BIOGEOCHEMISTRY OF CARBON IN TERRESTRIAL AND
LUNAR VOLCANIC SYSTEMS

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ABSTRACT

A study was undertaken to determine the conditions which are favorable for the formation and stability of minor amounts of organic substances from combinations of gases which have geological significance. The environmental conditions as they apply to terrestrial and lunar emanations were: temperatures within the range of active volcanism, partial pressures of component gases and the oxidation state of these gases and the basaltic lava. Because the concentration of observed organics often approached the limit of detection for flame ionization gas chromatography, reactor background and instrument sensitivity were critical problems.

It was concluded that the composition of present-day terrestrial volcanic gases erupting at 1400°K and an oxygen fugacity of about \(1.0 \times 10^{-9}\) atm is too oxidizing to permit the formation of most organic compounds, even when a volume of gas cools slowly in isolated confinement. Methane is the most conspicuous reduced organic substance, albeit appearing in extremely small quantities.

Analytical data for total carbon in Hawaiian basalt samples erupted on the ocean bottom with minimal volatile loss have been compared to surface erupted samples. The difference has been interpreted with respect to the volcanic contributions to the surface environment of Earth over geological time.

For crystalline lunar rock the oxygen fugacity at the erupting temperature seems to have been controlled to values not exceeding \(1.0 \times 10^{-11}\) atm and, in some instances, values as low as \(1.0 \times 10^{-14}\) atm.
are suggested. Despite the more reducing environment, high temperatures still suppress the formation of organic compounds. However, a mass of lunar volcanic gases composed predominantly of carbon monoxide will, as it cools to temperatures around 700°K, pass into a region of stability for simple hydrocarbons. The mode of formation of these hydrocarbons may be similar to the Fischer-Tropsch synthesis where the reduced lava behaves as a polymerization catalyst. At these lower temperatures the hydrocarbon type is primarily determined by the availability of hydrogen, which by its fugitive nature in silicate systems, may rapidly and selectively diffuse away from the gas phase which may be confined. Volatiles which cool slowly in confinements such as gas-formed vesicles or along grain boundaries offer the greatest potential for organic compound synthesis.

The role of condensed carbon and metal carbides is not completely clear, but experimental and theoretical evidence suggests the importance of both condensed forms in the laboratory experiments designed to study these reduced geological environments.

The chemistry of volcanic gases on the primitive Earth was examined on an equilibrium basis with respect to the formation of simple organic compounds which may have been important in the chemical origin of life. The composition of the major constituents and the trace quantities of organics were thought to be different from present-day volcanic systems. It appears that the origin of prebiotic compounds in significant amounts required some nonequilibrium concentration processes.
### TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABSTRACT</td>
<td>iv</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>v</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>vi</td>
</tr>
<tr>
<td><strong>I. BACKGROUND INFORMATION</strong></td>
<td>1</td>
</tr>
<tr>
<td>A. General Statement</td>
<td>1</td>
</tr>
<tr>
<td>B. Lava Degassing</td>
<td>3</td>
</tr>
<tr>
<td>C. Water and Carbon Contents of Volcanic Rocks</td>
<td>15</td>
</tr>
<tr>
<td>D. Lunar Geochemistry Highlights</td>
<td>20</td>
</tr>
<tr>
<td>E. Oxidation States in Natural Rock Melts</td>
<td>41</td>
</tr>
<tr>
<td><strong>II. EXPERIMENTAL DESIGN AND PROCEDURES</strong></td>
<td>60</td>
</tr>
<tr>
<td><strong>III. EXPERIMENTAL RESULTS</strong></td>
<td>92</td>
</tr>
<tr>
<td>A. High Steam Experiments</td>
<td>92</td>
</tr>
<tr>
<td>B. Anhydrous Experiments</td>
<td>100</td>
</tr>
<tr>
<td>C. Summary</td>
<td>109</td>
</tr>
<tr>
<td>D. Carbon and Sulphur Contents in Basalts</td>
<td>114</td>
</tr>
<tr>
<td><strong>IV. EXPERIMENTAL DISCUSSIONS</strong></td>
<td>120</td>
</tr>
<tr>
<td>A. Influential Factors</td>
<td>120</td>
</tr>
<tr>
<td>B. Water Gas Reaction Kinetics</td>
<td>123</td>
</tr>
<tr>
<td>C. Fischer-Tropsch Reaction</td>
<td>130</td>
</tr>
<tr>
<td>D. Carbon and Sulphur Contents in Basalts</td>
<td>142</td>
</tr>
<tr>
<td>E. Equilibrium Calculations</td>
<td>144</td>
</tr>
<tr>
<td><strong>V. GEOCHEMICAL DISCUSSIONS</strong></td>
<td>203</td>
</tr>
<tr>
<td>A. Influential Factors in Natural Systems</td>
<td>203</td>
</tr>
</tbody>
</table>
## Table of Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>B. Interpretation to Magmatic Systems</td>
<td>217</td>
</tr>
<tr>
<td>C. Magmatic Inputs and Atmospheric Evolution</td>
<td>225</td>
</tr>
<tr>
<td>VI. SUMMARY</td>
<td>241</td>
</tr>
<tr>
<td>VII. APPENDICES</td>
<td>244</td>
</tr>
<tr>
<td>VIII. BIBLIOGRAPHY</td>
<td>266</td>
</tr>
</tbody>
</table>
LIST OF TABLES

1. Selected Logarithms for Contamination Discussion .......... 83
2. Carbon and Sulphur Contents in Basalts .................. 116
3. Pyrolysis Data on Submarine Basalt ....................... 119
4. Equilibrium Results for Elemental Abundance Points for Equilibrium Calculations .................. 158
5. Equilibrium Results for Carbides and Graphite ............ 187
6. Equilibrium Results for Partially Oxygenated Organics .. 191
7. Comparison of Three Equilibrium Studies .................. 196
8. Selected Parameters Applicable to Fischer-Tropsch Synthesis .................................................. 211
9. Composition of the Atmosphere of Earth .................... 231
10. Complete Equilibrium Results .............................. 256
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Iron-Oxygen System</td>
<td>48</td>
</tr>
<tr>
<td>2.</td>
<td>Iron-Oxygen System</td>
<td>49</td>
</tr>
<tr>
<td>3.</td>
<td>Oxygen Controlling Buffers</td>
<td>59</td>
</tr>
<tr>
<td>4.</td>
<td>Laboratory Reactor</td>
<td>65</td>
</tr>
<tr>
<td>5.</td>
<td>Gas Handling System</td>
<td>67</td>
</tr>
<tr>
<td>6.</td>
<td>Chromatographic System</td>
<td>77</td>
</tr>
<tr>
<td>7.</td>
<td>Summary of Experimental Results with Buffers</td>
<td>113</td>
</tr>
<tr>
<td>8.</td>
<td>Equilibrium Diagram Demonstrating an Omission</td>
<td>149</td>
</tr>
<tr>
<td>9.</td>
<td>Equilibrium Diagram Demonstrating an Omission</td>
<td>151</td>
</tr>
<tr>
<td>10.</td>
<td>Elemental Abundance Points in C-H-O System</td>
<td>160</td>
</tr>
<tr>
<td>11.</td>
<td>Graphite Deposition Boundaries in C-H-O System</td>
<td>163</td>
</tr>
<tr>
<td>12.</td>
<td>Partial Equilibrium Diagram for L/W 2</td>
<td>167</td>
</tr>
<tr>
<td>13.</td>
<td>Partial Equilibrium Diagram for L/W 2</td>
<td>169</td>
</tr>
<tr>
<td>14.</td>
<td>Partial Equilibrium Diagram for L</td>
<td>171</td>
</tr>
<tr>
<td>15.</td>
<td>Partial Equilibrium Diagram for L</td>
<td>173</td>
</tr>
<tr>
<td>16.</td>
<td>Partial Equilibrium Diagram for L/H 3</td>
<td>175</td>
</tr>
<tr>
<td>17.</td>
<td>Partial Equilibrium Diagram for L/H 3</td>
<td>177</td>
</tr>
<tr>
<td>18.</td>
<td>Partial Equilibrium Diagram for L/H 4</td>
<td>179</td>
</tr>
<tr>
<td>19.</td>
<td>Partial Equilibrium Diagram for L/H 4</td>
<td>181</td>
</tr>
<tr>
<td>20.</td>
<td>Partially Oxygenated Compounds in C-H-O System</td>
<td>194</td>
</tr>
<tr>
<td>21.</td>
<td>Equilibrium Deviation from QFM</td>
<td>200</td>
</tr>
<tr>
<td>22.</td>
<td>Equilibrium Deviation from QFI</td>
<td>202</td>
</tr>
<tr>
<td>23.</td>
<td>Possible Planetary Atmosphere Evolution Patterns in C-H-O System</td>
<td>235</td>
</tr>
</tbody>
</table>
I. BACKGROUND INFORMATION

A. General Statement

Popular concepts about how the Earth and other planetary bodies formed are divided between either high temperature or relatively low temperature accretionary processes. Aside from this question it is pretty well agreed upon that the Earth in its most primitive form was devoid of an atmosphere. Whatever gases were present during the accretionary phase were not retained because of the high temperatures caused, in part, by intense unattenuated solar radiation and the absence of magnetic and gravitational fields. Further, the substances presently in the oceans and atmosphere, excluding those being introduced by human activity, are largely the result of degassing of the Earth throughout geological time. If the crust of the primitive Earth once contained the iron and transition metals believed to have formed the core, these volatiles when they came to the surface could be expected to have assumed equilibrium compositions different from those associated with present-day volcanism and fumarolic activity. Many excellent treatises on geochemistry and cosmochemistry review these subjects in detail (Kuiper, 1; Rankama and Sahama, 2; Poldervaart, 3; Urey 4; Brancazio and Cameron, 5). The factors which influence these compositions are the subject of this research project. Quite obviously neither all factors nor all compositions were investigated, but experimental results coupled with equilibrium computations reveal some of the important features of the chemical compositions of volcanic environments on the Earth and on the Moon.
The ultimate goal of these lines of investigation is an attempt to learn about the conditions necessary for the formation and stability of certain simple organic substances. These organics, termed prebiotics or biological precursors, are usually considered important in the chemical evolution of more complex organic structures presumed necessary for the formulation and propagation of the first life form. The premise upon which this research was conducted was that organic compounds may be synthesized from mixtures of gases derived from geological systems under the influence of thermal energies. Literature on the subject of the chemical origin of life is voluminous to say the least. Important contributions prior to 1965 may be found in several sources (Fox, 6; Oparin, 7; Rutten, 8; Kuiper, 9; Bernal, 10; Dauvillier, 11). Later review articles by Ponnampерума and Gabel (12), Lemmon (13) and Cloud (14) bring one up-to-date.

Thermal synthesis of prebiotics has not received as much attention as other sources of energy, such as ultraviolet radiation from the Sun or electrical discharges, because thermal energies comprise only a small fraction of the total input of energy at the present-day Earth's surface. Volcanic activity is believed to have been more important in altering the surface features of the primitive Earth than it is now. However, energy contributions from other sources may have escalated in the same manner. It should be emphasized that thermal energy is the only source which contributes high temperatures at or near thermodynamic equilibrium on the surface of the Earth. The importance of volcanic thermal energies in organic compound synthesis was first suggested by Bullard (15). Harada and Fox (16) synthesized many natural amino acids by passing mixtures of
methane, ammonia and water vapor over lava at 1275°K using a flow type reactor. Thermal energies have also been shown to initiate the polycondensation of free amino acids into a proteinoid substance which exhibited many properties of natural protein (Harada and Fox, 17). Hydrogen cyanide is also produced in high yield from ammonia and methane over hot silica or alumina (Kotake, et al., 18). This HCN with other gases has been shown to form many interesting organic substances which are known to be important biological intermediates (Miller, 19; Fox, 20; Miller and Urey, 21; Fox, et al., 22). The dimer of HCN cyanocarbene has been postulated as an intermediate in the formation of proteins (Kliss and Mathews, 257).

B. Lava Degassing

We may examine the situations normally encountered in active volcanism and how these conditions might bear upon the formation of simple organic constituents to be released through degassing or the weathering of basaltic rocks. It is evident from volcano watching that the eruption of lava is accompanied by huge volumes of volatiles. The amount of gases released is strongly dependent upon the composition of the lava. While hot fluid magmas of the tholeiitic type release their gases slowly during eruption, the more viscous lower temperature magmas, typical of continental volcanoes, release their gases with great mechanical and thermal energies which may lead to very destructive explosions.

Volcanic gases, separate from fumarolic emissions, always contain water vapor as the major component. A recent report by Tazieff (23), however, indicates that the water content from some vents on Etna falls to very low values during the quiescent periods of vent activity. This
would suggest that water vapor is the principal volatile causing fountain activity in an erupting vent. There are many factors related to the variability of composition of volcanic and fumarolic gases in various parts of the world. White and Waring (24) have presented a comprehensive review and assessment of worldwide volcanic gas data. In general, the three most abundant volatiles are water, carbon dioxide and sulfur dioxide—all highly oxidized species. There are localities where hydrogen, carbon monoxide and hydrogen sulfide are prevalent, but this would reflect some peculiarity in the subterranean environment. Hydrocarbons heavier than methane have not been reported in high temperature samples. Methane is not common and a magmatic origin under present-day conditions is doubtful (Basharina, 25; Finlayson, 26). It can be shown for a Hawaiian type volcanic gas composition that the equilibrium concentration of methane for high temperature samples is far below the amount which can be measured with even the most sensitive analytical instrumentation. A special problem in the collection of gases which might contain reduced species, such as CH₄, is combustion in the presence of atmospheric oxygen. Equilibrium considerations of the combustion reaction indicate the low tolerance of reduced species toward oxygen. Some of these equilibria will be considered in the discussion of reactor contamination and its elimination in the experimental section.

Those environmental situations present in a volcanic system will now be discussed in relation to previous investigations concerning organic substances. Organic substances, including carbon, found in various forms in sedimentary and metamorphic terrains will be neglected since a biogenic origin is strongly supported.
In their natural setting volcanic gases are released from the melt and escape to the atmosphere in several ways. In the spectacular eruptions on the surface of the Earth, where lava is thrown into the atmosphere by the force of expanding gases, rapid cooling of lava and gases occurs to form tephra with a high glass content and a depleted gaseous phase which will have a high temperature quenched composition. Obviously gases emitted in this manner offer an unsatisfactory opportunity for study. The energy dissipated by the cooling lava causes thermally-induced turbulence above the eruption which aids in the mixing of the gases with the ambient atmosphere. Energy lost by the gases during cooling is radiated away.

In spite of the usually difficult task of approaching an eruption site with spectrographic equipment, several investigations have collected limited spectral information on the constituents of volcanic gas and fumes. In the last century Brigham, Emerson and Libbey (27) conducted modest spectral color investigations at Kilauea and concluded that the colors observed resembled H$_2$ flames in a Bunsen burner. Libbey claims to have seen emission bands in the red and the blue portions and a continuum over the yellow-orange-red section which contained a couple of absorption features. Verhoogen (28) identified emission lines for Na, K and N$_2$ in flaming gases at Nyamalagira volcano in Africa. Three other bands not assignable by Verhoogen were later identified as CuCl by Murata (29). Using a low dispersion Gaertner quartz prism spectrograph, Murata observed four strong emission bands of CuCl and Na in flames issuing from a vent during the 1960 flank eruption of Kilauea. A provisional identification for lines assigned to diatomic sulphur was also made. Sulphur is
common in volcanic areas but its deposition on cool surfaces is believed to belong to the reaction

\[ 2\text{H}_2\text{S} + \text{SO}_2 = 3\text{S} + 2\text{H}_2\text{O} \]

rather than condensation from the gaseous phase (Naughton, et al., 30; Heald, et al., 31). Delsemme (32) has also obtained spectroscopic CuCl data from Nyiragongo volcano in Africa.

The same spectrograph used by Murata was used in an attempt to record absorption spectra in drill holes in Makaopuhi lava lake in the summer of 1965. The lava lake holes, bored and maintained by the U.S.G.S. Volcano Observatory for mineralogical and physical measurements, extended into the molten lava. The spectrograph was oriented to accept light emanating from the melt at distances of approximately 5-8 meters in complete darkness. No absorption features were detected because the source intensity was so low that several exposures of up to three hours during the night produced only a weak continuum between about 750 and 550 nm on photographic plates. We had hoped to be able to investigate the green-blue portion of the spectrum, the most useful region for the study of molecular species. The quartz dispersion element which compresses the shorter wavelengths and low sensitivity photographic emulsions were contributing problems.

Using a portable infrared spectrophotometer Naughton, et al. (33) were able to measure the infrared absorption spectrum of gases emitted during lava fountaining in Halemaumau crater in 1968. Measurements in the 2.5-14.5 micron region were taken with \( \text{H}_2\text{O}, \) carbon dioxide
and sulphur dioxide being identified. Quantitative estimations at wavelengths of least overlap and interference permitted values of 95% H$_2$O, 4% CO$_2$ and 1% SO$_2$ to be calculated. The only information on unexpected compounds was a hint for CH$_4$ at 7.7 microns in a poor portion of the spectrum.

Recently Cruikshank, et al. (34) have identified H$_2$O emission bands at two wavelengths which were attributed to the combustion of H$_2$ with atmospheric O$_2$.

While the cooling of magmatic gases during surface eruption is akin to quenching in an oxygenated environment followed by extensive dispersion, the cooling of volatiles in isolated confinement, such as gas-formed pockets common in vesiculated basalts or confined gases trapped within separate mineral grains, offers protection against atmospheric intrusion. This permits slower cooling which would be favorable from the standpoint of achieving equilibrium at a temperature more favorable for organic synthesis. Roedder (35) found in his investigations of certain types of fluid inclusions that the predominant gas was CO$_2$. This fact led him to conclude that many magma bodies are saturated with it. He also showed that the contents of almost all of the inclusions lacked appreciable amounts of water. Since these inclusions were formed at depths between 8 and 16 kilometers within the magma column, the pressure dependent difference in the pH$_2$O/pCO$_2$, as compared to gases erupted on the surface, is attributed to extensive solubility of water in the liquid silicate mass. The field evidence by Moore (36), as well as the laboratory studies on the solubility of water in magma under pressure,
support the idea of magma being undersaturated with water at depth
greater than about one to two kilometers. A probable result of this line
of reasoning would predict that vesicles filled with magmatic gas, and
thermally sealed to prevent their escape, will have a composition nearly
devoid of water.

The equilibrium constant for the reaction

\[ C + CO_2 = 2CO \]

is about \( E+03 \) at 1400°K and \( E-09 \) at 500°K, with a constant of unity at
approximately 950°K. This thermodynamic consideration indicates favorable
conditions for the stability (and possibly the deposition) of carbon at
temperatures under 900°K, but only if water is absent. Water serves as
an oxidizing agent for carbon and could under widely varying conditions
prevent its stability. A small number of the cavities containing high
pressure \( CO_2 \) studied by Roedder (35) appear to have a pale dark film on
their inner walls which he suggested might be carbon that deposited from
the gas phase.

Based on the preceding studies these fluid inclusions may be a
reasonable environment for the stability of reduced organics if \( H_2 \), or an
extremely limited source of \( H_2O \), is available for chemical reactions
leading to their formation. Whether or not enough water to participate
in chemical reactions could exist in the mineral material making up the

*In order to be consistent with computer notation for exponential
numbers, all exponential numbers will be formatted as \( E+03 \) which should
be read as \( 10^{+03} \). When it is quantitatively important, numbers pre­
ceding the exponent will be used, e.g., \( 5.5E+03 \).
confining crystal is difficult to predict. On the other hand, if \( \text{H}_2 \) is a high pressure magmatic gas, its presence in a fluid inclusion would be expected. Roedder does mention that hydrogen is the most difficult gas to detect by the technique which he applied. Also \( \text{H}_2 \) would be subject to preferential diffusion though the solid silicates at a rate possibly hundreds of times greater than \( \text{CO}_2 \).

In the study of the Boudouard reaction

\[
2\text{CO} = \text{CO}_2 + \text{C}
\]

Ingles (37) showed that carbon deposited only to a small extent from a flowing \( \text{CO} \) stream at \( 1100^\circ \text{K} \) onto a pure carbon surface. The deposition rate was determined by analyzing the \( \text{CO}_2 \). The equilibrium constant for the reaction at this temperature is less than unity, which suggests equilibrium was not established in this study. It should follow that the deposition of carbon from a gas phase to a solid phase consisting of carbon ought to proceed easily because of surface nucleation effects, unless significant kinetic effects prevent this. If the deposition rate determined by Ingles is a realistic guide, the results of two runs in the present experimental study suggest that lava reacts with carbon monoxide more completely than does a carbon surface. This would further imply that the products of the reaction between lava and carbon monoxide are more stable than carbon itself.

Because opportunities to obtain gas samples in contact with molten magma are rare, sampling is most often conducted at nearby fumaroles. The significance of this data has been questioned by various investigators but it is usually agreed that these samples are better than none at all.
As the gases percolate to the surface extensive alteration of the rocks in their pathway occurs. These reactions will alter the gas composition by removing those constituents which are most reactive, viz., the sulphur and halogens containing volatiles (Iwasaki, et al., 38). Another factor influencing fumarole gas composition is the extent of meteoritic water input and the nature of its dissolved load. The geomorphology of the region will influence this feature as well as the degree of recycling of condensed water back into the subterranean plumbing.

The most frequently sampled site in the Kilauea complex is Sulphur Bank, which is believed to have a reasonably direct connection with the magma conduits beneath the mountain. Samples have been obtained here rather continuously in anticipation of the emergence of a long term relationship between the composition of the gases and the eruptive activity of Kilauea or its rift zones. The rocks through which these gases must pass are most probably altered to an extent where reaction with the gases is slowed to a rate controlled by diffusion through the layer of solid reaction product. Finlayson (26) has presented complete analytical data on twenty-six samples taken at this site over a 14 month interval. It is interesting that methane was not reported in any of these even though the possibility of ground water seepage carrying substances leached from vegetative decay seems likely. Some samples did contain substances detectable with a gas chromatographic flame detector. In general, the mass spectrometric fragmentation pattern showed the m/e spacing of 14 mass units typical of methylene scission, but the small amounts and recovery difficulties prevented the identification of the parent substances. Samples containing the unidentified organics without methane would
indicate that the organics entered the fumarole effluent at a temperature less than that required for pyrolysis to CH₄.

Recent observations of organics being degassed from fumaroles have been reported at Vulcano in the Lipari Islands (Chaigneau and Conrad, 39; Stoiber, et al., 40) and Santiaguito in Guatemala (40). Analyses of fumarolic gases reveal saturated, unsaturated and aromatic hydrocarbons through C₈*, alcohols, carbonyls as well as several halogenated organics. Stoiber, et al., (40) failed to note the temperature at Sapper Fumarole where the samples containing the organics were obtained, but a highest surface temperature of 640°K was reported in an earlier publication (Stoiber and Rose, 41). The proposed origin of these organics at Sapper Fumarole, Santiaguito is a soil layer at a depth of 200 meters which is being heated by its proximity to intruding magma. Strontium isotope determinations on the lava do not support extensive crustal contamination, however.

Lava tubes or tunnels are fairly characteristic features in the structure of volcanoes that erupt very hot and highly fluid basaltic lava. These tunnels form as a result of solid crust formation over flowing rivers of lava. These tunnels vary greatly in cross-sectional area and may extend for miles. When the source of magma is withdrawn, the tube will drain leaving a hollow shell. While the tube is transporting lava the gases which exsolve from the melt will escape through available openings to the surface. At times the physical setting permits access to one of these "ideal" sampling sites where samples not altered in composition by air contamination may be collected.

*This notation refers to the number of carbon atoms in the specie.
A factor influencing the composition would be an overall loss of volatile phase which would be related to its distance of lateral flow from the main source and turbulence in the erupting chamber. Whether or not the loss of volatile phase also includes differentiation has not been studied. It is improbable that the conditions and physical setting would exclude all atmospheric gas from entering any particular void once the source of lava was terminated and cooling started. The presence of oxygen in the present-day atmosphere would have a deleterious oxidative effect on reduced volcanic gases. In later sections, however, we will examine the composition of magmatic gases proposed for the primitive Earth. This setting is believed to have contained little, if any, free oxygen. Therefore the carbon-containing volcanic gases could have cooled under conditions which might have allowed some interesting substances to form.

Lava flowing into any depression from a nearby vent forms a body of molten lava which cools slowly with considerable degassing. The amount of volatiles initially present in the lava lake will be largely determined by the distance it flowed, the character of its route, the degree of eruptive turbulence in the source vent and, of course, the original volatile content.

The March, 1965 flank eruption within Makaopuhi crater filled the preexisting depression with 950 meters of lava at its greatest depth. A petrographic study was conducted by scientists at the Hawaiian Volcano Observatory which necessitated drilling holes through the solid crust into the melt in order to obtain specimens of the mushy lava at its liquidus temperature just below the crust. Concurrently a gas collection
program was initiated before the outpouring of lava had subsided and continued periodically during the following seventeen months using these drillholes as sampling sites (26). The results indicated that the degassing trends for this lava body would be difficult to establish. The trouble in part was caused by extensive vertical and probably horizontal contraction jointing in the crust, which produced easy routes of escape for those gases which might normally have diffused to the bore hole. These joint cracks also allowed air and water to permeate into the crust.

Having been inactive for many years, Makaopuhi pit crater had a vegetative cover prior to the eruption. As the lava crept up the walls, many trees ignited spontaneously and burned while others burned away at the base and toppled into the lava. Even though a significant proportion of the vegetation did burn away, much was buried to slowly decompose by pyrolysis to give methane and presumably carbon monoxide, although CO was not detected in lava lake emanations. In those samples containing methane its partial pressure was consistently many orders of magnitude greater than the amount predicted by equilibrium calculations (Heald, et al., 31). One is therefore led to conclude that the quantities of methane measured in drillhole samples represented a contaminated situation.

The remaining terrestrial environmental entity to be described as a possible place for the formation and stability of simple organic substances is the minute volatile phase contained within solid rock. The open structure of silicates offers an extensive volume to accommodate low molecular weight gases which may be either chemically bound or free to move within the matrix. These gases may be extracted from lava by low temperature comminution in a controlled atmosphere or by heating in a
pure gas stream or in a vacuum with suitable trapping. Crushing at low
temperature liberates predominantly those gases occluded in vesicles,
vugs and along grain boundaries, while heating to temperatures near its
liquidus will degas vesicles and those gases inside the matrix. Even
though rocks which are heated evolve hundreds of times the amount of gas
liberated by crushing, the analysis of this gas suffers from the drawback
that the gases may interact in the presence of the rock to make the re-
results difficult to interpret. The sample crushing technique has been
utilized quite extensively in conjunction with the analysis of gases in
lunar specimens and will be discussed in a later section.

The selection of a specimen for a gas evolution study must be done
cautiously since differences can be expected between similar samples as
well as portions of the same sample. The reasons are absorption of
minerals by volatiles, the fact that volatiles appear to be enriched in
those phases (residual liquids) which are last to crystallize, and con-
tamination. It has been noted recently that volcanic gases exhibit very
short term fluctuations in composition and this may be reflected in the gases
which become trapped in cooling ejected lava (Tazieff, 23).

Comprehensive large scale investigations of volcanic gases trapped
in rocks have been carried out by Shepherd (42) and Chamberlin (279).
They included many rock types in this study but singled out Hawaiian basalts
since gas phase data was available for comparison. In spite of his aware-
ness of probable gas-gas and gas-solid reactions at high temperatures,
Shepherd was able to conclude, "that the results of gases collected in
vacuum tubes in the flaming vents and those of gases released by heating
may be interchanged without difficulty. There is no more constancy in one than in the other. The residual gases of the lava are the same and as variable as the gases of the vacuum tubes."

Using laser melting to liberate the gases and omegatron mass spectrometry to analyze quantities of gas as small as a few standard nanoliters, Ernsberger (43) has reported on the measurement of gas contents in a single grain of rock. This advancement will offer distinct advantages for the study of localized gas concentrations.

C. Water and Carbon Contents of Volcanic Rocks

Before proceeding to the other geological environment of interest to this project, namely the Moon, we must evaluate the prevalence of water in terrestrial rocks and the information which is available on the content and chemical forms of carbon. Both water and carbon are crucially important in lunar sample studies because water is an important oxidizing agent and oxidation state along with temperature controls the chemical form of carbon.

Water is reported in almost all analyses of terrestrial rocks and lavas using the Penfield technique until constant weight at both 380° and at 1225°K is attained. The low temperature water, reported as $H_2O(-)$, is that portion absorbed on the surface and trapped in vesicles but able to escape through cracks. The high temperature water, released between 380° and 1225°K, is the fraction chemically bonded to the various silicates and oxide minerals in the matrix. This water has the ability to alter crystal chemistry and affect the mineralogy of a cooling lava.

Studies of water solubility in various rock melts were also underway as the relationships between crystallization in silicate melts and
oxygen fugacity were being established by Osborn (129). A basic criterion for water solubility in any rock melt at specified conditions of temperature and pressure is the thermodynamics of the introduction of water into the melt (water content \( a \) + steam = melt (water content \( b \)).

The studies by Adams and Williamson (149) and Goranson (89, 90) concluded that the uptake of water by a melt undersaturated in water is thermodynamically favorable. A melt of granitic composition can admit up to 10% water by weight without the appearance of an aqueous phase at 1175°C and 3000 bars confining pressure, corresponding to a depth in the Earth of 11 kilometers. In view of the importance of water in any consideration of the oxygen pressure, water solubility studies on basalts and andesites were investigated by Hamilton and Burnham (152, 153). They reported water solubilities for a Columbia River basalt and a Mt. Hood andesite at 1375°C and water pressures between one and six kilobars. The andesite, perhaps due to its higher silica content, was able to dissolve about 50% more water than the basalt. If the silica content is the most important factor controlling water solubility, then many oceanic lava types could be expected to incorporate even less water since their silica fraction is typically about 50%. A weakness in this study is that the total test pressure consisted only of water vapor and its dissociation products. It did not take into account other volatiles which may be expected to dissolve in proportions not readily predictable by theoretical considerations. Furthermore, a recurrent problem for high temperature mineralogists is the loss of hydrogen through the container walls (recall drillhole anomaly). This results in an oxidation of the melt and a probable disequilibrium between the water vapor and the melts. In the studies by Burnham and
Hamilton this problem was overcome through the addition of hydrogen to the argon used as the compressing fluid.

The solubility of water in a basalt and a granite was measured by Khitorov (154) at 1175° and 1275°K and about 3 kilobars. The basalt with 52.1% silica dissolved about 3.4% by weight while the granite with 72.6% silica solvated 6.7% H₂O. Measurements at 1275°K on these samples suggest that a common value of about 7.4% may be reached at a temperature higher than that. This value would be significant since it would be independent of the rather great differences in chemical composition.

Experimental water solubility data is lacking at low pressures but a reasonable extrapolation from high pressures to 1 atm passes through typical values of H₂O(+) in many types of surface erupted volcanic rocks lying in range of 0.3-0.8% H₂O(+) by weight. Extensive compilations of volcanic rock compositions including water have been reported by Macdonald (155), Macdonald and Katsura (156), Nockolds (157) and Manson (158).

The water content of 22 samples of basalt which erupted on the ocean bottom on the southeast rift zone of Kilauea volcano at depths between 0.5 and 5.0 kilometers showed a rather constant water content at 0.45 ± 0.15% by weight (Moore, 36). Experimental data on the solubility of water in basaltic melts suggest that these samples could dissolve up to 1.5% H₂O(+) by weight at 0.5 kilobar pressure. Variations in the diameter of vesicles, the volume percent of vesicles and the specific gravity all suggest that when the confining pressure decreased to the equivalent of 0.3-0.5 kilometers of liquid magma (density 2.0-2.2 grams/cm³) significant changes in composition occurred in the volatile phase. This compositional change is attributed by Moore (36) to the exsolution of water vapor.
the water content of a surface erupted basalt of the same bulk chemistry, he used 0.1% H₂O(+), a value several times smaller than the range noted earlier. This does not invalidate his conclusions, however. The physical changes in the submarine basalts appear to be more dependent on a reduction in confining pressure than on a preferential exsolution of water into the volatile phase.

While the H₂O(−) value is related to environmental contamination, H₂O(+) is highly significant since it has a definite effect on the melting relationships, the viscosity and the course of crystallization for that body of lava. It is now well known that water vapor under pressure lowers the melting point of rock-forming silicates in part because of its ability to disrupt extensive silicate bonding (Eitel, 159; Bottinga and Weill, 160).

A recent report comparing the melting of an anhydrous basalt and two systems containing basalts, one with water alone and the other with water and CO₂(50:50 mole percent), showed a large reduction in the liquidus temperature, i.e., 300° at 5 kilobars (Hill and Boettcher, 161). The difference between water alone and water and CO₂ was less dramatic but points out that CO₂ raises the liquidus temperature by more than 100° for all pressures up to 15 kilobars. This is attributed to the appreciable solubility of carbon dioxide in this silicate melt.

The question of carbon in volcanic rocks with respect to amounts, chemical forms and its effect upon the mineralogy or the oxygen fugacity is largely unanswered. There is sufficient data to establish an approximate value for the concentration of carbon in terrestrial volcanic rocks. Samples crushed in a controlled atmosphere will release only that carbon
which is in the form of gases trapped during crystallization and cooling (see section on gases in rocks). Samples powdered and combusted in an excess of oxygen will produce stoichiometric amounts of CO$_2$.

Craig (162) has reported 140 µg/g and 80 µg/g for two specimens of olivine basalt and 300 µg/g and 160 µg/g for two andesites from Hawaii. Andesite lavas are generally regarded as being a fractionated residuum and thus the somewhat higher values for them may not be representative of the original magma. Carbon contents of two less common types of oceanic lavas were not reported because they contained carbonate. The isotopic distribution of $^{12}$C and $^{13}$C in these samples did not conclusively determine the chemical form, but carbonate was probably excluded. The values for the rock specimens were bracketed by isotopic ratios for graphite and terrestrial organic material, which makes the decision about contamination unresolvable.

Hoefs (163) has presented the most extensive survey of carbon in rocks, however, no Hawaiian samples were analyzed. He reported six analyses on tholeiites with an average carbonate carbon content of 850 µg/g and an average elemental carbon value of 175 µg/g. He also included 23 analyses on alkaline basalts, classified as melilites, nephelinites and basanites. The average carbon as carbonate averages 1.86 mg/g, and 215 µg/g in the undefined elemental form. The anomalously high value for the fractionated basalts is in accord with the decision of Craig (162) not to report his values.

A Hawaiian basalt of unidentified type and origin containing 120-150 µg carbon/g rock was reported by Burlingame, et al., (164). It was used as a "standard" to calibrate carbon monoxide release from lunar fines by hydrogen fluoride attack.
Moore (165) has furnished some unpublished data on a scoriaceous basalt containing 220 μgC/g rock from the 1965 eruption in Makaopuhi Crater, Hawaii. He also reported 144, 72 and 170 μgC/g rock for tephra, and a bomb interior from the 1970 eruption of Hekla Volcano, Iceland and an altered basalt from the new volcano Surtsey, respectively.

