

# Data of Geochemistry

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## *Sixth Edition*

### *Chapter K. Volcanic Emanations*

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GEOLOGICAL SURVEY PROFESSIONAL PAPER 440-K



# Data of Geochemistry

## *Sixth Edition*

MICHAEL FLEISCHER, *Technical Editor*

### *Chapter K. Volcanic Emanations*

By DONALD E. WHITE and G. A. WARING

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GEOLOGICAL SURVEY PROFESSIONAL PAPER 440-K

*Tabulation and discussion of about 300 chemical analyses of volcanic gases, volcanic sublimates, incrustations, and reaction products, and gases driven from igneous rocks by heating*



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# DATA OF GEOCHEMISTRY, SIXTH EDITION

Michael Fleischer, *Technical Editor*

The first edition of the Data of Geochemistry, by F. W. Clarke, was published in 1908 as U.S. Geological Survey Bulletin 330. Later editions, also by Clarke, were published in 1911, 1916, 1920, and 1924 as Bulletins 491, 616, 695, and 770. This, the sixth edition, has been written by several scientists in the Geological Survey and in other institutions in the United States and abroad, each preparing a chapter on his special field. The current edition is being published in individual chapters, titles of which are listed below. Chapters already published are indicated by boldface.

- CHAPTER
- A. The chemical elements
  - B. Cosmochemistry
  - C. Internal structure and composition of the Earth
  - D. Composition of the earth's crust
  - E. Chemistry of the atmosphere
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  - L. Phase equilibrium relations of the common rock-forming oxides except water
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DATA OF GEOCHEMISTRY

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VOLCANIC EMANATIONS

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By DONALD E. WHITE and G. A. WARING

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ABSTRACT

About 250 chemical analyses of representative volcanic gases are tabulated, with emphasis given to analyses with measured temperatures and minor-element data. The most sustained attention has been given to volcanic gases by Russian and, more recently, Japanese geochemists.

Compositions of gases are clearly related in part to temperature at the point of collection. In spite of long-standing interest in the changes in composition of exhalations with time and distance—as distinct from temperature and other factors—little critical information has been obtained.

The study of compositions of fumarolic sublimates and incrustations is largely qualitative, or consists largely of identification of minerals. Problems in determining which components were precipitated from vapor and which were derived by acid attack on surrounding rocks have seldom been resolved with confidence.

Little interest has been shown in the compositions of gases in rocks since E. S. Shepherd's classic work. Selected analyses by Shepherd are reconsidered. Much can be learned from gases in rocks, as a valuable supplement to studies of natural fumaroles and theoretical approaches.

INTRODUCTION

Relatively little attention has been given to the volatile components of volcanic rocks as compared to the solid phases; doubtless this is due more to difficulties involved with collecting and analyzing reliable samples than to lack of interest. Careful systematic work has in general been attempted for only short periods of time, as at Hawaii (Shepherd, 1921), the Katmai region (Allen and Zies, 1923), Showa-shinzan (Nemoto, Hayakawa, Takahashi, and Oana, 1957), and Vulcano (Sicardi, 1956). In contrast, Kliuchevskii and Sheveluch in Kamchatka have been studied systematically for more than 20 years. (See reviews by Basharina, 1958a, and Naboko, 1959b.)

Much effort was made in this compilation to find all analyses of volcanic gases that have been published; a few may have been overlooked. Particularly close attention was given to literature published since Allen's review of volcanic-gas analyses in 1922 (Allen, 1922). Special interest was given to analyses that were accompanied by temperature measurements and that included minor components.

The great variety of forms that have been used in reporting gas analyses has presented special problems.

Most analyses are stated in volume percent, but a few are in weight percent; where neither is clearly stated, volume percent is assumed.

The analysts' methods of stating or computing data for contents of water and air have differed greatly with time and place. Steam, when determined, is sometimes included in the summation of 100 percent; where excluded from the principal summation, it has been stated in either weight or volume percent of total gases, or in milligrams per liter of other gases. Air has likewise been stated in a variety of forms; N<sub>2</sub> and O<sub>2</sub> have been included in the principal summation, O<sub>2</sub> and equivalent N<sub>2</sub> for air have been excluded from the principal summation, or all N<sub>2</sub> and O<sub>2</sub> have been excluded on the assumption that essentially all N<sub>2</sub> was from air but some O<sub>2</sub> was consumed in oxidizing reactions. Gas analyses have been published in at least a dozen different forms, no one of which is directly comparable to the others. Much thought has been given to the problem of deciding the most useful form for reporting this compilation; all the determined gases other than H<sub>2</sub>O, O<sub>2</sub>, N<sub>2</sub>, and Ar are for convenience included in a group called the "active" gases, and are here recomputed to 100 percent (Naboko, 1959a). We believe that this method permits the most useful comparisons; O<sub>2</sub>, N<sub>2</sub>, Ar, and H<sub>2</sub>O where given in original published analyses are also included in separate columns. The reader should note that air, O<sub>2</sub>, and H<sub>2</sub>O not included in the author's principal summation of 100 percent are shown in parentheses.

This system of presenting the data has required a minimum of recomputation, and has the major advantage that the "active" components, which are commonly of greatest interest, can be directly compared. The major problems of atmospheric and (or) volcanic origin of H<sub>2</sub>O, N<sub>2</sub>, and even O<sub>2</sub> are also thereby isolated to a considerable extent.

In many gas analyses, the published record indicates that effort was made to determine only one, two, or three of the "active" gases. A relatively thorough search for many gases has been made in some of the samples from the Hawaiian, Alaskan, and, in recent years, the Kamchatkan volcanoes. An outstanding



example of completeness of search is that made by Oana at Showa-shinzan (Nemoto, Hayakawa, Takahashi, and Oana, 1957, p. 122-123; written communication, 1961; and this report tables 1A and 4). Many components of special interest are present in the original gases in such vanishingly small quantities that precise analysis is most difficult. A large number of these components of special interest are soluble in or are precipitated with condensates of steam, and can then be determined with considerable precision (tables 2, 3, 4).

#### VOLCANIC GASES AND CONDENSATES

The chemical composition of a fumarolic gas is presumably dependent upon the following: (a) Original abundance of each volatile component in the magma. (b) Temperature of evolution of the gaseous mixture from the magma, and temperature at the point of collection. (c) Time since evolution started; if differences in solubility exist, the more insoluble gases should be enriched in early emanations. (d) Place of evolution: crater fumaroles above a vertical vent should contain gases evolved from different depths but gases from lava vents and flows may be evolved from negligible depth. (e) Degree of mixing and reaction with air and meteoric water. (f) Reaction with rocks between places of evolution and collection. In addition to the above, some reaction may occur in unstable mixtures between times of collection and analysis, and amounts reported by the analyst depend on the quality of his work and the specific components for which he searched. Analyses of volcanic gases clearly represent at least to some extent unstable or changing conditions intercepted at some chance moment.

The data in tabular and graphical form (tables 1-5 and figs. 1-6) demonstrate the great ranges of concentration that have been reported for all components. An effort will first be made to generalize on quantities of components that may be present and possible direct relations to temperature at time of collection.

1. Steam, where determined, is with few exceptions the greatly dominant gas, generally in excess of 90 percent of total gases.
2. Total air, when reported, commonly exceeds the "active" gases and may be greatly dominant over these gases even when much effort was made to exclude it. Air is a particularly abundant contaminant of gases escaping through porous lava and is generally less important in gases escaping directly from molten lava or from water of hot springs; it is also notably minor at Showa-shinzan (table 1A).
3. CO<sub>2</sub> is generally the dominant "active" gas, particularly at low temperatures. The proportion of CO<sub>2</sub>

in the "active" gases commonly decreases with increasing temperature (fig. 1), probably because of an increase in other gases rather than an absolute decrease in CO<sub>2</sub> per unit of source lava. An increase in "active" gases with increasing temperature, relative to H<sub>2</sub>O, is particularly well shown in the 1954 series of analyses from Showa-shinzan, Japan (tables 1A and 4), and from some other localities.

4. CO has been reported in excess of CO<sub>2</sub> in many Kamchatkan analyses (table 1B), particularly from the fumaroles above 150°C from basaltic Kliuchevskii volcano. In other areas, CO has been reported in excess of CO<sub>2</sub> in only a single sample from Hekla in Iceland (table 1F); only minor CO was found in the careful study of fumaroles of the hypersthene dacite dome of Showa-shinzan (tables 1A and 4), and from Hawaii. This anomaly demands careful study; it suggests that the environment of some basaltic volcanoes is an unusually reducing one.
5. CH<sub>4</sub> is commonly not reported; where found, quantities seldom exceed 1 percent. Novarupta, Alaska (4 to 14 percent, table 1C), and "The Geysers", California (15 percent, table 1C), are notable for relatively high contents of CH<sub>4</sub>; even larger amounts are reported in single analyses from Mount Pelee (table 1F) and from a submarine eruption in the Azores (table 1F). CH<sub>4</sub> is most erratic in occurrence, and a volcanic origin for it is doubtful (Basharina, 1960, p. 21), although thermodynamic considerations (Krauskopf, 1957, p. 797) indicate that CH<sub>4</sub> is to be expected under rather strongly reducing conditions.
6. A search for NH<sub>3</sub> has been made in only a few volcanic gases. When looked for, it is generally minor or absent. Ammonia is suspected to be nonmagmatic by some (Shepherd, 1938, p. 322; Rubey, 1955, p. 642-645; White 1957, p. 1672), but is believed to be magmatic by others (Rayleigh, 1939; Urey, 1952; Ellis, 1957, p. 423; Krauskopf, 1957, p. 797; Stevenson, 1960). Recently Wlotzka (1961) has found that nearly all igneous rocks contain from 5 to 50 ppm of NH<sub>3</sub>-N, with an average close to 20 ppm; this evidence is strong support for a magmatic origin for some ammonia. It may also result from high-temperature reactions between volcanic H<sub>2</sub> and atmospheric N<sub>2</sub> (Nemoto, and others, 1957, abs. p. 20), and much is clearly of organic origin.
7. The abundance of H<sub>2</sub> is highly erratic; H<sub>2</sub> is commonly absent, but exceeds 40 percent of the "active" gases in many samples from the basaltic

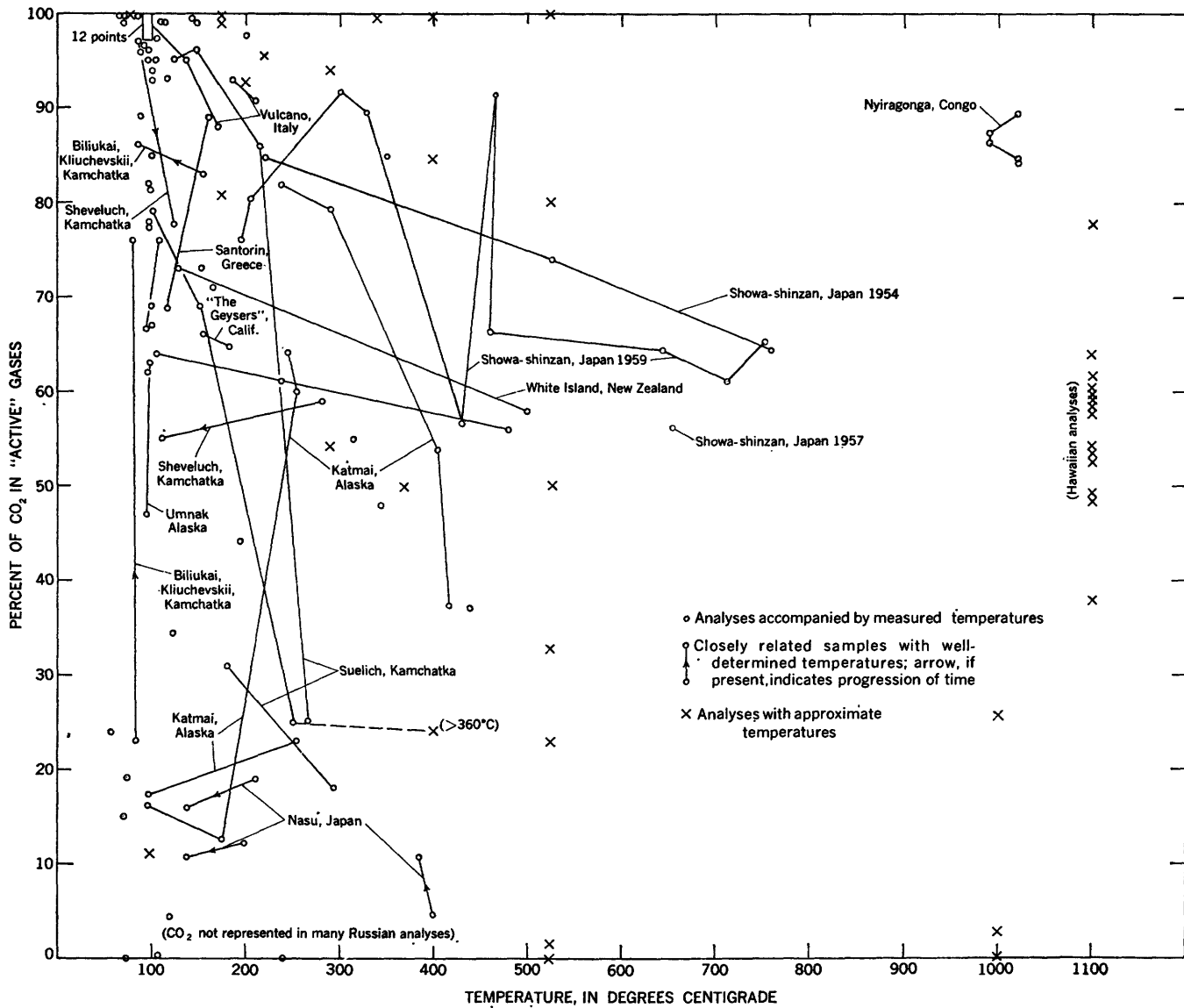


FIGURE 1.—Content of  $\text{CO}_2$  in "active" gases, relative to temperature.

- volcano Kliuchevskii (fig. 2), also notable for its high proportion of CO to  $\text{CO}_2$ . Lava of this volcano seems to be unusually deficient in oxygen.  $\text{H}_2$  in general decreases with falling temperature at Showa-shinzan, Japan (fig. 2), and also at times in the Kamchatkan volcanoes Kliuchevskii and Sheveluch; one series of samples from Zavaritskii crater of Kliuchevskii, however, clearly show a decrease in  $\text{H}_2$  with increasing temperature (fig. 2).
8. The HCl content shows little tendency to increase with increasing temperature (fig. 3); many high-temperature fumaroles contain little or no detected HCl, and other low-temperature fumaroles are notable for its abundance. It was the greatly dominant acid gas of the Katmai region (table 1C; Zies, 1929, 1938).

