THE GASES IN ROCKS AND SOME RELATED PROBLEMS.

E. S. SHEPHERD.

ABSTRACT.

This report had its origin as far back as 1911 when we made our first effort to determine the nature and composition of volcano gases, and the studies naturally led to the investigation of the gases in lavas and the analogous plutonic rocks.

INTRODUCTION.

When observed phenomena are not readily explained by forces whose limitations are known to us we naturally invoke other forces whose limitations are less well understood. Such explanations are of course tentative and compel a search for the limitations of the new forces invoked. Frequently these studies show that the forces postulated are insufficient to account for the observed facts and the investigation appears to lead to wholly negative results. Such negative findings are often quite useful in closing one line of speculation and turning attention to others more fruitful. Years ago geologists sought solace in the phrase "at high temperatures and pressures" and volcanologists perhaps invoke "the volatiles" of a magma as a simple and sufficient explanation of phenomena which are anything but simple. The volatiles have long been the deus ex machina for the many bewildering phenomena of volcanism, and the following paper is intended to supply a few, if often negative, details concerning these dei ex machina.

The amazing volumes of gas given off by some volcanoes, along with the vesicularity of lavas, indicate that at least some of the gases were brought to the surface by the lavas and that a study of these gases would furnish an explanation of volcanic phenomena. For over a century students have stood looking at the boiling lava in Kilauea and almost unanimously deduced that the lava was kept boiling by a continuous supply of gas from the parent magma below. It seems almost unamiable to remark that we now know that the lake is not the top of a column of liquid lava coming directly from a magma chamber below, and that the volumes of gas necessary to keep the lava molten by gas heating are too great to rise through this

hundred-meter orifice without sweeping all the lava along with it. We do not mean that gas is not a source of heat but that it is far from sufficient. Amazing rushes of gas are reported from volcanoes, for example, the great gas phase of Vesuvius,[1] but this gas the writer believes to have a somewhat different origin.

Many gas collections were made during the last century, and these were summarized by Allen,[2] but none of these is satisfactory from our viewpoint. It is necessary that the gas be collected from live lava in the crater uncontaminated by other gases. Experience at Kilauea, where gas may be collected directly from the molten lava, has shown us that even under these unusually favorable conditions contamination of the gases is difficult to avoid, and that gases from fumaroles, whether primary or secondary, are most interesting but bear no definable relation to the gases of the magma itself.

In an earlier paper[3] we called attention to this problem of contamination. At one extreme in gas-collecting we have the collection of gases at Kilauea where it is at times possible to insert the collecting tube directly through the flame source in the molten lava of the lake. At the other extreme are gases collected as they bubbled up through meters of sea water and where one could not know which constituents of the original had been washed out by passage through water or which were added by contact of hot lava with the organic debris of the sea bottom. In between lie the fumaroles where we must take into account not only the original gases but also those resulting from contact of the hot lava with the country rock—or ash or older lavas—together with the unpredictable reactions between the hot gases and the cracks or orifices from which they issue. That such secondary or fumarolic gases may be of the greatest interest, especially when the traces of other elements are determined, has been beautifully shown by Zies,[4] but a direct correlation with the so-called juvenile gases remains impossible and for our present purposes irrelevant; all of which is merely to

[1] Perret, F. A.: The Vesuvius eruption of 1906, Carnegie Inst. Wash. Pub. No. 339, p. 44, 1924.

[2] Allen, E. T.: Chemical aspects of volcanism, J. Franklin Inst., 193, 29-80, 1922.

[3] Shepherd, E. S.: The analysis of gases obtained from volcanoes and rocks, J. Geol., 33, 289-370, 1925. See also Chamberlin, R. T.: The gases in rocks, Carnegie Inst. Wash. Pub. No. 106, 1908.

[4] Zies, E. G.: The fumarolic incrustations in the Valley of Ten Thousand Smokes, Nat. Geogr. Soc., Contrib. Tech. Papers, Katmai series No. 3, 159-179, 1924.

state the obvious fact that gases which have passed through what is essentially an absorption tower (the earth's crust) can not at present give us any definite clue as to the composition of the original gases of the magma.

SELECTION AND HANDLING OF MATERIAL TO BE STUDIED.

The first difficulty which we meet is a lack of definable material. It is easy to analyze the rock or lava, though even here we must remember that the water content as determined in a chemical analysis is, as regards the rock itself, irrelevant. The chemist necessarily determines the purely arbitrary "plus" and "minus" water, but these data refer only to the powder he has prepared for analysis. It is to be regretted that more accurate data are not available, since a number of investigators have taken the figures in Washington's Tables for the water content of various rocks.

The problem of suitable vessels in which to heat the rock during evacuation was solved only when silica glass tubes became available, and these must be out-gassed before use. It is now well known that in "out-gassing" a glass, as in vacuum tubes after treatment at one temperature, if the temperature be raised above that used initially, more gas will be given off. In fact, there is no practical limit to this evolution. Only by adopting a definite procedure can one hope to duplicate one's results. The same statement applies to rocks and glasses, so the analyst must follow a definite schedule. The last traces of gas do not seriously affect the results if the same experimental conditions are followed, but without such a schedule no comparisons of the results are permissible.

Another difficulty is to find material which is definite in composition. Rock analysts usually demand that the rock be fresh and unaltered. Alteration in the sense in which we use it does not necessarily imply decomposition. To a limited extent one expects some bound water in crystalline rocks. Small amounts of water present in a magma may be completely used up to form normal hydrated minerals, as for example the micas and hornblende. But the amount which can be accounted for in this way is not large. As a maximum, assume ten per cent of mica in the rock with a water content of five per cent which at 1200° gives about 30 cc./g. In addition there will be the water present in hornblende and some adsorbed water for surfaces and cavities. As we find later, this 30 cc./g. is the average volatile content for the plutonic material studied which

we selected as free from alteration. It is evident that if there is more water it can only be present by combining with other minerals or by partially decomposing those originally present. It is this decomposition which we call alteration. It may be due to volatiles initially present in the magma, or it may be due to volatiles originating elsewhere and condensing in the rock. In the studies of rock types and relationships this demand for unaltered material is undoubtedly sound. On the other hand, in the intensive study of a rock series, the altered rocks become quite as important as the unaltered rocks, though this fact has not always been realized.

For purposes of gas study one first seeks rock showing as little alteration as possible. Later, the altered material may be even more interesting, but only when the geological relationships are being studied simultaneously. We have therefore confined our attention whenever possible to unaltered materials.

But even supposing that we can obtain fresh material—and a recently extruded lava is the only rock to which the term can apply—it is necessary that such material be handled with care. With the exception of the dense, glassy obsidians, where by chipping away the surface one can obtain the uncontaminated interior, there is always the certainty that more or less foreign matter will be present.

The vesicular lavas, and especially pumice, which have been exposed for any period will be contaminated with organic residues from various sources—bacteria, fungi, dust, and rain. One has but to heat such material and the odor betrays it. A particular case may illustrate this. In a collection of material from Little Glass Mountain, California, for which we are indebted to Professor Larsen, we found this condition:

	H_2O	
Dense, black glass	0.11%	No wood distillate
Type V coarsely vesiculated	0.12	A little wood distillate
Type IV more vesiculated	0.19	Appreciable wood distillate
Lightest pumice	0.36	Much wood distillate

With the exception of the dense glass, all gave the usual empyreumatic odor on heating. As these rocks had been exposed to the weather for at least a century in a rather dry climate, they furnish an excellent illustration of the adsorptive capacity of pumice.

We have mentioned care in handling; a simple example will clarify the point. Let us assume that in the collecting and

transportation of the sample the wrappings, labels, etc., deposit a centigram of cellulose on and in the specimen (very easily the case with rough vesicular lavas), and let us further assume the simplest possible dissociation of this cellulose on heating in vacuo, to give, say, 5 volumes CO, one volume CH_4, and 3 volumes H_2; then at our standard conditions (1200° C., 760 mm.) the yield will be about

CO	23.9 cc.
CH_4	8.3 cc.
H_2	20.1 cc.

that is, about 52 cc. of gas to be included in the total. We have grossly oversimplified the problem since these reducing gases would react with iron oxides, sulphur, and other lava constituents and seriously affect the relative quantities of fixed gases inferred. The degree to which vesiculated material can be contaminated can be appreciated only by those who have had occasion to examine such rocks. Clean material is therefore desirable, but unfortunately this ideal condition is not attainable for most rocks.

A priori one would imagine that the bubbles in a vesicular, glassy lava or pumice would be admirable places to look for fresh, uncontaminated primitive gases, and that all one needs to do is to crush the material cold in vacuo. This supposition, of course, ignores adsorption phenomena on the outside of the gas-containing vesicles. In agreement with Chamberlin's experiments, we found that no gas could be obtained in this way; the vesicles are intercommunicating.

With crystalline rocks, the case is no better. While it is true that some fine-grained rocks (certain quartzites) are relatively solid, yet there are few types which do not show one per cent or more porosity. Thus Adams and Williamson[5] show that a pore space of one per cent is a fair average for dense rocks. Many, however, will have greater pore space, and contrary to the common notion of "solid rock," from our viewpoint it would be better to regard all holocrystalline, and especially the coarsely crystalline rocks, as appreciably shattered. This "shattering" is due to several causes; it is a natural and unavoidable condition. A crystallizing magma apparently concentrates its volatiles in the liquid portion, which means that near the end the concentration of volatiles in the last liquid may

[5] Adams, L. H., and Williamson, E. D.: The compressibility of rocks and minerals at high pressures, J. Franklin Inst., 195, 512, 1923.

be very high even though the total volatile content of the magma was low. The spine of Mt. Pelée and the boulders carried by the nuées ardentes illustrate this point. These lava blocks are of a sugary texture—almost as if every crystal was separated from every other. In this case we know that some of the interstitial lava was highly charged, even to the explosion point; the remaining blocks left by a nuée were apparently less charged but enough so to be extremely porous. We may suppose that however free the passages for escape may have been, there will always be room for a thin film of the gas phase between many of the crystals, whatever the pressure may be. The crystals always include a small amount of water and may even include vesicles containing water and at times CO_2. The result is that rocks contain an infinite number of minute cavities and surfaces for adsorption effects. Quite as important in producing and maintaining porosity is the differing thermal expansion of crystals not only of one mineral compared to another but with differing axes of the same crystal. The constant shifting of the geotherms with time, the changing pressures with isostatic readjustments, loading and unloading, and the daily warping of the earth's crust by tidal stresses[6] keep the crystals in a continuous if minute state of movement.

There must be a usually slow but continuous movement of gases or vapors through the rocks, partly induced by these minute but definite shifting movements, therefore one can not believe that we shall ever be certain that the gases obtained from even the best holocrystalline rocks will bear any definite relation to those initially present. We can not know how much of the alteration observed in a rock is due to reaction with its initial volatiles and how much is due to foreign volatiles which have contaminated the mass in later periods.

