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By

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A chemical study has been made of volcanic gases from a variety of sources at Kilauea Volcano on the island of Hawaii. During a recent flank eruption, gas samples were taken from the molten surface of a lava lake as it was forming in Makaopuhi pit crater. Sampling was continued for more than a year by means of holes drilled through the crust of the lava lake by the staff of the Hawaiian Volcano Observatory, U. S. Geological Survey. Additional samples were collected from fumaroles on the summit area of Kilauea, and the majority of these were taken at the piped fumarole of Sulfur Bank.

The collection of gas samples was made by using evacuated, silica gel-filled, glass sampling tubes, developed by previous workers. Considerable effort was spent on making further improvements on these tubes, and on investigating collecting techniques suitable for the available sampling sites. A gas chromatographic method of analysis was developed, which required only two chromatographic columns for the analysis of a gas sample. The analyses from selected samples were used to initiate computer calculations of the thermodynamic equilibrium composition of the different gas sources investigated.

The analysis of samples from all collecting sites showed varying degrees of air contamination. Investigations were made to determine its cause. The results indicated that the majority of the air
contamination took place after the sample had been taken and the tubes were being resealed. Some air, however, may have infiltrated the gas source below ground, perhaps coming from air-saturated ground water.

As with most previous investigations of volcanic gases, relatively large compositional variations were often found in samples from the same source, even when they were taken only minutes apart. It is felt that this is in part a reflection of the air contamination, but is also due to the relatively poor precision of gas analyses.

The results of this first investigation of the degassing of a large, isolated body of cooling lava (Makaopuhi lava lake) showed a gradual depletion of the principle carbon and sulfur gases with time. This trend is apparently associated with the solubility of these gases in the rock melt. A similar trend was not found in the analyses of the Sulfur Bank samples. The relatively constant composition found for gases from this source, however, may be due to its connection with the magma reservoir beneath Kilauea caldera.

Sulfur Bank samples were also examined for compositional changes that might allow prediction of eruptions, as suggested by previous workers. The results have not established this, but do indicate that total sulfur gas content may be the key.

The results of this research imply that the interpretation of the role played by the gas phase in volcanics would be greatly aided by more frequent and systematic sampling of volcanic gases.
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I. INTRODUCTION

A. The Importance of Volcanic Gases

1. Introductory remarks

Volcanoes, or the remnants of them, are a geologic feature common to much of the surface of the earth. Some 500 active volcanoes are known today, and all are located on or near the major fault systems of the earth's crust. The molten rock or magma and the volatiles associated with it no doubt provide the best direct evidence as to the nature of the processes occurring within the interior of the earth.

2. The role of gases in eruptive phenomenon

Volcanic gases undoubtedly play an important role in eruptions. It is generally believed that the gases which appear during a volcanic eruption were originally dissolved in the magma. As the lava nears the surface these gases would be released, due to a loss of confining pressure. The rapid liberation of gases at that time produces the spectacular lava fountains that are associated with Hawaiian volcanoes, and the violent explosions common to volcanoes with more viscous lavas.

Changes in the composition of certain gases issuing from volcanic vents and fumaroles, have been suggested by some investigators\(^1\), \(^2\) as being indicative of impending eruptions. Ballard and Payne\(^3\) and Heald et al.\(^4\) found some evidence that increasing concentrations of the sulfur gases, (especially \(\text{H}_2\text{S}\)), from Sulfur Bank fumarole at Kilauea Volcano, Hawaii,
were associated with eruptive phases. A study by Noguchi and Kamiya\(^5\) of Japanese volcanoes showed that changes in total sulfur and chlorine taken up in solutions of NaOH set around the main vent of a volcano, could be used to predict the approach of an eruption within an active crater. Similarly, a paper by Surina and Voronova\(^6\) reported evidence which suggested that changes in the composition of halogen gases and \(\text{H}_2\text{S}\) indicated approaching eruptions for Ebeko Volcano on the Kurile Islands.

3. The role of gases in the formation of minerals and ore deposits

Ore deposition is generally believed to occur from a liquid medium, which becomes a supercritical fluid at greater depths in the crust. The volatility of certain metal compounds, especially the chlorides, makes a strictly gaseous transportation of some metal compounds a very probable likelihood, at least in the early stages of metal concentration. Studies of fumarolic sublimes indicate volatile transfer of Na, K, Fe and Cu salts, and direct sublimation has been confirmed for Ca and Mg.\(^7\) Murata\(^8\) has detected CuCl in volcanic flames, using spectrometry, during the 1960 eruption of Kilauea Volcano. The transportation of ore forming compounds at depth by solution in condensed supercritical magmatic gases has been discussed by Krauskopf\(^9\) and Barton.\(^10\)
4. The role of volcanic gases in the formation of atmospheres and oceans.

There is considerable evidence that the agglomeration of the earth occurred with the complete loss of any primordial atmosphere, and that the subsequent evolution of the present fluid envelope of the earth occurred entirely from a self-contained secondary source.\textsuperscript{11} It is currently believed that the most probable mechanism for the formation of this secondary atmosphere, and the oceans as well, was the degassing of the early crust in a process that is still taking place in present-day volcanoes, fumaroles and hot springs.\textsuperscript{12,13,14}

Thus the study of volcanic gases may shed some light on the various phases of the growth of these important bodies during the history of the earth, and account for the atmospheres presently being observed in detail on other planets with increased space exploration and discovery.

B. Statement of the Problem

The object of this research, in its broadest sense, was to obtain an increased insight into the composition and the function and importance of the gas phase associated with the active Hawaiian volcanoes. To this end the following objectives were included in the problem. Improved gas collecting devices and techniques were to be devised, based on existing designs and methods. A gas analysis system based on gas chromatography was to be developed. In addition, other analytical methods, such as mass spectrometry, were to be employed to supplement the
chromatographic analyses. During the course of the study, any source of volcanic gases (vents, fumaroles, lava lakes, etc.) that became accessible were to be sampled.

With the hope of gaining more knowledge of equilibrium conditions in Hawaiian volcanic gases, the results of selected samples from various collecting sites were to be used as a basis for thermodynamic equilibrium calculations, via an electronic digital computer.

C. Review of Volcanic Gas Collecting Techniques

It is probably true that man's first gas collecting and analyzing device was his nose. The human nose is capable of detecting, by their distinctive odors, H₂S, SO₂, and HCl, which are components of most volcanic gases. This method suffers in that it does not detect all of the gases and is only qualitative.

In some recent investigations of volcanically active areas, however, when a more formal program of collection and analysis of gases was not possible, this technique has provided the only information on the gases present. Judd has described another "qualitative technique" which was used at one time to illustrate the presence of large amounts of carbon dioxide in an active fumarole area near Naples, Italy. According to him, a dog was thrust into the invisible gas, and its suffocating effect on the animal indicated the presence of this gas. The dog was then withdrawn and revived with water.

Fortunately for dogs, scientists have been interested in a more complete and quantitative method of analysis of volcanic
gases. The design of a collecting technique for volcanic gases, ideally, must meet two requirements if the sample is to be representative of the gases. First, it must take in the gases to be collected while excluding all possible air. Secondly, the collected gases must not be allowed to react between themselves within the collecting device. Because volcanic gas sampling sites are always surrounded by an ocean of air and because of the hot, corrosive nature of the gases, meeting these two requirements is a very difficult task. This difficulty is often compounded by the inaccessibility of sampling sites, which limits the type and amount of equipment that can be brought to the area. A survey of the literature since the beginning of this century shows that five basic methods have been employed for taking volcanic gas samples: displacement of air from the sample container, displacement of water or mercury, vacuum tubes or bottles, condensation, and adsorption. These methods are essentially the same as those developed for sampling industrial gases, with modifications toward meeting the requirements and difficulties encountered in sampling volcanic gases. By far, the most popular method has been displacement of air in the sampling device with the volcanic gases. In 1912 Day and Shepherd used this method to take samples from cracks in a dome of lava built up over a lava fountain on the floor of Halamaumau caldera in Hawaii. Their apparatus contained 20 half liter glass tubes connected in series. One end of this series was connected through several lengths of glass tubing (with pure rubber joints) to a piece of iron pipe
which extended for 12 inches into the lava dome. The other end was attached to a hand pump to pull the gases through the sample tubes. They pumped gases through this system for 15 minutes to be sure all of the air originally present had been displaced before the ends of the sample tube series were closed off. Some disadvantages of this technique may be noted. First, considerable water condensed in the sample tubes (chiefly in the first three or four tubes) so that it was not possible to determine the proportion of this constituent relative to the total volcanic gases discharged from the lava dome. Second, there was no way to prevent alteration of the gas composition once the sample had been collected. The acid gases were soluble to a slight extent in the water that condensed out, thus removing some of these gases from the original composition. More troublesome is the reaction between $SO_2$ and $H_2S$:

$$2H_2S + SO_2 = 3S + 2H_2O.$$  

This reaction apparently occurs below 100°C in the presence of liquid water, leaving only that gas which was originally in excess and a sulfur deposit on the sides of the collecting device. Another reaction that would alter the composition of the collected gases, especially when there has been air contamination, is:

$$2H_2S + O_2 = 2S + 2H_2O.$$  

These workers found the iron intake pipe to be badly corroded after the collections, so it seemed likely that the primary composition of the gases as they were collected was affected by
this factor, especially with regard to the sulfur gases. The temperature at the iron pipe was estimated at 1000°C. Although the analyses indicated, by their high \( \text{N}_2 \) content (11 to 60 volume percent), that air contamination took place, it is not possible to determine how the contamination occurred. The air may have been sucked into the dome of lava by the motion of the molten lava inside, or it may have been due to incomplete removal of air from the collection train.

This first attempt by Day and Shepherd was designed to collect fixed gases only, as they did not expect to find any gases capable of condensing in the sampling system. In order to collect samples in which the condensed water vapor would be in its correct proportion to the fixed gases they turned to a vacuum tube. Their design consisted of a 500 ml bulb to which a long glass tube was attached. The sampling end of this tube was closed with a thin, glass bulb. It was planned to take the sample by inserting the thin bulb end into the gas vent or crack. The heat of the molten lava and the vacuum in the tube would cause the thin bulb to collapse, allowing the main bulb to fill with gas. This sampling end of the tube could then be resealed quickly in the molten lava. Unfortunately sampling conditions in Halemaumau crater had changed by the time these tubes were ready, and they were not able to test them under good sampling conditions.

From 1917 through 1919, Jagger and Shepherd\(^20\) took advantage of the excellent sampling conditions created in Halemaumau when
its lava lake would at intervals fill to its rim. For these gas collections they chose a vacuum tube. Shepherd was aware that the most critical part of the design of a vacuum tube was its collecting tip. The ideal tip would remain unbroken during transportation to the site, would break easily in the gas source, and would be capable of sealing before air could be drawn in by the cooling of the hot gases in the tube. The usual design had the tip drawn out to a fine point which can be broken on the walls of the collecting site, allowing the tube to fill. This tip had the disadvantage that if the sampling vent temperature was above the softening point of the glass, the tip might collapse and thicken, refusing to break. In another design, the tip was deliberately thickened, so that when placed in a hot vent, the reheating causes it to crack. Shepherd\textsuperscript{19} considered these tip designs as well as his "thin-bulb" model used in 1912 as unreliable. When placed in the source of volcanic gas, they often would not break as designed or just not break at all, but would break regularly during transportation to the source. For his 1917-1919 collecting tubes Shepherd followed the design of his early vacuum tube except for the tip. Here he used a small bulb with a moderately thick wall. A thin disc of soft glass was fused into the rounded end of this bulb, which curved inward when the tube had been evacuated. The idea was that the soft glass disc would melt and pull through before the thicker walls of the bulb reached their softening point. The tube also had a constriction near the main bulb end of stem leading to the tip. This allowed removal in the field of the
long stem by a gas torch, facilitating return of the collected sample to the lab for analysis. The collecting procedure began by tying the vacuum tube to a long bamboo rod, as heat from the lava lake would not allow hand-held tubes. The tip of the tube was thrust into openings of the lake surface from which small flames were rising. When they believed that the tip had opened, often signaled by a sudden clouding of the tube, they would attempt to seal the softened tip against the hot lava before removing the tube from the opening. Often, however, the tip cracked when it was pulled out. In this case it was sealed with a rubber tube until the stem could be sealed at its constriction with a gas torch.

Analyses of these samples showed a range of 0 to 100 percent air in the collected gases. All of the sample tubes in which the tip cracked on pulling from the gas source, showed considerable air. Those that stayed sealed, provided some of the best volcanic gas samples ever collected. Still, these samples suffered from the same major disadvantage as those taken by the displacement of air technique described above; that is, no provision was made for preventing sample alteration after collection.

On a National Geographic Expedition in 1919 to the Valley of Ten Thousand Smokes in the Katmai region of Alaska, Allen and Zeis\textsuperscript{21} collected gas samples from some of the many active fumaroles created by the 1912 eruption of Mt. Katmai. They rejected collection by vacuum tubes because the cooling gases in the tube usually pulled in air before the tube could be sealed, thus
contaminating the sample. In addition, since the fumarole gases consisted of almost 100 percent water vapor, they could not collect a large enough sample of the other gases to satisfy their method of analysis without resorting to impossibly large sample tubes. They chose to collect the "fixed" gases (CO₂, O₂, CO, H₂, CH₄, N₂) and "water soluble" gases (H₂S, HCl, HF) in separate operations.

For the "fixed" gases and water vapor determination, they used a water displacement technique. Their apparatus, consisting of a sample bulb with stopcocks at each end, a leveling bulb, and connecting tubing, was filled with water, including a copper intake tube which was to be placed into the sampling vent. On applying suction at the leveling bulb end of the apparatus train, a sufficient amount of the fumarole gas was pulled into the sample bulb. The volume of the condensed water was then determined and a measured volume of "fixed" gases was trapped in the sample bulb.

For the H₂O "soluble" portion of the gases they had planned to use a technique developed by Shipley, in his collections from the same area in 1917. This apparatus consisted of a glass tube leading from the vent to a catch bottle (a small filter flask) which was attached to one arm of a U-tube filled with solid Ba(OH)₂. The other arm of the U-tube was attached to a suction pump of known capacity. To collect a sample, a recorded number of strokes on the pump was performed. Some H₂O vapor would condense in the flask, some in the U-tube and some escaped through the pump. The H₂O in the flask was drawn into the U-tube of Ba(OH)₂ and this tube was stoppered until analysis.
Several objections can be raised against this collecting technique. A major objection was that the gases must be collected in two parts, due to the water solubility of some of the gases. Allen & Zeis were prevented from collecting the second portion of their samples, the "soluble" gases, due to bad weather. This made a complete analysis of the gases impossible, although they were able to gain some information about the "soluble" gases from Shipley's samples. They discovered on analyzing Shipley's four year old samples, that their original assumptions of negligible concentration of "soluble" gases was wrong. Instead, the "soluble" gases were found to have a concentration equivalent to that of the fixed gases. Even with this correction, the amount of water vapor was still greater than 99 volume percent. Another source of error was to include CO₂ with the "fixed" gases, whereas it is quite readily soluble in water (1713 ml of CO₂ per liter of water at 0°C).²³ They found a considerable amount of Ba(CO₃)₂ in Shipley's Ba(OH)₂ collecting tubes, but attributed this to atmospheric contamination, rather than CO₂ in the fumarole gases. Finally, the copper intake tube on their collection apparatus altered the composition of the gases by its reaction with H₂S. Because this reaction produces H₂, it was necessary to report these two gases as a total of H₂ + H₂S. No other sulfur gases were considered. These samples do not appear to have been entirely free of air contamination as the percentage of N₂ is high in almost all of their samples (25 to 80 volume percent of the fixed gases). This may have been due, however, to air mixing with the gases in the fumarole before they were collected.
E. T. Allen sampled gases from the steam wells of Sulfur Banks at Kilauea Volcano, Hawaii, in 1922 using an air displacement method. He determined sulfur vapor, sulfur dioxide and the ratio of water vapor to the remaining gases. For these three determinations it was necessary to take three separate samples. For sulfur vapor collection, a glass intake tube, which extended below the iron casings of the wells to prevent contamination from this source, led the gases into a series of two small bottles. The gases were pulled through the bottles by a 10 liter metal, gas aspirator. A small measured amount of water was added to each bottle to aid condensation and the first bottle was kept in an ice water bath, causing most of the water vapor to condense in this bottle. When 10 liters of gas had been pulled through the bottles, the condensed water vapor and precipitated sulfur were determined as a ratio of sulfur vapor to water vapor. The same apparatus was used for sulfur dioxide, with the addition of a flask containing 20 percent NaOH. The water in the bottles was also replaced with this solution, which adsorbs all of the other acid gases (CO₂, H₂S, HCl) as well as SO₂. Condensed water vapor was determined from the increased volume of the solutions and adsorbed SO₂ as BaSO₄. From this data a ratio of SO₂ vapor to water vapor was determined. To determine the water vapor to "fixed" gas ratio, a bulb with stopcocks on each end was placed between the condensing bottles and the aspirator. The first bottle was not cooled in an ice bath, but allowed to remain hot so that CO₂ would not be absorbed. Very little water
condensed in the second bottle and none in the gas bulb. After aspirating 10 liters of gas through this train, a sample of "fixed" gases was trapped in the bulb for later analysis (which was not reported). The amount of water vapor was determined from the condensed water and the difference between this and the 10 liters of the aspirator gave the "fixed" gas volume.

Since no "fixed" gas analysis was given it is not known how efficiently this method displaced air originally in the apparatus. The two major objections to this technique are the necessity of having ice and considerable amounts of water available and that three separate collections are required for determination of the different components of the gases.

Gases from fumeroles in the crater of White Island, one of New Zealand's most active volcanic areas, were sampled in 1927, 1928 and 1929 by I. L. Grange. The 1927 samples were taken by placing a small funnel attached to a gas bottle in the vent to be sampled. When it was felt that all air had been displaced, the bottle was removed and sealed. These samples were badly contaminated with air, the two reported having 87 percent and 97 percent, respectively. For the 1928 and 1929 collections they chose a liquid displacement technique. The gas was led from the fumerole vent by a small diameter copper tube to a sampling bottle filled with mercury or water, which it displaced. These samples also were air contaminated but to a lesser extent. Of the three reported, the highest air concentration (O₂ percent plus the atmospheric ratio equivalent of N₂) was 19 percent and the lowest
zero percent. While this second technique reduced air contamination considerably, it has several drawbacks. First the inlet tube was copper which would react with acid gases like H₂S and HCl. Neither of these gases were found when this technique was used, while large amounts of H₂ were detected (greater than 20 percent of the water and air free gases). With the air displacement method, HCl was found but no H₂. There was no H₂S detected, but this may have been oxidized to sulfur due to the large amount of air contamination. While a glass intake tube would have corrected this problem, the use of mercury as the displacing liquid would cause further problems. When water was used, some of the water soluble gases were lost by solution, also resulting in an altered gas composition.

An air displacement technique was used in 1929 and 1930 to sample solfataric gases from volcanoes in the former Netherlands East Indies.²⁵ The gases were led from the fumerole by a tube through three condensing bottles in series and then into a 15 liter aspirator. For each sample 10 liters of water was allowed to flow out of the aspirator, thus pulling 10 liters of gas into it. Although no further details were given, the author stated that he followed the procedures used by Allen at Sulfur Banks, Kilauea in 1922.¹

An air displacement method which sampled all of the gases with one collection was used in 1935 to sample fumarole gases from the summit area of Mount Hood, Oregon.²⁶ The collection train consisted of a Pyrex intake tube, a condenser, a Woulff
bottle containing barium hydroxide (evacuated to keep it free from CO₂), a copper gas holder, and an aspirator bottle. In taking a sample, most of the water vapor was collected in the condenser and then drained into the Woulff bottle. The Ba(OH)₂ in this bottle served as an adsorbent for H₂S and CO₂. The remaining gases were then collected in the copper gas holder. Water draining from the aspirator created the suction necessary to pull the sample through the gas train. The Woulff bottle and the copper container were then sealed until their contents could be analyzed in a laboratory.

In this technique, reactions between the apparatus and acid gases were avoided by using glass equipment until these gases were removed. Still some problems remained with the method. Water condensation in the intake tubing was a problem which is common to all methods of this type. It was especially serious when the position of the intake tubing allowed this water to drain back into gas vent, as happened with one of their reported samples. Air contamination did not seem to be too great a problem. Their best samples had less than one percent of air. The samples in which the condensed water vapor drained back into the vent had almost 100 percent air even though its intake tube extended 5 feet into the vent. The adsorption of the acid gases with Ba(OH)₂ prevented reactions between these gases and adding the volume of the condensed water vapor to the Ba(OH)₂ allowed analysis of any of these gases that dissolved in this water. Reactions, such as the one between H₂S and SO₂ which occurs readily at less than 100°C, could not be prevented in this apparatus. The authors of this
work did not report if any free sulfur was found in the intake tubing or in the water condenser which would have indicated the occurrence of this reaction.

A Russian scientist, I. Z. Ivanov, used the air displacement technique with some variations, to sample gases from satellite volcanoes of Kliuchevskoi volcano in 1937. In an attempt to prevent air contamination of the sample during collection, Ivanov buried a large iron funnel in a pit dug into the fumerole. Glass and rubber tubing led gases from the funnel into a collecting bulb with stopcocks on either end. A water aspirator, attached to the outlet end of the sample bulb, was used to pull the gases through the sample train. In some cases he replaced the sample bulb and aspirator with a one liter evacuated bulb. The tip of the bulb, which had been drawn-out to a capillary tube, was scratched and connected to the intake tube by thick-walled rubber tubing. By squeezing the rubber tubing, the tip was broken and the bulb filled with gas. Samples collected with either of these methods were used to determine the general mixture of the gases and the water vapor content. A separate collection of acid gases was made by pulling the fumarole gases through an adsorbing tube filled with a concentrated potassium hydroxide solution. The reported results of the samples show the dry gases (water percentage excluded) to be almost 100 percent air, indicating that the burial of the intake funnel did not help to reduce air contamination. A glass funnel would have been better than the iron funnel as the acid gases probably reacted with the iron funnel.
From 1936 to 1940, Ballard and his associates\textsuperscript{28,29,30} collected fumerolic gases from Kilauea volcano on the island of Hawaii. Almost all of these samples were taken from the manifold connecting the three wells drilled in the Sulfur Bank fumarole area in 1922.\textsuperscript{31} They were interested only in determining the composition of the 3.7 percent "fixed gases" reported by Allen’s 1922 study of Sulfur Bank gases,\textsuperscript{1} and made no attempt to collect water or sulfur vapor. A simple air displacement technique was first used by pulling the gases, with a hand pump, through a sample bulb attached to the manifold connecting the wells. The sample bulb was placed in a vertical position above the gas source and packed with ice so that water vapor would condense out and flow back into the wells. When it was believed that the tube had been thoroughly flushed with vent gases, stopcocks at each end were closed and the sample was ready for laboratory analysis. Detection of rare gases in these samples was obscured by the large amounts of CO\textsubscript{2} and SO\textsubscript{2} found. To eliminate these gases the collection train was altered by adding two water condensers followed by two adsorption tubes containing 50 percent KOH, and then the sample bulb. Only air argon was found in the rare gas analysis of these samples.

From 1938 to 1940 their interest was in the measurement of the SO\textsubscript{2}:CO\textsubscript{2} ratios in order to determine if any correlation existed between variations in gas composition and volcanic activity. For these collections they used the same air displacement method without the KOH adsorption tubes. For more efficient removal of
water vapor, they passed it through a coiled copper tube packed in ice. The sample bulbs were connected to the coil through a trap which prevented any water from entering the sample bulbs. Three sample bulbs were used, connected in series, and a hand-pump pulled the gases through the collection train. One sample tube was used for \( \text{SO}_2 \), one for \( \text{CO}_2 + \text{SO}_2 \) and the third was a spare in case of accidents.

There are two objections to their technique. First, the use of copper tubing with these highly reactive gases and second, the gases had to bubble through previously condensed water vapor before entering the sample bulb. Both of these could alter the composition of the collected gases. Air composition varied from zero to 40 per cent. This could mean air was not efficiently flushed from their sample train or that it had mixed with the fumarole gases underground. It is not likely to have entered at the intake to their sample train, as they had gas tight connections to the manifold connecting the wells.

Ballard\(^2\) also designed a vacuum sampling tube to collect gases from molten lava during eruptions. He changed the design of the Shepherd and Jagger tubes\(^2\) in an attempt to overcome the difficulties in opening and sealing vacuum gas collecting tubes. To insure that the tube could be opened when the sample was to be taken he used a crook-necked tip which had been scratched with a file. A wire was attached to the tip to pull it off at the proper time. To seal the tubes before air could be drawn in, Ballard placed a glass vacuum stopcock between the main bulb (an 800 cc
Kjeldahl flask) and the tube leading to the tip. Before removing
the sample tube from the gas source this stopcock would be closed,
preventing air contamination. The sample tube also could be tied
to a long pole as Shepherd and Jagger did, if sample conditions
required it, and the stopcock would then be closed by a remote
control device. Unfortunately, no opportunity occurred for
testing these tubes during an eruption while Ballard was conducting
his volcanic gas research at Kilauea.

A. U. S. Government study of Alaskan volcanoes in 1946 in-
cluded some investigations of fumarolic gases. Two methods were
described for taking gas samples. The first, which was used to
take partial samples of gas from Umnas Island fumaroles, allowed
the gas to bubble through 250 ml. absorption bottles containing
about 150 ml of a strong KOH solution. No other details of the
collection were given. Analysis reported only CO₂ and SO₂ in the
KOH solution and gave approximate volumes of unabsorbed gases
drawn through the collection bottles and the approximate volume
of condensed water vapor. The other gas samples were taken from
fumaroles on Great Sitkin Island. For these collections a 25 ml
Pyrex glass pipette was inserted in the fumarole opening. The
pressure of the fumarole gases was used to displace the air in
the tube and fill it with the gas sample. When the pipettes were
judged to be filled, they were sealed with an oxy-butane torch.
Unfortunately no analysis of these samples were reported.

Another very simple air displacement technique was used to
take gas samples near Helka volcano in Iceland in 1948. The
samples were taken by placing an inverted funnel over the vent opening. A rubber tube connected the funnel to a gas sampling tube or in some cases directly to a field gas analyzer. Air in the gas train was washed out by allowing the gas to flow through it for half an hour. The analyses showed large amounts of CO₂, O₂, and N₂ and less than one percent CO. The O₂ and N₂ are almost certainly atmospheric and probably were pulled in through the loose fitting edge of the funnel.

A simple air displacement technique was used by Wilson [34] to collect fumarolic gas samples in New Zealand. The gas train consisted of an intake tube which was attached to one side of a bolt head flask. An air condenser, attached to the other side of the flask was situated so that any condensate would drain into the flask. The top of the condenser was attached to the sample bulb set up vertically so that any further condensation would drain out of it into a flask attached to its bottom. This flask served as a trap for a pump used to pull gases through the train. The condensed steam was to be analyzed for soluble gases and the sample bulb for noncondensables, but no results were given.