9. HF has been determined in relatively few fumarolic gases; it is generally less than 10 percent of the reported HCl, but it is relatively very abundant at Katmai (table 1A) and at Showa-shinzan (table 1A and 4). Analyses of fumarolic condensates (tables 2 and 3) indicate that the ratio F/Cl is commonly 1:1,000 to 1:10. The relative abundance of F in fumaroles of the dacite dome of Showa-shinzan and the rhyolite ash deposits of Katmai suggest that F/Cl may increase with increasing silica content of lavas. The analyses by Oana of the remarkable collection from Showa-shinzan in 1959 (table 1A) indicate that the HF/HCl ratio is relatively constant in fumaroles above  $300^\circ\text{C}$ , but that HF decreases notably below that temperature. This relationship sug-

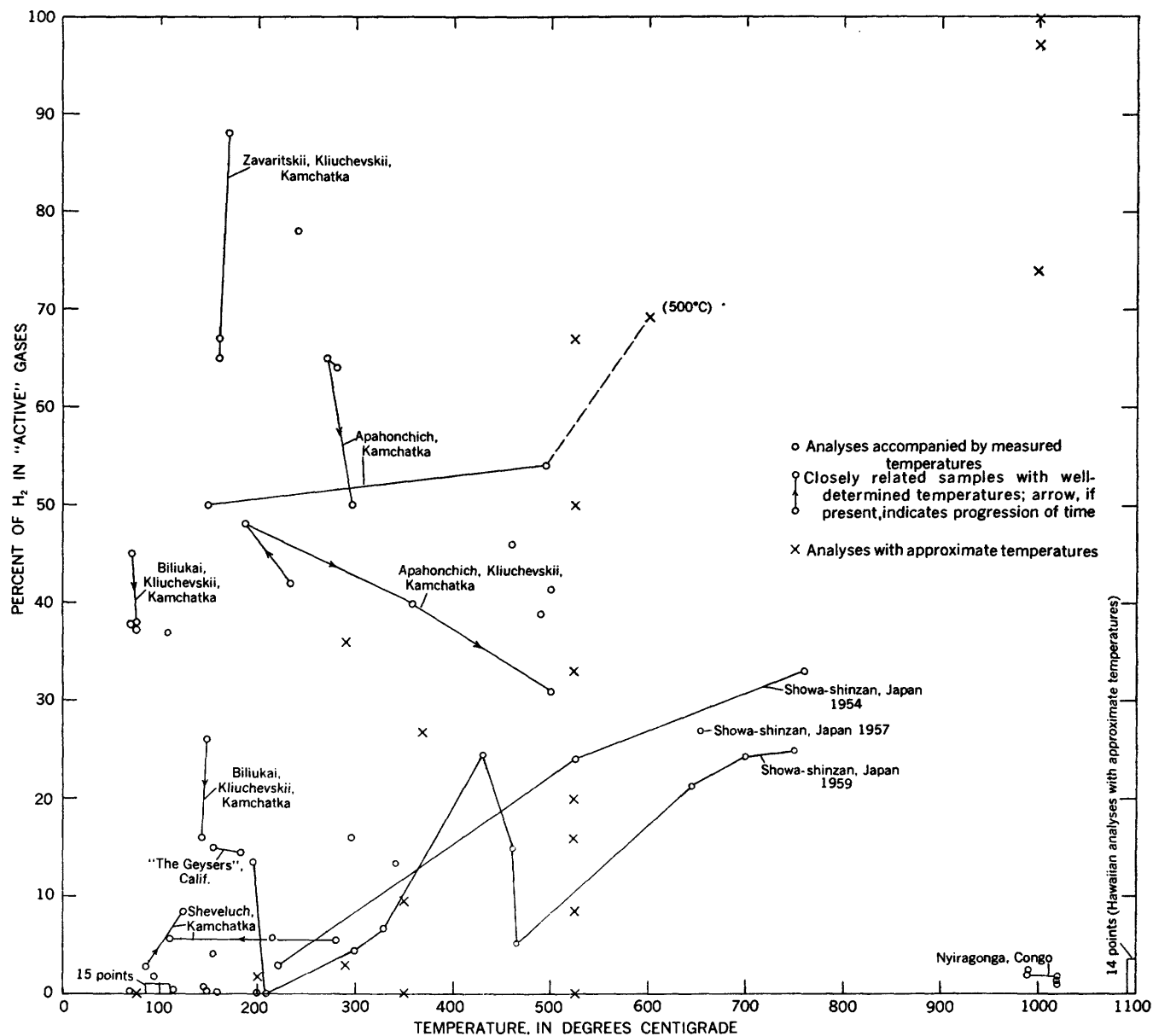


FIGURE 2.—Content of  $H_2$  in "active" gases, relative to temperature.

- gests that furometasomatism, mentioned in a later section, takes place largely at temperatures between  $100^\circ$  and  $300^\circ C$  and results from fixation of F from the superheated fumarolic gases.
10.  $H_2S$  seldom exceeds 20 percent of the "active" gases (fig. 4), but is astonishingly high in the fumaroles of Nasu volcano, Japan (table 1A), where large quantities of native sulfur are deposited (Hayase and Ahimazu, 1957). The proportion of  $H_2S$  in the "active" gases not uncommonly increases with increasing temperature (fig. 4), at least up to an intermediate range. At Showa-shinzan, however,  $H_2S$  decreases above  $200^\circ C$ .
  11.  $SO_2$ , nearly always the dominant oxidized sulfur gas (tables 1 and 2; fig. 5), exceeds 20 percent of total "active" gases in nearly one-third of the samples in which it was determined. Its content may be relatively high in many low-temperature fumaroles.
  12. The data also give some support to the concept that  $SO_2$  is the dominant sulfur gas at high temperatures (table 1; fig. 6), but its dominance is not as universal as is generally assumed.  $SO_2$  can also be the dominant sulfur gas at low temperatures, particularly where extensive reaction with atmospheric oxygen has occurred.

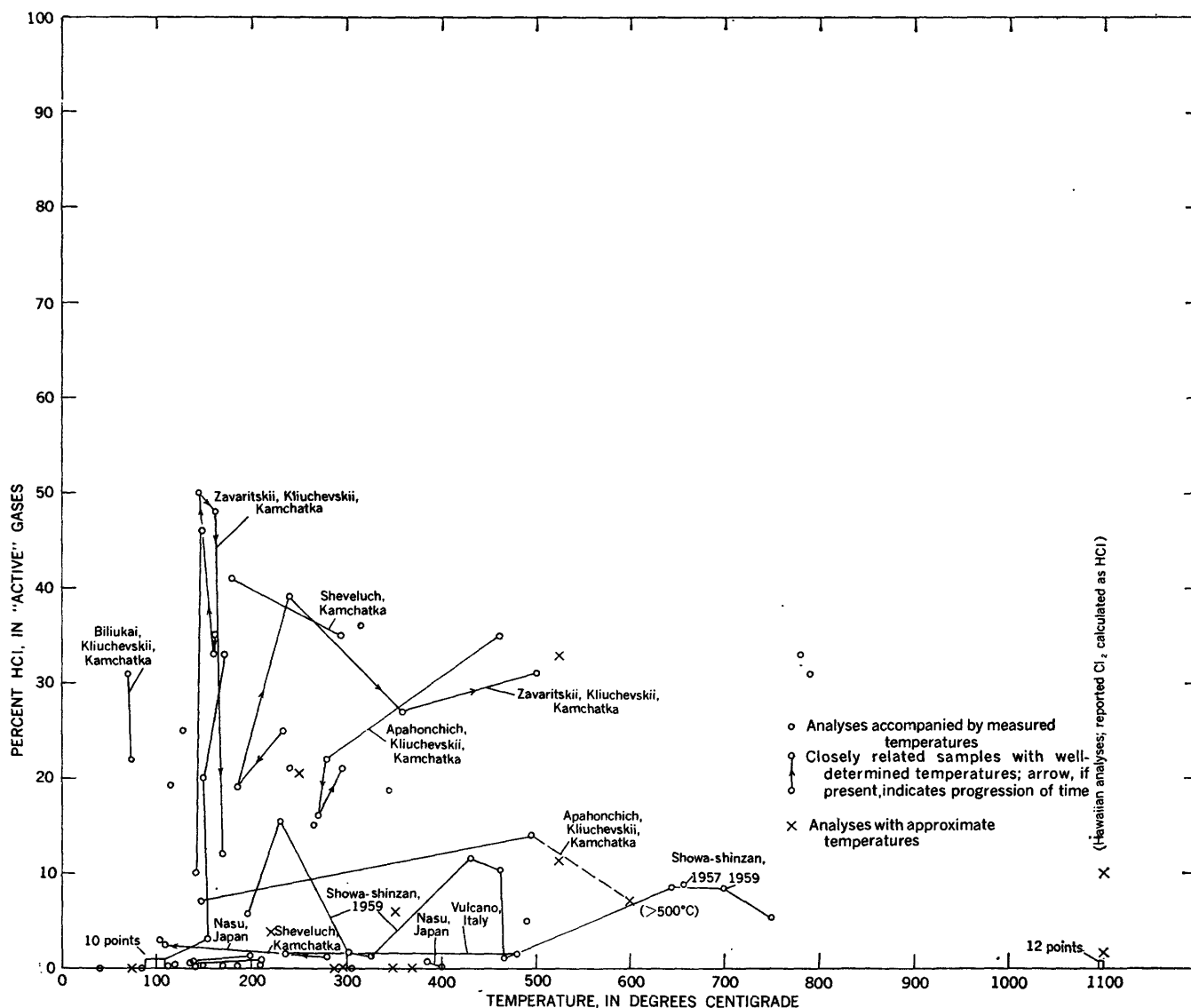


FIGURE 3.—Content of HCl in "active" gases, relative to temperature.

13.  $\text{SO}_3$  has seldom been determined in addition to  $\text{SO}_2$ ; it may be relatively minor, but it may also be the dominant sulfur gas (table 1, *D* and *F*). The  $\text{SO}_3$  dissolved in fumarolic condensates (as sulfuric acid, tables 2 and 3) commonly exceeds HCl; this suggests that  $\text{SO}_3$  is more abundant than is generally suspected.
14. Boron has not been determined directly in volcanic gases, but fumarolic condensates indicate that the ratio  $\text{H}_3\text{BO}_3/\text{HCl}$  generally ranges from 1:1,000 to 1:20 (tables 2, 3, and 4).
15. Bromine has been determined in only a few fumarolic condensates (tables 2, 3, and 4). Except for one analysis from Suelich Dome of Sheveluch volcano, the Br/Cl ratios range from about that of sea water (0.0034) to less than one-tenth that of sea water. Volcanic hot-spring waters also tend to be slightly lower in Br/Cl than sea water (White, 1960).
16. Iodine has been determined in only a very few fumarolic condensates (tables 2, 3, and 4). More data are needed because of the suggestion that I/Cl ratios are critical in distinguishing saline components of different origin (White 1960).
17. Components of low volatility such as  $\text{SiO}_2$ , Na, Ca, and Mg have been found in condensates from low-temperature fumaroles in much larger quantities than can be accounted for by their volatilities (table 3). Transport in droplets of water in wet steam (aerosols) is suspected (Naboko and Ryabichkina, 1957; Naboko, 1959a, p. 127).
18. The same low-volatile components, as well as significant quantities of minor metals, have also been detected in high-temperature fumarolic

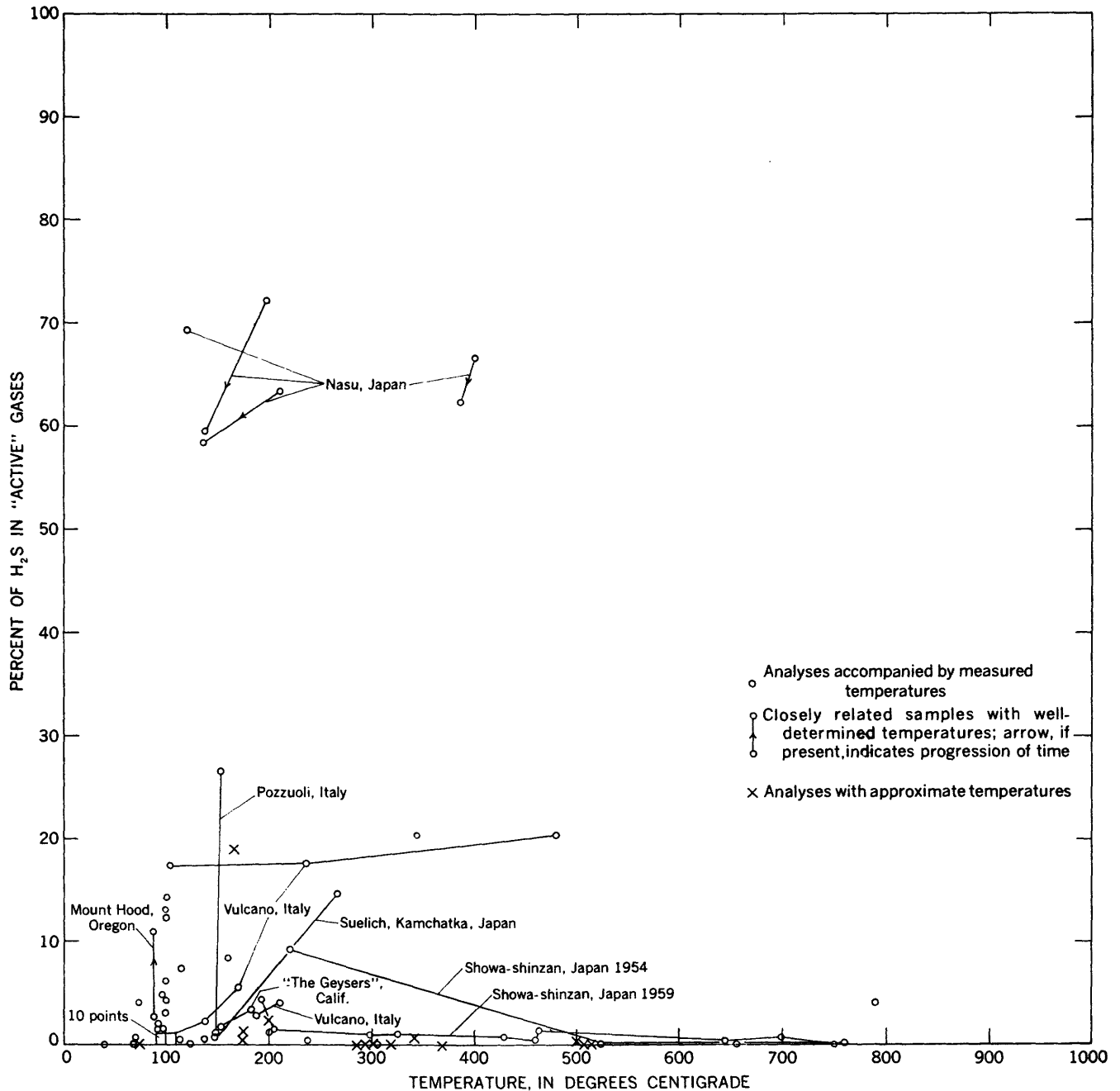


FIGURE 4.—Content of H<sub>2</sub>S in "active" gases, relative to temperature.

vapors. Many of these components are probably soluble in dense steam under high pressure but are probably present as aerosols in low-pressure steam. The quantities of Zn, As, Sn, and Ag reported in Showa-shinzan fumaroles (table 4) are especially notable; these metals and other components of low volatility are in general more abundant at higher temperature.