Samples of submarine basalts collected and described by James Moore (36) were analyzed for total carbon and sulphur by the high temperature oxygen combustion techniques of Carleton Moore, et al., (91). These values will be included with the experimental results.

D. Highlights of Lunar Geochemistry

Being probably the most exhaustive environmental study in the history of science, the investigations on rocks and soils returned from the Moon by the Apollo teams have generated thousands of N.A.S.A. authorized reports and articles. There is much information from these studies which has a direct bearing upon this experimental project in chemical volcanology. This discussion will summarize the pertinent findings from the Apollo 11 Lunar Science Conference, the Apollo 12 Proceeding of the Second Lunar Science Conference and Apollo 14 and 15 Preliminary Proceedings of the Third Lunar Science Conference. The Apollo landing sites were: Apollo 11--Mare Tranquillitatis, Apollo 12--Oceanus Procellarum, Apollo 13 (aborted mission), Apollo 14--Fra Mauro and Apollo 15--Hadley Rille. Instinctively, one might assume that the first two landing sites might be similar since they were on the lunar "seas". Likewise, the last two sites were in the lunar highlands where orogenic processes were prominent at one time.
The lunar literature reviewed for this discussion falls into the following categories: (a) the oxidation state of iron and the mineralogy of the iron-titanium minerals, since they have been studied extensively and have been shown to be reliable indicators of oxygen partial pressures, (b) the occurrence of minerals not found in terrestrial volcanic rocks, (c) the evidence for indigenous water vapor, (d) the occurrence of indigenous carbon compounds and the role of the solar wind in their origin, and (e) the evidence for volcanic activity and vapor transport on the lunar surface.

1. Mineralogy

The crystalline rocks, which have typical igneous textures, range from very fine-grained vesicular rocks to vuggy, medium-grained holocrystalline specimens. The most common minerals are pyroxene, often with highly zoned rims, plagioclase, ilmenite, olivine and the cristobalite form of silica. Silicate minerals are usually clear, a result of the complete absence of hydrothermal alteration. Melting experiments indicate that 98% of the primary igneous liquid crystallized in the temperature range 1400° to 1325°K with the absolute liquidus at 1225°K. The crystalline rocks are generally regarded as the most valuable source of information since they cooled and "equilibrated" in the lunar magmatic environment. Their earthly counterparts would be the differentiated basalts in a batholithic or monolithic structure which has been exposed through erosion and perhaps also slow-cooled surface basalts such as those in lava lakes.

The returned lunar materials are categorized as being regolith core samples, crystalline rocks (holocrystalline or normal), breccias
and fines or soil. The soil is a diverse mixture of single crystals, crystalline agglomerates and glass, and commonly contains meteoritic fragments. The crystalline fragments are usually related to igneous rocks near the site, but fragments which appear to be totally different can also be found. These constituents are most likely clastic in nature and are referred to as the crytic or magic components. The fines are the result of impact processes and erosion and will, by virtue of their high surface areas, be most affected by extralunar forces, viz., ions streaming from the sun and other galactic sources.

Numerous analytical studies on Apollo 11 and 12 specimens by several methods show total iron contents ranging between 14-20%. The iron content on fines (Type D lunar material) is usually several percent less in the range of 10-15%. Those investigations which used analytical methods which resolve total iron into its ferrous and ferric states such as Mossbauer spectroscopy, a tedious volumetric technique and electron microscopy concluded that within the accuracy of the methods ferric iron was absent (Engel and Engel, 49; Maxwell, et al., 50; Wiik and Ojanpera, 51; Rose, Cuttitta, et al., 52, 74; and Scoon, 69; Smales, 70).

In wet chemical methods where the sample is solvated in acid, a quantity called the total reducing capacity, expressed as FeO, often exceeds the total iron. This excess is suggested as being due to trivalent titanium, metallic iron, or small quantities of lesser important elements in oxidation states lower than expected (Maxwell, et al., 50; Keil and Prinz, 53; Haggerty, et al., 54; Agrell, et al., 55; and Scoon, 69; Cuttitta, et al., 68).
Another possible explanation for the excess reducing capacity is that the element to oxygen stoichiometry is not an integer ratio. Ehrmann and Morgan (71) have made oxygen determinations and show that lunar materials have an apparent oxygen deficiency of approximately 1.6% compared to the assumed ratio.

Most analytical methods could not reveal the presence of metallic iron if it was present. The procedure must begin with a separation of mineral components and analyses by X-ray diffraction or electron micro-probe spectroscopy. Metallic iron is found in lunar materials but iron found in breccias and fines must be accompanied by analyses for nickel, cobalt and chromium to determine whether it is indigenous or of meteoritic origin. A so-called Ni-Co criterion (Ni > 4.5% and Co = 0.2-1.0%) established by Goldstein (44) assists in the decision to specify a meteoritic origin for the sample in question.

Iron metal in crystalline rocks is highly significant since it assists in defining the oxygen partial pressure of the rock mass when the iron-containing phase crystallized. Iron is most often found as intergrowths with troilite (FeS) and ilmenite (FeO·TiO₂) (Ware and Lowering, 56; Skinner, 57). Troilite is a mineral found on the Earth associated only with meteorite recoveries and serpentinized alteration products. The mineral assemblage free iron-troilite-ilmenite has often been observed in holocrystalline lunar rocks in petrographic relationships strongly suggesting equilibrium. Using phase data on the iron-titanium-oxygen system (Webster and Bright, 87) and the thermodynamic data of formation of FeS (Larimer, 88), Wellman (89) was able to compute the equilibrium oxygen fugacity and the partial pressure of diatomic sulphur.
gas at the temperature of exsolution for these minerals. He arrived at an $O_2$ fugacity of $4.0E-15$ atm and a $S_2$ fugacity of $2.5E-07$ atm at $1300^\circ$K. Complete equilibrium calculations for our proposed lunar chemical composition will be presented later and comments on Wellman's values will be made there.

Terrestrial basalts contain between 7-12% iron distributed amongst various mineral phases. It is the most abundant element with stable multivalent oxidation states. The geochemistry of these oxidation states in terrestrial basalts is substantially controlled by the omnipresence of magnetite and olivine. Stoichiometrically magnetite is $FeO\cdotFe_2O_3$ while olivine is a ferrous iron silicate in solid solution with magnesium silicate. The bulk chemical ferrous iron to ferric iron ratio is almost always greater than unity and in the oceanic basalts (Hawaiian type) the ratio is three to seven. This ratio appears to be related to the silica content (Muan, 86).

While magnetite is the most abundant iron-bearing mineral in terrestrial basalts, its discovery in lunar samples has been restricted to minute quantities for which special mechanisms have been suggested for its appearance (Jeddub, et al., 58). The failure to detect ferric iron, mentioned previously, also supports the absence of magnetite. It is a conclusion of Buddington and Lindsley (90) that a high titania content and low oxygen partial pressures can effectively prevent the exsolution of magnetite from a melt. Without magnetite the opaque phase minerals in lunar rocks favor high ilmenite contents, but ulvospinel and a heretofore unknown mineral called ferropsuedobrookite are common. The last two minerals apparently form a solid solution series (Keil, et al.,
The reasonably high chromium content of lunar basalts (about 0.5\%) have in some instances formed chrome spinels (Cameron, 60; El Goresy, 45).

In summary, the presence of troilite, native iron and the less oxidized end members ulvospinel, ilmenite and ferropsuedobrookite in their respective series all indicate oxygen fugacities much lower than in terrestrial volcanic systems. There are, however, a few observations of the oxidized species hematite and rutile (Haggerty, et al., 54; Vobecky, et al., 72) and phyllosilicates (Arrhenius, 61) but these appear to have been formed by special mechanisms such as being impacted by water-rich meteorites or irradiation by galactic protons.

2. Carbon geochemistry

With the present extent of knowledge about the lunar geochemistry of carbon there seems to be no gross differences among analyzed samples from the various landing sites and sampling locations. They are all equally difficult to understand. There are, however, very marked differences between both the contents and the chemical forms of carbon in lunar fines of uncertain or mixed origin and the rocks which are assumed to have crystallized from a melt on the Moon.

The analysis and distribution of carbon in lunar materials have been studied by (a) total combustion in an oxygenated high temperature environment, (b) low temperature techniques of sample comminution under controlled atmospheres and chemical attack by mineral acids, (c) pyrolysis studies at elevated temperatures and (d) liquid extraction by ultrapure solvents. Each of these techniques has its own special advantage for certain classes of compounds and disadvantages in the interpretation of results.
a. Combustion

The technique of high temperature combustion in an oxygenated atmosphere is designed to convert all forms of carbon into carbon dioxide (Moore and Lewis, 91). Heating the samples to near its liquidus temperature liberates indigenous trapped gases and oxidizes them with the aid of a combustion catalyst, while condensed forms of carbon such as carbides and graphite are oxidized in situ in the stream of flowing oxygen. The CO₂ thus produced can be analyzed by gas chromatography after suitable fractionation from oxygen. For extremely small amounts of carbon the range of the method may be extended by converting the carbon dioxide into methane to be measured by flame ionization detection.

In general, the bulk carbon content of soils, breccias and igneous rocks returned from the Moon ranges between 50-250 micrograms per gram. The highest concentrations occur in the fine-grained portion of the soil while the lowest concentrations are found in the igneous rocks (Moore, et al., 62; Maxwell, et al., 50; Kaplan and Smith, 63; Moore, et al., 73; Chang, et al., 68; Oro, 75; Moore, et al., 46, 84; Kaplan and Petrowski, 80). The fact that the bulk carbon content for lunar and for fresh terrestrial lavas is approximately the same will tend to simplify interpretations about the comparative geochemistry and permit a greater emphasis upon chemical forms.

b. Sample Crushing at Low Temperatures

This technique liberates only those gases which have
been trapped along grain boundaries and those gas-formed vesicles which are comminutated during the treatment. Two very serious disadvantages to this technique are the loss of volatiles during sample preparation and prolonged storage and the very low efficiencies. Despite the poor recoveries these results are important because they identify the chemical forms without the concern for gas-solid reactions that complicate extraction procedures at high temperatures. The most common species released from the samples are \( \text{H}_2, \text{N}_2, \text{CH}_4, \text{CO}_2, \text{CO}, \text{H}_2\text{S}\) and \( \text{SO}_2 \) all in ppb levels and variable in amounts, while the existence of indigenous vapor phase water is doubtful. Vacuum crushing of breccias releases hydrocarbons through propane in addition to those gases listed above (Funkhouser, 76; Gibson and Johnson, 77; Belsky and Kaplan, 92; Abell, et al., 78).

c. Pyrolysis

The technique of sample pyrolysis liberates those gases generally procured by low temperature crushing in addition to the gases from the very smallest vesicles which mechanical crushing cannot break open. Also any gases which can adsorb to mineral surfaces will be vaporized during heating. The volatiles may be trapped and fractionated for slug injection in the case of gas chromatography or monitored semi-continuously by mass spectrometry as the sample temperature is programmed either stepwise or directly to its liquidus temperature. Pyrolysis data may lead to complicated interpretations due to gas-gas reactions, possibly catalytic, and mineral decompositions--most notably carbonates.
Carbon dioxide evolution data between 625°K and 775°K may be due to carbonates (Gibson, et al., 77) or that contained in microvesicles. About the only evidence to differentiate this CO₂ is the pressure surges observed when microvesicles erupt.

The pyrolysis investigations have yielded a huge amount of data which has not as yet been unified into an acceptable pattern. Aside from the heterogeneous character of the specimens, experimental variables such as heating program (time at constant temperature and rate of heating) and the gas phase environment in the pyrolysis chamber (gas composition and degree of vacuum) all add their complexing influences. One important point which does seem consistent between studies is the ubiquitous nature of carbon monoxide (and to a lesser extent CO₂) at almost all temperatures. Gibson and Chang (265) have considered the high temperature reaction between carbides and silicates to produce CO, and presumably some CO₂, during pyrolysis of lunar samples.

A study designed to investigate the occurrence of high molecular weight organics in lunar materials by Preti, et al., (79) has offered evidence for species with molecular mass units near 100 amu, but their indigenous origin is doubtful. The presence of high molecular weight species would reduce the discrepancy between total carbon by combustion, which is assumed to be quantitative, and the sum of components already established as being present by other techniques. This group performed pyrolysis studies at both high vacuum and under one atmosphere of
helium. At high vacuum, evidence for the tropylium ion of toluene and also the benzene ion was obtained along with C₂ and C₄ heteroatomic species containing oxygen and nitrogen above 800°K. High vacuum heating of deep core specimens gave similar results. Samples heated to a similar temperature but under an atmosphere of helium produced entirely different—yet still positive results. They attributed the differences in the organic spectra to the pressure dependence on the mean free path of gases. At very low pressures species may migrate several meters before intermolecular collisions occur, while at higher pressures these distances approach molecular diameters. Preti, et al., feel that the CO and H₂ being evolved at high temperatures and high pressures are synthesizing certain gaseous hydrocarbon species. They tested their hypothesis by passing CO and H₂ at 1:1 and 1:1.9 w/w over previously pyrolyzed lunar material. Although the experimental details are not complete only traces of benzene were observed which does not lend much support to their theory since benzene is not a prominent species formed in the hydrogenation of CO (see later section on Fischer-Tropsch synthesis). A way this experimental data could support this hypothesis is if an extremely selective catalytic mechanism leading to aromatic hydrocarbons was operative.

d. Liquid Extraction

Another analytical approach often applied was either conventional or ultrasonically facilitated liquid extraction. Common solvents are water for polar compounds such as amino acids, sugars,
alcohols and organic acids, while benzene-methanol mixtures are frequently used for hydrocarbons. Many exotic organics, least expected to be present, such as sugars, fatty acid residues, nucleic acids, porphyrins, high molecular weight hydrocarbons, et cetera, were not observed. Amino acids, aliphatic and aromatic hydrocarbons were sometimes observed. The analyses of the lunar samples for amino acids or peptide residues exhibit some of the most sophisticated analytical methodology regarding the problems of contamination by the laboratory environment and the handling of apparatuses and samples. Amino acid contamination, extendable to organics in general, is now commonly measured in units of Hamiltonian fingerprints (Hamilton, 93).

e. Etching

References to the procedures called etching or hydrolysis by acids are similar in that the silicate matrix is destroyed to allow the indigenous gases to escape. Surface etching took on greater significance once it was shown that hydrocarbons are concentrated in the shallow layers of the rocks. This shallow deposition of hydrocarbons to C₃ and other gaseous species is currently thought to be due to solar wind (ion) bombardment followed by \textit{in situ} deactivation by chemical reactions with carbon and oxygen in the lunar surface material. In defense of the present experimental study the formation of simple hydrocarbons through gas-solid reactions during magmatic cooling cannot be disregarded. However, the fact that most of these lunar hydrocarbons appear localized
near surfaces exposed to the solar influx supports the solar wind hypothesis. Irradiation studies are presently being conducted to simulate solar wind conditions in order to establish a threshold energy and flux hypothesized species (Chang, 94). The thermal formation idea would necessitate a highly restrictive and selective mechanism to explain the surface localization effects.

Chemical attack during etching will also hydrolyze the surface carbides, if they are present, to form hydrocarbons (see next section). A way to discriminate between hydrocarbons from these two sources is by isotopic labelling of the acid, i.e., DCl or DF in D$_2$O. The deuterated hydrocarbons will have a carbide origin, while the others are indigenous and assumed inactive in isotope exchange reactions. The gases are separately chromatographically and analyzed by moderate resolution mass spectrometry to define the ratio.

3. Lunar Carbides

Perhaps the most important result of the investigations into the carbon compounds in Apollo 11 and 12 samples is the poor agreement between total carbon determined by combustion (assumed to be quantitative) and the sum of carbon as determined by the various techniques just discussed. In many cases relative recoveries ranging from 40% down to 5% were reported. This suggests a non-volatile form of carbon unstable under the conditions of combustion in O$_2$, but resistant to thermal treatment under reducing atmospheres such as those used in either vacuum degassing or pyrolysis studies. Metal carbides, graphite and certain carbonates meet these requirements to some degree. Using standard thermochemical reference
states, the free energies of combustion for graphite and titanium carbide are about \(-94.7 \) and \(-219.5 \) kcal/mole at 1400°K, respectively. The free energy for the formation of methane from graphite and H\(_2\) at 1400°K is +15.2 kcal/mole and might serve as a guide for the stability of reduced carbon under reducing conditions. In a poorly documented experiment (Johnson and Davis, 64) heated carbonates, graphite and the carbides of silicon and zirconium to 1075°-1175°K and observed no evidence of carbon-containing volatiles.

The formation and stability of carbides are of importance to the ferrous metallurgy industry because of their case-hardening properties in the annealing of tooling steel. Aside from their study in meteorites the role of carbides in the geological sciences remained only academic until our space program returned lunar specimens for analysis. Carbides are generally recognized as belonging in one of three groups: (a) the salt-like carbides, formed chiefly by the elements of groups I, II and III, (b) the interstitial carbides, formed by most transition metals especially those in groups IV, V and VI and a borderline group formed by a few transition metals with small atomic radii, namely Fe, Co, Ni, Cr and Mn, and (c) the covalent carbides (Cotton and Wilkinson, 95; Richardson, 96; Copenhaver and Bigelow, 97). Compounds of carbon with nonmetals are not called carbides since their electronegativities are higher than that of carbon.

Most carbides react with protonated solvents, generally dilute acids and water, to form hydrocarbons ranging between methane and solid paraffin waxes. The salt-like (NaCl structure) carbides containing the C\(^+\) anions generally hydrolyze to CH\(_4\) while those with C\(^2-\) favor the
formation of C\textsubscript{2} unsaturated hydrocarbons. The latter group is commonly called acetylides which are industrially important catalysts. Sears and Ferris (98) have studied the mono-, the di-, and the sesquicarbides of uranium and thorium and aluminum toward various hydrolytic agents under varying conditions of acid strength, acid type and temperature. The monocarbides seem to behave as the salt-like group, while the dicarbides and the non-stoichiometric sesquicarbides yield extremely complex mixtures of organic compounds.

The carbon-carbon bond distance in uranium monocarbide is about 3.50 Angstroms. With a carbon-carbon bond distance of 1.34 Angstroms in UC\textsubscript{2} and the observation that it yields mostly hydrocarbons containing two or multiples of two carbon atoms, Sears and Ferris (98, 99) concluded that crystal structure is an important factor. However, if crystal structure was the only factor governing hydrolysis products, UC would give only CH\textsubscript{4} and UC\textsubscript{2} would give only ethane (or ethylene). Since this is not the case polymerization must be occurring or there are crystal defect structures whereby some carbon atoms are closer than 3.50 Angstroms in UC. It is in the borderline interstitial subgroup where the carbon fits into a distorted structure and associates with itself rather than with the metals. It is these carbides which have a tendency to form high molecular weight waxes. The covalent carbides SiC, B\textsubscript{4}C and Be\textsubscript{2}C are important industrially for their hardness but are chemically inert.

The small amounts of carbides in lunar samples cannot be studied by optical or spectrographic methods and are always determined by their instability toward dilute mineral acids on mild heating for various lengths of time. Several investigators have pointed out some problems
which are likely to affect the carbide values of the total carbon reported in the lunar samples. Abell, et al., (78) showed that the hydrolysis of a known carbide cohenite, \((\text{Fe,Ni})_3\text{C}\), is an extremely low yield reaction under their conditions, i.e., the quantity of hydrocarbons produced by acid hydrolysis accounts for less than 1% of the total carbon present—CO and CO\(_2\) were not determined. This result would be dependent upon:

(a) Grain size and the surface area exposed to the acid.

When the carbides are contained within a silicate matrix, the crystallographic orientation of the grain also becomes important. It may be that as the hydrolysis proceeds, the hydrated metal-containing by-product renders the carbide surface more or less passive to further attack by the acid.

(b) Acid strength and temperature and exposure time to the acid.

The type of acid apparently has little influence since all common ones have been used.

The failure of Abell, et al., (78) to look for CO or CO\(_2\) might have been critical with respect to their stated low carbide carbon conversion to gaseous products. Chang, et al., (68) also did not find either of these carbon gases in the hydrolysis of lunar fines. CO\(_2\) was reported to have been produced by acid hydrolysis of both Apollo 11 and 12 lunar fines (Burlingame, et al., 164; Henderson, et al., 243; Oro, et al., 75). At least CO\(_2\) was observed in some of the hydrolyses on lava samples carburized in the present study.

It is possible through isotopic labelling to discriminate between indigenous hydrocarbons and those produced by carbide hydrolysis. Since CO and CO\(_2\) do not exhibit this type of exchange, one must be aware that
they are indigenous and trapped in vesicles which when destroyed through acid attack release their gases.

Based on carbon isotope data on hydrocarbons released by acid hydrolysis, there seems to be a difference between carbides found in lunar fines and carbides of known meteoritic origin. This suggests four possibilities: (a) the carbides in the fines were formed on the Moon but with a different isotopic ratio, (b) the carbides are of meteoritic origin and have through some mechanism become enriched in $^{13}$C, (c) the isotopic composition of meteoritic carbides differs and the fragments found in lunar fines is representative of not one but many meteorites, (d) the isotopic composition of the hydrocarbons released during the hydrolysis is not representative of the isotope ratio of the carbon in the carbide. Of these only the second one has received much attention. A process described by Berger (100) and Kaplan and Smith (63) called hydrogen stripping involves the preferential loss of the lighter isotopes of $^{12}$carbon and $^{32}$sulphur by bombardment with solar protons. This leads to an apparent enrichment of $^{13}$C and $^{34}$S through the loss of isotopically light methane and hydrogen sulphide (Sakai, et al., 264). As the light isotopes are being lost through this process, carbon and sulphur atoms of unknown isotopic composition are being implanted into the lunar soil and into the surface layer of the solid rocks by the solar wind. It is a tentative conclusion of Chang, et al., (94) that carbon atoms implanted by the solar wind into metal grains and inclusions could generate submicroscopic moieties having the stoichiometry of carbides. The necessary metal particles are available from both meteorites and lunar igneous rocks.

Irradiation of a number of targets including lunar fines with $^{13}$C+ and
\(D_2^+\) at energies similar to those in the solar wind showed upon acid hydrolysis evidence for carbide-like substances (Cadogan, et al., 47).

The solar wind hypothesis gains considerable support from the reasonably clear relationship between particle size (surface area) and the depth of penetration (attenuation of ions) and the solar wind influx. Aliquots of six different Apollo 12 fines showed widely variable total carbon contents. Three of them described as dark in color had high carbon contents and yielded high values for methane and ethane; the other three light-colored ones contained a small amount of methane as the only indigenous hydrocarbon. The same relationship between carbon content and apparent color is evident in all lunar fines analyzed to date (Moore, et al., 73, 46). It may be that the apparent color differences are not of chemical origin but may be due to the effect of particle size on light scattering. Furthermore, it is apparent that methane can be correlated with particle size. The amount of methane and \(\text{CD}_4\) released by DCl is directly proportional to the reciprocal of the mean grain radius for particles between 48 and 152 microns. For particles 152 microns to 2 mm the relationship is null, but there appears to be an additional source of both methane and carbide component associated with the microbreccias and glassy aggregates in the course fractions (Cadogan, et al., 47).

Oro, et al., (75) initiate a discussion on the possibility of hydrolysis of lunar carbides by terrestrially adsorbed water vapor. They reason that a DCl/D_2O treatment which fails to release deuterated hydrocarbons should not be interpreted to mean that carbides were absent at the time the specimen was collected on the Moon. They calculated that only \(0.25 \text{ cm}^3\) of air at \(298^\circ\text{K}\) and 75% relative humidity contains sufficient
water to hydrolyze an amount of carbide which yields on the average the amounts of methane and other hydrocarbons normally being reported. Hydrolysis by this means would be slow and complicated by factors such as the weakly acidic nature of water, surface polarization phenomena and the morphological arrangement of the carbide grains in the silicate matrix. The possible hydrolysis of lunar carbides by terrestrial water vapor has also gained support in experiments by Abell, et al., (78), but nonsupportive evidence on other samples has been collected by Flory, et al., (48). It should be noted, however, that the evidence for the formation and deposition of lunar carbides by solar wind implantation places them on the surface where contact with water vapor would occur easily.

4. Water on the Moon

Based on the analyses of returned lunar materials the amount of indigenous water vapor is a most difficult question. Many investigators have shown that the water content is below measurable amounts. However, it should be emphasized that those techniques utilizing conventional methods for water analysis in rocks such as the Penfield (gravimetric) are least likely to be meaningful at trace levels (Rose, et al., 52; Maxwell, 50; Wilk and Ojanpera, 51; Scoon, 69; Friedman, et al., 81). The technique of mass spectrometry is required for the very low levels of water generally reported (Funkhouser, et al., 76; Epstein and Taylor, 82). Gibson and Johnson (77) have summarized the subject of water in lunar rocks with respect to its formation by the solar wind and its strong tendency to escape from the lunar surface.

The rather uniform oxygen isotope ratios of separated mineral phases and the implied high temperature of equilibration (1400°K) have
been attributed to the amount of water vapor (Onuma, et al., 65; Friedman, et al., 66; Epstein and Taylor, 82; Clayton, et al., 83).

Terrestrial rocks have an isotopic equilibration temperature significantly lower than their solidus temperature. It has been hypothesized that the lack of water vapor in the lunar magmatic gas phase and the lunar cooling conditions were responsible for the minimal subsolidus oxygen isotope exchange.

Friedman, et al., (66) reported water contents in lunar breccias ranging from 130-455 ppm and in lunar fines up to 810 ppm. These values are many times greater than reported in later analyses and therefore lack credibility. However, extreme sample heterogeneity is a possible explanation. Other lunar anomalies can be noted. The fine-grained structure of lunar anorthosites may also be taken as evidence for a lack of volatiles rather than rapid cooling (Wood, et al., 67).

The very high seismic dissipation factor of the lunar regolith relative to the crust of the Earth is another kind of evidence for a lack of volatiles on the Moon. These values are derived from the damping of seismic signals as the pressure wave is attenuated by the solid material through which it passes (Sutton, 101).

Three of the experiments deployed in the Apollo lunar surface experiment packages (ALSEP) are the suprathermal ion detector experiment (SIDE), the cold cathode gage experiment (CCGE) and the passive seismic experiment (PSE). This experiment telemetered complementary sets of data back to Earth on the 6th and 7th of March, 1971 which offers possible explanations for flashes of light from the Moon and the hazy regions occasionally recorded in photographs from lunar orbiter missions (NASA
At sunrise on the 6th of March, 1971 the concentration of un-ionized gaseous particles increased two orders of magnitude within two minutes. Possibly as much as one-half of this may be attributed to lunar surface heating by solar radiation. But another event on the 8th of March from a higher starting value was also recorded. These two different "background levels" may be representative of nighttime and daytime lunar surface pressures. On the 7th of March (the second day of that lunar cycle) the SIDE package detected three series of bursts over a 12 hour period.

Mass and other properties indicated that the ion cloud was 99% water vapor. On the same day data from the PSE revealed that a swarm of moonquakes had started two hours prior to the detection of water vapor by SIDE. A similar series of events also occurred on the 19th and 20th of March, 1971, at the end of that lunar cycle. Venting from the lunar module and other discarded equipment can be ruled out on the basis of timing relative to sunrise and by the magnitude of the event.

Recently Mukherjee and Siscoe (103) have calculated that water in the liquid form can exist at depths greater than 100 km on the Moon. Emissions of pure water from depths that great, as suggested by the March 7th SIDE event, are unlikely. Averaged over all of the available data there is an almost zero correlation between seismic events and signals generated by either SIDE or CCGE (Duenebier, 104). There is, however, good correlation between the deep lunar quakes (600-900 km) and the tidal cycle on the Earth (Sutton, 101; Chapman, 261). Also fluctuations recorded by the CCGE correlate well with the onset of the lunar day or the lunar night which induces very shallow "moonquakes" (less than one meter
deep) through thermal expansion and contractions caused by the abrupt change in temperature. The daytime lunar surface pressure has been measured at $1.0 \times 10^{-10}$ torr, while during the night it drops about two orders of magnitude. The CCGE in this special situation is probably responding to solar wind derived species which are not captured by the surface, but which are given escape velocities sufficient for their release as the solar radiation heats the surface. Gibson and Johnson (77) state that the lunar escape velocity is 2.38 km/sec. At the lunar noon temperature of about $390^\circ$K any gaseous specie whose molecular weight is below 43 amu would escape from the Moon while those gases with higher molecular weights would be retained.

5. Lunar Volcanology

Volcanic activity has not been observed on the Moon, although evidence from localities such as Hadley Rille reveal lava flow structures in the regolith. Smith (105) has attempted to categorize small craters on the Moon into volcanic-explosion types and meteorite-impact types based on their depth to diameter ratios. Elston (106), Holcomb (107), DeHon (108) and Green (109) all interpret certain lunar features as being definitely of volcanic origin. The vesiculated basalts with their depleted gas contents is evidence that at one time a gas phase was present.

Gold (110) has presented an interesting theory concerning water on the Moon, one which is supported by some experimental evidence. He claims that radioactive heating within the body of the Moon would, as it probably did on Earth, create enough heat to degrade hydrated silicates and generate steam. The steam would percolate upward but not reach the surface, as it does on Earth, because the sub-surface temperature there
is well below the freezing point of water. Any water coming upward in cracks and fissures would thus tend to freeze and block its own route of escape. Therefore the Moon would contain, at some level beneath the surface, a layer of permafrost in which all the pores are filled with ice. He estimates that at a depth of 150 meters ice is indefinitely stable. The diurnal heating of the surface would not affect this depth. He further considers the result of a meteor impact penetrating deep enough to puncture the permafrost and release the liquid water trapped beneath it. The finale to his line of reasoning is an explanation for certain lunar surface features, namely those craters associated with a system of rilles.

E. Determination of Oxidation States in Natural Rock Melts

There are several methods which have been used to estimate the oxygen fugacity in volcanic systems.* One involves only the bulk chemistry of the iron oxides while another considers only certain iron-containing minerals in equilibrium with each other. The fugacity of oxygen as derived from the chemistry of the gas phase at equilibrium forms the basis of another. In the field measurements involve the least computations and are the most direct way of obtaining this data.

A requirement for the theoretical study of natural systems of rock melt and their associated volatile phase is the assumption that thermodynamic equilibrium has been established between the components of interest. It would be desirable to have the entire system in complete

*Fugacity, abbreviated \( f \), and partial pressure, abbreviated \( p \), of oxygen may be used interchangeably since at the very low values—less than \( \times 10^{-8} \) atm—the fugacity coefficient may safely be assumed unity. Some investigators prefer to use fugacity to denote the essential absence of a molecular oxygen phase.
equilibrium, but this can be achieved only under special natural and controlled laboratory conditions. Because of kinetic factors it is possible to study equilibrium relationships for components which are independent of other components suspected to be out of equilibrium. An example is the substitution of CaO for MgO in the alkalic suite of volcanic rocks while the carbon gases are in disequilibrium because the lava contacted a buried layer of soil. In the following discussions equilibrium in the melt will not be critical except in those cases where certain constituents clearly can influence the composition of the volatile phase.

Another requirement in the theoretical treatment is the assumption that the components in the rock melt and in the volatile phase, including the oxide and halide vapors of the gaseous phase, can be treated as an ideal mixture. A nonideal thermodynamic treatment of any system requires values of activity and fugacity coefficients which for the most part are unavailable.

The data obtained on the gas samples from Halemaumau are regarded as the best ever obtained and the most representative of juvenile magmatic gas. It is therefore understandable that many investigators have thoroughly evaluated this data for equilibrium relationships in the gas phase (Nordlie, 111; Ellis, 112; Jaggar, 113; Matsue, 114). These evaluations have revealed that these gases were in equilibrium at the temperature of their collection. If the volatile phase can be shown to approach equilibrium and the problems of gaseous diffusion and material transport in a highly viscous melt have been considered, the components of the condensed phase can be expected to be near equilibrium also. Low temperature fumarolic and hot spring gases must be considered with caution from an equilib-
rium viewpoint since certain compounds interact with rock surfaces and ground water during their escape and may be out of equilibrium with other components of the gaseous mixture.

1. Bulk Iron and Iron-Titanium Minerals as Oxygen Barometers

Iron is the most abundant transition metal in rocks and Kennedy (115) was first to recognize the utility of the oxidation states of iron as an indicator of the partial pressure of oxygen in equilibrium at the time of the crystallization of the iron-bearing minerals. In the rock melt--volatile system he applied the equilibrium

$$2\text{Fe}_2\text{O}_3 = 4\text{FeO} + \text{O}_2$$

and experimentally determined the equilibrium constant between 1475° and 1700°K. The constant was computed for a natural basalt by analytically determining the amounts of ferrous and ferric iron in the rock after the specimen had equilibrated with air. Applying water vapor dissociation data, Kennedy was able to relate the pressure of a known volcanic gas constituent to the ferrous--ferric iron equilibrium through the reaction

$$2\text{Fe}_2\text{O}_3 + 2\text{H}_2 = 4\text{FeO} + 2\text{H}_2\text{O}.$$  

By asserting that the volatile phase was predominantly water vapor at ten atm, he computed a partial pressure of hydrogen which was in fair agreement with data obtained on gas samples collected by Jaggar (113) at Halemaumau. The Hawaiian basalt studied by Kennedy contained 1.40% Fe$_2$O$_3$ and 9.90% FeO on an assumed bulk composition basis. Flood (116) has suggested that the reaction
may represent a better approximation to the real equilibrium involved. Several years later Kennedy (117) was able to suggest that the oxygen pressure may be an important parameter in the processes of differentiation of a magma into many rock types as exhibited in the Skaergaard intrusion. Basaltic fractionation is also evident on a limited scale in Hawaii where andesite–dacite lavas seem to characterize the late stages of eruptive activity on Mauna Kea and Haleakala.

Applying only the data on ferrous and ferric iron to determine the oxygen fugacity at the time of crystallization suffers the drawback that chemical analysis is performed on the whole rock specimen. This ignores solid phases which solidified under different environmental conditions and those which were never melted. Typical olivine with a melting point in excess of 1900°K is a noteworthy example. The oxygen fugacity acting on the melt can influence these olivine xenocrysts only to the extent permitted by solid state diffusion at the erupting temperature. The extensive zoning of olivines in alkali olivine basalts indicates that these crystalline phases have reacted with the melt and were not in equilibrium at eruption (Johnston, 118; Wilkinson, 119; Richter and Moore, 120; Albarede and Bottinga, 121).

The question of the derivation of magmas with widely varying chemical and mineralogical compositions had been argued by many investigators before the laboratory procedures for the study of high temperature melts were developed (Fenner, 122; Wager and Deer, 123; Waters, 124; Tilley, 125; Bower, 126). Muan and Osborn (86, 127, 128, 129) at the College of
Mineralogical Industries at Pennsylvania State University have made significant progress on systems which approach natural magmas in composition. The oxygen partial pressure has been shown by them to be important in controlling the mineralogical composition of a cooling rock melt.

Much of the preliminary information about the chemistry of condensed phases in liquid melt systems is a direct outgrowth of investigations in the metallurgical sciences. Phase equilibrium studies on silicate systems containing iron are complicated since iron exhibits a degree of trivalency which depends on the oxygen partial pressure and the temperature. The system Fe-FeO-Fe$_2$O$_3$ at various temperatures and oxygen pressures was studied by Darken and Gurry (130, 131). Bowen and Schairer (132) applied the high temperature quench technique to melts in the FeO-Fe$_2$O$_3$-SiO$_2$ system.

