AN AERODYNAMIC SIZING AND CHEMICAL ANALYSIS OF THE VOLCANIC FUME PARTICULATE MATTER FROM KĪLAUEA VOLCANO, HAWAI'I

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I. INTRODUCTION

A. Background

A growing concern has arisen over the past couple of decades about the quality of the Earth's atmosphere and, more specifically, the extent to which man's technological "progress" may be affecting it. One of the biggest problems that has arisen as a major pollution concern is the suspended particulate matter and aerosols which are so often a part of the exhaust emissions from various industrial and transportational activities. Studies of this matter have shown that not only are its chemical properties important in determining how toxic the matter may be, but the particle size also has a major influence. Natusch and Wallace (1974) have demonstrated how the smaller size particles (0.01-1 microns) can reach into the pulmonary regions of the respiratory system, where they can remain for weeks or months. The larger particles (>1 micron), in contrast, are trapped in the nasal and pharynx regions, from which they are usually removed in a matter of hours to the digestive system.

It is in the pulmonary region where the most efficient extraction of toxic compounds is found to occur. This is most likely due not only to the long residence time of the particles, but also to the small particle size since extraction rate per unit mass depends on the ratio of the particle's surface area to its volume, which of course increases as particle size diminishes. Chemical effects may also play a significant role.

So it would seem that the careful studies being conducted into the pollution emissions of man's activities are necessary, especially the studies of the particulate matter being emitted. However, to be able to ascertain how significant an influence man's activities have on the overall aerosol and particulate matter levels, one must have some idea of what the natural levels are. Also important is the rate at which natural sources are injecting matter and gases into the atmosphere. One of the most important of these natural sources is volcanic activity--fumaroles and steam vents, active fountaining, and explosive eruptions.

Explosive eruptions, such as Krakatoa in 1883, Mt. Agung (in Bali) in 1963, and others, eject large quantities of material into the atmosphere, much of which may remain there for as long as 3-5 years. (Castleman, 1973) However, eruptions such as these are infrequent (fortunately), one-shot types of injection, acting more as the principal source perturbations of the normal background levels than as the major controlling factors of the normal atmospheric particulate concentration level.

A more likely source for the major volcanic contribution to the natural particulate production is felt to be the "constantly" venting fumaroles, solfataras, and steam vents almost always associated with volcanic activity of any kind. Though the actual generating processes of the particulate matter usually found in this effluent are not definitely known in most cases, a few theories have been proposed over the last few decades.

Naboko (1957) describes a gaseous fluorometasomatism where the silicates in the lava rock are decomposed and, as the result of complex reactions, some of the elements of the rock combine with compounds in the venting gases. These form other compounds which are volatile and are carried away at the temperatures and pressures prevailing during the process.

White and Waring (1963) suggest different sources for different compounds. For substances such as NH_4Cl, which is quite rare in basaltic rocks, the compounds are most likely associated with the original magmatic gases. Other compounds, such as those which are often found associated with sublimate incrustations, are probably the products of reactions of the magmatic gases with the vent wallrocks. Such reactions can result in the concentrating of certain elements even though those elements may be present in the rocks in very low concentrations. These reactions are described as acid-leaching reactions, involving H_2SO_4 in the lower temperature, sulfur-rich fumaroles, and halogen acids (HCl and HF) in the higher temperature vents.

Iwasaki et al. (1964) also suggest that the non-volatile portions of the volcanic fume have originated from acid-leaching and alteration of the vent rocks by the acid gases in the fume. The volatile components of the fume, the chloride, sulfate, carbonate, sulfide, etc., are more likely of magmatic origin, differentiating out of the magma as the temperature and pressure conditions drop near the surface.

Stoiber and Rose (1970), in their study of six Central American volcanoes, condensed the fume for collection, rather than trying to analyze it as an aerosol. Their analysis dealt mainly with chemical variations among different collection sites. Analyzing for Na, K, Ca, Mg, Cl, F, and SO_4, the authors found the best correlations when ratios of the different ion weights were compared. The ratio of Cl/SO_4 was described by the authors as most promising in having potential eruption prediction capabilities. Quantitative data collected in their study seems to suggest that the Cl/SO_4 ratio decreases at fumaroles at or near active vents before an eruptive period and rises after the eruption. The authors suggested that the most likely explanation for this was one advanced by Krauskopf (1948) where he suggested that the haloid gases, HCl and HF, were more soluble in the magma than the sulfur gases. The haloids would tend to persist in the magma longer while the sulfur gases would be expelled more rapidly and be depleted in the fume sooner.

Stoiber and Rose also compared the concentrations of the major cations with each other. In this case they found that the alkali metals (Na and K) were almost always enriched relative to the alkaline earths (Ca and Mg) in the condensate solutions when compared to the same cation ratios in the fumarole wallrocks. Since the authors found themselves in agreement with White and Waring, and with Iwasaki, as to the source of these cations, that is the acid leaching and alteration of the fumarole wallrocks, an extra source was suggested to account for the extra Na and K. Stoiber and Rose proposed that the Ca and Mg concentrations in the fume, as well as part of the Na and K, were the results of the acid leaching process of the wallrocks, giving an aerosol portion to the fume. This portion would have cation ratios equivalent to those found in the vent wallrocks. The extra Na and K would then come from a volatile component of the fume, increasing the overall relative concentration of Na and K in the fume. This volatile component would probably be a differentiation product from the magma body, as its content slowly disappear over time after an eruption.

Activity off the south coast of Iceland, at Syrtlingur and Surtsey in 1965, and at Heimay in 1973, provided opportunities for the collection and analysis of fume matter from Icelandic-type eruptions.

In 1965 McClaine et al. (1968) were able to obtain particulate and volcanic smoke samples from the eruption of the building volcano Syrtlingur, just east of the island of Surtsey. Samples were collected on aerosol monitor type millipore filters from a light airplane flying through the smoke clouds, and also from a boat downwind of the volcano. Analysis by a AMR Probescope gave largely qualitative results. Scanning individual particles in the range of 1-5 microns, results showed that the particles consisted mainly of Si, Ca, Cr, Ni, Fe, and Cl. K, Al, P, Mg, Cu, and Ti were also detected. By taking into account relative detection sensitivities, it was determined that the relative concentrations of the major constituents found were significantly different from their source magma, and that the particles themselves vary in composition to a large extent. A likely reason proposed to explain this was the existence of a selective vaporization step from the magma in the overall particulate formation process, rather than the formation of the particles by some kind of simple mechanical dispersion of the erupting magma. (McClaine et al., 1968) Thermodynamic calculations performed for the species and conditions under study indicate that the compounds mentioned as being concentrated, nickel and chromium among others, are most likely released as chlorides and hydroxides.

An eruption on the island of Heimay, again off the southern coast of Iceland, in 1973 provided another opportunity for the sampling of the smoke and fume clouds of an Icelandic-type eruption. Mroz and Zoller (1975) were able to obtain collections using a six-stage Scientific Advances cascade impactor. The samples were collected on 47mm. Nucleopore filters and were analyzed by neutron activation analysis. Though Cl, Na, and Ca were found to be among the principal elements in the analysis, their relative concentrations (in the microgram per cubic meter of air range) suggested that their main source in this case was the ocean. Other elements detected which were more likely of volcanic origin were Fe and Al (also in the μ gram/m^3 of air range), and to a lesser extent Zn, Mn, V, Se, and Co (in the nanogram/m^3 of air range). Most of these elements, as well as other minor elements in the nano- and pico-gram range, showed relative concentrations which corresponded to average crustal concentrations. However, a few elements, such as Sb, Zn, Se, Br, showed significantly higher concentrations in the fume aerosols relative to their concentrations in crustal material, suggesting some kind of enriching process. Sizing from the cascade impactor showed that these enriched elements seemed to be concentrated in the smaller particles, while the more common elements, Na, Ca, Al were associated more with larger particles. From this, the authors suggested that the enriched elements were volatilized out of the magma, possibly as halides. This vapor would escape to the atmosphere and form small particles, through condensation and coagulation processes.

One of the more heavily studied volcanic areas in the world has been the island of Hawai'i, specifically Kīlauea Volcano. Frequent activity over the past few decades has provided considerable opportunity for researchers to study the gaseous and particulate composition of the fume associated with it.

An extended eruption period in Kīlauea's east rift zone from 1969 through 1971 allowed Naughton et al. (1974) to collect a series of fume sublimate samples. Collection was accomplished using quartz tubes packed loosely with quartz wool, and on one occasion, a stainless steel tube packed with stainless steel wool. The tubes were hung in the vent above the heavily fuming lava lake at Mauna Ulu for periods ranging from 3 to 24 hours, with the solid material and vapors in the fume collecting on the "wool" in the tubes. The sublimate collected was analyzed for eight elements by atomic absorption spectrophotometry (Na, K, Ca, Mg, Fe, Zn, Cu, Ni), four elements (Al, B, Si, Ti) by spectrophotometric techniques, Cl and F by specific ion electrodes, and SO_4 and NH_3 by wet chemical and spectrophotometric methods.

The mole fractions of the various constituents of the sublimates were then used in computer equilibrium calculations as developed by Heald and Naughton (1962). Using this method, it is possible to calculate what the molecular forms of the major components should be at the various conditions associated with the active fountaining of Hawaiian type eruptions. An example of the results of such calculations is shown in Figure 1.

As can be seen, many of the compounds which eventually go to form the fume particulates vaporize from the magma as halides. As the vapors begin to condense and form particulates, reactions between the halide compounds and the

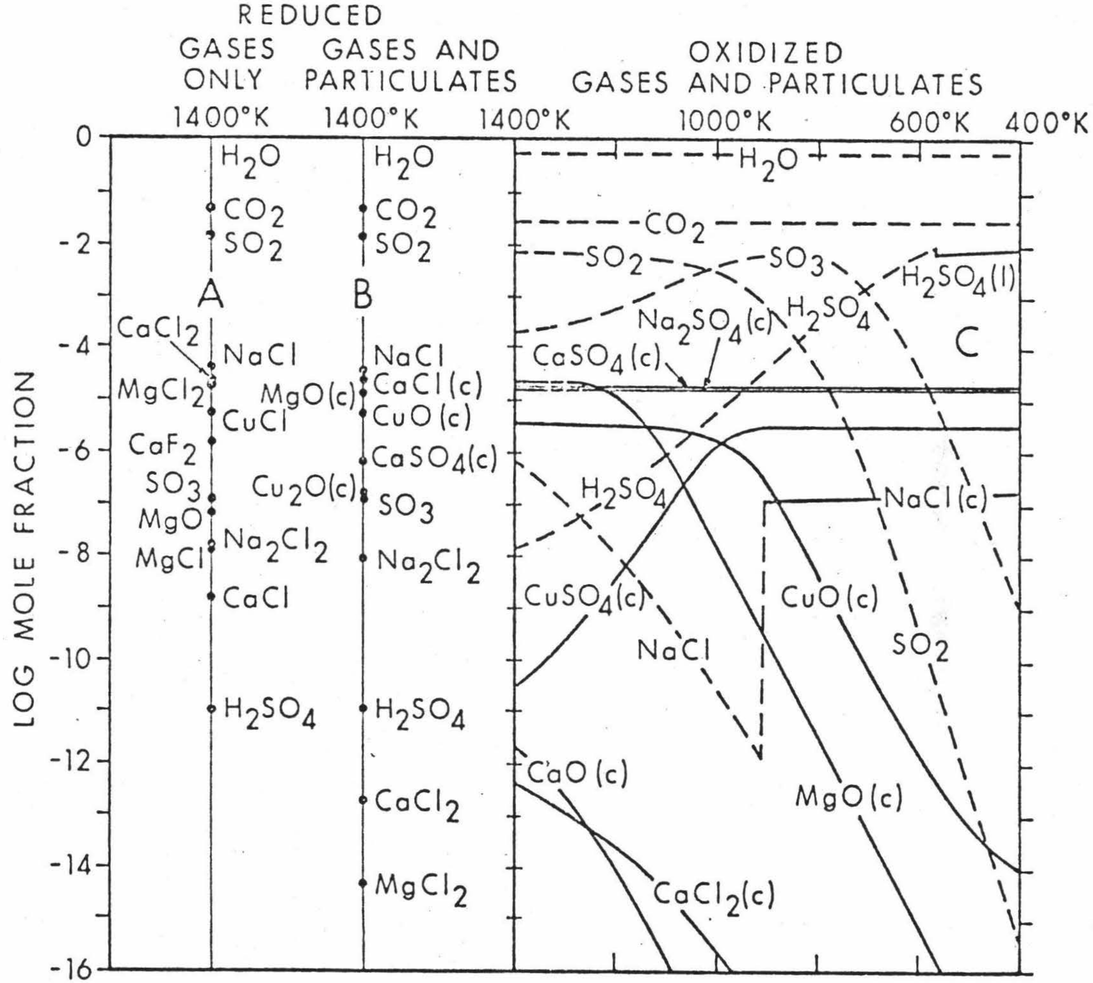

Fig. 1. Computer Calculated Equilibrium Compositions (from Naughton et al., 1974).

SO_3 and H_2O in the fume become important, increasing the concentrations of the sulfate compounds. Increasing the oxygen content in the fume by mixing with the atmosphere, should cause the sulfate compounds to become the main constituents of the fume. Throughout this entire process, it is assumed that chemical equilibrium exists with respect to all the compounds involved. This is most likely the case at the high temperatures existing in and around the fountaining lava, where the fume is vaporizing out and as the particulates begin to nucleate. However, at the lower temperatures, with increasing particle size, the reaction kinetics play a more important role. Realistically, as Naughton (1974) explains, the fume composition derived from the equilibrium calculations represents a composition toward which the reactions should trend and possibly reach if given sufficient time.

A later study by Naughton et al. (1975) performed a bulk collection of the fume particles on Whatman 41 filter paper in conjunction with collections of the gaseous portions of the fume with impingement-type bubblers. Collections were obtained at three main sites: 1) the Halema'uma'u pit crater, where the fume was quite heavy, but there was no lava activity; 2) the lava lake at Mauna Ulu, where the fountaining was low to moderate; and 3) near the August 1971 and July 1974 fissure eruptions on the caldera floor of Kīlauea. Fume concentrations in the air ranged from 111 milligrams/m^3 of air sampled at Mauna Ulu and 115 mg/m^3 at

Halema'uma'u to 3500 mg/m^3 at the Kīlauea fissure eruptions. Though these numbers can serve as gross indicators of fume level associated with the different kinds of activity, the variability of wind direction and strength, as well as variability in fume source emission, prevents any kind of precise measurements.

The results obtained were expressed in mole fractions and weight ratios. They indicated that the particulate matter in the fume was between 50% and 90% sulfates, it being the highest under conditions of least activity (Halema'uma'u). Also, an increase of K relative to Na in conjunction with an increase in activity was noted as well as a considerable increase in SO_4 with respect to Cl.