This uncertainty is accentuated when some of the characteristics of gas reactions are considered. The determination of gas equilibria is one of the tantalizing jobs which chemists encounter; not only are the reactions themselves subject to complications, but they are also seriously affected by the walls of the containing vessel. Adsorption phenomena together with catalytic effects, as of the iron oxides altered by small amounts of other metals, enter in. Then, too, the reactions shift with temperature, pressure, the relative proportions of the gases entering into the reaction or diluting the mixture, and also with

[6] There should be an appreciable heat effect involved in earth tides, though no one seems to have tried to evaluate it.

the rate of removal of one or more reaction products from the field of action. It is clear that even if we had imprisoned in the rock the "warranted genuine" magmatic gases, the effort to extract them, involving as it does changes of temperature and pressure, along with the uncertainties as to the length of time the mixture remains in contact with catalytic surfaces, defeats any attempt to interpret the analytical data in terms of the original composition of the gases in the cooling magma.

For those who may not have considered this aspect of the problem we may list a few of the reactions involved. First and foremost is the "water gas" equation

$$CO_2 + H_2 \rightleftharpoons H_2O + CO.$$

This classic equation has been intensively studied and the effect of concentration, temperature, and pressure definitely established for a limited range of conditions. But the results can not be applied to our problem because of extraneous factors introduced by the varying composition of the rocks themselves. We know what happens under carefully predetermined conditions, but in nature we find the gases of this equation contaminated by sulphur, halogens, silicon, iron, copper, zinc, lead, nickel, chromium, molybdenum, vanadium, etc., ad infinitum, some acting as catalysts, others poisoning the catalysts, and the whole chaotic mess enclosed by and enclosing the unpredictable pore spaces with unpredictable surfaces. In other words, we are not yet able to make any use of this equation without straining our present data inexcusably.

Reactions between mixtures of the following elements will be present: H_2, O_2, S_2, Cl_2, F_2, and Si, in greater or lesser degree.[7] Perhaps the only gas reactions which have not been

[7] Many gas reactions have been suggested in a search for energy sources for volcanoes. Most of these are based upon the tables for heat of formation which tables are far from satisfactory for the purpose since the whole hypothesis is an extrapolation with very scanty experimental checks. Thus there has appeared from time to time the dissociation of water into hydrogen and oxygen at high temperatures, the gases then being recombined later to produce the desired heat. According to our present knowledge this dissociation, if appreciable in amount, involves temperatures far above 2000° C. and therefore belongs, if anywhere, in a region far removed from any with which we have to deal. Another suggestion is to use ferrous oxide to react with water, thus giving ferric oxides and hydrogen. The hydrogen so obtained is then to be used to reduce the ferric oxides to ferrous, furnishing heat. Quite aside from the problem of moving the gases about and having them react at the precise spot needed and without loss of energy, there remains the regrettable fact that we are not dealing with ferrous oxide but instead with ferrous silicates, in which case the sign of the heat change is reversed.

exploited heretofore are those involving Si, S_2, and H_2. We elsewhere pointed out that SiH_4 is a probable constituent of magmatic gases at the higher temperatures. Any place where free hydrogen and a silicate are in contact at temperatures around 1100° will show some SiH_4 formation. Of even greater significance are the silicon sulphides which Hempel believed he has shown to be present in Vesuvian lava.[8] These sulphides form with great ease whenever sulphur and silica are heated to about 1100° under reducing conditions; the reaction is a commercial one used in the purification of bauxite. At some depth, therefore, silicon sulphide may be expected

Then, too, if all the iron in our richest iron-bearing lavas could be induced to obey our will there would remain the fact that the heat so obtainable would have to be distributed through the remaining ninety per cent of the rock and could at best raise the temperature only a few degrees. With the andesites and rhyolites the heat available from this source approaches zero. These reactions should not be invoked.

Of the purely gaseous reaction between CO_2, H_2O, and S_2, shifting equilibria can furnish heat if we are allowed to run the reaction just as we please and where we please. But before one indulges in such speculation one should also arrange to move the tremendous quantities of gas about and also compute the quantities needed. The results of this arithmetic are sure to be discouraging. Such gas reactions are no doubt a factor in supplying energy, but a very minor factor, and none of those suggested bears any relation to the average composition of volcano gases as we might expect it to do were it a dominant factor.

There is no limit to the arithmetic which can be expended in an effort to secure volcanic energy. As an example of this sort we shall consider one mode, that is, simple heating by hot gases. Approximations as to the heat loss at Kilauea using various reasonable assumptions give the order of magnitude around 400,000,000 calories per second as a conservative estimate. We shall assume all the gas to be water vapor with a specific heat of 0.5. One gram of steam at 1200°, 760 mm. has a volume of about 6.77 liters. Assume further a temperature drop of 300° in the gas, say 1400 to 1100°. Then for every 6.77 liters of gas evolved there would be available 150 calories. To supply the 4,000,000 calories we should need 2,666,600 grams or 18,040,000 liters per second, that is, 18,040 cubic meters per second. Assume a circular lake 100 meters in diameter. Then 18,040 cubic meters corresponds to a cylinder of gas 100 meters in diameter and 2.3 meters high. Therefore the gas would have to issue at such a rate as to pass this 2.3 meter cylinder each second, or in terms of wind velocity, about five miles an hour. As a matter of fact the lake is always largely covered with floating crusts so that the available free surface of fresh lave is more nearly a hundredth part of the assumed area, which would raise the required rate of gas evolution accordingly. To reduce these figures to every-day experience one need only consider the rate at which a pan of water must boil in order to furnish a steam jet of its own diameter issuing at the rate of seven feet per second. Transfer this concept to the more viscous lava, say more viscous than hot porridge, and one sees the impossibility of any such rate of gas evolution from the crater. This does not preclude intense gas blasts from suitable openings but does exclude gas heating as the main factor at Kilauea.

[8] Hempel and Haasy: Z. anorg. Chem., 23, 32, 1904; Dolch, P.: Chem. Fabrik, pp. 512-514, 1935.

and a slow but continuous removal of silicon from depth toward the surface may be expected to have been under way from the beginning. While we are not used to considering silicon compounds as "volatiles," they evidently must be so treated. Silicon halides are also formed and hydrolyzed readily. Thus we have not only SiF_4 easily formed at high temperatures but also the fluosilicic acid H_2SiF_6 quite stable in acid solutions and volatile with steam. Furthermore, the fluosilicates, most of which are quite soluble, add their mite to the chemist's confusion when he considers the various possible solutions with which rocks are contaminated. In addition to the unexpected volatility of the compounds is the stability of colloidal silica solutions, so that this element which the chemist regards as inert and insoluble is really surprisingly mobile.

The above considerations show that the gases which we find in the crystalline rocks are too indefinite in origin to answer the questions asked in the problem as originally stated. Neither the amount nor relative compositions tell anything definite about the "juvenile gases."

Even though we can not hope to learn much about the magmatic gases from our data, yet these same data will yield information that will be useful in studying the rôle of the gases in later stages of the igneous activity. After all, the phenomena with which we are concerned are much nearer the surface of the earth than the primitive magma. Thus it is important to know what gaseous elements, and the total amounts thereof, can be set free on reworking or reheating rock in nature, for with these gases we have to deal. For this purpose it seemed wise to determine at least the minimal amounts of gas which might be expected, letting the state of combination be what it might. We do not know what may have been the distribution of the gaseous constituents of, say, a granite magma, but we can know what gases and volumes will be given off when a particular granite is reheated. We have therefore examined a number of lavas and the corresponding plutonics to see what volatiles were available in the various transformations to which rocks are subjected in the crust. We selected material showing a minimum of alteration of whatever kind and compared this with such lavas and volcano gases as were available. The reason for selecting material that showed a minimum of alteration was similar to that which made earlier investigators omit water from their determinations. Since they were unable to say how much of the water belonged properly to the rock and

how much was adventitious, they excluded all of it. In our work it developed that the water must be included, though alteration in a rock introduces an indefinite quantity of total volatiles. However, if we are not concerned as to the primitive magmatic volatiles but are interested instead in the volatiles available for surface and near-surface phenomena, then water of whatever origin becomes of first importance.

VOLCANO GASES.

It will be better, perhaps, if we begin our examination of the gases with a review of the work on volcano gases.

Our first interest in volcano exhalations was aroused by observations made at Kilauea. The analyses of these gases were published long ago,[9] but they will be reprinted here (Table I) in order to compare the gases obtained from the active lava with those obtained by "out-gassing" the same lavas in vacuo. The Hawaiian gas analyses were made on samples collected in vacuum tubes. All the samples were obtained at Kilauea with the exception of ML 1 and 2 which were collected by Dr. T. A. Jaggar from a Mauna Loa eruption. The analyses listed with a J are that splendid series of tubes collected for us by Doctor Jaggar in 1919. By carefully choosing the time and place of collection, using both his knowledge of the crater activity and a very real courage, Doctor Jaggar has given us here what is unquestionably the most satisfying, indeed the only satisfying collection of volcano gases that has ever been made. To him we are deeply indebted for what may be characterized as the crucial test of the Kilauea gases. The S series was collected by Shepherd in 1917 and was taken from the most favorable sources available. The tubes were, however, more frequently contaminated with air, owing to less favorable sources than those of the J series.

The one obvious fact brought out by the analyses shown in Table I is the lack of any definite relationships among the constituents involved. As is well known, Kilauea remains active over long periods and one would therefore infer that foreign volatiles would long since have been swept away. When these collections were made, the lake had been active for many years. Surely here, if anywhere, we might expect some sort of equi-

[9] Shepherd, E. S.: Bull. Hawaiian Volcano Obs., 9, 83-88, 1921. Day, Arthur L., and Shepherd, E. S.: Water and volcanic activity, Bull. Geol. Soc. Am., 24, 573, 1913.

TABLE I.

Volume percentages at 1200°, 760 mm., for Kilauea gases from vacuum tubes.

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

librium and here we surely should be able to collect the true juvenile, that is, magmatic gases. Nothing of the sort appears in the data, and while one of the factors in furnishing heat may very well be the heat resulting from the shifting equilibria of the gases involved, as suggested by Day,[10] this must be a minor factor in view of the quantities of gas involved in comparison with the heat losses and specific heat of the lava itself. Any effort to compute such heat effects is vitiated by the absence of data as to the total volume of gases per unit of time, and even more so by our inability to handle theoretically mixtures of such complexity and subjected to such indeterminable conditions. It is clear that the "water gas" reaction is involved, with the equilibrium well over toward the water side. All the gases are well oxidized, and though enough sulphur is usually present to give occasional flames, the absence of any quantity of free

[10] Day, Arthur L.: Some causes of volcanic activity, Franklin Institute, 24 pp., 1925. Also J. Franklin Inst., 200, 161-182, 1925.

hydrogen is shown by the absence of explosions when great bubbles of gas (as in the fountains) break out from the surface.

