

An Acid Fumarolic Gas From Kilauea Iki Hawaii

By K. J. MURATA

THE 1959-60 ERUPTION OF KILAUEA VOLCANO, HAWAII

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*A study of a highly acid fumarolic
gas and of its chemical effect on
basaltic pumice*



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AN ACID FUMAROLIC GAS FROM KILAUEA IKI, HAWAII

By K. J. MURATA

ABSTRACT

A condensate of fumarolic gases, collected from the degassing pumice-cinder cone of Kilauea Iki during the 1959 eruption, proved to be essentially 2*N* HCl. The acid gases were observed to decompose surficial pumice thoroughly, leaving opaline pseudomorphs of pumice fragments and forming subsurface nodular deposits of mixed chlorides of aluminum, iron, magnesium, and other elements leached out of the pumice. Native sulfur deposited around the fumaroles contained almost 3 percent selenium.

INTRODUCTION

The purpose of this paper is to record the composition of a single sample of a fumarolic gas collected on the pumice-cinder cone of Kilauea Iki, formed during the 1959 summit eruption of Kilauea Volcano, and to describe the chemical alteration of basaltic pumice by this gas. When condensed, the water-rich gas formed a solution that was essentially 2*N* HCl. Only a few of the high-temperature Kilauea gas samples analyzed by Shepherd (1921, 1938) were rich in chlorine, most of them containing more sulfur compounds, such as S₂, SO₂, and SO₃, than chlorine. The emphasis placed in recent decades on gases from the solfatara at Sulphur Bank on Kilauea (Macdonald, 1944; Payne and Mau, 1946; Naughton and Terada, 1954) has also tended to draw attention away from chlorine toward carbon dioxide, hydrogen sulfide, and other components that predominate in low-temperature exhalations.

That the composition of fumarolic gases is temperature dependent has been known for a long time from the investigations of Deville and Leblanc (1858), Allen and Zies (1923), Nemoto and others (1957), Ellis (1957), and Naboko (1959), among others. Thus, a single sample represents only a brief interval in the history of a cooling chemical system that changes continuously. The nature of the sample from Kilauea Iki indicates that it represents an early high-temperature exhalation.

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LOCATION OF FUMAROLE AND METHOD OF COLLECTING THE SAMPLE

The gas sample was collected on the large cone of pumice, cinder, and spatter that formed downwind from the lava fountain at Kilauea Iki. Hot pyroclastics, many incandescent and some still fluid, were heaped continuously for a week on the bluff above the vent during the first phase of the eruption. The resultant cone was first explored on November 23, 1959, 2 days after the end of the first eruptive phase, and samples of the gas and altered pumice were collected on the summit of the cone at that time. Further additions of pyroclastic debris to the cone were made intermittently during 16 spasmodic eruptions that occurred subsequently over a period of a month.

The cone is a "rootless" structure perched on the rim of Kilauea Iki pit crater and has no direct connection to an underground supply of magma or magmatic gas. Owing to the low heat conductivity of the outermost cooled blanket of pumice and cinder, the interior part remained hot after the eruption, with only negligible cooling in the 2 days between the end of activity and sampling. It is supposed that magmatic gases dissolved in basaltic glass were expelled through devitrification and crystallization of the glass as the cone cooled slowly.

Acid vapors were being exhaled at the summit along minor faults that formed as a result of slumping and sliding of the cone into the pit crater. The fault lines were delineated on the surface by conspicuous yellow deposits of native sulfur and decomposed pumice. The localization of gas emission along faults may have been due to the presence within the cone of relatively impermeable layers of spatter material which were fractured locally by the faults.

Fortunately for our purpose, there was very little rain during the first eruptive phase of Kilauea Iki. During this period only about an inch fell, and for 2 days prior to the date of gas collection, less than 0.1 inch (W. U. Ault, written commun., 1961). It is therefore believed that the fumarolic gas was almost entirely of magmatic origin and had a minimum of contamination by meteoric water. However, some air was introduced owing to the generally porous nature of the pumice-cinder cone (Ault, 1960). The separate question of possible contamination of the magma by sea water deep within the volcano is considered later.