Another series of studies conducted at Kīlauea over the past decade was carried out by researchers from the National Center for Atmospheric Research in Boulder, Colorado. (Cadle et al. 1967, 1968, 1969, 1971, 1973)

Collections were first taken in 1965-1966 between eruption periods, using a Unico multistage impactor, and separately, polystyrene fiber filters. Cadle et al. (1967) reports that practically all of the particles and droplets were collected on the third and fourth stages of the impactor, indicating mass median diameters for the particles of less than 5 and 3 microns, respectively, assuming average densities of 1 gram/cm^3. Wet chemical analysis indicated dilute sulfuric acid droplets with some dissolved ammonia. Some of the particles captured on the polystyrene filters measured between 1 and 10 microns in diameter and analyzed as ammonium sulfate.

A later study was performed during the eruptive period in 1967. (Cadle and Frank, 1968) Collection was again accomplished using a Unico impactor, with a Gelman pump. This time, however, the samples were collected onto microscope slides and onto electron microscope grids. Optical examinations of the slides revealed largely hygroscopic, water-miscible droplets. A few solid particles were also observed. Chemical tests again indicated the presence of ammonium and sulfate, as well as the probability of sulfur. Electron diffraction patterns of some of the solid particles collected indicate elemental sulfur, ammonium chloride, and ammonium sulfate. A few of the crystals were judged to be calcium sulfate, mainly from their appearance. From the data obtained in this study, the authors concluded that the particulates and aerosol particles in the fume consist of over 95% dilute sulfuric acid droplets with a few cations such as NH_4^+ and Ca^{+2} in solution.

Another collection was made in May 1968 during the same eruptive period which began in 1967 (Cadle et al. 1969). This time fume samples were collected with the Unico impactor used previously, with collection again occurring on microscope slides. Also, a midget impinger-bubbler was used with the fume being bubbled through a few millimeters of distilled water. The results of these collections reinforced earlier findings, showing ammonium, sulfate, calcium, as well as the presence of magnesium. The impinger solutions were also analyzed for total inorganic nitrogen. Absolute amounts of the different compounds found were not reported, merely relative concentrations.

Continuing their study, more collections were taken in 1972 at two different locations on three different occasions--Mauna Ulu in October, and Halema'uma'u in April and December. (Cadle et al. 1973) This time collection was obtained on polystyrene fiber filters in open-faced holders. Most of the filters were extracted with distilled water and analyzed by wet chemical, atomic absorption, and neutron activation procedures.

The main object of this study by Cadle was to see if the relative proportions of the minor constituents varied to any large extent with changes in volcanic activity. Since, as Naughton (1974) noted, the large variability in fume concentration can considerably reduce the significance of any absolute amounts collected, a more relevant evaluation may be obtained by comparing certain ion weight ratios. Though a great deal of comparative significance cannot be given to Cadle's data from this one study, based as they are on single collections, a rough comparison can be made with similar ratios obtained by Naughton et al. (1974, 1975). Such a comparison shows that though the Ca/Mg ratio demonstrates a fairly good correlation with Naughton's data, the Cl/SO_4

ratio shows a significantly lower average, by as much as two orders of magnitude at Halema'uma'u, in Cadle's work.

The possible effects of all this volcanic fume aerosol and particulate matter on the overall global environment, atmospheric heating and cooling trends, weather patterns, and other aspects have been demonstrated by several different studies which have been conducted in recent years.

Castleman et al. (1973) describes how large scale injection of sulfur compounds, in the form of gases and aerosols, by volcanic activity can cause significant fluctuations in the stratospheric aerosol later described by Junge et al. (1961). The authors (Castleman et al.) describe how the sulfate concentration in this aerosol layer at approximately 20 kilometers altitude increased by as much as two orders of magnitude after large eruptions such as Mt. Agung in 1963, Mt. Taal in 1965, and Fernandina in 1968, as well as others.

Heidel (1972) describes another effect from volcanically injected aerosol matter, increases in atmospheric turbidity, which other researchers have tried to link to decreases or increases in world temperatures. Using pyrheliometric observations from Mauna Loa and from Tucson (University of Arizona), the author describes significant increases in the atmospheric turbidity following the eruption of Mt. Agung in March of 1963 and Mt. Awu in 1966.

Along similar lines, Shaw (1976), using precision multiwavelength measurements of the total vertical optical atmospheric transmission from the South Pole and the Mauna Loa Observatory, was able to calculate values for the parameters of the background global aerosols. His results seem to indicate a total column number density for aerosol particles of 1.1×10^8 for a column of 1 cm^2 cross section, with 70% of this amount in the stratosphere. The particle radius value at which the concentration appears to be the highest is 0.04 microns. In addition, the Mauna Loa data seem to indicate a second maximum at 0.09 microns, with an additional columnar number concentration of 7.6×10^8 cm^{-2}. While the first values cited should correspond to the normal background concentration of Aiken nuclei, that is, nuclei in the 0.1-1.0 micron size range, the second set of values, from Mauna Loa, may relate to the volcanic sulfate layer mentioned previously. (Castleman, 1973; Junge, 1961)

Using an estimated value for the "imaginary" portion of the aerosol matter's index of refraction, Shaw calculates that the aerosols cause a slight heating (of about 0.06°C, averaged over the entire year) in the polar regions, and a slight cooling (of about 0.2°C) in the Equatorial zones. Though the author admits that the values given are tentative, considering the rough determination of the value for the imaginary part of the index of refraction, calculations using other values for this n_i component still indicate the same polar heating-equatorial cooling trends. Shaw goes on to indicate that this aerosol induced heating-cooling trend can affect atmospheric circulation and may result in a net cooling of the polar regions.

Relating again to the stratospheric sulfate layer, Meinel (1967) discusses the length of time it apparently takes for the excess material injected by such eruptions as Krakatoa and Mt. Agung to settle out, bringing the aerosol concentrations back to normal. Studying this aspect from the relationship of the phenomenon of volcanic-dust sunsets and their persistence long beyond (3-5 years) the settling time expected (<1 yr.) for the approximately 1 micron dust particles involved, Meinel suggests a chemical source for the persisting particles. Though an initial injection of dust and aerosol particles into the troposphere and stratosphere does occur, they settle out within the first months after the eruption. The aerosol particles which seem to end up and stay for so long in the stratosphere at an altitude of roughly 20 kilometers are actually the result of a large-scale diffusion of the SO_2 given off in the eruption. Once it reaches the general area of the stratospheric "Junge" layer, this large influx of SO_2 enters into the ozone-SO_2 reactions which are believed to occur in this region (Junge, 1961; Kellogg et al., 1972; Bufalini, 1971), forming sulfate particles which precipitate onto condensation nuclei present, effectively "replenishing" the dust particles which settle out.

Thus, the light scattering layer of aerosol particles is maintained far longer than what would be expected by simple injection of all the particles with which one is confronted.

B. Purpose

The purpose of this research is to extend the chemical study of the particulate matter in volcanic fume by performing aerodynamic sizings of the particulates in the fume and studying these chemically and physically.

By taking repeated collections at established sites, it was hoped to be able to detect any chemical or physical change at a site over time. Aspects such as Cl/SO_4, Na/K, or alkalis/alkaline earths, as noted previously, have been known to change significantly over time, this being especially the case with Cl/SO_4 before an eruption. Other aspects that were studied were to determine the actual sizes of the particulates being emitted at the various collection sites, as well as any significant changes in the size of the particles coming out at a particular site over time. This latter aspect was probably unlikely, but was looked for anyway.

The collections were also studied to observe any chemical or more likely physical changes of the particulates with varied distance from the fume source. Hopefully, what would be observed here would be the occurrence of any atmospheric reactions between the particles which would add or remove certain elements from the fume, changing it chemically, or more likely, causing a condensation or coagulation of the smaller particles, forming larger ones, thus changing the fume physically.

Since samples could only be obtained infrequently, due to cost and limited available collection time, and to extend the observation period by an additional year or so, this work will also consider several sets of data obtained by Virginia Greenberg, using the same analysis procedures.

II. COLLECTION TECHNIQUES

A. Anderson Sampler

The main collection system in this study was an Anderson non-viable particle sampler. This collection system is considered better in some respects than regular, single-orifice cascade impactors in that by its unique design, the Anderson collector is able to perform an aerodynamic sizing of the particles being sampled. This type of sampling is much more useful than just a physical sizing of the particles in that it gives a better indication of how the particles will behave in the atmosphere. Since this aerodynamic sizing simulates to a significant degree the human respiratory system, the Anderson sampler operates quite well in determining respiratory health hazards.

> "The Anderson samplers consist of a series of stacked stages and collection surfaces. Depending on the calibration requirements, each stage contains from 150 to 400 precisely drilled jet orifices identical in diameter in each stage but decreasing in diameter on each succeeding stage. As a constant flow of air is drawn through the sampler so that as the air passes from stage to stage through the progressively smaller holes, the velocity increases. As the airstream makes a turn at each stage and the particle gains enough inertia to lose the aerodynamic drag, it is hurled from the airstream and impacted on the collection surface. The particle has been aerodynamically sized the moment it leaves the turning airstream." (Anderson, 1972)

The stated size ranges of the particles that are collected on each stage are given in Table 1, as well as the

TABLE 1

PARTICLE SIZE RANGES FOR COLLECTION STAGES OF ANDERSON NON-VIABLE PARTICLE SAMPLER AND CORRESPONDING AREAS OF HUMAN RESPIRATORY SYSTEM

Stage 0 (1)*	>11 microns	
Stage 1 (2)	7-11 microns	nasal passages
Stage 2 (3)	4.7-7 microns	pharynx
Stage 3 (4)	3.3-4.7 microns	trachea & primary bronchi
Stage 4 (5)	2.1-3.3 microns	secondary bronchi
Stage 5 (6)	1.1-2.1 microns	terminal bronchi
Stage 6 (7)	0.65-1.1 microns	alveoli
Stage 7 (8)	0.43-0.65 microns	alveoli

*number in parantheses represents sample stage number in data tables region of the respiratory system to which that stage is supposed to correspond.

Before being assembled, the collection stages, plates, and rubber O-ring gaskets are cleaned in an ultrasonic cleaner with a commercial cleaning solution. They are rinsed with deionized-distilled water (DDW), dried, and the sampler is assembled with a set of prepared collection discs. The inlet orifice is covered with a plastic cap to prevent preliminary contamination of the collection discs.

Though the sampler has been laboratory calibrated for the appropriate size ranges associated with each stage, using unit-density spherical particles or uranine and methylene blue dyes, the actual sizes being collected on each stage were not as crucial as the change in stage of maximum concentration, so this calibration was not repeated here.

The fume particles were collected onto discs which had been cut from 0.0015 inch thick polyethylene bags. The collection surfaces were cleaned by soaking 6-8 hours in 5-10% nitric acid solution, then rinsed with deionized-distilled water. The discs are dried, weighed on an analytical balance, and placed in plastic bags. Contamination is controlled by placing two discs collection sides together, and forcing out most of the air, before sealing the bag. After exposure, the discs are removed from the sampler, folded in half, and placed back into a plastic bag, which is ziplocked sealed. They were then returned to the laboratory for analysis.

Electrical power for the Anderson pump was provided by a "portable," 1800 watt gasoline generator.

Back in the laboratory, the exposed discs were again weighed to see if a detectable amount of material had been collected. They were then visually examined under a binocular microscope to observe any distinct solid particles that may have been collected and the spatter pattern of any collected solution droplets. The discs were rinsed off with a few drops of DDW which had been further purified by subboiling distillation in all-quartz equipment (QDW). (Naughton, 1975) This was diluted to 10 milliliters of total solution with QDW, transferred to polyethylene vials which had been nitric acid soaked (10% solution), DDW rinsed, and dried in a laminar flow clean bench, in which all of the sample preparation had occurred. These vials were then placed in a freezer until analyzed.

B. Nucleopore Filters

Another sampling system which was used on occasions involved a GE 47mm cascade impactor arrangement using 0.4, 0.2, and 0.1 micron Nucleopore filters as the size discriminators and collection surfaces. These filters, after exposure, were placed in individual hard plastic containers for storage until returned to the laboratory. Back in the lab, these filters were also observed under a microscope to ascertain if any visible solid particles had been collected. They were then rinsed off with QDW, diluted to 10 ml. in a volumetric flask, and transferred to polyethylene vials, which were also placed in a freezer until analyzed.

C. Scientific Advances Cascade Impactor

One other sampling system was tried out in January of 1976. This system was a six-stage Scientific Advances cascade impactor. In contrast to the Anderson impactor, this sampler uses a single orifice pumping design, with sample collection occurring on the center of, in this case, a polyethylene disc. These discs are similar to the collection discs used in the Anderson sampler, only of a much smaller size, about 11.3 cm^2, supported by round glass slides.

A certain degree of difficulty was encountered in the transporting and use of this sampler. Since the impactor stages were significantly larger than the Anderson stages, and being made out of stainless steel, the entire set-up was considerably heavier and therefore somewhat harder to transport.

A problem arose in shipping the impactor stages, when the packing case the stages were in partially broke open, dislodging three of the stages from their packing and knocking the collection plates in stages 1 and 3 loose. The collection disc from stage 3 came loose from its supporting glass disc and was found stuck to the outside of the impactor stage. The plastic collection discs were rinsed off with QDW before reassemblying the stages at the Observatory but it is most likely any analysis from stage 3 at least, and probably from stage 1 also, has little if any reliability due to contamination.

The impactor was tried anyway at Halema'uma'u on January 13, 1976, taking a sampling at the same time as a sampling was being taken with the Anderson sampler. The collection times as well as the fume and weather conditions were the same as those described for sample 12. (See Results) The pumping rate for the Scientific Advances impactor was measured at 0.75 cubic feet per minute.

D. Collection Sites

Collection was performed regularly at 4 different sites, with one time samplings obtained at a few other sites. See Figure 2.

One of the regular sites was at Sulfur Bank, a solfatara or fumarole whose gases include a significantly higher proportion of sulfur gases. Located at the northern edge of the Kīlauea caldera just west of the Park Headquarters, in a shallow graben just within the caldera's outer boundary faults, the area is the largest of the solfataras on Kīlauea. (Jaggar, 1924) The collection site itself is the remains of a well manifold connecting three holes drilled in 1922-1923 to depths of 15, 15, and 70 feet.

