DETERMINATION OF THE MASS RATIO OF THE ISOTOPES OF CARBON AND HYDROGEN PRESENT IN VOLCANIC EFFLUVIA

A THESIS SUBMITTED TO THE GRADUATE DIVISION OF THE UNIVERSITY OF HAWAII IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE

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I INTRODUCTION

The concept that the earth has a molten interior was once widely accepted and is still strongly held in the popular mind. However, among geologists, the most widely held present day view on the structure of the earth and on volcanism may be briefly stated as follows. It is thought that the earth consists of a nickel-iron core about 3500 kilometers in diameter surrounded by a silicate shell. The rocky shell is divided into layers that are seismically rather well defined. They may be characterized as (1) an inner layer or mantle of a rigid but weak glassy layer and (2) the outside layer or crust which contains the familiar crystalline rocks and extends to a depth of perhaps 100 kilometers. The inner layer is considered to be at a temperature far in excess of the melting point of its constituents (2000° - 5000° C), as such things would be conceived at the surface of the earth. However, because of the excessive pressures that exist deep within the earth, the rock is in a rigid, glassy state.

The crust of the earth is in no sense petrified and immobile but is a field of movement and action forever faulting and cracking, heaving and sinking, shrinking and expanding, for example, as in earthquakes. As a consequence of such disruptions, it is conceived that the pressure is relieved on the deep-seated glassy layers which are thereby liquified and occupy such cracks or faults as may be available. Outpourings of liquid rock, known as lava, may occur through such faults giving us tremendous areas of plateau basalts such as the Deccan in India and the Columbia plateau in our own Northwest. Usually however the lava is conceived to enter the fault and therein to maintain lava or magma chambers which in turn feed
volcanoes along the fault line, hence the lines or chains of volcanic peaks or islands. Emphasis has been placed on the rocky silicate magma in the above picture but it logically follows that the minor elements and volatiles that form a part of the lava will follow it through its course. Indeed it is the escape of the volatiles that lends much of the spectacular character to volcanic eruptions. The present research was undertaken as an effort to add a grain of evidence to support or disprove these ideas.

It was felt that with the increase of our knowledge of isotopes and of their relative abundance, the time was ripe to attempt to apply isotopic studies to the problems of volcanism. Also, the better understanding of the processes that lead to the separation of the isotopes of the elements and the development and refinement of tools for the determination of isotopic abundances were encouragements for the pursuit of the work. It was believed that either (1) the presence of unique ratios of the isotopes of the elements present might be used as "tracers" as to the source of the elements, or (2) the graded changes in the abundances of the isotopes due to volcanic processes could be interpreted in terms of the nature of such processes. For the former it was felt that isotopic ratios differing from or similar to surface values would disprove or prove the surface origin of some of the volcanic gases and rocks, a subject of some controversy. As to the use of graded isotopic differentiation, it was felt that such gradations might occur as a result of any of the following processes: (1) diffusion differentiation in the course of time that would be exhibited as differences in the isotopic ratios between ancient and more recent lavas; (2) gravitational differentiation, such as is supposed
to occur for rocks in the magma chamber, might also have a concomitant isotopic separation; and (3) when crystallization of rock components occurs in the cooling magma it might be expected that differences in the isotopic abundances might be manifest between the separated crystalline material, phenocrysts, and the groundmass of the rock. The plan of this thesis was to investigate all of these points. The \( \frac{\text{H}_2}{\text{H}_1} \) ratio in the water vapor and the \( \frac{\text{C}^{13}}{\text{C}^{12}} \) ratio of the carbon dioxide in the volcanic volatiles were chosen as the isotopic ratios to be investigated in this research. It was felt that these would be most revealing because these isotopes are known to be readily differentiated in nature and because of the ease of handling of the hydrogen and carbon dioxide which would be used in mass spectrometer determinations.\(^1\)

The isotopic ratio determinations were done with a mass spectrometer by the Consolidated Engineering Corporation in Pasadena, California.

Because the general procedure rendered it feasible, during the separation of the volatiles for the isotopic abundance determinations of the hydrogen and carbon present, the analysis of the gases present in the volcanic rocks and effluvia was carried on. It was considered that these analyses might throw some light on the genesis of volcanic rocks or effluvia.
(1) The Volcano Problem

Men have viewed volcanic eruption with terror and have usually linked them with the displeasure of their gods. Certainly an eruption is one of the most awesome spectacles of nature. Men could not view such a phenomenon without being struck by the thought of the tremendous forces at work within the earth. When they were able to overcome their superstitious dread of volcanoes their observations gave rise to what might be called the first scientific geological hypothesis. They saw the incandescent outpourings of lava as evidence that the interior of the earth was at a sufficiently high temperature to produce molten rock and hot ash. In turn, they were led to speculate on the source of this heat and ultimately on the history of the earth that would account for such a hot interior.

Here was the first evidence of a high temperature in the interior of the earth. A large part of volcanological literature deals with the superficial and descriptive aspects of eruptions and volcanoes, such, for example, as the frequency and types of eruption, the size and shape of cones and craters, and their geographical distribution. The essential problems of volcanism stem from the hypothesis almost universally held that present day volcanic activity is the direct or indirect result of injection of lava into the crust from the hot basaltic layer that underlies the crust of the earth. The problems that this theory evokes may be listed as follows:

1. The reason for the localization and the opening of the vent through which the passage of the magma takes place.

2. The explanation of the persistence of activity at intervals
through thousands of years.

3. The reason for the intermittent activity.

4. The origin of the heat of volcanism.

5. The explanation of the stages of eruptive evolution of volcanoes, and the changes in the character of the lava emitted.

The effort to solve these problems has been the consuming passion of a whole generation of volcanologists such as Perret and Jaggar. Attempts to answer one or all have given rise to a multitude of hypotheses, which, because of the nature of the problems, are extremely difficult of proof or disproof.

Magmaic injection and passage through the crust is thought to occur through fissures in the earth's crust. The source of the cracking of the crust has been sought in downwarping under loads of sediment, geosynclines, in the classical theory of the contraction of the earth, in continental migration and tensions of speculative origin in the crust due for example, to convection, differential radioactivity or decrease in the velocity of rotation of the earth. The upwelling of magma in the fissures has been variously ascribed to pressure due to the weight of the adjacent crust and to the kinetic action of the release and motion of imprisoned gas.

The studies of Jaggar at the Hawaiian volcano, Kilauea, conducted over a period of years, have been useful in supplying data to afford an explanation of the persistence of volcanic activity. Both gas fluxing and liquid lava convection have been invoked as suppliers of heat to keep the volcanic furnace going. The stopping of the lava column by conductive and radiative cooling has been repeatedly observed in active volcanoes and accounts for the ensuing dormancy. The revival of activity has been ascribed to the build-up of gas pressure and to the
purging action of the hot gas beneath the stopping plug. Both the residual heat from the primitive molten earth, and the heat of radioactivity, or, more probably, a combination of these, have been held responsible for the source of the heat concomitant with eruptions. Finally, to explain the evolution and ageing of volcanoes and the accompanying rock types, it was postulated that the volcano has its "roots" in a magma chamber that is either an abyssolith, giving the volcano a long life and intense activity, or a smaller, parasitic magma body, laccolith, with a shorter and less energetic life for the volcano. The evolutionary stage of the volcano depends on the age and degree of cooling of its magma chamber, and the difference in lava types is a consequence of magmatic differentiation in the chamber. An excellent summary of Hawaiian rock types and hypothesis as to their source was given by MacDonald in a recent paper.

Many subsidiary problems in volcanism arise as a consequence of the hypotheses herein outlined. The question whether or not the gases in magma have their origin from deep within the earth or from the atmosphere, for one, would bear further scrutiny.

(2) **Gases in Rocks**

From a very early date attention was focused on the gases in rocks by the decrepitation of rock crystals and gems for upon heating such stones the evolution of gas bubbles was evident. Sir Humphrey Davy, Brewster, Simler, and Sorby all directed their attention to the isolation and chemical analysis of the gases enclosed in crystal bubbles and found them to be largely water and carbon dioxide. With the investigation of the gases in meteorites by Graham a broader field was opened up. He subjected the samples to heat under a vacuum
and analyzed the gases given off by the samples. Subsequent investigators have tended to use this method almost exclusively, variations being due to improvement in materials and apparatus for work in vacuum and at high temperatures. Chamberlin was one of the leaders in the investigations of gases in rocks of a general nature by the hot extractive method. He gave an excellent resume and concluded that the gases found were either the result of reactions between the components of the rock at the temperature of extraction or were in solution in the body of the rock, with a very minor portion being due to bubble inclusions17. Subsequently the leader in this field of investigation was E. S. Shepherd18 who commented on the generally unsatisfactory nature of the results of such studies and the difficulty of interpretation. Recently Nash and Baxter19 have abandoned the hot extractive method and have used a cold solution technique to release and investigate the gases in meteorites.

