NASA TECHNICAL REPORT

NASA TR R-348

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NASA TR R-348

THE COMPOSITION OF THE BASALTIC GAS PHASE

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • MAY 1971

1. Report No.
NASA TR R-348

2. Government Accession No.

3. Recipient's Catalog No.

4. Title and Subtitle
The Composition of the Basaltic Gas Phase

5. Report Date
May 1971

6. Performing Organization Code

7. Author(s)
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8. Performing Organization Report No.
G-971

9. Performing Organization Name and Address
Goddard Space Flight Center
Greenbelt, Maryland 20771

10. Work Unit No.

11. Contract or Grant No.

12. Sponsoring Agency Name and Address
National Aeronautics and Space Administration
Washington, D. C. 20546

13. Type of Report and Period Covered
Technical Report

14. Sponsoring Agency Code

15. Supplementary Notes
Formerly submitted to the University of Chicago in partial fulfillment of the requirements for the degree of Doctor of Philosophy in geophysical sciences.

16. Abstract

Volcanic gas collections are used to calculate the composition of the original magmatic gas. Alteration from this original gas, to varying degrees, by surface or near-surface modifying processes is hypothesized. Four methods of removing atmospheric contamination give, for each sample, four atomic compositions, which yield equilibrium (molecular) compositions from 650° to 1250°C at 1 atm. The compositions are used to examine other modifying processes.

It is shown that water contamination causes all variations in hydrogen content. Sulfur content changes considerably from loss of SO_2. Atmospheric and water contamination and SO_2 loss are shown to account for all modifications.

Although all samples were derived from an equilibrium composition at magmatic temperatures, examination shows that none is at equilibrium as collected. Imperfect quenching during--and oxidation during and after--collection caused nonequilibrium.

The various contaminations and losses are discussed as they affect the total gas composition, quantitative amounts of additions, and losses being presented for each sample.

17. Key Words Suggested by Author
Basaltic
Magmatic
Kilauea volcano
Volcanic gas

18. Distribution Statement
Unclassified--Unlimited

19. Security Classif. (of this report)	20. Security Classif. (of this page)	21. No. of Pages	22. Price*
Unclassified	Unclassified	81	$3.00

*For sale by the National Technical Information Service, Springfield, Virginia 22151

SUMMARY

Fourteen volcanic gas collections from Kilauea, Hawaii, are used to calculate the composition of the magmatic gas from which the samples were derived. It is hypothesized that all samples originally had the same magmatic composition and were altered to varying degrees by modifying processes occurring at or near the surface. Atmospheric contamination is present in all samples; removal of atmospheric gases by four different methods results in four atomic compositions for each sample. These atomic compositions are used to compute equilibrium (molecular) compositions from 650° to 1250°C at 1 atmosphere pressure. The validity of each method is judged, in part, on the basis of the partial pressure of oxygen (PO_2). The four atomic and equilibrium compositions of each sample are used to examine the effects of other modifying factors which have altered the original magmatic gas composition.

Simultaneous consideration of atmospheric and water contamination defines the best method of atmospheric gas removal and shows that all variations in hydrogen content are due to contaminating water. Contaminating water is present in the gas collections in amounts up to 100 times the original amount.

The carbon content of the magmatic gas has not been significantly changed by the modifying processes, but large changes in sulfur content have occurred from loss of SO_2. It is shown that other sulfur gas species are not responsible for compositional changes to any significant degree. When atmospheric contamination, water contamination, and SO_2 loss are considered simultaneously, all differences in sample compositions are accounted for. This complete agreement shows that all samples are related, having been modified by these processes.

The compositional changes caused by these processes are then "reversed" to remove their effects and return each sample to the original magmatic composition. All samples lead to the same magmatic gas composition; this internal consistency supports the original hypothesis and the methods used.

The samples are then examined for the degree to which they approach equilibrium compositions as collected. Although none of the samples are at equilibrium, each was derived from an equilibrium composition at magmatic temperatures. Imperfect quenching during collection, and oxidation during and after collection, caused nonequilibrium. Oxidation of H_2S and SO_2 resulted in the formation of (S_2 + H_2O) and SO_3, respectively. The study shows that various groups of gases quench at different rates, thereby exhibiting a "spectrum" of quenching temperatures.

The various contaminations and losses are discussed as they affect the total gas composition. Quantitative amounts of additions and losses in each sample are also presented.

FOREWORD

This report concerns the deduction of the chemical composition of the volatile fraction of basaltic magma before contamination by surface effects and atmosphere constituents. The results achieved differ from and, I believe, represent a considerable improvement over, previous interpretations because the investigator has for the first time combined rigorous mathematical analysis and geologic know-how to correct for the ever-present contaminants. Although this work is of obvious importance to geology, it is even more significant in its bearing on the planetology of the terrestrial planets and on selenology. It is very likely that volcanic magmas have, through the ages, brought volatiles to the surfaces of these bodies. It is also likely that these volatiles have been important in forming the present surface layers and atmospheres of these bodies, just as on Earth. In the case of the Moon, studies of this kind may ultimately show what volatiles have been lost to space.

It may seem curious that these collections from Hawaii, dating back to 1917, were used. Of course, there have been numerous later analyses of volcanic gases; however, many of these analyses refer to volcanoes of diverse types and lack the homogeneity of composition necessary for a study of this kind. In addition, the personal skills of the collectors and analysts (T.A. Jaggar and E.S. Shepherd) appear to have compensated for the lack of modern techniques. In any case, the high quality of their data is brought out by the results of Nordlie's analysis.

Although the uncorrected chemical analyses of the Kilauean gases have been published for a long time, the interpretation of these analyses has generally been approached in a spirit of pessimism. Typical is the remark of Shepherd himself (1938) that "The one obvious fact brought out by the analyses...is the lack of any definite relationships among the constituents involved." Although the subsequent work of Ellis (1957) and of Heald, Naughton, and Barnes (1963) brought some order out of this chaos, Nordlie's work has revealed for the first time the great significance of the collection. Some of the most important results of his work are as follows:

(1) Identification of nature of the contaminants and the relations between them and the magmatic gas. (Especially important are the correlations made with the theoretical "water addition" and "sulfur subtraction" curves.)

(2) Classification of the various gases in terms of their reaction kinetics.

(3) Increasing our knowledge of the role of N_2 and Ar in volcanic processes.

(4) Showing the importance of SO_2 and CO_2 in volcanic processes.

(5) Calculation of the equilibrium composition of the magmatic gas (uncontaminated by surface effects and atmospheric constituents).

The basaltic Hawaiian volcanoes are among the most suitable of all volcanoes for the determination of the so-called juvenile component of the magmatic gas (that fraction which comes directly from the magmatic source), since they are far from the influence of continental rocks and are thought to come directly from the mantle. To the extent that this juvenile component can be identified — and here we are still in some doubt — the corrected analyses should represent a sample of the volatile fraction that is being emitted today by the upper mantle and is being contributed to the crust, hydrosphere and atmosphere. The corrected data thus have considerable significance in the study of terrestrial volcanology and the evolution of Earth's outer layers.

Among the planets the results of this study should apply most directly to Venus since its mass and density so closely approach those of Earth. We should also expect that on Venus basaltic lavas not much different from our own, and with similar complements of volatiles, should have reached the surface throughout geologic time. The high CO_2 content of the Hawaiian gases found by Nordlie would seem to imply a similar ultimate source of this gas on Venus. However, on Venus, the surface temperatures are too high for CO_2 to combine with crustal rocks to the extent it does on Earth, and much of it remains in the atmosphere. Then, too, the abundance of SO_2 in Hawaiian gases hints that sulfur should be approximately as abundant on Venus as on Earth. Perhaps on Venus more of this element occurs as SO_2 in the atmosphere. The important point here is that, although no sulfur compounds have yet been detected on Venus, they should continually be reaching the surface from the interior.

Although the characteristics of the magmatic gas as deduced here may apply directly only to Venus, the general method of approach is relevant to the other terrestrial planets. It is possible, for example, that the volcanic emanations of Mercury are considerably less than for the other terrestrial planets because the density of Mercury seems to imply that it is rich in metallic iron. In particular, this would be reflected in high CO/CO_2 and H_2/H_2O ratios of emitted gases. Conversely, the low density of Mars may imply a more highly oxidized state than obtains on either Earth or Venus. Whatever detailed differences may be revealed by future planetary probe data, it is likely that these data will be evaluated by methods similar to those developed here.

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CONTENTS

PART 1

MAGMATIC GAS COMPOSITION

INTRODUCTION

The gaseous (volatile) phase that coexists with magmas is of fundamental significance in many Earth processes. The great influence of volatiles on mineral equilibria and the importance of gases in rock melting, differentiation, and crystallization are well established. Contact metamorphism is often intimately related to the volatiles released by the intruding magma. Many metalliferous ore bodies are considered to be deposited by magma-derived volatiles, and thermal areas around the world are believed to be the surface expressions of deeper magmatic activity. Volcanic rocks and present volcanic activity give abundant evidence of the important role that gases play during their development. The atmosphere and hydrosphere are usually considered to be derived mainly from gases that were once associated with magmas. The composition of the paleoatmosphere and, ultimately, the origin of the Earth are also intimately linked with the magmatic gaseous phase.

In view of the importance of magmatic gases, the need for adequate knowledge of their composition and behavior is evident. Several approaches have been used to gain insight into the composition of the magmatic gaseous phase, and all have merit, since each adds information that must be considered. No one method alone can be used if a complete picture of magmatic gases is desired; however, most methods greatly oversimplify the chemical system involved and/or use data that are far removed from the magmatic environment. Arbitrary choices of variables are often necessary, and it is seldom possible to consider more than one or two gas species simultaneously. The results thus unavoidably involve large errors.

The most direct method of studying the composition of magmatic gases involves collecting these gases at their points of escape from the Earth. In the past, however, this method has not often yielded the most useful or reliable information about the true composition of the gases coexisting with magmas. Collections are usually made far from the source, at hot springs and geysers. Collections have been made at active volcanoes, but these usually must be obtained some distance from the magma at fumaroles and solfataras. Samples of gas have been obtained near erupting lavas, but the rare opportunities and hazards of this work have limited the number of such collections to a handful. This limited number of collections from lava lakes comprises the most reliable information about magmatic gas compositions.

Until recently, little has been done with the data beyond comparison of analyses and discussion of the sources of contaminants and probable original compositions. Ellis (1957) made a pioneering effort, using chemical thermodynamics, to investigate equilibrium compositions. Using relatively simple systems and estimates of compositions, his calculations showed that equilibrium compositions and the results of actual analyses are similar. Heald et al. (1963) applied computer methods to a gaseous system of complexity like that of natural systems. Using the composition of one of their collected samples, equilibrium compositions over a range of temperatures and pressures were computed. They also found that actual analyses and calculated compositions were similar, particularly after gross adjustments for contamination. A quantitative treatment of individual samples from a series of collections has not been attempted. Previous work has yielded several important suggestions concerning the processes in operation in a magmatic gas and some of the difficulties involved in making collections; however, satisfactory correlations among the diverse compositions collected from a single volcano during a relatively short interval have not yet been found. The processes leading to these varying compositions have not been distinctly separated. Most important, a clear picture of the composition of the original magmatic gas has not yet been obtained.

This report attempts to deduce the composition of a magmatic gas before its modification by surface and near-surface processes. The method of approach simultaneously shows the changes occurring in a volcanic gas in the surface and near-surface environment and during collection. The diverse compositions of samples collected from a volcano during a relatively short interval are shown to be the result of these changes. It is shown that each sample in the series of analyses used was derived from the same magmatic gas composition. Part 2 of this study examines the attainment of equilibrium in the samples before collection, the effects of the collection process on the samples, and the behavior of the magmatic gas during various modifying processes. Part 3 considers the effect of additions and losses of various gas species on the total gas composition and the magnitude of these additions and losses in each sample.

DATA USED

The data used in this study are analyses of gas collected at Kilauea volcano, Hawaii. Samples from Kilauea were chosen for several reasons:

(1) It is one of the most thoroughly studied active volcanoes.

(2) The geological setting of Kilauea is such that its magmas and gases are less likely to involve complicating factors such as those inherent in continental volcanoes.

(3) Basic lavas have a more fundamental relationship to Earth processes such as degassing of the mantle.

(4) The best data available are from Kilauea.

Table 1 shows the analyses of gases collected by Jaggar and Shepherd from 1917 to 1919. These collections were made when the volcano was active for an extended period.

Table 1 — Kilauea gases from vacuum tubes (Shepherd, 1938): volume percentages at 1200°C, 760 mm Hg.

Sample		CO	CO_2	H_2	H_2O	S_2	SO_2	SO_3	SO_2 + SO_3	Cl_2	N_2	Ar
J- 2	(P)	0.00	5.79	0.00	75.09	0.00	4.76	2.41	7.17	4.08	7.92	udt
J- 3	(P)	0.22	6.63	0.15	80.31	0.00	3.23	5.51	8.74	1.11	2.37	0.56
J- 4	(P)	0.14	6.79	0.17	84.98	0.15	1.38	3.43	4.81	0.62	2.33	0.00
J- 6	(P)	0.16	0.87	0.07	78.71	0.00	0.01	0.13	.14	0.03	20.01	0.00
J- 8	(E)	1.46	47.68	0.48	36.18	0.04	11.15	0.42	11.57	0.04	2.41	0.14
J-10	(E)	0.11	16.44	0.10	50.88	0.05	13.57	3.56	17.13	0.03	15.03	0.21
J-11	(E)	0.59	20.93	0.32	61.56	0.25	11.42	0.55	11.97	0.00	4.13	0.31
J-12	(P)	0.05	1.42	0.08	97.09	0.07	0.51	0.00	.51	0.03	0.68	0.05
J-13	(E)	0.58	16.96	0.96	67.52	0.09	7.91	2.46	10.37	0.10	3.35	0.66
J-14	(F)	0.47	14.81	0.17	76.84	0.10	3.65	1.03	4.68	0.00	2.91	0.00
J-15	(F)	0.13	11.53	0.10	73.89	0.03	6.14	1.70	7.84	0.10	6.20	0.16
J-16	(E)	0.56	18.03	0.67	66.25	0.15	8.53	2.53	11.06	0.08	3.11	0.08
J-17	(G)	0.37	11.61	0.58	79.31	0.24	6.48	0.00	6.48	0.05	1.29	0.04
J-18	(E)	0.74	17.55	0.83	61.88	0.22	10.81	3.22	14.03	0.13	4.50	0.12
S- 1	(F)	1.04	2.65	4.22	67.99	0.70			0.16	udt	23.22	udt
S- 2	(F)	0.36	17.95	1.35	38.48	0.49			3.51	udt	37.84	udt
S- 3	(E)	1.42	33.48	1.56	17.97	1.79			29.83	0.17	12.88	0.45
S- 4	(P)	3.92	11.12	1.42	77.50	8.61			0.00	0.02	0.00	0.51
S- 5	(E)	1.12	9.54	1.53	64.71	2.72			9.90	0.00	10.47	0.00
S- 6	(P)	0.82	1.97	0.21	89.77	2.70			0.95	0.00	3.50	0.07
S- 7	(E)	0.62	17.25	0.76	64.18	1.07			9.75	0.25	5.88	0.18
S- 8	(G)	0.45	15.27	0.70	75.08	0.49			6.98	0.00	0.87	0.14
S- 9	(G)	0.82	8.32	1.82	59.97	2.48			16.80	1.01	8.92	0.29
S-10	(P)	0.43	1.54	0.37	89.93	3.56			0.00	1.34	2.44	0.39
ML-1	(P)	0.03	3.84	0.00	75.44	0.00	1.22	2.08	3.30	0.00	16.80	0.58
ML-2	(P)	0.19	6.42	0.01	67.43	0.00	1.95	8.12	10.07	0.00	15.39	0.42

Collecting conditions were particularly favorable and several samples were obtained from the edge of the lava lake. The actual collection sites are described in Jaggar (1940) and Shepherd (1921). These samples constitute the best set of systematic collections ever made from an active volcano. The analyses were carried out and published by Shepherd (1919, 1920, 1921, 1938). The analytical technique (Shepherd, 1925) involved the absorption of each gas species by a proper compound and measurement of the change in volume accompanying this absorption. In Shepherd's hands this technique was at its best. What it may have lacked in accuracy and precision was more than compensated for by the excellence of the samples used, since a greater amount of the minor gases is present in a less contaminated sample.

The data in Table 1 are reproduced as given by Shepherd in the original publications, except for the addition of the (SO_2 + SO_3) column. The S-series of samples was analyzed before the apparatus was perfected to separate SO_2 from SO_3. The J-series of samples is the best because the collector (Jaggar) was more familiar with Kilauea, collecting conditions were better, and the analytical technique had been improved. Only the J-series is considered in this report. The letters in parentheses (P, F, G, E) refer to Jaggar's estimate (1940) of the quality of each sample (P = poor, F = fair, G = good, E = excellent) as to place of collection, success of collecting technique, and so on. A shorter interval of Kilauea's activity is considered if only one series is studied. In addition, the collections and analyses are superior for the J-series.

MODIFYING PROCESSES

Modifying processes alter the magmatic gas and cause samples from different places in a volcano to have diverse compositions. These processes may affect only the relative proportions of various molecular species, or they may affect both the molecular and atomic proportions. When considering individual modifying processes, it is useful and instructive to consider atomic and molecular compositions separately. A short outline of the various significant processes and their general effects on compositions will serve as a preface to later sections of this report.

The terms "magmatic gas" and "contaminating gas" must be defined. "Magmatic gas" is that part of the magma present in the gaseous phase, having a distinctly lower density than the liquid melt that crystallizes to form volcanic rocks. Under those surface and near-surface conditions considered here, the distinction between liquid and gas presents no difficulty. Magmatic gas is that portion of the collected sample which is an intimate part of the subsurface magma, and has not been modified by processes such as those considered here. Magmatic gas may be composed both of juvenile gas, which has never been involved in near-surface processes, and of other gases of deep origin that are not actually part of the magma at its source. It is inherent in this definition that the composition of the magmatic gas may change as the magma moves from its source to the surface if other gases mix with the juvenile gas and become an intimate part of the magma.

"Contaminating gas" is that part of the collected sample which cannot be classed as magmatic gas. Contaminating gas may come from a source foreign to the magma or may actually originate in the magma itself. Contaminating gases are thus considered as additions to the magmatic gas leading to false compositions in the collected samples.

Atmospheric Contamination

Volcanic gas samples free from contaminating atmospheric gases have rarely, if ever, been collected. The normal processes in an active lava lake cause ingestion of air. Convective overturn, assimilation of previously solidified porous lava blocks, and the possible subsurface mixing of magmatic and atmospheric gases make atmospheric contamination a probability in any gas sample collected at the surface. In addition, in the conventional collecting method using vacuum tubes, it is often difficult to seal the tube before air is sucked in. Places in an active volcano accessible to the collector (cones, grottos, and cracks on or near the edge of solidified crusts) are likely to be points where air mixes with gases escaping from the lava.

The gases added in significant amounts to magmatic gas by atmospheric contamination are O_2, N_2, and Ar, with CO_2 less important. Addition of these gases thus leads to increases in the atomic amounts of O, N, Ar, and C in the collected sample. The effect on molecular composition depends upon other factors discussed below, but in general, the total percentage of magmatic gas in the sample is reduced.

Contaminating Water

Contaminating waters (sea water, deep ground water, connate water) from deep sources are not directly treated in this report. Although such contaminants are not truly part of the original magma at its source, they are intimately mixed with the magma at the time of its extrusion and play a direct role in the physicochemical processes of the extrusive lava. Such contaminants are considered part of the magmatic gas as defined above and would not be reflected by rapid or large changes in the compositions of samples collected during a short length of time. Distinction between these contaminants and the original magmatic gas requires a further division of the magmatic gas into deep source contaminants and juvenile gas.

Water may be added to the magmatic gas by external sources such as rain or rain-derived ground water. Following the usage of White (1957), water that has recently been involved in atmospheric circulation is called "meteoric water." Such contaminations are near-surface phenomena and can be expected to vary from place to place in the volcano. Other sources of contaminating water more directly related to the volcano would also vary in importance, depending upon the location of the collecting site. The assimilation of lava blocks falling into the lake, or reaction with partially formed crusts, would release water included in the rock. Atmospheric processes above the lava lake may lead to "volcanic rain," and condensation on rocks surrounding the lake may return escaping water to the lava.

Contaminating water can carry gases in solution. This would add additional amounts of the atmospheric gases O_2, N_2, Ar and CO_2. The importance of such additions depends upon the relative amounts of contaminating water, atmospheric contamination, and magmatic gas. Gases in solution in water will be quantitatively considered in a later paper; they are of minor importance in good collections from volcanoes.

Reactions With Rocks

Lava and gases may react with rocks at all points from the source to the surface. If sufficient heat is available, reactions may lead to assimilation of rocks with accompanying changes in the composition of the lava and its gases. Compositional changes of the gas may reflect changes in the bulk composition of the liquid lava and will also result from the release of gases from the rock. Gases may either be held in the crystal structures of the rock, or be present as occluded gases. The particular species of gases released will depend in a complex manner on the rock type and its history, and any combination of known Earth gases in widely varying proportions is possible.

Reactions between the lava and its gases and rocks, when complete assimilation does occur, will have effects similar to those accompanying assimilation when chemical components are added to the lava. In addition, these reactions may result in a loss of components from the rising magma, particularly those components that form the gas phase at the surface. Numerous probable reactions can be written; the more important of these fit roughly into three main categories: (1) hydration reactions, resulting in the loss of atomic oxygen and hydrogen from the gas phase; (2) oxidation or reduction of iron-bearing minerals, causing respectively a decrease or increase in amount of atomic oxygen in the magmatic gas; (3) acid gas reactions with the formation of chlorides, fluorides, and sulfides from previously existing oxides and silicates. These reactions lead to a decrease in the amount of atomic Cl, F, and S, and an increase in O in the gas phase. At times, acid gas reactions may be reversed because of changing conditions. In general, decreasing temperature favors hydration, oxidation, and fixation of acid gases.

Reactions with rocks may, therefore, cause either an increase or a decrease in the relative amounts of various atomic species. The molecular composition of the analyzed sample will be influenced by additional factors. The quantitative importance of contaminations due to rock reactions in a collected sample will be determined by the importance of the reaction processes as a whole, as well as the relative volumes of gas to condensed phases in the lava and the rocks. Reactions with rocks at depth should not lead to large differences in gas composition during a single collection period because of the continual mixing of the magma as it moves upward. At the surface, however, these reactions can be expected to cause important variations from place to place because of great differences in the physicochemical environment.

Gas Reactions

If temperature and pressure remain constant, the molecular composition of the gas phase can vary from a change in the relative proportions of one or more atomic species. For example, contamination of a high-temperature gas by atmospheric oxygen will cause a decrease in the ratios CO/CO_2, H_2/H_2O, S_2/SO_2, and so on. Equilibrium requirements dictate that the various pairs of gases (e.g., CO and CO_2) will adjust their ratios to differing degrees. The result is a complex set of interdependent reactions leading to an equilibrium composition that is not easy to predict accurately. As an additional example, consider the reaction of HCl with wall rocks to form chloride-bearing minerals. Chlorine is removed from the gas phase, simultaneously releasing free hydrogen, thus causing hydrogen to be present in excess of its equilibrium amount. Reactions in the gas phase will cause a large portion of this released hydrogen to combine with sulfur and oxygen, causing a change in the relative proportions of all the other molecular species. The importance of such processes in modifying the composition of the collected sample is determined by: (1) the amount of the atomic species lost or gained relative to the total amount of atoms present, and (2) the relative amounts of the various molecules in which the atom is found at equilibrium. For example, the addition of a small amount of inert gas will affect the sample composition very little, while the addition of a large amount of inert gas will decrease the percentages of all other molecules significantly, but still will not alter the relative amounts of molecular species present. A significant increase or decrease of a chemically reactive substance, such as sulfur, will cause a complete readjustment of the molecular composition of the sample.

At constant atomic composition, the molecular composition will change because of variations in temperature and pressure. The pressure decrease accompanying the rise of magma toward the surface tends to drive reactions toward volume increase, in gas reactions toward the side with the larger number of moles of gases. Changing temperature also shifts the equilibria according to Le Chatelier's principle. The direction of temperature change in a rising and extruding lava is not always downward, however, and reactions may reverse one or more times as the lava rises to the surface, extrudes, flows on the surface, and solidifies.

Summary

Changes in the composition of a magmatic gas resulting from the processes outlined above cause differing compositions. Several of the processes acting simultaneously or in sequence, each varying in intensity with respect to time and place, make an infinite number of collected compositions possible. If a correlation is to be found among a series of samples from an individual volcano, it must be shown that the diverse compositions are related to a limited number of modifying processes. The difficulties met when such correlations are sought are perhaps best summed up in a statement by Shepherd (1938) after over 20 years of work with volcanic gases: "The one obvious fact brought out by the analyses. . . is the lack of any definite relationships among the constituents involved." Shepherd concluded that the gases must vary at their source. It seems probable, however, that, with some of the data and methods now available, more information can be obtained from such collections.

Various physical and chemical homogenizing processes will tend to cause the gas phase to have a uniform composition throughout the magma, and this tendency toward homogenization will spread the effects of modifying processes evenly through the magmatic body. Modifications occurring only in limited portions of the magmatic body, such as incomplete reactions at the contact between the magma and surrounding rock, will spread throughout the body more slowly. Such modifications would have a limited effect on the body as a whole, however, and the bulk composition of the gas phase would change only slightly. Modifications of significant importance to the magmatic body as a whole may cause a large change in the composition of the gas phase; however, such a change would be quickly spread throughout the magma because of the mixing of more nearly equal volumes. A long-established volcano might be expected to have coated its channels with its own products and completed its more favorable reactions with wall rocks thus establishing a pseudoequilibrium with respect to composition. The earlier lavas may have "swept-out" conduits. Inflowing contaminants, such as deep ground water, should tend to establish a steady state.

In essence then, the various modifying processes occurring at depth may not be reflected in varying compositions of collected volcanic gases. The deeper these changes occur, the less likely they are to be reflected in diverse gas compositions. The large differences always found in a series of systematic gas collections are likely to be expressions of surface and near-surface modifications. Drastic changes in the surface physicochemical environment would be expected to cause large variations in volcanic gas compositions. In addition, the release and escape of the gas phase from the magma, which occurs at or near the surface, is likely to be a unique event in the history of a volcanic magma. Finally, the collection of samples can be expected to augment the modifying processes, since atmospheric contamination and gas reactions are strongly influenced by collecting techniques.

A series of gas collections should be examined, emphasizing surface modifying processes. Elimination of the various effects of each process can shed light upon the importance of each modification and expose more subtle modifications that have occurred. If the composition of a volcanic gas, previous to changes caused by surface and near-surface modifications, can be deduced, then more deep-seated processes can be attacked with some hope of success.

METHOD OF APPROACH

It is hypothesized in this study that each sample was derived from a magmatic gas in which the atomic composition remained constant throughout the collection period. Thus, all samples had, at some time in their history, the same composition as the magmatic gas, and the varying compositions in the analyses are a consequence of surface and near-surface modifications. This hypothesis seems reasonable, in view of the discussion above. In addition, all samples have a common source and were collected during a relatively short interval. The magmatic compositions of Kilauea's eruptions have been remarkably constant over a long period, and the investigators making the collections found no evidence that the volcano had changing products during the collection period (Jaggar, 1947). The relative importance of each modifying process in altering the atomic and molecular composition of each sample varies with the site and conditions of collection.

The modifying processes are identified, and the effect of each process on the magmatic gas is examined independently and quantitatively with respect to each sample. The combined effects of all modifying processes are then considered simultaneously, so that a true picture of their complex interactions can be obtained. In this manner, the atomic and molecular compositional changes that have occurred in each sample are determined. By "reversing" the various changes, each sample is recalculated to its original magmatic composition. If all samples lead to the same magmatic gas composition, then the basic hypothesis is supported, and the identification and treatment of modifying processes are apparently correct.

ATMOSPHERIC CONTAMINATION

Ratio Ar/Ar + N_2

The ratio Ar/(Ar + N_2), or R, has long been used to indicate the extent of atmospheric contamination in hot-spring, fumarole, and volcanic gas samples. The numerical value of this ratio in a collected sample is a function of the fraction of the total sample that each source of gas contributes, as well as the fraction of Ar and N_2 in each source. Three sources could contribute significant amounts of Ar and N_2 to a collected volcanic gas sample: (1) the magmatic gas itself; (2) atmospheric contaminating gases; and (3) atmospheric gases in solution in contaminating water. An expression relating R for each of these sources to R for the collected sample is given below:

$$R_{\text{sample}} = \frac{XR_{\text{mag}}(\text{Ar}+\text{N}_2)_{\text{mag}} + YR_{\text{atm}}(\text{Ar}+\text{N}_2)_{\text{atm}} + ZR_{\text{sol}}(\text{Ar}+\text{N}_2)_{\text{sol}}}{X(\text{Ar}+\text{N}_2)_{\text{mag}} + Y(\text{Ar}+\text{N}_2)_{\text{atm}} + Z(\text{Ar}+\text{N}_2)_{\text{sol}}} \qquad (1.1)$$

where

X = magmatic fraction of total sample,
Y = atmospheric contamination fraction of total sample,
Z = water contamination fraction of total sample,
$X + Y + Z$ = 100,

and

$$\frac{X\,(10^2)}{X+Y+Z} = \text{\% magmatic gas,}$$

$$\frac{Y\,(10^2)}{X+Y+Z} = \text{\% atmospheric contamination.} \qquad (1.2)$$

$$\frac{Z\,(10^2)}{X+Y+Z} = \text{\% water contamination,}$$

R_{mag} = inert gas ratio in uncontaminated magmatic gas,

R_{atm} = inert gas ratio of atmosphere at Earth's surface,

R_{sol} = inert gas ratio in saturated water solution at temperature T,

$(\mathrm{Ar} + \mathrm{N_2}) = \left(\frac{\mathrm{Ar} + \mathrm{N_2}}{\Sigma \text{ gases}}\right)_{\mathrm{mag}}$ = fraction of inert gases in uncontaminated magmatic gas,

$(\mathrm{Ar} + \mathrm{N_2}) = \left(\frac{\mathrm{Ar} + \mathrm{N_2}}{\Sigma \text{ gases}}\right)_{\mathrm{mag}}$ = fraction of inert gases in atmosphere at Earth's surface,

$(\mathrm{Ar} + \mathrm{N_2}) = \left(\frac{\mathrm{Ar} + \mathrm{N_2}}{\Sigma \text{ gases}}\right)_{\mathrm{mag}}$ = fraction of inert gases in saturated water solution at temperature T.

