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"Search for Biological Precursor Molecules in Volcanic Volatile Systems

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2. Title: "Search for Biological Precursor Molecules in Volcanic Volatile Systems."

3. Abstract.

The general plan of research consists of the following two parts as outlined in previous reports - (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. (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 the recent period we may list the following: (I) Further analysis results following the trends in the gas composition of Makaopuhi lava lake and Sulfur Bank fumarole during this period. (II) The construction and testing of a high dispersion spectrometer for the measurement of emission and absorption spectra. This now is ready for field use during the next eruption. (III) The setting up of refluxing

systems over lava lake drill holes to simulate the thermal system which might evolve prebiotics in a volcanic or fumarole situation. (IV) Further work on the extraction and analysis of gases from inclusions in ultrabasic nodules from deep crustal sources.

No results of a real "breakthrough" nature can be reported as of this period from the above work.

4. General Results.

(A) Gas Collections - For the volcanic gas collection phase, in work of this character depending on the unpredictable conditions at erupting vents, the field investigations are very much "researches-of-opportunity." Since 1960 they have been patterned by the occurrence of three flank eruptions of Kilauea (Kilauea Iki 1959-60, Alae - 1963, and Makaopuhi - 1965) which partly filled old pit craters with molten lava lakes. The lakes quickly crusted over, but have molten lava cores which will continue to solidify for some years (Kilauea Iki and Makaopuhi--Alae has solidified completely). Procedures for drilling through the crust and into the liquid core have been developed by the staff of the Hawaiian Volcano Observatory, U. S. Geological Survey. These lakes have given us an unprecedented opportunity for studies of the geology, mineralogy, physics and chemistry of large molten rock bodies and the solidification processes in such systems. In our recent researches on volcanic gas, we have concentrated on collections and measurements made to follow the degassing process at these unique sites. On Christmas Eve 1965, a short eruption occurred

adjacent to Aloi crater. Currently the imminence of an outbreak is indicated by the seismic pattern and summit swelling at Kilauea Volcano.

5. Specific Accomplishments.

(I) Results of Gas Analysis - Details of gas collection procedures, analysis techniques, and results obtained from preliminary work have been given in previous reports. No unusual or spectacular observation which would be relevant to a search for prebiotics has been made during recent work.

Recent collections made from Makaopuhi lava lake have reinforced our conclusions as to the general trends in the gas composition as mentioned in our last report. These trends may be noted, as follows:

1. The thermodynamic variation of oxidized to reduced species is found as one goes from cold to hot areas--say, from edge to center of lava lake, or from top to bottom in a drill hole. These are noted mainly in the oxygen partial pressure variations, and have been mentioned previously.

2. A large decrease in the carbon dioxide content from the active lava immediately after eruption, to the present lava lake, when the content becomes minor and constant at approximately 0.03% (air free).

3. A possible decrease in the free nitrogen content during the history of the cooling of the lake.

4. The appearance of methane in small amounts in the later history of the lava lake. This would seem to preclude a contribution from pyrolyzing vegetation as an important

component of the gases. Collections made from lava flows covering vegetation always show a large content of methane, and this is predominant mainly in the early phases of cooling of these flows.

5. A trend in the sulfur gases which to some degree parallels the behavior of carbon dioxide--a large content in newly erupted lava, decreasing to minor amounts in the later history of the cooling lava lake. This gas is usually SO_2 (approx. 0.2%), with H_2S appearing on occasion. Sulfur gases are difficult to preserve unreacted during collection and analysis.

A graphic indication of these trends is presented in Figure I, with a comparison to some of the most favorable collections made previously during eruptions. The disparity in the carbon dioxide content is notable while the concentration of sulfur dioxide is little changed. This emphasizes the difference between a degassing lava system present in the lava lake and the primary volcanic vent, and probably indicates for one thing the lower relative solubility of carbon dioxide in lava compared to that of sulfur dioxide.

