

HYDROCARBON GASES IN SOME VOLCANIC AND GEOTHERMAL SYSTEMS

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Introduction. The analysis of hydrocarbon gases in volcanic and geothermal systems has traditionally been limited to methane and occasionally ethane. Stoiber, et al. (1971) analyzed three gas samples from a fumarole on Santiaquitio Volcano, Guatemala and identified a wide range of organic compounds including aliphatic and aromatic hydrocarbons, aldehydes, ketones, alcohols, halogenated hydrocarbons, and sulfur compounds. Gunter (1978) analyzed several samples from Yellowstone National Park for the C-1 to C-4 hydrocarbons. The normal alkanes, isobutane, ethene, and propene were identified. The present work reports on the analysis of C-1 to C-6 hydrocarbons, including normal and branched alkanes, alkenes, and cyclic compounds, from a variety of volcanic and geothermal systems.

Method. Samples were collected in evacuated bottles containing NaOH using a procedure similar to that described by Giggenbach (1975). After analysis of residual gases (in headspace over NaOH), a 1-10 cc aliquot was taken in a gas-tight syringe and analyzed on a Hewlett-Packard 5700A gas chromatograph equipped with a flame ionization detector. Dual columns 6' by 1/8" were packed with Porapak Q and helium carrier gas was used at 60 psi inlet pressure. Each analysis was temperature programmed as follows: 30°C for 2 min, 8° per min to 150°C, and held at 150°C for 16 min. Representative chromatograms are shown in Figs. 1 to 4, and their peaks are identified in table 1. Identification of the gases was based on retention time and confirmed on representative samples by GC-MS using a Perkin-Elmer 990 gas chromatograph coupled through a membrane separator to a Bell and Howell 21-491 mass spectrometer. A 6-foot Porapak Q column was used with a helium flow of 20 ml/min. The analysis was temperature programmed as given above. The membrane separator was held at 20°C until the water was eluted, then held at 0° for the remainder of the analysis.

Discussion. Samples were obtained from several volcanic and geothermal systems. These systems were arranged in four groups on the basis of the gas analyses:

1. Fumaroles from the active volcanoes of Kilauea, Hawaii; St. Augustine, Alaska; and Mount Hood, Oregon.

2. Hot springs and fumaroles associated with igneous or crystalline rocks represented by samples from Steamboat Springs, Nevada and Lassen National Volcanic Park, Calif.
3. Steam and hot water wells associated with sedimentary rocks at Cerro Prieto, Mexico; Larderello, Italy; and The Geysers, Calif.
4. Systems such as Yellowstone National Park, Wyoming in mixed igneous and sedimentary terrane.

Gases from fumaroles in recent lava flows at Kilauea and St. Augustine are probably of volcanic origin with no contribution from sedimentary or organic sources (Fig. 1A and 1B). These samples are characterized by a generally low content of hydrocarbons; only the C-1 to C-4 normal alkanes and the corresponding alkenes are present. The difference in the size of the peaks between different chromatograms is likely due to dilution of the samples by varying amounts of carbon dioxide or by near-surface atmospheric contamination. A sample from a crater fumarole at Mount Hood, Oregon, produced a similar chromatogram (Fig. 1C), although Mount Hood last erupted in the 1700's and the fumaroles are now well below boiling.

Methane is thought to be one of the gases originally present in a degassing magma (Ellis, 1957). The other hydrocarbon gases are in reasonable ratios to have been formed by the pyrolysis of methane (Gordon, 1948).

Distribution of gases from igneous and crystalline rock areas related to past volcanism such as Steamboat Springs, Nevada, and Lassen Volcanic National Park, Calif. (Figs. 2A and 2B) show a strong resemblance to the volcanic gases. Methane concentrations are higher, often constituting 1 percent or more of the total gases. A triplet identified as 1-butene, n-butane, 2-butene is characteristic of these samples and also appears in the Kilauea chromatogram. C-5 and C-6 hydrocarbons are generally present in small amounts.