(3) Isotopes in Geology

The investigation of the isotopic composition of the elements has been proceeding at an increasing pace in recent years with the result that the literature on this topic is very extensive. An excellent review and report on the current status of the subject have been made by Bainbridge and Miln20. This section will be restricted to a consideration of the development of our present knowledge with respect to the variations in the relative abundances of the isotopes of hydrogen and carbon, the atoms of concern in this research. With respect to isotopes in geology, an excellent and very pertinent review and consideration of current and future problems has been published very recently by Ingerson21.
Urey and Greiff\textsuperscript{22} were the first to show from theoretical considerations that the isotopes of hydrogen, lithium, boron, carbon, nitrogen and oxygen was expected to differ slightly in their chemical properties and that a slight fractionation of the isotopes of these light elements was expected to occur in nature. These early predictions have been verified by many experimenters and recent work has indicated that the variations in the isotopic abundances of the elements are more widespread than was previously thought\textsuperscript{23}.

The early work on hydrogen isotopes was done by the very exact measurement of the variation in density of water containing the hydrogen in question. The assumption was that the variations in the density were entirely due to variations in the H\textsubscript{2}/H\textsubscript{1} ratio. A comprehensive review and compilation of data was given by Kirshenbaum\textsuperscript{24} along with a detailed description of both the density and mass spectrometric method of measurement of the isotopic abundance of hydrogen. Measurement of the ratio of H\textsubscript{2}/H\textsubscript{1} has been made for water from many natural environments including rivers, oceans, lakes, glaciers, stars, hydrates, and fumaroles\textsuperscript{25}. The best value for this ratio was 6700 as selected from density determinations of water by Bainbridge and Nier\textsuperscript{26}.

The first investigation of the variability of the ratio of the stable isotopes of carbon, C\textsuperscript{13}/C\textsuperscript{12}, in nature was made by Nier and Gulbranson\textsuperscript{27} and was continued by Murphy and Nier\textsuperscript{28}. They found a concentration of the heavy isotope in carbonates, and of the lighter one in biological material, such as wood, and particularly in petroleum. No age effect was noted. A large amount of data had accumulated since that time, but had all tended to uphold this basic pattern\textsuperscript{29}. The newer
work of Craig\textsuperscript{30} reporting 300 new measurements made with the ratio type mass spectrometer was particularly interesting. In the main the work of Hie and his coworkers was confirmed. Pertinent to the present research were his results on igneous rocks which were high in the lighter isotope, carbon-12, and Yellowstone Park gases, methane, high in the lighter isotope and carbon dioxide, high in the heavier isotope.
The gases used for the experiments, except the Sulfur Bank "volcanic" gas, were obtained by melting weighed lava rock samples under high vacuum. The gases were stripped of the water vapor and carbon dioxide for mass ratio determination of the stable isotopes of carbon and hydrogen. Both were purified by low temperature distillation; the carbon dioxide by liquid air and the water vapor by a dry ice-acetone mixture as coolants. The water vapor was treated further with zinc at about 450° C for conversion to hydrogen gas before bottling. The carbon dioxide was purified by total distillation before being further treated before bottling.

A small amount of the gases was analyzed by a micro method. It consisted of measuring the pressures due to each component by condensing them with appropriate coolants, such as liquid air for carbon dioxide. The noncondensables, such as carbon monoxide and hydrogen, were determined later in the same sample by oxidizing them to carbon dioxide and water vapor, respectively. Their percentages were then determined as was previously done for the other condensables.

In addition it was decided to collect and purify carbon dioxide from the Sulfur Bank, Hawaii National Park, for carbon-14 determinations.

(1) Collection of Samples

The samples were obtained with the aid of professional geologists, E. Ingerson* and G. A. MacDonald**. Consequently, they were unweathered as possible and representative samples. The identification of the samples was also made by the two geologists.

Chief, Division of Petrology and Geochemistry

* U. S. Geological Survey and a visitor in the islands during the 1952 eruption of Kilauea.

** Director of Hawaii Volcano Observatory, U.S. Geological Survey.
The Sulfur Bank gas collections were made by a method similar to that described by Ballard and Payne (1940). The source of the gas was the manifold atop the three pipes which were sunk 18 to 50 feet deep at the Sulfur Bank in 1922. The collections were made by drawing the gases through a safety bottle to collect water vapor and through a sample collecting tube by means of a manually operated suction pump. Pumping was continued until all the air in the sample tube was replaced by the Sulfur Bank gases.

For the carbon-14 determination, a separate collection was made since the two grams of carbon that were required for the determination could not be obtained by the method described above. The gases from the Sulfur Bank were drawn through a series of freeze-out traps by the pump. The carbon dioxide was collected in a high pressure cylinder by freezing it out and condensing it within the cylinder with liquid air.

See insert 4.

(2) Description of Apparatus

The entire apparatus was an integral unit with distinct sections having definite functions. It was utilized primarily for the preparation of volatiles and the analysis of gaseous mixtures. Figure 1 is a schematic diagram of the various sections in assembled form, and Plate 1 is a photograph of the entire apparatus.

The basic vacuum was maintained through a manifold by a diffusion pump backed by an oil pump as shown by Figure 1 and Plate 1. This system maintained a vacuum of about 0.1 of a micron in the apparatus.

The next section, shown in Figure 2 and Plate 2, was the sample degassing system where the lava was heated and melted under vacuum. A transparent quartz tube was used as the furnace chamber in order to withstand the high temperatures involved. The water-jacketed ground
joint connected the quartz to the glass system and facilitated the changing of samples and cleaning of the tube. An induction furnace was necessary in order to heat the sample to the high temperatures that were used. As an induction furnace heats only conductors, the lava samples were melted in a platinum crucible. After extensive tests platinum was found to be a suitable crucible material in that it could withstand high temperatures, did not react appreciably with the melt, and could be repaired in case of burnout or melting. The temperature was determined with a filament type optical pyrometer, obtained from Kees and Northrup Co., Philadelphia, focused through the viewing window. A mercury diffusion pump maintained a high vacuum in the furnace tube and pumped the gases into the water vapor measuring section, as shown by Figure 3, which consisted of a trap surrounded by a dry ice-acetone mixture as coolant and a two-liquid manometer. This type of manometer made use of mercury and a low vapor pressure oil and gave sensitive pressure readings up to about 2 centimeters. In this system water was determined as a vapor by measuring its pressure in the known volume of the system. This was possible as long as the total pressure did not exceed the vapor pressure of water at the prevailing room temperature, 27°C = 27 mm Hg. The system was calibrated by noting the pressure produced by weighed samples of water.

It should be noted at this point for future reference that the water vapor was transferred from the measuring system, by freezing with dry ice-acetone, to the zinc containing tube used to convert water to hydrogen. This was connected to the shipping tube where the resultant hydrogen was stored and shipped for mass spectrometer determinations. The shipping tube is shown in Figure 4.

Figure 5 shows the next section which consisted of a Toepfer
pump used to collect and transfer the gases into the calibrated volume where the total quantity of permanent gases was measured. Thence gases were transferred either to the analyzing section as shown by Figure 6 and Plate 3, or to a series of traps, illustrated by Figure 5, where carbon dioxide was extracted and purified by low temperature distillation using liquid air as coolant.

It should again be noted for future reference that the pure carbon dioxide was stored in the sealed-off shipping tubes and shipped for mass spectrometer determination of the isotopic ratios.

For the analysis of the gases evolved by the rocks the so-called "low pressure" method was used. The apparatus used was a modification of one described previously by Naughton (Duschkite, 1944, p. 645).