Sainte-Claire Deville (1857) was the first to suggest that the composition of volcanic gases was a function

of time since evolution of gases started, and of distance from the volcanic throat. These ideas have been supported at least to some extent by many geologists and geochemists, but clear-cut quantitative evidence on the importance of either time or distance, as distinct from temperature and other possible factors, is still surprisingly scanty (see review by Lovering, 1961, p. 84-87). At Biliukai, a lava vent of Kliuchevskii volcano, fumaroles between 100° and 200°C were relatively high in halogen acid gases and H<sub>2</sub> in 1946; fumaroles of the same temperature range were higher in sulfur gases by

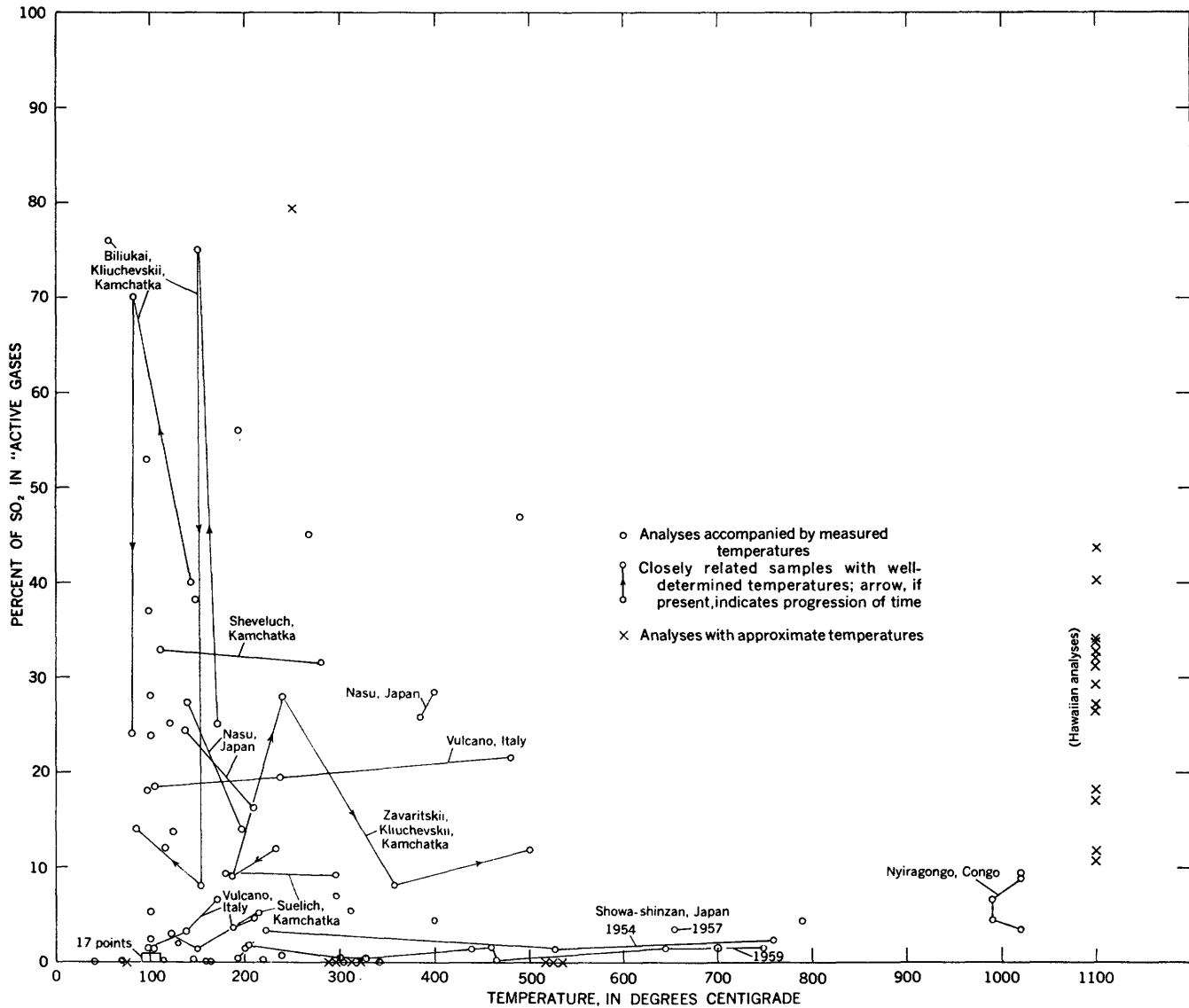


FIGURE 5.—Content of total SO<sub>2</sub> in "active" gases, relative to temperature.

1947 and were finally highest in CO<sub>2</sub> by 1948 (Naboko, 1959a, p. 88-90). Naboko (1959a, p. 91) also found that the fumaroles of explosive craters were higher in sulfur gases than were fumaroles of similar temperature on effusive vents, which were enriched in HCl and HF.

The fumaroles of Showa-shinzan showed surprisingly little change in temperatures between 1954 and 1959. During this time interval, the proportion of "active" gases to steam seems to have decreased (table 1A) and, for similar temperatures, the content of sulfur gases decreased slightly (fig. 4 and 5) but the ratio of H<sub>2</sub>S to SO<sub>2</sub> increased (fig. 6). Because of the method of reporting, the halogen acids are not directly comparable. The possible influences on composition of time and position are still in need of much critical attention.

It is appropriate to end this section with a brief mention of theoretical discussions of magmatic gases

as mixtures of components in chemical equilibrium. Shepherd (1938) took the pessimistic view that such treatments were not warranted by the data. Ellis (1957) more hopefully has calculated the equilibrium proportion of the major constituents of magmatic gases at various temperatures and pressures, for selected starting compositions. The computed trends of variation of gas compositions with temperature are in generally good agreement with trends observed for the fumarolic gases of Showa-shinzan but not always with gases from other localities.

Krauskopf (1957) has calculated equilibrium compositions of a magmatic gas phase at 600 °C and has considered the heavy-metal content of the vapors, and the influence of different oxygen pressures on the major and minor constituents. His calculations indicate for this temperature that SO<sub>2</sub> should exceed H<sub>2</sub>S only

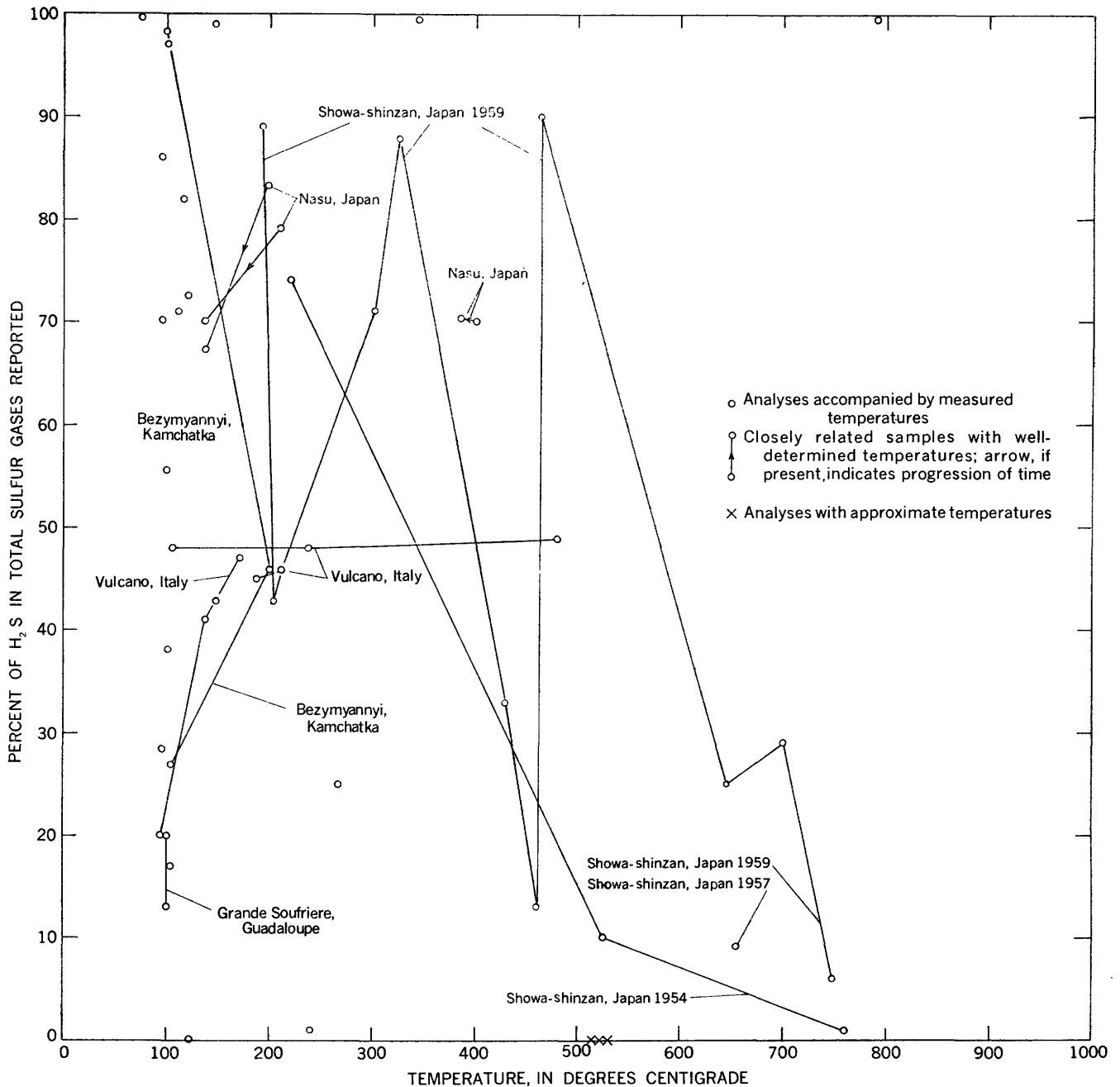


FIGURE 6.—Proportion of H<sub>2</sub>S to total sulfur gases reported, relative to temperature.

under very oxidizing conditions; CO and CH<sub>4</sub> are to be expected where conditions are strongly reducing; CO should not exceed CO<sub>2</sub> unless oxygen pressure is even lower than those considered; H<sub>2</sub> and H<sub>2</sub>S are important components from moderately oxidizing to strongly reducing conditions.

Matsuo (1960) has considered theoretically the differences in composition of gases that should exist in equilibrium with basaltic, dacitic, and granitic magma at different temperatures and pressures. If other conditions are equal, the H<sub>2</sub> content is highest in basaltic

magma; the total sulfur and especially the SO<sub>2</sub> content is highest in silicic magma; SO<sub>2</sub> is very sensitive to temperature and pressure, increasing with increasing temperature and decreasing pressure, and it may be useful in forecasting eruptions.

Computations by Ellis, Krauskopf, and Matsuo may serve as tentative bases for judging the extent of deviation from equilibrium compositions, and of differences in oxygen pressure, including effects of intermixture with air.

### SUBLIMATES, INCRUSTATIONS, AND REACTION PRODUCTS

Much qualitative work has been done on incrustations surrounding volcanic fumaroles. A major problem that has seldom been resolved with confidence is to determine which components were precipitated from vapor and which were derived by acid attack on surrounding rocks. Substances such as  $\text{NH}_4\text{Cl}$ , whose constituent elements are very rare in adjacent rocks, all were with little doubt transported in the fumarolic gases. Other incrustations, especially sulfates, are likely to be products of reaction of fumarolic gases, air, and adjacent rocks. The strong physical and chemical gradients surrounding volcanic fumaroles may result in high local concentrations of elements from surrounding rocks even though original concentrations are very low. Acid leaching of the surrounding rocks and local concentration of some metals is particularly obvious in low-temperature fumaroles characterized by abundant  $\text{H}_2\text{SO}_4$ . In high-temperature fumaroles,  $\text{HCl}$  and other acids may condense in cooler surroundings, with acid solutions attacking the rocks and then migrating toward and evaporating in the superheated gases. Some metals derived from the rocks could be selectively concentrated greatly by these processes.

Table 5 includes a few chemical analyses of substances that are likely to be largely sublimates from fumarolic gases. Products of Kamchatka fumaroles have been studied extensively, especially by Naboko (1945, 1953, 1959a, p. 93-169, and 1959b) and by Borovik and Vlodayets (1938), Popkov (1946), and I. Z. Ivanov (1937, 1938, 1940). Volatile transport appears to be confirmed for Na and K in approximately the same proportions as in the magma, and for Fe and Cu. Other metals that have been found in higher concentrations in encrustations than in surrounding lavas are Li, Be, Pb, Sn, Ag, Zn, Co, Ni, Zr, Mo, Bi, Ga, Te, Cr, V, Ba, Sr, As, Ag, and Cd. Direct sublimation of Ca and Mg has also been confirmed. Fluometasomatism and other rock alterations have been studied by Naboko (1957, 1958).

Zies (1924, 1929) found relatively high concentrations of Cu, Zn, Mn, and Mo in fumarolic magnetite in the Valley of Ten Thousand Smokes (table 5); other elements more enriched in magnetite or in other incrustations than in surrounding rhyolitic ash were Pb, As, Sb, Sn, Ag, Ni, Co, Ti, Bi, Se, and Te. Lovering (1957) has described fluometasomatism that surrounded one of the fumaroles; as suggested earlier, the data from Showa-shinzan (table 1A) indicate that fixation of F occurs largely between 300° and 100°C.

