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# Surface and Elemental Properties of Mount St. Helens Volcanic Ash

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Sized fractions of Mount St. Helens volcanic ash were examined by SEM, EDXA, and ESCA. Particle size distributions, density, and specific surface area were determined. The size distribution was bimodal. Both EDXA and AAS demonstrated the presence of Si, Al, Fe, Na, K, Ca, and Mg. The EDXA demonstrated that Si and Al were present in all particles, except one, which was over 99% Si. Particle-to-particle variation in composition was large. X-ray diffraction demonstrated the presence of labradorite (plagioclase), albite, orthoclase, and anorthite, with a high background from amorphous mate-

rial. ESCA demonstrated the presence of Na as a surface contaminant. No surface sulfur was detected, nor hydrocarbons at levels exceeding those normally found on air-exposed surfaces. The variation of specific surface area with particle size showed that the surface of the ash has a fractal dimension of  $2.23 \pm 0.03$ . Specific surface areas ranged from  $1 \text{ m}^2 \text{ g}^{-1}$  to  $10 \text{ m}^2 \text{ g}^{-1}$ . From our study we estimated that the total surface area of the respirable particles emitted during this eruption equals that of all fly ash emitted from coal combustors worldwide during 1980.

## INTRODUCTION

Volcanic eruptions, although intermittent, make a significant contribution to the background atmospheric aerosol (Fruchter et al., 1980; Walker, 1981). Anthropogenic emissions have been the subject of considerable study with toxicity (Seinfeld, 1975), modification of visibility and absorption of sunshine (Lodge et al., 1981), and surface catalysis of atmospheric reactions (Corn et al., 1971) as important facets of the resulting air pollution. Determination of the physical and chemical characteristics of volcanic emis-

sions is essential to complement studies of anthropogenic emissions. A major emphasis of this article is the characterization of the amount and type of surface of the airborne particulate emitted by Mount St. Helens. We supplemented this by a fairly detailed study of a bulk sample, using an array of tests including leaching studies to determine which of the materials present on the surface would be readily released to the environment.

This paper reports sample characterization by scanning electron microscopy (SEM), energy dispersive x-ray analysis (EDXA), x-ray diffraction, electron spectroscopy for chemical analysis (ESCA), and nitrogen adsorption studies. The specific surface area was  $> 1 \text{ m}^2 \text{ g}^{-1}$ , but no adsorbed sulfur nor significant hydrocarbons were detected. The surface was similar to that of other solids formed by pulverization. The volcanic eruption contributed as much airborne particle surface as all the worldwide emissions from coal combustors in 1980.

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## MATERIALS AND METHODS

A bulk sample of volcano ash was collected on the morning of May 19, 1980, from an undisturbed sidewalk in Pullman, Washington (about 400 km from Mount St. Helens). The well-mixed Mount St. Helens ash was aerosolized, using a 2-inch diameter fluidized bed aerosol generator (Carpenter and Yerkes, 1980) and sampled using a Lovelace aerosol particle separator (LAPS) (Kotrappa and Light, 1972) and a five-stage cyclone train (Smith and Wilson, 1978). The cyclone was operated at 14 L/minute to provide samples of aerodynamic-sized particles, with cut-points ( $R$ ) at 7.50, 3.05, 2.10, 1.25, and 0.71  $\mu\text{m}$  in aerodynamic diameter. Each sized cyclone fraction was weighed.

Samples of sized and bulk volcano ash were collected on formvar grids for examination by transmission electron microscopy to determine particle size distributions. Other samples were ultrasonically dispersed in alcohol and a drop placed on carbon planchets for examination by scanning electron microscopy and for EDXA of individual particles. A JEOL model JSM-35 SEM with KeveX 5100 x-ray detector attachment was used.

Elemental composition of the surface of dispersed particles from the 7.5- $\mu\text{m}$  size cut was studied using a Hewlett-Packard 590B ESCA analyzer, with an aluminum anode ( $K_\alpha = 1486$  eV) and monochromator. The spectrum from the sample was examined at low resolution and selected peaks were reexamined at high resolution. The sample was then ion-etched for 15 min using a 2-keV argon ion beam to remove any surface concentrated materials. An equivalent ESCA spectrum was taken after the etching period.

Specific surface areas ( $S$ ) were determined from nitrogen adsorption isotherms by procedures identical to those previously reported (Rothenberg, 1980). Plotting  $\log S$  vs.  $\log R$ , a straight line is obtained with a slope  $s$ . The corresponding fractal dimension  $D$  is (Mandelbrot, 1982):

$$D = 3 + s \quad \text{with} \quad 2 \leq D \leq 3. \quad (1)$$

This noninteger value,  $D$ , is an indicator of the complexity of the surface.