Now, since

$$(\mathrm{Ar} + \mathrm{N_2})_{\mathrm{sample}} = X(\mathrm{Ar} + \mathrm{N_2})_{\mathrm{mag}} + Y(\mathrm{Ar} + \mathrm{N_2})_{\mathrm{atm}} + Z(\mathrm{Ar} + \mathrm{N_2})_{\mathrm{sol}}, \tag{1.3}$$

Equation 1.1 can be restated as

$$R_{\mathrm{sample}}\,(\mathrm{Ar} + \mathrm{N_2})_{\mathrm{sample}} = XR_{\mathrm{mag}}\,(\mathrm{Ar} + \mathrm{N_2})_{\mathrm{mag}} + YR_{\mathrm{atm}}\,(\mathrm{Ar} + \mathrm{N_2})_{\mathrm{atm}} + ZR_{\mathrm{sol}}\,(\mathrm{Ar} + \mathrm{N_2})_{\mathrm{sol}}. \tag{1.4}$$

It will be shown in Part 2 of this study that the contribution of Ar and $\mathrm{N_2}$ form contaminating water in the Kilauea gases examined in this paper is negligible in even the most heavily contaminated samples. These terms can thus be eliminated from Equation 1.4, leaving $Z = 1.00 - X$, and Equation 1.4 can be rewritten in the form

$$R_{\mathrm{mag}} = \frac{R_{\mathrm{sample}}\,(\mathrm{Ar} + \mathrm{N_2})_{\mathrm{sample}} - R_{\mathrm{atm}}\,(\mathrm{Ar} + \mathrm{N_2})_{\mathrm{atm}}}{x(\mathrm{Ar} + \mathrm{N_2})_{\mathrm{mag}}} + \frac{R_{\mathrm{atm}}\,(\mathrm{Ar} + \mathrm{N_2})_{\mathrm{atm}}}{(\mathrm{Ar} + \mathrm{N_2})_{\mathrm{mag}}}. \tag{1.5}$$

Equation 1.5 can be used with Ar and $\mathrm{N_2}$ amounts expressed as partial pressures, volumes, volume percents, or molefractions; e.g., when mole fractions are used, Equation 1.5 reduces to

$$\left(x_{\mathrm{Ar}}\right)_{\mathrm{mag}} = \frac{\left(x_{\mathrm{Ar}}\right)_{\mathrm{sample}} - \left(x_{\mathrm{Ar}}\right)_{\mathrm{atm}}}{X} - \left(x_{\mathrm{Ar}}\right)_{\mathrm{atm}}, \tag{1.6}$$

where

$\left(x_{\mathrm{Ar}}\right)_{\mathrm{mag}}$ = mole fraction of Ar in the magmatic gas,

$\left(x_{\mathrm{Ar}}\right)_{\mathrm{sample}}$ = mole fraction of Ar in the sample,

$\left(x_{\mathrm{Ar}}\right)_{\mathrm{atm}}$ = mole fraction of Ar in atmosphere at Earth's surface.

Use of Equation 1.6 requires knowledge of the processes that have occurred after mixing of the gases from both sources. For example, if atmospheric oxygen has reacted with the magmatic gases, the value of $(Ar + N_2)_{atm}$ will be greater than its normal value in the atmosphere. The use of the ratio R in expressions such as 1.5 and 1.6 requires the general assumption that the inert gases have retained their identity by not entering into gaseous- or condensed-phase compounds. Evidence of such losses of Ar or N_2 would require adjustments to the values used in the formulas. Such evidence has not been found in the Kilauea gases examined here.

Table 2 shows the percentages of Ar and N_2 from the data reported by Shepherd (1919, 1921, 1938) and listed in Table 1. The ratio R_{sample} given by these percentages is also shown; the values are irregular and usually quite high. These values were noted and discussed by Shepherd (1921), Allen (1922), and Jaggar (1940). The great differences between the Kilauea R_{sample} values and the value for the atmosphere allow various interpretations. Allen (1922) concluded that either N_2 and Ar are wholly magmatic and highly variable, or else atmospheric gases have been absorbed to varying degrees by the magma. A satisfactory explanation of the variability between the limits has not been given. Any quantitative determination of atmospheric contamination must be compatible with R_{sample}.

The anomalous values of R_{sample} in Table 2 are a result of the method chosen to report the data in Table 1. The percentages in Table 1 are not the actual percentages of the original collected samples. Shepherd made the assumption that any free O_2 found in the samples was due to atmospheric contamination. He thus deleted O_2 and atmospheric proportions of N_2, Ar, and CO_2 from his reported analysis. To quote Shepherd (1925):

> We have uniformly interpreted oxygen really present as due to air in the supposedly evacuated tube or, more commonly, mixing with the gas after collection and before sealing off. . . . Consequently, we make it a regular practice to subtract from any gas composition, as analyzed, oxygen with the normal equivalent of nitrogen, carbon dioxide, and argon, before computing the composition of the gas under analysis.

In Equation 1.5 all the variables are known except X, $(Ar + N_2)_{mag}$, and R_{mag}. It can be seen that mixing a high value of R_{mag} with the atmospheric value for this ratio will lead to an intermediate value in the sample somewhere above 1.18×10^{-2}. If $X(Ar + N_2)_{mag}$ is estimated by some means, the value of R_{mag} can be determined. If $X(Ar + N_2)_{mag}$ is overestimated, the value obtained for R_{mag} will be too low, and if $X(Ar + N_2)_{mag}$ is underestimated, R_{mag} will be too high. In essence, when R values are computed from Table 1, one is estimating $X(Ar + N_2)_{mag}$ on the basis of the free O_2 present in the collected sample, and the values of R in Table 2 are estimates of R_{mag}. The strong probability that some of the O_2 from the atmosphere has reacted and that the amount lost due to reactions varies from sample to sample explains the lack of correlation among the values in Table 2. The samples in Table 2 with the highest values of R are those that have lost the smallest fraction of their atmospheric O_2 to reaction, and give ratios nearest to the true value of R_{mag}.

Table 2 — Ratios of argon to the total inert constituents from data of table 1.

Sample		N_2 (percent)	Ar (percent)	$R_{\text{sample}} \times 10^2$
Atmosphere		78.084	0.934	1.18
J- 2	(P)	7.92	udt	. . .
J- 3	(P)	2.37	.56	19.11
J- 4	(P)	2.33	.00	0.00
J- 6	(P)	20.01	.00	0.00
J- 8	(E)	2.41	.14	5.4
J-10	(E)	15.03	.21	1.3
J-11	(E)	4.13	.31	6.9
J-12	(P)	.68	.05	6.8
J-13	(E)	3.35	.66	13.9
J-14	(F)	2.91	.00	9.00
J-15	(F)	6.20	.16	2.5
J-16	(E)	3.11	.08	2.5
J-17	(G)	1.29	.04	3.0
J-18	(E)	4.50	.12	2.6
S- 3	(E)	12.88	.45	3.38
S- 4	(P)	0.00	0.51	100.00
S- 5	(E)	10.47	0.00	0.00
S- 6	(P)	3.50	.07	1.96
S- 7	(E)	5.88	.18	2.97
S- 8	(G)	.87	.14	13.87
S- 9	(G)	8.92	.29	3.15
S-10	(P)	2.44	.39	13.78
ML-1	(P)	16.80	.58	3.34
ML-2	(P)	15.39	.42	2.66

It is possible to restore the J-series of Table 1 to gas percentages including the O_2, N_2, and Ar removed by Shepherd. Shepherd (1921) and Jaggar (1940) report two values in the notes accompanying each of the J-series samples. Jaggar lists these values under columns headed "*Ab*" and "Oxygen" and states in the text that "*Ab* = *ratio* CO_2 + SO_2 to the *figure* for *O*" (p. 319), and later (p. 324) ". . . *Ab* is the *sum* of the volcanic gases CO_2 and SO_2 . . . and *O* is the *percentage* of free oxygen that the analyst eliminated." Careful examination of the original publication (Shepherd, 1921) and the description of Shepherd's methods (Shepherd, 1925) shows that "*Ab*" and "*O*" are actually the volumes in cm^3 of these gases found during the analysis, so that

"Ab" = volume of $CO_2 + SO_2$ in cm^3, and

"O" = volume of O_2 in cm^3.

Comparison of the values given for "Ab" with the volume percentages of Table 1 supports this conclusion. Knowing the volume of O_2 removed by Shepherd, the volumes of N_2, CO_2, and Ar removed can also be determined. The known volume of $CO_2 + SO_2$ allows calculation of the volume of each other gas species in Table 1. Combining the volumes removed by Shepherd with the volumes of Table 1, and dividing each species volume by the total volume results in a new table of gas percentages (Table 3). Table 3 shows the "restored" compositions of the collected samples as analyzed before removal of any assumed contamination from the data.

New values of R can now be calculated from Table 3. These true values for R_{sample} are shown in Table 4, together with the ratios from Table 2 and the "restored" percentages of atmospheric gases from Table 3. The values for Ar obtained by Shepherd are actually analysis residues. It was assumed that these residues contained small amounts of other inert gases (Kr, Xe, Ne, He); they could have also contained other gases not considered in the analysis, thus causing R_{sample} to be higher than the atmospheric value. Further, errors resulting from analyses for other gas species may have accumulated in the residue analysis; such errors might account for the apparent absence of Ar in samples J-4, J-6, and J-14 in Table 1, leading to minimum values in the restored ratios.

Table 3 — Restored volume percentages of J-series samples (as analyzed before removal of assumed atmospheric contamination).

Sample	CO	CO_2	H_2	H_2O	S_2	SO_2	SO_3	Cl_2	N_2	Ar	O_2	Total
J- 2 (P)	0.000	0.336	0.000	4.35	0.000	0.276	0.140	0.239	75.9	0.009	19.0	100.
J- 3 (P)	.150	4.51	.102	54.7	.000	2.20	3.75	.756	26.6	.683	6.73	100.
J- 4 (P)	.111	5.36	.134	67.1	.118	1.09	2.71	.490	18.2	.195	4.39	99.9
J- 6 (P)	.115	.626	.0504	56.7	.000	.00719	.0935	.0216	36.2	.262	5.88	100.
J- 8 (E)	1.32	43.2	.435	32.8	.0362	10.2	.0381	.0362	9.67	.315	2.00	100.
J-10 (E)	.0736	11.0	.0669	34.1	.0334	9.10	2.38	.0201	35.8	.448	6.90	99.9
J-11 (E)	.508	18.0	.276	53.0	.215	9.82	.473	.000	14.3	.396	2.90	99.9
J-12 (P)	.0413	1.18	.0662	80.4	.0580	.422	.000	.0248	14.0	.202	1.60	98.0
J-13 (E)	.471	13.8	.780	54.8	.0730	6.42	2.00	.0812	17.4	.711	3.95	100.
J-14 (F)	.218	6.89	.0792	35.8	.0465	1.70	.480	.000	43.1	.501	11.2	100.
J-15 (F)	.0858	7.60	.0660	48.7	.0198	4.05	1.12	.0660	30.5	.413	7.13	99.8
J-16 (E)	.449	14.4	.538	53.2	.120	6.85	2.03	.0642	17.9	.248	4.15	100.
J-17 (G)	.276	8.67	.433	59.2	.179	4.84	.000	.0374	20.8	.267	5.33	100.
J-18 (E)	.576	13.7	.646	48.2	.171	8.41	2.51	.101	20.7	.299	4.64	100.

The restored R_{sample} ratios in Table 4 are close to, and generally greater than, the atmospheric value of 1.18×10^{-2}. Consideration of the preceding discussion suggests the following possibilities to explain the ratios:

(1) A significant fraction of the total N_2 is magmatic, and R_{mag} is only slightly above the atmospheric value.

Table 4 — Ratios of argon to the total inert constituents restored Kilauea J-series.

Locality	O_2 (percent)	N_2 (percent) (Restored)	Ar (percent)	$R \times 10^2$ (Restored)	$R \times 10^2$ (Shepherd, 1938)
Atmosphere	20.946	78.084	0.934	1.18	
Kilauea J- 2 (P)	19.0	75.9	.009	1.12	. . .
Kilauea J- 3 (P)	6.73	26.6	.683	2.01	19.11
Kilauea J- 4 (P)	4.39	18.2	.195	1.09 (min)	0.00
Kilauea J- 6 (P)	5.88	36.2	.262	.753 (min)	0.00
Kilauea J- 8 (E)	2.00	9.67	.215	2.18	5.4
Kilauea J-10 (E)	6.90	35.8	.448	1.23	1.3
Kilauea J-11 (E)	2.90	14.3	.396	2.70	6.9
Kilauea J-12 (P)	1.60	14.0	.202	1.42	6.8
Kilauea J-13 (E)	3.95	17.4	.711	3.73	13.9
Kilauea J-14 (F)	11.2	43.1	.501	1.15 (min)	0.00
Kilauea J-15 (F)	7.13	30.5	.413	1.34	2.5
Kilauea J-16 (E)	4.15	17.9	.248	1.36	2.5
Kilauea J-17 (G)	5.33	20.8	.267	1.26	3.0
Kilauea J-18 (E)	4.64	20.7	.299	1.40	2.6

(2) A small fraction of the total N_2 is magmatic, and R_{mag} is very high (infinite if no N_2 is magmatic).

(3) N_2 was removed from the gas phase by the formation of nitrogen compounds. (This is probably not important since such compounds were not detected.)

(4) Values are high because of analytical errors and all N_2 and Ar are contributed by atmospheric contamination.

The following sections of this report show that numbers 2 and 4 are the most likely possibilities.

Removal of Atmospheric Contamination From the Analyses

Gases added in significant amounts to the magmatic gas by atmospheric contamination are N_2, O_2, Ar, and CO_2. The amount of CO_2 added to even the most heavily contaminated samples is very small relative to the total percentage of CO_2; this contamination can usually be neglected. Argon will be present as an uncombined gas, due to its inert character, while N_2 can be expected to form compounds to a limited degree. The amount of N_2 in compounds depends largely on the total composition of the gas. Depending upon the temperature-pressure conditions, O_2 will react with one or more of the magmatic gases. Since N_2 may be partly magmatic and may react to form compounds, its abundance in a collected sample may not be a reliable estimate of the amount of atmospheric contamination. The extremely reactive nature of O_2 makes it even more unreliable. Another parameter is therefore required in order to estimate atmospheric contamination and delete it from the analyses.

Thermodynamic equilibrium in a magmatic gaseous system is not only the usual limiting case from which to work, but at magmatic temperatures and atmospheric pressure it is very likely to be closely approached, because of the rapid reaction rates involved. Just before exposure to the cold atmosphere and/or collection tube, the partial pressures of all gas species should closely approach equilibrium values. (This subject is discussed in detail in Part 2 of this study.) Under these conditions, the partial pressure of oxygen will be a sensitive indicator of the amount of atmospheric contamination. The mixing of a gas of atmospheric composition with the magmatic gas is effectively the addition of oxygen plus inert gases. This mixing should be reflected in the equilibrium oxygen pressure to a degree proportional to the relative mixing volumes. If, according to our basic hypothesis, all samples initially had the same oxygen pressure, then removal of the proper amount of atmospheric oxygen from each sample should return its equilibrium oxygen pressure to a value closer to the true magmatic value; the P_{O_2} obtained in this way may not be the correct magmatic value, because of other modifying processes that have occurred. The proper way of removing atmospheric contamination should, however, bring the oxygen pressures of all the samples closer together within some limited range of variation; this can serve as a qualitative criterion for the correctness of the contamination estimates.

A second criterion for removal of atmospheric contamination is that the resulting P_{O_2} should be compatible with minerals known to crystallize in unaltered basalts. Iron has been used by several authors as an indication of oxygen pressure. It has been shown experimentally and theoretically that the oxidation state of iron in the melt and in the minerals crystallizing from it is a function of P_{O_2}. In this study, the stability fields of iron metal, wustite, magnetite, and hematite are used as indicators of magmatic oxygen pressures. The stability fields of these minerals were calculated using information from the JANAF Thermochemical Tables, Kelley (1960), and Robie (1966). Petrological studies of many basaltic lavas have shown that magnetite is the primary iron oxide; this is also true at Kilauea. The abundance of hematite in volcanic rocks is attributed to late oxidation of more reduced iron-bearing minerals by exposure to the atmosphere. While hematite can crystallize as a primary mineral under the extremely oxidizing conditions of a lava flow at the surface, studies of unaltered basalts show that magnetite is the stable iron oxide under normal conditions.

The equilibrium oxygen pressures obtained for each sample, after the removal of atmospheric contamination, should fall within the magnetite field. Oxygen pressures in the wustite field or in the magnetite field very close to the magnetite-wustite boundary would suggest that the gas is deficient in oxygen and that contamination is overestimated. Oxygen pressures in the hematite field indicate that atmospheric oxygen is still present in the sample and more atmospheric gases must be removed. It is shown later that large amounts of contaminating H_2O have a relatively small effect on the partial pressure of oxygen.

Equilibrium Calculations

The equilibrium compositions (molecular compositions) of each of the J-series samples have been computed at 50°C intervals from 650° to 1250°C. The total gas pressure in all computations is 1 atm. These temperature-pressure conditions are considered to cover all likely natural conditions encountered during the time the collections were made. In effect, using equilibrium compositions removes the changes in molecular compositions which were caused by changes in temperature and pressure; the samples can then be studied under conditions of equal temperature and pressure. By examining the equilibrium compositions of each sample individually, the effects of modifying processes on each sample can be assessed, and parameters, such as oxygen pressure, can be studied without relating all samples to some arbitrary standard. In addition, compositional differences between samples and changes within a single sample can be determined accurately. This is important, because minor compositional changes may reflect large variations in the modifying processes.

Four sets of data have been obtained for each sample over the temperature range 650° to 1250°C; each set corresponds to a different method of removing atmospheric contamination. These four methods (Cases 1, 2, 3, and 4) are stated below:

Case	Method of Atmospheric Contamination Removal
1	Based on total free O_2 present
2	Based on total N_2 present
3	Based on total free O_2 present plus total SO_3
4	Combination of Cases 1, 2, and 3

Atmospheric gases are removed from the atomic compositions of each original sample as determined from either Table 1 or Table 3. The gases are removed according to their atomic proportions in the atmosphere at the Earth's surface, but in each case the amount of gases removed differs. The four atomic compositions that result for each sample are then used to compute equilibrium (molecular) compositions in the temperature range considered. The complete molecular compositions are used in Part 2 to examine equilibrium in the samples, quenching of collections, and so on. In this report, the oxygen pressures resulting from the calculations are used as atmospheric contamination criteria.

The thermochemical data for gases used in this study are based on spectroscopic measurements of excellent quality. Calculations made with these data are quite accurate, and the accuracy of the equilibrium calculations is limited by the analytical data rather than the thermochemical data. Portions of the following discussion assume that the gaseous system behaves ideally and closely approximates equilibrium (see Part 2). Partial pressures rather than fugacities are used to emphasize the total pressure of 1 atm and the assumed ideality.

The equilibrium composition is not easily calculated. Computations by hand require estimates of some atomic ratios and use of simple systems. The time required for these methods prevents numerous calculations. Such calculations do provide approximations to equilibrium compositions, which are useful in further work. At attempt was made to use the method of simultaneous equilibrium constant and abundance ratio equations in a computer program. While it is possible to write a successful program for this method, it becomes very inflexible when complex systems are considered. The adjustments required as the system is changed become impractical; this difficulty is due mainly to the nonlinear equations involved in the method.

To include all compounds likely to be important in a volcanic gas, a system of 7 to 9 atomic species and 12 to 15 molecular species must be considered. The method used to solve for the equilibrium composition of such a system in the present study is based on the minimization of the total free energy. This method was originally presented by White et al. (1958) and is outlined in the Appendix. While the use of the method in this paper follows that of White et al., some refinements have been made, and a few points are more completely outlined in the Appendix to present a clearer physical picture of what the method achieves. In addition, some different terminology is included, which may be more familiar to many readers.

The method, as used in this study, requires a minimum of input data. Once the system is defined and corresponding coefficients supplied, equilibrium compositions over any range of temperatures and pressures can be obtained. With the system defined, it is necessary to provide values for the amount of each atomic species present and any total molecular composition for the gas system that corresponds to these amounts. The necessary information can be obtained from an analysis of an actual gas collection or by assuming some desirable hypothetical composition.

Case I

The first set of equilibrium (molecular) compositions to be considered is computed from atomic compositions obtained after removal of atmospheric gases according to Case 1. Using the restored data of Table 3, all free O_2 present in each sample is removed, as well as atmospheric proportions of N_2, Ar, and CO_2. This results in atomic compositions indentical to those obtained from Shepherd's original data (1938) shown in Table 1. Figure 1 shows the equilibrium P_{O_2} for each sample over the temperature range under consideration after the removal of atmospheric contamination according to Case 1. Superimposed on the graph are the stability fields of the iron-oxide minerals. Although free oxygen has been removed from the samples, most of the curves still fall well within the hematite field. The hematite-magnetite boundary shows that an oxygen pressure (P_{O_2}) of about 10^{-3} atm is the greatest to be expected in a basaltic melt (about 1200°C) at the Earth's surface. As the melt cools and crystallizes, P_{O_2} must decrease by orders of magnitude. The O_2 shown in Table 3 is undoubtedly due to atmospheric contamination;

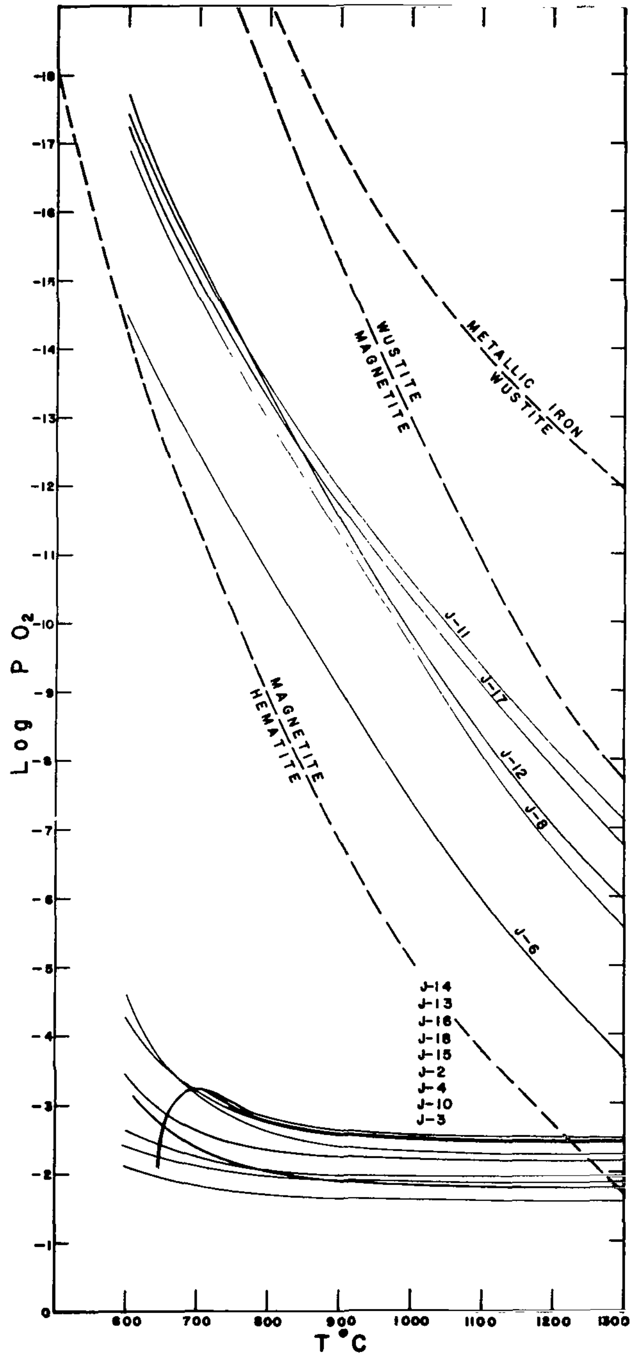

Figure 1–Equilibrium partial pressures of oxygen (P_{O_2}). Atmospheric contamination removed on basis of Case 1; i.e., molecular compositions computed after removal of free O_2 and atmospheric proportions of N_2, Ar, and CO_2 from atomic compositions of Table 3. Dashed lines are boundaries of iron oxide stability fields.

however, estimation of atmospheric contamination on the basis of the free O_2 present in the samples must be considered as the minimum possible amount.

The most abundant nitrogen compound, other than N_2, in a magmatic gas is ammonia. Since a minimum amount of atmospheric N_2 is removed by Case 1, it is a corollary that a maximum amount of magmatic N_2 is assumed in the calculations. Even under this assumption, the equilibrium calculations show that the partial pressure of ammonia P_{NH_3} is always less than 10^{-7}atm (see Part 2) in all samples over the entire temperature range. It can, therefore, be safely stated that the amount of N_2 mixed with the magmatic gas during atmospheric contamination will not be significantly decreased by reactions. This agrees with Shepherd's observation (1925, 1938) of the absence of NH_3. This also supports the assumption made earlier that R values are not significantly changed by losses of atmospheric N_2 due to reactions.

The equilibrium oxygen pressure curves in Figure 1 show a wide range of variation, with most of them falling in the hematite field. This method of removing atmospheric contamination has not brought the equilibrium oxygen pressures closer together, but instead has caused a wider variation than that shown in Table 3. The samples in the hematite field evidently contain contaminating oxygen in excess of the free oxygen of Table 3.

Case 2

The second set of equilibrium compositions is computed from atomic compositions obtained after the removal of all N_2 along with atmospheric proportions of O_2, Ar, and CO_2. The study of the [Ar/(Ar + N_2)] ratios in an earlier section suggested the

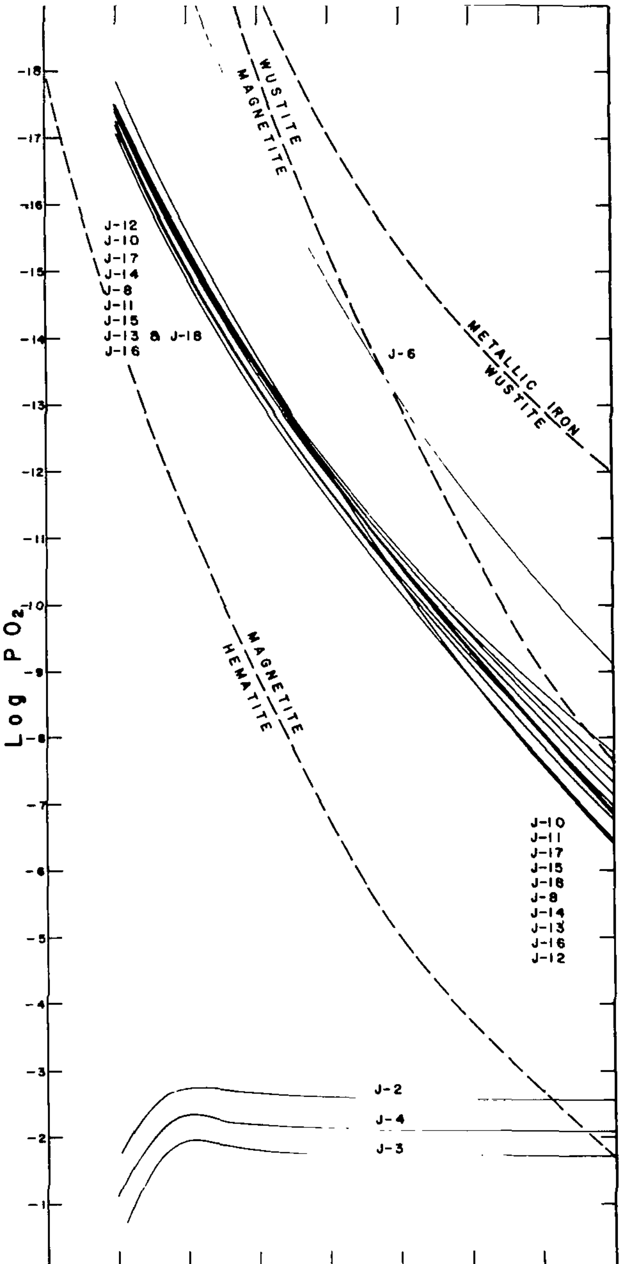

Figure 2–Equilibrium partial pressures of oxygen (P_{O_2}). Atmospheric contamination removed on basis of Case 2; i.e., molecular compositions computed after removal of all N_2 and atmospheric proportions of O_2, Ar, and CO_2 from atomic compositions of Table 3.

the possibility that all N_2 present in the samples is atmospheric. As discussed under Case 1, this contaminating N_2 will not be noticeably depleted because of gas reactions; the amount of N_2 shown in Table 3 can be considered as the maximum possible amount of atmospheric N_2. Removal of atmospheric gases on the basis of the total N_2 present in Table 3 will consequently be a maximum estimate of atmospheric contamination, and oxygen in excess of the free O_2 shown in Table 3 must be removed.