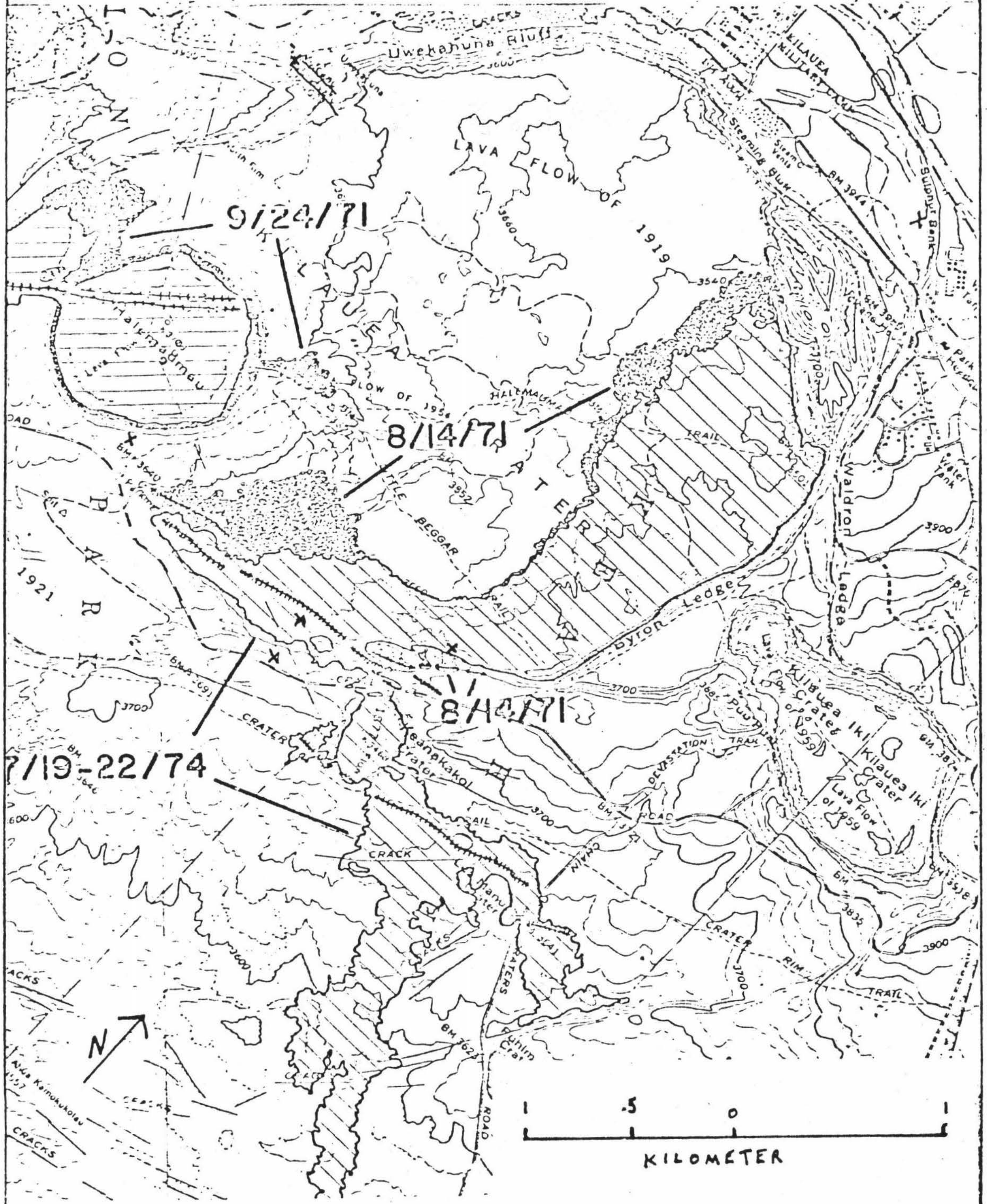

Fig. 2. Map of Kīlauea Volcano, Hawai'i (from Monthly Report of H.V.O. 12/21/74-1/20/75).

The iron well pipe is essentially gone, corroded away, and has been plugged off, except from one of the shorter holes. The gas flows out at a rate of about 10 liters per minute and at a temperature of about 95-96°C., the boiling point of water at that elevation. The rocks piled around the mouth of the vent are encrusted with deposited sulfur. (Keeling, 1973) Due to the fact that the fume emanating from this site was largely steam just above its condensation point, condensation on the collection stages was always a problem, with the collection films, and the rest of the collection apparatus, always having considerable amounts of water on them.

Another one of the regular collection sites was downwind of the August 14, 1971, and the July 19, 1974, fissure eruption sites on the caldera floor. See Figure 2. Though the site was sampled several times, the actual site of collection varied from right up to the venting fissures to as far away as the bluff near the crater rim road downwind (S-SSW) of the fissures. This is a distance of roughly 300 meters from the 1974 fissure and about 500 meters from the 1971 fissure site. An examination of the different samplings done in this study, and more so, of data obtained in earlier samplings by Dr. J. Naughton suggests that most of the material collected with each downwind sampling was from the 1971 fissure site.

A third collection area was of the fume emanating from the Halema'uma'u pit crater itself. Collection here was taken roughly 5-6 meters downwind of the crater rim (roughly south), approximately on a line between the crater and the crater lookout parking lot. Often the fuming at this point was fairly dense due to the close proximity of its source and consequently, reasonably good samples were often obtained there.

Another frequent, though somewhat irregularly, sampled site was the caldera rim in front of the Volcano Observatory, WNW of the pit crater. Due to a nearby electrical source, one of the equipment sheds at the Observatory, it was possible to make arrangements to set up the collector in the evening and allow it to run overnight. When Kona winds were encountered overnight, reasonably good samples were obtained. However, more often than not the prevailing trade winds carried the fume from Halema'uma'u and the surrounding caldera floor off to the south or southwest, away from the Observatory. The samplings obtained at such times usually showed concentrations hardly above background levels and often were not significantly greater than blank concentrations.

A site which was sampled just once was at the end of the Mauna Loa strip road at an elevation of approximately 2000 meters. Since the site is roughly northwest of the Kīlauea summit, and the tradewinds were blowing off and on that day, the fume from Kīlauea, which was quite visible from the collection site, was being blown away from the site. Though Mauna Loa had erupted several months previous, no fuming was in evidence anywhere around Mauna Loa's summit, which was completely visible from the Observatory. Therefore, it is assumed that the collection obtained at the site is roughly representative of the atmospheric background concentrations in that region.

One other site that was sampled on one occasion was of the fume from Halema'uma'u after it had been blown a few hundred meters out over the Ka'ū Desert. Though any large scale chemical differences were not expected, what was looked for were any significant changes in the size range of the maximum concentration of any of the species being studied.

III. ANALYTICAL PROCEDURES

A. Atomic Absorption Spectrophotometry

Since the end results of these collection and work-up procedures are, on the most part, quite dilute, near neutral or weakly acidic aqueous solutions, analysis of the cations of interest is well-suited to atomic absorption spectrophotometry. Since the concentrations are all quite low, interferences between different constituents were considered unlikely to be a problem.

The samples were analyzed by atomic absorption for Na, Ca, Mg, K, Fe, Zn, and Cu, using the routine procedure of bracketing the sample concentrations with mixed standard solutions. (Perkin-Elmer, 1972) These standard solutions had been made up by dissolving a known amount of a reagent grade salt of the elements desired to obtain a stock solutio of 1000 parts per million (ppm) concentration, as given in Table 2. Standards in the desired concentration range were made by diluting these stock solutions down to the desired values with QDW.

The concentration measurements were obtained from a Perkin-Elmer model 303 atomic absorption spectrophotometer, using a model 303-0401 3-slot burner head and an air-acetylene oxidant-fuel mixture. Operating parameters for the different elements were obtained from the Standard

TABLE 2

REAGENTS USED TO PREPARE STANDARD STOCK SOLUTIONS

Na	NaCl	Fe	$FeCl_3$
K	K_2SO_4	Cu	$CuCl_2$
Mg	$MgCl_2$	Zn	$ZnCl_2$
Ca	$CaCl_2$	Cl	NaCl
total S	K_2SO_4		

Conditions tables in the Perkin-Elmer Analytical Methods Handbook. The light sources used were Perkin-Elmer Intensitron hollow cathode lamps for all elements except Zn, for which a Westinghouse hollow cathode device was used. Distilled-deionized water was aspirated between samples to help control the flame noise and temperature, and to aid in maintaining a steady baseline.

The percent absorption of the samples and standards were printed out on a Perkin-Elmer model 165 chart recorder. The percent absorption values were converted to their corresponding absorbance values. These values for the standards were used to calculate a standard curve using a least squares calculation. The sample absorbance values were compared to this calculated curve and their corresponding concentration values were obtained.

B. Specific Ion Electrodes

Chloride analysis was performed using an Orion model 94-17 solid state Cl specific ion electrode and an Orion model 90-02-00 double junction reference electrode with 1M KNO_3 in the outer chamber. The sample solutions were titrated with a 2.82×10^{-3}M $AgNO_3$ solution with the resulting millivolt readings being plotted on 10% volume corrected Gran's Plot paper. Two different pH meters were used during the course of all of the analyses. Originally a Beckman Expandomatic pH meter was used, utilizing the expanded scale of the meter. Then in April of 1976, an Orion Research model 801A digital analyzer pH meter was obtained and the remaining samples were analyzed with this instrument.

The procedure consisted of pipeting 4 ml. of the sample solution into a 100ml. Teflon beaker, adding a drop of 1M KNO_3 solution to give a constant ionic strength background, and diluting to a total volume of 20ml. with QDW. This solution is titrated with the $AgNO_3$ solution in 0.10ml. increments and the +millivolt reading is taken after each increment. The readings are plotted on the Gran's Plot paper and the chloride ion concentrations are obtained from the axis intercept when the samples are plotted against a blank and standard solutions.

Normally a blank of 20ml. of QDW is titrated first to determine the millivolt range for the standards and samples. Then 20ml. portions of the standard solutions are titrated, continuing the 0.10ml. additions of the $AgNO_3$ solution until 4 to 6 millivolt readings are obtained in the range spanned by the QDW blank titration. The sample intercepts are then compared with the "best-fit" line intercepts of these standards.

C. Wet Chemical--Ultraviolet-Visible Spectrophotometry

Total sulfur in each sample was analyzed by a procedure adopted from Johnson and Nishita (1952). In this procedure one milliliter of the sample or standard solution was refluxed at 115°C with a reducing solution consisting of red phosphorus, concentrated HI, and concentrated formic acid, under a nitrogen atmosphere for an hour. The resulting hydrogen sulfide vapor was bubbled through a washing solution consisting of a 50-50 mixture of $NaH_2PO_4 \cdot H_2O$ and pyrogallol ($C_6H_3(OH)_3$) dissolved in DDW. This solution is designed to remove any agents which could reoxidize the hydrogen sulfide. The hydrogen sulfide was then absorbed in a 4-1 mixture of $Zn(C_2H_3O_2)_2 \cdot 2H_2O$ and $NaC_2H_3O_2 \cdot 3H_2O$ dissolved in DDW. After the hour of refluxing, 5ml. of an amine solution, prepared from Kodak #1333 p-aminodimethyl aniline sulfate dissolved in DDW and sulfuric acid, was added to the absorbing solution. The resulting acidic solution was transferred to a 50ml. volumetric flask containing a milliliter of a ferric ammonium sulfate solution, and diluting to volume with DDW or QDW, forming a methylene blue dye solution. The solutions prepared one day, blank, standards, and samples, were allowed to develop overnight and their absorbance at 670 nanometers was measured the next morning on a Beckman DU Spectrophotometer. A diagram of the refluxing apparatus is shown in Figure 3.

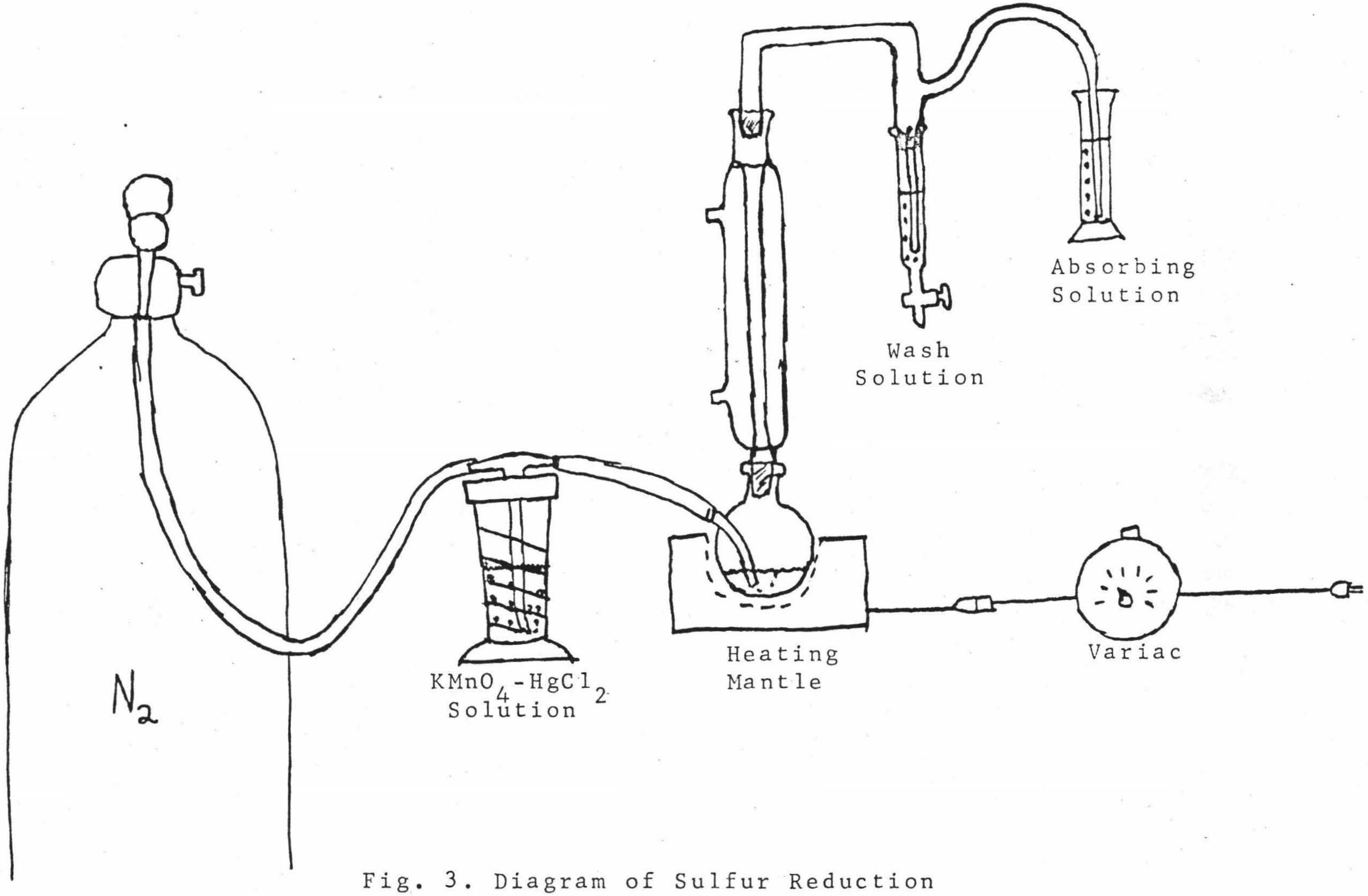

Fig. 3. Diagram of Sulfur Reduction Refluxing Apparatus

IV. RESULTS AND DISCUSSION

A. Results

Compiled tables of the results obtained from the chemical analyses in this study can be seen in Table 3 through 25. The values reported in these tables are the net values obtained after subtracting an average blank value from the amounts obtained in each analysis. The total weights reported for each stage in Tables 3 through 25 are the totals of just the cations that were found in each analysis. This was done since with many cases, if the total sulfur content had been added to the total cation amount, the latter would have contributed little. The collections themselves are described below.