The increased methane may be generated from the reaction of carbon dioxide with hydrogen in the presence of liquid water (Hulston, 1964). Sediments may contribute small amounts of methane

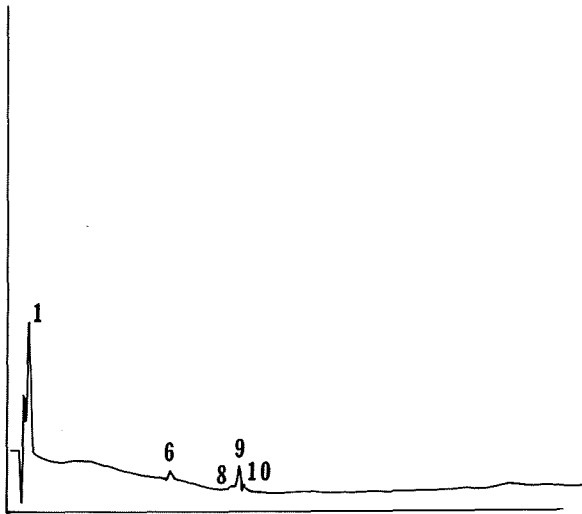


Fig. 1a KILAUEA, HAWAII

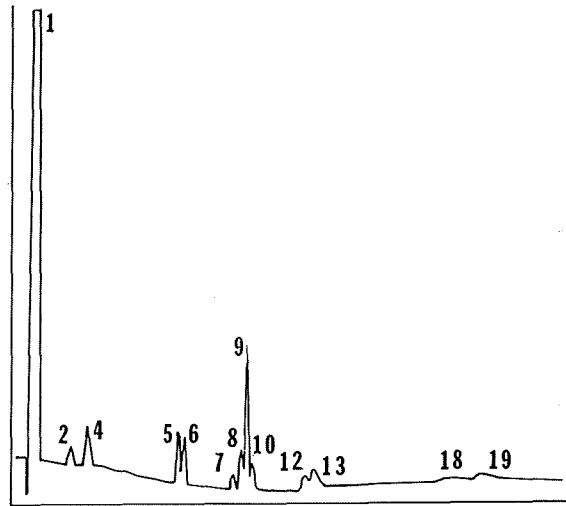


Fig. 2a STEAMBOAT SPRINGS, NEVADA

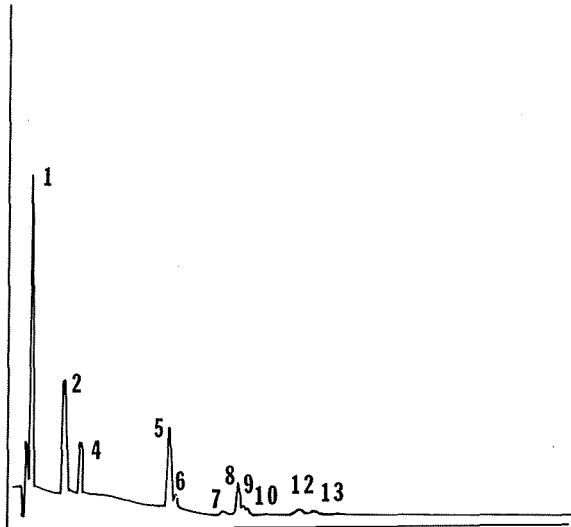


Fig. 1b ST. AUGUSTINE, ALASKA

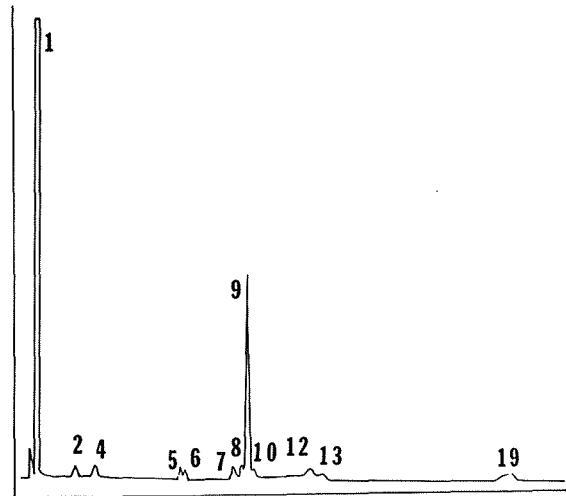


Fig. 2b LASSEN VOLCANIC NATIONAL PARK, CALIFORNIA

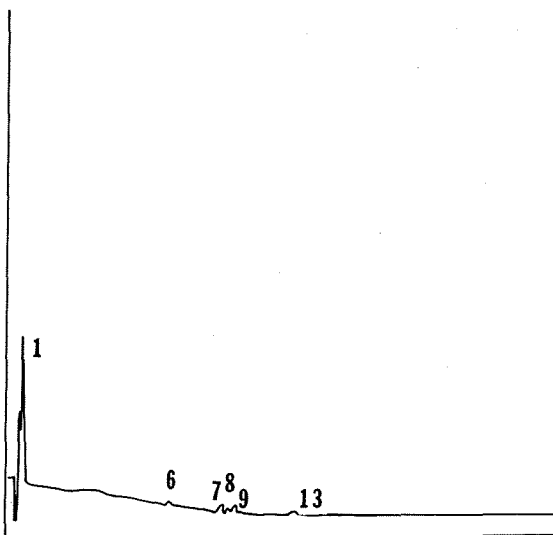


Fig. 1c MT HOOD, OREGON

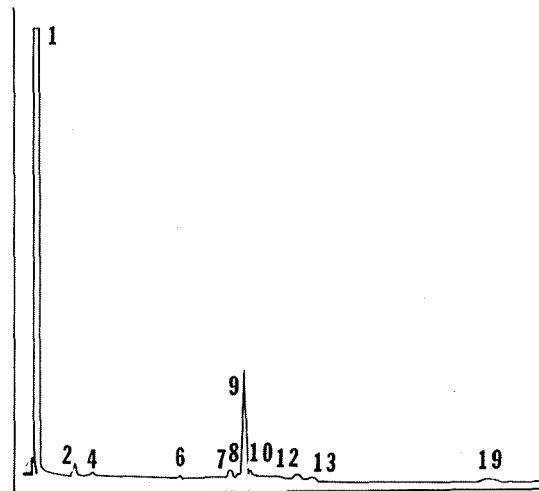


Fig. 2c MORGAN SPRINGS, CALIFORNIA

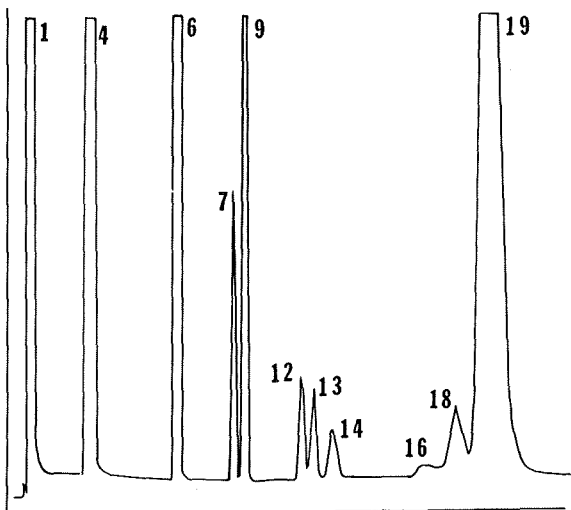


Fig. 3a CERRO PRIETO, MEXICO

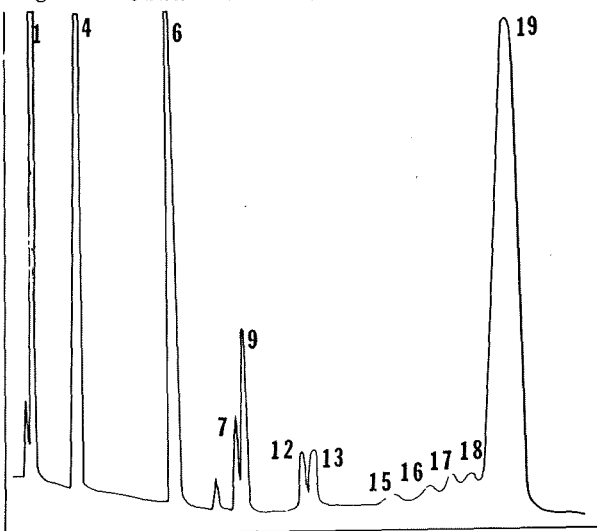


Fig. 3b LARDERELLO, ITALY

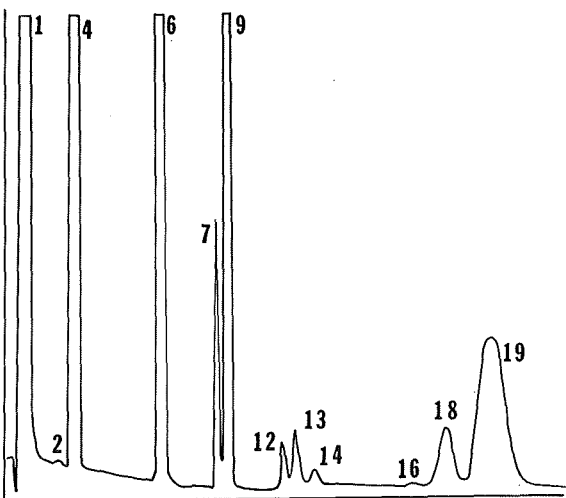
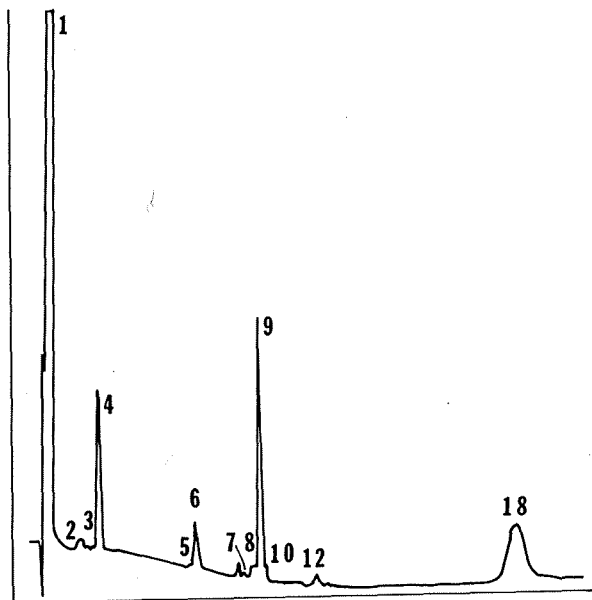
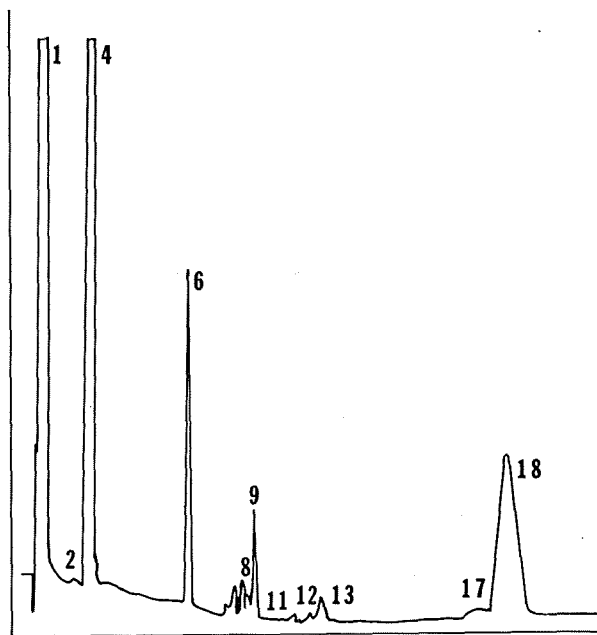


Fig. 3c THE GEYSERS, CALIFORNIA



YELLOWSTONE NATIONAL PARK, WYOMING

Fig. 4a



YELLOWSTONE NATIONAL PARK, WYOMING

Fig. 4b