The equilibrium oxygen pressures of all samples computed for Case 2 are shown in Figure 2. Most of the samples now fall in the magnetite field, but J-2, J-3, and J-4 still contain too much oxygen. Sample J-6 falls in the stability field of wustite at temperatures corresponding to a basaltic liquid; many of the other samples also have oxygen pressures above 1050° -1100°C which approach the stability field of wustite. These low equilibrium oxygen pressures suggest that contaminating oxygen has been overestimated in these samples. If all samples are considered, the spread of values for the oxygen pressure is greater than that of either Table 3 or Case 1.

Case 3

A third set of equilibrium compositions uses atomic compositions obtained after adjustment on the basis of free O_2 plus SO_3. The equilibrium compositions obtained in Case 1 and Case 2 show that when oxygen pressures are low enough to be out of the stability field of hematite, SO_3 is always present as a trace molecule only; partial pressures of SO_3 (P_{SO_3}) are always below = 10^{-7} atm in the temperature range considered. This fact strongly suggests that the high pressures of SO_3 shown in Table 3 are a result of an oxidation process that is not indigenous to normal magmatic processes. The evident source of excess oxygen to the magmatic gas is the atmosphere. The information obtained in this study consistently indicates that essentially all of the SO_3 in the samples is formed by the oxidation of SO_2, rather than S_2 or H_2S, according to the reaction

$$2\,SO_2 + O_2 \rightleftarrows 2\,SO_3.$$

The following points are among those leading to this conclusion:

(1) The amounts of S_2 and H_2S in equilibrium compositions are completely inadequate to supply the amount of sulfur in the SO_3.

(2) In several samples, oxidation of S_2 or H_2S would require more atmospheric oxygen than could be supplied by even the maximum amount of atmospheric contamination of Case 2.

(3) The ratios of O/H discussed in this paper are consistent only with the oxidation of SO_2.

(4) Equilibrium considerations (Part 2) show that SO_3 was derived from oxidation of SO_2 only.

Therefore, in Case 3, all free O_2 in Table 3 is considered to be atmospheric and, in addition, all O_2 required to form SO_3 (one-half the amount of SO_3 in Table 3) is also atmospheric. This amount of atomic oxygen is deleted from the samples, as well as N_2, Ar, and CO_2 in atmospheric proportions.

Figure 3 shows the equilibrium oxygen pressures corresponding to Case 3. The oxygen pressures satisfy the two criteria used for judging the validity of atmospheric contamination estimates: (1) All oxygen pressures fall within a limited range at any specified temperature; (2) all curves are at oxygen pressures significantly below those corresponding to the stability field of hematite at all temperatures but are not so low as to be in the field of wustite.

Case 4

The fourth set of equilibrium calculations uses atomic compositions obtained after removing atmospheric gases by combining the concepts of Cases 1, 2, and 3. The discussion above points out the evidence suggesting that all N_2, all free O_2, and all SO_3 in Table 3 may be present as a result of atmospheric contamination. In Cases 1 and 3, the amounts of N_2, Ar, and CO_2 deleted were based on the O_2 removed and the atmospheric ratios. In Case 2, O_2, Ar, and CO_2 were removed on the basis of complete N_2 removal and the atmospheric ratios. In Case 4, the removal of O_2 and N_2 are independent, each being determined by different evidence. As in Case 2, all N_2 is removed with Ar and CO_2 removed in atmospheric proportions; O_2 is removed in the same manner as in Case 3. The amounts of O_2 and N_2 removed in Case 4 do not correspond to the atmospheric ratio of O/H; this discrepancy will be discussed in detail in a later section. However, the exact history of the contaminants that could lead to such variations is not vital to the argument leading to an unmodified magmatic gas.

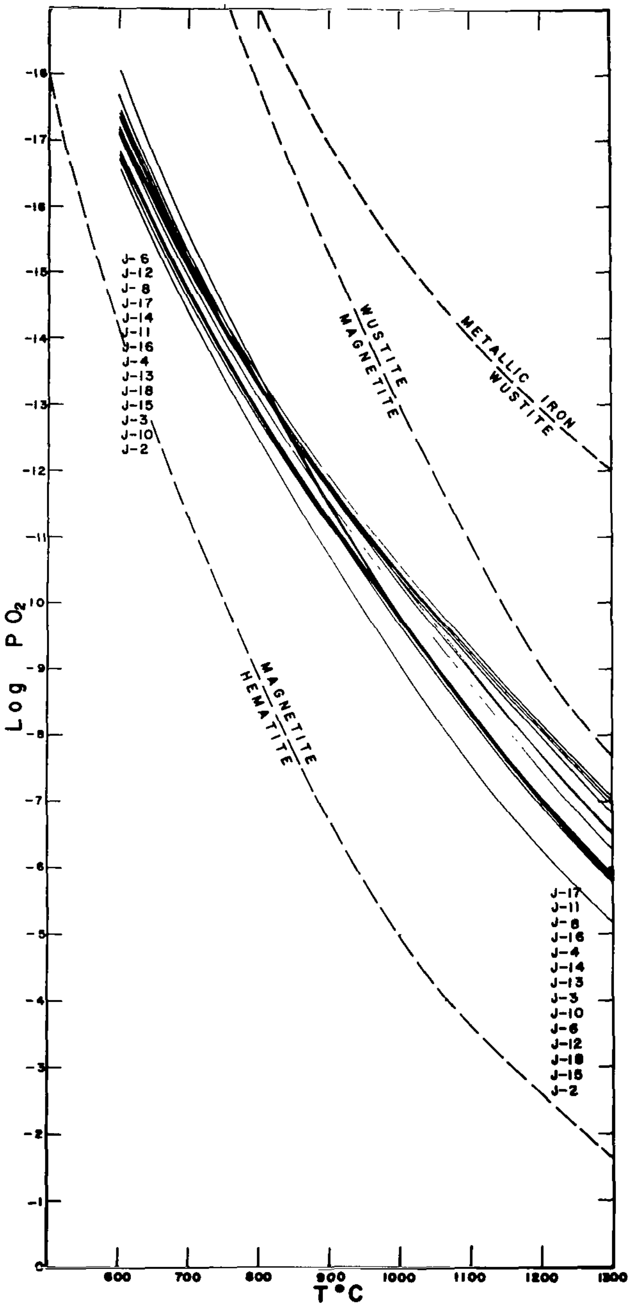

Figure 3–Equilibrium partial pressures of oxygen (P_{O_2}). Atmospheric contamination removed on basis of Case 3; i.e., molecular compositions computed after removal of free O_2 plus O_2 used to form SO_3, and atmospheric proportions of N_2, Ar, and CO_2 from atomic compositions of Table 3.

The equilibrium oxygen pressures obtained under the conditions of Case 4 are shown in Figure 4. The general appearance of Figures 3 and 4 is the same in view of the two criteria being used; however, the oxygen pressures of most of the samples are slightly higher in Case 4. The sequence of samples from higher to lower oxygen pressures at each end of the temperature scale is also different, but there is little to suggest a choice between Case 3 and Case 4.

Conclusions

The previous discussion has considered the simultaneous effects of two important modifying processes: 1) the changes in molecular compositions accompanying gas reactions that occur during changing temperature-pressure conditions, and 2) the changes in both atomic and molecular compositions that result from contamination by atmospheric gases. The modifications involved in the first process were eliminated by examining the equilibrium compositions of all samples under the same temperatures and pressures, i.e., their appearance in the magmatic environment was recreated. The effects of the second modifying process were assessed by removing atmospheric contamination in four different ways. The *R* values and equilibrium oxygen pressures indicate that atmospheric contamination is indeed present and that it is most accurately estimated by using the methods of Case 3 or Case 4. The choice between Case 3 and Case 4, as well as further information concerning the accuracy of the methods, must be determined from additional lines of reasoning. The following discussion will be enlarged to include other modifying processes. The processes already considered and the information already obtained must also be simultaneously considered. This increasing complexity is necessary to obtain a realistic picture of the magmatic gas.

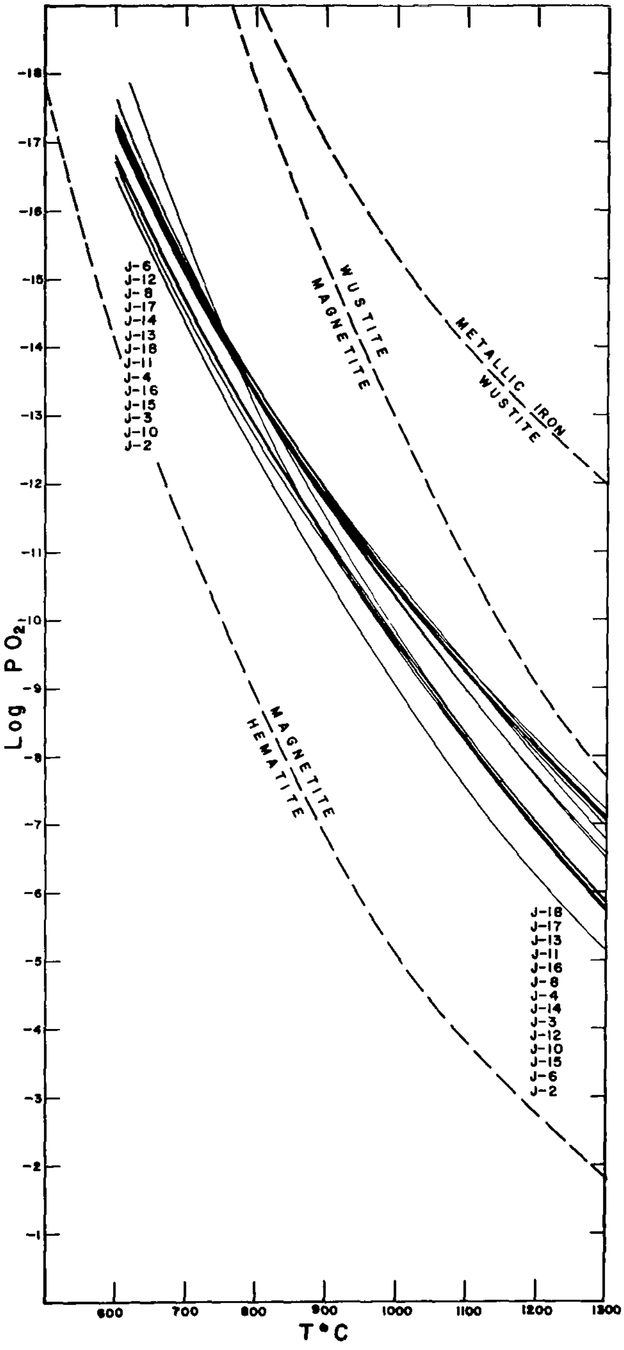

Figure 4–Equilibrium partial pressures of oxygen (P_{O_2}). Atmospheric contamination removed on basis of Case 4; i.e., molecular compositions computed after removal of free O_2 plus O_2 used to form SO_3, all N_2, and atmospheric proportions of Ar and CO_2 from atomic compositions of Table 3.

WATER CONTAMINATION

The analyses of Tables 1 and 3 show widely varying amounts of H_2O. Equilibrium compositions of all samples over the entire temperature range for all four cases of atmospheric contamination removal show that H_2O is always the dominant hydrogen-containing compound. The values of H_2O/H_2 and H_2O/H_2S are never less than about 100 at 1200°-1300°C, and increase by orders of magnitude as the temperature decreases (see Part 2). The equilibrium value of H_2O/H_2 approximates the same ratio computed from Tables 1 and 3, and Shepherd (1925, 1938) was unable to find H_2S in the samples. Therefore, it is extremely unlikely that the varying amounts of H_2O can be attributed to differential surface oxidation of a magmatic gas containing a large percentage of either H_2 or H_2S. It is evident that the varying amounts of water in the different samples are the result of phenomena not directly related to atmospheric contamination. If, in addition, the basic hypothesis is maintained that all samples had the same atomic composition before various modifying processes occurred, then the differences shown in Tables 1 and 3 must be the result of surface or near-surface changes in the hydrogen and oxygen content in the ratio $O/H = 1/2$. Although there are alternative possibilities, it is likely that these differences in atomic composition result from varying amounts of water contamination.

A change in the hydrogen and oxygen content of a magmatic gas at magmatic temperatures and low pressure can be expected to result in numerous reactions involving all the molecular species present. Regardless of how hydrogen and oxygen have reacted or what molecular species are involved, such changes will be reflected in the total atomic composition of the gas. Examination of the hydrogen and oxygen composition of each gas collection will show how these atomic species vary from sample to sample. The variation of atomic hydrogen and oxygen should not be considered separately from the atmospheric contamination already discussed; these two modifications should be simultaneously examined to ascertain their joint effect on a magmatic gas. The following discussion will consider the hydrogen and oxygen content of each sample for four different cases — each case corresponding to one of the methods of removing atmospheric contamination. The atomic compositions used are the same as those of the four cases in the preceding section.

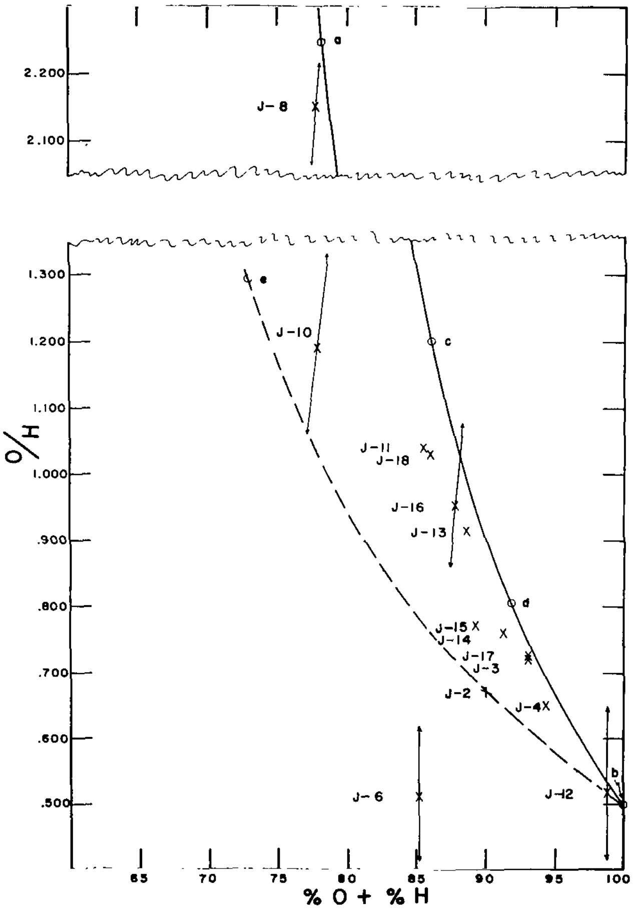

Figure 5—Atomic oxygen and atomic hydrogen contents. Atmospheric contamination removed on basis of Case 1 (*X*'s). Solid and dashed curves are H_2O addition curves, showing how compositions at *a* or *e* move toward *b* as oxygen and hydrogen are added in the ratio O/H = 1/2. Lines through J-10, and so on, show composition change when only oxygen is added or removed. Solid H_2O addition curve same as in Figures 6, 7, 8, and 10.

Case I

Figure 5 is constructed from atomic compositions corresponding to removal of the minimum amount of atmospheric contamination (Case 1). The data in Figure 5 correspond with equilibrium P_{O_2} values shown in Figure 1. The ratio of atomic oxygen to atomic hydrogen is plotted in Figure 5, against the sum of the atomic percentages of oxygen and hydrogen, where

$$\%O = \frac{O}{C+H+S+O+N} \text{ and } \%H = \frac{H}{C+H+S+O+N}$$

The solid curve from point *a* to point *b* at O/H = 0.500, (%O + %H) = 100 can be called an "H_2O addition curve." The significance of this curve can be appreciated from the following: (1) Assume a complex gas whose oxygen and hydrogen contents are such that they fall on point *a*. (2) If oxygen and hydrogen are now continually added to this complex gas in the ratio O/H = 1/2, point *a* will move down along this curve toward *b*. Hence, each point on the curve is related to any other point on the curve with respect to oxygen and hydrogen content by the ratio 1/2 (e.g., points *c* and *d*), or alternatively, all points on the curve *a*-*b* are related to *a* by the addition of H_2O. A family of curves, all terminating at point *b*, can be drawn. For example, if a complex gas has oxygen and hydrogen contents plotting at point *e*, continual addition of H_2O will cause *e* to move along the curve toward *b*. One value of *e* + H_2O will correspond to the oxygen and hydrogen content of sample J-2. The curve *a*-*b* is plotted on all subsequent figures showing O/H versus (%O + %H); the reason for the use of this particular member of the family of curves will become evident. It should be emphasized, however, that this curve is superimposed upon the other data which appear on these figures and in no way depends upon the sample data. The short lines passing through samples J-6, J-8, J-10, J-12, and J-16 are "O_2 addition lines." These lines indicate the directions in which the O/H versus (%O + %H) plots of these samples would move if pure oxygen were added or subtracted from the samples. Addition or subtraction of N_2 would move the points horizontally, parallel to the %O + %H axis.

The J-series points in Figure 5 tend to parallel curves *a* - *b* and *e* - *b* suggesting an H_2O addition relationship among the samples. No single "H_2O addition curve" would pass through all the points, however, and individual curves drawn through each of the points would show a wide dispersion. The O_2 addition lines form wide angles with the trend of the sample points, and there is no suggestion that the O/H versus (%O + %H) plots can be related by a change in oxygen alone. Similarly, a change in nitrogen content alone does not explain the J-series plots. It is evident from Figure 5 that addition or subtraction of various amounts of O_2 or N_2 from each sample could bring all the points to a single H_2O addition curve. Also, simultaneous changes in O_2 and N_2 could do likewise, but changes in the O_2 and N_2 content of each sample would have to be consistent with previous considerations concerning atmospheric contamination. Comparison of Figures 1 and 5 shows that samples J-8, J-11, J-12, and J-17 probably have the most nearly magmatic oxygen content. Removal of oxygen alone from the other samples to reduce the oxygen pressures in Figure 1 would move their positions in Figure 5 farther away from some common H_2O addition curve. It thus seems clear that a different combination of O_2 and N_2 changes is required, such as in Cases 2, 3, and 4.

Case 2

The O/H versus (%O + %H) plots of the J-series corresponding to removal of the maximum amount of atmospheric contamination (Case 2) are given in Figure 6. The solid curve is curve *a* - *b* of Figure 5. Figure 6 should be considered in conjunction with Figure 2. The samples show a much closer relationship to the single H_2O addition curve shown. J-6 is a poor fit, however, and its position could only be explained as a deficiency in oxygen. This deficiency corresponds to the extremely low P_{O_2} of J-6 in Figure 2. Removal of oxygen from samples J-3 and J-4 to reduce the P_{O_2} of these samples in Figure 2 would move their plots in Figure 6 toward the H_2O addition curve.

Case 3

In Figure 7 the oxygen and hydrogen contents are plotted, using the atomic compositions of Case 3. The oxygen pressures in Figure 3 are from the equilibrium molecular compositions of Case 3. The position of J-6 in Figure 7 is improved over its position in Figure 6. Many of the other points have moved away from the curve, however, and no single H_2O addition curve would fit as well as the curve in Figure 6.

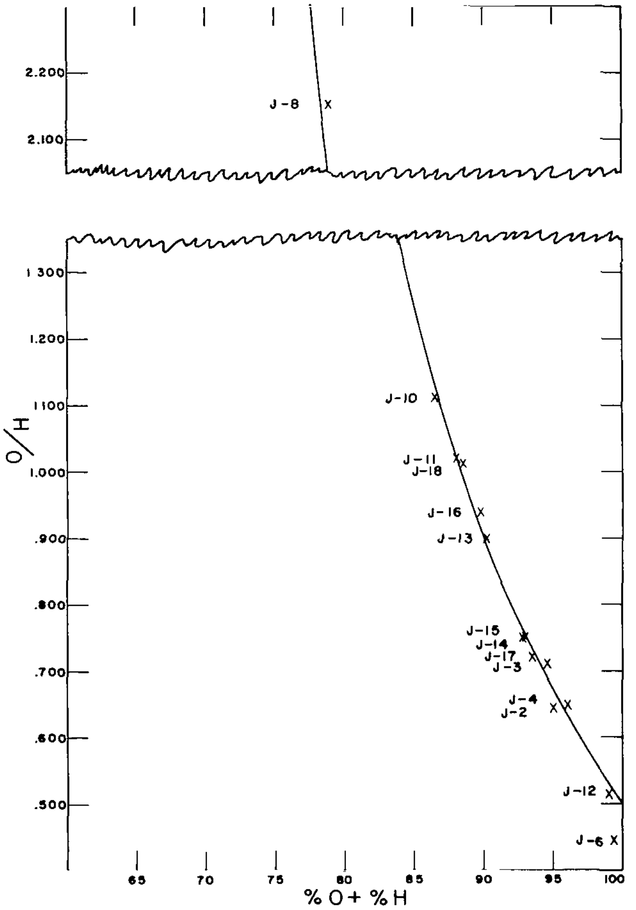

Figure 6–Atomic oxygen and atomic hydrogen contents. Atmospheric contamination removed on basis of Case 2 (*X*'s). Solid curve is H_2O addition curve of Figure 5.

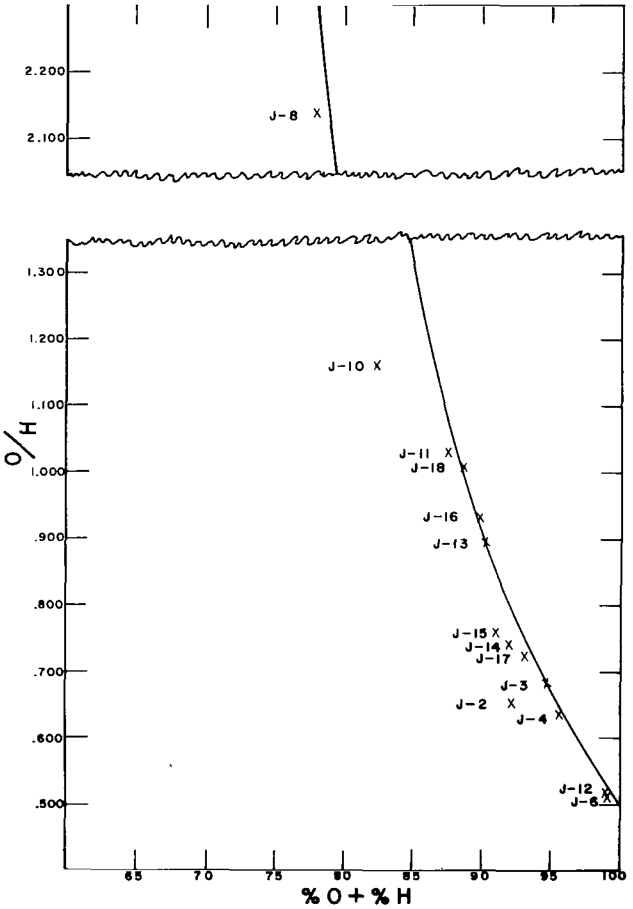

Figure 7–Atomic oxygen and atomic hydrogen contents. Atmospheric contamination removed on basis of Case 3 (*X*'s). Solid curve is H_2O addition curve of Figure 5.

Although the oxygen pressures obtained in Case 3 are superior to those of Case 2, the correlation among the J-series with respect to H_2O addition is better in Case 2 than in Case 3.

Case 4

Figure 8 shows the J-series plotted on the basis of Case 4 atomic compositions. The coincidence of the sample points and the H_2O addition curve is remarkable. The oxygen pressures of Figure 4, which are also for Case 4, fit the two criteria for atmospheric contamination removal very well. The letters in parentheses in Figure 8 are taken from Table 1 and show the quality of the field collecting conditions as judged by Jaggar (1940). The correlation between increasing water content and decreasing quality of collection is striking; only sample J-17 is out of order.

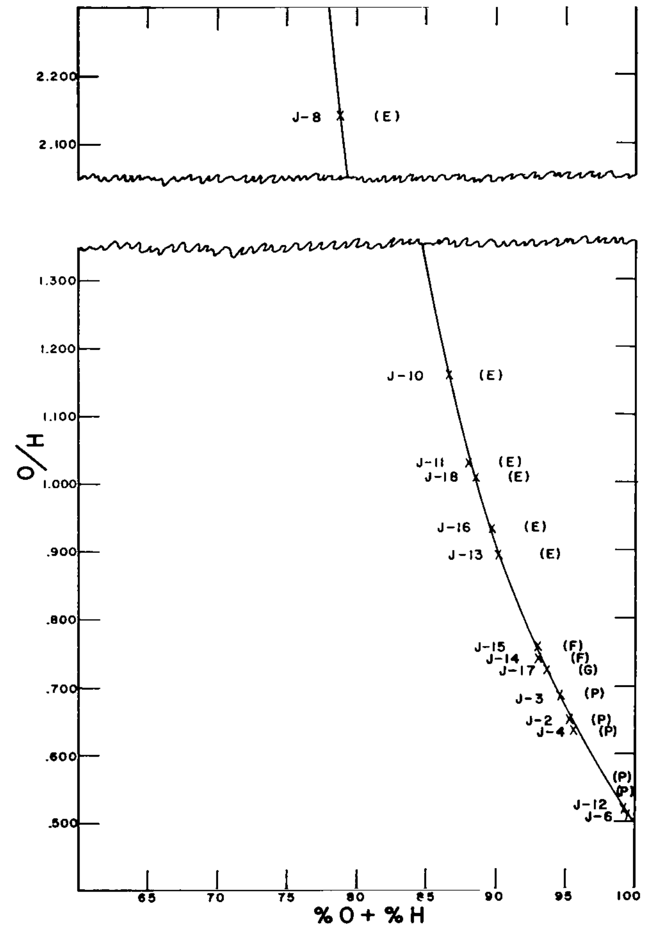

Figure 8–Atomic oxygen and atomic hydrogen contents. Atmospheric contamination removed on basis of Case 4 (*X*'s). Solid curve is H_2O addition curve of Figure 5. Letters indicate quality of sample collection: E = Excellent, G = good, F = fair, P = poor.

Tentative Conclusions

The discussion regarding atmospheric contamination led to the conclusion that either Case 3 or Case 4 was the best method for deleting contaminating atmospheric gases. This conclusion was based upon two criteria that should be satisfied by the graphs of the equilibrium oxygen pressure for each sample as a function of temperature. This section, concerning water contamination, uses the atomic composition of each sample. It is shown that the oxygen and hydrogen contents of all the samples can be precisely related to a difference in water content when the compositions of Case 4 are used. These two independent lines of reasoning strongly suggest that the estimates of the amounts of contaminating atmospheric gases (O_2 and N_2) on the basis of Case 4 closely approximates the true amounts. The section discussing *R* supports this conclusion also, in suggesting that all N_2 may be atmospheric.* In addition, the computation of equilibrium compositions also supports Case 4, since large amounts of SO_3 and free O_2 have no place in a magmatic gas even if thermodynamic equilibrium is only roughly approximated. The discussion to this point strongly suggests that, after the removal of atmospheric gases on the basis of Case 4, all remaining differences with respect to oxygen and hydrogen are due to the addition of contaminating water. The remarkable coincidence of points with the independent H_2O addition curve, plus the correlation between H_2O addition and quality of sample, seems to be beyond the realm of chance.

These conclusions must, however, be considered as only temporary. Variations in carbon and sulfur content among the samples have not yet been considered. Before the preceding conclusions can be accepted on a more concrete basis, the complexity of the discussion must be increased to include these variables, since their simultaneous effects must be investigated to study the natural system realistically.

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*Allowance for small amounts of magmatic N_2 and Ar will not noticeably alter the figures or conclusions based on Case 4. This is discussed in more detail in Part 3.

CARBON AND SULFUR

The investigation of carbon and sulfur variations among the J-series samples requires a parameter which independently shows these variations without being affected by variations in the amounts of other atomic species present. In addition, due to their reactive character, variations in the amount of either carbon or sulfur can be expected to change the partial pressures of many molecules. This suggests that atomic rather than molecular compositions be used for comparison. A parameter that satisfies these needs is the ratio C/S, where C and S are the atomic amounts of carbon and sulfur present in each sample. The considerations of the previous sections have not involved carbon and sulfur, thus C/S ratios can be computed from Table 1 or 3 or from the atomic compositions corresponding to any of the Cases 1, 2, 3, or 4. Regardless of which of these is used, the C/S ratio will be the same for any particular sample. In Table 5, the C/S ratios for the J-series samples are listed; the S-series ratios are shown for comparison. There is wide variation in values. According to the basic hypothesis, all samples had the same C/S ratio before the modifying processes changed compositions. Table 5 gives no information about the modifying processes leading to the various C/S ratios; they could be the result of addition or loss of carbon or of sulfur or some combination of these changes.

Table 5 — C/S Ratios of Shepherd's analyses (1938).