Of much less importance, but perhaps significant, is the content of rare gases. These we have listed as argon. A large part of this may properly be attributed to admixed air. This contamination may occur in filling the vacuum tube and can be partly corrected if the analysis shows free oxygen. This correction, however, is obviously far from perfect. We may also expect that the air carried down by sinking crusts at Kilauea will account for a further unpredictable amount.[11] Some argon might be supposed to enter the lava at still greater depths since the lava has to work its way up through a brecciated, and therefore adsorptive, mass of old lava. But there is no intelligible relation between the figures for argon and nitrogen. We have often tested for helium in the course of our analyses and with negative results. It may be present but certainly in no significant amount. If, as some maintain, the energy of volcanoes derives in part from radioactivity, one might hope that volcano gases would show at least appreciable quantities of helium, but neither in the rocks from Kilauea nor in other rocks and lavas examined is the total of rare gases significant.[12] Nitrogen is believed to come partly from nitrides. Gautier, the most critical student in this field, made a number of interesting tests which satisfied him that the rocks studied contained iron nitride which would account for traces of NH_3 commonly appearing in accounts of volcano gases. One can not accept this conclusion without reserve. Experiments made upon fresh, carefully handled basalt might be more conclusive, but no such tests have been made. It is not probable that any nitride could withstand the age-long soaking in water which the plutonics have endured, nor could one distinguish between NH_3 derived from this source and NH_3 of meteoric origin. The presence of nitrides or NH_4Cl in fumaroles together with the rarer elements needs much more study before one would feel any confidence that it originated in the juvenile gases, and this remains true even though we grant that at some depth in the earth nitrides ought to be stable and common.

The explanation of the lack of any uniformity of com-

[11] Jaggar developed his "surface combustion" hypothesis on the assumption that the sinking crusts would carry down enough oxygen to burn combustible gases. The great excess of nitrogen which combustion by trapped air implies is not borne out by the analyses of the gases.

[12] For example, there are helium-bearing strata in Southeastern Utah (the San Rafael swell) but our No. 29, the Marvine laccolite in the Henry Mountains, shows no abnormal rare gas content.

position in these Kilauea gases appears from the following observations. Most fountains burst without any visible flame, whatever the "seeing." Then a fountain breaks, emitting a purplish-brown vapor apparently almost pure sulphur vapor. One sees fumed wall rock (highly impregnated with sulphur) avalanche into the lake with great boiling and spattering as the condensed volatiles are revolatilized. Other blocks may slip into the lake with little or no disturbance. It is a fair inference that the variable streaming of the lava, the chilled lava crusts which instantly coat sinking blocks and the irregularly sinking crusts (for the lava lake is barely above its freezing temperature), and the shallow character of the lake itself all tend toward a most irregular mixing of whatever gases may be present.

The older conception of the lake, which in 1912 we fully shared, wherein the lake was thought to be merely the top of a column of molten magma, the column going down directly to the hypothetical magma reservoir below, would have implied a rather efficient mixing of gases and hence some sort of uniformity. The absence of any such uniformity of composition is quite in accord with those physical features of the lake which Doctor Jaggar's long series of observations and tests has established.

Jaggar's remarkable sounding-experiments and observation of the lake at times when a sudden drop of lava level exposed the bottom, the input, and the drainage openings, give us a wholly different picture.

To the writer it now seems clear that the lava lake is not the top of a column of liquid lava but that it is a lava spring with subterranean drainage. The actual lake is a shallow pool poised on top of a breccia through which several small streams of lava work their way to the surface, the original lava coming probably from under Mauna Kea or Mauna Loa and thence drained off, for the most part, under the sea. Frequently it breaks out along the line of the pit craters or out on the Kau desert.

Jaggar[14] has shown that at times of subsidence a tremendous volume of talus avalanches into the heart of the mountain. This talus acts as a condenser for the fumes of the receding lava. With a renewal of activity the new lava must work its way up through this old talus, in doing which the condensed fumes are once more set moving to contaminate whatever gases the new lava may bring with it.

[14] Bull. Hawaiian Volcano Obs., 12, No. 12, 1924.

To those who have not followed the record of Kilauea's eruptions, this concept may seem fantastic. To all such we commend the record both of outbursts in the Kau region and particularly Father Coan's description of the 1840 Kilauea flow.[15] The difficulty some have in understanding these craters lies in a preoccupation with the over-simplified textbook diagrams. There are great differences between a basaltic edifice resting on basaltic flows and a volcano of more viscous lava resting on or penetrating a sedimentary or solid igneous platform.[16] In the case of Hawaii, the volcano is a pile of loose flows and tubes, or tiles. It is an extremely porous mass without the coherence of our continental edifices. Not only that, but the flows are never welded together.[17] Typical pahoehoe lava has a density of about 2.0 whereas the specific gravity is about 3.0. The macro-porosity is well shown in Goranson's computations,[18] according to which the mountains, above sea level, at least, have a density (as determined by gravity measurements) of between 2.1 and 2.8. This means that many lava channels must be present.

These channels can produce changes in the composition of the gases issuing from the lava. If one channel is blocked, the lava seeks a new outlet. This phenomenon is readily observed in watching both the rising and the sinking pools at the edges of the lake. But in changing channels the lava passes through fumed areas in which both magmatic gases and drainage from above have been active. One result will be a sudden increase in the total sulphur content because sulphur is one of the most easily condensed of the common volatiles present. Consider this action to be going on in the breccia underneath the lake, and we see why no constancy of composition is to be expected.

[15] Brigham, W. T.: The volcanoes of Kilauea and Mauna Loa, on the island of Hawaii, their variously recorded history to the present time, Bishop Museum Press, Honolulu, p. 50, 1909.

[16] Consider Vesuvius, where the lava works its way up through several thousand feet of limestone and pieces of more or less altered limestone are erupted; or Mt. Pelée and Lassen Peak, where the lava is so viscous that it reaches the crater as domes and spines, and a free-flowing lava—a good lava flow—is rare.

[17] The record of the outbreak of Hawaiian lava flows is consistently the same; lava wells up in the crater, building up pressure of the lava column until at some point a pathway through the mountain opens, then the surface flow begins, not from the crater but out of some point on the mountain's flanks. This is the regular course of eruption for Mauna Loa and even with the more accessible subterranean-submarine exits which we assign to Kilauea, breaks through the side toward the pit craters (the pit craters are on the side of the mountain toward the sea) or in the Kau desert are not infrequent.

[18] Goranson, R. W.: This Journal, 16, 117, 1928.

GASES FROM LAVAS.

It seemed reasonable that if we could pump the residual gases out of the freshly collected Hawaiian lava it might be of interest to compare it with the gases which the lava gave off as collected in vacuum tubes at the volcano. The results of this study are given in Table II. Obviously, Tables I and II could be interchanged without difficulty. There is no more constancy in one than in the other. The residual gases of the lava are the same and as variable as the gases of the vacuum tubes. The hydrogen averages a little higher and the nitrogen lower, but we feel justified in assuming that extracting the gases from fresh lava by heating in vacuo will tell us just as much about the gases of an eruption as will vacuum tubes. The only additional information would be that of the fumaroles and incrustations, which in carefully handled cases (Zies' paper on the incrustations at Katmai is a beautiful example) is likely to be even more instructive now that the general character of the main gas content is established.

We next examined a series of six other types of lava. In Table II, with descriptions in Table III, we have assembled the entire series, both lavas and the analogous plutonic rocks.

In the first section are given the results for obsidians; in the second group, the andesites from Mt. Pelée, Martinique, and Lassen Peak, California; then the basalts of Kilauea and Mauna Loa; and finally typical plutonics. These last are: granite from Stone Mountain, Georgia; the Barre and North Jay granites from Vermont; a selected specimen from the Henry Mountains, Utah (Marvine laccolite); the Maryland diabase from near New Market, Maryland; and the diabase from Granton, New Jersey. About the only tendencies visible in the tables are the dominance of H_2O and a clustering of the total cc./g. around 5 or 6 for lavas. The few exceptions such as Numbers 2, 5, and 6 of the obsidians; 11 and 14 of the andesites are readily accounted for by the nature of the specimens, as described in Table III, and in a succeeding discussion.

In the selected plutonics examined, the tendency is for the total volatiles to cluster around 30 cc./g. (approximately). This figure of course may become much greater if alteration is present. The Barre granite contains visible calcite of whatever origin, and it was the threefold increase in total volatiles from the Granton diabase that first called our attention to the fact that the rock was altered. The earlier examination had over-

TABLE II.

Gases from rocks in vacuo.

Lava Numbers*		CO_2	CO	H_2	N_2	A	S_2	Cl_2	F_2	H_2O	cc./g.
					Obsidians (Rhyolitic)						
(1)	1	1.402	0.705	0.101	2.897	0.000	0.367	2.965	3.163	88.386	1.19
(2)	2	1.595	0.035	0.174	1.420	0.000	0.014	0.499	0.516	96.299	27.10
(3)	3	0.179	0.073	0.501	3.897	0.002	0.000	1.820	7.795	89.246	1.45
(4)	4	0.075	0.008	2.253	1.153	0.000	0.039	1.498	2.205	94.434	4.89
(5)	5	0.672	0.007	0.377	0.138	tr	0.000	1.713	4.329	92.761	55.3
(6)	6	0.077	0.032	0.080	0.053	udt	0.000	0.069	1.136	98.551	214.8
					Andesitic Lavas						
(7)	MP/4	8.609	1.473	0.199	1.228	udt	1.732	0.934	2.575	83.248	7.1
(8)	MP/5	10.109	2.007	0.252	0.854	0.008	0.422	0.387	3.317	82.525	4.8
(9)	MP/6	20.260	1.391	0.185	2.494	0.023	1.908	1.575	1.420	70.726	4.3
(10)	MP/1	7.441	1.256	0.435	2.371	0.007	2.892	10.495	4.289	70.812	5.9
(11)	MP/7	0.824	0.214	0.427	0.213	tr	0.053	0.991	1.038	96.227	26.5
(12)	LP	2.070	0.623	0.412	0.577	0.003	0.882	0.297	1.524	93.658	9.5
(13)	LP	1.187	0.310	0.210	0.116	0.018	0.215	0.428	nd	97.519	7.8
(14)	LP	1.959	0.503	1.187	0.029	0.0003	0.123	0.129	nd	96.067	10.6
					Basaltic Lavas						
(15)	P 1911	5.673	0.601	1.085	0.269	0.003	1.384	0.404	udt	90.580	5.4
(16)	P 1919a	11.757	0.148	0.376	0.280	tr	1.662	1.334	3.609	80.834	6.9
(17)	P 1919b	11.172	0.045	0.464	1.305	tr	1.674	1.030	6.203	78.100	7.3
(18)	KMP 1923	6.262	0.038	0.435	2.047	0.003	0.988	1.152	14.115	74.953	5.0
(19)	KMA 1923	7.893	1.877	0.520	2.564	0.005	0.454	0.544	11.733	74.402	4.2
(20)	KAA	6.80	3.83	6.18	1.31	0.01	0.72	0.26	udt	80.17	9.8
(21)	K 1924	9.337	0.026	0.382	2.109	0.042	1.094	0.127	5.218	81.663	0.69
(22)	KJ 1917	2.339	0.069	3.131	2.516	0.002	1.957	0.739	13.331	75.914	6.6
(23)	Loa 1926	15.304	1.426	4.410	5.193	0.015	0.236	0.213	0.000	73.199	6.2
(24)	ML 3a	12.982	0.985	3.872	1.749	0.037	0.475	0.055	0.000	79.892	2.9
(25)	Niuafoua	10.358	8.276	1.108	7.207	0.018	1.278	0.430	0.000	71.322	3.9
					Plutonic Rocks						
(26)	Stone Mt. Granite	1.965	0.081	4.823	0.334	0.007	0.268	0.007	1.970	90.512	34.2
(27)	N. Jay Granite	4.236	0.536	11.603	1.228	0.024	0.159	0.051	2.563	79.599	29.4
(28)	Barre Granite	19.634	2.215	5.502	2.190	0.025	0.724	0.180	0.254	69.276	57.3
(29)	Marvine Laccolite	9.463	0.814	13.455	0.566	0.002	4.042	0.300	1.914	69.439	31.2
(30)	Maryland Diabase	0.894	0.023	4.813	1.911	tr	1.844	0.189	0.275	90.059	30.0
(31)	Granton Diabase	2.425	0.026	2.944	0.797	0.000	0.079	0.986	0.341	92.399	89.9