With collections of gas made at Sulfur Bank fumarole during the past summer we have sufficient data to begin to note a relationship between the concentration of the sulfur components of the gas and the stage of activity of the associated volcano Kilauea. These results are shown in Figure 2, where the sum of the sulfur gases (H_2S and SO_2) divided by the carbon dioxide content (which is used as reference since it is relatively

Change of Lava Lake Gas Composition
with Time after Eruption

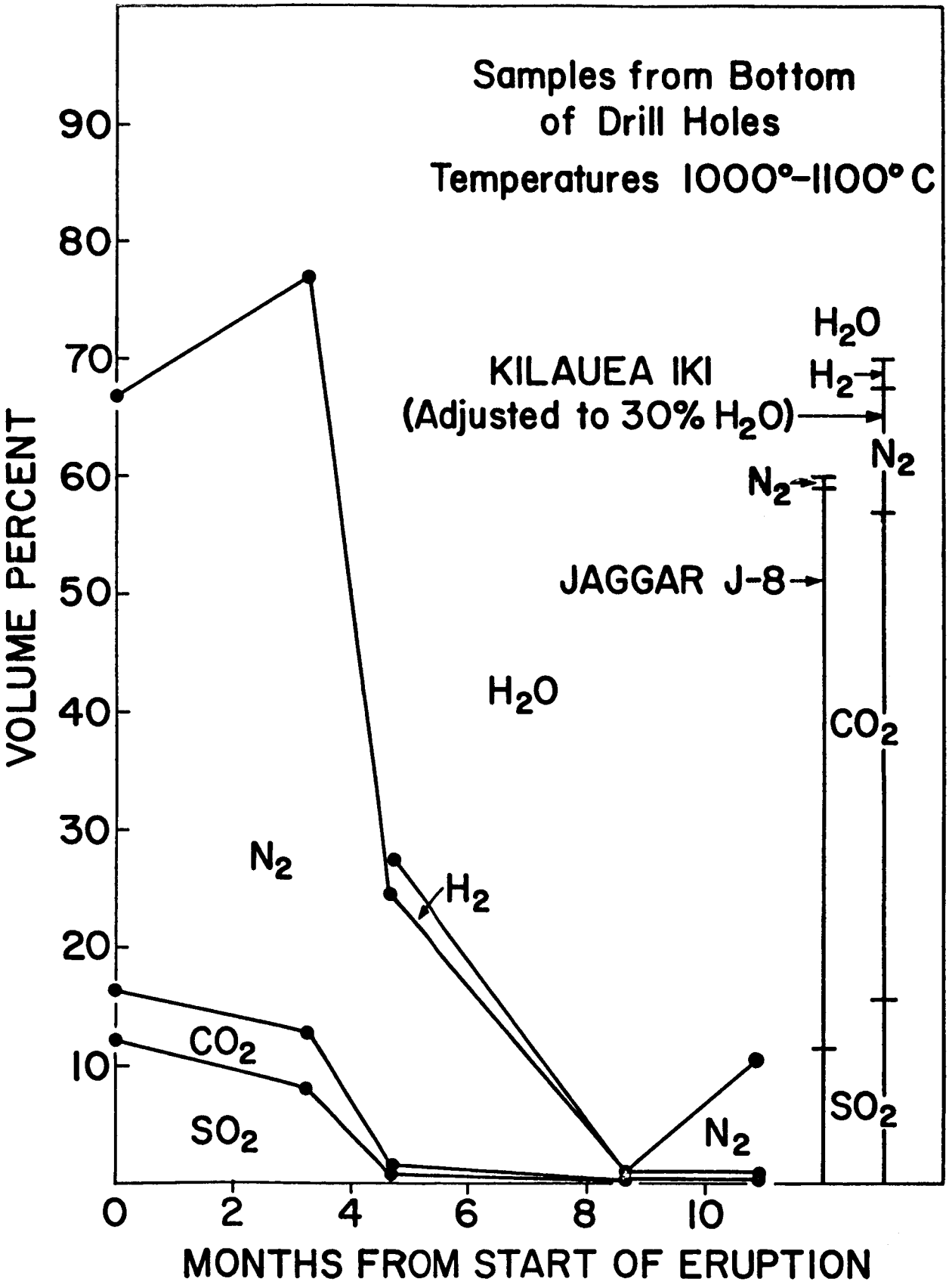

FIG. 1

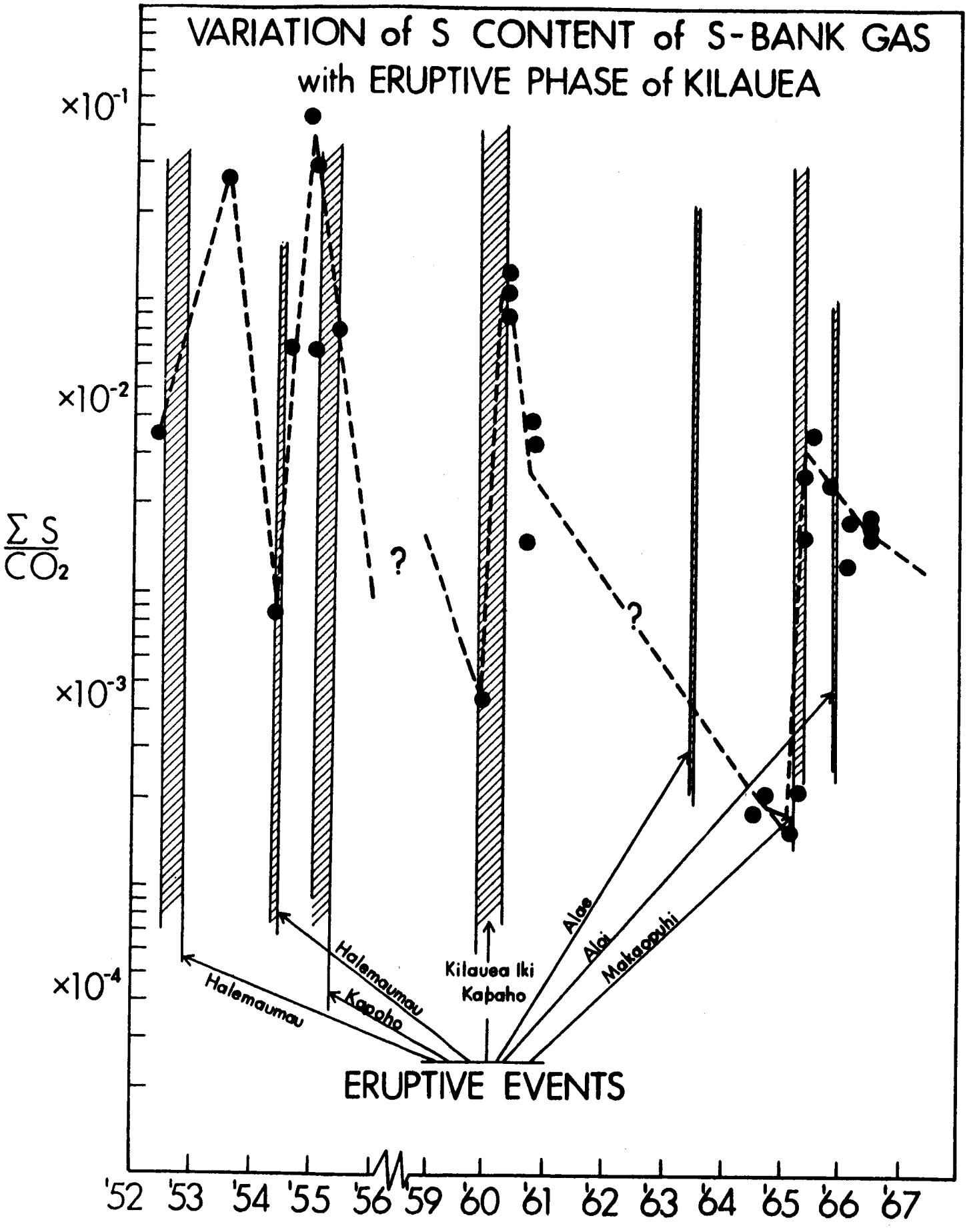
VARIATION of S CONTENT of S-BANK GAS
with ERUPTIVE PHASE of KILAUEA
×10⁻¹
×10⁻²
×10⁻³
×10⁻⁴
Σ S / CO₂
?
?
Halemaumau
Halemaumau
Kapaho
Kilauea Iki
Kapaho
Alae
Alai
Makaopuhi
ERUPTIVE EVENTS
'52
'53
'54
'55
'56
'59
'60
'61
'62
'63
'64
'65
'66
'67

FIG. 2

constant), is plotted against time. Volcanic eruptive events at Kilauea are shown by the stippled vertical bars. It will be noted that there is a definite indication that sulfur gases increase greatly during activity, and there is some thought that this phenomenon might be used to indicate imminence of volcanic eruptions.