The gas sample was collected as a steam condensate. A spot marked by copious evolution of steam was first selected, and the temperature of the gas was determined by W. U. Ault to be 328° C at a depth of 1½ feet beneath the surface. A hole about 2 feet deep and 1 foot in diameter was then dug, and a large inverted glass funnel provided with a long glass stem was buried in the hole. The stem of the funnel was connected to an inclined length of Pyrex glass tubing 8 feet long, which served as an air condenser. A 500-ml (milliliter) Ehrlenmeyer Pyrex flask immersed in a bucket of water served as the receiver, and the gas was led to it by pumping on an outlet in the stopper of the flask with a suction pump, manually operated. Periodic addition of solid carbon dioxide kept the water in the bucket reasonably cool, and condensation of steam was almost complete. After several hours of pumping, about 450 ml of condensate was obtained.

A solution of cadmium nitrate left exposed in a beaker within the steaming area of the collection site for 2 hours gave no indication of the presence of hydrogen sulfide. The strong choking odor of sulfur dioxide must have affected our sense of smell because we did not recognize the presence of hydrochloric acid in the issuing vapors. Some elemental sulfur condensed with water in the air condenser. Part of the sulfur was drawn into the receiver, but that remaining in the air condenser was not recovered.

COMPOSITION OF THE CONDENSATE

The chemical analysis of the steam condensate, made by S. M. Rogers and H. C. Whitehead, is presented in table 1. The condensate is virtually 1.9*N* HCl. The content of sulfate is a measure of the total quantity of both sulfurous and sulfuric acid in the fumarolic vapor. Although the elemental sulfur that deposited in the air condenser was not recovered, there is no doubt that chloride was more abundant than sulfur and its compounds.

TABLE 1.—*Chemical analysis of a steam condensate from the pumice cone of Kilauea Iki*

[Analysts: S. M. Roger and H. C. Whitehead]

Constituent	Parts per million	Equivalents per million
<i>Cations</i>		
H (total acidity)-----	1,910	1,894.84
Na-----	4.9	.21
K-----	1.1	.03
Li-----	.0	.0
NH ₄ -----	0	0
As-----	.0	.0
Total-----	1,926.0	1,895.08
<i>Anions</i>		
Cl-----	68,600	1,934.52
Br-----	246	3.08
I-----	4.5	.04
F-----	20	1.05
SO ₄ -----	430	8.95
B-----	3.2	-----
SiO ₂ -----	.0	-----
S (elemental)-----	400+	-----
Se (elemental)-----	12+	-----
Total-----	69,715.7+	1,947.64

Density at 20°C-----grams per milliliter...1.031

A small part of the sample was neutralized with sodium hydroxide, and the resulting salt was analyzed spectrographically by Joseph Haffty in order to detect constituents other than those reported in table 1. A blank sample prepared by neutralizing reagent-grade hydrochloric acid with the same sodium hydroxide was analyzed at the same time. The salt prepared from the fumarolic condensate was found to contain no element at a significantly higher concentration than the blank.

Although an extensive discussion of the Kilauea Iki condensate does not seem warranted, comparisons with a few previously described volcanic gases and gases extracted from Kilauea basalts will serve to place the nature of the condensate in a proper light. The comparisons are made in table 2 in which the elemental compositions are expressed as gram atoms per 1,000 grams of water. A natural fumarolic condensate very similar to the sample from Kilauea Iki has been described from the andesitic volcano Ebeko in the Kuriles (Ivanov, 1957). Its composition is given in column 2 of table 2. Another somewhat similar material is a condensate obtained during the 1950-51 eruption of the basaltic volcano Oshima in Japan (Iwasaki, 1951). It proved to be a strong solution of ferric chloride in 1.4*N* HCl and contained no sulfate. A part of the ferric chloride of this material may have been derived from the iron pipe that was used in its collection.

TABLE 2.—Composition of steam condensates, volcanic gases, volatiles extracted from lavas, and sea water

[Gram atoms per 1,000 grams water]

Element	Steam condensates		Kilauea gases			Volatiles in Kilauea lavas				Sea water
	1	2	3	4	5	6	7	8	9	10
F	0.0011	0.0039				15	6.86	20.90	19.49	0.000068
Cl	2.0140	1.8508	6.03	1.53	0.81	5	1.65	1.71	1.08	.5544
Br	.0032	.0006								.00083
I	.00004	.000003								.0000004
S	.0177+	.0107	5.30	6.04	3.34		2.33	1.46	2.86	.0286
C	Present	Present	4.28	4.73	4.53	4	8.07	4.66	1.76	.0024
B	.00031	Present								.00043
<i>Atomic ratio</i>										
F:Cl	.0055	.00211				3	4.15	12.22	18.05	.0000123
Br:Cl	.0016	.0003								.00150
S:Cl	.0088+	.0058	.879	3.95	4.12		1.41	.85	2.65	.0516
B:Cl	.000015									.00078