Sample	C/S	Sample	C/S
J- 2 (P)	0.806	S- 1 (F)	2.36
J- 3 (P)	.783	S- 2 (F)	4.10
J- 4 (P)	1.36	S- 3 (E)	1.04
J- 6 (P)	7.36	S- 4 (P)	.873
J- 8 (E)	4.22	S- 5 (E)	.695
J-10 (E)	.962	S- 6 (P)	.440
J-11 (E)	1.73	S- 7 (E)	1.51
J-12 (P)	2.26	S- 8 (G)	1.98
J-13 (E)	1.66	S- 9 (G)	.420
J-14 (F)	3.13	S-10 (P)	.277
J-15 (F)	1.48		
J-16 (E)	1.63		
J-17 (G)	1.72		
J-18 (G)	1.27		

The previous discussion concerning the atomic species N, O, and H does not lead to any direct conclusions concerning the variation in C/S ratios. The atomic compositions of Case 4 show no variations in N, O, or H which cannot be, at least temporarily, attributed to the modifying processes already discussed. The differences in C/S ratios must, therefore, be considered with regard to carbon and sulfur alone. Since neither the direction of change (increase or decrease) nor the amount of change of either member of the ratio is known it is necessary to establish a reference point from which to work. Further deductions using this reference point can then be made. The validity of such deductions can be tested from several points of view, and the original reference point can then be evaluated. This somewhat circular approach is unavoidable; its strength lies in its internal consistency and its ability to explain the observed facts while simultaneously supporting conclusions reached from several other lines of reasoning.

In establishing a reference point for the following discussion a few facts are outlined below:

(1) Large deposits of native sulfur are found closely associated with modern thermal areas such as those of Iceland, Japan, Hawaii, Italy, and New Zealand (see e.g., Barth, 1950).

(2) Extrusions of liquid sulfur have been observed in some thermal areas (see e.g., Watanabe, 1940).

(3) Native sulfur is commonly found around fumaroles, solfataras, and volcanic vents. In particular, a deposit of sulfur around the orifice from which sample J-6 was collected is described in Jaggar's field notes (Shepherd, 1921). Sample J-6 has the highest C/S ratio of the J-series.

(4) Several other sulfur-bearing minerals (sulfides, suplhates) are found in significant quantities in volcanic and thermal areas.

(5) The C/S ratios of gases collected at hot spring areas are orders of magnitude larger than those of volcanic gas collections. The ratios increase as collections are made farther from the source of the gases.

This list is presented to emphasize the point that there is strong evidence that sulfur is lost from magmatic and/or hot spring gases as they move toward the surface and escape into the atmosphere.

The evidence pertaining to carbon suggests the opposite tendency:

(1) Carbon-bearing minerals that can be related to emanations from volcanic or thermal areas are almost nonexistent.

(2) The carbon content of primary minerals in basic volcanic rocks is negligible.

(3) The equilibrium calculations discussed previously show that CO_2 and CO are the only carbon-bearing molecular species present in significant quantities in any of the samples studied; of these two, CO_2 is by far the most abundant.

(4) With few exceptions, CO_2 is abundant in gas collections from thermal areas. The percentage of CO_2, and thus the C/S ratios of gases from hot spring areas, increases in collections made farther from the source of the gases (Barth, 1950).

These facts point out the difficulty of finding evidence to suggest that carbon is lost from magmatic and/or hot spring gases in noticeable quantities. The possibility of adding carbon to a volcanic gas near the surface is apparently equally unlikely. Contact with carbonate rocks, such as at Vesuvius, seems doubtful in a long-established, deep source volcano such as Kilauea. Addition of CO_2 in solution in sea water is of negligible importance.* Such phenomena are not expected to be the cause of large compositional variations in the surface collections studied here, according to the basic hypothesis stated at the beginning of this paper. There is no source of significant amounts of carbon within the crater itself unless it is in the gas phase, and no reasonable method presents itself to explain how great differences in carbon concentration can occur in the gas phase.

The conclusions derived from the facts above lead to the following choice of reference point from which to continue: It will be assumed that carbon has been neither added to nor lost from the magmatic gas and that the variations observed in C/S ratios are due to a change in sulfur content alone. This means that all samples can now be put on an "equal carbon" basis; the atomic composition of each sample can be multiplied by an appropriate factor to bring its carbon content to some arbitrary value. That is, after choosing some convenient equal carbon reference value, the atomic carbon of each sample is made equal to that value by multiplying the total atomic composition by the appropriate factor. This multiplication factor is given by the expression

$$\frac{\text{reference value for C}}{\text{value of C in sample}} .$$

This operation changes neither the relative amounts of atomic species present nor their percentages, since each species is multiplied by the same factor. In effect, it simply changes the total volumes of the samples so that they all contain the same amount of atomic carbon.

Variation in Sulfur Content

The comparison of carbon and sulfur contents of the samples can be made on a plot of C/S versus (%C + %S), where

$$\%C = \frac{C}{C + H + S + O} \text{ and } \%S = \frac{S}{C + H + S + O} .$$

These parameters are similar to the ones used for the figures showing O/H versus (%O + %H); an independent parameter (C/S) is shown, along with parameters that depend upon the total atomic composition (%C and %S). The J-series, plotted in this

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*This was mentioned earlier in connection with water contamination. It will be quantitatively considered later in this study.

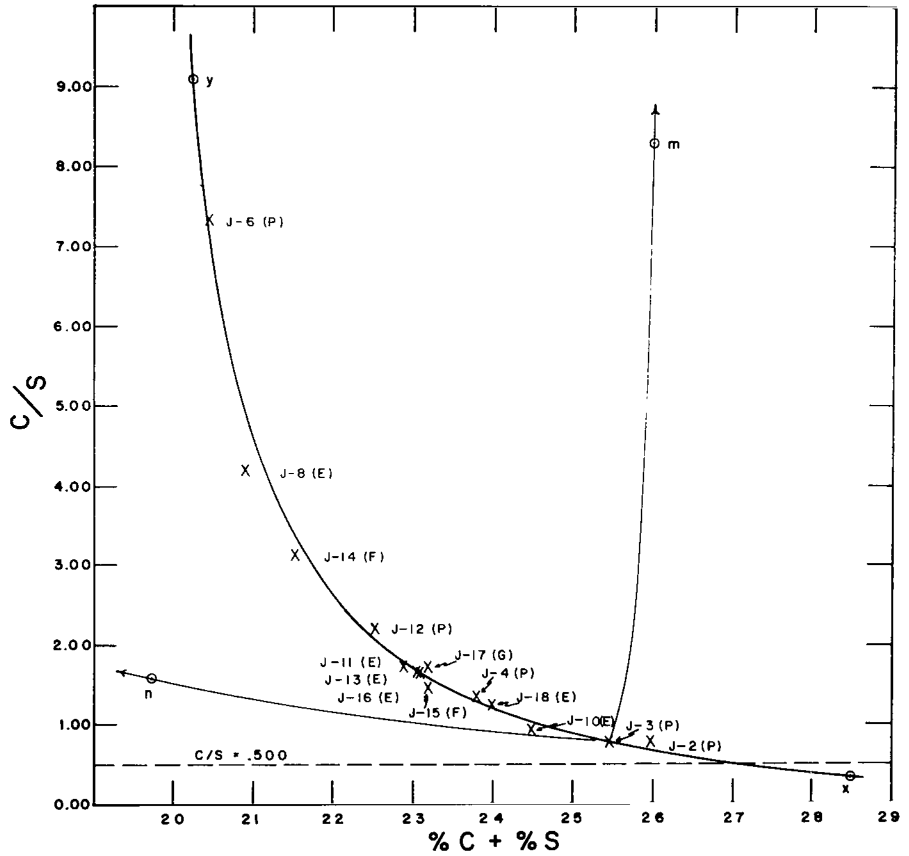

Figure 9—Atomic carbon and atomic sulfur contents. Samples adjusted to an equal carbon reference point. Curve *x-y* shows how composition changes as SO_2 is lost from point *x*. Curve J-3-*m* shows change as SO_3 is lost from J-3. Curve J-3-*n* shows change as S_2 is lost from J-3. C/S = 0.500 is value from which all samples could be derived.

manner, is shown in Figure 9; each point was plotted using these conclusions from the foregoing discussion:

(1) Atmospheric contamination has been removed on the basis of Case 4.

(2) It is assumed that the carbon content of every sample has remained essentially unchanged; therefore, the samples are brought to an equal carbon condition by multiplying the atomic compositions as described above. The carbon content of sample J-8 is used as the equal carbon reference value.

(3) The H_2O contamination suggested by Figure 8 is then removed. Figure 8 shows that sample J-8 contains the smallest amount of water and suggests that all the other samples contain contaminating water in amounts at least as great as their excess over sample J-8. This excess can be removed, in each sample, by removing oxygen and hydrogen in the ratio 1/2 until the amount of hydrogen equals that of J-8. This procedure is equivalent to stating that "essentially all of the atomic hydrogen exists as H_2O";

the analyses show that this is indeed the case. Sample J-8 itself may contain contaminating water, but there is no basis for its estimation, and further removal of contaminating water is not justified. It should be mentioned that even though all atomic hydrogen contents are now the same, the O/H values are not, because of the variable amounts of oxygen in other molecular species.

Columns A, B, and C of Table 6 show the atomic compositions of the J-series as each of the above adjustments is made. The points plotted in Figure 9 are computed from column C of Table 6 and allow comparison of the carbon and sulfur contents without the superimposed complications of atmospheric and water contamination. The validity of the three conclusions used in constructing this figure will be strongly supported if a correlation can be shown among the points of Figure 9.

Table 6 — Atomic compositions of J-series samples.

Sample	After removal of atmospheric contamination on basis of Case 4				After adjusting all samples to an "equal carbon" basis (J-8 is reference value)				After removal of H_2O contamination in excess of amount in J-8			
	(A)				(B)				(C)			
No.	C	H	S	O	C	H	S	O	C	H	S	O
J- 2 (P)	0.058	1.543	0.072	1.010	0.491	13.068	0.610	8.555	0.491	0.734	0.610	2.378
J- 3 (P)	.069	1.620	.088	1.113	"	11.620	.628	7.984	"	"	.628	2.541
J- 4 (P)	.069	1.710	.051	1.083	"	12.124	.362	7.679	"	"	.362	1.983
J- 6 (P)	.010	1.576	.001	.809	"	75.175	.067	38.585	"	"	.067	1.414
J- 8 (E)	.491	.734	.117	1.561	"	.734	.117	1.561	"	"	.117	1.561
J-10 (E)	.166	1.020	.172	1.181	"	2.968	.511	3.508	"	"	.511	2.390
J-11 (E)	.215	1.238	.125	1.279	"	2.823	.284	2.916	"	"	.284	1.872
J-12 (P)	.015	1.943	.007	1.010	"	64.935	.217	33.734	"	"	.217	1.633
J-13 (E)	.175	1.371	.106	1.228	"	3.839	.295	3.438	"	"	.295	1.886
J-14 (F)	.153	1.540	.049	1.163	"	4.943	.158	3.733	"	"	.157	1.628
J-15 (F)	.117	1.483	.079	1.128	"	6.173	.333	4.749	"	"	.333	2.029
J-16 (E)	.186	1.340	.114	1.250	"	3.551	.301	3.313	"	"	.301	1.904
J-17 (G)	.120	1.598	.070	1.159	"	6.560	.286	4.758	"	"	.286	1.845
J-18 (E)	.183	1.255	.145	1.258	"	3.376	.389	3.384	"	"	.389	2.063
Sample	After addition of SO_2 C/S = 1.500				After addition of SO_2 C/S = 1.000				After addition of SO_2 C/S = 0.500			
	(D)				(E)				(F)			
—												
J- 2 (P)	0.491	0.734	0.328	1.813	0.491	0.734	0.491	2.140	0.491	0.734	0.983	3.123
J- 3 (P)	"	"	"	1.940	"	"	"	2.268	"	"	"	3.251
J- 4 (P)	"	"	"	1.914	"	"	"	2.242	"	"	"	3.224
J- 6 (P)	"	"	"	1.935	"	"	"	2.263	"	"	"	3.246
J- 8 (E)	"	"	"	1.983	"	"	"	2.311	"	"	"	3.297
J-10 (E)	"	"	"	2.024	"	"	"	2.352	"	"	"	3.334
J-11 (E)	"	"	"	1.958	"	"	"	2.286	"	"	"	3.269
J-12 (P)	"	"	"	1.854	"	"	"	2.182	"	"	"	3.165
J-13 (E)	"	"	"	1.950	"	"	"	2.278	"	"	"	3.261
J-14 (F)	"	"	"	1.970	"	"	"	2.297	"	"	"	3.280
J-15 (F)	"	"	"	2.019	"	"	"	2.347	"	"	"	3.329
J-16 (E)	"	"	"	1.930	"	"	"	2.285	"	"	"	3.267
J-17 (G)	"	"	"	1.928	"	"	"	2.256	"	"	"	3.239
J-18 (E)	"	"	"	1.940	"	"	"	2.267	"	"	"	3.250

The curve *x*-*y* in Figure 9 can be called an "SO_2 loss curve." It is based on the same concept as the H_2O addition curve of previous figures. If SO_2 is steadily removed from a gas in which the atomic composition is such that it plots on point *x* of Figure 9, then point *x* will steadily move up the curve toward point *y*. Similarly, since J-16 happens to fall on curve *x*-*y*, steady removal of SO_2 will cause J-16 to move toward point *y* or steady addition of SO_2 will cause J-16 to move toward point *x*. A family of curves similar to *x*-*y* can be drawn with the exact position of each member depending upon the particular point from which calculations are made, in a manner analogous to that described for H_2O addition curves. The correspondence between the independently calculated SO_2 loss curve shown and the J-series sample points is quite good and strongly suggests that the variation in C/S ratios is due to a difference in SO_2 content. The possibility that the sample points are related by a difference in SO_3 content was examined. Curve J-3-*m* shows how point J-3 would move if SO_3 were continually removed from J-3. The wide deviation between the trend of the sample points and curve J-3-*m* shows difference in SO_3 content to be of minimal importance. Curve J-3-*n* shows the movement of J-3 as S_2 is removed from the atomic composition. Again, the trend of sample points cannot be explained on this basis. If H_2S is removed from sample J-3, the sample point moves toward *y* on the SO_2 loss curve. This suggests that variations in H_2S content could also explain the distribution of points in Figure 9. However, removal of hydrogen and sulfur in the ratio 2/1 soon removes all hydrogen from the sample so that J-3 is able to move toward point *y* only as far as the position C/S = 1.88, (%C + %S) = 22.82; at this point all hydrogen has been removed. A similar situation occurs with samples J-2 and J-10. These three samples could not be related to points at the upper end of curve *x*-*y* through loss of H_2S alone.

Additional information supports the conclusion that the samples are all related by a loss of SO_2. The equilibrium compositions computed and discussed earlier in this report show that SO_3, S_2, and H_2S are always present in small amounts relative to SO_2. The relatively large amounts of CO_2 that are always present, plus the great differences in C/S ratio, imply that a sulfur-containing gas was lost in large amounts. Shepherd (1925, 1938) found small amounts of S_2 and was unable to detect H_2S; moreover, it has been shown that large amounts of SO_3 are present only as a byproduct of atmospheric contamination. The analyses thus bear out equilibrium calculations showing that SO_2 was probably the only gas abundant enough to account for sulfur losses.

The O/H versus (%O + %H) plots further support the loss of SO_2. The excellent coincidence of sample points with the H_2O addition curve in Figure 8 strongly suggests a definite relationship among the samples. The variations in carbon and sulfur content should also agree with this relationship. If the explanation for C/S variations destroyed the relationship shown in Figure 8, then the explanation would be of doubtful validity. In Figure 10, the sample positions of Figure 8 are reproduced as *X*'s, with sample numbers left of the curve. Sample J-16 is used in Figure 10 to test the SO_2 loss curve of Figure 9. Curve *r*-*s* in Figure 10 shows the effect of changing the SO_3 content of J-16; curve *v*-*w* shows the effect of changing S_2, and curve *t*-*u* shows the effect of changing the H_2S content. These three curves show that addition or removal of these gases to sample J-16 will move it away from the H_2O addition curve; the same is true for the other samples. If the variation in C/S values is explained by changes in these gases, an attempt to move each sample back to the magmatic value for C/S would move the sample off the H_2O addition curve by a different amount. The result would be to completely destroy the correspondence found in Figure 8. If, however, SO_2 is added to sample J-16, the point moves up the H_2O addition curve and the correspondence between points is not destroyed. Since all samples lie on the H_2O addition curve, the same is true for all samples; it can, therefore, be stated that the H_2O addition curve and the SO_2 loss curve are one and the same in Figure 10.

The differences in the sample positions plotted as *x*'s in Figure 10 are due to different contents of both H_2O and SO_2. The samples can all be brought to the same C/S value by putting the lost SO_2 back into the analyses. When this is done, the points on the H_2O addition-SO_2 loss curve will then show differences in H_2O content only. In Figure 10, all samples have been returned to a value of C/S = 0.500. This is considered to be the most likely magmatic value as will be discussed in the next section, and is, therefore, used as an example. The O/H versus (%O + %H) values corresponding to C/S = 0.500 are shown in Figure 10

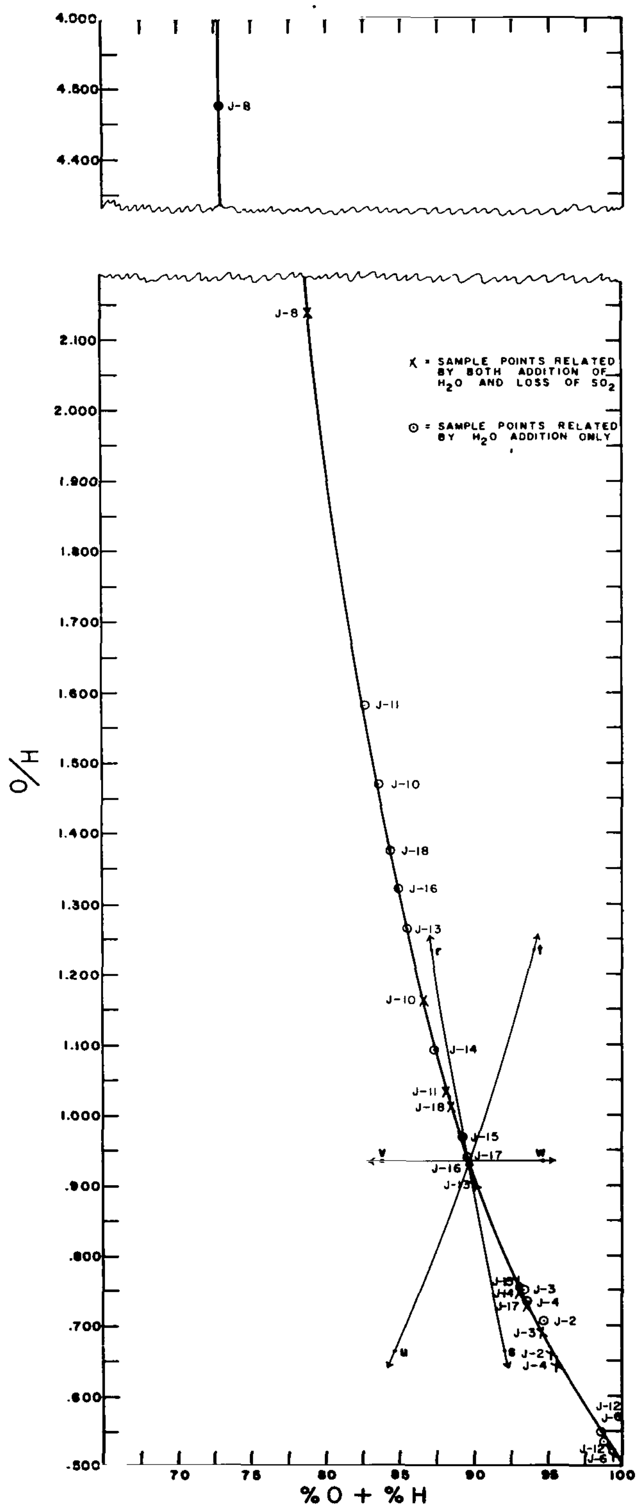

Figure 10—Atomic oxygen and atomic hydrogen contents. Atmospheric contamination removed on basis of Case 4. *X*'s are compositions with C/S values equal to those shown in Figure 9 and are same as *X*'s of Figure 8. ⊙'s are compositions after all C/S values are corrected to C/S = 0.500 by addition of SO_2 to atomic compositions of Figure 8. Curve *r-s* shows change of J-16 as SO_3 content varies. Curve *t-u* shows change of J-16 as H_2S content varies. Curve *v-w* shows change of J-16 as S_2 content varies.

as circled points, with their numbers to the right of the curve. The circled points all lie at higher O/H values. The order of points on the curve is somewhat changed, but they still tend from poor to excellent collections with less H_2O content.

Conclusions

Examination of the carbon and sulfur contents of the J-series samples shows that differences in the values of C/S can be resolved when: (1) The atomic carbon content of all samples is considered to be unchanged throughout the modifying processes, and (2) the variations in the amounts of atomic sulfur are attributed to losses of SO_2. The complexity of the study was increased to consider simultaneously variations in all atomic species. The earlier conclusions concerning atmospheric and water contamination were based on excellent correlations among sample compositions, and these correlations are in agreement with the above explanation for changes in C/S values. In fact, the earlier correlations are destroyed if atomic sulfur changes are attributed to significant changes in any sulfur gas other than SO_2. This mutual agreement among all of the conclusions constitutes an internally consistent picture, which relates all of the variations observed in the collected samples. The temporary conclusions presented earlier remain valid with the following modification: The relationship between sample points shown in Figure 8 expresses a difference among compositions with respect to both H_2O addition and SO_2 loss, and so the curve should be correctly called an H_2O addition-SO_2 loss curve. The compositional variations of the analyzed samples have been related to a relatively small number of changes brought about by the modifying processes. It is now possible to attack the problem of deducing the composition of the magmatic gas.

COMPOSITION OF THE MAGMATIC GAS

The definition of the magmatic gas should be restated at this point. "Magmatic gas" is considered to be the composition of a sample before it was altered by the processes discussed in this paper. According to the basic hypothesis of this study, all samples had the same composition before the modifying processes took place. It follows that if the effects of the modifying processes are eliminated from each sample, the same composition should result for all samples. In other words, every sample should be brought back to the magmatic gas composition. This can be accomplished by applying the conclusions of the preceding discussion.

The original molecular compositions of the J-series samples as collected are given in Table 3. Atmospheric contamination can be removed from these compositions by applying the concepts of Case 4:

(1) Remove all N_2.

(2) Remove all free O_2 and the oxygen required to form SO_3 by the reaction

$$2SO_2 + O_2 \rightleftharpoons 2SO_3.$$

This brings all samples to a common H_2O addition-SO_2 loss curve (Figure 10). The atomic compositions are shown in Table 6, column A. The atomic species now left in the samples (ignoring chlorine) are carbon, hydrogen, sulfur, and oxygen. It was concluded that the carbon content has not changed; hence, all samples can be put on an equal carbon basis (Table 6, column B). Differences in atomic composition still remain with respect to atomic hydrogen, sulfur, and oxygen. Figures 9 and 10 show that the variations in these three atomic species are the result of changes in the molecular composition, viz., changes in H_2O and SO_2 content.

Water contamination can now be considered. The positions of sample points in Figure 10 are influenced by changes in both H_2O and SO_2; however, the amount of hydrogen in a sample is significantly influenced only by H_2O. The trend of quality of collections in Figure 8 and the earlier discussion on water contamination strongly suggest that the sample containing the least water is the closest to a magmatic composition with respect to water content. This contaminating water can be removed from each sample by deleting hydrogen and oxygen in the ratio 2/1. Since sample J-8 contains the least water, it is used as the standard for hydrogen content. H_2O is removed from each sample until its hydrogen content equals that of J-8. This "equal hydrogen" basis effectively puts the samples on an "equal H_2O" basis. The atomic compositions are now as shown in Table 6, column C. With this adjustment made, the contaminating water has been removed from each sample.

To correct the changes in SO_2 content caused by the modifying processes, the C/S ratio in the magmatic gas must be known. This value is not known, and so it must be estimated from Figure 9. It was concluded earlier that the evidence points to a loss of sulfur from the magmatic gas. This in turn means that the sample with the lowest C/S value is closest to the magmatic composition; this is sample J-2 or J-3 with values near C/S = 0.800. All other samples are then related to J-2 or J-3 by a loss of SO_2. The grouping of samples rated "excellent" by Jaggar around C/S = 1.500 should also be considered. If this value is the magmatic C/S value, then the samples are related to this value by both a loss of SO_2 and an addition of SO_2. It is difficult to find a method to concentrate SO_2 in the gas by some modifying process and perhaps the criteria used by Jaggar to rate the collecting conditions had little to do with the SO_2 content. The position of an "excellent" sample, J-8, far up the curve and "poor" samples at either end imply that the quality rating is indeed a bad indicator for SO_2 content. These considerations lead to three C/S values that have been chosen as possible magmatic values: (1) C/S = 0.500 is considered to be the magmatic value that the SO_2 loss curve is approaching at the lower end; there is no justification to go to lower values on the curve. (2) C/S = 1.500 is used in deference to the sample quality. (3) An intermediate value of C/S = 1.000 is used for comparison. When all samples are brought to equal C/S by adding or removing SO_2, their atomic compositions are all identical with respect to carbon, hydrogen and sulfur. The atomic compositions corresponding to these three C/S values are given in columns D, E, and F of Table 6.

The oxygen contents corresponding to the three C/S values are given under the O headings of columns D, E, and F. Although the C, H, and S values are identical for all samples, some variation remains in the oxygen content. This variation reflects the imperfections in the methods used to arrive at the compositions of columns D, E, and F. The conclusions discussed above and the resulting methods used to return carbon, hydrogen, sulfur, and oxygen to their proper magmatic values are gross corrections, which do not consider small variations of other kinds. For example, there may actually be slight differences in the carbon content due to the loss of small amounts of carbon, or the differences in sulfur content may be due to small differences in S_2 or H_2S, or perhaps not all atmospheric oxygen has been accounted for. Such complications should be expected in a natural system; however, the variations in oxygen content in columns D, E, and F are remarkably small. This small variation in a parameter that reflects the accumulation of errors from all of the modification corrections strongly suggests that the corrections were valid. Possible variations such as mentioned above which were not considered are apparently of minimal importance in arriving at the total atomic composition of the magmatic gas.

The atomic composition shown in column F, Table 6, is the magmatic gas composition resulting from this study. The compositions in columns D and E are presented as alternative possibilities and differ only in SO_2 content. If the compositions with C/S values of 1.000 or 1.500 are used as magmatic compositions, then a process must be identified that can both increase and decrease C/S values. Equilibrium compositions for these three atomic compositions have been computed over the temperature range 650° to 1250°C at intervals of 50°C and a total pressure of one atmosphere. The atomic oxygen value of sample J-8, Table 6, columns D, E, and F was used rather than an average over all samples; this is due to the excellence of the J-8 collection shown earlier and in a following part of this study. The partial pressures (see Tables 7-9) of the major molecular species are plotted as a function of temperature in Figures 11-13. To show the partial pressures of trace molecules accurately, their values are shown as numerical values at the temperatures for which compositions were computed. Figure 11 shows the change in molecular composition of the magmatic gas with variation in temperature in the absence of any modifying processes. Figures 12 and 13 show the changes for the two alternative magmatic compositions, or a combination of the three figures shows the simultaneous effects of temperature change and SO_2 loss from a magmatic gas with an original C/S = 0.500.

Figures 11-13 have features in common that have been referred to in preceding portions of this paper:

(1) CO_2 is the dominant carbon-bearing species over the entire temperature range. CO is next in abundance, but the value of CO_2/CO increases by orders of magnitude with decreasing temperature.

(2) H_2S becomes more abundant at lower temperatures, but this is balanced by a decrease in H_2; therefore, essentially all atomic hydrogen is contained in H_2O.

(3) SO_2 is always the dominant sulfur-bearing molecular species and is the only species that could account for large changes in the abundance of atomic sulfur. Sulfur could be drained from the system by a mechanism such as the sublimation of sulfur from

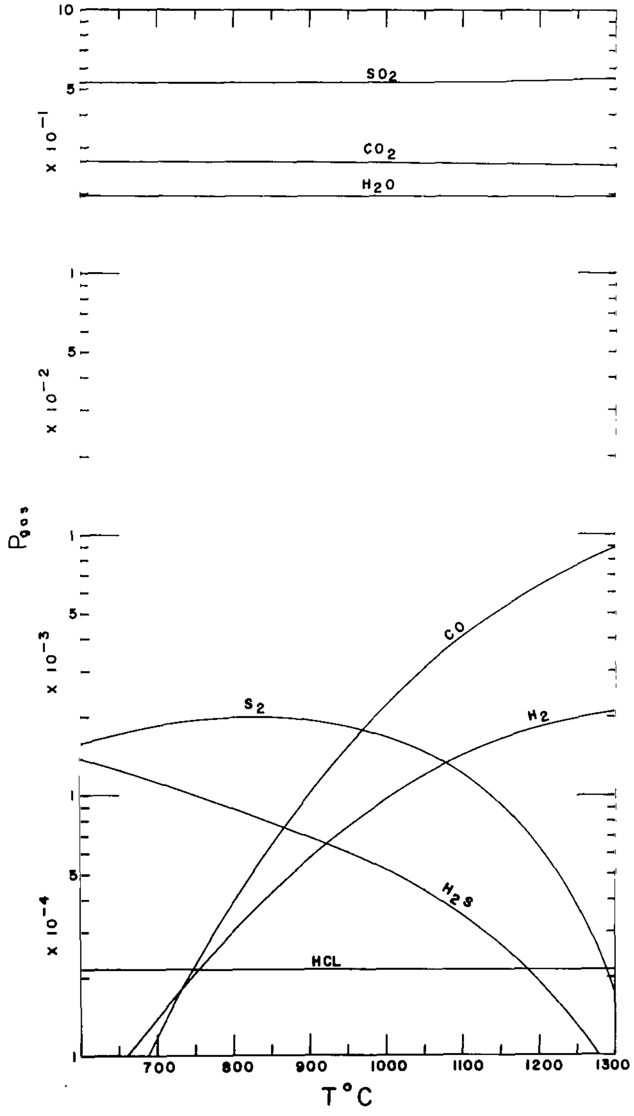

Figure 11—Equilibrium composition of the magmatic gas. Partial pressures of molecular species given as a function of temperature. Total pressure is 1 atm. C/S = 0.500.