Samples were digested with acid in pressurized Teflon digestion vessels and analyzed for elemental content by flame and graphite furnace atomic adsorption spectroscopy (AAS).

X-ray diffraction measurements were made on samples mounted on a 0.8- $\mu\text{m}$  pore size silver membrane filter (Selas®) (which served as an internal calibration standard) using a Philips APD-3500 diffractometer equipped with a copper target X-ray tube. Crystalline components were identified by comparison of the patterns obtained with patterns for standards (Joint Committee on Powder Diffraction Standards, 1980).

## RESULTS

The light gray ash collected was similar in texture to a fine sand. The particles were of irregular shape (Figure 1). Weighing each fraction collected in the cyclone stages demonstrated a bimodal size distribution, mass median aerodynamic diameter (MMAD)  $\approx 13$   $\mu\text{m}$ ,  $\sigma_g$  2.6, in agreement with data obtained by microscopy, count median diameter 0.6  $\mu\text{m}$ ,  $\sigma_g$  2.6. The values are rough approximations because the formula for a log-normal distribution cannot be correctly applied to bimodal distributions.

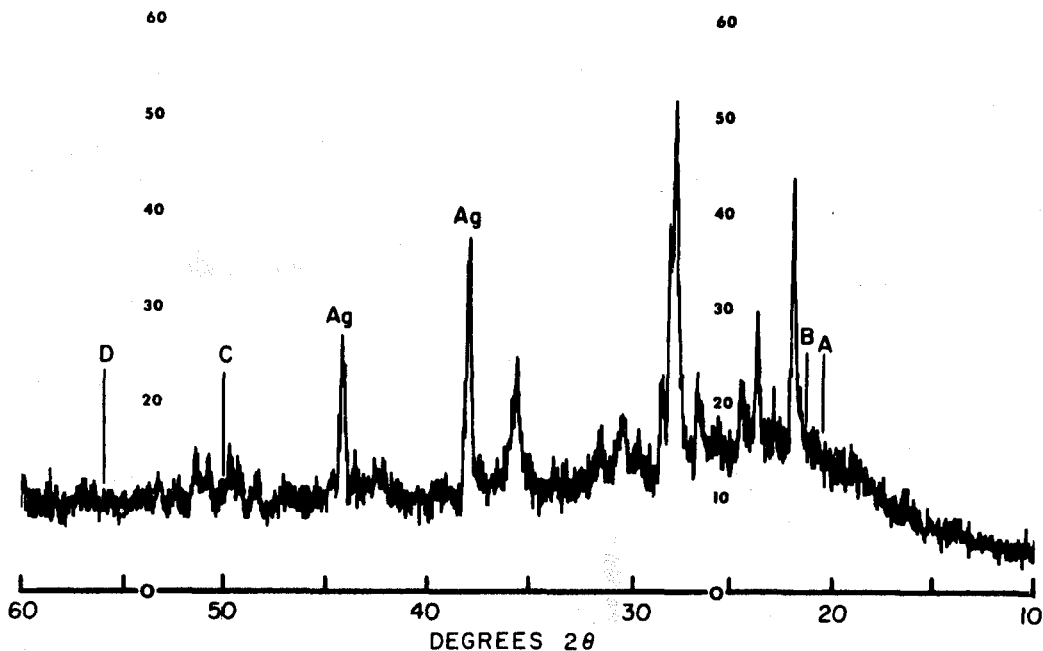
Density, determined by analysis of electron photomicrographs of LAPS samples, was  $2.1 \pm 0.2$   $\text{g cm}^{-3}$ .

The x-ray diffraction pattern (Figure 2) shows a high background, especially for  $2\theta$  between  $5^\circ$  and  $40^\circ$ , indicating amorphous material in a mixture of feldspar minerals including: labradorite (plagioclase), albite, orthoclase, and anorthite.

The EDXA analyses demonstrated that the sample contained Si, Al, Fe, K, P, Ca, Mg, and Na with over 80 atom % of the sample being Si and Al. Variation between particles was considerable. Only one particle with over 99% silica was found. This was presumed to be quartz, although EDXA does not determine the form of  $\text{SiO}_2$  present.