A preliminary investigation of fumarolic gases of Mount Pele and Grande Soufrière volcanoes in the West Indies by Fabre and Cha igneau [35] in 1958, led them to suspect that the gases were interacting after collection (particularly water vapor, H₂S and SO₂). To investigate this further they devised a vacuum tube collecting technique. Three bulbs of about 300 cc capacity were evacuated to about 10⁻² mm of Hg before sealing. In one bulb
they had put an excess amount of powdered $P_2O_5$ (12-15 grams) so that all water vapor would be quickly removed from the gas mixture during collection. The second bulb contained a weighed tube of $P_2O_5$ adsorbed on pumice, so that the amount of water vapor in the sample could be determined. The third bulb contained no absorbent, so that a comparison of the affect of interactions during collections on the gas composition could be made with the first two bulbs. To take a sample, gas from the fumarole opening was pulled through a funnel and tubing by means of a bulb-type aspirator until it was felt all air had been displaced. The aspirator was then replaced with one of the evacuated sample bulbs, fitting the intake tube over the sample bulb's capillary tip. This tip was then broken and the sample bulb filled with gas. It was then sealed by melting some Golaz cement which had previously been introduced into the intake tube. Because of the low temperature of these fumaroles ($100^\circ$C) the funnel and intake tubing were of polyvinyl plastic which should be inert to volcanic gases.

The results showed that the use of $P_2O_5$ as a dessicant was quite successful in preventing the reaction between $SO_2$ and $H_2S$. As an example, the gas from a Grande Soufriere fumarole had about 0.8 percent (by volume) $H_2S$ and about 15 percent $SO_2$ according to the analysis of the sample bulb with no dessicant. When $P_2O_5$ was used, the $H_2S$ was found to be about 5 percent and the $SO_2$ 21 percent. These percentages were calculated without including the water vapor. The other gases found, $CO_2$, $O_2$, $CH_4$, $N_2$ and rare gases, were not affected by the presence or lack of the dessicant.
A sample taken from a Mount Pele fumarole, in which no \( \text{H}_2\text{S} \) or \( \text{SO}_2 \) were found, had the same composition with the dessicant as without.

In later collections, these workers used \( \text{CaC}_2 \) to determine the water vapor content of the gases. The \( \text{P}_2\text{O}_5 \) on pumice was replaced with 12-15 grams of powdered \( \text{CaC}_2 \) which reacts with water according to the equation:

\[
\text{CaC}_2 + \text{H}_2\text{O} = \text{CaO} + \text{C}_2\text{H}_2.
\]

The volume of acetylene (\( \text{C}_2\text{H}_2 \)) liberated corresponds to an equal volume of water vapor and so no weighing was involved in this method. Chaigneau et al. felt that the \( \text{CaC}_2 \) reacted with water vapor more efficiently than the \( \text{P}_2\text{O}_5 \) adsorbed on pumice. They did not compare these two methods, but did use collecting tubes containing excess \( \text{P}_2\text{O}_5 \) to determine all gases except water vapor. Comparison of these results showed both methods gave the same composition (excluding the water vapor).

Several research groups in Japan have in recent years developed techniques for the collection and analysis of volcanic gases. Mizutani has developed a technique, based on a method originally devised by Oana, which required that four separate samples be taken for a complete analysis. In each case a syringe with two needle heads was used to pull the gases through the sampling train. The first sample was used to determine the total alkali soluble gases (\( \text{CO}_2 \), \( \text{H}_2\text{S} \) and \( \text{SO}_2 \)), oxygen, and the residual gases. The sample train in this case consisted of the glass intake tube from the vent, and the syringe. Using the syringe, air was displaced by the volcanic gases. The exhaust head of the syringe was sealed.
and the syringe was cooled in water. Then more gas was drawn into it. Condensed water vapor dissolved any hydrogen halide gases and the remaining gases were transferred to a gas burette for analysis. For the second sample, used to determine H$_2$S and SO$_2$, a volumetric tube cooled in H$_2$O and containing 4N NaOH was placed between the intake tube from the vent and the syringe. After purging air from the system, the syringe was used to bubble the fumarolic gases through the NaOH solution. Water vapor condensed and the alkali gases were dissolved in the basic solution. Pumping was continued until about 50 cc. of water had condensed. The solution was then analyzed for H$_2$S and SO$_2$.

The same sampling train and procedure was used for the third sample, to determine HCl, HF and the ratio of the remaining gases to the original water vapor, but the alkali solution was replaced with 10 ml of distilled water. When a measurable amount of water had condensed in the tube the system was closed-off. After the system had cooled, the volume of gas remaining in the syringe was measured and the volume of condensed water vapor was determined. The water was saved for the determination of the dissolved HCl and HF. A final gas sample was taken to determine the alkali-unadsorbed fraction (H$_2$, N$_2$, CH$_4$, CO and Ar). For this sample a gas collecting tube was placed between the vent intake tube and the syringe. After air had been displaced from the sample train by pumping the syringe a concentrated NaOH solution was pumped via the syringe into the collecting tube, until it was half-full.
The collecting tube was closed off from the syringe and tilted so that the fumarolic gases bubble through the solution and the un-adsorbed fraction collected above it. Both ends of the collecting tube were sealed with a torch and the sample was returned to the lab for analysis.

Mizutani was aware of several sources of error in his procedure. Air contamination was always possible and a large amount of oxygen in the first portion was reason for rejecting the sample. Some error was introduced due to the solubility of $\text{H}_2\text{S}$, $\text{SO}_2$, and $\text{CO}_2$ in the condensed water vapor in the first and third samples. He was also aware of the error due to the reaction that occurs between $\text{H}_2\text{S}$ and $\text{SO}_2$, but felt that when volcanic gases were poor in both $\text{H}_2\text{S}$ and $\text{SO}_2$, the error was negligible. When volcanic gases contained considerable amounts of $\text{H}_2\text{S}$ and $\text{SO}_2$ he altered his sampling procedure and method of analysis. The third sample was eliminated and the $\text{HCl}$, $\text{HF}$ and ratio of unadsorbed gases to water vapor were determined from the second sample (taken with $\text{4N NaOH}$ solution). The major disadvantage of this technique is that at least three samples are required to make a complete analysis.

An extremely simple collection technique was developed by Noguchi and Kamiya$^5$ in their studies on predicting volcanic eruptions. Their gas collection device was a glass dish 15 cm in diameter and 15 cm deep, containing 500 ml of 25 percent KOH. The dish was covered by a protective wooden box whose sides were full of holes to allow gas to enter. Several of these boxes were placed on stands one meter high situated around the main crater.
and a sulfataric zone of the volcano being studied. The KOH solution was changed every 7 to 10 days and analyzed by the authors for its CO₂, total sulfur, and total chlorine content. Although a complete analysis could not be obtained by this method it provided the information the authors needed.

The research group led by Iwasaki developed sampling techniques similar to Oana's and Mizutani during their studies of a number of Japanese volcanoes in the 1950's. They tried and rejected iron tubes and glass vacuum tubes because of poor precision. Fumarolic gases were sampled by inserting silica or hard glass tubes into the vent to a depth sufficient to prevent air contamination. A syringe was used to pump gas through this tubing until all air had been displaced, if the pressure of the gases was low. For a complete determination, two samples of gas were taken. A 100 ml syringe containing 20-30 ml of 5N KOH was attached to the vent intake tube and opened to the volcanic gases. When necessary the syringe was cooled with water. When the gases were drawn into the syringe, water vapor condensed and the acid gases dissolved in the alkaline solution. The other components remained in the gas phase. The volume of these residual gases and of the alkaline solution were determined in the syringe, and then both were analyzed. From this sample, H₂O, CO₂, HCl, F, total sulfur and fixed gases (H₂, N₂, etc.) were determined. A second sample was necessary to determine the ratio of the sulfur gases. For this purpose they bubbled the fumarole gases through potassium iodide solution containing known amounts of iodine. This solution was
analyzed for total sulfur (iodine consumed) for $SO_2$ (as sulfate), and $H_2S$ was determined by the difference. Laboratory tests showed the precision and accuracy of this technique to be quite satisfactory. The disadvantages were that a complete analysis requires two samples and that liquids, one of them caustic, must be transported to and from the collection site.

During this same decade of European and Japanese activity, Naughton was developing gas sampling techniques for his studies on Hawaiian volcanic gases. Like most investigators at the time, Naughton was aware that one of the main problems involved in obtaining representative samples of volcanic gases was the prevention of interactions among the gases during and after collection. This is particularly true of the sulfur gases, as illustrated above by the work of Fabre and Chaigneau. Naughton noted that whether the sample was taken in a vacuum bulb or by displacing air in a sample bulb, free sulfur deposited in the liquid condensate on the walls of the bulb. This sulfur was believed to result from the interaction of $H_2S$ and $SO_2$. To overcome this problem, Naughton chose a vacuum tube design similar to that used by Jagger and Shepherd, but with an adsorbent occupying a major portion of the tube. Of the many adsorbents tested, both liquid and solid, the most successful was 20 to 60 mesh silica gel. The sample tubes were made from approximately three foot lengths of 3/8" diameter Pyrex glass tubing with break-off tips added to each end (one for sampling and one for analysis). About two feet of the length was filled with silica gel which was held in place by glass wool plugs,
and the tube was baked at 350°C under vacuum to activate the silica gel. To take a sample, the sampling tip was broken against the wall of the volcanic vent, filling the tube with gas in only a few seconds. Sealing the tube was still as much a problem as it was for Jagger and Shepherd. If the vent was above the softening temperature of glass, the glass tip could be resealed in it. Otherwise, when the tube was removed from the vent, it was temporarily sealed with a short piece of closed-end fluorocarbon or rubber tubing. A torch was used to seal the tip later. When a sample was to be taken deep in a high temperature vent, the tubes were placed in an iron pipe and surrounded by an insulating layer of powdered diatomaceous earth. The glass break-off tip protruded from the end of the pipe so it could be broken as before. This pipe could be held in an 800°C vent for about one minute before the temperature of the vacuum tube exceeded 100°C.

Naughton and co-workers\(^{40}\) made a comparison of their silica gel tube and Shepherd's vacuum bulb by taking samples of a known mixture of CO\(_2\), H\(_2\)S, SO\(_2\) and steam passing through a large glass tube. Free sulfur was invariably deposited on the walls of the Shepherd tubes and when the remaining gases were analyzed, only that sulfur gas (H\(_2\)S or SO\(_2\)) originally present in a stoichiometric excess was found. Analysis of the gases collected in the silica gel tubes showed they had the same composition as the prepared mixture. Other tests showed that the silica gel adsorbed the acid gases and water vapor in the same way as a chromatographic column, separating each component. The adsorbed gases showed no
tendency to migrate or remix, allowing a sample to be stored for long periods without alteration of its contents. The fixed gases \((\text{H}_2, \text{O}_2, \text{N}_2, \text{etc.})\) were not adsorbed and filled the free volume of the tube. In field tests during the 1959-1960 Kilauea eruption, the composition of gases collected by this method corresponded to the equilibrium composition calculated for such volcanic systems. Not even an approximate equilibrium composition was found in samples taken by any of the other methods tested. While this collecting tube had many advantages over previous designs it still had the disadvantage of being difficult to seal before air contamination occurs.

Both Naughton and Murata sampled gases from the pumice-cinder cone of Kilauea Iki, which was built-up during the 1959 Kilauea eruption. While Naughton was interested in determining all of the components of the gas, Murata was interested only in finding the amount, if any, of halogen acid gases present. For this purpose the latter used the following technique. A two feet deep hole was dug into the cone at a point where copious steam was being emitted (the temperature was about 328°C at this point). A large inverted glass funnel was buried in this hole and its protruding stem was attached to a long, inclined piece of glass tubing. This tube, which served as a condensor, ran into a 500 ml receiving flask immersed in a bucket of dry ice cooled water. A suction pump was used to pull the fumarole gases through the gas train, and after several hours of pumping about 450 ml. of condensate was collected and analyzed by standard chemical methods.
The use of all glass equipment prevented the interaction of the halogen acid gases with the collecting equipment. Air contamination was not important in this type of collection, as only the condensed steam was collected for analysis.

In November of 1963 a submarine eruption off the southern coast of Iceland, began building the island of Surtsey. Four attempts were made in 1964 to collect gases from Surtsey’s still erupting volcano by Sigvaldason and others. The collections were made by inserting a tube into the vent to be sampled. This was attached to a Dewar bottle, which served as a water trap, and this in turn was attached to the sample tube. The sample tubes were made from Pyrex glass with stopcocks on each end. On the first and second visits to the island, samples were taken using a copper inlet tube. This proved to be a poor choice due to the high temperature of the vent ($84^\circ$C) and the corrosive gases. Air cooling was used to condense water vapor in the Dewar bottle and a pump was used to pull the remaining gases into the sample tube. Analysis of these samples showed only water and air. Sampling conditions had changed on the third visit to Surtsey. This time lava was flowing from the main crater through closed channels. Samples were taken from a hole in the roof of one of these channels where burning gases were escaping at a high velocity. Since the temperature of this vent was about $1100^\circ$C, the copper intake tubing was replaced with stainless steel tubing. The high velocity of the emitting gas efficiently removed air from the sample train and made pumping unnecessary. The reported analysis of a sample taken from
this vent showed a number of active gases to be present \((H_2, CO_2, CO \text{ and } SO_2)\) with less than one percent air. Tests with lead acetate paper at the end of the stainless steel tube indicated the presence of \(H_2S\) and its odor had been noted from the beginning of lava production. Considerable free sulfur was noted in the condensed water vapor, which also indicated the presence of \(H_2S\). Sampling conditions had changed again when the fourth visit to Surtsey was made. Again a stainless steel tube was inserted into a hole in a lava tunnel, but this hole was very large and the gases did not have as high a velocity as before. It was necessary to use a pump to pull the gases through the sample train. The composition of this sample was like that of the first two, mostly water and air with some \(CO_2\).

The results of the analysis indicated that Sigvaldason's collecting technique worked best at high pressure gas vents. Air was probably pulled in through the intake tube by the pump and its \(O_2\) plus the metal intake tube apparently removed all of the active components from the gases before they reached the sample tube. While a quartz intake tube would have been better than the metal ones used, very little could have been done to prevent interactions between the gases as they cooled in the sample train before reaching the sample tube. This probably was the reason \(H_2S\) was not found in the gases analyzed.

This review has shown that a wide variety of volcanic gas collecting techniques have been developed since the beginning of the century. While some techniques seem superior to others, no
clear favorite has emerged. It is not always obvious from the reported research why a particular method was used. Many factors not always evident in the report must be considered, such as the location of the sampling site and difficulty or ease in reaching it. Sometimes, because of heat or other dangers, it is not possible to get close enough to a vent to use a particular method. Lack of some of the necessary material and equipment may also prevent the use of more desirable techniques.

D. Review of volcanic gas analysis techniques

In the past, as with the collecting techniques, the methods used for analyzing volcanic gases have relied heavily on the technology developed for studying mine and industrial gases. This has most often been an absorption apparatus based on the Hempl or Orsat principle. In both cases, the sample is admitted to a gas burette and its volume measured. The gases are then exposed to a pipette containing an absorption reagent specific for one gas. The volume is redetermined, and the difference corresponds to the absorbed gas. With the Hempl apparatus, the absorption pipettes are attached one at a time as they are needed, while with the Orsat apparatus they are permanently attached to the gas burette by means of a manifold. Absorption reagents used by Allen and Zies in their studies of volcanic gases from Katmai, Alaska are typical. In order of their use they were: potassium hydroxide for carbon dioxide, pyrogallol for oxygen, ammoniacal cuprous chloride for carbon monoxide. Methane and hydrogen were determined
in a combustion pipette and nitrogen was adsorbed on hot calcium. Any residual gases were assumed to be noble gases. Their laboratory apparatus, based on the Orsat principle, was developed by U.S. Bureau of Mines' scientists. Allen and Zies took a portable model into the field, which, for convenience, used water instead of mercury in the gas burette. This resulted in a loss in accuracy, however, due to the solubility of the gases in water.

Until recent years $\text{H}_2\text{S}$ was not detected in volcanic gases, due to the collecting techniques, so a method of analysis was rarely reported for this gas. If $\text{SO}_2$ was present it was absorbed in the sodium or potassium hydroxide used to adsorb $\text{CO}_2$. The $\text{SO}_2$ was then determined gravimetrically by oxidizing and precipitating as $\text{BaSO}_4$ or volumetrically by adding a standard iodine solution and back-titrating the excess iodine. This latter method was used by Shepherd in the analysis of the famous samples collected with Jagger in Hawaii in 1918 and 1919. Shepherd's apparatus was based on the Orsat principle, but was more elaborate than the usual equipment employed and undoubtedly contributed a great deal to the excellence of their 1918-1919 analyses. His apparatus was designed around the fact that volcanic gases consist of a few components present in large amounts and the majority present in trace quantities. So that a simple solubility would not be mistaken for absorption, Shepherd used solid reagents for absorbents and mercury to move the gases around within the system. Tests indicated his apparatus was accurate for its purposes and considerably more accurate than the gas collecting techniques used.
Absorption methods based on the Hample or Orsat apparatus were also used by Ivanov in Russia, Ballard and Payne in Hawaii and Forkelsson in Iceland. Using a similar technique, Wilson made a partial analysis of his samples in the field. After determining the sample pressure and temperature, CO₂ and H₂S were removed with a NaOH solution. The pressure was remeasured and from this and the amount of H₂S found in the NaOH solution by iodine titration, the amount of CO₂ was determined. The remaining gas was transported to his laboratory for analysis by a standard adsorption pipette method. Fabre and Chaigneau used an absorption method developed by Lebeau and Damie that, like Shepherd's technique, used solid reagents to avoid errors from the solubility of some of the gases in the reagents. Their analysis included specific reagents for absorbing H₂S and SO₂, since these gases were preserved by their collecting technique. Hydrogen sulfide was absorbed by cupric sulfate crystals and SO₂ by an agglomeration of small balls of PbO₂.

Allen's 1922 study of gases from the drill holes at Sulfur Bank, Kilauea, Hawaii, involved extremely simple methods for a partial analysis of the samples. Sulfur vapor was considered a component of the gases and was determined by drying and weighing the free sulfur that precipitated in the condensing water vapor during collection of the sample. Sulfur dioxide, which was collected in a NaOH solution, was determined by precipitating it from this solution as BaSO₄. The remaining components, water
vapor and the fixed gases (CO₂, N₂, etc.), were determined by measuring the volume of fixed gases that accompanied a measured amount of condensed water vapor. He took care to avoid solution of CO₂ in water by using hot water whenever the two came into contact. This same procedure was followed by Stehn in his gas studies of volcanoes in the former Netherlands East Indies.²⁵

In their recent study on the use of volcanic gas composition for the prediction of volcanic eruptions, Noguchi and Kamiya⁵ were concerned only with the gases that would be adsorbed by dishes of a NaOH solution set around the volcano. Total sulfur gases (H₂S and SO₂) were determined by oxidizing these gases to sulfate with thirty percent hydrogen peroxide. The resulting sulfate was then precipitated with barium chloride and determined gravimetrically as barium sulfate. They determined chlorine by titrating with silver nitrate, using potassium chromate as an indicator (the Mohr method). After oxidizing an aliquot of the potassium hydroxide, they titrated it with a 2N hydrochloric acid solution to determine carbon dioxide.

Murata's⁴¹ search for halogen acid gases at Kilauea Iki also made use of standard wet chemical methods of analysis, since his gas samples were collected as a steam condensate.

The use of instrumental methods for the analysis of volcanic gases has largely replaced the absorption pipette and wet chemistry techniques. While this has been mostly a recent
development, one instrumental technique, spectroscopy, has been applied to the study of volcanic gases for some time. Judd's book, "Volcanoes," published in 1881, proposes the use of a spectroscope to study the flames of burning volcanic gases as they are emitted from a vent.\textsuperscript{48} Since that time many investigators have used hand-held, visual spectrometers to observe volcanic flames, but only qualitative information could be obtained in this way. In 1938, Verhoogen\textsuperscript{49} made the first quantitative studies of volcanic flames by obtaining spectrograms from the eruption of the African volcano, Nyamalagira. His results showed that the major emitting atoms were minor components of the gases, such as sodium and potassium. Nothing of the nature of the major burning gases was revealed by the spectrograms. It was suggested that this was most likely due to the poor emitting ability of the molecules and radicals involved in the major gases. His instrument was a Hilger constant deviation camera spectrometer with a range of 3800-9000 Å. K. J. Murata\textsuperscript{8} made a study of gas flames during the 1960 flank eruption of Kilauea volcano, using a small Gaertner quartz spectrograph. His spectrograms showed the presence of CuCl in the flames and suggest that this molecule is more volatile in basaltic magmas than had been suspected. Emission spectroscopy was sometimes used to analyze the residual gas fraction from the adsorption pipette techniques,
since this fraction contained only rare gases, which almost always consisted of only argon. Ballard and Payne attempted to analyze all of the gases in a sample by spectroscopic means but were not successful, because the large amount of CO₂ in the sample masked the other components. They then switched to the absorption pipette method of analysis, using spectroscopy only for the rare gases.

The two analytical techniques, mass spectrometry and gas chromatography, have in recent years been developed to a high state and are proving to be extremely valuable tools for the study of volcanic gases. Sakai and Nagasawa have studied the fractionation of sulfur isotopes in fumarolic gases from Shirane and Showashinzan volcanoes in Japan by means of mass spectrometry. During collection of the sample the gases were bubbled through a KI-I₂ solution, which oxidized SO₂ and H₂S to sulfate ions and free sulfur. The free sulfur was filtered-out and the sulfate precipitated as BaSO₄ and converted to a sulfide. Each of these was then converted to sulfur dioxide for the analysis by mass spectrometry. In this way they were able to determine S³²/S³⁴ ratios for the SO₂ and the H₂S in the original sample. They used a CHD Model 21-103A mass spectrometer.

Rafter and Wilson in New Zealand have made sulfur isotope measurements on a variety of specimens, including gases
and condensates from fumaroles in their studies on the origin and genesis of sulphide and sulfate minerals. In their sampling technique the reactive gases were adsorbed in a concentrated sodium hydroxide solution. In addition to H₂S and SO₂, polythionates were also found in the gases and condensates from the fumaroles sampled. To separate these compounds, they used a stream of N₂ to drive the two gases out of the NaOH solution into an acidified H₂O₂ solution. This solution oxidized the SO₂, which was later precipitated as BaSO₄, and the H₂S, which passed through it, was trapped in a AgNO₃ solution and precipitated as Ag₂S. The sulfur isotope abundances for each of these components could then be determined.

Other New Zealand investigators have used mass spectrometry to study gas discharges in the thermal areas of that country, in hopes of obtaining more information on the cause of such discharges. Their analyses included determinations of N₂, O₂, H₂, Ar, CH₄ and CO₂. Collected samples were prepared for the mass spectrometer in a vacuum system where water, CO₂ and the residual gases, as a group, were separated. The pressure and volume of the CO₂ and of the residual gases were measured and break-seal tubes taken for analysis. The mass spectrometer used was a sixty degree Nier type using magnetic ion selection and manual peak height
measurement. They estimated an accuracy of ± 3 percent for Ar/N ratios reported and approximately 10 percent for the other components reported.

The high sensitivity of mass spectrometry makes it a particularly advantageous technique for the study of the rare gas component of volcanic gases. An example is the work of Mazor and Wasserburg\(^{54}\) on gas emanations from Yellowstone and Lassen volcanic parks. The purpose of their study was to determine the nature and the juvenile component, if any, of the rare gases associated with some of the thermal waters in these National Parks. Their samples, which involved only gases bubbling-up through the hot springs and mud pools of these thermal areas, were first analyzed volumetrically for CO\(_2\), N\(_2\), CH\(_4\), H\(_2\)S and the total rare gases in a vacuum system. The individual rare gases were then determined by isotopic dilution and mass spectrometry using a tracer mixture containing each rare gas to be determined. They used a mass spectrometer with a 6-inch radius of curvature and two detectors, one with an electron multiplier and the other a simple Faraday cage, to measure the argon, krypton and xenon in their samples. Experimental errors of the results were in the range of 10 percent or less.

Gas chromatography is undoubtedly the most suitable technique available for the analysis of volcanic gases. Its sensitivity range is such that both the major components and the trace components can be determined from a relatively small sample (a few milliliters). While not as sensitive as mass spectrometry
for the trace components, this disadvantage is completely out-
weighed by the low cost and simple operating procedures of a gas
chromatograph. Naughton et al., 40 used a gas chromatographic tech-
nique for the analysis of their gas samples taken during the 1959-
1960 Kilauea eruption in Hawaii. They used five chromatographic
columns to obtain a complete separation of the gas sample. Their
analysis involved essentially three steps. First the permanent
gases (H₂, O₂, N₂, CH₄ and CO), which were not adsorbed on the
silica gel in their collecting tubes, were analyzed with a molecu-
lar sieves 5A column, using argon as the carrier gas. Another
molecular sieves 5A column was run at -78°C with He carrier gas to
separate Ar and O₂ and a third column of silica gel and cupric oxide
was used to determine CO and CO₂ (some of which apparently did not
stay adsorbed on the collecting tube silica gel). In the second
step of the analysis, the gases adsorbed on their silica gel col-
lecting tubes were driven off and analyzed. Here they used a
column of tricresyl phosphate on a base of C-22 firebrick to sep-
arat H₂S, CO₂ and SO₂ and a distillation trap with silica glass to
separate CO₂, SO₂ and CS₂. Both were used with He carrier gas. In
the third step, water was driven off the collecting tube into a re-
movable trap and weighed. They used a thermal conductivity detector
throughout. Using air samples, they found the accuracy and pre-
cision of their apparatus varied with the sample size. The
accuracy of analysis was usually within 5 percent of the known
values, but as high as 20 percent for very small samples.

Suwa83 in Japan has developed a gas chromatographic method
to analyze the "residual gases" which remain after washing a
volcanic gas sample with a concentrated alkali solution. These gases ($H_2$, $N_2$, $O_2$, $CH_4$, $CO$ and the rare gases) were analyzed on columns of molecular sieves 5A and 13X run at room temperature with argon as a carrier gas. The 5A sieves gave a better separation of $H_2$ and $O_2$ than the 13X sieves. Since a molecular sieve column will not separate $O_2$ and $Ar$ at room temperature, Suwa determined $O_2$ using argon as the carrier gas and then determined $Ar$ using oxygen as the carrier gas. When there was so much $H_2$ present that it interfered with the determination of $Ar$ and $O_2$, she removed the $H_2$ with a palladium leak. Helium was also determined by first removing $H_2$ with a palladium leak, as these two gases have the same retention time on molecular sieve columns at room temperature. To determine the precision and accuracy of her technique, Suwa measured the Ar content of different volumes of air. She found a relative standard deviation of 2.4 percent and an average value of $0.93 \pm 0.02$ percent for argon in air, which compares favorably with the accepted value (0.93 percent).

A recent study of gases from hydrothermal sources in Yellowstone National Park was made by Gunter and Musgrave using gas chromatography for the analysis. With their system they were able to determine $CO_2$, $H_2$, $H_2S$, $O_2 + Ar$, $N_2$, $CH_4$, $CO$, and $SO_2$ with one run of a gas sample through the chromatograph. Carbon dioxide, $H_2S$ and $SO_2$ were separated on a sulfolane on firebrick column, which also produced a composite peak for the other gases. A molecular sieves 13X column was used to separate the "composite" gases, while the $H_2S$, $SO_2$ and $CO_2$ were irreversibly
adsorbed on this column. As the "composite" gases (H₂, O₂, etc.) were eluted from the 13X column, they were detected on the reference side of the detector. A polarity switch was necessary to obtain positive recorder peaks for these gases. To obtain a separation of Ar and O₂, they switched to a molecular sieves 5A column which was run at less than zero degrees centigrade. The reliability of their system was monitored periodically by comparing the total number of moles of gas observed with the number calculated from the sample pressure, volume, and temperature. On the average, they were found to agree within 3 percent of each other. It should be noted that in their technique the continued irreversible absorption of CO₂, H₂S and SO₂ on the 13X column would eventually destroy the separating ability of this column for the other gases. This would necessitate continued reactivation or replacement of the 13X sieves column.

