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ISOTOPIC FRACTIONATION IN
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ABSTRACT

A complete mass spectrometer has been constructed around a mass spectrometer tube originally designed by Nier. Modifications of this single collector device have permitted its use as a medium precision instrument in the determination of isotope abundances in carbon dioxide.

In addition, a previous gas chromatograph design has been modified to allow a one step separation and collection of carbon dioxide from a volcanic gas matrix, thus eliminating the usual and tedious volumetric method.

To qualitatively predict the magnitude and direction of the isotopic fractionation in volcanic gases at higher temperatures (600°K-1500°K), equilibrium constants were calculated for numerous reactions involving carbon or oxygen isotope exchanges, such as \( \text{^{12}C} \text{^{16}O}_2 + \text{H}_2 \text{^{18}O} = \text{^{12}C} \text{^{18}O}_2 + \text{H}_2 \text{^{16}O} \). The validity of these calculations was discussed on a basis of high temperature anharmonicity, and the resultant effect on the partition function ratios was estimated.

Samples from a Hawaiian volcanic system were collected and analyzed for carbon and oxygen isotope abundances, in the form of carbon dioxide. Samples were taken from several areas, including fumarolic gases from Sulfur Bank in Kilauea Iki Crater, on Hawaii Island, gases from the drill holes in the lava lake of recently erupted Makaopuhi Crater, also on Hawaii, and assorted carbonaceous samples of marine origin.
The results of this work have illustrated the need for
(1) a further investigation, on a more detailed and precise basis,
of the fundamental properties of isotopic species at elevated
temperatures, and (2) a further analysis of the Hawaiian volcanic
system incorporating more precise isotope measurements.
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I. INTRODUCTION

A. Purpose of research

As one of the keys to an understanding of the fundamental processes by which the earth was formed and later altered, the study of volcanology is of unqualified importance. Such a study can be approached from many directions, each of which offers a uniqueness in its explanation of these processes. The purpose of this research was to probe the enigma of volcanic gases, using basic chemistry as the mode of inquiry.

More specifically, by determining the isotopic structure of carbon dioxide in volcanic gases, and by investigating the relation of the structure to its geological environment, it was anticipated that information would be derived which would lead to at least a partial evaluation of the following points:

1) the ultimate origin of volcanic gases containing carbon and oxygen,
2) the establishment of isotopic equilibrium in the gaseous phase, and the temperature of equilibration,
3) the processes intrinsic to isotopic fractionation, other than basic equilibrium.

Finally, the development of analytical techniques of sample treatment and analysis have been considered as an important and integral part of the investigation.
B. Distribution of isotopes in nature

1. General distribution

In 1914, J. J. Thompson published his discovery of the existence of isotopes of neon \(1\). His study of these "positive rays" initiated the development of what turned out to be an extremely potent tool for scientists in almost every discipline. The geologically oriented sciences have been no exception to the influence of mass spectrometry.

Following such leaders in the mass spectrometry field as Aston and Dempster, A. O. Nier, in 1935, refined previous developments in mass spectrometers and emerged with an instrument which has served as the basis for many modern instruments used in isotope measurements \(2\).

Utilizing such instruments, progressively more work has been done toward elucidating the distribution of isotopes within each element and in the different compounds incorporating this element in nature. The distribution of the isotopes of virtually every stable element has been examined. From such work, the number of isotopes per element has ranged from as many as nine to ten for the heavier elements such as xenon and tin, to only a single isotope of beryllium \(3\). Falling in between, the commonly found elements in the earth's crust and/or atmosphere, such as carbon, oxygen, nitrogen, silicon, etc., have two common isotopes in the case of carbon and nitrogen, and three
isotopes in the case of oxygen. In addition to the range in the number of isotopes per element, there is an even greater range of per cent abundance of isotopes per element. For example, silicon has isotopes of masses 28, 29 and 30, which are 92.21, 4.70 and 3.09 per cent abundant, respectively (3). Lastly, and most important from the aspect of the present work, the intraelement isotopic distribution has been shown to be different among various compounds incorporating a given element. Such differences have been shown to vary from essentially zero to several per cent.

2. Distribution of carbon isotopes

Within the above framework of isotope abundances in nature, carbon is one of the two elements which has been of major concern in this research.

The distribution of carbon isotopes in nature has been the object of considerable study over the last decade and a half, and probably the most ubiquitous assay of carbon in natural surroundings was published by Craig in 1953 (4). In this work, which substantiated and extended previous work (5, 6), the two stable carbon isotopes ($^{12}$C and $^{13}$C) were shown to have a ratio which varied as much as five per cent.

This variation occurred over a wide gamut of carbon-containing compounds of geological interest, from coal and
carbonates to calcareous marine organisms and plants. The present work has dealt with a more specific distribution of the carbon isotopes within the above range.

3. Distribution of oxygen isotopes

In 1935 Dole published work establishing the existence of a variation of oxygen isotope abundances in nature (7). Atmospheric oxygen was found to be enriched in the $^{18}O/^{16}O$ ratio over oxygen found in fresh water by about 3.1 per cent.

Since the above work, many analyses have verified the widespread fractionation of oxygen isotopes in nature (5, 6). As a result of these analyses, it has been determined that oxygen in nature consists of three stable isotopes—$^{16}O$, $^{18}O$ and $^{17}O$, which are 99.759, 0.2039 and 0.0374 per cent abundant, respectively (3).

C. Isotopic differentiation

1. Notation used in isotope ratio measurements

Although the widest range of differences in isotope ratios is easily expressed in terms of percentage, a slightly different standard notation has evolved in the field for two reasons: (1) it is often desirable to measure small differences in the isotope ratios of an element from closely related sources, and (2) differences recorded in this fashion are easily compared with calculated equilibrium constants, as shown later.
The notation usually used (and in this work) has been the per mil difference:

\[
\delta_{\%} = \left[ \frac{\text{Isotope Ratio}_{\text{Sample}}}{\text{Isotope Ratio}_{\text{Standard}}} - 1 \right] \times 1000
\]

This equation has also been set up so that a difference between the ratios of sample and standard is automatically known to be positive or negative, simply by virtue of a plus or minus delta value.

2. Differentiation through chemical processes

From the geological standpoint, one of the major reasons for measuring isotope ratios has been to provide aid in the elucidation of natural processes which cause the fractionation to occur. These processes may be conveniently divided into two types—chemical and physical.

Equilibrium between different species containing the same isotopes was one of the earliest recognized factors contributing to differentiation of isotopes (8). Using such reactions as

\[ ^1\text{H}_2 + ^2\text{D}_2 = \text{HD} \]

and

\[ ^1\text{H}_2\text{O} + ^1\text{H}_2\text{O} = ^1\text{H}_4\text{O}_2 + ^1\text{H}_2\text{O}_2 \]

equilibrium constants have been calculated via statistical mechanics, and confirmed by experiment (9). Since then many other reactions similar to the above have been shown to exist. Of even greater significance to this study has
been the application of isotope equilibrium to reactions occurring in nature. Isotope exchanges of carbon, nitrogen, oxygen, sulfur and hydrogen have been studied in this respect. For example, Thode, et al., worked on the problem of sulfur isotope distribution in a geological setting (10), and were able to make significant conclusions based on isotope equilibrium predictions.

Perhaps the most striking use of isotope equilibrium in nature has made use of the $^{16}\text{O}^{18}\text{O}$ exchange between carbonate ion and solid carbonate in an aqueous system (the ocean in this case) to calculate the temperature at which a particular marine carbonate was deposited in the ocean sediment (11). Thus in these and many other cases, the validity of the application, under suitable restrictions, of isotope equilibrium theory to natural settings has been amply proven.

Also of major importance, particularly in carbon isotope studies, has been the course of photosynthesis in plants. Isotope enrichments of $^{13}\text{C}$ have been observed in plant materials (4). Plants, in turn, have varying isotope effects on their geological environment. Therefore, any analysis of isotope distribution in a geological setting must have included the possibility of plant-derived carbonaceous material embodied in the specimen destined for analysis.
A third source of chemically derived isotope fractionation is the kinetic isotope effect. It has been observed that different isotopes within an atom or molecule cause the latter to react at different rates. For example, Urey and Washburn showed that water grows richer in deuterium as it is electrolyzed (12). Many other reactions have since been substantiated as having a fractionating effect on the participating isotopes, due to the kinetics of the reaction (13). The application of theory to natural settings has not been thoroughly investigated, however, because of the number of interfering parameters.

Lastly, isotope fractionation effected by chemical interaction may have occurred in a unidirectional, or irreversible, manner (14). Thus any interpretation of equilibrium reactions must include this possibility.

3. Differentiation through physical processes

In the same manner that fractionation of a mixture of compounds occurs during distillation, a single compound containing different isotopes of the same element have also been shown to be separated upon distillation. In the lighter elements, such as hydrogen, carbon and nitrogen, the vapor pressure of different isotopes of the same element have been proven to differ slightly. This difference has been used in efficient distillation columns to provide an isotope mixture which is enriched in one
of the components. Heavy water, for example, has been prepared in this fashion (15).

Thermal diffusion has also been employed in the separation of isotopes of atoms or molecules in gaseous form. As an illustration, Hoering has analyzed the isotope ratios of nitrogen taken from petroleum producing areas, and partially explained the observed fractionation by using a model employing diffusion through a porous rock structure (16).

D. Volcanism as a setting for isotopic fractionation

Having considered the basic processes which induce a fractionation of isotopes, there has remained the question of the validity of their application to volcanic gases.

The question of equilibrium has always plagued investigators of the Hawaiian volcanic system. However, it has been verified that this condition is satisfied, at least for the gross components involved (17, 18, 19, 20). It has appeared reasonable, then, to expect at least some degree of isotopic equilibrium to exist. In addition, it has been firmly established that volcanic gas temperatures vary from about 373°K to about 1500°K. Thus the idea of equilibration at various temperatures, via isotope exchange, is an attractive one.

Incorporation of plant materials into lava flows during an eruption has been visually observed in numerous cases. The effect of this contamination on the measurement of the
endemic gases has also been in question. Again isotope analysis offers an attractive solution.

The influence of kinetic and unidirectional processes on isotope differentiation is also possible in volcanic gases, but more difficult if not impossible to assess.

Perhaps the most attractive possibility is the analogy between diffusion-distillation processes and the situation prevailing inside a volcanic and/or fumarolic system.

The varying porosity of Hawaiian lavas is well known, as is the thermal nature under which they exist. Thus these conditions offer a setting which is very similar to one needed for the separation of isotopes by thermal diffusion.

Considering again the thermal nature of the Hawaiian system, and its abundance of water, it is not difficult to envision a natural distillation column leading to isotope fractionation.

From the above considerations it is evident that, on a qualitative basis at least, the investigation of isotope fractionation in volcanic gases is potentially a very fruitful one. In fact, the danger involved in such a study is not from a lack of potential, but that there are possibly too many sources of fractionation to permit a precise elucidation of any one of them.
E. Review of the literature

1. Origin of atmospheric gases and water

   a. General Hypotheses

   Hypotheses dealing with the origin of atmospheric gases and water fall into two general categories. The first assumes that the atmosphere and hydrosphere were "captured" as a whole in the initial stages of the formation of the earth, and that the present state of the atmosphere, in terms of composition and density, is a result of subsequent interaction of the primary gases with the surface of the earth through geologic time.

   The second hypothesis results from a belief that the present atmosphere is composed of excess volatiles which have accumulated as the result of a gradual and continuous degassing of the earth's interior, since the early period of its postulated accretion.

   Founded on the idea that the best way to interpret the origin of the present atmosphere and hydrosphere is by considering their present composition and extrapolating back, most of the work undertaken to refute or support either of the above hypotheses has been based on an evaluation of their interactions with each other, and with their geological environment.

   Carbon dioxide and water have been the two chief constituents of interest in this work. Their isotope composition and abundance reflect not only their own
origin but also the genesis and history of other species capable of interacting. For this reason, the origin of these components is reviewed specifically.

b. Origin of carbon dioxide

Equilibrium constant calculations by Rubey (21) for interactions among common gases, such as hydrogen, methane, carbon monoxide, carbon dioxide, water and nitrogen, have shown that the early dense atmosphere could have been composed of over 90 per cent (by volume) carbon dioxide and 6.4 per cent nitrogen.

On the other hand, similar calculations (21) showed that a gradual degassing of the earth's interior could lead to a less dense atmosphere, whose primary constituents were still carbon dioxide and nitrogen. Some evidence is lent to the latter hypothesis because of the amount of limestone deposits and dissolved rocks required to correspond to the large amount of carbon dioxide in the former hypothesis. Such large deposits and dissolutions were not consistent with observed geological evidence (22).

Additional evidence for the atmospheric nature of volcanic exhalations has been given by Rubey (21), who noted that excess volatiles closely approximate the average composition of volcanic gases.

Not all carbon dioxide from thermal areas appears to be necessarily of magmatic origin. Craig (4)
investigated the $^{13}C/^{12}C$ ratio in carbon dioxide from Yellowstone gases and concluded that the carbon dioxide was derived from the reaction between limestone rocks and acidic water.

Thus, although some general conclusions have been drawn concerning the origin of carbon dioxide in volcanic gases, each individual case must be assessed in view of its natural surroundings.

c. Origin of water

Rubey (21) has proposed that the hydrosphere is also ultimately of volcanic origin, and is the result of continuous degassing of the earth's interior. This implies that present day thermal areas, such as volcanoes and fumaroles, should show some evidence of juvenile water (i.e., water which has never been at the surface before).

In opposition, however, Craig (23) has observed no evidence of juvenile water in his studies on hot spring systems. All of the departures of isotope ratios from those of standard waters could be easily explained on a basis of the water's interaction with its immediate surroundings.

Thus juvenile water is as yet more of a concept than a firmly established reality. It has been postulated (24) that juvenile or magmatic water should have an $^{18}O$ content similar to the oxygen in silicate rocks,
based on equilibrium exchange at high temperatures.

2. Origin of Hawaiian volcanic gases
a. Origin of carbon dioxide

Matsuo (25) has considered the carbon dioxide observed in volcanic gases to be largely of crustal (i.e., not magmatic) origin. This was postulated on the basis of the interaction of hot magma with inter-lacing coral reefs, according to the chemical reactions

\[ \text{CaCO}_3 + \text{SiO}_2 = \text{CaSiO}_3 + \text{CO}_2 \]

and

\[ \text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2. \]

The possibility of these reactions was buttressed by earlier geological speculations. To explain the origin of Hawaiian nepheline basalts, Daly (26) proposed the existence of a widespread layer, 500-600 meters thick, of limestone material underlying the Hawaiian Islands. In moving to the surface, then, the hot magma tended to assimilate the limestone, which showed up later as a higher lime content in the basalt.

Macdonald (27) has largely disagreed with this theory, maintaining that although the possibility of limestone assimilation exists, there is no evidence of inter-lacing limestone, as such, in any of the lavas of the main shield volcanoes. The latter author has also indicated that the coral reefs surrounding the islands are
superficial; i.e., frequent lava inundations in the area of the volcano itself prevented the growth of marine organisms in the abundance necessary for coral reefs. This hypothesis has also been advanced by Winchell (28).

As mentioned above, carbon dioxide has been reported to be a contamination arising from pyrolysis of vegetation by hot lava (29). Naughton, et al., (30), have also suggested that samples taken in areas of deep lava flows are very possibly contaminated by buried organic material, as indicated by the occasional presence of unusually large quantities of hydrogen, methane, carbon monoxide and carbon disulfide.

b. Origin of water

Hawaiian volcanic gases have always been found to contain an abundance of water, ranging from about fifty to practically one hundred per cent of the total sample (25, 30, 31, 32).

