Reports

Volcanic Gases: Hydrogen Burning at Kilauea Volcano, Hawaii

Abstract. *Spectroscopic evidence for hydrogen burning in air was obtained at Kilauea Volcano. The abundance of hydrogen required to support combustion is consistent with that predicted for gases in equilibrium with typical Hawaiian tholeiitic basalt.*

Volcanic gas is usually collected under low-temperature fumarolic conditions, and, as a result, the composition of the gas may have been altered by reaction with subsurface rocks and perhaps groundwater. Only on rare occasions, and then with some difficulty, can collections be made at high temperatures where gas and molten lava are in intimate contact. The gases collected under these conditions are in thermodynamic equilibrium (*1*), but in the special case of gases burning at a vent thermodynamic equilibrium with the ambient air is achieved after combustion. In Hawaii flames are occasionally seen from burning volcanic gas, usually during or immediately after an eruption, and can, in certain exceptional cases such as that reported here, be studied by spectroscopic methods.

Previous attempts at flame spectroscopy at several volcanoes (*2–4*) have revealed emission bands of CuCl, lines of Na and K, and some unidentified continua, but have given little information on the combustion process occurring in the flames. We report here the identification of spectral features observed at Kilauea Volcano that establish the flames as originating from the combustion of H_2 in air. Although the burning of H_2 had long ago been suggested as the cause of certain volcanic flames (*4*), reliable evidence for H_2 burning was previously unavailable and the possibility remained that other combustibles, such as CO, were the prime cause of the flames seen at Kilauea and elsewhere.

An 11-hour episode of lava fountaining on the caldera floor of Kilauea Volcano, Hawaii, began at 0855 H.S.T. on 14 August 1971. Considerable portions of the caldera floor were covered with new lava from en echelon lines of vents preventing access except to the southwesternmost extremity of one fissure. Large and colorful flames were seen emanating from these vents after sunset, following the termination of fountaining.

Our observing party approached to within 20 m of a line of flaming vents, and at the edge of a fresh lava flow we set up a small field spectrograph (*5*) especially constructed for the study of volcanic flames. The line of vents was about 35 m long and consisted of six separate flaming orifices. Flames at one end of the line were greenish-blue, and those at the other end were yellow-orange, with intermediate colors between. Hour-long exposures, shown in Fig. 1, were made of both the greenish-blue and the yellow-orange flames between 2005 and 2400 H.S.T. (by 2400 H.S.T. their intensities had diminished greatly). At maximum activity the flames rose about 2 m above the rims of the orifices. The most striking differences between the two extremes of flame color are the intensity of the Na doublet (blended because of overexposure) and the faint continuum from about 5800 to 6200 Å.

Between 4900 Å, where the filter begins to transmit, and 5300 Å no radiation was recorded. A weak continuum appears between about 5300 and 5500 Å. This is most likely part of the Na system; flames showing strong resonance lines of alkali metals also exhibit continuous emission (*6*). The resonance lines of atomic Na at 5890 and 5896 Å are seen as an impurity in nearly all flames. The dark gap in the spectrum near 6200 Å corresponds to a dip in the sensitivity of the Eastman Kodak class F plates used in this study. In the spectral region covered by this series of plates, emission features of CO_2, due to the combustion of CO in air, occur (*6*) but are not seen in our records. We originally considered CO combustion