Melts may be studied at partial pressures of oxygen ranging between 0.21 and 0.001 atm by using air and the proper amount of oxygen-free inert gas. Partial pressures of O$_2$ lower than 0.001 atm must be achieved indirectly using gases which dissociate to yield oxygen in amounts defined by the thermodynamics of the reaction. Since the dissociation constants for CO$_2$ and H$_2$O are of the proper magnitude and reliably known, these gases are usually used. CO$_2$ and H$_2$ react with each other to form CO and H$_2$O according to the water gas reaction

$$\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2.$$  

The ratio of either pCO$_2$/pCO or pH$_2$O/pH$_2$ can define the oxygen partial pressure at a given temperature by the following reactions
\[ H_2O = H_2 + 1/2O_2 \]
\[ p_{O_2} = (pH_2O)^2(K \text{ dissociation})^2 / (pH_2)^2 \]

and

\[ CO_2 = CO + 1/2O_2 \]
\[ p_{O_2} = (pCO_2)^2(K \text{ dissociation})^2 / (pCO)^2. \]

The selection of gases to study equilibrium phase relationships in a melt system must be made consistent with the limitations imposed by the phase rule. For instance, if CO\textsubscript{2} or H\textsubscript{2}O is used alone at constant pressure in the Fe-0 system, the partial pressure of O\textsubscript{2} is univariant with temperature. If some H\textsubscript{2} is added to the water vapor or some CO to the CO\textsubscript{2}, the pressure of oxygen becomes a divariant function of temperature and the mixing ratio water/hydrogen or carbon dioxide/carbon monoxide. By then varying the mixing ratios Muan (86, 127, 128) was able to define the phase relationships in the iron-iron oxide system encompassing all three oxidation states. Bulgakova and Zaitsev (133) have verified data points along the Fe0-Fe\textsubscript{3}O\textsubscript{4} phase boundary in terms of the water dissociation equilibrium.

Figures 1 and 2 show the phase relationships between metallic iron and the iron oxides in their solid and liquid states as functions of both temperature and the partial pressure of oxygen indicated by either the ratio of pH\textsubscript{2}O/pH\textsubscript{2} or pCO\textsubscript{2}/pCO.
Figures 1 and 2. Stability Regions for the Iron Oxides in the Iron--Oxygen System as a Function of Temperature and the Ratios of Carbon Dioxide (CO$_2$) to Carbon Monoxide (CO) and water to Hydrogen (H$_2$) at 1.0 Atmosphere Total Pressure. Superimposed on both phase diagrams are the oxygen isobars which relate to the ratio of gases involved in the dissociation at the indicated temperature. The long dash--short dash line labelled (H$_2$O) in Figure 1 is the equilibrium dissociation curve for pure water. At temperatures above 1375°K magnetite is the stable phase in equilibrium with water, while temperatures below that favor hematite.

The long dash--double short dash labelled graphite in Figure 2 represents the boundary of the stability field for graphite by the reaction

$$2\text{CO} = \text{CO}_2 + \text{C(graphite)}.$$  

The heavy line drawn on both Figures 1 and 2 and extending almost vertically through the magnetite stability field represents the oxygen fugacity--temperature relationship for the quartz--fayalite--magnetite buffer system to be defined in the next section.
There are two fundamentally different courses of crystallization of magmas. The details of the fractionation mechanisms in two identical melts allowed to cool under these differing constraints can be found in Osborn (129). In summary, the two pathways result in a substantially different array of mineral phases, one scheme favoring the formation of a magnetite phase, whereas the other predicts its absence. Aside from the presence or absence of magnetite the most notable difference between the two pathways concerns the mass of the volatile phase which either contributes oxygen-donating species from the surroundings, or which is operative only within the mass of magma with no exchange with the surroundings. Presnall (134) introduced the term "buffered" to describe the effect of a volatile phase, whatever its origin, on a crystallizing melt. The variations in the courses of crystallization, depending upon the source of the volatile phase, have been labelled as internal or external buffering, respectively (Carmichael and Nicholls, 135, 136).

It can be estimated for hot, fluid Hawaiian lavas that the mass of the iron-bearing condensed phase is 500-1000 times the mass of the gas phase. It should be pointed out that if at any time during the fractionation a volatile phase of sufficient magnitude becomes available to the melt the crystallization course may be altered. A slow cooling plutonic rock mass could exhibit this fractionation pathway alteration since the volatiles exsolved in one part may influence the oxygen reservoir in a different portion.

The information contained in Figures 1 and 2 must be used with caution in reference to natural magmatic melts for the following reasons. First, it is only reliable for the Fe-O system and does not include other
major components such as silica, magnesia, alumina and lime. In the Fe-O system the addition of silica below the point of saturation causes the \( \text{Fe}_2\text{O}_3/\text{FeO} \) ratio in the melt to decrease, but with no large increase in the liquidus temperature (Muan, 86). As the silica saturation content is approached and exceeded the increase in the liquidus temperature further magnifies the decrease in \( \text{Fe}_2\text{O}_3/\text{FeO} \). The addition of either \( \text{Al}_2\text{O}_3 \) or \( \text{MgO} \) has a slight neutralizing effect on the acidic \( \text{SiO}_2 \) but at the same time causes an increase in the liquidus temperature since these oxides also interact with the melt to increase its viscosity and melting point.

A released disadvantage in the use of planar phase diagrams, such as Figures 1 and 2, is the influence of added components upon phase boundaries. It is possible to lessen this problem if the diagram represents mineral assemblages instead of component oxides. In their classic paper on the origin of basalt magmas Yoder and Tilley (137) were able to represent all mineral assemblages present in the alkali, olivine tholeiite and tholeiite group on a regular tetrahedron. The obvious drawback here is that one does not know the composition of a mineral used to establish the diagram. Roeder and Osborn (138) have used an anorthite saturation diagram to depict the course of crystallization with tetrahedral diagrams even though six component oxides were involved. A second drawback to the use of such a simplified diagram is that it does not take into account the other components of the volatile phase, such as sulphur gases and the halogens.

From the developments in the \( \text{FeO-Fe}_2\text{O}_3-\text{MgO-SiO}_2 \) system and other systems containing components of basaltic rocks, the equilibrium rela-
tionships between the iron-bearing phases and their effect upon the composition has become evident. In their experimental work on annite, a ferrous iron biotite, Eugster and Wones (139) developed the basis for an important approach to understanding these complex systems. Drawing extensively from previous phase studies involving iron constituents they developed a series of temperature dependent oxygen buffer combinations which thermodynamically will control the oxygen partial pressures over an extremely wide range. These buffer pairs range between quartz-iron-fayalite for low oxygen pressures to the magnetite-hematite buffer at high oxygen requirements. They concluded that the buffer system which gave the best fit to a basaltic composition and its associated gas phase was the quartz-fayalite-magnetite assemblage (hereafter QFM). The values used to establish the QFM line in Figures 1 and 2 were interpolated from graphical plots covering two different parts of the temperature span (Carmichael and Nicholls, 135; French and Eugster, 140). A list of the numerical values may be found in the Appendix. It should be cautioned that while these high temperature values are based on mineralogical data at equilibrium, the values below about 1200°K are subject to errors of unknown magnitude because of oversimplified thermodynamic assumptions (Eugster and Wones, 139; Richardson and Jeffes, 141).

Fudali (142) extended the iron oxidation state concept by experimentally defining the oxygen fugacity at the time of crystallization. He reasoned that a rock melted in a gaseous environment will change its \( \text{Fe}_2\text{O}_3/\text{FeO} \) ratio unless the oxygen fugacity under natural conditions and under laboratory conditions coincided. He chose nine andesites and basalts from Hawaii, the Columbia River plateau and the
Cascade province. These specimens retained a ferrous/ferric iron ratio indicating oxygen fugacities between $E-9.0$ and $E-6.5$ atm at $1475^\circ K$.

His limited sampling prevented a broad interpretation on the subject of magmatic differentiation.

Perhaps the most elaborate mineralogical approach to the determination of temperature of formation and oxygen fugacity is by Buddington and Lindsley (90). In the system FeO-Fe$_2$O$_3$-TiO$_2$ they have shown that the composition of coexisting magnetite-ulvospinel and hematite-ilmenite pairs in equilibrium are both oxygen pressure and temperature dependent. Although examples in nature do support the existence of solid solutions between magnetite and ilmenite and between hematite and ulvospinel, they do not provide proof of their general occurrence. Therefore a basic prerequisite of this approach must incorporate the assumption of the formation of these solid solutions at high temperatures. The technique is applicable only for compositions typical of plutonic rock masses. The accuracy of the temperature estimation is $30^\circ$ and one order of magnitude for the oxygen fugacity. Since fresh tholeiitic lavas do not contain hematite, lavas of a Hawaiian composition can be treated only if the useful limits of the concept are exceeded. From this data a Hawaiian basalt may be expected to yield an oxygen fugacity of $E-10.5$ atm at $1300^\circ K$.

2. Computational Methods Based on Gas Analyses

The second method of understanding equilibrium in the gaseous components of volcanic systems is the technique developed by Heald and others (31, 143, 144) at the University of Hawaii. It is completely independent of equilibria in the condensed phase, although it has been
shown that the methods are complementary (Carmichael and Nicholls, 135) (see Figure 3). This computer assisted technique is identical to the one described later in this report and only important applications to the chemistry of a volcanic gas phase will be mentioned here. Beside the necessary thermodynamic functions at the temperature of interest, the only input required is an account of the mass balance (elemental abundance) for the number of gram-atoms for each element to be included. These values should be selected judiciously in order to avoid over-emphasizing the contribution of an element in its equilibrium distribution. They chose the gram-atomic values based on samples thought to be representative of the gases being emitted under the conditions prevailing at the time of sample collection. In this manner the variability in molecular composition between many samples may be neglected.

The potential of water vapor to control the composition was demonstrated. High partial pressures of water, common in the majority of volcanic gas samples, favor the oxidized species, while low pressures of water and higher partial pressures of reduced species are compatible. A most important feature of this technique is that one may compare the calculated and the actual composition in order to examine the degree of attainment of equilibrium. This provides some evidence about sources of contamination for the gases as they are collected in the field. One can also learn about the rate of attainment of equilibrium since the calculated and actual composition may agree but at widely different temperatures.

In an attempt to define the conditions which might exist in the fugitive gas phase in equilibrium with a plutonic body of magma
Krauskopf (145) calculated the composition and concentrations for heavy metal containing species. This application to the genesis of ore bodies limited his choice of volatiles to the sulphides, the halides and the oxides of those metals found in igneous rock masses. He presented the maximum and the minimum concentrations to be expected depending upon whether the equilibrium conditions were oxidizing or reducing. The mass balance relationship used for the composition was based on the results of magmatic gas analyses by Shepherd (42).

3. Direct Measurements

The third method of determining the oxygen fugacity is the direct measurement in situ either in a stream of magmatic gas or in a crystallizing melt by the technique developed by Sato and Wright (146). The device is a solid-state electrochemical cell employing a Ni-NiO reference and a zirconia-lime (85:15) electrolyte and a platinum sensor. This cell operates reversibly at temperatures above 875°K and at pressures of oxygen greater than E-22 atm. Prolonged high temperature operation in high oxygen environments, however, destroys the reference half-cell through oxidation of the finely divided nickel powder. It is portable and requires only a potentiometer and a thermocouple for its field operation.

As part of an on-going program in the 1960s to study petrogenesis in newly erupted masses of lava, crews from the Hawaiian Volcano Observatory, a U.S. Geological Survey facility, bored holes through the crusts of cooling bodies of lava in order to obtain core samples of basalt in the crust and samples of the mushy lava beneath the crust. Drilling equipment and procedures are described by Richter and Moore (120). These drill holes were reasonably convenient sites for gas phase collections
and sublimate sampling. Using the equipment described above oxygen fugacity measurements and thermometric data was collected by Sato and Wright (146) in order to plot the oxygen profile and calculate the heat flow from the mass of lava which filled Makaopuhi Crater. About 50 measurements were taken in eight drill holes in this lava lake. With one exception the logarithm of the oxygen fugacity decreased almost linearly with a decreased temperature. The $f_{O_2}$--temperature function for this data fell within the magnetite stability field as defined by Muan (86), and at high temperatures was in excellent agreement with the QFM predicted value. This report appears to be the only instance where this oxygen probe was used in the field. It is believed to be buried in the new lava filling Alae Crater at this time.

The exception to the well-behaved plot of log $f_{O_2}$ versus temperature appeared in only one drill hole. At $1050^\circ K$ the oxygen fugacity turned sharply upward and increased from $E-14$ to almost $E-05$ atm. After several high values the function plunged back to $E-21$ atm at about $825^\circ K$, the lower limit of cell stability and reversibility. The core samples removed from this anomalous hole showed reddening due to the appearance of hematite and an increased magnetic susceptibility probably due to paramagnetic ferric iron. Downward diffusion of atmospheric oxygen is a possibility but the return of the function to its extrapolated "normal" value of $E-21$ atm cannot be held in support of this. Furthermore, if atmospheric $O_2$ diffusion through the solid crust was occurring it would be expected to affect the data from all holes. The tentative explanation offered is that crystalline basalt between $1050^\circ$ and $825^\circ K$ behaves as a semi-permeable membrane for the preferential diffusion of
hydrogen. Diffusion measurements for He and H$_2$ in fused silica and various crystalline substances by Norton (147) suggest the ease by which H$_2$ may escape across a pressure gradient. High vacuum mass spectrometers are usually operated in a dynamic mode since the diffusion of atmospheric H$_2$ and He will cause significant pressure elevations if the system is isolated.

Finlayson (26) has shown the extreme difficulty in obtaining drillhole gas samples free of atmospheric constituents. Even though the sample tubes were sealed after being withdrawn from the hole, it appeared that air was indeed penetrating deeply into the holes. He suggested the sinking of cool dense air along the wall of the bore hole to a depth where its density becomes the same as the gases being evolved by the cooling lava. A simple estimation employing the ratio of the density of air to the density of lava lake gases at any temperature shows that air intrusion is extensive, especially in those holes with low gas velocities.

The petrology of the cool tholeiite lava in Alae lava lake (1963 eruption) suggested that oxidation with maximum intensity between 825° and 885°K moved downward during its cooling history. This was followed by a low temperature reducing period (Peck, et al., 148).

In summary, each of the four methods commonly utilized to obtain the O$_2$ fugacity of a rock melt, namely, the ferrous-ferric iron chemistry of the bulk sample, the iron-titanium coexisting mineralogy, equilibrium calculations on the gas phase and in situ fO$_2$ measurements offers certain advantages to the investigator for certain samples and situations. Figure 3 summarizes the high temperature agreement between the various methods of obtaining oxygen fugacity determinations.
Figure 3. Oxygen Fugacities (as $-\log f_O^2$) Plotted Against Temperature in Degrees Centigrade.

The solid curves labelled HM and FMQ (sic) are the hematite-magnetite and the quartz-fayalite-magnetite buffers (Eugster and Wones, 139). The dashed curve shows the calculated equilibrium oxygen fugacity of analyzed volcanic gas (Heald, et al., 31). P refers to the measured oxygen fugacity in the Alae lava lake at 1065°C (Peck and Wright, 148). The range of oxygen fugacities obtained by Fudali (142) at 1200°C is represented by two connected open circles and labelled F. The remaining notation in this figure is relatively unimportant to this study, but its description may be found in Carmichael and Nicholls (135) from which the figure was taken.
II. EXPERIMENTAL DESIGN AND EXPERIMENTAL PROCEDURE

This research was undertaken to study the environmental conditions favorable for the formation of minor amounts of carbonaceous substances from gases which have geological significance in volcanic systems on Earth or on the Moon. The environmental conditions considered were temperatures up to 1400°K, partial pressures of component gases and the oxidation state of the system which will be reflected in the composition of gases and the surface chemistry of the lava which was present to simulate the condensed phase in a volcanic system.

A. Laboratory Studies

The experimental phase of this study consisted of (a) performing gas phase-lava investigations in the laboratory, (b) submitting lava samples for carbon and sulphur analyses, (c) calculating thermodynamic equilibrium concentrations for various compositions of geological significance.

Data was collected on two series of experimental runs referred to as steam and anhydrous. Experiments in the steam series are those in which liquid water was boiling in the round-bottomed flask to produce a high partial pressure of water vapor inside the furnace and in contact with the lava (see Figure 4). These steam experiments were performed to study the possibility of organic synthesis under conditions of terrestrial volcanism where water vapor is the major component. Partially oxidized substances, namely, formaldehyde, methanol and formic acid, were expected to solvate in the aqueous phase and remain there until the analysis was performed for them. The partial pressure of any of these polar, oxygen-
ated organics above an aqueous solution containing traces of them was not expected to be high enough to detect their gas phase contribution in the gas samples. For this reason primary consideration was given to hydrocarbons in the volatile phase.

All experiments performed in conjunction with this project are numbered sequentially and are preceded by the letter E. Experiments to study reactor operating parameters and sample loop calibrations are designated by I. Many runs with designations earlier than E-25 have little bearing on the final conclusions. They were principally exploratory. A record of reactor parameters (furnace temperature and pressures), sampling notes (time and date), and chromatographic details (column and oven temperatures) was kept on all experiments. All necessary information concerning the chromatographic readout (range attenuation, recorder sensitivity and sample numbers) was noted directly on the strip chart record.*

1. Reactor Design

The first reactor design resembled, in principle, the closed apparatus described by Harada and Fox (16). Besides being fragile and difficult to repair in place, it suffered from a serious drawback. The gases were drawn by the pumping action of the venturi through a water-cooled condensor prior to their entry into the reaction zone (furnace). Assuming complete condensation this feature reduced the water vapor pressure to its value at the temperature of the wall of the condensor--

*A terse summary of experimental details for all experiments which resulted in significant data may be found in the Appendix.
a value approximately 30-40 torr. Since the reactions of concern were to be related to volcanism, partial pressures of water vapor this low were unrealistic. Hence, the new reactor design positioned the condenser at the exit of the furnace and allowed steam along with other gases to be injected directly into the furnace (see Figure 4). It will be shown in a later section that the oxidizing potential of the high partial pressures of steam suppressed the formation of hydrocarbons.

The only experimental results to be reported here on an experiment conducted in the first reactor design will indicate a probable relationship between the lower partial pressure of water vapor and the formation of hydrocarbons in gas phase-lava reactions. At the time the reactor design was being altered this relationship was not apparent.

Within the limits of reasonable construction restraints and availability of suitable materials the reactor was designed to resemble the flow of gases over hot surfaces in volcanic activity. A most important consideration was always that the gases remain in contact with the hot surfaces of the lava for long periods of time or come in contact with it many times during an experiment. This repetitive contact of gases and hot lava (or the hot walls of the furnace tube) would insure that an equilibrium composition was at least approximated when the experiment was terminated. This was important since it is recognized that volcanic gases and volatiles and the molten lava are in a close approximation to thermodynamic equilibrium on eruption.

Results of experiments conducted in flow-type or one-pass reactors must always be examined critically in regard to equilibrium since the partially reacted hot gases will, on being pushed from the reaction
zone, have a tendency to quench and preserve their composition. Unless these gases remained in the hot reaction zone long enough to achieve equilibrium, their analysis will reveal only partial equilibration. At the outset, it was suspected that any organics which were to form as a result of the experimental work would do so at low concentrations. Because of the extreme sensitivity of the flame detector it was readily apparent that background contamination was to be the most annoying problem to overcome. Because of its importance a thorough discussion of the sources and elimination of contaminants will be made in a separate section.

The reactor had to be built from materials which could not contribute organics to the gas phase or involve substances, i.e., polymers or greases, which would pyrolyze in the furnace of the reactor. The final design excluded ground glass joints, greased stopcocks and plastic tubing. The furnace tube and the holder for the bits of lava which comprised the heated reaction zone were made of quartz which could withstand the high temperatures under vacuum and which subsequently showed only minimal reactivity. All other parts of the reactor were made of Pyrex glass. The sampling loop (see description later) and the gas chromatograph were joined with tubing made of copper and a non-ferrous alloyed material.

2. Reactor Operation

The steam produced by the boiling water escapes through the venturi jet and the constricted channel into the lower portion of the furnace tube (see Figure 4). The obstruction caused by the liquid water in condensate trap 2 prevents steam from bypassing the venturi and the varying heights of the water.
Figure 4. The Laboratory Reactor (The Final Design).
Figure 5. The Inlet Manifold and the Vacuum System Associated with the Laboratory Reactor

See pages 68-69 for a description of the function of the traps (T) and the Teflon valves (V).
The Function of the Valves (V) and the Traps (T) in the inlet

T1 Unpacked trap cooled with dry ice to minimize backstreaming of oil vapors from the pump.

T2 Trap packed with 8 mesh molecular sieve 5A and used uncooled to further reduce oil vapor contamination.

T3 Trap packed with 8 mesh molecular sieve 5A and used to purify cylinder gases before their introduction into the reactor. Either liquid nitrogen or dry ice–acetone slush was used depending upon the boiling point of the gas being introduced. Both T2 and T3 were frequently heated with a torch under vacuum to desorb previously introduced gases and impurities.

T4 Trap packed with 8 mesh molecular sieve and used uncooled to reduce oil vapor contamination.

T5 Unpacked trap cooled with liquid nitrogen to protect the sampling loop (and reactor) from contamination.

"A" Vacuum system–sampling loop connection with Teflon sleeve.

"B" Vacuum system–reactor connection by glass tubing.

V1 Isolates the cylinder gases from inlet section and was closed when T2 and T3 required evacuation and conditioning.

V2 Isolates the rotary oil pump from the inlet section and was closed when gases are being prepared for reactor introduction. This is the only greased stopcock in system.

V3 No specific application.

V4 Isolates inlet section from room atmosphere and opened during purging of the inlet with purified gas just prior to introducing gases to the manometer section of the inlet. When carbon monoxide was in the inlet, this atmospheric vent was purged with room air with a water aspirator to prevent the escape of CO.

V5 Used in conjunction with each other to permit small quantities of gas to be introduced into the manometer section. The volume of the manometer section and the volume of the reactor were measured by pressure differences.

V7 Used to expand versatility in controlling the pressure in the manometer section during the course of an experiment.
V8 Isolates the manometer--but usually remained open. A wad of gold foil was inserted between glass wool plugs in the valve to minimize the introduction of mercury vapor into the reactor. A long term color change from gold to silver indicated an amalgamation reaction had occurred.

V9 Isolates the inlet section from the reactor at "B". During an experiment it remained closed and was opened only to observe a pressure and then closed again.

All valves described here (excluding V2) and those used in the reactor sampling loop assembly are Lab-Crest quick opening variety made of a glass body, Teflon plug and one Viton O-ring.
columns give an indication of the pressure differential across the venturi. This pressure difference has an aspirating effect upon the noncondensable gases in the reactor and forces them along with the steam into and across the bits of lava which are contained in a shallow quartz canoe-styled insert. It is within these bits of hot lava where the reactions of interest between the gases occurs. Having been heated in the furnace the gases are pushed out of the furnace into the upper portion by the venturi pump. Uneven heating within the furnace gave rise to a significant thermal gradient along the furnace tube and thus along the lava-containing boat. To evaluate this situation a temperature profile was recorded at four points within the furnace with a calibrated thermocouple. The water-cooled condenser removes the majority of the steam and the resulting water trickles through condensate trap 1 (see Figure 4) and into condensate trap 2 and eventually back into the boiler which is at a temperature of about 350°K depending upon the reactor pressure. During proper operation there is evidence through the heating of sections of the apparatus that the gases are circulating.

a. Sampling

The uncondensed volatile phase flows through the sampling loop in order to bypass the liquid water obstruction in condensate trap 1. The sampling loop wrapped in asbestos and nichrome wire is heated to about 352°K with a variable a.c. voltage so that droplets of water do not foul the flow path of the gases. If this blockage should occur, the forementioned evidence for circulation would reveal it and corrective action could be taken. The effect of the heated sample loop was accounted for in the
calculations. The sampling loop arrangement consists of two Teflon valves to isolate the loop from the carrier gas stream and two valves to isolate the loop from the reactor. This proved to be very convenient for troublefree repetitive sampling without the addition of air to the sample or extraneous gases to the reactor. The valve at point "A" (see both Figures 4 and 5) permits the sampling loop to be evacuated after sampling so that the residual carrier gas is not added to the reactor contents. The volume of the sampling loop relative to the volume of the reactor was small enough so that repetitive samples do not deplete the system of a significant amount of gas. One additional valve is required to divert the carrier gas from its bypass configuration into and through the sampling loop and into the chromatographic system. The valves of the sampling loop are sealed together so that dead volumes (where sample flow may be delayed) are kept to a minimum. This is especially important for the sampling loop bypass valve near the downstream end of the bypass leg and for the valve isolating the sampling loop from the vacuum system.

A system containing so many valves isolating atmospheric pressure from moderate vacuums did on several occasions develop leaks traceable to valve stem leakage. The simple task of replacing the Viton O-rings on the valve stem corrected the problem. Furthermore, three of the six Teflon valves in the sampling loop assembly have an overpressure of pure helium on one side and the reactor operating pressure (always less than one atm) on the other side, so that leakage of atmospheric gases across these would be
nearly impossible. The critical nature of even a minute leak over a several day period is evident in consideration of the low states of oxidation which are being studied. To see the tiny $N_2$ peak on highest sensitivity (shown to be an impurity in the cylinder CO) remain unchanged over several days is a satisfactory indication of the vacuum integrity of the entire reactor assembly.

When it became apparent that water vapor was a constituent of great importance, a series of experiments was performed where liquid water and steam were excluded from the reactor. In these runs the partial pressure of water vapor was limited to a value controlled in part by reactions between the gases and the lava. An initial residual water vapor pressure will be present in any vacuum system, especially one having contained liquid water at one time. For these experiments the reactor was obviously overdesigned since the venturi and the condensate traps had no functions. The circulation of gases during these dry experiments was much slower than if steam had been present. The pumping action of the lighter heated gases served to produce circulation and was depended upon to produce a homogenous gas phase composition which could be sampled with precision. As previously noted, experiments were generally discontinued when the $CO_2$ to $CO$ ratio approached constancy.

At the end of most experiments the gas phase was pumped from the reactor and condensed onto a bed of glass chips at 77°K in a tiny Pyrex glass trap. These traps were from three to five cm$^3$ in volume and equipped with a rubber septum for syringe sampling. The condensation trap was preceded by a dry adsorbent
foretrap consisting of Drierite and Ascarite both of which had been thoroughly checked to ascertain that neither exhibited irreversible adsorption of the traces of hydrocarbons being drawn through them. The flow of reactor gases through these three traps was regulated by a Teflon valve so that trapping would be effective. Once the reactor pressure had fallen, the microtrap still at 77°K was isolated by melting the glass. It was the usual practice to analyze an aliquot of the trap immediately upon its isolation since there was some concern that the traces of hydrocarbons might dissolve in the rubber septum. Although this seems to be a valid concern, repetitive samplings days after preparation and storage at ambient temperature showed no serious degradation.

With H₂O and CO₂ chemically removed and H₂ and CO non-condensable at 77°K, the microtraps were usually under a good vacuum. The reason for the removal of CO₂ by Ascarite and H₂O by Drierite stems from an attempt to analyze by mass spectrometry some of the earlier concentrated samples where no adsorbents were used. It was learned that a volume of gas large enough to analyze for traces of the hydrocarbons contained too much CO₂ and H₂O to permit a good mass spectrum to be obtained.

3. Chromatographic System

The chromatographic system for analysis of the reactor contents is basically a standard design, although several modifications were made in order to increase sampling convenience. These changes were:

(a) The insertion of a carrier gas/combustion air purification element was used to increase the signal to noise ratio in
the flame ionization detector by removing those traces of organic vapors commonly found as contaminants in cylinder gases. This easily prepared purification substrate is an oxidation catalyst made from silver nitrate supported on alimuna and held at about 420°K (Hoffman, et al., 167). When the detector showed evidence of a rapidly fluctuating flame background, not traceable to other causes, the catalyst was replaced and within a day the unit was back in operation.

(b) The permanent installation of the chromatographic columns in the oven, selectable via column switching valves, was very helpful. All necessary analytical data on the gases could be obtained utilizing only two different column substrates. A third column shown in the chromatographic oven (see Figure 6) with different plumbing is the column used to analyze the aqueous fraction in those experiments which contained liquid water. These samples were introduced as usual with a syringe through the standard heated injection port (see later discussion). The details of the chromatographic columns may be found in the Appendix.

(c) Two separate detectors with independent readouts were utilized in series (see Figure 6). This arrangement permits simultaneous analysis of the inorganic gases with the thermistor-equipped thermal conductivity cell (T.C.D.) and the organic vapors with the H₂ flame ionization detector (F.I.D.). The T.C.D. is mounted in an aluminum box filled with lead shot and kept warm with a heating tape connected to the in-
strument power supply. The normal plumbing arrangement for a flame ionization detector employs a stream splitting device which vents up to 99% of the total sample plus carrier gas to a fraction collecting device. Here the F.I.D. inlet was changed to allow all of the sample contained in the reactor sampling loop to enter the flame detector after passage through the column and the T.C.D. This arrangement sacrifices some baseline stability due to pressure surges caused when sampling valves are actuated and to the effect of non-combustible gases, but it affords maximum sensitivity for those substances of interest in the quantities normally encountered.

When a concentrated sample contained in the microtrap offered chromatographic indication for substances heavier than the readily recognized C_2 hydrocarbons, the sample was submitted for analysis by combined gas chromatography coupled to a mass spectrometer (G.C/M.S). Although this is a powerful analytical tool, it often suffers some disadvantages due to its complexity. The system used here was shown to have a lower overall sensitivity than the flame ionization equipped gas chromatographic detector used in this project. The primary reason was an unfavorable split ratio at the inlet to the mass analyzer. This did not prove to be a critical drawback since gas chromatographic retention times provide almost certain identification as long as the sample does not contain organic compounds with similar boiling points and retention properties on the column being used. The C_5 hydrocarbons formed in some experiments could not be identified on the G.C/M.S system even though the flame responses were well above background noise levels.
Figure 6. The Chromatographic System.
The static mixing technique using syringes was used in the detector calibration procedures. Because the very lowest end of the concentration range for CH₄ was of interest, the static calibration using pure CH₄ in air (or helium) was least accurate. The problem was that a sufficiently small amount of pure methane could not be reproducibly sampled for dilution. Despite this shortcoming, the detector was checked on three different occasions within a two year period and was found not to suffer any noticeable change in response. Access to a cylinder of primary standard CO dilution analyzed at 5.1 ppm by volume afforded the opportunity to calibrate the detector and establish its limit of detection. Since the flame detector does not respond to CO, a hydrogenation reactor (Porter and Volman, 168) was built and placed between the column and the detectors. Assuming that the catalytic reduction of CO to CH₄ is complete it was shown that under the best conditions of baseline stability and signal to noise ratio the detector was capable of responding reproducibly to about 2.5E-07 standard cm³ or 1.5E-10 grams or 7.5E-12 moles of CH₄. This value may represent the limit of detection but under normal operating conditions the electrometer output voltage was attenuated by a factor of four to accommodate minor changes in the noise level. The integrated detector response, at least over the lowest end of its response scale, is linear with respect to the amount of substance being ionized. It was therefore determined that 6.0E-09 grams was the working limit of detection or the least amount of CH₄ analyzed for during the background checks for contamination. When this value was applied to the reactor a partial pressure of CH₄ of less than 2.2E-07 atm was considered free of contamination.
4. Contamination, Sources and Elimination

At the outset of the experimentation it was realized that any organic substances synthesized in the reactor would occur at very low concentrations. For this reason the F.I.D., used in the modified manner, was chosen as the best detector for this application. Through a consideration of the equilibrium values for reactions producing CH₄ from CO or CO₂ with hydrogen we knew that the conversion of CO₂ or CO to organic compounds would not exceed 1% and would most likely be much less.

To begin an experiment with any background contamination would not be wise because the assumption that it would remain constant could not be made with confidence and also because even a small amount of CH₄ may affect the relative proportions of the other gases which are being sought. Because of its stability among hydrocarbons we knew that methane would be the major constituent of the sum of all hydrocarbons. Due to its better elevated temperature stability relative to other hydrocarbons and its ease of analysis, methane was chosen as an index of residual contamination (see Table 1).

The highest CH₄ backgrounds, indicating contamination, were routinely observed whenever the reactor had been opened to the laboratory environment. This was necessary in order to change the charge of lava inside the furnace or to add a new batch of water to the boiler. Both of these operations required pressurizing the reactor and minor glass-working manipulations where contamination by my expired breath, room dust and oily aerosols and rubber tubing particles from my blow tube were possible sources of pyrolyzable organic material. On occasion the reactor was held under a helium purge to lessen the chances of contaminant
introduction. Another obvious possible source of contamination was the
gases which are intentionally introduced into the reactor. The purity
of every new cylinder of gas was checked chromatographically using a
large volume injection. In several instances, badly contaminated
cylinders were identified and either rejected or used elsewhere in a
noncritical application.

It is important to point out that the carbon, appearing as
methane, and being applied as an indicator of contaminations is not in-
troduced into the reactor as methane. If this was the case, extensive
pumping would remove it. It is thought to be a thermal pyrolysis prod-
uct of some higher molecular weight contaminant for which gas chromato-
graphic evidence was not readily possible. Support for this hypothesis
is that CH₄ was often observed to increase with time during background
contamination checks. Also during some contamination checks analyses
for methane, ethylene and ethane were conducted. The relationship be-
tween the quantities of these three pyrolysis products was variable and
unpredictable. It is suspected that this stems from the chemical nature
of the initial contaminant and its fragmentation behavior in a hot zone
under the conditions present at that time.

Table 1 lists selected thermodynamic formation constants for
some low molecular weight hydrocarbons. An inspection of these values
clearly shows why methane is the best indicator of organic contamination.
A comparison of the constants for methane at 800° and 1000°K, which are
usual reactor temperatures for background checks, with those for other
hydrocarbons is a measure of its dominance over its higher homologs.
The magnitude of these values for CH₄ indicates its intermediate temper-
ature stability.
With respect to the chromatographic analysis for CH₄, its well resolved early elution (about 1.5 mins.) with good peak symmetry is an advantage. A slight disadvantage, however, in using methane is the fact that the flame ionization detector responses least sensitively to the one carbon atom member of any homologous series of organic compounds. Older literature refers to the F.I.D. as the carbon counting detector. This carbon atom dependency is related to the formation by thermal ionization and the detection of the C⁺ species in the flame (Sternberg, et al., 169).
Table 1. Selected Logarithms of Equilibrium Constants for Reactions Producing Hydrocarbons from Hydrogen and Carbon Monoxide with Water as the Oxygenated Byproduct.