* The numbers in parentheses in the first column are serial cross-reference numbers for Tables II and III. In the second column is listed the name or symbol that identifies a particular rock.

Computing these analyses to the third decimal is made necessary by the method and composition. In analyzing the gas, water is determined gravimetrically and this large volume added to the analysis of the fixed gases. These may vary anywhere from one to fifteen cc. and no extraordinary precision can be claimed for them; if small but definite quantities of the fixed gases are to appear in the final computation the figures must be carried past the one-tenth cc. limit as usually computed.

NOTE FOR TABLES II AND III.

In the analysis of gases collected in vacuum tubes it is often feasible to separate the sulphur gases into free sulphur and its oxides. This separation illustrates the inherent difficulty in such analyses. The gases are not in equilibrium even as collected. We find, then, a mixture of SO_2, SO_3, with free sulphur and in exceptional cases H_2S. In such a mixture on standing, for example during the interval between collection and analysis, rearrangements are certain to take place. Hence, the figures represent merely what was present at the time of analysis. With gases extracted from lavas in vacuo, this separation is more difficult and often out of the question, so that as work progressed we tended more and more to state all sulphur as S_2 because its distribution in the possible combinations would be fortuitous. Similarly, fluorine is not to be determined in vacuum-tube collections, though nowadays the determination is possible for lavas or for gases pumped from the lavas. With these exceptions Tables I and II can be compared directly.

It may be repeated here that the gases obtained from out-gassing lavas and rocks represent the volatiles which can be obtained from the material under our conditions. No method of attack will deliver all the volatiles in one operation.

TABLE III.

Rock Analyses.

Lavas—Big Glass Mountain, California.

Ser. No.*	1 (1)	2 (2)	#19103	Type C
SiO_2	73.34	73.38	73.59	72.64
Al_2O_3	13.35	13.69	13.78	14.07
Fe_2O_3	0.58	1.84	0.60	0.77
FeO	1.27	0.13	1.30	1.45
MgO	0.37	0.37	0.33	0.49
CaO	1.41	1.38	1.39	1.60
Na_2O	4.13	3.92	4.19	4.25
K_2O	4.45	4.22	4.32	4.08
H_2O+	0.33	0.34	0.14	0.11
H_2O-	0.03	0.05	....	....
CO_2	....	....	....	....
TiO_2	0.30	0.28	0.27	0.36
ZrO_2	0.01	tr	....	....
P_2O_5	0.18	0.08	0.12	0.11
SO_3	....	....	....	....
Cl	0.08	0.12	....	....
F	....	....	....	....
S	0.10	0.03	....	....
Cr_2O_3	....	....	....	....
V_2O_3	....	....	....	....
MnO	0.02	0.02	0.02	0.02
NiO	....	....	....	....
BaO	....	....	....	....
SrO	....	....	....	....
Li_2O	p.n.d.	....	....	....
Cu	....	....	....	....

* The numbers in parentheses are serial cross-reference numbers for Tables II and III; they refer also to the appended notes.

TABLE III—Continued.

Lavas—Little Glass Mountain, California.

	Type 1	Type 2	Type 3	Type 4	Type 5	Type 6
SiO_2	73.59	73.34	73.22	73.47	73.46	73.49
Al_2O_3	14.03	13.96	13.65	13.72	13.72	13.65
Fe_2O_3	0.42	0.51	0.40	0.61	0.46	0.60
FeO	1.43	1.31	1.41	1.24	1.27	1.29
MgO	0.36	0.36	0.21	0.37	0.41	0.40
CaO	1.38	1.53	1.38	1.38	1.57	1.40
Na_2O	4.04	4.22	4.23	4.21	4.21	4.17
K_2O	4.34	4.35	4.30	4.27	4.30	4.27
H_2O+	0.12	0.10	0.39	0.34	0.33	0.31
H_2O-	0.06	0.07	0.16	0.12	....	....
CO_2	....	....	....	....	....	....
TiO_2	0.31	(0.36)	0.29	0.28	0.28	0.31
ZrO_2	....	....	....	....	....	....
P_2O_5	0.09	0.13	0.11	0.22	0.13	0.14
SO_3	....	....	....	....	....	....
Cl	0.03	....	0.09	....	....	....
F	0.03	....	....	....	....	....
S	0.02	0.05	0.02	0.04	0.03	0.03
Cr_2O_3	....	....	....	....	....	....
V_2O_3	....	....	....	....	....	....
MnO	0.02	0.03	0.03	0.02	0.02	0.03
NiO	....	....	....	....	....	....
BaO	....	....	....	....	....	....
SrO	....	....	....	....	....	....
Li_2O	p.n.d.	....	....	....	....	....
Cu	....	....	....	....	....	....

TABLE III—Continued.

	Lavas—							
	Coso Mts., Calif.		Mono Craters	Mt. Morrison Quadrangle	Newberry Volcano, Oreg.	Cerro Noagua, N. Mex.		Obsidian Cliff Yellowstone
Ser. No.*	Type 1 (3)	Type 2 (4)			No.75	Black Obsidian (5)	Pitchstone (6)	
SiO_2	76.09	75.92	76.13	76.27	73.40	76.35	73.14	76.78
Al_2O_3	12.60	12.31	12.49	12.24	13.98	12.34	13.41	12.09
Fe_2O_3	0.49	0.40	0.36	0.50	0.24	0.47	0.33	0.56
FeO	0.85	0.68	0.72	0.76	1.76	0.60	0.20	0.81
MgO	0.14	0.08	0.02	0.02	0.18	0.03	0.08	0.10
CaO	0.58	0.59	0.54	0.60	1.35	0.38	0.58	0.57
Na_2O	4.03	4.26	4.68	4.90	4.15	4.29	4.28	3.79
K_2O	4.43	4.36	4.72	4.49	4.10	4.39	4.31	4.93
H_2O+	0.26	0.98	0.20	0.15	0.40	0.91	3.10	0.12
H_2O-	0.06	....	0.09	0.06	0.10	0.00	0.12	0.08
CO_2	....	....	....	....	....	....	....	....
TiO_2	0.09	0.06	0.08	0.10	0.20	0.09	0.06	0.08
ZrO_2	....	0.01	0.00	0.00	....	tr	tr	0.01
P_2O_5	0.06	0.15	0.02	0.04	tr	0.02	0.01	0.09
SO_3	....	....	....	....	....	....	....	....
Cl	0.08	0.06	0.13	0.11	....	0.06	0.08	0.05
F	0.13	0.14	0.07	0.06	0.06	0.08	0.15	0.15
S	0.00	0.00	....	0.01	tr	0.01	0.00	0.06
Cr_2O_3	....	....	....	....	....	....	....	....
V_2O_3	....	....	....	....	....	....	....	....
MnO	0.02	0.02	0.02	0.01	....	0.06	0.14	0.02
NiO	....	....	....	....	....	....	....	....
BaO	0.00	....	....	0.00	tr	....	tr	0.00
SrO	....	....	....	....	....	....	....	....
Li_2O	....	p.n.d.	....	....	....	....	....	....
Cu	....	....	....	....	....	....	....	....

* The numbers in parentheses are serial cross-reference numbers for Tables II and III; they refer also to the appended notes.

TABLE III—Continued.

	Granites			Marvine Laccolite
Ser. No.*	Stone Mt., Ga. (26)	Barre, Vt. (28)	N. Jay, Vt. (27)	H 3 (29)
SiO_2	73.39	70.48	73.41	63.73
Al_2O_3	14.41	14.42	14.17	17.71
Fe_2O_3	0.09	0.63	0.22	2.09
FeO	0.70	1.59	1.19	2.15
MgO	0.27	0.89	0.19	1.16
CaO	1.05	1.68	1.02	5.69
Na_2O	3.96	3.98	3.33	4.56
K_2O	5.07	4.48	5.35	1.76
H_2O+	0.39	0.43	0.31	0.34
H_2O-	0.05	0.05	0.02	0.05
CO_2	....	0.54	p.n.d.	....
TiO_2	0.27	0.44	0.19	0.45
ZrO_2	tr	0.01	0.02	0.03
P_2O_5	0.57	0.31	0.12	0.25
SO_3	....	....	....	....
Cl	0.03	0.02	0.04	0.02
F	0.04	....	....	0.06
S	0.02	0.03	0.01	0.02
Cr_2O_3	....	....	....	....
V_2O_3	....	....	....	....
MnO	....	0.03	0.02	....
NiO	....	....	....	....
BaO	....	....	0.02	....
SrO	....	....	....	....
Li_2O	....	....	....	....
Cu	....	....	....	....

* The numbers in parentheses are serial cross-reference numbers for Tables II and III; they refer also to the appended notes.

TABLE III—Continued.

Lavas—Lassen Peak.

