

INVESTIGATION OF OXIDATION-REDUCTION IN SOME
SILICATE SYSTEMS AND ITS RELATIONSHIP TO
DIFFERENTIATION AND GAS CONTENT

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I. INTRODUCTION

Statement of Problem

Oxidation-reduction of silicate systems at elevated temperatures as a geological or mineralogical phenomenon seems to have been largely neglected in research up to the present time. Many authors have mentioned the importance of oxidation-reduction in rocks in relation to past history and differentiation; also, the interrelationship of oxidation-reduction in rocks with the gas content has been suggested and, in fact, investigated in a preliminary way.^{1,2,3} There has been very little published on the quantitative study of oxidation-reduction in rocks and on how oxidation or reduction might alter the rock type and affect the nature and composition of the gases that exist in equilibrium with the rock, and that can be extracted or evolved from it. The present investigation is an attempt to elucidate this point, especially in regard to the interrelation between oxidation-reduction and gaseous systems at elevated temperatures (1100°C).

Fundamental Concepts

(1) Oxidation-reduction System in Solids and Melts

The extent of oxidation-reduction in a natural silicate system is determined by all the ionic and molecular species present that have a bearing on the oxide ion activity, $a_{O^{2-}}$.

in the system. Some of the important components to consider are the ferric-ferrous ion ratio, the extent of oxidized and reduced forms of various polyvalent ions such as Cr(III), Ti(IV), and Mn(IV), and the molecular species related by oxidation-reduction equilibria such as H_2-H_2O , $CO-CO_2$ and H_2S-SO_2 . Fundamental to all of these is the oxide ion, O^{--} , and in a subsidiary way, the sulfide ion, S^{--} , and fluoride ion, F^- contents, and their stoichiometric relationship to the cations present.

Studies in metallurgical slags have led to an acid-base classification for the slag forming oxides. The G. N. Lewis definition of a basic molecule as an electron pair donor and an acidic molecule as an electron pair acceptor is utilized. If the extension of this theory, that is carried out in the Usanovich concept, is adopted, the situations involving oxidation and reduction may be treated as a special aspect of acid-base theory. Usanovich has defined an acid as any material which forms salts with bases through neutralization, gives up cations, or combines with anions or electrons. Conversely, he has defined a base as any material which neutralizes acids, gives up anions or electrons, or combines with cations.⁴ Oxidation-reduction in slags may be explained by referring to the typical and ever-present base--the oxide

ion, O^{--} . The oxide ion, although a stronger base, is comparable in importance and behavior to the hydroxyl ion, OH^- , which is the typical base in aqueous solutions. Because there is nothing in the chemistry of slags that can be called a solvent, there is nothing analogous to the acid ion, H_3O^+ , commonly encountered in aqueous solutions, so that any molecule or ion that will accept electron pairs is an acid. All oxide slags and silicate systems contain oxide ions, O^{--} . The higher the oxide ion concentration, or more accurately, its activity, the more basic or oxidizing is the slag. The oxide ion activity, and thus the oxidizing or reducing strength of any oxide, is based upon the relative strengths of the metal-oxygen bond. The fluoride ion, F^- , and sulfide ion, S^{--} , also contribute to the basicity but to a relatively small degree because of their low concentrations in slags.⁵ These ions, however, can be important in natural silicate systems. Their behavior is analogous to the oxide ion, O^{--} .

In this work, where adsorption effects are excluded, the gases in oxide or silicate systems such as are present in minerals and slags are the result of the presence of atoms such as carbon, sulfur, nitrogen and hydrogen which are capable of combining with the oxide ion to produce gases. The exact role of these elements in solid or liquid systems

is uncertain, but it is known that their presence leads to lowering of the viscosity of silicate melts. Thus hydrogen and carbon could serve in this role by forming hydroxyl and carbonate groups, respectively, on reaction with the oxide ions.

Volumetrically the oxide ion is overwhelmingly predominant in silicate and oxide systems, and its tendency to produce gases with certain elements gives rise to important industrial and geological processes. These gas producing reactions have been studied to some degree in the glass, ceramic and metallurgical industries, and also speculated on in geological work. It is rather obvious that in any volcanic eruption gaseous expansion supplies at least part of the kinetic energy of the eruption, and the claim has been made that the emitted gaseous mass exceeds the solid mass ejected.⁶ The permeation of "hydrothermal liquid" and gases through crustal rock systems, and its action as an agency of material transfer and differentiation has also long been recognized and studied.⁷

In the usual case for polyphase systems where oxidation or reduction is of no consequence because there is no readily alterable oxidation-reduction system present, the condensed phases which occur are a function of temperature and composition of the melt. No special precautions for control

