BULLETIN OF THE GEOLOGICAL SOCIETY OF AMERICA
VOL. 68, PP. 1637–1658, 5 FIGS. DECEMBER 1957

THERMAL WATERS OF VOLCANIC ORIGIN

BY DONALD E. WHITE

ABSTRACT

Waters of widely differing chemical compositions have been considered at least in part volcanic in origin, and are commonly associated with each other in the same area. Do any or all of these types contain volcanic components, and if so, how are the different types derived?

To determine the probable characteristics of volcanic waters, the writer has selected hot-spring groups that are particularly high in temperature and associated heat flow, are associated with late Tertiary or Quaternary volcanism, and are therefore most likely to contain some water and chemical components of direct volcanic origin. Of the different types of water that occur in these groups, one of the most common is characterized chemically by a dominance of sodium chloride.

Isotopic evidence indicates that the contribution of water of direct volcanic origin is not large and is probably no more than 5 per cent in typical sodium-chloride springs.

The compositions of volcanic waters are believed to be determined by: [1] type of magma and stage of crystallization; [2] temperature and pressure of the emanation at different stages during and after departure from the magma; [3] chemical composition, relative quantity, and depth of penetration of mixing meteoric water and water of other origin; and [4] reactions with wall rocks. Although the type of magma and its stage of crystallization are of major interest and have been emphasized in the past, the outstanding characteristics of volcanic emanations at and near the surface of the earth seem to be controlled for the most part by the other factors.

Nonvolatile compounds are slightly to highly soluble in steam at high pressure, and high-density steam has solvent properties similar to those of liquid water. In the volcanic sodium-chloride waters, the high ratio of lithium to sodium and potassium is shown to indicate that alkalies were transported as alkali halides dissolved in a dense vapor. This in turn demands a deep circulation of meteoric water for steam to condense at high pressure and for the halides to remain in solution. The depth of circulation of meteoric water in the sodium-chloride spring systems is believed to be in the order of 2 miles. Where circulation of meteoric water is shallow, the vapors rise and expand at low pressure, which does not permit transport of substances of low volatility; some type of water other than the sodium-chloride type is formed. The common volcanic sodium-chloride waters are therefore concluded to be the diluted product of high-density emanations, modified by reactions with wall rocks and by precipitation of the less soluble components.

Emanations at high temperature and relatively low pressure consist almost entirely of steam and volatile components. Their compositions are therefore relatively simple, and their ability to transport matter of low volatility is very limited.

The sodium-chloride type is probably gradational into acid-sulfate-chloride waters. There is some evidence that, under conditions not well understood, sulfur may be emitted as SO_2, SO_3, or other sulfur species of intermediate valence, rather than as H_2S or S. Other major types of volcanic waters are called sodium bicarbonate, acid sulfate, and calcium bicarbonate; the first two tend to be distinct, but the calcium-bicarbonate type clearly grades into the sodium-chloride type. The writer concludes that, in general, all these are derived from the sodium-chloride waters as a result of physical environment or of reactions with wall rocks.

CONTENTS

TEXT

	Page
Introduction	1638
Scope	1638
Definitions	1638
Thermal spring	1638
Hydrothermal	1638
Magmatic water	1638
Plutonic water	1639
Volcanic water	1639
Mixed water	1639
Acknowledgments	1639
Evidence for volcanic water	1639
Factors that probably influence chemical composition	1643
Volcanic emanations at or near the surface	1644
Superheated volcanic fumaroles	1644
Sodium-chloride waters	1644
Acid-sulfate-chloride waters	1647
Sodium-bicarbonate waters	1649
Acid-sulfate waters	1651
Calcium-bicarbonate waters	1652
Outline of possible modes of origin of the major types of volcanic waters	1653
References cited	1656

ILLUSTRATIONS

Figure	Page
1. Pressure-temperature-enthalpy diagram for steam and water	1644
2. Suggested genesis of volcanic sodium-chloride waters by two mechanisms	1645
3. Suggested genesis of acid-sulfate-chloride waters	1645
4. Suggested genesis of volcanic sodium-bicarbonate waters by three possible mechanisms	1650
5. Suggested genesis of volcanic calcium-bicarbonate water	1653

TABLES

Table	Page
1. Analyses of hot springs that are characterized by high temperatures and associated heat flow	1640
2. Maximum measured temperatures and estimated heat flow of some areas that contain analyzed thermal waters of probable volcanic origin	1642
3. Analyses of gases from areas of volcanic hot springs	1648
4. Suggested environmental relationships of the major types of volcanic waters	1654

INTRODUCTION

Scope

Waters of widely differing compositions have been considered volcanic in origin. Table 1 contains typical analyses of the principal types that have been recognized and shows the differences that are to be found in the major components. Are these waters entirely or in part of volcanic origin, and if volcanic, how are their greatly differing compositions explained? These questions have puzzled not only those geologists who have searched the literature for average or typical analyses, but also those who have studied hot springs in detail. Barth (1950, especially p. 39–43), for example, has considered some of the problems but has reached conclusions that are completely unacceptable to the writer.

The purpose of this paper is to describe the principal types of volcanic hot springs and to suggest processes that may account for their compositional differences.

Definitions

Thermal spring.—G. K. Gilbert (1875, p. 149) considered springs as thermal if their temperatures were more than 15°F. above mean annual temperature of the area. Stearns *et al.* (1935, p. 61) included some springs in their thermal list even though temperatures were not more than 10°F. above mean annual temperature. A temperature significantly above the mean annual temperature of the region characterizes the thermal springs. In general, 5°C. or 10°F. is considered significant.

Hydrothermal.—Of or pertaining to any water that is appreciably warmer (5°C. or more) than the surrounding environment. According to Holmes (1928, p. 121) the term refers to "magmatic emanations rich in water", and the same view is held by many geologists, but this was clearly not the intent of Morey and Niggli, (1913, p. 186–188), who first brought the term into popular use. It should refer to any water that is warm or hot relative to its surrounding environment, and it should have no genetic implications.

Magmatic water.—Water that is in, or is derived from, magma. It is a general term without restriction to depth or ultimate origin. Some magmatic water is probably juvenile, never having appeared previously at the surface, but much may actually be recycled, through remelting or partial melting of sedi-

mentary and volcanic rocks, or by absorption from intruded rocks.

Plutonic water.—Water that is in, or that has separated from, magma at considerable depth. The minimum depth is not known but is that of plutonic rocks—probably in the order of several miles.

Volcanic water.—Water that is in, or that has separated from, magma at the surface or at relatively shallow depth. The precise depth that separates volcanic from plutonic processes is not yet known; complete gradations are assumed. The waters with which this paper is concerned are in areas of recent or active volcanism. Considerations of heat flow appear to demand magma chambers at depths as great as 2–3 miles or somewhat more. The thermal activity is considered to be a phase of the volcanism.

Mixed water.—Many waters are believed to be mixtures of waters of different origins. If known, a mixture should ordinarily be identified by its components. Waters of deep origin, however, are ordinarily diluted near the surface by meteoric water. It is useful to refer to such mixtures by the deep component, which, if not diluted too extensively, largely determines the chemical and physical characteristics of mixture. In this paper the term volcanic water is used for all mixtures of volcanic and meteoric water even though the latter is greatly dominant. The deep component before dilution is called water of direct volcanic origin. Allen and Day (1935) applied the term "mixed" to acid waters high in chloride and sulfate, a usage that should not be continued.

Acknowledgments

The writer wishes to express his great indebtedness to James Healy of the Geological Survey of New Zealand, to C. J. Banwell, Dominion Physical Laboratory of New Zealand, and to Gunnar Bodvarsson of the Iceland Electricity Authority for stimulating discussions and correspondence concerning volcanic waters, and for reviews of the manuscript. Banwell has generously permitted use of Figure 1 of this paper. E. G. Zies, G. C. Kennedy, and R. M. Garrels have kindly read the manuscript and have offered many helpful suggestions and criticisms.

The writer owes much to his colleagues of the U. S. Geological Survey and in particular to Edgar Bailey, H. L. James, A. H. Lachenbruch, Ray Wilcox, P. F. Fix, H. R. Cornwall, C. H. Sandberg, P. E. Cloud, Jr., Siegfried Muessig, J. H. Feth, and Wilbur Burbank. None of these friends, however, is to be held responsible for the views that are expressed.

Evidence for Volcanic Water

A major problem is that of distinguishing volcanic or magmatic from non-magmatic waters. What criteria are conclusively diagnostic? The writer knows of no specific tag or label, such as the presence or absence of a particular element or isotope, to identify with certainty a volcanic water; in fact, he believes that no such tag exists.

Although it is possible to collect fumarolic gases, deep volcanic waters obviously cannot be sampled at their sources. Without prior definite knowledge of the compositions of deep emanations, nonchemical criteria must be used to point to those waters that are most likely to contain volcanic components. The most significant are held to be high temperatures and associated heat flow. In this paper, a few spring groups have been selected for critical examination, because of their abnormally high temperatures and heat flows (Table 2).