From this we judge that Sulfur Bank fumarole may have a unique connection to the Kilauea magma chamber, and would be a site which is indicated for future collections for this research. Additionally this is the one collecting point from which we have been able to obtain samples with zero or negligible air contamination, another indication of the primordial nature of its volatiles, and freedom from contamination by air or meteoric waters.

(II) Volcanic Spectrometry - In a previous report, some encouraging results were shown for absorption spectra taken by pointing a small spectrometer down into lava lake drill holes. Further work has not verified these results, and it has been found that even with a high intensity zirconium source present at the bottom of the hole, no significant absorption spectra could be obtained from the column of gas. It was concluded that the previous results were accidental and spurious, and that the experiment conducted in the drill holes at this late stage of the lava lake development was not hopeful because of the very small contribution of absorbing species from rock degassing. It was also concluded that spectrometry would be a valuable approach to the detection of significant concentrations of prebiotic

molecules or fragments during an actual eruption, or in a lava lake immediately after eruption when the concentration would be maximal. Accordingly it was decided to proceed with the construction of a high resolution field spectrometer. Reiner Goguel, who holds the post doctoral fellowship under this grant, has devoted a good deal of his time during the past months to the perfection of this instrument. Construction was carried out by purchase of a small Jarrel-Ash monochromator and the extensive modification of it to take a variety of film holders (to accomodate Polaroid and 35 mm infrared film). Arrangements also were made for taking comparison spectra, for distant focusing, and for a continuum source for absorption work. The instrument has been finished in anticipation of an eruption which is expected momentarily from all auspices, and has been tested by obtaining good spectra from small neon advertising signs about three miles distant. It is believed that the instrument will be most useful and it is hoped that it will give some unique information from the next eruption.

(III) Lava Drill Hole Reflux System - In an effort to simulate the conditions which might exist at a fumarole or degassing lava body, where primitive volatiles could percolate through and exchange with an earlier evolved condensed phase (presumably aqueous), a field condenser system was set up at one of the drill holes at Makaopuhi lava lake. This might be considered to be a field version of the classic Miller-Urey experiment, or perhaps of the Sidney Fox variation of it, since the energy source is thermal. The set-up used is shown in

Figure 3. A single preliminary run was made for only a few hours, and the system performed very well. Tests of the collected fluids were positive for ammonium ion and chloride, negative for cyanide, and "in process" for carbonyl and amino acids. It is hoped to set up the system for a prolonged run of a few weeks in the near future, when the experiment would be more meaningful.

(IV) Gases from Ultrabasic Nodules in Volcanic Lava - It is well known that under the usual circumstances certain high melting materials (for example, olivine) crystallize in the magma body beneath a volcano, and that the lava as erupted is a dilute mush of solids suspended in the major liquid. It can be shown that in some cases this crystallization takes place deep in the earth (4-10 kilometers), and recently it has been found that most such early crystallites contain a gas phase, frequently consisting of liquified carbon dioxide. In dating these nodules we have found that the gas contains radiogenic helium and argon and that the "ages" obtained may go back to 6 billion years. These fluid inclusions most certainly contain gas which is uncontaminated and primordial, and would be a possible place to look for biological precursors of the most primitive type.

Currently we are working on methods for detailed analysis of the gaseous component. Microscopy has shown that the majority of the bubblets exist along healed fracture planes, and crushing preferentially releases the gas from along these planes of weakness. Accordingly most of the work depends on a release of gas by crushing, although decrepitation and melting also are used.