Although no isotopic work has been done on the oxygen isotopes of water in Hawaiian volcanic gases, some gross composition work by Heald, Naughton, and Barnes (30) indicated the possible presence of magmatic or juvenile water. They showed evidence for non-attainment of equilibrium in some volcanic gas samples, due to a contamination of the sample by ground water. This, of course, would imply that juvenile water does exist in Hawaiian volcanic gases.
3. Analyses of gases from the Hawaiian volcanic system

a. General analyses

Realizing the importance of the gases in the Hawaiian volcanic system, many analyses of these gases have been carried out in the last few decades. Based on the first extensive series of gas sampling from Kilauea in 1917-1919, Shepherd (33), and later Jagger (34), performed classic analyses of the major gaseous components. The emphasis in these investigations was placed on the method and accuracy of analysis, and any rough correspondence of the gross composition with variation in location of sampling, etc.

Naughton and Terada (35) determined the composition of fumarolic gases from Sulfur Bank that were collected in 1952-1953 during alternating periods of quiescence and eruptive activity. It was shown that a considerable change occurred in the composition of the gas samples, which in turn was indicative of atmospheric contamination in the samples taken during the inactive period.

The eruption of Kilauea Iki Volcano in 1959-1960 gave impetus to two series of gaseous analyses by independent laboratories. A chemical and isotopic analysis (the isotopic work is discussed in the next section) of gases collected from drill holes in the
resultant lava lake was undertaken by Wasserburg, et al. (29). From their work, the group concluded that the presence of methane, carbon dioxide and hydrogen was most likely from the water gas reaction, and therefore of superficial—not volcanic—origin.

Conversely, concurrent work by Naughton, Heald and Barnes (19, 30), also based on analyses of drill hole samples from Kilauea Iki (as well as from fumarolic gases), showed that the gases collected were in near chemical equilibrium.

It has also been demonstrated by Matsuo (18) that the gas samples analyzed by Jagger were in chemical equilibrium.

More generally, Ellis (36) has concluded that the composition of volcanic gases from various locations in the world corresponds to that composition which was predicted by computer-oriented equilibrium calculations.

b. Isotopic analyses of volcanic gases

Investigation of $^{12}\text{C}/^{13}\text{C}$ variations in Hawaiian volcanic gases was begun by Naughton and Terada (35). Using the same inactive-active cycle, it was observed that the $^{12}\text{C}/^{13}\text{C}$ ratio in Sulfur Bank carbon dioxide did not vary with volcanic activity, remaining a constant 89.0 ($^{13}\text{C}/^{12}\text{C} = .0112$). Carbon dioxide in the gas taken from the 1950 Mauna Loa lava flow,
However, proved to be "light," with a $^{12}\text{C}/^{13}\text{C}$ ratio of 91.2 ($^{13}\text{C}/^{12}\text{C} = 0.0110$).

Eruption of Kilauea in 1955 again provided samples on a basis of the active-inactive cycle. Samples were analyzed by Hoering (37) for $^{15}\text{N}$ and $^{36}\text{A}$ variations. These analyses showed no variations from the values expected from atmospheric samples.

Carbon dioxide was analyzed by Wasserburg's group as a part of their chemical analysis of the Kilauea Iki lava lake gases. Two samples of carbon dioxide yielded delta values of $-24$ and $-18$ per mil for the $^{13}\text{C}/^{12}\text{C}$ ratio, with respect to a reference limestone. These values fell into the general range of the carbon isotope ratios for igneous rocks and terrestrial plant material, and was therefore explained by the authors as due to the incorporation of plant material by the lava flow. The significant difference in the delta values of the two carbon dioxide samples was judged to be due to fractionation arising from the sampling technique or from the partial purification procedure prior to analysis.

c. Isotopic analyses of gases from rocks

In addition to the fumarolic carbon dioxide analyses by Naughton and Terada, carbon dioxide was extracted from the olivine basalt of the 1959 Mauna Loa lava and analyzed (35). A $^{12}\text{C}/^{13}\text{C}$ ratio of 90.7
was recorded \((^{13}\text{C}/^{12}\text{C} = .0110)\). This represented a delta value \((^{13}\text{C}/^{12}\text{C})\) of \(-24.0\) per mil with respect to the ratio for Sulfur Bank carbon dioxide.

As a portion of Craig's survey of the distribution of carbon isotopes in nature (4), several samples of igneous rock from Hawaii were analyzed for the carbon isotope distribution. Analyses of two olivine basalts, melilite-nepheline basalt, basaltic andesite, andesite and trachyte yielded delta values of \(-24.8\) and \(-25.4\), \(-26.0\), \(-25.2\), \(-24.8\) and \(-19.0\) per mil, respectively. An apparent correlation between the increasing negative value of delta and the percentage of iron oxide in the sample was also observed.

4. Methods of isotope ratio measurements

a. Early developments

It should be mentioned at the outset that whereas the research in this work has dealt with a mass spectrometer employing an electron impact ion source, the following review has been limited largely to work involving similar sources.

Mass spectrometry has been the major tool used in the past for stable isotope abundance measurements. As indicated previously, the work of Thomson (1) on neon isotopes was among the earliest performed on isotopic distribution within an element. Using a parabolic mass spectroscope, Thomson (38) was also able to record
the spectra of isotopic species contributing to hydrogen, oxygen, carbon monoxide and carbon dioxide. These measurements, although outstanding at the time, were crude by today's standards, and permitted only a semi-quantitative estimate of the relative abundance of the individual species contributing to a particular molecule. The resolving power of Thomson's instrument was only about one part in fifteen.

A major refinement of Thomson's analyses by Aston (39) led to the determination of the presence of $^{124}\text{Xe}$ and $^{126}\text{Xe}$, each of which represented about 0.1 per cent of natural xenon. This work involved an instrument capable of a resolution of about 130. Although later work by Aston (40) and Costa (41) improved the available resolution to about 2000, the former resolution marked the emergence of a mass spectrometer (Aston's instrument was actually a mass spectrograph) potentially capable of making precise isotope ratio measurements.

b. Single collector instruments

With the resolution available from direction-focusing instruments, Nier (42) developed the 60° sector mass spectrometer, which proved to be a milestone in mass spectrometer determinations of isotope abundance ratios.

Nier's original 60° sector instrument used a slit which collected the ion beam of a specific species, or
mass-to-charge ratio, and was thus a single collector instrument. Measurements were made by manually scanning the peaks (effected by sweeping the accelerating voltage) and recording the galvanometer deflections resulting from an ion beam-induced current. In this way the $^{13}\text{C}/^{12}\text{C}$ ratio could be determined accurately to three decimal places.

Other single collector instruments of varying types (i.e., $90^\circ$, $180^\circ$, etc.) were used for isotope abundance measurements during and following Nier's work of 1940 (43, 44, 45, 56), but these efforts produced results of approximately the same accuracy, and usually at a disadvantage of more complexity.

Basically, commercial instruments designed around the $60^\circ$ sector device have changed very little since 1940, and merely represent refinements of Nier's instrument. These refinements, however, have permitted the best single collector mass spectrometer (using extreme care in making measurements), to determine isotope abundance ratios with an accuracy of one to two per mil.

Sakai (47), in 1957, used a CEC Model 21-103A (a single collector instrument) to make measurements of sulfur isotope ratios with a "standard error" of slightly less than $\pm$ one per mil. This accuracy required that a standard sulfur dioxide be run immediately before and after each sample, with care taken to avoid memory effects from successive runs.
More elaborate methods of measuring isotope ratios with single collector instruments have been employed in an effort to measure isotope ratios with an accuracy comparable to that attainable with double collector instruments. The high precision double collector arrangement for mass spectrometers (described later), however, has distinct disadvantages. Errors can be contributed from changes in the gain of the two separate detection and amplifying systems used. Also, the double collector instruments suffer from a lack of versatility in the ion pairs that can be measured, since the double collector slit system is usually fixed. Even with adjustable slits, the versatility is at best limited.

For the above reasons, several ratiometers have been described which use single beam mass spectrometers in conjunction with various means of rapid and alternate focusing of two ion beams, resulting in the near-simultaneous measurement of two ion beam intensities.

Butement and Finkelstein (48) described a single collector instrument which employed a photomultiplier scintillation detector in conjunction with a set of counters to record the mass ratio of $^{84}\text{Kr}/^{86}\text{Kr}$. In addition, high voltage electrostatic focusing plates were used between the magnet and collector, which permitted an alternating, rapid and automatic focusing
of the $^{84}\text{Kr}$ and $^{86}\text{Kr}$ mass peaks on the detector. Using this ratiometer, a standard deviation of less than one per mil was observed for abundance ratios measured on different days.

A different focusing scheme was employed by Pelah, Dattner and Fischler (49) to determine the $(^{17}\text{O}_2 + ^{16}\text{O}^{18}\text{O})/^{16}\text{O}_2$ and $(^{13}\text{C}^{16}\text{O} + ^{12}\text{C}^{17}\text{O})/^{12}\text{C}^{16}\text{O}$ ratios. Two accelerating voltages (corresponding to the two masses of interest) were obtained by rapidly (25Hz) and alternately short-circuiting a small fraction of the total accelerating voltage to alternately focus the two ion beams on the detector. A synchronous switch (also 25 Hz) at the detector permitted the emerging signals to be cyclically directed to two amplifier channels. The square wave signal thus produced was then amplified, filtered and compared by a potentiometer galvanometer system. In this manner the oxygen and carbon monoxide ratios were determined (on single samples) with a precision of ± 2.5 per mil, respectively.

c. Double collector instruments

Straus (50) first employed a ratiometer device (a general name for a device permitting measurement of isotope ratios simultaneously or nearly simultaneously) in 1941. However, since a spark source was used by Straus, the mass spectrometer is noteworthy here only because of its position as the first of the double
collecting instruments. A dual collector slit system was used by Straus to simultaneously measure two nickel isotopes.

Nier (51) later developed a mass spectrometer similar to the single collector described in 1940, but modified to include a double collector. The double collector consisted of a slit system designed to collect two adjacent ion beams (m/e = 44 and 45, from carbon dioxide) simultaneously. The individual ion currents were then fed to separate amplifying systems, and compared with each other via a null balancing system. Using this setup, the measurement of the $^{13}C/^{12}C$ ratio for fourteen samples on two different days yielded 1.005 for an average of the individual sample ratios. In terms of per mil deviation of the average ratio from unity, this would represent an absolute value of five per mil. In view of an apparent systematic change in the apparatus in between analysis days, an accuracy slightly better than five per mil was probably obtained. Nier's precision, however, was about ± one per mil.

Improvements on Nier's double collector instrument were made by McKinney, et al. (52). An alternating sample inlet valve assembly was added to a double collector mass spectrometer tube, so that replacing the standard gas in the ion source with a sample gas
resulted in a shift of the null balance point on a potentiometric recorder. The shift, in turn, was proportional to the difference in the isotope ratios of sample and standard. Taken over a large number of runs, the isotope ratio difference of a sample and standard could be determined with a standard deviation of ± 0.1 per mil.

More recently, Nier, Eckelmann and Lupton (53) have refined the McKinney instrument, via an ultra-stable emission regulator and electronic components, to permit isotope ratio difference measurements with a standard deviation of ± 0.06 per mil.
II. EXPERIMENTAL WORK

A. Construction of mass spectrometer

1. Description of tube and supporting electronics

   The mass spectrometer tube as a whole was originally designed by Nier, and later modified by Schaeffer (54). It was a 60° sector single focusing, single collector instrument, utilizing an electron impact source. The radius of curvature was approximately six inches.

   Supporting electronics for the instrument were either purchased commercially or constructed in the laboratory, and were standard power supplies except for the modifications enumerated below.

   The magnet coils were wound according to the specifications of Nier (42), and required about twenty watts of power under normal operating conditions.

2. Ion source modifications

   Although the mass spectrometer ion source was designed to incorporate a slit system for collimation of the electron beam, there was none in the mass spectrometer tube as received. Therefore, one was designed and constructed, approximately following the system described by Schaeffer (54). Schaeffer's desire for a pressurized source to decrease the hot filament contributions to the background led to a design with unusually small slits.

   However, since superior stability and better resolution
were of greater importance here, the slits were made larger to allow a stronger (but collimated) flux of ionizing electrons and a commensurate increase in ion intensity. The ions then exited through a larger slit in the ionization chamber. The dimensions are shown in Figure 1. Like the original Schaeffer slit system, this one was designed so that all electrons entering the ionization chamber impinged on the trap, or collector, plate.

In addition, the .001 x .010 mil tungsten filament was replaced by a more rugged .001 x .015 mil tungsten filament.

3. Signal output modifications

A vibrating reed electrometer (Cary Model 31) was used to monitor and amplify the current generated by the ion beam falling on a metal collector plate. Of the voltage signal thus generated, a small portion (10 millivolts) was tapped off and fed to a potentiometric recorder in the usual fashion.

Measurement of small differences in the heights of mass peaks was difficult with the above standard setup, which has normally been used for accuracy and precision of a few per cent. Therefore a circuit was designed and constructed which employed a well known method of depressing the zero line of the 10 millivolt signal coming into the recorder. The signal zero was depressed in nominal (but calibrated) steps of 1 millivolt until the signal to the recorder was
Figure 1. Electron collimating slits and ion exit slit in the ion source.

A = PRIMARY COLLIMATING SLIT
B = SECONDARY COLLIMATING SLIT
C = ION BEAM EXIT SLIT
less than 1 millivolt. This voltage was then expanded to full scale on the recorder. As a result of the suppression-expansion, a five-fold increase in accuracy was realized, thus extending the accuracy to a fourth decimal place.

As another aid to the attainment of more precise peak height measurements, the magnetic field was adjustable via ten-turn potentiometers to two exact positions so that rapid manual switching could be performed. In this manner two ion beams could be brought to focus alternately and rapidly, eliminating most of the error contributed by slight drift and instability under expanded scale conditions. Only occasional and slight readjustment of the potentiometers was required to maintain a maximum peak height. A sample of the signals recorded in this way is shown in Figure 2. Rapidity of data taking was also increased, allowing a greater number of "scans" during a given period of time.

As a final contribution to stability, the collector slit in the mass spectrometer tube was adjusted to a width of 1.4 millimeters. Since the exit slit was then wider than the ion beam for a specific mass, flat-topped or nearly flat-topped peaks were obtained, samples of which are also shown in Figure 3. The slightly sloping tops of the 45 and 46 peaks were due to overlapping of the adjacent 44 and 45 peaks, respectively. It was observed that lower analyzer tube pressures gave perfectly flat peaks for 44, 45 and 46. However, it was necessary to run the instrument at a pressure sufficient to give readily measurable peak heights.
Figure 2. Traces for expanded scale recorder signal.
Figure 3. Mass-to-charge peak shapes recorded with magnetic scanning of the mass spectrometer.
Thus, less stringent requirements were placed on the power supplies in order to "sit" on top of a peak. The peak shapes described above also insured that the total beam intensity was observed for a given m/e peak, rather than "seeing" only a fraction of it, as would be the case for a slit smaller than the ion beam.

A schematic picture of the mass spectrometer analysis system is shown in Figure 4.

4. Range and capabilities

As constructed and modified, the mass spectrometer used in this work had a magnetic field strength continuously variable from 0-8000 gauss, making it potentially applicable to all species from m/e = 1 to m/e = 225.

Under analysis conditions (i.e., with an analyzer tube pressure of about 3 X 10^{-5} millimeters of mercury), and with the ion source parameters empirically adjusted for maximum peak height, the resolution of the instrument was about 82 for masses 44, 45, and 46. This value was calculated as M/ΔM, where M = the mass of the ion considered, and ΔM = the peak width, in atomic mass units, at five per cent of the total peak height.

Optimum stability of the instrument permitted the 13C/12C ratio of a sample to be measured with a standard deviation of less than ± 1 per mil. The usual precision, however, was about ± 2 per mil.
Figure 4. Sample inlet and mass spectrometer system.
Measurement of the $^{18}_6/^{16}_6$ ratio of a sample was performed with a typical standard deviation of about ±4 per mil. A more detailed account of the precision and accuracy of the measurements in this work is given in the section dealing with the treatment of data.