Some investigators have used a combination of different techniques to achieve a complete analysis. Mizutani, 37 who collected his samples in four parts, used an Orsat type analyzer to determine CO₂, H₂S and SO₂ as a group, O₂ and residual gases in his first fraction. Hydrogen sulfide and SO₂ in the second fraction and HCl and HF in the third fraction were determined by standard titrametric methods. A gas chromatographic technique was used to analyze H₂, N₂, CH₄, Ar and CO in the fourth fraction. Multiple samples were also used by Iwasaki et al., 39 to obtain a complete analysis. They used standard "wet chemistry" techniques for the determination of H₂S and SO₂. For CO₂ they used a diffusion
technique and for HCl and HF, photometric methods. Fixed gases (H₂, N₂, O₂, etc.) were determined by mass spectrometry in their laboratory and by an Orsat apparatus in the field.

The techniques described above involve two steps, the collection of the sample in the field and the analysis of the sample in the laboratory (in some cases a partial analysis was made in the field). Elskens et al.,⁵⁷ have, however, devised a technique that analyzed the sample as it was being collected. Their technique completed the collection and analysis in a few seconds or less and was capable of detecting H₂O, CO₂, H₂S and SO₂ + H₂S.

To accomplish this they adapted an air-pollution detection unit manufactured by Draeger and Co. in Lubeck, Germany, for use with volcanic gases. The Draeger unit operates by selectively adsorbing one component of the gases being sampled on a solid reagent contained in a small (10-20 cc), calibrated glass tube. A measured amount of gases is pulled through this tube by a calibrated suction pump. The length of adsorbent that changes color then gives directly the concentration of that component. To compare their Draeger tube technique with laboratory analyses, these investigators took a number of samples from Stromboli volcano in Italy. Samples taken for laboratory analysis were collected on silica gel, molecular sieves, or other absorbents. They found the field results to be within 5 percent of the laboratory results, on the average, for H₂O, CO₂, H₂S and SO₂ + H₂S. Determinations of CO, HCl and Cl₂ were not successful due to interferences.
E. Chemical Equilibria in Volcanic Gases

The discouraging compositional variations found in the analyses of volcanic gas collections, led early investigators to conclude that such studies would contribute little to understanding the role of gases in volcanism. Crude collecting and analyzing techniques no doubt contributed to the variability in composition, but variations remained even when these factors were improved upon. Recent studies have taken into account the possible attainment of chemical equilibrium in volcanic gas systems, which could be used to explain the variations on the basis of temperature and pressure changes and the admixture of various quantities of air or ground water, or some combination of these.

Calculations made by Ellis\textsuperscript{58} in 1957 showed that the composition of the gases in some of the best volcanic gas collections were nearly the same as the chemical equilibrium compositions which would be expected for similar situations of distribution of atomic species, pressure and temperature. Krauskopf,\textsuperscript{59} has calculated the composition of a magmatic gas phase assumed to exist at 600°C and 1000 atmospheres, including the degree of oxidation of the gas and reactions of it with minerals in the magma. Several Japanese workers also have made studies of thermodynamic equilibria in volcanic gas systems.\textsuperscript{60,61} Extensive studies on the establishment of chemical equilibrium in recent collections of Hawaiian volcanic gases and the effects of temperature, pressure and water variations on these equilibria have been made by Heald et al.\textsuperscript{4} They reduced the considerable labor involved
in the theoretical calculations by programming them for a com-
puter. 62

F. Description of the Sampling Sites

The Hawaiian Archipelago consists of a series of volcanic
islands stretching for 1,600 miles along a line northwest to
southeast across the central Pacific. As described by Stearns,
these islands are actually shield-shaped basaltic domes built
over a fissure 1,600 miles long in the ocean floor. 63 He esti-
mates that the islands started from this fissure about 25,000,000
years ago in the Miocene epoch. Volcanic activity has apparently
moved down the chain from the northwest and is now centered on
Hawaii, the youngest island, at the southeastern end of the chain.
Of the five volcanoes on the island of Hawaii, only three have been
active in historic times. Hualalai, which is on the western part
of the island, last erupted in 1801. Mauna Loa and Kilauea,
which cover the southern end of Hawaii, are still active.

Both Kilauea and Mauna Loa are shield-type volcanoes, built
largely by eruptions occurring along their rift zones, which ex-
tend in two directions from their summit calderas at an angle of
approximately 135 degrees. Kilauea is the smaller of the two
volcanoes and lies against the southeastern flank of Mauna Loa.
Its rift zones extend to the southwest and to the east from its
summit crater. A map of the summit area is shown in Figure 1.
Kilauea's fame as a volcano is due mainly to the active lava
lake which occupied its summit through most of the 19th century
Figure 1. Summit Area of Kilauea Volcano
and the first quarter of this century. While other lava lakes existed for short periods on the caldera floor, the principle activity was centered in the pit crater Halemaumau, which is believed to be the point where the main lava conduit of Kilauea reaches the surface. The establishment of the Hawaiian Volcano Observatory in 1912 allowed continuous study of this unusual feature until the lava lake was destroyed by an explosive eruption in 1924.

Before this lava lake disappeared, however, it provided the first samples of gases collected from Hawaiian volcanoes. The first attempts to collect gases from this source were made by Day and Shepherd in May of 1913 shortly after the Volcano Observatory began functioning. Their samples were taken from a dome which had formed over a small fountain of lava at the edge of the lake. At the time they made their collections, the level of the lava lake was several hundred feet below its rim, requiring a rather difficult climb to reach the sampling point. Jagger and Shepherd took advantage of more favorable sampling conditions when they made their classic collections from the lava lake during 1917, 1918 and 1919. At times during these years, Halemaumau was filled to its rim, allowing these investigators to stand at the edge and collect their samples from openings in the crust as it floated by. These collections represent the only gas samples to be taken from this important source. The 1300 feet deep crater left by the 1924 explosion has been reduced to about 750 feet by several outbreaks of magma on the floor of Halemaumau. Still
this important source of gases (apparently the top of the main lava conduit of Kilauea volcano) remains inaccessible due to the steep, continually sloughing walls of the crater.

For the past decade, eruptive activity at Kilauea volcano has been centered along the east rift zone. Near the summit of the volcano, this rift zone is characterized by a series of pit craters formed by a collapse due to removal of support. Since 1959 a number of eruptions have occurred in or near these pit craters, partially filling some of them with molten lava. The lava lakes thus formed were not true lava lakes in the same sense as the active lake that existed for so long in Halemaumau, since they were not connected to any source of magma. Nevertheless, they are important for they have provided an unequalled opportunity to study the cooling and degassing of large bodies of basaltic lava. The 1959 eruption in Kilauea Iki pit crater resulted in a lake of this type, some 380 feet deep. About seven months after the end of this eruption, a study of this lake was begun by drilling holes through the crust and into the still molten interior of the lake. This program was initiated by U.S. Geological Survey geologists to make a long-term study of the cooling and crystallization of the lava lake. These drill holes also proved to be an excellent source of gases from the cooling lake. Naughton, Heald and Barnes were able to take a few samples of these gases by lowering their collecting tubes into one of the drill holes. An eruption in 1963 produced a similar but smaller lava lake in Alae crater, further down the
rift zone. This lake, only 50 feet deep, was also studied by core drilling. The initial gas samples taken for the present investigation came from these holes during the last stages of solidification of this lake.

During a week-long, flank eruption in March of 1965, another "rootless" lava lake was formed, this time in Makaopuhi pit crater, which is located about seven miles down the east rift zone from Kilauea's summit. By the end of the eruption, vents on the crater wall had poured into the deep western pit of this double pit crater approximately 6.5 million cubic yards of lava, creating a 290 feet deep lake. Twice during the course of this eruption, collecting trips were made down to the surface of the forming lake, and, under somewhat hazardous conditions, a number of gas samples were taken. These have been included in the present study. In April of 1965, when the surface of the new lava lake had cooled sufficiently and a crust about six feet thick had formed, the U.S. Geological Survey began a core drilling study of the cooling lava. This investigation took advantage of these drill holes to make a rather extensive collection and analysis of the gases emanating from them during the first year of cooling of Makaopuhi lava lake.

The rootless lava lakes are unusual, but the fumaroles found around Kilauea are a common feature of almost all volcanoes. A fumarole is defined as a hole or vent from which fumes or vapors are emitted, and those associated with volcanoes have been a major source of samples for studies of volcanic gases. Primary
fumaroles are best for this purpose, as they are situated over cracks in the calderas or rift zones of a volcano and are active for many years. The best known example at Kilauea is the solfataric fumarole known as Sulfur Bank, which is situated on an old rim of the main caldera, near the National Park headquarters. In 1922, T. A. Jagger conducted a drilling program at Kilauea to study changes in temperature, gas composition and mineral formation with depth in Kilauea volcano. During that time three holes were drilled at Sulfur Bank, one 70 feet deep and two on either side 15 feet deep. The middle hole was cased with cement and all three holes were joined at the top by an iron manifold. Since that time almost all Sulfur Bank gas samples have come from this source, rather than the natural fumarole. Allen, in 1922, was the first to sample and analyze these drill hole gases. From 1935 to 1940, Ballard and Payne conducted a study of gases from this source, and Naughton et al. samples these gases in the 1950's. Although the iron manifold topping these drill holes has corroded extensively and is now mostly crystalline sulfur retaining the form of the pipes, they have provided a continuous, reliable source of gases for this investigation.

Two previously unsampled fumaroles have also been included in this study. One is located on the southeastern edge of Kilauea Caldera about one mile east of Halemaumau (82 fumarole in Figure 1). As is the case at Sulfur Bank, the gases from the cracks and vents at this fumarole have caused considerable alteration of the surrounding rock. Both of these fumaroles
have been operating for some time; their activity apparently was first recorded in 1823. The other fumarolic area sampled is much more recent, and lies adjacent to the Chain of Craters Road between Aloi and Alae pit craters on Kilauea's east rift zone (83 fumarole in Figure 1). This region has had active steaming vents for some time, but after a small eruption in December, 1965, covered portions of the area, sulfur began depositing around many of the vents, indicating a more interesting site for gas sampling.
II. Experimental

A. Sampling

1. Gas collecting tubes

The gas collecting tubes used in this investigation were based on the vacuum sampling tubes developed by Naughton et al. The main feature of their design was the inclusion of an adsorbent, silica gel, which prevented the reactive gases, H$_2$S and SO$_2$ in particular, from interacting with each other. As shown by them, the silica gel acts like a chromatographic column, adsorbing and separating the acid gases and water vapor (CO$_2$, H$_2$S, SO$_2$ and H$_2$O in that order). The present form of the tube is shown (not to scale) in Figure 2, as it appears just prior to evacuation. A description of the construction of these sampling tubes follows; the numbers in parentheses correspond to those in Figure 2. Pyrex glass tubing was used in constructing the tubes, employing conventional glassblowing techniques. A 60 cm. length of 10 mm. O.D. (outside diameter) tubing (4) was joined to a 15 cm. length of 17 mm. O.D. tubing (6) to form the main body of the sampling tube. To the opposite end of (6) was added a break-seal (8), 10 mm. O.D., to allow transfer of the gas sample to the analyzing system. A side-arm (7) was attached for evacuating the sampling tube; it was constricted at its base so it could be more easily sealed. The indentations at (2) and (3) were made and a plug of glass wool was pushed into position at (5). Section (4) was then filled with about
Figure 2. Silica Gel Gas Sampling Tube
20 grams of 40 to 60 U.S. Standard mesh silica gel and a plug of glass wool was placed in position at (3). The glass wool plugs at (3) and (5) keep the silica gel in place. To complete the construction of the tube, a short section of small diameter glass tubing was added at (1). This was softened and pulled into the desired hook-shaped to form the sampling tip. The length of the completed sampling tube was about one meter. A protective glass bulb was fitted over this fragile tip and butted-up against the end of the sampling tube. It was held in place by asbestos tape during bake-out and by masking tape afterward. To remove all gases and water absorbed on the silica gel, thus "activating" it, the tube was bake-out at approximately 360°C while under vacuum. This step could be completed in 2 or 3 hours, but was usually done overnight for convenience. The vacuum system consisted of a manifold capable of handling eight sampling tubes, a dry ice-acetone trap and a high vacuum, rotary oil pump. The sampling tubes were removed from this system under vacuum by sealing the side-arm (7) at its base.

The silica gel used in the sampling tubes was of "Chromatographic grade" (Micro-Tek Instruments, Inc., Baton Rouge, Louisiana). Before using it in the sampling tubes, the silica gel was heated in a Pyrex tube which was swept with oxygen. This treatment was a precautionary measure to insure the removal of any organic matter that might have been adsorbed on the silica gel. The same pretreatment was applied
to the glass wool used in the sampling tubes.

When the silica gel from used sample tubes was examined for suspected adsorbed volatiles (iron compounds, for example) not removed during the gas analysis (see Section II-B-4), an additional pretreatment of this silica gel was required to remove the large background amounts of iron found on the commercially available product. For this purpose, the silica gel was placed in a vertical glass tube and washed with a dilute hydrochloric acid solution until iron was no longer found in the effluent by standard spot tests. The column was then flushed with distilled, deionized water until a negative chlorine spot test with AgNO₃ was obtained. Later in this investigation, a dilute perchloric acid solution was used for this prewashing, as the hydrochloric acid left a high chloride ion background, which was not easily washed-out by the water elution. The perchloric acid was flushed from the silica gel column with distilled, deionized water until a neutral eluate was obtained.

The sampling environment of the lava lake drill holes resulted in slight alterations to the design of the collecting tube just described. Temperatures in these holes varied from ambient to 1000°C and the sampling range was usually between 400°C and 900°C. To protect the evacuated
sampling tubes and retain the adsorption feature of the silica gel in them, it was necessary to insulate them from this high temperature environment. This was done by placing the sampling tube inside a protective jacket or shield, and filling the annular space with crushed firebrick (Johns-Manville and Company). Originally the jackets were made from steel conduit, but these were replaced with quartz shields to prevent reactions with the hot gases present in the drill holes. The quartz shields were made in two foot sections of heavy-wall, vitrified silica tubing (Thermal American Fused Quartz Company), and were closed on one end, except for two small holes, through which a chromel wire loop was fastened to secure the lowering cable. The other end was constricted slightly to help contain the insulation material. Because of this constriction, it was necessary to limit the diameter of the sampling tube to 10 mm. The diameter of the quartz shields was restricted to 2.5 cm.; the next larger size would not fit into the approximately 3 cm. diameter drill holes. The one meter length of the sampling tubes was reduced to about 55 cm., maintaining the same scale of the various sections. This resulted in a drill hole sampling device (tube and shield) of about 60 cm., which was a less awkward size to work with in the drill holes.
When the firebrick insulation had been packed around the inner tube and thoroughly tamped-down, it was covered with a plug of moistened asbestos paper. The sampling tip of the collecting tube was allowed to protrude beyond the lower end of the quartz shield. Partial protection of the tip from heat was provided by quartz wool packed around its base. The completed drill hole sampling apparatus is shown in a cutaway view in Figure 3. The break-off wire is packed inside the shield at the same time as the inner sampling tube, but is only attached to the tip just prior to lowering the apparatus into a drill hole.

2. Sampling techniques

During the course of this investigation, gas samples were collected from five different sites at Kilauea Volcano. A general description and history of them has been given in a previous section.

At Sulfur Bank all samples were collected from a small hole in a pipe attached to the manifold connecting the three holes drilled by Jagger in 1922. A sample was collected by pushing the evacuated tube into this hole until the tip touched the back wall of the pipe (a distance of about 15 cm.). The tip was then pulled off with a wire loop attached to the tip prior to inserting the tube into the hole (see detail of
Figure 3. Drill Hole Gas Sampling Device
Figure 2. The pull-off wire and loop was made from a piece of nickel-chromium wire slightly longer than the sampling tube. After 15 minutes the tube was sealed-off with a gas-oxygen torch. In the present design of the collecting tube, which is the one shown in Figure 2, it is possible to seal the tube without removing the tip from the vent, because of the slightly extended sampling end and the constriction at (2). Most of the samples reported in this work were collected before this change in design was made, and were sealed after removing the tube from the gas source. In this case it was helpful to use a glass rod to pull off the tip when it was softened by the torch, thus effecting a good seal.

The other low temperature sampling sites included in this study were the fumarole on the east rim of Kilauea Caldera (S2 fumarole) and the steaming area between Aloi and Alae pit craters on the east rift zone of Kilauea Volcano (S3 fumarole). These were sampled by the same techniques used at Sulfur Bank. The vents chosen for sampling were small cracks or holes in these areas, the edges of which were coated with sulfur crystals.

Samples were collected at two periods during the formation of the lava lake in Makaopuhi pit crater. The same general technique used at Sulfur Bank was followed, but some alterations were necessary due to the conditions at that time. All samples were taken at the edge of the lake from cracks in the crusting surface or from holes made in fresh lava "squeeze-outs"
as shown in Figure 4. The holes were made by ceramic combustion tubes used to pull-out samples of the still molten, but very viscous lava. The wire pull-off technique for opening the tubes had not been developed at the time these collections were made. Instead, the tubes were opened by crushing the fragile tip against wall of the crack or hole. Because of the great heat radiating from the lake surface, it was not possible to hold sample tubes in place for more than about 10 seconds. Sealing of the tubes was sometimes accomplished by holding the opened tip against the wall of the hole until it softened and collapsed. These were usually not good seals as they were a combination of lava and glass, and cracked easily. If the vents were not hot enough for this type of seal, a closed-end teflon tube was slipped over the tip to plug it. All of these tubes were sealed later at the Volcano Observatory by gas-oxygen torch.

Special sampling techniques were necessary for collecting gas samples from the drill holes in Alae and Makaopuhi lava lakes. As described previously, the high temperatures encountered required an insulated sampling tube. Since it was of interest to obtain samples from any level in a particular hole, it was necessary to suspend the tube by a cable so it could be lowered to the desired depth. For this purpose a woven-wire, stainless steel cable was attached to the quartz shield of the sampling tube by means of stainless steel fittings and the chromel wire at the top of the shield. Depth
Figure 4. Gas Sampling Technique at Makaopuhi Lava Lake Surface
and temperature data for each drill hole was supplied by the staff of the Hawaiian Volcano Observatory.

To collect a sample, the drill hole tube was first attached to the lowering cable. The pull-off wire packed in the thermal insulation was worked back and forth to insure freedom of movement when the tip was to be pulled-off. The loop of the pull-off wire was then hooked on to the sampling tip and an extension, the same length as the lowering cable was attached to the upper end of this wire. Being careful not to put any strain on the pull-off wire, the assembly was lowered rapidly to the desired depth, where the tip was pulled-off. The length of time which the sampling apparatus could be left in a hole at 1000°C without the inner tube and its adsorbent exceeding 100°C was determined from laboratory experiments to be one minute. Sampling at any depth in the drill holes was therefore confined to a one minute period. At this point the tube was pulled-out and the tip sealed with a gas-oxygen torch and returned to the laboratory for analysis.

B. The Gas Analysis System

1. Description of the extraction and measuring system

The gas samples were analyzed on the system shown in Figures 5 and 6. In the following discussion, the letters enclosed in parentheses refer to corresponding letters in these diagrams.

The extraction and measurement system (Figure 5) was used to remove the gas sample from the collecting tubes, perform a
Figure 5. Gas Analysis System: Extraction and Measuring Section
Figure 6. Gas Analysis System: Gas Chromatographic System
preliminary separation of the gases, and determine the pressure and volume of the gases. A metal break-off bar (detail of Figure 5), which was used to open the sample tube, was jacketed with glass to avoid any gas-metal reactions. Gases adsorbed on the sample tubes silica gel (CO₂, H₂S, SO₂ and H₂O) were desorbed by gradually heating the sample tube in an oven (A) to a maximum of 300°C. As these gases came off the silica gel they were collected in traps, the H₂O at (C) in a trap cooled with dry-ice acetone and the other gases (CO₂, H₂S, SO₂) at (E) in a trap cooled with liquid N₂. The water U-trap (C) was made large purposely on the sample tube side to prevent clogging with the condensed water (ice). During the extraction of the condensable gases, it was necessary to heat that portion of the system between (A) and (C) by wrapping with a heating tape. This prevented premature condensation of H₂O which seemed to act as a catalyst for the reaction:

\[ 2H₂S + SO₂ = 3S + 2H₂O \]

depositing a sulfur film on the glass wall of the system. Unfortunately, this reaction could not be prevented entirely by this means. When these gases were present in high concentrations (as in Sulfur Bank samples, for example), a sulfur film formed around the top of the frozen water in the U-trap (C). In such cases this film was oxidized at a later stage in the analysis and analyzed as SO₂. During the calculations, proportional amounts of H₂S and SO₂ were determined from this "extra" SO₂ and added to the H₂S and SO₂ concentrations found
in the gas U-trap (E). It should be noted, however, that this
"reacted" \( \text{H}_2\text{S} \) and \( \text{SO}_2 \) represented only a small portion of the
total concentration of these two gases found in such samples.

A removable trap (D) was attached to the system by means
of a ball and socket joint. The condensed water collected in
the U-trap at (C) and was transferred to the removable trap
for weighing.

A three-way stopcock at (F) served to connect or isolate
the extraction system to the left of it and the measuring
system to the right, and provided the extraction system with
a direct connection to the vacuum pump.

In the measuring portion of the system (Figure 5) a cold
finger (G) was utilized for transferring gases to this section
and a breakseal tube (I) provided a means of collecting por­
tions of the gas sample for further analysis by mass spect­
rometry. The expansion bulb (H) was used to determine the
volume in the system that the permanent gases (He, \( \text{H}_2 \), \( \text{Ar} \),
\( \text{O}_2 \), \( \text{N}_2 \), \( \text{CH}_4 \) and \( \text{CO} \)) filled when they were released from the
sample tube (the volume in which the pressure of these gases
was measured). It was necessary to determine this volume
for each sample since the volume of each sample tube and the
tubing connecting it to the system at (B) was different. This
problem did not exist with the condensable gas, which were
pulled over to the cold finger (G) by means of liquid \( \text{N}_2 \) and
expanded into the known volume of the measuring system. If
the pressure was greater than one atmosphere the condensable
gases were expanded further by using the expansion bulb.

Pressures were measured by a fused quartz precision
pressure gauge (J) manufactured by Texas Instruments,
Incorporated, Houston, Texas (Model Number 140). This unit
consisted of a quartz Bourdon tube contained in a capsule and
an optical readout system. The capsule was attached to the
vacuum system so that both it and the Bourdon tube could be
evacuated and the readout unit zeroed. In this way pressure
readings were independent of changes in atmospheric pressure.
The capsule was designed for a range of zero \(10^{-3}\) mm. of Hg
to one atmosphere, and was calibrated by the manufacturer.

The pumping system used a two-stage mechanical vacuum
pump (Welch Duo-Seal) capable of producing a vacuum of 0.1
micron, separated from the system by dry ice-acetone cooled
trap (N). A small McLeod gauge (K) was used to determine
when the system or a particular part of the system was pumped-
down to the limit of the pump. Mercury vapor from this gauge
was kept from diffusing into the system by the U-trap (M)
cooled with a dry ice-acetone mixture.

Samples were introduced into the gas chromatographic
system by means of a sample loop (L) formed with two four-way
stopcocks. A single bore plug was necessary for the stopcock
on the measuring system side of the loop to control access
of the measuring system and the loop to the vacuum pump. The
sample loop stopcocks are shown in the position for filling the loop in Figure 5. They have been turned, in Figure 6 (L), to the position for sweeping the sample from the loop into the gas chromatographic system by the carrier gas.

2. Description of the gas chromatographic system

The separation and determination of the individual gases in each sample was performed by means of the gas chromatographic system shown in Figure 6. Gas chromatography is a procedure that separates a gaseous mixture by passing a moving gas phase over a stationary adsorbent. The gas phase consists of a non-absorbed carrier gas plus the sample. The technique is called gas-liquid chromatography (GLC) when the stationary phase is a non-volatile liquid distributed over an inert solid phase, and gas-solid chromatography (GSC) when the adsorbent is a solid with surface active properties. The latter technique was used in this work.

The permanent gases were separated on a molecular sieves 5A column (0). The column was constructed from a six foot section of aluminum tubing one-quarter inch in outside diameter, and was filled with 60-80 U.S. Standard mesh molecular sieves number 5A. The column was activated by heating at a temperature of 360°C for at least two hours while passing a stream of He gas through it. Whenever the separating ability of this column deteriorated, it was reactivated by means of an oven (0). During an analysis the oven chamber insulated the column against variable air.
currents, but was not used to operate the column at an elevated temperature. The working temperatures used with the molecular sieves column were -78°C and room temperature. At -78°C and with Ar as the carrier gas, separation was achieved for He and H₂ among the permanent gases. At this same temperature, but with He carrier gas, Ar and O₂ were separated. Low temperature operation was achieved by placing the column in a Dewar flask of dry ice-acetone. At room temperature the column separated H₂ (+He), O₂ (+Ar), N₂, CH₄ and CO in that order with He as the carrier gas. The carrier gas flow rate for each case was 40 cc. per minute. The use of molecular sieves 5A columns under these temperature conditions to achieve these separations has been described in the literature.\textsuperscript{70}

Condensable gas were separated in a 2 feet by 1/4 inch outside diameter aluminum column filled with 80-100 U.S. Standard mesh silica gel. Activation of the silica gel was achieved by heating it to about 300°C for several hours while purging with He. The column (P) was run at 100°C, with He as carrier gas at a flow rate of 40 cc. per minute, and would separate gases in the following order: air (composite peak), CO₂, COS, H₂S, CS₂ and SO₂. Hodges and Matson\textsuperscript{71} reported this separation for this column in 1965. Either this column or the molecular sieve column, but not both at the same time, could be switched into the carrier gas flow-stream by means of a six-way gas sampling valve (Perkin-Elmer Corporation, Norwalk, Connecticut) adapted for this purpose (S).
The concentration of the separated gas components in the column effluent was measured with a thermal conductivity detector (V) manufactured by the Gow-Mac Instrument Company, Madison, New Jersey (Model 9234 - Hot Wire Detector). A home-made transistorized D.C. power unit supplied the detector voltage. The detector current was set at 200 milliamperes when He was used as the carrier gas and at 170 milliamperes with Ar carrier gas, and it was operated at 100°C. A thermal conductivity cell operates by comparing the conductivity of the pure carrier gas in the reference chamber to that of the carrier gas plus sample in the sample chamber. This results in an out of balance potential in a Wheatstone bridge circuit, which is used to produce a chromatogram on a potentiometric recorder (T). A Wheelco Series 8000 recorder, with a chart speed of 3 minutes per inch and a full scale deflection of 1 millivolt, was used with the thermal conductivity detector (Barber-Colman Company, Rockford, Illinois). A polarity switch was provided to reverse the output signal from this detector when Ar carrier gas was used, so that positive peaks were obtained for He and H₂, which have greater thermal conductivities than Ar.