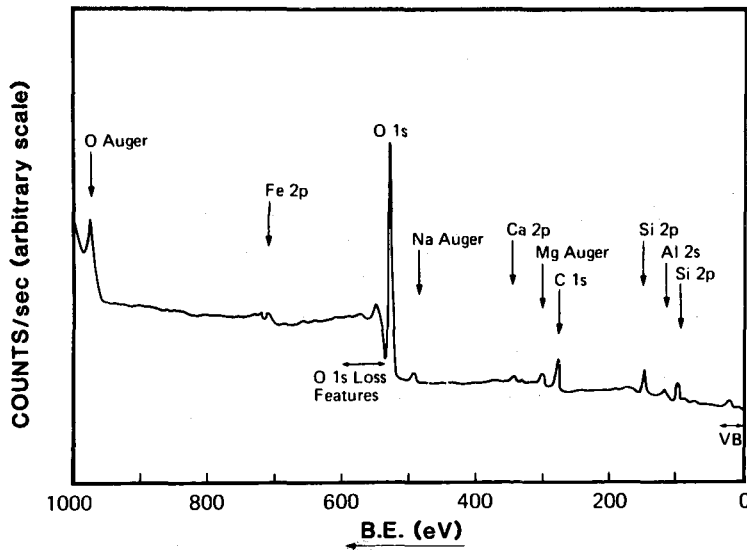
**FIGURE 1.** Scanning electron micrographs of the 3.1- $\mu$ m size cut.

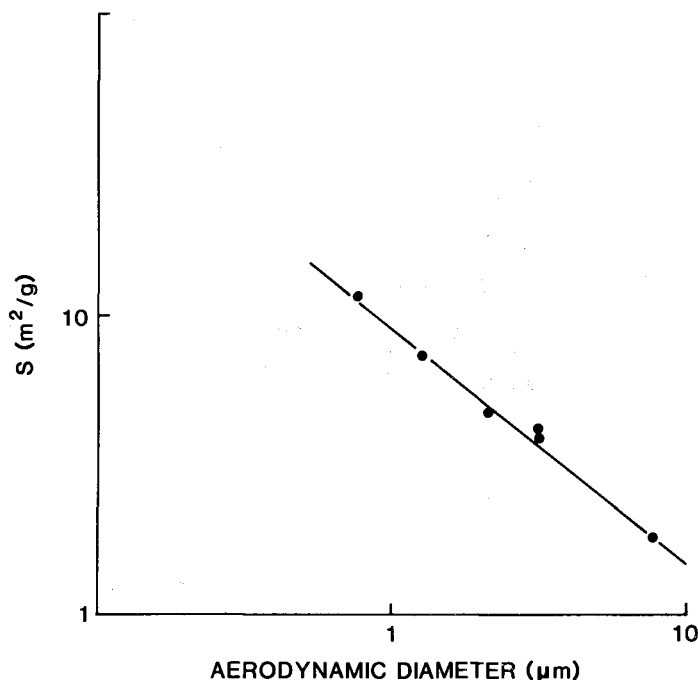


**FIGURE 2.** X-ray powder diffraction pattern of 2.1- $\mu$ m aerodynamic diameter volcano ash particles. The upper limit for crystalline silica is estimated to be 5% by weight.

The ESCA analysis of the surface (Figure 3) showed major amounts of O, Si, and Al within the probing depth ( $\sim 30$  Å) with trace amounts of Ca, Fe, Mg, and Na. The Na was a surface contaminant, as demonstrated by a light ion etch which removed it. The Ca, Mg, and Fe were present at the  $\sim 1\%$  surface concentration levels: Carbon, in the form of

**FIGURE 3.** ESCA analysis of the 7.5- $\mu$ m aerodynamic diameter particles.





**FIGURE 4.** Richardson plot of the variation of specific surface area with particle size. The straight line has a slope indicative of a fractal dimension of  $2.23 \pm 0.04$  for the surface.

hydrocarbon contamination on the surface was surprisingly low for an air-exposed sample. Figure 3, taken overnight to increase counting statistics, demonstrates hydrocarbon buildup on the surface under the cracking influence of the x-ray beam. A prior spectrum taken in 3% of the time used to collect the spectrum shown in Figure 3 showed a much smaller carbon 1s level. From peak areas at high resolution, the O:Si:Al stoichiometry was found to be 66:26:8. This was very close to that expected for a mixture of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ . The chemical shift determined from the accurate Al 2s and Si 2p binding energies also indicates the oxidized mixture of these elements.

Analysis by AAS of the samples confirmed the presence of Si, Al, Fe, K, Ca, Mg, and Na and demonstrated the presence (at lower concentrations) of trace elements not readily detected by EDXA or by ESCA. The elements Ni, Pb, Mo, As, Sb, and Cd were present in the respirable fraction at greater than fourfold their crustal abundances. About 3% of the Na, 1% of the K and less

than 1% of all other elements was dissolved from the ash during 24 hours reflecting its relatively insoluble nature.

The variation of specific surface area with particle size is shown in Figure 4.

