 contained very little H_2SO_4 liquid on them when examined under an electron microscope. Also, the number of ash particles appeared to diminish greatly in subsequent flights.
14. The National Center for Atmospheric Research is sponsored by the National Science Foundation.

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Trace Element Composition of the Mount St. Helens Plume: Stratospheric Samples from the 18 May Eruption

Abstract. *Atmospheric particulate material collected from the stratosphere in the plume of the 18 May 1980 eruption of the Mount St. Helens volcano was quite similar in composition to that of ash that fell to the ground in western Washington. However, there were small but significant differences in concentrations of some elements with altitude, indicating that the stratospheric material was primarily produced from fresh magma, not fragments of the mountain.*

The effects of aerosols in the earth's atmosphere on climate are the object of constant study and interest, especially the effects of sudden changes in the aerosol composition such as those produced by a large-scale volcanic eruption (1). Most studies of volcanoes have involved only the measurement of the number particles or the total mass or particle size distributions in plumes (2). Studies of the chemical compositions of particles from volcanic plumes have used aircraft sampling systems to collect tropospheric samples (3, 4). However, none of these projects included samples from a large-scale primary eruption, nor did they include samples from the stratosphere.

Mount St. Helens erupted catastrophically on 18 May 1980, sending clouds of ash and debris into the stratosphere to an altitude in excess of 18 km. The first sampling of the volcanic plume in the stratosphere took place on 19 May 1980, less than 24 hours after the major eruption. The sample collection flight covered areas over Oregon, Idaho, Montana, and Wyoming; samples were taken from the plume at various altitudes between 13 and 18 km. On 22 May, samples from a similar geographic area were collected at altitudes of about 20 km. These samples were taken to monitor chemical changes with time as the volcanic cloud dispersed. On 27 May, after the 25 May eruption, samples were collected along the Canadian coastline at an altitude of about 17 km.

A multifilter sampling device mounted in a wing tank of a NASA U-2 aircraft was used (5). Samples were collected on IPC cellulose filter papers and had a collection time of about 20 minutes each. Blanks were also taken in between each pair of samples (1 minute or less collection time) to correct for elements contained in the filter papers. Blanks collected immediately after the first and biggest eruption became heavily loaded with particles after just 1 minute of collection and were thus useless as blanks; the abundant elements suggest extremely high levels of contaminants even at these high sampling altitudes. In these cases, blanks collected on days when the clouds were not as thick were used to make the corrections.

One-half of each filter was sent to us, and it was pressed into a pellet and sealed in a clean polyethylene bag before being counted for natural radioactivity. The other half of the filter was analyzed by Gandrud and Lazrus (5) for water-soluble species. The pellets were analyzed by prompt γ-ray activation analysis (PGAA) (6) and instrumental neutron activation analysis (INAA) (7). Both procedures were carried out at the National Bureau of Standards reactor. The PGAA was done first and used a neutron-beam facility developed specifically for the rapid analysis of samples by prompt γ-rays emitted while samples were being irradiated (6). For INAA, samples were irradiated along with the appropriate standards in a flux of 6×10^{13} neutrons per square centimeter per second for a

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period of 2 minutes for short irradiations and 4 hours for long irradiations. Gamma rays from the induced activity were measured with Ge-Li detectors coupled to a Tennecomp TP-5000 data acquisition system, and the resulting spectra were analyzed by computer programs in the minicomputer of the TP-5000 system.

Usually 35 elements were measured in each of the samples by the combined nuclear techniques. There was excellent agreement between INAA and PGAA results for each of the elements measured by both methods (including Al, K, Ti, Fe, and seven others). Prompt gamma-ray activation analysis was especially crucial in the detection of Si and B, which were impossible to detect from INAA.

The concentration of ash throughout the cloud was quite large, as indicated by the high concentrations of Si, Al, Fe, and other elements associated with ash. Concentrations of total sulfur and chlorine are given in Table 1 for all samples that contained significant levels above blanks. The concentration of ash is inferred from the Al concentration in the plume; we assume that the Al concentration of the ash in the plume is the same as that of the ash collected at Pullman, Washington (8.9 percent), by the U.S. Department of Agriculture and analyzed in our laboratory (*8*). These results show that the plume contained between 1.5 and 3 mg/m^3 (at standard temperature and pressure) of ash, over the entire region sampled on 19 May. Samples collected on 22 and 27 May yielded much lower levels of ash and chlorine but larger quantities of sulfur. The sulfur data as obtained by Gandrud and Lazrus (*5*) on the same filters are in excellent agreement with results of our measurements by nondestructive techniques and do not show large systematic variations with altitude; large fluctuations at the same altitude were observed in the case of geographical variations, especially at 20.1 km on 22 May (Table 1).