Thus, this mass spectrometer has been developed into an instrument suitable for medium precision isotope ratio measurements, falling in between the ultra-precise instruments (designed for measuring isotope ratio differences to within ±0.1 per mil) and the more common instruments capable of obtaining measurements with an accuracy of a few per cent.

To aid in any future use of the mass spectrometer described above, a complete list of the operating parameters, as finally adjusted, is given in Appendix A.

5. Vacuum system

A standard pumping system was used, which employed a 120 liter/second mechanical pump in tandem with a 70 liter/second, three-stage mercury diffusion pump. Liquid nitrogen trapping brought the pressure down in the ion source region to about $10^{-6}$ millimeters of mercury, after baking the mass spectrometer tube out at approximately 250°C.

Approximately one hour of pumping was required to reduce the mass 44 peak to an acceptable level before running another sample.
B. Gas inlet system

Two types of leaks allowing gaseous sample flow into the mass spectrometer have been widely used. Molecular leaks were investigated by Honig (55) in his study on gas flow in mass spectrometers. Molecular flow occurs when the mean free path of the gas involved is much greater (usually about twenty times) than the diameter of the orifice. Under these conditions a small amount of gas is required because of the low inlet pressure, being on the order of 100 microns of mercury. On the other hand, a large volume is required for a sample container since the sample flow rates for species of differing molecular weights are not the same. Thus the composition of the sample would change, becoming richer in the heavier component.

Viscous flow occurs when the mean free path of the species involved is several times less than the corresponding leak dimension. Although no enrichment, under suitable conditions (56, 57), occurs in the sample container, a higher pressure sample must be used to maintain flow conditions.

A molecular flow sample input was chosen for this work for the following reasons:

(1) Since the separation procedure involved here was the trapping of a gas chromatographic effluent, small sample sizes were important.

(2) Molecular flow (and therefore fractionation) must occur in the region of the ion source, introducing an uncertain fractionation with a viscous leak. Thus,
if necessary, the molecular flow measurements were easier to put on an absolute basis.

A molecular leak in glass tubing was constructed according to Honig (55). The mean diameter of the leak was .0027 centimeters. Since the mean free paths of carbon dioxide at the pressures of 75 microns to 100 microns were equal to .045 centimeters to .070 centimeters, molecular flow was insured.

To satisfy the volume requirement mentioned above, a 5 liter flask was used. The expected fractionation for carbon dioxide under dynamic conditions for a given percentage diminution of mass 44 pressure was calculated according to

\[
\left(\frac{P_1}{P_0}\right)_{44} = \left(\frac{P_1}{P_0}\right)_{45} \left(\frac{M_{45}}{M_{44}}\right)^{1/2}
\]

where

- \(P_0\) = initial pressure
- \(P\) = final pressure
- \(M_{44}\) = molecular weight of \(^{12}_0{C}\text{^{16}O}_2\)
- \(M_{45}\) = molecular weight of \(^{13}_0{C}\text{^{16}O}_2\)

and the results are shown in Figure 5.

This plot shows that for any consumption of \(^{12}_0{C}\text{^{16}O}_2\) less than about 8 per cent, the change in reservoir composition was less than 1 per mil. Since it was experimentally observed that the consumption of carbon dioxide was always less than 5 per cent during a run, the error involved was roughly half of the above.

However, because a comparison standard was run under conditions identical with the sample, the error due to the above
Figure 5. Effect of molecular flow on the isotopic composition of carbon dioxide in the sample reservoir.
effect became negligible in relation to the accuracy of the isotope measurements themselves.

C. Collection of samples

1. Sulfur Bank samples

A number of gaseous samples were collected at Sulfur Bank, in Kilauea Iki Crater on the island of Hawaii. Sulfur Bank is an easily accessible collection site consisting of a pipe sunk into a fumarolic area in the 1920's.

Collection was formed by inserting the end of an evacuated one liter flask (which was equipped with a break-off tip) into the pipe. The tip was broken and the flask allowed to slowly fill for two to three minutes, and the tube sealed off under partial vacuum.

The outlet temperature of the fumarole, where the samples were taken, was about 96°C (at about 4000 feet elevation). Thus, at this temperature, considerable water was collected in its vapor state.

2. Drill hole samples

In April of 1965, Makaopuhi Crater, located along the Chain of Craters Road in Hawaii Volcanoes National Park, erupted along a side vent sending tons of lava and entrapped gases down its slopes to form a new lava lake. After a sufficient crust had formed on the lake, the United States Geological Survey drilled a series of holes, 1-1/8 inches in diameter, through the crust and down to the molten lava, using a technique developed earlier when drilling
holes in Kilauea Iki lava lake (58).

Samples were taken from the holes in evacuated one liter pyrex containers by inserting the end of the tube several inches below the surface and opening a stopcock to fill the flask.

3. Solid samples

In addition to the gaseous samples, a number of carbonaceous solid samples were acquired. These were selected to be of use in linking the isotope structure of the gaseous carbon dioxide samples to their geological environment. All the solid samples were of marine origin, consisting mostly of aragonite, with a calcite content from 8.7 to 17.9 per cent, and were taken from selected inland sites around the island of Oahu.

A detailed explanation of the sampling locations for the solid samples is given in Appendix B.

4. Standard samples

To avoid the determination of an absolute abundance each time a measurement of the isotope ratio was made, a standard sample was used. Since all samples were run under closely identical conditions, the procedure used was to measure the isotope ratio of a standard carbon dioxide and then measure the same ratio in a sample carbon dioxide. The ratio could then be computed simply by subtracting the sample ratio from the standard ratio according to the equation for determination of delta values, as described
earlier. A few small corrections to this procedure will be described later.

The standard samples used in this work were both calcium carbonate. One was National Bureau of Standards Reference Sample Number 20, a limestone from Solenhofen, Bavaria. The second was a calcite used by Clayton (59) as a laboratory standard.

Craig (4) used a standard carbonate whose delta values have been widely adopted. This standard was PDB, "a Cretaceous belemnite, Belemnitella americana, from the Peedee formation of South Carolina." This material is, however, no longer available for distribution.

The delta values of the National Bureau of Standards Number 20 and Clayton calcite standards, relative to PDB, are as follows:

\[
\begin{align*}
\delta^{(18O)} \% & \quad \delta^{(13C)} \% \\
\text{NBS 20} & \quad -4.14 \quad -1.06 \quad (60) \\
\text{Clayton calcite} & \quad -12.32 \quad -10.32 \quad (59)
\end{align*}
\]

D. Preparation and purification of samples

1. Gaseous samples

a. Gas matrix involved

Hawaiian volcanic gases, as determined by many previous analyses, consist largely of water vapor, carbon dioxide, nitrogen, carbon monoxide, sulfur dioxide, hydrogen sulfide, methane and argon. Thus
the separation and purification of carbon dioxide in the presence of the above matrix was a major problem. Most methods previously used by investigators on similar analyses have taken advantage of selective freezing out of components—based on their differing condensation temperatures—in conjunction with specific chemical reactions to convert the desired constituent(s) into a more usable form, all of which is very tedious and time-consuming.

b. Prechromatographic sample treatment

After collection, the one liter sample flask was attached to a vacuum system and heated to about 125°C, with a heating tape, following breakage of the breakoff-ski on the sample flask. A liquid nitrogen trap then collected all the condensables. Replacing the liquid nitrogen by a dry ice-acetone mixture resulted in liberation of the carbon dioxide and sulfur dioxide, while retaining the water. At this point the sample could be run on the chromatograph, since the column was capable of separating the remaining noncondensables (nitrogen, oxygen and hydrogen sulfide). However, in the initial analyses, the sample was usually refrozen with liquid nitrogen and the noncondensables pumped away, thus insuring a minimum of column contamination. In addition to prevention of contamination, the refreezing and pumping reduced the sample composition
to essentially carbon dioxide and sulfur dioxide (almost 100 per cent carbon dioxide). This allowed a more accurate carbon dioxide pressure determination, and consequently a proper choice of the aliquot U-tube size (see Figure 7) to provide a given mass spectrometer reservoir pressure.

c. Gas chromatographic purification

Based on intralaboratory volcanic gas analyses concurrent with this work (31), and on work by Hodges and Maéson (61), gas chromatography appeared to be an ideal, ultrasimple method of separation and purification of carbon dioxide. The latter authors were able to separate carbon dioxide, sulfur dioxide, hydrogen sulfide and carbonyl sulfide on a one foot silica gel column (80/100 mesh). A flow rate of 40 milliliters of helium per minute and a temperature of 100°C were also used.

A similar column was prepared in this laboratory, using a one foot silica gel column, also 80/100 mesh, employing a column temperature of 75°C. A slow flow rate of 5 milliliters per minute of a helium carrier gas was used to maximize the effluent trapping efficiency, as described below. The thermal conductivity detector was a GOW-MAC, Model JDC-133.

Insulation from temperature eddies was provided by placing the column and detector block in a box made
of one inch thick meranite (Johns-Manville Company) and lined with glass wool. With this protection, the temperature could be maintained constant to plus or minus one-half degree centigrade with a variac-controlled, 40 watt household appliance light bulb.

Aluminum tubing, \( \frac{3}{8} \) inch O.D., was used to make the column. All other construction materials downstream from the sample injection point were made from aluminum or stainless steel to avoid corrosion problems from the sulfur gases.

d. Effluent trapping procedure

As noted by Hodges and Matson (61), the order of chromatographic elution of the major gases present in a volcanic sample (following the above preparative treatment) is air, carbon dioxide and sulfur dioxide. Under the column conditions mentioned above, the same effluent order was noted. Retention times of 1.3 minutes for the air peak, 5.2 minutes for the carbon dioxide peak, and 45.3 minutes (at about 40 milliliters of helium per minute) for the sulfur dioxide were observed. The exit of the sulfur dioxide peak was hastened by increasing the helium flow rate to 40 milliliters per minute after the carbon dioxide was eluted.

Prior to the sample injection, the glass trapping coil was cooled with liquid nitrogen for a period of thirty to forty-five minutes, while being flushed with
helium carrier gas. A typical carbon dioxide isolation was then begun by injecting a measured aliquot of the sample, via a double four-way stopcock arrangement (see Figure 7), into the helium carrier gas flow. The imbalance of a Wheatstone bridge circuit (based on a diagram supplied by GOW-MAC for the JDC-133 thermal conductivity detector) was followed with a Honeywell Electronik 19 recorder.

Since any permanent gases (which elute as a single air peak) incorporated in the sample aliquot are not condensable at liquid nitrogen temperatures, these were allowed to flow through the trapping coil. Thus the flow needed to be diverted only after the carbon dioxide peak.

A trapping period of thirty-five minutes was used during emergence of the carbon dioxide. This amount of time was necessary due to the unusually slow flow rate, which increased the tailing effect of the peak.

Following the carbon dioxide isolation, the coil was transferred directly to the mass spectrometer inlet reservoir, while the carbon dioxide remained in the liquid nitrogen and thus was still frozen. The non-condensables were pumped off, the liquid nitrogen replaced by an acetone-dry ice mixture, and any necessary pressure adjustments made. The sample was then ready for mass spectrometric analysis.
Based on previous gross composition analyses of Sulfur Bank gases (31), a standard gas chromatographic injection loop was modified to allow the isolation of a quantity of gas suitable for the five liter inlet reservoir at a pressure of about 75 to 100 microns of mercury. A permanent volume of 0.75 milliliters could be added to five detachable volumes to provide aliquots of one, two, three, four and five milliliters. The reproducibility and efficiency of the gas chromatographic isolation of carbon dioxide is shown in Table I.

The possibility of helium-derived carbon dioxide impurities (as well as atmospheric carbon dioxide contamination) was checked by running a blank determination on the trapping procedure. Upon making the final expansion into the five liter reservoir, a two micron pressure rise was noted. This unknown gas was admitted to the mass spectrometer while monitoring the m/e=44 peak, and a rise above background of about three millivolts was recorded. Since the 44 signal output during a sample run was about 5 x 10^3 millivolts, this represented a maximum possible error of 0.78 per mil in the measurement of a 45/44 ratio. This was within the experimental limits defined earlier.

Any back diffusion of atmospheric gases into the trapping coil was prevented by the placement of a second liquid nitrogen trap and a dibutylphthalate
<table>
<thead>
<tr>
<th>Sample</th>
<th>Calculated Reservoir Yield, µ Hg</th>
<th>Observed Reservoir Yield, µ Hg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfur Bank Number 1</td>
<td>110</td>
<td>115</td>
</tr>
<tr>
<td>Varona Coral</td>
<td>88</td>
<td>86</td>
</tr>
<tr>
<td>Sulfur Bank Number 3</td>
<td>168</td>
<td>180</td>
</tr>
</tbody>
</table>
bubbler, respectively, downstream from the trapping coil.

To further prove the efficacy of gas chromatography as a preparative tool for gas analyses, pre- and post-chromatographed carbon dioxide samples were analyzed for purity of carbon dioxide. A portion of Sulfur Bank sample number two, after being chromatographed and isolated, was analyzed on the Hitachi-Perkin Elmer RMU-6E mass spectrometer. Another portion of the sample, taken before being chromatographed, was analyzed in the same manner. Both were preceded by background spectra to show the magnitude of the residual gases in the instrument. The results are shown in Figure 6. No presence of sulfur dioxide, as indicated by the level of the m/e=64 peak, was evident in the chromatographed portion. However, the unchromatographed aliquot showed a sizeable peak at m/e=64.

Thus it appears that the sulfur dioxide was completely removed from the carbon dioxide (within the limits of mass spectrometer sensitivity) by chromatographic purification. The amount of sulfur dioxide in Sulfur Bank gases, as indicated on the mass spectrum and previous Sulfur Bank analyses (31) is small. However, it has been observed that small amounts of impurities in the carbon dioxide samples appeared to cause the trap current regulation to be erratic, which in turn
Figure 6. Effectiveness of chromatographic sample purification.
rendered the instrument unusable for accurate ratio determinations. Also, it was desired to keep all corrosive sulfur gases away from the copper section of the mass spectrometer tube. For these reasons, it was desirable to remove even small quantities of sulfur dioxide from the gaseous samples.

A diagram of the complete preparative vacuum and gas chromatographic system is shown in Figure 7.

2. Preparation of solid samples

The method for releasing carbon dioxide from calcium carbonate has been thoroughly investigated by McCrea (62). Briefly, the carbonate was treated in a vacuum system with 100 per cent orthophosphoric acid, which released the carbon dioxide reproducibly to within ± 0.1 per mil on replicate runs of the same sample. The carbon dioxide thus produced was then frozen out with liquid nitrogen and the non-condensables pumped off. After releasing the liquid nitrogen, the carbon dioxide was measured, refrozen in a sample tube, and transferred to the mass spectrometer for analysis.

All of the solid samples analyzed here were prepared for analysis in the above way, after being ground to powder.
Figure 7. Preparative vacuum and gas chromatographic purification system for gaseous samples.
III. THEORETICAL WORK

A. Isotopic exchange equilibrium calculations

1. General aspects

The first widespread calculations of equilibrium constants for isotope exchange reactions were made by Urey (63). Equilibrium constants for reactions involving isotopes of H, Li, B, C, N, O, Cl, Br, and I were calculated using the methods of statistical mechanics.

A more detailed development of the final equation used in the calculation of the following equilibrium constants is given in Appendix C, but a brief summary of these details is as follows:

For a typical isotope exchange reaction,

\[ aA_1 + bB_2 = aA_2 + bB_1, \]

where A and B are molecules having a common atom whose isotopes are denoted by 1 (the light isotope) and 2 (the heavy isotope), the equilibrium constant is given by

\[ K = \frac{\frac{Q_{A2}'}{Q_{A1}'}}{\frac{Q_{B2}'}{Q_{B1}'}} \]

where the Q's are the partition functions of the molecules.