Table 7 — Trace molecules (partial pressures). See Figure 11.

	Trace Molecules (Partial pressures)				
T(°C)	SO_3	Cl_2	CH_4	COS	CS_2
650	3.92×10^{-8}	2.38×10^{-15}	2.65×10^{-11}	6.90×10^{-11}	8.85×10^{-10}
700	6.90×10^{-8}	5.34×10^{-15}	4.56×10^{-11}	7.82×10^{-11}	1.08×10^{-9}
750	1.16×10^{-7}	1.10×10^{-14}	7.39×10^{-11}	8.59×10^{-11}	1.27×10^{-9}
800	1.86×10^{-7}	2.14×10^{-14}	1.14×10^{-10}	9.18×10^{-11}	1.43×10^{-9}
850	2.89×10^{-7}	3.92×10^{-14}	1.67×10^{-10}	9.51×10^{-11}	1.55×10^{-9}
900	4.35×10^{-7}	6.85×10^{-14}	2.35×10^{-10}	9.56×10^{-11}	1.62×10^{-9}
950	6.41×10^{-7}	1.16×10^{-13}	3.15×10^{-10}	9.50×10^{-11}	1.61×10^{-9}
1000	9.24×10^{-7}	1.89×10^{-13}	4.03×10^{-10}	8.75×10^{-11}	1.52×10^{-9}
1050	1.31×10^{-6}	3.01×10^{-13}	4.88×10^{-10}	7.83×10^{-11}	1.34×10^{-9}
1100	1.84×10^{-6}	4.70×10^{-13}	5.54×10^{-10}	6.41×10^{-11}	1.05×10^{-9}
1150	2.59×10^{-6}	7.28×10^{-13}	5.86×10^{-10}	4.95×10^{-11}	7.60×10^{-10}
1200	3.30×10^{-6}	1.23×10^{-12}	6.82×10^{-10}	6.02×10^{-11}	1.16×10^{-10}
1250	4.41×10^{-6}	2.07×10^{-12}	8.41×10^{-10}	6.94×10^{-11}	7.67×10^{-11}

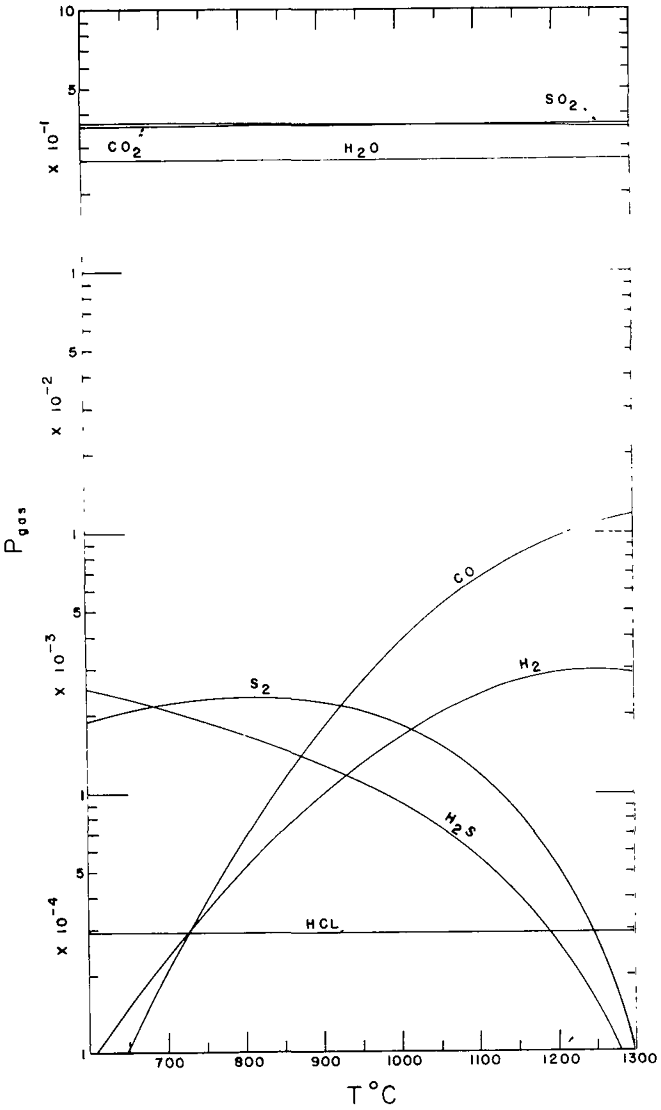

Figure 12–Equilibrium composition of the magmatic gas. Partial pressures of molecular species given as a function of temperature. Total pressure is 1 atm. C/S = 1.000.

Table 8 — Trace molecules (partial pressures). See Figure 12.

Trace Molecules (Partial pressures)					
T(°C)	SO_3	Cl_2	CH_4	COS	CS_2
650	2.12×10^{-8}	3.61×10^{-15}	4.83×10^{-11}	4.32×10^{-10}	2.14×10^{-9}
700	3.72×10^{-8}	5.80×10^{-15}	8.39×10^{-11}	4.98×10^{-10}	2.68×10^{-9}
750	6.23×10^{-8}	1.20×10^{-14}	1.38×10^{-10}	5.55×10^{-10}	3.21×10^{-9}
800	1.00×10^{-7}	2.32×10^{-14}	2.13×10^{-10}	5.95×10^{-10}	3.66×10^{-9}
850	1.55×10^{-7}	4.26×10^{-14}	3.14×10^{-10}	6.21×10^{-10}	3.98×10^{-9}
900	2.34×10^{-7}	7.50×10^{-14}	4.37×10^{-10}	6.22×10^{-10}	4.12×10^{-9}
950	3.46×10^{-7}	1.27×10^{-13}	5.79×10^{-10}	5.95×10^{-10}	3.99×10^{-9}
1000	5.05×10^{-7}	2.08×10^{-13}	7.24×10^{-10}	5.42×10^{-10}	3.60×10^{-9}
1050	7.28×10^{-7}	3.36×10^{-13}	8.45×10^{-10}	4.62×10^{-10}	2.95×10^{-9}
1100	1.05×10^{-6}	5.36×10^{-13}	9.20×10^{-10}	3.61×10^{-10}	2.14×10^{-9}
1150	1.51×10^{-6}	8.54×10^{-13}	9.05×10^{-10}	2.54×10^{-10}	1.33×10^{-9}
1200	2.22×10^{-6}	1.36×10^{-12}	8.09×10^{-10}	1.59×10^{-10}	6.86×10^{-10}
1250	3.33×10^{-6}	2.20×10^{-12}	6.50×10^{-10}	8.75×10^{-9}	2.93×10^{-10}

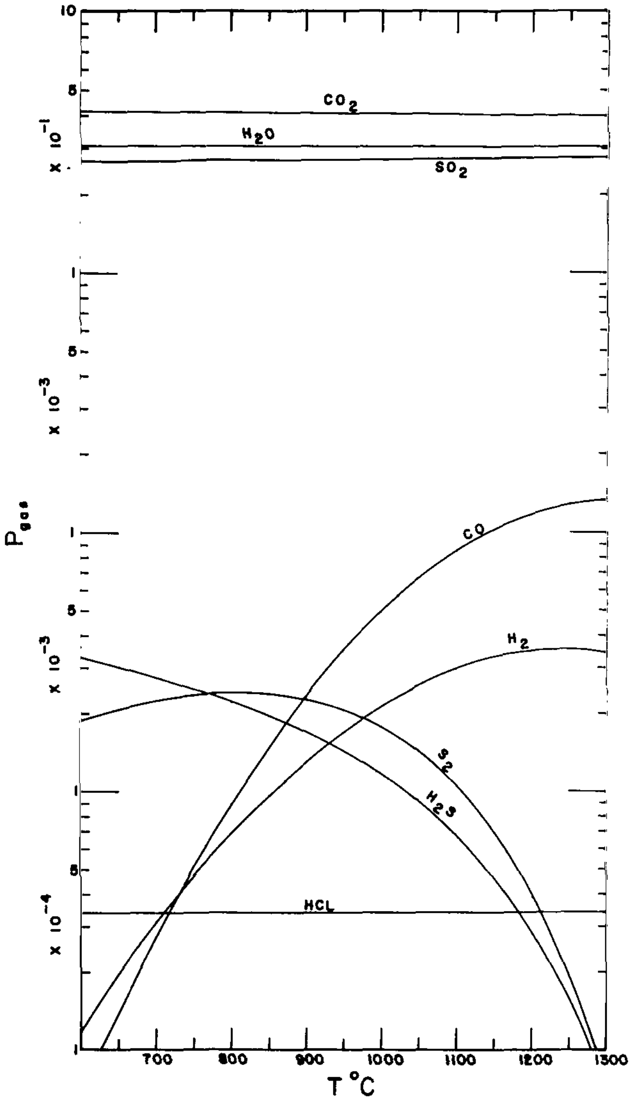

Figure 13–Equilibrium composition of the magmatic gas. Partial pressures of molecular species given as a function of temperature. Total pressure is 1 atm. C/S = 1.500.

Table 9 — Trace molecules (partial pressures). See Figure 13.

Trace Molecules (Partial pressures)					
T(°C)	SO_3	Cl_2	CH_4	COS	CS_2
650	1.38×10^{-8}	2.58×10^{-15}	6.32×10^{-11}	1.12×10^{-9}	3.22×10^{-9}
700	2.43×10^{-8}	5.74×10^{-15}	1.11×10^{-10}	1.30×10^{-9}	4.09×10^{-9}
750	4.05×10^{-8}	1.18×10^{-14}	1.82×10^{-10}	1.46×10^{-9}	4.94×10^{-9}
800	6.50×10^{-8}	2.29×10^{-14}	3.82×10^{-10}	1.58×10^{-9}	5.66×10^{-9}
850	1.01×10^{-7}	4.20×10^{-14}	4.15×10^{-10}	1.64×10^{-9}	6.15×10^{-9}
900	1.53×10^{-7}	7.40×10^{-14}	5.76×10^{-10}	1.63×10^{-9}	6.29×10^{-9}
950	2.28×10^{-7}	1.26×10^{-13}	7.54×10^{-10}	1.52×10^{-9}	5.95×10^{-9}
1000	3.33×10^{-7}	2.08×10^{-13}	9.20×10^{-10}	1.35×10^{-9}	5.15×10^{-9}
1050	4.86×10^{-7}	3.39×10^{-13}	1.05×10^{-9}	1.10×10^{-9}	3.95×10^{-9}
1100	7.10×10^{-7}	5.49×10^{-13}	1.08×10^{-9}	8.08×10^{-10}	2.63×10^{-9}
1150	1.05×10^{-6}	8.95×10^{-12}	1.01×10^{-9}	5.29×10^{-10}	1.46×10^{-9}
1200	1.59×10^{-6}	1.46×10^{-12}	8.42×10^{-10}	2.99×10^{-10}	6.54×10^{-10}
1250	2.43×10^{-6}	2.40×10^{-12}	6.26×10^{-10}	1.49×10^{-10}	2.40×10^{-10}

S_2 gas, with gas phase equilibrium being maintained and continually supplying new S_2 gas. However, the examination of C/S ratios has shown that such a mechanism is incompatible with the sample compositions.

(4) SO_3 is always present as a trace molecule only. Its abundances in Tables 1 and 3 are not in agreement with a gas which approaches equilibrium and the amounts in the samples strongly suggest atmospheric oxidation of SO_2.

Chlorine is added to the atomic compositions of Table 6 in the dimensionless proportion Cl = 0.0004. This is done in order to include the most important chlorine-bearing species (Cl_2 and HCl) in the equilibrium calculations. It was Shepherd's policy (Shepherd, 1925) to report all chlorine as Cl_2, although he suggested that it could actually be HCl. The chlorine content of the J-series samples is notably small, and there is no apparent relationship between the variability of chlorine and the variations in H_2O and SO_2. The equilibrium compositions show that Cl_2 is always present in insignificant amounts and that essentially all chlorine is contained in HCl molecules. This suggests that the amounts of Cl_2 shown in the original analyses (Table 1) were actually volumes of HCl detected by Shepherd. In spite of this, the amounts present are too small to have any significant effect on the total atomic composition or percentages of other molecular species.

The equilibrium partial pressures of oxygen corresponding to the compositions of Figures 11-13 are shown in Figure 14. A fourth curve is also shown. The atomic composition used for this curve is the same as those in Table 6, except for a further depletion in SO_2 such that C/S = 4.22. This C/S value is the same as that of sample J-8, which is one of the most sulfur-deficient samples collected. The decreasing SO_2 content from the magmatic gas with C/S = 0.500 to sample J-8 with C/S = 4.22 causes a steady decrease in the partial pressure of oxygen; however, the curves all fall well within the magnetite field. Also included in Figure 14 are dot-dash curves of actual oxygen pressure measurements at Makaopuhi, Hawaii. These measurements were made by Sato and Wright (1966) in drill holes through the crust of the lava lake. The higher pressure curve represents measurements made 6 days after drilling; the lower pressure curves are from measurements made 4 to 6 weeks later. The coincidence of the oxygen pressures obtained from this study and those from the field measurements is excellent. The points marked by X's in Figure 14 are oxygen pressures determined by Fudali (1965) in an experimental study of FeO/Fe_2O_3 ratios. The points shown are for basalts which correspond most closely to the tholeiitic basalts of Kilauea. Although these points extend over a wider range of oxygen pressures, they correspond well with the 1200°C values of the curves obtained in the present study.

SUMMARY

The foregoing investigation of Kilauea gas collections has examined the effects of various modifying processes that alter the composition of the magmatic gas in the surface and near surface environment. These processes were identified and evaluated qualitatively. Quantitative study of the processes shows that all the collected samples can

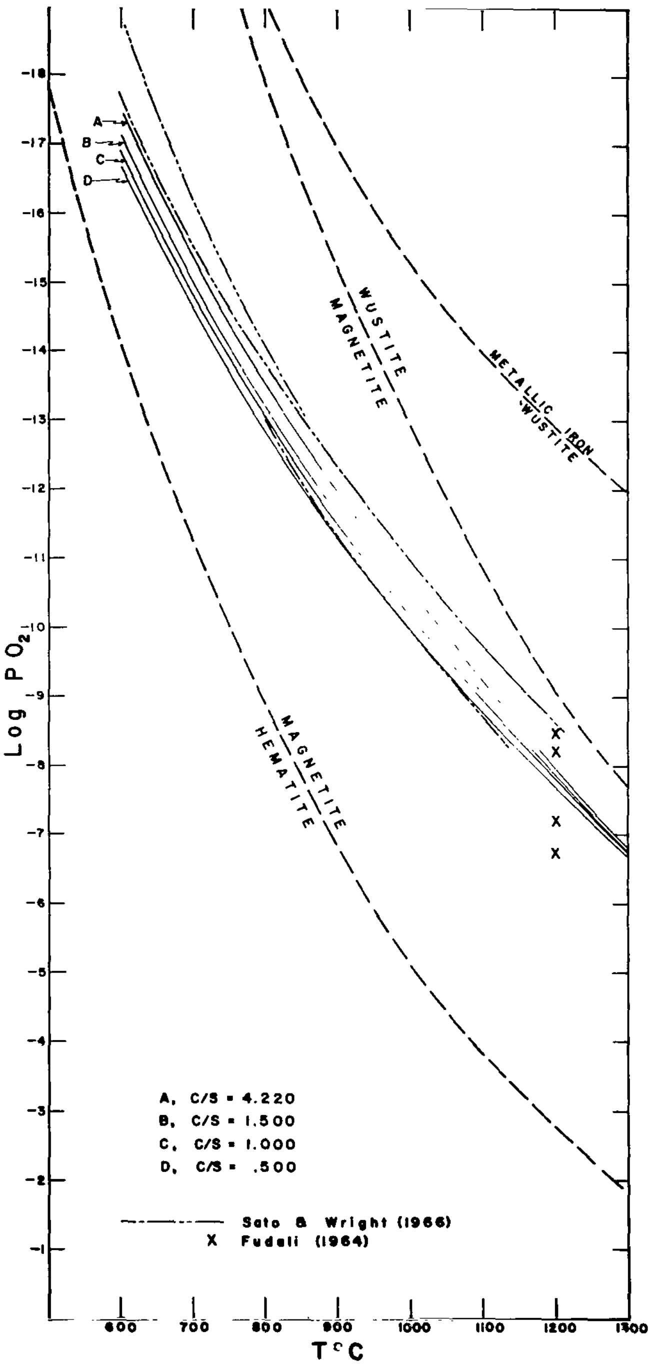

Figure 14–Equilibrium partial pressures of oxygen (P_{O_2}) of magmatic gas. Curve *D* is for magmatic gas with C/S = 0.500. Curves *C*, *B*, and *A* show decrease in P_{O_2} as SO_2 is removed from gas of curve *D*. Dash-dot curves are values measured in drill holes (Sato and Wright, 1966). *X*'s are experimental determinations in basalts (Fudali, 1964).

be related to a single magmatic gas composition by eliminating the effects of a limited number of modifying processes. The processes found to be of significant importance are:

(1) Molecular compositional changes caused by changes in temperature. These are eliminated by comparing computed equilibrium compositions over a range of temperatures at 1 atm pressure. (Part 2 of this study shows that pressure effects are not important.)

(2) Atomic and molecular compositional changes caused by atmospheric contamination. This contamination is removed by the best of four methods examined.

(3) Atomic and molecular compositional changes due to contamination by water. This water is removed by returning all samples to the composition of the sample with the lowest water content.

(4) Atomic and molecular changes caused by the loss of SO_2 from the samples. These effects are removed by replacing the lost SO_2 in each sample.

The effects of all of these changes were simultaneously considered so that their interactions could be quantitatively evaluated.

The magmatic composition that results in each sample supports the basic hypothesis that all of the gas collections were derived from a single magmatic gas with approximately equal portions of H_2O, CO_2, and SO_2. Other molecular species are of minor importance quantitatively. The effects of modifying processes other than those listed above are not of great significance in determining the gross composition of collected samples, but may have interesting and important chemical results. The magmatic gas composition resulting from this study is that of the near surface gas that was released from the magma during the collection period (approximately 1 year). The gas may have been altered further by the processes considered here or other modifying processes during its ascent to the Earth's surface. The composition presented here is thus a starting point from which to work to assess the behavior and composition of the magmatic gas before its release from the erupting lava. The compositional changes occurring during the release of the gas from the magma and its collection result in variable collected compositions. Earlier effects that may have occurred have been homogenized in the magma so that they cannot be readily detected in gross compositional changes. An optimistic viewpoint would suggest that the magmatic composition derived is actually close to the juvenile gas composition present at depth. However, compositional changes brought about by increased pressure, varying solubilities in the magma, contamination at depth, and so on, must be evaluated before this becomes a tenable conclusion.

The concepts and approaches used in this study lead to additional information concerning the validity of assuming equilibrium, the effectiveness of the collecting technique, the behavior of gases during compositional changes, gas reaction rates, and the relationship between the gases of thermal areas and magmatic gases. These subjects are discussed in Parts 2 and 3 of this study.

PART 2

EQUILIBRIUM AND REACTION RATES

INTRODUCTION

The volcanic gas samples collected from Kilauea by Jaggar in 1918-19 and analyzed by Shepherd (Shepherd, 1921) are the best set of systematic samples yet obtained. In Part 1 of this study, these samples were examined to determine the quantitative effects of various modifying processes that altered the sample compositions from their original magmatic composition. By identifying and evaluating these effects, the composition of the magmatic gas from which these samples were derived was deduced. As part of the method of approach used, it was stated that thermodynamic equilibrium is likely to be closely approached in nature in a gas phase under the high temperatures and low pressures of an extruding magma. It was also assumed that the gases obey ideal gas laws. The validity of these assumptions needs to be more firmly established, not only in support of the earlier part of this study, but also because of their great significance in acquiring a knowledge of the behavior of magmatic gases in general.

A knowledge of the behavior of volcanic gases before and during collection is of prime importance to those involved in the collection, analysis, and interpretation of gas samples. A better understanding of this behavior would assist in the design of collecting apparatus and collecting techniques. One of the objectives of the usual collecting technique, using vacuum tubes, is to "quench" the composition issuing from the collecting site by adiabatic expansion cooling. This quenching technique has not been closely examined, but it should be evaluated to determine its effectiveness, so that equipment can be designed that will produce the desired result. Another important objective of gas collecting is to eliminate as much contamination, especially atmospheric, as possible. It has been realized since the first volcanic gas collections were made that atmospheric gases are almost always included in the samples. Part 1 of this study has shown that this is also true in all of the Kilauea samples and that, in addition, other gases have been both added and lost. We do not know, however, to what extent these additions and losses result from the collecting techniques and equipment and how much is due to volcanic processes before collection. A better knowledge of this would assist in designing equipment and in understanding volcanic processes.

In this section, the J-series samples, collected by Jaggar, are examined to study some of the problems outlined above. The approach to equilibrium in the samples before and after collection is evaluated. The times at which compositional modifications occurred and rates of gas reactions are also considered, in order to deduce the behavior of each sample both before and during the collection. Several conclusions can then be drawn about the processes occurring in the volcanic environment and the effectiveness of the collecting technique.

METHOD OF APPROACH

In general, gas phase reactions are rapid at high temperatures and low pressures, with experimentally determined reaction rates far exceeding those usually found in condensed phases. This leads to the thought that gas phase equilibria will adjust to temperature, pressure, and compositional changes relatively quickly, with a rapid reestablishment of equilibrium compositions. Numerous factors will determine how successfully a volcanic gas achieves and maintains equilibrium, but the reaction rates suggest that true equilibrium may be closely approached at the temperatures of basaltic magmas with the pressure near 1 atm. This behavior would have obvious advantages in interpreting gas analyses and predicting magmatic processes by eliminating the doubts that are often a part of equilibrium studies of condensed phases. In contrast to studies of most rocks and minerals, however, the collection of gas samples is likely to alter drastically the equilibrium composition present in the natural environment. The evidence of former equilibrium is then destroyed and proof of its existence becomes difficult. This possibility has led to the attempts to "quench in" high-temperature compositions. On the plus side of equilibrium studies in gases are the excellent thermodynamic data that have become available over the past few years. The quality of these data is such that the accuracy of calculations is usually limited by the quality of the analyses available. If analytical data are good, then thermodynamic calculations are quite reliable. The data used in this report are from Shepherd (1921, 1938) and are reproduced in Part 1 of this study. At the completion of the work discussed below, it became evident that these analyses are of excellent quality — remarkably so, considering the methods available at the time of Shepherd's work.

Previous work has suggested that volcanic gas compositions at least approximate equilibrium compositions. Ellis (1957) made calculations by hand to obtain equilibrium compositions of relatively simple gaseous systems. Starting ratios for the atomic species he considered were chosen to approximate the values found in analyzed samples. By comparing his calculated equilibrium compositions with some of the better sample analyses available, he found that the compositions were quite similar; some of the J-series and S-series collections from Kilauea were included in his comparisons. Heald et al. found correlations (1963) by comparing the average equilibrium composition of twelve of Shepherd's sample analyses (1938) with the analyzed compositions of samples J-18, S-2, and S-7. Their calculations were made by computer methods and involved chemical systems with a complexity like that of natural gases. These papers have provided valuable clues concerning the processes affecting volcanic gas compositions, especially the gross effects of atmospheric and water contamination. Although correlations were found between the major features of calculated and collected compositions, the questions of equilibrium and the real chemical effects of contamination are still moot.

Compositions made by using atomic ratios that only approximate the ratios in actual analyses will always show some discrepancies when comparisons are made. It cannot be determined whether these discrepancies are caused by disequilibrium or by differences in atomic compositions, because small variations in equilibrium compositions may reflect very large variations in either gas temperatures or atomic composition. In this section, the equilibrium composition of each sample is considered individually and compared to the actual analysis. By using the true atomic composition of each sample in the calculations, the deviations from equilibrium are accurately evaluated. Then, adjustments are made to the calculated compositions so that the causes of these deviations can be determined.

Equilibrium compositions were computed, using the method presented by White et al. (1957); this method is discussed in Part 1 and the Appendix. Equilibrium compositions have been obtained from the atomic compositions of each of the fourteen J-series samples. Four different atomic compositions were used for each sample, corresponding to four different methods of removing atmospheric contamination from the analyzed compositions. These methods are termed Cases 1, 2, 3, and 4 and are discussed in Part 1 of this study. In each Case, the equilibrium composition is compared to the sample compositions as analyzed (Shepherd, 1938; Part 1, Table 1, of this study). The methods of removing atmospheric contamination and the atomic and molecular species considered in the calculations for Cases 1, 2, 3, and 4 are given in Table 10. The actual atomic compositions used can be referred to in Table 6. The sample analyses are tested for thermodynamic equilibrium as follows:

(1) The equilibrium (molecular) compositions are computed from atomic compositions over the temperature range 650°-1250°C at intervals of 50°C; atomic compositions are obtained by removing atomic nitrogen and oxygen from the analyses in amounts corresponding to the case being considered. The total pressure equals 1 atm, and ideal gas laws are assumed to be followed (i.e., activity coefficients are equal to unity).

(2) The equilibrium compositions are then plotted on P_{gas} versus T°C graphs as curves connecting the calculated points.

Table 10 — Atomic and molecular species used in equilibrium calculations.

Basis of Atmospheric Contamination Removal	Atomic Species	Molecular Species
Case 1 (Remove all O_2 plus atmospheric proportions of nitrogen and argon)	C, H, S, O, N, Cl	CO, CO_2, H_2, H_2O, S_2, SO_2, SO_3, O_2, N_2, NH_3, Cl_2, HCl, H_2S
Case 2 (Remove all N_2 plus atmospheric proportions of argon and oxygen)	C, H, S, O, Cl	CO, CO_2, H_2, H_2O, S_2, SO_2, SO_3, O_2, Cl_2, HCl, H_2S
Case 3 (Remove all O_2 and oxygen used to form SO_3 plus atmospheric proportions of nitrogen and argon)	C, H, S, O, N, Cl	CO, CO_2, H_2, H_2O, S_2, SO_2, SO_3, O_2, N_2, NH_3, Cl_2, HCl, H_2S
Case 4 (Remove all N_2 plus atmospheric proportion of argon. Remove oxygen as in Case 3.)	C, H, S, O, Cl	CO, CO_2, H_2, H_2O, S_2, SO_2, SO_3, O_2, Cl_2, HCl, H_2S

(3) N_2 is removed from the analyses in an amount corresponding to the case being considered, and the remaining volumes are recomputed so that their totals equal 100%. The volumes of the analyses are then plotted on the right-hand side of the P_{gas} scale on the equilibrium composition graphs. The volumes are equal to partial pressures, since the total pressure equals 1 atm. Hence, four graphs are made for each sample, one for each of the Cases 1, 2, 3, and 4. On each graph, the equilibrium compositions and sample analyses are plotted after they have been adjusted for atmospheric contamination. Comparisons are then made, to look for a correspondence between equilibrium compositions and analyses. If the analysis value for a molecular species falls somewhere on its equilibrium curve, the point is marked on the curve and the temperature is noted. If the analysis and equilibrium values for all molecular species are coincident at the same temperature, then the analysis represents an equilibrium composition. If correspondence is not found for all gas species at the same temperature, then the analysis does not represent an equilibrium composition, and the problem then becomes a matter of finding reasons for the lack of correspondence.

CASE I

A typical example of the approach used can be shown by discussing sample J-18, Case 1. In Case 1, all free oxygen (O_2) present in the analysis is removed, along with atmospheric proportions of nitrogen and argon. After this adjustment, the analysis is retotalled to 100%, so that the total pressure again equals 1 atm. The atomic ratios resulting from this adjustment are used to compute equilibrium compositions and the equilibrium curves are then plotted as in Figure 15. The equilibrium partial pressures of H_2, CO, S_2, and Cl_2 are too low to be shown on the graph. The labeled arrows at the right mark the pressures of the molecular species in the analysis after it has been adjusted according to Case 1. This procedure is equivalent to assuming that this amount of atmospheric contamination was added to the volcanic gas after it had cooled to a point where reactions would no longer occur at a significant rate. Therefore, oxygen and nitrogen added at this time did not react with the gases already present and should not be included in the search for an equilibrium composition. If this assumption is in error, then it will become evident when comparisons are made.

Figure 15 shows that equilibrium would require H_2O, CO_2, and SO_2 pressures above those present in the analysis over the entire temperature range considered. Therefore, even though all free oxygen has been removed, the amount of oxygen left in the atomic composition is too large to give calculated H_2O, CO_2, and SO_2 pressures as low as those in the analysis. To have the two compositions match, more oxygen must be removed before making calculations. Figure 15 also shows that H_2, CO, and S_2 are present in the analysis in amounts that are orders of magnitude above those in the equilibrium composition. This again suggests that the calculated composition is too highly oxidized, because increasing atomic oxygen suppresses these molecules. Furthermore, equilibrium would require a partial pressure of oxygen which is easily measurable, yet the analysis contains no oxygen after the Case 1 adjustment. The evidence above shows that it was correct to remove free oxygen from the original analysis as a nonreacting gas. If this oxygen had been included in the calculations, the equilibrium amounts (pressures) of H_2O, CO_2, and SO_2 would be considerably higher and the amounts of H_2, CO, and S_2 would be much lower than those of Figure 15. Therefore, the reaction of this oxygen with the samples would have affected the analysis values similarly, giving values much different from those actually found. Figure 15 shows that even more oxygen must be removed for calculated values to approach analysis values. In contrast to these relationships, SO_3 shows the opposite comparison, i.e., this oxidized gas species is present in the analysis in greater abundance than in the equilibrium composition. At first glance this would appear to be in opposition to the conclusions reached above; however, this discrepancy can be resolved and is, in fact, in complete agreement.