When the molecular sieves column was run at room temperature or when the silica gel column was used, a flame-ionization detector (U) was attached to the effluent vent of the thermal conductivity cell, to determine CH₄ and search for other organic gases in the sample. The flame-ionization detector,
which is extremely sensitive to these compounds, produces an electric current, due to the release of electrons and negative ions when organic matter is burned in the hydrogen flame of the detector. The current is amplified by an electrometer and applied to a strip-chart recorder to produce the chromatogram (Q). A Wilkens Flame Ionization Detector (Varian-Aerograph, Walnut Creek, California) was used in conjunction with that company's Model 650 Hydrogen Generator (Z). The recorder (Q) was a Honeywell Electronik 19 single pen lab recorder (Honeywell, Philadelphia, Pennsylvania) operated at one millivolt full scale and with a chart speed of one-half inch per minute.

The carrier gases, He and Ar, were used directly from the tanks, except for passing them over two drying agents (W), indicating silica gel and Aquasorb (Mallinckrodt Chemical Works, New York). A three-way stopcock (X) allowed one to select the desired carrier gas. Tank pressure for the carrier gases was set at 40 p.s.i., and column head pressure was varied between 5 to 12 p.s.i., depending on the column and column temperature being used. The pressure regulator at (Y) controlled the column head pressure and flow rate. Flow rate was measured with a soap-bubble flow meter placed at the detector effluent vents.

The column and detector operating conditions are summarized in Table I along with the column retention times and the thermal conductivities (where available) for each gas.
<table>
<thead>
<tr>
<th>Gas</th>
<th>Retention time, minutes</th>
<th>Thermal conductivity, cal./cm.sec./deg. (100°C)</th>
<th>Column Parameters</th>
<th>Detectors</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>1.4</td>
<td>39.8</td>
<td>Molecular sieves 5A</td>
<td>Thermal conductivity (170 m. amps)</td>
</tr>
<tr>
<td>H₂</td>
<td>1.8</td>
<td>49.9</td>
<td></td>
<td>-78°C Ar carrier gas</td>
</tr>
<tr>
<td>Ar</td>
<td>10.5</td>
<td>5.1</td>
<td>Molecular sieves 5A</td>
<td>Thermal conductivity (200 m. amps)</td>
</tr>
<tr>
<td>O₂</td>
<td>14.5</td>
<td>7.4</td>
<td></td>
<td>-78°C He carrier gas</td>
</tr>
<tr>
<td>H₂(+He)</td>
<td>1.5</td>
<td>49.9</td>
<td>Molecular sieves 5A</td>
<td>Thermal conductivity</td>
</tr>
<tr>
<td>O₂(+Ar)</td>
<td>3.1</td>
<td>7.4</td>
<td></td>
<td>(200 m. amps) ambiant flame</td>
</tr>
<tr>
<td>N₂</td>
<td>7.0</td>
<td>7.2</td>
<td>Molecular sieves 5A</td>
<td>Temperature ionization</td>
</tr>
<tr>
<td>CH₄</td>
<td>10.6</td>
<td>7.2*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>35</td>
<td>5.4*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>air</td>
<td>0.8</td>
<td>7.5</td>
<td>Silica gel</td>
<td>Thermal conductivity</td>
</tr>
<tr>
<td>CO₂</td>
<td>1.7</td>
<td>5.1</td>
<td></td>
<td>100°C He carrier gas (200 m. amps)</td>
</tr>
<tr>
<td>(COS)</td>
<td>3.5</td>
<td>---</td>
<td></td>
<td>flame ionization</td>
</tr>
<tr>
<td>H₂S</td>
<td>4.1</td>
<td>3.0*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(CS₂)</td>
<td>13.1</td>
<td>3.7*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SO₂</td>
<td>16.3</td>
<td>2.0*</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

# Abstracted from Jeffery and Kipping, 72
*Available only for O°C.
**Thermal conductivity detector run at 100°C.
*Carrier gas flow rate always set at 40 cc./min.
The detectors were calibrated by a syringe injection technique developed by Jeffery and Kipping\footnote{72} using a by-pass syringe valve (R) of their design. Their method combines the advantages of sample loop injection with the speed and simplicity of syringe injection. The four-way stopcock of the valve was turned so that carrier gas would flush the small sample loop. It was then returned to the position shown in Figure 6. The high pressure of the carrier gas trapped in the loop was equalized to atmospheric pressure to make sample injection easier. This was done by inserting an empty, gas-tight syringe, and allowing the barrel of the syringe to be pushed-out until the pressure was equalized. A calibration gas sample was then injected into the loop using a gas-tight syringe with a Chaney adaptor (Hamilton Company, Whittier, California) which was possible without the high back pressure of the carrier gas. This sample was then swept into the gas stream by opening the 4-way stopcock.

Air was used for the \( \text{O}_2 \) and \( \text{N}_2 \) calibration and the remaining gases came from commercial gas cylinders or lecture bottles. A glass bulb with stopcocks on either end and an injection port in between was flushed and filled with a sample from a cylinder, and calibration samples were removed from the bulb with the gas tight syringe by way of the injection port. When \( \text{Ar} \) and \( \text{He} \) were included in the gas analysis scheme, these gases were calibrated by introducing them into the measuring system at (D) and running aliquots into the gas chromatograph
via the sample loop (K). Calibration curves for each gas were constructed by plotting peak area versus the number of moles injected into the system.

3. Operating procedure

An outline of the procedure for analyzing a gas sample on this system follows. The sample tube was usually attached to the system (B) the evening before a run was to be made, and the system in Figure 5 pumped-out overnight. The molecular sieves column (O) was also purged overnight with Ar carrier gas with a Dewar flask of dry ice-acetone cooling the column.

a. All stopcocks were closed and dry ice-acetone was placed on the H₂O U-trap (C) and liquid N₂ on the traps at (D) and (E).

b. The sample was opened and the pressure of the permanent gases measured.

c. The permanent gases were pumped from the extraction system and heating of the sample tube was started.

d. H₂ and He were determined in the permanent gases with the molecular sieves column (O) at -78°C and Ar carrier gas.

e. The carrier gas was changed to He, and Ar and O₂ in the permanent gases were determined on the molecular sieves column still at -78°C.

f. The molecular sieve column was warmed to room temperature and the flame-ionization detector (U) was attached to the effluent vent of the thermal conductivity detector (V).
g. The remaining permanent gases (O₂, N₂, CH₄ and CO) were analyzed on the molecular sieves column at room temperature with He as carrier gas.

h. If a sample of the carrier gas was to be saved for further analysis, it was trapped and sealed in the break-seal tube (I).

i. The permanent gases were pumped from the measuring system.

j. The condensable fraction was transferred from traps (D) and (E) to the cold finger (G).

k. The silica gel (P) column was switched (S) into the gas flow, replacing the molecular sieves column.

l. The condensable gases were expanded in the measuring system and into the expansion bulb (H) if necessary.

m. The pressure of the condensable gas was determined.

n. These gases (CO₂, H₂S and SO₂) were analyzed with He carrier gas on the silica gel column (P).

o. The water in trap (C) was transferred to the removable trap (D) and weighed.

p. If the condensable gases were to be saved for further analysis, they were collected in a breakseal tube at (D).

q. The volume, in which the permanent gas pressure was measured, was determined.

r. If a sulfur film had formed in the water U-trap (C), it was oxidized and the SO₂ formed analyzed on the silica gel column.
Steps q and r were usually carried out on the day following an analysis. At least two aliquots were necessary for each run (steps d, e, g and h) in order to correct for bad guesses on the attenuation of the signals to the recorders.

4. Analysis of the volatiles on the sampling tube silica gel

After the completion of the gas analysis, the gas sampling tubes were removed from the system for elution analysis of volatiles that were not desorbed from the silica gel during the gas analysis. The top and the tip of the sampling tubes were broken-off and a separatory funnel containing the eluting solution was attached to the top with a short piece of Tygon plastic tubing. Both were mounted on a rack in a vertical position, with the separatory funnel above the sampling tube. An Erlenmeyer flask was placed beneath the tip of the sampling tube to receive the effluent.

Elution was by gravity, and the first washing was with 100 ml. of methanol which removed iron. If iron was found by spot test (NH$_2$OH $\cdot$ HCl and 0-phenanthroline) in the last 0.5 ml. of effluent from this washing, an additional 50 ml. of methanol were passed through the silica gel. This was repeated until the test for iron was negative.

The silica gel was then eluted with 250 ml. of distilled, deionized water. The calcium, hydrogen, chloride, and ammonium ion concentrations in the effluent from this step were determined from different aliquots of that solution. Sulfate ion was determined only qualitatively at this time.
The methods of analysis were based on procedures reported in the literature. Iron was determined colorimetrically with o-phenanthroline according to Sandell. The photometric method of Zall et al., using mercuric thiocyanate, was adapted for the analysis of chlorine. A photometric method was also used for the ammonium ion analysis, based on the formation of a blue color when an ammonium solution is treated with phenol and sodium hypochlorite. Calcium was determined by titration with ethylene diamine tetracetic acid (EDTA) after the method of Brown and Sallee.

C. Sublimate Collection and Analysis

1. Sampling technique

Two devices were designed and used to scrape sublimates from the walls of the drill holes at different depths. The first type consisted of a long steel tube with two slots at the bottom end along the wall of the tubing. From these slots, strips of spring steel would extrude when a rod inside the tube was pushed against them from the other end of the tube. The extruded springs would then scrape against the walls of the drill hole, knocking loose bits of sublimate, which would fall into the tubing. The pressure on the springs was released and the tube pulled into the hole. A steel plug, held by screws in the slotted end of the tube was removed and the sample taken out.

The second type of sublimate collector was made from four foot lengths of stainless steel rod which could be connected
together to any multiple lengths of four feet. Two sampling end pieces were used on these rods. The first, which was constructed from two one-half inch tapered reamers was used to punch a hole or make a bigger hole (at least one-half inch by one inch) through the sublimate formation in the drill hole. The rod was then pulled from the hole and this end piece replaced with the second one.

The second or collecting end piece consisted of two cylinders, 7/16 of an inch in diameter formed by drilling two holes in one piece of stainless steel. The horizontal dimensions of this end piece were the same as those of the reamer, one-half inch by one inch. The cylinders were closed on the bottom by a plate held by screws.

Sampling was achieved by pushing these cylinders through the hole opened in the sublimate by the reamer. The rod was then turned 90 degrees and pulled-up through the sublimate collecting the sample in the cylinders. The rod was then pulled from the hole, the plate on the bottom of the cylinders removed, and the sample pushed into a collecting bottle and returned to the laboratory for analysis.

Sublimate samples were collected with these two devices by the author and Dr. I. L. Barnes, who designed the first collector, and Dr. Reiner Goguel, the designer of the second collector (both of the staff of the University of Hawaii).
2. Extraction and analysis techniques

The extraction and analysis of the sublimate samples collected were performed by Dr. Reiner Goguel using a scheme devised by him. A brief abstract of his techniques is given here.

Three solvents, acetone, methanol and water, were used to separate the samples into fractions by extraction. The extraction was done by shaking the sample with three, 20 ml. portions of a particular solvent. Acetone was used to separate the halides of polyvalent cations from the halides of the alkali metals. Since the samples contained very large amounts of CaSO$_4$, and methanol does not dissolve great amounts of this compound, it was easier to tell from the balance of cations and anions in the acetone and methanol fractions, if cations had been overlooked. If there were excess cations, sulfate was expected as the anion. The difference was therefore called sulfate.

The extracted solutions were dried at room temperature in a dessicator above magnesium perchlorate. The dry residue was dissolved in 25 ml. of 0.2N H$_2$SO$_4$ and extracted with water. This was followed by an extraction with 100 ml. of 10 percent NaCl solution, with four hours of shaking, to remove all CaSO$_4$.

The insoluble residue was investigated separately by x-ray diffraction techniques and differential thermometrical analysis techniques.
The acetone, methanol, and water fractions were analyzed for Cu, Zn, Fe, Mn, Mg, Ca, Na, K, and Rb by atomic adsorption spectroscopy.

A potentiometric titration with 0.01 N ceric sulfate was used to determine Fe (II), which was found in the acetone fraction of two of the samples.
III. Results and Discussion

A. Introduction

The results of the analyses of the gas samples collected from the various gas sources investigated have been summarized in Tables II and III. Two compositions are given for each sample. The first lists the actual composition of gases found in the sample tubes, and the second the air free composition of the sample. The latter was determined by subtracting all O₂ and N₂, and corresponding amounts of the other atmospheric gases (CO₂, Ar, He + Ne, and H₂) based on the amount of N₂ found and their N₂ ratio in air. The computer program in Appendix I illustrates the necessary calculations. The tables also include the mole percent of air in each sample, which was determined by adding together the portions of gas subtracted to make the air free corrections. This percentage of air provides a simple basis for judging whether or not the sample is any good. The less air contamination in a sample, the less chance for alteration of the gas composition by air oxidation; thus a better sample. Samples which were analyzed on a low temperature column to obtain a separation of H₂ from He and O₂ from Ar are so noted, as are those in which a partial separation of He and H₂ was obtained at room temperature. For all other samples, the O₂ concentration actually represents (O₂ + Ar) and the H₂ percentage represents (H₂ + He). The temperatures given in the tables were provided through the courtesy of the staff of the U.S. Geological Survey, Hawaiian Volcano Observatory.
# TABLE II

## ANALYSES OF MAKAOPUHI LAVA LAKE SAMPLES

### PART A - Surface Samples

<table>
<thead>
<tr>
<th>Sample No. and Date</th>
<th>$H_2O$</th>
<th>He</th>
<th>$H_2$</th>
<th>Ar</th>
<th>$O_2$</th>
<th>$N_2$</th>
<th>$CH_4$</th>
<th>$CO_2$</th>
<th>$H_2S$</th>
<th>$SO_2$</th>
<th>Air</th>
</tr>
</thead>
<tbody>
<tr>
<td>27-M 3/7/65</td>
<td>9.39</td>
<td>0.023</td>
<td>—</td>
<td>—</td>
<td>20.36</td>
<td>73.31</td>
<td>0.004</td>
<td>0.178</td>
<td>—</td>
<td>—</td>
<td>94.57</td>
</tr>
<tr>
<td>28-M 3/7/65</td>
<td>11.78</td>
<td>0.023+</td>
<td>0.003</td>
<td>—</td>
<td>15.89</td>
<td>68.00</td>
<td>—</td>
<td>0.18</td>
<td>0.63</td>
<td>0.63</td>
<td>84.73</td>
</tr>
<tr>
<td>29-M 3/7/65</td>
<td>4.95</td>
<td>—</td>
<td>0.047</td>
<td>—</td>
<td>22.30</td>
<td>73.80</td>
<td>—</td>
<td>0.095</td>
<td>—</td>
<td>—</td>
<td>97.01</td>
</tr>
<tr>
<td>30-M 3/7/65</td>
<td>16.71</td>
<td>—</td>
<td>—</td>
<td>0.11</td>
<td>10.22</td>
<td>57.15</td>
<td>—</td>
<td>1.38</td>
<td>—</td>
<td>12.30</td>
<td>68.07</td>
</tr>
<tr>
<td>36-M 3/14/65</td>
<td>18.19</td>
<td>0.0019+</td>
<td>—</td>
<td>0.67</td>
<td>15.86</td>
<td>66.78</td>
<td>—</td>
<td>0.16</td>
<td>—</td>
<td>0.35</td>
<td>83.46</td>
</tr>
<tr>
<td>37-M 3/14/65</td>
<td>31.25</td>
<td>0.00007+</td>
<td>0.012</td>
<td>0.76</td>
<td>12.08</td>
<td>65.74</td>
<td>—</td>
<td>0.34</td>
<td>—</td>
<td>1.73</td>
<td>78.63</td>
</tr>
<tr>
<td>38-M 3/14/65</td>
<td>95.62</td>
<td>0.011</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.49</td>
<td>—</td>
<td>3.89</td>
<td>59.47</td>
</tr>
</tbody>
</table>

---

*Surface temperature, 1100°-1200°C.*

+Corrected to "air free" conditions by subtracting $O_2$ and $N_2$ and equivalent amounts of other air gases based on $N_2$ atmospheric ratios.

*Low temperature (-78°C) column used to separate He from $H_2$ and Ar from $O_2$.

+Partial separation of He from $H_2$ obtained at room temperature.
### TABLE II

**ANALYSES OF MAKAOPUHI LAVA LAKE SAMPLES**

**PART B - Drill Hole Samples**

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Depth-ft. and Date (Temp.)</th>
<th>H₂O</th>
<th>He</th>
<th>H₂</th>
<th>Ar</th>
<th>O₂</th>
<th>N₂</th>
<th>CH₄</th>
<th>CO₂</th>
<th>H₂S</th>
<th>SO₂</th>
<th>Air</th>
</tr>
</thead>
<tbody>
<tr>
<td>50-MD9</td>
<td>9, 6/18/65 (950°)</td>
<td>96.48</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>0.67</td>
<td>2.64</td>
<td>---</td>
<td>0.021</td>
<td>0.044</td>
<td>0.017</td>
<td>3.34</td>
</tr>
<tr>
<td>54-MD8</td>
<td>1.5, 6/18/65 (160°)</td>
<td>68.14</td>
<td>0.0007</td>
<td>0.056</td>
<td>0.33</td>
<td>1.36</td>
<td>31.65</td>
<td>---</td>
<td>0.27</td>
<td>---</td>
<td>0.035</td>
<td>33.40</td>
</tr>
<tr>
<td>55-MD10</td>
<td>1.5, 6/18/65 (160°)</td>
<td>38.19</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>8.61</td>
<td>55.71</td>
<td>---</td>
<td>0.14</td>
<td>---</td>
<td>0.18</td>
<td>65.01</td>
</tr>
<tr>
<td>63-MD11</td>
<td>5, 7/20/65 (500°)</td>
<td>28.12</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>14.76</td>
<td>53.52</td>
<td>---</td>
<td>0.077</td>
<td>---</td>
<td>---</td>
<td>68.95</td>
</tr>
<tr>
<td>64-MD11</td>
<td>7, 7/20/65 (600°)</td>
<td>80.75</td>
<td>---</td>
<td>0.042</td>
<td>---</td>
<td>4.58</td>
<td>15.03</td>
<td>---</td>
<td>0.21</td>
<td>---</td>
<td>---</td>
<td>19.80</td>
</tr>
<tr>
<td>66-MD11</td>
<td>5, 7/20/65 (500°)</td>
<td>26.32</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>11.43</td>
<td>60.87</td>
<td>---</td>
<td>0.068</td>
<td>---</td>
<td>---</td>
<td>73.05</td>
</tr>
<tr>
<td>67-MD11</td>
<td>7, 7/20/65 (600°)</td>
<td>86.51</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>1.19</td>
<td>7.57</td>
<td>---</td>
<td>0.14</td>
<td>---</td>
<td>---</td>
<td>8.85</td>
</tr>
<tr>
<td>69-MD8</td>
<td>4, 7/21/65 (500°)</td>
<td>98.00</td>
<td>---</td>
<td>0.011</td>
<td>---</td>
<td>0.04</td>
<td>1.62</td>
<td>---</td>
<td>0.020</td>
<td>---</td>
<td>0.33</td>
<td>1.68</td>
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TABLE II
ANALYSES OF MAKAOPUHI LAVA LAKE SAMPLES

PART B - Drill Hole Samples (Continued)

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Depth-ft. (°C)</th>
<th>H₂O</th>
<th>He</th>
<th>H₂</th>
<th>Ar</th>
<th>O₂</th>
<th>N₂</th>
<th>CH₄</th>
<th>CO₂</th>
<th>H₂S</th>
<th>SO₂</th>
<th>Air</th>
</tr>
</thead>
<tbody>
<tr>
<td>71-MD8</td>
<td>9/21/65 (900°)</td>
<td>90.81</td>
<td>0.16</td>
<td>1.50</td>
<td>6.96</td>
<td>0.002</td>
<td>0.032</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>72-MD14</td>
<td>11/21/65 (950°)</td>
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<td>1.92</td>
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<td>33.62</td>
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<td>7/22/65 (600°)</td>
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<td>74-MD14</td>
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<tr>
<td>76-MD16</td>
<td>12/21/65 (1000°)</td>
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<tr>
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<td>0.080</td>
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<tr>
<td>78-MD11</td>
<td>13.9/27/65 (810°)</td>
<td>97.43</td>
<td>0.008</td>
<td>0.39</td>
<td>1.91</td>
<td>0.0005</td>
<td>0.067</td>
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### TABLE II

**ANALYSES OF MAKAOPUHI LAVA LAKE SAMPLES**

**PART B - Drill Hole Samples (Continued)**

<table>
<thead>
<tr>
<th>Sample No.</th>
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<td>$H_2O$</td>
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<td>------------</td>
<td>-----------</td>
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<tr>
<td>79-MD10</td>
<td>5</td>
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<td>11/27/65</td>
<td>(370°)</td>
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<tr>
<td>80-MD10</td>
<td>8</td>
<td>60.50</td>
</tr>
<tr>
<td>11/27/65</td>
<td>(550°)</td>
<td>99.96</td>
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<td>81-MD10</td>
<td>10.1</td>
<td>82.70</td>
</tr>
<tr>
<td>11/29/65</td>
<td>(700°)</td>
<td>98.78</td>
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<tr>
<td>82-MD20</td>
<td>6</td>
<td>98.60</td>
</tr>
<tr>
<td>11/29/65</td>
<td>(420°)</td>
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<td>83-MD20</td>
<td>14.5</td>
<td>96.52</td>
</tr>
<tr>
<td>11/29/65</td>
<td>(900°)</td>
<td>99.62</td>
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<tr>
<td>86-MD21</td>
<td>3</td>
<td>97.35</td>
</tr>
<tr>
<td>1/31/66</td>
<td>(150°)</td>
<td>99.72</td>
</tr>
<tr>
<td>88-MD21</td>
<td>10</td>
<td>94.46</td>
</tr>
<tr>
<td>1/31/66</td>
<td>(560°)</td>
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<td>89-MD21</td>
<td>13</td>
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<tr>
<td>1/31/66</td>
<td>(720°)</td>
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### TABLE II
**ANALYSES OF MAKAOPUHI LAVA LAKE SAMPLES**

**PART B - Drill Hole Samples (Continued)**

<table>
<thead>
<tr>
<th>Sample No. (Temp.)</th>
<th>Concentration, Moles Present</th>
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</thead>
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<td></td>
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<tr>
<td></td>
<td>Sample Bo. (!remp.)</td>
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<td>90-MD21 15 1/31/66 (810°)</td>
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<tr>
<td>91-MD20 3 1/31/66 (250°)</td>
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</tr>
<tr>
<td>92-MD20 7 1/31/66 (450°)</td>
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<td>93-MD20 10 1/31/66 (630°)</td>
<td>96.50</td>
</tr>
<tr>
<td>96-MD14 3 2/1/66 (150°)</td>
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</tr>
<tr>
<td>97-MD16 8 2/1/66 (465°)</td>
<td>97.42</td>
</tr>
<tr>
<td>98-MD23 10 2/1/66 (619°)</td>
<td>97.75</td>
</tr>
<tr>
<td>99-MD23 15 2/1/66 (840°)</td>
<td>77.38</td>
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</table>
### TABLE II

**ANALYSES OF MAKAOPUHI LAVA LAKE SAMPLES**

**PART B - Drill Hole Samples (Continued)**

<table>
<thead>
<tr>
<th>Sample No. (Temp.)</th>
<th>Depth-ft.</th>
<th>H₂O</th>
<th>He</th>
<th>H₂</th>
<th>Ar</th>
<th>O₂</th>
<th>N₂</th>
<th>CH₄</th>
<th>CO₂</th>
<th>H₂S</th>
<th>SO₂</th>
<th>Air</th>
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<tr>
<td>104-MD24</td>
<td>7</td>
<td>98.58</td>
<td></td>
<td>0.16</td>
<td></td>
<td>0.02</td>
<td>1.16</td>
<td></td>
<td>0.049</td>
<td>0.010</td>
<td>0.044</td>
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<td>6/7/66 (327°C)</td>
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<td>99.74</td>
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<td>0.16</td>
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<td></td>
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<td>0.049</td>
<td>0.011</td>
<td>0.045</td>
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<td>108-MD24</td>
<td>14</td>
<td>94.91</td>
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<td>0.20</td>
<td>0.056</td>
<td>0.31</td>
<td>4.24</td>
<td>0.0007</td>
<td>0.027</td>
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<td>4.61</td>
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<tr>
<td>6/7/66 (683°C)</td>
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<td>99.75</td>
<td></td>
<td>0.22</td>
<td>0.008</td>
<td></td>
<td></td>
<td></td>
<td>0.0008</td>
<td>0.027</td>
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<tr>
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<td>4.5</td>
<td>80.28</td>
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<td>0.016</td>
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<td>18.73</td>
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<td></td>
<td>20.50</td>
</tr>
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<td>8/9/66 (210°C)</td>
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<td>99.51</td>
<td>0.003</td>
<td>0.020</td>
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<td>0.44</td>
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<td>116-MD22</td>
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<td>8/9/66 (217°C)</td>
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<td>99.98</td>
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<td></td>
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<td></td>
<td></td>
<td>0.021</td>
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<td>118-MD22</td>
<td>7.5</td>
<td>96.43</td>
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<td>3.64</td>
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<td>3.78</td>
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<td>8/9/66 (288°C)</td>
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<td>99.99</td>
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<td></td>
<td></td>
<td>0.011</td>
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*Corrected to "air free" conditions by subtracting O₂ and N₂ and equivalent amounts of other air gases based on N₂ atmospheric ratios.

#Low temperature (-78°C) column used to separate He from H₂ and Ar from O₂.