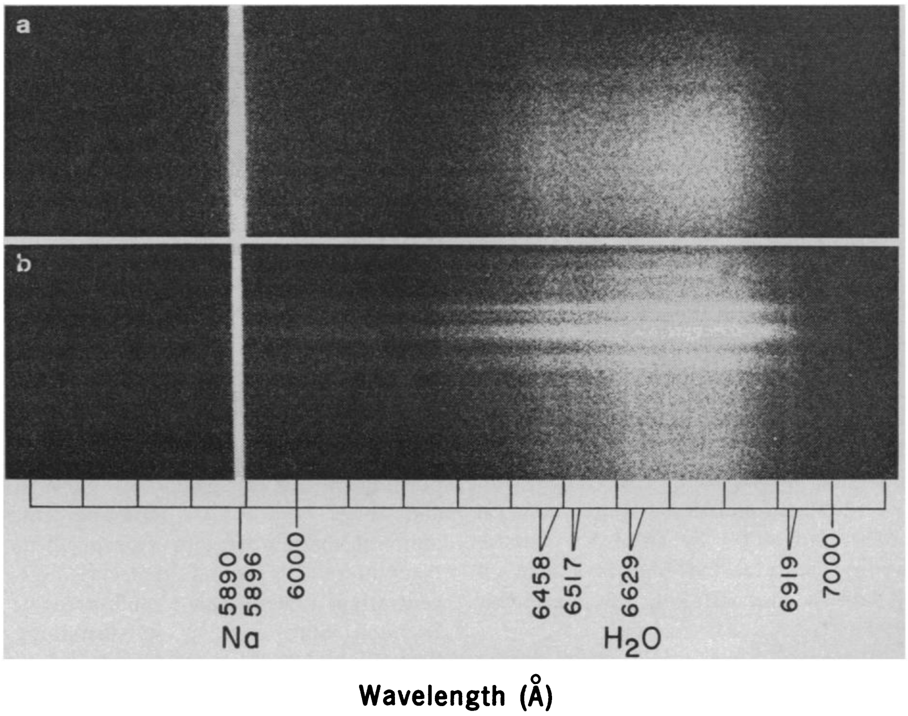

Fig. 1. Spectra of volcanic flames, 14 August 1971. (a) Hour-long exposure of a yellow-orange flame; (b) similar exposure of a greenish-blue flame emanating from a nearby vent. The Na lines are blended by overexposure, but note the relative intensities in the two flames. The four most intense bands of the H_2O emission spectrum are indicated.

to be the prime candidate for the generation of volcanic flames, owing to the often relatively high concentration of this gas in volcanic emanations. We are unable to establish an upper limit on the concentration of CO in the flames we observed. Bands of S_2, which should result from combustion of H_2S in air, are not seen in our records, but in a spectrum of the lava fountain at the 1967–1968 eruption of Halemaumau Cruikshank found marginal evidence for one relatively intense S_2 band (*7*).

Between about 6450 and 6915 Å there appears a series of bands corresponding to the four most intense members of a system of H_2O emission bands first discovered in high-pressure premixed H_2-O_2 flames (*8*). A reproduction of a laboratory spectrum showing these bands is given by Gaydon [plate 1 in (*6*)].

In a laboratory study of the H_2O bands, Kitagawa (*8*) considered their formation by the reactions

$$2H_2 + O_2 = 2H_2O + 114 \text{ kcal} \quad (1)$$

$$H + OH + H_2O = 2H_2O + 112 \text{ kcal} \quad (2)$$

Since the shortest wavelength bands of the observed system require about 50 kcal/mole, these reactions would lead to the necessary excitation if most of the energy goes into the vibration states of the H_2O molecule. The nonmetathetical reaction (Eq. 1) does not normally occur, although it is stoichiometrically correct. In order to determine which of the two reactions occurs in the flames at Kilauea, the emission features of OH were sought. The strongest accessible emission bands (0, 0 and 0, 1) occur in the ultraviolet region between 3064 and 3472 Å (*6*, p. 79). These bands were invisible in spectra of the Halemaumau lava fountain in 1967 and 1968 (*9, 10*). We observed flames at another eruption of Kilauea in late September 1971 but could not detect the ultraviolet bands. Delsemme (*3*) failed to detect OH emission in flames in the Congo, and we found no emission features between 3000 and 4000 Å from an intense yellow flame at the Alae lava lake on Kilauea's east rift on 13 December 1972.

Present evidence, then, suggests that excited H_2O molecules form without the intermediate formation of the OH radical. Bimolecular branching reactions involving H and O and the many combinations of radicals and stable molecules all have activation energies too low to yield the observed bands of H_2O (*11*). The OH radical, if present, presumably would enter into the flame chemistry by Kitagawa's Eq. 2.