	LP 32	LP 18	LP 2	LP 34	LP 7	BH 1
SiO_2	70.17	67.98	66.06	65.56	64.80	64.53
Al_2O_3	14.98	15.69	15.93	15.41	16.26	16.60
Fe_2O_3	0.87	2.93	1.53	2.38	1.11	1.76
FeO	1.78	0.42	2.36	2.16	3.17	2.34
MgO	1.28	1.47	2.15	2.37	2.39	2.55
CaO	3.16	3.86	4.53	4.92	4.83	5.18
Na_2O	4.49	4.42	4.18	3.51	4.13	3.87
K_2O	2.74	2.33	2.28	2.35	2.13	2.09
H_2O+	0.35	0.20	0.16	0.34	0.09	0.23
H_2O-	0.02	0.11	0.11	0.15	....	0.16
CO_2	....	....	....	....	....	....
TiO_2	0.39	0.45	0.55	0.48	0.53	0.61
ZrO_2	0.05	0.03	0.03	0.01	....	0.03
P_2O_5	0.25	0.15	0.19	0.19	0.26	0.25
SO_3	....	....	....	....	....	....
Cl	....	....	....	....	....	....
F	....	....	....	....	....	....
S	0.01	0.01	0.01	0.02	....	....
Cr_2O_3	....	....	....	....	....	....
V_2O_3	....	....	....	....	....	....
MnO	0.03	0.07	0.08	0.07	0.08	0.07
NiO	....	....	....	....	....	....
BaO	....	....	0.03	0.05	....	0.01
SrO	....	(0.01)	(0.06)	(0.07)	(0.03)	(0.02)
Li_2O	(0.02)	....	(0.01)	(0.01)	(0.01)	(0.02)
Cu	....	....	....	....	....	....

TABLE III—Continued.

Lavas—Lassen Peak.

	LP 10	LP 28	BH 3	CC 6	LP 21	CC 7b
SiO_2	64.49	63.45	60.55	59.76	58.77	57.54
Al_2O_3	16.33	17.20	16.90	16.96	18.16	17.86
Fe_2O_3	2.55	1.80	1.95	2.31	3.02	2.81
FeO	1.85	2.42	3.12	3.18	2.92	3.45
MgO	2.65	2.62	3.14	3.80	4.35	3.67
CaO	5.04	5.28	5.89	6.71	7.30	7.29
Na_2O	4.38	4.13	3.42	4.20	2.97	4.04
K_2O	2.13	1.65	2.02	2.16	1.19	1.65
H_2O+	0.08	0.83	1.30	0.15	0.10	0.13
H_2O-	0.01	0.32	0.27	0.08	0.02	0.12
CO_2	....	....	....	....	....	....
TiO_2	0.56	0.50	0.71	0.74	0.72	0.78
ZrO_2	0.01	0.01	0.01	....	0.01	0.01
P_2O_5	0.17	0.20	0.38	0.34	0.20	0.26
So_3	....	....	....	....	....	....
Cl	....	....	....	....	....	....
F	....	....	....	....	(0.01)	....
S	0.01	....	....	....	0.01	....
Cr_2O_3	....	....	....	tr	....	tr
V_2O_3	....	....	....	....	....	....
MnO	0.09	0.08	0.09	0.08	0.08	0.10
NiO	....	....	....	....	....	....
BaO	0.04	0.07	0.03	0.07	0.04	0.02
SrO	(0.03)	(0.05)	....	(0.07)	(0.06)	(0.06)
Li_2O	(0.02)	(0.03)	(0.02)	(0.02)	....	(0.08)
Cu	....	....	....	....	....	....

TABLE III—Continued.

Lavas—Lassen Peak.

Ser. No.*	LP 25	CC 1	LP 35	LP 20	CC 3	LP 45 (12) (13)
SiO_2	57.27	56.62	55.55	55.81	54.71	63.21
Al_2O_3	17.53	16.41	18.68	18.94	15.55	17.15
Fe_2O_3	1.62	1.03	3.51	4.25	1.65	1.30
FeO	5.00	5.30	3.73	3.00	5.54	3.00
MgO	4.10	6.77	4.60	4.42	8.55	2.96
CaO	7.27	7.79	9.06	8.88	8.52	5.23
Na_2O	4.10	2.99	2.33	2.87	3.18	4.12
K_2O	1.17	1.49	1.05	0.78	1.23	2.10
H_2O+	0.28	0.31	0.35	0.35	0.26	0.31
H_2O-	0.14	0.03	0.01	0.09	0.03	0.04
CO_2	....	....	....	....	....	....
TiO_2	0.88	0.76	0.74	0.77	0.66	0.48
ZrO_2	0.01	....	0.07	0.02	....	0.02
P_2O_5	0.38	0.22	0.12	0.16	0.15	0.16
SO_3	....	....	....	....	....	....
Cl	....	....	....	0.01	....	0.02
F	....	(0.01)	(0.02)	....	....	....
S	....	....	0.03	0.04	....	0.03
Cr_2O_3	....	0.06	....	tr	0.06	tr
V_2O_3	....	....	....	tr	....	....
MnO	0.12	0.10	0.10	0.09	....	0.07
NiO	....	....	....	....	....	0.07
BaO	0.03	0.04	0.05	0.02	0.03	....
SrO	(0.07)	(0.08)	(0.07)	(0.06)	(0.03)	....
Li_2O	....	(0.02)	....	....	....	....
Cu	....	....	....	....	....	....

* The numbers in parentheses are serial cross-reference numbers for Tables II and III; they refer also to the appended notes.

TABLE III—Continued.

Lavas—Mt. Pelée.

Ser. No.*	MP 4 (7)	MP 5 (8)	MP 6 (9)	MP 1 (10)	MP 7 (11)
SiO_2	62.05	63.53	62.79	62.51	62.87
Al_2O_3	17.99	17.02	17.61	17.56	17.35
Fe_2O_3	2.11	2.80	3.36	1.94	1.54
FeO	4.13	3.25	2.66	4.15	4.31
MgO	2.21	2.08	1.98	2.12	2.08
CaO	6.48	5.83	6.15	6.19	6.05
Na_2O	3.39	3.59	3.27	3.22	3.41
K_2O	0.97	1.05	0.95	0.98	1.04
H_2O+	0.08	0.16	0.08	0.60	0.42
H_2O-	0.01	0.09	0.03	0.08	0.00
CO_2	....	....	....	....	....
TiO_2	0.50	0.47	0.50	0.50	0.46
ZrO_2	0.003	0.02	0.01	0.02	0.01
P_2O_5	0.23	0.16	0.30	0.20	0.23
SO_3	....	....	....	....	....
Cl	0.03	0.02	0.02	0.09	0.09
F	p.n.d.	p.n.d.	....	p.n.d.	p.n.d.
S	....	0.003	....	0.003	0.01
Cr_2O_3	....	0.00	....	....	....
V_2O_3	....	....	....	....	....
MnO	0.14	0.14	0.14	0.14	0.16
NiO	....	....	....	....	....
BaO	0.02	0.00	0.02	0.02	0.01
SrO	....	....	....	....	....
Li_2O	....	....	....	....	....
Cu	....	....	....	....	....

* The numbers in parentheses are serial cross-reference numbers for Tables II and III; they refer also to the appended notes.

TABLE III—Continued.

Lavas—Hawaii.

Ser. No.*	P 1919 (16) (17)	KMP 1923 (18)	KMA 1923 (19)	KAA (20)	K 1924 (21)	ML '26 1 (23)	ML '26 2
SiO_2	50.19	49.33	49.42	50.50	47.45	51.82	51.34
Al_2O_3	13.34	11.57	11.83	13.31	8.83	13.66	12.94
Fe_2O_3	1.23	2.31	3.83	1.21	1.07	1.50	3.48
FeO	9.85	9.48	8.08	10.03	10.57	9.68	8.42
MgO	7.96	12.41	12.04	6.73	19.66	7.24	7.88
CaO	11.65	9.14	9.28	11.30	7.93	10.09	10.36
Na_2O	2.09	2.20	2.35	2.20	1.72	2.30	2.24
K_2O	0.54	0.44	0.59	0.53	0.13	0.30	0.37
H_2O+	0.09	0.11	0.16	0.26	0.07	0.11	0.04
H_2O-	0.00	0.01	0.02	0.00	0.01	0.01	0.05
CO_2	....	....	....	....	....	....	....
TiO_2	2.60	2.85	2.42	3.63	1.77	2.07	2.22
ZrO_2	....	....	....	....	....	....	....
P_2O_5	0.41	0.37	0.39	0.47	0.37	0.39	0.26
SO_3	....	....	....	....	....	....	....
Cl	0.02	0.03	0.02	0.02	0.03	0.01	0.01
F	....	....	....	....	....	....	....
S	0.07	0.03	0.01	0.08	0.02	0.02	0.09
Cr_2O_3	....	0.08	0.13	....	0.15	0.04	0.04
V_2O_3	....	....	....	....	....	....	....
MnO	0.15	0.14	0.14	0.15	0.17	0.13	0.15
NiO	....	....	....	....	....	....	....
BaO	....	0.02	0.04	....	0.01	tr	tr
SrO	....	....	....	....	....	....	....
Li_2O	....	....	....	....	....	....	....
Cu	....	....	....	....	....	....	....

* The numbers in parentheses are serial cross-reference numbers for Tables II and III; they refer also to the appended notes.

TABLE III—Concluded.

	Lavas—Hawaii			Lava—Niuafoua	Diabases	
	ML '26 3 A	ML '26 3 B	ML '26 4		Md 9 1	NJGD
Ser. No.*	(24)			(25)	(30)	(31)
SiO_2	51.55	51.67	51.38	50.37	51.28	52.40
Al_2O_3	13.59	13.42	13.39	14.65	15.07	13.67
Fe_2O_3	2.33	2.05	2.43	2.19	1.12	1.15
FeO	9.04	9.04	8.80	9.24	9.31	9.16
MgO	8.02	7.97	7.79	7.13	7.97	7.86
CaO	10.31	10.39	10.54	11.74	11.42	10.42
Na_2O	2.43	2.39	2.43	1.88	2.03	2.11
K_2O	0.27	0.27	0.28	0.31	0.27	0.64
H_2O+	0.07	0.26	0.09	0.13	0.39	0.69
H_2O-	0.02	0.01	0.03	0.03	0.09	0.23
CO_2	....	....	....	....	....	....
TiO_2	1.98	2.15	2.08	1.75	0.78	1.19
ZrO_2	....	....	....	0.00	....	....
P_2O_5	0.24	0.49	0.60	0.17	0.13	0.21
SO_3	....	....	....	....	....	....
Cl	....	....	....	0.02	0.00	0.03
F	....	....	....	....	....	0.02
S	....	....	....	0.05	0.06	....
Cr_2O_3	0.08	0.08	....	....	0.05	0.03
V_2O_3	....	....	0.15	0.13	....	0.06
MnO	0.12	0.14	....	....	0.16	0.15
NiO	....	....	....	....	....	....
BaO	....	....	....	0.01	0.00	0.03
SrO	....	....	....	0.00	....	....
Li_2O	....	....	....	....	....	....
Cu	....	....	....	....	....	....

* The numbers in parentheses are serial cross-reference numbers for Tables II and III; they refer also to the appended notes.

NOTES FOR TABLE III.