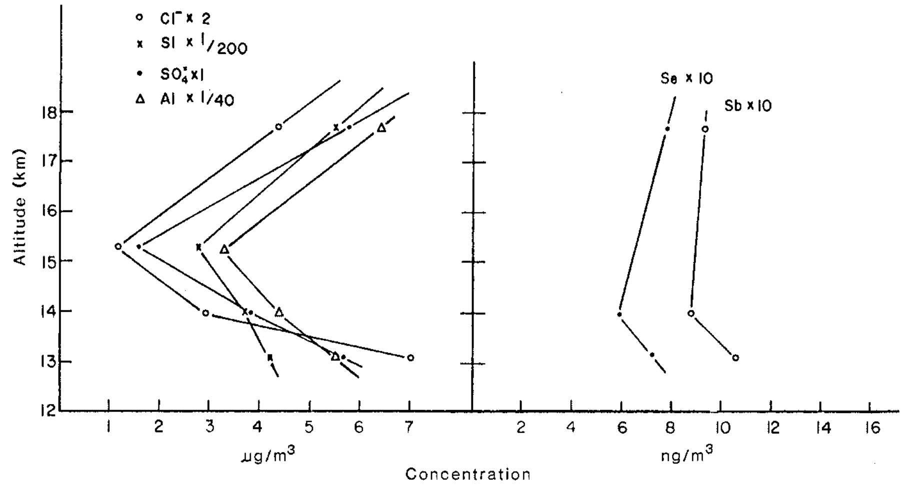

Fig. 1. Vertical profiles of the concentration of some chemical species in the Mount St. Helens plume on 19 May 1980.

Table 1. Mass per unit volume (at standard temperature and pressure) of major components in the plume of Mount St. Helens.

Altitude (km)	Ash* (µg/m^3)	Sulfur† Total (µg/m^3)	Sulfur† Soluble (µg/m^3)	Volcanic (%)	Chlorine Total (µg/m^3)	Chlorine Soluble‡ (%)
			19 May 1980			
13.1	2870	5.6	4.5	95	3.5	14
14.0	1460		3.0	94	1.4	24
15.3	1960		1.2	99	3.1	10
17.7	2460	5.8	4.4	94	2.2	86
			22 May 1980			
18.8 to 20.1	30		21.2	96	2.1	3.3
20.1	110	190	263	99	2.1	40
20.1	~ 60	63	82	91	1.3	28
20.7	~ 7		3.1	74		
			27 May 1980			
16.8	59	21	27.8	98		

*We assumed that the Al concentration of plume particles is the same as that for ash collected at ground level (*8*). †Data taken from Gandrud and Lazrus (*5*) for comparison with the total sulfur measurements: the fraction of volcanic origin is corrected for background sulfate. ‡Soluble chloride from Gandrud and Lazrus (*5*) for comparison with the total chlorine measurements.

The sulfur measurements from the 22 May flight differ, and we believe these differences may be due to inhomogeneities in the filters or analytical problems with the nuclear analysis because sulfur is not very sensitive by neutron activation analysis. Both measurements do show that the sulfur levels are much larger on 22 May than on 19 May.

The ash and chloride concentrations in samples collected at the highest and lowest altitudes yielded significantly higher concentrations than did the samples at other altitudes. This result is probably due to large inhomogeneities of the plume that was sampled. Some regions of the plume, therefore, contain higher concentrations of ash and other components as was indicated on photographs. Vertical concentration profiles for several elements in the plume on 19 May are shown in Fig. 1. As seen in Table 2 and Fig. 1, concentrations of elements increase above 15 km. Because of the inhomogeneities of the plume, it is difficult to interpret the absolute concentrations; therefore, we analyzed the enrichment factors of elements on the collected particles.