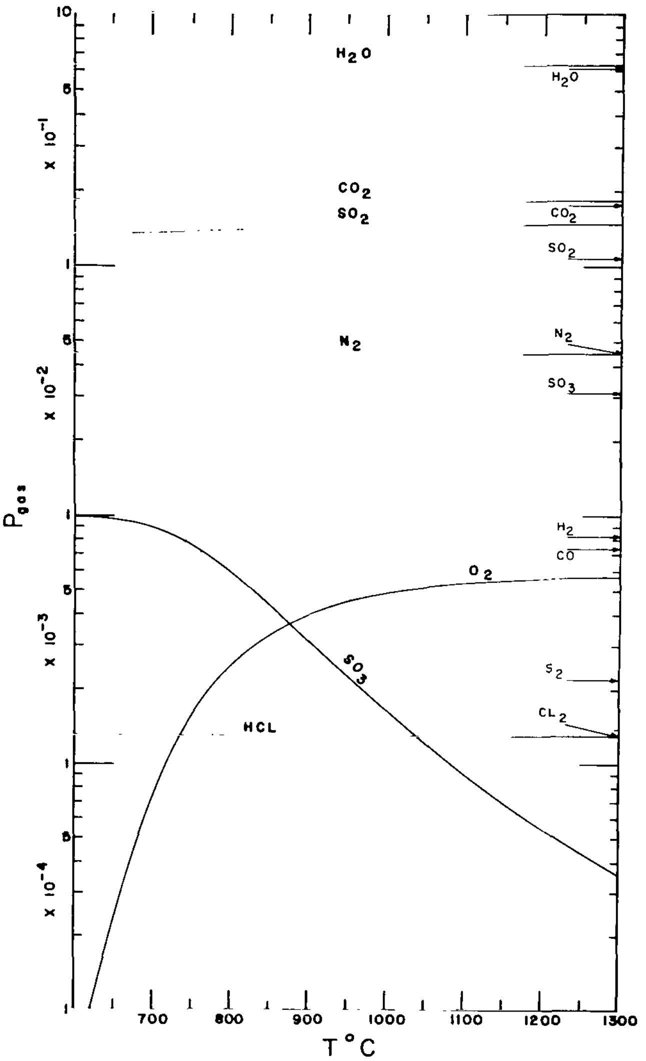

Figure 15–Equilibrium composition (partial pressures) of sample J-18. Atmospheric contamination removed on basis of Case 1. Arrows at right indicate analysis values after adjustment to conditions of Case 1.

Figure 15 shows that the original analysis of sample J-18 does not represent an equilibrium composition. Removal of atmospheric gases according to Case 1 gives a residual analysis which is identical to that published by Shepherd (1921, 1938). This residual analysis contains the oxidized gases H_2O, CO_2, and SO_2 in amounts that are relatively close to equilibrium values, but the other gas species (H_2, CO, S_2, O_2) are too abundant by orders of magnitude. The graphs for Case 1 shows the same general relationships in every J-series sample; none of the samples represents equilibrium compositions either before or after removal of atmospheric contamination by the methods of Case 1. Equilibrium compositions are always considerably more oxidized than the molecular compositions of the analyses. If the calculated compositions are to match the analyses, additional oxygen must be removed from the atomic compositions used in the calculations. This suggests that if the analyses do represent equilibrium amounts for most of the species, then one or more of the species are too highly oxidized. The calculated composition spreads this excess oxygen over all molecules in the equilibrium composition and makes every species appear to be out of equilibrium. Since all free oxygen has been removed, this excess oxygen must be combined in one or more other types of molecules. The anomalously large amounts of SO_3 present in every sample indicate that the excess oxygen is present in this gas. It is reasonable to assume that this excess oxygen was added as a result of atmospheric contamination; it was shown in Part 1 of this study that this is indeed what has occurred.

The relationships of the nitrogen- and chlorine-bearing gases in sample J-18 are the same in all of the other J-series samples. In all the calculations made in this study, the species NH_3 and Cl_2 are present in trace amounts only. Essentially all nitrogen and chlorine are contained in the species N_2 and HCl. Because of this, the calculated amount of N_2 does not vary significantly over the temperature range considered, and the equilibrium and analytical abundances are always the same. The equilibrium amounts of HCl are also constant over the temperature range and always equal the analytical amounts of Cl_2. The Cl_2 reported by Shepherd in his analyses must actually be HCl. Shepherd (1925) suspected that this might be true, but he followed the policy of reporting all chlorine as Cl_2.

CASES 2, 3, AND 4

Three other methods of removing atmospheric contamination (Cases 2, 3, and 4) from the analyses are considered in this study. The methods and the resulting compositions are discussed in detail in Part 1. The methods are outlined below to emphasize what each method accomplished in relation to the subject presented here. In Case 2, all N_2 is removed from the analyses, along with atmospheric proportions of O_2 and Ar. Whereas Case 1 removes the minimum probable amount of total atmospheric contamination, Case 2 removes the maximum probable amount. In Case 1, the only oxygen removed was the free O_2 found in the analysis; in Case 2, free O_2 plus some additional oxygen is removed. This additional oxygen is removed to account for and estimate the excess oxygen that apparently remains in the samples after the adjustments according to Case 1. The amount of oxygen removed in Case 2 is such that the excess oxygen must be assumed to be held in more than one molecular species; i.e., contamination caused the oxidation of several molecular species. Case 3 assumes that all excess oxygen is held in SO_3 molecules. Atmospheric contamination is removed in Case 3 by excluding free O_2 plus the excess in SO_3, along with atmospheric proportions of N_2 and Ar. The amount of oxygen and atmospheric contamination removed in Case 3 is intermediate between the amounts in Cases 1 and 2. In Case 4, oxygen is removed in the same way as in Case 3, with N_2 and Ar removed in the same way as Case 2; therefore, in Case 4 the atmospheric gases are not removed in their atmospheric proportions. Plots similar to Figure 15 were made for each sample for each of Cases 2, 3, and 4. The information obtained from these plots shows that the samples fall into four groups, depending upon the correspondence between equilibrium compositions and adjusted sample analyses.

Group I

Sample J-8 is the only sample which falls into this group. An examination of the three plots for J-8 shows that Case 4 is the most correct method of removing atmospheric contamination; Cases 2 and 3 are similar to Case 1, in that calculated and

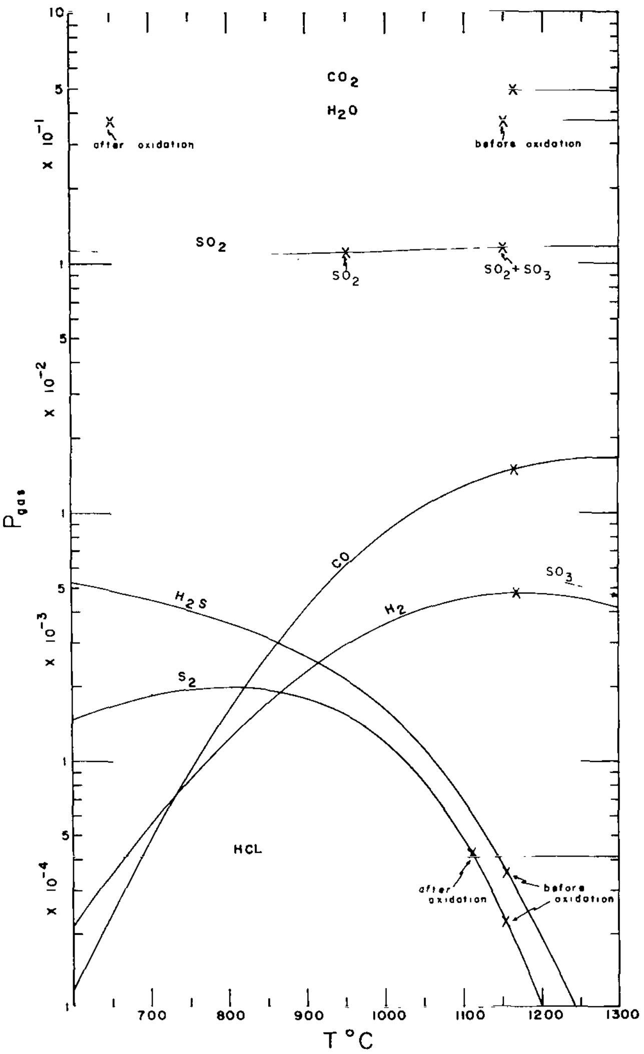

Figure 16—Typical temperatures of correspondence of Group 1. Curves show equilibrium partial pressures of molecular species in sample J-8 when atmospheric contamination is removed on basis of Case 4. *X*'s mark the points at which equilibrium values correspond to analysis (N_2 in analysis adjusted to conditions of Case 4). Temperatures of correspondence before and after the analysis is corrected for low temperature oxidation of SO_3 and H_2S are given. Temperatures of correspondence are all between 1150° and 1160°C after oxidation correction is made.

adjusted compositions show discrepancies that cannot be reconciled. The equilibrium plot for Case 4 is shown in Figure 16. Following the procedure outlined above, the analyses are recomputed to a total of 100% (1 atm) after the removal of free O_2 and N_2; as the analysis stands after this adjustment, the excess oxygen held in SO_3 has not yet been removed. The analysis is plotted in Figure 16 as *X*'s on the equilibrium curves where these values correspond to equilibrium values; the H_2O and S_2 points are marked "after oxidation." The analysis value for SO_3 is shown by an arrow at the right; H_2S cannot be plotted, since it is not present in the analysis. The temperature values of those points that are the same as the equilibrium value at some point on the curve are called "temperatures of correspondence." The temperatures of correspondence are quite variable, but are close enough to a single temperature to suggest an approach to equilibrium. Ignoring for the moment the points marked "before oxidation," the anomalous values appear to be H_2O at 650°C, SO_2 at 950°C, and S_2 at 1110°C. In addition, the equilibrium values for SO_3 are too low to be shown in the figure (approximately 10^{-7}) and are far below the analysis value of 4.31×10^{-3} over the entire temperature range. Finally, the calculations show that H_2S should be present in amounts comparable to CO, H_2, and S_2; however, H_2S was not detected in the sample. These discrepancies now need to be considered.

Case 4 assumes that all excess oxygen is contained in SO_3 molecules; if this assumption is valid, then SO_3 is present because of the oxidation of some other sulfur-bearing molecule. In Part 1, it was shown that SO_3 was derived from oxidation of SO_2, since quantitative tests eliminate all other sulfur-bearing species as significant sources but are in complete accord with the oxidation of SO_2. Therefore, in Case 4 (and Case 3), the amount of excess oxygen can be determined by considering the reaction

$$2SO_2 + O_2 = 2SO_3.$$

The amount of excess oxygen present (atmospheric O_2) is equal to one-half the amount of SO_3. This oxygen has been removed from the equilibrium composition in Figure 16, but has not yet been removed from the analysis. It can now be removed from the analysis simply by adding the amounts of SO_2 and SO_3 which, in effect, returns the amount (pressure) of SO_2 to its preoxidation value. This is shown in Figure 16 by the point (SO_2 + SO_3) on the SO_2 curve; the reaction has been run backwards to the amount of SO_2 before contamination. With this correction made, the SO_2 temperature of correspondence becomes 1150°C.

Further examination of Figure 16 gives information that leads to another correction. Shepherd (1921, 1925) was unable to find H_2S in any of the samples; however, Figure 16 shows that at equilibrium, sample J-8 should contain even more H_2S than S_2. Further, if J-8 contained slightly less H_2O, the temperature of correspondence for H_2O would be higher. H_2S should be decreased and H_2O increased if oxidation occurred by the reaction

$$2H_2S + O_2 = 2H_2O + S_2.$$

The temperatures of correspondence for CO_2 (SO_2 + SO_3), CO, and H_2 are all very close to 1150°C; the amount of H_2S that would be present at that temperature is $P_{H_2S} = 4.35 \times 10^{-4}$ atm. If this amount of H_2S actually was present originally and has since been oxidized out of detectable existence by the reaction above, then an equal amount of H_2O and one-half this amount of S_2 would now be present in the analysis. This oxidation can be "re versed" in a manner similar to the SO_2 oxidation discussed above; i.e., P_{H_2S} is increased to 4.35×10^{-4} atm; P_{H_2O} is decreased by 4.35×10^{-4} atm, and P_{S_2} is decreased by 2.17×10^{-4} atm. This correction has been made in Figure 16; the new temperatures of correspondence are marked with x's labeled "before oxidation." It should be mentioned that although the oxygen required for H_2S oxidation is not removed by Case 4, the amount is so small that it does not significantly affect the total amount of atomic oxygen present. The calculated equilibrium compositions do not noticeably reflect this slight difference.

The temperatures of correspondence for all gas species in Figure 16 now fall between 1150° and 1160°C. The conclusion to be drawn from this is that sample J-8 represents an equilibrium composition at approximately 1150°-1160°C, which has been altered by the superimposed modifications of atmospheric contamination. The ability of atmospheric oxygen to react with the volcanic gas depends upon when contamination took place. If contamination occurs when the volcanic gas is at a high temperature, when reaction rates are rapid, then oxygen should react quickly with many gas species; if contamination occurs at a low temperature, reactions may be too slow to be measurable. In sample J-8, the gas was apparently at a temperature above 1160°C before it was collected. Expansion into the vacuum tube successfully "quenched in" a composition that was at equilibrium at 1150°-1160°C. After the gas was quenched, atmospheric contamination gases entered the tube and reactions then occurred between H_2S and O_2 and between SO_2 and O_2. It is reasonably certain that this contamination and oxidation occurred below 1150°C. Rapid reactions involving H_2, H_2O, CO, and CO_2 were occurring above this temperature, and if the contaminating oxygen had been present, it would have reacted with these molecular species. The two oxidation reactions used above apparently indicate the processes that actually occurred because the preoxidation temperatures of correspondence all fall within such a narrow temperature range. Using other reactions to reconcile postoxidation compositions would completely destroy this close agreement and it seems most unlikely that such agreement would be achieved by chance. This is particularly true considering the sensitivity of temperature-composition changes shown by preoxidation and postoxidation points.

Group 2

The phenomena exhibited by this group are shown using sample J-17 as an example. As in Group 1, Cases 1, 2, and 3 do not give temperatures of correspondence that can be reconciled in any reasonable manner. The plot for Case 4 is shown in Figure 17. As in Group 1, equilibrium compositions for Group 2 are computed from atomic compositions resulting from the Case 4 adjustment, but analyses are plotted with the oxygen in SO_3 not yet removed. Since the J-17 analysis contains no SO_3, no further adjustment must be made, but it is made for all other members of the group in the way already described.

The temperatures of correspondence "after oxidation" are again quite variable, with H_2O too low at 650°C, H_2S not present in the analysis, and S_2 much too abundant in the analysis. CO and CO_2 agree at 1119°C. The temperature of correspondence for SO_2 is 900°C, suggesting that SO_2 ceased to react when the temperature dropped below 900°C; evidently, atmospheric oxidation was introduced below this temperature — i.e., at a later time. Since H_2S and S_2 would be expected to interact with SO_2, it can be assumed that these species were present in their equilibrium amounts at this temperature, if this assumption is incorrect, the oxidation adjustments will reveal the error. Again considering that H_2S has disappeared because of oxidation, the same correction is made as for Group 1 using the equilibrium partial pressure of H_2S at 900°C. The partial pressures of H_2S, S_2, and H_2O before oxidation are shown in Figure 17. All the sulfur-bearing gases now show temperatures of correspondence that fall between 900° and 905°C; in addition, the temperatures of correspondence for H_2 and H_2O are quite close to the same value.

The relationships in Figure 17 can be summarized as follows:

(1) The adjustment made for SO_3 in sample J-8 (and all other samples) is supported by the agreement between analysis and equilibrium in J-17 in which no SO_3 was found.

(2) The adjustment made for oxidation of H_2S again brings all sulfur gases to the same temperature of correspondence (900°-905°C) with the pair H_2-H_2O within a few degrees of this temperature range.

(3) The temperature of correspondence of the CO-CO_2 pair (1119°C) is much higher than that of the other gases.

The H_2S correction again results in a close agreement of temperatures of correspondence, suggesting that the oxidation did occur; since SO_2 is included in this agreement, the assumption of former equilibrium at 900°C is also supported. The spread of temperatures of correspondence shows a new phenomenon not present in Group 1, viz., that during the cooling of sample J-17 the reaction between the pair CO-CO_2 was effectively stopped at 1119°C while the other gases continued to react until they were quenched at 900°-915°C. Thus, in this sample, cooling was slow enough to allow the different reaction rates to be spread out with the slowest reaction (between CO and CO_2) quenching first. The precollection temperature had a minimum value of 1119°C. Atmospheric contamination occurred below 900°C and caused oxidation of H_2S only.

Samples J-2, J-4, and J-16 give results similar to J-17. Case 4 is the most accurate method of estimating atmospheric contamination in each sample. These samples require an adjustment for oxidation of SO_2. After making this correction, the temperatures of correspondence for all of the sulfur- and hydrogen-bearing gases fall within a 20°C temperature range in every sample. Their plots are not shown, in order to avoid repetition, but their average temperatures of correspondence are shown in Table 11. Table 11 also shows that the temperatures for the carbon gases are always higher.

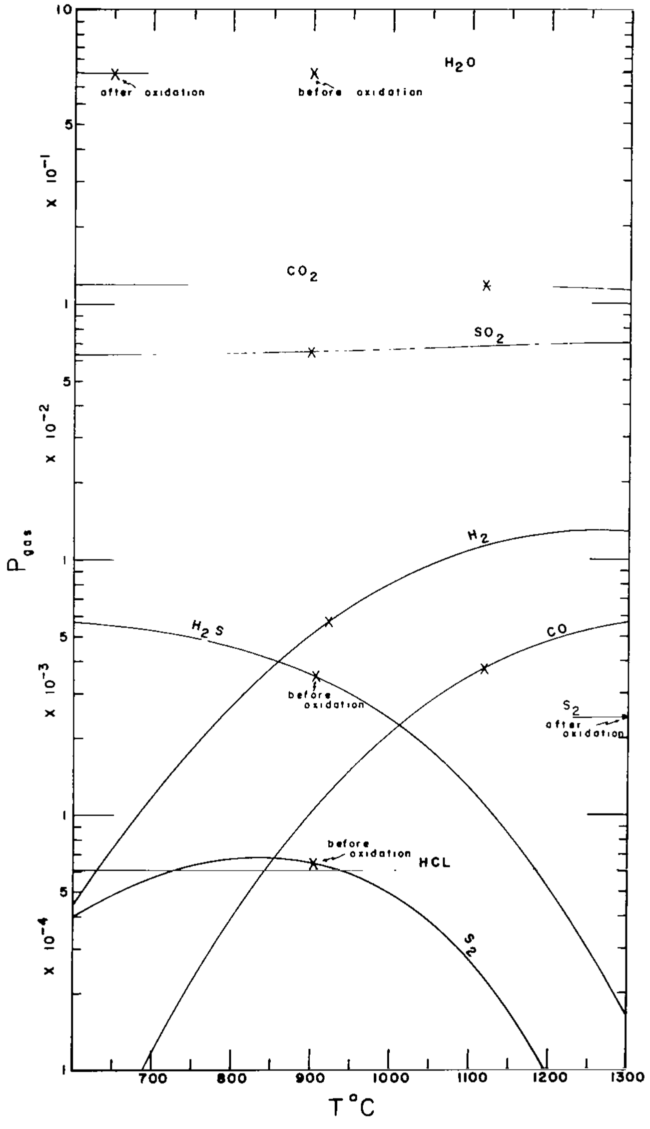

Figure 17–Typical temperatures of correspondence of Group 2. Case 4 of sample J-17 used as the example. Temperatures of correspondence are at two values after the correction for low temperature oxidation. In the example, carbon gases = 1119°C, sulfur and hydrogen gases = 900° to 920°C.

Group 3

An example of the characteristics of the third group of samples is given in Figure 18; this is the Case 4 plot of sample J-14. The analysis values before oxidation corrections are again shown as arrows at the right, or *x*'s for temperatures of correspondence. The corrections for oxidation of SO_2 and H_2S were made and are shown in the figure. As before, the correction for SO_3 causes analysis and equilibrium to coincide. The H_2S adjustment, based on the temperature of correspondence for SO_2 + SO_3, brings all sulfur-bearing gases to the same temperature of correspondence (within 5°C). The pair H_2-H_2O have also been brought to a common temperature (within 10°C) but at a lower temperature of correspondence than the sulfur gases.

Table 11 — Temperatures of Correspondence

Gases	Group 1		Group 2		Group 3		Group 4	
	Sample	Temperature	Sample	Temperature	Sample	Temperature	Sample	Temperature
Carbon	J-8	1165°C	J-2	900°C	J-3	1300°C	J-6	875°C
			J-4	1130°C	J-10	1012°C	J-12	1300°C
			J-16	1145°C	J-11	1111°C		
			J-17	1119°C	J-13	1300°C		
					J-14	1160°C		
					J-15	1300°C		
					J-18	1295°C		
Sulfur	J-8	1150°C	J-2	650°C	J-3	1050°C	J-6	760°C
			J-4	700°C	J-10	900°C	J-12	770°C
			J-16	1050°C	J-11	950°C		
			J-17	910°C	J-13	1025°C		
					J-14	880°C		
					J-15	850°C		
					J-18	970°C		
Hydrogen	J-8	1150°C	J-2	650°C	J-3	810°C	J-6	550°C
			J-4	700°C	J-10	850°C	J-12	660°C
			J-16	1050°C	J-11	900°C		
			J-17	910°C	J-13	1200°C		
					J-14	750°C		
					J-15	790°C		
					J-18	1185°C		

The samples in this group show a continuation of the trend from Group 1 to Group 2, i.e., a spreading out of quenching temperatures. In J-14 the cooling rate was such that the pair CO-CO_2 quenched at 1160°C. As cooling continued, the remaining gases continued to react until the sulfur gases quenched at approximately 1000°C. Below 1000°C, only the pair H_2-H_2O continued to react until they were finally quenched at about 750°C. At some temperature below 750°C, oxygen contamination caused the oxidation of SO_2 and H_2S. Although it could be inferred from Figure 18 that this oxidation may have occurred anywhere below 1000°C (the quenching temperature of sulfur gases), the pair H_2-H_2O would have also been oxidized above 750°C. Since this pair apparently did not become strongly oxidized, the contamination must have occurred below the temperature at which they ceased to react.

Samples J-3, J-10, J-11, J-13, J-15, and J-18 show phenomena identical to sample J-14. Their temperatures of correspondence are given in Table 11. Only sample J-18 shows a different sequence of quenching temperatures; here the pair H_2-H_2O apparently quenched at a higher temperature than the sulfur gases. In all the samples, atmospheric contamination is removed on the basis of Case 4.

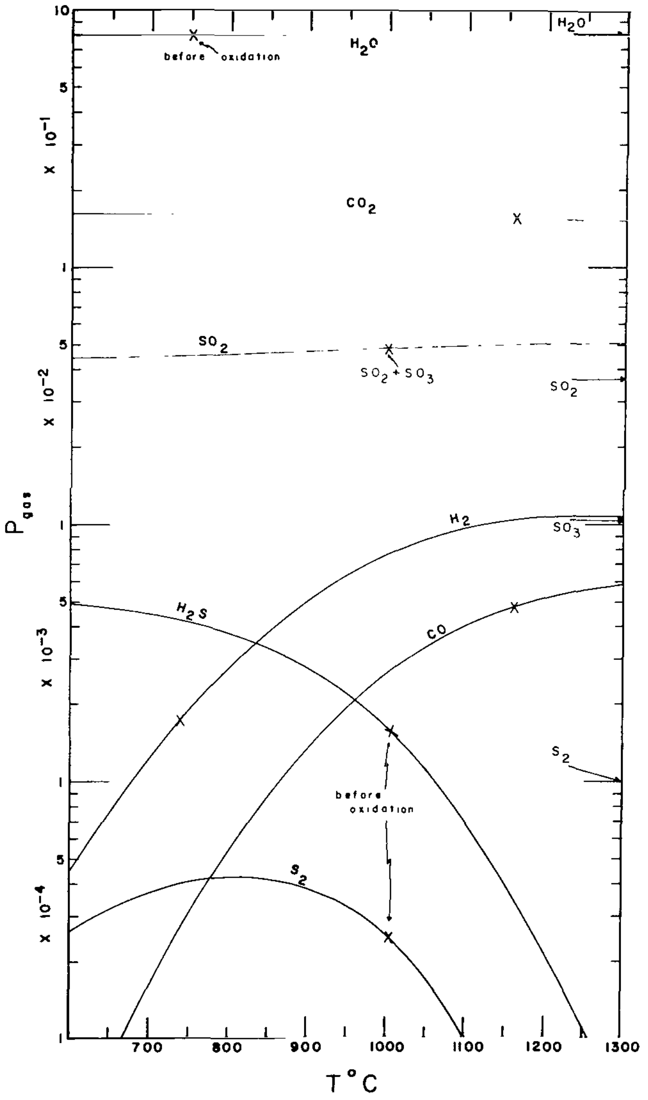

Figure 18—Typical temperatures of correspondence of Group 3. Case 4 of sample J-14 is used as the example. Temperatures of correspondence are at three values after the correction for low temperature oxidation. In the example, carbon gases = 1160°C, sulfur gases = 1000°C, hydrogen gases = 750°C.

Group 4

The remaining two samples, J-6 and J-12, have characteristics that put them into a fourth group. These phenomena are shown in Figures 19 and 20, which are both for sample J-6. Figure 19 is for removal of atmospheric contamination on the basis of Case 2, the maximum amount of oxygen removed; Figure 20 shows the situation for Case 4. Temperatures of correspondence can be found for CO and CO_2 only under the conditions of Case 2, but the equilibrium compositions for all other gases are then much too reduced to agree with the analyses. Temperatures of correspondence for the hydrogen and sulfur gases can be found only under the conditions of Case 4, but the pair CO-CO_2 is then too highly oxidized. The usual SO_3 and H_2S adjustments were made in both Figures 19 and 20.

The proposed explanation for the anomaly expressed in these two figures is as follows:

(1) Cooling occurred before contamination by oxygen and all gases reacted forming a near-equilibrium composition down to a temperature of approximately 875°C, where the pair CO-CO_2 ceased to react (Figure 19).

(2) Below 875°C but above 760°C, limited oxygen contamination occurred (Figure 20). The hydrogen and sulfur gases reacted with this oxygen, thus becoming more oxidized as cooling continued.

(3) At about 760°C, the reactions between sulfur gases were quenched, preserving their more oxidized state.

(4) As cooling continued below 760°C, the hydrogen pair H_2-H_2O continued to react until they were finally quenched in their more oxidized state at about 650°C.

(5) Below 650°C, further oxygen contamination caused the formation of SO_3 and loss of H_2S.

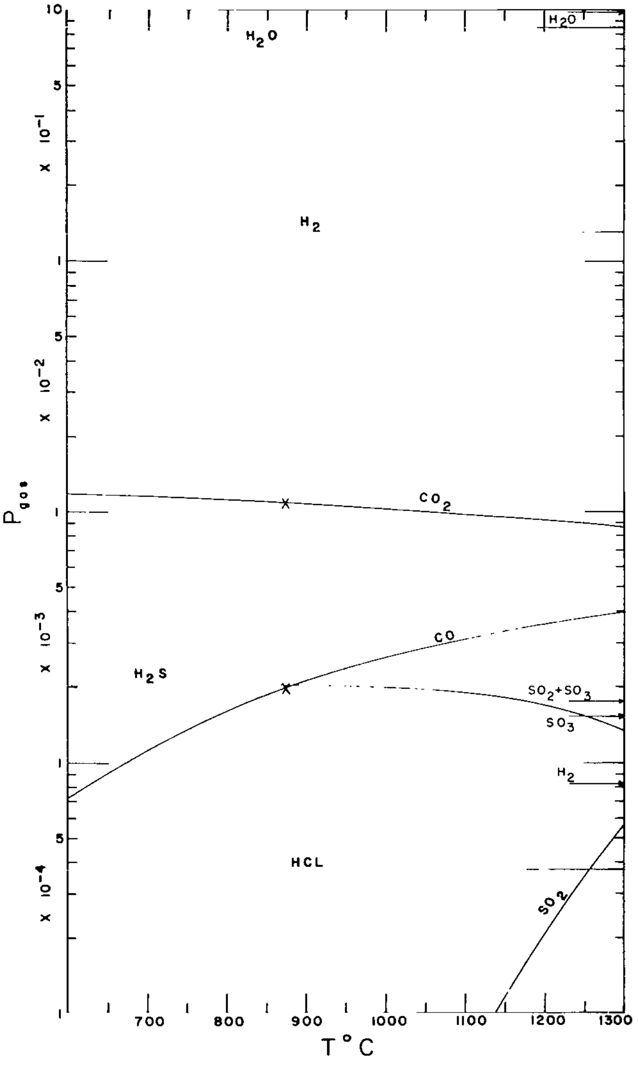

Figure 19—Typical temperatures of correspondence of Group 4. Sample J-6 used as the example. Atmospheric contamination removed on the basis of Case 2. Temperature of correspondence for carbon gases (875°C) indicates quenching before oxygen contamination (see Figure 6).