Hydrogen is normally a minor constituent of volcanic gases collected from fuming vents (*12*). Its concentration can be understood in terms of the equilibrium with O_2; the O_2 fugacity is established by the oxidation states of iron in a rock melt-volatile system (*13*). The quartz-fayalite-magnetite buffer system (QFM), defined by Eugster and Wones (*14*), has provided a reliable approximation of the O_2 fugacity in equilibrium with basaltic melts at temperatures near the liquidus (*15*). Calculated O_2 fugacities for analyzed volcanic gases (*1*) are in excellent agreement with those predicted for gases coexisting with the QFM buffer at temperatures above about 1200°K. Electron microprobe analysis of coexisting ilmenite-magnetite in a Hawaiian tholeiite (*16*) and in situ measurements of O_2 concentrations (*17*) at 1300°K agree closely with the values predicted for the QFM system. Thus the O_2 fugacity of the gas phase coexisting with Hawaiian tholeiite can be adequately specified for the temperature range from 1300° to 1525°K. If we assume thermodynamic equilibrium at these high temperatures in a typical melt, the knowledge of O_2 fugacity permits computation of the ratio of partial pressures. In the temperature range considered, $p_{H_2O}/p_{H_2} = 54 \pm 2$ and is relatively insensitive to temperature.

The value of p_{H_2} can be readily calculated once p_{H_2O} in the volcanic gas is determined. From infrared absorption studies, Naughton *et al.* (*10*) assigned a value of 95 percent for the H_2O content of Hawaiian volcanic fume, a value which is supported by analyses of collected samples. At 1475°K, p_{H_2} is 14 torr (1.8 mole percent). This should be considered an upper limit because various processes tend to deplete H_2 selectively (*18*).

The lower flammability limit of H_2 burning in air is given by Coward and Jones (*19*) as 4.0 mole percent, although the temperature is unspecified. Naughton (*20*) found that, at concentrations of less than 2 mole percent, H_2 will burn with a self-sustaining flame in air if the orifice temperature is greater than 975°K, whereas gas containing less than 0.5 mole percent H_2 can ignite if the orifice temperature is about 1125°K. In addition to the hot orifice walls, condensed solids in the fume may provide the source of heat for ignition. Large flames that immediately follow the cessation of lava fountaining from fissures at the summit and on the flanks of the mountain normally persist for several hours after fountaining and then slowly diminish and disappear. Their disappearance is probably related to the cooling of the orifice below the flammability limit for the molar fraction of H_2 at that particular eruptive event, rather than to a change of gas composition.

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5. The spectrograph uses a plane grating (600 lines per millimeter, blazed for 12,000 Å, first order) and is used in the first and second orders. Dispersion in the second order is 100 Å/mm. This project began in 1967 under the sponsorship of G. P. Kuiper and was supported through 1968 by a NASA institutional grant to the University of Arizona.
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18. Once the gas phase has been exsolved from the melt, the O_2 and H_2 pressures are no longer buffered. Any process selectively removing H_2 will induce a degree of disequilibrium, which will be followed by the dissociation of H_2O vapor. (This will restore the H_2 to approximately its previous pressure but will greatly increase the O_2 pressure.) Two possible processes are the introduction of small amounts of atmospheric O_2 and the diffusion of H_2 through solid lava crusts, the latter having been postulated by Sato and Wright (*17*) to explain the oxidation of solidified basaltic lava.
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21. We thank Dr. D. W. Peterson, scientist-in-charge of the Hawaiian Volcano Observatory, U.S. Geological Survey, and his staff, particularly Dr. D. A. Swanson. We thank the superintendent of the Hawaiian Volcanoes National Park for permission to conduct the spectroscopic project at Kilauea. Research supported under funds from the National Geographic Society.

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Ground-Based Thermal Infrared Surveys as an Aid in Predicting Volcanic Eruptions in the Cascade Range

Abstract. *Detailed, ground-based thermal surveys of selected slopes of Mt. Rainier and Mt. Lassen have provided quantitative data for the construction of thermal contour maps of portions of the flanks of these volcanoes. Preliminary surveys substantiate the existence of one suspected thermal anomaly on Mt. Rainier.*

Recent eruptions of supposedly extinct volcanoes such as Mt. Arenal in Costa Rica in 1968 and the recognition of large, geologically recent, lahars (mudflows from a volcano) in volcanic areas have led to an increase in the monitoring of potentially hazardous volcanoes. Volcanic eruptions often produce destructive quantities of lava and ash. However, lahars may pose even greater destructive threats because of their possible speed and size. Lahars covering tens of square miles have been found, for example, in many of the valleys adjacent to Mt. Rainier, Washington (*1*). It is possible that many of these lahars formed as a result of volcanic warming of portions of the ice- and debris-covered volcano and were not necessarily related to simultaneous outpourings of volcanic materials.