One possible source of confusion should be noted. It is well known that there is a layer of high concentrations of sulfate and other particulate matter at about 20 km—the stratospheric sulfate layer (*9*). We have used the ^{7}Be/SO$_4^{2-}$ ratio obtained from previous U-2 flights (*10*) to correct the observed sulfur concentrations for sulfur (sulfate) normally present in the stratosphere. This correction assumes that the ^{7}Be/SO$_4^{2-}$ ratio is relatively constant and that the ^{7}Be determined for these samples is that which occurs naturally. Most of the particulate sulfur measured on 19 May (Table 1) is associated with the volcano, predominantly with the ash present. It is not associated with gas-to-particle conversion, as judged by the values of the enrichment factor (EF$_{\text{ash}}$) of only 2.3 and 2.7, indicating that the quantity of sulfur present on particles in the plume is only two to three times that present on ash that fell in western Washington. For the samples collected on 22 and 27 May, the sulfur concentrations were as high or higher than those from 19 May, but as there was much less ash present, this sulfur appears to be highly enriched relative to the quantity of ash present. This sulfur probably represents sulfate aerosols formed from gaseous precursors from the plume in the stratosphere, presumably by heterogeneous processes since there was a great deal of ash and water vapor present.

We detected chlorine by INAA and PGAA only in the samples from 19 May and three from 22 May, due to the excessively high blanks from the IPC filters. Soluble chloride was measured on all of the filters by Gandrud and Lazrus (*5*); when the total chloride measurements are compared, the fraction of the chlorine that is water soluble is highest at the greatest altitude (Table 1). This result suggests that the chlorine in the lower altitude samples was physically tied up in the ash, as indicated by the relatively low enrichment factors (Table 2). The increase in the soluble chloride on the particles at the higher altitude is probably the result of gas deposition on the surfaces of the ash particles (*11*).

Concentrations of all elements measured in the highest and lowest altitude samples collected on 19 May are listed in Table 2. In order to remove effects of inhomogeneities of the plume and make comparisons of the composition of the plume particles with the volcanic ash, we have also listed enrichment factors, defined by

$$\mathrm{EF}_{\mathrm{ash}} = \frac{(\mathrm{X/Al})_{\mathrm{plume}}}{(\mathrm{X/Al})_{\mathrm{ash}}}$$

where X/Al is the ratio of the concentration of element X to that of Al in particles collected from the plume, or in ash deposited at Pullman, Washington (*8*, *12*). Our ash sample, from its composition, represents predominantly material from the breakup of the mountain. Ranges of $\mathrm{EF}_{\mathrm{ash}}$ values observed in the plume of 19 May are shown for all of the elements in Table 2 and are plotted in Fig. 2.

The $\mathrm{EF}_{\mathrm{ash}}$ values for most elements are close to unity, indicating that few elements are fractionated in the stratospheric samples as compared to the ash that fell on the ground. This observation is in sharp contrast with results of studies of particles from other volcanoes or high-temperature sources, which usually show enrichments of one or more orders of magnitude for several moderately volatile elements (for example, As, Se, Pb, Cd, and Zn) on the small airborne particles with respect to the larger ash that remains behind (*3*). These observations are explained by a mechanism in which moderately volatile species are vaporized in the high-temperature zone and, upon cooling, condense preferentially on small particles that have greater surface area to mass ratios. The generally small $\mathrm{EF}_{\mathrm{ash}}$ values observed for Mount St. Helens suggest that most of the plume material was simply airborne ash injected into the stratosphere by the energetic eruption, with little influence of high-temperature processes that would enhance the release of volatile elements. Some elements are depleted (that is, $\mathrm{EF}_{\mathrm{ash}} < 1$), possibly indicating that the plume may be enriched in Al relative to other lithophile elements in the ash. The ash we are using for comparison has a slightly different composition as it contains more material from the breakup of the mountain than merely erupted magma. If one calculates an enrichment fac-

