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titled

"Search for Biological Precursor Molecules

in Volcanic Volatile Systems"

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1. Subject: Semi-Annual Status Report
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2. Title: "Search for Biological Precursor Molecules in Volcanic Volatile Systems."

3. Status of Work during this Period

The general plan of research consists of the following two parts as outlined previously - (1) an investigation of the natural volcanic gaseous system for its elemental and molecular composition, with particular emphasis on compounds of biological importance which might be present in trace quantities; and (2) a field and laboratory investigation of the equilibrium molecular and free radical components to be found in gaseous systems which contain the major elements (O, H, C, S, N) of volcanic gas. This last is pertinent since we have found from work on Hawaiian volcanoes that the gases are a homogeneous system in thermodynamic equilibrium. Investigations of pockets or vesicles of gas in newly erupted lavas, and of similar gaseous or fluid inclusions in ultrabasic nodules found in lava, which seem to have a deep-seated source, also are being made with the search for prebiotic components as the objective.

For accomplishments during this period we may list the following:

a. Volcanic Gas Collections. Collection of gases have continued at Makaopuhi lava lake. In addition the staff of the

Volcano Observatory has started a drilling program through the thick crust (ca. 60 feet) of the Kilauea Iki lava lake which resulted from the 1959 eruption at that site. A new rig is being used which will drill a large diameter hole (3") which should enable us to obtain samples without the difficulties due to contamination and tube jamming which were experienced in the previously used 1" diameter drill holes.

Collections also have been continued at the Sulfur Bank (S-1) and Aloi (S-2) fumarole sites.

No eruption occurred during this period, although seismic and tilt evidence indicated the imminence of activity.

b. Other Field Work. A glass reflux system was set up at Sulfur Bank fumarole in an effort to simulate a low temperature (96°) thermal system which might have been involved in the evolution of prebiotics. The reflux solution was tagged with carbonate-C^{14} as a sensitive indicator of any exchange which might take place, or trace amounts of prebiotics (cyanides, carbonyl compounds) which might form. Runs of twenty-four hours were made, but no indication of the formation of any radioactive substance other than carbon dioxide was obtained.

Inorganic volatiles from the drill holes of Makaopuhi lava lake were collected. It was believed that it would be important to be aware of the metallic substances present in the volatile system, since these may have a catalytic or chelating function in prebiotic formation. Collections were made at various temperature zones in the holes, and these were analyzed by

emission spectroscopy, atomic absorption, and x-ray diffraction and fluorescence. In the hotter zones (to 600°C) elements were present generally as chlorides, with sulfates and oxides becoming prevalent in the cooler (100°C) regions. Cations found have been copper, iron (both ferrous and ferric), magnesium, sodium, potassium, zinc, manganese and calcium. In addition to chlorides, silica and calcium sulfate were much in evidence. It is believed that the primary transport takes place as chlorides, whereas sulfates and oxides are secondary products. Some iron-aluminum compounds were present which have not been identified as yet.

c. Laboratory Work - Analyses. Analyses of collected gases have continued by the use of gas chromatography, with no carbon containing substances beyond carbon dioxide and methane being revealed with certainty. On occasion an unexpected peak would appear in the flame ionization detector, which was indicative of carbon compounds of unknown nature. Portions of some of these samples were saved for investigation on the mass spectrometer when this instrument became operative and available for the work. Most samples showed only a very minor indication of unambiguous organic peaks (m/e -- 41, 42, 43 -- 53, 54, 55, 56 -- 69, 70, 71, 72 -- 82, 83, 84, 85), but one sample in particular showed a range of peaks to a maximum m/e of 121. The vestigial peaks in the other samples reflect, to some extent, the peaks of this most abundant material. Unfortunately we seem to be dealing with a mixture so that interpretation is very difficult. There is indication of isoprenoid groupings, and perhaps some sulfur containing compounds.

A comparative representation of these results is shown in Figure 1. Samples from two lava lake sites (Alae and Makaopuhi), from the liquid lava lake at Makaopuhi (30-M and 37-M), fumaroles (S-1, S-2) and White Island in New Zealand (NZ-1, NZ-3) are represented. These have been arranged in order of increasing organic content going "backward" in Figure 1. Lines have been drawn connecting the peaks, which bring out the interrelationships which are not apparent when single spectra are examined. The subtraction technique has been applied to remove gross peaks due to H_2O, CO_2 and SO_2. Peak grouping around m/e --91, 84, 77, 64, 56, 53, 48, and 43 are evident, as well as lower m/e values due to molecular fragments.