The quantity of uranium demanded to account for the heat flow at Steamboat Springs, Nevada, is approximately 300 million tons, an amount so large that magma rather than radioactivity is demanded. The thermal conductivity of bedrock granodiorite at Steamboat Springs is approximately 0.006 cal./cm sec. deg. If the quantity of heat that is flowing to the surface at Steamboat is at any depth transferred entirely by conduction through a cross-sectional area equal to Steamboat's surface area (5 sq. km), the geothermal gradient required is about 1°C. per 1¼ feet of depth. If this heat flow were transferred to the surface entirely by conduction, magmatic temperatures of 600°C. should exist at depths of only 750 feet.

In fact, however, the heat is transferred almost entirely in hot water that is dominantly meteoric in origin. It must be heated at depth by conduction, by high temperature (volcanic) stream, or by a combination of the two. If steam is lacking and meteoric water is heated by conduction the necessary thermal gradient is a function of the effective surface area of the walls of the fissure controlling circulation of the water. A fissure 2 km long and 1 km deep has a maximum effective surface area (both walls) of 4 square km; the average horizontal temperature gradient in the walls must then be about 1°C. per foot. Even a fissure 5 km long and 3 km deep requires an average horizontal gradient of 1°C. per 7½ feet. These gradients,

TABLE 1.—ANALYSES OF HOT SPRINGS THAT ARE CHARACTERIZED BY HIGH TEMPERATURES AND ASSOCIATED HEAT FLOW, IN PARTS PER MILLION

	Steamboat Springs Washoe County Nevada[1]	Morgan Springs Tehama County California[2]	Norris Basin Yellowstone Park Wyoming[3]	Upper Basin Yellowstone Park Wyoming[4]	Well 4 Wairakei New Zealand[5]	Norris Basin Yellowstone Park Wyoming[6]	Frying Pan Lake New Zealand[7]	Well 5 Wairakei New Zealand[8]	Acid Pool, Norris Yellowstone Park Wyoming[9]	Mammoth Yellowstone Park Wyoming[10]
Type of water	Sodium chloride	Sodium chloride	Sodium chloride	Sodium chloride	Sodium chloride	Acid sulfate chloride	Acid sulfate chloride	Sodium bicarbonate	Acid sulfate	Calcium bicarbonate
Temp. °C.	89.2	95.4	84	94.5	>100	87	59	>100	70	70.5
pH	7.9	7.83	7.45	8.69	8.6	2.47	3.0	6.7	2.2	6.9
SiO_2	293	233	529	321	386	496	428	191	364	56
Fe				Tr.		0.8	3		2.9	
Al				0		1.5	4		1.6	
Ca	5.0	79	5 8	4	26	6.5	17	12	2.6	209
Mg	0.8	0.8	0.2	Tr.	<0.1	nil	4	1.7	1.0	78
Sr	0.1	10								
Na	653	1398	439	453	1130	243	607	230	27	129
K	71	196	74	17	146	61	70	17	24	56
Li	7.6	9.2	8.4		12.2	3.2		1.2	0.1	1.4
NH_4	<1	<1	0.1	0	0.9	3.4		0.24	10	
As	2.7	2.2	3.1							
Sb	0.4	0.0	0.1							
CO_3	0	0	0	66						
HCO_3	305	52	27	466	35	nil	(nil)	670	nil	526
SO_4	100	79	38	15	35	454	262	11	482	529
Cl	865	2427	744	307	1927	408	953	2.7	6.0	169
F	1.8	1.5	4.9	21.5	6.2			3.7		
Br	0.2	0.8	0.1							
I	0.1	<0.1	<0.1							
B	49	88	11.5	3.7	26	6.9	14	0.5	1.5	4.4
S_2O_3				2						
H_2S	4.7	0.7	0	0	1.1		nil	0		2.4
CO_2					11			0		
Sum	2359	4577	1885	1676	3742	1684.3	2362	1141.04	922.7	1760.2

Ratios										
HCO_3/Cl[11]	0.35	0.021	0.036	1.9	0.018	0.000	0.000	250	0.00	3.1
SO_4/Cl	0.12	0.033	0.051	0.049	0.018	1.1	0.28	4.1	80	3.1
F/Cl	0.0021	0.0006	0.0066	0.070	0.0032			1.4		
Br/Cl	0.0002	0.0003	0.0001							
I/Cl	0.0001	<0.00004	<0.0001							
B/Cl	0.057	0.036	0.015	0.012	0.013	0.017	0.015	0.2	0.25	0.026
K/Na	0.11	0.14	0.17	0.038	0.13	0.25	0.12	0.074	0.89	0.43
Li/Na	0.012	0.0066	0.019		0.011	0.013		0.0052	0.004	0.011
Ca + Mg/Na + K	0.0080	0.050	0.012	0.008	0.020	0.021	0.031	0.055	0.071	1.6

[1] Spring 8, collected 8/9/49, analyzed by W. W. Brannock, U. S. Geological Survey. Sr by spectrographic analysis but is probably about 0.6 ppm judging from samples collected at Steamboat in 1954.

[2] Black Growler Spring, collected 7/29/49, analyzed by W. W. Brannock, U. S. Geological Survey. Sr by spectrographic analysis.

[3] Unnamed spring with periodic discharge depositing abundant silica, 200 feet southwest of Pearl Geyser. Collected 8/13/51, analyzed by P. W. Scott and W. W. Brannock, U. S. Geological Survey.

[4] Sapphire Pool (Allen and Day, 1935, p. 103, 249). Analyzed by E. T. Allen.

[5] Erupting well in eastern part of Wairakei area (Wilson, 1955, p. 37).

[6] Green Dragon Spring, collected 8/27/54. Analyzed by Henry Kramer. Estimated discharge, 40 gpm.

[7] Estimated discharge "greater than 1,000 gpm." (Grange, 1937, p. 93, 103, analysis 28).

[8] Erupting well in western part of Wairakei area (Wilson, 1955, p. 37).

[9] Spring with seeping discharge, 45 feet west of Norris Basin drill hole described by Fenner (1936, p. 282–285). Collected 8/25/54, analyzed by Henry Kramer.

[10] Blue spring, crest of Main Terrace, collected 8/25/54, analyzed by Henry Kramer.

[11] All carbonate computed as bicarbonate.

if continued for considerable distances under steady-state conditions, require magmatic temperatures within about 600 feet of the fissure for the first example and 4200 feet for the second.

necessary to supply stored heat at submagmatic temperatures.

The volumes, length of time, and required gradients also suggest that an inert crystallizing magma chamber does not satisfy the demands.

TABLE 2.—MAXIMUM MEASURED TEMPERATURES AND ESTIMATED TOTAL HEAT FLOW OF SOME AREAS THAT CONTAIN ANALYZED THERMAL WATERS OF PROBABLE VOLCANIC ORIGIN

Locality	Max. temps., degrees C.		Heat flow 10^6 cal./sec.	Equiv. km^2 of "normal" area[1]	Approx. size of thermal area, km^2	Multiple of "normal" for area	Yearly requirement of magma, km^3 [2]
	Surface	Drill Holes					
Steamboat Springs, Nevada[3]	boiling	172	7	600	5	120	0.00047
Morgan Springs, California[4]	boiling						
Yellowstone Park							
Norris Basin	boiling	205[5]	8[6]	660	3	220	0.00053
Upper Basin		180[5]	90[7]	7500	10	750	0.0060
Mammoth and Hot River area	75°		34[8]	2800	8	350	0.0023
New Zealand							
Wairakei area	boiling	270	110[9]	9200	15	610	0.0075
Frying Pan Lake	55°		23[10]	1900	1	1900	0.0015

[1] Heat flow from "normal" areas is about 1.2×10^4 cal./sec. sq. km (Birch, 1954).

[2] The magma is assumed to be granite initially liquid at 900° C. and is assumed to cool and be entirely crystalline at 500° C. The mean heat of crystallization is assumed to be 75 cal./gm (Goranson, 1942, p. 235–236) and the heat capacity through this temperature range, ¼ cal./gm° C. (Goranson, 1942, p. 237–238). The total available heat of the magma above 500° C. is thus 175 cal./gm, or about 4.7×10^{17} cal./km^3, assuming a density of 2.7.

[3] Data, in part not previously published.

[4] On the south border of Lassen Volcanic National Park, an area with historic volcanic eruptions (Day and Allen, 1925, p. 98–100, 113).

[5] Fenner, 1936, p. 237, 291.

[6] Allen and Day, 1935, p. 135. Discharge, 39 liters/sec. of water containing 3.1×10^6 cal./sec. excess heat at discharge temperatures. If all has cooled from the maximum recorded fluid temperature of 205° C. (at depth of 246 feet), the heat flow is 7.8×10^6 cal./sec. This is a more realistic figure and allows for very abundant steam flow at Norris.