*Partial separation of He from H₂ obtained at room temperature.
### TABLE III

**ANALYSES OF FUMAROLE SAMPLES**

**PART A - Sulfur Bank Samples**

<table>
<thead>
<tr>
<th>Sample No. and Date</th>
<th>H₂O (Moles)</th>
<th>He (Moles)</th>
<th>H₂ (Moles)</th>
<th>Ar (Moles)</th>
<th>O₂ (Moles)</th>
<th>N₂ (Moles)</th>
<th>CO₂ (Moles)</th>
<th>H₂S (Moles)</th>
<th>SO₂ (Moles)</th>
<th>Air (Moles)</th>
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<tr>
<td>4-81 9/21/64</td>
<td>84.24</td>
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<td>0.0007</td>
<td>—</td>
<td>2.64</td>
<td>9.09</td>
<td>4.51</td>
<td>0.007</td>
<td>0.002</td>
<td>11.84</td>
</tr>
<tr>
<td>9/21/64</td>
<td>94.91</td>
<td>—</td>
<td>0.0008</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>5.08</td>
<td>0.008</td>
<td>0.002</td>
<td>—</td>
</tr>
<tr>
<td>20-81 2/3/65</td>
<td>91.59</td>
<td>—</td>
<td>0.0006</td>
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<td>0.012</td>
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<td>6.39</td>
<td>—</td>
<td>0.010</td>
<td>0.38</td>
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<tr>
<td>2/3/65</td>
<td>93.46</td>
<td>—</td>
<td>0.0008</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>6.53</td>
<td>—</td>
<td>0.010</td>
<td>—</td>
</tr>
<tr>
<td>33-81 3/7/65</td>
<td>92.76</td>
<td>—</td>
<td>0.0008</td>
<td>—</td>
<td>0.006</td>
<td>0.35</td>
<td>7.36</td>
<td>0.018</td>
<td>0.013</td>
<td>0.36</td>
</tr>
<tr>
<td>3/7/65</td>
<td>92.63</td>
<td>—</td>
<td>0.0009</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>7.34</td>
<td>0.018</td>
<td>0.012</td>
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</tr>
<tr>
<td>34-81 3/7/65</td>
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<td>0.00007³</td>
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<td>0.12</td>
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<td>0.064</td>
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<tr>
<td>6/17/65</td>
<td>93.68</td>
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<td>0.0007</td>
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<td>0.025</td>
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<td>0.016</td>
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<td>7/19/65</td>
<td>93.18</td>
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<td>0.0001</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>7.16</td>
<td>0.029</td>
<td>0.098</td>
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</tr>
<tr>
<td>62-61 7/19/65</td>
<td>95.25</td>
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<td>0.078</td>
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<td>0.08</td>
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<td>94.90</td>
<td>0.00001</td>
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<td>7.16</td>
<td>0.029</td>
<td>0.098</td>
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<td>84-61 11/29/65</td>
<td>92.47</td>
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<td>0.088</td>
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<td>0.015</td>
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<td>11/29/65</td>
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## TABLE III

### ANALYSES OF FUMAROLE SAMPLES

#### PART A - Sulfur Bank Samples (Continued)

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<th>Sample No. and Date</th>
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<th>Ar</th>
<th>$\text{O}_2$</th>
<th>$\text{N}_2$</th>
<th>$\text{CO}_2$</th>
<th>$\text{H}_2\text{S}$</th>
<th>$\text{SO}_2$</th>
<th>Air</th>
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</thead>
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<td>102-S1 2/1/66</td>
<td>91.07</td>
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<td>0.0003</td>
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<td>9.78</td>
<td>0.026</td>
<td>0.15</td>
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<tr>
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<tr>
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<td>0.00003</td>
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<td>8.71</td>
<td>0.020</td>
<td>0.24</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>


**TABLE III**

**ANALYSES OF FUMAROLE SAMPLES**

<table>
<thead>
<tr>
<th>Sample No. and Date</th>
<th>Concentration, Moles Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$H_2O$</td>
</tr>
<tr>
<td>22-S2 2/3/65</td>
<td>58.69</td>
</tr>
<tr>
<td>39-S2 6/17/65</td>
<td>66.90</td>
</tr>
<tr>
<td>40-S2 6/17/65</td>
<td>72.64</td>
</tr>
<tr>
<td>41-S2 6/17/65</td>
<td>70.84</td>
</tr>
<tr>
<td>57-S2 7/19/65</td>
<td>88.23</td>
</tr>
<tr>
<td>58-S2 7/19/65</td>
<td>76.49</td>
</tr>
<tr>
<td>59-S2 7/19/65</td>
<td>73.71</td>
</tr>
</tbody>
</table>

---

*Note: All concentrations are given in moles percent.*
TABLE III
ANALYSES OF FUMAROLE SAMPLES

PART C - S3 and New Zealand Fumarole Samples

<table>
<thead>
<tr>
<th>Sample No. and Date</th>
<th>H₂O</th>
<th>He</th>
<th>H₂</th>
<th>Ar</th>
<th>O₂</th>
<th>N₂</th>
<th>CO₂</th>
<th>H₂S</th>
<th>SO₂</th>
<th>Air</th>
</tr>
</thead>
<tbody>
<tr>
<td>100-S3 2/1/66</td>
<td>93.57</td>
<td>0.0002</td>
<td>0.016</td>
<td>0.063</td>
<td>^</td>
<td>1.28</td>
<td>4.91</td>
<td>0.11</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>2/1/66</td>
<td>99.87</td>
<td>0.0002</td>
<td>0.017</td>
<td>0.005</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>101-S3 2/1/66</td>
<td>90.43</td>
<td>----</td>
<td>0.022</td>
<td>----</td>
<td>2.15</td>
<td>7.36</td>
<td>0.09</td>
<td>---</td>
<td>---</td>
<td>9.60</td>
</tr>
<tr>
<td>2/1/66</td>
<td>99.88</td>
<td>----</td>
<td>0.024</td>
<td>----</td>
<td>---</td>
<td>---</td>
<td>0.10</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>132-S3 3/18/67</td>
<td>91.15</td>
<td>----</td>
<td>0.004</td>
<td>0.079</td>
<td>^</td>
<td>2.08</td>
<td>6.77</td>
<td>0.16</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>3/18/67</td>
<td>99.82</td>
<td>----</td>
<td>0.005</td>
<td>----</td>
<td>---</td>
<td>---</td>
<td>0.17</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>127-WZ (1/67)</td>
<td>38.61</td>
<td>----</td>
<td>---</td>
<td>0.54 ^</td>
<td></td>
<td>12.95</td>
<td>46.27</td>
<td>0.18</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>99.59</td>
<td>----</td>
<td>---</td>
<td>0.54</td>
<td>---</td>
<td>---</td>
<td>0.41</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>129-WZ (1/67)</td>
<td>80.32</td>
<td>0.00004</td>
<td>0.008</td>
<td>0.14 ^</td>
<td></td>
<td>2.93</td>
<td>11.93</td>
<td>3.21</td>
<td>0.007</td>
<td>1.60</td>
</tr>
<tr>
<td></td>
<td>94.32</td>
<td>0.00005</td>
<td>0.010</td>
<td>0.007</td>
<td>---</td>
<td>---</td>
<td>3.77</td>
<td>0.008</td>
<td>1.88</td>
<td>---</td>
</tr>
</tbody>
</table>

#Corrected to "air free" conditions by subtracting O₂ and N₂ and equivalent amounts of other air gases based on N₂ atmospheric ratios.
^
Low temperature (-78°C) column used to separate He from H₂ and Ar from O₂.

*Partial separation of He from H₂ obtained at room temperature.
B. Evaluation of Sampling Tubes and Techniques

The gas sampling tube used in this research retained the basic design of the evacuated tube developed by Naughton et al. The main feature of this design was the inclusion of silica gel in the tube, which prevented reactions between the gases by absorbing and separating $H_2O$ and the acid gases, thus preserving the composition of the sample. While this solved one of the major problems of collecting good samples of volcanic gases, other problems remained.

The difficulties involved in opening a vacuum type sampling tube in the gas source have been considered by several workers. The technique of Naughton et al., which was used for early Sulfur Bank samples in this research (Samples 4, 20, 33 and 34 in Table III and the surface samples in Table II, was to smash a fragile tip on the sample tube against the wall of the vent being sampled. Similarly, for the first attempts to sample Alae lava lake drill holes, the tip was broken when the tube was allowed to drop the last few inches to the bottom of the hole. This was found to be a rather unreliable method (only two samples successfully collected). Often the main section of the tube would break above the tip, making it very difficult to seal after removing from the drill hole; these samples were usually discarded. At other times the tip refused to break, probably because slippage within the quartz shield prevented it from striking the bottom. In addition, gas samples could be collected only at the bottom of the drill hole by this opening method. Therefore, investigations were made to devise a more reliable technique that would allow the sample tube to
be opened at any level in a drill hole. Borrowing from oceanographic technique, an attempt was made to open the tip by dropping a "messenger" made of glass down the lowering cable. In this case the quartz shield was lowered upside down, with the lowering cable passing through the firebrick insulation, alongside of the sampling tube, so the messenger could strike the tip. This method, which was used for the Alae lava lake samples 13 and 14 (Table II), allowed taking samples at any depth, but very often did not break the tip. The messenger either stopped before reaching the tip or broke on the way down. The present method, that of pulling the tip off with a fine, nichrome wire, was then adopted. It required a small change in the tip design; a hook-shape was necessary, so the loop of the break-off wire could be attached. This pull-off method also has the advantage that it leaves only a fine capillary-sized opening, which is easier to seal with a torch. This technique, which was used for the Makaopuhi drill hole samples, was also adapted to the sample tubes used at Sulfur Bank and the other fumaroles, where it had an added advantage. At these sites, when the tip was opened by smashing as in the older designs, it often became partially plugged with sulfur crystals or other fumarolic deposits. When this happened, it was necessary to reseal the tube above the tip, where it had a larger diameter; this took longer, increasing the chances of air contamination. Pulling the tip off with a wire eliminated this difficulty.
Of the many problems encountered by past investigations of volcanic gases, the collection of samples free from air has been the most persistent. An examination of the results of this investigation listed in Tables II and III show varying degrees of air contamination in the samples. It was of interest to determine the cause of this contamination and if it could be prevented because of the possible alteration of the composition of the gas sample by air oxidation. The question as to what was the source of the air found in the samples, was considered. There are two possibilities, the accidental contamination by the atmosphere surrounding the site during sampling, and the natural infiltration and mixing of air with the volcanic gases underground. The former was considered first, as the most likely source. In this case, contamination by air would occur during sampling, and would depend on the collecting technique used and the conditions at the sampling site. At Sulfur Bank samples were taken from a small hole in a pipe capping a cased drill hole. There appeared to be little chance for air to mix with these gases at this point. Indeed Sulfur Bank samples were found to have relatively little air contamination compared to samples taken from the other sites. Air infiltration apparently occurred during the time when the tube was removed from the hole in the pipe and was being resealed by a gas torch. It was noted that as the glass tip was softened by the torch, it pulled-in as though there was still a vacuum in the tube. This would be expected, with the cooling of the hot gases just collected and undoubtedly would pull in some air. Normally the
tubes were left open in the gas source for one minute before re-sealing. It was found, however, that if they were left open in the vent for at least fifteen minutes before closing them, their air content was greatly reduced. This can be seen in the results for Sulfur Bank (Table III), starting with the June 1965 samples (43-81). The most likely explanation for this is that the hot gases, which fill the tube, are given time enough to reach a temperature equilibrium with the air surrounding most of the length of the collecting tube and the continually emitted gases from the vent. Leaving the tip in the vent during this time keeps it immersed in the fumarolic gases, preventing air infiltration.

In an attempt to eliminate the remaining air contamination, the design of the collecting tube was altered so that it could be sealed off while still in the vent. This involved extending the tip end of the tube several inches beyond the silica gel section of the tube. A constriction was included as shown in Figure 2 to facilitate closing by torch. In Table III, Sulfur Bank samples 124 and 126 were sealed while still in the vent and sample 125 was sealed after removing it from the vent. While there was a reduction of air in those tubes closed in the hole, it was not especially great, and in fact several other samples had an equally low air content (Sample 85, for example). A convenient explanation as to why this technique did not reduce air contamination to zero, was provided by the discovery of another, larger hole in the "sampling pipe," which had been hidden by the pile of
rocks covering the pipe and manifold of the sulfur well. It is not unlikely, that some air is being drawn into the pipe through this hole, which lies below the sampling hole.

Air contamination of samples taken at other low temperature sources (approximately 100°C) was greater than at the piped fumarole of Sulfur Bank. This was expected because the cracks and vents sampled at these sites were much larger and more irregular than the small hole used at Sulfur Banks and, therefore, were more open to mixing with atmospheric gases. In addition none of these samples were sealed while still in the vents. The effect on the air contamination of leaving the tubes in the vents for at least 15 minutes is apparent with the S2-fumarole samples. As at Sulfur Bank, this technique was begun with the June, 1965, samples. The three samples taken at the S3-fumarole, which were collected in the same manner, still had considerable air contamination. The cause of this was not investigated further, but may be due to a shallow underground mixing of air with the rising fumarolic gases. The air could have entered through lava tubes and cracks at lower levels on the uneven ground where these vents were located.

Air contamination was considerable for the samples taken from the surface of Makaopuhi lava lake during its formation. This was not unexpected because of the unfavorable sampling conditions at that time. The holes from which the samples were taken were shallow enough to allow considerable mixing of air with the emitted gases. A more likely cause was the sampling difficulty
due to the intense heat radiating from the surface, which allowed one to hold the sample tubes in these holes for only a few seconds. Because of this the tubes could not be sealed sufficiently against the red-hot walls of these holes. When the tubes were removed to be sealed, they began cooling, creating in them a partial vacuum, which drew in the air.

The situation appeared to be different for samples taken from the drill holes in Makaopuhi lava lake. It was often noted that when a sample tube was pulled from a drill hole, gas was blowing-out of its tip, making it difficult to seal. In most cases closure was not achieved until this effect had stopped and the softened glass tip was pulled-in by a vacuum in the tube. A number of tubes, however, were apparently sealed-off under this ideal "blowing-out" condition. Like all of the other drill hole samples, though, these tubes were contaminated with air. Air, which ranged from one to ten percent for the best samples, was found at all depths in the drill holes. Investigations were made to determine how this air might be getting into the drill holes. If air permeation through the crust of the lava lake has extended down to the hot zone near the bottom of the holes, one would expect with time an approach to equilibrium conditions with the gases present. Thermodynamically, equilibrium conditions with such high concentrations of air (O₂) would preclude any measurable quantities of reduced gas species such as H₂, H₂S and CH₄. All of these gases, however, were found in the drill hole samples. Further evidence against the presence of large concentrations of air in these holes was provided by the
determination of the oxygen partial pressure for the gaseous
composition found in the holes. Heald et al., 4 have shown that
volcanic gases seem to represent a system in thermodynamic
equilibrium, with partial pressures of oxygen extending from $10^{-8}$
atmospheres at 1200°C to even smaller values at lower tempera-
tures. Using their computational method, 62 the oxygen partial
pressures for two drill hole samples (72 and 73 in Table II) were
calculated for the temperature range (400°C to 1000°C) found in
these holes. These have been compared with oxygen partial pres-
sure measurements made directly by U. S. Geological Survey
scientists, 78 using an electrochemical device. A plot of the
limits of variation of the oxygen partial pressure measured both
ways is shown in Figure 7. The area between the hematite-
magnetite and hematite-wustite boundaries represents the stability
field of magnetite according to the data of Eugster and Wones. 79
Within the crust of the earth, variations in oxygen partial pres-
sure will occur largely between these boundaries. It should be
noted that they found the direct measurements were not reliable
below 500°C. The straight lines shown below this temperature are
extensions of the high temperature results. Nevertheless, these
results indicate that the air found in the samples taken at the
lower depths (the high temperature zones) of the drill holes is
not present in the holes before sampling. Other sources or causes
for this air contamination was therefore investigated.

One possibility considered was that cooler, more dense atmos-
pheric air was seeping down into the drill holes in a current
Figure 7. Oxygen Partial Pressure Variation Within a Drill Hole: High (Low) $H_2O$—Theoretically Determined $O_2$ Partial Pressures; High (Low) Probe—Experimentally Determined $O_2$ Partial Pressures (Sato and Wright78)
counter to the evolved gases, which were mainly steam. As it sank in the hotter and lighter volcanic gases, it would be heated until its density matched that of the rising gases, which would then carry it back out of the hole. This might cause the poor reproducibility of the oxygen partial pressure probe in the upper reaches of the drill holes (below 500°C). To determine if seepage could occur, a simple "drill hole" consisting of a vertical glass tube was set-up in the laboratory. To stimulate the light volcanic gas, air was passed up through the tube. Neither the tube nor the air, however, were heated. A heavy gas atmosphere was created at the top of the "drill hole" with carbon dioxide, which was generated by adding "dry ice" to water. The usual ice fog produced allowed one to follow the movement of the heavy gas, which did indeed infiltrate the laboratory drill hole, flowing down the walls of the glass tube. The flow rate for the lighter gas was varied over a wide range, including the approximate flow rate determined for the actual drill holes. It was found that the heavy gas penetrated to as much as seven feet at this latter rate (600 cc. per minute).

It is conceivable then that a similar effect could occur in the field and would be heightened by the piston-like effect of lowering a sampling tube into the hole. This latter effect was not observed with the laboratory model. In fact the opposite occurred, and as the tube was withdrawn the heavy gas appeared to be pulled down and around it. In either case, this seems to be a likely cause for air infiltration into the hole during the sampling procedure,
and a possible source of air contamination of the samples.

The crushed firebrick used as insulation for the drill hole sampling tubes, was also examined as a possible source of introduction of air into the drill holes. It was believed that air trapped between the particles of firebrick when the sampling tubes were packed into their quartz shields, would be released when the apparatus was lowered into the hot holes. To counteract this possible effect, a double-walled quartz shield was constructed, in which the space between the walls was filled with crushed firebrick and sealed-off under vacuum. The results of this experiment are illustrated by Makapuhi drill hole samples 116 and 118 (Table II), which were collected using this shield. The considerable amount of air found in these samples would seem to eliminate the firebrick as a major source of the sample contamination.

A second, but more sophisticated artificial drill hole was constructed in the laboratory in a further attempt to establish the cause of the air contamination in the drill hole samples. For this model, a vertical glass tube with the same diameter as the lava lake drill holes, was fitted to a round bottom flask. In operation, carbon dioxide from a cylinder was bubbled through boiling water in the flask, and the glass tube was heated with heating tapes to 350°C in the lower four foot section and to slightly greater than 100°C in the upper four feet. Only freshly boiled, distilled water was used and the system was allowed to purge itself of air for at least one-half hour after each addition
of fresh water, before taking any samples. In addition to the usual drill hole sampling tubes, with quartz shields and firebrick insulation, samples were also taken with a special collecting device, that could be closed while still in the "drill hole." It consisted of a one-meter long, small diameter glass tube with a break-off tip on one end and a cylindrical sample bulb connected to the other end by means of a stopcock. No silica gel was used in this tube. In practice, the entire tube was evacuated, sealed, and placed in the "drill hole." After 10 minutes which allowed any air pushed in by the tube to be flushed-out, its tip was pulled-off, and after one additional minute, the stopcock was closed and the tube removed for analysis. Table IV summarizes the results of this experiment; samples 141, 142, and 143 being collected with the usual sampling tubes and samples 144 and 145 being taken with the specially designed tube. According to these results, a considerable reduction in air contamination occurred when the samples were closed while still in the "drill hole." The small amount of air that was found in these samples was a mystery until a sample of gas from the carbon dioxide cylinder was analyzed directly and found to contain oxygen and nitrogen. For samples of the same size, the O₂ and N₂ found in the cylinder and in samples 144 and 145 were in the same concentration range. Of the three samples collected by the usual means, and sealed outside the hole, 141 was opened as soon as it was lowered into the "drill hole," and 142 and 143 were opened after waiting one minute for purging of air that might have been pushed into the "drill hole" by the sample
### TABLE IV

**ANALYSES OF ARTIFICIAL DRILL HOLE SAMPLES**

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Type of Sampling Device</th>
<th>Depth, feet (Temp.)</th>
<th>H₂O</th>
<th>O₂</th>
<th>N₂</th>
<th>CO₂</th>
<th>Air</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>141</td>
<td>regular drill hole device</td>
<td>7 (350°)</td>
<td>96.53</td>
<td>0.28</td>
<td>1.08</td>
<td>2.63</td>
<td>1.36</td>
<td>Opened immediately. Removed after 1 min. Sealed by torch.</td>
</tr>
<tr>
<td>142</td>
<td>&quot;</td>
<td>&quot;</td>
<td>95.33</td>
<td>0.09</td>
<td>0.36</td>
<td>4.59</td>
<td>0.45</td>
<td>Opened after 1 min. Removed after 1 min. Sealed by torch.</td>
</tr>
<tr>
<td>143</td>
<td>&quot;</td>
<td>&quot;</td>
<td>94.29</td>
<td>0.61</td>
<td>2.21</td>
<td>3.56</td>
<td>2.82</td>
<td>Opened after 1 min. Removed after 1 min. Sealed by torch.</td>
</tr>
<tr>
<td>144-1</td>
<td>Stopcock tube</td>
<td>3 (100°)</td>
<td>94.69</td>
<td>0.002</td>
<td>0.03</td>
<td>5.90</td>
<td>0.03</td>
<td>Opened after 10 min. Sealed in the hole by stopcock.</td>
</tr>
<tr>
<td>144-2</td>
<td>&quot;</td>
<td>&quot;</td>
<td>94.69</td>
<td>0.004</td>
<td>0.02</td>
<td>6.11</td>
<td>0.02</td>
<td>Same as 144-1, except composition was determined from a different aliquot.</td>
</tr>
<tr>
<td>145</td>
<td>&quot;</td>
<td>&quot;</td>
<td>96.37</td>
<td>0.004</td>
<td>0.009</td>
<td>4.48</td>
<td>0.01</td>
<td>Opened after 10 min. Sealed in the hole by stopcock.</td>
</tr>
</tbody>
</table>
tubes. The results indicate that if air is pushed into the drill holes by the sample tubes it is not a significant factor in the air contamination of the samples. The conclusion then is that the majority of the air contamination of the drill hole samples occurred, as with the samples taken at the other sites investigated, when the sampling tube was removed from the gas source and before it could be sealed-off.

Additional evidence, that at least the major fraction of the oxygen and nitrogen found in all samples came directly from atmospheric air, was provided by considering air-saturated ground water as a possible source for air contamination of the gases. This was done by plotting the ratio of nitrogen to water versus the ratio of oxygen to water (expressed as cubic centimeters of $O_2$ or $N_2$ per liter of liquid $H_2O$) for each sample. The relationships for nitrogen to oxygen in atmospheric air and in air-saturated water were then superimposed on this plot, which is shown in Figure 9. As is seen in the diagram, the majority of the points are clustered about the atmospheric air line, while the air solution line is completely ignored, eliminating air dissolved in ground water as a major source of air contamination. These points represent, in most cases, samples which had massive air contamination. The position of the remaining points, all of which lie to the left of the air line, is most probably due to oxygen consumption caused by reactions of this gas during collection and before analysis of the sample. A less likely explanation is that they have been displaced from the atmospheric air line by the presence of primary magmatic
Figure 8. Oxygen and Nitrogen in the Gas Samples:
Solid Line—O$_2$:N$_2$ in Atmospheric Air;
Dashed Line—O$_2$:N$_2$ in Air-Saturated Water
nitrogen in the gases. Although such "juvenile" nitrogen is believed to exist in magmatic gases, it is not thought to be present in concentrations as great as this interpretation indicates. Perhaps the displacement of these points is due to both factors, with oxygen consumption the main cause. These results support a similar study described recently by Yuhara. In his case oxygen and nitrogen found in water samples from hot springs in Japan were compared with the air-saturated water relationship. His results indicate an atmospheric source for the oxygen and nitrogen found, and he concludes that oxidizing reactions account for the oxygen consumption found.

C. Evaluation of the Gas Analyzing System

1. Introduction

The characteristics and advantages of gas chromatography as a method of separation and analysis of gases, liquids or even metallic compounds of sufficient volatility, have been well documented in many papers and texts since this technique was first described by James and Martin. The three chief advantages may be succinctly described as speed of analysis, simplicity of apparatus, and sensitivity of detection. The combination of these factors with relatively low cost in comparison with other instrumental techniques, has led many to refer to gas chromatography as the poor man's mass spectrometer.
2. Sensitivity of the gas chromatograph

Sensitivity data for the two detectors used for each gas analyzed by the gas chromatographic system is presented in Table V. The minimum detectable number of moles was determined by estimating the smallest peak area that could be measured above the background noise of the detector systems. This area depended a great deal on the peak shape for the individual gases at this concentration limit, and varied from approximately $4 \times 10^{-3}$ square inches for CH$_4$ to 0.12 square inches for Ar. For comparison, the minimum detectable concentration in parts per million (ppm) were calculated from the moles for a four milliliter sample which was the approximate volume of gas introduced into the chromatographic system during a run. In actual practice, the concentrations of the individual gases in the samples, often approached their sensitivity limits. Commonly found concentrations were: $10^{-6}$ moles (Ar, N$_2$), $10^{-7}$ moles (O$_2$, CO$_2$, H$_2$S, SO$_2$), $10^{-8}$ moles (He, H$_2$), and $10^{-9}$ moles (CH$_4$). Concentrations in these ranges increase the likelihood for inaccuracies in determining chromatogram peak areas and in measuring pressures, as discussed in the following section. Carbon monoxide, COS, and CS$_2$ were not found in any samples, and this is believed to be due to the relatively low sensitivity of the thermal conductivity detector used in this study for these gases. Previous investigations of Hawaiian volcanic gases have found CO and CS$_2$ to be present.$^4$
TABLE V
SENSITIVITY OF THE GAS CHROMATOGRAPH DETECTORS FOR GASES INVESTIGATED

<table>
<thead>
<tr>
<th>Component</th>
<th>Moles</th>
<th>ppm*</th>
<th>Component</th>
<th>Moles</th>
<th>ppm*</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>3.7x10^{-10}</td>
<td>2.1</td>
<td>Ar</td>
<td>8.2x10^{-8}</td>
<td>461</td>
</tr>
<tr>
<td>H₂</td>
<td>2.8x10^{-10}</td>
<td>1.6</td>
<td>O₂</td>
<td>5.6x10^{-9}</td>
<td>31</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>N₂</td>
<td>5.5x10^{-9}</td>
<td>31</td>
</tr>
<tr>
<td>CO</td>
<td>2.7x10^{-8}</td>
<td>151</td>
<td>CO₂</td>
<td>3.0x10^{-9}</td>
<td>17</td>
</tr>
<tr>
<td>H₂S</td>
<td>5.4x10^{-9}</td>
<td>31</td>
<td>SO₂</td>
<td>1.6x10^{-8}</td>
<td>88</td>
</tr>
</tbody>
</table>

Flame Ionization Detector

<table>
<thead>
<tr>
<th>Component</th>
<th>Moles</th>
<th>ppm*</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>3.2x10^{-12}</td>
<td>0.02</td>
</tr>
</tbody>
</table>

*Calculated for the sample size analyzed (4cc.) at S.T.P.
3. Sources of error

Errors associated with gas chromatographic techniques and in particular with its application to the study of volcanic gases have been discussed by Heald and by Suwa. Consideration of these and other errors as they apply to this investigation will be given here.

The inaccuracies in measuring the peak areas of the chromatograms are believed to be one of the most important sources of error. Three factors influence this measurement: 1) The method used to determine the area; 2) the size of the peak; and 3) the shape of the peak. An excellent comparison of the most common methods for measuring peak areas (planimetry, triangulation, height x width at half-height, cutting and weighing, disc integration and electronic digital integration) has recently been presented by Gill and Tao. Their results show that height times the width at half-height, the method used in this study, to be comparable to the other mechanical methods, but not as precise generally as the electronic integration techniques.

Another important relationship illustrated by their data is that precision and reliability of the results decreases as the peak size decreases. The peak size for a particular component will depend on its concentration in the sample and the detector's sensitivity to it.

Peak shape is particularly important when using height times width at half-height and other triangulation methods. When used on assymetrical peaks, poor results will often be obtained.
Symmetrical peaks are more common in the usual method of gas-liquid chromatography than in the gas-solid technique used in this investigation. This error was somewhat minimized by selecting the most symmetrical peak for each component from the several aliquots usually run from each sample. The effect on the results of measuring different peaks from different aliquots of the same sample is illustrated by samples 144-1 and 144-2 in Table IV.

Mechanical errors inherent in the gas chromatograph no doubt contributed to lack of precision in the results, but compared to peak measurement errors they play a minor role. These errors include nonlinearity of the detector response, variations in flow-rate and in the temperature of the columns and detectors. By keeping the sample size within the linearity range of the detector, and maintaining constant flow-rates and temperatures from sample to sample, these errors can be kept to a minimum.

A constant error may have been introduced into the results by the calibration curves, since they were subject to the inaccuracies of the measurement of peak areas when they were constructed. In addition, the syringe method used for calibrating the gas chromatograph may have added to this error, because air was always introduced with the calibrating gas. Correcting for this air included the uncertainty involved in measuring the oxygen and nitrogen peaks produced. When the determination of He and Ar was included in the analysis scheme, the instrument was calibrated for these gases by introducing them directly into the vacuum system. All air was excluded, eliminating one source of
error. This method then should lend itself to a more accurate calibration of the gas chromatograph.