1. Kilauea Iki, condensate recalculated from table 1.
2. Ebeko Volcano, upper crater, natural condensate, Paramushir Island, the Kuriles; S. S. Krapivina, analyst (Ivanov, 1957).
3. Jaggar's sample 2, gas from Halemaumau lava lake, Mar. 1, 1918 (Shepherd, 1938).
4. Jaggar's sample 3, gas from Halemaumau lava lake, Mar. 2, 1918 (Shepherd, 1938).
5. Jaggar's sample 4, gas from Halemaumau lava lake, Mar. 2, 1918 (Shepherd, 1938).
6. Kilauea Iki eruption, average content of volatiles in lavas of the first phase, calculated from conventional rock analyses (K. J. Murata and D. H. Richter, unpub. data) and water determinations (I. I. Friedman, unpub. data).

7. Gas extracted from lava dipped out of Halemaumau lava lake in 1919 (Shepherd, 1938).
8. Gas extracted from pahoehoe lava of the 1923 Kilauea eruption (Shepherd, 1938).
9. Gas extracted from lava collected from Halemaumau lava lake in 1917 (Shepherd, 1938).
10. Average sea water (Rankama and Sahama, 1950).

Columns 3–5 of table 2 represent chlorine-rich gas samples collected from the molten lava of the Halemaumau lava lake by T. A. Jaggar in March, 1918. Shepherd's work (1938) indicated that Kilauea gases usually contained only a tenth to a hundredth as much chlorine as do these samples. But the three samples show that magmatic gases with chlorine content comparable to that of the Kilauea Iki condensate have been found previously on Kilauea. Likewise some samples of volatiles extracted from Kilauea lavas by heating under vacuum (Shepherd, 1938) were as rich in chlorine (cols. 7–9, table 2). Even the conventional chemical analyses of Kilauea Iki lavas suggest the possibility of gases containing molal concentrations of chlorine or hydrochloric acid (col. 6, table 2). Thus, a condensate like the 1.9*N* HCl of Kilauea Iki would not be entirely unexpected and would represent pristine exhalation from Kilauea magma.

The concentrations of fluorine and total sulfur in Kilauea gases and lava volatiles are about equal to or greater than that of chlorine. Shepherd (1938) did not determine fluorine in most of his gas samples from the lava lake of Halemaumau, but in one sample he found the F:Cl atomic ratio to be 4.62 and the S:Cl ratio, 1.03 (Day and Shepherd, 1913), in harmony with proportions indicated by the lava volatiles (cols. 6–9, table 2). The condensate from Kilauea Iki is thus deficient in fluorine and sulfur relative to chlorine when compared to the high-temperature gases of Kilauea. Like all previously analyzed gases from Kilauea, the Kilauea Iki gas also contained appreciable amounts of CO₂ as

a "fixed" component (Ault, 1960), which would not appear in the analysis of the acid condensate.

On the basis of the chlorine content, the condensate is 3.6 times more concentrated than normal sea water (col. 10, table 2). Although the derivation of hydrochloric acid by contamination of the magma with sea water at depth is conceivable, this difference in concentration and the discrepancies in the ratios of fluorine, sulfur, and boron to chlorine in the two materials (even after making allowances for possible metasomatic reactions of the fumarolic gas) seem to argue against sea water as the major source of the acid.

The ratio of bromine to chlorine in the condensate is very close to that in sea water, but White (1957, 1960) called attention to the fairly prevalent constancy of this ratio in nature, which renders it of uncertain diagnostic value. Fumarolic vapors of the dacitic volcano Showa-Shinzan also contained bromine and chlorine in a ratio close to that of sea water (Nemoto and others, 1957, p. 115–133). On the other hand, Br:Cl ratios substantially higher and lower than that of sea water have been reported for solfataric gases of the andesitic volcano Sheveluch (Basharina, 1956).

The presence of hydrochloric acid in gases exhaled by many volcanoes far removed from the sea or saline deposits has led to the general belief that hydrochloric acid is a common primary constituent of magmas. The Hawaiian Islands, however, are immersed in and impregnated with sea water, and the possibility of entry of sea water into magma conduits is ever present. A brief episode of such an entry at shallow depths was observed

during the 1960 flank eruption of Kilauea at Kapoho. Sea salts not only could yield hydrochloric acid through hydrolysis but also could add soda to the magma, thereby possibly helping to form hyperalkalic magmas. The possibility of a marine contribution to magmas thus remains one of the outstanding questions in Hawaiian volcanism.