The analyzing section, depicted by Figure 6 and Plate 3, consisted basically of a circulating diffusion pump, a McLeod gauge, freeze-out traps and a catalytic combustion furnace. The method was based on Dalton's law of partial pressures. During analysis the gases were circulated by the diffusion pump around the closed analyzing system through freezing mixtures which took out various components of the gases. The release of these frozen components at various temperatures caused decreases in pressures which were measured with a McLeod gauge. The pressure measurements were made in a known volume in the system, situated between the mercury cutoff and the outlet of the diffusion pump as shown by Figure 6 and Plate 3. It was found by Naughton and Uhlig (1945) that this volume varied with the pressure of the gas in the system. A small water-cooled condenser was sealed into the diffusion pump to eliminate this variability. Selective separation of carbon dioxide and sulfur dioxide by distillation was possible by a slow heat-up of the freeze-out trap from liquid air temperature,
and the collection and measurement of each gas as it was distilled off. A copper-constantan thermocouple was connected to the freezing trap to determine the temperatures involved. The results of the analysis showed that the deviations from the true values were in no case greater than 0.7% as shown in Table I.

For the oxidation of combustibles a quartz furnace containing a platinum catalyst was used, as depicted by Figure 6 and Plate 3. This furnace was maintained at 1750° C and the temperatures were determined with a chromel-alumel thermocouple. Other accessories to the analyzing procedure were bulbs for oxygen and hydrogen storage as shown by Figure 1 and Plate 1. These gases were used in the analysis for the combustion of carbon monoxide and hydrogen, and oxygen, respectively. A Pirani gauge, illustrated by Figure 6 and Plate 3, was not used for quantitative pressure measurements but for the indication of the presence or passage of gases. Its use will be described more fully in the analytical procedure.

Details of procedure are given in Flow Sheets F and G.
Figure 1 - Schematic Diagram of System for Degassing Rocks, Purifying and Bottling the $\text{H}_2\text{O}$ and $\text{CO}_2$ Extracted and Analyzing the Extracted Gases.
Plate I. The Entire Apparatus
Figure 2 - System Used for Heating and Degassing Rock Samples
Plate II. The Degassing Section
Figure 3 - Water Freeze-out and Measuring System.
Figure 4 - Water-to-hydrogen Conversion Tube with Shipping Tube Attached.
Figure 5 - Toepler Pump with System for Measuring Permanent gases, and System for Purifying and Bottling Carbon Dioxide.
Figure 6 - Low Pressure Gas Analysis System.
Plate III. The Gas Analysis Section
### Table I. Analysis of a Prepared Gas Mixture

<table>
<thead>
<tr>
<th>Gas</th>
<th>Vol. % Prepared</th>
<th>Vol. % Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>8.0</td>
<td>7.7</td>
</tr>
<tr>
<td>Carbon Monoxide</td>
<td>15.2</td>
<td>15.9</td>
</tr>
<tr>
<td>Sulfur Dioxide</td>
<td>5.4</td>
<td>5.5</td>
</tr>
<tr>
<td>Carbon Pioxide</td>
<td>48.0</td>
<td>49.0</td>
</tr>
<tr>
<td>Oxygen</td>
<td>4.8</td>
<td>4.1</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>18.0</td>
<td>17.4</td>
</tr>
<tr>
<td></td>
<td><strong>Average deviation</strong></td>
<td><strong>0.4</strong></td>
</tr>
</tbody>
</table>
(3) Procedure:

In the degassing process samples were weighed on an analytical balance and in most cases about 2 grams were used. The individual pieces were about the size of a pea to minimize the effects of adsorbed atmospheric gases that have been reported when powdered samples were used. The samples were placed in the side-arm tube, as illustrated, Figure 2, by blowing out the end of the tube. A small iron rod was placed in the tube behind the sample before sealing the tip. This rod was later used to push the sample into the degassed crucible by manipulating it with a magnet from outside.

In the center of the quartz tube, Figure 2 and Plate 2, was placed a ceramic crucible on top of which a platinum crucible was balanced. When the funnel tube was placed as illustrated the bottom of the platinum crucible could be seen when observed through the viewing window. The water-jacketed ground joint was then greased with a low vapor pressure vacuum grease, Apiezon N, and slipped into place as illustrated.

The diffusion pump was switched on and the stopcocks opened to the high vacuum manifold to degas the furnace tube and crucible in preparation for degassing the sample. This preliminary step consisted of heating the sample with a low flame to drive off any adsorbed gases. Subsequently, the platinum crucible was degassed thoroughly using the induction heater to bring it to the same temperature as the maximum degassing temperature of the lava sample.

After about 2 hours of evacuation prior to degassing the sample, the Pirani gauge on the system usually gave a zero reading. The stopcocks to the high vacuum manifold were closed and the increase in pressure on the gauge was noted. The standard increase of 1 micron
(3) Procedure

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After about 2 hours of evacuation prior to degassing the sample the Pirani gauge on the system usually gave a zero reading. The stopcocks to the high vacuum manifold were closed and the increase in pressure on the gauge was noted. The standard increase of 1 micron
per 20 seconds was chosen as the maximum blank acceptable before the
addition of the sample into the hot platinum crucible. This blank
contributed little to the gases that were collected from the rock samples.
The lava sample was heated at 3 different temperatures. The initial tempera-
ture was about 1100 degrees C with the next two about 100 and 200 degrees
higher. In all cases the sample was completely melted at the highest
temperature and in some the sample was melted at the initial setting. Most
of the gases was evolved as soon as the sample was dropped into the
hot crucible even before melting. This was in agreement with the
work of Chamberlin. As quickly as the gases were evolved, the diffusion
pump pulled them from the furnace tube. Then, the Teeppler pump
operated manually, pumped the gases through the water-vapor trap seen
in Figure 3, which was cooled by a freezing mixture of crushed dry ice and
acetone. The temperature of this mixture was sufficient to freeze
out the water vapor which has a vapor pressure of about $10^{-3}$ mm at this
temperature. The rest of the gases were pumped into the calibrated
volume above the Teeppler pump shown by Figure 5.

When the lava sample was considered to have been sufficiently degassed,
the pressure of the water vapor from the rock sample was measured with the
two-liquid manometer depicted in Figure 3. The stopcocks leading to the
rock exhausting system and to the permanent gas measurement system were
closed to isolate the calibrated water vapor measuring section. The
stopcock to the two-liquid manometer was opened for the zero reading of
the water vapor pressure. The removal of the freezing mixture released
the water vapor, which gave the final pressure reading on the manometer.
The water vapor was then drawn into the storage tube, illustrated by
Figure 4, by cooling the tube with a dry ice and acetone freezing mixture.
The water vapor was converted to hydrogen for mass ratio determination. 

The amount of permanent gases in the calibrated volume above the Toepler pump was determined by raising the mercury level to one of the lines marking the calibrations as shown by Figure 5. The pressure was found by measuring the mercury height in relation to the adjacent mercury level as depicted by Figure 5. The difference in the mercury heights was accurately measured with a cathetometer.

For analysis, a small amount of the gases was transferred into the analyzing region. From the remainder of the gases, carbon dioxide was extracted and purified for mass ratio determination. Usually about 0.1 cc to 0.3 cc at standard conditions was used in the analysis. Due to the small amount of gases involved the slightest leakage of air grossly contaminated the samples. With a view to reducing contamination and leakage all stopcocks in the analyzing system were substituted by the mercury cutoffs shown in Figure 6 and Plate 3. Four cutoffs were used, and were operated by three way stopcocks attached to the mercury well about 760 mm below. The stopcocks connected the wells either to the atmosphere or to a vacuum. Connection of the well to the vacuum made it possible to lower the mercury in the cutoff, while connection to the atmosphere raised it. One of these cutoffs was used in the gas introduction section and another led to the high vacuum manifold illustrated by Figure 6 and Plate 3. The third, between the Pirani gauge and the furnace, and the fourth, between the diffusion pump and the Pirani gauge, played an important part in the actual analysis. These latter two in the description of the procedure will henceforth be referred to as cutoffs 1 and 2, respectively.

As the first step in the analysis, the gases were allowed to circulate through the closed circuit with liquid air around the
freeze-out trap. The liquid air condensed the carbon dioxide and sulfur dioxide and after 10 minutes the noncondensable gases were collected by the pump into the measuring volume by raising cutoff 2. Carbon dioxide and sulfur dioxide have immeasurably low vapor pressures at liquid air temperatures. These were negligible in comparison with the 0.1 micron pressure of the system. The mercury level of the cutoff was always kept at the same point to maintain the pressure determining volume constant. When all the noncondensable gases had been collected in the measuring volume, the pressure was determined using a McLeod gauge. Two identical pressure readings in succession were considered necessary before a reading was accepted. The liquid air was lowered just free from the trap. The temperature was allowed to rise sufficiently for the carbon dioxide to distill. This was observed on the Pirani gauge which the carbon dioxide must pass on its way to the measuring volume. As soon as the Pirani gauge returned to the zero point indicating the escape of all the carbon dioxide, the freeze out mixture was replaced around the trap to prevent the escape of sulfur dioxide. The carbon dioxide distilled off at about -140° C. The pressure in the measuring volume was again measured, the increase in pressure being due to the carbon dioxide. Sulfur dioxide was allowed to escape by replacing the liquid air with a dry ice-acetone mixture. Sulfur dioxide at this temperature has a vapor pressure of approximately 15 mm., sufficient for it to be distilled off. As soon as the sulfur dioxide had escaped, the mercury cutoff was raised. The residual water vapor which passed through the freeze out trap, at this temperature had a very small vapor pressure, but it was still sufficient to cause an increase in the pressure readings with time.
and had to be guarded against. The pressure readings after the sulfur
dioxide was released was considered to be the initial total pressure.