[7] Allen and Day, 1935, p. 135. Discharge, 518 liters/sec. of water containing 44×10^6 cal./sec. at discharge temperatures. If all has cooled from the maximum recorded fluid temperature of 180° C. (at depth of 406 feet), the total heat flow is 90×10^6 cal./sec.

[8] Allen and Day, 1935, p. 135, 386. Heat flow in discharging water, probably close to total because temperatures are relatively low with little heat loss in vapor or by conduction.

[9] Approximate average of physical methods (133×10^6 cal./sec., Healy, 1953; Banwell, 1955, p. 50) and chemical methods (82×10^6 cal./sec., Ellis and Wilson, 1955, p. 629).

[10] Assuming 1000 gpm, 55° C. at outlet (Grange, 1937, p. 92), and mean annual temperature of 15° C., the excess heat content of the flowing water is 2.5×10^6 cal./sec. The evaporative heat loss from the lake, about 5 acres in area, is approximately 20×10^6 cal./sec., according to John Banwell of the Dominion Physical Laboratory, New Zealand (Personal communication).

For young spring systems, the necessary heat could come from a stored supply, but Steamboat Springs, for example, has been active for all the post-Pleistocene, and its age is more probably in the order of 100,000 years. The present heat flow, if representative of such an interval, requires a total volume of magma of 47 km^3 (Table 2). A much larger volume is

A magma chamber with convection is indicated in order to maintain high temperatures near the chamber walls.

The necessary heat can also be supplied entirely by volcanic steam. The temperature of the hot spring water at shallow depth in the Steamboat Springs system, for example, is about 170°C., and its enthalpy (or heat con-

tent above 0°C.) is about 170 cal./gm (Fig. 1). If steam at the critical point is heating cold meteoric water, approximately 35 per cent of volcanic steam, with an enthalpy of 500 cal./gm., is required. Steam at any likely volcanic temperature cannot have an enthalpy of more than about 1000 cal./gm. If such steam supplies all the heat, about 17 per cent is required.

These calculations clearly indicate the need for magma. They also point out the function that volcanic steam may play in supplying at least part of the heat. Regardless of the relative importance of conduction and steam in supplying heat, a magmatic source is clearly required for old thermal systems. If magma contains water, and water is evolved during cooling and crystallization, then the springs of Table 2 are likely places to look for volcanic water.

Lindgren (1933, p. 47–49, and earlier work) was one of the first to conclude that the varied waters found intimately associated in these volcanic environments contain relatively high concentrations of substances such as CO_2, sulfur, boron, chlorine, and alkali metals. In general, this paper concludes that most of these waters are derived from dense supercritical vapor containing much sodium chloride. In a companion paper (White, 1957), the sodium-chloride waters from volcanic environments are compared with other waters high in sodium chloride. Chemical criteria then become apparent for distinguishing volcanic sodium-chloride waters from non-volcanic waters.

Near the surface, waters of volcanic association clearly consist dominantly of meteoric water. This has long been suspected by most geologists, but strong isotopic evidence for this view is shown by Craig, Boato, and White (1954; 1956; and forthcoming papers). The surface waters of New Zealand, Lassen Park, Yellowstone Park, Steamboat Springs, and Iceland differ isotopically from each other, but the hot springs of each area are very similar to the surface water of the same area. In the waters that have been studied, the volcanic component probably does not exceed 5–10 per cent of the total, and the isotope evidence does not actually demand the existence of any volcanic water. If the primary volcanic emanations have salinities similar to or greater than that of sea water, and are diluted 10–20 times by meteoric water, all data pertaining to heat flow, chemical composition, and isotopes are found to be mutually compatible. If, in view of the isotopic evidence, it is assumed that no hydrous volcanic emanations are involved, then all the heat flow must be accounted for by conduction, and most chemical components must be derived from wall rocks. Some quantitative aspects of this possibility have already been described, and others will be examined. The possibility is found to be very unlikely.

Factors that Probably Influence Chemical Composition

The compositions of volcanic waters and vapors are believed to be determined by the following: [1] type of magma and stage of crystallization; [2] temperatures and pressures of the volcanic emanation during and after departure from the magma; [3] the chemical composition, relative quantity, and depth of penetration of mixing meteoric water or water of other origin (White, 1957); and [4] reactions with wall rocks. The type of magma and its stage of crystallization are of major interest, but the dominant characteristics of volcanic emanations at and near the surface of the earth seem to be determined to a major extent by the other factors.

The physical state of volcanic water as it leaves the magma and while it migrates toward the surface is believed to account for the greatest differences in composition. Recent work has demonstrated that many compounds of low volatility are soluble in water vapor near and above the critical point (Schröer, 1927; Kennedy, 1950; Morey, 1953; 1954; Morey and Hesselgesser, 1951a; 1951b; Olander and Liander, 1950; Straub, 1946). Smith (1953, p. 25–30) and Morey (1957) have reviewed the recent evidence. In general these compounds have very low solubilities in steam of low density, but the solubilities increase with increasing density of the steam. At constant density solubilities increase with temperature, but at relatively low constant pressures they decrease with increasing temperature because of decreasing density of the vapor. Of particular importance is the relative insolubility of NaCl and other alkali halides in steam at low pressure and density, but solubilities increase greatly near the critical point of water (Schröer, 1927; Straub, 1946; Olander and Liander, 1950).

Figure 1 is a pressure-temperature-enthalpy diagram for water and steam. Solubility data for NaCl in supercritical steam (Olander and Liander, 1950) are superposed on the diagram without regard for effects on the enthalpy and critical relations.

Volcanic Emanations at or Near the Surface

Superheated Volcanic Fumaroles

Volcanic fumarole gases consist almost entirely of components of relatively high volatility. Components that are nonvolatile at the fumarole temperatures and that do not form somewhat volatile halogen compounds are very rare. The halogens are transported largely as halogen acids (Zies, 1929) and possibly as free halogens (Shepherd, 1925, p. 366; 1938, p. 321, 326), although sublimates of KCl and NaCl were found by Lacroix (1906) in high-temperature fumaroles at Vesuvius (700°–800°C.). Many but not all high-temperature fumarolic gases give acid reactions when condensed (Sborgi, 1939).

Volcanic fumarole gases are ordinarily superheated, and temperatures are far higher than equilibrium temperatures of saturated water vapor at the existing pressures. Nonvolatile substances have low solubilities in water vapor of such low density. Under favorable conditions, as in some crater lakes, the steam and acid-forming gases are no doubt completely condensed by meteoric water. The mixture, with free halogen and sulfur acids, then attacks wall rocks and dissolves most metallic elements, roughly in proportion to their abundance in the rocks.

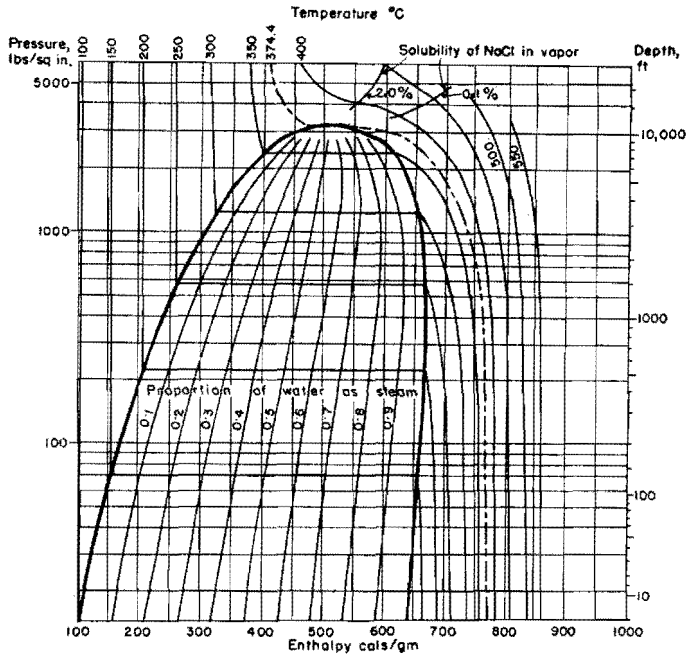

FIGURE 1.—PRESSURE-TEMPERATURE-ENTHALPY DIAGRAM FOR STEAM AND WATER

(Diagram prepared by C. J. Banwell, Dominion Physical Laboratory, D. S. I. R., New Zealand.) Solubility of NaCl in gas from Olander and Liander (1950). Depth assumes hydrostatic pressure, boiling throughout Effects of NaCl on critical temperature and enthalpy have been neglected.