Table 3. This sampling was collected over the night of January 14-15, 1975, at the Hawaiian Volcano Observatory (HVO) over a timespan of about 14 hours. Conditions over much of the evening and night were rainy, foggy, with intermittent Kona winds, but clearing by the end of the collection run the next morning. Typical collection patterns for the Anderson impactor were visible only on the last three stages.

Table 4. This sample was obtained at the August 1971 caldera floor fissure eruption site on January 15, 1975. The collection was obtained within 2 meters of one of the main fume vents, towards the upper end of the rift area, over a period of about 45 minutes. The fume was quite heavy in the immediate vicinity around the vent, and contained very noticeable amounts of SO_2, as detected by its smell.

Table 5. Sulfur Bank was sampled on January 16, 1975, for about 45 minutes. The steam and fume were funneled over the impactor stages, which were placed right beside the vent about 3/4 of a meter off of the ground, by draping a large plastic sheet over the cairn built up around the vent. This was arranged such that the fumes escaped out by passing over the impactor stages. Upon examination back in the laboratory, after drying in a desiccator for 3.5 to 4 hours, the discs showed a whitish scaling on their reverse (non-collection) sides such as what one would obtain from evaporating a dilute solution of dissolved salts.

A collection was obtained at Halema'uma'u on July 7, 1975, by Don Thomas. He reported that the sample was taken on the edge of the Halema'uma'u pit crater downwind of a densely fuming crack near the overlook parking area. The collection run was carried out for an hour and a half. The sample was analyzed but the results were dropped when it was found that the stages had not been sitting squarely on their base such that the fume had not been drawn through the whole system but only over the last stage.

Table 6. This collection was taken on August 8, 1975, directly downwind of the fume issuing from Halema'uma'u, by Don Thomas. Taken over a 90-minute timespan, this sample contained significant amounts of moisture upon removal and showed typical collection patterns. No information was available on weather conditions at the time of collection.

Table 7. This sampling was obtained August 13, 1975, by Don Thomas. The collection site was described as being 231 paces out into the Ka'ū Desert from the Crater Rim Road, downwind of the fuming area at Halema'uma'u. The collection was conducted over 134 minutes under conditions which were only described as quite windy.

Table 8. The fume from the Kīlauea caldera fissure eruptions of 1971 and 1974 was sampled from the overlooking bluff near the Crater Rim Road on August 20, 1976, by Don Thomas for approximately 350 minutes. The weather at the time was described as gusting, variable winds, with a drizzling rain falling.

Table 9. This sampling, obtained at Sulfur Bank January 12, 1976, was collected in the same manner as earlier Sulfur Bank samples, by having a large plastic sheet draped

over the vent, funneling the steam and fume over the impactor stages. The collection proceeded for 90 minutes. Upon removal, the discs were quite wet from condensed steam.

Table 10. Collected at the H.V.O., this sampling was obtained over a 9¼-hour period during the night of January 12-13, 1976. Unfortunately the prevailing wind that night blew the fume off to the southwest away from the Observatory. Rain was expected during the night so a partial wind block was placed on the upwind side of the collector. This may also have shielded the collector somewhat from any residual particulates which might have been carried over to the Observatory by the wind. This collection also used a different pump due to the regular Anderson pump having frozen up. The air flow from this pump was measured at approximately 1.25 cubic feet per minute.

Table 11. This sample was obtained January 13, 1976, on the bluff overlooking the August 1971 fissure eruption area. This area is still actively fuming, though it has died down considerably over the past year or so, at least with respect to particulate matter. The wind was blowing quite strongly during the two-hour collection period, carrying the fume in the general direction of the impactor most of the time. Because of the blowing rain, a shield was

Table 3

Sample stage no.	1	2	3	4	5	6	7	8	Total
μg Na	1.85	2.16	0.79	2.86	2.01	4.06	4.87	8.32	26.94
" Ca	1.02	0.14	0.36	1.39	0.23	0.23	0.58	1.47	5.42
" K	1.01	0.80	0.54	1.35	1.82	1.52	1.95	3.90	12.89
" Mg	n.d.*	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	-
" Fe	-+	-	-	-	-	-	-	-	-
" Zn	0.04	0.014	-	-	-	-	0.051	0.11	0.21
" Cu	-	-	-	-	-	-	-	-	-
μg/ml Cl	-	-	n.d.	10	1.8	3.5	4.5	n.d.	
as SO_4 μg total S	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	30	
Δmg	0.1	0.1	-	-	0.1	-	-	-	
Total (excluding S&Cl)	3.92	3.11	1.69	5.6	4.06	5.83	7.45	13.8	

Collected: 1/14-15/75 at Hawai'i Volcano Observatory

*n.d. - not determined

+ - below average blank levels

Table 4

Sample stage no.	1	2	3	4	5	6	7	8	Total
μg Na	12.3	8.62	4.55	9.47	4.54	7.50	7.50	11.0	65.48
" Ca	1.39	0.29	0.36	1.66	0.29	1.32	0.87	1.09	7.27
" K	4.08	2.92	1.73	3.63	1.52	5.57	3.40	5.90	28.75
" Mg	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	-
" Fe	-	-	-	-	-	-	-	-	-
" Zn	0.07	-	0.10	-	trace	-	0.18	0.04	0.39
" Cu	-	-	-	-	-	-	-	-	-
μg/ml Cl	n.d.	-	n.d.	~3.6	n.d.	~2	n.d.	~3.6	
as SO_4 μg total S	22	n.d.	17	n.d.	210	n.d.	18	n.d.	267
Δmg	-	-	-	-	-	-	-	-	
Total (excluding S&Cl)	17.8	11.8	6.64	14.8	6.35	14.4	12.0	18.0	

Collected: 1/15/75 at 1971 Fissure Eruption Site

Table 5

Sample stage no.	1	2	3	4	5	6	7	8	Total
μg Na	1.90	3.30	1.32	1.10	2.33	0.80	0.67	3.33	14.75
" Ca	0.29	0.23	0.14	-	0.23	0.23	0.08	0.36	1.56
" K	0.74	1.48	0.48	0.54	1.05	0.38	1.14	1.48	7.29
" Mg	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	-
" Fe	-	0.17	-	0.20	-	-	-	-	-
" Zn	0.22	0.11	-	0.05	-	0.023	-	0.02	0.42
" Cu	-	-	-	-	-	-	-	-	-
μg/ml Cl	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	~2	~2	
as SO_4 μg total S	-	n.d.	18	30	18	53	n.d.	n.d.	-
Δmg	0.6	0.2	0.1	-	0.1	0.2	-	0.4	
Total (excluding S&Cl)	3.15	5.12	1.94	1.69	3.61	1.43	1.89	5.19	

Collected: 1/16/75 at Sulfur Bank

Table 6

Sample stage no.	1	2	3	4	5	6	7	8	Total
μg Na	0.23	0.52	6.27	0.50	10.0	0.50	0.67	2.05	20.74
" Ca	0.56	0.17	0.56	0.34	2.01	-	-	0.11	3.75
" K	-	0.12	0.83	-	2.15	0.38	0.12	0.49	4.09
" Mg	0.02	-	1.13	0.04	0.87	1.38	0.55	0.48	4.47
" Fe	-	-	-	0.65	1.18	1.27	1.03	0.84	4.97
" Zn	0.11	0.25	0.97	0.25	1.37	0.34	0.25	0.25	3.79
" Cu	-	-	0.25	-	0.47	-	-	-	0.72
μg/ml Cl	0.54	0.54	~3	0.66	~2	0.63	0.63	0.24	
as SO_4 μg total S	62	6.5	45	244	540	1420	1200	840	4358
Δmg	-	-	-	-	1.6	3.0	3.8	2.0	
Total (excluding S&Cl)	0.92	1.06	10.0	1.78	18.0	3.87	2.62	4.22	

Collected: 8/8/75 at Halema'uma'u

Table 7

Sample stage no.	1	2	3	4	5	6	7	8	Total
µg Na	2.92	4.63	3.09	5.70	4.50	0.21	0.25	-	21.3
" Ca	0.46	0.57	1.56	1.51	0.88	0.45	0.25	0.25	5.93
" K	0.80	1.45	0.23	1.10	1.18	-	-	-	4.76
" Mg	0.055	0.086	0.004	0.14	0.25	0.02	0.02	-	0.57
" Fe	-	-	-	-	-	-	-	-	-
" Zn	0.45	0.21	0.50	0.14	0.21	0.26	0.30	0.18	2.25
" Cu	-	-	-	-	-	-	-	-	-
µg/ml Cl	0.36	0.6	1.3	n.d.	0.1	-	-	-	
as SO_4 µg total S	91	1380	22.2	n.d.	10-11	12.6	2.8	2.7-5.5	1840
△mg	-	-	-	-	-	-	-	-	
Total (excluding S&Cl)	4.68	6.95	5.38	8.59	7.02	0.94	1.76	0.43	

Collected: 8/13/75 at Ka'ū Desert from Halema'uma'u

Table 8

Sample stage no.	1	2	3	4	5	6	7	8	Total
µg Na	6.82	6.11	1.10	0.41	0.60	0.88	0.27	0.77	16.96
" Ca	1.02	0.90	1.40	0.15	0.21	0.04	-	0.19	3.91
" K	2.63	0.49	0.27	0.08	-	0.18	-	0.65	4.73
" Mg	o.276	1.06	-	-	-	-	-	0.012	1.35
" Fe	-	-	-	-	-	-	-	-	-
" Zn	0.26	0.76	0.29	0.21	0.09	-	-	0.25	1.86
" Cu	-	-	-	-	-	-	-	-	-
µg/ml Cl	-	-	-	-	-	-	-	-	-
as SO_4 µg total S	4.1	5.7	3.6	2.1	1.1	-	3.1	2.6	22.3
Δmg	-	-	-	-	-	-	-	-	
Total (excluding S&Cl)	11.0	9.32	3.06	0.85	0.90	1.1	0.27	1.87	

Collected: 8/20/75 at 1971-1974 Fissure Eruption Site

Table 9

Sample stage no.	1	2	3	4	5	6	7	8	Total
µg Na	0.91	0.29	-	0.82	2.12	-	-	-	4.14
" Ca	-	0.09	-	0.01	0.31	-	0.20	0.50	1.11
" K	0.46	0.15	-	0.56	1.22	-	0.10	-	2.49
" Mg	1.97	4.37	3.17	2.25	1.40	1.36	0.49	0.55	15.6
" Fe	-	-	0.46	0.41	0.26	0.29	-	-	1.42
" Zn	-	0.25	0.19	0.22	0.12	0.05	-	-	0.83
" Cu	-	-	-	-	-	-	-	-	-
µg/ml Cl	0.60	0.55	0.60	0.92	-	trace	-	0.40	
as SO_4 µg total S	22.4	25.2	24.5	15	8.1	7	7.4	2.8	112
Δmg	0.6	0.7	0.5	0.3	0.2	0.1	-	0.5	
Total (excluding S&Cl)	3.34	5.15	3.82	4.27	5.43	1.70	0.79	1.05	

Collected: 1/12/76 at Sulfur Bank

Table 10

Sample stage no.	1	2	3	4	5	6	7	8	Total
μg Na	0.16	-	1.32	0.25	-	0.24	0.31	-	2.28
" Ca	0.05	-	0.23	-	-	0.18	0.41	-	0.87
" K	0.05	-	0.70	0.01	-	0.03	0.09	-	0.88
" Mg	0.023	0.007	0.12	0.064	0.012	0.082	0.17	-	0.478
" Fe	-	-	-	-	-	-	-	0.57	0.57
" Zn	-	-	-	-	-	0.12	1.18	-	1.30
" Cu	-	-	-	-	-	-	-	-	-
μg/ml Cl	-	0.2	-	-	-	0.4	-	-	
as SO_4 μg total S	n.d.	-	-	-	-	-	-	-	-
Δmg	0.05	0.1	-	0.1	0.1	0.1	-	-	
Total (excluding S&Cl)	0.28	-	2.25	0.26	0.01	0.57	1.99	0.57	

Collected: 1/12-13/76 at Hawai'i Volcano Observatory Overlook

Table 11

Sample stage no.	1	2	3	4	5	6	7	8	Total
μg Na	1.3	-	-	-	0.05	-	0.68	-	2.03
" Ca	0.24	-	-	0.05	0.01	-	0.01	-	0.31
" K	0.73	-	-	-	0.06	-	0.12	-	0.91
" Mg	0.12	0.019	0.023	0.055	0.046	-	0.084	0.009	0.36
" Fe	-	-	-	-	-	-	-	-	-
" Zn	-	-	-	0.22	-	-	-	-	0.22
" Cu	-	-	-	-	-	-	-	-	-
μg/ml Cl	0.63	0.2	0.2	0.2	0.4	0.2	n.d.	0.2	
as SO_4 μg total S	1.2	1.5	1	-	-	-	n.d.	trace	3.7
△mg	-	-	-	-	-	-	-	-	
Total (excluding S&Cl)	2.40	0.019	0.023	0.32	0.17	-	0.89	0.009	

Collected: 1/13/76 at 1971-1974 Fissure Eruption Site

Table 12

Sample stage no.	1	2	3	4	5	6	7	8	Total
µg Na	0.16	-	-	-	-	-	-	-	0.16
" Ca	0.09	-	0.01	-	-	1.42	0.31	0.84	2.67
" K	0.12	-	-	-	-	-	-	-	0.12
" Mg	0.082	0.039	0.053	0.030	0.019	0.98	0.048	0.039	1.29
" Fe	-	-	-	-	0.32	0.80	0.41	0.55	2.08
" Zn	0.39	0.22	0.25	-	-	0.93	0.22	0.12	2.13
" Cu	-	-	-	-	-	-	-	-	-
µg/ml Cl	-	trace	0.2	0.2	trace	5	-	0.12	
as SO_4 µg total S	6	2.6	20	50	128	566	256	159	1188
Δmg	0.05	0.05	0.05	0.15	0.35	1.35	0.85	0.45	
Total (excluding S&Cl)	0.84	0.26	0.31	0.030	0.34	4.13	0.99	1.55	

Collected: 1/13/76 at Halema'uma'u

Table 13

Sample stage no.	1	2	3	4	5	6	7	8	Total
μg Na	-	-	0.13	-	0.43	0.56	0.20	-	1.32
" Ca	-	-	0.01	-	0.05	-	-	-	0.06
" K	-	-	0.01	-	0.33	0.19	0.06	-	0.59
" Mg	0.028	0.017	0.037	0.035	0.058	0.067	0.055	-	0.30
" Fe	-	-	-	-	-	-	-	-	-
" Zn	-	-	-	-	-	-	-	-	-
" Cu	-	-	-	-	-	-	-	-	-
μg/ml Cl	-	-	-	0.5	-	-	-	-	
as SO_4 μg total S	-	2.5	-	-	-	16	5	-	23.5
Δmg	-	-	0.05	0.05	0.05	0.15	-	-	
Total (excluding S&Cl)	0.028	0.017	0.19	0.035	0.87	1.73	0.32	-	