To determine combustibles a pressure of oxygen equivalent to at
least half the pressure of the noncondensable gases was added and
measured. Sufficient oxygen was thus used to insure complete combustion
even if all the remaining gases were either carbon monoxide or hydrogen
or both. The gases were circulated through a liquid air freeze out
trap, a furnace at about 450 degrees C, and a pair of traps with dry
ice-acetone mixtures around them on both sides of the furnace. About one
to one and a half hours were necessary for the complete combustion of any
carbon monoxide or hydrogen that was present in the gases. The carbon
monoxide was oxidized to carbon dioxide and the hydrogen to water.
The products were then taken out of circulation by the freeze out
mixtures. The dry ice-acetone mixtures on both sides of the furnace
prevented the mercury vapor in the system from entering the hot
furnace. It had been noted previously that platinum could catalyze a
reaction between the mercury and oxygen, consume oxygen and thus ruin
the analysis. The pressure at this stage showed a drop. The carbon
dioxide and sulfur dioxide pressures were again determined as previously
described. If any carbon monoxide and hydrogen sulfide had been
present in the gases, the initial pressures of carbon dioxide and
sulfur dioxide would have increased. From these and previously
measured pressures, the carbon monoxide and hydrogen content of the
gas were determined.

To determine oxygen, pure hydrogen was added and its pressure
measured. The gases were circulated through the system with liquid
air around the freeze-out trap and with the furnace at 450 degrees C
as previously explained in order to reduce all oxygen to water and
remove it from circulation. After combustion the pressure in the measuring system was again measured, this step made it possible to calculate the oxygen originally present.

Method of calculation for gas analysis:

CO₂ and SO₂ pressures were obtained directly,

\[
\frac{\text{pressure of CO}_2}{\text{Initial total pressure}} \times 100 = \% \text{ CO}_2
\]

CO calculation

The increase in the pressure of CO₂ at the second CO₂ pressure measurement after combustion was due to the CO.

\[
\frac{\text{Increase in CO}_2 \text{ pressure}}{\text{Initial Pressure}} \times 100 = \% \text{ CO}
\]

H₂ calculation

Let \( A \) = pressure drop due to first combustion.

This drop in pressure was due to reactions:

\[
2 \text{ CO} + \text{ O}_2 \rightarrow 2 \text{ CO}_2
\]

\[
2 \text{ H}_2 + \text{ O}_2 \rightarrow 2 \text{ H}_2\text{O}
\]

The products were condensed in the freezing mixtures.

Knowing the CO pressure B:

\[
\frac{1}{2} B = \text{O}_2 \text{ used in the CO combustion}
\]

Thus \( 3/2 B \) was the pressure drop due to CO combustion, and \( A = 3/2 B = C \) pressure drop due to H₂ combustion.

Since 2 moles of H₂ react with 1 mole of O₂:

\[
\frac{1}{3} C = \text{O}_2 \text{ used in H}_2 \text{ combustion}
\]

\[
\frac{2}{3} C = \text{pressure of H}_2 \text{ present in the gases;}
\]

\[
\% \text{ H}_2 = \frac{2/3 C}{\text{Initial Pressure}} \times 100
\]
O₂ calculation

The drop in pressure after the second combustion was due to H₂ and O₂ reaction, with H₂ in excess.

Let D = pressure drop

2/3 D = pressure drop due to H₂ combustion

1/3 D = pressure drop due to all the O₂ that was left.

1/3 C = O₂ used in first combustion

1/2 B = O₂ used in CO combustion

Let E = O₂ added before first combustion

E = 1/3 C + 1/2 B = F O₂ that was added still uncombined

1/3 D - F = O₂ that was originally present in the gases

% O₂ = O₂ originally present \times \frac{X}{100}

Original presence

N and A calculation

Let G = final pressure reading

Let H = added H₂ in excess

G = H = pressure of N and A

% N and A = Pressure of N and A \times \frac{X}{100}

Original Pressure

From this point on the experimental procedure deals with the preparation of samples for shipping away to the Consolidated Engineering Corporation in Pasadena, California, for the determination of isotopic ratios of carbon-13 to carbon-12 and hydrogen-2 to hydrogen-1 and to Dr. Kulp at Columbia University in New York City, for the carbon-14 determination.

It was mentioned previously on page 13 that the gases in the calibrated volume not used for analysis were stripped of the carbon
dioxide, which was then purified and sealed in shipping tubes for \(^{13}C/^{12}C\) isotopic ratio determinations. The purification of the carbon dioxide was accomplished by repeated low temperature distillation of the gas. The section of the apparatus used for this operation is illustrated in Figure 5. The gases were passed through the carbon dioxide freeze-out trap cooled by liquid air. Using the same procedure as in the analysis, the carbon dioxide trap was allowed to warm sufficiently for the gas to escape and was passed into the second trap cooled by liquid air. The passage of the gas was observed on the Pirani gauge between the two traps. After all the gas distillable in the carbon dioxide range was transferred, the stopcock beside the Pirani gauge was closed to isolate the traps. Any contaminants present were pumped out of the traps and the carbon dioxide was redistilled back and forth in this manner two more times. Finally the coolant was placed around the shipping tube and, after the purified carbon dioxide had condensed in it, it was sealed off under vacuum.

For the preparation of hydrogen for \(H_2/H^1\) isotopic ratio determination, it was mentioned previously, pages 12 and 26, that the water vapor was transferred from the measuring system to the storage tube shown in Figure 4. The storage tube containing the water vapor was sealed off and removed from the rest of the system by carefully heating the thickened constricted area, seal-off point No. 1 depicted in Figure 4. This was placed in a furnace at 450°C for at least three hours. The zinc reacted with the water vapor to form hydrogen gas and zinc oxide which was observable as a whitish substance in the zinc. The zinc tube was separated from the shipping tube by heating the seal-off point No. 2 seen in Figure 4. Before separating the shipping tube of hydrogen from
the zinc tube, the latter was immersed in liquid air to freeze out any condensable contaminants from the shipping tube.

The Sulfur Bank carbon dioxide that was collected for carbon-14 determination was converted to calcium carbonate and was purified by the method described by Arnold and Libby\textsuperscript{37}. The procedure consisted of passing the carbon dioxide into a solution of 6 N ammonia and precipitating calcium carbonate by the addition of calcium chloride to the solution. The mixture was filtered and the precipitate was thoroughly washed until the wash water was no longer basic to litmus. After drying, the sample was bottled and shipped for carbon-14 determination.

A summary of the procedure just described follows on pages 34-36 in the form of flow sheets.
Flow Sheet I - Degassing of the Samples to the Bottling of CO₂ and H₂

Rock sample

Heated under vacuum 1000°C to 1350°C

Gases evolved

Water vapor condensed by passing the gases through a trap cooled by a dry ice-acetone mixture

Remainder of gases

Amount determined in measuring volume Figure 5

Most of gases

CO₂ extracted and purified by fractional low temperature distillation

CO₂ sealed in shipping tube

.1-.3 ml of gases

Pumped into analytical section for analysis—see Flow sheet 2

Pressure measurement on two liquid manometer Figure 3

Purified by low temperature distillation

Sealed in storage tube Figure 4

Heated for 3-6 hours at 450°C

Zinc tube removed from shipping tube
Flow Sheet II  Gas Analysis

Total pressure of gases measured
Gases passed through liquid air

Pressure measured
\( \text{H}_2, \text{CO}, \text{O}_2, \text{A} \) and \( \text{N}_2 \)

Pressure measured
\( \text{H}_2, \text{CO}, \text{O}_2, \text{CO}_2, \text{A} \) and \( \text{N}_2 \)
*increase due to \( \text{CO}_2 \)