The reaction may be generalized by the following:

alkanes: \((2n+1)H_2 + nCO = C_{n+2}H_{2n} + nH_2O\)

alkenens: \((2n)H_2 + nCO = C_nH_{2n} + nH_2O\)

alkynes: \((2n-1)H_2 + nCO = C_{n+2}H_{2n-2} + nH_2O\)

There is also a similar set of equations but with \(CO_2\) as the byproduct (see later section of Fischer-Tropsch synthesis).
<table>
<thead>
<tr>
<th>Compound</th>
<th>400°</th>
<th>600°</th>
<th>800°</th>
<th>1000°</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>15.61</td>
<td>6.30</td>
<td>1.73</td>
<td>-1.31</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>22.11</td>
<td>6.42</td>
<td>-1.26</td>
<td>-6.34</td>
</tr>
<tr>
<td>C₂H₄</td>
<td>10.57</td>
<td>0.97</td>
<td>-3.75</td>
<td>-6.89</td>
</tr>
<tr>
<td>C₂H₂</td>
<td>-6.32</td>
<td>-8.10</td>
<td>-9.04</td>
<td>9.64</td>
</tr>
<tr>
<td>C₃H₈</td>
<td>29.69</td>
<td>7.24</td>
<td>-3.70</td>
<td>-10.95</td>
</tr>
<tr>
<td>C₃H₆</td>
<td>20.17</td>
<td>3.25</td>
<td>-5.04</td>
<td>-10.53</td>
</tr>
<tr>
<td>C₄H₁₀</td>
<td>37.48</td>
<td>8.23</td>
<td>-6.03</td>
<td>-15.44</td>
</tr>
<tr>
<td>C₄H₈</td>
<td>27.77</td>
<td>4.13</td>
<td>-7.41</td>
<td>-15.04</td>
</tr>
</tbody>
</table>
A simple test using ethane, propane and butane in equal proportions was performed on this particular detector. A surprisingly strong linear relationship between integrated detector response and carbon atom number was demonstrated. This relationship will be applied in the quantitative work-up of the results for those substances for which calibration data was not available.

A major contributor to contamination was Tygon tubing in the inlet system without provision for trapping potential impurities. U.S. Stoneware, the manufacturer of Tygon (polyethylene plastic), indicates in their sales brochure that the standard laboratory formulation has a vapor pressure of about $5.0 \times 10^{-6}$ atm at the normal room temperature of $301^\circ K$. It also has a slight odor which is an obvious indication of a significant vapor pressure. Another source of contamination originating from Tygon, beside the vapors, may have been a release of aerosols to a flowing gas stream from the inside surface once that polished surface became pitted or otherwise damaged through physical or chemical abuse. In order to gather more definite information on the Tygon problem the same length of tubing used in the inlet connection was stuffed into a small volume glass cell and allowed to degas on the inlet of our mass spectrometer for several days. The spectra clearly showed sample responses at $m/e$ 41, 55 and 56. Based on this information the inlet system was completely rebuilt using Teflon valves, metal valves, molecular sieve traps, glass tubing and permanent copper tubing, cleaned by the recommended suite of solvents to remove industrial residues (Mon, 271). These changes resulted in an immediate reduction in background to levels which could be removed by means to be discussed next.
Once gross contributors of contamination were eliminated the following procedure evolved to further reduce the organic background to or below the limit of detection for methane as described earlier.

(a) After the insertion of new lava or new water the reactor was sealed and checked for leaks in the new work. Roughly 0.2 atm of helium was added, the water was brought to a boil and the furnace was set to about 800°K. Sequential sampling while the system stabilized would almost invariably result in a gradually increased CH₄ signal.

(b) The boiler was shut off and allowed to cool, the furnace temperature increased to about 1200°K and the reactor was evacuated. Oxygen was added to a pressure of about 0.4 atm, the boiler was started and steam was allowed to reflux through the furnace overnight under these oxidizing conditions. The thermodynamic equilibrium constant for the stoichiometric combustion of methane with oxygen at 1200°K is about $E+35$, which attests to its extreme high temperature instability under oxidizing conditions.

(c) After the overnight treatment the O₂ was removed either by pumping (after the boiler cooled) or by purging with helium while the water continued to boil. The sampling loop valve assembly had another advantage in that helium could be made to flow in at 'B' and exit at 'A' (see Figure 4) which effectively purged the furnace tube and the steam which was being ejected through the venturi. This arrangement, along with cooling under a slowly flowing helium stream, permitted
complete removal of oxygen.

(d) The final check for contamination usually was performed at a furnace temperature of about 800°K and with H₂ present since these conditions would favor the stability of methane more than if helium was used. If after several hours (or overnight) the flame detector produced a satisfactory background an experiment could be initiated; otherwise the oxidation procedure was repeated. It was usual that one extended oxidation step was sufficient to remove the organic contaminants.

The really stubborn problem of contamination was eventually whipped and it became possible with a relatively short expenditure of time to proceed from a moderately contaminated reactor to a completely clean flame background which showed no tendency to increase over a 24 hour period prior to the introduction of the reactant gases.

There was an extremely important ramification of these decontamination procedures which will be referred to as the noncontrolled redox problem. Fresh Hawaiian basalt, like that used in these experiments, generally has an Fe(II)/Fe(III) of about four to eight, expressed as oxides. The Fe(III) is contained in magnetite, a reduced iron mineral, which is subject to oxidation under many conditions, as are the remainder of the ferrous iron-bearing minerals.

Conditions inside the reactor furnace during decontamination were, as just described, always oxidizing since the organic contaminants are unstable in a high temperature, high oxygen pressure medium. Parameters which affected the degree of oxidation of the lava during de-
contamination were: the initial oxidation state, partial pressures of water and oxygen, temperature and the length of treatment. This last item was important since once the surface was oxidized, diffusion-controlled processes would take oxidizing conditions to the subsurface lava. The manner in which these factors were affecting the experimental results was not fully recognized until a certain set of experiments was performed and the observations studied in terms of the thermodynamic stability of iron oxides as a function of the partial pressure of oxygen. The following reactions and equilibria values at 875°K (the experimental temperature of these tests) will be used with the assumption that the condensed phases will have unit activity and the fugacities for the gases will be equivalent to their partial pressures.

\[
\begin{align*}
3\text{FeO} + \text{H}_2\text{O} &= \text{H}_2 + \text{Fe}_3\text{O}_4 & K = \frac{\text{pH}_2}{\text{pH}_2\text{O}} &= 2.2 \\
\text{Fe} + \text{H}_2\text{O} &= \text{H}_2 + \text{FeO} & K = \frac{\text{pH}_2}{\text{pH}_2\text{O}} &= 3.0
\end{align*}
\]

These equilibrium ratios may be interpreted to mean that when the \(\text{pH}_2/\text{pH}_2\text{O}\) is less than 2.2, water dissociates to form \(\text{H}_2\), and \(\text{Fe}_3\text{O}_4\) is the stable iron oxide (Storch, 170). They also mean that ratios between 2.2 and 3.0 favor the stability of FeO while at values greater than 3.0, iron is stable and any FeO or \(\text{Fe}_3\text{O}_4\) reacts with \(\text{H}_2\) to shift toward an equilibrium composition more favorable for metallic iron. When the logarithms of the inverted ratios \(\text{pH}_2\text{O}/\text{pH}_2\) are taken (log 1.0/2.2 = -0.34 and log 1.0/3.0 = -0.48) and compared with the phase boundaries Fe-FeO and FeO-Fe\(_3\)O\(_4\) at 875°K in Figure 1, the agreement is good.

Also from Figure 1 the equilibrium constant for the reaction

\[
2\text{Fe}_3\text{O}_4 + \text{H}_2\text{O} = 3\text{Fe}_2\text{O}_3 + \text{H}_2
\]
can be seen to be about $1.38 \times 10^{-5}$ at 875°C. When combined with the water dissociation equilibrium the new reaction

$$2\text{Fe}_3\text{O}_4 + \frac{1}{2}\text{O}_2 = 3\text{Fe}_2\text{O}_3$$

has a constant at 875°C equal to about $1.5 \times 10^{-7}$. An equilibrium constant of this magnitude clearly shows the strong tendency for oxygen to cause the oxidation of magnetite. Also it can be seen that the oxygen fugacity value from the QFM diagram (see Figure 1) at 875°C is about $10^{-21}$ atm; a value which is obviously many orders of magnitude lower than oxygen partial pressures used in the decontamination procedures.

This situation means that even though the decontamination procedures were effective in reducing the reactor background, the noncontrolled redox problem was constantly changing the surface oxidation state of the lava in a way rather difficult to predict. Reversal of the surface oxidation by a hydrogen treatment would be reasonable except that the basic problem of deciding the final state of reduction would be as difficult as in the oxidized situation. The oxidation state of the lava, be it oxidized or reduced, may be thought of as a source for either oxygen or hydrogen which upon the introduction of the initial carbon gas will influence the position of equilibrium in the water-gas expression

$$\text{H}_2 + \text{CO}_2 = \text{CO} + \text{H}_2\text{O}$$

and this form of the Fischer-Tropsch reaction

$$3\text{H}_2 + \text{CO} = \text{CH}_4 + \text{H}_2\text{O}.$$
As a final result of these complex gas–solid interactions involving uncertain oxidation states, the pCO₂/pCO ratios were variable and produced differing small amounts of methane and ethylene and ethane. Hydrocarbons heavier than C₂ were not observed in the high steam experiments.

5. Analysis of Aqueous Phases

Depending upon the choice of column the analysis by gas chromatography or mixtures containing large concentrations of water may cause difficulties such as severe tailing or masking of the peaks of interest, liquid phase degradation by hydrolysis and detector corrosion. The development and use of cross-linked polystyrene polymers, which require no liquid phase, helped alleviate some of these problems (Hollis and Hayes, 172).

The statement that the flame ionization detector is insensitive to water applies only in small amounts. This is probably due to the fact that the H₃O⁺ is the predominant species in the flame envelope (Sternberg, et al., 169). Hill and Newell (173), Lucero (174) and Eggertsen and Stross (254) have all reported a decreased sensitivity for organic substances when water vapor is intentionally introduced into either the carrier gas or into the burner fuel gases. These reduced responses are attributed to a drop in the flame temperature which lowers the ionization efficiency.

It is well known that within a series of organic compounds of the same carbon number the hydrocarbon will generate the strongest ionization current. The substitution of oxygen, sulphur or a halogen reduces the strength of this current (Sternberg, et al., 169; Ettre, 175; Perkins,
et al., 176). Compared to methane this effect achieves its extreme for the substances CO, CO₂, HCHO and HCOOH which are regarded as being insensitive (Perkins, et al., 176; Emery and Koerner, 177; Ackman and Burger, 178).

At the conclusion of each high steam experiment the aqueous phase was withdrawn from the reactor boiler and carefully stored until an appropriate method of analysis was selected. The technique used in this study may be termed "column-detector flooding". References to it could not be found in the literature, although Nomaka (275) has described a chromatographic system employing steam as the carrier gas. It was observed that the injection of a slug of distilled water caused the generation of a "flame ionization signal" so strong that the electrometer was swamped to an extent that complete recovery required about 40 minutes. Having determined retention times for vapors of methanol, ethanol, n-propanol, i-propanol, acetaldehyde, propionaldehyde and acetic acid, it was evident that all of these organics would elute from the column within this nonresponsive period of detector operation. It was subsequently demonstrated that despite the water vapor background the detector could be made responsive to these organics if the electrometer controls were twiddled to attain a new state of dual flame balances. This state of metabalance was temporary, but it allowed enough time to inject a large volume of sample with only an additional minor disturbance to the baseline.

Using carefully prepared dilutions of the simple alcohols, aldehydes and acids, it was shown that the limit of detection for the above water-soluble organics was about 20-70 times less than that of the hydrocarbon with the same carbon number.
6. Carbon and Sulphur Analyses in Volcanic Rocks

a. Combustion

Samples of submarine basalts collected and described by James Moore (36) were analyzed for total carbon and sulphur by the high temperature combustion technique developed by Carleton Moore and Lewis (91) and Carleton Moore et al., (278). The sample is heated to a high temperature in excess of its liquidus by an induction furnace for a predetermined period of time in a stream of oxygen gas with the aid of a combustion catalyst. The combustion products are measured either chromatographically ($\text{CO}_2$) or by an automated iodiometric titrator ($\text{SO}_2$). The reported precision for both gases is ±5% and the accuracy is ±8%.

b. Pyrolysis

A 185 mg piece of sample 4 and 5 was subjected to thermal mass spectroscopy by the technique of Gibson (277). This specimen was heated continuously under vacuum to its liquidus temperature. During the heating cycle multiple mass spectra are taken—in this instance every 50 degrees. Total pressure in the pyrolysis chamber is monitored so that quantitative data is available from the spectra of the volatiles.
Compositions extending over wide ranges in partial pressures of $H_2$, $CO$, $CO_2$ and water vapor in the presence and absence of basaltic lava chips were studied at temperatures between 1300° and 600°K. The temperatures most often studied may be referred to as either the high (1150-1300°K), intermediate (850-1050°K) or low (600-750°K) range. The experimental assembly limited the total pressure to less than one atmosphere.

A. The Results of the High Steam Experiments

1. The Effect of the Initial Oxidation State of Lava on the Gas Phase Composition

The two pairs of experiments which gas quantitative data on the influence of the lava on the position of equilibrium in the water-gas reaction were E37/E38 and E39/E40. The primary difference was that prior to E37 and E39 the lava was conditioned with hydrogen gas while prior to E38 and E40 the lava was conditioned with oxygen gas. A new charge of lava from the same batch was used in each run with conditioning times, temperatures and sampling times held constant. The results of the principal carbon constituents are summarized below.

<table>
<thead>
<tr>
<th></th>
<th>Hydrogen Conditioned</th>
<th>Oxygen Conditioned</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E371</td>
<td>E392</td>
</tr>
<tr>
<td>CO_2/CO</td>
<td>2.4</td>
<td>0.6</td>
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<tr>
<td>H_2/CO_2</td>
<td>6.7</td>
<td>3.8</td>
</tr>
<tr>
<td></td>
<td>37.0</td>
<td>22.0</td>
</tr>
<tr>
<td></td>
<td>0.27</td>
<td>0.08</td>
</tr>
</tbody>
</table>

During the removal of $H_2$ from the reactor prior to the introduction of $CO$ (in E37 and E39) evidence for an internal source of gas, which was

1. The water in the flask was brought to a boil.
2. The water in the flask was left at room temperature.
analyzed as hydrogen, was observed. At first it was thought that a combination of H₂ sorption onto the surface of the lava and H₂ diffusion out of vesicles may be responsible, but it turned out that the magnitude was much greater than could be attributed to these combined sources. Cadenhead, et al., (171) determined the extent of H₂ sorption on lunar fines below 175°K and showed that it decreases sharply above this temperature, which is 50 degrees above the boiling point for hydrogen.

When CO and H₂O are the initial reactants, the stoichiometric amounts of H₂ and CO₂ ought to be equal when no other sources or sinks exist. However, upon analysis of the final composition, i.e., when the ratio stopped changing significantly, the amount of H₂ present was several times (see 6.7 and 3.8) greater than the amount produced by the water-gas reaction. Likewise, it can be seen that the gas phase was depleted of H₂ when the lava was initially oxidized.

This evolution of H₂ from the hydrogen-conditioned lava was due to a reversal of the ratio pH₂/pH₂O from iron stable during conditioning, i.e., pH₂/pH₂O greater than 3.0, to FeO stable when the H₂ was evacuated and the pH₂/pH₂O became less than 2.2 (see page 87). The principal reason for performing these parallel experiments where the lava was either oxidized or reduced was to emphasize its role on the chemistry of the gas phase. One can see then that the composition of the gas phase, including the organics, may be highly variable due in part to some of the considerations discussed here.

It is unlikely that volcanic gases will come into contact with hot surfaces more reduced than those at their origin. On the other hand, reduced volcanic gases interacting with more oxidized lava surfaces would
be common along the walls of vents through which volatiles and occasional lava fountains are ejected. In vents produced in recent eruptions the limit of downward intrusion of atmospheric oxygen is clearly visible as a demarcation line separating reddish oxidized surfaces from the original black reduced lava color.

The role of lava was anticipated to be catalytic toward establishing equilibrium in the water-gas reaction as well as catalytic toward the synthesis of organic compounds. As it turned out the lava had not only a catalytic influence, but also an extremely important role in the position of chemical equilibrium. The participation of the lava (assumed to be due to the iron minerals) may be depicted by adding the dissociation reactions

\[
\begin{align*}
\text{CO} + \frac{1}{2}\text{O}_2 &= \text{CO}_2 \\
\text{H}_2\text{O} &= \text{H}_2 + \frac{1}{2}\text{O}_2 \\
3\text{Fe} + \frac{3}{2}\text{O}_2 &= 3\text{FeO} + \frac{1}{2}\text{O}_2 = \text{Fe}_3\text{O}_4 \\
3\text{FeO} + \text{CO}_2 &= \text{Fe}_3\text{O}_4 + \text{CO} \\
\text{Fe} + \text{H}_2\text{O} &= \text{FeO} + \text{H}_2.
\end{align*}
\]

These equations along with \(2\text{CO} = \text{CO}_2 + \text{C}\) are essentially those which are used to develop Figures 1 and 2.

It must be noted that the formal definition of catalysis does not include provisions for allowing a catalyst to enter into the chemical reaction to an extent greater than the formation of intermediate activated complexes which do not appear as stable components of the reaction. The catalyst does not change the energy relationship between the reactants
and the products, but simply reduces the activation energy which may act as an energy barrier for the approach to equilibrium.

2. Effect of Presence or Absence of Lava

All but a few experiments were conducted with lava in the furnace and any without it would have little geochemical interest. They did, however, help elucidate the influence of lava upon the gas phase composition. Experiments E31 through E35 furnished the data to evaluate the role of the lava in establishing equilibrium in the water-gas reaction

\[ H_2 + CO_2 = H_2O + CO. \]

These few runs were performed with only the quartz insert, which would normally contain the lava bits. One would naturally want to investigate the influence of the necessary parts of the reactor, in this case the silica furnace tube and insert. After 36 hours it was shown that equilibrium had been established only to the extent of 0.2% at 900°K and 6% at 1200°K. The degree of establishment of equilibrium as defined here is simply the experimental \( pCO_2 / pCO \) divided by the theoretical equilibrium ratio at the furnace temperature. The experimental \( pCO_2 / pCO \) values for experiments containing lava can be shown to be in near complete equilibrium in time periods much shorter than 36 hours. A discussion of the kinetics of the water-gas equilibrium reaction will be presented later.

3. Effect of Major Components in the Gas Phase on Organic Composition

   a. Hydrogen

In experiments where steam was injected into the furnace along with the permanent gases the position of equilibrium was always in favor of \( CO_2 \), as it is in terrestrial volcanic systems.
In some experiments hydrogen in addition to that produced by the oxidation of CO was added to the gas phase, most often after the pCO₂/pCO appeared to reach a constant value. As expected the increased partial pressure of H₂ always tended to shift the apparent equilibrium ratio of CO₂ to CO to lower values. The increased reducing potential caused by this added hydrogen never had a significant effect upon either the quantity or the number of hydrocarbons appearing, as long as steam was the major component in the reactor.

In high steam experiments the maximum concentration of CH₄ never exceeded 5.0E-05 atm and for ethylene plus ethane the maximum concentration was about 4.0E-07 atm. Hydrocarbons beyond C₂ were not observed in high steam experiments. A most important point for these experiments is the high temperature instability of these simple hydrocarbons, excluding CH₄. In order to study this, an experiment equilibrated to include the small amounts of hydrocarbons noted above then had its furnace temperature increased. Increasing the furnace temperature to about 1200°C or higher would cause the almost immediate disappearance of ethylene and ethane to below their limits of detection.

In those cases which were frequently sampled during the furnace heatup from an intermediate to a high temperature, an interesting temperature dependent transition was noticed. The saturated hydrocarbons (S.HC) disappeared quickly while the unsaturated ones (U.HC) increased to a slight maximum and then decreased rapidly and completely. This apparent greater stability
of the U.HC also was observed during the anhydrous experiments to be discussed later. The high temperature portion of the runs shifted the pCO₂/pCO in the direction expected from the equilibrium relationships. Upon reducing the temperature to the intermediate range the C₂ hydrocarbons reappeared but never in amounts greater than before the high temperature phase. This reappearance of hydrocarbons after the high temperature phase is sound evidence that they are not related to system contamination. The nonconstant U.HC/S.HC ratio was apparently due to a slow hydrogenation process. As nearly as could be determined the unsaturated species appeared first, reaching its maximum while its saturated counterpart was just appearing and increasing in prominence. Then as a function of time the relative concentrations reversed making the saturated species dominant when the experimental run was terminated and the concentrated sample was prepared.

This unsaturated-saturated hydrocarbon transition was not observed in all cases because the ethylene-ethane response in some experiments was so small that the unsaturated contribution to the incompletely resolved signal from the flame ionization detector could not be made. The concentrated sample usually contained enough of both to make the distinction. Thermochemical equilibrium calculations to be presented later in detail, show a high-temperature to low-temperature convergence pattern for the ratio of U.HC/S.HC for a fixed composition. The ratios ethylene/ethane and propylene/propane both decrease about three orders of magnitude going from 1000° to 400°K (see equilibrium composition
printouts in Appendix). There also exists a decreasing ratio pattern as a function of increased hydrogen pressure (but necessarily with a variable composition) at constant temperature. Despite the nonconstant composition the concentration trends of unsaturated and saturated hydrocarbons are more strongly influenced by temperature than by hydrogen pressure. In other words, hydrogenation of unsaturated hydrocarbons occurs best at low temperatures in the presence of excess hydrogen gas.

The unsaturated/saturated hydrocarbon dependency upon hydrogen is shown in the results of a pair of parallel experiments (E37 and E38) at about 900°K. In E37 the lava (conditioned initially in H₂) caused the pCO₂/pCO ratio to remain low and gave a C₂H₄/C₂H₆ ratio of 0.3 at a pH₂ of 0.59 atm. In E38 where the lava was conditioned initially in oxygen, substantial oxidation of the CO occurred and a C₂H₄/C₂H₆ value of 6.0 was obtained at a pH₂ of only 0.02 atm.

b. Water

There were a small number of experiments which were performed at water vapor pressures about 30 torr. These experiments—few in number—have no special geological significance to this study. They were conducted primarily to demonstrate the ability of water vapor to control the oxidation state which, as already described, also regulates the ratio of pCO₂/pCO and the amounts and types of hydrocarbons. In the final reactor design these experiments were done by simply not boiling the water in the venturi assembly (see Figure 4). The partial pressure of water in the reactor is then the vapor pressure of water at room temperature.
These low water pressures had a definite effect upon the oxidation of carbon monoxide. This is shown in the results of E39 and E40 (on page 92) and in E41. Even though these low partial pressures of water did influence the oxidation of CO, they were not low enough to allow the formation of hydrocarbons at concentrations above the values previously stated to apply to high steam experiments. This observation will support a statement to be made later in this chapter that the critical water vapor pressure is probably in the range of one to 30 torr at one atmosphere total pressure. The critical value is one which seems to separate reactions into either (a) the water-gas dominant reaction at high pressures of water with a small hydrocarbon contribution, or (b) some form of the Fischer-Tropsch synthesis which produced significant quantities of hydrocarbons in the presence of a reduced iron catalyst.

There is one experiment (E7) which was conducted in the reactor with the first design (see experimental reactor design section) that deserves a special notation. With the furnace temperature at 1200°K hydrogen was introduced in small amounts over a two week period. During this interval the pCO₂/pCO ratio decreased, while the methane signal increased slightly. After several days a dark, mirror-like deposit was observed to have formed in the tube leading out of the furnace. When the furnace temperature was reduced to about 850°K, at least five flame-active substances were formed. Although some of these species persisted, some process—probably hydrogenation—was responsible for altering their distribution. The dark substance was not
analyzed, but it readily burned-off in air. The disposition of carbon, as soot, from a gas phase is a common occurrence. The circumstances of this experiment do not permit a conclusion about which factor (the reduction in furnace temperature or the dark substance) was most responsible for the appearance of these hydrocarbons.

Additional evidence for the importance of water vapor in controlling the oxidation state of the gases in contact with lava was provided in E41. During the initial phase of the experiment CO was allowed to oxidize to CO$_2$ in the presence of about 30 torr water vapor. The steam pressure was controlled by simply not boiling the water. During the 21 hours preceding initiation of boiling, the pCO$_2$/pCO barely exceeded unity at 975$^\circ$K. Within two hours at a high steam pressure the ratio was 2.8 increasing to 19.0 during the following 20 hours.

4. The Results of the Aqueous Phase Analyses

Employing the analytical techniques described earlier, the aqueous samples retained from most of the high steam experiments did not reveal any soluble flame-active substances in concentrations above their limit of detection. Sample volumes were often as large as three milliliters. An aqueous specimen was crudely concentrated from about 80 to several milliliters, but no benefit was evident when the "concentrate" was chromatographed.

B. The Results of the Anhydrous Experiments

The results of the high steam experiments, although variable in pCO$_2$/pCO and the vary limited organic complement, were consistently indicative of a strong influence by an oxidizing agent. Upon removal of liquid water from the reactor in E28 and its dramatic effect upon the gas phase
composition, the dominating role of water in the water-gas reaction to suppress Fischer-Tropsch reactions started to become clear. Concurrently literature on lunar studies was becoming available and, as already described, the subject of water and its effect upon lunar geochemistry was receiving such attention.

In order to understand how the composition of carbon-containing gases would be affected by the surface compositions of the lava in an anhydrous system, a pair of parallel experiments E29 and E30 were run where the only difference was the preconditioning of the lava. One common trait of all anhydrous experiments was that they exhibited a decreasing pressure trend. Thirty-eight percent of the initial quantity of CO in E29 was transformed into CO$_2$ while 18% disappeared from the gas phase. Forty-two percent of the initial gas phase CO disappeared in E30 and 37% of it oxidized to CO$_2$. If the CO$_2$ had been formed by the water-gas reaction H$_2$ would have appeared (it didn't) and the pressure would have increased instead. The difference between the two experiments was that the lava was conditioned in a slowly flowing stream of O$_2$ in E29 and likewise by H$_2$ in E30. The experimental results cannot positively identify the form of the nonvolatile carbon in either case but a phenomenon did occur which strongly suggests either the formation of a carbide or the deposition of carbon (graphite?). The possible pressure decreasing reactions between lava and CO in the absence of water are as follows.

When the lava is oxidized, the Fe$_2$O$_3$ may react as

$$3CO + 3Fe_2O_3 = 2CO_2 + 2Fe_3O_4 + \text{carbon}$$

$$CO + Fe_2O_3 = CO_2 + \text{an iron carbide}$$
When the lava is reduced, the FeO or Fe can react as

\[ 2\text{CO} + \text{FeO} = \text{CO}_2 + \text{Fe} + \text{carbon} \]
\[ 2\text{CO} + \text{FeO} = \text{CO}_2 + \text{an iron carbide} \]
\[ \text{CO} + \text{any constituent} = \text{CO}_2 + \text{any carbide} \]

The last equation, which can also apply in the oxidized case, was included since there is no evidence in which the condensed phase might be involved.

There are two iron carbides, cementite and the Hagg carbide. The best known is the Hagg form, Fe₂C (probably not stoichiometric), which is encountered in iron catalysts for the Fischer-Tropsch reactions (see later section). The Hagg carbide decomposes to cementite, Fe₃C, and carbon above 725°C. Another low temperature carbide, E-iron carbide, may be produced at lower temperatures from iron oxide and carbon monoxide.

There are many variable gas phase compositions suitable for the formation of carbides, a process known as carburization (Driver and Barrand, 258; Wyss, 259).

Once H₂ was made available to these two systems, E29 and E30, the pCO₂/pCO ratios changed immediately with a strong tendency to converge to a common value of about 0.9 which offers evidence that a new controlling parameter was responsible. The final gas phase results of these two runs were very similar both in composition of permanent gases and the amounts and types of hydrocarbons. It was calculated that near the end of both of these runs the water vapor pressure was about 20 torr. It may have been that water vapor at about this pressure was responsible for the apparent convergence in these two runs. It will be shown later that a value slightly lower than 20 torr might be important in the formation of carbides.
The hydrocarbons formed under the lower pH2O conditions of E29 and E30 were dominated by saturated species. The ratio of C2H6/C2H4 in the condensed sample was near 300 and propylene barely showed as a trace preceding propane. A comparison of these results to those obtained in experiments in which water vapor pressure was high showed that the total amounts of hydrocarbons formed at any temperature was very strongly limited by water vapor. The partial pressure of total hydrocarbons (always dominated by CH4) in the anhydrous experiments was always at least 400–700 times greater than the total in an experiment dominated by steam at the same temperature.

1. The Effect of Temperature on the Formation of Organics

Despite the tendency toward higher partial pressures of hydrocarbons in the anhydrous systems, high temperatures still have a suppressing effect upon their formation. The amount of CH4 formed in a low temperature, high steam environment barely exceeded the CH4 formed in a high temperature, anhydrous system. Anhydrous experiments in the intermediate temperature range produced methane in amounts about five to 15 times that produced at high temperatures. The condensed gas samples from intermediate temperature anhydrous experiments showed only a trace of C2 hydrocarbons and nothing higher. Based on results of the low temperature, anhydrous runs (to be described next) there appears to be a very strong temperature dependency on the amounts of hydrocarbons formed below about 8000K.

There can be no question that the star of the entire series of experiments was EH4. Within two hours of adding the component gases CO and H2, the products ethylene, ethane, propylene, propane, and C4 hydro-
carbons were observed along with methane in large amounts. Samples the next day showed amounts of C₂, C₃ and C₄ hydrocarbons never observed in any experiments conducted theretofore. Because of their early appearance in easily observable amounts the transition of unsaturated hydrocarbons to saturated hydrocarbons could easily be observed. The unsaturated compounds definitely formed more readily. Their disappearance and the apparent quantitative formation of saturated analogs indicate hydrogenation. However, carbon monoxide addition reactions involving unsaturated hydrocarbons, i.e., the Oxo reaction, cannot be ruled out. Studier, et al., (187) have concluded that the Fischer-Tropsch reaction proceeds by the addition of two hydrogen atoms per mole of CO to yield predominantly unsaturated species probably through an alcohol intermediate. Mass spectrometric analysis of the components condensed in E44 positively identified the above mentioned hydrocarbons plus isobutane, isobutene, 2-butene and n-butane. Four C₅ hydrocarbons in quantities close to the limit of detection for the available G.C/M.S system were clearly seen on the flame detector but could not be identified. One would expect that they would also include saturated and unsaturated species. A trace of one and possibly two C₆ hydrocarbons was also noted. The absence of acetylenic hydrocarbons in E44 and the following anhydrous experiments may be attributed to either the use of copper plumbing in the chromatographic system (Jeffery and Kipping, 188) or to their thermochemical instability under the reactor conditions. In the section on equilibrium computations we shall see that the amount of C₂H₂ is always present in lesser amounts than ethylene or ethane, but is still strongly hydrogen dependent. The complexity (relative to previous experiments) of the hydrocarbon distribu-
tion was most reasonably determined in part by catalytic effects of the lava acting as a reduced catalyst in the Fischer-Tropsch reaction, which forms the basis of the synthetic petrochemical industry. A characterization of this synthesis will follow.

Because of the significance of E44 a mention of the possibility of contamination is in order. Neither the inside of the reactor nor the lava was exposed to any room air between the start of E42 and E46. At the termination of all experiments cylinder oxygen was introduced into the furnace to combust any residuals remaining on the lava (recall decreasing pressure implications) and each experiment was preceded by the already described check for organic contaminants.

When O₂ was added at the end of E42 a mild explosion with an emission of light occurred inside of the furnace tube. This phenomenon, affably referred to as my lunar flash, could have been caused by any of three possibilities; carbon (graphite?), carbides or a pyrophoric form of metallic iron. One-half hour after the flash CO₂ was appreciable but its maximum concentration was not reached for four hours. The same procedure in E43 did not produce any visible explosion and manometric observations indicated a much less significant uptake of O₂. The CO₂ produced was only about 1/4 of that formed in E42. The oxygen is in competition between the carbonaceous residue and the reduced lava. Based on this partial evidence it was concluded that there was a residual solid form of carbon. A consideration of the thermochemical properties of carbon in the iron oxide system (see Figure 1) would suggest that carbon caused the flash. At 1000°K the log of the pCO₂/pCO for E42 falls on the border of the graphite stable region at an oxygen fugacity of
1.0E-21 atm. This evidence, however, cannot discount the contributions of carbides for which support will be forthcoming. The overall results of initial decontamination (prior to E42) plus the two terminal residual combustion determinations reduced the likelihood of contamination pyrolysis appearing in E44 to a negligible level of concern.

There is more data on pCO2/pCO values in the high steam experiments than there is for the anhydrous ones. The limited anhydrous data does, however, strongly indicate that the quartz-fayalite-iron (QFI) buffer controlled the oxygen partial pressure. The pCO2/pCO ratios were 0.14 in E42, 0.32 in E43 and 0.75 in E44. When the logarithms of these values are plotted in Figure 7, they lie very close to the QFI buffer which has been derived by Eugster and Wones (139).

Regardless of how the experiment was performed all evidence indicated the deleterious effect which high temperatures had on the stability of simple hydrocarbons. It is felt that this was due to equilibrium conditions in a chemical system containing oxygenated species. Steck, et al., (189) and Gulbransen (190) in their studies of the reaction products between graphite and hydrogen in an "approach-to-equilibrium" flow type reactor with short contact times produced every hydrocarbon entity up to 140 amu. The amounts of hydrocarbons actually increased with temperatures between 1900 and 2400°K. They admit that trace amounts of metals in the graphite may have been influential in these results. One experiment in the present study reacted powdered graphite and hydrogen at an intermediate temperature to produce large amounts of methane and other simple hydrocarbons.
2. The Experimental Formation of Carbides on Lava

Considering the effort being expended in the lunar analytical program to resolve the carbide question, it seemed important to consider their role in this project, and E46 revealed some convincing evidence for their formation. Again the same charge of lava used previously was thermally reduced for 24 hours under \( \text{H}_2 \) at about 700°K. Being cautious not to cause another explosion or introduce contamination, the reactor was opened and about 1/2 of the lava bits were removed and placed in a clean storage vessel. The reactor was sealed and \( \text{CO} \) flowing through a molecular sieve/dry ice trap (T3 in Figure 5), contacted the lava for 22 hours. This rock was removed and stored until the hydrolysis procedure was readied. The procedure for identification of carbides was exactly as developed by Chang, et al., (191) for the lunar samples. Chromatographic analysis of the headspace gases after chemical attack by 4.8N HCl at 370°K for 20 hours showed significant amounts of ethylene, ethane, propylene and propane, with traces of \( \text{C}_4 \) hydrocarbons. \( \text{CO}_2 \) was detected but not measured. The hydrocarbon constituents were confirmed by the \( \text{G}, \text{C}/\text{M}, \text{S} \) techniques already mentioned. Hydrolysis of the sample treated only under hydrogen did not reveal the evidence for carbides. An interesting point, but of unknown importance, in this carbide hydrolysis test is that the ratio of saturated to unsaturated was almost exactly unity for both the \( \text{C}_2 \) and \( \text{C}_3 \) hydrocarbons.