(1) Dense black obsidian, Big Glass Mountain, California.
(2) Pumiceous phase of same block.
(3) Dense black obsidian (No. 4), Coso Mountains, California.
(4) Coarsely vesiculated portion of same block as No. 3.
(5) Dense black obsidian, Cerro Noagua, New Mexico.
(6) Pitchstone, Cerro Noagua, New Mexico. Apparently a compressed pumice, or incipient pumice.
(7) Hypersthene andesite, Mt. Pelée, Martinique, F. W. I. The series of 1902 lavas. A piece of the old summit pinnacle (Morne Lacroix) which rose above the rim of the old crater. Very fine-grained groundmass but nearly or quite holocrystalline with cavities containing tridymite.
(8) Mt. Pelée. Portion of the "spine" of 1902-3. Groundmass contains pyroxene, feldspar, tridymite, and glass. Fragments of a highly feldspathic and more crystalline rock are present.
(9) Mt. Pelée. Summit of new cone near eastern edge of spine of 1902-3. Ferromagnesian phenocrysts (probably hypersthene) are surrounded by reaction products of a deep red-brown color having strong birefringence and high refractive index.
(10) Mt. Pelée. "Pumice from a nuée ardente July 1902. Lacroix." The cellular glass has few microlites. After heating in vacuo the phenocrysts in some parts of the glass were completely dissolved. Small amounts of hypersthene crystals were filled with a meshwork of glass and embedded in dark glass but no distinct reaction border appeared.
(11) Mt. Pelée. Shell of a breadcrust bomb, 1902-3. Phenocrysts in a slightly bubbly light colored glass.

[In the Mt. Pelée series (Nos. (7) to (11), inclusive), SO_2 was determined instead of listing all sulphur as S_2.]

(12) Lassen Peak, California. A breadcrust bomb, 1915. Surface.

(13) Interior of same bomb as No. 12.

(14) "The volcanic activity and hot springs of Lassen Peak," Arthur L. Day and E. T. Allen, Carnegie Inst. Wash., Publ. No. 360, 1925.

(15) Kilauea lava dipped from the middle of the active lake in 1911 by F. A. Perret. See "Water and volcanic activity," Arthur L. Day and E. S. Shepherd, Smithsonian Report for 1913.

(16) Kilauea. Dipped by pot and chain by T. A. Jaggar. This and the following were parallel runs used to check the analytical method.

(17) Same as No. 15.

(18) Pahoehoe from Makaopuhi flow, 1923.

(19) Aa from Makaopuhi flow, 1923.

(20) Aa from an old flow within the crater.

(21) A peculiar lava erupted from an unknown depth in the 1924 explosions at Kilauea. It looks as though baked and slightly burned, but the ferric iron is not increased and may be slightly low. The olivines are iridescent and shot through with a brownish powder too fine to be determined.

(22) Kilauea. Lava brought up on the sounding-rod used by Jaggar. Lava not analyzed.

(23) Pumice phase of the 1926 eruption of Mauna Loa. From the summit crater, collected by T. A. Jaggar.

(24) From the 1926 eruption of Mauna Loa (Jaggar) from the 1400-foot level. No change could be found.

[Determinations of F_2, SrO, and Li_2O were made much later; the analytical sum has not been readjusted thereto.]

(25) Lava collected by T. A. Jaggar, Niuafoua Island, 1930. From 1929 eruption.

(26) Granite from Stone Mountain, Georgia. Our standard granite used in a number of different studies.

(27) Granite from North Jay, Vermont.

(28) Granite from Barre, Vermont. Contains calcite.

(29) Marvine laccolite, Henry Mountains, Utah. Selected as showing the least alteration of the specimens collected. The feldspars of most specimens were cloudy.

(30) Diabase from near New Market, Maryland. Our standard diabase for various studies.

(31) Diabase from Granton, New Jersey. Shows slight alteration on careful examination.

LASSEN PEAK ANALYSES.

LP/32 Schistose rock from just below the present peak.
LP/18 South wall of the old crater slope. Lookout Point.
LP/2 Top of cliff just above Drakesbad.
LP/34 Gray dacite one-third way up peak.
LP/7 Loose inclusion in flow near west side of crater.
BH/1 North wall above Bumpass Hell.
LP/10 Lava (old?) flow in crater. West end near edge of mass.
LP/28 From shore of Lake Hellen.
BH/3 Southwest lip of basin, Bumpass Hell.
CC/6 Flow between Snag and Grassy Lakes.
LP/21 Inclusion near source of "flow" of 1915 in Lassen Peak crater.
CC/7b Trail between Snag and Grassy Lakes. Half a mile from Grassy Lake.
LP/25 Basalt flow between Tartarus and Geyser.
CC/1 Wall rock, source of the Cinder Cone flow.
LP/35 Inclusion in gray dacite one-third way up southeast slope of Lassen Peak.
LP/20 Inclusion in old wall of the Lassen crater. Large block with dates carved in it going back to 1884.
CC/3 End of Cinder Cone flow containing a few very large quartz masses.
LP/45 Lassen Peak crater. From the 1915 extrusion described by Day and Allen, op. cit., p. 46.

looked a small amount of sericite present.[19] As to the effect of alteration on the volatile content, a little arithmetic may be illuminating. Take the figure 30 cc./g. of rock and note that this means about 90 cc. per cc. of rock of density about 3. A cubic meter of such rock would yield about 90 cubic meters of gas at 1200°, and a cubic kilometer might yield an amount of the order of 90 billion cubic meters of gas if all gas were available. Our table shows that with relatively slight alteration this figure will be trebled, and with noticeably altered material, increased indefinitely.

Table III is added to give the chemical analyses of all materials studied in Tables I and II, and has been extended to include all the analyses which we have made on the suites of rocks from which we selected those examined for volatiles. The remaining analyses may be of service to petrologists, though many of them, especially the Lassen suite, were made before we decided that no advantage would result from outgassing all the series.

Before taking up the geological implications of these gas studies we shall summarize the results thus far.

The following inferences seem to be justified:

1. The distribution of the volatiles in rocks and lavas is largely fortuitous.
2. There is as yet no reasonable way in which either the composition or quantity of the primitive magmatic exhalations can be deduced.
3. This uncertainty follows from the ineluctable contamination to which such gases are subjected on their way to the surface of the earth.
4. With the Kilauea crater as an example it has been shown how this contamination occurs and why no constancy of composition is to be expected.
5. Approximate figures are found for the minimum volatile content of unaltered rocks and lavas, and some light is thereby thrown on the questions of condensation, redistillation and recondensation with the concurrent unpredictable enrichment in one or another element. The importance of this process is emphasized.
6. Chemically the volatiles show the predominance of water, 80 per cent or more, the nearly complete oxidation of the gases, and the absence of notable amounts of hydrocarbons and rare gases.

[19] Obviously there is nothing to be gained by increasing the number of analyses of the altered rocks. There may well be some profit in a series of such analyses if done in connection with an elaborate chemical and geological study of some particular rock mass.

It seems clear that chemical reactions do not constitute the important factor in volcanism that some had supposed. On the other hand, this investigation opens up a more promising field which concerns itself with phenomena much nearer the earth's surface and more accessible to investigation. To this aspect we may now turn our attention.

Once we know definitely what volatiles are present in igneous rocks and their average minimal amounts we may turn to the special considerations and investigations which grow out of our observations. Always in the background hovers the question as to the condition in which the volatiles are present.

If we begin with the simplest case, gases dissolved in solid glassy obsidian, the answer is apparently simple. The gases are in solution in the glass and our interest centers on the possible solubility of these volatiles in the glass. Here we are on solid ground, for we have glasses with determinable quantities of volatiles in them and we have also Goranson's work on the solubility of water in these particular silicate solutions. The field specimen can be checked against the laboratory determinations.

In the first section of Table II we have "selected" field material. We collected a great many obsidians from many sources. This material was then exhausted in vacuo and the water content determined. With a few notable exceptions the majority of obsidians tested were astonishingly dry, for example, No. 1 and No. 3 (Tables II and III) may be taken as typical. The water content is of the order of 0.01 per cent taken on the unground material and the total volatile content is only about 1.5 cc./g.

Of the dozens of obsidians tested, this dryness is the outstanding, if irritating, characteristic. Adjacent vesiculated parts of the same block, such as No. 2 and No. 4 (Table II) show more gas, but one can not tell with certainty how much was in solution in the glass and how much adsorbed on the surface.

Numbers 5 and 6 are of quite different behavior. These two specimens we owe to Doctors Ross and Larsen, who collected them near Cerro Noagua, New Mexico. No. 5 is a splendid black (transparent in thin section) glass with over one per cent of volatiles, and yields 55 cc./g. It is the best material thus far received, though it was not found in place and a further supply has not been obtainable on search. No. 6 is a cream-colored rock with somewhat resinous fracture like a

pitchstone and contains a few large albite phenocrysts which appear to be undissolved residues rather than the beginnings of crystallization. It was examined by H. E. Merwin, who found in it very fine elongated vesicles.[20] Computed to a dry basis, these two rocks are identical (see Table III). Although the water may be in solution in both glasses, the physical behavior is different. Upon being heated, No. 5 remains unaltered until (depending on the time and temperature) at 800° after 15 minutes vesiculation begins and continues until the gases are expelled. The mass puffs up into a pumice with large thin-walled vesicles. No. 6 remains unaffected under these conditions and can be induced to puff only by very rapid heating to nine hundred or a thousand degrees. The difference is that No. 5 loses only surface water until vesiculation begins—that is, the water is held firmly in the solid glass. No. 6 begins to lose water as soon as heat is applied and evidently there is no difficulty in the escape of the volatiles. The very slight puffing of this glass seems to be confined to water in solution in the septa between the pores. Heated in vacuo to 1200° for some hours, the chips of No. 6 slump down to a viscous clear glass, whereas No. 5 puffs and after losing its water is too viscous to flow together under its own weight, though, given time, it slowly slumps down.

In heating these obsidians one very important phenomenon appears at once. For these "wet" glasses (and the same would be true of the mother liquor of a crystallizing magma) a rapid change in the apparent viscosity is caused by relatively insignificant concentrations of volatiles, when a block of No. 5 (1.25 per cent volatiles) reaches the vesiculating temperature it flows, i.e. froths, around and through small obstacles, or in a tube it froths all over the inside. But once the volatiles are out, the septa and shreds of glass remain indefinitely rigid. It requires much time and a much higher temperature before the mass begins to gather itself together again. This quick shift from

[20] There is no satisfying criterion by means of which one can discriminate between an incipient pumice, that is, a magma whose pressure has been reduced enough to permit vesiculation to start and which if brought to the surface would expand to a pumice, and a magma supersaturated at the pressure and temperature acting on it, so that the second phase, silicate in water, appears in accordance with Goranson's data. We have one tuff (showing 5.3 per cent total H_2O) from the Salton Sink region many of the glass shards of which were found by H. E. Merwin to contain liquid with various-sized bubbles. Such material seems to fit the two-phase picture. The absence of such vesicles in the Cerro Noagua No. 6 would seem to place it in the incipient pumice class. No sharp dividing line would be expected.

fluid to rigid glass has obvious importance both for volcanology and petrology.