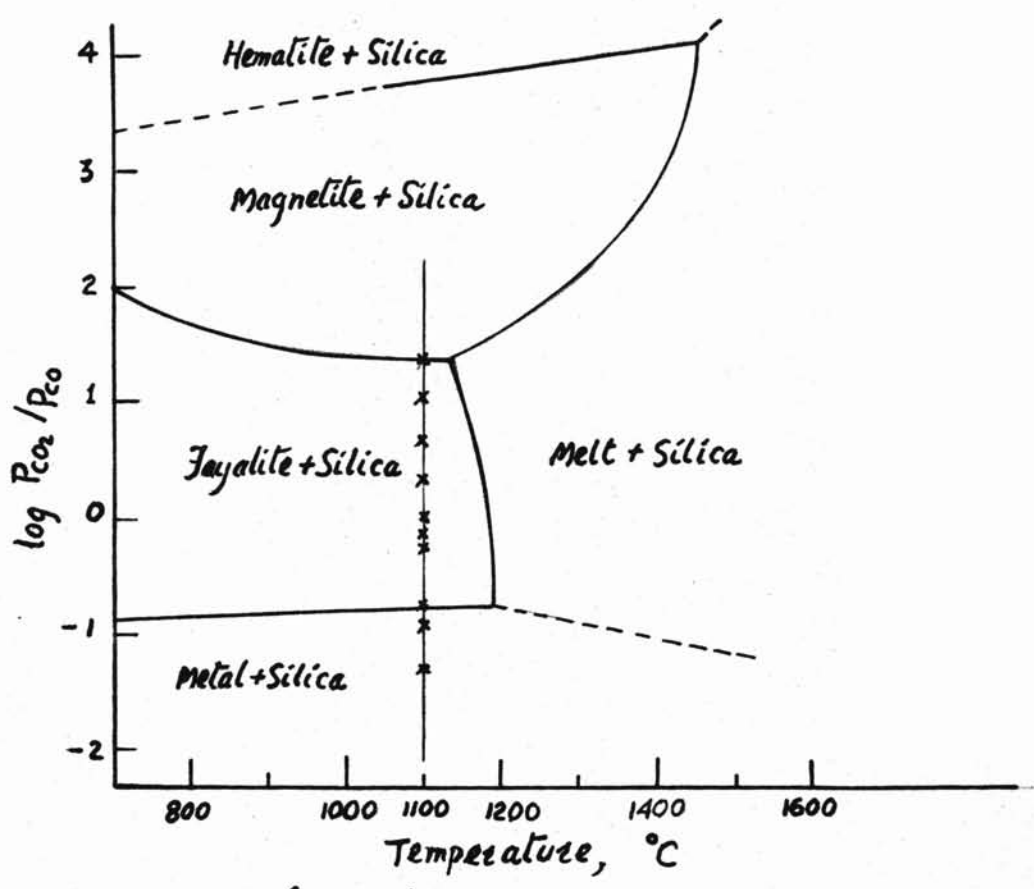
of the atmosphere to which the melt is exposed need be taken. In the study of the iron oxide-silica system, however, the final composition of the condensed phase is definitely dependent on the atmosphere to which it was exposed. The multivalent character of iron gives rise to the complicating factor that the existence of more than one solid phase is possible. The possibility of iron existing in three oxidation states--Fe(II), Fe(III), and Fe(O)--makes it imperative that the atmosphere to which the system is exposed in the equilibrium or phase studies be carefully controlled and of known composition if comprehensible results are to be obtained.⁸ The above statement is true also for natural rock systems that contain such components.

A diagram showing the stable phases of the system Fe-O-Si in the presence of excess silica is reproduced exactly on the following page from previous work by Darken.⁹ The ordinate is the $\log \frac{P_{CO_2}}{P_{CO}}$ of the equilibrating atmosphere and the abscissa, the temperature. The isotherm at 1100°C has been drawn and points on this line represent the data from the present research.

(2) Gas-Solid Systems in Igneous Differentiation

The problem of genesis of igneous rock from parent magma has been the subject of considerable discussion by

Figure 1



Stable phases of the system Fe-Si-O in the presence of solid silica

petrologists. The process by which basaltic magma separates into allied but chemically or mineralogically unlike portions is called differentiation. One of the more widely accepted views is that the various rock types form in sequence by fractionally crystallizing from the slowly cooling liquid magma.¹⁰ Another view is that gases are effective agents of differentiation.¹¹ Proponents of this hypothesis reason that gases bubbling through the magma from the lower levels toward the surface take up certain materials into solution while precipitating others depending upon the conditions of temperature and pressure. This results in a selective transfer of material from lower to upper levels. A third school suggests that recrystallization of pre-existing rocks under the influence of abundant gaseous mineralizers, or recrystallization where solid diffusion is the important agent of transfer is responsible for differentiation.¹² Other theories have been advanced such as liquid immiscibility and thermal diffusion-convection being the basis of the process.¹³

No one mechanism explains igneous rock differentiation satisfactorily and it is likely that a combination of one or more of these views represents the actual process. Whatever the mechanism involved, the result is that, as differentiation

continues the remaining liquid becomes richer in volatile content and silica. Rocks such as andesite and trachyte which are formed in the later stages of differentiation have a relatively high silica and volatile material content, whereas the early formed basalt contains relatively small amounts of silica and volatiles. In general, the later stages of differentiation yield magmatic rocks with a relatively high degree of oxidation. It appears that the extent of oxidation of a magmatic rock may be used as a measure of the degree of differentiation which it has undergone, and may possibly be used to corroborate geological evidence of differentiation.¹

(3) Role of Gases and Volatiles in Silicate Systems

The influence of volatiles on the physical and chemical properties of solids in which they are dissolved or enclosed is of fundamental interest to investigators in many fields. To those engaged in the field of geology, the action of volatiles as mineralizers is important. One of the more widely accepted theories about the mechanism of magmatic differentiation is that of fractional crystallization. It has been proposed that the laws of solution are followed; i. e., not the highest melting but least soluble constituent crystallizes first. The small amounts of volatiles which

are dissolved like other non-volatile constituents are called mineralizers, fugitive constituents, or simply volatiles. These volatiles do not enter into mineral crystallization in the early stages and tend to concentrate in the residual portion. They are of importance in several ways. Their presence lowers the temperature of crystallization (hence "mineralizer") and reduces the viscosity of the magma, and they may be incorporated into the compounds being formed, thus affecting the composition of the minerals formed.¹⁴

Magmatic differentiation is connected intimately with the viscosity. When gravitative sedimentation takes place in heterogeneous melts by a segregation of crystals from the magma, the velocity of the rising or settling of the crystals follows Stoke's law and is a function of the viscosity of the liquid in which the crystals move. The rate of sedimentation, therefore, is dependent to a large extent upon the volatile content, which is relatively high in acidic magma and low in basic magma.¹⁵ The viscosity of magmatic effusion determines the mode of solidification of lava. Low viscosity lavas of the Hawaiian Islands build shield volcanoes of low profile. The two principal types of flows, "aa" and "pahoehoe" are differentiated by their degrees of fluidity. The fluidity of "pahoehoe" lava is much greater than that of "aa", a

probable consequence of its higher gas content. Chemically, in the non-volatile components, these two lavas are quite similar.¹⁶

Water vapor appears to be the most prevalent volatile constituent in volcanic, fumarolic and rock gases, surpassing by far the other constituents--carbon dioxide, carbon monoxide, hydrogen sulfide, hydrogen, nitrogen, carbonyl sulfide, sulfur dioxide and oxygen--in quantity. The geochemical significance of water is difficult to evaluate because the ratio between primary and secondary water is often not known. Three sources of secondary water are proposed. Some say the source of the secondary water is the water assimilated by the magma from its surroundings on its ascent to the surface.¹⁷ Others contend that the original magma is rich in hydrogen which on contact with the atmospheric oxygen react to form water.¹⁸ A third group suggests that the heating of ground water might explain the high content of water vapor in the analyzed gases.¹⁹ What remains to be observed and studied is the solidified rock under entirely new conditions. A careful study of the available rock and gas samples, however, may be of value for it may explain what happens to magma on its ascent toward the surface.