Experiments E47 and E48, which were similar to E44 in temperature, were conducted at different initial ratios of hydrogen to carbon monoxide (see Appendix). Hydrocarbons through \( \text{C}_4 \) were observed in the gas phase of both experiments. Their distribution was only slightly different from the
results of $E_4$ which employed an initial $H_2CO$ ratio to two. At the end of the run, the lava was removed and hydrolyzed as described previously. Both specimens gave clear evidence that carbides had been produced at the same time hydrocarbons were synthesized. It seems reasonable to propose that the hydrocarbons themselves might have been the carburizing agents here. Methane and butane are commonly used industrially in annealing and carburizing ovens. In addition a sample intentionally contaminated with coffee, perspiration, saliva and a bit of skin was hydrolyzed according to the same procedure and no carbide evidence was noted. An important question concerning carbide formation under these conditions, which cannot be answered unambiguously: what is the upper limit of water vapor which can be tolerated before the reaction ceases to produce carbides? Using the equilibrium constant for the water-gas reaction it is estimated that 8 torr water vapor might be an upper limit for the formation of carbides. Although descriptive information on the Fischer-Tropsch synthesis is forthcoming, it seems pertinent to mention here that water vapor pressures somewhere between 0.013-0.034% (one to 30 torr at 1 atm) may be the critical range of values in that reaction with respect to catalytic activity.

In one poorly documented instance some additional evidence pertaining to carbide formation also was observed. An experiment with steam was begun using lava upon which some anhydrous experiments had been conducted. As the steam began condensing in the upper portion of the reactor between the furnace and the condenser a layer, which displayed hydrophobic properties, appeared on the inside surface. One possible explanation is that it was an optical phenomenon associated with the wetting of a glass surface. Another is that carbide hydrolysis produced wax-like hydrocarbons
on the lava, which desorbed and were carried out of the furnace by the steam. The first drop of condensate was reddish colored.

C. Summary of High Steam and Anhydrous Experiments

Certain of these experiments with high partial pressure of steam can be evaluated in terms of terrestrial volcanism. The slightly oxidizing environment associated with high temperatures and high water vapor in the presence of basaltic lava with an iron composition dominated by magnetite maintains an oxygen fugacity in close approximation to the QFM buffer system. This buffer favors pCO₂/pCO ratios near or in excess of ten at all temperatures. Some experiments yielded pCO₂/pCO and pH₂O/pH₂ ratios in excellent agreement with equilibrium values. Theoretical values were never found to be exceeded. The inability to consistently arrive at equilibrium values as interpreted from Figures 1 and 2 must be related to the effects (sometimes intentional) of not matching the oxidation state of the lava at the start of an experiment with the gas phase composition to be studied for the formation of organic substances in that experiment. This was discussed under the noncontrolled redox problem. Another reason is that Figures 1 and 2 relate to a condensed phase consisting wholly of iron oxides which overlooks the oxidation-reduction potentials for other constituents of lava and other gases in the volatile phase. The oxygen fugacity can be estimated with about one order of magnitude accuracy from either of these figures where the QFM line intersects an oxygen isobar at the respective temperature.

The results of the attempts to synthesize organic compounds from "magmatic gases" at a high pressure of water vapor were indeed discouraging until the influences of the experimental parameters on the final state
of oxidation were elucidated and appreciated. A typical set of results would show that the degree of conversion of CO into methane ranged upward from 0.0003%, i.e., 1 part CH₄ in 3.0E+06 parts CO (or sum CO plus CO₂) to perhaps 0.002% under the best thermal conditions and generally with a considerable amount of hydrogen present. Due to the very small response, usually just above the limit of detection, the sum of both C₂ hydrocarbons would be estimated at 0.00001% in most instances. Ethylene was the most conspicuous of the two, generally appearing first under all modes of reactor heating.

While the experiments containing high concentrations of steam favored fairly high degrees of oxidation, all of the anhydrous ones maintained pCO₂/pCO ratios less than unity. The highest ratios were associated with the highest temperature. The water-gas reaction

\[ \text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2 \]

in the anhydrous experiments appears to have been suppressed since the data suggests that some reaction which favors the removal of gas species is more important. These reactions have been suggested as involving either the deposition of carbon or the formation of carbides, or both.

The amount of CH₄ formed at high temperatures and anhydrous conditions was only slightly greater than the largest amount of CH₄ formed under the most favorable thermal conditions employing large amounts of steam as a reactant. At about 800°K (the exact temperature is uncertain) a region of hydrocarbon stability is approached and many unsaturated, saturated and branched hydrocarbons appear along with a large amount of methane. In this instance the unsaturated hydrocarbons
were least stable because they became hydrogenated readily in the presence of the substantial amounts of molecular hydrogen and the low partial pressures of water vapor. It is proposed that the Fischer-Tropsch synthesis involving CO and H\textsubscript{2} is responsible for these results. The reaction is probably catalyzed by the free iron which was formed on the lava during its reduction and maintained in that state of oxidation by the composition of the gas phase.

It is crucial to recognize that despite the differences between the outcome of the high steam and the anhydrous experiments, the controlling factor in both series is the fugacity of the oxygen present in the gas phase as well as the oxygen associated with the surface of the lava. Therefore, whatever oxygen fugacity value is evaluated with respect to organics one must imply gas phase--solid phase surface equilibrium.
Figure 7. The Stability Field for the Oxides of Iron as a Function of $p_{CO_2}/p_{CO}$, Temperature and Oxygen Fugacity Showing the Approximate Ranges for the Experimental Data on the Ratio of Carbon Dioxide to Carbon Monoxide in the Two Systems Studied.

Cross-hatched area in magnetite region and on the reduced side of the QFM buffer represents high steam data. The dashed line in the metallic iron region is the oxygen buffer requirements for the QFI assemblage (Eugster and Wones, 139). The $p_{CO_2}/p_{CO}$ data obtained in the anhydrous experiments B42, B43 and B44 is shown as the shaded area.
D. Results of the Carbon and Sulphur Analyses on Basalts

In order to establish the amount of carbon and sulphur introduced into the environment through volcanic eruptions, samples of submarine basalt collected and described by James Moore (36) were analyzed for these elements by the high temperature oxygen combustion techniques of Carleton Moore (91). Since these samples have not been analyzed previously, the entire raw data will be included here in Table 2. The sample numbers are identical to those reported by Moore (36) and reveal the depth and the location of sample retrieval. It should be pointed out that samples 4 and 5 and samples 6, 7 and 8 have been grouped accordingly, since the depth of collection are the same. However, each represents a different sampling of possibly the same lava flow. Some of the surfaces of the specimens exposed to the seawater are coated by a rust colored scale. Both interior as well as crustal chips (with and without the scale) were selected to test for surface contamination. Also included for comparison are two surface erupted lavas from Kilauea—collected fresh and stored to minimize laboratory contamination.
Table 2. The Results of the Carbon and Sulphur Analyses on Hawaiian Submarine and Subserially Erupted Basalts.

The underlined carbon values were obtained from samples weighing about 100 mg, while all others represent the results on 200 mg or larger specimens.
<table>
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<th>Sample Number, Description and Depth of Coll' n.</th>
<th>Total Carbon in $\mu gC/g$ lava</th>
<th>Total Sulphur in $\mu gS/g$ lava</th>
</tr>
</thead>
<tbody>
<tr>
<td>#2, inside chips</td>
<td>42, 57, 52</td>
<td>144</td>
</tr>
<tr>
<td>#2, crustal chips, no brownish scale, 1400 meters</td>
<td>72, 73, 86</td>
<td>108</td>
</tr>
<tr>
<td>#4 and 5, inside chips, 3420 meters</td>
<td>107, 80, 107, 99, 95</td>
<td>974</td>
</tr>
<tr>
<td>#4 and 5, crustal chips, no brownish scale, 3420 meters</td>
<td>94, 71, 80</td>
<td>1077</td>
</tr>
<tr>
<td>#6, 7 and 8, inside chips, 4680 meters</td>
<td>98, 60, 70</td>
<td>2041</td>
</tr>
<tr>
<td>#6, 7 and 8, crustal chips, brown scale removed by analyst, 4680 meters</td>
<td>100, 109, 111</td>
<td>998</td>
</tr>
<tr>
<td>#6, 7 and 8, crustal chips, brown scale left intact</td>
<td>159, 153, 148</td>
<td>929</td>
</tr>
<tr>
<td>Pele's Tears Mauna Ulu, 1969</td>
<td>28, 37, 43</td>
<td>119</td>
</tr>
<tr>
<td>Alae Crust, 1969 exposed to atmosphere about three weeks before coll'n</td>
<td>29, 16, 45, 47</td>
<td>129</td>
</tr>
<tr>
<td>Average on all submarine samples</td>
<td>83</td>
<td>895</td>
</tr>
<tr>
<td>Average on all submarine samples excluding #2</td>
<td>91</td>
<td>1204</td>
</tr>
</tbody>
</table>
The technique of thermal analysis using mass spectroscopy generates amounts of data which generally require the utilization of a small laboratory computer. Table 3 summarizes the data obtained on the previously described submarine basalt. Only at temperatures above 950°C did signals at mass numbers greater than 44 appear. The heaviest ion recorded was 80 amu and many lighter ones disappeared from the spectrum as the liquidus temperature was approached. This could be attributed to either a depletion of certain elements or high temperature instability. At these high temperatures, gas-solid chemistry is undoubtedly a major factor in determining the composition of the volatiles.
Table 3. Summary of Mass Spectral Data of the Volatiles Released from 185.6 mg of Submarine Basalt No. 4 and 5.

The data has been corrected for background contribution. Probable peak assignments are given with the molecular weight of the species (the ion charge has been omitted).

- \(x\) denotes that this ion generated a signal greater than 10% of the total intensity at that temperature.
- \(\times\) denotes that this ion generated a signal greater than 1%, but less than 10%, of the total intensity at the specified temperature.
- \(\dagger\) denotes that the ion was detected, but at less than 1% of the total ion intensity.
- A blank indicates that the ion was not detected above background levels.
<table>
<thead>
<tr>
<th>amu</th>
<th>Possible species</th>
<th>Temperature in Degrees Centigrade</th>
</tr>
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<tbody>
<tr>
<td></td>
<td></td>
<td>600</td>
</tr>
<tr>
<td>1</td>
<td>H</td>
<td>x</td>
</tr>
<tr>
<td>2</td>
<td>H₂</td>
<td>x</td>
</tr>
<tr>
<td>12</td>
<td>C</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>O, CH₄</td>
<td>x</td>
</tr>
<tr>
<td>17</td>
<td>OH</td>
<td>x</td>
</tr>
<tr>
<td>18</td>
<td>H₂O</td>
<td>x</td>
</tr>
<tr>
<td>24</td>
<td>C₂</td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>CO₂, N₂</td>
<td>d</td>
</tr>
<tr>
<td>30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>32</td>
<td>O₂</td>
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</tr>
<tr>
<td>34</td>
<td>H₂S</td>
<td>d</td>
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<tr>
<td>44</td>
<td>CO₂</td>
<td>d</td>
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<tr>
<td>48</td>
<td>SO</td>
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<td>50</td>
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<td>64</td>
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<td>66</td>
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</tr>
<tr>
<td>76</td>
<td>CS₂</td>
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</tr>
<tr>
<td>80</td>
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</tr>
</tbody>
</table>
IV. EXPERIMENTAL DISCUSSIONS

A. Experimental Factors which may Influence Results

Because of my own difficulties in obtaining reproducible results (see discussion on the noncontrolled redox problem) definite proof for the following discussion cannot be supplied, but suspicions are strong that experiments conducted in the manner described by Yoshino, et al., (179) and Hayatsu, et al., (180) and some of my own may lead to some unfounded conclusions especially when results are being weighed against thermodynamic equilibria. The point in question is the heating cycle impressed upon a reactive mixture with an initial makeup far from its equilibrium composition.

Another related consideration in the discussion of prebiotic synthesis, organic constituents in meteorites or the possibility of organics in low pressure interstellar space is the time factor involved. Quite obviously laboratory experiments cannot be studied on a geological time scale and the results obtained must be interpreted accordingly. To place a mixture of gases in a vessel at ambient temperature, heat it overnight in the presence of a reduced catalyst, analyze the contents and interpret the results as being of cosmological significance puts one in a precariously defensive position, especially when the often illdefined problems of contamination must also be reckoned with by the investigator.

It was my occasional observation that two experiments performed as nearly alike as possible gave different results depending upon the heating cycle employed. These geochemical experiments normally are
performed with heating cycles of one of the following three types. The first is the introduction of gases with a cool furnace and either direct or stepwise heating to the desired temperature. The second is to have the furnace at temperature when the gases are introduced thus avoiding chemical changes associated with lower temperatures. The third approach is to have the furnace at a high temperature initially and begin a stepwise or continuous temperature decrease once a high temperature "equilibrium" has been established. It is hypothesized here that all three of these may be applied to the same composition leading to variable results in the molecular distribution of products within a reasonable expenditure of laboratory time. This variability must tend to distort the interpretation.

In regard to a mass of cooling magmatic gas the last type of heating program is best since we know that volcanic gases are exsolved from the melt at about 1400°K and are either cooled rapidly by quenching or cooled in the presence of lava possessing possible catalytic properties. Experimental cooling cycles as described were used in some runs while the remainder were conducted in one of the other two ways (see Appendix 1 for experimental details). Bringing the gases initially to the highest possible experimental temperature has the obvious benefit of "seeing" the high temperature composition, which in the case of the terrestrial experiments is closely predicted by the oxidation state for the QFM system.

The disadvantage to a cool start with the temperature increasing, such as might be proposed for studies related to small particle agglomeration in micrometeor interactions or planetary accretion, is that organics may be formed at the lower temperatures in substantial concentra-
tions. At the final experimental temperature, where these concentrations may be metastable, the kinetic readjustment to final equilibrium concentrations may be too slow with respect to the time which can be allocated to the experiment. The termination of an experiment with nonequilibrium quantities of certain components present may lead the investigator to improper conclusions. This situation would easily apply to polymerization reactions which kinetically are slow. Isothermal experiments which are somewhat slower to equilibrate, especially at low or intermediate temperatures, avoid this low temperature difficulty of interpretation.

Experiments designed to probe geological settings other than magmatic systems, which exhibit predominantly cooling or isothermal conditions, may need to consider a nonuniform temperature program. Variable temperatures with wide extremes would be related to phenomena such as the short duration of high temperatures in electrical discharges, high intensity ultraviolet radiation, or the high temperatures created during cosmic particle bombardment, or meteor agglomeration and impact. The latter would be associated with localized melting. A brief discussion later will consider the nonequilibrium aspects of the chemical origin of life.

A method to determine if a composition is representative at a certain temperature is to approach that temperature from both directions. This was often done in the course of the experimentation because it additionally permitted an evaluation of the two carbon atom complement with respect to contamination. The appearance of any one specie at about the same concentration from either side of the temperature gives confidence that the quantity is representative and may indeed be an equilibrium amount.
In summary, each method of conducting an experiment has some advantages and one must be aware of the heating or cooling cycle employed along with the experimental results. It may have been factors related to the experimental approach used by Studier, et al., (182), with whom Yoshino and Hayatsu collaborated, which lead them to conclude that their results for aliphatic hydrocarbons were an embarrassment to an equilibrium hypothesis. The equilibrium computations in reference are those by Dayhoff, Eck and others (183, 184, 185) who chose to delete graphite as an equilibrium substance through the kinetics consideration described elsewhere. However, his experimental results also embarrass the equilibrium computations reported later in this study, which included graphite.

B. Kinetics of the Water-Gas Reaction

The important equilibrium controlling the proportions of the main carbon gases, CO and CO₂, in the system under investigation is known as the water-gas reaction. It is important to understand the rate at which the equilibrium for this reaction is attained. Experimental evidence for the attainment of equilibrium in the isolated water-gas reaction, i.e., one occurring in a "nonreactive vessel" points toward a homogeneous mechanism. A homogeneous mechanism, in contrast to a heterogeneous one, proceeds wholly within the gas phase. The heterogeneous mechanism, on the other hand, involves the chemisorption of a reactant species onto a solid surface—which may in fact be the wall of the reaction vessel. It is likely that the two mechanisms will share some chain propagating steps and, of course, will yield the same products in the same concentration regardless of the pathway. The major factor
which will be different between the two mechanisms is the time required to reach an equilibrium composition.

Experiments by Hadman, et al., (192) concluded that in a static system the CO and steam reaction does occur on a silica surface. These results could not be verified by Ingles (193) or Doehlmann (194) in studies on flowing systems. Based upon the observation that increasing the silica surface area in the reactor reduced the rate of the reaction, two other investigations claimed that CO\textsubscript{2} and H\textsubscript{2} (Kondrat'ev and Ziskin, 195) and CO and steam (Long and Sykes, 196) both reacted by homogeneous mechanisms. Evidence of an opposite nature, i.e., an accelerating influence, led Tarama et al., (197) to conclude that a heterogeneous mechanism occurs in a packed quartz vessel. The homogeneous mechanism initiated by the dissociation of either water or hydrogen and terminated by an atom-radical recombination was found to support most of the kinetic data of Graven and Long (198).

The two most important parameters affecting the length of time before equilibrium is attained are the reaction rate and the activation energy, which are interrelated through the Arrhenius rate constant equation. The activation energy is a barrier above which the energy content of the reacting system must exceed before products may be formed and the mechanism usually involves the formation of an unstable activated complex. In some systems the activation energy barrier reduces the reaction rate to essentially zero. It is in these kinds of systems that catalysts play such an important role. The catalyst does not change the energy relationship between the reactants and the products, only that between the activated complex and products or reactants. The
activation energies in the water-gas reaction as they apply to this project were of no concern, especially when weighed against other problems. However, some data became available during the search for kinetics data and will be included here for possible reference.

The activation energy is normally derived from experimental data since a theoretical basis for its calculation is difficult. It is determined from the temperature coefficient of the rate constant. Graven and Long (198) observed that the activation energies for the two opposing reactions in the water-gas equilibrium differed by slightly more than ten kilocalories. They also calculated theoretical values which fell in a reversed order.

\[ \text{H}_2 + \text{CO}_2 = \text{CO} + \text{H}_2\text{O} \]

observed \( E_{\text{act.}} = 56.9 \text{ kcal/mole} \)

calculated \( E_{\text{act.}} = 84 \) " "

\[ \text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2 \]

observed \( E_{\text{act.}} = 67.3 \text{ kcal/mole} \)

calculated \( E_{\text{act.}} = 75 \)

They attributed these discrepancies to the fact that their activation energies are derived from data representative only of the initial stages of the reactions. Their flowing gas reactor techniques, as opposed to the static, limited all reaction times to within 0.5 seconds which prevented the degree of conversion to products from exceeding one to two percent. Actually this was necessary in order to prevent a hinderance caused by the back reaction as the system approached equilibrium.
Tarama, et al., (197) offered a heterogeneous mechanism with an activation energy less than half of the value given by Graven and Long. Masuda (199) arrived at an activation energy value similar to that of Tarama but used a platinum catalyst to achieve the reaction. This suggests that even though Tarama, et al. studied the reaction in a quartz reactor (generally regarded as nonreactive) they may have observed a heterogeneous mechanism, but called it homogeneous for lack of experimental verification. Many authors note the drastic influence of even trace quantities of impurities, especially the transition metals. It has recently been pointed out that lengthy storage of carbon monoxide in steel cylinders at the filling pressures normally encountered can lead to a substantial buildup of high trace levels of iron pentacarbonyl in the gas (Harris and Yakel, 200). The investigators were more concerned with the extreme toxicity of Fe(CO)$_5$ than other effects. The fact that iron is common in water-gas reactions may suggest a heretofore unknown catalytic effect. The synthetic organic work by Reppe (Copenhaver and Bigelow, 97) showed that iron group carbonyls and their carbonyl hydrides exhibit catalytic activity in the Oxo process, a modification of the Fischer-Tropsch synthesis. Many of the more sophisticated kinetic investigations were performed using evaporated metal foils and films or single crystals all of which are available in high purity (Stotz, 201; Masuda, 199). The means of measuring kinetic data have also changed in recent work from the originally used Orsat volumetric gas analyzers to gas chromatography and finally to electrical relaxation techniques.

According to basic concepts the equilibrium composition may be approached from any combination of species provided all elements are
present in some molecular or elemental form and a suitable source of energy is available. This is to say that the water-gas composition for the QFM equilibrium conditions might arise from \( \text{CO} + \text{H}_2\text{O}, \text{CO}_2 + \text{H}_2, \text{CO}_2 + \text{H}_2\text{O}, \text{graphite} + \text{water}, \text{et cetera}. \) In preliminary experiments in this project \( \text{CO}_2, \text{H}_2\text{O} \) and \( \text{H}_2 \) were used, while later a switch to \( \text{CO} + \text{H}_2\text{O} \) was made. The combination \( \text{H}_2 \) plus \( \text{CO}_2 \) is obviously valid, but the amount of water which could be formed would never have fulfilled the requirements of an experiment at high steam vapor pressures. One of two situations would have prevailed:

(a) The vapor pressure of water might exceed its condensation dew point in the condensor and perhaps a few drops of liquid water would form. The way the reactor was designed \( \text{pH}_2\text{O} \) would never have exceeded its partial pressure at room temperature, about 30 torr (see Figure 4).

(b) The vapor pressure of water would have been held to very low values—not exceeding condensation parameters—through its reactions with iron minerals in the lava to produce hydrogen. This would be largely controlled by the initial oxidation state.

An irony arises from this situation since if \( \text{H}_2 \) and \( \text{CO}_2 \) had been used instead of \( \text{H}_2, \text{H}_2\text{O} \) and \( \text{CO}_2 \), the secret of these inexplicable reactions would have been discovered much earlier. The \( \text{H}_2 \) and \( \text{CO}_2 \) mixture would have led to substantial hydrocarbon synthesis. The water vapor was an oxidizing agent of such magnitude that catalytic activity by the reduced lava was inhibited.
The oxidation of CO by steam was generally observed to approach a satisfactory equilibrium composition within 48 hours at the temperatures studied, but only when lava was present in the reactor furnace. There is a fair amount of literature available on the kinetics of the \( \text{H}_2 + \text{CO}_2 \) reaction, but a noticeable lack of same for the opposing reaction. Graven and Long (198) and Tingey (202) both present rate expressions for the homogeneous reduction of \( \text{CO}_2 \) in quartz which when evaluated at 1125°K differ by a factor of only four and are essentially equal at 1325°K. Factors such as reactor flow dynamics, trace quantities of \( \text{O}_2 \) in the feed gases and induction period differences were mentioned as reasons for imperfect coincidence of experimental rates. Further, Tingey resolved his data to fit two very different rate expressions, one valid above and one below 1175°K. The activation energy for the low temperature equation was more in line with those arrived at by Tarama et al. (197) and Masuda (199). Tingey did not study the reverse reaction, but calculations using data supplied by Graven and Long show equal rates in the initial stages for both reactions.

Barkely (203) studied the kinetics of the \( \text{H}_2 \) and \( \text{CO}_2 \) reaction in the presence of an iron—copper water-gas catalyst and derived an equation for the reaction rate which was related to the weight of catalyst and parameters defining residence time in the bed. The slow step in the proposed mechanism was the fixation of \( \text{CO}_2 \) on an active site. Kul'kova, et al., (186) showed in their investigations that oxygen isotope exchange occurred between gas-phase oxides of carbon and iron catalysts.
Both Ingles (193) and Tingey (202) studied the water-gas reaction in the presence of solid carbon and agreed that it does not significantly influence the equilibrium, i.e., the contribution of CO and H₂ from the reaction

\[ \text{H}_2\text{O} + \text{C} = \text{CO} + \text{H}_2 \]

is small. Ingles (193) and Brown (204) agreed in their partial kinetic study of the reaction

\[ 2\text{CO} = \text{CO}_2 + \text{C} \]

that the behavior closely follows a prediction based only on equilibrium considerations, and further that isotopic exchange between the two phases occurred only at temperatures above about 975°K, the temperature where the equilibrium constant is about unity.

The role of catalysis in any reaction is complex and little comparison of data is possible since it is generally recognized that catalyst performance is highly dependent on its preparation with the chemical composition sometimes of secondary importance. In summary, a catalyst will hasten the establishment of equilibrium by reducing the activation energy and providing active sites for chemisorption. If a substrate causes serious deviation from predicted equilibrium composition, then it is most likely that a different reaction is involved. In the system under study it is concluded that the lava did have a catalytic effect in the establishment of the water-gas equilibrium. The experimental data on page 95 supports this statement.
In some respects concern for the kinetics of a system which is going to be applied to a geological system is unnecessary because either the period of time for equilibration is rather short (a few seconds) or very long (years). The very long periods of time, of course, refer to volatiles which are trapped within a silicate matrix or in vesicles formed by expanding gases. In either instance the rate of cooling is dependent upon the mass, its thermal conductivity and the heat flow to its surroundings. The short reaction times would apply where volcanic eruptive activity is happening and the contact time between volatiles and the walls of the vent or with condensed particulates in the fume is brief. Short contact times and rapid cooling are essentially quenching processes and would have a tendency to stabilize the high temperature composition, which in a body of molten erupting lava has been shown to be in equilibrium.

C. Characterization of the Fischer-Tropsch Synthesis

It is important to examine the characteristics, mechanisms and the poisoning of catalysts in the Fischer-Tropsch (herein abbreviated F-T) process. A discussion of the results of the role of the Fischer-Tropsch synthesis in geochemical systems will be presented later. The use of the phrase Fischer-Tropsch reaction should not be accepted to mean a specific reaction, instead a set of poorly understood reactions produces a suite of substances referred to as a F-T distribution. The term F-T process ought to be held in reference to the industrial methodology which includes the manufacture and purification of the feed gases, the product synthesis and its recovery.
1. Mechanisms and Product Distributions

Prior to widespread availability of substances manufactured from petroleum products the Fischer-Tropsch process was the industrial route to the production of light and medium boiling synthetic hydrocarbons. Its technology began in Germany in 1923 and reached its state of highest development there in the pre-World War II years. For the high molecular weight paraffin waxes not found in natural petroleum it retains its industrial stature (Kolbel, 205). The stoichiometry of the process can be illustrated by the following generalized equations where $C_nH_{2n+2}$ represents paraffin hydrocarbons, $C_nH_{2n}$ is for olefinic hydrocarbons and $C_nH_{2n+1}OH$ is an alcohol. The ideal ratio of $H_2$ to CO for each reaction is also given.

<table>
<thead>
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<th>$H_2/CO$</th>
<th>Generalized Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>$(2n+1)H_2 + nCO = C_nH_{2n+2} + nH_2O$</td>
</tr>
<tr>
<td>0.75</td>
<td>$(n+1)H_2 + 2nCO = C_nH_{2n+2} + nCO_2$</td>
</tr>
<tr>
<td>2.0</td>
<td>$2nH_2 + nCO = C_nH_{2n} + nH_2O$</td>
</tr>
<tr>
<td>0.5</td>
<td>$nH_2 + 2nCO = C_nH_{2n} + nCO_2$</td>
</tr>
<tr>
<td>2.0</td>
<td>$2nH_2 + nCO = C_nH_{2n+1}OH + (n-1)H_2O$</td>
</tr>
<tr>
<td>1.0</td>
<td>$(n+1)H_2 + (2n-1)CO = C_nH_{2n+1}OH + (n-1)CO_2$</td>
</tr>
</tbody>
</table>

The feed gas, called synthesis gas, usually has a $H_2/CO$ of about 2.0. An examination of the stoichiometries above shows that feed gases in that ratio will favor the synthesis reactions resulting in the water byproduct, which is easier to remove in an exhaust gas--feed gas recycling operation.
The feed gases were normally made from the reaction

\[ \text{C(coke)} + \text{steam} = \text{CO} + \text{H}_2. \]

In order to obtain the higher \( \frac{\text{H}_2}{\text{CO}} \) ratio it was necessary to further react a portion of these products with excess steam by the water-gas reaction

\[ \text{CO} + \text{steam} = \text{CO}_2 + \text{H}_2. \]

In this manner two moles of hydrogen gas are produced per mole of initial carbon. Even an outline of the effect of varying operational parameters and catalysts upon the distribution of hydrocarbons is not in order here but may be found in chapters and books devoted to the subject (Storch, 170, 206, 207). There are, however, a few items which have a bearing upon the experimental work and its interpretation in the geological systems of interest.

The original catalyst used in the Ruhrchemie process contained cobalt, thorium and magnesium and the overall process underwent only nominal modifications to increase yields. During this period other companies were developing iron catalysts which ultimately resulted in higher temperature, high pressure processes with better yields. The iron catalysts almost invariably started with a ferric iron salt which after being impregnated into the support by precipitation was reduced either in dry \( \text{H}_2 \) at a temperature well above the synthesis temperature or in moderately dry synthesis gas.

The economic lifetime of a catalyst is finite but it may be extended by a variation in operational parameters which leads to a slightly
different product distribution. Several mechanisms are involved in the gradual loss of catalytic activity and the fact that many spent catalysts are deficient in the cobalt or iron suggests that carbonyl formation contributes to the catalytic process as well as the degradation of the active substrate. It was subsequently shown that carbide formation played an important role in the production of a long-lived and durable catalyst.

The Fischer-Tropsch process is always conducted in the presence of a solid substrate specifically selected to either speed up the attainment of equilibrium (mode A) or to alter the distribution of products in a predictable way (mode B), or both. Obviously a substrate performing only the first role is a catalyst in the traditional sense, whereas in the second role it is more than "just a catalyst". It may be regarded as either an essential reactant for that particular reaction or its catalytic effect is being felt in a reaction different from the one considered in mode A. Literature on the subject of catalytic Fischer-Tropsch processes and equilibrium must be read with caution.

The proposed catalytic reaction mechanism involves the formation of long methylene chains between active sites on the substrate surface. Parameters affecting competition between the two adsorbed species, CO and H₂, directly influences the chain length of the desorbed hydrocarbons. Two experimental facts tend to withdraw support from the methylene polymerization concept. The first is that alcohols appear to be formed early in the synthesis and then dehydrate to give olefins. The second is the low conversion to non-linear hydrocarbons with branching restricted to methyl groups. The latter is presumably a steric
hinderance between the catalyst surface and free rotation of the chemisorbed intermediate. This supports the hypothesis that the principal surface reaction occurring is the interaction of CO and a specie containing an olefinic linkage, a reaction analogous to the Oxo reaction.

The treatment of kinetic data for heterogeneous catalytic reactions is always complicated, especially those involving porous catalysts. The rate for the F-T synthesis (expressed as %CO converted per unit time) has been postulated as being directly proportional to the partial pressure of hydrogen and inversely proportional to the fraction of the reduced iron in the reaction zone, which is in turn determined by the partial pressure of water vapor and carbon monoxide. The activity of iron catalysts is enhanced by carbiding while cobalt ones are rendered nearly passive by it. The beneficial effect of precarbiding iron catalysts is probably related to the slower oxidation of iron carbide compared to iron produced by the reduction of magnetite.

It is well established that normal alkanes are the major components in typical F-T distributions (Storch, 170; Friedel and Sharkey, 209). The product distribution is highly variable for hydrocarbons up to C₄, but appears to become exponentially decreasing beyond C₅, at least for cobalt catalysts (Underwood, 210). Iron catalysts are generally better than cobalt ones and have a minimum at C₂ with large amounts of methane. The results of experiment E44, which have been suggested as being due to a F-T synthesis, show a clear exponential decrease in product concentrations continuous between CH₄ and the C₆ hydrocarbons, and presumably beyond. A possible reason for not having observed the discontinuities in the C₁-C₄ range may have been a furnace temperature
higher than optimum. Gelpi (211) reported an optimum temperature of 575°K for the production of paraffins and that a 50° increase had a profound effect upon the product distribution.

The tendency for the F-T synthesis to form olefins increases from nickel, cobalt to the iron catalysts. Many of the factors which tend to enhance or reduce the olefin contents are the same for these three metals. Some of these are: (a) H₂ to CO ratio, (b) space velocity within the catalyst bed (not applicable in an equilibrium system), (c) temperature, (d) nature of the catalyst besides its metal, and (e) the pressure (Storch, 170, p. 562, ff.). Another feature about the olefin complement in an iron-catalyzed Fischer-Tropsch experiment is that alpha-olefins dominate over internally unsaturated isomers (Friedel and Anderson, 212, 213). In a distribution of hydrocarbons the C₄ grouping offers the first opportunity to study the alpha to beta unsaturated relationship. The fact that hydrogenation was consuming the butenes, prevents a conclusion on the alpha-olefin dominance in these experimental results.

Another chapter has been recently added to the strong controversy on whether the isoprenoid hydrocarbons pristane and phytane are indeed products of the Fischer-Tropsch synthesis (Studier, et al., 187). The keen interest in these two polymers is that 2-methylbutane (isoprene), a common F-T product, can be considered a precursor of the amino acids leucine and isoleucine and also "probably" the monomeric unit in the formation of these saturated polyisoprenoids (Oro, 214). In their investigations of gas--liquid inclusions in quartz crystals in Precambrian rocks, Kvenvolden and Roedder (166) have suggested that phytol might be
considered the precursor of these isoprenoid hydrocarbons. Blumer and Snyder (208) have suggested that phytol, a photosynthetic byproduct, is a probable precursor of phytane, but that pristane depends upon a phytane cleavage for its formation.

Much of this controversy concerning the isoprenoid hydrocarbons phytane, pristane and norpristane evolved from the results of meteorite analyses for organics and experiments to attempt to elucidate their origin (Hayes, 253) and Nooner and Oro (215) found relatively large amounts of these saturated isoprenoids in a large number of meteorite samples. They were claimed to be indigenous to the samples, albeit of unknown origin. They also showed that meteorites exhibit a bimodal distribution of hydrocarbons which suggests either (a) the hydrocarbons originated from two sources, e.g., indigenous and acquired through contamination or (b) fractionation processes (polymerization) or selective loss of a certain molecular size range had been involved. Analyses of surface and interior pieces of the specimens, a common analytical technique for meteorites, showed only a quantitative difference which tends to rule out contamination unless, of course, the entire sample was contaminated.

In attempts to simulate laboratory experiments based on the Fischer-Tropsch synthesis they were unsuccessful in synthesizing (or analyzing for) the isoprenoid hydrocarbons. This group typically uses a flowing gas (one-pass) reactor. The analysis of a complex distribution of Fischer-Tropsch products requires very sophisticated capillary gas chromatographic and mass spectrometric instrumentation since high molecular weight species have many possible isomers which must be resolved from each other.
On the other side of the controversy Studier, et al., (187) have also found isoprenoid hydrocarbons in meteorites. Contrary to their opposition they were able to show through dueterium labelling that the isoprenoids in question are products of a F-T distribution. They also use what can be termed a static reactor in that the gases are placed in a quartz cell and allowed to equilibrate for a period of time before analysis. An experimental feature of their reactor which raises a question is that a portion of the cell protrudes outside of the furnace. This permits less volatile constituents to distill away from the reaction zone and no longer participate in the "equilibration". Another feature of their experimental design is the irregular and sporadic heating cycle which is used. The consequences of these were discussed in the experimental section of this report.

Another feature of similarity between the hydrocarbons found in meteorites and the Fischer-Tropsch synthesis is that normal alkanes predominate over their isomers in ratios of about three to one. Lancet and Anders (216) conclude through their investigation of isotopic fractionation in the Fischer-Tropsch reaction that organic compounds in meteorites are formed by similar processes.