A high concentration of Ni (1.64 percent) was found in an incrustation consisting dominantly of potassium

aluminum sulfate at Shirane volcano, Japan (Shima, 1956, 1957). The data do not prove vapor transport to the exclusion of concentration from surrounding rocks. Other data on Japanese sublimates and incrustations are given by Minami and Oosaka (1957), and Foster and Mason (1955).

Incrustations from White Island, an andesitic volcano of New Zealand, contained the following maximum concentrations in percent (Wilson, 1959, p. 48): Pb, 1; V, 0.03; B, 5; Cu, 0.4; As, 0.3; Zn, 0.3; and Sn, 0.5.

Many sublimates contain abundant NaCl, KCl, and  $\text{NH}_4\text{Cl}$  (LaCroix, 1906, 1936; p. 117-118; Perret, 1950, p. 102; Foshag, 1945, p. 95-100). Fluorine is abundant in some Vesuvian incrustations (Tonani, 1955, p. 280).

Relatively high concentrations of minor elements can be leached by distilled water from freshly fallen volcanic ash. Much leachable material was with little doubt in hot gas clouds, and condensed on associated ash as temperature and pressure decreased. The water extracts undoubtedly also include some matter dissolved from volcanic glass and silicate minerals. An analysis of leachate from ash of Bezymyanny is included in table 5. Leachates from ash of the same volcano were also studied by Tovarova (1958). Melted snow containing fresh ash from an eruption of Krenitzyn volcano, Onekatan Island of the Kuriles, contained 100 ppm  $\text{SO}_4$  and nearly 500 ppm Cl (Gorshkov, 1958, p. 75). Surface water runoff from Hekla during and after its 1947 eruption contained as much as 9.5 ppm F (Stefansson and Sigurjonsson, 1957). Fluoride that was leachable from fresh ash ranged from 60 ppm of coarse ash to 350 ppm from the finest fraction; grinding did not notably increase leachable F, indicating adsorption of soluble fluorides on surfaces of particles.

Many minerals have been identified as sublimates or reaction products of fumaroles. Kamchatkan fumarolic products have been thoroughly studied by Naboko (1959a, p. 93-169; 1959b, p. 128-129), and at least 75 different minerals have been identified. At least 15 additional minerals have been found elsewhere in fumaroles (quoted by Palache, Berman, and Frondel, 1944, 1951). About half of the total consist of various combinations of Na, K, Ca, Mg, and Al with sulfate, and with different degrees of hydration. Many of the other minerals are combinations of Cl and F with K, Na, Ca, Mg, Fe, Si, and Al.

Minerals containing minor elements include salamoniac  $\text{NH}_4\text{Cl}$ , kremersite  $(\text{NH}_4, \text{K})_2 \text{FeCl}_5 \cdot \text{H}_2\text{O}$ , chlormanganokalite  $\text{K}_4\text{MnCl}_6$ , atacamite  $\text{Cu}(\text{OH})_2\text{Cl}$ , hydromelanothallite  $\text{Cu}_2(\text{OH})_2\text{Cl}_2 \cdot \text{H}_2\text{O}$  (?), scacchite  $\text{MnCl}_2$ , cotunnite  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ , psuedocotunnite  $\text{K}_2\text{PbCl}_4$  (?), eriochalcite  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ , cryptohalite



and bararite,  $(\text{NH}_4)_2\text{SiF}_6$ , ferruccite  $\text{NaBF}_4$ , and avogadrite  $(\text{K,Cs})\text{BF}_4$ . Other fumarolic minerals containing high concentrations of minor elements include larderellite and ammonioborite  $(\text{NH}_4)_2\text{B}_{10}\text{O}_{16} \cdot 5\text{H}_2\text{O}$  (?), sassolite  $\text{B}(\text{OH})_3$ , tenorite  $\text{CuO}$ , realgar  $\text{As}_2\text{S}_3$ , orpiment  $\text{As}_2\text{S}_3$ , and selenian sulfur (S, Se).

Because of great uncertainties regarding derivation of minor elements by vapor transport or by reactions with surrounding rocks, much more effort should be made to determine minor quantities of elements in fumarolic gases and condensates, as done in Japan (table 4) and Kamchatka (tables 2 and 3).

#### GASES IN ROCKS

Travers (1899), Gautier (1906), Chamberlin (1908), and Stutzer (1910) were among the first geologists interested in gases contained in rocks, in the hope that much could thereby be learned about the gases these same rocks gave off while cooling, or might have given off in a different environment. A few analyses selected from the literature are included in table 6. Obvious difficulties concern lack of equilibrium, oxidizing reactions, contamination with air, and absorption of ground water, but the study of fumarolic gases also involves these same considerations.

The influence of ground water on the water contents of volcanic glasses, and the manner in which water is driven off upon heating, have been studied by Shepherd (1931, 1938, p. 313-315), Keller and Pickett (1954), Ross and Smith (1955), and Friedman and Smith (1960). Fresh natural glasses are very low in water content (generally less than 0.1 percent), but absorb water with time. Friedman and Smith have shown that the rate of absorption is relatively constant, and is even of value in geochronometry; they have also shown that absorbed water is similar in deuterium content to associated meteoric waters and is clearly of local origin.

Special studies of individual gases in rocks include that of  $\text{CO}_2$  in granites (Khitarov and Rengarten, 1956), and  $\text{N}_2$  and the inert gases (Rayleigh, 1939). Mayne (1957) has found that  $\text{N}_2$  ranges from 0.002 to 0.05  $\text{cm}^3$  per gm;  $\text{N}^{15}$  is high in rocks low in nitrogen and low where  $\text{N}_2$  is high relative to the atmosphere. Wlotzka (1961) has shown that nearly all igneous rocks contain ammonia, with an average  $\text{NH}_3\text{-N}$  content of about 20 ppm. Large enrichments of  $\text{Ar}^{40}/\text{Ar}^{36}$  relative to the atmosphere have been found in gases from Larderello, Italy, and other thermal areas (Boato and others, 1951, 1952). Chemical compositions of fluid inclusions in rocks are summarized in another chapter of this report.

E. S. Shepherd's careful work on gases in rocks was summarized in 1938 (p. 326-337). Analyses of rocks that from his descriptions appear to be fresh and that

include all or most major gaseous components (F not determined in four) are recalculated in table 7 to exclude water. Shepherd was impressed with the wide and apparently random proportions of gaseous components, and he made few broad generalizations in his final summary. It is true that random variations occur with no obvious explanation, perhaps in part because of inconsistent reactions between gases and oxidizable elements during the extraction processes. Examples are the  $\text{CO}$  and  $\text{H}_2$  in paired analyses 1 and 2, 3 and 4, 5 and 6, and 13 and 14 of table 7. Other paired analyses, 11 and 12, and 16 and 17, are more nearly alike.

Shepherd may have been unduly cautious in drawing conclusions from his work. Shepherd's generalizations and others that can be made, if these relatively few analyses are typical, are:

1. Total gases from unaltered rocks range from about 1 to perhaps 200 cc per gram of rock.
2. Total gases other than  $\text{H}_2\text{O}$  are more consistent in quantity, ranging from 0.14 to 6 cc per gram of rock.
3. Obsidians exhibit the maximum range in total gas content, with the higher amounts clearly caused by absorption of meteoric water with little gain or loss of other gases. The  $\text{H}_2\text{O}$  content of total gases range from about 90 percent in low-gas obsidians to nearly 99 percent in the high-gas rocks.
4. Fresh andesites and basalts tend to have about 6 cc of gases per gm, with  $\text{H}_2\text{O}$  constituting approximately 80 to 90 percent of the total in andesites and 75 percent in fresh basalt.
5. Fresh plutonic rocks have about 30 cc of gases per gm, with water constituting about 80 to 90 percent of the total. Presumably because of cooling and crystallization under high pressure, much more of the original gases of plutonic rocks were retained than in near-surface volcanic environments.
6. Rhyolitic pumice contains more gas exclusive of  $\text{H}_2\text{O}$  than obsidian (Nos. 1 and 2, 3 and 4); basaltic pahoehoe (No. 13) and pumice (No. 16) contain more gas than associated aa lavas (No. 14, and also No. 17, which is aa according to K. J. Murata (oral communication, 1961).
7.  $\text{CO}_2$  is generally the most abundant gas next to  $\text{H}_2\text{O}$ ; it is relatively more abundant in gases from andesites, basalts, and granites than from obsidians, in which other gases may be more abundant.
8.  $\text{CO}$  is commonly somewhat more abundant in gases from andesites and basalts than from obsidians or granite, and it does not exceed  $\text{CO}_2$  in any of Shepherd's analyses.

9. The abundance of  $H_2$  is very erratic and shows little relation to any known characteristic, except that it is particularly abundant in the two granitic rocks.
10.  $N_2$  shows considerable variation in abundance; similar although not identical concentrations in related pairs of samples indicate that most  $N_2$  is from the rocks rather than from atmospheric contamination.
11.  $S_2$  is relatively more abundant in andesites and basalts than in obsidians and fresh granite.
12.  $Cl_2$  is about equally abundant in obsidians and andesites and is lower in relative abundance in basalts and particularly in fresh granites. The indicated great difference in  $Cl_2$  content of Kilauea and Mauna Loa gases needs further study.
13.  $F_2$  is relatively abundant in obsidians and is somewhat less abundant in many other rocks. The indicated great difference in abundance of F between Kilauea and Mauna Loa volcanoes is surprising.

The data suggest that renewed interest should be shown in the gases contained in rocks. Extensive geochronologic studies that are now being made on argon and helium contents of rocks and minerals could be broadened with relatively little effort to include quantitative study of other gases driven off in the extraction process.

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TABLE 1.—Chemical analyses of volcanic fumaroles, in volume percent

A. JAPAN

[For many important new analyses of volcanic gases of Japan see: Iwasaki, I., Ozawa, T., Yoshida, M., Katsura, T., Iwasaki, B., Kamada, M., and Hirayama, M., 1962, Volcanic gases in Japan: Tokyo Inst. Technology Bull. 47, 54 p. (in English)]

No.	Location	Date collected	Temp. °C	"Active" gases (recalculated to 100 percent)											Gases reported in original analysis						
				CO <sub>2</sub>	CO	CH <sub>4</sub>	NH <sub>3</sub>	H <sub>2</sub>	HCl	HF	H <sub>2</sub> S	S	SO <sub>2</sub>	SO <sub>3</sub>	Total "active" gases, recalculated	O <sub>2</sub>	N <sub>2</sub>	Ar	H <sub>2</sub> O	HF HCl	H <sub>2</sub> S SO <sub>2</sub>
<b>Hokkaido</b>																					
<i>Shouwa-shinzan, Utsu Volcano</i>																					
1	Fumarole A-1 (9081)	Sept. 1954	760	64.4	0.18	0.090	(?)	33.0	(?)	0.022	0.011	2.3	0.026	1.879	0.0032	0.057	0.000025	98.1	0.00044		
2	A-3 (9051)	do	525	74.2	.15	.16	23.9	(?)	9.1	.16	.007	1.41	.019	1.442	.0027	.054		98.5			
3	C-3 (9063)	do	220	84.8	.12	.17	27.2	(?)	8.7	.39		3.2	.009	1.632	.0013	.089	.000066	99.3	.00074		
4	east side	Aug. 1957	655	65.0	.08	.08	25.0	8.7	3.5	1.0	1.66	3.7		5.16	.0000	.014	.00005	99.48	.0036		
5	A-1 (9081)	July 7, 1959	750	61.1	.14	.14	24.5	8.61	3.54	.62	1.50	1.50		5.92	.0000	.026	.00009	99.25	.0037		
6	A-6a	July 9, 1959	700	64.3	.14	.14	21.3	8.61	3.51	.63	1.60	1.60		5.92	.0000	.021	.00006	99.39	.0029		
7	C-2	July 1, 1959	645	91.1	.14	.14	10	5.12	1.07	1.07	1.12	1.12		8.59	.0000	.042	.00007	99.41	.0017		
8	B-4b	July 4, 1959	464	91.1	.06	.06	15.1	10.6	5.96	.28	1.86	1.86		8.59	.0050	.209	.00012	99.24	.011		
9	A-4a	July 8, 1959	460	66.1	.11	.11	24.7	11.8	4.06	.79	1.57	1.57		5.67	.0000	.023	.00009	99.41	.0023		
10	C-4	July 4, 1959	430	57.0	.15	.15	6.96	1.48	6.65	1.05	1.4	1.4		9.48	.0000	.062	.00012	99.00	.0039		
11	B-1	July 6, 1959	328	89.5	.15	.15	4.45	1.76	5.3	1.02	1.44	1.44		8.53	.0017	.274	.00027	99.07	.0042		
12	B-4b	July 4, 1959	300	91.7	.00	.00	4.00	1.71	1.07	1.07	1.44	1.44		4.86	.067	.274	.0032	99.1±	.012		
13	A-6b	July 10, 1959	203	80.3	.16	.16	13.6	4.86	4.43	4.27				2.58	.0000	.026	.00007	99.72	.0027		
14	C-3 (9063)	July 1, 1959	194	76.4																	
<b>Honshu</b>																					
<i>Nasu Volcano, Chauayama</i>																					
15	Mugen No. 2	June 1956	400	4.7										61.13	2.79	36.0		(96.46)			
16	do	Sept. 1956	385	10.8						66.6		28.5	.08	85.76	3.06	11.2		(96.89)			
17	Chokoman No. 1	June 1956	198	12.1					75	62.2		25.8	.49	90.82	1.11	8.0		(98.52)			
18	do	Sept. 1956	138	10.7					1.11	72.1		13.9	.78	83.96	3.10	13.0		(98.66)			
19	Chokoman No. 2	June 1956	210	19.0					.73	59.6		27.3	1.7	71.04	3.23	24.8		(97.87)			
20	do	Sept. 1956	136	16.0					.72	63.3		16.2	.70	88.29	2.56	9.3		(98.44)			
21	Oana No. 2	do	120	4.3					.34	69.2		25.1	1.1	70.52	5.50	24.0		(96.26)			
<i>Asamayama Volcano</i>																					
22	Jigokudani Fumarole	Aug. 9, 1934	3.2	84.8	1.25	*13.95	0.0			0				92.68	.95	6.26					
<b>Izu Islands</b>																					
<i>O-shima Volcano, Miharayama</i>																					
23	Lava lake sample—	April 1951	1000±	26.2										16.4	17.0	65.4	1.2				
24	E	do	1000±	3.0										57.3	0.0	41.9	.8				
25	E'	do	1000±	3.0										26.7	0.0	72.5	.8				
<b>Kyushu</b>																					
<i>Aso Caldera, Naka-dake Cone</i>																					
26	Immediately after explosion	June 1958	76.32							5.61	0.43	10.03									
27	One month later	July 1958	79.0							4.5		8.7									

1 Hypersihene dacite dome extruded 1944-45; Ibusi Prefecture.  
 2 See table 10 for complete analyses.  
 3 Two-pyroxene andesite flows and pyroclastics; fumaroles of sulfur mine area; Tochiigi Prefecture.  
 4 Andesite-dacite volcano, Nagano and Gumma Prefecture.  
 5 Includes 10.8 CH<sub>4</sub> and 3.15 "higher hydrocarbons."  
 6 Basalt lava lake active March-April 1951.  
 7 Basaltic andesite volcano; strong explosive eruption June 24, 1958.