Another source of error in the analyses was the pressure measurements. Here the error was mainly due to uncertainties in reading a mercury manometer. Sample pressures in the vacuum system varied from approximately 0.1 mm of Hg to 300 mm of Hg. The uncertainty involved in reading the manometer when sample pressures were in the low range, probably contributed as great an error in the results as the area measurements did for the size peaks produced by these samples. A great improvement in the reliability of the pressure readings, especially when the pressures were low, was achieved when the manometer was replaced by the quartz pressure gauge. This improvement was apparently masked in the results, however, by the still present errors in measurement of peak areas. The determination of the sample volume involved pressure measurements before and after expansion from a known volume. Error in these measurements was kept to a minimum by using a relatively high pressure range (250 to 350 mm of Hg).

The determination of the condensed water vapor by weighing is subject to error, as is any physical measurement. This is usually the most reliable step, however, in a chemical analysis, and errors normally amount to fractions of a milligram. The weight range for the analyses in this study were approximately 0.001 gram for surface and drill hole samples, to 3 grams for Sulfur Bank samples. Again the greatest error would be expected in the low range.
4. Precision and accuracy of the gas analyzing system

To assess the precision and accuracy of the gas analyzing system, seven samples of a gas mixture of known composition were analyzed in the same manner as the volcanic gas samples. The results are presented in Table VI. The gas mixture, which was prepared by Philips Petroleum Company and designated by them as Gas Mixture G-7 (Lot 8), contained acetylene, but it was excluded from the results, since the instrument was not calibrated for this gas. The sample size of the Philip's mixture used for these runs was within the range found for the volcanic gas samples. For the permanent gas portion this range varied from \(10^{-3}\) moles for Makaopuhi lava lake surface samples to \(10^{-6}\) moles for Sulfur Bank samples. The condensable gas range varied from \(10^{-2}\) moles for Sulfur Bank samples to \(10^{-6}\) moles in Makaopuhi drill hole samples.

The precision reported in Table VI is poorer than that indicated for the Philip's analysis, but no information is available on the method of analysis used by this supplier or the size of sample taken by them. Other investigators of volcanic gases, and especially those using gas chromatography for their analyses, usually have reported better precision and accuracy. It might be remarked, however, that these data almost always involve only a simple gas mixture, such as oxygen and nitrogen (air). The column of relative standard deviations shows that the precision generally decreases with a decrease in concentrations. As was explained in the preceding section, this is most likely due to
TABLE VI

PRECISION AND ACCURACY OF THE GAS ANALYZING SYSTEM: SEVEN RUNS OF PHILIPS GAS MIXTURE G-7 (LOT 8)*

<table>
<thead>
<tr>
<th>Component</th>
<th>Median, Mole Percent</th>
<th>Range</th>
<th>Estimated Standard Deviation**</th>
<th>S_relative ( \frac{S}{\text{median}} \times 100 )</th>
<th>Philips Analysis of G-7 (Lot 8) Mole Percent</th>
<th>Philips Deviation Mole Percent</th>
<th>Present Deviation (Philips-Median), Mole Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{N}_2 )</td>
<td>69.83</td>
<td>8.71</td>
<td>3.22</td>
<td>4.6</td>
<td>67.91</td>
<td>0.5</td>
<td>1.9</td>
</tr>
<tr>
<td>( \text{H}_2 )</td>
<td>13.13</td>
<td>3.26</td>
<td>1.21</td>
<td>9.2</td>
<td>11.23</td>
<td>0.2</td>
<td>1.9</td>
</tr>
<tr>
<td>( \text{CO} )</td>
<td>9.13</td>
<td>7.51</td>
<td>2.78</td>
<td>30.4</td>
<td>14.52</td>
<td>0.2</td>
<td>5.4</td>
</tr>
<tr>
<td>( \text{CO}_2 )</td>
<td>5.10</td>
<td>2.82</td>
<td>1.04</td>
<td>20.4</td>
<td>4.82</td>
<td>0.2</td>
<td>0.3</td>
</tr>
<tr>
<td>( \text{Ar} )</td>
<td>0.95</td>
<td>0.78</td>
<td>0.29</td>
<td>30.1</td>
<td>0.94</td>
<td>0.1</td>
<td>0.01</td>
</tr>
<tr>
<td>( \text{CH}_4 )</td>
<td>0.041</td>
<td>0.008</td>
<td>0.003</td>
<td>7.3</td>
<td>0.58</td>
<td>0.1</td>
<td>0.5</td>
</tr>
</tbody>
</table>

*The acetylene component of this mixture has been deleted.

**S = (Range) (Km), where Km is a statistical factor based on the number of observations; for seven observations, the present situation, Km = 0.37.85
uncertainties in measuring peak areas. Any discrepancies in the
decreasing sensitivity with decreasing concentration can be ex-
plained on the basis of individual variation in sensitivities. As
seen in Table V, the sensitivity of the system is greater for CO₂
and CH₄ than it is for CO and Ar. Deviations of as high as
20-30 percent for gases present in low concentrations and devia-
tions of approximately 5 percent for gases of higher concentration
compare with the results of Naughton, et al.⁴⁰ For the size and
type of sample involved, and accepting the accuracy of the analysis
supplied with the standard sample, the accuracy of the method used
in this work is sufficient for noting the trends in composition
which are discussed in a later section. No detailed analysis of
the precision and accuracy can be given for the volcanic gas samples,
since no more than three were taken at the same site (or depth in a
drill hole) at the same time. The accuracy of the analyses of
these samples may be assessed in a general way by noting their
degree of air contamination. Samples containing a large amount of
air necessarily would have only a small concentration of volcanic
gases. These would suffer therefore from the errors inherent in
the analyses of low gas concentrations. The relatively large
compositional variations that were found when samples were taken
from the same site and only minutes apart, are common to most
previous investigations of volcanic gases. It is felt that, at
least in this investigation, these variations are due not only to
the vagaries of sample collection (such as air contamination), but
also reflect the effects of all the factors discussed previously
which lead to the relatively poor precision and accuracy of the gas analyses. In view of this work, and with some recent developments in gas chromatography, several changes could be suggested for the analysis system to improve its accuracy and precision: 1) adoption of an electronic integration technique for chromatogram peak area measurements; 2) use of a more sensitive thermal conductivity detector or the ultra sensitive helium ionization detectors recently developed; and 3) adoption of the calibration technique used for Ar and He to the other gases.

D. Discussion of the Gas Samples

1. Makaopuhi lava lake samples

An examination of the results of the gas analysis of the Makaopuhi lava lake samples in Table II shows a characteristically variable composition for the gases with position on the lava lake at a given time, with depth in a given drill hole at a given time, and with time since eruption. The change in the average composition of the gases with time and the range of the measurements for each collecting date are shown in Figure 9. Similar data from Heald's collections at Kilauea Iki are shown for comparison.

As has been noted previously, a great variation in composition is almost a general phenomenon in collections of volcanic gases, and may occur even over short periods of time for gases issuing from a given natural vent. It would not be unreasonable, however, to expect a more uniform composition in gases collected from an isolated body of lava such as Makaopuhi lava lake, at
Figure 9. Variation of the Makaopuhi Lava Lake gases with Time After Eruption (similar data from Heald's collections at Kilauea Iki are shown for comparison)
least at a given time. This did not prove to be the case.

Further evidence of this compositional variation was found in the
degassing at the natural crack system on the surface of the lake,
which left some with a coating of sulfur and other volatile
deposits, and others nearby with no deposits at all. Why this is
so is not yet known. In discussions with the staff of the
Hawaiian Volcano Observatory, the hypothesis that convection cells
are formed in the molten lava beneath the crust due to lower heat
transfer through areas where the crust is thicker, such as the
island-like wellings on the surface of the lake and at the lake
edges. While there is no definite experimental proof of this
phenomenon, the slow flowing action in these regions could lead to
the concentration of volatiles. Deposits along the natural crack
system in the vicinity of these regions of thicker crust indicate
higher concentrations of gases rich in volatiles.

Since the gases collected from the drill holes appear to repre-
sent a system in thermodynamic equilibrium, as will be shown in a
following section (III-E), a variation in gas composition with
increasing depth within in a given drill hole and at a given time,
would be expected due to the accompanying temperature increase.
As may be seen from the results in Table II, there were a number
of cases where a series of samples were collected at varying depths
within a given drill hole and at a given time. Unfortunately only
one series, numbers 72, 73 and 74 from drill hole 14, was complete
enough (i.e., had a variety of gases at all three depths sampled)
to allow any conclusions to be drawn with respect to trends with depth. The gases found in this series show evidence of an approach to the equilibrium situation, particularly with respect to the H₂O to H₂ ratio. The compositional trends for CO₂ and H₂S, however, are in the reverse order to what would be expected theoretically. In addition, the CH₄ concentration found at each level sampled in this drill hole is much greater than the calculated equilibrium concentrations at these depths. These problems will be explored further in the discussion of the equilibrium calculations made for this investigation.

The variations in the composition of the gases of Makaopuhi lava lake with time, as illustrated in Figure 9, show a rapid depletion of all of these gases, with the exception of water, during the first few months after the eruption. The composition of the gases then became essentially constant for the remaining period in which samples were collected (some 16 months). This trend strongly supports the hypothesis presented by Peck et al. to explain the formation of vesicles found in drill cores extracted from Alae lava lake. The decrease in the solubility of a rapidly ascending magma, due to falling pressure, is believed to result in a supersaturation of the gases in the magma before any bubbles are formed. When the bubbles do form, the high viscosity of the magma would result in negligible movement of the bubbles relative to the magma. Abundant exsolution of gases would then occur as the magma reaches the surface. In Alae lava lake, then, evolution of the gas held in a supersaturated condition in this body of
lava for the first two months after it was created is believed to have formed the large number of vesicles found in the first three or four feet of the crust. Below this depth, as solidification proceeded, exsolution of the gases became nearly constant, relative to the amount of lava solidifying, forming less abundant tiny angular vesicles. This same decrease in abundance and size of vesicles with depth has been found for other similar situations at Kilauea Volcano. In this case, the gas is believed to have resulted from the "second boiling" effect during crystallization of the lava. Second boiling differs from ordinary boiling in that it is a response to cooling. This is a pressure effect; a result of an increase in vapor pressure due to confinement of dissolved gases in a smaller and smaller body of liquid as it is removed from other portions by crystallization.

Essentially no variation occurred in the water concentration of Makaopuhi gases with time from the eruption. This would be expected, since water comprises almost one-hundred percent of the gases found, and small variations would not be as noticeable as with the other gases where variations were of the same magnitude as the gas concentrations.

2. Fumarolic gas samples

The results of the gas analyses of samples collected at Sulfur Bank (S1), at the solfatara on the east rim of Kilauea Caldera (S2), and at the steaming area between Aloi and Alae pit craters on the east rift zone of Kilauea volcano (S3) are summarized in Table III. The location of these fumaroles at Kilauea may be seen in Figure 1.
The analyses of two samples obtained from fumaroles on White Island, New Zealand, have also been included in the table.

A comparison of these analyses shows a wide variation in composition from site to site, which is an almost universal feature of volcanic gas collections throughout the world. These variations may be attributed to several factors, one or all of which may be in effect, such as air contamination either during sampling or in the gas source, poor precision in the gas analyses, infiltration and mixing of meteoric waters with the gases, and the effect of temperature on the gas composition.

A lack of sulfur gases in the samples collected at the S3 fumarole was surprising, considering the sulfur deposition that occurred around many of the cracks and vents after an eruption on Christmas Eve, 1965, poured lava over much of that area. Also the first samples were collected only a month after the eruption. The composition of the gases at this site, mostly H2O with a small amount of CO2 and H2, is similar to that found for late Makaopuhi samples collected from "old" drill holes in which the bottom no longer extended through the lava lake crust (Sample 97 in Table II, for example). This indicates that a similar mechanism of gas exsolution is operative in both cases, but reaches the final degassing composition (H2O and some CO2 and H2) at a faster rate at the shallow lava flows found in the S3 area.

The location of Sulfur Bank (S1) and S2 fumaroles on faults of Kilauea Caldera and the long activity, as evidenced by the considerable rock alteration around them, indicates that they may be closely
associated with the main magma chamber of Kilauea volcano. For this reason Sulfur Bank has long been a prime source of gases. Since the first samples collected from the piped wells at this fumarole,\textsuperscript{1} it has been suspected that a consistent and thorough study of these gases would provide an indication of impending eruptions. Ballard and Payne,\textsuperscript{3} and later Heald \textit{et al.}\textsuperscript{4} presented data indicating that the sulfur gases particularly $\text{H}_2\text{S}$, were very sensitive in this respect, increasing significantly preceding eruptions that occurred during their studies.

The data of the present study has been examined for this effect. The change of concentration of the gases found with respect to time are shown in Figure 10, and the time periods for the two eruptions that occurred during the investigation have been included. Although there are variations in the $\text{H}_2\text{S}$ and $\text{SO}_2$ composition with time, they are not clearly related to the times of eruption. In fact the concentration for these gases remains nearly constant as the Aloi eruption is approached and passed. The possibility that the total sulfur gas concentration might be the indicating factor was also considered. This data is shown in Figure 11 as a total sulfur gas to $\text{CO}_2$ ratio versus time. The $\text{H}_2$ to $\text{CO}_2$ ratio was also included, as the data in Figure 10 showed a curious "mirror image" relationship between the sulfur gases and $\text{H}_2$. To keep them on the same scale for comparison it was necessary to divide this latter ratio by two. Neither of the ratios show a particular trend with respect to the occurrence of the eruptions. Before any definite conclusions can be drawn, as
Figure 10. Variation of the Gases from Sulfur Bank Fumarole with Time
Figure 11. Total Sulfur Gas to $\text{CO}_2$ and $\text{H}_2$ to $\text{CO}_2$ variations with time at Sulfur Bank Fumarole
to whether or not the variation in the Sulfur Bank gaseous composition can be used to predict eruptions, it is believed that a more frequent, periodic sampling than was carried out for this investigation would be needed. A program has already been initiated in this direction, with the collection of samples proceeding at a rate of one a week.

The gases from the S2 fumarole have never been sampled and analyzed before this study, and too few samples were collected in this study to lend much light on the effect of approaching eruptions on the gas content of S2. The data, which comprise three sampling periods, is shown in Figure 12 versus time. The period covered included the Makaopuhi eruption, but no trends relative to this eruption are noted in these gases. It might be worthwhile to make more frequent collections from this source also, with regard to eruption prediction.

These two gas sources are discussed further in a later section with regard to the equilibrium situation (see section III-E).

3. Miscellaneous

Up to this point very little has been said about CH₄ and the rare gases, Ar and He, which were found less frequently than the so-called major gases. Methane was found only in samples taken from Makaopuhi lava lake. Equilibrium calculations (section III-E) predict a much lower concentration than was found in the Makaopuhi samples, in fact so low as to be beyond the limits of the flame ionization detector (10⁻⁶ mole percent). Collections of gases made from lava flows covering vegetation usually show on analysis a
Figure 12. Variation of the Gases from S2 Fumarole with Time
large content of this gas, predominantly in the early phase of
degassing. Stereo photos made before the eruption in Makaopuhi
pit crater show a rather sparse covering of vegetation. Rough
calculations based on a tree count from these photos, indicate
the carbonaceous gases would be exsolved from the lava in less
than one day. Methane was not found, however, until about four
months after the eruption. At present there is no way to explain
its presence in the drill hole gases.

The results of the gas analyses in Tables II and III show Ar
and He to be present in some samples. The gas chromatographic
techniques for separating these two gases (from O₂ and H₂
respectively) on the molecular sieves column were not worked out
until late in this study so only a few analyses have included
these gases. Ratios of N₂ to Ar in the sample generally indicate
an atmospheric source for these gases. This is in agreement with
results found by Hoering for isotope studies on N₂ and Ar in
volcanic gases. Nitrogen to He ratios indicate the same source
for this gas, with best agreement in samples having high air con-
tamination. Isotopic studies by Wasserberg et al. also indicate
an atmospheric origin for these gases in samples from Kilauea Iki.

In some analyses, unidentifiable peaks were produced on the
flame-ionization detector trace. As this was an indication of
the presence of organic compounds other than the methane sometimes
found, provisions were made in the gas analyses to collect these
samples in a breakseal tube for mass spectrometric analysis. Pre-
liminary analyses of these samples were attempted using an eight-inch,
single focusing mass spectrometer, with a resolution of 2500, operated in the dynamic mode. Figure 13 shows the results of a number of condensable gas portions of samples plotted to emphasize the similar peak intensity pattern that appeared throughout in varying degrees of intensity. A full interpretation has not yet been made but indications are that unsuspected organics (m/e = 26, 27, 41, 42, 43) other than methane are present. A further investigation of these results has been initiated.

E. Equilibrium Calculations

1. Introduction

A theoretical study was made with the hope of gaining more knowledge about the nature and extent of attainment of chemical equilibrium in volcanic gas systems. Because sublimate deposits contain metal compounds common to those found in ore deposits, a study was initiated to investigate equilibrium systems that included sublates.

A method of calculating complex equilibria, which was developed by White, et al. and is based on the principle that the free energy of a system has a minimum value at equilibrium, was adapted by Heald and Naughton for computer calculation of volcanic gas equilibria using the analysis of an actual sample as a starting composition. The present study follows their methods and uses a program written by Heald, but represents a more advanced form of his original program. A listing of the program is given in Appendix II. It was written in the
Figure 13. Residual Peaks from Condensable Gases from Assorted Volcanic Gas Samples; CO$_2$, SO$_2$ and H$_2$O Subtracted; Peak Height Equals Percent Abundance
Fortran IV computer language for use on the IBM 7040 computer system and was adapted here for use with the University of Hawaii Computing Center's IBM 360 computer.

As with Heald's original program, the effect of temperature and pressure variations on the equilibrium composition under study may be determined, and the variety and number of components that make up the system of study may be varied. The larger "memory" (data storage capacity) of today's computers and the availability of free energy data for a larger number of compounds allows one to study systems of considerably greater complexity than heretofore. At present the program is capable of handling up to 15 elements and 40 compounds. Unlike Heald's original procedure, which required two separate program runs, one to determine the major components and the other the minor components based on the output of the first program, the compositions of both major and minor components are determined in the same run with the present system.

There are some limitations to this program and to the resulting calculations of equilibria in volcanic gas systems that should be noted:

a. At present the program cannot take into account non-ideal situations; therefore the calculations are made assuming all compounds are present as ideal gases.

b. Although the program is designed to handle more than one phase, lack of data prevents the use of this feature.
c. Free energy data often are lacking for compounds believed to be important in volcanic systems, such as sulfides and some chlorides (CaCl₂ for example).

d. The lack of knowledge as to the concentration of many of the suspected components in volcanic gases forces one to make guesses in order to supply the computer with a starting composition. The resulting calculated composition may give a false picture of the equilibrium situation in the system under study.

2. Results

The calculations were made using the analyses of samples selected from Tables II and III as starting compositions. Low air contamination was used as the basis for selection of analyses from Sulfur Bank (No. 126) and S2 (No. 58) fumaroles. The variety of components present determined which Makaopuhi surface analyses were to be used (Nos. 28 and 38), as air contamination was considerable in all of these samples. Equilibrium calculations also were made using two drill hole samples, one from a high temperature zone during the early stages of cooling (No. 72) and one from a low temperature zone in the later stages of cooling (No. 91).

Free energy data was obtained from the J.A.N.A.F. (Joint Army, Navy, Air Force) tables and from the literature, and for each component represented the free energy of an ideal gas phase.

The results of the equilibrium calculations indicate that, in general, equilibrium between the gases has been achieved, at least
for the major components, as shown in Table VII. With regard to
the drill hole samples, however, the observed composition appears
to represent an equilibrium at temperatures higher than those
found at the temperature of collection. This same effect was
found by Matsuo for gases of Showa-Shinzan volcano, and has
been interpreted by him as a quenching of the original equilibrium
as the gases reached the lower temperature at the point of col-
lection. The temperature which the observed equilibrium composi-
tion of the Makaopuhi surface samples represented is not accur-
ately known. Heat was lost by radiative transfer, and the molten
lava at the points of collection cooled very rapidly. Therefore
only an estimated temperature range can be given (800 to 900°C or
1100°C to 1200°C). It is surprising that under such rapidly
changing conditions these samples would represent an equilibrium
composition at any temperature whatsoever.

That equilibrium was achieved in the Sulfur Bank and S2
fumarole gases, was also surprising. One might expect that the
low temperatures involved would hinder the reactions leading to
an equilibrium situation. When the Sulfur Bank wells were drilled
by Jagger in 1922 it was found that the temperature remained
constant, at 95°C (the boiling temperature of H2O at that alti-
tude), throughout the length of the drill hole (70 feet). Per-
haps this effect, which may extend deeper, gives hotter gases
coming into the fumarole area, sufficient time to reach a new
equilibrium at this lower temperature before they reach the top
of the well. The Sulfur Bank vent temperature was measured
### TABLE VII

**OBSERVED AND EQUILIBRIUM COMPOSITIONS OF THE MAJOR GAS COMPONENTS AT THE SAMPLING SITES**

<table>
<thead>
<tr>
<th></th>
<th>126-81</th>
<th>58-82</th>
<th>28-M</th>
</tr>
</thead>
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<tr>
<td></td>
<td>0#</td>
<td>C#</td>
<td>0#</td>
</tr>
<tr>
<td></td>
<td>368°K</td>
<td>400°K</td>
<td>368°K</td>
</tr>
<tr>
<td>H₂O</td>
<td>91.03</td>
<td>91.03</td>
<td>74.16</td>
</tr>
<tr>
<td>H₂</td>
<td>0.00003</td>
<td>0.00002</td>
<td>0.00007</td>
</tr>
<tr>
<td>CH₄</td>
<td>--</td>
<td>10⁻¹²</td>
<td>--</td>
</tr>
<tr>
<td>CO₂</td>
<td>8.71</td>
<td>8.71</td>
<td>23.47</td>
</tr>
<tr>
<td>H₂S</td>
<td>0.02</td>
<td>0.02</td>
<td>--</td>
</tr>
<tr>
<td>SO₂</td>
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<table>
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<tr>
<th></th>
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<th>72-MD14</th>
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<tr>
<td></td>
<td>0#</td>
<td>C#</td>
<td>0#</td>
</tr>
<tr>
<td></td>
<td>1100-1200°K</td>
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<td>1233°K</td>
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<tr>
<td>H₂O</td>
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<tr>
<td>SO₂</td>
<td>3.89</td>
<td>3.89</td>
<td>2.22</td>
</tr>
</tbody>
</table>

* O = Observed composition and the temperature at the time of collection.

* C = Calculated equilibrium composition and temperature at which agreement with the experimental value is closest.

* # Estimated temperature range.
during this investigation and found to be 94.5°C. No temperature data was collected at the S2 fumarole, but the assumption that the temperature at the vents is the same as at Sulfur Bank appears reasonable.

As was mentioned earlier and is shown in Table VII, the CH₄ found in the drill hole samples had not established equilibrium with the other gases in these samples. In each case the observed values were several orders of magnitude larger than the calculated equilibrium values at each temperature. Matsuo has found an excess concentration of CH₄ in the fumarolic gases of Showashinzan Volcano with respect to the concentration his equilibrium calculations predicted. He concluded that this CH₄ was not of magmatic origin, but was added to the original gases at a shallow point beneath the ground, and did not establish equilibrium with the other components before reaching the fumarole outlet. According to the previous discussion, however, reactions between these rising gases should be fast enough that at least an approach to equilibrium would be achieved. The concentration of methane found in the drill hole samples remain an anomaly.

The components listed in Table VII represent only those gases found in the actual analyses after corrections for air contamination. A large number of related compounds that might be expected in a volcanic gas system were also included in the calculations. These comprised compounds of nitrogen and of sulfur, the halogen acids, and metal halides. The latter two groups of compounds will be covered in the discussion of sublimates.
In the past, discussion of the very important component, nitrogen, in magmatic gas has always centered around the gases $N_2$ and $NH_3$ and the equilibrium:

$$N_2 + 2H_3 = 2NH_3$$

Considering $N_2$, $H_2$ and $NH_3$ independently of the other gases in a volcanic gas system, Ellis 58 has shown that $NH_3$ would be expected at temperatures below $400^\circ K$ and at increased pressures, would become more stable at higher temperatures. Matsuo, 96 studying this same equilibrium, considered the possible role of $NH_4^+$ and concluded that its contribution would be negligible. Free energy data for $NH_4^+$ (as the gaseous ammonium ion) has recently become available 94 and was incorporated into the equilibrium calculations of this study along with $N_2$ and $NH_3$ data. There is direct proof of the existence of $NH_3$ or $NH_4^+$ in the gases of Hawaiian volcanoes, ammonium compounds having been found in the sublimes ($NH_4Cl$) 97 and in the fume ($NH_4)_2SO_4$ 98 associated with these volcanoes. In addition $NH_4^+$ ion has been found in the water eluate of the silica gel in the collecting tubes of this investigation.

Originally the $N_2$ content of the analyses in this work were corrected for atmospheric $N_2$ according to the amount of $O_2$ found (assumed to be completely atmospheric) and the air ratio of these two gases. This often left a large amount of $N_2$ (greater than 10 mole percent). Preliminary equilibrium calculations were made using these large concentrations of $N_2$ and $10^{-3}$ mole percent for $NH_3$ and $NH_4^+$ in the starting composition. In the resulting equilibrium composition, $N_2$ changed very little, while $NH_3$ became
very small \((10^{-10})\) and \(\text{NH}_4\) increased by a factor of ten. This surprising situation was explored further in the present set of calculations. All gas analyses now are corrected by assuming all \(N_2\) found (as well as \(O_2\)) to be atmospheric, as has been indicated by isotopic studies,\(^8\) so smaller starting concentrations were used for \(N_2\) in equilibrium calculations \((10^{-4} \text{ and } 10^{-2} \text{ mole percent})\). Starting compositions for \(\text{NH}_4\) and \(\text{NH}_3\) were \(10^{-4} \text{ mole percent}\) and \(10^{-9} \text{ mole percent}\) respectively. These were guesses; the \(\text{NH}_3\) was started very small according to the results of the preliminary calculations. The resulting equilibrium calculations are summarized below:

<table>
<thead>
<tr>
<th>Component</th>
<th>Starting Composition</th>
<th>Equilibrium Composition (400^\circ\text{K})</th>
<th>Equilibrium Composition (1400^\circ\text{K})</th>
<th>Starting Composition</th>
<th>Equilibrium Composition (400^\circ\text{K})</th>
<th>Equilibrium Composition (1400^\circ\text{K})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(N_2)</td>
<td>(10^{-4})</td>
<td>(10^{-56})</td>
<td>(10^{-31})</td>
<td>(10^{-2})</td>
<td>(10^{-43})</td>
<td>(10^{-28})</td>
</tr>
<tr>
<td>(\text{NH}_3)</td>
<td>(10^{-9})</td>
<td>(10^{-21})</td>
<td>(10^{-21})</td>
<td>(10^{-9})</td>
<td>(10^{-18})</td>
<td>(10^{-20})</td>
</tr>
<tr>
<td>(\text{NH}_4)</td>
<td>(10^{-4})</td>
<td>(3 \times 10^{-4})</td>
<td>(3 \times 10^{-4})</td>
<td>(10^{-4})</td>
<td>(10^{-2})</td>
<td>(2 \times 10^{-2})</td>
</tr>
</tbody>
</table>

(Concentration in moles percent)

It is obvious from these results that \(\text{NH}_4\) is the important form of nitrogen in the volcanic gas systems studied, while \(N_2\) and \(\text{NH}_3\) play very minor roles.