Sodium-Chloride Waters

Slightly acid to alkaline waters dominated by sodium chloride and bicarbonate constitute a group that was called alkaline waters by Allen and Day (1935, p. 71–72), but are here called sodium-chloride waters. In the past the halogens were generally assumed to be transferred as volatile acids in steam, as in Figures 2*B* and 3*B*. When the steam was condensed, the acids reacted with the wall rocks and were neutralized. Some sodium-chloride waters may form in this way. The acid-sulfate-chloride waters, such as those of Norris and Frying Pan Lake (Table 1) are logical suspects, but they are also characterized by particularly high sulfate. The acidity, as will be seen, appears to be due to sulfuric rather than to hydrochloric acid. In

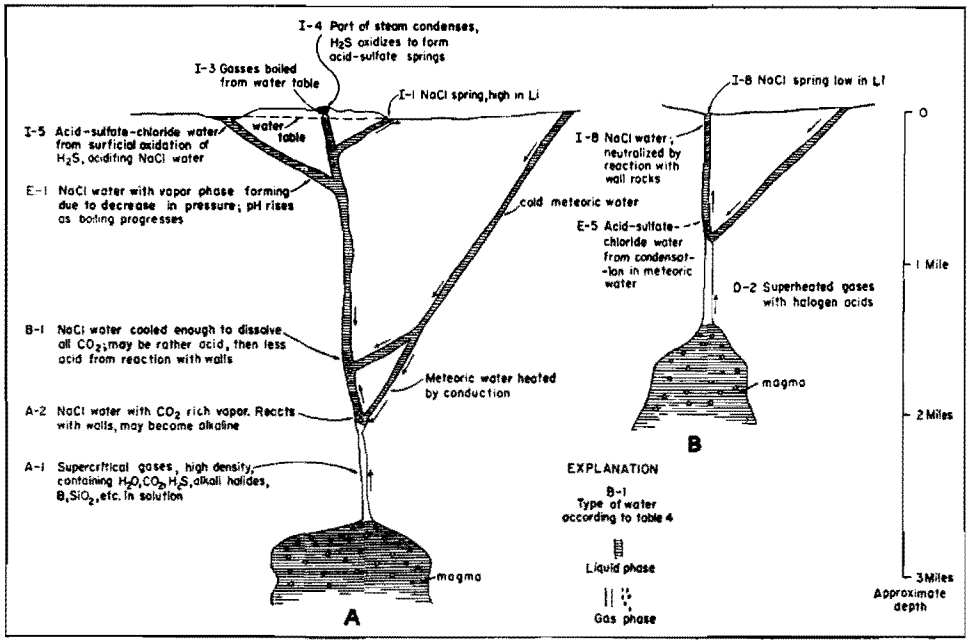

FIGURE 2.—SUGGESTED GENESIS OF VOLCANIC SODIUM-CHLORIDE WATERS BY TWO MECHANISMS

Method A seems to be the most common. Widths of fissures greatly exaggerated to permit distinguishing liquid and gas phases. Sodium-chloride water of probably high sulfate content can also be formed by sufficient reaction of acid-sulfate chloride water of Figure 3 with wall rocks.

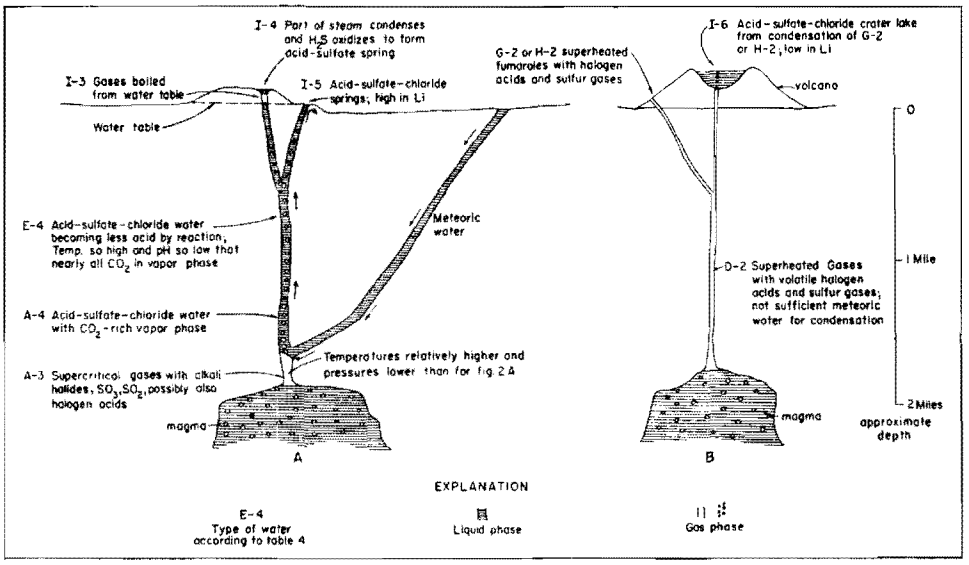

FIGURE 3.—SUGGESTED GENESIS OF ACID-SULFATE-CHLORIDE WATERS

A third method is illustrated in Figure 2*A*, I-5. Widths of fissures greatly exaggerated; lava filling of volcanic vent of *B* not shown.

view of their acidity, their surprisingly low content of calcium and magnesium (Table 1) is not consistent with the theory that their alkalies and silica were obtained entirely or even largely by leaching of wall rocks. Minor leaching of alkalies, however, is probable.

Superficial alteration by sulfuric acid is not uncommon in oxidizing sulfide deposits and hot springs (White, 1955). Deep alteration by sulfuric acid seems to be relatively rare. Of other hydrothermal alterations that may be caused by acid solutions, CO_2 rather than HCl is indicated as the active component.

When volcanic steam is evolved under sufficient pressure, the halogens are soluble in the dense vapor as alkali halides (Schröer, 1927; Ingerson, 1934; Straub, 1946; Olander and Liander, 1950), and probably little or no dissociation occurs. The alkali ratios of most if not all sodium-chloride springs favor transport of the halogens as alkali halides dissolved in the magmatic vapor phase (Table 1; Fig. 2*A*). Lithium, relative to other components, is higher in the chloride springs than in any other known type of natural water (White, 1957). The Li/Na ratios are in the order of 0.01 in these springs, 0.0008 in average igneous rocks (Rankama, 1954, p. 135), and perhaps as much as 0.005 in rhyolites in the western United States (Coats, 1956, p. 76). If the alkali content of the volcanic sodium-chloride springs is a result of leaching, a strong selective removal of lithium is necessary. As will be seen, this is not found in the acid-sulfate springs, and there is no reason to suspect that halogen acids could leach lithium so selectively in the required amounts and over the probable long lives of some of the spring systems.

For example, at Steamboat Springs, Nevada, thermal water with an average lithium content of 8 ppm is being discharged at and below the surface at a rate of about 700 gpm. Lithium is discharged at a rate of 1.1×10^7 gms or 11 metric tons per year. If Steamboat granodiorite, with an average lithium content of about 30 ppm, is completely leached of its lithium, 140,000 cu.m. are required per year. This is equivalent to 14 km^3 of granodiorite over a period of 100,000 years, which is believed to be the probable age of the spring system. Stated in another way, each pound of water must come in contact with a quarter of a pound of fresh rock and leach all the lithium from it. This may be conceivable in a new spring system where much surface area of unaltered rocks is accessible in fault and breccia zones but is highly improbable in a system as old as that of Steamboat Springs. The accessible altered rocks, moreover, indicate that lithium may be added rather than leached. Rocks containing secondary micas appear to be particularly high in Li, and as much as 300 ppm is reported in some analyses. A much more reasonable hypothesis to explain all the evidence is that lithium and the other alkali metals were concentrated in residual magma and were then transported as soluble alkali halides in a dense vapor phase. The writer suspects that the alkali metals in the emanations that leave silicic magmas are in the approximate proportions, by weight, of 1 Na:0.5 K:0.25 Li. The proportions found in surface springs (Table 1) are changed by reactions, including cation exchange with wall rocks. The other alkali metals, rubidium and cesium, probably remain for the most part in the magma and are fixed in silicate minerals. Fluorine may be relatively low in high-pressure emanations for the same reason.

Much silica is no doubt transported in solution in the dense vapor phase (Kennedy, 1950; Morey and Hesselgesser, 1951b; Morey, 1954), and additional silica is dissolved from the wall rocks. Volcanic sodium chloride waters have the highest silica content of known natural waters (White, Brannock, and Murata, 1956).

Meteoric water is believed to circulate to depths that are in the order of 10,000 feet to provide the hydrostatic pressures and vapor densities required to transport alkali halides in solution rather than as volatile compounds (Olander and Liander, 1950, p. 1443). For a column of water that is everywhere at its boiling point, hydrostatic pressure is equal to the critical pressure at a depth of about 2 miles (Fig. 1). Where vapor pressure of the emanation exceeds the hydrostatic pressure, ground water cannot penetrate to condense the vapor or to dissolve its low-volatile components. Condensation of the vapor at high pressure seems to be an essential stage in the continuous transfer of substances like sodium chloride from the magma to the surface.