Pressure measured
\( \text{H}_2, \text{CO}, \text{O}_2, \text{CO}_2, \text{SO}_2, \text{A} \) and \( \text{N}_2 \)
*increase in pressure due to \( \text{SO}_2 \)

Gases circulated through liquid air trap

Pressure measured
\( \text{H}_2, \text{CO}, \text{O}_2, \text{A} \) and \( \text{N}_2 \)

\( \text{O}_2 \) added
Pressure measured
increase due to \( \text{O}_2 \)

\( \text{CO}_2 \) and \( \text{SO}_2 \) condensed in trap cooled by liquid air

Trap warmed to allow only \( \text{CO}_2 \) to sublime

\( \text{SO}_2 \) condensed

Trap warmed to allow \( \text{SO}_2 \) to sublime

\( \text{CO}_2 \) and \( \text{SO}_2 \) condensed in trap cooled by liquid air
Gases oxidized and passed through liquid air trap

Pressure measured $O_2$, $A$, and $N_2$

Pressure measured $O_2$, $CO_2$, $A$, and $N_2$ increase due to $CO_2$ increase in $CO_2$ due to $CO$

Gases circulated through liquid air

Pressure measured $O_2$, $A$, and $N_2$

$N_2$ added pressure increase due to $N_2$

Gases oxidized and passed through liquid air

Pressure measured $N_2$, $A$, and $N_2^*$

$CO_2$, $SO_2$, and $H_2O$ condensed

Trap warmed to allow $CO_2$ to sublime

$SO_2$ and $H_2O$ condensed

$CO_2$, $SO_2$, and $H_2O$ condensed

*At these stages enough data were available for the calculation of volume percent of $CO_2$, $SO_2$, $CO$, $H_2$, $A$, and $N_2$, and $O_2$, respectively.
(1) **Analysis of Gases in Rocks**

It was hoped that with increasing knowledge and experience in the extraction and analysis of gases in metals, similar techniques might be applied to rocks for the achievement of results that might be interpretable in terms of the composition or genesis of the rocks. Table II gives the results obtained for the analysis of gases obtained from rocks by the methods described in the previous sections.

Within recent years much has been done in an effort to understand the chemistry of the slags which are of importance in metallurgical practice. These slags approximate the composition of volcanic lavas, and it was thought that an application of some of the findings of workers in this field could be made to lava systems. The structure of solid silicates is well known from the work of Bragg and since the entropy of fusion is low, it appears that the solid structure is maintained in a vestigial form in the liquid. It was deduced that this structure is composed of silicon tetraoxide tetrahedra of various degrees of polymerization with cations having no fixed position save for a few that can replace silicon in the tetrahedra. Water and carbon dioxide exist in the melt in the form of hydroxyl and carbonate ions and profoundly influence the viscosity by affecting the degree of polymerization of the tetrahedral chains. The ferrous, ferric-carbon monoxide, carbon dioxide equilibrium has been established for liquid and solid systems and an attempt has been made to apply the ferrous-ferric equilibrium with gaseous mixtures to volcanic systems.
<table>
<thead>
<tr>
<th></th>
<th>cc of permanent gas per gm sample</th>
<th>mg H₂O per gm sample</th>
<th>CO₂</th>
<th>SO₂</th>
<th>CO</th>
<th>H₂</th>
<th>O₂</th>
<th>N₂</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Kahuku Basalt 0.25</td>
<td>1.6</td>
<td>18.2</td>
<td>0.0</td>
<td>21.7</td>
<td>21.2</td>
<td>34.7</td>
<td>4.6</td>
<td>Personal collection. Old lava. Mauna Loa. Road south of Pahala.</td>
</tr>
<tr>
<td>2.</td>
<td>Nepheline Basalt 2.48</td>
<td>5.6</td>
<td>82.5</td>
<td>8.1</td>
<td>4.4</td>
<td>5.0</td>
<td>0.0</td>
<td>1.0</td>
<td>Personal collection. Koililili Quarry.</td>
</tr>
<tr>
<td>3.</td>
<td>Oceanite Picrite Basalt 1868 0.77</td>
<td>0.7</td>
<td>18.2</td>
<td>0.0</td>
<td>40.2</td>
<td>23.4</td>
<td>14.1</td>
<td>3.9</td>
<td>Collected by G. A. MacDonald. Mauna Loa.</td>
</tr>
<tr>
<td>4.</td>
<td>Oligoclase Andesite 1.42</td>
<td>1.2</td>
<td>48.7</td>
<td>4.1</td>
<td>25.4</td>
<td>21.5</td>
<td>0.0</td>
<td>0.3</td>
<td>Collected G. A. MacDonald. Kohala Mountain.</td>
</tr>
<tr>
<td>5.</td>
<td>Pumice Kilauea 1952 0.28</td>
<td>0.8</td>
<td>21.2</td>
<td>14.5</td>
<td>42.0</td>
<td>17.3</td>
<td>0.0</td>
<td>6.9</td>
<td>Personal collection during eruption.</td>
</tr>
<tr>
<td>6.</td>
<td>1859 Basalt 0.09</td>
<td>0.9</td>
<td>15.3</td>
<td>5.1</td>
<td>33.4</td>
<td>36.2</td>
<td>4.7</td>
<td>6.5</td>
<td>Collected by G. A. MacDonald. Mauna Loa.</td>
</tr>
</tbody>
</table>
Table II. (Continued) Volume and Analyses of Gases Extracted From Volcanic Rocks and From Sulfur Bank Fumarole

<table>
<thead>
<tr>
<th>7. Olivine Basalt 1950</th>
<th>0.45</th>
<th>0.5</th>
<th>5.2</th>
<th>0.0</th>
<th>21.1</th>
<th>7.5</th>
<th>6.3</th>
<th>60.0</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Collected with Dr. Ingerson. 1952. Mauna Loa. From point where flow crosses road. SW part of island.</td>
</tr>
<tr>
<td>8. Andesine Andesite</td>
<td>0.80</td>
<td>0.5</td>
<td>22.4</td>
<td>0.0</td>
<td>20.3</td>
<td>15.8</td>
<td>9.6</td>
<td>31.9</td>
<td>Comments</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>From Mauna Kea. Road cut at Popoe Gulch NW side of island. Collection with Dr. Ingerson. 1952.</td>
</tr>
<tr>
<td>9. Trachyte</td>
<td>1.09</td>
<td>3.0</td>
<td>34.6</td>
<td>0.0</td>
<td>12.4</td>
<td>13.3</td>
<td>36.8</td>
<td>2.9</td>
<td>Comments</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>From Hualalai, Puu Waawaa flow - road out. W side of island. Collection with Dr. Ingerson. 1952.</td>
</tr>
<tr>
<td>10. Mauna Loa</td>
<td>1.73</td>
<td>0.6</td>
<td>6.4</td>
<td>7.3</td>
<td>14.3</td>
<td>1.7</td>
<td>9.2</td>
<td>60.7</td>
<td>Comments</td>
</tr>
</tbody>
</table>
Table II. (Continued) Volume and Analyses of Gases Extracted From Volcanic Rocks and From Sulfur Bank Fumarole

<table>
<thead>
<tr>
<th>cc of permanent gas per gm sample</th>
<th>mg H₂O per gm sample</th>
<th>CO₂</th>
<th>SO₂</th>
<th>CO</th>
<th>H₂</th>
<th>O₂</th>
<th>N₂</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>12. Sulfur Bank Gas 1952</td>
<td>---</td>
<td>---</td>
<td>96.4</td>
<td>1.6</td>
<td>1.7</td>
<td>0.4</td>
<td>0.0</td>
<td>0.0 Permanent gas emitted at Sulfur Bank fumaroles. Personal collection July 1952. Kilauea in eruption.</td>
</tr>
</tbody>
</table>
It was hoped that it would be possible to relate the ratio of the ferrous to ferric ion concentration of these various rocks to the ratios of the concentrations of the gaseous oxidation-reduction systems, CO₂/CO; H₂O/H₂. Superficially it was seen that a rough relationship existed between the acidity, per cent silica, of the rock and the CO₂/CO ratio; the ratio increased with the acidity as shown in Table III. Nepheline basalt, however, was completely out of line as seen in Graph 1. A similar increase in the total gas content with rock acidity was also evident.