REFERENCES AND COMMENTS FOR SAMPLES 1 TO 27

- 1-3. Nemoto, Hayakawa, Takahashi, and Oama, 1967, p. 121-123; see also table 4 for complete analyses of all gases and condensates of these samples.
- 4. Mizutani and Matsuo, 1959, p. 121; repeat sample August 1968 essentially the same; see table 3 for condensate.
- 5-14. S. Oama, written communication, 1960; also contain in mg per 1,000 l. gas:
  - 5. B, 14.6; N (nitrate), 0.000; P, 0.0080; As, 0.550.
  - 6. B, 15.1; N (nitrate), 0.000; P, 0.0096; As, 0.520.
  - 7. B, 14.4; N (nitrate), 0.112; P, 0.0061; As, 0.650.
  - 8. B, 8.8; N (nitrate), 0.490; P, 0.0096; As, 0.180.
  - 9. B, 20.2; N (nitrate), 0.000; P, 0.011; As, 0.420.
  - 10. B, 20.3; N (nitrate), 0.660; P, 0.027; As, 0.610.
  - 11. B, 8.8; N (nitrate), 0.088; P, 0.015; As, 0.210.
  - 12. B, 9.0; N (nitrate), 0.610; P, 0.0068; As, 0.230.
  - 13. B, 21.1; N (nitrate), 0.510; P, 0.0042; As, 0.285.
- 14. B, 6.1; N (nitrate), 0.085; P, 0.017; As, 0.510.
- 15-21. Hayase and Ahimazu, 1957; also contains—
  - 15. 70 mg free S per cu.m. gas; pH of condensate, 1.0.
  - 16. 1,670 mg free S per cu.m. gas; pH of condensate, 1.2.
  - 17. 6,140 mg free S per cu.m. gas; pH of condensate, 0.6.
  - 18. 5,650 mg free S per cu.m. gas; pH of condensate, 1.0.
  - 19. 2,830 mg free S per cu.m. gas; pH of condensate, 0.6.
  - 20. 4,180 mg free S per cu.m. gas; pH of condensate, 1.2.
  - 21. 2,860 mg free S per cu.m. gas; pH of condensate, 1.0.
- 22. Noguchi, 1935, p. 1508; 1 of 4 analyses; temperature, written communication, 1961; original analysis includes 2.72 percent "higher hydrocarbons."
- 23-25. Iwasaki, 1951; see also table 3 for analysis of condensate. Sample E' same fumarole as E but different date.
- 26-27. Matsumoto and Tanaka, 1959, p. 155.

B. USSR

No.	Location	Date collected	Temp. °C	"Active" gases (recalculated to 100 percent)							Gases reported in original analyses (in percent except as noted)							
				CO <sub>2</sub>	CO	CH <sub>4</sub>	NH <sub>3</sub>	H <sub>2</sub>	HCl	HF	H <sub>2</sub> S	SO <sub>2</sub>	Total "active" gases recalculated	O <sub>2</sub>	N <sub>2</sub> , Ar, and other inert gases	H <sub>2</sub> O (mg/l of other gases unless noted)		
<b>Kamchatka</b>																		
<i>Shiveluch Volcano</i> †																		
1	Summit Crater	Sept. 27, 1946	85	97.0	0.2				2.8				Trace	13.8	7.12	19.60	73.29	† (92.0)
2	Southern fumarole 2	Aug. 3, 1946	122	77.6	.3				8.3				Trace	2.4	7.22	19.20	73.58	† (91.5)
3	do	Feb. 16, 1947	100	94.3	.2								3.0	21.05	16.60	32.35	† (83.0)	
4	Autumnal fumarole 1	Aug. 21, 1949	86	97.0					1				2.1	67.75	6.65	26.6	† (86.0)	
5	Central 1	Sept. 2, 1953	280	59.3	3.0				5.3					31.5	13.50	17.45	69.05	(1080)
6	do	Dec. 13, 1953	110	55.2	3.8				5.6					11.76	11.76	18.20	70.04	(900)
7	do	do	70	100.0										32.9	2.85	20.30	76.85	
<i>Snellich Dome</i> †																		
8	Fumarole 1	Sept. 11, 1946	122	95.0	2.0									3.0	2.64	19.95	77.42	(16.6)
9	Fumarole 2	do	149	96.0	2.0								.9	1.2	2.33	19.20	78.20	(14.0)
10	Fumarole 3	do	214	85.0	3.0				6.0					5.0	.70	20.2	78.32	(9.5)
11	Kipyaschnaya	do	266	25.0									15.0	43.0	.14	20.1	79.45	(4.5)
12	Dome, central part	Sept. 2, 1953	256	15.0	22.0				16.0					9.0	2.76	19.64	77.60	(180)
13	Dome, eastern part	do	180	31.0	19.0				41.0					9.0	1.60	19.40	78.20	(102)
<i>Karan Dome</i> †																		
14	Fumarole 1	Sept. 4, 1953	92	97.0	.3								2.6		85.09	2.60	12.31	(6500)
15	Fumarole 2	do	70	89.0	1.0								.7		71.76	5.05	22.65	(6000)
16	Fumarole 17	Sept. 29, 1957	90	96.5	1.0	1.8			.6				.1	0	71.62	9.40	15.98	(3860) (110)
<i>Klyuchevskii Volcano</i> †																		
<i>Bilulskai Crater</i> †																		
17	Fumarole B-1	Sept. 28, 1946	170	42	42				33					25	.060	19.55	20.00	79.95
18	do	Sept. 16, 1947	160	6	6				20					73	1.050	18.88	50.08	(240)
19	do	May 6, 1948	154	83	2				4					8	.35	19.86	73.72	(365)
20	do	May 6, 1948	156	86					0					14	.35	19.86	74.70	(360)
21	Fumarole B-2	Sept. 28, 1946	143	25	25				26					40	.165	19.84	78.92	(280)
22	do	Sept. 16, 1947	145	34	34				16					70	.63	19.84	78.90	(360)
23	do	Sept. 7, 1948	81	76	7				45					24	.35	19.82	79.85	(984)
24	do	May 6, 1948	81	76	7				45					24	.35	19.82	79.82	(1300)
25	Fumarole B-3	Sept. 28, 1946	70	24	24				31					76	.165	19.82	79.87	(1345)
26	do	Sept. 16, 1947	71	40	40				38					76	.165	20.10	79.67	(1300)
27	do	May 7, 1948	54	24	24				22					76	.165	20.10	79.67	(1200)
28	Crater fumarole	Sept. 16, 1957	71	0	100	0			0				Trace	76	.10	19.60	80.30	(1000)

See footnotes at end of table.

B. USSR—continued

No.	Location	Date collected	Temp. °C	"Active" gases (recalculated to 100 percent)								Gases reported in original analyses (in percent except as noted)					
				CO <sub>2</sub>	CO	CH <sub>4</sub>	NH <sub>3</sub>	H <sub>2</sub>	HCl	HF	H <sub>2</sub> S	SO <sub>2</sub>	Total "active" gases re-calculated	O <sub>2</sub>	N <sub>2</sub> , Ar, and other inert gases	H <sub>2</sub> O <sup>1</sup> (Mg/l of other gases unless noted)	
<b>Kamchatka—Continued</b>																	
29	<i>Kitchevskii</i> Volcano—Continued																
30	Obrucheva Crater: <sup>8</sup>	July 19, 1945	790							31		4				19.5	78.5
31	Incarescent fissure	Sept. 17, 1945	780							33						20.6	78.6
32	Crater wall	Dec. 26, 1946	232							25						19.65	80.11
33	Crater B-1	Sept. 12, 1947	186							19						19.92	79.87
34	do	May 5, 1948	240							39						20.15	79.87
35	do	May 9, 1949	358							27						20.05	79.32
36	do	Aug. 9, 1949	500			.8				31						19.50	79.69
37	Crater (?)	Mar. 8, 1953	107							35		Trace				19.40	80.06
38	Lava flow B-2	Dec. 26, 1946	160			.68				33						20.05	79.72
39	do	Sept. 12, 1947	145							50						20.15	79.70
40	Lava flow B-3 (same as B-2)	May 5, 1948	162							48						20.20	79.68
41	do	May 9, 1949	170							52						20.50	79.42
42	do	Aug. 4, 1949	170							12						20.8	78.97
43	Apahonchich Crater: <sup>10</sup>																
44	Flow fumarole 1	Dec. 25, 1946	>500							7						19.58	79.34
45	do	do	495							14						19.75	79.20
46	do	do	147							7						19.75	79.87
47	Cone fumarole 1	Sept. 13, 1947	460							35						19.85	78.85
48	do	do	280							22						19.92	79.70
49	do	do	270							16						19.45	80.24
50	do	May 5, 1949	296							50						20.20	79.50
51	do	Aug. 5, 1949	70							21						20.20	79.50
52	Crater fumarole	Sept. 13, 1957	15.1	3.8	43.2				37.9							19.70	78.98
53	Levinson-Lessig Crater: <sup>11</sup>																
54	Cone fumarole	Aug. 5, 1949	490				.5		39							20.05	79.28
55	Crater fumarole 9	Sept. 13, 1957	73						38							19.30	80.44
56	Bylinkin Crater: <sup>12</sup>																
57	Crater fumarole	May 1955	220±				.79			3.8							
58	do	Sept. 1955	312				4.1			35.8							
59	do	May 8, 1958	240							21						19.3	79.3
60	do	do	240														
<b>Bezmyuznnyi Volcano<sup>14</sup></b>																	
61	Gas cloud of most violent eruption	Mar. 30, 1956	Cold <sup>7</sup>														
62	Agglomerate flow	Sept. 9, 1956	200														
63	Agglomerate flow, sulfate area	do	105														
64	Agglomerate flow, native-sulfur area	do	100														
65	Cupola of agglomerate flow	Aug. 1957	95														
66	do	July 29, 1958	344														
<b>Paramshir Island, Kuriles</b>																	
67	Upper Crater:																
68	Fumarole I-1	Aug. 30, 1955	100														
69	do S-3	1957 <sup>9</sup>	114														
70	Central Crater:																
71	Fumarole S-1	1957 <sup>9</sup>	95														
72	do S-8	1957 <sup>9</sup>	102														
73	Lower Crater:																
74	Fumarole S-5	1957 <sup>9</sup>	110														
75	do S-6	1957 <sup>9</sup>	94														

<sup>1</sup> Values given in parentheses are not included in original author's total.  
<sup>2</sup> Andesite volcano.  
<sup>3</sup> Percent of total weight.  
<sup>4</sup> Andesite dome extruded 1945-50.  
<sup>5</sup> Old andesite extrusion.  
<sup>6</sup> Basalt volcano, frequently active.  
<sup>7</sup> Accessory crater erupted 1938-39.  
<sup>8</sup> Erupted 1945.  
<sup>9</sup> Erupted 1945.  
<sup>10</sup> Erupted October 1946.  
<sup>11</sup> Erupted 1945.  
<sup>12</sup> Erupted 1951.  
<sup>13</sup> Reported in percent. Included in original author's total.  
<sup>14</sup> Violently active 1955-56; two-pyroxene andesite (Gorshkov, 1959).

REFERENCES AND COMMENTS FOR SAMPLES 1 TO 66

- 1-15. Basharina, 1963a, p. 33-34; 1963b, p. 58; 1956, p. 22-26; a few of many analyses; see table 2 for analyses of condensed steam.  
 16. Borisov, 1960, p. 15; one of six analyses.  
 17-27. Basharina, 1963a, p. 37; 1963b, p. 57; Naboka, 1969a, p. 64.  
 28. Borisov, 1960, p. 13; one of four analyses, 1957-58.  
 29-30. Pilp, 1956, p. 273; 0.818 percent "heavy" rare gases included with N<sub>2</sub>.  
 31-35. Basharina, 1963a, p. 38-39; 1963b, p. 52, 57.  
 36. Borisov, 1960, p. 13.  
 37-48. Basharina, 1963a, p. 37-39; 1963b, p. 52, 57.  
 49. Borisov, 1960, p. 13; one of three analyses, 1957-58.  
 50. Basharina, 1963b, p. 58; most complete of 15 analyses, 1946-49.  
 51. Borisov, 1960, p. 13; one of three analyses, 1957-58.  
 52. Gorskho'v, 1957, p. 11; recalculated from condensate; also contains 0.0016 percent HBr and 0.00022 percent HI.  
 53. Idem; recalculated from condensate; also contains .0065 percent HBr and .0012 percent HI.  
 54. Borisov, 1960, p. 13; one of six analyses.  
 55. Basharina, 1963b, p. 38-41; one of three samples; see table 5 for leachate from fresh ash.  
 56. Surrina, 1969, p. 469-470; fumarole no. 2; reported sum 101.15 percent.  
 57. Basharina, 1960, p. 19-20; highest SO<sub>2</sub> of 15 from sulfate areas.  
 58. Idem; highest H<sub>2</sub>S of 12 from native-sulfur areas.  
 59. Idem; one of two analyses of vent fumaroles; see table 3 for condensate.  
 60. Borisov, 1960, p. 8; highest temperature of two analyses; 18 other analyses from agglomerate flow, 1957-58.  
 61. Ivanov, 1957, p. 68; air deducted, gases escaping through water.  
 62-66. Surrina, 1969, p. 470; reported sum of no. 66 is 98.98 percent.