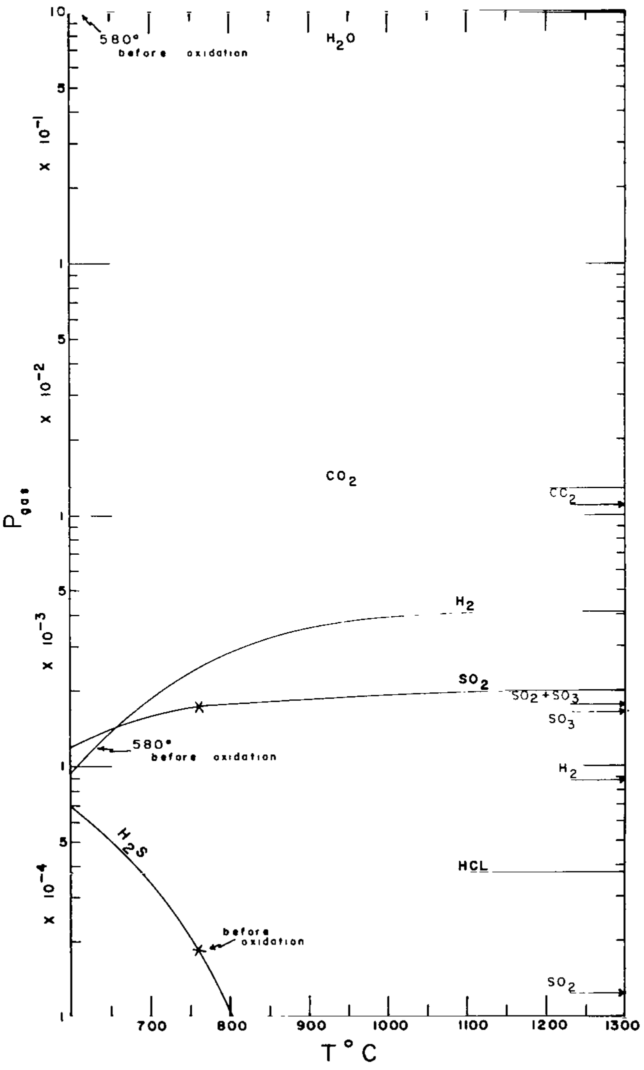

Figure 20—Typical temperatures of correspondence of Group 4. Sample J-6 used as the example. Atmospheric contamination removed on the basis of Case 4. After quenching of carbon gases (see Figure 5), slight oxygen contamination occurred. Temperatures of correspondence show that sulfur and hydrogen gases quenched at 760°C and 650°C, respectively, before low temperature oxidation of SO_3 and H_2S.

In sample J-12, where no SO_3 was found in the analysis, the final oxygen contamination may have occurred at a temperature too low for oxidation for SO_2 to proceed at a measurable rate.

The Group 4 samples reflect the further effects of the two modifying processes of cooling and oxidation. In this group the quenching temperatures of the sulfur- and hydrogen-bearing gases are lower than in the other groups (Table 8). Oxidation is more severe and occurred during cooling of the sample. The final result shown in the original analysis is a highly contaminated gas that is far out of equilibrium but, as in all other samples, it can be traced back to a former uncontaminated, equilibrium composition.

DISCUSSION

The results of the preceding study are summarized in Figure 21. The compositions of the samples reported by Shepherd (1921, 1938) are not equilibrium compositions. Every sample does, however, represent a former equilibrium composition that has been modified by imperfect quenching and atmospheric contamination. In each sample, the gas was at equilibrium above its quenching temperature for the carbon gases. The desired effect of expanding the volcanic gas into a cold vacuum tube would be to quench the entire gas sample at its precollection temperature. This may have been achieved in one sample only (J-8). All other samples were imperfectly quenched, so that reactions between the three groups of gases (carbon, sulfur, and hydrogen) were quenched at successively lower temperatures, creating a sample that exhibits a spectrum of quenching temperatures. The resulting compositions are thus not equilibrium compositions, except in the instance of sample J-8 (Group 1). The final modification, causing all samples to be nonequilibrium compositions, was caused by atmospheric contamination. This contamination added N_2, O_2, and Ar to the samples, with some of the free O_2 reacting to form SO_3 from SO_2 and oxidizing H_2S out of detectable existence. In all samples, except J-18, the sequence of quenching for the three groups of gases, from highest to lowest temperatures, is carbon gases—sulfur gases—hydrogen gases. In Group 4, atmospheric contamination occurred during the quenching process as well as after complete quenching. SO_2 and H_2S again became active after the contamination, due to the large amounts of O_2 present in the collection tube.

The trend of an increasingly widened spectrum of quenching temperatures from Group 1 through Group 4 is apparently caused by decreasing rates of cooling. If equilibrium is to be maintained, reactions occurring between any two or more molecular species will be reflected by, and intimately tied to, reactions between the other molecular species present, such that there is a complete readjustment to a change in temperature, pressure, or compositional variations. The rapidity of this readjustment depends upon the reaction rates involved; when reaction rates are so slow that readjustment cannot keep pace with changing conditions, disequilibrium occurs. The rates of gas reactions typically decrease drastically with a decrease in temperature. At high temperature a volcanic gas can evidently maintain equilibrium, but as cooling takes place, reaction rates will decrease to the point where compositional readjustments will lag behind equilibrium requirements. When the temperature becomes low enough, compositional changes due to reactions will be too slight to be measurable. The temperature at which reactions "stop," the "quenching temperature," will depend largely upon the cooling rate, since a slower cooling rate will give more time for readjustment. If the cooling rate is extremely rapid relative to all of the reaction rates involved, then the entire

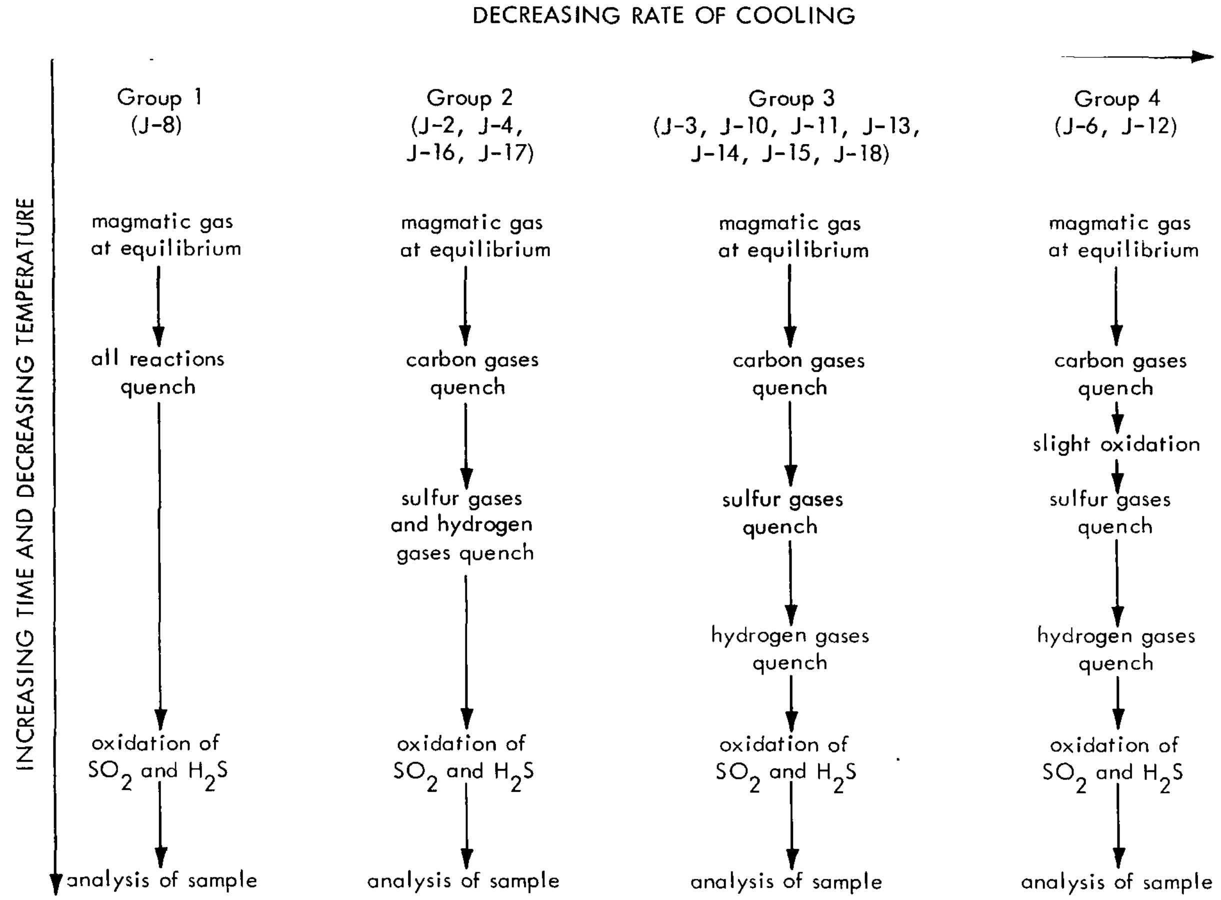

Figure 21—Summary of equilibrium relations in J-series samples. Vertical and horizontal spacings are not quantitative and show relative positions only.

gas collection will quench at the same apparent quenching temperature. Slower cooling rates will allow the various reaction rates involved to be expressed as different quenching temperatures, with the slowest reaction having the highest quenching temperature and vice versa. Once the reaction between a given group of gas species has been quenched, these species are, in effect, removed from the system. The remainder of the system may then continue its adjustment as equilibrium requires until another group of gas species is quenched. In this way, a "pseudo-equilibrium" may be maintained for part of the system while equilibrium for the system as a whole no longer exists.

Some of the methods of approach used in Part 1 were based on the assumption that volcanic gases behave ideally and maintain equilibrium compositions; this section uses the same premise. These idealized concepts, of course, cannot be realized in any actual system; however, the results above show that the volcanic gas approaches such behavior within the limits of error involved. For practical purposes, ideality and equilibrium can be assumed to prevail in the surface and near-surface magmatic environment. The concept of a spectrum of quenching temperatures outlined above is also apparently a useful working model. The discussion shows that Figures 15—20 are only approximate. To be rigorous, the equilibrium curves should be valid only down to the temperature where the carbon gases are quenched. At this point, CO_2 and CO should be removed from the atomic composition, with the new composition being used in calculations at lower temperatures. This procedure would then be repeated with respect to sulfur gases at their quenching temperature. These corrections, however, have a small effect on the equilibrium, as shown by the close agreement in the temperatures of correspondence.

The particular quenching temperatures obtained in the equilibrium analysis should not be considered to be quantitatively diagnostic. The quenching temperatures of a particular sample reflect not only cooling rates, but other factors as well, such as: (1) initial gas temperature; (2) completeness of tube filling; (3) size and shape of collection tube; and (4) temperature of tube, which is affected by its position over the collecting area and the time during which it is held there. A collected sample may cool quickly past the carbon gas-quenching temperature and then cool rather slowly because of the relatively high temperature of the tube. The different sizes of tubes used by Jaggar (Shepherd, 1921) would have different surface effects on reaction rates. A tube that remains at a temperature of a few hundred degrees for some time could cause all reactions to move slowly, but measurably, toward lower temperature equilibria, even though largely quenched at higher temperatures. The relative positions of the three groups of gases on the temperature scale apparently are indicative, however, and the temperatures obtained do indicate the range over which the gases are reactive. The fact that all members of a group cease to react at the same temperature shows the interdependence of all members of the group. For example, if SO_2 effectively ceases to be reactive because of decreasing temperature, S_2 and H_2S are so inhibited in their reactions that they too are quenched. SO_2 and H_2S are reactive again at lower temperatures only after the introduction of large amounts of free O_2 into the system. In spite of some of the above comments, the equilibrium analysis is valid when each sample is examined independently and the conclusions concerning the sequence of events from equilibrium compositions to analyzed samples can be deduced.

The Timing of Contamination

It was shown previously (Part 1) that the amount of atmospheric contamination present in the samples is closely approximated by using the methods of Case 4; equilibrium studies support this conclusion. In Groups 1, 2, and 3, discussed above, atmospheric contamination is apparently completely eliminated by removing all N_2 along with an atmospheric proportion of Ar plus all free O_2 and the oxygen required to form SO_3. In Group 4, the contamination is nearly completely removed on the basis of Case 4, but small amounts of atmospheric oxygen remain in the hydrogen and sulfur gases; also, the small amounts of oxygen used to oxidize H_2S are not considered in Case 4. It is evident that the small amounts of oxygen not removed by Case 4 are of insignificant importance relative to the total atomic composition. The equilibrium study shows that this contamination occurred after collection and quenching of the volcanic gas. The exceptions to this are samples J-6 and J-12 (Group 4), where some contamination occurred during cooling. These samples may have been partially cooled and contaminated in the volcano before collection, but it is more probable that volcanic and atmospheric gases were simultaneously pulled into the tube during collection. The timing of this contamination shows that the volcanic gas was relatively free of atmospheric gases in the lava lake before its collection, or at least at those sites around the lake chosen by Jaggar for sampling. This result is in agreement with the general observation that lava lake crusts and flows are not extremely oxidized when fresh. Admitting that the nature of Kilauea was particularly suitable for gas collections during his work, this result also shows remarkable experience and skill on the part of Jaggar.

It was shown previously (Part 1) that the volcanic gas samples contain large amounts of contaminating H_2O and have lost a large percentage of the SO_2 originally present in the magmatic gas. The equilibrium tests show that equilibrium was reestablished after, and probably during, the occurrence of these additions and losses. If these changes had occurred after reactions had ceased to establish equilibrium, anomalous amounts of H_2O and SO_2 would be present. The fact that the analyses can be so closely related to equilibrium apparently eliminates the changes in H_2O and SO_2 content as late occurrences. These changes occurred at high temperatures as an intimate part of the volcanic processes before the gases cooled past their various quenching temperatures. The rapid rate of gas reactions at these high temperatures evidently maintained thermodynamic equilibrium in the gas phase all the while these compositional changes were taking place. It has been shown that all the samples were derived from a single magmatic composition with the modifications occurring in the near-surface environment. Therefore, H_2O and SO_2 abundance variations must be explained by a mechanism that takes place locally in the lava lake and causes wide compositional variations from one collection site to another. This problem is discussed in Part 3 of this report.

Collecting Techniques

The techniques and equipment used to collect volcanic gases should achieve two main objectives: (1) quench in the exact precollection molecular composition without further modification; (2) avoid the introduction or loss of any gas species as a consequence of the collecting method. The fact that these objectives have seldom, if ever, been simultaneously and perfectly accomplished indicates the difficulty of such a task. The physical conditions under which collections must be made at any volcanic site put obvious limitations on what can be achieved. In addition, accessibility and favorable conditions equal to those during the time of Jaggar's collections are rarely available. However, collection methods need to be developed that will make the most of these rare opportunities or provide the best information available in less desirable collecting areas. It is not within the scope of this paper to discuss equipment design, but the foregoing study does suggest some aspects that need to be considered when making gas collections and designing equipment. These are listed below:

(1) A series of collections from various sites in the collecting area is desirable. This study has shown that various modifying processes occurring in the surface environment drastically alter gas compositions. Widely varying compositions can be obtained

from different places in the collecting area, and the best sample is not always obtained from the apparently best site. A representative set of collections can be used to determine the various changes that have occurred and will give more information about the true nature of the magmatic gas.

(2) Further attempts should be made to design equipment that will quench in gas compositions more effectively. Extremely rapid reaction rates at high temperatures allow the composition to change even during rapid cooling. The vacuum tube technique can apparently largely achieve this goal, as shown by sample J-8, but it apparently is not safe to assume that successful quenching occurs routinely. Tube dimensions, surface area, precollection temperature, and so on, are important in determining cooling rate, and apparatus should be designed to minimize undesirable effects.

(3) A technique should be devised whereby vacuum tubes can be opened and closed at will. Samples should be admitted at the most opportune time and then immediately sealed. Introduction of large amounts of oxygen, even after a successful quench, causes low-temperature oxidation. The sealing of tubes after their removal from the collecting site makes it extremely difficult to keep atmospheric gases from entering the tube. The atmospheric contamination present in the gas before collection cannot be distinguished, and the percentage of volcanic gas available for analysis is seriously decreased. The problems of analysis and interpretation are thus increased.

(4) Compositional changes between the times of collection and analysis should be minimized. Reactions between halogen gases and collection tubes may occur at low temperatures, and gas reactions may cause measurable compositional changes even at low temperatures. Oxidation is apparently a problem at low temperatures and can be expected when it is not possible to eliminate all atmospheric contamination. An important step was taken by Naughton, et al. (1963) to reduce these changes. By packing their collection tubes with silica gel, a general chromatographic separation occurs, which hinders postcollection reactions. Further advances in tube design and storage after collection may also be helpful.

The suggestions above must obviously be considered in view of practicality in the field. It is hoped, however, that the results of this study have more distinctly indicated where the emphasis should lie in future developments in this area of research.

PART 3

EFFECT OF MOLECULAR ADDITIONS AND LOSSES ON TOTAL GAS COMPOSITION

The preceding discussion has shown that the variations in atomic composition of the J-series samples are caused by additions or losses of various molecular species. In this section the amounts of molecular additions or losses that occurred in each sample will be determined. The illustrations presented earlier can then be used to examine the effect of these changes on the molecular composition of the gas phase.

The effect of additions and losses on a magmatic gas can be appreciated if the relative volumes of such changes are considered. In the earlier discussion of $Ar/(Ar + N_2)$ values, the method of obtaining Table 3 was described. As part of this method, the actual volumes (in cm^3) of gases present in the collection tubes were obtained. These volumes are useful to the present discussion and are presented in Table 12 in a modified form. The collections, made in tubes of different sizes and at different temperatures, resulted in different total volumes for each sample. The sample series can be compared volume to volume only if a common reference value is chosen. The reference volume used in Table 12 is the equal carbon concept discussed earlier. Since it is postulated that no carbon has been lost from the samples, the sum of the volumes of carbon gases in Table 12 has been assigned an arbitrary value of 50.0 cm^3. This value is chosen purely for convenience, to keep numbers close to the decimal point. The actual volumes in cm^3 of all molecular species have been multiplied by a factor such that the volume of the carbon gases equals 50.0 cm^3. The value of the factor for each sample is given by the expression

$$\text{Multiplication Factor} = \frac{50.0\ (cm^3)}{\text{actual volume of } CO_2 + CO\ (cm^3)} .$$

All samples in Table 12 have an equal amount of atomic carbon. The volumes of Table 12 are thus the volumes that would have been collected if the collector had been able to seal the tube after exactly 50.0 cm^3 of $(CO_2 + CO)$ had entered. Using Table 12, samples can be compared to determine the relative amounts of additions and losses. The three magmatic gas compositions obtained earlier are also shown. The equilibrium compositions obtained from the computation are expressed in moles of each molecular species. The compositions at 1100°C showing the relative numbers of moles (relative volumes) have been multiplied by the appropriate factors to bring them to an equal carbon basis with the samples.

Table 12 — Volumes (accurate to three significant figures) of molecular species J-series samples (cm^3); samples adjusted to an equal carbon basis of CO_2 + CO = 50.0 cm^3.

Sample	CO	CO_2	H_2	H_2O	S_2	SO_2	SO_3	HCl	N_2	Ar	O_2	H_2S
J- 2 (P)	0.00	50.0	0.00	649.	0.00	41.0	20.8	35.5	11,300.	...	2,850.	
J- 3 (P)	1.61	48.4	1.10	589.	0.00	23.6	40.4	8.15	288.	7.36 (3.91)	72.7	
J- 4 (P)	1.02	48.9	1.23	615.	1.08	9.97	24.6	4.49	166.	1.78 (-.202)	40.1	
J- 6 (P)	7.75	42.3	3.41	3,830.	0.00	.484	6.33	1.46	2,510.	18.2 (-11.4)	410.	
J- 8 (E)	1.44	48.6	.489	36.9	.0407	11.5	.0428	.0407	10.9	.242 (.111)	2.25	
J-10 (E)	.334	49.7	.302	154.	.151	41.0	10.8	.0909	162.	2.02 (.0989)	31.0	
J-11 (E)	1.38	48.6	.746	143.	.581	26.5	1.29	0.00	38.4	1.06 (.609)	7.76	
J-12 (P)	1.69	48.3	2.71	3,290.	2.38	17.3	0.00	1.02	574.	8.28 (1.43)	147.	
J-13 (E)	1.69	48.3	2.73	192.	.254	22.4	7.00	.284	54.1	2.22 (1.76)	12.3	
J-14 (F)	1.53	48.5	.555	252.	.327	11.9	3.38	0.00	302.	3.52 (-.112)	78.7	
J-15 (F)	.557	49.5	.429	316.	.128	26.2	7.25	.429	198.	2.74 (.373)	46.2	
J-16 (E)	1.51	48.5	1.82	179.	.404	23.0	6.85	.216	60.2	.835 (.129)	14.0	
J-17 (G)	1.54	48.5	2.42	329.	.999	27.0	0.00	.208	115.	1.48 (.103)	29.6	
J-18 (E)	2.02	48.0	2.26	169.	.599	29.4	8.79	.354	72.5	1.05 (.180)	16.3	
Magmatic Gas I at 1100°C C S = .500	.770	49.2	.270	37.0	.227	99.6	1.27×10^{-4}	.0407	0.00	...	$1.27 \cdot 10^{-6}$	0.0649
Magmatic Gas II at 1100°C C S = 1.000	.919	49.0	.322	36.9	.165	49.5	1.43×10^{-4}	.0407	0.00	...	1.34×10^{-6}	.0787
Magmatic Gas III at 1100°C C S = 1.500	.103	49.0	.358	36.8	.127	32.9	8.55×10^{-5}	.0407	0.00	...	$1.41 \cdot 10^{-6}$	.0821

The mixing of a single molecular species with the magmatic gas will have two main effects. First, it may react with the molecular species already present as dictated by thermodynamic equilibrium. This will cause an adjustment in the proportions of molecular species, which will be reflected in the partial pressures and in the volumes (numbers of moles). Second, there is a dilution effect due to a decrease in the percentage of magmatic gas. This dilution effect will cause a decrease in the partial pressures of all molecular species in the magmatic gas. The reactions occurring in the surface environment of an erupting volcano are under conditions of constant pressure rather than constant volume; therefore, the dilution does not directly affect the relative volumes of molecular species already present. These relative volumes will remain unchanged unless reactions occur. The loss of a given volume of one of the molecular species in the magmatic gas will have the same two effects, but they will be in the opposite sense to the changes caused by additions. The importance of additions or losses thus depends upon the amount of the species added or lost, and its chemical nature.

ADDITION OF NITROGEN AND ARGON

Atmospheric contamination has added N_2 to every sample. Sample J-8 was the only sample for which the collection tube was sealed by melting the tip in the glowing cavity before it was withdrawn. J-8 contained the smallest amount of N_2. The reason for the absence of CO, H_2, and S_2 in sample J-2 is now obvious. Since only about 0.5 liter of this gas was collected, these three species were present in amounts too small to detect; i.e., atmospheric N_2 diluted them out of detectable existence.

It was shown previously that atmospheric N_2 does not enter into reactions with other molecular species in significant amounts. NH_3 will be the most abundant nitrogen-bearing molecular species present (other than N_2). After the addition of atmospheric N_2 to the hot magmatic gas, equilibrium will be established between N_2 and NH_3 according to the reaction:

$$N_2 + 3H_2 \rightleftharpoons 2NH_3. \tag{3.1}$$

The equilibrium constant for this reaction is

$$K_1 = \frac{(NH_3)^2}{(N_2)\ (H_2)^3} .$$

Over the temperature range 650°-1250°C, the value of K_1 will vary between

$$K_1 \text{ at } 1250^\circ C = 3.12 \times 10^{-8}, \text{ and}$$
$$K_1 \text{ at } 650^\circ C = 1.03 \times 10^{-5}.$$

These values show that, even in the most N_2-rich samples, the amount of NH_3 is negligible; this is true if equilibrium is only roughly approximated. The partial pressure of NH_3 in the calculated equilibrium compositions of contaminated samples is approximately 10^{-7} to 10^{-8} atm.

Contaminating N_2 thus behaves essentially like an inert gas, and its effect on the total magmatic gas is that of a diluent only. When it is removed from an equilibrium composition as a contaminant, the relative amounts (volumes, moles) of the remaining molecular species will be unaffected. The partial pressures of the remaining species will be increased by removal of N_2.

Removal of N_2 as atmospheric contamination requires the removal of an atmospheric proportion of Ar. Ar behaves as a diluent only, because of its inert character, and its effect is like that of N_2. The Ar values in parentheses in Table 12 are the volumes after removal of atmospheric contamination on the basis of Case 4. After this removal, N_2 is absent.

The best method of removing atmospheric contamination eliminates all N_2 from the samples. The study indicates that this procedure, indeed, reconciles the data and that significant amounts of N_2 remaining in the samples as magmatic N_2 would destroy the relationships found. It is reasonable to expect, however, that N_2 (and Ar) is a proper constituent in primary magmatic gases, especially in view of the composition and source of atmospheric gases. An assessment of the actual rate at which primary N_2 has been added to the atmosphere by volcanic processes is an involved and risky undertaking. However, a simple calculation can show the order of magnitude involved and put the problem in the proper perspective. As an oversimplified starting point, it can be assumed that the primary N_2 production from volcanoes at present represents the average production rate over all geologic time. Further, it may be assumed that the total amount of N_2 now in the atmosphere and hydrosphere approximates the total amount of N_2 produced since the Earth began retaining its atmosphere. The same assumptions can then be made with respect to H_2O. Geochemical abundance calculations show that these gases are present today in the following amounts:

$$H_2O = 283.\ \text{kg/cm}^2 \text{ of Earth,}$$

$$N_2 = .849\ \text{kg/cm}^2 \text{ of Earth.}$$

These values give a weight ratio of

$$H_2O/N_2 = 334,$$

or a volume ratio, at STP, of

$$H_2O/N_2 = 5.18 \times 10^2.$$

This study has shown that the volume percentage of H_2O in magmatic gases before contamination is considerably below 100%; however, to maximize the calculation it can be assumed that the volcanic gas is composed totally of H_2O and N_2. The ratios above show that volcanic gases steadily producing H_2O and N_2 in the following percents would result in the amounts of these gases present today:

$$H_2O = 99.807\%,$$

$$N_2 = .193\%.$$

Although this calculation has little resemblance to reality, it lends validity to the following statement: There is no compelling reason to assume that magmatic gases must contain notable quantities of N_2. A small quantity of the N_2 removed as atmospheric contamination in this study (a few tenths of a percent) may be primary magmatic N_2. The inclusion of this amount in the foregoing analysis would have no detectable effects.

ADDITION OF OXYGEN

Oxygen was present in all of the samples, and undoubtedly accompanied N_2 as atmospheric contamination. Sample J-8 contained the least O_2; J-2 contained the most. The effect of O_2 addition on the magmatic gas will depend upon when the contamination occurs. If O_2 is mixed with a magmatic gas at high temperatures, equilibrium will be established. The equilibria involving the more important species of the carbon, hydrogen, and sulfur gases are expressed by the independent reactions:

$$2CO + O_2 \rightleftharpoons 2CO_2, \qquad (3.2)$$

$$2H_2 + O_2 \rightleftharpoons 2H_2O, \qquad (3.3)$$

$$S_2 + 2O_2 \rightleftharpoons 2SO_2, \qquad (3.4)$$

$$2SO_2 + O_2 \rightleftharpoons 2SO_3. \qquad (3.5)$$

The corresponding equilibrium constants will vary as shown below:

$$\begin{aligned}
K_2 = \frac{(CO_2)^2}{(CO)^2(O_2)} &= 1.99 \times 10^{10} \text{ at } 1250^\circ C, \\
&= 7.50 \times 10^{22} \text{ at } 650^\circ C; \\
K_3 = \frac{(H_2O)^2}{(H_2)^2(O_2)} &= 1.55 \times 10^{11} \text{ at } 1250^\circ C. \\
&= 1.92 \times 10^{22} \text{ at } 650^\circ C; \\
K_4 = \frac{(SO_2)^2}{(S_2)(O_2)^2} &= 1.61 \times 10^{17} \text{ at } 1250^\circ C, \\
&= 2.25 \times 10^{33} \text{ at } 650^\circ C; \\
K_5 = \frac{(SO_3)^2}{(SO_2)^2(O_2)} &= 1.60 \times 10^{-1} \text{ at } 1250^\circ C, \\
&= 1.36 \times 10^{0} \text{ at } 650^\circ C, \\
&= 3.66 \times 10^{24} \text{ at } 100^\circ C.
\end{aligned}$$

From these values, it follows that large amounts of atmospheric contamination will cause CO, H_2, and S_2 to react until they are present in only trace amounts. For example, if the partial pressure of oxygen after contamination were $P_{O_2} = 0.05$ atm., then at 1250°C, $H_2O/H_2 = 8.80 \times 10^4$.

When atmospheric contamination occurs at lower temperatures, O_2 may have the effect of a diluent only, or it may react at measurable rates with only a limited number of molecular species. It has been shown in the equilibrium study that this was the case in all of the samples. In the J-series collections, O_2 entered the collection tube after filling and quenching of the magmatic gas. At these low temperatures, only H_2S and SO_2 reacted with O_2. The equilibrium constant K_5 for reaction 3.5 shows that, at low temperatures, both SO_2 and SO_3 are present in large amounts of O_2. The amounts of SO_2 and SO_3 in Table 3 or Table 12 show the tendency to establish this low-temperature equilibrium. The removal of atmospheric contamination on the basis of Case 4 thus eliminates all O_2 plus the oxygen required to form SO_3 from SO_2 according to reaction 3.5.