The question of how the volatiles affect the viscosity of silicate melts has received considerable attention.

In laboratory studies of silicate melts, results show that small amounts of water have a great influence on viscosity.²⁰ The high viscosity of silicate melts has been attributed to the presence of complex silicate anions and it is known that the extent of glass formation and the viscosity of these silicates is markedly affected by the Si:O ratio. A reaction such as $H_2O + O^{--} \rightleftharpoons 2(OH)^-$, which effectively removes an oxide ion from the silicate structure, reduces the glass forming ability of the silicate anions and thereby decreases the viscosity of the melt. Carbon dioxide reacts similarly to form the carbonate anion. $CO_2 + O^{--} \rightleftharpoons CO_3^{--}$.

(4) Solubility of Gases in Silicates

The work of Shepherd and Jaggard showed that natural rocks when fused in a vacuum will yield gases that are either dissolved in the rock or formed by the decomposition of compounds that exist in the rock.^{21,22} The technique of studying gases in silicate systems, however, has been developed primarily by investigators in the glass industry. The quantity and nature of the gases in the glass influence the quality of the glass. Glasses have been shown to contain water which exists apparently as part of the silicate structure in the glass.²³ The water content of glass depends on the partial pressure of the water vapor in the atmosphere of the furnace

in which the glass is prepared. The infra-red absorption peak at $\lambda = 2.8 \mu$ of water containing glasses was especially studied by A. J. Harrison.²⁴ R. H. Dalton while determining the gases dissolved in glass, found appreciable amounts of water, carbon dioxide, and oxygen but very little nitrogen, carbon monoxide, hydrogen and other reducing gases.²⁵ The important question of how the chemical character of the gases dissolved in glass depends on glass composition has been investigated by E. E. Schumacher.²⁶ He attempted to distinguish between surface adsorbed gases and those which are evolved at higher temperature from the interior of the glass melt, and are therefore really dissolved in it. The correlation between alkalinity of the melt and carbon dioxide content was demonstrated--the carbon dioxide content rising with increase in alkalinity.

Survey of Pertinent Literature

(1) Previous Work

The miscellaneous work on gases in minerals dating back to the time of R. W. Bunsen (1853) has been ably reviewed and summarized by F. W. Clarke.²⁷ Much of this is fragmentary and qualitative and is of little value as a contribution to the understanding of such systems. One of the important earlier studies of gases in rocks was made by Chamberlin in 1908.²

Some data are presented by Chamberlin to support his proposals as to the possible sources and states of gases in rocks. Some attempts, attended by limited success, have been made to relate gas composition to rock composition, particularly to the iron oxides.^{21,22} Shepherd in 1938 compared the composition of the gas extracted from cooled lava by heating the rock to redness in vacuum, to the composition of the gas collected from the volcano, but obtained poor correlation because of difficulty in obtaining rock samples containing the original magma gases. Shepherd concluded that any such relationship is non-existent or obscured in gases extracted from rocks and in volcanic gases. Jaggard, in a study of Hawaiian volcanic gases suggested gas chemistry as the "heart of the volcano magma problem". He had difficulties, however, in obtaining any consistent correlations between the composition of the rock and the composition of the gas. Poor sampling techniques were suggested as reasons for the inconsistency of his results.

A recent application of the gas content of minerals has been its use in determining the age of rocks. This method involves extracting the gas from the rock samples and determining the argon⁴⁰:potassium⁴⁰ ratio in the extracted gases.²⁸ An isotopic dilution method was employed and the argon extracted from the rocks was purified and its isotopic

composition was determined with the aid of a mass spectrometer.

In 1948, George C. Kennedy in studying the equilibrium of volatiles and iron oxides in igneous rocks, determined the value of the equilibrium constant, K, for the reaction $2 \text{Fe}_2\text{O}_3 \rightleftharpoons 4 \text{FeO} + \text{O}_2$ at different temperatures between 1200°C and 1420°C where K may be expressed as $K = \frac{(\text{FeO})^4 (\text{O}_2)}{(\text{Fe}_2\text{O}_3)^2}$. He suggested that the evaluation of the ferrous-ferric iron ratio would clarify several important problems of volcanology and petrogenesis and discussed applications of the result to problems of field geology. Although Kennedy later stated that on some of his assumptions were erroneous, concerning the hydrogen partial pressure in the above expression, two of these applications may be cited here as examples.²⁹ (1) The ratio of ferrous to ferric iron in an unalterable, cold, igneous rock will allow the calculation of the partial pressure of oxygen under which the melt crystallized, if a good estimate of the temperature of crystallization can be made. (2) The partial pressure of oxygen in a rock melt is a function of the total pressure due to all volatile material as well as of gas composition. Because the ferrous-ferric ratio is also dependent on this oxygen partial pressure, this ratio serves as an indication of the total pressure due to volatiles in the melt at the time the iron bearing minerals

crystallized.³

N. F. Bowen and J. F. Schairer investigated the system FeO-SiO₂ in 1932, one of the early significant contributions to the study of oxidation-reduction in silicates.³⁰ They recognized the important fact that the existence of a low concentration of ferric ions in this system cannot be avoided and that in effect they were studying a three-component system. Although iron oxide is the third most abundant constituent of rocks, being exceeded by silica and alumina, relatively little work had been done on the FeO-SiO₂ system prior to 1932. The silicates of aluminum oxide, Al₂O₃, calcium oxide, CaO, sodium oxide, Na₂O, magnesium oxide, MgO, and potassium oxide, K₂O, however, had been the subject of numerous investigations.