Where the vapor channel is very restricted and low in permeability, opening suddenly into permeable channels filled with meteoric water, it is possible for the zone of intermixture to be less than 10,000 feet in depth and still maintain the relationships essential for continuous transport of alkali halides. The minimum depth in these special circumstances is about 3000 feet, where lithostatic pressure is equal to the critical pressure of water.

Drilling at Wairakei, New Zealand (Healy, 1953; Banwell, 1955; Ellis and Wilson, 1955)

to depths of more than 3000 feet indicates that water, dominantly of meteoric origin, circulates to depths that are unknown but are certainly greater than the drill holes. Vapor pressures with rare exceptions do not exceed hydrostatic pressures and are always far below lithostatic pressures. Meteoric water and volcanic steam apparently mix with proportions that attain a single liquid phase at a temperature that is close to 270°C. The water rises as a liquid phase to depths of 2000–1500 feet where hydrostatic pressure becomes sufficiently low to permit a vapor phase, at least locally.

Drilling at Steamboat Springs, Nevada, to depths as great as 685 feet has revealed a similar situation, except that the mixing temperature of meteoric water and volcanic steam is probably little above 175°C., and the near-surface vapor phase is limited to the upper 350 feet of the spring system.

Some geologists may object to the concept that meteoric water circulates to depths of 2 miles or more. The dryness of many deep mines is commonly cited as evidence against deep circulation, but this proves only that present permeabilities are low and that deep circulation does not occur to a prominent extent under existing conditions. Most of the examples are not from epithermal deposits; in addition, the deposition of vein material may have greatly decreased original permeabilities.

The paucity of fluorine relative to chlorine may be due to condensation of the volcanic fluid of the sodium-chloride springs at sufficient depth and with sufficient distance and travel time, so that much F can be fixed in hydrothermal micas and fluorite. Zies has been impressed with the abundance of fluorine relative to chlorine in volcanic fumarole gases and igneous rocks (Zies, 1929, and personal communication). In these substances, chlorine is seldom greatly dominant over fluorine. In contrast, the highest F/Cl ratio of the sodium-chloride springs of Table 1 is only 0.07. The fluoride content of these waters is seldom more than 15 ppm and is consistently lower in the nearly neutral springs containing appreciable calcium.

At all temperatures below the critical temperature of steam (374.4°C.), the water of the sodium-chloride springs is either in the liquid phase or is in part in saturated steam (Fig. 2*A*). Steam in contact with liquid water cannot be superheated, but the thermodynamic relations of steam and water are such that steam separated from water at high temperature and remaining out of contact with water can become slightly superheated. The maximum superheat obtainable in this way is when steam at about 250°C. is removed from contact with water and is allowed to expand to atmospheric pressure without loss of heat (Fig. 1); the resulting steam has a temperature of about 170°C., or 70° of superheat.

At temperatures appreciably below the critical temperature, all the low-volatile components that had been transported in solution in the high-density volcanic steam are dissolved in the liquid phase. A vapor phase, if present, contains only volatile components such as steam, CO_2, sulfur gases, and nitrogen.

Acid-Sulfate-Chloride Waters

Some volcanic hot springs are similar in composition to the near-neutral or alkaline sodium-chloride springs except that their pH's are less than 5, combined CO_2 is therefore virtually absent, and sulfate is relatively high.

Acid waters of rather similar compositions can probably originate in four different ways: [1] mixing of different sodium-chloride and acid-sulfate waters; [2] near-surface acidification of near-neutral sodium-chloride waters by oxidation of H_2S (Fig. 2*A*, type I-5); [3] deep condensation of dense vapors that contain alkali halides and oxidized sulfur (Fig. 3*A*), probably with little or no free halogen acids; and [4] surficial condensation and oxidation of low-density volcanic gases containing halogen acids and sulfur (Fig. 3*B*). Allen and Day (1935, p. 73, 460–504) used the term "mixed waters" for what is here called the acid-sulfate-chloride type. They were believed to form by the first or second method, the latter involving acidification of "alkaline" sodium-chloride water as a result of surficial oxidation of H_2S in the gases (Table 3). Low rates of discharge of water and inadequate flushing, combined with abundant discharge and oxidation of H_2S contained in the gases were viewed as favoring the formation of these acid waters. The present writer agrees that many acid-sulfate-chloride springs originate in this way. The alkali ratios in the waters are largely inherited from the parent sodium-chloride waters. The K/Na ratios may be modified, but important changes in the Li/Na ratios are unlikely.

A few acid springs are similar to the above in composition, but their discharges are so high that surficial production of sulfuric acid in the required quantities is unlikely; their origin is not yet well understood, but the mechanism suggested in Figure 3*A* may be applicable.

Two outstanding examples have been described briefly by White (1955, p. 106–107). The Green Dragon spring in the southern part of Norris Basin has a discharge that is difficult to estimate but is in the order of 40 gpm. Free acid, calculated as H_2SO_4 by balancing excess hydrogen ions with sulfate, is being produced at a rate of about 90 kg per day. This is far in excess of the rate of production of sulfuric acid in areas of similar size containing acid-sulfate springs, where much H_2S is oxidized to SO_3, and where the most-favored conditions appear to be: porous ground with a high ratio of particle surface area to volume, a position above the water table, temperature not far from boiling, and possibly catalytic effects of opal or other substances to foster the reaction. These conditions are represented diagrammatically in Figure 3*A* near the acid-sulfate spring, type I-4.

Frying Pan Lake in the Tarawera region of New Zealand (Grange, 1937, p. 93, 103) is probably a more striking example of the same type of water. Its rate of discharge of water has been estimated at "more than 1,000 gpm"; the discharge of free sulfuric acid is as much as 800 kg, or nearly a metric ton, per day. Porous ground of the type that appears to be most favorable for surficial oxidation of H_2S to SO_3 is of only local extent on the margins of the lake (diameter about 500 feet) and can hardly account for more than an insignificant part of the total production of sulfuric acid.

The high lithium-sodium ratio of the Green

TABLE 3.—ANALYSES OF GASES FROM AREAS OF VOLCANIC HOT SPRINGS, IN VOLUME PER CENT

	Well 4/1 Wairakei, N. Z.[1]	Well 6 Wairakei, N. Z.[2]	Steamboat Springs, Nev.[3]	Upper Basin Yellowstone[4]	Lassen Park, Calif.[5]	The Geysers, Calif.[6]	Lardarello, Italy[7]
CO_2	82.73	98.06	97.23	95.10	95.05	63.50	92.17
CO			none		none		
H_2S	8.36	0.63	0.77	0.55	0.55	1.69	2.44
H_2	2.37	0.18	none	0.10	0.30	14.67	1.75
CH_4	0.11	0.12	<0.03	0.10	0.15	15.29	0.92
C_2H_6	0.39	0.05	none				
NH_3	5.36	0.06				1.28	1.71
H_3BO_3	0.03	0.007				(0.14±)	0.47
O_2			0.14	none	0.10		
H_2	0.65	0.89	1.82	4.15	3.85	3.53	0.54
A, He, Ne			0.04		0.05		0.002
Total	100.00	99.997	100.00	100.00	100.05	100.0	100.002
Gas content of steam, vol. per cent	0.04	0.51				1.94	1.06

[1] Gas in steam from well erupting sodium-chloride water, eastern part of thermal area (Wilson, 1955, p. 29).

[2] Gas in steam from well erupting sodium bicarbonate water, western part of thermal area (Wilson, 1955, p. 29).

[3] Spring 16, Main Terrace (Brannock *et al.*, 1948, p. 222). Temperature of water 94½° C.; pH 7.2.

[4] Upper Basin drill hole behind Old Faithful Inn (Allen and Day, 1935, p. 86).

[5] Pool with precipitated sulfur, Bumpass Hell (Day and Allen, 1925, p. 133, analysis 4). Temperature 84–85° C. Six miles north of Morgan Springs.

[6] Well 1 (Allen and Day, 1927, p. 60, 76). Temperature 154° C.; sample contained boric acid, " . . . not . . . more than 20 to 40 ppm by weight" of total gases, including H_2O. A sample of completely condensed steam from well 4, collected Sept. 10, 1954, contained by partial analysis 18 ppm of H_3BO_3, and 0.13 ppm of Hg (analyst, J. O. Pera, Buckman Laboratories, Inc.). A similar sample from well 6 contained by partial analysis 13.1 ppm of H_3BO_3, 109 ppm of NH_4, and 0.5 ppm of Cl (Scott and Brannock, analysts).

[7] Average Larderello steam (Mazzoni, 1951, p. 34–35) recalculated to volume per cent. Temperatures of wells range from 140° to 230° C.