The controversy then boils down to the fact that isoprenoids may be formed under catalyzed conditions of prolonged heating but not in catalyzed, single pass experiments using essentially the same gaseous compositions. It should follow that experiments involving prolonged heating of a reactive gas mixture would tend toward equilibrium more than those of short duration followed by quenching. This approach to equilibrium composition as a function of time has been demonstrated in
nearly all of the experiments in the present study. The appearance of
the isoprenoids with other hydrocarbons of similar molecular weight in
prolonged heating experiments would suggest that they are polymeriza-
tion products of their constituent monomers. It has been pointed out
by Breger (217) that equilibrium in organic geochemical systems tends
toward the ultimate and most stable form of carbon, graphite, or its
high pressure form diamond. This is well substantiated by investiga-
tions into the course of metamorphism from organic matter of biogenic
origin through diagenesis and coalification. One is therefore tempted
to conclude that the presence of these controversial isoprenoids is
simply representative of varying degrees of equilibrium.

2. Catalytic Poisoning

Any discussion of catalysis cannot overlook the subject of
poisons and their part in altering the rates of heterogeneous reactions.
Poisons are divided into three groups: (a) the nonmetals of group V and
VI, (b) the metals and their metallic ions, and (c) molecules contain-
ing triple bonds (Maxted, 218). Only species in the first category
need to be considered here since they include the sulphur gases and
water, both of which relate to this project. Most of the work on cata-
lytic poisons has been done in hydrogenation systems and Fe, Co, Ni,
Cu, Ru, Rh, Pd, Os, Ir and Pt have been found to be the most susceptible
metals. In the original Ruhrchemie process utilizing the cobalt-
thorium catalyst the feed gas could not exceed 2.0 mg total sulphur per
cubic meter. These gases were purified in two separate processes, one
for $\text{H}_2\text{S}$ and the other for organically bound sulphur. $\text{H}_2\text{S}$ is a very
powerful poison on many substrates and as a result has been studied
extensively. All sulphur compounds are not poisons, e.g., the catalytic oxidation of SO₂ in the manufacture of sulphuric acid can be held in proof. The toxicity of sulphur compounds diminishes as the oxidation state of sulphur increases (Deem and Kaveckes, 219). However, it is very possible that an oxidized sulphur gas may be reduced and become a poison under the conditions present within the reaction zone.

Poison toxicity can be related to the strength of the chemical bond between species and substrate. Within the series of sulphur-containing species commonly encountered in industrial processes: H₂S, S₂, SO₂, thiols and sulphides, it is possible to predict the relative toxicity with reasonable certainty on the basis of electronic configuration. On the macroscale it has been known that catalysis and poisoning are directly related to chemisorptive interactions, but on the atomic level the role of molecular orbitals in the forementioned metals is just emerging. Toxicity appears to be confined to those metals in which all five orbitals of a d shell, immediately preceding the s and p valency orbitals, are occupied by either electron pairs or at least a single unshared electron. There is a strong correlation between the strength of the chemisorptive bonding, the d orbital configuration of the acceptor (substrate) and the free electron pair character of the donor (poison). The strong poisoning by H₂S is therefore attributed to its two pairs of unshared electrons. SO₂, on the other hand, has one pair of unshared electrons but these are involved in intramolecular resonance bonding and are much less accessible for donation to the substrate (Maxted, 218). A factor restricted to the organosulphur substances is the number and length of the methylene portion of the ad-
sorbed species. In this respect sulphides (two alkyl constituents) are generally always more toxic than organothiols.

Fujimura, et al., (220) observed, and it was confirmed by Herington and Woodward (222), that the addition of small amounts of hydrogen sulphide, which was apparently consumed by the catalyst since it did not appear in the off gases, had the unexpected effect of increasing catalytic activity and conversion yields at the expense of higher operating temperatures. The usual industrial connotation associated with poisoning is more a shift from the desired distribution of products than a drastic decline in yields, the latter occurring in severe cases of deactivation. The problem of catalyst poisoning may be circumvented in some cases by utilizing active substrates containing sulphur, such as molybdenum disulphide (Stewart, 222, Kirkpatrick, 270). Catalyst preparation methods in many instances are just as important as the chemical makeup or the operating parameters (Christian and Boyds, 223). Bridger (224) has reported that catalysts prepared from iron oxides are not susceptible to sulphur poisoning. A special preparation is claimed for a water-gas catalyst which is resistant to H₂S poisoning. Karschawin, et al., (Berkmer, et al., 280) have shown that a methane oxidation catalyst operating at a high temperature does not lose its activity even though the sulphur content in the feed is considerably greater than that reported to completely deactivate other susceptible ones.

It has been reported by Bone (225) that water influences the combustion of carbon monoxide with oxygen. The removal of water and its readmission to the system had entirely different effects depending upon whether porcelain or metals were used to aid in combustion.
One very important industrial process where water vapor is regarded as a catalytic poison is the ammonia synthesis from the elements (Nielsen, 226). Iron oxides are almost universally used in batch operations and are reduced at high \( \frac{pH_2}{pH_2o} \) ratios before their utilization. The surface area increases linearly with the degree of reduction and a crystallographic phase change from the spinel structure of magnetite to cubic iron occurs as the reduction proceeds to completion. If the oxygen content exceeds about 100 ppm in the synthesis gas \( (H_2:N_2:3:1) \), poisoning is indicated. This inactivity, however, is reversible by simply eliminating the sources of the contaminant. The easily reversible nature is attributed to oxidation of the high energy iron sites in contrast to the usual concept of poisoning which involves rather stable substrate to poison bonding.

Even though iron and its oxides are important catalysts they do not supersede those containing other metals in the hydrogenation reaction of the Fischer-Tropsch synthesis. Several investigators of catalytic processes now favor the concept that it is the strength of the oxygen to metal bond on the surface of the substrate which is the most important factor involved in the ability to catalyze a reaction. A review of the work leading to this hypothesis may be found in Klier (227) and Stone (228). This theory predicts that the best catalysts for many processes are \( MnO_2, Co_3O_4, CuO \) and \( NiO \)—indeed the same ones usually used in industrial reactions. Further, it predicts the low effectiveness of iron oxides and supports the observations that chromium oxides have no catalytic activity. In spite of this, Seelig and Weck (229) claim that \( Al_2O_3, ZnS, Cr_2O_3 \) are catalysts which preferentially yield aromatic
hydrocarbons. On the basis of their semiconducting properties Gallagher (230) has considered the potential of iron oxides to catalyze certain reactions involving carbon gases. Hematite, Fe$_2$O$_3$, and Fe$_3$O$_4$, magnetite, are $n$-type conductors and FeO is a $p$-type. The latter group generally exhibits superior catalytic properties.

With regard to the natural systems of volcanic gases and lava, it can be seen that the components for a catalytic F-T type reaction are available. Deactivation of lava surfaces by $H_2S$ might be important, but only at lower temperatures when favorable conditions for this type of substrate poisoning are met.

D. The Carbon and Sulphur Values in Volcanic Rocks

The carbon values for the surface erupted samples and #2 (the shallowest submarine) are somewhat lower than values reported by other investigators (see pages 19-20). The high temperature technique for carbon has been checked against N.B.S. standard steels and many may be assumed to be quantitative. The basalts of Hawaii are generally regarded as being pristine with respect to the interaction with metamorphosed sediments and country rock, both of which could readily contribute carbon.

There is a trend in these values (see page 116), suggestive that the carbon content increases with the depth of extrusion. This is reasonable since the pressure of the overlying burden of water would suppress the exsolution of a gas phase, and that which did develop would be retained to some extent by the quenched skin. The specimen analyzed with the brownish scale intact indicated surface contamination, which is not surprising.
In general, the volatiles of the one specimen analyzed by mass spectrometry during heating to its liquidus was rather uninteresting (Gibson, 265). The sample revealed no evidence for carbonates, however, CO$_2$ was detected at about 975°K. It probably resulted from the rupture of CO$_2$ rich vesicles or fluid inclusions which are common in terrestrial as well as lunar rocks (Roedder, 35; Roedder and Weiblen, 67; Kvenvolden and Roedder, 166).

A parallel trend in support of volatile loss during eruption is more clearly evident in the total sulphur contents. The 1400 meter depth for sample #2 corresponds to that pressure where a rapidly developing gas phase seems to begin to exsolve from the melt (Moore, 36).

Moore and Fabbi (260) have analyzed some of the same submarine samples for sulphur by the method of X-ray fluorescence. They reported an average of 680 ppm for 38 samples. There is an apparent enrichment of 10-15% in sulphur in the glassy crust compared to internal specimens which cooled more slowly. They also reported sulphur contents for nine subaerially erupted samples with an average of 107 ppm from elsewhere on the island of Hawaii.

There is a strong probability that sample heterogeneity is an important factor in the sulphur contents of these submarine samples. It has been reported by Moore and Calk (255) that they contain metal sulphide spherules of iron, copper and nickel. It must follow that a tiny chip containing one of these sulphide blebs would be expected to result in an anomalously high sulphur value. This might explain the high value for the sample 6, 7 and 8.
There is a particularly interesting aspect of the carbon and sulphur chemistry in volcanic systems. It has no obvious relationship with the potential to form organic compounds, however. In submarine basalts the carbon to sulphur ratio is low—on the order of 0.01, while the C/S value in magmatic gases is greater than unity. This presumably is related to the reactivity of sulphur with constituents in the lava thereby hindering its volatilization and release. The lunar samples also exhibit a low C/S value. Whether there is a relationship between this ratio and oxidation state or the tendency to form organic compounds remains to be investigated.

E. The Results of the Equilibrium Calculations

1. Procedure

The thermodynamic equilibrium computations carried out as part of this project are based on the method developed by White, et al. (231). It has been used extensively by Eck, Dayhoff, Lippincott, et al. (183, 184, 185, 232) to study complex inorganic and organic equilibria, and in our group to study the composition of terrestrial volcanic fumes at various degrees of oxidation (Naughton, et al., 233). The computer assisted procedure determines the minimum free energy for the system once temperature, pressure and composition (expressed as gram-atomic abundances) have been selected.* The partial molal free energy is the only value required in this computation. For those substances contained in the newest compilation of thermochemical data (Stull and *For clarity the word abundance or elemental abundance will be used here to designate a composition expressed in gram atomic values such as those listed in Table 4. The word composition will refer to the molecular distribution.
Prophet, 234) the necessary values are available through the free energy function. For substances not in this publication, e.g., all of the organic compounds, one must derive the appropriate free energy value by finding the difference between the free energy of formation and the free energies of the elements in the stoichiometric amounts which make up the compound of interest. Care is required regarding the standard reference states used, especially when data from two sources are being combined.

A large effort on the part of several persons has resulted in a composition for volatiles emitted during periods of active degassing in Hawaiian volcanoes.

The amounts of those elements, namely H, O, C, S and N, which predominantly occur as noncondensable species at ambient temperatures were derived from numerous samples collected over a long period of time and analyzed by various techniques, and therefore are reasonably representative.

The amounts of metals and other nonmetals, however, are based on very limited field samplings and are probably good only to an order of magnitude (Naughton, 235). As previously mentioned, the expression of a composition by its gram-atomic abundances circumvents the problems of defining it in terms of molecular forms. With normal assumptions concerning activity and fugacity, the composition of a volatile phase will, by Raoult’s law, be proportional to the elemental composition in the lava. The typical composition of Hawaiian lava coupled with the composition of lunar lavas also permits an estimation of the elemental composition of a magmatic gas phase in equilibrium with an erupting lunar
basalt. The two elemental composition lists corresponding to a lunar and a terrestrial magmatic gas phase may be found in Table 4.

In order to proceed from an elemental composition to a molecular one, a list of substances likely to be present must be selected and their free energies determined by one of the two methods mentioned above. It should be emphasized that if a particular major component is overlooked, this method, which ultimately arrives at an equilibrium composition, gives no hint that it should have been included.

Two sets of computations run at 1000°, 800°, 600° and 400°K for a composition including only carbon, hydrogen, oxygen and sulphur are included in Figures 8 and 9 to demonstrate this point. The only difference between the two sets is that H₂S was intentionally omitted in one but not in the other. It is interesting that the deletion of an important substance such as H₂S affects only those compounds present in lesser amounts. Based on this example it appears that the substance at the concentration level closest to the deleted species, had it been present, assumes the controlling role for those substances lying below either of them. In this case S₂ being second most abundant S species, below SO₂, has a strong controlling influence on COS and CS₂ in the absence of H₂S. SO and SO₃, on the other hand, are unaffected and seem to be dependent upon only SO₂ and O₂. Likewise, the pairs H₂O and H₂ and CO₂ and CO are not dependent on the H₂S-S₂ relationship. This observation leads to a conditional statement that some equilibria may be considered independent of the overall distribution. However, the safest approach is to consider all species in an elimination process as described next.
The usual practice to avoid the potentially serious error of overlooking an important compound is to derive an elimination list for the composition to be studied. Since the molecular amounts of many substances are strongly interdependent on one another, a better elimination list can be defined if the composition is permitted to vary.
Figure 8. Equilibrium Distribution for a Limited Composition to Demonstrate the Omission of a Major Constituent.

The elemental abundance is: Hydrogen, 1.90E+02; Oxygen, 1.04E+02; Carbon, 4.02E 00 and Sulphur, 1.00E 00.

The compound omitted in Figure 8 is H₂S.
Figure 9. Equilibrium Distribution for a Limited Composition to Demonstrate the Omission of a Major Constituent.

The elemental abundance is: Hydrogen, $1.90 \times 10^2$; Oxygen, $1.04 \times 10^2$; Carbon, $4.02 \times 10^0$ and Sulphur, $1.00 \times 10^0$.

In Figure 9 $H_2S$ has been included.
It would be a senseless endeavor to run equilibrium computations on an extremely large number of substances since many would be vanishingly small under most conditions anyway. The FORTRAN program being exercised was limited to 75 constituents, so a procedure to define a final list of compounds was a necessity. The inorganic complement used here was the product of an extensive investigation into the dominant species at various temperatures and oxidation states in volcanic environments (Naughton, 235). The procedure used to arrive at the organic selection list was as follows. From the equilibrium compilation of Dayhoff, et al., (185), who investigated 340 compounds, all substances at points C, A and D, at 500° and 1000°K, and where either N was predominant or where the sum of N, P, S and Cl was 0.01% of the total, were compiled if their mole fractions exceeded 1.0E-15 atm. The highest temperature considered was 1000°K since organic stability decreases sharply above it. All computations were performed at one atmosphere total pressure. This gave a list of 48 organics including some rather complex ones, e.g., substituted aromatics, heterocyclics and partially oxygenated simple organics. A few additional substances suggestive of a lunar occurrence and most of the hydrocarbons observed in my anhydrous experiments were combined with these to give an initial list of 70 compounds. This list, used in conjunction with both the proposed lunar and the terrestrial elemental compositions, gave an interim list comprised of 52 organics which exceeded 1.0E-20 atm under all conditions of temperature between 400° and 1000°K and composition fluctuations. This list did not include any substances with more than two carbon atoms, but did contain about a dozen marginally important organics containing Cl and S which were later shown to drop out when more
thermodynamically favorable inorganic substances containing the same two elements were introduced. The next concentration cutoff value was $1.0 \times 10^{-12}$ atm and all substances exceeding that value were included along with the inorganics to give a final list of 71 compounds of which only 17 contained either the methyl or the ethyl skeleton. Because of the extensive elimination procedure incorporated into this final list, it was deemed suitable for both the terrestrial and the lunar equilibrium studies. The entire list of substances is included in the Appendix in Table 10 and following.

Another consideration which concerns itself only with the less volatile inorganic complement is possible phase changes as a function of temperature. At temperatures between 1500°K (the erupting temperature) and about 1000°K condensation of certain species occurs in volcanic fumes. It is condensation which is in part responsible for the bluish haze which develops in proximity to the lava fountains. At temperatures of 1000°K and lower condensation is substantially complete except for the gases and the organics since both have relatively low boiling points. For this reason all of the inorganics included in this computation are present in their condensed (c) form. With possible exception of a few Cl and S containing organic substances, the contribution of the inorganics, e.g., oxides and halides of the alkali and alkaline earth metals, can be computed independently with only minimal disturbance to the organic distribution and vice versa. Notable exceptions are the metal carbidies and oxides since their carbon and oxygen would be added to the respective pools. No condensed nitrogen compounds were included so all of it was distributed between $N_2$ plus nine other gaseous species.
Similarly for phosphorus which was incorporated exclusively into P$_{4\,0\,6}$ since PH$_3$, P$_{2\,0\,10\,4}$, P and P$_{4\,0\,4}$ were eliminated. P$_{4\,0\,6}$ is the major phosphorus specie only within the oxidizing region (see Figure 11) while PH$_3$ remains low throughout the entire region under the CO--H line (Dayhoff, et al., 134, p.66, 67, 68). As noted previously, the "equilibrium concentration" of P$_{4\,0\,6}$ is invariant with changes in temperature and with changes in composition excluding, of course, the amount of phosphorus.

Due to the probable formation of carbides in a cooling lunar magma and the experimental evidence that carbides were formed in some of the anhydrous runs, a separate computer computation was devised to study their stability. One gram of lava, expressed as oxides, with a composition given by Moore (36) was "equilibrated" on a mole for mole basis with carbon monoxide at 1000°K and 1.0 atm. The carbon distributed itself between SiC and TiC with graphite, CO$_2$, CO, Mg$_2$C$_3$, Al$_2$C$_3$, Fe$_2$C, Fe$_3$C and CaC$_2$ in total contributing less than 1 ppm. Almost all of the oxygen remained as metal oxides. No hydrogen was introduced into the computation, hence no water or H$_2$ could form. The composition was extremely reduced. Hydrogen was then "allowed" to enter the computation as H$_2$ to probe the hypothetical reactions

$$\text{metal oxide} + H_2 = \text{metal} + H_2O$$

$$\text{metal carbide} + H_2O = \text{metal oxide} + CO(\text{or } CH_4).$$

The addition of hydrogen as H$_2$ had almost no effect upon this limited composition. The oxygen fugacity remained at E-36 atm. The addition of water, still at 1000°K, had some interesting effects upon the
composition. While the H/O changed from 350.0 to 2.0 SiC, TiC and Mg C decreased by about 10 orders of magnitude and Al C decreased by 30 orders. Even though only Fe C is stable at 1000°K, both iron carbides appeared reasonably stable. Although this problem was of limited scope it displayed a spectacular carbide sensitivity toward H 2 O and metal oxide stability toward hydrogen. Thermochemical data for the carbides is by Richardson (96) and was presented in the form of a virial equation.

2. The Computations

An arbitrary decision was made to use the proposed lunar composition as a starting point. Even though the lunar and the terrestrial compositions vary by factors of between two and ten for most elements, the primary difference is in the amounts of H and O (see Table 4). This accounts for the fact that the terrestrial composition with respect to C, H and O lies nearly on the straight line between the lunar point, L, and H 2 O (see Figure 10). From the lunar point the overall composition was altered by (a) adding water and (b) adding hydrogen. The addition of water, as mentioned above, directs the composition toward the H 2 O point. On this line are composition points L/W 1 and L/W 2. L/W 2 is very close to the terrestrial point, T, with respect to H, C and O but significantly different for the other elements since L/W 2 was derived from the lunar composition. Composition point L/W 2 was selected over the terrestrial point for graphical display (see Figures 12 and 13) because its composition, excluding H and O, is identical to all the other points except, of course, the terrestrial. This will permit an easier graphical comparison of equilibrium trends in terms of oxidation parameters.
Altering the lunar composition through the addition of hydrogen defines the line L/H on which lie L/H 1, L/H 3 and L/H 4. L/H 2 is slightly off this line. The distribution of these eight composition points permits an arbitrary assignment to one of several zones: (a) T and L/W 2 are in the high water, low carbon region and are typical of present-day terrestrial volcanic gases, (b) L/H 3 and L/H 4 are in the extremely high hydrogen zone which will be designated the cosmic zone since its C to O ratio compares favorably with the solar abundance and the high hydrogen abundance seems to fit in well with estimates of the cosmic abundance (Anders, 236), (c) L/H 1, L/H 2 and perhaps also L/H 3 fall near the top of a crudely defined zone resembling a composition(s) similar to that proposed to have existed on planets similar to Earth during that period of evolutionary history before the appearance of free oxygen in the atmosphere when the essential prebiotic chemicals necessary for the origin of life were being synthesized through processes mentioned in the Introduction.
Table 4. The Elemental Abundances for the Eight Points where Equilibrium Calculations Were Performed.

The designations, i.e., L/H 2, and their geochemical significance are described in the text and are shown in Figures 10 and 11.
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Figure 10. Ternary Diagram Showing the Position of the Eight Composition Points in the C-H-O System for Which Thermodynamic Equilibrium Composition Were Determined at Four Temperatures.
Carbon CO/LUNAR (L)
\[ \sum N, P, S, Cl = 95.2\% \sum H, C, O \]

TERRESTRIAL (T)
\[ \sum N, P, S, Cl = 0.7\% \sum H, C, O \]

LUNAR (L)
\[ \sum N, P, S, Cl = 95.2\% \sum H, C, O \]
In Figure 11 the eight composition points are shown relative to the threshold for the deposition of solid carbon as defined by Cairns and Tevebaugh (237). These temperature dependent curves (only the $300^\circ$, $1000^\circ$ and the $1500^\circ$K ones have been reproduced) are boundaries above which solid carbon, as graphite, would precipitate under conditions of complete equilibrium. According to a formally strict definition of thermodynamic equilibrium, graphite must be included. However, graphite may be considered the end product of the polymerization of higher aromatic compounds—a relatively long sequence of reactions. If the activation energy for these reactions is high and the temperature is low the final product, graphite, may be essentially forbidden. All other compounds involved in the reaction leading to it may achieve only metastable equilibrium quantities. For these kinetic reasons, for which experimental evidence is only implied, some investigators choose to eliminate graphite from their computations and consider only a limited equilibrium distribution (Dayhoff, Eck, et al., 183, 184, 185; Studier, et al., 187). These authors prefer to substitute "asphalt" for graphite since they assume the kinetic hinderance for asphalt is much less than for graphite. Asphalt is a composite of 100 isomers containing six benzene structures with a molecular formula $C_{22}H_{12}$.
Figure 11. Ternary Diagram Showing the Position of the Graphite Deposition Boundaries at Three Temperatures in the C-H-O System.
This substance was included in the earliest computer elimination runs but it consistently caused the underflow condition for the system 360 to be activated, i.e., values less than about E-76 cannot be accepted. It was replaced with C_{7}H_{8} and C_{10}H_{8} which did not underflow but nevertheless were far below my arbitrary cut-off value. It has been shown (Dayhoff, et al., 183) that the threshold for C_{6}H_{6} at the 1.0E-06 level and for asphalt at the 1.0E-06 level at all temperatures in the range of interest and pressures 1 atm or above generally lie on or near the CH_{4}--CO tie line. Lowering the pressure to the E-03--E-06 range brings the C_{6}H_{6} and asphalt thresholds in near coincidence with the H--CO line at 10000K, which is close to the L/H line (see Figure 11) defined in this study. Therefore, it is concluded that at one atmosphere all compositions studied are well removed from any influence of aromatic constituents. This was confirmed since C_{7}H_{8} and C_{10}H_{8} values approached 1.0E-40 atm at L/H 3 and L/H 2. Based in part on my experimental evidence for some condensed form of carbon it was finally decided to include graphite, keeping in mind the foregoing kinetic considerations.

There is a strong division between points T, L/W 1 and L/W 2 (see Figures 10 and 11) and those on the L/H line with respect to graphite. Points L(lunar) and L/H 1 were the two most carbonaceous points examined and exhibit a more or less constant graphite content between 400° and 1000°, albeit not the highest graphite value. This observation is interesting in that it shows that the gram-atomic abundance of carbon and the mole fraction going into graphite, the most stable form of carbon, are not directly proportional. The maximum graphite value appears at L/H 2 at 400°K. As the composition approaches the intersection of the high and low temperature graphite boundaries on the CH_{4}--H_{2}O tie line,
in Figure 11, the graphite values demonstrate a temperature dependence consistent with the relative position of the composition point and the carbon boundary at the temperature of interest. It should be pointed out that these boundaries were defined in a three component system, whereas our calculations involve 19 elements, all of which have the potential of influencing the position of the graphite value. This difference, however, does not seem to have caused any large distorting effect. The graphite value at L/H 2 decreases by one order of magnitude as the temperature increases between 400° and 1000°K. This trend is in line with the movement of the boundary through L/H 2 at about 800°K. On the other side of the \( \text{CH}_4--\text{H}_2\text{O} \) tie at L/H 3 and L/H 4 the change in the graphite value over the same temperature interval is about five orders of magnitude increasing to a lower absolute value at L/H 4 in the carbon deficient zone. These two points lying under the low temperature boundary (unstable) do, as the temperature increases, approach the graphite stable composition.

The gas phase composition for the major expected compounds are consistent with their position on the ternary diagrams in Figures 10 and 11, e.g., at L/H 3 and L/H 4, \( \text{H}_2, \text{H}_2\text{S}, \text{H}_2\text{O}, \text{CH}_4 \) and \( \text{NH}_3 \) in about that order are dominant since they share the common trait of containing mostly hydrogen. Compounds with high concentrations and selected minor constituents of the equilibrium distribution have been graphically displayed in the figures to follow. Only L/W 2, L, L/H 3 and L/H 4 are presented because these represent "special geochemical abundance". In order to prevent the Figures from becoming too crowded, compounds with mole fractions greater than \( \text{E-16 atm} \) which were omitted are listed on the caption page.

The entire list of compounds and their equilibrium values may be found in the Appendix.
Figure 12. The Change in Thermochemical Equilibrium Concentrations for Selected Compounds between 400 and 1000°K and One Atmosphere Total Pressure for Elemental Abundance Point L/W 2 Representing the Present-day Terrestrial Environment.

Compounds omitted for graphical clarity are: N\textsubscript{2}, NH\textsubscript{2}, NH\textsubscript{3}, HCN, HNCO, NH\textsubscript{3}O\textsuperscript{-}, P\textsubscript{4}O\textsubscript{6}, S, CS, HS and CH\textsubscript{2}SO. The remainder lie at concentration levels less than E-16 atm. See Table 10J for the data.
Figure 13. The Change in Thermochemical Equilibrium Concentrations for Selected Compounds between 400 and 1000°K and One Atmosphere Total Pressure for Elemental Abundance Point L/W 2 Representing the Present-day Terrestrial Environment.

See caption for Figure 12 for those substances which have not been included but which have mole fractions exceeding $E^{-16}$ atm.
Graphite

\( \text{CH}_2\text{O}_2 \)

\( \text{CH}_4 \)

\( \text{H}_2 \)

\( \text{CO} \)

\( \text{CO}_2 \)

\( \text{H}_2\text{O} \)
Figure 14. The Change in Thermochemical Equilibrium Concentrations for Selected Compounds between 400 and 1000°K and One Atmosphere Total Pressure for Elemental Abundance Point L Representing the Lunar Environment.

Compounds omitted for graphical clarity are: CH₂O₂, P₄O₆, S, and HS. The remainder lie at concentration levels less than E-16 atm. See Table 10E for the data.
Figure 15. The Change in Thermochemical Equilibrium Concentrations for Selected Compounds between 400 and 1000°K and One Atmosphere Total Pressure for Elemental Abundance Point L Representing the Lunar Environment.

See caption for Figure 14 for those substances which have not been included but which have mole fractions exceeding $10^{-16}$ atm.
Figure 16. The Change in Thermochemical Equilibrium Concentrations for Selected Compounds between 400 and 1000°K and One Atmosphere Total Pressure for Elemental Abundance Point L/H 3 Representing a Primitive Terrestrial Environment.

Compounds omitted for graphical clarity are: C₂H₆O, C₂H₄O, CH₂O₂, NH₂, CH₂N, C₂H₃N, HNCO, NH₃O, CH₃NO, HCl, P₄O₆, S, CS, HS and CH₂SO. See Table 10C for the data.
Figure 17. The Change in Thermochemical Equilibrium Concentrations for Selected Compounds between 400 and 1000°K and One Atmosphere Total Pressure for Elemental Abundance Point L/H 3 Representing a Primitive Terrestrial Environment.

See caption for Figure 16 for those substances which have not been included but which have mole fractions exceeding E-16 atm.
Figure 18. The Change in Thermochemical Equilibrium Concentrations for Selected Compounds between 400 and 1000°K and One Atmosphere Total Pressure for Elemental Abundance Point L/H 4 Representing the Cosmic Environment.

With the exception of many compounds at concentrations greater than $10^{-16}$ atm only at 1000°K all substances included in the calculations are presented in the two following figures. See Table 10D for the data.
Figure 19. The Change in Thermochemical Equilibrium Concentrations for Selected Compounds between 400 and 1000°K and One Atmosphere Total Pressure for Elemental Abundance Point L/H 4 Representing the Cosmic Environment.

See caption for Figure 18 for notation on omitted substances.
A point of consistency between all of these plots is that as the temperature is lowered the concentrations of all substances with the exception of NH$_3$ decrease. First thoughts about this may seem contrary to the behavior of organic compounds with temperature, i.e., most organics decompose at temperatures above 500°K. The compounds included in these computations are being formed from their constituent atoms in the stoichiometric amounts called for by their empirical formulas. While the free energies for the atoms are the same at a given temperature, the free energies for the molecular species vary widely in response to internal bond types and geometry. It is apparent that two compounds will be thermodynamically "competing" for those atoms required for each to form. It is this situation which is in part responsible for the steeply declining mole fractions for the minor compounds. Each molecular distribution will have one or perhaps two dominant low temperature species containing the major elements C, H, O, N and S. For example in L/W 2, (see Figures 12 and 13) H$_2$O, CO$_2$, H$_2$S, SO$_2$ and N$_2$ are the dominant species at low temperatures and would thus be expected to contain all but an extremely small fraction of the total available atoms.

Even though there is no unambiguous proof of this point there are some data here which suggest that the maximum concentration for the two carbon member of a homologous series, i.e., the alcohols, occurs at a lower temperature than for the one carbon member of the same series. This hypothesis is consistent with the observations made on the Fischer-Tropsch process. The metal containing portion of the list is not of primary concern although certain interesting points will be discussed.

As previously mentioned, if the condensable species CaF$_2$ and NaCl among
others were not included the concentrations of HF and HCl would have much higher values. This would in turn use more H and affect the entire distribution and the oxidation state. As it is, HCl and HF are among the components changing most dramatically as a function of temperature, which may be an indication of the effect of F and Cl-containing condensable species.

The calcium compounds would not normally be of special interest when the emphasis is on organic compounds except that calcium carbide, CaC₂, happened to be one of the constituents included in the final list along with CaF₂ and CaCl₂, all in their condensed forms. It must be remembered that the computation started with the lunar abundance which was altered both toward (a) high water and (b) high hydrogen contents. Throughout the series L (lunar) through L/H 4, CaCl₂ and CaF₂ exhibited trends which for lack of comparison information were not particularly interesting (see Tables 5 and 10A through 100). A summation of thermochemical data for the carbides has been compiled in Table 5. Calcium carbide, in contrast, remained at high values, decreasing only modestly between L and L/H 4 and remaining constant at all temperatures between 400 and 1000°K at a fixed composition. This observation lead to suspicions about the authenticity of the free energy equation (Richardson, 96). The same trend was observed between L and L/W 2. Noting CaC₂ as an important constituent in a composition which is 99% water only strengthened the faulty data suspicion. A decision to remove CaC₂ at that point was dismissed since it would have necessitated several recomputations. The last elemental abundance point to be computed was the terrestrial; interestingly the CaC₂ value fell 17 orders of magnitude at
1000°K and at least 74 orders at 4000°K, yet nothing unusual happened to CaF$_2$ or CaCl$_2$. The gram-atomic abundances (see Table 4) for Cl, F and C are all greater in the terrestrial makeup than in the lunar one. This would suggest that the fluoride, chloride and carbide of calcium, along with other halogens, would be more prominent in the terrestrial distribution. This is not the case, at least for calcium halides. A partial explanation is that the lower amount of Ca in the terrestrial abundance is responsible. The changes in CaC$_2$ mole fraction noted above for a 68.5% reduction in Ca certainly indicate an extreme sensitivity toward that element, especially when the increase in carbon abundance was almost three times the decrease in calcium.

This extra attention being directed toward CaC$_2$ stems from a statement made in connection with the problems of accounting for chemical forms of carbon in lunar samples. Oro, et al., (75) hinted that there may be components in lunar samples, such as carbides, which are stable on the Moon but decompose upon being subjected to the relatively humid conditions of the lunar sample receiving laboratory and subsequent environments. It is well known that alkaline earth carbides are explosively reactive with H$_2$O and produce predominantly acetylene. The overwhelming value for CaC$_2$ under such widely varying conditions of composition and temperature tends to support such a hypothesis.
Table 5. Negative Logarithms of the Equilibrium Values for the Carbides and Graphite at 800 and 1000°K for All Elemental Abundance Points.
<table>
<thead>
<tr>
<th>Elemental Abundance Point</th>
<th>Temp. °K</th>
<th>CaC₂</th>
<th>Fe₃C</th>
<th>SiC</th>
<th>TiC</th>
<th>Grap.</th>
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</table>
Of course, there are some aspects of the computations which can have an effect. First, a change in the abundance of Ca will, as already described, have a drastic effect upon the CaC$_2$ value. Secondly, the inclusion of another Ca-containing compound more stable than CaC$_2$ will also be influential. This entire discussion of CaC$_2$ may be based on coincidences, but when theoretical evidence, experimental evidence and independent hypotheses begin to converge the coincidence, if it is one, becomes more credible.

Contrary to the predominantly wayward behavior of CaC$_2$ in the equilibrium computations, the other carbides TiC, SiC and Fe$_3$C followed expected trends, that is, marked deviations appear as the elemental abundance moves away from the L/H line toward the compositions on the L/H$_2$O line. Here it can be concluded that the presence of water distinctly affects the equilibrium mole fraction for these carbides. Carbide values also maximize in L/H 2 at about 8000°K exactly like most of the organics. This suggests that in an all-inclusive equilibrium the carbides are competing with the organic constituents for the available carbon. Fe$_3$C, the form known as cementite, demonstrates the least variability at high temperatures throughout those points defining the L/H line. The absolute values of its mole fractions lie just inside the boundary of detectability if the carbon hydrolyzed to produce mainly CH$_4$. The Fe$_3$C information derived here along with that from the hypothetical equilibration of Hawaiian basalt (described earlier) implies that this carbide may be important in dry magmatic environments such as that which probably occurred on the Moon.
In Table 6 equilibrium values for the alcohols, aldehydes and acids and the corresponding hydrocarbons have been compiled in a manner permitting some general observations on the role of these partially oxygenated organics in the various compositions which have been studied here. These partially oxidized organics are generally regarded as important in prebiological chemistry because they are water soluble, chemically reactive and polar.