Ferrous and ferric ions exist together in solid and liquid lavas. This system is considered to be in equilibrium with oxygen supplied in the melt by the CO₂/CO or H₂O/H₂ systems. Thus:

\[ 2 \text{Fe}^{++} + \frac{1}{2} \text{O}_2 \rightleftharpoons 2 \text{Fe}^{+++} + \text{O}_2 \]

For the high concentrations of \( \text{O}_2 \) and low concentrations of the ferrous and ferric ions that exist in rocks, the equilibrium expression may be written as:

\[ K = \frac{[\text{Fe}^{+++}]^2}{[\text{Fe}^{++}]^2 \text{pO}_2^{\frac{1}{2}}} \quad \text{or} \quad K' = \frac{[\text{Fe}^{+++}]^2}{[\text{Fe}^{++}] \text{pO}_2^{\frac{1}{2}}} \]

where the square brackets indicate gram-ion concentrations and \( \text{pO}_2 \) the partial pressure of oxygen. If the oxygen is assumed to be in equilibrium with CO₂-CO then the following equation will hold:

\[ \text{CO}_2 \rightleftharpoons \text{CO} + \frac{1}{2}\text{O}_2 \]

and the equilibrium:

\[ K'' = \frac{\text{pCO} \times \text{pO}_2^{\frac{3}{2}}}{\text{pCO}_2} \]

so that:

\[ \text{pO}_2^{\frac{3}{2}} \propto \frac{\text{pCO}_2}{\text{pCO}} \]
<table>
<thead>
<tr>
<th></th>
<th>SiO₂</th>
<th>CO₂/CO</th>
<th>(CO₂/CO)²</th>
<th>Fe⁺⁺/Fe⁺⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>48.4</td>
<td>0.82</td>
<td>0.91</td>
<td>-0.086</td>
</tr>
<tr>
<td>2.</td>
<td>38.6</td>
<td>18.70</td>
<td>4.33</td>
<td>1.272</td>
</tr>
<tr>
<td>3.</td>
<td>49.3</td>
<td>0.46</td>
<td>0.68</td>
<td>-1.167</td>
</tr>
<tr>
<td>4.</td>
<td>52.0</td>
<td>1.92</td>
<td>1.39</td>
<td>+1.283</td>
</tr>
<tr>
<td>5.</td>
<td>48.4</td>
<td>0.50</td>
<td>0.71</td>
<td>-1.301</td>
</tr>
<tr>
<td>6.</td>
<td>52.3</td>
<td>0.46</td>
<td>0.68</td>
<td>-1.337</td>
</tr>
<tr>
<td>7.</td>
<td>48.4</td>
<td>0.24</td>
<td>0.49</td>
<td>-0.620</td>
</tr>
<tr>
<td>8.</td>
<td>48.8</td>
<td>1.11</td>
<td>1.05</td>
<td>+0.045</td>
</tr>
<tr>
<td>9.</td>
<td>62.8</td>
<td>2.81</td>
<td>1.68</td>
<td>+0.949</td>
</tr>
<tr>
<td>10.</td>
<td>48.4</td>
<td>0.45</td>
<td>0.67</td>
<td>-3.047</td>
</tr>
</tbody>
</table>
Graph 1. Relationship between Acidity and Gas Content of Rocks, and between Acidity and CO₂/CO Ratio
Substituting in the ferrous-ferric equilibrium expression we get: 
\[ \frac{Fe^{++}}{Fe^{+++}} \propto (pCO_2/pCO)^{\frac{1}{2}} \]

A plot of this relationship gave an approximation to a straight line for most of the rocks studied, with trachyte falling outside as shown in Graph 2. No consistent relationship between the ferric-ferrous and water-hydrogen ratios was discovered. It was expected that the fit to the line would be rather poor because the calculations assumed that equilibrium was reached at the same temperature for all the rocks and was frozen in by a rapid quench. The only rocks that achieve this condition are spatter and pumice from the lava fountains. In addition, analysis for the ferric-ferrous content was not performed on these rocks, but the average values given by MacDonald were used for each type of rock. These average values were an approximation for individual rocks. The process of rapid heating and removal of gases from the hot zone in the extraction procedure did not cause reactions to disturb the equilibrium conditions that existed in the rocks. This was concluded from the mixtures of gases found that would be incompatible if allowed to attain equilibrium in the hot zone. Also Kennedy has found that many hours were necessary for the achievement of equilibrium in silicate oxidation-reduction systems even at 1300° C.
Graph 2. Relationship between Fe$^{++}$/Fe$^{++}$ and (CO$_2$/CO)$^{1/2}$ Ratios
The presence of rather large concentrations of free oxygen in some of these samples came as somewhat of a surprise. It was believed that this gas, and possibly also the nitrogen, resulted from the decomposition of certain of the oxide and nitride components of the melt under the conditions of high vacuum and high temperature achieved in the process of extraction. It was noted that the delivery of gas from the molten rock proceeded interminably, with each increase of temperature giving a new burst of gas that tended to be exhausted in time. At the higher temperatures, above 1200°C, this drop-off was less noticeable so that a termination of the extraction had to be based on the observation of quiescence in the melt at an arbitrarily set final exhaust temperature. Brewer* in a recent review gave the high temperature behavior expected for many oxides. He listed the decomposition of sodium oxide at 1060°C, potassium oxide at 880°C, magnetite at 1570°C, and phosphorus pentoxide at 380°C, as occurring when the total pressure of the gaseous products was $10^{-2}$ atmosphere. Under the condition of high vacuum that prevailed in the furnace the decomposition was expected to occur at a somewhat lower temperature. All of these oxides are present in the lava melt, although what effect the mixture with themselves and with the other components may have on their decomposition temperatures cannot be exactly predicted. It was to be expected, then, that a degree of decomposition of the rock would be observed.

Table IV shows the amount and composition of gases extracted from a sample of 1952 Kilauea pumice at successively higher temperatures. It was noted that the gases that were probably physically dissolved, hydrogen and carbon monoxide, or were contained in chemical
combinations that were unstable at high temperatures, carbon dioxide in carbonate ion, sulfur dioxide in sulfite ion and water in hydroxyl ion, were released in the main at lower temperatures. The oxygen that formed the major portion of the gases released at the highest temperature was that which resulted from the decomposition of the rocks.

In Table II, comparison of composition of the permanent gases emitted by the Sulfur Bank fumarole during and after an eruption of Kilauea showed a radical change in the constituents of the gases. The onset of this change might be used to predict the rising of magma in a volcano, and the probability of an eruption, by regular analyses of the gases at the fumarole. This was suggested previously by Ballard and Payne45.

In conclusion it may be said that the analyses of gases obtained in this work gave some evidence for a high gas content for acidic rocks. This was expected since these were the light residuals that were presumed to occupy the upper layers in the process of magmatic differentiation. These rocks contained a preponderance of the components that were the last to crystallize and into which the volatile impurities were concentrated. A rather tenuous relationship was noted between the ferrous-ferric content of the rock and carbon dioxide-carbon monoxide ratio in the gases extracted therefrom.
Table IV. Volume and Analyses of Gases Extracted From 1952 Kilauea Pumice at Various Temperatures

<table>
<thead>
<tr>
<th></th>
<th>First Heating 1075°C</th>
<th>Second Heating 1250°C</th>
<th>Third Heating 1300°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>cc of permanent gas per gm sample</td>
<td>0.260</td>
<td>0.019</td>
<td>0.109</td>
</tr>
<tr>
<td>mg H₂O per gm sample</td>
<td>0.794</td>
<td>0.003</td>
<td>0.000</td>
</tr>
<tr>
<td>Percent</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>12.7</td>
<td>32.2</td>
<td>1.8</td>
</tr>
<tr>
<td>SO₂</td>
<td>20.6</td>
<td>1.6</td>
<td>0.0</td>
</tr>
<tr>
<td>CO</td>
<td>40.4</td>
<td>13.6</td>
<td>3.2</td>
</tr>
<tr>
<td>H₂</td>
<td>19.3</td>
<td>4.9</td>
<td>0.0</td>
</tr>
<tr>
<td>O₂</td>
<td>0.0</td>
<td>38.6</td>
<td>87.2</td>
</tr>
<tr>
<td>A and N₂</td>
<td>7.6</td>
<td>7.8</td>
<td>4.6</td>
</tr>
<tr>
<td>Total</td>
<td>100.6</td>
<td>98.7</td>
<td>96.8</td>
</tr>
</tbody>
</table>
In agreement with the findings of previous workers in this field, the extreme variability of the results of the analyses of gases in rocks was noted. There was also a lack of correlations between the gas analyses and the chemical analyses of the rocks or with the postulated history of the rocks, except the rather tenuous ones already mentioned. The reasons for this variability may be found in the complexity of the equilibrium and rate processes that the liquid and solid lava has passed through in its history from magma to extraction. A few of these factors can be envisioned as follows:


2. Rate of cooling - varies from fast in thin dikes and splatter to very slow in large flows and batholiths - controls "freeze-in" of equilibria.