Dragon water (Table 1) is believed to indicate that most of the alkalies were derived from magma and transported in dense volcanic steam as dissolved alkali halides and were not for the most part leached from wall rocks. Unfortunately, no lithium analysis is available for Frying Pan Lake. The low content of alkaline-earth metals and of aluminum and iron, all of which are appreciably soluble at existing pH's of 2½–3, is believed to be additional evidence that these acid waters have not extensively attacked their wall rocks.

The high content of sulfate in these waters suggests that sulfur may be emitted from some magmas as oxidized sulfur gases, SO_2 and SO_3 and intermediate-valance sulfur rather than as H_2S or S, and that the acidity is caused by these oxidized gases. R. M. Garrels has suggested (Personal communication) the possibility of reactions of sulfur with water to form polybisulfides, which could in turn decompose to give sulfate and sulfide plus free acid, with decreasing temperature and pressure. On the other hand, George Kennedy (1948) has concluded that the ferric-ferrous ratio of volcanic rocks indicates low O_2 pressure and, therefore, very low SO_2 and SO_3. Are these relationships quite different in certain circumstances, perhaps related to type of magma, or is essentially all sulfur oxidized only after it leaves the magma? It is known that many volcanic fumaroles at high temperature and low pressure are very acid and contain oxidized sulfur gases (Shepherd, 1938, p. 321). When and how does the oxidation occur in fumaroles and the acid-sulfate-chloride springs?

It may be significant that geothermal gradients at Norris Basin in Yellowstone Park are very high, and with little doubt the same is true of Frying Pan Lake in New Zealand. Fenner (1936, p. 291) measured a temperature of 205°C. at Norris at a depth of only 246½ feet, which is the highest temperature that has been found at a similar depth in any explored hot spring system. No holes have been drilled at Frying Pan Lake, but the existence of very high temperatures at relatively shallow depths is indicated by the fact that volcanic eruptions occurred at the site of the lake in 1886 and 1917 (Grange, 1937, p. 93).

Burbank (1950) has presented evidence for generation of acid solutions at depth in a relatively shallow volcanic environment, and Lovering (1950) has favored acid solutions for some stages of alteration at Tintic, Utah. These solutions were apparently dense enough to transport matter of low volatility and may have been similar in nature and origin to the acid-sulfate-chloride waters here described.

The above stated lines of evidence suggest that volcanic emanations with oxidized sulfur gases and alkali halides may characterize at least some moderately shallow volcanic environments. The deep acid waters with high lithium-sodium ratios (Fig. 3*A*) may be formed by condensation of emanations that occur within a critical range of temperature and pressure. Without supporting evidence, it is suggested that optimum conditions may be provided by relatively high temperature and moderately low pressure, but with pressure still sufficiently high for the alkali halides to be appreciably soluble in a rather dense vapor; some halogen acids may also be present. The hypothesis assumes that at greater pressures and perhaps lower temperatures, sulfur is driven off as H_2S or S in vapors that form the sodium-chloride waters.

Acid-sulfate-chloride waters may also form by near-surface condensation of low-density volcanic gases containing free halogen acids. The waters of some acid crater lakes are probably of such an origin (Fig. 3*B*). The alkali metals are leached from the wall rocks. The Li/Na ratios are presumably similar to those of the wall rocks and are probably lower than in the acid-chloride waters previously discussed. This mechanism could account for the water of Frying Pan Lake; a lithium determination is needed to clarify its origin.

Sodium-Bicarbonate Waters

A little-known and relatively rare type of volcanic water is here called the sodium-bicarbonate type. Its outstanding characteristics are its low chloride and relatively high bicarbonate content; it is nearly neutral in pH. Possible modes of origin of the sodium-bicarbonate waters are illustrated in Figure 4.

A number of cold and warm waters are known to be relatively high in sodium bicarbonate, but only a few areas are definitely known to contain such waters in environments that demand a close relation to volcanism. These include the Wairakei, Waiotapu, and Rotorua areas of New Zealand (James Healy, personal communication), and Steamboat Springs, Nevada. At Wairakei and Steamboat, the sodium-bicarbonate waters are found only in wells; several springs of this type have been found associated with sodium-chloride water at Waiotapu and Rotorua. The writer suspects that volcanic sodium-bicarbonate water nor-

mally occurs below the zone of easy access of air and is present in some areas where it has not been suspected. With surficial oxidation of associated H_2S, the sodium-bicarbonate waters may change to acid-sulfate waters.

The existence of the volcanic sodium-bicarbonate type was first demonstrated in the western part of the Wairakei area, New Zealand (Healy, 1953; Wilson, 1955, p. 37; *see* analyses of well 5, Table 1, and well 6, Table 3). Healy and Wilson suggest that steam with CO_2 has separated from sodium-chloride water at depth (at least 1000 feet) and at some higher level is condensed in meteoric water, perhaps as in Figure 4*C*. Dissolved CO_2 reacts with the wall rocks; at high temperatures calcium and magnesium carbonates are only slightly soluble, potassium is commonly fixed in clay minerals and feldspars, and sodium bicarbonate becomes the dominant component of the dissolved solids.

In the central and eastern parts of the explored Wairakei area, normal sodium-chloride water (*see* analyses of well 4, Tables 1, 3) rises to high levels and is locally discharged in springs. One well (No. 7) must have been near the contact between these two distinctly different types of water; immediately after being drilled it discharged sodium-bicarbonate water, but after some months the composition changed to that of the sodium-chloride type.

Albite with little or no potassium feldspar characterizes the hydrothermal alteration of the western part of the Wairakei area, containing sodium-bicarbonate water, and adularia with minor albite is typical of a major deep zone of alteration in the central and eastern area, containing sodium-chloride water (Steiner, 1953; 1955). Adularia has also been found with the sodium-chloride waters of Steamboat Springs and the Upper Basin of Yellowstone Park, but hydrothermal albite is rare or absent in other explored hot spring systems (White, 1955, p. 104). Is hydrothermal albite closely related to the sodium-bicarbonate waters, and adularia to sodium-chloride waters?

A dilute sodium-bicarbonate water was found at depth in the western part of the Steamboat Springs thermal area. The drill hole apparently went through a zone of this water and into saturated steam mixed with CO_2 and H_2S that apparently rises into and is condensed by the overlying water. Although the bottom of

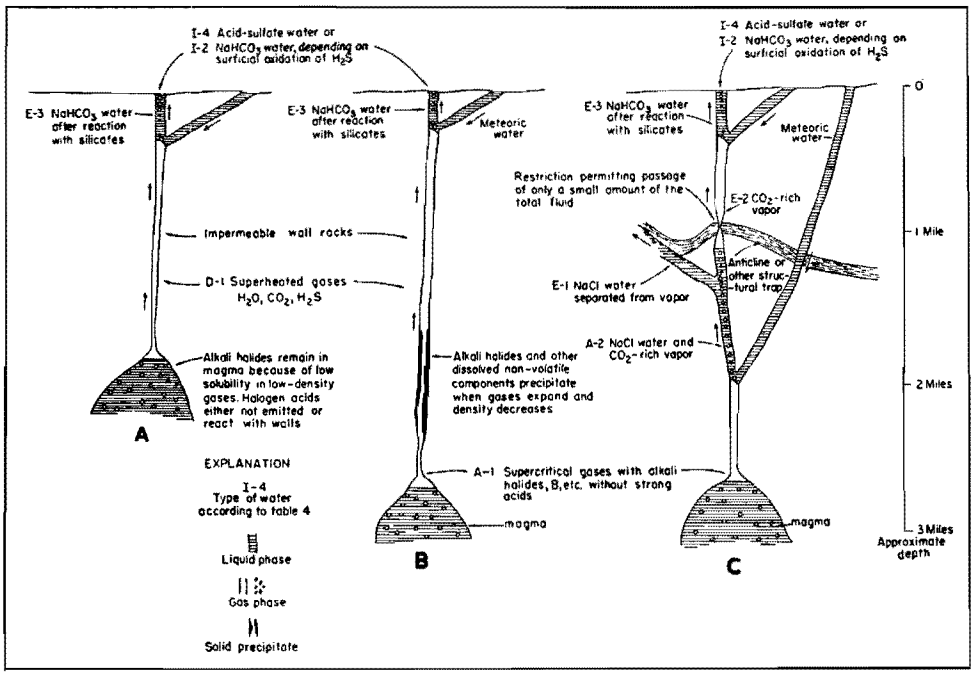

FIGURE 4.—SUGGESTED GENESIS OF VOLCANIC SODIUM-BICARBONATE WATERS BY THREE POSSIBLE MECHANISMS

Depending on depth of penetration of meteoric water and density of gas phase. Widths of fissures greatly exaggerated.

the drill hole is at a lower altitude than the water table of sodium-chloride water to the east, chloride water is completely absent.