(2) Metallurgical Studies

In recent years, much work has been done in the study of the chemistry of metallurgical slags. It is coincidental that the same fundamental system, iron oxide-silica, is of interest to both the metallurgist and the petrologist. This system is tied in intimately with the problems of iron production. Some of the more important and pertinent publications in this field may be mentioned. The equilibrium $\text{FeO} + \text{H}_2 \rightleftharpoons \text{Fe} + \text{H}_2\text{O}$ at temperatures up to the melting point of iron has been studied³¹

and indirect calculation of the equilibrium constant was obtained from a study of equilibria in the Fe-H-O system, on the basis of the partial pressures of H_2O and H_2 .³² A major contribution to the knowledge of the iron oxide system at high temperatures was made by L. S. Darken and R. W. Gurry.³³ They determined the CO-CO₂ ratios in equilibrium with iron and wüstite at temperatures between 1038°C and 1365°C and that in equilibrium with wüstite and magnetite between 1096°C and 1388°C. The thermodynamics of liquid oxide and other phases in the iron-oxygen system was worked out from the studies on the equilibrium relations between partial pressure of oxygen, temperature and composition of oxide.³⁴ Controlled gas pressures in a range covering oxygen partial pressures up to one atmosphere were used. In subsequent work Darken and Gurry investigated the effect on the equilibrium of the addition of calcium oxide, CaO, and manganese oxide, MnO, to the iron oxide.³⁵ Chipman and Larson have employed similar methods of gas-slag equilibria to study similar iron oxide systems.^{36,37}

The study of the iron silicate system was the natural extension of the iron oxide investigations. Darken determined the phase equilibria in the system Fe-Si-O as a function of gas composition and temperature.⁹ R. Schuhmann and his group

studied the constitution of the ternary system, $\text{FeO-Fe}_2\text{O}_3\text{-SiO}_2$ at slag making temperatures and also worked out the thermodynamics of iron silicate slags.^{38,39,40} Recently, Arnulf Muan has investigated the phase equilibria in this same system and he has discussed the difficulties arising from the fact that the composition of the condensed phase containing iron or iron oxide as a component is dependent on the gas phase.⁸

A careful study of all the work to date leads to a fairly good understanding of the iron oxide system, and of the conditions at the liquidus in the iron oxide-silica systems, at temperatures up to 1600°C.

Object of the Research

The object of the research described here is to investigate the relationship between the equilibrating atmosphere, the extracted gases and the ferric-ferrous ratio in both a synthetic model system, Fe-O-Si, and natural rock systems. The nature of the work is to a great extent exploratory, for the existence of such relationships have thus far not been shown experimentally, and there is no certainty that this work will demonstrate the existence of any such relationships. Considerable refinement in techniques,

particularly of gas extraction and analysis, and of ferrous-ferric iron analysis was necessary for the research, and much preliminary work was devoted to this.

II. EXPERIMENTAL

Preparation of Samples

(1) Iron Oxide-Silica Sample

The stock iron oxide-silica slag was prepared according to the procedure described by Schuhmann and Ensio.⁴⁰ 3.350 g. Baker's c. p. hydrogen reduced iron powder, 9.582 g. Baker's c. p. ferric oxide, and 5.405 g. powdered silica--prepared by crushing and grinding clear quartz tubing and screening to #100 mesh--were thoroughly mixed and ground in an agate mortar. The proportions used were calculated to yield a slag corresponding approximately to fayalite (Fe_2SiO_4). The mixture was packed firmly in a clean 25 ml. iron crucible which was fitted with a cover made from another iron crucible. Figure 2 shows the equipment which was used during the heating of the crucible.

Oil pumped (c. p.) nitrogen--purified by bubbling through (1) ammoniacal cuprous chloride solution, (2) water, (3) 12 N H_2SO_4 solution, and (4) a trap placed in a dry ice-acetone bath--was used to flush out air from the system before and during the preparation of the sample. After a preliminary nitrogen flush for ten minutes, the induction heater was switched on and the crucible was heated at approximately 800°C for five minutes to remove moisture and adsorbed or