C. NORTH, CENTRAL, AND SOUTH AMERICA

No.	Location	Date collected	Temp. °C	"Active" gases (recalculated to 100 percent)										Gases reported in original analysis, (in percent except as noted)				
				CO <sub>2</sub>	CO	CH <sub>4</sub>	NH <sub>3</sub>	H <sub>2</sub>	HCl	HF	H <sub>2</sub> S	SO <sub>2</sub>	Total "active" gases recalculated	O <sub>2</sub>	N <sub>2</sub>	Ar	H <sub>2</sub> O*	
United States																		
<i>Alaska</i>																		
1	Umnak Island, Okmok Caldera Cone A. <sup>3</sup>	Sept. 26, 1946	96.5	47														
2	A-1	do	98.0	62.6														
3	A-2	do																
4	Ten Thousand Smokes: S-3	1917	400															
5	S-5	1917	400															
6	S-20	1917	350															
7	S-21	1917	300															
8	S-10	1917	300															
9	S-16	1917	250															
10	S-15	1917	250															
11	S-8	1917	100															
12	S-1	1917	100															
13	Lower Valley: 29-G	1919	255	59.6	0.3	0.2												
14	28-G	1919	244	63.6	.2	.3												
15	26	1919	177	12.6	.2	0												
16	98	1919	98	16.5	.4	.2												
<i>Novarupta:</i>																		
17	108-2	1919	414	37.5	.7	4.4												
18	107	1919	403	54.1	.9	10.1												
19	110-1	1919	290	79.4	.2	12.5												
20	110-2	1919	238	81.6	.7	14.0												
<i>Upper Valley:</i>																		
21	133	1919	253	23.1	.2	.7												
22	113-1	1919	96	17.0	.7	1.3												
<i>Broken Mountain Valley:</i>																		
23	132-G	1919	122	34.6	1.0	0												
24	134	1919	98(?)	10.7	.2	.6												
<i>Knife Creek Valley:</i>																		
25	144	1919	440	37.2	.9	2.1												
<i>Oregon</i>																		
26	Mount Hood Volcano, <sup>4</sup> Fumarole D	1935	89	96		.1												
27	do	1951	89	89		.04												
<i>California</i>																		
28	"The Geysers", <sup>5</sup> Well 1	1925	154	65.9		15.9	1.3	15.2										
29	Well 6	1925	181	64.8		15.3	1.8	14.5										

See footnotes at end of table.



C. NORTH, CENTRAL, AND SOUTH AMERICA—continued

No.	Location	Date collected	Temp. °C	"Active" gases (recalculated to 100 percent)										Gases reported in original analysis, (in percent, except as noted)						
				CO <sub>2</sub>	CO	CH <sub>4</sub>	NH <sub>3</sub>	H <sub>2</sub> <sup>1</sup>	HCl	HF	H <sub>2</sub> S <sup>1</sup>	SO <sub>2</sub>	Total "active" gases recalculated	O <sub>2</sub>	N <sub>2</sub>	Ar	H <sub>2</sub> O <sup>1</sup>			
Mexico																				
<i>Paricutin</i> <sup>1</sup>																				
29	March, 1943 lava flow	June 1943	(?)	62			12	Trace	26						0.05	20.759	79.190			26.5
30	Taqui lava flow	Apr. 19, 1944		5.4					84.0						8.81	18.83	72.36 (by difference)			106.5

<sup>1</sup> H<sub>2</sub> probably present but included with H<sub>2</sub>S in samples 12 to 24.  
<sup>2</sup> Parentheses indicate percent of total gases; not included in author's total.  
<sup>3</sup> Active 1945-46, erupting basaltic lava flows. \* Superheated steam at depth, no nearby recent volcanism.  
<sup>4</sup> Great eruption of rhyolite ash and probably welded tuff, June 1912. † Basaltic andesite volcano, active 1943-52.  
<sup>5</sup> Andesite volcano, no recent activity. ‡ Milligrams per liter.

REFERENCES AND COMMENTS FOR SAMPLES 1 TO 30.  
 1-2. Byers and Brannock, 1949, p. 723.  
 3-11. Allen and Zies, 1923, p. 142, 148; CO<sub>2</sub>, CO, CH<sub>4</sub>, and H<sub>2</sub> not determined, are included with H<sub>2</sub>O and not with "active" gases.  
 12-24. Allen and Zies, 1923, p. 122.

D. MOLTEN LAVAS OF HAWAII

[Values in parentheses are not included in original author's total]

No.	Location	Date collected	Temp. °C	"Active" gases (recalculated to 100 percent)										Gases reported in original analysis (in percent)			
				CO <sub>2</sub>	CO	H <sub>2</sub>	Cl <sub>2</sub>	S <sub>2</sub>	SO <sub>2</sub>	SO <sub>3</sub>	Total "active" gases recalculated	O <sub>2</sub> (of orig. analysis)	N <sub>2</sub>	Ar	H <sub>2</sub> O		
<i>Kilauea</i>																	
Halemauamau:																	
1	S-3	1917	1100±	49.1	2.1	2.3	0.3	2.6	43.7	66.25	(8)	12.88	0.45	17.97			
2	S-7	1917	1100±	58.1	2.1	2.6	.8	3.6	32.8	29.70	(9)	5.88	.18	64.18			
3	S-8	1917	1100±	64.0	1.9	2.9	.0	2.1	29.2	23.89	(11)	8.77	.14	75.08			
4	J-4 Flaming crack	Mar. 2, 1918	1100±	53.6	1.1	1.3	4.9	1.2	10.9	12.68	(15.0)	2.33	.00	84.98			
5	J-8 Cone at flow source	Mar. 25, 1918	1100±	77.8	2.4	.8	.07	.07	18.2	61.27	(3.0)	2.41	.14	36.18			
6	J-10 Flaming crack, fountain roof	do	1100±	48.6	3.3	.3	.09	.15	40.1	33.86	(11.0)	15.03	.21	50.88			
7	J-11 Flaming crack, south cone	do	1100±	61.5	1.7	3.9	.0	.7	33.5	34.06	(6.0)	4.13	.31	61.56			
8	J-13 Flaming hole in cone	Mar. 13, 1919	1100±	58.4	2.0	3.3	.35	.3	27.2	29.06	(9.0)	3.35	.66	67.52			
9	J-15 Flaming crack, lava lake	Mar. 15, 1919	1100±	58.4	1.7	6.6	.6	.2	31.1	19.73	(14.0)	6.20	.16	73.89			
10	J-16 Flaming vent over flow	Mar. 16, 1919	1100±	59.1	1.9	2.2	.3	.5	27.9	30.55	(9.0)	3.11	.08	66.25			
11	J-17 Soft bursting lava bubble	Mar. 17, 1919	1100±	60.1	1.9	3.0	.3	1.2	33.6	19.33	(13.0)	1.29	.04	79.31			
12	J-18 Hole in dome over fountain	do	1100±	52.4	2.2	2.5	.4	.7	32.3	33.50	(9.0)	4.50	.12	61.88			
Suphur Bank fumarole:																	
13	Well sample	Nov. 17, 1939	97±	81.8					18.2	97.8	(2.2 percent air in original analysis)						
14	do	Mar. 14, 1940	97±	98.4					1.6	100	0	0					
15	Well sample 1	July 1952	97±	97.4	1.0	.4			1.5	100	0	0					
16	1a	do	97±	96.2	1.7	.4			1.6	100	0	0					
17	1b	do	97±	77.4	22.7	.0			.0	14.1	13.6	71.5					
18	2	do	97±	78.0	22.1	.0			.0	13.1	13.2	71.8					
<i>Mauna Loa</i>																	
19	ML-1	Oct. 19, 1919	1100±	54.0	.4	.0	.0	.0	17.	7.17		16.80	.58	75.44			
20	ML-2	do	1100±	38.5	1.1	.06	.0	.0	11.7	16.69		15.39	.42	67.43			

REFERENCES AND COMMENTS FOR SAMPLES 1 TO 20

1-12. Shepherd, 1938, p. 320-324; Jaggar, 1940, p. 313-330; of 24 analyses, these 12 include all that contain less than 15.1 percent original O<sub>2</sub>, and less than 15.1 percent residual N<sub>2</sub>; after air has been subtracted.  
 13-14. Ballard and Payne, 1940, p. 3; two of 45 analyses; analysis of Mar. 14, 1940, includes some H<sub>2</sub>S with SO<sub>2</sub>.  
 15-16. Naughton and Terada, 1954; two of three samples while Kilauea in eruption; C<sub>2</sub>H<sub>4</sub>/C<sub>2</sub>H<sub>6</sub> ratio, 89.0.  
 17-18. Naughton and Terada, 1954; two of three samples while Kilauea not erupting; C<sub>2</sub>H<sub>4</sub>/C<sub>2</sub>H<sub>6</sub> ratio, 89.0.  
 19-20. Shepherd, 1938, p. 320-324; Jaggar, 1940, p. 313-330.

E. OTHER ISLANDS OF THE PACIFIC AND INDIAN OCEANS, AND AFRICA

No.	Location	Date collected	Temp. °C	"Active" gases (recalculated to 100 percent)								Gases reported in original analysis								
				CO <sub>2</sub>	CO	CH <sub>4</sub>	NH <sub>3</sub>	H <sub>2</sub>	HCl	H <sub>2</sub> S	SO <sub>2</sub>	COS	Total "active" gases recalculated	O <sub>2</sub>	N <sub>2</sub>	H <sub>2</sub> O				
<b>Rennion</b>																				
1	Piton de la Fournaise:	1936(?)																		
2	Crater fumaroles:	1936(?)	"High"						Present					(?)						
3	do		"Inter-med."																	
3	do	1936(?)	"Low"							Present										
<b>Indonesia</b>																				
4	Papandajan, Java	1908	192	44									56		54	8	38			
5	Merapi, Java. 1	Feb. 25, 1931	96	62.0			.01		Trace		Trace		.02		6.743		1.82		91.423	
6	Fumarole near above	Feb. 26, 1931	96	66.6			.01		Trace		Trace		.016		10.473		1.86		87.63	
7	do	Mar. 27, 1931	108	76.4			.01		Trace		Trace		.2		9.801		1.69		87.98	
<b>New Zealand</b>																				
8	White Island: 3	1927	500±	84.0			Present		11.5				4.5		85.0		3 (98.7)		15.0	
9	Big Donald Fumarole	1928	500	57.9		0.5			41.5						75.6		3 (3.3)		24.4	
10	do	1927	129	73					26				2		100				1.1	
11	Fumarole near Lot's Wife	1928	(?)	73.1					22.9				4.0		98.9		(.0)		1.1	
12	Schubert's Fri King	1939	340±	99.4									.6		10.77				84.2	
13	Seven Dwarfs:	1939	175±	88.9									1.1		97.90				2.1	
14	West Northwest	1939	175±	99.7									.3		98.7				1.3	
15	Small vent	January 1955	(?)	95.2					1.9				2.7		99.6				1.35	
<b>New Hebrides</b>																				
16	Ambrym Volcano, Santa Cruz	1938(?)		87.8	1.2	1.2									33.5		9.2		34.6	22.7
<b>Congo</b>																				
17	Nyragongo lava lake:	1959	1,020	89.15					1.95				3.40		97.95		0.40		1.65	
18	Analysis 1	1959	990	86.30	5.45				2.00				6.55		88.50		.95		10.55	
19	do	1959	990	87.75	5.45				2.30				4.45		82.80		3.10		14.10	
20	do	1959	1,020	84.30	4.95				1.50				9.20		85.50				14.50	
21	do	1959	1,020	84.35	5.05				1.55				9.05		48.50				8.30	

1 1930(?) eruption of pyroxene andesite.  
 2 Hypersihene andesite volcano with vigorous fumarolic activity and with minor eruptions 1928, 1933-40 (Luke, 1959, p. 20-22).  
 3 Air, not included in original author's total.  
 4 Percent of total gases, water not included in original author's total.  
 5 "Residual gas", stated to be "mostly air"; summation of original analysis is 94.97 percent, suggesting "air" may be 89.2 percent.  
 6-11. Grange, 1959, p. 27; see table 2 for 1939 condensate from Big Donald Fumarole.  
 12-15. Wilson, 1959, p. 42-43; see table 2 for condensates.  
 16. Chaigneau, Tazieff, and Fabre, 1960a, p. 1762.  
 17-21. Chaigneau, Tazieff, and Fabre, 1960b, four of 13 analyses.

REFERENCES AND COMMENTS FOR SAMPLES 1 TO 22



VOLCANIC EMANATIONS

G. EUROPE AND THE MEDITERRANEAN

No.	Location	Date collected	Temp. °C	"Active" gases (recalculated to 100 percent)							Gases reported in original analysis							
				CO <sub>2</sub>	CO	CH <sub>4</sub>	NH <sub>3</sub>	H <sub>2</sub>	HCl	HF	H <sub>2</sub> S	SO <sub>2</sub>	Total "active" gases recalculated	O <sub>2</sub>	N <sub>2</sub>	Ar and other inert gases	H <sub>2</sub> O	
<b>Italy</b>																		
1	Vesuvius: <sup>1</sup>	1906	300±	84.5	0	0	0	0	9.5	6.0	0	0	0	0	13.05	3.72	15.49	67.74
2	Near summit of cone	1906	300±	100	0	0	0	0	Trace	Trace	0	0	0	0	6.68	6.00	24.88	62.44
3	Valley NE of crater	1907	280-300	54	10	0	0	0	36	0	0	0	0	0	1.49	4.59	21.23	72.60
4	do	1907	280-300	94	3	(?)	0	0	3	0	0	0	0	0	.70	3.68	17.62	77.76
5	Fumarole in crater	1917±	220-286							20.6	0.08				12.98		0.243	87.00
6	Phlegrean fields: <sup>2</sup>	1869	115	92.7											95.8	0.7	4.5	
7	Great solfatara of 1867	1907	152	73.3											93.8	0.2±	6.0±	
8	do	1933±	147	99.4	Trace	.01		.07	Trace	Trace					8.95	Trace	.0002	91.03
9	Solfatara Pozzuoli	1938±	149	98.9		.04		.10							96.74	0.0	.261	97±
10	do																	
11	Larderello: <sup>4</sup>	1950±	200±	92.67		.92	1.72	1.76							96.46		.002	98.94
12	Average steam	?	(?)	98.60		.99		4.45							98.50		.42	99.8
13	Ischia Island: <sup>5</sup>	?	(?)	93.56											96.94		.84	99.8
14	Monticorvo fumarole 1	?																
15	do 2	?																
16	Etna, Sicily: <sup>6</sup>	1863	150-180	80.9		0									62.4	7.1	30.5	Present
17	Fissure fumarole	April 1947	305			0				Trace(?)								Do.
18	Fumarole "G", 1947 eruption	Sept 1947	40															
19	do																	
20	Vulcano, Lipari Islands: <sup>7</sup>	1865	360±	24.1											97.20	0.52	2.28	
21	do	1865	250	25.0											88.0	2.4	9.6	
22	do	1865	150	68.7											86.81	2.20	10.99	
23	do	1865	100	79.3											86.8	2.7	11.2	
24	Fumarole	1923	480	56.3											20.4		1.9	
25	do	1923	237	61.3											12.3		2.7	
26	do	1923	104	63.9											17.8		2.4	
27	do	1923	170	87.8											19.4		2.7	
28	do	1937	138	94.5											17.4		2.4	
29	do	1937	99.5	90.8											18.6		2.0	
30	do	1951	210	90.8											98.0		2.3	
31	do	1951	187	93.0											96.2		1.8	
32	do	1951	187	93.0											96.2		1.8	
<b>Greece</b>																		
33	Santorin, Cyclades Islands: <sup>8</sup>	1866	160	89.0		2.5			Trace	19.4					19.41	14.12	66.47	Much
34	West slope of George	1870	115	68.6											96.9	(?)	(?)	(?)
35	200 feet from cone of George																	

<sup>1</sup> Tephrific leucite volcano, major eruptions 1906 and 1944.  
<sup>2</sup> Dominantly alkali trachyte cones.  
<sup>3</sup> Percent of total gases; water not included in original author's total.  
<sup>4</sup> No nearby recent volcanoes, but steam with temperatures of 200°C and more encountered at depth.  
<sup>5</sup> Dominantly trachyte volcanic rocks but no eruption since 1801.  
<sup>6</sup> Basalt volcano, frequently active.  
<sup>7</sup> Trachyte volcano, frequently active until 1892, dormant since then.  
<sup>8</sup> Includes SO<sub>2</sub>.  
<sup>9</sup> Andesite or rhyodacite volcano.