Collected: 1/14/76 at Mauna Loa strip road

Table 14

Sample stage no.	1	2	3	4	5	6	7	8	Total
μg Na	2.06	0.76	-	0.39	0.08	0.12	0.21	-	3.62
" Ca	0.09	0.09	-	0.20	-	-	-	-	0.38
" K	2.19	0.85	0.08	0.33	-	0.29	0.45	-	4.19
" Mg	3.66	0.38	0.013	0.096	0.066	0.65	8.52	0.028	13.4
" Fe	-	-	-	0.54	-	-	0.63	-	1.17
" Zn	0.97	0.05	-	-	-	0.05	0.78	-	1.85
" Cu	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	-
μg/ml Cl	-	-	0.55	-	-	0.57	0.73	0.53	
as SO_4 μg total S	175	16	28	179	451	1610	1130	1720	5309
Δmg	0.75	0.15	0.2	0.8	1.3	5.1	4.7	5.8	
Total (excluding S&Cl)	8.97	2.13	0.093	1.56	0.15	1.11	10.6	0.028	

Collected: 4/15/76 at Halema'uma'u

Table 15

Sample stage no.	1	2	3	4	5	6	7	8	Total
μg Na	0.39	-	0.19	-	0.20	0.20	0.76	-	1.74
" Ca	0.02	-	-	-	-	-	-	-	0.02
" K	0.22	-	0.24	0.38	0.13	0.18	0.69	-	1.84
" Mg	0.064	0.014	0.026	0.033	0.044	0.042	0.039	-	0.26
" Fe	-	-	-	-	-	-	-	-	-
" Zn	0.02	-	0.02	-	-	-	-	-	0.04
" Cu	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
μg/ml Cl	-	0.67	0.73	0.78	-	-	0.43	-	
as SO_4 μg total S	12	-	-	-	2.6	-	-	3.6	18.2
Δmg	-	-	-	-	-	-	-	-	
Total (excluding S&Cl)	0.71	0.014	0.48	0.41	0.37	0.42	1.49	-	

Collected: 4/15/76 at 1974 Fissure Eruption Site

Table 16

Sample stage no.	1	2	3	4	5	6	7	8	Total
μg Na	n.d.	0.16	0.15	0.26	1.06	0.32	1.16	-	3.11
" Ca	n.d.	-	-	-	-	-	0.02	-	0.02
" K	n.d.	0.10	0.13	0.29	0.47	0.13	0.70	-	1.82
" Mg	n.d.	-	-	-	0.009	-	0.025	-	0.034
" Fe	n.d.	-	-	-	-	-	-	-	-
" Zn	n.d.	-	-	-	-	-	-	-	-
" Cu	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	-
μg/ml Cl	n.d.	0.15	0.43	1.1	-	0.2	1.1	0.15	
as SO_4 μg total S	n.d.	8.9	1.7	12.9	6.2-42	2.4-5.4	28.7	4.8	
Δmg	0.1	0.2	0.1	0.2	-	-	0.1	0.15	
Total (excluding S&Cl)	-	0.26	0.28	0.55	1.54	0.45	1.90	-	

Collected: 4/16/76 at Sulfur Bank

Table 17

Sample stage no.	1	2	3	4	5	6	7	8	Total
μg Na	9.68	1.80	2.88	2.54	3.47	3.54	0.66	4.76	29.33
" Mg	2.00	0.12	0.16	0.13	0.33	0.22	0.12	0.40	3.48
" Ca	1.83	0.63	0.86	0.70	0.79	0.97	0.79	1.42	7.99
" K	0.98	0.58	1.25	0.67	0.94	0.81	0.68	1.43	7.34
μg/ml Cl	-	-	-	-	-	-	-	-	
Total	14.5	3.13	5.16	4.04	5.53	5.51	2.25	8.01	

Collected: 12/2-3/74 at Hawai'i Volcano Observatory overlook

Table 18

Sample stage no.	1	2	3	4	5	6	7	8	Total
μg Na	1.18	1.24	0.92	1.04	1.30	1.20	0.79	1.61	8.28
" Mg	0.21	0.27	0.11	0.086	0.094	0.12	0.14	0.13	1.16
" Ca	1.03	2.09	0.62	0.47	0.56	0.67	0.41	0.68	6.54
" K	0.69	1.02	0.35	0.31	0.44	0.50	0.30	0.57	4.18
Total	3.11	4.61	1.99	1.91	2.39	2.49	1.64	2.99	

Collected: 12/3/74 at Sulfur Bank

Table 19

Sample stage no.	1	2	3	4	5	6	7	8	Total
µg Na	1.52	1.25	0.91	1.47	1.09	2.41	0.38	1.80	10.83
" Mg	0.20	0.075	0.06	0.19	0.17	0.50	0.14	0.41	1.74
" Ca	0.26	0.20	0.12	0.35	0.26	0.50	0.26	0.15	2.11
" Zn	-	-	-	-	-	-	-	-	-
" Cu	n.d.	n.d.	n.d.	-	-	-	-	-	-
" Ni	n.d.	n.d.	n.d.	-	-	n.d.	n.d.	n.d.	-
as SO_4 µg total S	-	35	95	540	4675	4735	1110	195	10385
Δmg	0.4	0.1	0.4	2.0	12.9	8.4	2.9	0.7	
Total (excluding S)	1.96	1.53	1.09	3.10	4.62	3.41	0.78	2.36	

Collected: 5/15/74 at Halema'uma'u

Table 20

Sample stage no.	1	2	3	4	5	6	7	8	Total
μg Na	4.10	0.94	1.60	1.76	1.87	1.85	1.97	1.05	15.14
" Mg	0.25	0.074	0.14	0.23	0.19	0.14	0.19	0.30	1.50
" Ca	0.85	0.43	0.85	1.02	0.85	0.56	0.85	0.43	5.84
" K	0.52	0.40	0.61	0.61	0.40	0.52	0.82	0.52	4.40
" Fe	-	-	-	-	-	-	1.37	-	1.37
" Zn	-	-	-	-	-	-	-	-	-
Total	5.72	1.84	3.20	3.62	3.31	3.07	5.20	2.30	

Collected: 7/22/74 at 1974 Fissure Eruption Site

Table 21

Sample stage no.	1	2	3	4	5	6	7	8	Total
μg Na	0.70	0.68	1.00	5.37	1.28	1.67	1.76	2.38	14.85
" Ca	0.27	0.19	0.27	1.00	0.035	0.31	0.20	0.62	2.88
" K	0.27	0.21	0.13	0.28	0.18	0.39	0.39	0.14	2.00
" Mg	0.18	0.12	0.18	0.29	1.01	0.14	0.84	0.33	3.09
" Zn	-	-	-	-	-	-	-	-	-
" Fe	-	-	-	-	-	-	-	-	-
μg/ml Cl	-	-	n.d.	-	n.d.	n.d.	n.d.	n.d.	-
as SO_4 μg total S	59	75	185	652	1650	1530	496	149	4796
$\triangle$mg	0.3	0.2	0.5	2.2	4.4	4.7	1.3	0.5	
Total (excluding S&Cl)	1.42	1.20	1.57	6.94	2.51	2.51	3.20	3.47	

Collected: 12/3/73 at Hawai'i Volcano Observatory overlook

Table 22

Sample stage no.	1	2	3	4	5	6	7	8	Total
μg Na	-	0.87	2.71	5.46	5.64	2.30	1.39	3.84	22.21
" Ca	-	0.18	0.57	0.63	0.74	0.53	0.48	0.64	3.77
" Mg	-	0.13	0.42	0.71	0.85	0.32	0.25	0.26	2.94
" K	-	0.10	0.54	0.92	0.50	0.06	0.84	0.31	3.26
" Zn	-	-	0.04	0.12	-	-	0.06	-	0.22
Total	-	1.28	4.28	7.84	7.73	3.21	3.02	5.05	

Collected: 8/7-20/73 at Hawai'i Volcano Observatory overlook

Table 23

Sample stage no.	1	2	3	4	5	6	Total
μg Na	-	0.24	0.17	0.30	-	0.07	0.78
" Ca	0.06	0.33	0.17	0.22	0.09	0.08	0.97
" K	-	0.27	0.28	0.31	-	-	0.86
ng Mg	3	17	50	75	235	42	422
μg Fe	-	-	-	0.65	1.06	0.93	2.64
" Zn	-	-	0.28	0.45	-	0.15	0.88
" Al	-	-	-	-	-	-	-
μg/ml Cl	0.95	0.4	-	-	0.45	-	
as SO_4 μg total S	-	-	-	13	48	117	178
Total (excluding S&Cl)	0.063	0.86	0.95	2.0	1.38	1.27	

Collected: 1/13/76 at Halema'uma'u

Scientific Advances cascade impactor

Table 24

Location & Date	Halema'uma'u	7/7/75		1971 Fissure Eruption Fumarole-7/7/75		
Size of filter	0.1μ	0.2μ	0.4μ	0.1μ	0.2μ	0.4μ
μg Na	1.5	0.86	4.2	2.1	1.1	2.9
" K	0.46	0.31	1.6	1.9	0.52	0.93
" Mg	0.1	0.016	0.1	0.13	0.021	0.1
" Ca	0.34	-	0.37	0.33	0.18	0.47
" Fe	-	-	0.57	-	-	-
" Cu	-	-	trace	-	-	-
" Zn	-	-	-	-	-	-
μg/ml Cl	-	0.62	0.7	-	0.7	0.7
as SO_4 μg total S	1.0	9.3	n.d.	2.4	n.d.	-
Total (excluding S&Cl)	2.4	1.19	6.84	4.46	1.82	4.4

Table 25

Location & Date	1/14-15/75			1974 Fissure Eruption Overlook-1/14-15/75		
Size of filter	0.1µ	0.2µ	0.4µ	0.1µ	0.2µ	0.4µ
µg Na	2.30	13.40	9.86	12.39	5.33	3.09
" K	0.72	4.65	5.27	n.d.	1.98	0.97
" Mg	2.20	1.93	2.84	4.80	1.25	0.79
" Ca	0.38	0.98	1.23	2.49	0.58	0.25
" Fe	-	-	-	-	-	-
" Zn	0.42	0.081	-	-	-	-
µg/ml Cl	1.5	1.0	1.0	-	1.0	0.35
as SO_4 µg total S	86-87	18	-	14	18	n.d.
Total (excluding S&Cl)	6.02	21.04	19.2	19.7	9.14	5.1

placed immediately upwind of the impactor which may again have shielded it from some of the fume.

Table 12. This collection was obtained from the fume being emitted directly from Halema'uma'u. It was collected on January 13, 1976, over a time span of about 135 minutes. The wind was gusting strongly, though the rain from that morning had diminished to a wind-blown light rain and sprinkles. The impactor stages were placed within about 4-5 meters of the crater edge and no more than 15-20 meters downwind from where the fairly heavy, localized fume rose out of Halema'uma'u. Consequently, the fume was being blown directly over the collector most of the time. Again, a rainshield was placed on the upwind side of the collector, which may have shielded out some of the fume. Upon removal, though, several of the plastic collection discs showed the typical patterns of collected droplets associated with Anderson impactors.

Table 13. A sample was also obtained at a picnic site at the end of the strip road on Mauna Loa, at an elevation of approximately 2000 meters. The weather was generally clear and sunny during most of the roughly 160-minute collection period on January 14, 1976, with the wind blowing unsteadily from the east-northeast. Practically all of Kīlauea and most of the surrounding country was visible from the collection site. Some fuming was seen to be occurring

from Kīlauea but was being blown off to the southwest away from the collection site. This sampling is viewed mainly as a clean air sample.

Table 14. Collected on April 15, 1976, directly downwind of the largest concentration of fuming at Halema'uma'u, this sampling ran for roughly three hours. The wind was blowing intermittently, gusting the fume back and forth over the collection site, such that the fume was actually over the impactor roughly half of the collection run. Collection was stopped twice for 5-10 minute periods to refill the generator with gas.

The collection discs from this sampling, upon removal from the collector assembly, were placed in individual clean, Pyrex petri dishes and taped shut for transporting back to the lab. The discs were examined visually under a microscope and photomicrographs were taken of individual collection spots that were felt to be representative of each stage. See Figures 4-8.

Table 15. This sampling was taken at a site roughly 25-30 meters downwind from one of the July 1974 caldera floor fissure outbreaks, on April 15, 1976. The collection period covered about two hours and though there was a significant amount of visible fume being emitted, the variable winds kept shifting the direction the fume was blowing in

that day. Consequently the fume was again actually over the impactor less than half of the collection period.

Table 16. Sulfur Bank was again sampled, on April 16, 1976, over an 84-minute timespan. The procedure was the same as before, with a large plastic sheet draped over the vent, channeling the fume over the impactor stages. On this occasion, however, a drying tube containing silica gel was placed in the system just before the pump to prevent any condensed steam from getting into the pump chamber. The assembly was tested with a flowmeter back in the lab the next day, where a flow rate of roughly 38 cubic feet per hour was measured. The reduced pumping rate seemed to significantly affect the amount of material collected as the discs, upon removal, did not appear to be nearly as wet as previous collections at Sulfur Bank. Though this could also possibly be a result of a significantly lower atmospheric humidity at the time of collection, further analysis also indicated a poor yield.

The next six sets of samples were obtained by Dr. J. J. Naughton before my start on this project. The first two sets were analyzed by this author, while the other four sets were analyzed by Ms. Virginia Greenberg, using identical or very similar procedures.

Table 17. This collection was an overnight run at the Hawai'i Volcano Observatory. Taken over December 12-13, 1974, it covered a period of 20 hours and 35 minutes.

Table 18. This sample was obtained at Sulfur Bank on December 13, 1974, over a half-hour period.

Table 19. This sampling was taken over a two-hour period on May 15, 1974, immediately downwind of the fume issuing out of Halema'uma'u.

Table 20. This collection was obtained immediately after the July 19, 1974, fissure eruption on the caldera floor at Kīlauea, on the 22nd. It covered a timespan of about 90 minutes. The fountaining from the eruption had stopped, though the lava was still extremely hot and there was a considerable amount of fume still being given off.

Table 21. A collection of the fume from Halema'uma'u was obtained at the H.V.O. during a period when Kona winds were blowing, on December 3, 1973.

Table 22. The date of this collection taken at the H.V.O. is uncertain but it was obtained sometime between August 7-20, 1973.

Table 23. This sampling was obtained with the Scientific Advances cascade impactor. The sample was taken at the same time as the sample described in Table 12, at Halema'uma'u on January 13, 1976, for the same length of time, about 135 minutes. The pumping rate was measured at 0.75 cubic feet per minute.

Table 24. Two sets of Nucleopore samples were taken on July 7, 1975. One set was taken at Halema'uma'u, for 20 minutes, with a measured flow rate of 2.8 liters per minute. The other set was taken down along the 1971 fissure eruption area, about 100-150 feet downwind from a heavy H_2S fuming area. The collection period ran for about 21 minutes at a flow rate of 3.2 liters per minute.