and also account for the presence of the C-5 and C-6 hydrocarbons. The proximity of the acid hot springs and fumaroles in Lassen National Volcanic Park and the high-chloride springs at Morgan Hot Springs suggests that they belong to a single geothermal system. That hydrocarbon gases from the two areas show identical peaks and similar ratios (although the actual concentrations are less at Morgan) adds support to this theory (Figs. 2B and 2C).

Gases from sedimentary (and metamorphosed sedimentary) areas have a much higher concentration and wider variety of hydrocarbons. This type is represented by samples from Cerro Prieto, Mexico; Larderello, Italy; and The Geysers, Calif. (Figs. 3A, 3B and 3C). Methane frequently constitutes 10-30 percent of the total gas. Unsaturated hydrocarbons are absent, but branched hydrocarbons are present in large amount and variety. Benzene is usually one of the dominant peaks, and cyclopentane has also been identified.

These hydrocarbons probably originated, for the most part, from the breakdown of more complex organic substances. Magmatic heat sources are hypothesized for all these areas and may make minor contributions to the hydrocarbons.

Mixing of the preceding gas types is possible and evident in samples from Yellowstone National Park, Wyoming. Comparison of Fig. 4A with 4B shows an increase in both the number of hydrocarbons and the amount of the normal hydrocarbons and benzene. Apparently, a gas of igneous origin is mixing with differing amounts of a sedimentary gas as the igneous gas moves away from its source.

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Table 1. Peak identification

| Number | Name |
|--------|----------------------------|
| 1 | Methane |
| 2 | Ethene |
| 3 | Ethyne |
| 4 | Ethane |
| 5 | Propene |
| 6 | Propane |
| 7 | 2-Methylpropane |
| 8 | 1-Butene |
| 9 | n-Butane |
| 10 | 2-Butene |
| 11 | 2,2-Dimethylpropane |
| 12 | 2-Methylbutane |
| 13 | n-Pentane |
| 14 | Cyclopentane and 2-Pentene |
| 15 | 2,2-Dimethylbutane |
| 16 | 3-Methylpentane |
| 17 | 2-Methylpentane |
| 18 | n-Hexane |
| 19 | Benzene |