3. Degree of exposure to air and moisture while at high temperatures - leads to a variation in degree of oxidation, and to adsorption or loss of gases.

4. Surface area of sample - controls amount of adsorption of atmospheric moisture and carbon dioxide - can be excessive in powders.

5. Decomposition of oxides during extraction - variable depending on the amounts and types of oxides present.

6. Time at extraction temperature - can lead to equilibrium readjustments.

It was felt that until analyses are run with samples wherein we are certain that all of these factors save one are held constant, this type of seemingly unaccountable variability of extracted gas composi-
tion will be the rule. The difficulty of securing natural rocks for such work is obvious, so an approach through artificially prepared melts in which these factors could be controlled would perhaps be most fruitful.

(2) **Carbon-14 Content of Sulfur Bank Gases**

The determination by Kulp of the radioactivity due to carbon-14 in Sulfur Bank gases collected during the Kilauea eruption of 1952 gave negative results, showing that the carbon in the carbon dioxide had not been in equilibrium with atmospheric carbon dioxide for about 25,000 years. This is directly interpretable as another point toward the proof that the fumarolic carbon dioxide was not derived from the surface, but was of magmatic origin.

(3) **Isotopic Ratios of the Stable Isotopes of Carbon and Hydrogen in Volcanic Gases**

The measured values for the $^{15}\text{C}/^{12}\text{C}$ mass peak ratio for carbon dioxide and the $^{3}/^{2}$ mass peak ratio for hydrogen from the sources indicated are given in Table V. The relative differences in parts per thousand between $^{13}\text{C}/^{12}\text{C}$ and $^{2}/^{1}$ ratios and those of the standards used, $\delta^{c}$ and $\delta^{h}$, were calculated from these data by the methods indicated below and also are listed in Table V. This is the usual form in which such data are expressed.

Since the mass spectrometer determinations were performed elsewhere no effort will be made to describe this familiar instrument in detail. Suffice it to say that it spreads out a beam of ions from the gas to be analyzed into individual beams whose positions depend on the charge and mass of the ions, and whose intensities are functions of the concentrations of the ions. Both position and intensity
are measured and recorded as mass units and ion currents, respectively; thus a quantitative and qualitative analysis of the ion beam, and of the gas which is the source of the ion beam, is possible. The instrument used in this work was the Consolidated-Nier Type, Model 21-401, that measures the ratio between peaks at a given instant. It was specially designed for isotopic abundance work.

Carbon dioxide is an ideal gas for making measurements of the $^{12}/^{13}$ ratio in that it is easy to purify and behaves well in the mass spectrometer. The mass 45 peak found with this gas was due to the ions $^{13}O^{16}O^{16}^+$ and $^{12}O^{16}O^{17}^+$, and the 44 peak was due to $^{12}O^{16}O^{16}^+$. To determine $\delta_c$ from the ratio of the 45 to 44 peaks it was necessary to make a correction for $^{17}$ in the 45 peak. The abundance of this isotope of oxygen was taken to be 0.0374 atomic percent and was assumed to be constant. The possibility of a fractionation of $^{17}$ existed, but the resultant variation would have served only to amplify the effects sought in this work, since the heavy oxygen isotope would vary in a manner similar to the heavy carbon isotope. This is an additional factor in favor of the use of carbon dioxide for the determination of total differentiation effects. To make the calculation for carbon, two times the relative $^{17}$ abundance, 0.000748, was subtracted from the 45/44 peak ratio. This correction was made both for the sample and for the standard and gave the $^{13}/^{12}$ ratio for each. The difference value, then, was obtained from the following equation:

$$\delta_c \text{ in } 0/00 = \frac{\left(\frac{^{13}}{^{12}} \text{ Ratio for sample} - \frac{^{13}}{^{12}} \text{ Ratio for Standard}\right) \times 1000}{^{13}/^{12} \text{ Ratio for Standard}}$$

Thus a negative value for $\delta_c$ indicated that the sample contained a
lesser concentration of carbon-\textsubscript{13} than the standard, and conversely, a positive value indicated that the sample contained a greater concentration of carbon-\textsubscript{13}, the heavy isotope. The standard carbon dioxide used throughout the research was a sample taken from dry ice that was produced by the calcining of ancient reef coral. All ratios were relative to this sample.
Table V. Variation of the Isotopic Abundances of Carbon and Hydrogen in Volcanic Rocks and Fumaroles with Respect to Standard Samples

### Carbon from Carbon Dioxide

<table>
<thead>
<tr>
<th>Sample Description</th>
<th>45/44 Ratio</th>
<th>δ₁₃C/₀₀</th>
<th>%SiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Dry Ice Standard</td>
<td>0.011234</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>2. Picrite Oceanite Basalt</td>
<td>0.011072</td>
<td>-15.4</td>
<td>49.3</td>
</tr>
<tr>
<td>Mauna Loa 1868</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3. Kilauea Pumice 1952</td>
<td>0.011063</td>
<td>-14.4</td>
<td>48.9</td>
</tr>
<tr>
<td>4. Kahuku Series Basalt</td>
<td>0.011073</td>
<td>-15.4</td>
<td>48.4</td>
</tr>
<tr>
<td>5. Mauna Loa Basalt 1950</td>
<td>0.011126</td>
<td>-10.1</td>
<td>48.4</td>
</tr>
<tr>
<td>6. Mauna Loa Basalt 1859</td>
<td>0.011083</td>
<td>-14.4</td>
<td>52.3</td>
</tr>
<tr>
<td>7. Andesine Andesite</td>
<td>0.011087</td>
<td>-14.0</td>
<td>48.8</td>
</tr>
<tr>
<td>8. Oligoclase Andesite</td>
<td>0.011093</td>
<td>-13.5</td>
<td>52.0</td>
</tr>
<tr>
<td>9. Trachyte</td>
<td>0.011210</td>
<td>-2.3</td>
<td>62.6</td>
</tr>
<tr>
<td>10. Nepheline Basalt</td>
<td>0.011201</td>
<td>-3.2</td>
<td>38.6</td>
</tr>
<tr>
<td>11. Sulfur Bank 1952 - during Kilauea eruption</td>
<td>0.011324</td>
<td>+8.4</td>
<td></td>
</tr>
<tr>
<td>12. Sulfur Bank 1953 - Kilauea dormant</td>
<td>0.011340</td>
<td>+10.1</td>
<td></td>
</tr>
</tbody>
</table>

### Hydrogen from Water Vapor

<table>
<thead>
<tr>
<th>Sample Description</th>
<th>3/2 Ratio</th>
<th>δ₂H/₀₀</th>
<th>%SiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Pacific Ocean Water (Off Kaneohe Bay, Oahu)</td>
<td>$5.25 \times 10^{-4}$</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>2. Mauna Loa 1950</td>
<td>$5.75 \times 10^{-4}$</td>
<td>+95</td>
<td>48.4</td>
</tr>
<tr>
<td>3. Kilauea Pumice 1952</td>
<td>$5.30 \times 10^{-4}$</td>
<td>+9</td>
<td>48.4</td>
</tr>
<tr>
<td>4. Andesine Andesite</td>
<td>$5.26 \times 10^{-4}$</td>
<td>+2</td>
<td>48.8</td>
</tr>
<tr>
<td>5. Trachyte</td>
<td>$5.61 \times 10^{-4}$</td>
<td>+69</td>
<td>62.8</td>
</tr>
<tr>
<td>6. Sulfur Bank 1952 Kilauea in Eruption</td>
<td>$4.88 \times 10^{-4}$</td>
<td>-70</td>
<td></td>
</tr>
</tbody>
</table>
Hydrogen gas has been found to be the most convenient substance for use in the determination of relative abundance of the $^1\text{H}$ and $^2\text{H}$ isotopes of hydrogen in the mass spectrometer. The mass peaks found for hydrogen gas and the ions causing them were 1 - $^1\text{H}^+$, 2 - $^1\text{H}^1\text{H}^+$, 3 - $^1\text{H}^2^+$ and $^1\text{H}^1\text{H}^+$, and 4 - $^2\text{H}^2^+$ and $^2\text{H}^1\text{H}^2^+$. These are the peaks used in working with gases, such as in the samples of the present research, that are poor in deuterium. The $^2\text{H}/^1\text{H}$ ratio is usually determined by a comparison of the 3 and 2 peaks, but the problem is complicated by the interfering pressure-sensitive peak due to the formation of triatomic ions of a secondary source. To get the true $^2\text{H}/^1\text{H}$ ratio from the 3/2 peaks it is necessary to determine the peaks at various pressures and extrapolate to zero pressure. However with the more accurate type of ratio mass spectrometer used and with the comparative types of results that are important to this work, it is possible to use the 3/2 peak ratio directly provided the determinations are made at similar pressures, approx. 200 mm.