Rigorously, the partition function ratio is given by

\[ \frac{Q_2'}{Q_1'} = \frac{\sigma_1}{\sigma_2} \left( \frac{M_2}{M_1} \right)^{3/2} \sum e^{-E_2/kT} \sum e^{-E_1/kT} \]
where $\sigma_1$ and $\sigma_2$ are the symmetry numbers for the two molecules, and $M_1$ and $M_2$ are their molecular weights.

Assuming that the potential functions are the same for isotopic molecules, that the temperature is sufficiently high so $kT$ is large compared with the rotational energy level separations, and that the vibrational levels are sufficiently harmonic, it can be shown that for an isotopic molecule, the partition function ratio is given by

\[
\ln \frac{Q_2}{Q_1} = \ln \frac{\sigma_1}{\sigma_2} + \sum_i \ln \frac{u_{2i}}{u_{1i}} + \sum_i \left[(\coth x_i) \delta_i + \frac{1}{12} \coth x_i (\coth^2 x_i - 1) \delta_i^3 + \ldots \right]
\]

where $u_{1i}$ and $u_{2i}$ are $\hbar \omega_{1i}/kT$ and $\hbar \omega_{2i}/kT$, respectively; $x = \frac{u_{1i} + u_{2i}}{4}$, and $\delta_i = \frac{u_{1i} - u_{2i}}{2}$.

Thus the partition function ratio (and therefore the equilibrium constant) can be calculated from a knowledge of the molecular vibration frequencies.

Many applications and confirmations of the above equations have been made, both in the laboratory and in nature. The original calculations were carried out from 273.1°C to 600°C. However, in dealing with volcanic gases, it was of interest to compute the approximate magnitude and direction of isotopic enrichment at higher temperatures, from 600°C to 1500°C. To this
end, the above equation was used to calculate (via the IBM 7040 Computer) the equilibrium constants for reactions between selected species peculiar to a volcanic environment. All vibration frequencies used in the calculations were those of Urey (63), with the exception of the methane frequencies. The carbon 12 frequencies were taken from Herzberg (64) and the carbon 13 frequencies from Craig (4).

Initially it was desired to work with the isotopes of nitrogen, carbon and oxygen. Therefore calculations were performed which utilized a postulated equilibrium between various molecules containing these isotopes.

2. Nitrogen isotope exchanges

The recorded presence of ammonium compounds in solidified magma (37) and as ammonium compounds in volcanic gases (31), as well as molecular N₂ (30), prompted the calculation of equilibrium constants for reactions involving these three nitrogen-containing species: nitrogen, ammonia and ammonium ion.

A few high temperature equilibrium constants for nitrogen exchange reactions were calculated by Hoering (37), which agree with the corresponding values calculated here. All constants and partition function ratios for the nitrogen exchanges are shown in Table II.

As an aid in determining the significance of these equilibrium constants in terms of per mil isotope ratio
### Table II

**Partition Function Ratios and Equilibrium Constants for Nitrogen Isotope Exchange Reactions**

<table>
<thead>
<tr>
<th>$Q_2/Q_1$</th>
<th>$15\text{NH}_4^+/14\text{NH}_4^+$</th>
<th>$(15\text{N}_2/14\text{N}_2)^{\Delta}$</th>
<th>$15\text{NH}_3/14\text{NH}_3$</th>
<th>$T, \text{°K}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0264</td>
<td>1.0200</td>
<td>1.0178</td>
<td>800</td>
<td></td>
</tr>
<tr>
<td>1.0184</td>
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<td>1.0125</td>
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<td></td>
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deviations, it has been pointed out by Craig (4) that the per mil notation used in measuring isotope ratio differences between compounds A and B is related to the equilibrium constant $K$, by

$$\delta_A - \delta_B = (1-K)(\delta_A + 1000).$$

Thus the difference, in per mil, between compounds A and B is equal to the deviation of the equilibrium constant from unity, except for a small factor.

For convenience in comparison of all constants appearing here with those of Urey (63) the former results were tabulated in the same manner as the latter. An equilibrium constant greater than unity indicated that the compound listed in the left column would be enriched in the heavier isotope.

Employing these observations, then, the equilibrium constants for the ammonium-nitrogen exchange at 1200$^\circ$K would predict a 4 per mil enrichment of $^{15}$N in the ammonium. A similar enrichment was predicted for the ammonium-ammonia exchange, also at 1200$^\circ$K. However, the equilibrium constant for the nitrogen-ammonia exchange at the same temperature predicted only a one per mil enrichment in the $^{15}$N of molecular nitrogen.

3. Carbon isotope exchanges

The abundance of carbon-containing gases in volcanic emanations (particularly carbon dioxide) made carbon an
especially useful element for observation of isotope ratio deviations, in the form of $^{13}\text{C}/^{12}\text{C}$.

Carbon dioxide, carbon monoxide, methane and the carbonate anion were used as the most likely volcanic species. The results of these calculations are shown in Table III.

Again, the expected enrichment was small, with the carbon dioxide-carbon monoxide exchange being most promising. The $\text{CO}_3^2-\text{CO}_2$ exchange exhibited a directional reversal of a few per mil. However, Craig has pointed out (4) that the deviation from unity of the equilibrium constants calculated by Urey for this exchange are probably too high, by a factor of about two. The partition functions were calculated in reverse for the carbonate anion, beginning with the $^{13}\text{C}/^{12}\text{C}$ abundances in natural carbonate, as observed by previous investigators. In addition to this inaccuracy, the carbonate anion was treated as a gas in the partition function calculations, thus leading to errors in the application of these values to the solid carbonate. Finally, recognizing the semi-quantitative nature of the extension of these calculations to high temperatures, as described later, the reversal in direction of this equilibrium may or may not be a real one.

However, it has been observed that the above reversal is not unique (63). Numerous reactions exhibit
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such reversals, involving compounds whose physical form and temperature of calculation are not subject to the above criticisms. Also, the carbonate–carbon dioxide reversal actually shows up at lower temperatures, thus disallowing much of the criticism based on high temperature speculations.

It has also been noted by Craig (4) that the unusually "heavy" carbonate from travertine deposits by the Tivoli River near Rome, Italy, could easily be explained by such a reversal of equilibrium at higher volcanic temperatures.

It should be noted that although methane and carbon monoxide are found in volcanic gases, their quantity is sufficiently small so that less importance should be accorded to correlations involving these compounds.

On the other hand, carbon dioxide and carbonates should assume a more important role, in view of the abundance of the former and the recently demonstrated presence of the latter in drill hole sublimates (31).

4. Oxygen isotope exchanges

Based on the abundance and uncertain origin of water in volcanic gases, it was observed that a measurement of the fractionation of oxygen isotopes would be a good way to follow the interaction of water with its environment. Other oxygen-containing molecules
of volcanic prominence (CO₂, SO₂, CO₃²⁻, O₂, CO), as well as water, were included in the equilibrium calculations for oxygen isotopes. The equilibrium constants for these interactions are shown in Table IV.

In the CO₂-CO and CO₃²⁻-H₂O exchanges, an apparent reversal in equilibrium was again observed. Inaccuracies of the same type as the ¹³C/¹²C reversal described above are still possible. Thus the reversals may be only apparent. The remaining exchange constants rapidly approach unity, at higher temperatures, with an enrichment of zero to four per mil.

B. Accuracy of equilibrium calculations

It was mentioned by Urey (63) that for precise calculations, even at the temperatures covered in the original isotopic equilibrium calculations (0-600°K), it was necessary to consider the contribution of the anharmonic terms to the total vibrational energy.

Also, the rotational terms would tend to be non-classical at higher temperatures. Thus a degree of uncertainty was introduced into the calculation of partition functions (and therefore the equilibrium constants) via the equation of Urey (63).

Calculations needed to indicate the magnitude and direction of the error introduced by the above uncertainties have been limited by a knowledge of the anharmonicity constants. A secondary reference (65) reported that anharmonicity "can
| Q2 | 1.0238 | 1.0249 | 1.0163 | 1.0196 | 1.0204 |
| Q1 | 1.0159 | 1.0169 | 1.0106 | 1.0152 | 1.0155 |
| Q1 | 1.0113 | 1.0122 | 1.0074 | 1.0121 | 1.0127 |
| Q1 | 1.0085 | 1.0092 | 1.0055 | 1.0098 | 1.010 |
| Q1 | 1.0074 | 1.0081 | 1.0048 | 1.0082 | 1.0087 |

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be of significance at high temperatures" in the calculation of equilibrium constants with the Urey equation.

Partition functions for $^{12}\text{C}^{16}\text{O}_2$ have been calculated rigorously for high temperatures and compared with the corresponding values using the harmonic oscillator and rigid-rotor approximations (66). At 1200°K an increase of two percent was observed for the rigorously calculated expressions over the corresponding approximations. This amount of error would render the high temperature calculations useless. However, the actual quantity of interest here was the partition function ratio for the isotopic molecules, and not the individual partition functions. For this reason the errors should tend to cancel somewhat. The remaining error would then be related to the extent that the $^{13}\text{C}$ substitution affected the population of the individual vibrational and rotational energies at a specific temperature. The implications of this residual error were beyond the scope and intent of the present research. However, because of the cancellation effect, it was believed that the calculations of equilibrium constants at higher temperatures were qualitatively correct, and it was within this context that the calculations have been employed throughout the portion of the work pertaining to their use.
IV. RESULTS AND DISCUSSION

A. Treatment of data

1. Measurement of peak heights

As described earlier, the accurate measurement of peak heights was facilitated by rapid manual switching from one peak to the next. However, the general drift of the recorded signal under expanded scale conditions still produced isotope ratios slightly more imprecise than desired. This was partially compensated for by measuring the height of the m/e=44 peak on either side of its companion peak (45 or 46), and using the average of the two m/e=44 measurements, together with the height of the intervening peak, to calculate the isotope ratio of interest. This procedure was usually performed eight to ten times to obtain an average value for the isotope ratio in a sample. In this manner the precision of measurements was increased by a factor of about two.

The peak heights thus obtained were then multiplied by a previously determined calibration factor (.003838 mv/mm) for the 1 mv full scale range on the recorder used (a Beckman 10-inch linear laboratory potentiometric recorder). This value represented the height of the tip of the incoming signal, as described earlier. The remainder of the signal was obtained directly from the calibrated value of the nominal supressor ranges; i.e., any value from 1 to
10 mv, depending on the magnitude of the exsunt electrometer signal. A total signal intensity was then found by adding the values of the suppressed signal and that of the expanded signal.

Following the above procedure, the total signal values for the 45 and 46 peaks were multiplied by a constant factor to correct for the difference in electrometer scale ranges. The end result was individual isotope peak heights in terms of millivolts. These values were the ones used in the final calculation of the isotope ratios.

2. Correction factors

There were several correction factors required in making accurate isotope ratios measurements. The first correction was that for background contribution to measured peak heights. At the background pressure in the analyzer tube, and with the sensitivity of the instrument, the only background correction worthwhile was the m/e=44 peak. The average correction value was found to be .004 mv, or .00008 per cent of the total signal.

A second correction factor for $^{13}\text{C}/^{12}\text{C}$ analyses was that involving the small contribution of $^{12}\text{C}^{16}\text{O}^{17}\text{O}$ (m/e=45) to the height of the $^{13}\text{C}^{16}\text{C}^{16}\text{O}$ peak (m/e=45). Nier (67) measured the value of $^{17}\text{O}^{16}\text{O}/^{16}\text{O}_2$ in air and found an average of $749 \times 10^{-6}$. This value was then subtracted from the measured 45/44 ratio in carbon dioxide to yield the correct $^{13}\text{C}/^{12}\text{C}$ value. It was later shown by
Craig (60) that this correction factor should and did differ by a small amount, depending on the source of carbon dioxide. However, in this work, the accuracy and precision were such that Craig's small correction to the correction factor was insignificant. Therefore, all the measured 45/44 ratios were corrected in this work by subtracting 749 X 10^-6.

In any mass spectrometer of this type there is a definite amount of overlap of adjacent mass peaks. To do an absolute abundance determination, then, this overlap must be corrected. Here it has been assumed that the expedient of running samples and standards under nearly identical conditions of mass spectrometer parameters and sample inlet pressure has made any corrections of this nature unnecessary. That this was justified is seen in the following section.

All experimental \(^{13}\text{C}/^{12}\text{C}\) and \(^{18}\text{O}/^{16}\text{O}\) ratios were first measured relative to the NBS 20 ratios, and then referred to PDB via the known relationship between the latter two. Thus, all delta values following are with respect to the PDB standard.

3. Precision and accuracy

A number of analyses of NBS 20 for \(^{13}\text{C}/^{12}\text{C}\) and \(^{18}\text{O}/^{16}\text{O}\) yielded the values shown in Table V. This represented an average of .01190, and .004159, for \(^{13}\text{C}/^{12}\text{C}\) and \(^{18}\text{O}/^{16}\text{O}\), respectively, and a standard deviation of 4.5 per mil for
TABLE V
PRECISION AND ACCURACY OF NBS-20 ANALYSES

<table>
<thead>
<tr>
<th>Analysis</th>
<th>$^{13}\text{C}/^{12}\text{C}$</th>
<th>$^{18}\text{O}/^{16}\text{O}$</th>
<th>Intra-run Std. Dev., ±%o</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.01195</td>
<td>0.004191</td>
<td>3.8</td>
</tr>
<tr>
<td>2</td>
<td>0.01196</td>
<td>0.004178</td>
<td>4.1</td>
</tr>
<tr>
<td>3</td>
<td>0.01197</td>
<td>0.004205</td>
<td>2.8</td>
</tr>
<tr>
<td>4</td>
<td>0.01187</td>
<td>0.004150</td>
<td>2.3</td>
</tr>
<tr>
<td>5</td>
<td>0.01183</td>
<td>0.004063</td>
<td>2.7</td>
</tr>
<tr>
<td>6</td>
<td>0.01192</td>
<td>0.004160</td>
<td>2.4</td>
</tr>
<tr>
<td>7</td>
<td>0.01192</td>
<td>0.004165</td>
<td>8.4</td>
</tr>
</tbody>
</table>
$^{13}\text{C}/^{12}\text{C}$ and 11.1 per mil for $^{18}\text{O}/^{16}\text{O}$.

The standard deviations derived from all the NBS 20 analyses are somewhat misleading, however, since there appeared to be systematic changes in the mass spectrometer over a period of a few days. This was illustrated by two observations. The intra-run standard deviation for $^{13}\text{C}/^{12}\text{C}$ analyses (also seen in Table V) was almost always less than the average $\pm 4.5$ per mil. Also, two sets of analyses, each consisting of a Sulfur Bank sample and a standard were carried out on successive days. The $^{13}\text{C}/^{12}\text{C}$ ratios of the Sulfur Bank samples (taken consecutively in the field) were almost identical when compared against their respective standards, which also agreed almost exactly. However, when several days separated the analysis of the same coral sample, a difference of sever per mil in the $^{13}\text{C}/^{12}\text{C}$ ratio was noted, with a commensurate change in the standard $^{13}\text{C}/^{12}\text{C}$ ratio. From this evidence it was concluded that, for the most accurate results, the average of the NBS carbon and oxygen ratios taken over a period of time should not be used in calculating the isotope ratio deviations of individual samples. Instead, a standard was run before each sample, and the ratios of the former used to calculate the delta values of the latter. As a result, the accuracy of the calculations of the ratio differences for each sample should be that which corresponds closely to the intra-run precision for the standard--
sample pair concerned. This was usually about ± 2 to ± 2.5 per mil for the $^{13}$C/$^{12}$C ratios and ± 3.5 to ± 4.5 per mil for the $^{18}$O/$^{16}$O ratios, which represented roughly half of the standard deviation of the carbon and oxygen isotope ratios recorded over a period of time.