**REFERENCES AND COMMENTS FOR SAMPLES 1-29**

12. Idem; 2.2 liters of gas per kg vapor; also contains 0.011 percent He, Ne.  
 13. Quoted by Allen, 1922, p. 73; one of three analyses.  
 14-15. Silvestri and Fonte, 1948; other fumaroles have NH<sub>4</sub>Cl.  
 16-19. Quoted by Allen, 1922, p. 74.  
 20-24. Sicaardi, 1956, p. 164.  
 25. Sicaardi, 1940, p. 137.  
 26-27. Sicaardi, 1956, p. 164.  
 28-29. Quoted by Allen, 1922, p. 75; two of 24 old analyses.

TABLE 2.—Chemical analyses of fumarole condensates, expressed as compounds in milligrams per liter of water

No.	Location	Date collected	Temp. °C	H <sub>2</sub> S	H <sub>2</sub> SO <sub>4</sub>	HCl	HF	HBr	HI	CO <sub>2</sub>	H <sub>2</sub> BO <sub>3</sub>	NH <sub>3</sub>	H <sub>2</sub> SO <sub>4</sub>
USSR													
1	Kamohatka; Sheveluch volcano: <sup>1</sup>												
2	Central crater, central 1	Sept. 2, 1953	280		7,050	10,244	21.0	2.71			9.59		
3	2	Dec. 13, 1953	210		2,565	2,055	34.0	6.01		410	6.28		
4	Suelich dome, central part	do.	70										
5	180	Sept. 2, 1953	295		70.0	2,720	84.0	2.65			4.56		
6	eastern part	do.	180		18.5		14.0	4.46	1.81	499.4			
7	Karan dome 1	Sept. 4, 1953	92	35	Trace					460.0			
	2	do.	70	26	0								
Guatemala													
8	Santa Maria <sup>2</sup>	1932	300±		330	8,800	20.4	1.8	2.2		9±	(i)	
Iceland													
9	Hekla volcano: <sup>4</sup>												
	Shoulder Crater	Aug. 10, 1952	530		10,200	3,300	13				23		
New Zealand													
10	White Island: <sup>5</sup>												
11	Big Donald fumarole	1939	305		9,000	4,900	19				0	9	0
12	Schaubert's Earl King	1939	340±	800	3,000	3,000	260				0	6	0
13	Seven Dwarfs, B/1	1939	175±	40	1,100	24,300	44				730	50	80
14	A/5	1939	175±	Trace	2,000	15,000	10				260		0
15	A/6	1939	175±	Trace	0	16,000	15				190		0
16	B/20	1939	175±	Trace	2,000	26,000	38				490		650
	B/22	1939	175±	510	7,400	7,900	65				180	12	1,120

REFERENCES AND COMMENTS FOR SAMPLES 1-16

<sup>1</sup> Andesite volcano, periodically active. See table 1E.<sup>2</sup> Andesite volcano that extruded Santiago dome, beginning 1923 and continuing at least to 1939.<sup>3</sup> Looked for but not found.<sup>4</sup> Basalt volcano, major eruption 1947. See table 1F.<sup>5</sup> Hypersthene andesite volcano with vigorous fumarolic activity, eruptions 1933-40. See table 1E.

1-7. Basharina, 1956, p. 22, 26, 27.

8. E. G. Zies, written communication, 1957.

9. B. Lindal, written communication, 1958; temperatures by T. Sigurgeirsson, decreasing from 620 °C on September 23, 1951, to 385 °C on September 9, 1954.

10-16. Wilson, 1959, p. 45.

TABLE 3.—Chemical analyses of fumarole condensates, expressed in parts per million by weight

	Mendeleev Kunashir Is., Kuriles USSR	Mendeleev Kunashir Is., Kuriles USSR	Golovkina Kunashir Is., Kuriles USSR	Ebevo Paramushir, Kuriles USSR	Zavaritskii Kamchatka USSR	Bezmyannyi Kamchatka USSR	Bezmyannyi Kamchatka USSR	Miharayama O-shima Volcano Izu Japan	Showa- shimzan Hokkaido Japan	Kilauea Iki Hawaii USA
	1	2	3	4	5	6	7	8	9	10
SiO <sub>2</sub> .....	16	9.8	-----	231	4.2	9.2	22	-----	-----	0.0
Al.....	26	1	1.7	80	1.6	6.0	10	Some (?)	-----	-----
Fe <sup>++</sup> .....	( <sup>1</sup> )	( <sup>1</sup> )	( <sup>1</sup> )	0	.2	2.5	6.8	58,000	-----	-----
Fe <sup>+++</sup> .....	( <sup>1</sup> )	( <sup>1</sup> )	( <sup>1</sup> )	45	67	.6	-----	-----	-----	-----
Ti.....	( <sup>1</sup> )	( <sup>1</sup> )	( <sup>1</sup> )	0	-----	-----	-----	0	-----	-----
As.....	( <sup>1</sup> )	( <sup>1</sup> )	( <sup>1</sup> )	-----	-----	-----	-----	-----	-----	0
Ca.....	165	41	71	104	7.9	35	120	-----	4.6	-----
Mg.....	17	16	11	50	.7	5.6	11	0	1.1	-----
Na.....	-----	-----	-----	-----	59	15	36	-----	-----	4.9
K.....	64	-----	-----	1,396	48	3.0	11	-----	<7	1.1
Li.....	-----	-----	-----	-----	-----	-----	-----	-----	-----	.0
NH <sub>4</sub> .....	.2	2.0	1.5	.6	1.0	-----	-----	-----	-----	0
H.....	2.8	.3	.4	.8	-----	8	.2	-----	-----	1,910
HCO <sub>3</sub> .....	( <sup>1</sup> )	( <sup>1</sup> )	( <sup>1</sup> )	-----	6.1	-----	121	-----	-----	-----
H <sub>2</sub> SO <sub>4</sub> .....	11	.9	1.9	82	-----	12	-----	-----	-----	-----
SO <sub>4</sub> .....	77	81	75	1,296	279	176	266	0	<30	430
Cl.....	Trace	6.6	13	1,892	35	24	96	56,000	772	68,600
F.....	-----	-----	-----	2.4	-----	-----	-----	-----	195	20
Br.....	Trace	-----	-----	Trace	-----	-----	-----	-----	-----	246
I.....	-----	-----	-----	0	-----	-----	-----	-----	-----	4.5
NO <sub>2</sub> .....	-----	( <sup>1</sup> )	( <sup>1</sup> )	1.8	-----	-----	-----	-----	0	-----
NO.....	( <sup>1</sup> )	( <sup>1</sup> )	( <sup>1</sup> )	-----	-----	-----	-----	-----	21	3.2
B.....	( <sup>1</sup> )	( <sup>1</sup> )	( <sup>1</sup> )	0	-----	-----	-----	-----	-----	-----
CO <sub>2</sub> .....	-----	-----	-----	-----	3,150	-----	-----	-----	-----	-----
S.....	-----	-----	-----	-----	-----	195	-----	130	-----	400+
Se.....	-----	-----	-----	-----	-----	-----	-----	-----	-----	12+
H <sub>2</sub> S.....	19	( <sup>1</sup> )	( <sup>1</sup> )	-----	-----	7.5	-----	-----	-----	-----
Total, as reported...	398	159	176	5,180	3,660	492	700	114,000	994+	71,600+
pH (or acidity).....	2.56	3.46	3.40	3.0	5.48	3.1	4.1	(1.4N)	1.9	(Very low)
Temp. °C.....	98	98	97	115(?)	87	100±	95	1000±(?)	653±2	328

<sup>1</sup> Looked for but not found.

## REFERENCES AND COMMENTS FOR SAMPLES 1-10

- 1-2. On border of dacite dome (Naboko and Ryabichikina, 1957, p. 109-11, anal. 13 and 16). No. 2 also contains (in ppm) by semiquantitative spectrographic analysis, approximately: Zn, 10; Sb, 1; Pb, Sr, Ba, 0.1; Sn, Cu, Ag, 0.01. Collected August, 1955.
3. Andesite-dacite dome of Golovkina Caldera (Naboko and Ryabichikina, 1957, p. 110-111, anal. 22). Also contains (in ppm) by semiquantitative spectrographic analysis, approximately: Sb, Zn, 1; Pb, Sr, 0.1; Sn, Cu, Ba, 0.01; Ag, 0.001. Collected August, 1955.
4. Augite andesite crater, last erupted 1934-35 (Gorshkov, 1958, p. 94); see table 1B.
5. Basalt cone of Kliuchevskii volcano, erupted 1945; condensate from cupola (Tovarova, 1960, p. 53). Collected 1957; see table 1B.
- 6-7. Andesite agglomerate flow erupted 1956 (Basharina, 1960, p. 23-24). No. 6, collected September 9, 1956, is the most acid of 11 condensates from the flow; No. 7 is from the vent area of the eruption, collected August 25, 1957; see table 1B.
8. Basaltic lava lake (Iwasaki, 1951, p. 141); Fe from iron collecting pipe (?); re-computed from g/l, assuming density of 1.20; see table 1A.
9. Hypersthene dacite dome extruded 1944-45 (Mizutani and Matsuo, 1959, p. 125-126); average of 16 "normal" samples collected August 17, 1958; see table 1A.
10. Collected from basaltic pumice cone, temperature from depth of 1½ feet, November 23, 1959 (K. J. Murata, written communication, 1960); analysis by S. M. Rogers, U.S. Geological Survey; not all of S and Se recovered; density 1.031 g/l.

## DATA OF GEOCHEMISTRY

TABLE 4.—*Chemical analyses of fumarolic gases of Showa-shinzan, Japan, including all detected components of high and low volatility, expressed in parts per million*

[Samples collected September 1954 and analyzed by S. Oana (Nemoto, Hayakawa, Takahashi, and Oana, 1957, p. 122-123). Volatile components in volume percent in original analyses and components of low volatility in mg per 1000 l. gas; all re-computed here to ppm by weight]

	A-1(9081)	A-3(9051)	C-3(9063)
Temperature.....°C..	760	525	220
SiO <sub>2</sub> .....	253	289	48
Al.....	15	14	1.3
Fe.....	1.3	1.2	5.9
Ca.....	4.6	4.3	21
Mg.....	32	14	7.9
Na.....	22	22	13
K.....	15	11	1.7
CO <sub>2</sub> .....	29,200	25,800	13,000
CO.....	50	34	716
SO <sub>2</sub> .....	1,490	716	2.7
SO <sub>3</sub> .....	21	11	1,080
H <sub>2</sub> S.....	8.0	42	1.8
S.....	3.7	1.8	433
Cl.....	728	420	35
F.....	238	169	1.2
Br.....	1.1	.9	5.6
B.....	39	21	.8
PO <sub>4</sub> .....	2.8	3.0	.008
NO <sub>2</sub> .....	.01	.001	23
O <sub>2</sub> .....	51	47	20
H <sub>2</sub> .....	685	381	17
NH <sub>3</sub> .....	1.3	.8	1,250
N <sub>2</sub> .....	567	676	1.5
Ar <sup>40</sup> .....	.6	18	.0007
CH <sub>4</sub> .....	1.5		.004
Ni <sup>1</sup> .....	<.01	.0007	.02
Cu <sup>1</sup> .....	.03	.03	.0007
Zn <sup>1</sup> .....	.5	.4	.007
Ge <sup>1</sup> .....	<.01	.003	Trace
As <sup>1</sup> .....	.7	.3	<.0001
Mo <sup>1</sup> .....	Trace	Trace	.001
Ag <sup>1</sup> .....	.003	.0007	<.005
Sb <sup>1</sup> .....	.03	.006	.005
Pb <sup>1</sup> .....	<.1	<.01	<.002
Bi <sup>1</sup> .....	.03	.03	
Bt <sup>1</sup> .....	<.05	<.005	
Rn.....curies 10 <sup>-7</sup> ..	(1.3)	(2.1)	(12.6)
Total reported.....	33,432	28,698	16,685

<sup>1</sup> Semiquantitative spectrographic analysis of solids in condensate, here computed to parts per million of total, assuming intermediate value of range.