## DISCUSSION

### Particle Aerodynamic Properties

Particle sizing by the cyclone train showed ~ 9% had an aerodynamic diameter less than  $2 \mu\text{m}$ . Predicted atmospheric residence times for particles less than  $2 \mu\text{m}$  exceed 1 week (Lodge et al, 1981, Seinfeld, 1975). The density ( $2.1 \pm 0.2 \text{ g cm}^{-3}$ ) is less than that expected for an aluminosilicate material ( $\sim 3 \text{ g cm}^{-3}$ ). Our SEM demonstrated that most of the particles had an irregular shape with numerous prominences (Figure 1).

### Crystalline Components

Because of the potential toxicity of quartz, we searched the diffraction pattern for alpha-quartz, cristobalite, and trydimite. Interference of labradorite peaks with those of the three forms of quartz, and the high background, precluded quantitative analysis for quartz content. These problems have been addressed previously (Borman, 1980). In Figure 2, the primary [101] alpha-quartz peak expected at  $26.6^\circ 2\theta$  ( $d = 3.343 \text{ \AA}$ ) is masked by the broad background structure. The resolved peak was assigned to the labradorite  $\bar{1}12$  peak ( $d = 3.325 \text{ \AA}$ ). The angles in the region *A-B* correspond to the secondary [100] peak of alpha-quartz at *A*, the three most intense trydimite peaks and the primary [111] beta-cristobalite peak at *B*. None are above background intensity.

We estimated the quartz content based on EDXA measurements of individual particles. This represents an upper bound, because EDXA measures both amorphous and crystalline  $\text{SiO}_2$ . One hundred-fifteen particles were analyzed; one was found to contain only Si. According to the binomial probability distribution, the fraction of particles in the respirable ash was estimated at 7% or less, with 99% confidence. These results agree with those of Davis et al. (1981) who reported trace amounts to an upper limit of 7.9% quartz in ash samples from the same eruption.

Those elements which are present at higher than normal concentrations in the respirable particles are As, Cd, Mo, Ni, Pb, and Sb. Excluding Mo, they have all been designated as Priority Pollutants by the Environmental Protection Agency (EPA). When individual particles were examined by EDXA, the material was found to be very heterogenous, although nearly all the particles demonstrated peaks for Si and Al.

Surface sulfur was not detected (Figure 3), in agreement with data of both Wightman (1982) and Gardella and Hercules (1983), but in marked contrast with data reported for the volcanoes Pacaya, Fuego,

and Santiaguito, where sulfuric acid droplets were ubiquitous in the particles collected (Rose et al., 1980). The absence of surface sulfur was somewhat surprising, as both sulfur dioxide and hydrogen sulfide were measured in the gases emitted by Mount St. Helens (Fruchter et al., 1980; Hobbs et al., 1982). The very low levels of hydrocarbons detected on the ash surface is equally unexpected. Results of the leaching study show that some of the surface sodium demonstrated present by ESCA was in a readily soluble form.

### Specific Surface Area and Fractal Dimension of the Surfaces

Specific surface area values obtained are in good agreement with those reported by Cannon et al. (1982) for other samples of respirable Mount St. Helens ash. The values for the specific surface area obtained for the sized fractions (Figure 4) lie on a straight line, indicating self-similarity of their surfaces (Mandelbrot, 1982) between  $2 \times 10^{-4}$  and  $3 \times 10^{-2} \mu\text{m}$ . The surfaces themselves are not too complex (porous) because the fractal dimension,  $D = 2.23$ , lies in the lower quarter of the theoretical range of 2–3. The nature of the surface is thus similar to that of coarse soil and particles formed by grinding or pulverizing materials (Avnir et al., 1985).

The smallest particles make a significant contribution to the surface area of airborne dust. The specific surface area ( $> 5 \text{ m}^2 \text{ g}^{-1}$ ) for particles smaller than  $2.1 \mu\text{m AD}$  is similar to that of coal combustion fly ash (Rothenberg, 1980). Thus, by mass, Mount St. Helens volcanic ash can be directly compared to fly ash. On May 18th, 4 cubic kilometers of ash were emitted, with a mass of  $10^{16} \text{ g}$  (Walker, 1981). On the basis of our own and other sizing data, at least 1% of Mount St. Helens ash was in the fine-particle ( $< 2 \mu\text{m}$ ) mode. Thus  $\sim 10^{14} \text{ g}$  of material, specific surface area  $\sim 10 \text{ m}^2 \text{ g}^{-1}$  was emitted. This is similar to total annual worldwide emissions of coal combustion fly ash,  $4 \times 10^{13}$

g (Seinfeld, 1975). Thus, volcanic ash must be considered a nonspecific adsorbent and a potential catalyst for atmospheric chemistry comparable to coal combustion fly ash.

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