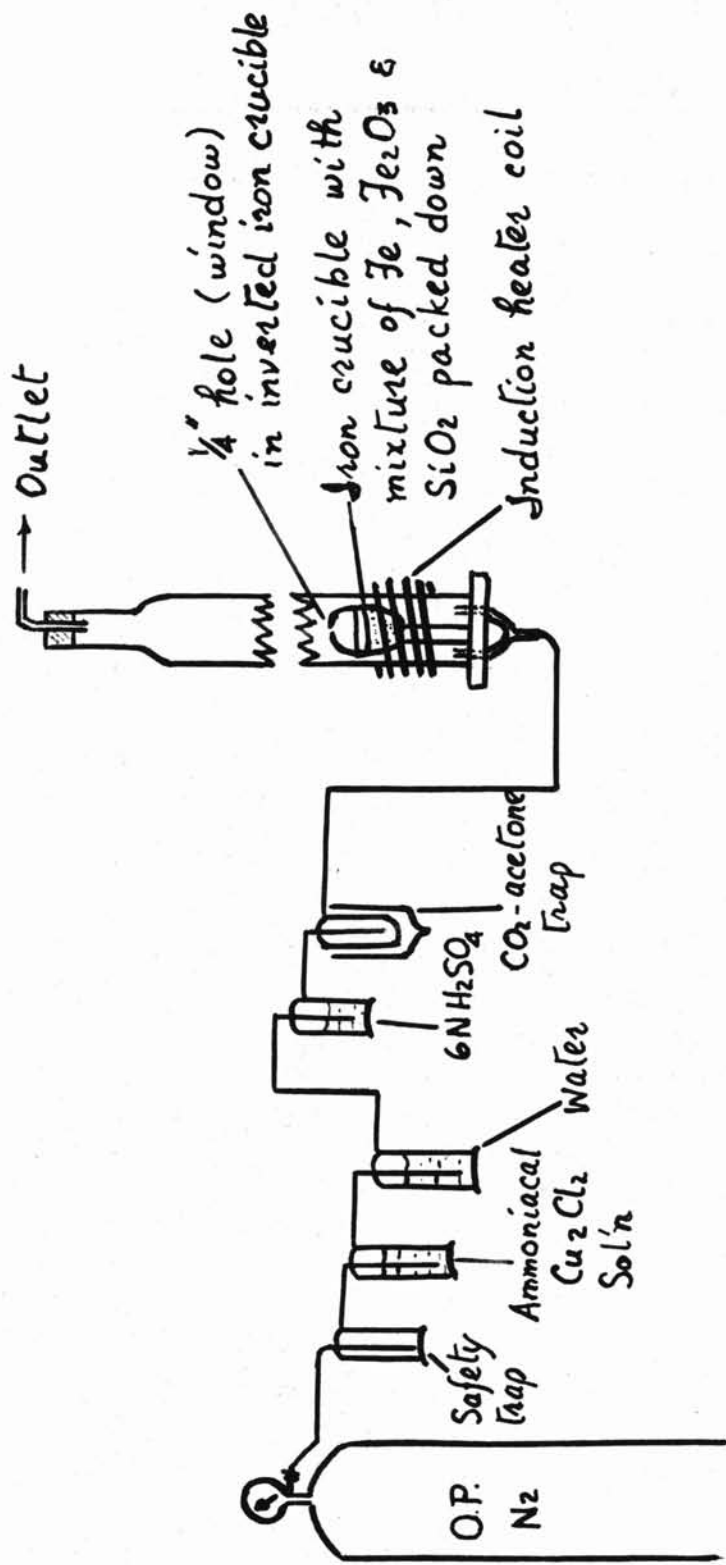


Figure 2. Equipment for Preparation of Synthetic Melts

absorbed gases. Following a 15-30 minutes cooling period during which purging with purified nitrogen was continued to remove the gases evolved in the preliminary heating, the induction heater was turned on and the crucible was heated gradually up to approximately 1300°C. At this temperature the melt was completely fluid, and the heating was continued for 25-35 minutes until the iron crucible started to melt. The melt was removed from the crucible, crushed, and remelted in a new iron crucible under the same conditions as for the first melting period to assure that the sample was homogeneous. A Leeds and Northrup optical pyrometer was used for temperature measurements.

The cooled slag was removed from the crucible, with great care being taken not to include any pieces of the molten crucible, crushed in a diamond mortar, and screened. The #20-40 mesh particles were collected and a tiny magnet was raked over the screened product to remove any pieces of iron that might have been accidentally included. The yield of screened sample from the original 18 g. of starting material was approximately 9 g.

(2) Calcium Oxide-Iron Oxide-Silica Sample

The same amount of iron, ferric oxide and silica as in the preparation above were used with the addition of 1.650 g. of

Baker's c. p. calcium oxide. This weight of calcium oxide is 8% of the total weight of the mixture, which is the approximate percentage of calcium oxide reported for Hawaiian rocks.⁴¹ The procedure employed was the same as in the preparation above, 8 g. of screened sample being obtained.

(3) Andesine Andesite and Olivine Basalt Samples

The andesine andesite and olivine basalt samples were previously collected and identified by qualified geologists.⁴² Adequate amounts were crushed and screened; the #20 -40 mesh particles were collected.

Equilibration of Samples in H₂-H₂O and CO-CO₂ Atmospheres

(1) Construction of Furnace

Figure 3 shows the furnace used in the equilibration. The heating element was approximately 50 ft. of Kanthal wire, 0.081 in. size and with a resistance of 0.132 ohm/ft., wound $\frac{1}{4}$ in. apart around an alundum tube ($2\frac{1}{2}$ in. inner diameter) 24 in. long. Norton's refractory cement was used to set the wire. The ends of the furnace were fashioned out of transite and the outside covering was 1/16 in. thick aluminum sheets. The insulation material was "Sil-O-Cel".

(2) Equilibration in H₂-H₂O Atmospheres

The H₂-H₂O saturator is essentially one described by L. Himmel, R. F. Mehl, and C. E. Birchenall and is shown in