If we assume that the gas initially released from the hot pumice within the Kilauea Iki cone had the usual composition of high-temperature magmatic gases of Kilauea, the relative paucity of fluorine and sulfur in the fumarolic condensate suggests that these elements were removed through interaction with the pumice as the gas migrated to the surface. An extensive fluorine- and sulfur-metasomatism of the interior pumice may have been in process (Naboko, 1957; Lovering, 1957). Observations at the surface revealed an intense decomposition of the pumice by hydrochloric acid, to a lesser extent, sulfuric and hydrofluoric acids.

ACID ALTERATION OF THE PUMICE

Along the gas-emitting faults on the pumice hill, the uppermost few inches of the pumice was thoroughly decomposed to siliceous pseudomorphs of pumice fragments. The highly porous pseudomorphs had absorbed much ferric chloride and consequently had a deep orange color in sharp contrast to the black of the unaltered or slightly altered pumice. Below this surficial layer, the black pumice fragments did not appear to be much affected, although the fumarolic gas was streaming all around and through them. At many points, the sub-surface fragments were cemented into hard irregular nodules, as much as 6 inches long, by crystallization of various salts (mostly chlorides) leached out of the surface layer. No nodules were found at a depth greater than about a foot below the surface. It must be remembered that these observations pertain only to a very early stage in the degassing of the hot interior pumice and alteration of the surface pumice. Later observations by Ault (1960) indicated increasing contamination of the fumarolic gas by air.

The localization of the zone of intense alteration to the uppermost few inches of pumice was very striking and was attributed at first solely to the formation of sulfuric acid in the surface layer through air oxidation of sulfur dioxide. Later, when the preponderance of hydrochloric acid in the fumarolic vapor and of chlorides in the crystallized salts were realized, it became apparent that access of air may also have been promoted the action of hydrochloric acid on the pumice. The oxidation of its ferrous iron to ferric iron probably rendered the glassy pumice more susceptible to attack by hydrochloric acid. Also, the acid solution that formed

in the surface layer of pumice through condensation of the vapor may have been a more potent agent for decomposing the pumice than the original vapor (Naboko, 1959).

A sample of the pseudomorphic surficial material was washed with 1*N* HCl and with water to remove the occluded ferric chloride; it was then air dried and assayed by rapid-analysis methods (Shapiro and Brannock, 1956). The analysis is given in table 3.

TABLE 3.—Analyses of altered and original pumice from Kilauea Iki

[Analyst of altered pumice: Rapid analysis group, Washington; analyst of unaltered pumice, sample S-9: D. F. Powers (K. J. Murata and D. H. Richter, unpub. data)]

	Altered Pumice		Fresh pumice
	Composition	Recalculated to anhydrous basis	
SiO ₂	79.2	95.2	48.41
Al ₂ O ₃	1.0	1.2	11.62
Fe ₂ O ₃	1.46	1.55	1.36
FeO.....			10.29
MgO.....	.17	.20	13.34
CaO.....	.14	.17	9.77
Na ₂ O.....	.06	.07	1.94
K ₂ O.....	.04	.05	.47
H ₂ O (total).....	17.0		.04
TiO ₂	2.0	2.4	2.30
P ₂ O ₅14	.17	.23
MnO.....	.01	.01	.17
CO ₂01
Cl.....			.02
F.....			.03
Subtotal.....	100	100	100.00
Less O.....			.01
Total.....	100	100	99.99

¹ Total iron as Fe₂O₃.

The composition shown in column 1 of table 3 corresponds to that of hydrous silica with minor amounts of the other common constituents of basalt. According to B. J. Skinner, the X-ray diffraction pattern of this sample shows a single diffuse maximum typical of amorphous silica. On an anhydrous basis (col. 2, table 3) the material is 95 percent silica. Hydrochloric and sulfuric acids had decomposed the surficial pumice thoroughly and left behind only siliceous pseudomorphs of the pumice fragments.

Nodules of the previously mentioned cemented pumice were first examined qualitatively in the chemical laboratory of the Hawaiian Volcano Observatory. The crystallized salts that constituted the yellow cement were readily soluble in water, and the resulting solution gave strong test for Cl⁻, Fe⁺², Fe⁺³, Ca⁺², Mg⁺², Al⁺³, and Na⁺. Tests for sulfate and fluoride indicated only a moderate amount, and negative tests were obtained for ammonium ion and for elemental sulfur.