This has been the most promising lead in this research thus far, and currently is being pursued vigorously along the following lines: (1) The collection of large samples which would enable gas chromatographic work as well as a more thorough mass spectrometric investigation to be carried out. (2) A search for contaminents which might lead to the presence of organic compounds in the volatiles. An effort is being made to collect samples where buried vegetation could not make a significant contribution (old lava lakes), or where materials introduced during drilling would not play a role (fumaroles), and, of course, collection from a new eruption for this type of analysis is anticipated. (3) Continued effort to make positive identification of the compounds responsible for the spectra. This should be simplified with larger organic samples from these sources which we are now attempting to collect.

4. Personnel

During this period the work was conducted with the help (half-time) of one graduate student (K. Lennon), and the full-time participation of the post doctoral fellow (R. Goguel). In addition, staff and other graduate students gave part-time help to the project.

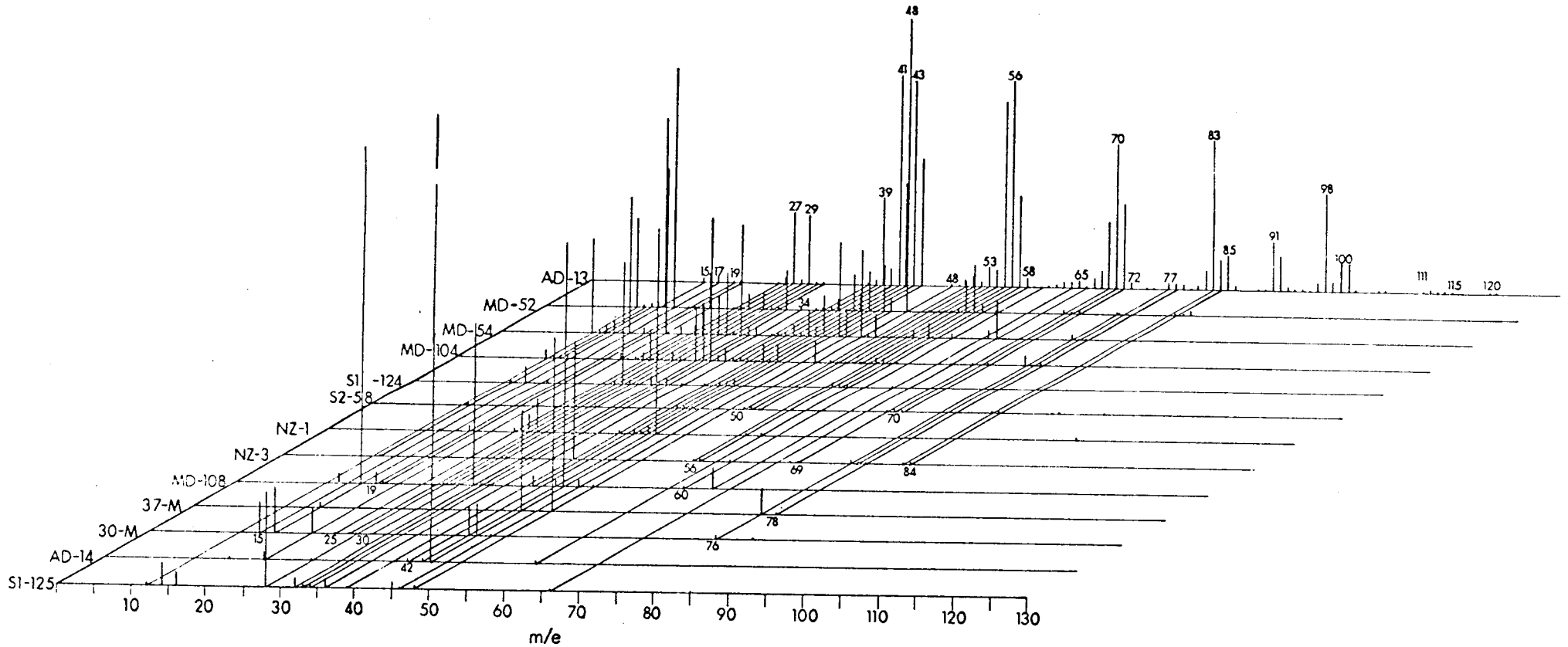

FIGURE 1. RESIDUAL PEAKS FROM CONDENSABLE GASES FROM ASSORTED VOLCANIC GAS SAMPLES CO_2, SO_2, AND H_2O SUBTRACTED