The effect of small amounts of atmospheric contamination can be seen by referring to sample J-18 in Figures 1, 4, and 15. Free O_2 has already been removed in all of these figures. The equilibrium composition of Figure 15 and the corresponding oxygen pressure in Figure 1 still contain the oxygen used to form SO_3. The equilibrium composition after removal of this oxygen (Case 4) gives the oxygen pressure of J-18 shown in Figure 4. The ratio of total atomic oxygen in J-18 before this removal to the total atomic oxygen after the removal is

$$\frac{\text{Case 1}}{\text{Case 4}} = \frac{\begin{array}{l}\text{Total atomic oxygen in}\\ \text{J-18 including that used}\\ \text{for reaction 3.5}\end{array}}{\begin{array}{l}\text{Total atomic oxygen in}\\ \text{J-18 without that used}\\ \text{for reaction 3.5}\end{array}} = 1.03.$$

The decrease in oxygen pressure of J-18 in Figure 4 from the oxygen pressure in Figure 1 is caused by a decrease in the total atomic oxygen content of only 3%. The effect of this 3% change on the other molecular species is shown by the ratios given in Table 13 for the equilibrium compositions at 1100°C. The addition of relatively small amounts of uncombined (free) oxygen to a magmatic gas has drastic effects on the total composition if temperatures are high enough for reactions to proceed rapidly. The contamination of a magmatic gas by free oxygen at low temperatures, however, may have only a dilution effect, since reaction rates are then extremely slow. Only those molecular species that react quickly will be affected by low temperature oxygen contamination.

Table 13 — Effect of oxygen on gas ratios and P_{O_2} (equilibrium ratios at 1100°C.

Sample	$\frac{CO_2}{CO}$	$\frac{H_2O}{H_2}$	$\frac{SO_2}{S_2}$	$\frac{SO_3}{SO_2}$	P_{O_2}
J-18 Case 1	1.16×10^{5}	2.49×10^{5}	1.63×10^{16}	6.30×10^{-3}	5.30×10^{-3}
J-18 Case 4	3.42×10^{1}	7.32×10^{1}	1.22×10^{2}	1.86×10^{-6}	4.45×10^{-10}

LOSS OF SULFUR DIOXIDE

It was shown earlier that the SO_2 content of the magmatic gas was changed by the modifying processes. The evidence indicates that all samples were derived from an original magmatic gas with a value of C/S = 0.500; therefore, SO_2 has been lost in varying amounts in all samples. An alternative possibility is that the magmatic gas had a value of C/S = 1.500, and SO_2 had been added to some samples and lost from others (see Figure 9). The value of C/S = 0.500 is preferred, because of the difficulty of finding a method whereby SO_2 is added to the magmatic gas; however, both values will be considered in the following discussion.

The actual amounts of SO_2 in each sample, relative to the two postulated magmatic compositions, are shown in Table 12. For comparison the values of (SO_2 + SO_3) should be used, because they show the amount of SO_2 present before low-temperature oxidation. Also, the amounts of S_2 in the samples are actually the amounts of S_2 present before low-temperature oxidation plus the S_2 formed by low-temperature oxidation of H_2S. It was shown in the equilibrium study that thermodynamic equilibrium was reestablished after the losses of SO_2 occurred. Although the loss of atomic sulfur is due almost entirely to the loss of SO_2, during and after this loss all of the sulfur gas adjusted their volumes to reestablish equilibrium. Therefore, to compare the samples and the magmatic gas, the total atomic sulfur contents must be compared. The total atomic sulfur lost from each sample can then be stated as SO_2 lost, and this in turn can be compared to the amount of SO_2 in the magmatic gas. Sample J-6 has lost the most SO_2. Samples J-2 and J-3 are closest to the amount originally present in the magmatic gas (C/S = 0.500). If the comparison is made with C/S = 1.500, then J-2 and J-3 have had the largest amount of contaminating SO_2 added. The relationship between the original atomic sulfur content and the sample contents are shown in Table 14 as ratios; percents of original SO_2 content lost or added are also given.

Table 14 — SO_2 change in J-series samples.

Sample	$\frac{\text{S (sample)}}{\text{S (magmatic gas)}}$ (C/S = 0.500)	Magmatic SO_2 lost (percent)	$\frac{\text{S (sample)}}{\text{S (magmatic gas)}}$ (C/S = 1.500)	Magmatic SO_2 lost or added (percent)
J- 2 (P)	0.620	-37.8	1.86	+87.9
J- 3 (P)	.640	-35.7	1.92	+94.6
J- 4 (P)	.359	-64.0	1.08	+ 9.13
J- 6 (P)	.0681	-93.2	.204	-79.4
J- 8 (E)	.115	-88.5	.345	-65.1
J-10 (E)	.520	-47.8	1.56	+58.1
J-11 (E)	.284	-71.5	.853	-13.7
J-12 (P)	.197	-80.1	.591	-40.2
J-13 (E)	.297	-70.2	.891	- 9.73
J-14 (F)	.156	-84.3	.469	-52.6
J-15 (F)	.336	-66.2	1.01	+ 2.12
J-16 (E)	.303	-69.5	.910	- 7.91
J-17 (G)	.280	-71.9	.840	-14.9
J-18 (E)	.388	-61.0	1.16	+17.9

The effect of SO_2 loss can now be examined. In Table 12, the three magmatic gas compositions are expressed as volumes at equilibrium at 1100°C. The only difference in total atomic composition is a difference in atomic sulfur and atomic oxygen in the ratio $S/O = 1/2$. Therefore, these three columns show the change in total molecular composition after SO_2 has been removed in going from magmatic gas I to magmatic gas III; the relative volumes of other molecular species have changed very little. This shows that only the volume of SO_2 itself is significantly changed by a loss of SO_2; the ratios of all other species remain nearly the same. The effect of SO_2 loss on oxygen pressure is of particular importance. The change in volume of O_2 in Table 12 is relatively small. When partial pressure is considered, however, the diluent effect of SO_2 removal must also be taken into account. Figure 14 shows the oxygen pressures of the three magmatic gas compositions plus J-8. J-8 is identical to the magmatic gases, except for a further reduction in SO_2 content. In Figure 14, the combined effects of dilution and equilibrium adjustment are shown. The effect is relatively small. The decrease in oxygen pressure with increase in SO_2 content is largely caused by the dilution of the magmatic gas.

The small effect of large changes in SO_2 content on the total gas composition is explained by the equilibrium constants for reactions 3.4 and 3.5. At the oxygen pressures prevailing in magmatic gases (Figure 14), nearly all of the atomic sulfur is contained in SO_2 molecules. If SO_2 is added to the magmatic gas, only a small fraction of the amount added will dissociate into S_2 and O_2 molecules or combine with O_2 to form SO_3. The loss of SO_2 has a similar but opposite effect; i.e., very little S_2 and O_2 will need to combine to reestablish equilibrium.

ADDITION OF WATER

Water was added to the magmatic gas, causing the amount of atomic oxygen and hydrogen to vary from sample to sample. The amount of water in sample J-8 is used as the magmatic value because of its position on the H_2O addition curve in Figures 8 and 10. In Table 12, the three magmatic gases contain volumes of water equal to the volume of J-8. All other samples contain a larger volume of water; J-6 and J-12 have the largest volumes. It has been shown that equilibrium was reestablished in all samples after the water contamination occurred. It was also shown that low-temperature oxidation added a small amount of water to the amount present at equilibrium. Since the amount of H_2 and the amount of water added by H_2S oxidation are small, the O and H relations of Figures 8 and 10 are accurately calculated by considering H_2O only. In addition, the different volumes of water shown in Table 12 can be considered to be the result of differences in the amount of water contamination.

The ratios of the volumes of water in the samples to the magmatic volume are given in Table 15. The correlation between sample quality and water contamination observed in Figure 8 is also shown in Table 15. The amount of contamination in J-6 and J-12 is extremely large and it is very significant in all samples other than J-8. Such extreme contamination is not immediately obvious from tables of volume percentages such as Tables 1 and 3. Natural processes are concerned with volumes rather than percents. It is important to make this distinction when the mixing of gases is being considered.

Table 15 — Amount of contaminating water in the J-series samples.

Sample	Volume of H_2O in sample / Volume of H_2O in magmatic gas
J- 2 (P)	17.6
J- 3 (P)	16.0
J- 4 (P)	16.7
J- 6 (P)	104.
J- 8 (E)	1.00
J-10 (E)	4.17
J-11 (E)	3.87
J-12 (P)	89.1
J-13 (E)	5.20
J-14 (F)	6.82
J-15 (F)	8.56
J-16 (E)	4.85
J-17 (G)	8.91
J-18 (E)	4.58

It is obvious that, if other molecular species of gas are present, it is impossible to add enough water to make a sample of 100% water. The addition of increasing amounts of water to a sample affects the water percentage decreasingly. This can be seen by comparing the circled points of Figure 10 with the values of Table 15. Therefore, it can be misleading to compare partial pressures or volume percentages. Tables such as Table 12 compare mixing volumes directly.

The greatly differing volumes of gas, which were present in the collecting tubes, require explanation. Jaggar's field notes (Shepherd, 1921) describe the appearance of the collected gas as it entered the tube. He notes that there was ". . . some water within (a few drops)." The quenching of the hot gas caused water to condense (also S_2) which greatly decreased the gas volume. The tube, therefore, continued to fill with gas as water was condensed. All but a small part of the total tube volume was filled with molecular species that remain gaseous at low temperatures.

The large amount of contamination occurring within the volcano also can be explained on this basis. The sources of contaminating water were discussed at the beginning of this report. If this contamination is introduced as liquid water, relatively small amount are required to produce the effect shown in Table 15. A simple calculation shows that 1 cm^3 of liquid water at STP will vaporize to form 5875 cm^3 of water at 1000°C. Water would be condensed out of the escaping volcanic gas as it cools. It could then return to the lava lake through cracks, porous lava, and so on, where it would be vaporized, heated, and mixed with the magmatic gas. The volcanic gas would in effect contaminate itself by a distillation process. CO_2, SO_2, and so on, would escape into the atmosphere as H_2O accumulated in the crater. This contaminating water would probably be abundant at the edges of the lake farthest from the source. It would be most abundant near cones on the lake crust (J-12) and in cracks in the crater wall (J-6). Small amounts of liquid water added in this manner would result in greatly differing volumes such as shown in Table 12.

During the discussion of atmospheric contamination, it was stated that the amount of atmospheric gases in solution in contaminating water is insignificant. Such a solution could occur only if the contaminating water reached the vicinity of the magma as a liquid The approximate maximum amounts of atmospheric gases present in saturated water between 0°C and 100°C at 1 atm total pressure (Lang, 1961) are shown below:

$$\frac{N_2}{H_2O} = \frac{1.20 \times 10^{-2}\ (cm^3)}{(cm^3)},$$

$$\frac{O_2}{H_2O} = \frac{6.19 \times 10^{-3}\ (cm^3)}{(cm^3)},$$

$$\frac{Ar}{H_2O} = \frac{3.17 \times 10^{-4}\ (cm^3)}{(cm^3)},$$

$$\frac{CO_2}{H_2O} = \frac{2.37 \times 10^{-4}\ (cm^3)}{(cm^3)}.$$

These ratios can be compared with the same ratios in any of the samples, and this comparison indicates that the contribution of gases in solution is negligible.

The discussion above shows that the large amounts of contaminating water in the samples had a strong dilution effect. The effect on the equilibrium composition should also be considered. The equilibrium constant for reaction 3.3 shows that the effect is small. As water is added to the magmatic gas, only a small fraction of it will dissociate into H_2 and O_2. These small changes will in turn have little effect on the other molecular species present, and the total gas composition will change only slightly. The effect on oxygen pressure is especially important. The atomic compositions of the samples in Figure 4 differ by only about 5%, while the H_2O contents differ by a factor of 104. Similarly, the oxygen pressures differ by a relatively small amount. It is apparent that P_{O_2} is a poor indication of the amount of water contained in the magmatic gas.

ACKNOWLEDGEMENTS

The writer is grateful to Dr. Robert F. Mueller for reading the manuscript and for valuable discussions and advice during the course of this work. Computer costs were defrayed by National Science Foundation Grant CNHM NSF GP 3688.

Goddard Space Flight Center
National Aeronautics and Space Administration
Greenbelt, Maryland, January 14, 1970
195-42-01-02-51

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APPENDIX

CALCULATION OF EQUILIBRIUM COMPOSITIONS

The equilibrium compositions in this work were obtained by the method of steepest descent described originally by White et al. (1958). The problem was programed in the FORTRAN language; an IBM 7094 computer was used for problem solving. Although the original paper was closely followed, it contains terminology that differs from that most generally used. In addition, a clearer physical picture of what the method achieves emerges if it is presented in a somewhat different form. Finally, key punching and computer time have been reduced in this study by having the computer calculate the values of thermodynamic functions needed for each solution. In this way, a series of calculations can be made more economically.

The total free energy of a mixture of β gaseous molecular species containing n_i moles of the i^{th} species can be expressed as

$$G_{\text{total}} = \sum_{i=1}^{\beta} n_i \mu_i , \tag{A.1}$$

where

$$\mu_i = \mu_i^0 + RT \ln \frac{P}{P^0} + RT \ln \left(\frac{n_i \gamma_i}{\sum_{i=1}^{\beta} n_i \gamma_i} \right) , \tag{A.2}$$

in which

μ_i = chemical potential of i,

μ_i^0 = standard chemical potential of i.

P = pressure,

P^0 = standard pressure,

γ_i = activity coefficient of i.

In an ideal gaseous system at standard pressure (1 atm),

$$\mu_i = \mu_i^0 + RT \ln P + RT \ln \frac{n_i}{\bar{n}_i}, \tag{A.3}$$

$$\bar{n}_i = \sum_{i=1}^{\beta} n_i . \tag{A.4}$$

Equation A. 1 now becomes

$$G_{\text{total}} = \sum_{i=1}^{\beta} n_i \left(\mu_i^0 + RT \ln P + RT \ln \frac{n_i}{\bar{n}_i} \right). \tag{A.5}$$

It is convenient to eliminate the factor RT from the last term in the parentheses. Equation A. 5 is then written as

$$\frac{G_{\text{total}}}{RT} = \sum_{i=1}^{\beta} n_i \left(\frac{\mu_i^0}{RT} + \ln P + \ln \frac{n_i}{\bar{n}_i} \right). \tag{A.6}$$

Equation A. 6 is one of the two basic equations used by the method. At equilibrium, the total free energy will be a minimum. The equilibrium composition will be obtained when the one set of values for the n_i's is found that minimizes G_{total} at a specified temperature and pressure.

The equilibrium composition must also satisfy mass balance constraints. These constraints can be expressed in the second basic equation as

$$b_j = \sum_{i=1}^{\beta} a_{ij} n_i , \tag{A.7}$$

where

b_j = total number of moles of the atomic species j present in the mixture of molecular species i, and

a_{ij} = formula number indicating the number of atoms of atomic species j in a molecule of species i.

The a_{ij}'s can be expressed in a "formula matrix." An example for a system of five atomic species and 11 molecular species is shown in Table A.1. The equilibrium composition must satisfy A.7 while simultaneously minimizing A.6.

Table A.1
Atomic and molecular species occurring in magmatic gas.

Compound	Value of i	C J = 1	H J = 2	S J = 3	O J = 4	Cl J = 5
CO	1	1	0	0	1	0
CO_2	2	1	0	0	2	0
H_2	3	0	2	0	0	0
H_2O	4	0	2	0	1	0
S_2	5	0	0	2	0	0
SO_2	6	0	0	1	2	0
SO_3	7	0	0	1	3	0
O_2	8	0	0	0	2	0
Cl_2	9	0	0	0	0	2
HCl	10	0	1	0	0	1
H_2S	11	0	2	1	0	0
CH_4	12	1	4	0	0	0
COS	13	1	0	1	1	0
CS_2	14	1	0	2	0	0

The values for the b_j's must be obtained from independent information. They may be supplied by specifying the ratios of atomic species in hypothetical systems to be studied. In analyzed gas samples, the molecular composition is known. Even though the analyzed composition does not represent an equilibrium composition, Equation A.7 can be used to obtain values for the b_j's.

There is an unlimited number of sets of values for the n_i's which will satisfy A.7; each set will give a different value for G_{total}. Only the equilibrium set of values will cause G_{total} to be a minimum.

In order to obtain the equilibrium composition, any set of values for the n_i's that satisfies A.7 can be used. Corrections are then added to those values that cause the total free energy (G_{total}) to decrease the greatest amount. That is, if a surface is visualized that gives the total free energy values for all sets of values for the n_i's, then the initial set of values corresponds to a total free energy somewhere on this surface. The corrections are added to the set of values so that the value of the total free energy descends along the steepest path. The assumption is that this steepest descent will lead to the minimum value. The free energy surface of a system of many molecular species must be expressed in multidimensional space. Although this cannot be visualized, it is possible for the method of steepest descent to lead to a lower value for the total free energy, which is not the true minimum. In such a case, the method will fail. For this reason, the use of any set of values satisfying A. 7 may not lead to the desired result. It is better to use values that are likely to be in the range of the equilibrium values rather than random values. The amounts of molecular species in an analyzed sample that are used to obtain the b_j's are appropriate initial values for the computation.

The equations used to approximate the equilibrium composition can now be discussed. The initial set of values for the numbers of moles of the molecular species are denoted by m_i's. Equation A. 6 then becomes

$$F(m) = \frac{G_{\text{total}}}{RT} = \sum_{i=1}^{\beta} m_i\left(\frac{\mu_i^0}{RT} + \ln P + \ln\frac{m_i}{\bar{m}_i}\right). \tag{A. 8}$$

where

$$\bar{m}_i = \sum_{i=1}^{\beta} m_i .$$

Now let

$$\Delta_i = n_i - m_i$$

and

$$\bar{\Delta} = \bar{n}_i - \bar{m}_i .$$

Since all m_i's are positive, we can form a Taylor-series expansion about these m_i's. This gives the first approximation to $F(m)$:

$$Q(m) = F(m) + \sum_{i=1}^{\beta} \left.\frac{\partial F}{\partial n_i}\right|_{n=m} \Delta_i + \frac{1}{2}\sum_{i=1}^{\beta}\sum_{k=1}^{\alpha} \left.\frac{\partial^2 F}{\partial x_i \partial x_k}\right|_{n=m} \Delta_i\Delta_k . \tag{A. 9}$$

$$Q(m) = F(m) + \sum_{i=1}^{\beta}\left(\frac{\mu_i^0}{RT} + \ln P + \ln\frac{m_i}{\bar{m}_i}\right)\Delta_i + \frac{1}{2}\sum_{i=1}^{\beta} m_i\left(\frac{\Delta_i}{m_i} - \frac{\bar{\Delta}}{\bar{m}_i}\right)^2 . \tag{A. 10}$$

The second partial derivatives of both $F(m)$ and $Q(m)$ are nonnegative; hence, both functions are convex.

The next approximation to $F(m)$ can now be derived. To minimize $Q(m)$ in equation A.10, the stationary value of the function must be found. Since $Q(m)$ is a convex function, this stationary value will be a minimum. To minimize $Q(m)$, we set $\partial Q(m)/\partial X_i = 0$,

$$\frac{\partial Q(m)}{\partial x_i} = 0 = \left(\frac{\mu_i^0}{RT} + \ln P + \ln \frac{m_i}{\overline{m}_i}\right) + \left(\frac{n}{m_i} - \frac{\overline{n}}{\overline{m}_i}\right). \tag{A.11}$$

The equilibrium set of values for the n_i's must satisfy A.7. The mass balance constraints must, therefore, be incorporated into Equation A.11. There are i independent increments in Equation A.11. Equation A.7 shows that the number of constraints that must be satisfied is equal to the number of atomic species (j). This effectively reduces the number of independent increments from i to $i - j$. Hence, j of the increments i must be considered to be functions of the remaining ones. The j dependent increments can, in effect, be eliminated from A.11 by using the Lagrange method of undetermined multipliers. Each of the equations of constraint, A.7, is multiplied by a constant π_j:

$$\sum_{j=1}^{\gamma} \pi_j b_j = \sum_{j=1}^{\gamma} \pi_j \left(\sum_{i=1}^{\beta} a_{ij} n_i\right). \tag{A.12}$$

$$0 = \sum_{j=1}^{\gamma} \pi_j \left(- \sum_{i=1}^{\beta} a_{ij} n_i + b_j\right). \tag{A.13}$$

Differentiate A.13 with respect to n_i:

$$0 = - \sum_{j=1}^{\gamma} \pi_j a_{ij}. \tag{A.14}$$

If Equation A.14 is now added to A.11, we obtain

$$\frac{\partial R(m)}{\partial n_i} = 0 = \left(\frac{\mu_i^0}{RT} + \ln P + \ln \frac{m_i}{\overline{m}_i}\right) + \left(\frac{n_i}{m_i} - \frac{\overline{n}_i}{\overline{m}_i}\right) - \sum_{j=1}^{\gamma} \pi_j a_{ij}. \tag{A.15}$$

The values for the n_i's that solve A.15 satisfy the two conditions required for the equilibrium composition.

Since all m_i's are positive, we can solve A.15 for n_i:

$$n_i = - m_i\left(\frac{\mu_i^0}{RT} + \ln P + \ln\frac{m_i}{\bar{m}_i}\right) + m_i \sum_{j=1}^{\gamma} \pi_j a_{ij} + \frac{m_i \bar{n}_i}{\bar{m}_i}. \qquad \text{(A. 16)}$$

By summing over i in A. 16

$$\sum_{j=1}^{\gamma} \pi_j b_j = \sum_{i=1}^{\beta} m_i\left(\frac{\mu_i^0}{RT} + \ln P + \ln\frac{m_i}{\bar{m}_i}\right). \qquad \text{(A. 17)}$$

Substitution of A. 16 into A. 7 and using A. 17 gives

$$a_{ij} m_i\left(\frac{\mu_i^0}{RT} + \ln P + \ln\frac{m_i}{\bar{m}_i}\right) = m_i \pi_j a_{ij} a_{ik} - b_j + a_{ij} m_i\left(\frac{n}{\bar{m}_i}\right), \qquad \text{(A. 18)}$$

which can be written as a system of equations.

The procedure for obtaining the equilibrium set of values for the n_i's is as follows:

(1) The system of Equation A. 18 is solved first.

(a) m_i's are given as input data; $\bar{m}_i = \sum_{i=1}^{\beta} m_i$.

(b) a_{ij}'s are obtained from the formula matrix such as shown in the earlier example; b_j's are given as input data.

(c) P is assigned the desired value.

(d) μ_i^0/RT is obtained from published thermochemical data and given as input data.

(2) Equation A. 18 is then solved for the unknowns π_i and $\bar{n}_i$. The number of simultaneous linear equations in A. 18 is equal to $(\gamma + 1)$; i.e., the number of atomic species plus the value for $\bar{n}_i$.

(3) The improved values for the n_i's are then obtained from A. 16.

This is the end of one iteration cycle. In general, more than one cycle will be required to obtain values to the desired precision. The precision can be built into the program by having the cycle repeated until the difference between the initial m_i's of a cycle and the improved n_i's is less than a specified amount. For example, in the calculations obtained in this study, the iterations were repeated until the largest value of $n_i - m_i = \Delta i$ was less than 0.0001.

Trace Molecules

It is impractical to specify a precision that is significant for trace molecules present in amounts as small as 10^{-6} mole or less. The precision specified ($\Delta_i = 0.0001$) can be attained with relatively large values of Δ_i in trace molecules. For example, $\Delta_i = 1.0 \times 10^{-8}$ is a large change for a molecule present as 10^{-10} mole. This could be corrected by weighting the values of Δ_i for each molecular species. However, a simple method is available for obtaining accurate values for trace molecules. White et al. (1958) note that π_j represents the free energy contribution due to the presence of b_j mole of the atomic species j in the mixture. This is seen by examining Equation A. 17. This concept can be used to obtain improved values for the trace molecules in the system.

The equilibrium composition for the more abundant molecular species is first obtained to the specified precision. In Equation A. 15, the two terms in parentheses can then be replaced by the exact function given by Equation A. 6.

$$\frac{\partial R(m)}{\partial n_i} = \frac{\partial}{\partial n_i}\left\{\sum_{i=1}^{\beta} n_i\left(\frac{\mu_i^0}{RT} + \ln P + \ln\frac{n_i}{\bar{n}_i}\right) + \sum_{j=1}^{\gamma} \pi\left(- \sum_{i=1}^{\beta} an + b_j\right)\right\}. \qquad \text{(A. 19)}$$

When this differentiation is carried out and set equal to zero, it becomes

$$n_i = \bar{n}_i \exp\left(-\frac{\mu_i^0}{RT} - \ln P + \sum_{j=1}^{\gamma} \pi_j a_{ij}\right). \qquad \text{(A. 20)}$$

Equation A. 20 can then be used to obtain the equilibrium value for the trace molecule i. The accuracy of the value obtained is excellent, due to the small effect of trace molecules on the terms in the equation. The changes in values of $\bar{n}$ and π_j's due to changes in the amounts of trace molecules are insignificant. Therefore, even though the number of moles for a trace molecule at the end of the iterations may be quite inaccurate, the values of $\bar{n}$ and π_j's will still be correct.

Thermochemical Data

Values for the function μ_i^0/RT must be supplied to solve A. 18. This function can be calculated from the equation

$$\frac{\mu_i^0}{RT} = \frac{\left(G_t^0 - H_{298}^0\right)/T}{R} + \frac{\Delta H_{298}^0}{RT}. \qquad \text{(A. 21)}$$

The function $(G_t - H^0_{298})/T$ is called the "free energy function." Values for this function and for the heat of formation, ΔH^0_{298}, can be obtained at 100°C temperature intervals from the NANAF thermochemical data. Interpolations from these tables need to be made in order to calculate equilibrium compositions at temperatures other than those tabulated. If calculations are made for a series of temperatures, values must be supplied for each temperature. Supplying all data necessary for a study such as that carried out in this report would require a large amount of time and tedious hand calculations.

To avoid hand calculations, the computer was programed to supply its own data. Curves were fit to the tabular data of the free-energy function by the least-squares method, using the computer. The coefficients for the curves of each molecular species were then used as standard input data. For a calculation at any specified temperature, the computer used the coefficients to calculate the value of the free-energy function of each molecular species. These values were then used in Equation A. 21 to obtain μ_i/RT which were, in turn, used in Equation A. 18. As a side product of this, tables were developed giving the values of the free-energy function, μ_i/RT and μ_i^0 at 10°C intervals.

```
TEMPERATURE = 1373 DEGREES KELVIN

LARGEST COMPONENT OF DELTA =  0.00003565

NUMBER OF ITERATIONS =   5           LAMBDA =  1.01

            EQUILIBRIUM
MOLECULE    COMPOSITION       G(I)        TRACE MOLECULES    ATOM    FREE ENERGY (PI(J))

   CO       7.57260E-03  -3.15212E-01   7.55743E-03        C         -1.78998E 01
   CO2      4.84218E-01  -3.17522E 01                      H         -1.24724E 01
   H2       2.64778E-03  -6.57560E-02   2.64248E-03        S         -1.30212E 01
   H2O      3.63409E-01  -1.77161E 01                      O         -2.38674E 01
   S2       2.22624E-03  -5.79066E-02   2.22178E-03        CL        -2.92466E 01
   SO2      9.79106E-01  -5.94254E 01
   SO3      3.39318E-06  -2.87492E-04   3.38639E-06
   O2       1.24858E-09  -2.03031E-08   3.19097E-09
   CL2      8.66274E-13  -5.07111E-11   9.64539E-13
   HCL      3.99918E-04  -1.56584E-02
   H2S      6.37004E-04  -2.42212E-02   6.35730E-04
   CH4      1.01836E-09  -5.59106E-08   1.01632E-09
   COS      1.17765E-10  -8.05901E-09   1.17536E-10
   CS2      1.94882E-09  -8.60620E-08   1.94496E-09

        SUMMATION G(I) = -1.09374E 02
```

Figure A.1—Example of data obtained from computer. Equilibrium composition in moles in column 2, with refined values of trace molecules in column 4. Free energy contributions of molecular species and atomic species in columns 3 and 6, respectively.

An example of a typical output page is shown in Figure A. 1. The temperature and molecular species considered are shown. The equilibrium composition at this temperature is given in the second column, with refined values for trace molecules in column 4. In addition, the free-energy contribution of each molecular species is shown in column 3. The total free energy [summation *G(I)*] is the minimum free energy for the system at this temperature. Column 5 lists the atomic species involved in the system and column 6 gives the free-energy contribution of each atomic species. This was noted by White et al. (1958) to be a characterization of the system giving the relative importance of each species. The total free energy [summation *G(I)*] can be obtained from the values in column 6 using the method described above.

Equilibrium compositions obtained for an individual sample over the entire temperature range can be plotted as in Figures 11-13. Although a small-scale plot extending to partial pressures as small as 10^{-15} atm or less could be used, it would understate the accuracy of the data obtained in this study. The important molecular species will be present at pressures greater than 10^{-4} atm; trace molecules can be considered on separate plots. The equilibrium composition shown in Figure A. 1 is expressed in moles of each gas; the number of moles has been converted to partial pressure for plotting on graphs. Since the total pressure is 1 atm, the input data were usually adjusted so that the total number of moles of gas was equal to unity. The equilibrium compositions shown in Figure A. 1 are thus the number of moles to the specified accuracy and also the mole fractions and partial pressures to nearly the same accuracy. It should not be assumed that the values given in Figure A. 1 are valid to five decimal places. The accuracy of the input data of Tables 1 and 3 limits the accuracy of the corresponding output. The precision of the values of Figure A. 1 (expressed by the delta function) is to within 0.0001 on the major molecules, with further refinements made on trace molecules.

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