Heated in vacuo, both No. 5 and No. 6 lose water; surface water escapes rapidly, and the remainder diffuses out slowly. Thus an 8 gram cylinder of No. 5 lost only 0.006 per cent in weight (about 7 per cent of its total water) in three months at 400° C. Under similar treatment, No. 6 lost 2.3 per cent (70 per cent of the total) out of its total of 3.25 per cent water in 1 hour and at only 300°, after which rapid loss in weight the rate dropped to about 0.01 per cent in twelve hours. Since the surface of No. 6 is indefinitely greater than that of No. 5, only the general form of the curves is comparable. To obviate as far as possible the effect of the difference in surface, both No. 5 and No. 6 were powdered, placed in a capsule, and heated at 300° in vacuo. In thirty minutes No. 5 lost 0.16 per cent (about ten per cent of its total water) and No. 6 lost over 70 per cent of its content. After nine hours No. 5 had lost less than 30 per cent, and No. 6 about 87 per cent. The experiment can not be conclusive, but it points to the same inference as that made from the observations of the coarser material.

The search for a series of obsidians with increasing water content has been a bit trying, for the water is not uniformly distributed throughout any given field exposure. Only by testing each specimen in the field can one avoid collecting an unconscionable load of dry material.[21] Messrs. Greig and Schairer made some collections in the New Mexico area, testing the material with a blowpipe. From one exposure they secured a number of good specimens, but none with a high water-content. It was possible, however, to select from their collection a series running between one-tenth and eight-tenths per cent water. This series is very useful for experimental purposes as we are not yet able to make synthetic mixtures in sufficiently large pieces for all the tests one may wish to apply. Certain important tests can be made with the present series. The significant fact is that most of the dense glass found in the field contains very little water and can flow if at all only at temperatures far above those which for other reasons we have associated with eruptions. We have made a number of experiments touching the diffusion rate of water in obsidians.

[21] This is the more surprising because great masses of obsidian are known where there is no difference of chemical composition over great areas (Little and Big Glass Mountains, Table III), and although these masses are usually uniformly dry, occasional specimens may occur with varying degrees of wetness. Similar conditions obtain at Cerro Noagua.

The data are not yet ready for discussion, but we may say that up to 1.25 per cent of volatiles the rate is not noticeably different from that expected according to the usual diffusion formula. The implication is that water does not enter or leave these glasses with any unusual ease at temperatures up to 500° at any rate. Dehydration studies at temperatures above 500° are not feasible because above that a glass with one per cent or so of water will slowly develop vesicles, and at lower temperatures the rate of weight loss drops to practically zero. As Goranson's studies show, we are not to expect a high water-content in any glass which arrives at the surface hot. Fifty atmospheres of pressure, or more, are required to prevent these glasses from vesiculating. It follows that we may only hope to obtain water-rich material from dikes or sills which have been exposed by erosion, because notably wet glass will vesiculate or explode if brought to the surface at any temperature at which it is able to flow.

Although the time factor enters into our experiments and confuses our observation and deductions in both field and laboratory, we can show experimentally that the viscosity of these and presumably all magmas is profoundly altered by the amount of water present. For example, a weighted prism of the dry Coso Mountain glass (Table II, No. 3) showed no bending when heated 24 hours at 575° C., and the wet Cerro Noagua glass (No. 5) was slightly bent and breadcrusted under the same conditions. We know that in 15 minutes at 900° the Coso glass remains unaltered and the Cerro Noagua has expanded into a very light pumice. But for anything one would call flow in the field sense, temperatures above 600° are needed even with the Cerro Noagua glass. However, this same glass, given time, will start vesiculating at 600° or even lower, and with rising temperature vesiculates more and more readily unless the pressure is high enough to hold the water in solution. The time factor, that is, the time required for vesiculation to get under way, enters the problem unpredictably except for the general rule that the more water present the more readily vesiculation starts. This point is nicely shown in the following experiment, which is similar to the Seger cone method of temperature determination. Place a series of small chips of obsidian of differing water content on a refractory plate and set the plate in the furnace for a fixed time and at a series of temperatures. Take, for example, obsidian chips containing respectively 0.1, 0.3, 0.5, 0.7, and 1.2 per cent total volatiles

(we use gases, volatiles, and water interchangeably because water is so overwhelmingly dominant), and start at 800° with a 15-minute heating period. Except for the last (1.2 per cent water) which is unstable above 600°, none will show any change. The one with 1.2 per cent water may vesiculate. With a longer exposure or with slightly higher temperature, the 0.7 per cent glass may show changes. At 900° the 1.2 per cent will at once expand to pumice and the 0.7 per cent may start to vesiculate; the others remain unaffected except that at above 700° all these obsidians bleach more or less and do not darken on cooling down. As the experiment is continued the less hydrated samples will vesiculate in regular order as the temperature is raised, until at about 1200° the material with lowest water content will in time show a few scattered vesicles. The degree of vesiculation, the size of vesicles formed and the thickness of the septa between them, vary also with the water content. For the samples with little water content, temperatures around 1200° or more, as well as ample time, will be needed before they will deform under their own weight. In fact, the dry glass is so astonishingly rigid that we are not yet able to imagine its flowing in the ordinary sense of lava flows. That it may be slightly plastic is evident in the field but it seems more likely that these dry masses reach the surface carried along with and surrounded by a shell or shells of more fluid material, and that the latter is for the most part carried away explosively.

The above-cited experiments on the relation of volatile content to viscosity have an important bearing on the mechanism of extrusion and lava flows. In the interval where vesiculation occurs the glass is notably fluid, the expanding pumice can froth around and between obstacles. But once fully expanded, that is to say, once the volatiles have been liberated, the foam becomes rigid. Unlike most foams known to us, this material is no longer mobile. Expanding into a crack or fissure it can effectively seal it. Masses of foam act like solid objects in the magma. Instead of increasing mobility as with ordinary froths, this rock foam decreases it and may block movement by clogging the pathway. The reverse reaction is of course possible. A mass of this foam if trapped and subjected to heat and water at sufficient pressure will of course collapse and become fluid again. These observations are helpful when we try to picture the mechanism of flowing lava, of extrusion, or eruption. The fact that the effective viscosity varies so greatly

with relatively small change in the volatile content is very illuminating!

The experiments outlined above show that the time interval varies with temperature, pressure, and volatile content. Vesiculation both chills and stiffens the mass and some time must elapse before the temperature is readjusted to a point where further vesiculation or explosion will occur. This mechanism should be particularly noticeable for the final mother liquor of a partly crystallized rock.

Since the rate of diffusion of water vapor through the obsidian shows no unusual speed, that is, seems to obey the usual formula, and does not behave in a special manner, like hydrogen and palladium, it follows that these huge masses of dry obsidian as found in the field can hardly be thought to have lost their water content after arriving at their present emplacement. Apparently they have never been very wet. The possibility exists that these dry masses may represent lenses carried along by the wetter, less viscous envelopes. The Mono Craters as described by Russell[22] seem to have been formed in some such fashion. Each crater has a central plug of dry and rigid glass. In a few places the plug shows a slight bending, or overhang, of an otherwise vertical outer surface. Most of the plugs were evidently not plastic enough to bend under their own weight. The edifice is in all cases constructed of pumiceous material and ash. There is no way of knowing whether the entire glassy mass was originally laid down as a dry core with wet envelopes or whether the envelopes represent a reactivation of an originally dry magma, where the reactivation had not yet penetrated to the core before eruption occurred.

With the less acid crystalline rocks, andesites and dacites (Table II) we find 6 cc./g. to be the common and presumably average residual gas content of our selected material. The exception, MP 1 (Tables II and III) being a chilled breadcrust surface. The Lassen Peak material contains more gas and also shows slight alteration. This figure, 6 cc./g., continues through the Hawaiian lavas, with one notable exception, No. 21.[23]

[22] Russell, I. C.: Volcanoes of North America, p. 217, 1910.

[23] This No. 21 is a peculiar olivine basalt erupted during the phreatic explosions of Kilauea in 1924. It reached the surface apparently barely red hot, and in blocks, but not as fresh lava. As the analysis shows, it is not a fumed and decomposed rock. The iron is normal, it is not oxidized, magnesia is naturally high, and the alkalis a little low. The rock appears normal enough except that the olivines are iridescent. The indications are

The plutonics examined show a different order of "normal gas content." Here (Table II) the figure is about 30 cc./g., but it will be much greater if alteration of any kind has occurred during the rock's history.[24] Unfortunately, there is no clue as to what part of the volatiles belongs to the rock initially and what part is secondary. We can not determine the pore space or surfaces and can not distinguish between surface chemical reactions and adsorption. There is a tendency toward a low CO_2 for unaltered rocks, and where sulphides are present H_2S will appear in the gases given off. The sublimates as deposited in the SiO_2 tubes on out-gassing these rocks show much SiO_2 along with varying amounts of Fe, Cu, Zn, Mo, etc.[25] The study of such sublimates and their relation to fumarolic and mineral deposits has not yet been undertaken.

We do not know in what condition the gas is held in the rock and we do know, as Chamberlin found before us, that it is not a simple adsorption. The gas pumped out is not reabsorbed in any notable degree, just as the water pumped out of obsidians at relatively low temperatures, 300-500°, is not restored on subjecting the rock to an excess of water at atmospheric pressure. Then, too, as Chamberlin found, even though

that we have here a rock which has been reheated, but in an effectively neutral atmosphere. From the total volatiles alone (compare the other Kilauea lavas cc./g. in Table II) we get our idea as to the treatment to which this lava has been subjected just as an excessive gas content indicates a different record.

The absence of oxidation is suggestive of conditions at no very great depth in this volcano. The extremely porous nature of the Kilauea edifice would lead one to expect a free circulation of air and oxidizing conditions, yet these 1924 explosions which eviscerated the core of the volcano brought this and other products of a non-oxidized character to the surface. For example, there had existed for many years a series of hot cracks (the Devil's Kitchen) which exhaled a mixture of steam, SO_3, SO_2, and free sulphur. The surface rock was disintegrated to sulphates and sulphur, giving the impression of intense oxidizing action, and yet from beneath this area large quantities of ferrous magnesium sulphate were erupted. Oxidation, then, seems to be a surface phenomenon which requires a much greater freedom of air circulation than even the Hawaiian volcano structure permits. This point is significant for those who seek to derive volcanic heat from oxidation and reduction reactions. The Hawaiian type of edifice is so very open to air circulation that if such reactions are important they should be noticeable here. They are not.

[24] We found that the figure of about 30 cc./g. could be readily explained by taking into account the volatiles in micas and hornblende, and some adsorbed water, that is, the average minimum content as computed from the hydrous minerals is of the same order as the value found experimentally for carefully selected granites. If there is more than this amount of water and it is unable to escape readily, then alteration will be noticeable.