Table 25. These two sets of Nucleopore samples were belived to have been taken on January 15, 1975, but no exact time, date, or collection time period was apparently recorded. One sample was obtained downwind of Halema'uma'u, while the other was taken along the bluff overlooking the July 1974 fissure eruption area.

Most of the sample collection discs showed little or no visible evidence of any collected samples on them. Of those discs that did, the patterns of droplets resembled most closely water mist droplets or the dilute sulfuric acid droplets Cadle reported on different occasions. (Cadle et al. 1968, 1969, 1971) Photomicrographs were taken of the collection taken at Halema'uma'u April 15, 1976, specifically of the last five stages. The first two stages showed little visible evidence of anything having been collected, other than a few collection spots along the edge, none of them having much detail. The third stage showed a collection pattern typical of the Anderson impactor, with the individual spots composed of very fine mist-like droplets. Typical collection spots for the last five stages are shown in Figures 4-8. The characteristic "spatter" patterns of dilute sulfuric acid droplets as Cadle described them are most evident in Figures 6 and 7. Similar patterns were found on the collection taken at Halemau'uma'u January 13, 1976. The collection taken August 8, 1975, at Halema'uma'u may also have contained such collection patterns as the discs were visibly wet. However, in folding the discs after removal from the impactor assembly, most of the patterns of spots were smeared out and lost.

Collections taken at Sulfur Bank were generally the only other samples which contained visible amounts of material. The problem here, though, was that these samples were usually quite wet from condensed steam and any

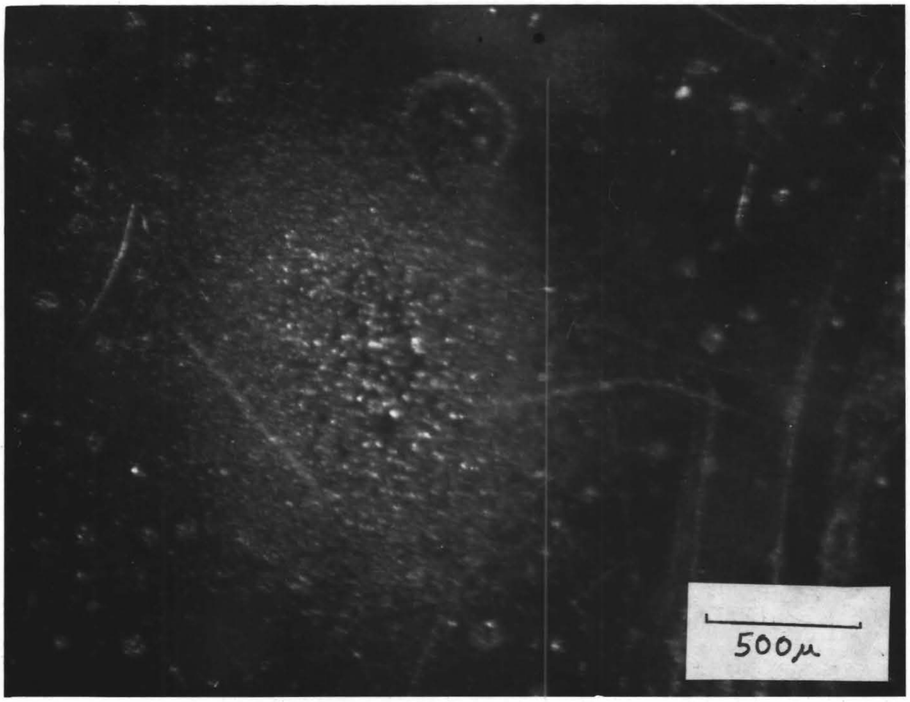

Fig. 4

Photomicrograph of Collection Pattern
Halema'uma'u, April 15, 1976
Stage 3

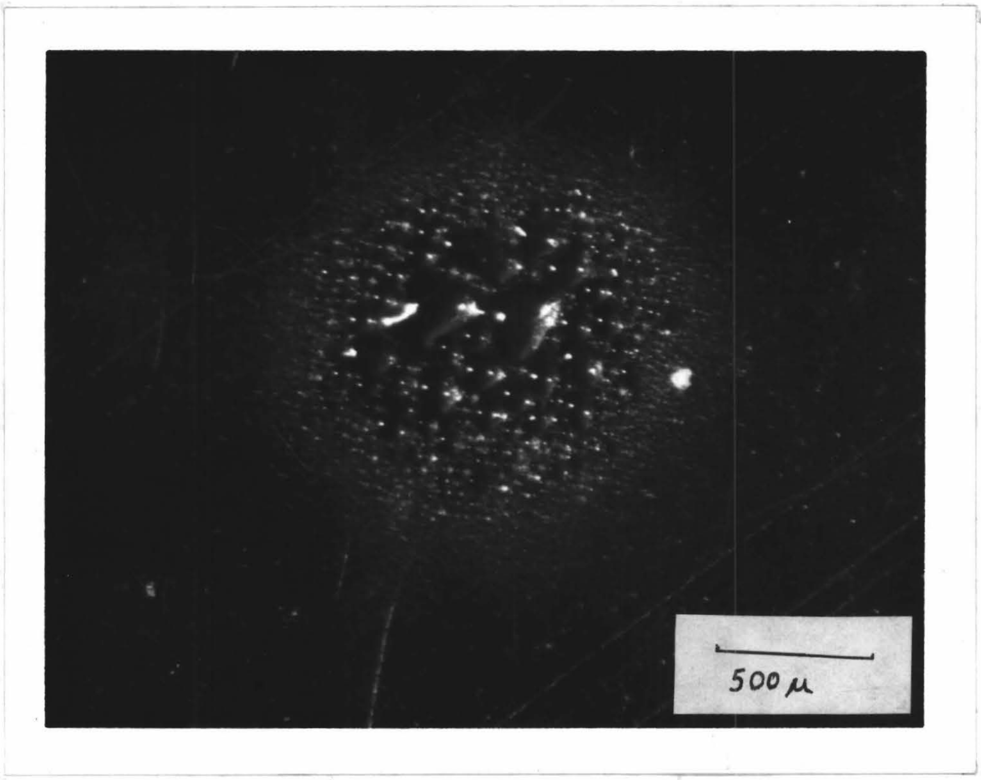

Fig. 5

Photomicrograph of Collection Pattern
Halema'uma'u, April 15, 1976
Stage 4

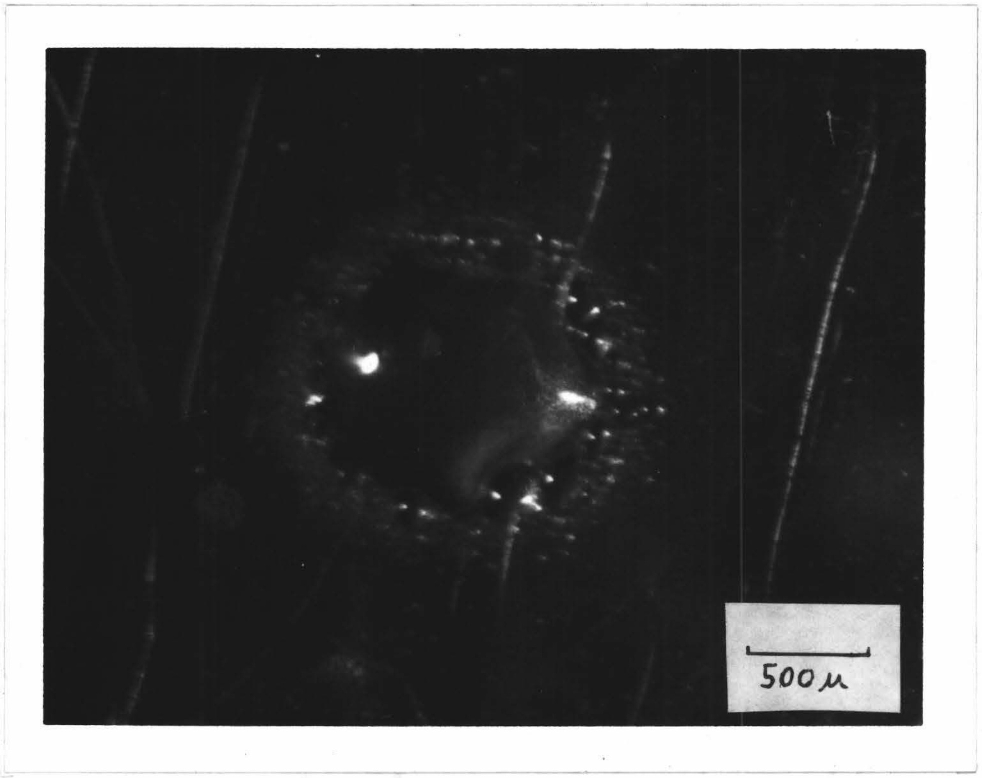

Fig. 6

Photomicrograph of Collection Pattern
Halema'uma'u, April 15, 1976
Stage 5

Fig. 7

Photomicrograph of Collection Pattern
Halema'uma'u, April 15, 1976
Stage 6

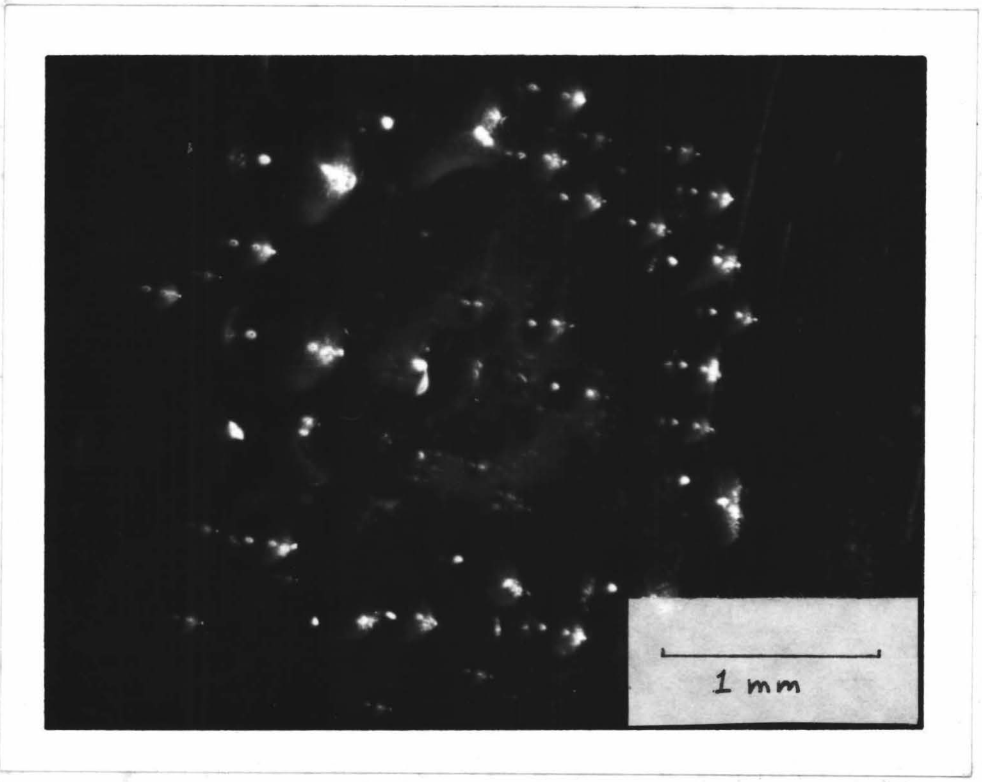

Fig. 8

Photomicrograph of Collection Pattern
Halema'uma'u, April 15, 1976
Stage 7

collection patterns which might have originally existed were lost in the excess moisture on the discs. On at least one occasion, the discs from a sampling at Sulfur Bank, after having been dried off, showed traces of a whitish scaling on the noncollection sides of the discs. This was probably due to the dissolved salts in the steam precipitating on the discs as the water evaporated away. It most likely consisted of alkali and calcium sulfates, though it was not directly analyzed.

In order to possibly obtain a better comparison with values obtained by Naughton et al. (1974, 1975), the major ion weight ratios were calculated for all of the samplings. See Table 26. One of the first aspects which becomes noticeable upon first glance is an apparent decrease in the Na/K ratio over time at Halema'uma'u. This seems to show up both in the collections taken immediately downwind of the heaviest fume issuing out of the pit crater, as well as in the collections taken at H.V.O. However, referring to the data from Naughton et al. (1975), the range of possible values for this ratio can cover as much as an order of magnitude either way from the values obtained in this study. What must also be considered is that the later collections contained much smaller amounts of material, with many of the stages showing blank concentration levels with respect to various elements. Since this would give quite low total amounts for these elements, the value of the ratio between two such elements would be much more sensitive to small

Table 26

CATION WEIGHT RATIOS

Collection Dates	8/73	12/73	7/74	12/74	1/75	8/75	1/76	4/76
Collection Sites								
Halema'uma'u								
Na/K	-	-	-	-	-	$5.07, 4.47^+$	1.33*	0.86
Ca/Mg	-	-	-	-	-	$0.84, 10.5^+$	2.07*	0.028*
1971-1974 Fissure Eruption Sites								
Na/K	-	-	3.46	-	2.28	3.59	2.23*	0.94
Ca/Mg	-	-	3.89	-	-	2.90*	0.86*	0.076*
Sulfur Bank								
Na/K	-	-	-	1.99	2.02	-	1.66*	1.71
Ca/Mg	-	-	-	5.64	-	-	0.071	0.59*
Hawai'i Volcano Observatory								
Na/K	6.81	7.43	-	4.00	2.09	-	2.59	-
Ca/Mg	1.28	0.93	-	2.30	-	-	1.82	-

$^+$Value of Halema'uma'u sample taken out in Ka'ū Desert

*Value unreliable due to low elemental weight values changes or large relative uncertainties. It would seem then that the suggested trend in Na/K values described above, varying by as much as a factor of five, is not as significant as one might initially suppose. A more reasonable statement would be that the range of values obtained in this study agrees quite well with those obtained by Naughton in his previous studies.

The Na/K values from the collections taken at Sulfur Bank show a much better consistency, averaging 1.84, and with individual values varying from each other by less than 20%. The collections from the 1971 and 1974 fissure areas showed fairly good consistency also, averaging around a value of 2.5.

The Ca/Mg values showed much less agreement between consecutive samples, in some cases ranging over as much as two orders of magnitude at the same collection site. Much of this variability is no doubt due to the extremely low Ca or Mg concentrations obtained for many of the samples. In many of the later collections taken, hardly any Ca was detected at all. However, on comparing the cation ratios measured in this study and those found in Naughton (1974) with the values given by Stoiber and Rose (1970) and in White and Waring (1963), one finds a general agreement.

B. Analytical Uncertainties and Errors

The total uncertainty value of the cation concentrations arises from several different sources. The standard solutions had an average uncertainty in their concentration value of about 1-1.5%, as determined by a propagation of errors calculation. However, on a few occasions it was noted, by comparing the absorbance of a particular standard against the other standards being used in a certain analysis, that an error had randomly arisen in the preparation of an occasional standard. If the relative error was more than 15%, the standard's value was dropped from the calculations and the standard curve was recalculated.