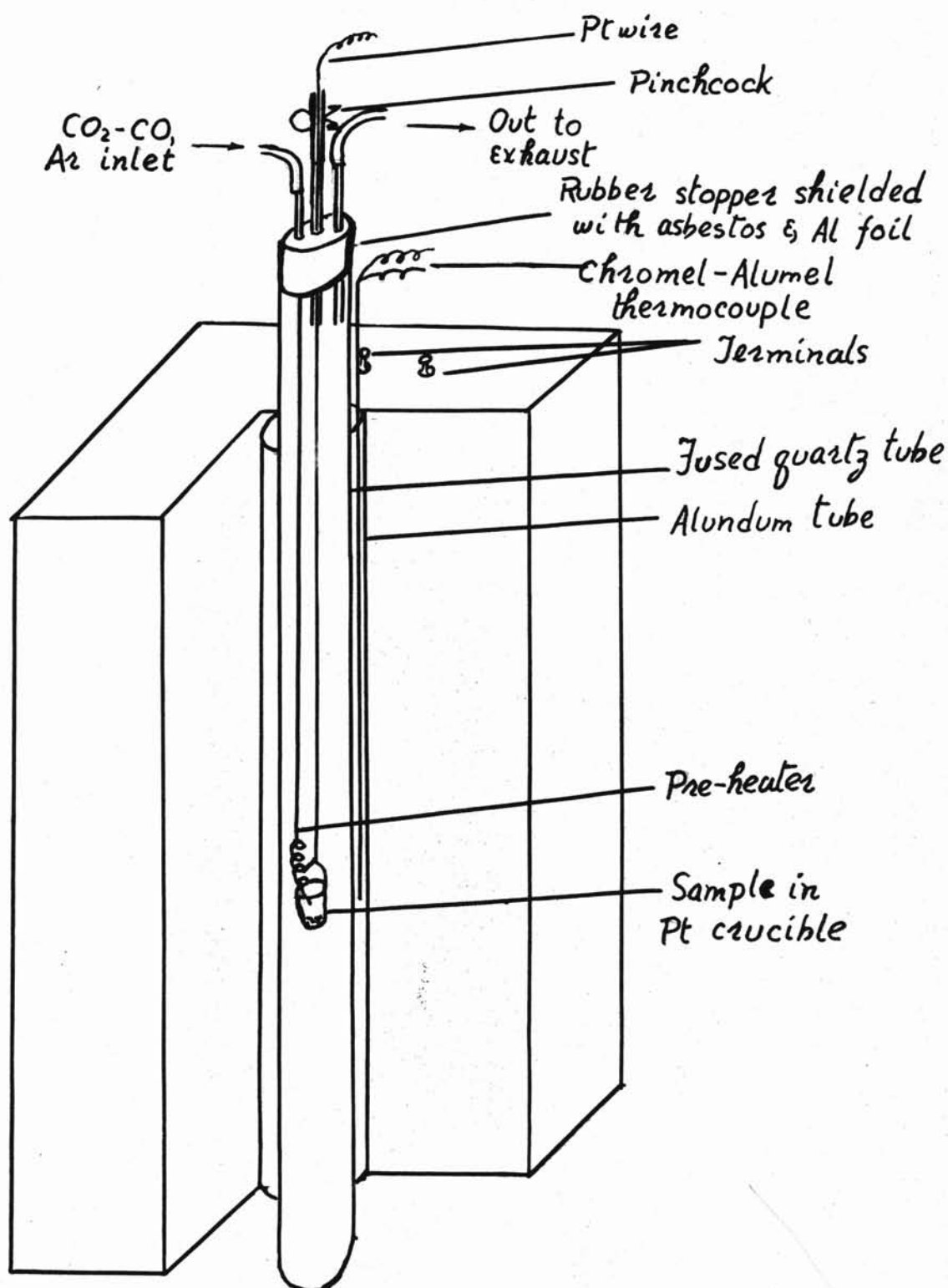


Figure 3. Furnace Assembly for Equilibration

Figure 4.⁴³ Flowmeters were used to control the proportioning of gases. Each flowmeter was calibrated by measuring the volume of water displaced per unit time by the gas. The chromel-alumel thermocouple used to measure the furnace temperature was calibrated against a standard Pt, Pt-Rh couple. In preliminary work with the iron oxide-silica slag samples, hydrogen and water vapor in varying ratios were used as the equilibrating atmospheres. The temperature of the bath used in heating the water vapor saturator was kept constant at 45°C, thus keeping the water vapor partial pressure constant. The H₂-H₂O ratios were varied by altering the hydrogen and argon flows. Although carbon monoxide, carbon dioxide and water vapor were found to be present, no hydrogen could be found in the iron oxide-silica samples on analysis. Therefore in all later runs, carbon dioxide and carbon monoxide mixtures were used for equilibrating the samples.

(3) Equilibration in CO-CO₂ Atmospheres

Purified tank carbon dioxide was used, and carbon monoxide was produced by reduction of carbon dioxide over hot carbon. Proportioned mixtures were obtained through control of the flow of respective gases measured by flowmeters and a controlled amount of argon was added to minimize thermal diffusion. Figure 5 shows the apparatus used. Traces of oxygen were