First, at most conditions of composition and temperature the acids are dominant over the alcohols of the same carbon number. One might wonder how this observation interacts with the hypothesis that the F-T synthesis proceeds through an alcohol intermediate. Second, the relative trends between these three partially oxidized types of substances are readily related to their positions on the C-H-O ternary diagram. The mole ratio of C, H and O in formic acid, formaldehyde and methanol are: 20:40:20, 25:50:25 and 17:66:17, respectively. These proportions change as the methylene portion of the molecule is lengthened, i.e., as it becomes more like a hydrocarbon. It can be seen that methanol followed by formaldehyde are the most hydrogenous compounds and also the least oxygenated. This would position them in the area of the ternary C-H-O diagram which includes abundance points L/H 3 and L/H 4. Formic acid is the most oxidized specie of the three and thus would be expected to attain prominence nearer the oxidized side of the diagram. These relationships are displayed in Figure 20.
Table 6. Summary of Equilibrium Concentrations at All Temperatures for Simple Hydrocarbons and Their Partially Oxygenated Alcohols, Aldehydes and Acids at the Seven Elemental Abundance Points Noted.

All values are negative logarithms of the mole fraction at one atm total pressure.
<table>
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<tr>
<th>Elemental Abundance Point</th>
<th>Temp. °K</th>
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<th>C(_2)H(_6)</th>
<th>C(_2)H(_4)</th>
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<td>CH(_2)O (_2)</td>
<td>C(_2)H(_4)O (_2)</td>
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Figure 20. Approximate Ranges of Dominance Amongst the Hydrocarbons and Their Partially Oxygenated Compounds.
Table 7. Selected Values of $\frac{pCO_2}{pCO}$, $\frac{pH_2O}{pH_2}$ and $pO_2$ from Two Thermochemical Equilibrium Calculations and the QFM at Three Temperatures and One Atmosphere Total Pressure.
Since the QFM had not yet been defined, Heald, et al., (31) could not have discussed the gross differences between their equilibrium values for pH$_2$O/pH$_2$ and pCO$_2$/pCO and the same ratios derived from an assumed water-gas equilibrium in the Fe-O system (see Figures 1 and 2). In the abbreviated Table below a few values are presented in reference to the following discussions and figures.

<table>
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<tr>
<th>Study</th>
<th>Temp °K</th>
<th>pCO$_2$/pCO</th>
<th>pH$_2$O/pH$_2$</th>
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<td>5.8E 00</td>
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</table>

Figure 21 shows both the QFM oxygen requirement as defined by Eugster and Wones (139) from Appendix 1 and those derived from this study (see Table 8C). Although 1000°K is highest temperature employed here, it can be seen that high temperature values will be in good agreement. But this agreement rapidly degrades as the temperature is reduced. Possible reasons for these divergencies will be discussed after the QFI buffer system is examined.

Because the QFM diverges at low to intermediate temperatures from the results of the present equilibrium study, it should be expected that the QFI would do likewise. In Figure 22 the theoretical QFI is shown to diverge very strongly from the results of the equilibrium calculations for our proposed lunar elemental abundance.
Williams (276) has considered the formation of both magnetite and hematite in lunar rocks through their equilibrium with the fluid phase. He concluded that at 875°K magnetite become stable, while at around 400°K hematite stability is attained. In an attempt to explain those few instances where magnetite and hematite have been observed in lunar rocks, he invoked the equilibrium hypothesis. Most other investigators simply chose some non-equilibrium special mechanisms to explain oxidized species in these strongly reduced environments. A problem to reckon with is the achievement of equilibrium in a natural system at these low temperatures. It seems reasonable to assert that equilibrium could only be attained on the surface of a rock which is in intimate contact with the volatile phase.

There are several contributing reasons for the discrepancies between both of the mineralogical buffers and the results of this study.

(a) It was pointed out by Richardson, et al., (141) and Eugster and Wones (139) that the extrapolation of high temperature mineralogical information to lower temperatures was subject to uncertainties. This statement applies specifically to the QFM and the QFI values in Appendix 1, and to the position of the QFM line in Figures 1, 2, and 21 and 22 and the QFI in Figure 22.

(b) The calculations presented in this study are, for the sake of simplicity, assumed to be a single gaseous phase. The condensed particles have been assumed to be finely comminuted and to be in equilibrium. Adler and Dluznieski (268) have recently revealed the development of a computer
programs for complex thermochemical equilibria capable of accommodating phase changes.

(c) It is possible that the inclusion of sulphur compounds into this study and the one by Heald, et al., (31) contributes to the strong tendency toward higher $f_{O_2}$ values at the lower temperatures.

In summary, it is not possible at this time to determine whether the QFM and the QFI are too reduced or the thermodynamic calculations presented here are too oxidized. The strong tendency toward oxidizing conditions is probably partially responsible for the sharply decreasing concentrations of organics observed at the lower temperatures. If the oxidation state predicted by the QFM and the QFI had prevailed instead of the more oxidizing ones (this study), these decreases might have been less dramatic or even absent for some compounds.
Figure 21. Stability Regions for the Iron Oxides in the Iron-Oxygen System as a Function of Temperature and the ratio of water to hydrogen at 1.0 Atmosphere Total Pressure.

The QFM line is drawn as in Figure 1 and 2. The lighter line (dashed above $1000^\circ$K) which deviates sharply from the QFM represents the results of the equilibrium calculations in this study for the terrestrial abundance point. Possible reasons for its deviation are given in the text.
Figure 22. Stability Regions for the Iron Oxides in the Iron-Oxygen System as a Function of Temperature and the Ratio of Water to Hydrogen at 1.0 Atmosphere Total Pressure.

The QFM line is drawn as in Figures 1 and 2. The QFI line has been included (see Appendix for QFI values). The lighter line (dashed above 1000°K) which deviates sharply from both the QFM and the QFI represents the results of the equilibrium calculations in this study for the lunar abundance point.
V. GEOCHEMICAL DISCUSSIONS

A. Factors Which May Influence Organic Compound Formation in Natural Systems

The following discussions will attempt to correlate the experimental observations derived from this study and the equilibrium computation in relation to volcanic environments on the Earth (both presently and earlier in its geological history) and on the Moon. Factors to be incorporated are: (a) the selective loss of hydrogen gas from lava containing its magmatic gases, (b) the mode of cooling (equilibrium or quenched), (c) potential catalysts in the lava and possible poisoning agents in the gas, (d) the gas phase composition (based on the equilibrium computations included herein).

1. The Selective Loss of Hydrogen

A consideration of general consequence to a cooling gas-solid system is the selective loss of certain gaseous constituents. First, it must be assumed that upon eruption the gas phase which is trapped within the congealed lava has the same composition as the volatile phase which is lost to the atmosphere and further that this composition represents an equilibrium mixture. Because of its molecular size (susceptible to diffusion) and its importance in hydrocarbon formation, hydrogen is the substance most likely to be affected by selective removal from its confinement to zones of lower pressure. The diffusion of $H_2$ would presumably be enhanced, especially at higher temperatures, if the silicate mass was highly vesicular. It may well be that hydrogen diffuses away so rapidly that by the time a temperature favorable for the Fischer-
Tropsch synthesis has been reached, the initial $H_2$ has all but left the "reaction vessel".

It should be recalled that hydrocarbon formation by the F-T synthesis is a rather low temperature occurrence (under $600^\circ$K). The only hydrogen then available would be through the dissociation of water which at low to intermediate temperatures could supply only very small amounts. Another factor in the loss of $H_2$ from the volatile phase might be the nature of the internal surface surrounding the gases. Naturally contractional cracking will provide avenues of ready escape. A glassy internal surface may be a reasonably good barrier to rapid gas transport out of the confinement, while a vuggy internal surface would be expected to loose its gases more rapidly. In our attempts to choose field samples suitable for residual gas measurements we select blobs of chilled lava free of gross surface cracking. It is thought that these might retain the magmatic gases in about the same relative proportions as the volatile phase. Preliminary investigations using both gas chromatography with in-line sample crushing and long path infrared spectrometry support this conclusion to at least a first approximation.

It should be recalled from an earlier section that Shepherd (42) claims one could transpose magmatic gas data with that derived from rock degassing and be accurate to within the normal deviation in both. If nonrepresentative field sampling of magmatic gases is a significant source of error, as suggested by Nordlie (111), then the gases retained in vesicles in chilled lava and along grain boundaries will exhibit a close correlation with the magmatic gases with which it erupted. A distinct advantage in studying gases from rocks over gases in sampling
flasks is that the nonrepresentativeness of vesicles is swamped by the number of them. There are, on the other hand, analytical difficulties associated with it. It may well be that the success in the comparison of volcanic gases with gases extractable from lavas by Shepherd is the direct result of the freshness of the specimens.

There is some information which may be called a $H_2$ diffusion anomaly, if the real situation is indeed governed by diffusion. It concerns the measurements of $O_2$ fugacities by Sato and Wright (146) which were described in the section on oxygen fugacity determinations. They were not definitely able to rule out the possibility that the observed anomaly was in some way related to the behavior of the solid-state electrochemical cell which formed the active part of the probe. It should be noted that if $H_2$ can selectively diffuse through lava as suggested here, this would have an important influence upon hydrocarbon formation in the following discussion since the optimum $F-T$ temperature is about 200° below the lower limit of the temperature range for the selective loss.

With the fragmented evidence just reviewed it is not possible to conclude whether differential losses of magmatic hydrogen occur from vesicles as the specimen cools. It is expedient simply to assume that it does not occur to any significant extent within the time span of the loss of heat from the mass of lava under consideration.

2. Catalytic Poisoning

The following discussion is hypothetical since there is no field or laboratory evidence to even suggest that magmatic gases may act as poisons in gas-gas reactions in a cooling melt. The nearest situation
is low temperature industrial catalytic poisoning which has been discussed earlier. An attempt to analyze qualitatively the possibility of catalytic poisoning in a complex gas-solid system such as a mass of magmatic gas trapped within vesicles in lava must take into consideration the following:

(a) The appearance of the catalyst and the poison relative to temperature. This point is rather clear since the catalyst (Fe or FeO) will have been exsolved from its parent residuum at a high temperature and will be present along the grain boundary or on the inside surface of the vesicle at temperatures well above those involved in the F-T synthesis. Although it is simplest to assume that the active form is directly exsolved from the melt, there are references to processes called subsolidus reduction which may mean that the active form appears at lower temperatures. Subsolidus reduction in the opaque minerals reported by El Goresy, et al., (45) and Haggerty (181) in Apollo 12 and 14 samples is of more than academic interest to this project. The minerals fayalite and chromium ulvospinel have been observed to breakdown completely to metallic iron and some oxide. The importance of iron as a catalyst in the F-T synthesis has been mentioned elsewhere in this report. The lowest inferred temperature in this process lies above those normally encountered in the F-T synthesis. One would therefore predict that CH₄ would be the dominant product of gas-solid reactions involving subsolidus catalytic activity.
Lunar magmatic gases have been shown elsewhere to be hydrogen deficient. In this case, the carbon monoxide in the presence of reduced lava might favor another reaction, perhaps one leading to carbides.

(b) Another consideration in this discussion is that the gas phase present upon eruption will most likely contain the poison, but there is evidence which suggests that volatiles which do not vesiculate are concentrated in that portion of the melt which solidifies last. In a careful analysis of the gas evolution characteristics of a cooling, crystallizing melt it may be necessary to study the chemistry of this residuum in order to predict the appearance of the catalytic poison.

(c) A third consideration to be accounted for is the heterogeneity of the host matrix in which the reactive gases and the catalytic poison are trapped. Even the most finegrained rock is heterogeneous on a microscale and thus there could be gases in vesicles and grain boundary confinements which do not necessarily have to be in contact with a mineral surface exhibiting some catalytic potential. Under most conditions the trapped gases would through their thermal motion be able to come in contact with these surfaces. Studier, et al., (187) attempted to utilize somewhat similar logic of localized heterogeneous catalysis only affecting its immediate gas phase environment. In their brief discussion it appears that the high mobility of gases may not have been fully considered.
Points L/H 2 and L/H 3 (see Figure 10) are the extremes in a range of compositions which represent optimum conditions in the F-T synthesis. Organic compounds with the greatest diversity and the highest concentrations occur between these two points. The overwhelming concentration of $H_2S$ (see Figure 16) hints at the importance of catalytic poisoning of the metallic iron fraction of the "equilibrium catalyst" (see Table 8A and 8B). Some indirect evidence, however, suggests that the $H_2S$ mole fraction is higher than it should be in an all-inclusive equilibrium. This is because no condensed sulphides, or even condensed sulphur-containing species, were included in the computations. It is proposed that the same situation would have affected the $H_2S$ concentration here. If FeS had been included, the $H_2S$ might still have been the major sulphur gas but its catalytic poisoning capacity, which is concentration dependent, would not be as important as the high mole fraction values might imply. We know that troilite, FeS, is a common mineral phase in lunar rocks. The presence of metallic sulphides is also known to form in terrestrial lavas (Moore and Calk, 255). In the latter, it is interesting to note that these sulphides form on the walls of the vesicles where the bulk of the gas phase would be expected to be located.

If, as already discussed, the F-T synthesis can be made to assume a degree of equilibrium (generally expressed as a CO conversion value) strongly dependent upon the choice of operating conditions, attempts to apply theoretical thermodynamic calculations to a normally non-equilibrium system can lead at best to a tenuous interpretation. The information contained in Tables 8A, B, C and D has been extracted and compiled from the computer generated equilibrium calculations. It is
grouped according to composition and lists some parameters helpful in assessing the importance of the Fischer-Tropsch synthesis in a system at complete equilibrium. The \( \text{H}_2\text{O}/\text{H}_2 \) and the \( \text{CO}_2/\text{CO} \) values have already been discussed.

Two factors important in the F-T process are the ratio of \( \text{H}_2/\text{CO} \) and the total pressure of their sum. It is interesting that the equilibrium \( \text{H}_2/\text{CO} \) changes from a slightly decreasing to a drastically increasing function with increasing temperature, as the composition changes from the lunar toward the hydrogen-rich end. The transition begins to appear in \( \text{L}/\text{H}_2 \) and continues into \( \text{L}/\text{H}_3 \) (see Tables 8A and 8B). In \( \text{L}/\text{H}_2 \) a maximum for many simple organics appears at about 800\(^\circ\)K (see Appendix 4, Table 10B). \( \text{CH}_4 \) is the organic constituent at maximum concentration at all temperatures and compositions. As the composition approaches the H-rich end, ethylene goes above ethane at 1000\(^\circ\)K despite the fact that \( \text{L}/\text{H}_3 \) lies further from the \( \text{C}_n\text{H}_{2n} \) point than it does from the \( \text{C}_n\text{H}_{2n+2} \) point. The extraordinary stability of \( \text{CH}_4 \) over other hydrocarbons maintains its dominance at all points, even at \( \text{C}:/\text{H}:/0::33:66:01 \) which is in near coincidence with \( \text{C}_n\text{H}_{2n} \) (Dayhoff, et al., 185, pp.24, 30, 33). Ethylene does maximize at this point but its mole fraction is seven orders of magnitude below \( \text{CH}_4 \) at the same point.
Table 8. Selected Parameters to Evaluate the Potential of the Fischer-Tropsch Synthesis to Contribute Hydrocarbons to an Equilibrium Distribution of Products.

These values have been derived and compiled from the equilibrium Tables given in Appendix 4.
### Composition Point L/H 1 at 1.0 atm

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<td>77% Fe 23% Fe0</td>
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### Composition Point L/H 4 at 1.0 atm

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<th>press.</th>
<th>$H_2$</th>
<th>$H_2O$</th>
<th>$CO_2$</th>
<th>$H_2$</th>
<th>press.</th>
<th>press.</th>
<th>Notes on Iron States</th>
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<td>$H_2$</td>
<td>$H_2O$</td>
<td>$CO_2$</td>
<td>$H_2$</td>
<td>press.</td>
<td>press.</td>
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<td></td>
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<td>3.8E+03</td>
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### Composition Point Terrestrial at 1.0 atm

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### Composition Point L/W 1 at 1.0 atm

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<tr>
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<td>8.0E-03</td>
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</table>

### Composition Point L/W 2 at 1.0 atm

<table>
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</thead>
<tbody>
<tr>
<td>400</td>
<td>1.4E-07</td>
<td>7.0E+06</td>
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<td>600</td>
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<td>5.2E-03</td>
<td>all FeO</td>
</tr>
</tbody>
</table>
3. Mode of Cooling: Equilibrium or Quenched

The concentration of simple organics of possible prebiological significance in the equilibrium Tables 10, Appendix 4, especially those of L/H 2 and L/H 3, and to a lesser extent L/H 4, can be interpreted as the equilibrium thermal contribution to the "prebiological soup"—a term commonly used to denote the medium in which life originated. As suggested earlier, equilibrium cooling of magmatic gases with their eventual liberation from the silicate matrix by diffusion or weathering is a tiny fraction of the total thermal volcanic contribution to the early atmosphere, as that source is relevant to the present atmosphere. A much larger bulk of primitive Earth magmatic gases would have been ejected into the atmosphere to be cooled by quenching. Because lava cools with a rather high temperature equilibrium composition this might additionally imply that the gases in the primitive atmosphere and the lava with which they erupted were probably in disequilibrium. A similar situation presently exists. Fresh lava containing iron predominantly as magnetite is out of equilibrium with the present-day terrestrial atmosphere. A partial consequence of this disequilibrium causes weathering of fresh lava to more stable constituents. In the case of the iron in magnetite, the product is hematite.

It can be seen through an examination of the equilibrium Tables 10 for L/H 2 and L/H 3 that large amounts of H₂, H₂O, N₂, CH₄ and H₂S could have been brought to the Earth's surface through volcanism by either equilibrium or rapid cooling. Because methane is the most stable low temperature form of carbon, the only means by which CO and CO₂ could have attained appreciable levels is through quenching at the eruptive
temperatures. \( \text{CH}_4 \) stability begins to drop off at about 800°K and is replaced by CO and \( \text{CO}_2 \). The CO molecule has been inferred as an important UV absorber in the initiation of photochemical reactions (Dauvillier, 11). The one substance which presents some difficulty is \( \text{NH}_3 \). It is unstable at high temperatures (recall one laboratory explosion and its low synthesis temperature from the elements). It appears that if it was ever an important primitive Earth atmospheric gas, it must have come to the surface in low temperature equilibrium situations, probably through fumarolic or hot spring activity. Furthermore, the residence time would be short if the oceans were acidic. At the other extreme hot springs made acidic by sulphur gases would probably not allow any basic \( \text{NH}_3 \) to be released. It would remain in solution as \( \text{NH}_4^+ \). The high temperature instability and the acidic aqueous sources seem to narrow the surface source of \( \text{NH}_3 \) to a magmatic source in low temperature equilibrium with the lava. The possible contribution of N as \( \text{NH}_4^+ \) (e.g., \( \text{NH}_4\text{Cl} \)) in the gas phase and its chemical behavior relative to \( \text{NH}_3 \) in photochemical and thermal reactions has not received much attention.

It is the temperature incompatibility between CO and \( \text{NH}_3 \) which led Studier, et al., (187) to have a concern for the kinetics of the competing reactions: \( \text{CO} = \text{CH}_4 \), \( \text{CO} = \) higher hydrocarbons, and \( \text{CO} + \text{NH}_3 = \) nitrogeneous organics. Hydrogen cyanide has been shown to form readily from CO and \( \text{NH}_3 \) on alumina catalysts (Tanaka, 241). \( \text{CO}, \text{H}_2 \) and \( \text{NH}_3 \) and their deuterated analogues have been shown to produce amino acids, purines and pyrimidines, as well as hydrocarbons under widely varying experimental conditions using thermal energies (Yoshino, et al., 179; Hayatsu, et al., 180; Harada and Fox, 16; Oro, 214). In some of the
very earliest experiments in this project thermal synthesis of a few amino acids from CH₄, NH₃, H₂ and H₂O was observed by thin-layer chromatography using ninhydrin, but they were not identified.

With the possible exception of gas phase NH₃ (or NH₄⁺) it is relatively easy, based on the concepts presented here, to propose a primitive atmosphere on Earth derived from volcanic emissions at thermodynamic equilibrium. This is the basis of the proposal by Oparin (7) and the "jumping off point" for the hundreds of laboratory experiments using CH₄, NH₃, H₂ and water activated by various forms of energies to produce rather complex organic compounds.

B. Interpretation of Equilibrium Calculations to Magmatic Systems

As a matter of convenience for the following discussion the terrestrial, the lunar and the primitive volcanic compositions will be designated each by one of the compositions points in Figure 10. The terrestrial volcanic composition (reasonably well established by Hawaiian-type data) will be, of course, the point T, or its lunar-derived analogue L/W 2. The lunar magmatic composition is designated L, although deviations from that will also be considered. The primordial composition will be L/H 3.

1. Present-day Terrestrial Magmatic Composition

Tables 10G and 10H in Appendix 4 show that the equilibrium quantities of magmatic gases at 1000°K agree with the results of field samplings of gases from lava lake drill holes and vents in intimate contact with molten lava (White and Waring, 24; Finlayson, 26; Shepherd, 42; Naughton, 238). Table 10I contains equilibrium values for the terrestrial composition at 1400°K from another source (Naughton, 235) and may be con-
sidered a partial high temperature extension of Table 10H. Hydrogen sulphide begins to taper off in importance at about 900°K and at the erupting temperature is a minor contributor to the sulphur-containing volatiles. This is in accord with its high temperature instability and reaction with water to form \( \text{SO}_2 \) and \( \text{H}_2 \) by

\[
\text{H}_2\text{S} + 2\text{H}_2\text{O} = \text{SO}_2 + 3\text{H}_2.
\]

Because of its oxidative reactivity with water which resulted in a minor interference for the other sulphur species \( \text{S}_2 \) and \( \text{SO}_2 \), Matsuo (114) has calculated \( \text{H}_2\text{S} \) concentrations at the erupting temperature for the samples analyzed by Shepherd (42). He arrived at a \( \text{H}_2\text{S}/\text{SO}_2 = 0.024 \) which is agreeable with Table 10I. The drillhole data by Finlayson (26), although containing many analyses without \( \text{H}_2\text{S} \), are also in agreement when that value was supplied. Although \( \text{CO} \) does not become more prominent than \( \text{CO}_2 \), it may, at high temperatures and in contact with the ambient atmosphere, be a minor contributor to magmatic gas flaming.

Examination of Figures 12 and 13 for selected simple organics reveals the paucity of organic compounds with equilibrium partial pressures high enough to exceed the lower limit used in these plots. There are no organics with equilibrium concentrations at any temperature which are high enough to warrant any special attention. The very small amounts of \( \text{CH}_4 \) observed in the high steam experiments in this study are due mainly to the larger amounts of carbon relative to water vapor in the experiments. No explanation can be advanced why the ratio of \( \text{CH}_4/\text{C}_2 \) hydrocarbons is 13 orders of magnitude in the equilibrium calculations and only about one in the experiments.
It ought to be noted that the highest mole fraction for simple organics occurs at 1000°C for all compounds investigated for this composition. This should not, however, be construed to predict that these values will continue to increase at higher temperatures. If equilibrium values for temperature exceeding 1000°C were available, it is believed they would not differ substantially from the 1000°C values and would most likely be less. This can be substantiated to some extent by observing the change in equilibrium mole fractions as a function of increasing temperature where a levelling off is apparent as the high temperature is approached. It is common knowledge that organic compounds are unstable in an oxidizing environment at reasonably low temperatures. The oxygen fugacity here at 1000°C is on the order of $10^{-19}$ atm, which is not oxidizing in any sense, but it does exert an important controlling influence over the equilibrium concentrations for the organics.

The absence of any significant organics under the terrestrial conditions is also supported by values in Table 8C and 8D. Here it can be seen that in the low to intermediate temperature interval conditions required for a Fischer-Tropsch synthesis are very poorly satisfied. For example in Table 8C at 600°C for the terrestrial composition the pressure of H₂ is $8.7 \times 10^{-6}$ atm, the H₂/CO ratio is 620.0 and the total pressure of H₂ plus CO is the same as that for hydrogen alone. This says that there is "no" carbon monoxide (note pCO₂/pCO value) and a

*It will be assumed for this discussion that the best conditions a Fischer-Tropsch synthesis will be a H₂/CO ratio in the general range of values on page 131. Additionally the total pressure of H₂ + CO must be as high as possible since the F-T process uses predominantly these two gases at moderately high pressures. One would easily predict that a total pressure reduction would have a significant effect upon the amounts of hydrocarbons and other organics. Both of these conditions must be met at low to intermediate temperatures.
severely depleted \( H_2 \) partial pressure. With the "catalyst" composition being less than ideal, i.e., no reduced iron, and a gas phase lacking favorable F-T chemical requirements, it can be concluded that this reaction is unimportant for this composition.

2. Proposed Lunar Magmatic Composition

The lunar and the terrestrial abundances share one similarity, i.e., both are deficient in one of the three elements used in Figures 10 and 11, the lunar in H and the terrestrial in C, relative to the other two elements. The manifestation of these deficiencies is that \( H_2O \) is the most important terrestrial magmatic gas and CO and \( CO_2 \) are the most important lunar magmatic gases, excluding \( N \) and \( S \)-containing gases which cannot be displayed on a C-H-O ternary diagram. The H deficiency in the lunar composition leads directly to another situation where the conditions, as defined, are unsuitable for hydrocarbon formation by the F-T synthesis. It can be seen in Table 8C that nowhere in the temperature interval does the \( H_2/CO \) ratio come close to the favorable values.

In the terrestrial composition two of the three F-T conditions are at least being approached but at a very high temperature. The "catalyst", however, was absent since the high value of water prevented the iron from becoming reduced. In the lunar composition the two parameters used to evaluate the potential for the F-T synthesis diverge with temperature, i.e., \( pH_2/pCO \) gets favorable at low temperatures while their total pressure decreases. This same relationship persists at L/H but to a lesser degree (see Table 8A).

Even though the stoichiometric ratio between hydrogen and CO fails to develop in the lunar or the terrestrial composition the F-T
synthesis may be thought to proceed to an extent limited by the amounts of the least abundant reactant. For example in the lunar composition at 600°K, it can be seen that (1000) (pH₂) = pCO and pH₂ = 2.3E-08 atm. Ideally then a F-T synthesis (assuming pH₂: CO::2:1) could proceed to the extent limited by (1/2) (2.3E-08) whereupon the available H₂ supply would be exhausted.

Of the two composition points expected to demonstrate the most favorable F-T conditions L/H 2 meets the requirements best since the two chemical parameters appear to optimize at a reasonably low temperature. The optimum F-T chemical requirements would naturally fall on the line joining H and CO which is similar to the line L/H defined earlier in this study. The pressure of H₂ plus CO increases going toward L/H 4, but the highest value is not optimum since the ratio is equally important. The values in Table 8A indicate that optimum chemical requirements are attained in L/H 2 at about 800°K. The "catalytic element" of having free iron is also met. This optimum is of course temperature dependent and appears to shift toward L/H 1 as the temperature is reduced. It should be noted in Table 10B that the concentration of almost all of the trace organics do indeed maximize at about 800°K in L/H 2 and this is the only elemental abundance point where this was observed to happen. In Figure 10 it is seen that L/H 2 is indeed very close to one of the stoichiometric proportions for the Fischer-Tropsch process. It would be interesting, but not presently possible with this FORTRAN program, to specify and hold constant partial pressures of hydrogen and carbon monoxide which fulfill optimum conditions of relative proportions and total pressure and have the remaining composition
equilibrate around them. This would give greater insight into the role of the Fischer-Tropsch reactions in an equilibrium distribution of products.

Based on our proposed lunar composition the agreement between volatile species released from lunar samples and the results of thermodynamic equilibrium is rather good. Our computations show in decreasing abundance the following: $S_2$, CO (0); $N_2$, CO$_2$, COS (1); CS$_2$, H$_2$S (2); H$_2$, SO$_2$=H$_2$O=SO (3) for the lunar composition at 1600°K and 1 atm. The numeral in brackets is the order of magnitude for the negative log of the mole fraction. Table 10F contains lunar equilibration concentrations for selected major components from another source but for exactly the same gramatomic composition. It may be considered a high temperature extension of Table 10E. The Compound abundance changes to $S_2$, COS (0); CO$_2$, CO=CS$_2$, $N_2$ (1); H$_2$S (2); H$_2$=H$_2$O (3) at 1000°K (the lowest temperature where equilibrium could be expected to be established in a reasonable length of time relative to the cooling of the specimen). Before one attempts any comparison it must be assumed that the distribution of molecular species is dependent upon total pressure in a uniform manner.

Due to insufficient data and the high variability between samples it is not possible to derive a typical volatile abundance distribution list for lunar samples, although H$_2$, N$_2$, CO$_2$, CO, H$_2$S and SO$_2$ are most frequently reported (Gibson and Johnson, 77; Funkhouser, et al., 76). Much of the H$_2$, most of the CO$_2$, and an undetermined portion of the others appear to have been derived through solar wind implantation. The most notable exception between the thermodynamic values and the qualitative list above is, as expected, in the sulphur compounds, which again are overemphasized because a condensible sulphur specie was
not included in the computations. Murphy, et al., (239) and Hamilton, et al., (240) do present mass spectrometric evidence for all sulphur-containing substances in the equilibrium list. An important question affecting any quantitative information concerning volatiles in lunar basalts which are residual from a magmatic origin is the total gas phase pressure upon eruption. Funkhouser, et al., (76) estimated a pressure of two to three torr from their measurements.

Strong evidence has already been presented that the simple hydrocarbons sometimes found in lunar samples are the results of solar wind interactions. Another possibility is the in situ hydrolysis of lunar carbides by water vapor once the samples are exposed to the terrestrial atmosphere (Oro, et al., 75). The equilibrium concentrations of CH₄ and the C₂ hydrocarbons calculated from our proposed lunar composition (Table 10E) would have to undergo sizeable concentration mechanisms in order to reach even the ppb range normally reported in lunar samples. About the only concentration process which might be invoked, and then only to a limited extent, is that which involves the concentration (actually a redistribution) of volatiles in the mineral constituents which are last to solidify. If, however, the actual lunar magmatic composition was closer to L/H 1 than L in Figure 10, the differences between equilibrium values and instrumentally detectable levels are not as great. At this point it should be recalled from an earlier discussion that our proposed lunar composition is only an approximation. It has been derived from rather basic assumption commonly used in similar situations when little experimental information is available.
3. Primitive Earth Magmatic Gases

As suggested elsewhere, L/H 2 and L/H 3 in Figures 10 and 11 are representative of popular concepts about the composition of the early terrestrial atmosphere, "In the beginning when God created ...," and perhaps the atmospheres on other planets in our solar system. If it is assumed that equilibrium magmatic gases were the major contributor to this early atmosphere (and this seems to be accepted) then the composition of the magmatic gases and the early atmosphere would exhibit similarities. The degree of dissimilarity would, of course, be dependent upon removal factors such as: (a) the removal of atmospheric constituents to the primitive oceans (solubility), (b) removal by reaction with surface rocks (weathering), (c) removal by reactions occurring in the atmosphere under the influence of other forms of energy capable of initiating chemical reactions. Despite strong tendencies for some substances to decrease sharply with temperature, a summary of constituents for L/H 2 and L/H 3 (see Tables 10B and 10C) are as follows: major components: H₂O, H₂, N₂S, CO and N₂; minor components: CO₂, CH₄, NH₃, COS, CS₂, CH₄S and S₂; trace components: HCN, C₂H₃N, HNCS, HNCO, C₂H₂O₂, CH₂O and CH₄O. In such a generalized summary, one must be aware of irregularities such as that demonstrated by CO₂, CO and CH₄ which will be touched upon in the next section. It is also important to note that NH₃ is always at its minimum at high temperatures.

One is directed to some of the readings suggested in the Introduction to see how these gases are proposed to have interacted with each other, with the solid crust of the primitive Earth, and with the oceans which are believed to have been acidic as opposed to the slightly alkaline conditions today.
C. Magmatic Gas Input and the Evolution of the Earth's Atmosphere

The major theme of this project was to examine compositional differences between terrestrial and lunar volcanic gases and potential for the formation of simple organic compounds from these gases under the influence of thermal energy. Volcanism is only a part of the environment of the Earth and therefore needs to be integrated into the whole. The assumption that the atmosphere and hydrosphere is a direct result of planetary degassing and crustal rock weathering is generally accepted (Rubey, 244; Sillen, 245). In this important role it becomes a challenge to attempt to relate volcanic and fumarolic gases to the present-day atmosphere and also, but in a less direct manner, to the origin and maintenance of life on Earth.

1. Magmatic Inputs to the Surface Environment

The comparison of total carbon content in Hawaiian submarine basalts with those erupted on the surface offers an opportunity to compute the amount of carbon as \( \text{CO}_2 \) which is released into the surface environment (atmosphere, hydrosphere and the biosphere).

The volume of lava extruded during two Halemaumau eruptions and the first seven months of the present Mauna Ulu eruption has been estimated by Swanson (266) at \( 2.05 \times 10^8 \text{ m}^3 \) on a nonvesicular basis. The volume estimates for the two Halemaumau contributions are quite accurate because the eruptions were confined to a crater of known dimensions. These estimates, however, do not take into account that the majority of the Halemaumau lava was confined to the firepit and that the 1952 lava was, for the most part, recycled in the 1967-68 eruption. For the purpose of the following calculation, it is assumed that the entire volume
was degassed upon eruption.

For surface erupted basalts the total amount of carbon can be computed using the following values: (a) vesicularity 15% by volume (Moore, J., 36; Swanson, 266), (b) specific gravity 2.2 grams per cm³ (Moore, J., 36), and (c) total carbon content 40 micrograms per gram of lava* (Moore, C., 165, see p. 116). With these values 2.05E+08 m³ of Hawaiian basalt would contain 2.7E+10 grams of carbon.

If this volume of lava had erupted on the ocean bottom such that the loss of carbon-containing volatiles was at a minimum, the total amount of carbon can be computed using the following values: (a) no vesicularity factor**, (b) specific gravity 3.0 grams per cm³ (Moore, J., 36), (c) total carbon content 91 micrograms per gram of lava# (Moore, C., 165, see p. 116). With these values 2.05E+08 m³ of Hawaiian basalt would contain 6.6E+10 grams of carbon.

It is herein proposed that the difference between these amounts of carbon realistically approximates the total amount of carbon released chiefly as CO₂ by these three eruptions. Hence, 6.6E+10 minus 2.7E+10 equals 3.9E+10 grams of carbon. This amount of carbon represents 1.4E+11 grams of carbon dioxide or 7.1E+10 standard liters. These large numbers serve to indicate the magnitude of volcanic inputs and their potential contribution to the surface environment.

*In the absence of carbon data for Halemaumau basalts we can use lava erupted in 1969 at Alae Crater for our accepted value.

**Moore, J., (36) reported a near zero volume percent vesicles for samples collected at or below 2.5 km.

#Average of 14 analyses (range 60-111) for samples 4 and 5 and 6, 7 and 8. The shallowest sample #2 was excluded because vesiculation and volatile loss was evident at this depth.
In a related computation, the Kilauea magma supply rate, $9.0 \times 10^6 \, m^3$ per month (Swanson, 266), taken over all geological time (4.53+0.9 years) would have produced $1.6 \times 10^{24}$ grams of lava. This value is only about one order of magnitude less than the mass of the crust of the Earth estimated by Mason (267). This is to say that ten volcanoes extruding lava at the present rate of Kilauea over all of geological time could have brought to the surface all of the material presently in the crust. This interpretation must, however, be considered in the light of present knowledge about crustal recycling by mantle convection cell motion.