The concentrations were obtained by measuring the percent absorption from a chart printout. These readings were generally accurate to ±0.2 percent absorption. This, however, can give a relative percent uncertainty in the reading of from 20% for a 1 percent absorption reading to 0.5% for a 40 percent absorption reading, the normal maximum working range used.

This percent absorption value was then converted to absorbance units. A calibration curve was calculated using concentration versus absorbance in a least squares calculation. The sample concentrations were then determined from this curve.

The detection limits for the various elements tested for are given in Table 27. The two different listings given are estimated values for the detection limits for the first set of samples analyzed in February of 1975 and for the last set of samples analyzed in May of 1976. The change is a result of the improvement in technique and expertise which was developed over the period of this study.

TABLE 27

ANALYTICAL DETECTION LIMITS

	February 1975		May 1976	
Na	0.02	μg/ml	0.01	μg/ml
K	0.04	"	0.02	"
Ca	0.08	"	0.02	"
Mg	n.d.*		0.005	"
Fe	0.04	"	0.04	"
Zn	0.03	"	0.03	"
Cu	0.03	"	n.d.	
Cl	0.4	"	0.2	"
total S	0.5	"	0.2	"

*n.d.= not determined

Though the prescribed analysis technique for atomic absorption spectrophotometry is to run each sample at least 3 times, due to the limited amount of sample available, (10ml.) for all of the analyses which were to be performed, only one analysis for each element could be made. The uncertainties in the actual sample concentration values were then estimated to possibly be as much as ±10%, though this was felt to be an extreme maximum value.

Uncertainties in the chloride determinations were largely due to the method of analysis. Any uncertainty in the actual concentration of the standards should have been no more than 1-2%, as calculated above. The error in the reading of the various pH meters used turns out to be somewhat larger. When using the Beckman pH meter, analyses were originally done by arbitrarily taking the largest value believed to be reached after each increment of $AgNO_3$. Later this procedure was modified somewhat to give more consistency to it by taking the + millivolt reading 30 seconds after the addition of each increment. The uncertainty in the reading itself, with the Beckman instrument, was about 1%, while the "accuracy" in the reading was only good to an estimated 3-5%.

Later when using the Orion digital pH meter, the same procedure was followed, adding the 0.10ml. of $AgNO_3$ solution, waiting 30 seconds, then taking the + millivolt reading. Precision may have improved somewhat due to the fact that the millivolt reading could be directly read off the digital display to at least three significant figures, while the third figure had to be estimated on the Beckman instrument.

The largest source of error and uncertainty lies in the plotting of the data on the Gran's Plot paper and trying to draw a best-fit straight line. Since the points tended to curve away from linearity at the lower readings, the first two, and occasionally three, points were generally dropped when determining the best-fit line. However, when plotting the data from sample determinations, "eyeballing" a best-fit line could often lead to an uncertainty of as much as 25%, especially with the lower concentrations, <1 microgram/milliliter.

The total sulfur determinations on the earlier samples were found to be largely unreliable due to a degradation in the electronics of the spectrophotometer which was used, and to a lesser extent in the strength of one of the reagents used. The standard solutions themselves were felt to be accurate to within 2-3%, and the absorbance readings had an uncertainty of ±0.002. But erratic results were often obtained for sequentially increasing standard concentrations in these early analyses. Though the instrument was eventually repaired, by the replacement of several tubes, it was impossible to repeat those sample analyses already done due to a lack of enough sample solution. Later analyses seemed to give more reliable, reproducible results. It was believed that by the last sets of samples to be analyzed, the uncertainty in the sample concentration absorbances had been brought down to ±0.001 absorbance units. However, with a 1 microgram/milliliter of solution sulfate concentration, this corresponds to a relative uncertainty of 20-25%, and about 1% for a sulfate concentration of 20 micrograms/ml. of solution.

C. Discussion

As can be seen from the number of blanks in the later samplings, the level and content of fume activity has died down considerably since the July 1974 eruption, and especially since the November 1975 earthquake and accompanying short-lived volcanic activity. Various indications over the past year have prompted Volcano Observatory scientists to suggest that the November 1975 earthquake may have so disrupted the internal magma operations of Kīlauea that it may not be able to build up sufficient pressure to erupt again in the near future. (Thomas, 1976) Such a disruption of Kīlauea's internal workings is more than likely the main cause for the considerable reduction in fume output. Any large scale shifting of the magma within the volcano may have closed off many of the fume vents. The large deflation in the volcano which has occurred since November 1975 earthquake also implies a draining away of a large amount of the magma from the reservoir. This removal of source material to greater depth would drastically reduce the amount of gas, and with it fume, given off by the magma, since it is at the lower pressures encountered nearer the surface that the gas and fume vapors differentiate out of the magma. Lower down in the crust and upper mantle, the higher pressures and temperatures prevailing would keep the magma gases dissolved in the magma body.

Comparison of the different analyses from the same source seems to show that the composition of the fume has also changed, such that it is now composed mostly of water and acid sulfur gases (and presumably carbon dioxide, also). A likely explanation is that since the fume content has diminished so much, the concentrations of most of the metals analyzed for have simply dropped to blank levels or below.

Using the total cation amounts and total sulfur, some observations can be made as to the variability in size range of the particulates. The collections taken downwind of the fume issuing from Halema'uma'u all indicate maximum particle concentration in the smaller size ranges, particles approximately in the 1 to 2 micron size range. This is especially apparent when one looks at the total sulfur content of the samples. See Figure 9. One can draw similar conclusions when one compares the total cation weights of the different stages in some cases, though with less reliability. Looking at the various results from the collections taken at the Volcano Observatory lookout, the data obtained suggest a slight shift in the size range of

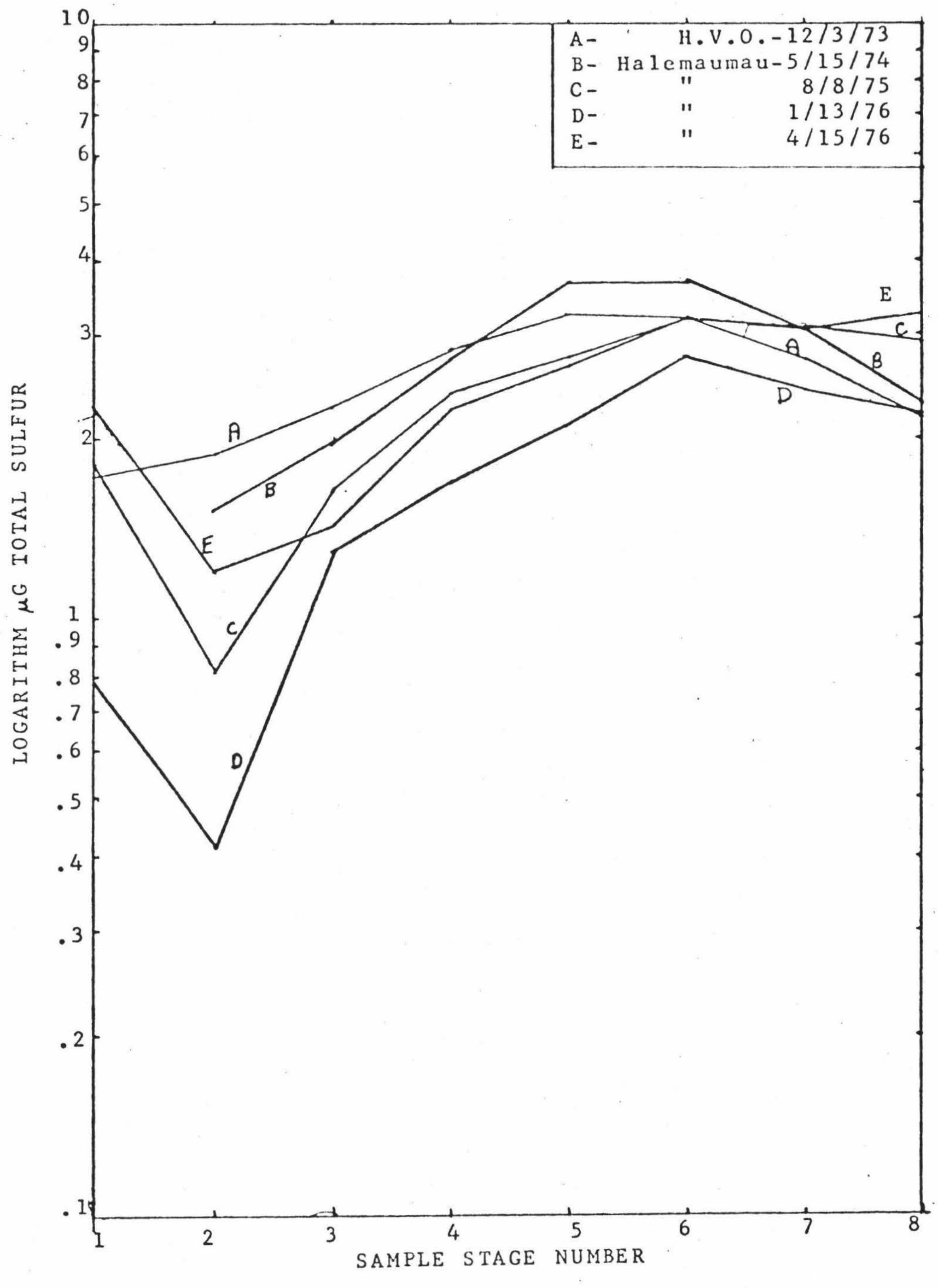

Fig. 9. Halemaumau samplings -- μg Total Sulfur vs. Sample Stage Number.

maximum concentration of particles to a slightly larger size, roughly 2-4 microns. See Figure 10. The results though should not be taken as entirely definitive. No explanation was derived for the sudden increase in the total cation amount for the smallest sizes.

However, if one compares the collections taken at Halema'uma'u with a sample that was collected a couple of hundred meters out into the Ka'ū Desert of the same fume issuing from Halema'uma'u, the change in particle size of maximum concentration is much more obvious. At this point downwind the data indicates a maximum concentration of particles around the 7-10 micron range. See Figure 11. One should be careful though, in making too definite of a conclusion from this comparison, as only one sample was ever obtained at this site.

This apparent shift in the maximum concentration of the total sulfur content in most of these cases, to the larger sizes suggests a "growing" of the particles or droplets in the fume as they are blown away from their source. This would agree quite well with descriptions of fume generation and growth proposed by Naughton (1974) and Cadle (1967, 1968) at Maunu Ulu and Halema'uma'u, respectively.

The fume coming directly off of an active lava lake or fountain is generally described as a clear, invisible gas cloud, or sometimes as brownish in color, which has been suggested to be a result of light scattering by lava drops and threads. As the fume rises and cools, various chemical

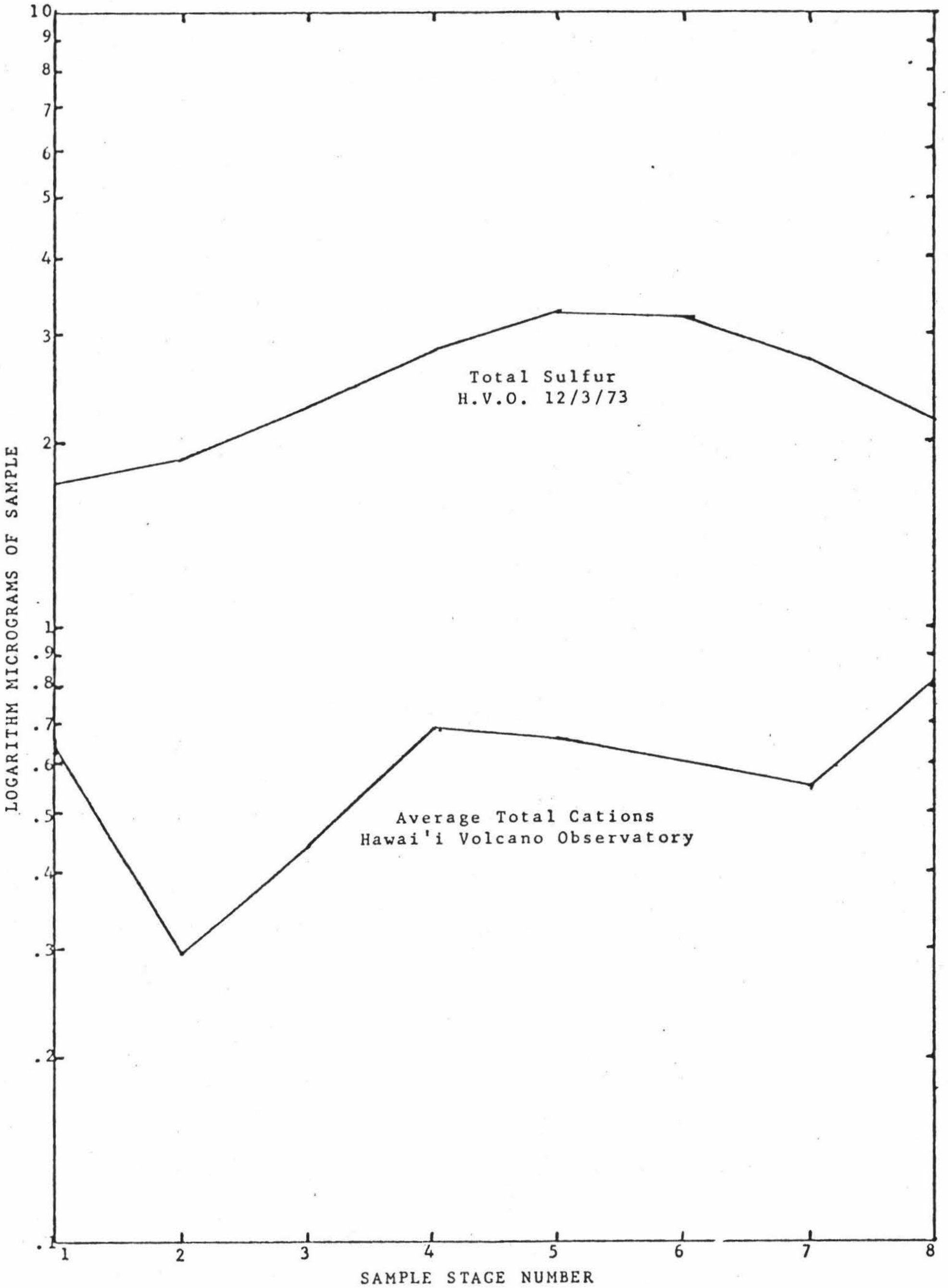

Fig. 10. Hawai'i Volcano Observatory Samples Average of Total Cation Weights and Total Sulfur from December 3, 1973, sample.