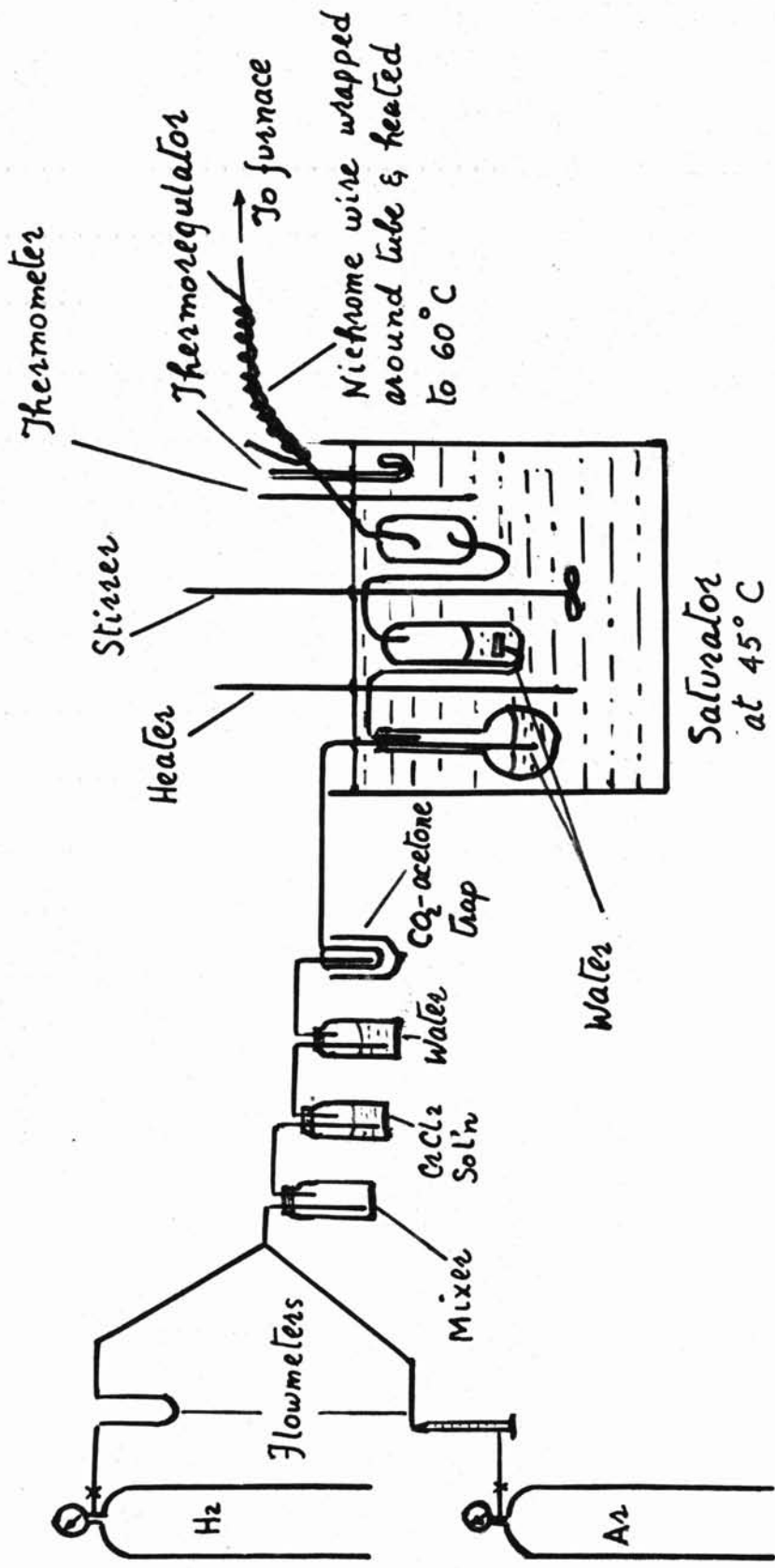


Figure 4. Equipment for Preparation of H_2 - H_2O Mixtures

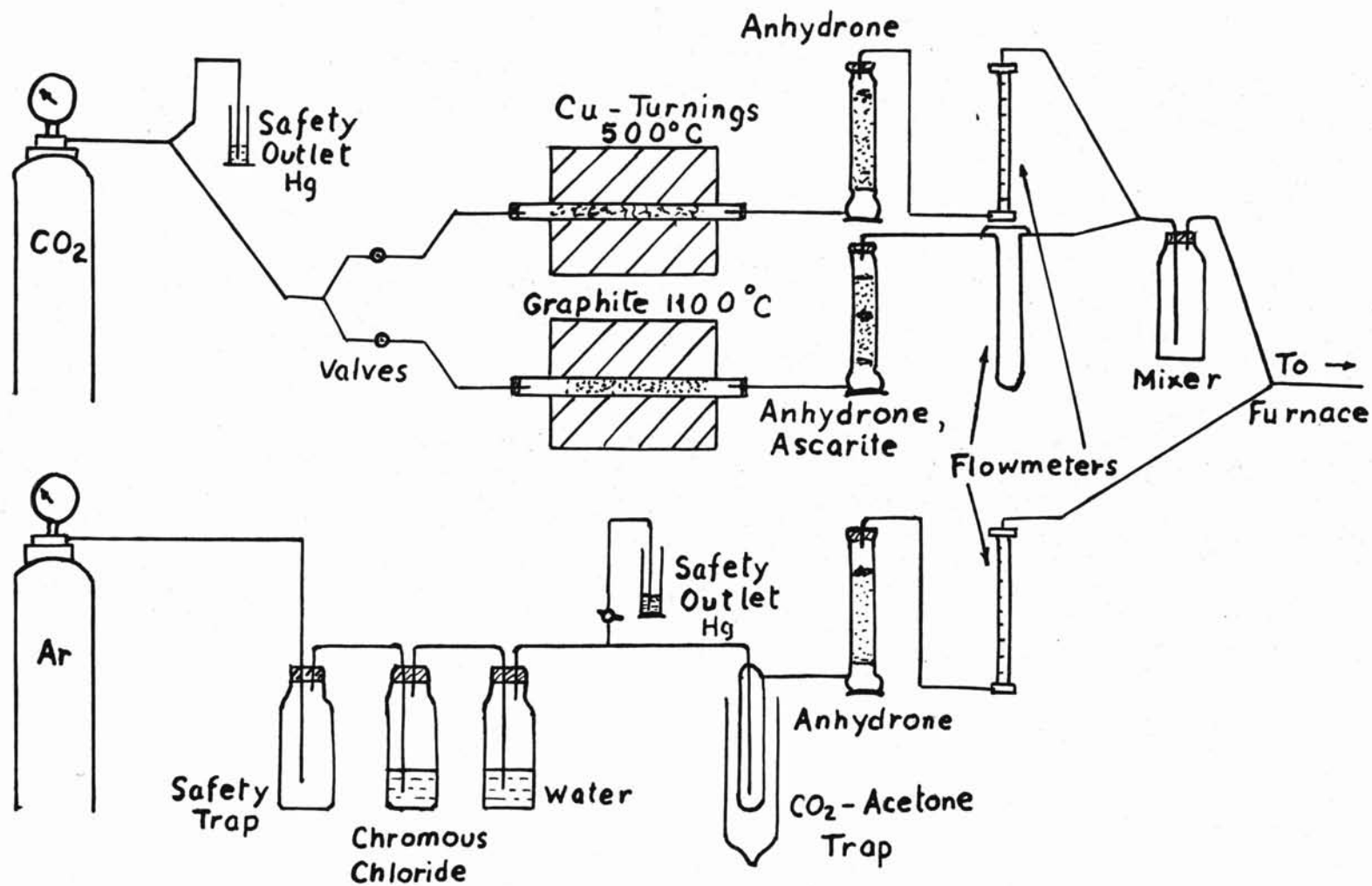


Figure 5. Equipment for Preparation of CO-CO₂ Mixtures

removed from the carbon dioxide by copper metal turnings heated to 500°C. Ascarite was used to remove traces of carbon dioxide from the carbon monoxide stream. Argon was purified by passing through a chromous chloride solution.⁴⁴ Anhydron (magnesium perchlorate) was used to dry all the gases before they entered the equilibrating chamber. The flowmeters were recalibrated for carbon monoxide and carbon dioxide by the same method used previously.

In an actual determination, 1.0-1.5 g. of sample was placed in the 25 ml. platinum crucible and this was kept at the bottom of the quartz tube until the furnace temperature of 1100°C to be used in the equilibration was reached, usually in about twelve hours. The system was purged with argon for 15-30 minutes. The carbon monoxide and carbon dioxide flows were adjusted to 100-200 ml. per min. The sample was then hoisted by the platinum wire into position directly below the quartz, gas pre-heater coil at the mid-point of the furnace. Preliminary trials showed that equilibrium was attained in about six hours. All determinations, however, were for ten hours to assure the attainment of equilibrium. At the end of a determination the sample was quickly lowered to the cooler portion of the quartz tubing. The carbon monoxide and carbon dioxide flows were stopped, the argon flow being maintained,

and the furnace was allowed to cool. After about one hour, the argon flow was stopped, the sample was removed and bottled for gas and iron analyses.

The choice of argon as the carrier gas and the use of the quartz, gas pre-heater coil were made to prevent any separation of the gas mixture entering the furnace by thermal diffusion. This important and perhaps unexpected phenomenon, whereby a mixture of a lighter and a heavier gas will be separated to some degree in the hot zone of a furnace, has been investigated, and means--such as those used in this work --of reducing or eliminating the effect has been discussed very thoroughly, by Darkin and Gurry,³³ and by Chipman.⁴⁵

Analysis of Samples for Fe(II) and Fe(III)

Two methods of analysis were tried. One a polarographic method reported by Bien and Goldberg⁴⁶ and the other a spectrophotometric method introduced by Harvey, Smart and Amis.⁴⁷ Both methods determined the Fe(II) and Fe(III) ion concentrations simultaneously. Because the spectrophotometric method was faster and free from the necessity of using special fluxes for the samples to meet the solubility requirements, it was used in this work.

Spectrophotometric Determination of Fe(II) and Fe(III)
Concentrations Using the 1, 10-Phenanthroline Complexes

A Beckman quartz spectrophotometer Model D. U. with a photomultiplier attachment and matched Beckman Corex cells with 0.998 cm. light paths were used for the absorbance readings.