Previous studies by Ellis\(^{58}\) and Heald et al.,\(^4\) have investigated, theoretically, the role that would be played by a variety of sulfur compounds that either have been found in volcanic gases or that might exist in such systems in trace quantities.

A similar group of compounds were included in the present study \((\text{H}_2\text{S}, \text{SO}_2, \text{S}_2, \text{COS} \text{ and } \text{CS}_2)\). In addition two other elemental
forms of sulfur (S and S₈), for which free energy data are now available, were included in this study, to determine which form would be more likely at the various temperatures involved. The results are in general agreement with what Ellis and Heald found, and are summarized as follows:

a. The chief sulfur gases are H₂S and SO₂, with H₂S more prominent at low temperatures.
b. At temperatures of 1200°C or greater the presence of COS and S₂ in the gas phase becomes probable.
c. CS₂, S, and S₈ are very small at all temperatures (10⁻⁷ mole percent or less).

3. Equilibrium and the trends in a drill hole

It was noted in section III-D-1, that the trend in the observed composition with depth (temperature) in drill hole No. 14 samples, 72, 73 and 74, (decreasing H₂O and increasing H₂, CH₄, CO₂, H₂S and SO₂) could not be completely explained as due to the effect of temperature changes on an equilibrium mixture. The theoretical variations, that the observed trends were expected to follow, were determined by calculating a series of equilibrium compositions at the temperatures found in this drill hole, using the analysis of the sample taken at 11 feet (sample 72) as the starting composition. This would be a correct approach if it could be assumed that nothing was added to the gas mixture moving upwards in the drill hole. If an admixture of water or air occurred at one or more points in the upper reaches of the hole, the effect on the calculated equilibrium mixture for the
temperature at that point (starting with the observed composition at 11 feet) would have to be considered.

To test this idea, Table VIII has been compiled. The composition at 11 feet (sample 72) is shown in the first column. In the second column the corresponding equilibrium composition has been listed. Using the composition in column 1 as a starting point, the equilibrium values at approximately the same temperature found at a depth of 5 feet are shown in column 3. In column 4, the actual composition found at 5 feet in drill hole 14 is shown. A considerable difference is noted, especially in the amount of H₂O present in each case. A sample collected at a shallow depth (91-MD 20) and having a high water content was used to calculate the equilibrium composition that would be expected at 5 feet (800°K) and this is listed in column 5.

A comparison of column 4 with the columns on either side of it shows that the observed composition at the 5 foot level in drill hole 14 is in better agreement with the equilibrium composition calculated from the shallow sample (column 5) than with the equilibrium values determined with the deep sample concentration (column 3). It would appear then that the compositional trend in drill hole 14 could reasonably be due to the effect of water (perhaps meteoric water) seeping into the upper portion of the drill hole and mixing with the gases present. This water addition, as well as any temperature change, must be considered in calculating the equilibrium composition of the drill hole gas.
<table>
<thead>
<tr>
<th>Component</th>
<th>Makaopuhi</th>
<th>Drill Hole No. 14</th>
<th>Drill Hole No. 20</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sample 72</td>
<td>Sample 73</td>
<td>Sample 91</td>
</tr>
<tr>
<td>H₂O</td>
<td>91.50</td>
<td>93.25</td>
<td>93.85</td>
</tr>
<tr>
<td>H₂</td>
<td>2.84</td>
<td>1.15</td>
<td>0.35</td>
</tr>
<tr>
<td>CH₄</td>
<td>0.032</td>
<td>10⁻¹¹</td>
<td>10⁻⁷</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.62</td>
<td>0.71</td>
<td>0.72</td>
</tr>
<tr>
<td>H₂S</td>
<td>2.72</td>
<td>3.23</td>
<td>3.62</td>
</tr>
<tr>
<td>SO₂</td>
<td>2.22</td>
<td>1.57</td>
<td>1.36</td>
</tr>
</tbody>
</table>

* 0 = Observed composition, mole percent.

C = Calculated equilibrium composition, mole percent.
4. Extension of the equilibrium studies to sublimates

It was pointed out in Section I-A-3 of this paper, that the most likely role of volcanic gases in the formation of ore deposits is that of a transport medium. Because sublimates are known to contain most of the metals commonly found in ore bodies, these deposits provide the best direct evidence for a gaseous transport of ore forming metals.

The preliminary experimental work on the collection and analyses of sublimates from the gas sampling sites has revealed a number of problems, chief of which is the low concentrations of these substances involved. It was discovered that most of the "ultrapure" silica gel used in the sampling tubes was contaminated with some of the compounds being sought: \( \text{NH}_4^+ \), \( \text{Fe}^{3+} \), \( \text{H}^+ \), \( \text{Cl}^- \), \( \text{Cu}^{2+} \), and \( \text{SO}_4^{2-} \). In most cases then, nothing was left when the background was subtracted. In the later stages of the work, when highly purified silica gel with a low background was used, the concentration range of the sublimates found was at the very limit of detection. To complicate the situation it was discovered that the washing procedure did not completely remove all of the chloride from the silica gel, resulting in low values for this important anion. In the few cases where some values were obtained there was some difficulty in making use of the data. Because one has no idea of how much of each cation goes with the anions found it is difficult to arrive at a concentration that will be meaningful. In spite of these difficulties, enough information was obtained to provide values for the starting composition
of the computer calculations. The particular sublimate compounds that could be included in the computer program depended on the availability of the free energy data for the compounds. Since free energy data is lacking for many of the $\text{NH}_4^+$, $\text{Cu}^{2+}$, $\text{Mn}^{2+}$ and $\text{SO}_4^{2-}$, compounds found in the sublimates, these could not be included in the equilibrium calculations. The compounds that have been used are listed in Appendix II with the program:

The calculations were made using sample number 72 (Table II) for the starting composition. The sulfur and nitrogen compounds were started at $10^{-9}$ mole percent, except for $\text{NH}_4$ and $\text{N}_2$ at $10^{-4}$ mole percent. The technique for selecting the starting composition of the sublimate compounds is outlined as follows:

a. All of the sublimate compounds (the metal chlorides, fluorides, and oxides), $\text{HBr}$, $\text{HF}$, $\text{MgS}$, and $\text{SiO}$ were started at $10^{-9}$ mole percent, and $\text{HCl}$ as 1.0 mole percent. From this first run one could determine which compound in a series would be the most likely form to be present in an equilibrium system. For example, $\text{FeCl}$, $\text{FeCl}_2$ and $\text{FeCl}_3$ were started at $10^{-9}$ and in the resulting equilibrium composition $\text{FeCl}_2$ increased while the other two became smaller by several powers of ten.

b. For each component in a series that increased, a new starting composition was selected based on the computational trend and on the estimates made from the analyses of the sublimates and the silica gel washings. A value for $\text{HF}$ was estimated from the data of Murata$^{41}$ on $\text{F}:\text{Cl}$ ratios in Hawaiian gases and the value of $\text{Cl}$ estimated from the elution analysis.
of the sampling tube silica gel. These compounds and the estimated concentration used are as follows:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>1.0 mole percent</td>
</tr>
<tr>
<td>HF</td>
<td>4 x 10^{-3}</td>
</tr>
<tr>
<td>FeCl₂</td>
<td>0.05</td>
</tr>
<tr>
<td>CuCl</td>
<td>0.01</td>
</tr>
<tr>
<td>MgCl₂</td>
<td>0.15</td>
</tr>
<tr>
<td>TiOCl</td>
<td>0.06</td>
</tr>
<tr>
<td>NaCl</td>
<td>0.18</td>
</tr>
</tbody>
</table>

The effect of increasing the starting composition of these dominant sublimate species on the concentration of all other components was very slight. The equilibrium concentrations of the major components changed very little at each temperature. The concentration of each of the other members of a series of metal compounds increased, but in proportion to the composition of the dominant species in that particular series. The silicon compound, SiO, was not included in this study, although it was run with the program. As there were no other silicon compounds, the concentration of SiO did not vary from the starting value (10⁻⁹ mole percent). Work with the mass spectrometry of molecular beams from solids heated to high temperatures has revealed the presence of many compounds in the high temperature gas phase which may seem unusual to those schooled in aqueous chemistry. Many such substances are pertinent to sublimes in volcanic gas systems, and where thermodynamic data was available these were included in the calculations. One may point to such substances as NH₄⁺, discussed previously, and to CuCl, FeF, FeCl₂, MgCl₂, Cu₃Cl₃ and ZnCl as examples. These calculations show that in some cases these unconventional compounds would have a relatively
high partial pressure in an equilibrium combination typical of volcanic systems.

Samples of sublimate have been extracted from various levels in the lava lake drill holes, and the salts present have been extracted by solvents and analyzed by Dr. R. Goguel. In the earliest stage at which such collections were made (August 1966), all metals were found to be present as chlorides, with some secondary sulfates and unidentified alumino-silicates. A rough estimate of the relative abundances of the sublimate salts at various temperature levels in the drill holes could be made from this work. This showed that NaCl and KCl were most abundant in the hottest zone (hypothermal), CuCl₂ and ZnCl₂ in the intermediate zone (mesothermal), and FeCl₂, MnCl₂ and Ca and Mg chlorides and sulfates in the coolest zone (epithermal). This distribution compares favorably to the presence of compounds of these elements in ore bodies, in relation to their position relative to the hot intrusive which presumably was the source of the ore substances. Also it is in general agreement with the equilibrium vapor pressure of the chlorides of these elements in volcanic equilibrium mixtures, where available data enabled the calculation of such compositions.

The full extension of equilibrium calculations to sublimates, and the utilization of this powerful tool in identification of transport species and their sequences, must await the availability of thermodynamic data for all compounds possible in such systems.
IV. CONCLUSIONS

The following conclusions are reached as a result of the research on volcanic gases presented in this dissertation:

A. Regarding the gas collecting techniques

1. An excellent method of collecting volcanic gas samples from any depth in a drill hole was found to be the use of an insulated silica gel sampling tube combined with a sampling tip pull-off wire.

2. Air contamination of volcanic gases collected for this study resulted during that time when the sample was removed from the gas vent and before sealing could be accomplished.

B. With regard to the gas analyzing system

1. A precision quartz bourdon tube pressure gauge is a major improvement in convenience and accuracy over the mercury manometer generally used for making gas pressure measurements in analyzing systems.

2. The by-pass valve-syringe injection technique provides a fast, reproducible calibration method, but calibration via the measuring system and sample loop should be more accurate.

3. The following recommendations are suggested for future work with the gas analyzing system:

   a. In order to determine the minor components in a volcanic gas sample, more sensitive detectors would be needed, such as a micro-volume thermistor detector or an ultra-sensitive He ionization detector.
b. An improvement in accuracy and precision of the results could be achieved through more accurate peak area measurement by means of an electronic digital integrator.

C. With regard to the gas samples collected during the course of this investigation

1. The compositional variations in gas analyses from sample to sample and source to source may be explained by any one or all of the following:
   a. Air contamination of the sample.
   b. Poor precision and accuracy in the gas analyses.
   c. The effect of temperature changes on gaseous equilibrium systems.
   d. The effect of the admixture of water on a gaseous equilibrium system.

2. The oxygen and nitrogen found in gas samples from each site is atmospheric air rather than air dissolved in ground or meteoric water.

3. The degassing trend of Makaopuhi lava lake with time may be explained as a two step process:
   a. A rapid and abundant exsolution of gas from a lava supersaturated with magmatic gases.
   b. Afterwards, a constant rate of degassing fed by gases from a "second boiling" process.

4. The degassing of the S3 fumarole area may have followed the same process as at Makaopuhi lava lake, but on a much shorter time scale.
5. Sampling as frequent as once a week may be necessary to determine if variations in the gas composition at primary fumaroles (such as Sulfur Bank) can be used to predict volcanic eruptions.

6. Systematic sampling and analysis should yield information on the link between certain fumaroles and the volcano, and on the nature of the gas source.

7. No explanation can be presented for the presence of methane in the Makaopuhi samples.

8. The argon and helium as found in the gas samples are of atmospheric origin.

9. The preliminary examination of condensable gas fractions for unsuspected organics shows indication of interesting compounds and should be extended.

10. The collection and analysis of sublimates from drill holes and on the silica gel tubes should be made a major part of the study of volcanic gas systems.

D. With regard to the thermodynamic equilibrium studies

1. The major volcanic gases issuing from Sulfur Bank, S2 fumarole, and Makaopuhi lava lake, represent, in general, equilibrium compositions.

2. The dominant nitrogen species in volcanic gases is $\text{NH}_4$; $\text{N}_2$ and $\text{NH}_3$ play only a small role.

3. With the presently available free energy data and knowledge of sublimate concentrations, it is not possible
to determine more than which metal compound of a series
(FeCl, FeCl₂, FeCl₃) would be most probable in a gaseous
ore transport phase.
V. SUMMARY

A chemical study has been made of Hawaiian volcanic gases from a variety of sources at Kilauea volcano on the island of Hawaii. These can be listed as follows:

1. The molten surface of a lava lake as it was forming in Makaopuhi pit crater during the 1965 flank eruption.
2. Gas from the holes drilled through the crust of the cooling lava lake at Makaopuhi crater by the staff of the Hawaiian Volcano Observatory, U. S. Geological Survey.
3. Gases from the piped-well at Sulfur Bank fumarole.
4. The natural venting gases of a solfatara (S2) on the east rim of Kilauea Caldera.
5. The steaming area (S3) between the Alai and Aloi pit craters on the east rift zone of Kilauea Volcano.

The gases were collected in evacuated, silica gel sampling tubes. For the drill holes the sampling tube was sheathed in a quartz jacket. Samples were opened by means of a pull-off wire.

Gas analysis was carried on by means of gas solid chromatography, using molecular sieves 5A and silica gel columns to separate the gases: He and H₂, Ar and O₂, N₂, CH₄, and CO on the molecular sieves, and CO₂, H₂S, and SO₂ on the silica gel.

Investigations were made to determine the source of air contamination in the samples, by considering the sampling techniques and the possibility of air entering the gas sources.

The lava lake sample compositions have been discussed in regard to the trends with depth in a drill hole, with position of drill holes on
the lava lake, and with time. A great variability in composition was noted for samples from one site to another. This has been attributed to air contamination, poor analyses, and the effect on an equilibrium composition of temperature changes and water influx. The compositional variations of the lava lake gases were related to the degassing processes of a cooling rock body. The S3 fumarole appeared to show trends indicative of the same process of degassing of a small molten rock flow or body.

Sulfur Bank and S2 fumarole analyses were examined for changes with time that could be used to predict volcanic eruptions. The results were inconclusive.

Chemical equilibrium calculations were made by computer, using a method of calculation based on minimizing free energy. The major gas sources samples were examined and found to represent, in general, systems in thermodynamic equilibrium. The important nitrogen gas system was studied and NH₄⁺ radical was found to be the most likely nitrogen gas under equilibrium conditions.

Results from a preliminary program of collection and analysis of sublimates in the drill holes and absorbed on the silica gel tubes were used to conduct a study of the equilibrium conditions in a volcanic gas phase that included sublimate compounds. An indication of the form in which some such solids were transported was obtained. In addition the levels of condensation of the compounds in the drill holes followed that expected from the partial pressure of those substances at the temperature of the respective levels. These studies
were limited by the lack of thermodynamic data for many sublimate compounds. When these become available, the application of thermodynamics to the study of ore-body forming processes can be greatly extended.
APPENDIX I

Calculation of Gas Sample Composition by Computer

The program for calculation of the mole percent of each component in an analyzed gas sample is presented here. Fortran IV computer language was used to write the program for the IBM 7040 computer of the University of Hawaii Computing Center. The gases included are: \( H_2O, He, H_2, Ar, O_2, N_2, CH_4, CO, CO_2, H_2S \) and \( SO_2 \). The meaning of the symbols used in order of appearance in the program follows:

\[
\begin{align*}
\text{AREA}(I) &= \text{chromatogram peak area.} \\
\text{AMOLE}(I) &= \text{moles of a particular gas in the sample loop.} \\
\text{BMOLE}(I) &= \text{moles of a particular gas in the permanent or condensable gas fractions.} \\
\text{PCMOLE}(I) &= \text{mole percent of a gas in the sample.} \\
\text{AFP}(I) &= \text{mole percent corrected for air contamination.} \\
\text{CORG}(K) &= \text{moles of a particular gas corrected for air contamination.} \\
\text{FG}(K) &= \text{CORG}(K). \\
M &= \text{number of gases analyzed, excluding water.} \\
P_1 \text{ and } P_3 &= \text{pressure of air in the expansion bulb, for system volume determination.} \\
P_2 \text{ and } P_4 &= \text{pressure after expansion of air from the bulb, for system volume determination.} \\
\text{PPERM} &= \text{pressure of the permanent gases.} \\
\text{PCOND} &= \text{pressure of the condensable gases.}
\end{align*}
\]
VCOND = volume of the sampling loop.
VTUBE = volume of the breakseal tube.
WH2O = weight of water in the sample.
NOS = sample number.
V SYS = volume of the system.
VPERM = volume of the permanent gases.
TMPERM = total moles of permanent gases.
TMCOND = total moles of condensable gases.
TMH2O = total moles of water.
PCH2O = mole percent of water.
TALL = chromatogram peak height.
W  = chromatogram peak width at half-height.
ATT = recorder attenuation.
PGL = pressure of an aliquot of gas in the sample loop.
SLOPE = slope of the calibration curve for a particular gas.
SO2L = peak height for the oxidized sulfur film (SO2).
PRUN = pressure of an aliquot of the oxidized gas.
POXID = total pressure of the oxidized gas.
VOXID = volume of the oxidized gas.
AIRHE = portion of He in the sample that is to be subtracted as air contamination (similarly for AIRH2, AIRAR, etc.).
PCAIR = mole percent of air contamination.
AFG = total moles of air-free gas.
Numerical factors:

\[ 2.30686 \times 10^6 \] = the gas constant (R) in terms of degrees of rotation for pressure readings by the quartz Bourdon tube.

2500 = necessary to convert peak areas to square inches, the units used in the calibration curves. The peaks are measured with a scale of 50 units per inch.

The atmospheric ratios of He, H₂, Ar, etc., to N₂ are included in the program to determine the amount of air contamination, i.e., AIRHE, AIRH₂, AIRAR, etc. The symbol NAR may be ignored.
DIMENSION AREA(10),AMOLE(10),EMOLE(10),PCMOLE(10),AFP(10),CORG(6),
1PG(6)
4 N = 1
WRITE(6,9)
9 FORMAT(1H1,77H
1 VOLCANIC GAS ANALYSIS,///73H
2 MOLE PER CENT,///TH SAMPLE,4X,11H H20
528 11H 802 ///)
33 READ(5,6)M,P1,P2,P3,P4,PPERM,PCOND,VCOND,VLOOP,VTUBE,WH20,NOS,NAR
6 FORMAT(I2,6F7.3,F7.2,F5.2,F7.4,I4,I2)
IF(M.EQ.99)STOP
VSYS1=601.7*(P1-P2)/P2
VSYS2=601.7*(Pe-P4)/Pr
VSYS=VSYS1+VSYS2/2.
VPERM=VSYS+VTUBE
TMPERM=PPERM/VPERM/2.302E6
TCOND=PCOND*VCOND/2.302E6
TMH20=WH20/18.02
TMMGAS=TMPERM+TCOND+TMH20
PCH2O=(TMH20/TMMGAS)*100.
DO2I=1,M
REAC(5,7)TALL,W,ATT,PG1,SLOPE
7 FORMAT(2F7.1,F4.0,F7.3,E8.2)
IF(TALL.EQ.0.)EMOLE(I)=0.
IF(TALL.EQ.0.)PCMOLE(I)=0.
IF(TALL.EQ.0.)GO TO 2
IF(I.GT.7)GO TO 55
AREA(I)=TALL*W*ATT/2500.
AMOLE(I)=AREA(I)*SLOPE
EMOLE(I)=(PPERM*VPERM/(PG1*VLOOP))*AMOLE(I)
PCMOLE(I)=(EMOLE(*)/TMMGAS)*100.
GO TO 2
55 AREA(I)=TALL*W*ATT/2500.
AMOLE(I)=AREA(I)*SLOPE
BMOLE(I) = (PCOND*VCOND/(PG1*VLOOP))*AMOLE(I)
PCMOLE(I) = (BMOLE(I)/TMGAS)*100.

2 CONTINUE
READ(5,8)SO2L,W,ATT,PRUN,POXID,SLOPE,VOXID
8 FORMAT(2F7.1,F4.0,2F7.3,E8.2,F7.2)
IF(SO2L.EQ.0.) GO TO 15
SAREA = SO2L*W*ATT/2500.
SMOLE1 = SAREA*SLOPE
SMOLE2 = ((POXID*VOXID)/(PRUN*VLOOP))*SMOLE1
BMOLE(9) = BMOLE(9) + (SMOLE2/3.)*2.
BMOLE(10) = BMOLE(10) + SMOLE2/3.
PCMOLE(9) = (BMOLE(9)/TMGAS)*100.
PCMOLE(10) = (BMOLE(10)/TMGAS)*100.
15 IF(NAR.EQ.1) GO TO 11
11 AIRHE = PCMOLE(5)*2.9E-5
AIRH2 = PCMOLE(5)*6.4E-7
AIRAR = PCMOLE(5)*1.19E-2
AIRCH4 = PCMOLE(5)*2.6E-6
AIRCO2 = PCMOLE(5)*3.8E-4
PCAIR = AIRHE+AIRH2+AIRAR+AIRCH4+AIRCO2+PCMOLE(4)+PCMOLE(5)
CORG(1) = PCMOLE(1) - AIRHE
CORG(2) = PCMOLE(2) - AIRH2
CORG(3) = PCMOLE(3) - AIRAR
CORG(4) = 0.
CORG(5) = PCMOLE(6) - AIRCH4
CORG(6) = PCMOLE(8) - AIRCO2
DO 40 K = 1,6
FG(K) = 0.
IF(CORG(K).GE.0.)FG(K) = CORG(K)
40 CONTINUE
APF = FG(1)+FG(2)+FG(3)+FG(4)+FG(5)+FG(6)+PCMOLE(7)+PCMOLE(9)+PCMOLE(10)+PCMOLE(11)
APP(1) = (PCH20/APF)*100.
APP(2) = (FG(1)/APF)*100.
APP(3) = (FG(2)/APF)*100.
APP(4) = (FG(3)/APF)*100.
\[
\begin{align*}
\text{AFP}(5) &= (\text{FG}(4)/\text{AFG}) \times 100. \\
\text{AFP}(6) &= (\text{FG}(5)/\text{AFG}) \times 100. \\
\text{AFP}(7) &= (\text{PCMOLE}(7)/\text{AFG}) \times 100. \\
\text{AFP}(8) &= (\text{FG}(6)/\text{AFG}) \times 100. \\
\text{AFP}(9) &= (\text{PCMOLE}(9)/\text{AFG}) \times 100. \\
\text{AFP}(10) &= (\text{PCMOLE}(10)/\text{AFG}) \times 100.
\end{align*}
\]

GO TO 22

20 P\text{CAIR} = 0.
DO 24 K = 1, 6
\text{CORG}(K) = 0.
24 CONTINUE
DO 28 I = 1, 10
\text{AFP}(I) = 0.
28 CONTINUE
GO TO 22

WRITE(6, 10) NOS, VS\text{YS}\text{A}, \text{TMP\text{PERM}}, \text{TM\text{COND}}, \text{TM\text{GAS}}, \text{TMB20}, \text{BM\text{OLE}}, \text{PC20}, \text{PCMOLE},
1 \text{P\text{CAIR}}, \text{CORG}, \text{AFP}

10 FORMAT(1X, 14, 3X, 13HSYSTEM VOLUME, 2X, 1PE12.5, 3X, 14HMOLES PERGAS, 2 
1X, EL2.5, 3X, 14HMOLES CONDGAS, 2X, EL2.5, 3X, 15HTOTAL MOLES GAS, 2X, EL2 
2.5/3X, 5HMOLES, 3X, 1LE11.4/2X, 7HPERCENT, 2X, 1LE11.4/4X, 3HAIR/3X, OPP5. 
32, 2X, 12HCORRECT GAS, 1PE11.4, 11X, 2E11.4, 11X, E11.4//2X, 7HPERCENT, 2 
4X, 4E11.4, 11X, 6E11.4//)
N = N + 1
IF(N-6) 33, 33, 4
END
APPENDIX II

Computer Program for Calculating Chemical Equilibria in Gas Mixtures

The Fortran IV computer program used for the calculation of thermodynamic equilibrium compositions of volcanic gases is presented here. It should be noted that the program is completely general; it will work with any gas mixture. This program, originally written by Heald, has been slightly modified to handle 15 elements and 40 compounds of those elements, which requires that the IBM 360 computer be used rather than the IBM 7040, due to the insufficient "memory" of the latter machine. All symbols and terms used are defined within the program.
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DEFINITIONS OF TERMS USED IN THIS PROGRAM

LIMIT    TOTAL NO OF CALCULATIONS IN A GIVEN RUN
Q        LIMITS THE CHANGES IN MOLE NUMBERS
IMAX     MAX NO OF PHASES (=1)
NPHASE    NAME OF PHASE(GAS)
JMAX     MAX NO OF ELEMENTARY COMPONENTS IN DATA TABLE
NATOMS   NAME OF ELEMENT
ITMAX    MAX NO OF TEMPERATURES IN DATA TABLE
T        TEMP TEMP = TEMP IN DATA TABLE
IMAXL    NO OF COMPOUNDS IN TABLE
NAME     NAME OF COMPOUND IN TABLE
A(I,J)   NO OF GRAM ATOMS OF ELEMENT J IN 1 MOLE COMPOUND I
FZERO    STD GIBBS FREE ENERGY
QD       CHANGE IN Q DEFINING JUMP TOWARD EQUI COMP
QL       LOWEST VALUE OF Q
QA       PARAMETER DEFINING PRECISION OF EQUI MOLE NUMBERS
NOL      MAX NO OF ITERATIONS
LG       INDEX OF GAS PHASE
INDEX    HEADING OF CALCULATION
INDMAX   NO OF WORDS IN HEADING, 360 WORD = 4, NORM = 54 = 3 CARDS
P        PRESSURE
JR       MAX NO OF COMPONENTS IN DATA TABLE
LR       MAX NO OF PHASES IN DATA TABLE  ALWAYS = 1
IR(L)    MAX NO OF COMPOUNDS IN PHASE L
JFIX     SELECTION NO OF COMPONENTS IN DATA TABLE
LFIX     SELECTION NO OF PHASES IN CALC
IFIX     SELECTION NO OF COMPOUNDS IN CALC
Y        STARTING VALUE OF MOLE NUMBER
IDEAL(L) IDEAL SET GREATER THAN 0 TO TREAT PHASE L AS IDEAL

PROGRAM M
C PROGRAM FOR CALCULATION OF CHEMICAL EQUILIBRIUM COMPOSITIONS
C IN SYSTEMS OF UP TO 10 ELEMENTARY COMPONENTS AND UP TO 10 PHASES.
C NON-IDEALITY OF ANY OR ALL PHASES.
C NON-IDEALITY OF ANY OR ALL PHASES.