The accuracy of the $^{13}$C/$^{12}$C analyses therefore compare favorably with Nier's (51) analyses utilizing a double collecting mass spectrometer. And, although a direct comparison with the ratiometer single collector instruments described earlier was not possible, it appeared that the $^{13}$C/$^{12}$C analyses here also compared favorably in precision with the results of the single collector ratiometer instrument described by Pelah, Dattner and Fischler (49). Thus, although the instrument described in this work is not nearly as precise or accurate as one using the differential technique (52), it has been shown that a single collector instrument, with the relatively simple modifications described here, can be used to obtain isotope ratios which are comparable to those usually associated with double collector instruments, or with some single collector instruments equipped with a fairly complex ratiometer device.

The reason for the larger error involved in making oxygen isotope ratio measurements in this work was judged to be due to the smaller signal output of the 46 peak (30 mv), which was more difficult to measure accurately
because of the greater noise level. Therefore, it is felt that in future analyses of the oxygen isotopes, a precision of measurement comparable to the carbon isotope ratios could be achieved by increasing the inlet pressure of the sample gas, which would result in a higher signal output and consequent greater ease and stability of measurement.

B. Isotope ratio results

1. Sulfur Bank samples

The results of the Sulfur Bank carbon dioxide samples are shown in Table VI. Since the samples were taken successively on the same day, one would expect fairly close agreement (within experimental limits) among the samples. The results agreed well within the experimental error as indicated by the intra-run precision for each sample and standard. The one exception was the oxygen ratio of Sulfur Bank Sample Number 1. The magnitude of the deviation of this value from the others, and its intra-run precision, indicated that it should be deleted when considering any equilibrium or temperature correlations.

2. Coral samples

Isotope ratio deviations for carbon and oxygen, relative to PDB, are also shown in Table VI. The Varona coral oxygen ratio deviation was the average of two analyses: -13.8 and -20.3 per mil. Although this result differed considerably from the other oxygen ratio deviations,
### TABLE VI

RESULTS OF CARBON AND OXYGEN ISOTOPE ANALYSES

#### SULFUR BANK SAMPLES

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>$\delta^{13}\text{C}, %o$</th>
<th>$\delta^{18}\text{O}, %o$</th>
<th>$^{13}\text{C}/^{12}\text{C}$</th>
<th>$^{18}\text{O}/^{16}\text{O}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-6.5</td>
<td>+31.0</td>
<td>3.0</td>
<td>31.2</td>
</tr>
<tr>
<td>2</td>
<td>-4.8</td>
<td>-23.1</td>
<td>2.0</td>
<td>3.2</td>
</tr>
<tr>
<td>3</td>
<td>-5.6</td>
<td>-27.9</td>
<td>1.9</td>
<td>4.0</td>
</tr>
</tbody>
</table>

#### CORAL SAMPLES

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\delta^{13}\text{C}, %o$</th>
<th>$\delta^{18}\text{O}, %o$</th>
<th>$^{13}\text{C}/^{12}\text{C}$</th>
<th>$^{18}\text{O}/^{16}\text{O}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Varona Coral</td>
<td>-0.6</td>
<td>-16.5</td>
<td>4.0</td>
<td>5.5</td>
</tr>
<tr>
<td>Kaena Point</td>
<td>-1.4</td>
<td>-0.2</td>
<td>2.9</td>
<td>6.7</td>
</tr>
<tr>
<td>Koko Head High Level</td>
<td>+4.5</td>
<td>-0.5</td>
<td>2.5</td>
<td>3.1</td>
</tr>
<tr>
<td>Koko Head</td>
<td>+8.7</td>
<td>-</td>
<td>1.7</td>
<td>-</td>
</tr>
</tbody>
</table>
it is unlikely that this represented experimental error alone, in view of the magnitude of the corresponding intra-run errors involved.

3. Drill Hole samples

It was later found that the drill hole samples did not contain sufficient carbon dioxide for even a guess at the isotope ratios.

Previous calculations on the amount of carbon dioxide available in drill hole samples were based on intra-laboratory analyses of gases collected at varying drill hole depths. Apparently there was insufficient carbon dioxide available at a point near the surface, where the present samples were taken. Air and water vapor appeared to be the major constituents, since abundant water was visually evident and almost no liquid nitrogen condensables were observed.

C. Major source correlations

1. Carbon isotopes

a. Sulfur Bank samples

The Sulfur Bank analyses occupy a range of -4.8 to -6.5 per mil, relative to PDB. From Appendix D, which was reproduced from Craig (4), the values for Sulfur Bank carbon dioxide were seen to fall within the range for carbonates, carbonate-derived carbon dioxide (Yellowstone Park gases), graphites, and diamonds. They are only slightly removed from marine invertebrates and plants, and from atmospheric carbon dioxide.
Graphites and diamonds were immediately ruled out as extremely unlikely geological specimens in the immediate crustal area of the Hawaiian volcanic system, in view of the fact that no samples of these forms of carbon have been reported. It is, however, possible that the carbon isotope results could indicate a high pressure and temperature source of carbon dioxide (necessary for the formation of carbon in the above forms), which in turn could correspond to a deep-seated magmatic source. The equilibrium considerations of a graphite-like source are discussed in the section dealing with equilibrium correlations.

The dividing line between carbon from marine origin and that from carbonates is a diffuse one, but the bulk of carbon ratios of the former fell between -10 and -16 per mil. And, since the bulk of the carbonates fell between +4 and -4 per mil, the values for Sulfur Bank fell almost exactly in between.

Atmospheric oxygen values overlap sufficiently to make this a possible source of contamination, were it not for the fact that such abundant quantities of carbon dioxide in Sulfur Bank would require inconceivable amounts of air (which contains only about 0.03 per cent carbon dioxide) to somehow be recycled, concentrated in carbon dioxide, and reappear at Sulfur Bank as almost 100 per cent carbon dioxide, exclusive
of water vapor. Thus this possibility was also regarded as extremely unlikely.

Origin of the carbon dioxide from plant combustion also appears very improbable, since all carbon values for plants and plant derived material (fossil wood, coal) are grouped fairly closely together with a mean delta value of about -25 per mil.

The average value of Naughton and Terada (35) for $^{12}\text{C}/^{13}\text{C}$ in Sulfur Bank gases was given as 89.0. Apparently this value represents an absolute abundance ratio. Assuming this to be true, then the delta value, using Nier's value of 88.89 (67) for Solenhofen limestone, is approximately -0.9 per mil. Since the NBS 20 standard is -0.4 per mil with respect to Nier's standard (60), Naughton's value became -0.2 per mil relative to PDB. Thus the average value found in this work agreed in approximate magnitude with that of Naughton and Terada; i.e., they both fell (within experimental accuracy) in the marine carbonate range. However, the average value found here was 5.4 per mil lighter. The implications of the slight disagreement between these values are discussed further in the equilibrium correlations.

A more recent summary of the distribution of carbon isotopes in carbonates and related materials in nature (68) showed that marine carbonates occupied a delta
range \(^{13\text{C}}/^{12\text{C}}\) of +3 to -4 per mil, hydrothermally altered limestone fell between +1.2 and -5.7 per mil, and carbonatites fell between -4 and -9 per mil, all relative to PDB. When compared with these ranges, the Sulfur Bank analyses were seen to be, within experimental error, on the light edge of the carbonatite range. Considering the average value of -5.6 per mil for the Sulfur Bank analyses, and the usual experimental accuracy of about ±2 per mil, the values for Sulfur Bank appeared to fall just inside the light end of the hydrothermally altered limestone range.

Thus, if one were to assign an origin of the Sulfur Bank carbon dioxide on the basis of the above correlations with previously observed ranges of carbon sources in nature, the several sources mentioned (marine carbonate, carbonatite, graphite-diamond, and hydrothermally altered limestone) could all be possible. Although no clearly dissected evidence was produced, it was possible that the carbon dioxide could well have been derived from a marine carbonate source, as has been suggested by Matsuo (26), or from a limestone source, as suggested by Daly (25). This would imply that the carbon dioxide was of crustal, or superficial, origin. On the other hand, the carbon dioxide could equally well have had a carbonatite
source or a graphite type source. Since carbonatites have generally been considered to be materials from deep in the earth, it was interesting to note that the assumption of either a carbonatite or graphite type source would imply a deep-seated origin of carbon dioxide. However, no carbonatite or graphite type carbon specimens have been observed in the Hawaiian volcanic system. Conversely, embedded marine carbonates have been observed in lavas on Oahu (see next section), and were believed to have been brought up from lower depths during an eruption. No corresponding embedded specimens have been observed on the island of Hawaii. It was possible that, since weathering has exposed the Oahu specimens of carbonate, natural weathering processes have not been operative on Hawaii (a geologically younger island) for a sufficiently long period of time to expose any embedded carbonate.

It should be reiterated that these conclusions were drawn without any consideration of equilibrium processes, and only as a correlation with previously observed ranges of $^{13}\text{C}/^{12}\text{C}$ ratios from natural carbon sources.

To attack the problem of the origin of carbon dioxide from a different direction; i.e., to consider the carbon dioxide as originating independently of the previously mentioned sources, it was altogether
possible that the Sulfur Bank carbon dioxide basically represents a gas endemic to the magma itself, existing as an occluded or dissolved gas under conditions of high temperature and pressure. There was no way, at the present time, to compare the Sulfur Bank $^{13}C/^{12}C$ results with a "known" magmatic carbon dioxide. Thus, although possible, the assignment of Sulfur Bank carbon dioxide as a truly magmatic gas remained purely speculative.

Based on the above discussion, perhaps the most likely source of Sulfur Bank carbon dioxide is a combination of two or more of the possibilities mentioned; i.e., a magmatic carbon dioxide adulterated with carbon dioxide from limestone and/or marine carbonate sources, or, vice-versa, a carbonate-derived carbon dioxide with significant quantities of magmatic carbon dioxide. Such a mixture would be very difficult to dissect in terms of its contributing carbon dioxide fractions. However, a concentrated and more precise isotopic study of Sulfur Bank carbon dioxide, together with corresponding isotopic evidence from nearby fumaroles and from significant geological samples, should yield some interesting results in the future.

b. Coral samples

A determination of the $^{13}C/^{12}C$ ratio in four coral samples yielded results ranging from -1.4 to +8.7 per
mil, all of which fell within the general range for carbonates.

The samples were comprised mostly of aragonite, with small percentages of calcite, as determined by others (using X-Ray diffraction) in the course of intralaboratory work (69). This data is reproduced in Appendix I.

Samples were of two general types. Coral from Kaena Point and Varona was found in inland reef deposits which were isolated by the withdrawal of the sea in the past. The Koko Head samples were embedded in lava. It is believed that these globules were broken loose during a volcanic eruption, brought near the surface, and retained there. Weathering in the case of the Koko Head, high level, and sea action in the case of Koko Head has exposed these embedded particles.

Ratios of $^{13}\text{C}/^{12}\text{C}$ fell in the same two groups, with an average of -1.0 per mil for the Varona and Kaena samples, and an average of +6.6 per mil for the Koko Head samples.

The latter value represents a considerable enrichment in $^{13}\text{C}$. Since the Sulfur Bank samples yielded such consistent isotope ratios for $^{13}\text{C}/^{12}\text{C}$, and the samples were very similar in composition, it was difficult to believe that the difference is due to
experimental error. In addition, the precision of analysis was good enough on the individual coral $^{13}\text{C}/^{12}\text{C}$ ratios to uphold this assumption.

A sample of coral limestone from Florida was analyzed by Craig (4), and a value of -1.5 per mil was found. The agreement between this value and the average value for the Kaena Point and Varona samples was good--perhaps fortuitous.

The fact that the values did agree so closely lent more strength to the analysis accuracy of the Koko Head samples, and also implied that the $^{13}\text{C}$ enrichment was at least partially real.

Enrichment in this type of sample could not readily be attributed to the type of marine organism which comprised the sample, since these are typically "light" in carbon (4).

Although some $^{13}\text{C}/^{12}\text{C}$ enrichments in dolomitic limestone have been observed (4), no such samples have been observed on Oahu; thus the incorporation of said material into the Koko Head samples analyzed here could offer an explanation of the heavy carbon isotope results, but was unlikely because of the lack of evidence for dolomitic limestone on Oahu.
2. Oxygen isotopes

a. Sulfur Bank samples

It should be reiterated that the oxygen isotope ratios recorded for all the samples in this work are more inaccurate than the carbon isotope determinations, by a factor of about two. Considering the accuracies involved in the oxygen isotope analyses, any conclusions regarding the major source of the carbon dioxide must be less reliable than the conclusions based on carbon isotope analyses.

Using a recent compilation of $^{18}O/^{16}O$ analyses of oxygen-containing species in nature (68), the oxygen isotopes in Sulfur Bank carbon dioxide (average = -25.5 per mil) were seen to fall generally in the ranges for sea water and fresh water, which were -27.6 to -29.6 per mil, and -29.6 to -48.0 per mil, relative to PDB.

The values of $\delta^{18}O$ in the above reference were relative to Standard Mean Ocean Water (S.M.O.W.), as defined by Craig (70, 60). The $\delta^{18}O$ PDB values of the water ranges above were calculated with the equation

$$\delta^{18}O_{\text{S.M.O.W.}} = (\delta^{18}O_{\text{PDB}})(1.03) + 29.5,$$

(68), and compared with the values in this work, which were relative to PDB.
The $\delta^{18}O$ average of the Sulfur Bank carbon dioxide apparently reflected an equilibrium exchange of the carbon dioxide oxygen isotopes with those of water. The only conclusion that could be drawn on the basis of the preceding information was that the Sulfur Bank carbon dioxide was probably intimately associated with water prior to and after its exit at the collection site. This, of course, was consistent with the observed abundance of water in the Sulfur Bank system.

b. Coral samples

Employing the same $\delta^{18}O$ compilation as in the previous section (68), and converting to the PDB standard, it was observed that the marine carbonates (syngenetic), fresh water carbonates, hydrothermally altered limestone, and carbonatites occupied ranges of +4.4 to -6.3 per mil, -3.9 to -18.5 per mil, -2.4 to -15.5 per mil, and -21.9 to -22.9 per mil, respectively.

Referring again to Table VI, it was observed that the Varona and Kaena Point analyses were -16.5 and -0.2 per mil. The latter result fell almost exactly in the middle of the marine carbonate range, as one might have expected. The Varona sample, however, fell within the fresh water carbonate range, and within experimental error, into the hydrothermally altered limestone range. Having observed the
consistency of the corresponding carbon analyses of the coral and that the other oxygen analyses of coral are consistent with each other, it was unlikely, as mentioned earlier, that this large difference was due to experimental error alone. However, no tenable explanation of this deviation could be advanced.

The Koko Head high level sample result (-0.5 per mil) fell in the middle of the marine carbonate range, in apparent agreement with the other coral samples.

D. Equilibrium correlations

1. Carbon isotopes

a. Sulfur Bank samples

Based on the previous conclusion concerning possible evidence for a marine carbonate source of carbon dioxide at Sulfur Bank, it was of interest to assume that this was indeed the case, and then estimate the isotopic structure of carbon dioxide evolved from such a source.

Assuming a carbonate source whose carbon isotopic delta value was the average of the Kaena Point and Varona corals, then a "fractionationless" reaction would release carbon dioxide with a delta value of -1.0 per mil. To reach the surface with a delta value of -5.6 per mil, a reaction or process must have occurred to enrich the gas in $^{12}C$. 
Looking at the equilibrium constants for $\text{CO}_2 - \text{CO}_3^-$ exchange, it was seen that the predicted equilibrium direction was the opposite of that required for a $^{12}\text{C}$ enrichment in the carbon dioxide. If a dolomitic limestone source were assumed, the required shift would be twice as large and in the same direction; i.e., the direction not favored by equilibrium.

Using the same model, the only equilibrium carbon isotope reaction resulting in $^{12}\text{C}$ enrichment would be the methane-carbon dioxide couple. This was unlikely, considering the amount of methane present in the gases. However, it cannot be completely discounted, for methane has been found in excess of the amount predicted by equilibrium calculations.