It is possible to proceed one more step with these types of calculations. Accepting the value of 91 micrograms carbon per gram of lava (Moore, C., 165) along with the previous figure for total extruded lava at the present Kilauea rate, we arrive at $1.5 \times 10^{20}$ grams carbon. This figure happens to be almost exactly the total amount of carbon chosen by Rubey (244) to be in the present-day atmosphere, hydrosphere and the biosphere. This is also close to the value arrived at by Cloud (14), who used Rubey's data, but modified it to allow for larger deposits of ferric oxides in the crust than were known to Rubey. This agreement is almost too good. It suggests that one volcano erupting as Kilauea does today with total weathering of its solid ejecta could over geological time be recycling all of the carbon in the forementioned near-surface entities.

It does not, however, account for the bulk of the carbon (99.9%) in the Earth's crust which is buried in ancient sedimentary rock. By a similar line of reasoning this much larger quantity of carbon would had to have been introduced by about 600 volcanoes erupting as Kilauea.
presently does, or any combination of total carbon release, extrusion rate and number of volcanoes which would result in a figure approximating this sedimentary carbon. With the modification by Cloud (14) the amount of sedimentary carbon has been significantly reduced.

In his volcanic furnace concept for the Earth, Cotton (269) has estimated that $6.4E+22$ grams of carbon has been introduced over geological time. This value compares favorably with estimates on the total carbon in the atmosphere, hydrosphere, biosphere and the ancient sediments—a sum which accounts for all crustal carbon.

It should be noted that the foregoing calculations have been expressed for convenience in terms of either elemental carbon or carbon dioxide. It has been the objective of this experimental study to show that the composition of volcanic gases on Earth probably have been in a state of evolutionary change over much of geological time. This has been due in part to oxidation state controlling mechanisms which have affected the chemistry of the carbon gases.

It should also be noted (and perhaps held in support of the previous discussion) that a similar set of calculations can be described to account for the water in the Earth's surface environment. Here we arrive at the conclusion that about 30 volcanoes erupting as Kilauea does with its amount of water could be responsible.

2. Evolution of the Atmosphere of Earth

The gross chemical composition of planetary atmospheres can be approximated to some degree as the thermodynamic equilibrium distribution of the constituent atoms. In the lower portion of the atmosphere, which is shielded from photodissociating UV radiation, a closer approximation to thermodynamic equilibrium can be expected since there is a strong
tendency for the degradation of molecules to their lowest energy states. Even in the presence of special mechanisms which favor the production of specific compounds, i.e., UV radiation or lightning, the thermodynamic equilibrium distribution of reaction products should be a useful first-order approximation. Since the equilibrium state is independent of particular reaction mechanisms and reaction rates, studies of equilibrium chemistry would appear to be a prerequisite to consideration of non-equilibrium processes.

In spite of the continual addition of trace compounds by biological activity, lightning, photochemical reactions, volcanism, pollution, planetary sweeping and emissions from natural petrochemical deposits, the constituents of the present atmosphere (considered as a closed system) are in approximate thermodynamic equilibrium at 1 atm and 280°K (Allen, 246; Hutchinson, 247). Table 9 lists the stable constituents of the Earth's atmosphere and the calculated equilibrium composition for the gram-atomic abundance.
Table 9. Actual and Calculated Composition of the Atmosphere of Earth
Based on a Gram-atomic Abundance Ratio of Nitrogen, 1.56E 00; Oxygen,
4.22E-01; Hydrogen, 2.00E-03 and Carbon, 3.30E-04.
<table>
<thead>
<tr>
<th>Substance</th>
<th>Adopted Chemical Composition of Terrestrial Atmosphere (225, 226)</th>
<th>Equilibrium Composition Computed from Gram Atomic Abundance in Previous Col.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$O_2$</td>
<td>0.2095</td>
<td>0.21</td>
</tr>
<tr>
<td>$N_2$</td>
<td>0.7808</td>
<td>0.78</td>
</tr>
<tr>
<td>$O_3$</td>
<td>E-08 -- E-07</td>
<td>E-32</td>
</tr>
<tr>
<td>$H_2O$</td>
<td>E-03</td>
<td>E-03</td>
</tr>
<tr>
<td>$H_2$</td>
<td>E-07</td>
<td>E-35</td>
</tr>
<tr>
<td>$NO_2$</td>
<td>E-10 -- E-08</td>
<td>E-11</td>
</tr>
<tr>
<td>$N_2O$</td>
<td>E-07</td>
<td>E-20</td>
</tr>
<tr>
<td>$NH_3$</td>
<td>E-08</td>
<td>E-35</td>
</tr>
<tr>
<td>$SO_2$</td>
<td>E-06</td>
<td>E-19</td>
</tr>
<tr>
<td>$CO_2$</td>
<td>3.3E-04</td>
<td>3.3E-04</td>
</tr>
<tr>
<td>$CH_4$</td>
<td>E-06</td>
<td>E-35</td>
</tr>
</tbody>
</table>
For the major constituents the agreement is excellent, while the concentration of all of the trace compounds are higher than thermodynamic values. It could be argued that the lack of agreement for O₃ and H₂ is due to UV photolytic reactions involving water vapor. The high values of NH₃ and CH₄ are probably due to decomposition of organic material. It has recently been reported that 90% of the atmospheric CO is produced by the oceans and that forests contribute amounts of hydrocarbons larger than man-made pollution.

The two straight lines radiating out from the hydrogen apex in Figure 23 and intersecting the carbon--oxygen boundary about equidistant on each side of the point CO₂ represent all compositions with total carbon to total oxygen ratios greater than 0.30 (the lower) but greater than 0.67. These two values form the extremes of the proposed cosmic abundance ratio (Suess and Urey, 242; Cameron, 250; Goldberg, et al., 251). It needs to be stated that there is no a priori necessity for a direct dependency between atmospheric evolution or magmatic gas compositions and the cosmic abundances for the elements hydrogen, carbon, oxygen, nitrogen, sulphur, et cetera.

It is possible, albeit highly hypothetical, to use Figure 23 as an aid in the evolution of the atmosphere. Within the limitations of plotting the elemental composition of the Earth's atmosphere in only three dimensions, i.e., C-H-O, it is obvious that for all intent and purpose the overwhelming contribution of life-supporting oxygen places it at the oxygen apex (far left).

As pointed out in another section, it is generally accepted that the primitive atmosphere of Earth had a composition somewhere near L/H₂ or L/H₃ and that this atmosphere was strongly influenced by the magmatic
inputs. At "time zero" the composition of the atmosphere would have been identical to the composition of the magmatic gases, if all of the residual atmosphere was swept away during accretion.

It is now possible to postulate that the atmosphere of Earth evolved from the hydrogen-rich side of the ternary diagram to the oxygen-rich side. Naturally it is impossible to define the exact course of this transition. It may have started as proposed by (a) with a high concentration of methane or it may have been influenced more by the C/O cosmic ratio and thus have proceeded as shown in (b). If Hawaiian-type volcanic gases had a persistent influence then a dip (dashed side track) near the water point in Figure 23 would be justified.

It can be seen in Figure 11 that the line joining the points H$_2$O and CO$_2$ may be called the oxygen threshold—a range of compositions which would allow free molecular oxygen to appear in the gas phase at equilibrium. Holland (248) and Berkner and Marshall (249) have proposed a time scale to correspond to major changes in the atmospheric composition so that free molecular oxygen began appearing about two billion years ago. Prior to that time O$_2$ from various sources was consumed in crustal weathering and the oxidation of reduced magmatic gases.
Figure 23. Ternary Diagram in C-H-O Denoting Suggested Cosmic Ratios of Carbon to Oxygen (see text) and Possible Paths of Atmosphere Evolution.
The onset of photosynthesis permitted \( O_2 \) to be formed faster than its consumption and it gradually accumulated in the atmosphere. Paleontologic evidence suggests that present-day oxygen levels occurred as far back as 0.3 billion years ago. Prior to the turning point for the appearance of free \( O_2 \), the composition of magmatic and fumarolic gases probably had a domineering influence over the atmospheric composition. It is within this time span that various processes are believed to have been operative on the surface environment which made conditions favorable for the formation and stability of organic compounds of biological importance. These processes and conditions are described in the literature referenced in the Introduction.

3. Prebiotic Synthesis

The stability of these prebiotic compounds under their environmental conditions is not a trivial point. One of two conditions (and probably both) must have prevailed during the period when the first life form evolved: (a) effective screening of UV radiation between 2600–2900 nm by atmospheric constituents. These frequencies are highly lethal to cellular functions (the absorption bands for nucleic acids and proteins fall in this region). Berkner and Marshall (249) claim that only atmospheric ozone can provide that protection, the formation of which is directly dependent upon molecular oxygen. Since the beginnings of life preceded the appearance of \( O_2 \), an alternative must be sought. (b) Screening by water. A ten meter depth of water will effectively screen the lethal UV radiation but yet transmit enough visible light for photosynthesis. Another requirement is a minimum of liquid turbulence to avoid circulation of primitive metazoa toward the lethal surface, but
gentle convection to provide organic nutrients synthesized photochemically at the surface, in the presence of UV radiation. Warm pools associated with volcanic hot springs, which are rich in nutrients and elementary compounds, seem prime candidates for the origin of life and photosynthesis. As so vividly described by Darwin; (Oparin, ?)

"It is often said that all the conditions for the first production of a living organism are now present, which could ever have been present. But if (and oh! what a big if) we could conceive in some warm little pond, with all sorts of ammonia and phosphoric salts, light, heat, electricity, etc., present, that a protein compound was chemically formed ready to undergo still more complex changes, at the present-day such matter would be instantly devoured or absorbed, which would not have been the case before living creatures were formed."

In retrospect, the geological history of Earth before the origin of life, before the appearance of free oxygen in the atmosphere and to the period when magmatic gases may have had a profound effect upon the surface environment, we may conclude that volcanic gases, more reduced than present ones, could have contributed low trace amounts of a few simple organic substances. This is substantiated by "some experimental evidence" and the thermochemical calculations pertaining to the primitive Earth. More importantly, the major volcanic gas constituents liberated to the atmosphere probably participated in photochemical reactions in the atmosphere and in the surface layers of aqueous environments to produce macromolecular organics which set into motion the processes of biogenesis. It can be asserted with confidence that these complex organics were not synthesized under thermal equilibrium conditions alone.

Hulett (272) has arrived at the same conclusion that nonequilibrium conditions were required to synthesize the prebiotics necessary for the origin of life. This statement may be taken as contrary
to the Oparin-Haldane hypothesis. As pointed out by Morowitz (273),
almost any compound can be synthesized from simple precursors containing
the required atoms and an appropriate energy flow. Thus the fact that a
compound has been synthesized under laboratory conditions is no real
indication of its presence in the "prebiotic soup" at concentration levels
of significance. The concentration of any compound in that medium would
have depended on the relationship between rates of synthesis and degrada­
tion at the energy levels present in the primitive environment. Hulet t
concluded that chemical evolution could have occurred only in localized
areas where high concentrations existed. Such areas might have been form­
ed if there were consistently high local generation rates or if uniform
mixtures could have been differentiated.

It is statistically possible for an equilibrium mixture to be
differentiated to give high local concentrations of a substance, but such
an event is so unlikely that it has not been seriously suggested as a
method of providing intermediates for chemical evolution. On the other
hand, several nonequilibrium pathways leading to such differentiation can
be envisioned.

One involves concentration of soluble intermediates with low
vapor pressures by evaporation of water from dilute pools. Another uses
phase separation such as the freezing of water which could trap trace
quantities of prebiotics in the unfrozen liquid water beneath the ice mass
and eventually concentrate it. Adsorption onto surfaces forms the third
way. Because of the omnipresence of environmental surfaces with diverse
properties this concentration mechanism has received some attention
(Siegel, 274; Akabori, et al., 278). Adsorption reduces the energy con­
tent for the component of interest. Most biosynthetic reactions, i.e.,
those postulated in chemical evolution, are energy consuming and will
tend to proceed in the opposite direction in the presence of a catalyst
(desorption). This is shown in the following reaction

\[
\text{prebiotic } 1 + \text{catalyst} \rightarrow \text{prebiotic } 1' \text{catalyst}.
\]

The only way to prevent this is to couple the process to an external
source of energy in such a way as to change the energy relationship be­
tween dissolved prebiotic species and the catalyst as shown in the re­
action

\[
\text{prebiotic } 1 + \text{catalyst} + \text{energy} \rightarrow \text{prebiotic } 1' \text{catalyst} + \\
\text{prebiotic } 2 \rightarrow \text{prebiotic } 3 + \text{catalyst}.
\]

It therefore appears that the origin of life could only have oc­
curred through many specific mechanism involving concentration of pre­
biotics, nonequilibrium chemical reactions, catalysis probably in an
aqueous medium, protection from the degrading UV radiation, low tempera­
tures and a mathematical probability known as luck.

The brief discussion to follow is admittedly extraneous, but
should be included for its potential importance. The point HB in Figures
10, 11 and 23 is the composition of an average human body which is 97% 
by weight hydrogen, carbon and oxygen (Lehninger, 252). Over the geo­
logical history of Earth, believed to be about 4.5 billion years life 
has, quite obviously, originated and flourished. If magmatic gases 
evolved from a composition similar to L/H 2 or L/H 3 to T the present 
terrestrial and if the carbon and other elements were incorporated into
the prebiotic soup from which life originated, it may not be a coincidence to find HB located in that zone. The premise upon which the inorganic origin of life is based is, in part, magmatic inputs, photochemical reactions, solubility in aqueous environments, polymerization, stability and organization.

Further the point HB lies to the right of the oxygen threshold which is in accord with the established criterion that prebiotic formation preceded the appearance of free oxygen in the atmosphere.

There is additionally another interesting feature which deals not with the origin of life but with its ultimate discontinuation. Figure 11 shows that HB is metastable with respect to the elemental and most stable form of carbon.
Oxidation states which have been shown to be important in terrestrial and lunar magmatic systems were reviewed. It was shown that the QFM (quartz-fayalite-magnetite equilibrium region) realistically represents the oxidation state of Hawaiian basalt at a high temperature, while the QFI (quartz-fayalite-iron) seems to fit the lunar magmatic conditions reasonably well. These mineralogical assemblages through their equilibrium with the volatile phase control the oxygen fugacity to very small values (see Figures 1, 2 and 3). The magnitude of the oxygen fugacity through its influence on the water-gas reaction regulates both the pCO₂/pCO and the pH₂O/pH₂ ratios. If the oxidation state is low enough to establish low values for the above ratios and if the temperature is favorable, the oxygen partial pressure may cross the graphite deposition boundary in Figure 2. This occurrence may favor reactions leading to the formation of hydrocarbons.

Using total carbon data on Hawaiian basalts along with an estimated magma extrusion rate for the active volcanoes on the Island of Hawaii, it was possible to estimate the total carbon introduced into the surface environment through volcanic activity. The magnitude of these values is the same as estimates derived by other investigators.

An experimental reactor and procedures were devised to study the influence of gas phase composition upon the formation of organic substances. The reactor was designed to prevent gross contamination. However, lengthy procedures were developed in order to reduce background organic levels to below the limit of detection for a flame ionization detector.
In the presence of basaltic lava and high partial pressures of steam, the results of the equilibrium studies showed that all chemical systems studied limited the formation of ethylene and ethane to concentration levels just barely in excess of their limit of detection. The partial pressures of methane in this set of experiments were also small under all conditions of temperature and gas phase composition, but it always exceeded the sum of C₂ hydrocarbons. There was no evidence for partially oxidized organic compounds such as alcohols or aldehydes. The pCO₂/pCO values in these experiments indicated that equilibrium in the lava catalyzed water-gas reaction was generally achieved. The kinetics of this reaction were reviewed, but the experimental data did not lend itself toward a satisfactory kinetic evaluation.

In the presence of basaltic lava and low partial pressures of water vapor, the set of experiments which approached lunar magmatic condition did, as favorable temperatures were reached, allow the formation of hydrocarbon up to C₆. These reactions were discussed in terms of reduced iron catalyzed Fischer-Tropsch synthesis. Although evidence is sparse, there is reason to imply that carbon gases in the presence of lava, but in the absence of appreciable water vapor, can form either metal carbides or a condensed form of carbon. The latter is commonly a prerequisite for the former. The pCO₂/pCO values observed in these anhydrous experiments appear to satisfy the oxygen fugacity requirements of the QFI buffer system.

Extensive thermodynamic calculations were performed on eight composition points for a large number of organic compounds in an all-inclusive equilibration with inorganic species and graphite. The
Fischer-Tropsch synthesis was interpreted with respect to hypothetical magmatic systems using these equilibrium values. Preferential loss of hydrogen, catalysis and catalytic poisoning by hydrogen sulphide were included.

Lastly, magmatic contributions to the atmosphere of Earth from its earliest composition to its present-day makeup were discussed. Photochemical and thermal reactions in the proposed primitive atmosphere are believed to have contributed certain simple, but reactive, organic constituents to the prebiological setting from which the first life form originated.
Appendix 1. Oxygen Fugacity Values for the Quartz-Fayalite-Iron (QFI) Buffer and for the Quartz-Fayalite-Magnetite (QFM) Buffer as a function of Temperature.

<table>
<thead>
<tr>
<th>Temp in °C.</th>
<th>-log fO₂ (QFM)</th>
<th>-log fO₂ (QFI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1250</td>
<td>7.7</td>
<td></td>
</tr>
<tr>
<td>1200</td>
<td>8.4</td>
<td></td>
</tr>
<tr>
<td>1150</td>
<td>8.9</td>
<td></td>
</tr>
<tr>
<td>1100</td>
<td>9.6</td>
<td>14.0</td>
</tr>
<tr>
<td>1050</td>
<td>10.4</td>
<td></td>
</tr>
<tr>
<td>1000</td>
<td>11.2</td>
<td>15.5</td>
</tr>
<tr>
<td>950</td>
<td>12.0</td>
<td></td>
</tr>
<tr>
<td>900</td>
<td>12.9</td>
<td>17.7</td>
</tr>
<tr>
<td>850</td>
<td>14.0</td>
<td></td>
</tr>
<tr>
<td>800</td>
<td>15.2</td>
<td>20.1</td>
</tr>
<tr>
<td>750</td>
<td>16.4</td>
<td></td>
</tr>
<tr>
<td>700</td>
<td>17.8</td>
<td>23.0</td>
</tr>
<tr>
<td>650</td>
<td>19.3</td>
<td></td>
</tr>
<tr>
<td>600</td>
<td>21.0</td>
<td>26.5</td>
</tr>
<tr>
<td>550</td>
<td>23.0</td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>25.0</td>
<td></td>
</tr>
<tr>
<td>450</td>
<td>27.5</td>
<td></td>
</tr>
<tr>
<td>400</td>
<td>30.3</td>
<td></td>
</tr>
<tr>
<td>350</td>
<td>33.6</td>
<td></td>
</tr>
</tbody>
</table>
Appendix 2. Details of Significant Experiments

Following these explanatory remarks is a terse summary of each experiment which yielded significant data to support the conclusions. The experimental number is given along with procedural information on gas phase composition, temperature and oxidation state of the lava.

(a) Steam: Liquid water was present in the reactor and that steam was the major component in the reaction zone. The partial pressure of steam is total pressure dependent and therefore was nonconstant.

(b) Lava: Lava was present in the quartz insert inside the furnace tube. If there is no additional note as to preliminary conditioning of the lava, the initial oxidation state was unknown.

(c) Initial Gas Phase Composition: In the steam experiments usually only one other gas was introduced and the equilibrium composition was derived through thermal reactions. Sometimes, however, two gases were used—in these cases they were added as closely following each other as the manifold could be prepared. In the anhydrous experiments which usually began with hydrogen conditioning of the lava, the H₂ was evacuated to the desired pressure and CO or CO₂ was added to meet initial ratio requirements.

(d) Temperature: The designation of temperature as either high, intermediate or low is as described on page 110.

(e) Temperature Program: Isothermal; furnace temperature increasing or furnace temperature decreasing.
El6  Steam; Lava; CO₂ introduced initially with furnace at 1250°K; Decreasing (stepwise) temperature program.

El7  Steam; Lava; CO₂:CO::9:1 introduced initially with furnace at 1250°K; Decreasing (stepwise) temperature program.

El8  Steam; Lava; CO₂:CO::1:1 introduced initially with furnace at 1250°K; Decreasing (stepwise) temperature program.

When the initial pCO₂/pCO falls short of the high temperature equilibrium value, oxidation of CO occurs in accordance with the initial excess. There was no indication of a change in pCO₂/pCO with decreasing temperature.

El9  Steam; No lava; CO introduced initially at 500°K and furnace set to heat directly to 1200°K.

E20  Steam; Lava; Same as El9.

Even though some CO oxidation did occur without lava, the degree of conversion was higher in E20 and it required less time. Electrometer not operating here.

E21  Steam; Lava; CO introduced initially at low temperature; Increasing followed by decreasing furnace temperature program.

E22  Steam; No lava; Same as E21.

With respect to the oxidation of CO, the notes on El9 and E20 apply. Methane and small amounts of C₂ hydrocarbons appeared at intermediate temperatures, but the C₂ disappeared as the lava heated up to high temperatures. As the temperature was reduced both C₂ hydrocarbons reappeared in about the same amounts. Terminal addition of H₂ significantly affected the pCO₂/pCO ratio, but had little influence upon the hydrocarbons.
E23  Steam; Lava; CO introduced initially at an intermediate temperature; Intermediate-High-Intermediate furnace temperature program. CO oxidation was evident. The failure of C₂ hydrocarbons to disappear at high temperatures and the observation of C₃ at intermediate temperatures suggests contamination.

E26  Steam; CO introduced initially; Isothermal intermediate temperature; Lava conditioned in O₂ prior to the entry of CO.

E27  Same as E26 except that the lava was conditioned in H₂. The effect of lava conditioning in these two experiments clearly shows that the degree of conversion of CO to CO₂ is dependent on pH₂ which in turn is dependent on the initial oxidation state of the lava.

E28  Anhydrous (first); Lava; CO introduced initially followed by hydrogen after the CO--lava reaction had proceeded for 24 hours. Large amounts of methane and C₂ hydrocarbons formed, but the experiment lacks geological significance.

E29  Anhydrous; Lava; CO introduced initially; Isothermal intermediate temperature; Lava conditioned in O₂ prior to entry of CO.

E30  Same as E29 except that the lava was conditioned in H₂.

E31  Anhydrous; No lava; CO introduced initially; Isothermal intermediate temperature; Furnace tube conditioned in O₂.

E32  Same as E31 except the furnace tube was conditioned in H₂. Anhydrous baseline experiments which resulted in only a small degree of conversion of CO to CO₂. Electrometer not operating here.

E33  Steam; No lava (quartz wool); CO introduced initially; Isothermal intermediate temperature.

E34  Steam; Same as E33 except experiment was run at high isothermal temperature.
E35 Steam; Same as E33 except experiment was run at low isothermal temperature.

The small degree of oxidation of CO (highest at the highest temperature) is consistent with previous observations. It was now clear that both steam and a catalytic surface are necessary for the oxidation of CO to achieve equilibrium values with CO₂. The small amount of H₂ produced by the oxidation of CO did not produce significant amounts of hydrocarbons.

E36 Steam; Lava; CO introduced initially; Isothermal intermediate temperature.

E37 Steam; Lava; CO introduced initially; Isothermal intermediate temperature; Lava conditioned in H₂.

E38 Steam; Same as E37 except the lava was conditioned in O₂.

E39 Low water vapor pressure; Lava; CO introduced initially; Isothermal intermediate temperature; Lava conditioned in H₂.

E40 Low water vapor pressure; Same as E39 except the lava was conditioned in O₂ prior to the entry of CO.

E41 Low water vapor pressure switched to high steam after 20 hours; Lava; CO introduced initially; Isothermal intermediate temperature. This result shows clearly the relationship between water vapor pressure and degree of conversion of CO to CO₂.

E42 Anhydrous; Lava; H₂/CO = 2.0 introduced initially; Lava conditioned with H₂; Isothermal high temperature.

E43 Same as E42 except the experiment was run at an intermediate temperature.

E44 Same as E42 except the experiment was run at a low temperature.
E45 Anhydrous; Lava; H₂/C₀₂ introduced initially; Isothermal low temperature; Lava conditioned with H₂ prior to the entry of C₀₂. Substantial hydrocarbons were formed but it seems that saturated species were dominant early in the experiment as opposed to E44 where unsaturated hydrocarbons were definitely formed more readily.

E46 Anhydrous; Lava; H₂ conditioning of lava followed by C₀ conditioning; Isothermal intermediate temperature. Experiment to show that C₀ could carburize lava.

E47 Anhydrous; Lava; H₂/C₀ = 1.0 introduced initially; Isothermal low temperature.

E48 Same as E47 except the H₂/C₀ ratio initially was 0.5. In both E47 and E48 gas phase hydrocarbons were observed to form in a manner similar to those in E44. At the experiment termination about one-half of the lava was hydrolyzed. This supplied evidence that carbides were formed under these experimental conditions.

E49 Steam; Lava; C₀ introduced initially; Isothermal low temperature.

E50 Steam; Lava; C₀ introduced initially; Isothermal high temperature.
Appendix J. Final Chromatographic Details, Procedures and Retention Times for the Substances Most Often Analyzed.
Column A: 10' x 1/8" copper tubing packed with Porapak Q (-80+100) operating at a column head pressure of 25.5 p.s.i.g. giving a helium flow of 19 cm³/minutes. This column was operated isothermally at 40°C for 5 minutes with discontinuous programming to 65°C at 5 minutes and 100°C at 11 minutes. This column heating program would yield the following retention times.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Retention Time</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂(CO, N₂)</td>
<td>0 mins, 52 secs.</td>
<td>1.</td>
</tr>
<tr>
<td>CH₄</td>
<td>1 min, 07</td>
<td>2.</td>
</tr>
<tr>
<td>CO₂</td>
<td>1</td>
<td>30</td>
</tr>
<tr>
<td>C₂H₄</td>
<td>2</td>
<td>23</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>2</td>
<td>45</td>
</tr>
<tr>
<td>Temp. to 65°C</td>
<td>5</td>
<td>00</td>
</tr>
<tr>
<td>H₂O</td>
<td>7-9 mins.</td>
<td>5.</td>
</tr>
<tr>
<td>C₃H₆</td>
<td>8</td>
<td>08</td>
</tr>
<tr>
<td>C₃H₈</td>
<td>8</td>
<td>53</td>
</tr>
<tr>
<td>Temp. to 100°C</td>
<td>11 mins.</td>
<td></td>
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<tr>
<td>Temp. to 140°C</td>
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<td>C₅ HC</td>
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1. The H₂(CO) combined peak was quantitatively useable for the CO data since it was strongly attenuated to ranges normally X50, X100 or
When using helium carrier gas the thermal conductivity detector exhibits very poor sensitivity toward H₂. This is caused by the similarity in thermal conductivity values between H₂ and He (124). It was shown that the H₂ contribution to the H₂ (CO₂,N₂) peak could not exceed 3% and thus was generally ignored unless the amount of H₂ in the sample was excessive. For highest accuracy CO and H₂ are determined on Column B. The amount of N₂ contribution to the combined peak was never significant.

2. The CH₄-CO₂ retention times do not offer full resolution. This was not a problem since CH₄ was usually determined on the flame ionization detector at levels far below the sensitivity of the thermal conductivity detector operating on the high ranges of attenuation which was necessary to record CO₂ data. The CO₂ and CO responses on the flame detector were small in relation to the usual CH₄ signals. The flame detector response to these two noncombustible carbon gases was calibrated and simply tolerated without concern for quantitative interference.

3. The thermal conductivity output record was usually terminated after the CO₂ peak was recorded.

4. Although the C₂H₄-C₂H₆ resolution was not complete the semiquantitative values on their amounts could be determined by the simple graphical deconvolution techniques.

5. The small and badly tailed H₂O peak was normally observed on the flame ionization detector between 7-9 minutes after injection. It caused no quantitative concern even though it formed the background for the recording of the C₃ HC. In the anhydrous experiments no H₂O
peak was observed, therefore no propene-propane interference.

Column B: 7' x 1/4" copper tubing packed with Molecular Sieve 5A (reg. trademark) (-80+160) operating at a column head pressure of 5 p.s.i.g. and a carrier flow rate of 20 cm³/mins. This column was operated isothermally at 40°C for 4 minutes and then set to heat up to 100°C to elute CO. The 4 minute program point came just after the CH₄ peak. H₂O and CO₂ are strongly adsorbed on this column and must be eluted at a rather high temperature. Under these heating conditions the following retention times were observed:

- H₂: 1 min. 15 secs.
- N₂: 2 mins. 15 secs.
- CH₄: 3 mins. 0 secs.
- Temp. to 100°C: 4 mins.
- CO: 5 mins. 20 secs.

This column was also used to determine quantitatively the H₂ in a sample using argon as the carrier gas. The Ar flow rate was adjusted to be the same as when He is used. The switch over He to Ar, and visa versa, usually required about 1 hour to stabilize. Therefore H₂ data was collected only when the CO₂/CO ratio suggested constancy.

Column C: 6' x 3/16" copper tubing packed with Porapak Q (-60+80) operating at a column head pressure of 20 p.s.i.g. and a flow of 24 cm³/mins. This column was operated at 145°C exclusively for the analysis of the aqueous samples. It was plumbed into the last column switching valve via the conventional heated injection port. Using vapor phase samples
from the headspace above mixtures of methanol, formaldehyde, formic acid, ethanol, acetaldehyde, acetic acid, propanol (iso and normal) and butanol. The characteristic retention times were determined.

Analyzing large volumes (several c.c.) of aqueous solutions for small quantities of soluble organic proved to be quite a perplexing problem until it became apparent that the system (column and detector) needed to be saturated with water vapor before the flame detector could respond in a sensitive mode to the organics. The overall procedure became: (a) inject 500 µl H2O, (b) at about 2 minutes the baseline disturbance caused by the water front appeared and was bucked out by the electrometer controls, (c) anytime between about 3-10 minutes the sample could be injected and the organics observed with only minimal baseline deformation caused by the second solvent water. Full resolution of the alcohols was possible whereas the acetaldehyde-ethanol composite was only of limited use. Formaldehyde and formic acid vapors do not generate a signal in the flame ionization processes.

They are arranged in the same order as are the entries in Tables 8A, 8B, 8C and 8D.
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Table 10A. Elemental Abundance Point L/H 1.
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Table 10B. Elemental Abundance Point L/H 2.
Table 10C: Elemental Abundance Point L/H 3.
Table 10D. Elemental Abundance Point L/H 4.
Table 10E. Elemental Abundance Point L.
Table 10F. Logarithms Mole Fractions for Selected Compounds at Temperatures above 1000°K at Elemental Abundance Point L at 1 atm.

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Table 10G. Elemental Abundance Point T.
Table 10H. Logarithms of Mole Fractions of Selected Magmatic Gases at 1400°K and 1 atm for the Elemental Abundance Point T.

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BIBLIOGRAPHY


74. Cuttitta, F., Rose, H., Annell, C., Carron, A., Christian, R.,
1217-29.

75. Oro, J., Flory, D., Gilbert, J., McReynolds, J., Lichtenstein, H.
and Wikstrom, S., "Abundances and Distribution of Organogenic
1913-25.

76. Funkhouser, J., Jessburger, E., Muller, O. and Zahringer, J., "Active
and Inert Gases in Apollo 12 and Apollo 11 Samples Released by
Crushing at Room Temperature and by Heating at Low Temperatures," ibid. pp. 1381-96.

77. Gibson, E. and Johnson, S., "Thermal Analysis-Inorganic Gas Release

78. Abell, P., Cadogan, P., Eglington, G., Maxwell, J. and Pillinger,
C., "Survey of Lunar Carbon Compounds: I. The Presence of
Indigenous Gases and Hydrolyzable Carbon Compounds in Apollo 11 and

79. Preti, G., Murphy, R. and Biemann, K., "Search for Organic Compounds
1879-89.

80. Kaplan, I. and Petrowski, C., "Carbon and Sulphur Isotope Studies on

81. Friedman, I., "The Carbon and Hydrogen Content and Isotopic Composi-

82. Epstein, S. and Taylor, H., "$^{18}O/^{16}O$, $^{30}Si/^{28}Si$, D/H and $^{13}C/^{12}C$

83. Clayton, R., Onuma, N. and Mayeda, T. "Oxygen Isotope Fractionation

84. Lunar Sample Preliminary Examination Team, "Preliminary Examination
of Lunar Samples" in Apollo 14 Preliminary Science Report, Chap. 5.

85. N.A.S.A. Manned Spacecraft Center Apollo 14 Preliminary Science

86. Muan, A., "Phase Equilibria at High Temperatures in Oxide Systems
Involving Changes in Oxidation State," Amer. J. Sci., 256, 171-
207 (1958).

87. Webster, A. and Bright, N., "System Iron-Titanium-Oxygen at 1200°C
and Oxygen Partial Pressures Between 1 atm and 25-14 atm," J.


104. Duenebier, F., Secondary investigator on Apollo passive seismic experiments project, Univ. of Hawaii, personal communication, 1972.


116. Flood in personal communication with Fudali, see reference 142.


138. Roeder, P. and Osborn, E., "Fractional Crystallization Trends in the System $K_2SiO_4-CaAl_2Si_2O_8-FeO-Fe_2O_3-SiO_2$ over the range of Oxygen Partial Pressures $10^{-11}$ to $10^{-0.7}$ atm," Bull. Volcanol 29, 659-70 (1966).


145. Krauskopf, K., "Heavy Metal Content of Magmatic Vapor," Econ. Geol. 52, 786-807 (1957).


234. Stull, D. and Prophet, H. (Eds.) Joint Army Navy Air Force Thermo-
(1971).


Compositions in Equilibrium with Carbon and Carbon Deposition
(1964).

238. Naughton, J., "Volcanic Flame: Source of Fuel and Relation to
Volcanic Gas-Lava Equilibrium," accepted for publication in

239. Murphy, R. and Preti, G., "Search for Organic Material in Lunar
Fines by Mass Spectrometry," Science: The Moon Issue 167,

240. Hamilton, P., Modzeleski, J., Modzeleski, V., Mohammed, J., Nagy,
L., Nagy, B., McEven, W. and Urey, H., "Carbon Compounds in
Apollo 14 Lunar Samples," in Lunar Science III. Watkins, C.

241. Tanaka, K., "Synthesis of Prussic Acid, I.X. Catalytic Activity
of Alumina," J. Res. Inst. Catalysis, Hokkaido Univ. 11,

Phys. 28, 53-74 (1956).

243. Henderson, W., Kray, W., Newman, W., Reed, W., Simoneit, B. and
Calvin, M., "Study of Carbon Compounds in Apollo 11 and 12
Returned Lunar Samples," Geochim. et Cosmochim. Acta Suppl. 2,

244. Rubey, W., "Geological History of Sea Water," in Origins and
Evolution of Atmospheres and Oceans. Brancazio, P. and
Cameron, A. (Eds.) John Wiley and Sons, New York 1964, pp. 1-
64.


(1963).