TABLE 5.—Chemical analyses of sublimates of volcanic fumaroles and eruption clouds, in weight percent

	Paricutin		Valley of 10,000 Smokes		Vesuvius		Papanda-	Merapi		Hokkaido, Showa-shin-		Berym-	
	Mexico		Alaska		Italy		Jan	Indonesia		zan Usu Volcano			ny Kam- chatka USSR
	1	2	3	4	5	6	7	8	9	10	11		
Temperature...°C...	294	120	239	350±	700	250	?	140±	100	720	730		
Date collected.....	1943(?)	1943(?)	1919	1919	1944	1944	?	2/26/31	2/23/31	9/54	9/54	10/55	
Li.....					( <sup>1</sup> )	Trace	<sup>2</sup> 0.0035						
Na.....	0.44	0.39	0.02	4.1	20.13	>10	<sup>2</sup> 0.0085	16.66	17.21	<sup>2</sup> 0.33	<sup>2</sup> 5.76	0.032	
K.....	.26	.20		.6	25.16	>10	.0039	5.64	3.57	<sup>2</sup> .16	<sup>2</sup> 5.49	.012	
Cu.....			.23		.1	.1	.0003			.005	.012		
Ag.....					.0005	.0014				.0002	.005		
Mg.....				2.7	.01	.1	<sup>2</sup> .0001	2.75	3.25	<sup>2</sup> .21	<sup>2</sup> 1.10	.017	
Ca.....				3.5	.07	1	.0030	Trace	Trace	<sup>2</sup> .50	<sup>2</sup> 1.24	.19	
Sr.....					1	.1							
Zn.....			.47	.01±	( <sup>1</sup> )	( <sup>1</sup> )	.0005				.25		
Pb.....			.005	.01±	.01	1				.001	.20		
Mn.....			<sup>2</sup> .13		.001	.01							
Fe.....			Dominant	<sup>2</sup> 1.0		.01	.0001	.73	1.43	<sup>2</sup> 18.30	<sup>2</sup> 6.57	.01	
Al.....				23.5	.03	.1	<sup>2</sup> .0012	1.65	1.93	<sup>2</sup> 3.41	<sup>2</sup> 24.09	.021	
Ge.....										.0015	.005		
Tl.....			<sup>2</sup> .005		( <sup>1</sup> )	.1	<sup>2</sup> .0001						
Sn.....			.004+					Trace	Trace	.04	.18		
P.....							.0000						
As.....			( <sup>1</sup> )	<sup>2</sup> .5			.0002			.01	.50		
Sb.....			Present				.0009				.025		
Ti.....					( <sup>1</sup> )	.001	.0030						
S.....					( <sup>1</sup> )		99.93	Trace	Trace			.018	
SO <sub>4</sub> .....			.27	19.1			.0059	26.0	47.17			.44	
F.....	.57	.53		14.9								.0067	
Cl.....	63.22	64.95	.03	1.9	53.43	52.82	( <sup>1</sup> )	23.96	4.35	.00	.00	.167	
NH <sub>4</sub> .....	30.65	30.17		< 1				.05	.40	.0082	.018		
CO <sub>2</sub> .....								.03	.92			.1	
SiO <sub>2</sub> , or insoluble.....			.53	26.5	.60	.01	.015	2.42	1.72	76.48	46.50	.015	
H <sub>2</sub> O.....					.26			20.45	17.4	.00	2.11		

<sup>1</sup> Looked for but not found.<sup>2</sup> Calculated as oxides.<sup>3</sup> With SO<sub>4</sub>.

## REFERENCES AND COMMENTS FOR SAMPLES 1-12

- 1- 2. Solid condensates in glass tubes (Foshag and Henderson, 1946, p. 686); No. 1 gives alkaline reaction, excess NH<sub>3</sub> is 1.19 percent; No. 2 gives acid reaction, excess HCl, 2.44 percent.
3. Zies, 1929, p. 6; analysis 148 of magnetite; Sb, "present"; Hg, Cr, V, Bi, "none"; Mo, 0.04 percent; Co, 0.02 percent; Ni, 0.01 percent.
4. Ibid, p. 23; analysis 131 of "incrustation"; also contains 0.2 percent Ba.
5. Cipriani, 1953, p. 39, 40, 45; Cu, Sr, Zn, Pb, Ti, Mn, from semiquantitative spectrographic analysis; Rb, Ni, not found; V, trace.
6. Ibid, p. 39, 40, 45; Na, K, Cu, Mg, Ca, Sr, Pb, Al, Ti, Mn, Fe, V, Tl, SiO<sub>2</sub> from semiquantitative spectrographic analysis; Rb, Ni, not found; V, 0.0001.
7. Neumann van Padang, 1951, p. 84; yellow native sulfur, also containing 0.0076 percent Se.
- 8- 9. Hartmann, 1933, p. 123; No. 8 is of yellow NaCl and alum; No. 9 is of white alum, contains 0.00 Br.
- 10-11. Nemoto and others, 1957, p. 122; No. 10 (9151) is of black highest temperature part of sublimate, with trace of Mo; No. 11 (9102) of reddish-gray low-temperature part of a different fumarole, with 0.002 percent of Bi.
12. Basharina, 1958b; analysis 749a of aqueous extract of sublimate on fresh ash, stated in percent of air-dried ash; pH, 4.0; some of cations presumably leached from ash. Also contain 0.0006 percent B, 0.0016 percent Br, and trace of I.



## DATA OF GEOCHEMISTRY

TABLE 6.—Gases in rocks, in volume percent

No.	Location or source	H <sub>2</sub> O	CO <sub>2</sub>	CO	S <sub>2</sub>	SO <sub>2</sub>	H <sub>2</sub>	O <sub>2</sub>	N <sub>2</sub>	Ar	Cl <sub>2</sub>	F <sub>2</sub>	H <sub>3</sub> BO <sub>3</sub>	CH <sub>4</sub>	Volume of gas per gram of rock (cc/g)
<b>Obsidians</b>															
1	Big Glass Mountain, Calif.....	88.386	1.402	0.705	0.367	-----	0.101	-----	2.897	0.000	2.965	3.163	-----	-----	1.19
2	Coso Mountains, Calif.....	89.246	.179	.073	.000	-----	.501	-----	3.897	.002	1.820	7.795	-----	-----	1.45
<b>Rhyolite</b>															
3	Kozu-shima, Japan.....	63.0	25.9	(*)	-----	(1)	-----	Trace	11.1	(1)	-----	-----	-----	-----	.36
<b>Andesites and dacites</b>															
4	Mount Pelée lava of 1902.....	82.525	10.109	2.007	0.422	-----	.252	-----	0.854	0.008	0.387	3.317	-----	-----	4.8
5	Mount Pelée pumice glass, 1902.....	70.812	7.441	1.256	2.892	-----	.435	-----	2.371	.007	10.495	4.289	-----	-----	5.9
6	Lassen Peak bomb, 1915.....	93.658	2.070	.623	.882	-----	.412	-----	.577	.003	.297	1.524	-----	-----	9.5
7	Andesites.....	97.20	1.64	.10	-----	-----	.38	-----	.05	0	0	0	0	0.03	-----
8	Asama-yama andesite, Japan.....	21.6	47.8	(*)	-----	10.2	-----	3.1	17.2	Trace	-----	-----	-----	-----	.241
9	Sambe-yama dacite, Japan.....	11.8	70.6	(*)	-----	.9	-----	2.6	14.1	-----	-----	-----	-----	-----	.506
<b>Basalts</b>															
10	Kilauea molten lava, 1916.....	80.834	11.757	0.148	1.662	-----	0.376	-----	0.280	Trace	1.334	3.609	-----	-----	6.9
11	Kilauea Pahoehoe, 1923.....	74.953	6.262	.038	.988	-----	.435	-----	2.047	0.003	1.152	14.115	-----	-----	5.0
12	Mauna Loa pumice, 1926.....	73.199	15.304	1.426	.236	-----	4.410	-----	5.193	.015	.213	.000	-----	-----	6.2
13	Niuafoua lava, 1929.....	71.322	10.358	8.276	1.278	-----	1.108	-----	7.207	.018	.430	.000	-----	-----	3.9
14	Higashiyama, Japan.....	22.7	58.0	(*)	-----	Trace	-----	2.3	17.0	Trace	-----	-----	-----	-----	.242
<b>Granites</b>															
15	Stone Mountain, Ga.....	90.512	1.965	0.081	0.268	-----	4.823	-----	0.334	0.007	0.007	1.970	-----	-----	34.2
16	North Jay, Vt.....	79.599	4.236	.536	.159	-----	11.603	-----	1.228	.024	.051	2.563	-----	-----	29.4
17	Granites and gneisses.....	95.54	1.70	.26	-----	-----	2.25	-----	.15	-----	0	0	0	.10	-----
<b>Other rocks</b>															
18	Marvine laccolite, Utah.....	69.439	9.463	0.814	4.042	-----	13.455	-----	0.566	0.002	0.300	1.914	-----	-----	31.2
19	New Market diabase, Md.....	90.059	.894	.023	1.844	-----	4.813	-----	1.911	Trace	.189	.275	-----	-----	30.0
20	Diabases and basalts.....	93.23	3.37	.84	-----	-----	2.31	-----	.11	-----	0	0	0	.14	-----
21	Gabbros and diorites.....	96.05	.28	.07	-----	-----	3.29	-----	.16	-----	0	0	0	.15	-----
22	Syenites.....	98.61	.13	.07	-----	-----	1.08	-----	.05	-----	0	0	0	.06	-----
23	Iron meteorites.....	-----	75.6	8.8	-----	-----	12.5	-----	3.1	-----	-----	-----	-----	.0	.016
24	Dunite, N. Urals, USSR.....	-----	-----	-----	-----	-----	66.5	3.8	20.5	.22	-----	-----	-----	9.5	-----

<sup>1</sup> Looked for but not found.

<sup>2</sup> N<sub>2</sub> includes CO.

<sup>3</sup> H<sub>2</sub> misprinted as 2.5 percent, but calculation of original data indicates 12.5 percent.

## REFERENCES AND COMMENTS FOR SAMPLES 1-24

- 1-2. Shepherd, 1938, No. 1 and 3, p. 326; analysis from Coso has total of 103.51 percent.  
 3. Iwasaki, and others, 1955, p. 780.  
 4-6. Shepherd, 1938, No. 8, 10, and 12, p. 326.  
 7. Nikogosyan, 1940.  
 8-9. Iwasaki, and others, 1955, p. 780.  
 10-13. Shepherd, 1938, No. 16, 18, 23, 25, p. 326.  
 14. Iwasaki, and others, 1955, p. 780.  
 15-16. Shepherd, 1938, No. 26-27, p. 326.  
 17. Nikogosyan (1940).  
 18-19. Shepherd, 1938, No. 29, 30, p. 326.  
 20-22. Nikogosyan, 1940.  
 23. Nash and Baxter, 1947; HCN, 0.0.  
 24. Gas escaping from borehole (Zavaritskii and Betekhtin, 1937, p. 72); He, absent.

TABLE 7.—Selected analyses of gases in rocks  
[Recalculated excluding H<sub>2</sub>O. After Shepherd, 1938, p. 326-337]

No.	Gases, including H <sub>2</sub> O, volume per gram of rock (cc/g)	H <sub>2</sub> O (percent of total gases)	Gases, excluding H <sub>2</sub> O		Gases (H <sub>2</sub> O excluded) recalculated to 100 percent							
			Percent of total gases	Volume per gram of rock (cc/g)	CO <sub>2</sub>	CO	H <sub>2</sub>	N <sub>2</sub>	Ar	S <sub>2</sub>	Cl <sub>2</sub>	F <sub>2</sub>
<b>Obsidians</b>												
1	1.19	88.386	11.60	0.138	12.09	6.08	0.87	24.97	0.00	3.16	25.56	27.27
2	27.10	96.299	4.253	1.15	37.50	.82	4.09	33.39	.00	.33	11.73	12.13
3	1.45	89.246	14.267	.207	1.25	.51	3.51	27.31	.01	.00	12.76	54.64
4	4.89	94.434	7.230	.354	1.04	.11	31.16	15.95	.00	.54	20.72	30.50
5	55.3	92.761	7.236	4.01	9.29	.10	5.21	1.91	.00	.00	23.67	59.83
6	214.8	98.551	1.447	3.11	5.32	2.21	5.53	3.66	Undet.	.00	4.77	78.51
<b>Andesitic lavas</b>												
7	4.8	82.525	17.356	0.835	58.24	11.56	1.45	4.92	0.05	2.43	2.23	19.11
8	5.9	70.812	29.186	1.72	25.50	4.30	1.49	8.12	.02	9.91	35.96	14.70
9	26.5	96.227	3.760	.998	21.91	5.69	11.36	5.66	Trace	1.41	26.36	27.61
10	9.5	93.653	6.388	.606	32.40	9.75	6.45	9.03	.05	13.81	4.65	23.86
<b>Basaltic lavas</b>												
11	6.9	80.834	19.166	1.32	61.34	0.77	1.96	1.46	0.00	8.67	6.96	18.83
12	7.3	78.100	21.893	1.60	51.03	.21	2.12	5.96	Trace	7.65	4.70	28.33
13	5.0	74.953	25.040	1.25	25.01	.15	1.74	8.18	.01	3.95	4.60	56.37
14	4.2	74.402	25.590	1.07	30.84	7.33	2.03	10.02	.02	1.77	2.13	45.85
15	6.6	75.914	24.084	1.59	9.71	.29	13.00	10.45	.01	8.13	3.07	55.35
16	6.2	73.199	26.797	1.66	57.11	5.32	16.46	19.38	.06	.88	.79	.00
17	2.9	79.892	20.155	.585	64.41	4.89	19.21	8.68	.18	2.36	.27	.00
18	3.9	71.322	28.675	1.12	36.12	28.86	3.86	25.13	.06	4.46	1.50	.00
<b>Granites</b>												
19	34.2	90.512	9.455	3.23	20.78	0.86	51.01	3.53	0.07	2.83	0.07	20.84
20	19.4	79.599	20.400	6.00	20.76	2.62	56.88	6.02	.12	.78	.25	12.56

## EXPLANATION OF SAMPLES 1-20

1. Dense black obsidian, Big Glass Mountain, Calif.; Shepherd No. 1.
2. Pumiceous phase of No. 1. Shepherd 2; poor summation, 100.552 percent.
3. Dense black obsidian, Coso Mountains, Calif. Shepherd 3; very poor summation, 103.513 percent.
4. Coarsely vesiculated part of No. 3. Shepherd 4; poor summation, 101.664 percent.
5. Dense black obsidian, Cerro Noagua, N. Mex. Shepherd 5.
6. Pitchstone, Cerro Noagua, N. Mex. Shepherd 6.
7. Spine, 1902-03, Mount Pelée, some glass; Shepherd 8.
8. Pumice, nuée ardente, July 1902, Mount Pelée; Shepherd 10.
9. Glassy shell, bomb from Mount Pelée; Shepherd 11.
10. Surface of 1915 breadcrust bomb, Lassen Peak; Shepherd 12.
11. Kilauea lava dipped from lava lake; Shepherd 16.
12. Kilauea lava, same time and conditions as No. 11; Shepherd 17.
13. Kilauea, pahoehoe, 1923 Makaopuhi flow; Shepherd 18.
14. Kilauea, aa, same flow as No. 13; Shepherd 19.
15. Kilauea, lava brought up on sounding rod; Shepherd 22.
16. Mauna Loa, pumice, 1926 summit eruption; Shepherd 23.
17. Mauna Loa, 1926 aa flow (Murata, oral communication, 1961) from 1,400-foot altitude; Shepherd 24.
18. Niuafoou Island, 1929 eruption; Shepherd 25.
19. Stone Mountain granite; Shepherd 26.
20. North Jay granite; Shepherd 27.



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