A representative sample of the nodules was sent to the Denver laboratory of the U.S. Geological Survey for mineralogical study. Because of an accident in transit the originally hard cementing substance decomposed into a pasty mass through hydration and oxidation. F. A. Hildebrand found most of it by X-ray examination to be amorphous. Only a small amount of halite and anatase could be identified in the X-ray diffraction patterns. The general instability of the cementing substance was also manifested in the gradual decomposition of the samples that were retained in covered jars in Hawaii. Although the crystalline phases constituting the cement remain mostly unidentified, there is no doubt that they were chlorides (and some sulfates and fluorides) of the major elements of basalt. They represented acid-soluble constituents of the surficial pumice, and the siliceous pseudomorphs of pumice fragments, the acid-insoluble residue.

SELENIUM CONTENT OF THE SULFUR

The elemental sulfur present as a sediment in the sample of steam condensate was filtered off and analyzed qualitatively by means of an X-ray fluorescence spectrometer. Because D. E. White and R. A. Gulbrandsen obtained strong indications of selenium in this sulfur, it and another sample, collected from the pumice cone of Kilauea Iki, were analyzed for selenium by J. W. Budinsky and Irving May, with the results shown for samples 1 and 2 in table 4. All previous determinations of selenium in sulfur from Kilauea volcano are included in table 4. The Kilauea Iki sulfur is remarkably rich in selenium and is only exceeded by sample 8 collected in 1840 by J. D. Dana, while a member of the Wilkes expedition.

Sulfur that was depositing in 1957 in and around the vents of the 1955 flank eruption of Kilauea contained about a tenth of a percent of selenium (samples 3-5, table 4). Sample 6 from the low-temperature solfatara of Sulphur Bank had only 4 ppm (parts per million) of selenium. The data of table 4 suggest that the concentration of selenium is highest in high-temperature exhalations and becomes progressively less in cooler vapors of fumaroles and solfataras.

The amount of selenium present in the primitive magma of Kilauea is not known but is probably only a few parts per million or less. Kilauea lavas studied by Davidson and Powers (1959) uniformly contained less than 2 ppm of the element. An idea of the order of magnitude of concentration of selenium in the magmatic gas of Kilauea is gained from the fact that Byers and others (1936) found 0.005 milligram selenium in 600 cubic centimeter of a sample that had been collected

in 1913 from the lava lake of Halemaumau. The seleniferous sulfur of Kilauea Iki constitutes an excellent example of a trace magmatic constituent becoming separated and concentrated through the process of vapor transport.

TABLE 4.—Selenium content of native sulfur from Kilauea Volcano

Sample	Source	Reference	Selenium (percent)
1	Steam condensate, Kilauea Iki cone. Collected Nov. 23, 1959, by K. J. Murata and R. T. Okamura.	J. W. Budinsky and Irving May, analysts.	2.9
2	Altered pumice, Kilauea Iki cone. Collected Nov. 23, 1959, by W. U. Ault. Sulfur extracted with carbon disulfide.	do	1.1
3	"Blowhole" cinder cone, 1955 flank eruption. Collected January 1957 by T. S. Lovering.	Lakin (1961); W. A. Bowles, Jr., analyst.	.16
4	New pit crater, Kalapana road, 1955 flank eruption. Collected January 1957 by T. S. Lovering.	do	.16
5	Spatter cone on roadcut northeast of Kalapana, 1955 flank eruption. Collected January 1957 by T. S. Lovering.	do	.09
6	Sulphur Bank solfatara at the summit. Collected January 1957 by T. S. Lovering.	do	.0004
7	Great Solfatara on the southwest rift near Halemaumau. Collected in 1921 by T. A. Jaggar before the great overflow of Mar. 7, 1921.	Byers and others (1936).	.22
8	Sulfur-impregnated lava, from unspecified locality on the volcano. Collected in 1840 by J. D. Dana.	Brown (1916)	5.18

SUMMARY

The lone sample of acid gas from the pumice hill of Kilauea Iki raises more geochemical questions than it answers. But it does call attention to the possibility of hydrochloric acid being a more common constituent of Kilauea gases than was hitherto realized. The attack of basaltic pumice by hydrochloric acid produces chlorides of ferrous iron, magnesium, calcium, and other major elements of basalt. In future studies, the need for special precautions to prevent the decomposition of these salts through hydration and oxidation is indicated.

The selenium in the sulfur associated with the gas recalls other minor elements, such as copper (Murata, 1960), that are exhaled during eruptions of basaltic volcanoes, and thereby emphasizes the importance of volcanic contributions to the oceans (Wedepohl, 1960).

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