The results for the determinations of the 3/2 peak ratio are listed in Table V along with the values of the relative differences in parts per thousand, $\delta^H$, calculated from them.

To calculate these values the 3/2 ratio for our standard, hydrogen from Pacific Ocean water, Hawaii, was applied in the following equation:

$$\delta^H \text{ in } 0/00 = \frac{(3/2 \text{ Ratio for sample } - 3/2 \text{ Ratio for Standard}) \times 1000}{3/2 \text{ Ratio for Standard}}$$

The data of Table V shows the low carbon-13 content of the carbon dioxide extracted from the volcanic rocks in contrast to the "heaviness" of the gas found in the selfatara, Sulfur Bank. Also it was noted that,
in general, the gas became heavier the more acidic the rock; nepheline basalt, however, was an exception. These were the two points that seemed to be most evident in this data and upon which conclusions were based. The number of specimens studied in this investigation was too small to merit generalizations; still it was felt that the trends noted were significant and it will be shown that they were in agreement with general expectations. Significant confirmation of the data was also found in similar measurements made by Craig.  

Urey and Grieff showed that in equilibrium systems involving isotopes, some concentration of one isotope of an element was expected, particularly for the lighter elements. Quantitative data were given for the degree of enrichment expected. Recently Urey has expanded these data and made further comment on their applications. It was discussed previously that the source of the carbon dioxide extracted from the rocks by vacuum fusion was probably carbonate in the rock. The carbon dioxide in the fumarolic gases that were examined may also be presumed to have had its origin largely in magmatic carbonates, but to have resulted from equilibrium attained at high temperatures within the earth. It was expected then that it was in this equilibrium between carbon dioxide and carbonates that an explanation for the trends noted in the data listed in Table V was to be found.  

The values in a table given by Urey for the equilibrium constants of the carbon dioxide-carbonate reaction at various temperatures are as follows:

\[ c^{13}O_2 + c^{12}O_3 = c^{12}O_2 + c^{13}O_3 \]
\[ K(273^\circ \text{ A}) = 1.016 \]
\[ K(298^\circ \text{ A}) = 1.012 \]
\[ K(400^\circ \text{ A}) = 1.004 \]
\[ K(500^\circ \text{ A}) = 0.9994 \]
\[ K(600^\circ \text{ A}) = 0.9975 \]

It was noted from these values that the higher the temperature the greater the tendency of the heavier isotope to concentrate in the carbon dioxide rather than in the carbonate with which it was in equilibrium. It was presumed, then, that some of the carbon dioxide that was released in fumaroles in the vicinity of a volcano contained the equilibrium isotopic concentration of the gas in contact with the magma at high temperatures. A high concentration of the heavy isotope was expected in such gases, and it was found to be true with the Sulfur Bank carbon dioxide. In Table V, the carbon isotopic ratio difference values for the eruption of Kilauea in 1952 and for gases obtained during the eruption and a year later, at the Sulfur Bank nearby, have been listed.

The increase in the carbon-13 content of the carbon dioxide in the Sulfur Bank gases when Kilauea, the adjacent volcano, was dormant, as compared to the value when Kilauea was in eruption indicated a higher temperature for the source of the carbon dioxide in the former case. This result was surprising but it might be the result of the higher temperature in a magmatic chamber cut off from direct access to the surface, as opposed to the temperature of a body of lava that was losing its heat to the surface during an eruption.

The next variation noted in Table V was the increase in carbon-13 content of the carbon dioxide extracted from the rocks.
with increase in acidity of the rocks. According to Urey's table, a decrease in temperature resulted in an increase of the heavy isotope in the carbonate, for the carbon dioxide-carbonate equilibrium. It seemed that at the last stage at which there was enough time and the temperature was high enough for the attainment of equilibrium, the more siliceous or acidic rocks were at the lower temperature. As it was discussed by MacDonald, the rock series present in the Hawaiian Islands are thought to have resulted from the gravitational differentiation from a parent olivine basaltic magma. The heavier ferro-magnesian minerals settled out with time and left an ultimate residue of lighter, more siliceous rocks. In the early stages of volcanism, the least differentiated lavas were obtained as in the olivine basalt so evident at Mauna Loa. After differentiation, eruptions tapped the magma chamber at various levels and gave lavas varying from the olivine rich picrite basalt to olivine poor basalt. In the old age of the volcano, differentiation proceeded to such a stage that andesites were erupted, and finally trachyte. In certain cases the anomalous nepheline basalts were erupted. In general agreement with expectations from the isotopic data, the temperatures for the erupted lavas were noted to be lower for the more acidic lavas in the few measurements that were available. It may be then said, that the increase in "heaviness" of the carbon dioxide extracted from the more acidic rocks was evidence of lower temperatures of the rock magma during last residence in the magma chamber before the equilibrium was "frozen in" by the quenching effect of an eruption. Also, this was in agreement with the available measurements of the temperatures of erupting rocks as a function of acidity of the rocks.
The data for the isotopic abundances of the hydrogen-2 and hydrogen-1 found in the water extracted from the rocks and in the Sulfur Bank fumaroles were less consistent with expectations that that for the carbon isotopes. Here the solfataric gas was found to be much richer in the light isotope than the gas extracted from the rocks. This was at a complete variance with the case for carbon and with what was expected from thermodynamic considerations. Also no noteworthy trend of variation was detected with the nature of the rock. These results were explainable on the probable contamination or weathering of the rocks by meteoric water and the certainty of an unknown degree of contamination of the fumarolic gases by surface water. They probably reflected the inaccuracies and difficulties of the mass spectrometric determination of the very small concentrations of deuterium present in water from natural sources.
In the few years since research on the variability of isotopic abundances in nature began, the subject has expanded rapidly and isotopic research is in progress in almost all fields of natural science.

This research was conducted to see whether or not such variability of the isotopic abundances existed in volcanism, inasmuch as it is to be expected that the high temperatures, pressure gradients, and tremendous time periods involved would be contributory to isotopic differentiation.

The gases used were extracted under vacuum at high temperatures from lava rocks from Hawaiian volcanoes and were obtained at the Sulfur Bank fumarole. From these gases, hydrogen and carbon dioxide were obtained and $\text{H}_2/\text{H}_1$ and $^{13}\text{C}/^{12}\text{C}$ isotopic ratios were determined for these components.

Comparison of the $^{13}\text{C}/^{12}\text{C}$ ratios of the carbon dioxide from the Sulfur Bank and from the volcanic rocks showed a higher concentration of carbon-13 in the Sulfur Bank gases. From thermodynamic considerations, it was thought that this is due to the higher temperatures at which the Sulfur Bank gases escape from the magma, as against the lower temperatures at which the equilibrium of the reactions in the volcanic rocks were "frozen".

In agreement with the findings of previous workers, the data obtained showed a tendency toward an increase of carbon-13 as the acidity of the lava rocks increased.

Comparison of the $^{13}\text{C}/^{12}\text{C}$ isotopic ratios of carbon dioxide collected from the Sulfur Bank during the eruption of 1952 and a year later during dormancy of Kilauea, showed a higher carbon-13
content for the gases collected during dormancy. This indicated that the gases were evolved from the magma in the latter case at a higher temperature.

No significant trends were discerned from the $\text{H}_2/\text{H}_1$ isotopic ratios, probably due to weathering and contamination of the samples by meteoric water, and uncertainties in the mass spectrometer sample preparation techniques.

The gases from the samples on which isotopic ratio determinations were made were also analyzed for water vapor, carbon dioxide, carbon monoxide, sulfur dioxide, hydrogen, oxygen and nitrogen and argon.

A pattern of increasing gas content with the increasing acidity of the lavas and a relationship between the ferric-ferrous oxidation-reduction couple and the carbon dioxide-carbon monoxide ratios were observed. However, little addition to the understanding of gas-rock relationships has been achieved by the more modern methods used in this research.

Carbon dioxide for carbon-14 determination was collected from the Sulfur Bank fumarole. The absence of the radioactive isotope is an indication of the magmatic origin of most of the permanent solfataric gases.
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