REAL*8 NAME
DIMENSION Y(45,20),YBAR(20),DEL(45,20),A(45,20,20),B(20),IMAX(20),
INDEX(140),NATOMS(20),NPHASE(20),FIDEAL(45,20),
2FZERO(45,20),BETA(45,50),PI(45,20),DEBAR(20),EXCESS(45,20),
3ALPHA(45,50),PI(45),U(20),IDEAL(20),X(45,20),W(45,20),XBAR(20),
4ALPHAV(2250)
COMMON NAME(45,20),X,EXCESS,LAC,NO,IMAX,
1 LM, Y, FZERO, A, T, P, NPHASE, IMAX, JR, QD,
2 QL, QA, NATOMS, INDEX, IDEAL, ROL, LG
C LIMIT # TOTAL NUMBER OF CALCULATIONS IN A GIVEN RUN
READ 17, LIMIT
17 FORMAT (15)
   LM = 0
10 NO = 0
    OVER = 0.
    NOTMIN = 0
    NOT = 1
C INPUT DATA PROVIDED BY SUBROUTINE INPUT
CALL INPUT
   LM = LM + L
   JMAX = JR + IMAX
   MAX = JMAX + 1
   JS = JR + 1
C CALCULATION OF MATERIAL BALANCE CONDITIONS
DO 1006 J = 1, JR
   B(J) = 0.
DO 1006 L = 1, IMAX
   IMAXL = IMAX(L)
DO 1006 I = 1, IMAX
   B(J) = B(J) + A(I,L,J) * Y(I,L)
C  CALCULATION OF FREE ENERGIES
    DO 200 L = 1, IMAX
    YBAR(L) = 0.
    IMAXL = IMAX(L)
    DO1150 I = 1, IMAXL
    YBAR(L) = YBAR(L) + Y(I,L)
1150 CONTINUE

C  CALCULATION OF FREE ENERGIES
    FTOT = 0.
    DO 200 L = 1, IMAX
    IMAXL = IMAX(L)
    DO 141 I = 1, IMAXL
141   X(I,L) = Y(I,L) / YBAR(L)
    DO 130 I = 1, IMAXL
      FTEMP = FZERO(I,L)/(1.98646*T)
      FIDEAL(I,L) = Y(I,L) *(FTEMP + ALOG(X(I,L)))
      IF (L-LG) 130, 170, 130
    170   FIDEAL(I,L) = FIDEAL(I,L) + Y(I,L) * ALOG(P)
C  CALCULATION OF NON-IDEAL CONTRIBUTIONS TO FREE ENERGIES DONE IN
C  SUBROUTINE ACTIV
C  VERSION OF ACTIV SUPPLIED HEREWITK IS A DUMMY, FOR THE PURPOSE OF
C  PERMITTING COMPIILATION OF THE PROGRAM
C  IN ACTUAL FACT, THEN THIS PROGRAM CANNOT CONSIDER NON-IDEAL
C  PHASES. WORKING VERSION OF ACTIV WILL FOLLOW LATER.
C  MUCH LATER, I FEAR.
    EXCESS(I,L) = 0.
    IF (IDEAL(L)) 142, 142, 150
142   LAC = L
    CALL ACTIV
    DO 151 I = 1, IMAXL
151   FTOT = FTOT + FIDEAL(I,L) + EXCESS(I,L)
200 CONTINUE
    IF (NOTMIN) 301, 202, 301
202 IF (NOT) 301, 301, 203
203 IF (NO-NOL) 210, 301, 301
210   NO = NO + 1
C SETTING UP OF MATRIX DEFINING SET OF SIMULTANEOUS SYMMETRIC LINEAR EQUATIONS
C
211 DO 300 K = 1, KMAX
212 DO 300 J = 1, JMAX
213 ALPHA(J,K) = 0.
220 IF (K-JR) 240, 240, 230
230 IF (K-KMAX) 250, 250, 260
240 IF (J-JR) 270, 270, 271
250 IF (J-JR) 241, 241, 300
260 IF (J-JR) 281, 281, 251
270 IF (K-J) 261, 261, 241
281 ALPHA(J,K) = ALFA(K,J)
242 GO TO 300
251 L5 = J-JR
   IMAXL = IMAX(L5)
   DO 252 I = 1, IMAXL
252 ALPHA(J,K) = ALPHA(J,K) + FIDEAL(I,L5) + EXCESS(I,L5)
   GO TO 300
261 DO 263 L = 1, IMAX
   IMAXL = IMAX(L)
   DO 263 I = 1, IMAXL
263 ALPHA(J,K) = ALPHA(J,K) + A(I,L,J) * A(I,L,K) * Y(I,L)
264 GO TO 300
271 L7 = J-JR
   IMAXL = IMAX(L7)
272 DO 273 I = 1, IMAXL
273 ALPHA(J,K) = ALPHA(J,K) + A(I,L7,K) * Y(I,L7)
274 GO TO 300
281 ALPHA(J,K) = B(J)
282 DO 284 L = 1, IMAX
   IMAXL = IMAX(L)
283 DO 284 I = 1, IMAXL
284 ALPHA(J,K) = ALPHA(J,K) + A(I,L,J) *(FIDEAL(I,L) + EXCESS(I,L))
300 CONTINUE
   GO TO 18
OVER = 1.
18 IF (OVER) 12, 12, 14
C SOLUTION OF SIMULTANEOUS EQUATIONS BY SUBROUTINE SIMQ
C STORE COEFFICIENT PART OF MATRIX ALPHA IN VECTOR ALPHAV
12 CALL ARRAY (2, JMAX, JMAX, 45, 50, ALPHAV, ALPHA)
C STORE CONSTANT COLUMN OF ALPHA IN VECTOR PI AS NEEDED BY SIMQ
DO 320 J = 1, JMAX
320 PI(J) = ALPHA(J, KMAX)
   CALL SIMQ (ALPHAV, PI, JMAX, NOTMIN)
   IF (NOTMIN - 1) 9330, 9340, 9330
9340 PRINT 340
   GO TO 16
.340 FORMAT (1HO, 15HSINGULAR MATRIX)
9330 CONTINUE
13 DO 523 J = JS, JMAX
522 LX = J - JR
523 U(LX) = PI(J)
524 Q = 1.
C CALCULATION OF CHANGES IN MOLE NUMBERS
C THE PARAMETER Q LIMITS THE CHANGES IN MOLE NUMBERS SO THAT
C 1) ALL MOLE NUMBERS ARE POSITIVE
C 2) THE MINIMUM IN THE TOTAL FREE ENERGY IS NOT PASSED
512 DO 600 L = 1, IMAX
541 DEBAR(L) = YBAR(L) + (U(L) - 1.)
   IMAXL = IMAX(L)
513 DO 600 I = 1, IMAXL
515 PIJ(I, L) = 0.
530 DO 531 J = 1, JR
531 PIJ(I, L) = PIJ(I, L) + PI(J) * A(I, L, J)
   DEL(I, L) = -FIDEAL(I, L) - EXCESS(I, L) + Y(I, L) * (PIJ(I, L) - 1.) + U(L - 1)
550 IF (Y(I, L) + Q * DEL(I, L)) 560, 560, 600
560 Q = Q * (L - QD)
561 IF (Q - QL) 9964, 550, 550
600 CONTINUE
610 DERFQ = 0.
620 DO 653 L = 1, IMAX
   IMAXL = IMAX(L)
630 DO 653 I = 1, IMAXL
640 QUOT = (Y(I,L) + Q*DEL(I,L)) / (YBAR(L) + Q*DEBAR(L))
642 IF (QUOT.GT.0.) GO TO 643
   EXP = 0.
   EXP = (QUOT-1.) - (((QUOT - 1.)*2)/2.) + (((QUOT - 1.)*3)/3.)
   DERFQ = DERFQ + DEL(I,L) * (FZERO(I,L)/(1.98646 * T) + EXP)
   GO TO 651
643 DERFQ = DERFQ + DEL(I,L) * (FZERO(I,L)/(1.98646*T) + ALOG(QUOT))
651 IF (I-LG) 653, 652, 653
652 DERFQ = DERFQ + DEL(I,L) * ALOG (P)
653 CONTINUE
660 IF (DERFQ) 711, 670, 670
670 Q = Q * (1. - QD)
680 IF (Q-QL) 9965, 610, 610
711 NOT = 0
CALCULATION OF NEXT-IMPROVED MOLE NUMBERS
710 DO 800 L = 1, IMAX
720 YBAR(L) = YBAR(L) + Q*DEBAR(L)
   IMAXL = IMAX(L)
730 DO 800 I = 1, IMAXL
740 Y(I,L) = Y(I,L) + Q*DEL(I,L)
760 ABEL = Q * ABS (DEL(I,L)) - QA * Y(I,L)
770 IF (ABEL) 800, 800, 780
780 NOT = NOT + 1
800 CONTINUE
GO TO 20
9968 PRINT 968, INDEX(L), I, L
968 FORMAT (1HL, A5,22H DIVISION BY ZERO, I = , 13, 4HL =, 13)
   NOTMIN = 1
GO TO 20
9969 PRINT 969, INDEX(1), I, L, QUOT
969 FORMAT (1HL, A5, 26H NEGATIVE ARGUMENT OF LOGARITHM, I = , 13, 4H L
1=, 13/10H QUOTIENT = , 1PE12.4)
   NOTMIN = 1
   GO TO 20
9964 PRINT 964, INDEX(1), I, L, DEL(I, L)
964 FORMAT (1HL, A5, 26H NEGATIVE MOLE NUMBER, I = , 13, 4H L =, 13,
1 6H DEL = , 1PE12.4)
9965 NOTMIN = -1
20 IF (NOTMIN) 11, 11, 16
920 FORMAT (1H/(1X, 18A4))
921 FORMAT (1HO, 10HGRAM ATOMS/ ( A4, 1X, 1PE12.4))
922 FORMAT (1HO, 13H TEMPERATURE = , F10.3, 2X, 14H DEGREES KELVIN )
923 FORMAT (1HO, 10H PRESSURE = , F10.3, 2X, 11H ATMOSPHERES )
924 FORMAT (1HO, 9H ITERATION, I5)
925 FORMAT (1HO, 8HLAMBD A = , F10.7 )
926 FORMAT (1HO, A4, 6X, 16H PHASE FRACTION = , 1PE12.4/3X, 8HC OMP OUND
   IND , 9X, 11H MOLE NUMBER, 7X, 13H MOLE FRACTION , 3X, 17H LOG MOLE PR
   2ACTION )
927 FORMAT (1H, 2X, A8, 1PE20.4, OPF16.5)
934 FORMAT (1HO, 19HTOTAL FREE ENERGY = , 1PE20.7)
935 FORMAT (1HO, A4/3X, 8HC OMP OUND, 3X, 17H IDEAL FREE ENERGY , 2X,
1 18H EXCESS FREE ENERGY )
928 FORMAT (1H, 2X, A8, 1PE20.4)
931 FORMAT (1HO, 23H UNKNOWN MULTIPLIERS, PI )/(1PE24.4)
932 FORMAT (1HO, 22H UNKNOWN MULTIPLIERS, U/ (1PE24.4))
933 FORMAT (1HO, 40H MOLE NUMBERS STILL CHANGING BY MORE THAN , F5.2,
18H PERCENT , 15)
936 FORMAT (1HO, A4/2X, 8H COMPOUND , 2X, 23H CHANGES IN MOLE NUMBER
18)
937 FORMAT (1H, 2X, A8, 1PE25.4)
14 YTOT = 0.
   QAX = 100. * QA
DO 9935 L = 1, LMAX
YTOT = YTOT + YBAR(L)
IMAXL = IMAX(L)
DO 9935 I = 1, IMAXL
W(I,L) = ALOG10(X(I,L))
9935 CONTINUE
DO 9936 L = 1, LMAX
XBAR(L) = YBAR(L) / YTOT
9936 CONTINUE

C PRINT-OUT OF THE ANSWERS WILL OCCUR IF ANY OF THE FOLLOWING
C CONDITIONS ARE SATISFIED
C
C 1) ITERATION NUMBER REACHES MAXIMUM ALLOWED VALUE
C 2) NO MOLE NUMBER CHANGES BY MORE THAN A FRACTION QA OF ITS
C PREVIOUS VALUE
C 3) ANY FURTHER CHANGE IN THE MOLE NUMBERS WOULD RESULT IN
C PASSING THE MINIMUM POINT FOR TOTAL FREE ENERGY
C 4) AN ERROR CONDITION (I.E., DIVISION BY ZERO) OCCURS
C IF CONDITIONS 2) OR 3) ARE SATISFIED, THE EQUILIBRIUM COMPOSITION
C IS OBTAINED IN THE ANSWERS
PRINT 920, (INDEX(JH), JH = 1, INIMAX)
PRINT 921, (NATOMS(J), B(J), J = 1, JR)
PRINT 922, T
PRINT 923, P
PRINT 924, NO
PRINT 925, Q
PRINT 933, QAX, NOT
DO 1 L = 1, LMAX
IMAXL = IMAX(L)
PRINT 926, NPHASE(L), XBAR(L)
PRINT 927, (NAME(I,L), Y(I,L), X(I,L), W(I,L), I = 1, IMAXL)
1 CONTINUE
PRINT 934, FTOT
DO 1261 L=1, LMAX
IMAXL = IMAX(L)
DO 1262 I = 1, IMAXL
1262 PUNCH 1260, T, NAME(I,L), W(I,L)
1260 FORMAT(5X, F5.0, 3X, A8, 4X, F16.5)
PRINT 1263
1263 FORMAT (5X, 23HCARDS HAVE BEEN PUNCHED)
1261 CONTINUE
   DO 2 L = 1, IMAXL
   IMAXL = IMAX(L)
   PRINT 935, NPHASE(L)
   PRINT 928, (NAME(I,L), FIDEAL(I,L), EXCESS(I,L), I = 1, IMAXL)
2 CONTINUE
   PRINT 931, (PI(J), J = 1, JR)
   PRINT 932, (U(L), L = 1, IMAXL)
   IF (NOTMIN) 4, 16, 4
   4 DO 5 L = 1, IMAXL
   IMAXL = IMAX(L)
   PRINT 936, NPHASE(L)
   PRINT 937, (NAME(I,L), DEL(I,L), I = 1, IMAXL)
5 CONTINUE
16 IF (LM-LIMIT) 10, 15, 15
15 STOP
END

C SUBROUTINE INPUT PART OF PROGRAM M
C SUBROUTINE FOR READING IN INPUT DATA
C STANDARD FREE ENERGIES IN DATA TABLE, WITH PROVISION FOR LINEAR
C TEMPERATURE INTERPOLATION
C SUBROUTINE INPUT
REAL*8 NAME, LAME
DIMENSION T(20), NPHASE(20), A(50, 20), NAME(50), FZERO(45, 50),
INATOMS(20), INDEX(140), JFIX(20), LFIX(20), IR(20), IFXI(45, 20),
2Y(45, 20), IPHASE(20), FZAP(45, 20), AB(45, 20), 20.
COMMON LAM((45,20),FAKE(90,20),IFAKE(2))

1 JR, QD, QL, QA, LATOMS, INDEX, IDEAL, NOL, LG

C I MAX = MAXIMUM NUMBER OF PHASES IN DATA TABLE
C NPHASE = NAME OF PHASE
C J MAX = MAXIMUM NUMBER OF ELEMENTARY COMPONENTS IN DATA TABLE
C NATOMS = NAME OF ELEMENT
C ITMAX = MAX. NO. OF TEMPERATURES IN TABLE. T = TEMPERATURE
C IMAXLE = NO. OF COMPOUNDS IN TABLE
C NAME = NAME OF COMPOUND IN TABLE
C A(I,J) = NO. OF GRAM ATOMS OF ELEMENT J IN 1 MOLE OF COMPOUND I
C FZERO = STANDARD GIBBS FREE ENERGY
C QD = CHANGE IN PARAMETER Q DEFINING EXTENT OF "JUMP" TOWARD
C EQUILIBRIUM COMPOSITION (ANSWER)
C Q L = LOWEST ALLOWABLE VALUE OF Q
C QA = PARAMETER DEFINING PRECISION OF EQUILIBRIUM MOLE NUMBERS
C NOL = MAXIMUM NUMBER OF ITERATIONS
C LG = INDEX OF GAS PHASE

100 READ 7, I MAX, (NPHASE(L), L = 1, I MAX)
100 READ 7, J MAX, (NATOMS(J), J = 1, J MAX)
9 READ 9, ITMAX
9 READ 2, (T(IT), IT = 1, ITMAX)
9 READ 9, IMAXLE
DO 110 I = 1, IMAXLE
110 READ 4, NAME(I), (A(I,J), J = 1, J MAX)
.210 READ 21,(FZERO(IT,I), IT = 1, ITMAX)
22 READ 22, QD, QL, QA, NOL, LG
C ABOVE DATA READ IN ONLY ONCE. FOLLOWING ARE NEEDED FOR EACH
C SEPARATE CALCULATION IN A GIVEN RUN
C INDEX = HEADING OF CALCULATION. INDMAK = NO. OF WORDS IN
C HEADING (WORD = 5 CHARACTERS, INCLUDING BLANKS)
C TEMP = TEMPERATURE. P = PRESSURE
C JR, LR = MAX. NO. OF COMPONENTS, PHASES IN CALCULATION
C IR(l) = MAX. NO. OF COMPOUNDS IN PHASE L
C JFIX, LFIX, IFIX = SELECTION NOS. FOR COMPONENTS, PHASES,
C COMPOUNDS IN A GIVEN CALCULATION
C Y = STARTING VALUE OF MOLE NUMBER IN A GIVEN CALCULATION
C IN ORDER TO TREAT PHASE L AS IDEAL, SET IDEAL(L) GREATER THAN ZERO

200 READ 9, INDMAX
READ 5, (INDEX(IND), IND = 1, INDMAX)
READ 11, TEMP, P, ISAME
IF (ISAME) 250, 250, 220

250 READ 8, JR, (JFIX(J), J = 1, JR)
READ 9, LR
DO 210 L = 1, LR
READ 6, LFIX(L), IR(L), IDEAL(L)
IRL = IR(L)
READ 10, (IFIX(I,L), Y(I,L), I = 1, IRL)

210 CONTINUE

220 DO 212 IT = 1, ITMAX
IF (T(IT) - TEMP) 212, 211, 211

211 IDIF = TEMP - T(IT)
IDIF = IT
GO TO 300

212 CONTINUE

300 DO 310 LA = 1, LR
LB = LFIX(LA)
LPHASE(LA) = NPHASE(LB)
IRL = IR(LA)
DO 310 IA = 1, IRL
IB = IFIX(IA,LA)
NAME(IA,LA) = NAME(IB)
FZAP(IA,LA) = FZERO(IDIF,IB) + TDIF * (FZERO(IDIF,IB) -
1 FZERO(IDIF-1, IB))
DO 310 JA = 1, JR
JB = JFIX(JA)
AB(IA,LA,JA) = A(IB,JB)

310 CONTINUE
DO 320 JA = 1, JR
JB = JFIX(JA)
320 LATOMS(JA) = NATOMS(JB)
RETURN
2 FORMAT (7F10.6)
4 FORMAT (A8, 1X, 15F3.2)
5 FORMAT (18A4)
6 FORMAT (315)
7 FORMAT (I4,17A4)
8 FORMAT (1614)
9 FORMAT (I5)
10 FORMAT (I5,5X,F10.9,I5,5X,F10.9,I5,5X,F10.9)
11 FORMAT (F10.6, F10.9, I10)
21 FORMAT (7F10.3)
22 FORMAT (3F10.9, 215)
END

C SUBROUTINE ACTIV (PART OF PROGRAM M)
C DUMMY VERSION, TO PERMIT OPERATION OF MAIN PROGRAM.
SUBROUTINE ACTIV
REAL*8 NAME
DIMENSION Y(45,20), FREE(45,20), IMAX(20)
COMMON NAME(45,20), Y, FREE, L, N, IMAX
IF (N) 10, 10, 20
10 READ 1,ICONST
CONST=ICONST
1 FORMAT (15)
20 IMAXL = IMAX(L)
DO 21 I = 1, IMAXL
21 FREE(I,L) = Y(I,L) * CONST
RETURN
END
SUBROUTINE ARRAY

PURPOSE

CONVERT DATA ARRAY FROM SINGLE TO DOUBLE DIMENSION OR VICE VERSA. THIS SUBROUTINE IS USED TO LINK THE USER PROGRAM WHICH HAS DOUBLE DIMENSION ARRAYS AND THE SSP SUBROUTINES WHICH OPERATE ON ARRAYS OF DATA IN A VECTOR FASHION.

USAGE

CALL ARRAY (MODE, I, J, N, M, S, D)

DESCRIPTION OF PARAMETERS

MODE - CODE INDICATING TYPE OF CONVERSION

1 - FROM SINGLE TO DOUBLE DIMENSION
2 - FROM DOUBLE TO SINGLE DIMENSION

I - NUMBER OF ROWS IN ACTUAL DATA MATRIX

J - NUMBER OF COLUMNS IN ACTUAL DATA MATRIX

N - NUMBER OF ROWS SPECIFIED FOR THE MATRIX D IN
DIMENSION STATEMENT

M - NUMBER OF COLUMNS SPECIFIED FOR THE MATRIX D IN
DIMENSION STATEMENT

S - IF MODE=1, THIS VECTOR CONTAINS, AS INPUT, A DATA
MATRIX OF SIZE I BY J IN CONSECUTIVE LOCATIONS
COLUMN-WISE. IF MODE=2, IT CONTAINS A DATA MATRIX
OF THE SAME SIZE AS OUTPUT. THE LENGTH OF VECTOR S
IS LJ, WHERE LJ=I*J.

D - IF MODE=1, THIS MATRIX (N BY M) CONTAINS, AS OUTPUT,
A DATA MATRIX OF SIZE I BY J IN FIRST I ROWS AND
J COLUMNS. IF MODE=2, IT CONTAINS A DATA MATRIX OF
THE SAME SIZE AS INPUT.
REMARKS
VECTOR S CAN BE IN THE SAME LOCATION AS MATRIX D. VECTOR S IS REFERRED AS A MATRIX IN OTHER SSP ROUTINES, SINCE IT CONTAINS A DATA MATRIX.
THIS SUBROUTINE CONVERTS ONLY GENERAL DATA MATRICES (STORAGE MODE OF O).

SUBROUTINES AND FUNCTION SUBROUTINES REQUIRED
NONE

METHOD
REFER TO THE DISCUSSION ON VARIABLE DATA SIZE IN THE SECTION DESCRIBING OVERALL RULES FOR USAGE IN THIS MANUAL.

SUBROUTINE ARRAY (MODE,I,J,N,M,S,D)
DIMENSION S(1),D(1)

NI=N-1

TEST TYPE OF CONVERSION

IF(MODE=1) 100, 100, 120

CONVERT FROM SINGLE TO DOUBLE DIMENSION

100 IJ=I*J+1
NM=N*J+1
DO 110 K=1,J
NM=NM-NI
DO 110 L=1,I
LI=LJ-1
NM=NM-1

IT0
SUBROUTINE SIMQ

PURPOSE
OBTAIN SOLUTION OF A SET OF SIMULTANEOUS LINEAR EQUATIONS, 
$\mathbf{A}\mathbf{x} = \mathbf{b}$

USAGE
CALL SIMQ(A,B,N,KS)

DESCRIPTION OF PARAMETERS
A - MATRIX OF COEFFICIENTS STORED COLUMNWISE. THESE ARE DESTROYED IN THE COMPUTATION. THE SIZE OF MATRIX A IS N BY N.

B - VECTOR OF ORIGINAL CONSTANTS (LENGTH N). THESE ARE REPLACED BY FINAL SOLUTION VALUES, VECTOR X.

N - NUMBER OF EQUATIONS AND VARIABLES

KS - OUTPUT DIGIT 0 FOR A NORMAL SOLUTION
1 FOR A SINGULAR SET OF EQUATIONS

REMARKS
MATRIX A MUST BE GENERAL.
IF MATRIX IS SINGULAR, SOLUTION VALUES ARE MEANINGLESS.
AN ALTERNATIVE SOLUTION MAY BE OBTAINED BY USING MATRIX
INVERSION(MINV) AND MATRIX PRODUCT (GMPRD).

SUBROUTINES AND FUNCTION SUBPROGRAMS REQUIRED
NONE

METHOD
METHOD OF SOLUTION IS BY ELIMINATION USING LARGEST PIVOTAL
DIVISOR. EACH STAGE OF ELIMINATION CONSISTS OF INTERCHANGING
ROWS WHEN NECESSARY TO AVOID DIVISION BY ZERO OR SMALL
ELEMENTS.
THE FORWARD SOLUTION TO OBTAIN VARIABLE N IS DONE IN
N STAGES. THE BACK SOLUTION FOR THE OTHER VARIABLES IS
CALCULATED BY SUCCESSIVE SUBSTITUTIONS. FINAL SOLUTION
VALUES ARE DEVELOPED IN VECTOR B, WITH VARIABLE 1 IN B(1),
VARIABLE 2 IN B(2),........, VARIABLE N IN B(N).
IF NO PIVOT CAN BE FOUND EXCEEDING A TOLERANCE OF 0.0,
THE MATRIX IS CONSIDERED SINGULAR AND KS IS SET TO 1. THIS
TOLERANCE CAN BE MODIFIED BY REPLACING THE FIRST STATEMENT.

SUBROUTINE SIMQ(A,B,N,KS)
DIMENSION(A(1),B(1))

FORWARD SOLUTION

TOL = 1.0E-20
KS = 0
JJ = N
DO 65 J=1,N
JY=J+1
JJ=JJ+H+1
BIGA=0
IT=JJ-J
DO 30 I=J,N

SEARCH FOR MAXIMUM COEFFICIENT IN COLUMN

IJ=IT+I
IF(ABS(BIGA)-ABS(A(IJ))) 20,30,30
20 BIGA=A(IJ)
IMAX=I

TEST FOR PIVOT LESS THAN TOLERANCE (SINGULAR MATRIX)

30 CONTINUE
IF(ABS(BIGA)-TOL) 35,35,40
35 KB=1
PRINT 10, LJ, BIGA
10 FORMAT (1H0,5Hlj = , 15, 5X, 7HBiga = , 1PE24.4)
RETURN

INTERCHANGE ROWS IF NECESSARY

40 II=J+H*(J-2)
IT=IMAX-J
DO 50 K=J,N
II=II+N
I2=II+IT
SAVE=A(I2)
A(I2)=A(I1)
A(I1)=SAVE
50 CONTINUE
DIVIDE EQUATION BY LEADING COEFFICIENT

50 A(II)=A(II)/BIGA
SAVE=B(IMAX)
B(IMAX)=B(J)
B(J)=SAVE/BIGA

ELIMINATE NEXT VARIABLE

IF(J-N) 55,70,55
55 IQS=N*(J-1)
DO 65 IX=JY,N
IXJ=IQS+IX
IT=J-IX
DO 60 JX=JY,N
IXJX=N*(JX-1)+IX
JJX=IXJX+IT
60 A(IXJX)=A(IXJX)-(A(IXJ)*A(JJX))
65 B(IX)=B(IX)-(B(J)*A(IXJ))

BACK SOLUTION

70 NY=N-1
IT=N*NY
DO 80 J=1,NY
IA=IT-J
IB=N-J
IC=N
DO 80 K=1,J
B(IB)=B(IB)-A(IA)*B(IC)
LA=IA-N
80 IC=IC-1
RETURN
END
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