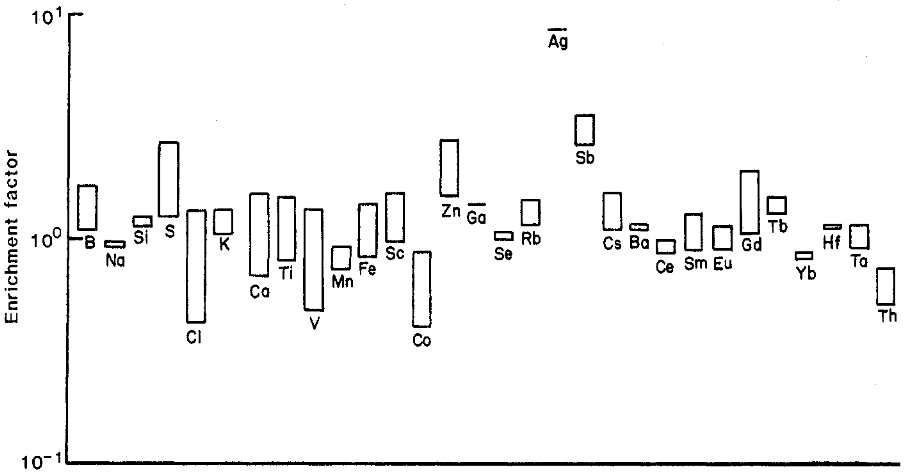

Fig. 2. The range of the ash enrichment factors for elements measured in the Mount St. Helens plume of 19 May 1980.

Table 2. Concentrations and relative enrichments in plume samples from 19 May 1980.

Element	Concentration (μg/m^3)		$\mathrm{EF}_{\mathrm{ash}}$*	
	17.7 km	13.1 km	17.7 km	13.1 km
B	0.051	0.068	1.10	1.71
Na	96	79	0.97	0.93
Mg		29		1.37
Al	260	220	1.00	1.00
Si	1100	840	1.26	1.13
S	5.8	5.6	2.35	2.70
Cl	2.2	3.5	0.72	1.37
K	46	41	1.22	1.27
Ca	130	56	1.52	0.76
Sc	0.035	0.019	1.60	0.97
Ti	16	8.2	1.56	0.95
V	0.18	0.082	1.38	0.72
Mn	1.3	0.90	0.94	0.74
Fe	110	72	1.46	0.96
Co	0.036	0.017	0.89	0.50
Zn	0.39	0.22	2.8	1.82
Ga	0.074		1.43	
As	0.0043	0.026	0.79	5.6
Se	0.00077	0.00072	1.00	1.08
Rb	0.14	0.15	1.19	1.52
Ag	0.0019			
Cd	0.099	0.00015	360	6.4
Sb	0.00092	0.00105	2.63	3.52
Ba	1.3	1.10	1.18	1.18
La	0.046	0.040		
Ce	0.11	0.079	0.99	0.87
Sm	0.012	0.0080	1.32	1.04
Eu	0.0039	0.0024	0.91	1.17
Gd	0.014	0.0074	1.73	1.08
Tb	0.0019	0.0013	1.32	1.57
Yb	0.0038	0.0033	0.84	0.87
Lu	0.00087	0.00049		
Hf	0.014	0.012	1.16	1.16
Ta	0.0014	0.00093	1.18	0.92
Th	0.0031	0.0039	0.51	0.75

*Ash data from (*8*, *12*).

tor from crustal abundances rather than the composition of ash, many elements are depleted, as the volcanic material is of dacitic composition (*12, 13*).

There are some significant changes with altitude in the plume. For example, the Si enrichment, which is constant for most samples, does show an increase in the higher reaches of the plume. A group of elements (Ca, Sc, Ti, Fe, Zn, and Th) shows a similar pattern of enrichment at higher altitudes. Although the enrichments are not large, they are significant for these elements that are not usually fractionated by volcanic processes. These enrichments may occur because the source of the higher altitude clouds is in part the hotter magmatic debris rather than simply that from the physical breakup of the material from the mountaintop. The volatile elements As, Se, and Sb show little or no enrichment, indicating either that portions of them were in the vapor phase and thus missed by particle collection, or that they were not fractionated significantly. Due to the temperatures in the stratosphere and the large quantities of ash present, it is doubtful that very much of the Se, As, and Sb would be in the vapor phase. On the other hand, there may have been some fractionation that was not observed because of the presence of the huge amounts of unfractionated ash that was released. We cannot explain the huge enrichment of Cd at high altitudes. Since the PGAA and INAA results are in good agreement, the analyses appear to be valid. There might have been Cd contamination on the filters, although no materials of high Cd concentration were used in the collection system. The source of contamination is under investigation.