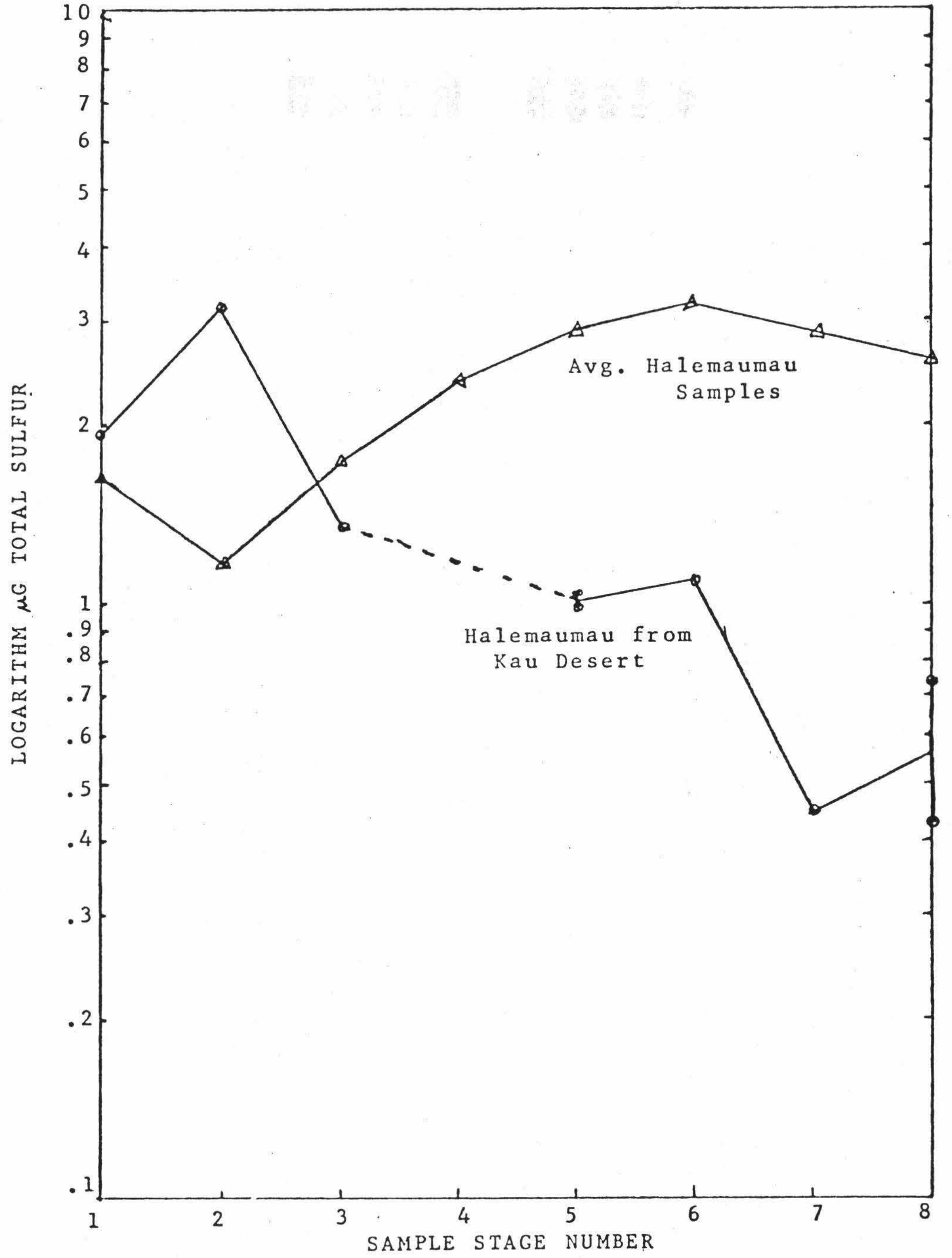

Fig. 11. µg Total Sulfur vs. Sample Stage Number Average of Halemaumau samplings compared to Kau Desert sampling of Halemaumau.

reactions proceed, forming particulate matter of a size which can scatter blue light, giving the fume the appearance of a bluish haze. The particulates at this point are most likely minute sulfuric acid droplets. As the fume continues to rise and dissipate, cooling further in the process, it forms the copious white clouds which are perhaps the most obvious form of volcanic fume. By now the fume has cooled to a point where solution condensation can occur.

As the fume is carried away from its source, the particulates and acid solution droplets continue to coalesce and grow in size. In addition, the sulfuric acid droplets are absorbing water from the water vapor of which most of the fume is composed.

How far the particles will continue to grow will depend on several different factors. Some of the more important of these would be the various reactions which would be occurring with the fume particulates, such as the oxidation of SO_2 to H_2SO_4. This reaction could proceed by several different routes.

In the very hot fume directly above the lava lakes or fountains, and possibly even in the more quiescent fumaroles, the SO_2 in the fume would be oxidized to SO_3 by mixing with atmospheric oxygen. This SO_3 would then react fairly quickly with water in the cooling fume to form H_2SO_4. (Cadle, 1971)

As the fume cooled, a more likely process to occur would be for the SO_2 to react with water in the fume first, forming sulfurous acid, H_2SO_3, which would react fairly quickly with any dissolved oxygen. This is a more likely process at this point especially if one considers the metal ions which are often dissolved in the fume droplets and which can serve as catalysts.

A much less likely process which could occur would be a photoexcitation of the SO_2 by absorbing solar radiation in the near-ultraviolet range. This excited SO_2 would react with atmospheric oxygen much more readily than unexcited SO_2, forming SO_3, which could go on to form sulfuric acid or sulfate salts. Though this process would be much slower than the other processes described, its relative importance could increase as the fume cooled, dissipated, and rose higher in the atmosphere, where the ultraviolet radiation would be stronger. (Kellogg, 1972)

In all of the possible reactions, once sulfuric acid has been formed, the significant hygroscopic nature of this substance would immediately cause it to start absorbing water vapor from the fume, which would result in growth of the particles.

However, this absorption of H_2O by the sulfuric acid droplets will not continue indefinitely but will be limited by the relative humidity, and more indirectly, by the temperature. Once the vapor pressure of the diluted sulfuric acid reaches the vapor pressure of water at the prevailing conditions, absorption should stop. At what stage or size this point would be reached is hard to predict.

Naughton et al. (1975) have described how on occasion the fume clouds from Kīlauea, during times when the fume activity was particularly heavy and under certain weather conditions, were observed to travel considerable distances from the volcano, spreading over much of the island of Hawai'i around the base of the volcanoes and up along the Kona coast. Other reports describe distinct SO_2 odors at considerable distance downwind and there have been reports of significantly acidic rainfall along parts of the Kona coast. (Virginia Greenberg, personal communication, 1976)

All of this points to an extensive pervasion of the fume, possibly to a larger extent than would be expected if a continued growth of the droplets were assumed, so that a sufficient size would eventually be attained to allow the droplets to settle out of the fume. If this latter situation prevailed, the pervasiveness of the fume could be explained by a slow though continual oxidation of the SO_2 in the fume to H_2SO_4 which could continue the water absorption and particle coalescing reactions. All sulfuric acid droplets from whatever source, and also the gaseous SO_2, could in time be removed by absorption into rain drops and washed out of the air in that manner.

However, since the sulfuric acid droplets will be limited in the amount of water they will be able to absorb by the relative humidity, an equilibrium in the particle size attained may be reached before a majority of the initial particulates reach a size sufficient to cause them to settle out at any significant rate. If this is the case then the pervasiveness of the fume is due as much to the nature of the initial particulates formed, with all of the dissolved salts which would be present, as to any continued oxidation of the SO_2 present to more H_2SO_4.

One possible way of determining which of the above mechanisms might predominate in the formation of the fume droplets would be to sample an area of extensive heavy fuming at regular distances downwind of the source. If a majority of the particles or droplets did grow to sufficient sizes to hasten their removal from the fume cloud, then the samplings suggested should show a steady increase in the size where maximum concentration occurs up to a point where they would be effectively removed from the cloud. Further samplings downwind would probably hold constant around this size range, but the chemical composition of the fume should change, especially with regards to the more abundant metal ions present which were analyzed for--Na, K, Ca, Mg, etc. As the initial particulates ejected from the source settle out, the concentration of these elements would go down as they became depleted, eventually approaching levels which would be more representative of, in this case, a marine environment.

If, however, the initial particulates formed were limited in the extent to which they could eventually grow, then the extent to which this initial material would pervade or disperse would be much larger. Such a collection series as described above should, in this latter case, again show a gradual increase to a certain size and then hold relatively steady around this size. The chemical composition, however, should also hold relatively constant, or at least drop off more slowly as the fume dispersed and mixed with marine particulates, since the components of the initial material, such as dissolved salts, would not be settling out of the fume.

The differences between these two cases would be most obvious in the cation weight ratios. In the first case a steady shift of the ratios to values more representative of a marine atmosphere should occur. In the latter case, these ratio values should remain relatively constant, or at most, change to a considerably lesser extent and much more slowly.

The reasons for all this concern about determining size ranges and maximum concentrations are mainly twofold:

First of all, the possible and actual effects of particulate matter on man have undergone considerable scrutiny over the past decade or two. As mentioned earlier, these suspended particulates can have a pronounced effect on man's health and well-being. It has been generally accepted that the particle size is a major factor in determining the toxic effects of airborne particulate matter. (Natusch and Wallace, 1974) More precisely, the smaller the particle, the more toxic it will behave in the respiratory system.

Though the volcanic fume particulates from Kīlauea probably do not become widespread, such as on the order of many hundreds or thousands of kilometers from the source, they can have quite noticeable effects locally. Thousands of people visit this area yearly and a large majority of them may be exposed to varying amounts of the fume. In addition, the local residents who live downwind of the volcano will have frequent exposure to the fume, especially when the activity is particularly heavy. What effects this fume could have should be determined.

Secondly, the effects of volcanic fume on the global environment have received considerable attention in recent years, as has already been described. Again it appears that with many of these effects being examined and studied; heating and cooling trends, and significant changes in the global weather patterns being among the more common, it is the smaller particles, <1 micron, which seem to make the largest contributions to these effects. It is these smaller particulates which will also have the most wide-spread influence, since they are capable of becoming much further dispersed than the larger particles.

Though the results of this study are unfortunately too sparse to give any effective overall indication of the behavior of the fume, some possible conclusions are suggested. At close range, of course, the fume particulates are still forming and growing, and the fume clouds are still dense enough, such that the particles are small enough and plentiful enough to constitute a respectable hazard with prolonged exposure. However, beyond this, it is believed that the particulates grow to a sufficient size, and in the process disperse to a low concentration, so that under most conditions, they need not be considered a significant hazard.

Since the particulates and solution droplets have been observed to grow to a relatively large size (7 μm diameter) while still relatively close to the volcano, it is believed that much of the material initially ejected in a particulate state or attaining such a state soon after being emitted, will be quite localized in any environmental effects it might show. The most significant of these will probably come from the absorption of SO_2 and H_2SO_4 into the rainfall and the resulting effects of this acidic rain on vegetation and man-made structures.

The SO_2 which does not get oxidized soon after emission is capable of being dispersed to a much greater extent. It is this component of the fume which Castleman (1973) and Meinel (1967) describe as diffusing far up into the lower stratosphere and entering into the sulfur-ozone reactions which have been described elsewhere. (See page 16)

How much of the SO_2 given off constantly by Kīlauea reaches this sulfate layer depends on many different factors, among them the extent to which the SO_2 undergoes the oxidation reactions described earlier while it is still at the lower altitudes.

V. CONCLUSION

The most obvious observation of this study is the drastic decline in fume output over the past 12-18 months at Kīlauea Volcano. Though this in itself is an interesting observation, its consequences severely limit any further study into any particular chemical aspects of the fume. Longer and longer collection periods have become necessary to obtain enough samples to raise concentration values above blank levels. Some reduction in the amounts of the more volatile elements in the fume is to be expected as the source wallrocks in the fumarolic vents become depleted through constant and prolonged interaction with the fumarolic gases. However, it is felt that this wallrock depletion accounts for only part of the reduction in fume content which is observed in this study.

The other factor which is believed to have had a major influence in the observed depletions, as discussed earlier, is the November 1975 earthquake and following deflation of the volcano. The large removal of source magma implied by such a deflation would of course cause a considerable reduction in the gas and fume output, since it is only in the lower pressure conditions existing near the surface that the magmatic gases can differentiate out of the magma, undergoing the various reactions described earlier in this paper.

As to the analytical techniques used in this study, indications suggest that the atomic absorption spectrophotometric procedures used are well suited to this type of analysis, considering the physical form into which the samples are worked up. The small amount of sample with which one has to work is somewhat of a problem, but with a continual gaining of experience in the various techniques employed, a significant decrease in the absolute uncertainty was felt to have been achieved.

The chloride analysis procedure gave more than a few problems, especially when trying to obtain any kind of good precision with a low uncertainty. Further work with this procedure should help in improving the reproducibility of this technique, which could prove useful in other areas where a quite low chloride concentration (0.1-1 ppm) needs to be measured. Greater care needs to be taken, however, in the addition of the $AgNO_3$ and with the taking of the millivolt reading. This may help reduce the large uncertainty resulting in plotting the millivolt values on the Gran's Plot paper.

The procedure for sulfure determination, though somewhat tedious and involved, has been developed to a point where it should now be fairly reliable even in the low (<5 μg/ml) sulfur concentrations, provided enough care is taken in the sample workup, and relatively fresh reagents are always used.

The collection procedure itself, utilizing the Anderson particle sampler, appears to work quite well. The sampler is lightweight, easily transported, and easily loaded and unloaded. The polyethylene collection discs used in this study, however, often gave some difficulties in its pretreatment, such as with the acid cleaning of the collection surface, and in the final rinsing off of the collected sample. Contamination, during both of these steps as well as elsewhere, was often a feared, if not always an actual, problem. It is believed that lower and/or more consistent blank levels would more likely be obtained by using a different collection surface, such as a Delbag Microsorban, polystyrene fiber, or similar filter.

The Nucleopore filters which were tried on a few occasions were harder to work with, especially considering their apparent ability to acquire a weak static charge, most noticeable when loading and unloading the filters into their plastic holders.

Further study of the fume is definitely warranted, considering the sparseness of samplings involved in this study. However, considering the present physical state of Kīlauea, unless one is prepared to spend several hours per collection, it would not really be worthwhile to pursue a regular sampling routine until conditions build up under Kīlauea again such that a renewal in fume activity will result.

One aspect which should be more closely studied, should the fume activity significantly pick up in the future, is the change in the fume matter with distance by taking collections at increasing distances downwind from Halema'uma'u or any other area at which activity may pick up. It would be useful to know how quickly the droplets grow in the dissipating fume cloud, as well as the approximate maximum size the particulates reach. Another point which may be able to be determined by such a sampling study would be whether the reactions of the gas and fume described earlier actually take place to a significant degree at these lower altitudes, eventually controlling the composition and size ranges, or whether the apparent persistence of the fume is merely due to a slow dissipation of the particulates initially ejected by the fumarole.

As it appears now, however, the particulates initially ejected grow quickly enough to a sufficiently large size that they need not be considered a serious health hazard, except in the immediate vicinity of the fumarole or vent and downwind for a short distance. The gases in the fume are another matter, especially if they do not undergo the reactions described at a very rapid rate, allowing them to eventually disperse to great distances and entering into a large variety of possible reactions.

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