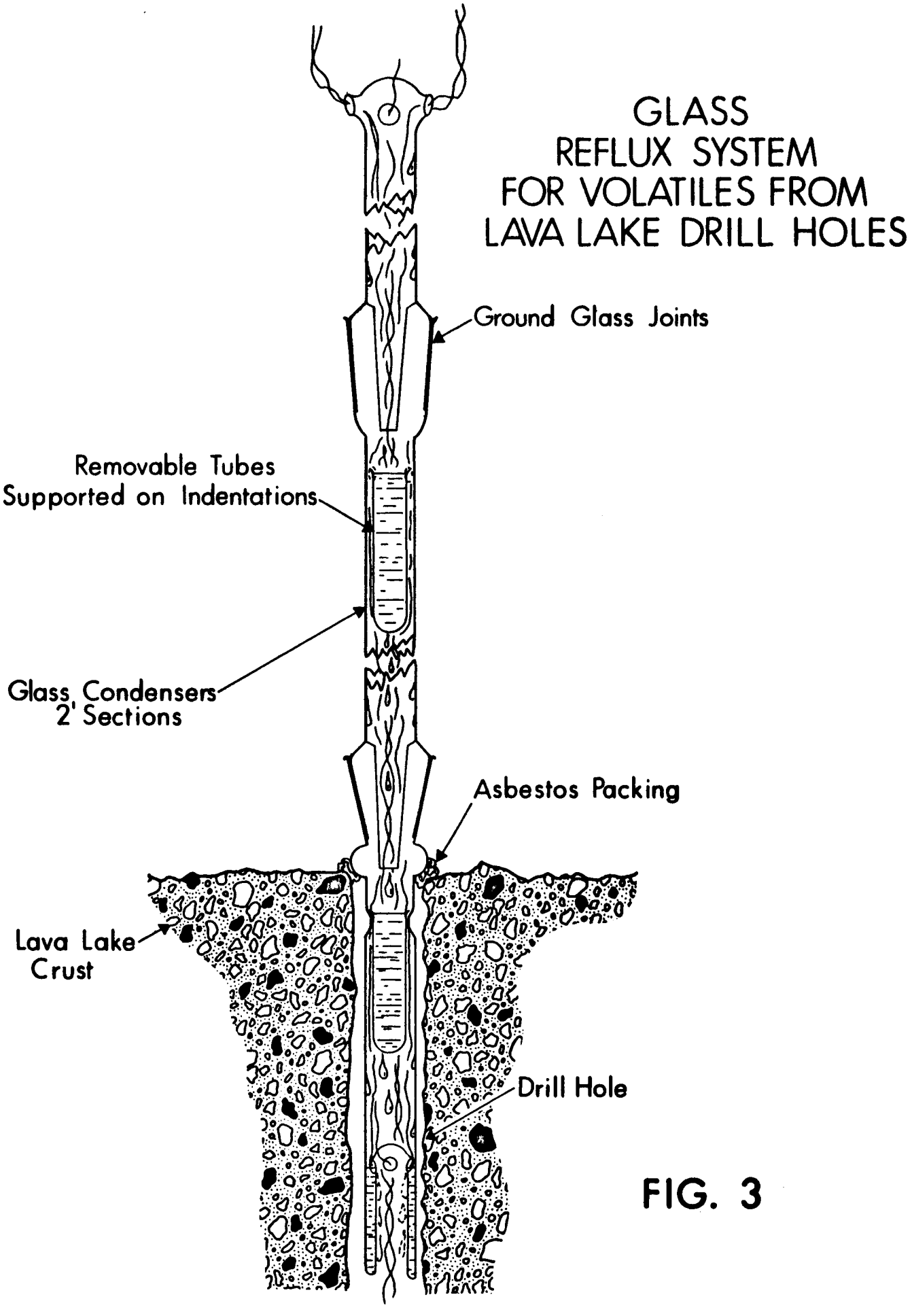
GLASS
REFLUX SYSTEM
FOR VOLATILES FROM
LAVA LAKE DRILL HOLES
Ground Glass Joints
Removable Tubes
Supported on Indentations
Glass Condensers
2' Sections
Asbestos Packing
Lava Lake
Crust
Drill Hole

FIG. 3

The work to date has consisted of the following: (a) Construction of a high pressure crushing device operating as a single action plunger (designed and built by Dr. Goguel). Currently this is under preliminary test. (b) Continued investigation of the inert gas occurrence pattern using mass spectrometry. (c) Development of gas chromatographic and mass spectrometric methods of analysis of the small quantities of gas involved. (d) Attemps to analyze the gas phase in situ in single crystals of the nodules by transmission and reflection infrared spectrophotometry. Since all of this work is in the early stages of development, no results are available as yet.

6. Personnel.

Currently the work is proceeding with the use of student help (V. Tesoro), one graduate student (K. Lennon), and the full time participation of a post doctoral fellow (R. Goguel). In addition staff and other graduate students give part time help to the project.