James Healy has suggested (Personal communication) that a CO_2-rich vapor phase can separate from sodium-chloride water that is flowing with a strong horizontal component; the vapor phase can later dissolve at higher levels in ordinary ground water heated by conduction and the vapor. Reactions with the containing rocks can then form sodium-bicarbonate water. He has pointed out that principles suggested by Hubbert (1953) for separating gas, oil, and water are also applicable to thermal systems.

Springs that are probably equivalent to sodium-bicarbonate water have been found at "The Geysers" in California (Allen and Day, 1927, p. 33). Steam containing CO_2, H_2S, and other gases (Table 3) apparently rises into near-surface meteoric water and is condensed. CO_2 reacts with the wall rocks and dissolves alkali and alkaline-earth metals as bicarbonates. Because of the facts that alkali-rich rocks are scarce, serpentine is abundant in the wall rocks and temperatures of some of the springs are low enough for appreciable solubility of calcium and magnesium bicarbonates, sodium is the dominant metallic ion in only one of the springs (Allen and Day, 1927, p. 33). In spite of their differences, all the volcanic bicarbonate waters are included for present purposes in the sodium-bicarbonate type although other subdivisions may be desired in the future. Most of the other springs of "The Geysers" area are of the acid-sulfate type, discussed below. Surficial oxidation of H_2S to sulfuric acid has probably changed some sodium-bicarbonate waters to the acid-sulfate type.

C. J. Banwell of the New Zealand Physical Laboratory and the writer made a series of temperature measurements on December 6, 1955, in a new steam well drilled to a depth of 600 feet at "The Geysers" late in October 1955. The well contained steam that was apparently saturated (wet) for the casing-head pressure to a depth of about 300 feet, and temperatures were near 160°C. Temperatures were determined by a geothermograph supplied by the New Zealand government, of the type described by Banwell (1955, p. 64–66). Total casing-head pressures ranged from 86 lbs./sq. in. at the start of the measurements to 97 lbs./sq. in. when the geothermograph was at 300 feet. From 350 to 450 feet the temperature rose to 178° C., and this temperature was maintained to the bottom of the hole. The final total casing-head pressure was 104 lbs. per sq. in.; steam in the lower part of the well was superheated by about 12° C. The presence of wet steam to a depth of 300 feet, and of zeolites and other hydrothermal minerals in altered rocks erupted from the well are evidence that, before drilling, there was a liquid phase in much of the upper part of the spring system. Where H_2S was not abundantly oxidized, this liquid phase was probably a sodium-bicarbonate type of water.

The thermal system of "The Geysers" is illustrated by Figure 4, type A or B. No trace of sodium-chloride water has been found, and none of the analyzed hot springs (Allen and Day, 1927, p. 33) contain more than 1.8 ppm of chloride. To test the possibility that unseen sodium-chloride water might be escaping into Sulphur Creek, water samples were taken immediately above the springs as well as near the Cloverdale quicksilver mine 4 miles below the springs. Both samples contained only 2 ppm of chloride, proving that no unseen sodium-chloride water is discharging near by from the system, and no possibility is known within a 10-mile radius of the area.

There is also no published evidence to suggest that sodium-chloride waters occur in the Larderello, Italy, thermal areas, where superheated steam is utilized to produce an important part of Italy's electric power (Mazzoni, 1951). Sodium-chloride water seems to be absent both here and at "The Geysers." Meteoric water probably mixes at such shallow depths and low pressures that the volcanic steam has not condensed at sufficiently high density to retain the alkali halides in solution. The latter may have precipitated from the vapor phase above the magma (Fig. 4*B*), as temperature and density of the vapor decreased, or pressure on the magma chamber may have been so low that no halogens were evolved in combination with alkali metals (Fig. 4*A*).

Acid-Sulfate Waters

The characteristics of acid-sulfate waters have been described by Allen and Day (1935, p. 65, 100–125, 393–448), who called them "acid waters", and briefly by White, Sandberg, and Brannock (1953, p. 493), and others. The waters contain relatively high sulfate and low chloride, and the pH is low (generally from 2 to 5). The near absence of chloride distinguishes these waters from the acid-sulfate-chloride type. An example from Norris Basin is shown in Table 1. Springs of this type are generally situated on relatively high ground, and discharges

are meager in comparison to typical sodium-chloride springs. Allen and Day believed that this type of water owes its origin to a shallow circulation of meteoric water, presumably because of lack of adequate supply or low permeability of the bed rocks. This permits superheated steam from a magma to approach nearly to the surface. Alkali halides, and other low-volatile components are either retained in the magma or are precipitated at depth as the steam expands and decreases in density (Fig, 4*A*, 4*B*). Steam that condenses near the surface becomes acid if associated H_2S is oxidized. The present writer agrees with Allen and Day that the mechanisms illustrated in Figures 4*A* and 4*B* are the best explanations for acid-sulfate springs not closely associated with chloride waters, as at "The Geysers", Larderello, and probably some thermal areas in Yellowstone and Lassen Parks and elsewhere.

Other acid-sulfate springs, however, are closely associated with or are surrounded by sodium-chloride waters (Allen and Day, 1935, p. 72). The writer believes that they result from steam that has boiled from chloride water at depth and has condensed again near the surface, and is then acidified by oxidizing H_2S (*see* type I-4 waters in Figs. 2*A*, 3, 4*C*). Where condensation occurs below the zone of extensive oxidation, sodium-bicarbonate water can first form and later be acidified near the surface. Some acid-sulfate springs are completely surrounded and underlain by sodium-chloride water in an environment that clearly points to direct boiling-off of steam and other gases, followed by condensation and acidification. An example was found by the writer on the Main Terrace at Steamboat Springs (spring 14). The terrace has been penetrated by 5 drill holes, all entering the chloride water table a few feet below the surface. The spring is a pure acid-sulfate type when the water level in its feeding fissure is 1 foot or more below the surface. When the water level rises, the spring changes gradually to the acid-sulfate-chloride type and eventually to nearly neutral sodium-chloride water. Other examples are known in the Upper Basin of Yellowstone Park and Beowawe Geysers in Nevada.

The compositions of the acid-sulfate springs are clearly related to the rocks that bound the spring pools. Iron, aluminum, calcium, and magnesium are abundant in the more acid springs if the wall rocks contain appreciable quantities of these metals. From the few available analyses, the Li/Na ratios of the acid-sulfate springs are considerably lower than those of the sodium-chloride springs (Table 1). The alkalies of the former are dissolved from the wall rocks in approximate proportion to abundance. There is no evidence for selective leaching of lithium relative to the other alkali metals.

Calcium Bicarbonate Waters

The compositions of all types of volcanic waters are influenced to some extent by reactions with wall rocks. This has been stated or implied in the previous discussion. When sodium-chloride waters come in contact with silicate rocks at high temperatures, sodium is typically enriched in the water by rock alteration as potassium is removed; some additional sodium is dissolved by reactions involving CO_2; the pH progressively increases (if all CO_2 is dissolved in the liquid phase without a reservoir in a vapor phase); and little Ca, Mg, Fe, and Al dissolve because of low solubilities at high temperature or because the waters are nearly neutral and contain H_2S.

In contrast to the above, the calcium-bicarbonate type of water is believed to form when sodium-chloride water is sufficiently cooled (Fig. 5) so that calcium bicarbonate is soluble in relatively large amounts (Garrels and Dreyer, 1952, p. 339–340; Miller, 1952, p. 175). This implies that sodium-chloride water can come into contact with limestone at 200°–300° C. with little change in composition, although solution and redeposition of calcite may occur. At temperatures near 100° C., sodium-chloride waters do not contain more than 20 ppm of calcium except when combined CO_2 is particularly low. The available solubility data for calcium carbonate at temperatures close to that of the Mammoth hot springs (Garrels and Dreyer, 1952, p. 339, 340; Miller, 1952, p. 175, 178) suggests that these springs, with 260 ppm of Ca and 500 ppm of HCO_3 (Table 1), are essentially saturated with calcium carbonate. Their subsurface temperatures have probably not been much higher than their vent temperatures. This is consistent with the writer's observations that calcium-bicarbonate springs seldom if ever emerge at boiling temperatures, and that discharging water starts to precipitate carbonate at or very near the spring vents. This type of water probably forms only when volcanic sodium-chloride water is so greatly diluted by cold meteoric water that the mixing temperature is in the order of 100° C. or less; if the mixture contains dissolved CO_2, and comes in contact with limestone for a sufficient time, it changes to the calcium-bicarbonate type by dis-

solving $CaCO_3$. The content of calcium bicarbonate of thermal waters may be useful as a crude geothermometer, indicating the maximum temperature the water has had since coming in contact with a supply of calcium carbonate.

by temperature and pressure of the environment in which the author believes them to occur. Degree and depth of mixture with meteoric water, depth and temperature of source intrusions, and reactions with different types of wall rocks are considered to some extent. A