Thus, at magmatic temperatures (about $1200^\circ\text{K}$-$1500^\circ\text{K}$) it appeared that, if the model was correct, the carbonate-carbon dioxide did not exist in equilibrium. This conclusion, even if based on a proper model, is purely qualitative.

If the carbon dioxide were released at magmatic temperatures and escaped rapidly to a lower temperature chamber (about $300$-$400^\circ\text{K}$) where carbonate equilibrium was achieved, this could account for the observed depletion in $^{13}\text{C}$ in the Sulfur Bank gases (see Appendixes E, F and G for Urey's low temperature calculations). This would correspond roughly to the
Sulfur Bank exhaust temperature of 369°K. As a qualitative measure, the depletion of Sulfur Bank $^{13}\text{C}$ under these conditions could also be enough to correspond to a dolomitic limestone source.

Recently, Thode, et al. (65), have published data on the fractionation of carbon isotopes for $\text{CO}_2(\text{g}) \rightarrow \text{CO}_3^2$ and $\text{CO}_2(\text{g}) \rightarrow \text{CO}_2(\text{aq})$ reactions, from 0° to 100°C. The equilibrium constants were calculated by Urey's method (i.e., using partition function ratios). Considering the abundance of water in the Sulfur Bank system, a check of the equilibrium exchange expected at Sulfur Bank exhalation temperature (96°C) might be useful. The partition function ratios and equilibrium constants @ 95°C are reproduced in Appendix H.

The equilibrium constants are perhaps large enough to make some contribution, but are in the wrong direction; i.e., they predict an enrichment on the $^{13}\text{C}$ of the $\text{CO}_2(\text{g})$.

Of course, it was also possible that both of the last two equilibrium systems are in operation, and the observed depletion of $^{13}\text{C}$ was due to a mean result of the two opposing equilibria.

If one assumed a vegetation-derived carbon dioxide source for Sulfur Bank, and pursued the same reasoning as that based on a carbonate source, the following
points were deduced:

(1) The mean $^{13}\text{C}/^{12}\text{C}$ delta value for land plants and wood is about -25 per mil.

(2) The required enrichment in $^{13}\text{C}$ to correspond to the Sulfur Bank analysis would be 25 per mil - 5.6 per mil = 19.4 per mil.

(3) Magmatic (high temperature) equilibrium of plant-derived carbon dioxide with methane would result in an enrichment in the latter, or in the wrong direction.

(4) Magmatic equilibrium of carbon dioxide with $\text{CO}_3^-$ would probably result in enrichment in the proper direction, but of insufficient magnitude.

(5) Magmatic equilibrium of the carbon dioxide with carbon monoxide would predict an enrichment in the proper direction, but also of insufficient magnitude.

(6) At Sulfur Bank exhalation temperatures (about $369^\circ\text{K}$), the carbon dioxide-methane equilibrium exchange is in the proper direction and of sufficient magnitude.

(7) At $369^\circ\text{K}$ the $\text{CO}_2-\text{CO}_3^-$ exchange is in the wrong direction.

(8) At $369^\circ\text{K}$ the carbon dioxide-carbon monoxide exchange is in the proper direction and of more than sufficient magnitude.
(9) The CO$_2$(g) - CO$_3^-$ and CO$_2$(g) - CO$_2$(aq) exchanges (at 3680K) is in the proper direction but of insufficient magnitude.

The results of the above considerations are summarized in Table VII. The aqueous-gas exchanges were omitted in view of their previously demonstrated insignificance.

Several conclusions can be drawn from a study of this table. For both sources, the possible exchanges of sufficient magnitude and direction at high temperatures were limited to the carbon dioxide-methane exchange with a carbonate source.

At exhaust temperatures, however, there was one possibility on the CO$_2$-CO$_3^-$ with a carbonate source. For a plant source, both the carbon dioxide-methane and carbon dioxide-carbon monoxide exchanges offered possibilities.

From this it appeared that, regardless of the source, the lower temperature exchanges could more readily explain the observed fractionation in Sulfur Bank carbon dioxide. Of the two sources, it would still be more reasonable to assign carbonate as the more likely source, since the reservoir of methane and carbon monoxide necessary to provide such a large fractionation effect in gross quantities of carbon dioxide just have not been observed in Sulfur Bank
### TABLE VII

EQUILIBRIUM CORRELATIONS OF SULFUR BANK
CARBON DIOXIDE USING ASSUMED SOURCES

<table>
<thead>
<tr>
<th>MAGMATIC TEMPERATURES</th>
<th>EXHAUST TEMPERATURES</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>EXCHANGE</strong></td>
<td><strong>CO₂ - CO₃</strong></td>
</tr>
<tr>
<td>Mag. Dir.</td>
<td>Y</td>
</tr>
</tbody>
</table>

**SOURCE**

| **CARBONATE** | --- | X | X | X | --- | X | X | X | --- | X | --- | X |
| **PLANT** | X | X | --- | X | X | X | --- | X | X | X | X |

**MAG.** = SUFFICIENT MAGNITUDE?
**DIR.** = PROPER DIRECTION?
**Y** = YES
**N** = NO
gases. On the other hand, a large reservoir of carbonate material serving as an isotope exchange medium is not difficult to imagine.

Another implication arises from the above discussion: if the lower temperature exchanges provided a more likely explanation of the observed fractionation, then the carbon dioxide should be associated with the limestone source at sub-magmatic temperatures, which would in turn indicate a crustal (i.e., not magmatic) origin of the carbon dioxide.

It was observed earlier in the major source discussion that the average values of the graphite, diamond and carbonatite ranges for $^{13}\text{C}/^{12}\text{C}$ fell within about one to two per mil of the observed average value for the Sulfur Bank $^{13}\text{C}/^{12}\text{C}$ analyses. Since this span was within experimental error, it was felt that any equilibrium correlations similar to those of the carbonate and plant material were of little use. Of equal interest, however, was the assumption of a carbon source of an average delta value equivalent to the observed Sulfur Bank analyses. If all reactions involving these carbon isotopes (after their primary release in a deep-seated volcanic region) occurred at magmatic temperatures of about $1500^\circ\text{K}$, it could be considered significant that very little fractionation of the carbon isotopes
would be expected under these conditions, since the equilibrium constant approximates unity at these temperatures. The significance of the lack of fractionation was important, because it then followed that one could assume that carbon dioxide was generated and/or released under magmatic conditions, ascended through a conduit and finally emerged at Sulfur Bank in essentially the same form as it was generated.

b. Coral samples

The Kaena Point and Varona coral samples have the expected carbon isotope composition for a typical coral sample, as discussed earlier. For this reason, no particular correlation with equilibrium processes was possible within experimental error. However, it should be pointed out that these delta values reflected the probable origin of the coral formations; i.e., they would appear to be of relatively late and superficial origin, and exhibit no evidence of having undergone any drastic enrichment or depletion due to equilibrium processes.

However, the enrichment of the Koko Head samples was interesting. Craig (4) has observed carbon isotope ratios of the same approximate range (+3 to +9 per mil) in dolomites for the lower delta values of enrichment, and in travertine deposits near volcanic areas for the higher delta values of enrichment.
The latter has been postulated as possibly arising from the predicted equilibrium reversal of the CO$_3^-$ - CO$_2$ reaction at elevated temperatures (4). This was also possible with the Koko Head samples, particularly since the embedded carbonate has probably been intimately associated with volcanic areas in the past.

2. Oxygen isotopes

a. Sulfur Bank

The delta value for Sulfur Bank sample number one should be discarded (\( \sigma = \pm 31.2 \) per mil) when considering the oxygen isotope ratio deviations. An average of the remaining values yields -25.5 per mil.

As in the previous section, where the carbonate source was assumed and the ensuing $^{13}C/^{12}C$ equilibrium consequences pursued, the oxygen isotopes can be treated in a similar fashion.

If a carbonate source of oxygen isotopic composition similar to that of PDB is assumed, this means that the oxygen is "lightened" by about 25 per mil before exiting from the Sulfur Bank fumarole.

Perusing the enrichment factors (equilibrium constants) predicted at magmatic temperatures for the reactions of carbon dioxide with other oxygen-containing species, it was observed that there was no reaction that would give rise to the required depletion of $^{18}O$. 
All values of the equilibrium constants approached unity, or closely approximated it.

At a temperature of about 369°K (the Sulfur Bank exhaust temperature), based on the lower temperature equilibrium constants, there is again no enrichment which would correspond either in magnitude or direction to the observed delta value of -25.5 per mil.

b. Coral samples

Oxygen isotope ratios of the coral samples averaged out as -5.7 per mil, although the range was from -0.2 to -16.5 per mil. No particular correlation could be made with the oxygen isotopes observed in the Sulfur Bank samples.

The results were not precise enough to allow any solid state equilibrium comparisons to be made, such as the possible exchange between the calcite and aragonite fractions of the samples.

Thus the oxygen isotopes of the corals did not (at least with the present accuracy of measurements) appear to be correlative with the volcanic history of the sample source, or in any way appear to aid in an elucidation of the Sulfur Bank oxygen analyses.
E. Summary

A condensation of the preceding text should include the following points:

1. A single collector mass spectrometer has been modified to permit isotopic analyses of carbon ($^{13}\text{C}/^{12}\text{C}$) and oxygen ($^{18}\text{O}/^{16}\text{O}$) with accuracies of two and four permil, respectively, making this instrument comparable in accuracy to a double collector mass spectrometer, and comparable to a more complex single collector instrument employing a ratiometer.

2. Gas chromatography has been used as a preparative tool for the separation and collection of carbon dioxide from a volcanic gas matrix. This tool has been shown to be effective in the complete removal of contaminating gases.

3. High temperature equilibrium calculations have been made for reactions among commonly found volcanic species, but were of qualitative use only in view of the uncertainties introduced by neglect of the departure from ideality of the vibrational and rotational contributions to the partition function ratios.

4. Using the above methods, carbon and oxygen isotope analyses of several Sulfur Bank and coral samples were performed. It was shown that the observed fractionation of the carbon isotopes in Sulfur Bank
carbon dioxide could be explained by a correlation with the major source of the carbon isotopes, and by a semi-quantitative correlation of carbon isotopic equilibrium under various temperature conditions.

5. The results of the source correlations and of the equilibrium correlations pointed to the possibility of a carbonate source for Sulfur Bank carbon dioxide. Major source correlations also showed the possibility of other solid sources for carbon dioxide.

6. A possible explanation for the apparent $^{13}$C enrichment in two coral samples was advanced on a basis of the probable history of the samples.

7. Oxygen isotope interactions were found to be of little use in explaining the observed delta $^{18}$O values of either the Sulfur Bank or coral samples.

8. The possibility of a carbon dioxide originally present in magmatic gases (therefore not requiring the assumption of a solid or other precursor) was discussed, although no direct correlation with the observed Sulfur Bank $^{13}$C/$^{12}$C ratios could be made.

F. Suggestions for further work

This research has indicated a need for:

1. A more ubiquitous assay of carbon isotopes in Hawaiian volcanic gases, to establish the prevalence of carbon dioxide derived from an apparent carbonate source.
2. More accurate analyses to provide a clearer and more precise picture of the low temperature equilibrium processes indicated by this work.

3. Theoretical work on the equilibrium distribution of isotopic molecules at elevated temperatures.

4. A wider investigation of the carbon isotopic distribution in Hawaiian corals, in an effort to relate the distribution to their previous volcanic history and to the fumarolic carbon dioxide.
APPENDIX A
OPERATING PARAMETERS FOR THE MASS SPECTROMETER

Ion Source:

\[ R_1 = \text{repeller plate \#1} = 1.45 \text{ units on potentiometer dial} \]
\[ R_2 = \text{repeller plate \#2} = 2.50 \text{ units on potentiometer dial} \]
\[ D = \text{draw-out plate} = 0.00 \text{ units on potentiometer dial} \]
\[ F_1 = \text{focusing plate \#1} = 0.00 \text{ units on potentiometer dial} \]
\[ F_2 = \text{focusing plate \#2} = 10.00 \text{ units on potentiometer dial} \]
\[ A = \text{case voltage setting} = 3000 \text{ volts (with respect to ground), or 3.25 units on potentiometer dial} \]

Trap current = 14 microamperes

Trap voltage = 105 volts (with respect to the filament)

Case current = 110 microamperes

Case voltage = 80 volts (with respect to the filament)

Collector:

Collector voltage (electron suppression voltage) = 90 volts

Collector slit width = 1.4 millimeters
APPENDIX B

SAMPLING LOCATIONS FOR CORAL SAMPLES

1. KAENA POINT: Kaena Point is at the extreme northwest tip of Oahu. The Kaena Point sample was obtained at an elevation of about 90 feet above sea level, at a location roughly two miles west of the Point. Samples taken here were freshly chipped from chunks of coral, which were interspersed with the lava.

2. VARONA: The Varona sample was taken near Varona Village, which is about 1.5 miles west and 1.6 miles south of Ewa, Hawaii. These samples were obtained at an elevation of about 40 feet above sea level, and from an area where the coral had been exposed by excavation.

3. KOKO HEAD: Koko Head is part of an extinct volcano located near the southeast tip of Oahu, and adjacent to Haunama Bay Beach Park. The actual sample was taken from a sea cave just below Highway 72, about 0.5 miles east of Haunama Bay.

4. KOKO HEAD, HIGH LEVEL: This sample was taken at roughly the same geographical location as the Koko Head sample, but from a chunk of coral embedded in lava above the sea cave where the Koko Head sample was taken.
APPENDIX C

DETAILED DEVELOPMENT OF PARTITION FUNCTION AND EQUILIBRIUM EQUATIONS*—

A typical exchange reaction may be written as:

\[ aA_1 + bB_2 = aA_2 + bB_1, \]

where A and B are molecules which have some one element as a common constituent and subscripts 1 and 2 indicate that the molecule contains only the light or the heavy molecule respectively. It is well known that the equilibrium constant \( K \) for any reaction is given by

\[ -RT \ln K = \Delta F^0 \]

where \( F^0 \) is the standard free energy. For a reaction of the type \( E(1) \), one obtains

\[ -RT \ln K = aF^0_{A_2} + bF^0_{B_1} - aF^0_{A_1} - bF^0_{B_2}. \]

The free energy is related to the partition function by the following equation:

\[ F = E_0 + RT \ln N - RT \ln Q, \]

where \( E_0 \) is the "zero point energy" of the molecule,

\( N \) is the Avogadro number, and

\( Q \) is the partition function of the molecule.

On substituting \( E(4) \) in \( E(3) \) and simplifying, one gets the relation

\[ K = \frac{(Q'_{A_2})^a}{(Q'_{A_1})^b} \frac{(Q'_{B_2})^b}{(Q'_{B_1})^a} e^{-\frac{aE_{OA_2} + bE_{OB_1} - aE_{OA_1} - bE_{OB_2}}{RT}} \]

Instead of taking \( E_0 \) as the "zero point energy" (which is unique for any molecule), one can take \( E_0 \) as the bottom of the "potential energy

*Taken, with slight modification, from Tudge and Thode (14).
curve" for the molecule. Since the potential energy curves are practically identical for isotopic molecules, then $E_{OA_2}$ equals $E_{OA_1}$, and $E_{OB_2}$ equals $E_{OB_1}$. Thus the exponential term in $E(5)$ becomes unity, and

$$K = \left( \frac{Q'_A}{Q'_B} \right)^a / \left( \frac{Q'_B}{Q'_A} \right)^b$$  \hspace{1cm} E(6)$$

Therefore, in order to calculate the value of $K$, it is first necessary to determine the $Q_2/Q_1$ ratio for substances A and B.