The general composition of the plume material is similar to that of the ash that fell to the ground in western Washington. Only minor enrichments of volatile elements are indicated; Cd, Sb, S, and Zn were the most enriched. The plume was fractionated vertically, as judged by the slight increases of EF_{ash} for some elements at higher altitudes. The fraction of water-soluble chlorine increased greatly with altitude, but the total chlorine concentration on particles was not much greater than for ash that fell to the ground. On the basis of $^7Be/SO_4^{2-}$ ratios, most of the sulfur observed resulted from the volcanic eruption.

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14. We thank A. Lazrus and B. Gandrud of the National Center for Atmospheric Research for their help and cooperation. The filter holder they designed and built allowed us to obtain valuable data on this unique stratospheric injection, and their efforts helped us to interpret our results. Supported by NASA grant NAG-2-28 and NSF Undergraduate Research Program grant STI-792-6820 to T.V. The PGAA studies were supported in part by DOE contract EY-76-S-05-5173.

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Characterization of Aerosols from Eruptions of Mount St. Helens

Abstract. *Measurements of mass concentration and size distribution of aerosols from eruptions of Mount St. Helens as well as morphological and elemental analyses were obtained between 7 April and 7 August 1980. In situ measurements were made in early phreatic and later, minor phreatomagmatic eruption clouds near the vent of the volcano and in plumes injected into the stratosphere from the major eruptions of 18 and 25 May. The phreatic aerosol was characterized by an essentially monomodal size distribution dominated by silicate particles larger than 10 micrometers in diameter. The phreatomagmatic eruption cloud was multimodal; the large size mode consisted of silicate particles and the small size modes were made up of mixtures of sulfuric acid and silicate particles. The stratospheric aerosol from the main eruption exhibited a characteristic narrow single mode with particles less than 1 micrometer in diameter and nearly all of the mass made up of sulfuric acid droplets.*

The quartz crystal microbalance cascade impactor (*1*) classifies aerosol particles by size from inertial impaction. Each of the ten impactor stages contains a piezoelectric crystal microbalance which senses the mass of particles on impact. This enables the device to weigh the particles in each size interval, in real time, as sampling proceeds. Size-fractionated aerosol samples from eruptions of Mount St. Helens were collected by several aircraft, and the samples were analyzed by scanning electron microscopy and energy dispersive x-ray techniques with an electron microprobe (*2*).

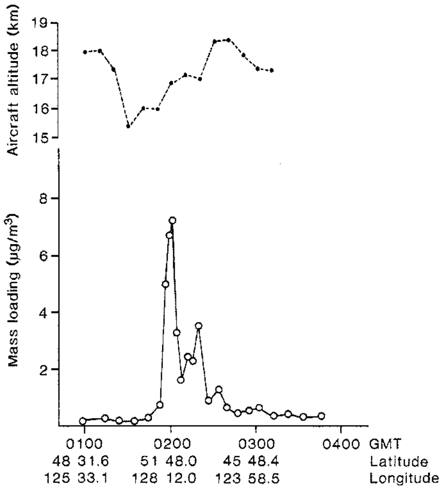

Fig. 1. Total mass loading as a function of time, position, and altitude measured by a U-2 aircraft in the eruption plume of Mount St. Helens on 27 May 1980; *GMT*, Greenwich Mean Time.

For sampling the plume in the stratosphere, the quartz crystal microbalance instrument is housed inside a NASA U-2 research aircraft. An externally mounted isokinetic sampling probe, designed for the U-2 airspeed, brings ambient air into the instrument through a control valve that is operated from the cockpit. A vacuum pump draws the sample through ten impaction stages. The geometric mean particle diameter for stage one is greater than 22 μm, and the diameters for stages two through ten are 14.8, 6.9, 3.2, 1.3, 0.54, 0.23, 0.11, 0.065, and 0.043 μm. Measurements in the plume near the volcano were made with the instrument mounted on a twin-engine QueenAire operated by the National Center for Atmospheric Research in April and on a small Navaho aircraft from the U.S. Geological Survey in August. An isokinetic sampling probe was used on the QueenAire, but a straight-through non-