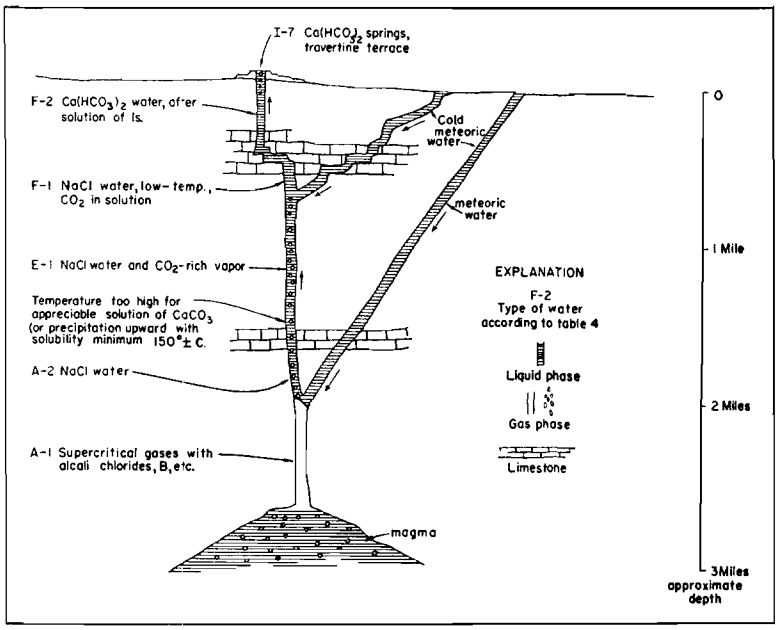

FIGURE 5.—SUGGESTED GENESIS OF VOLCANIC CALCIUM-BICARBONATE WATER
Widths of fissures greatly exaggerated.

In contrast to the above, volcanic sodium-chloride springs seem to be unsaturated with calcium carbonate at vent temperatures, except where the pH also rises greatly in geysers and spouting springs with loss of CO_2 (White, Sandberg, and Brannock, 1953, p. 496–498). At Steamboat Springs, calcite is absent in veins and altered rocks from the surface to depths of about 150 feet but is relatively abundant at greater depths (White, 1955, p. 112). George Kennedy has suggested to the writer (Personal communication) that the solubility of calcium carbonate attains a minimum at a temperature somewhat above 100° C. The Steamboat data are consistent with this hypothesis and suggest that the minimum for water of Steamboat's composition and CO_2 content is about 150° C.

OUTLINE OF POSSIBLE MODES OF ORIGIN OF THE MAJOR TYPES OF VOLCANIC WATERS

The types of water previously discussed by composition and origin are arranged in Table 4

wide variety of compositions and of histories are apparent. This table is not intended to be a complete outline of the possibilities, because our knowledge of the processes is much too inadequate.

Most of the waters are believed to be directly or indirectly related to dense volcanic vapors containing alkali halides in solution. The direct condensation of such a vapor is believed to yield the volcanic sodium-chloride waters. Most other waters are evolved from the latter; the exceptions appaer to be related to low-density superheated vapors that contain little matter of low volatility.

Specific ranges for temperatures are not stated but are in the general order of: low temperature $<100°$ to $150° \pm$ C.; intermediate temperature $150° \pm$ to $370° \pm$ C.; high temperature $>370°$C.

In groups A, E, and I, pressures are near those of saturated steam for the existing temperatures. In groups D and H, pressures are slightly lower than for saturated steam, and

TABLE 4.—SUGGESTED ENVIRONMENTAL RELATIONSHIPS OF THE MAJOR TYPES OF VOLCANIC WATERS*

Degree and depth of mixture with meteoric water, reactions with wall rocks, and depth of source intrusions are also involved. The list does not include all possibilities. Evolution of many are illustrated in Figures 2–5.

	High pressure	Intermediate pressure	Low pressure
High temperature	A. High P-high T 1. Dense volcanic steam—H_2S, alkali halides, B, SiO_2 *etc.* from moderately deep intrusion(?).† (Figs. 2*A*, 4*B*, 4*C*, 5) 2. NaCl water—A-1 condensed in deep meteoric water; associated CO_2-rich vapor.† (Figs. 2*A*, 4*C*, 5) 3. Moderately dense volcanic steam, very high temp. from local intrusion; alkali halides, SO_3, SO_2, possibly halogen acids. (Fig. 3*A*) 4. Acid-sulfate-chloride water from condensation of A-3; CO_2-rich vapor phase. (Fig 3*A*)	D. Intermediate P-high T 1. Superheated vapor from moderate depth intrusion or from sufficient expansion of A-1 to precipitate low-volatile components; CO_2, H_2S. (Fig. 4*A*, *B*) 2. Superheated vapor with SO_2, SO_3, possibly halogen-acid gases from moderate-depth intrusions, or from A-3 with precipitation of nonvolatiles.† (Figs. 2*B*, 3*B*)	G. Low P-high T 1. Superheated fumaroles with CO_2, H_2S, from D-1. 2. Superheated fumaroles with halogen acids, SO_2, SO_3, from D-2 or from lavas and shallow intrusions.† (Fig. 3*B*)
Intermediate temperature	B. High P-intermediate T 1. NaCl water, from enough cooling of A-2 by conduction or meteoric water to dissolve vapor phase with CO_2.† (Fig. 2A) 2. Acid-sulfate-chloride water from further cooling of A-4; may have a CO_2-rich vapor phase, insoluble because of acidity.	E. Intermediate P and T 1. NaCl water from A-2; from B-1 with little cooling; from A-4 or B-2 by neutralization; CO_2-rich vapor phase.† (Figs. 2*A*, 4*C*, 5) 2. CO_2-rich vapor, separated physically from A-2 or E-1. (Fig. 4*C*) 3. $NaHCO_3$ water from condensation of D-1 or E-2, then reaction with silicate wall rocks. (Figs. 4*A*, *B*, *C*) 4. Acid-sulfate-chloride water from A-4 or B-2; high in Li. (Fig. 3*A*) 5. Acid-sulfate-chloride water by condensation of D-2 and reaction with wall rocks; low in Li. (Fig. 2*B*)	H. Low P-intermediate T 1. Superheated H_2O-CO_2-H_2S vapors from D-1, E-2, E-4, or G-1. 2. Superheated vapors with strong acid-forming components from D-2 or G-2.† (Fig. 3*B*)

Low temperature	C. High P-low T 1. NaCl water by sufficient cooling of B-1. 2. $Ca(HCO_3)_2$ water by reaction of C-1 with limestone.	F. Intermediate P-low T 1. NaCl water from C-1, or sufficient cooling of B-1 or E-1; no vapor phase.† (Fig. 5) 2. $Ca(HCO_3)_2$ water from C-2 or from F-1 reacting with limestone.† (Fig. 5)	I. Low P-low T 1. NaCl water from E-1, E-4 (by reaction) or F-1; may have CO_2-rich vapor phase; high in Li.† (Fig. 2*A*) 2. $NaHCO_3$ water, from E-3 or condensation of H-1 and reaction. (Figs. 4*A*, *B*, *C*) 3. Steam with CO_2, H_2S, from Group E or from H-1 or I-1, separating above water table.† (Figs. 2*A*, 3*A*) 4. Acid-sulfate water from partial condensation I-3, and oxidation of H_2S; also by oxidation of H_2S in I-2.† (Figs. 2*A*, 3*A*, 4*A*, *B*, *C*) 5. Acid-sulfate-chloride water from oxidation of H_2S in I-1; high in Li. (Figs. 2*A*, 3*A*) 6. Acid-sulfate-chloride water from surficial condensation of G-2 or H-2; low in Li. (Fig. 3*B*) 7. $Ca(HCO_3)_2$ water from F-2. (Fig. 5) 8. NaCl water from neutralization of E-5 or I-6; low in Li.† (Fig. 2*B*)

* Assumptions for Table 4.

1. Alkali halides are appreciably soluble in superheated steam near and above the critical pressure of water.
2. Sulfur is generally emitted from the magma as H_2S or S. In certain little-understood conditions, perhaps where temperature is high relative to pressure, much sulfur may be emitted as SO_2 or SO_3 (*See* text).
3. Liquid phase of all types of water reacts with wall rocks, at least to some extent; the same presumably holds for high-density vapors.
4. Alkaline-earth metals are only slightly soluble in CO_2-bearing waters at high temperatures but become appreciably soluble at temperatures below 100°C. (*See* text).

† Probably relatively abundant.

group G is highly superheated. Pressures in groups B and F are somewhat higher than saturation pressures and are very high relative to temperature in group C.

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U. S. GEOLOGICAL SURVEY, MENLO PARK, CALIF.

MANUSCRIPT RECEIVED BY THE SECRETARY OF THE SOCIETY, MARCH 26, 1957

PUBLICATION AUTHORIZED BY THE DIRECTOR, U. S. GEOLOGICAL SURVEY