The ratio $Q_2/Q_1$ for a chemical compound (diatomic) is given by the equation

$$\frac{Q'_2}{Q'_1} = \frac{I_2 \sigma_2^{3/2} M_2^{3/2}}{I_1 \sigma_1^{3/2} M_1^{3/2}} \frac{\frac{u_2}{e^{-2(1-e^{-u_1})}}}{\frac{u_2}{e^{-u_1}(1-e^{-u_2})} e^{-\frac{u_1}{2}}}$$  \hspace{1cm} E(7)$$

where $\sigma_2$ and $\sigma_1$ are the symmetry numbers of the two molecules (identical for all compounds studied in this paper), $M_2$ and $M_1$ are their molecular weights, $u_2$ and $u_1$ are related to the fundamental vibrational frequencies by relations of the kind $u_i = \hbar \omega_i/kT$, and $I_2$ and $I_1$ are the moments of inertia.

If the right and left sides of Equation E(7) are multiplied by $(m_1/m_2)^{3/2n}$ (where $m_1$ and $m_2$ are the atomic weights of the isotopic atoms being exchanged and $n$ is the number of isotopic atoms being exchanged) and if the right side is multiplied and divided by the ratio $\frac{u_1}{u_2}$, it is possible to simplify this expression.

Thus E(7) becomes

$$\frac{Q'_2}{Q'_1} \left( \frac{m_1}{m_2} \right)^{3/2n} = \frac{u_2}{2^{u_1}(1-e^{u_2}) e^{-\frac{u_1}{2}}}$$  \hspace{1cm} E(8)$$
since
\[
\frac{I_2 M_2^{3/2}}{m_1^{2n}} \frac{3}{u_1} = 1
\]  
\[E(9)\]
and
\[
\frac{I_1 M_1^{3/2}}{m_2^{2n}} \frac{3}{u_2}
\]
according to the Teller and Redlick theorem. New partition functions are then defined where
\[
\frac{Q_2}{Q_1} = \frac{Q'_2}{Q'_1} \left(\frac{m_1}{m_2}\right)^{\frac{3}{2n}}
\]  
\[E(10)\]
It is obvious that the equilibrium constant \(K\) is given by
\[
\left(\frac{Q_{A_2}}{Q_{A_1}}\right)^a \left(\frac{Q_{B_2}}{Q_{B_1}}\right)^b = K
\]  
\[E(11)\]
Equation \(E(8)\) can be put in a more convenient form for purposes of calculation. Defining
\[
x = \frac{u_1 + u_2}{4} \text{ and } \delta = \frac{u_1 - u_2}{2}
\]  
\[E(12)\]
and expanding in terms of \(\delta\), \(E(8)\) becomes
\[
\ln \frac{Q_2}{Q_1} = \ln \frac{\sigma_1}{\sigma_2} + \ln \frac{u_2}{u_1} + (\coth x) \delta.
\]  
\[E(13)\]
Although the entire preceding treatment has been given for diatomic molecules, it is possible to go through similar reasoning for polyatomic molecules and obtain equations similar to \(E(12)\) and \(E(13)\).
\[
\ln \frac{Q_2}{Q_1} = \ln \frac{\sigma_1}{\sigma_2} + \sum \frac{u_{2i}}{u_{1i}} + \sum (\coth x_i) \delta_i
\]  
\[E(14)\]
\[ x_i = \frac{u_{2i} + u_{1i}}{4} \; ; \; \delta_i = \frac{u_{1i} - u_{2i}}{2}. \]

The vibrational frequencies are related to the various fundamental vibrational frequencies (in cm\(^{-1}\)) of the isotopic molecules as shown above. Therefore, although the calculation for a single partition function would be extremely complicated, the partition function ratio for isotopic molecules is easily obtained from a knowledge of vibrational frequencies alone.

In order to determine \(Q_2/Q_1\), it is necessary to obtain the vibrational frequencies of the molecules containing the most abundant isotope from spectroscopic data and then to calculate the frequencies of the rare isotopic molecules by means of well known "normal vibration equations." This method must be used because, in general, the rare isotopic molecule is in such low concentration that its vibrational frequencies cannot be experimentally determined.
APPENDIX D

$^{13}C/^{12}C$ IN $\%$ of various carbonaceous samples

[Diagram showing various samples with their $^{13}C/^{12}C$ ratios]
### APPENDIX E

**PARTITION FUNCTION RATIOS AND EQUILIBRIUM CONSTANTS FOR NITROGEN ISOTOPE EXCHANGES**

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<th></th>
<th>$\frac{N^{15}H_4^+}{N^{14}H_4^+}$</th>
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<th>$\frac{N^{15}H_3}{N^{14}H_3}$</th>
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**Notes:**
- $Q_2$ and $Q_1$ are partition function ratios.
- The table lists the ratios at different temperatures.
APPENDIX F

PARTITION FUNCTION RATIOS AND EQUILIBRIUM CONSTANTS
FOR CARBON ISOTOPE EXCHANGES

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## APPENDIX G

### PARTITION FUNCTION RATIOS AND EQUILIBRIUM

**CONSTANTS FOR OXYGEN ISOTOPE EXCHANGES**

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### APPENDIX H

PARTITION FUNCTION RATIOS AND $^{13}$C EXCHANGE EQUILIBRIUM

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<th>$K_2$</th>
<th>$\frac{Q(13CO_2(aq))}{Q(12CO_2(aq))}$</th>
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APPENDIX I

PER CENT CALCITE IN ARAGONITE SAMPLES, AS DETERMINED BY X-RAY DIFFRACTION

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<td>Koko Head, High Level</td>
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APPENDIX J

FORTRAN IV PROGRAM FOR THE CALCULATION
OF ISOTOPIC PARTITION FUNCTION RATIOS

C VOLCANIC GASES
C DETERMINATION OF PARTITION FUNCTION RATIOS FOR ISOTOPE
C EXCHANGE REACTIONS IN VOLCANIC GASES

101 FORMAT (8(F8.2))
      IF(W1A.EQ.99999.99) GO TO 300
112 T = 600.0
      GO TO 122
113 T = 700.0
      GO TO 122
114 T = 800.0
      GO TO 122
115 T = 900.0
      GO TO 122
116 T = 1000.0
      GO TO 122
117 T = 1100.0
      GO TO 122
118 T = 1200.0
      GO TO 122
119 T = 1300.0
      GO TO 122
120 T = 1400.0
      GO TO 122
121 T = 1500.0
122 H1 = (10.)**(27.)
C1 = (10.)**(+10.)
BK1 = (10.)**(-16.)
H = (6.6256)*(H1)
C = (2.997925)*(C1)
BK = (1.38054)*(BK1)
Z = (H*C)/((BK)*(T))

104 SR = 0
U1A = Z*(W1A)
U2A = Z*(W2A)
XA = (U1A + U2A)/4.
DELTA A = (U1A - U2A)/2.
YA = (U2A)/(U1A)
RA = ALOG(YA)

5 PAA = TANH(XA)
PA = (1./(PAA))*DELTA A
I = I + 1
IF(I.LE.30)GO TO 111

500 UIB = Z*(W1B)
U2B = Z*(W2B)
XB = (U1B + U2B)/4.
DELTA B = (U1B - U2B)/2.
2 YB = (U2B)/(U1B)
RB = ALOG(YB)
PBA = TANH(XB)
PB = (1./(PBA))*DELTA B
U1C = Z*(W1C)
U2C = Z*(W2C)
XC = (U1C + U2C)/4.
DELTA C = (U1C - U2C)/2.
3 YC = (U2C)/(U1C)
RC = ALOG(YC)
PCA = TANH(XC)
PC = (1./(PCA))*DELTA C
IF(I.LE.60) GO TO 111

412 U1D = Z*(W1D)
U2D = Z*(W2D)
XD = (U1D + U2D)/4.
DELTA D = (U1D - U2D)/2.

YD = (U2D)/(U1D)
RD = ALOG(YD)
PDA = TANH(XD)
PD = (1./(PDA))*(DELTA D)

CONTINUE

IF(I.GE.11) GO TO 400
GO TO (220,221,222,223,224,225,226,227,228,229), I

220 PR2TO = EXP(SR+RA+PA)
GO TO 113

221 PR2T1 = EXP(SR+RA+PA)
GO TO 114

222 PR2T2 = EXP(SR+RA+PA)
GO TO 115

223 PR2T3 = EXP(SR+RA+PA)
GO TO 116

224 PR2T4 = EXP(SR+RA+PA)
GO TO 117

225 PR2T5 = EXP(SR+RA+PA)
GO TO 118

226 PR2T6 = EXP(SR+RA+PA)
GO TO 119

227 PR2T7 = EXP(SR+RA+PA)
GO TO 120

228 PR2T8 = EXP(SR+RA+PA)
GO TO 121

229 PR2T9 = EXP(SR+RA+PA)
GO TO 1

400 CONTINUE

IF(I.GE.21) GO TO 401
GO TO (220,221,222,223,224,225,226,227,228,229,230,231,232,233,
1234,235,236,237,238,239), I
230 PR3TO = EXP(SR+RA+PA)
PR3TOA = SQRT(PR3TO)
GO TO 113
231 PR3T1 = EXP(SR+RA+PA)
PR3T1A = SQRT(PR3T1)
GO TO 114
232 PR3T2 = EXP(SR+RA+PA)
PR3T2A = SQRT(PR3T2)
GO TO 115
233 PR3T3 = EXP(SR+RA+PA)
PR3T3A = SQRT(PR3T3)
GO TO 116
234 PR3T4 = EXP(SR+RA+PA)
PR3T4A = SQRT(PR3T4)
GO TO 117
235 PR3T5 = EXP(SR+RA+PA)
PR3T5A = SQRT(PR3T5)
GO TO 118
236 PR3T6 = EXP(SR+RA+PA)
PR3T6A = SQRT(PR3T6)
GO TO 119
237 PR3T7 = EXP(SR+RA+PA)
PR3T7A = SQRT(PR3T7)
GO TO 120
238 PR3T8 = EXP(SR+RA+PA)
PR3T8A = SQRT(PR3T8)
GO TO 121
239 PR3T9 = EXP(SR+RA+PA)
PR3T9A = SQRT(PR3T9)
GO TO 1
401 CONTINUE
   J = J + 1
   IF(I.GE.31)GO TO 402
   GO TO(260,261,262,263,264,265,266,267,268,269),J
260  PR6TO = EXP(RA+PA)
     GO TO 113
261  PR6T1 = EXP(RA+PA)
     GO TO 114
262  PR6T2 = EXP(RA+PA)
     GO TO 115
263  PR6T3 = EXP(RA+PA)
     GO TO 116
264  PR6T4 = EXP(RA+PA)
     GO TO 117
265  PR6T5 = EXP(RA+PA)
     GO TO 118
266  PR6T6 = EXP(RA+PA)
     GO TO 119
267  PR6T7 = EXP(RA+PA)
     GO TO 120
268  PR6T8 = EXP(RA+PA)
     GO TO 121
269  PR6T9 = EXP(RA+PA)
     GO TO 1
402  CONTINUE
   IF(I.GE.41)GO TO 403
   GO TO(260,261,262,263,264,265,266,267,268,269,200,201,202,203,  
   1204,205,206,207,208,209),J
200  PROTO = EXP(SR+RA+(2.)*(RB)+RC+PA+(2.)*(PB)+PC)
     GO TO 113
201  PROTI = EXP(SR+RA+(2.)*(RB)+RC+PA+(2.)*(PB)+PC)
     GO TO 114
202  PROT2 = EXP(SR+RA+(2.)*(RB)+RC+PA+(2.)*(PB)+PC)
     GO TO 115
203  PROT3 = EXP(SR+RA+(2.)*(RB)+RC+PA+(2.)*(PB)+PC)
     GO TO 116
204  PROT4 = EXP(SR+RA+(2.)*(RB)+RC+PA+(2.)*(PB)+PC)
     GO TO 117
205  PROT5 = EXP(SR+RA+(2.)*(RB)+RC+PA+(2.)*(PB)+PC)
GO TO 118
206 PROT6 = EXP(SR+RA+(2.)*(RB)+RC+PA+(2.)*(PB)+PC)
GO TO 119
207 PROT7 = EXP(SR+RA+(2.)*(RB)+RC+PA+(2.)*(PB)+PC)
GO TO 120
208 PROT8 = EXP(SR+RA+(2.)*(RB)+RC+PA+(2.)*(PB)+PC)
GO TO 121
209 PROT9 = EXP(SR+RA+(2.)*(RB)+RC+PA+(2.)*(PB)+PC)
GO TO 1
403 CONTINUE
K = K + 1
IF(I.GE.51)GO TO 404
GO TO (270,271,272,273,274,275,276,277,278,279),K
270 PROTTO = EXP(SR+RA+(2.)*(RB)+RC+PA+(2.)*(PB)+PC)
PROTTOA = SQRT(PROTT0)
GO TO 113
271 PROT11 = EXP(SR+RA+(2.)*(RB)+RC+PA+(2.)*(PB)+PC)
PROTT1A = SQRT(PROTT1)
GO TO 114
272 PROT12 = EXP(SR+RA+(2.)*(RB)+RC+PA+(2.)*(PB)+PC)
PROTT2A = SQRT(PROTT2)
GO TO 115
273 PROT13 = EXP(SR+RA+(2.)*(RB)+RC+PA+(2.)*(PB)+PC)
PROTT3A = SQRT(PROTT3)
GO TO 116
274 PROT14 = EXP(SR+RA+(2.)*(RB)+RC+PA+(2.)*(PB)+PC)
PROTT4A = SQRT(PROTT4)
GO TO 117
275 PROT15 = EXP(SR+RA+(2.)*(RB)+RC+PA+(2.)*(PB)+PC)
PROTT5A = SQRT(PROTT5)
GO TO 118
276 PROT16 = EXP(SR+RA+(2.)*(RB)+RC+PA+(2.)*(PB)+PC)
PROTT6A = SQRT(PROTT6)
GO TO 119
277 \[ \text{PR7T7} = \exp(\text{SR}+\text{RA}+(2.)*(\text{RB})+\text{RC}+(2.)*(\text{PB})+\text{PC}) \]
\[ \text{PR7T7A} = \sqrt{\text{PR7T7}} \]
GO TO 120

278 \[ \text{PR7T8} = \exp(\text{SR}+\text{RA}+(2.)*(\text{RB})+\text{RC}+(2.)*(\text{PB})+\text{PC}) \]
\[ \text{PR7T8A} = \sqrt{\text{PR7T8}} \]
GO TO 121

279 \[ \text{PR7T9} = \exp(\text{SR}+\text{RA}+(2.)*(\text{RB})+\text{RC}+(2.)*(\text{PB})+\text{PC}) \]
\[ \text{PR7T9A} = \sqrt{\text{PR7T9}} \]
GO TO 1

404 CONTINUE

IF(I.GE.61)GO TO 405

GO TO(270,271,272,273,274,275,276,277,278,279,290,291,292,293,1294,295,296,297,298,299,K

290 \[ \text{PR9TOA} = \exp(\text{SR}+\text{RA}+\text{RB}+\text{RC}+\text{PA}+\text{PB}+\text{PC}+\text{PA1}+\text{PB1}+\text{PC1}) \]
\[ \text{PR9TO} = \sqrt{\text{PR9TOA}} \]
GO TO 113

291 \[ \text{PR9T1A} = \exp(\text{SR}+\text{RA}+\text{RB}+\text{RC}+\text{PA}+\text{PB}+\text{PC}+\text{PA1}+\text{PB1}+\text{PC1}) \]
\[ \text{PR9T1} = \sqrt{\text{PR9T1A}} \]
GO TO 114

292 \[ \text{PR9T2A} = \exp(\text{SR}+\text{RA}+\text{RB}+\text{RC}+\text{PA}+\text{PB}+\text{PC}+\text{PA1}+\text{PB1}+\text{PC1}) \]
\[ \text{PR9T2} = \sqrt{\text{PR9T2A}} \]
GO TO 115

293 \[ \text{PR9T3A} = \exp(\text{SR}+\text{RA}+\text{RB}+\text{RC}+\text{PA}+\text{PB}+\text{PC}+\text{PA1}+\text{PB1}+\text{PC1}) \]
\[ \text{PR9T3} = \sqrt{\text{PR9T3A}} \]
GO TO 116