[25] A preliminary spectroscopic examination for which the writer is indebted to his colleague Dr. E. G. Zies.

the gas be partly reabsorbed, it will have undergone a change of composition when re-evacuated. Not being able to determine the surfaces and dimensions of the cavities present we have no way of linking our analyses to what is now known about adsorption phenomena. We have found that traces of alteration (of whatever origin) increase the total volatiles notably above our averages for the best material obtainable and this increase in volatile content runs parallel with increased alteration.

For the granites Goranson[26] has given us our first definite data as to their melting temperatures. It has long been believed that instead of being a high-temperature rock as the early studies of the melting temperatures of rocks implied, granite was formed at relatively low temperatures, 500-600° C. being a not wholly absurd figure as judged by the minerals present. Goranson found that at 700 ± 50° the Stone Mountain granite No. 25 would be completely liquid with 6.5 per cent water at a pressure of 1000 bars. But our tabulated data involve no such water content; evidently the volatiles have largely escaped or were not present initially.

A relatively low water concentration would give to the last portion of the crystallizing mother liquor a rather high and at times explosive (Mt. Pelée) volatile content, yet if we consider the relatively few plutonics which show cavities or pronounced alteration by their own volatiles the implication is that their volatile content is not particularly high. Of course this point is a matter of opinion and not subject to proof. However, if one runs over in one's memory the innumerable igneous contacts where apparently little or no alteration showed, and other areas not apparently different as to the facilities for escape of volatiles in which profound alteration appears at the contact, it seems to us a fair inference that while in general the volatile content of the magma has not been at all high, in special cases there has evidently been a concentration of volatiles either in the magma or in the environing rock which has produced great changes. Those who prefer to consider the volatile content of magmas as high because of the enormous quantities of gas given off by volcanoes should not overlook this possibility of local enrichment either of the magma or country rock. That a magma can absorb water was shown in Adams and Goranson's work. Since they find that the solution of water in the

[26] Goranson, R. W.: The solubility of water in granitic magmas, Am. J. Sci., *22*, 481, 1931; Some notes on the melting of granite, ibid., *23*, 227, 1932.

melt is an exothermic reaction, the much disputed question of whether a magma can take up water, meteoric or other, and thereby be rendered "explosive" is answered in the affirmative.[27]

Of course our data can not tell us how much gas may have been in the lava before it reached the surface but we have Goranson's work which shows that not more than ten per cent of water can occur in a granitic magma without the appearance of a second phase, silicate dissolved in water. That being true, the relative scarcity of drusy granites indicates that we seldom have to deal with such excessive volumes of water in granites. Goranson shows that at 900° nine per cent of water will form a second phase, that is, develop drusy cavities at 3000 bars pressure corresponding to about eleven kilometers depth while with only six per cent of water cavities should appear at a mere four kilometers. It is a reasonable inference that such excessive amounts of water are uncommon. On the other hand, drusy plutonics are known, showing that under some special conditions these high volatile concentrations do occur.

We must not overlook the important fact that certain special conditions are required before a magma can absorb water. Some volcanologists have written as though all that was required was for a magma to come in contact with meteoric water. This is no more true in depth than at the surface, for while steam explosions do occur when a hot rock comes in contact with water, we now know that for the water to be

[27] A cubic kilometer is no great volume of the Earth's crust; much larger lava outpourings are common. With only the average volatile content for unaltered rocks (30 cc./g., a few tenths of a per cent by weight) a cubic kilometer might yield some ninety billion cubic meters of gas if raised to 1200°. To pass this volume of gas through a 100-meter conduit (i.e. an orifice of 7854 square meters) in twenty-four hours requires that the gas issue at a rate of 477,000 meters per hour, 296 miles per hour or nearly five miles per minute. With a more restricted orifice the phenomena would be even more impressive.

One would not expect any such complete release of volatiles, but the figures serve to indicate that a few hundred degrees rise in the geotherms of a region, especially if the rocks have been previously enriched in volatiles to the extent of only a per cent or so, will release enormous volumes of gas. Enough gas can evidently be obtained from the country rock to account for many volcanic phenomena without postulating excessive concentration of volatiles in the advancing magma.

If the water content is of the order of 3 per cent as with the pitchstone No. 6, or of 5 per cent as with some others, then the available gas reaches an amazing volume. These very "wet" rocks are comparable to explosives and act similarly if suddenly erupted. For example, black powder yields only 1500 cc./g. at 1200°, 760 mm., and the "high" explosives about 4300 cc./g. In comparison, the material with which we have been working does not class as a high explosive though Mt. Pelée developed such qualities at times.

absorbed by the magma this foreign water must be at such a temperature and pressure that the reaction moves in that direction, otherwise the heat merely evaporates or distills the water. Yet water under sufficient head or water trapped by impervious strata will be absorbed by advancing magma once the conditions are fulfilled.

It seems to us that a more reasonable and illuminating picture of subterranean phenomena is obtained if we take into consideration what may be expected to happen when magma from below advances into the crustal layers. The most casual field observation teaches us that although some large areas have been little disturbed, many show not one but repeated invasions of magma. For example, in the Crazy Mountains, or the Highwood Mountains of Montana and the neighboring country, as at Shonkin Sag Laccolith, we have a much troubled area shot through with sills and dikes in a most puzzling manner. For the majority of contacts observed there was no apparent alteration of the country rock but at certain places apparently the volatiles were trapped in such manner that intense alteration was produced (Haystack Butte). With the mechanism of injection we need not concern ourselves; it is sufficient that it occurred.

On a simpler scale, let us picture what happens to the volatiles of the country rock when subjected to such treatment. We shall assume (which is of course not true) a uniform distribution of volatiles in the country rock. If this area is invaded by hot magma, this by raising the geotherms will cause the volatiles in the affected area to move over to be recondensed in cooler areas. In addition, volatiles brought up by the magma may be expected to penetrate the area and be condensed also. Some of the strata of areas penetrated by the magma may be relatively impervious to the volatiles or their condensates. We have then a spotty distribution of volatiles scattered through the country rock. This is the fundamental explanation for what we have already observed in our analyses; that while rocks selected for the absence of alteration show a common volatile content, altered rocks may show many times that quantity; that the quantity which we find in any rock will be purely a chance figure depending on the past history of the rock.

Now it is common observation that the first phase of an eruption sends, primarily, the halogens (the most volatile) outward or upward, and it is equally true that the dying out of the eruption is accompanied by the exhalation of the sulphur

gas and other less volatile constituents. We are to expect, therefore, an enrichment in halogens at the greatest distance from the heated areas and enrichment in sulphur nearer the dike or conduits. A new rise in temperatures, as at the beginning of an eruption, will move the halogens first, the rest following according to their volatility. It is obvious that if the country rock is inhomogeneous (as it usually is) then some areas will be relatively impervious and others will allow free passage to the moving vapors. Again we have an unpredictable distribution of volatiles.

If, now, after a period of rest the area is again injected with magma, not only will new volatiles be introduced but old ones will again be set in motion. Certain areas have now been several times fumed and cooled. It is easily fancied that conditions being right this mass may have its temperature raised and its volatile content so increased that it will be either remelted or partially melted and rendered potentially mobile. It does not strain the imagination to account in some such way for the appearance of a rhyolite or andesite from a crater initially basaltic or vice versa.

Something of this sort may have happened at Katmai and the Valley of Ten Thousand Smokes. Here we may suppose that we have a sill of new magma injected beneath an old water-soaked valley. Had the load above been sufficient it was entirely possible that even if the magma was not already saturated, the water from the country rock would be absorbed until some balance was attained or until a break or other dynamic disturbance set it free. If some of the magma was initially more hydrated or acquired more water than other portions, or if the surface of the sill became hydrated, then there would be a very reactive shell around a mass which might be hot but less mobile in the interior. In such a case the Novarupta plug, which in some respects seems similar to the Mono Crater plugs, would be one manifestation while the lava which gave the "sand flow" also fits into the picture.

Meanwhile we must suppose that the long accumulation of volcano residues in the old valley has been providing its own kinds of entertainment. For our present purposes it is not too important whether the above picture of Katmai is the real picture or not, but it may serve to indicate why the gases in rocks are unpredictable in both amount and distribution and yet may be very important in relation to volcanology and related problems. The more one looks at the problems with this pic-

ture in mind the more clearly many field observations seem to fit into it. Hybrid rocks, and the slow digestion of xenoliths become intelligible since we are in this case dealing, not with the initial energy of the cooling magma but with energy from other sources working on separated portions of the old magma. That means that equilibrium conditions will be quite different. It means also that in a much disturbed region rocks may be worked and reworked not once but many times and elements not usually considered mobile be variously transported, concentrated, and recombined.

With Goranson's study of the melting of granite and the relation of water to it, we can see that the partial or complete remelting of the acid rocks, at any rate, can occur and at no great depth. The temperature observed at volcanoes average somewhere between 1000 and 1100°. To melt a granite, assuming a supply of heat from an invading magma and sufficient water under pressure,[28] involves not more than 750° and for partial remelting perhaps 600°. The solution of water in a magma is accompanied by a heat evolution as yet undetermined, but known to be large. But whether these speculations as to volcano mechanisms be true, partly true, or sheer nonsense, we still have left the irregularity of total volatiles, and from Goranson's studies ample means to explain the altered condition of most plutonics. The zoned and fractured feldspars may involve more movements than we formerly thought possible, but we must allow not only the reactions involving water, but also the secondary ones involving CO_2,[29] the halogens, and sulphur. We no longer need, as formerly, to try to explain such changes exclusively by shifting pressure during crystallization of the primary magma. It is evident that an attack can now be made in this formerly impregnable field of study. To this work our apparently negative results contribute their mite for purposes of orientation.

[28] Goranson's data also imply that meteoric water given opportunity need penetrate to no astonishing depth before the hydrostatic pressure becomes sufficient to enter into the reaction if the temperature has been raised to five or six hundred degrees by any mechanism one wishes to assume. The observed fact that some deep mines and bore holes are very dry is cancelled by the fact that others are very wet. Mines in highly porous strata can not be extended to great depths.

[29] Feldspars are evidently surprisingly reactive (see C. N. Fenner: Borehole investigations in Yellowstone Park, J. Geol., 44, 225, 1936). We may expect further any of the alkali-rich minerals to break down at least superficially in a water—CO_2 mixture to form various hydrated-carbonated mixtures whose effect on the gases potentially available will be unpredictable.

Some of these considerations may seem elementary, but they are not necessarily so to the chemist or laboratory worker who has some difficulty in extrapolating from test tubes to batholiths. To these we would point out, as we too have had to learn, that the earth's crust may be "solid" but is only relatively so, and it is certainly not static or dead. When we take into account the volatiles in the minute pores of the rocks, and the shift of these with the continuous changes in temperature and pressure, the effects of loading and unloading due to erosion, isostatic readjustments, shifting geotherms, and the continuous bending up and down due to the earth tides, the picture is that of moving, breathing masses, in constant flux.

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