A variety of techniques are now being used on Cascade Range volcanoes in the western United States to predict volcanic eruptions. These include seismic monitoring, intermittent periodic aerial thermal infrared imagery, tiltmeter studies, geodetic surveys, and ground-based quantitative thermal scanning.

We report here preliminary results of one of the field-monitoring techniques, namely, ground-based quantitative thermal scanning of the slopes of some of the most potentially dangerous Cascade Range volcanoes. This particular thermal technique was first used by Birnie (*2*) on certain Central American volcanoes. Radiometry was also used by Tazieff and Jatteau to determine the temperatures of gases emitted at Mt. Etna, Sicily (*3*).

In our thermal technique we utilize a PRT-5 precision radiation thermometer (Barnes Engineering Company) (*4*). The radiation thermometer measures the radiant exitance between 9.5 and 11.5 μm of any target within its 0.14° (2.44 milliradians) field of view. This particular band pass substantially reduces errors normally induced by atmospheric absorption. The 0.14° field of view of the instrument makes it possible to integrate the radiant exitance of a circular area 1.0 m in diameter at a distance of 401 m from the sensor. The PRT-5 yields precise readings of apparent surface temperatures ranging from −20° to +75°C. The precision of the instrument is 0.1°C.

The radiation thermometer is set up on prominent view sites around each volcano. The PRT-5 optical scanning head is mounted on a goniometer-equipped tripod capable of reproducible vertical and horizontal movements as small as 15′. Readings are taken in the very early morning before the first rays of the sun strike the mountainside, thus minimizing the differential solar heating of the surface material from the preceding day. The slope is scanned horizontally from the top down, and the temperatures are recorded at 20-minute intervals. No corrections are made for the emissivity of the surface material, the atmospheric absorption of the infrared radiation, or the temperature change due to the adiabatic cooling rate with increasing elevation. The vegetation-free volcanic surfaces are approximately constant in composition; therefore, the emissivity is approximately constant but not equal to unity.

The thermal data were collected on clear mornings in August and September 1972, the season of minimum mountain snow cover. Recorded temperatures were rounded off to the nearest degree Celsius and then they were plotted on photographs of the mountain slopes taken from the monitoring sites, and the isotherm contours were

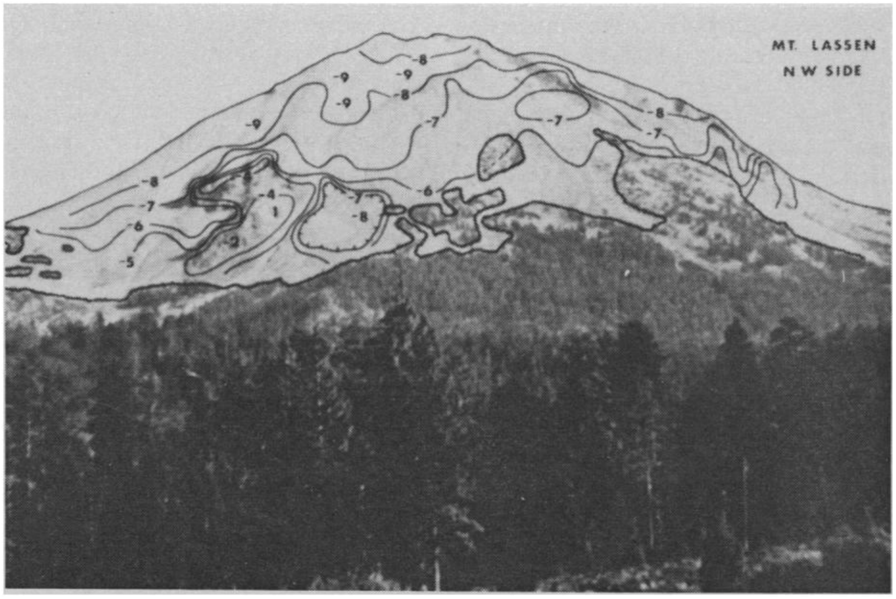

Fig. 1. Northwest side of Mt. Lassen (elevation, 3189 m), California, scanned 24 September 1972, from the north shore of Manzanita Lake (elevation, 1784 m). The distance between the station and the summit is approximately 8.1 km.