294 \[ \text{PR9T4A} = \exp(\text{SR}+\text{RA}+\text{RB}+\text{RC}+\text{PA}+\text{PB}+\text{PC}+\text{PA1}+\text{PB1}+\text{PC1}) \]
\[ \text{PR9T4} = \sqrt{\text{PR9T4A}} \]
GO TO 117

295 \[ \text{PR9T5A} = \exp(\text{SR}+\text{RA}+\text{RB}+\text{RC}+\text{PA}+\text{PB}+\text{PC}+\text{PA1}+\text{PB1}+\text{PC1}) \]
\[ \text{PR9T5} = \sqrt{\text{PR9T5A}} \]
GO TO 118

296 \[ \text{PR9T6A} = \exp(\text{SR}+\text{RA}+\text{RB}+\text{RC}+\text{PA}+\text{PB}+\text{PC}+\text{PA1}+\text{PB1}+\text{PC1}) \]
\[ \text{PR9T6} = \sqrt{\text{PR9T6A}} \]
GO TO 119
297 \[ PR9T7A = \exp(SR+RA+RB+RC+PA+PB+PC+PA1+PB1+PC1) \]
   \[ PR9T7 = \sqrt{PR9T7A} \]
   GO TO 120

298 \[ PR9T8A = \exp(SR+RA+RB+RC+PA+PB+PC+PA1+PB1+PC1) \]
   \[ PR9T8 = \sqrt{PR9T8A} \]
   GO TO 121

299 \[ PR9T9A = \exp(SR+RA+RB+RC+PA+PB+PC+PA1+PB1+PC1) \]
   \[ PR9T9 = \sqrt{PR9T9A} \]
   GO TO 1

405 CONTINUE
   \[ L = L + 1 \]
   IF(I.GE.71)GO TO 406
   GO TO(210,211,212,213,214,215,216,217,218,219),L

210 \[ PR1T0 = \exp(SR+RA+RB+(2.)*(RC+RD)+PA+PB+(2.)*(PC+PD)) \]
   GO TO 113

211 \[ PR1T1 = \exp(SR+RA+RB+(2.)*(RC+RD)+PA+PB+(2.)*(PC+PD)) \]
   GO TO 114

212 \[ PR1T2 = \exp(SR+RA+RB+(2.)*(RC+RD)+PA+PB+(2.)*(PC+PD)) \]
   GO TO 115

213 \[ PR1T3 = \exp(SR+RA+RB+(2.)*(RC+RD)+PA+PB+(2.)*(PC+PD)) \]
   GO TO 116

214 \[ PR1T4 = \exp(SR+RA+RB+(2.)*(RC+RD)+PA+PB+(2.)*(PC+PD)) \]
   GO TO 117

215 \[ PR1T5 = \exp(SR+RA+RB+(2.)*(RC+RD)+PA+PB+(2.)*(PC+PD)) \]
   GO TO 118

216 \[ PR1T6 = \exp(SR+RA+RB+(2.)*(RC+RD)+PA+PB+(2.)*(PC+PD)) \]
   GO TO 119

217 \[ PR1T7 = \exp(SR+RA+RB+(2.)*(RC+RD)+PA+PB+(2.)*(PC+PD)) \]
   GO TO 120

218 \[ PR1T8 = \exp(SR+RA+RB+(2.)*(RC+RD)+PA+PB+(2.)*(PC+PD)) \]
   GO TO 121

219 \[ PR1T9 = \exp(SR+RA+RB+(2.)*(RC+RD)+PA+PB+(2.)*(PC+PD)) \]
   GO TO 1
CONTINUE
IF(I.GE.81)GO TO 407
GO TO (210, 211, 212, 213, 214, 215, 216, 217, 218, 219, 240, 241, 242, 243, 
1244, 245, 246, 247, 248, 249, L
240 PR4TOA = EXP(SR + RA + (2.)*(RB) + (3.)*(RC+RD) + PA + (2.)*(PB) + (3.)*(PC+PD))
PR4TO = (PR4TOA)**(.2500)
GO TO 113
241 PR4T1A = EXP(SR + RA + (2.)*(RB) + (3.)*(RC+RD) + PA + (2.)*(PB) + (3.)*(PC+PD))
PR4T1 = (PR4T1A)**(.2500)
GO TO 114
242 PR4T2A = EXP(SR + RA + (2.)*(RB) + (3.)*(RC+RD) + PA + (2.)*(PB) + (3.)*(PC+PD))
PR4T2 = (PR4T2A)**(.2500)
GO TO 115
243 PR4T3A = EXP(SR + RA + (2.)*(RB) + (3.)*(RC+RD) + PA + (2.)*(PB) + (3.)*(PC+PD))
PR4T3 = (PR4T3A)**(.2500)
GO TO 116
244 PR4T4A = EXP(SR + RA + (2.)*(RB) + (3.)*(RC+RD) + PA + (2.)*(PB) + (3.)*(PC+PD))
PR4T4 = (PR4T4A)**(.2500)
GO TO 117
245 PR4T5A = EXP(SR + RA + (2.)*(RB) + (3.)*(RC+RD) + PA + (2.)*(PB) + (3.)*(PC+PD))
PR4T5 = (PR4T5A)**(.2500)
GO TO 118
246 PR4T6A = EXP(SR + RA + (2.)*(RB) + (3.)*(RC+RD) + PA + (2.)*(PB) + (3.)*(PC+PD))
PR4T6 = (PR4T6A)**(.2500)
GO TO 119
247 PR4T7A = EXP(SR + RA + (2.)*(RB) + (3.)*(RC+RD) + PA + (2.)*(PB) + (3.)*(PC+PD))
PR4T7 = (PR4T7A)**(.2500)
GO TO 120
248 PR4T8A = EXP(SR + RA + (2.)*(RB) + (3.)*(RC+RD) + PA + (2.)*(PB) + (3.)*(PC+PD))
PR4T8 = (PR4T8A)**(.2500)
GO TO 121
249 PR4T9A = EXP(SR + RA + (2.)*(RB) + (3.)*(RC+RD) + PA + (2.)*(PB) + (3.)*(PC+PD))
PR4T9 = (PR4T9A)**(.2500)
GO TO 1
407 CONTINUE
M = M + 1
IF(I.GE.91)GO TO 600
GO TO (250, 251, 252, 253, 254, 255, 256, 257, 258, 259), M
250 PR5TO = EXP(SR+RA+RB+(2.)*(RC+RD)+PA+PB+2.*(PC+PD))
GO TO 113
251 PR5T1 = EXP(SR+RA+RB+(2.)*(RC+RD)+PA+PB+2.*(PC+PD))
GO TO 114
252 PR5T2 = EXP(SR+RA+RB+(2.)*(RC+RD)+PA+PB+2.*(PC+PD))
GO TO 115
253 PR5T3 = EXP(SR+RA+RB+(2.)*(RC+RD)+PA+PB+2.*(PC+PD))
GO TO 116
254 PR5T4 = EXP(SR+RA+RB+(2.)*(RC+RD)+PA+PB+2.*(PC+PD))
GO TO 117
255 PR5T5 = EXP(SR+RA+RB+(2.)*(RC+RD)+PA+PB+2.*(PC+PD))
GO TO 118
256 PR5T6 = EXP(SR+RA+RB+(2.)*(RC+RD)+PA+PB+2.*(PC+PD))
GO TO 119
257 PR5T7 = EXP(SR+RA+RB+(2.)*(RC+RD)+PA+PB+2.*(PC+PD))
GO TO 120
258 PR5T8 = EXP(SR+RA+RB+(2.)*(RC+RD)+PA+PB+2.*(PC+PD))
GO TO 121
259 PR5T9 = EXP(SR+RA+RB+(2.)*(RC+RD)+PA+PB+2.*(PC+PD))
GO TO 1
600 CONTINUE
N = N + 1
GO TO (280, 281, 282, 283, 284, 285, 286, 287, 288, 289), N
280 PR8TO = EXP(SR+RA+RB+(2.)*(RC+RD)+PA+PB+2.*(PC+PD))
PR8TOA = (PR8TO)**(0.333333)
GO TO 113
281 PR8T1 = EXP(SR+RA+RB+(2.)*(RC+RD)+PA+PB+2.*(PC+PD))
PR8T1A = (PR8T1)**(0.333333)
GO TO 114
282 $\text{PR8T2} = \exp(SR + RA + RB + (2.)*(RC + RD) + PA + PB + (2.)*(PC + PD))$

$\text{PR8T2A} = (\text{PR8T2})^{0.333333}$

GO TO 115

283 $\text{PR8T3} = \exp(SR + RA + RB + (2.)*(RC + RD) + PA + PB + (2.)*(PC + PD))$

$\text{PR8T3A} = (\text{PR8T3})^{0.333333}$

GO TO 116

284 $\text{PR8T4} = \exp(SR + RA + RB + (2.)*(RC + RD) + PA + PB + (2.)*(PC + PD))$

$\text{PR8T4A} = (\text{PR8T4})^{0.333333}$

GO TO 117

285 $\text{PR8T5} = \exp(SR + RA + RB + (2.)*(RC + RD) + PA + PB + (2.)*(PC + PD))$

$\text{PR8T5A} = (\text{PR8T5})^{0.333333}$

GO TO 118

286 $\text{PR8T6} = \exp(SR + RA + RB + (2.)*(RC + RD) + PA + PB + (2.)*(PC + PD))$

$\text{PR8T6A} = (\text{PR8T6})^{0.333333}$

GO TO 119

287 $\text{PR8T7} = \exp(SR + RA + RB + (2.)*(RC + RD) + PA + PB + (2.)*(PC + PD))$

$\text{PR8T7A} = (\text{PR8T7})^{0.333333}$

GO TO 120

288 $\text{PR8T8} = \exp(SR + RA + RB + (2.)*(RC + RD) + PA + PB + (2.)*(PC + PD))$

$\text{PR8T8A} = (\text{PR8T8})^{0.333333}$

GO TO 121

289 $\text{PR8T9} = \exp(SR + RA + RB + (2.)*(RC + RD) + PA + PB + (2.)*(PC + PD))$

$\text{PR8T9A} = (\text{PR8T9})^{0.333333}$

GO TO 1

300 CONTINUE

301 WRITE(6,110)PROTO,PROT1,PROT2,PROT3,PROT4,PROT5,PROT6,PROT7,PROT8,ulen1,PROT9,PR10,PR11,PR12,PR13,PR14,PR15,PR16,PR17,PR18,PR19,ul2,PR20,PR21,PR22,PR23,PR24,PR25,PR26,PR27,PR28,PR29,PRO30,ulen3,PR31,PR32,PR33,PR34,PR35,PR36,PR37,PR38,PR39,PR40,ulen4,PR41,PR42,PR43,PR44,PR45,PR46,PR47,PR48,PR49,PR50,ulen5,PR51,PR52,PR53,PR54,PR55,PR56,PR57,PR58,PR59,PR60,ulen6,PR61,PR62,PR63,PR64,PR65,PR66,PR67,PR68,PR69,PR70,ulen7,PR71,PR72,PR73,PR74,PR75,PR76,PR77,PR78,PR79,PR8TOA,ulen8,PR8TOA,PR8TOA,PR8TOA,ulen9,PR8TOA,PR8TOA,ulen10,PR8TOA,PR8TOA,ulen11,PR8TOA,PR8TOA

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8B2A, PR8T3A, PR8T4A, PR8T5A, PR8T6A, PR8T7A, PR8T8A, PR8T9A, PR9T0, PR9T1,
PR9T2, PR9T3, PR9T4, PR9T5, PR9T6, PR9T7, PR9T8, PR9T9

110 FORMAT(6H C C02,10(F10.4)//6H C C03,10(F10.4)//5H C CO,10(F10.4)];//
13H N2,10(F10.4)//6H N NH4,10(F10.4)//6H N NH3,10(F10.4)//5H O CO,1
20(F10.4)//6H O CO2,10(F10.4)//6H O CO3,10(F10.4)//6H O H2O,10(F10.3
4))
STOP
END
ADDITIONAL INFORMATION FOR
THE FORTRAN IV PROGRAM

The parameters used in the preceding program were:

\[ T = \text{absolute temperature, } ^{0}\text{K} \]

\[ H = \text{Planck's constant} \]

\[ C = \text{velocity of light} \]

\[ B_K = \text{Boltzmann's constant} \]

\[ W_{1A}, W_{1B}, W_{1C}, W_{1D} = \text{fundamental vibration frequencies (cm}^{-1}) \]
\[ \text{of molecule 1 (containing light isotope)} \]
\[ = \omega_{1a}, \omega_{1b}, \omega_{1c}, \omega_{1d}, \text{respectively.} \]

\[ W_{2A}, W_{2B}, W_{2C}, W_{2D} = \text{fundamental vibration frequencies (cm}^{-1}) \]
\[ \text{of molecule 2 (containing heavy isotope)} \]
\[ = \omega_{2a}, \omega_{2b}, \omega_{2c}, \omega_{2d}, \text{respectively.} \]

\[ U_{1A}, U_{1B}, U_{1C}, U_{1D} = u_{1a}, u_{1b}, u_{1c}, u_{1d}, \text{respectively.} \]

\[ U_{2A}, U_{2B}, U_{2C}, U_{2D} = u_{2a}, u_{2b}, u_{2c}, u_{2d}, \text{respectively.} \]

\[ X_A, X_B, X_C, X_D = x_a, x_b, x_c, x_d, \text{respectively.} \]

\[ \text{SR} = \ln \frac{\sigma_1}{\sigma_2} \]

\[ \text{DELTA A, DELTA B, DELTA C, DELTA D} = \delta_A, \delta_B, \delta_C, \delta_D, \text{respectively} \]

\[ \text{PR2T0} = \text{partition function ratio for molecule number two at} \]
\[ \text{temperature number one.} \]

\[ \text{PR2T1} = \text{partition function ratio for molecule number two at} \]
\[ \text{temperature number two.} \]

\[ \text{etc.} \]
For the output FORMAT:

\[ \text{C0}_2 = \text{partition function ratio of the oxygen-18 and oxygen-16 isotopic molecules of CO}_2. \]

\[ \text{C CO}_3 = \text{partition function ratio of the carbon-13 and carbon-12 isotopic ions of CO}_3^+. \]

e tc.

The above program was set up to calculate the isotopic partition function ratios of ten different molecules, for each of ten different temperatures. Although the range of 600°K to 1500°K was used above, any desired combination of temperatures could be used by changing the temperature statements to incorporate the desired values.

Since each molecule had a characteristic pattern of degenerate vibrations, the final equation used for calculating the partition function ratio was specific. However, if two molecules had identical degeneracy patterns (e.g., \( \text{SO}_2 \) and \( \text{H}_2\text{O} \)) then the ratio for \( (\text{S}^{18}\text{O}_2/\text{S}^{16}\text{O}_2)^{1/2} \) could be calculated with the equation for the \( \text{H}_2^{18}\text{O}/\text{H}_2^{16}\text{O} \) ratio (correcting only for the square root) simply by substituting a data card containing the vibration frequencies of the \( \text{S}^{18}\text{O}_2 \) and \( \text{S}^{16}\text{O}_2 \) molecules. Therefore, although the original program was used for the molecules listed in the FORMAT statement, the above program was actually a modification to permit the calculation of partition function ratios for \( \text{O}_2 \) in place of \( \text{N}_2 \), \( \text{O} \text{SO}_4 \) in place of \( \text{N} \text{NH}_4 \), and \( \text{O} \text{SO}_2 \) in place of \( \text{O} \text{H}_2\text{O} \). The FORMAT statement detail was not changed to refer to the substitute molecules. Their presence was simply noted on the data output sheet.
The final equilibrium constants were computed with an electric calculator, since the simplicity of their calculation did not warrant use of the computer.
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