(1) Preparation of Solutions

(a) 0.3% 1,10-phenanthroline reagent solution. One gram of reagent grade 1,10-phenanthroline monohydrate obtained from G. Frederick Smith Chemical Co. was added to 100 ml. of hot distilled water. After all the reagent dissolved, 233 ml. of distilled water were added.

(b) Standard iron solutions. The standard Fe(II) solution was prepared by dissolving 7.0213 g. of Baker's reagent grade ferrous ammonium sulfate hexahydrate, $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6 \text{H}_2\text{O}$, in distilled water acidified with 3 ml. concentrated sulfuric acid and diluting to a liter. Similarly the standard Fe(III) solution was prepared from 8.6337 g. of Baker's reagent grade ferric ammonium sulfate dodecahydrate, $\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$. The concentrations of both solutions, checked gravimetrically as ferric oxide, Fe_2O_3 , were found to be 1.000 mg./ml. or 1000 p.p.m. in each case. Suitable aliquots were taken to make up the solutions used in obtaining the calibration curves.

(c) Buffer solution. Two buffer solutions were prepared from Baker's c. p. potassium hydrogen phthalate. One, a 0.2 M potassium hydrogen phthalate solution was used for making up the standard solutions for the calibration curves; the other, a 0.3 M potassium hydrogen phthalate solution was treated with 1.00 N sodium hydroxide solution. Enough sodium hydroxide solution was added to give a pH of 6.6, the pH reading being taken on a Beckman Model G pH meter. Approximately 30 ml. of 1.00 N sodium hydroxide solution were required for 100 ml. of 0.3 M potassium hydrogen phthalate solution to obtain a pH of 6.6. This second buffer solution was used in the actual analyses of the samples.

(d) Saturated aluminum nitrate solution. Excess Merck's reagent grade aluminum nitrate nonahydrate, $\text{Al}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$, was added to 500 ml. of distilled water and shaken. After saturation of the solution was assured, the excess solid was removed by filtration. This solution was used only in the analysis of the unknown solutions to reduce the fluoride ion concentration.

(2) Standard Absorption Curves

The work of Harvey, et al.⁴⁷ was repeated to obtain standard absorption curves for Fe(II) and Fe(III). The absorption spectra of Fe(II) and Fe(III) were determined.

for the wave length interval 380-600 μ . Each solution was prepared from 10 ml. of 0.1% 1,10-phenanthroline reagent, 5 ml. of phthalate buffer, 2.00 ml. of 100 p.p.m. iron solution diluted to 25 ml. which gave a solution containing 8 p.p.m. iron. The Fe(II) curve showed a maximum at 512 μ and an isosbestic point with the Fe(III) curve at 396 μ . The 396 μ reading indicated total iron concentration and since Fe(III) showed very little absorption at 512 μ , this reading represented approximately the Fe(II) concentration. Fe(III) concentration was determined by difference. The exact Fe(II) concentration was obtained after subtracting the very small absorption at 512 μ due to Fe(III). This new value subtracted from the original total iron gave the exact Fe(III) concentration. Calibration curves of concentration vs. absorbance for Fe(II) and Fe(III) were determined at 512 and 396 μ . The calculated slopes for the straight lines obtained were: (a) 0.196 p.p.m.⁻¹ for Fe(II) at 512 μ , (b) 0.054 p.p.m.⁻¹ for Fe(II) or Fe(III) at 396 μ , and (c) 0.005 p.p.m.⁻¹ for Fe(III) at 512 μ .

(3) Analysis of Unknown Samples

A major obstacle in analyses of mineral samples for both their Fe(II) and Fe(III) contents is getting the sample into solution without altering the Fe(II) and Fe(III) concentrations

through oxidation of Fe(II) by the oxygen of the air. In preliminary work, considerable difficulty in obtaining consistent results was encountered when the samples were put into solution by 48% hydrofluoric acid in a nitrogen atmosphere. The elapsed time for complete solution of the solid was about 10-12 hours and this long period undoubtedly affected the Fe(II) and Fe(III) concentrations even under the protecting nitrogen blanket. It was found that a mixture of ten parts hydrochloric acid (35%) and three parts hydrofluoric acid (48%) used by Soule⁴⁸ in Fe(II) determinations in magnetite was a satisfactory solvent provided a CO₂ atmosphere was used and the time of solution limited to one hour. Putting the samples into solution with hydrofluoric acid resulted in a high fluoride ion concentration which if higher than 25 p.p.m. interfered in the analysis. Two modifications of the procedure suggested by Harvey and his co-workers were introduced.⁴⁷ One was the addition of boric acid solution and the other the addition of saturated aluminum nitrate solution. Both solutions worked through complex formation to reduce the free fluoride ion concentration to a point where it no longer interfered. Because these solutions were acidic, a more basic phthalate buffer solution of pH 6.6 was used.

The following procedure was followed in the analysis.

(a) Two 0.0150-0.0250 g. samples were weighed and placed into small polyethylene bottles which had been dried and previously filled with carbon dioxide.

(b) Two to three ml. of HCl-HF mixture (10:3) were added to each bottle. The bottles were placed in a 400 ml. beaker filled with water kept at 40-50°C. A constant stream of carbon dioxide was passed over the mouths of the bottles by means of a funnel fitted snugly over the water bath, the lip on the beaker serving as the outlet for the gas.

(c) After one hour, the warm bath was replaced by an ice bath and 5 ml. of boric acid solution (25 g. Baker's c. p. boric acid in 500 ml. of solution containing 10 ml. of concentrated sulfuric acid) were added. The contents of the bottles were transferred to 25 ml. volumetric flasks and diluted to volume with oxygen free distilled water.

(d) For absorbance readings, the solutions were made up in 10 ml. volumetric flasks by adding the following in order: 2.00 ml. of phthalate buffer solution (pH 6.6), 0.40 ml. of saturated aluminum nitrate solution and 0.10 ml. of the solution prepared above. Readings were taken at 512 and 396 m μ for each solution and blanks subtracted before Fe(II) and Fe(III) concentrations were calculated from the predetermined slopes.

(4) Precision and Accuracy of the Iron Determination

The precision and accuracy of the iron analysis were determined by analyzing a Bureau of Standards iron ore magnetite sample no. 29. An average deviation of 8/1000 and an accuracy of 2.1% were calculated for a series of four independent analyses. The figures are based on the value of 1.92 for the Fe(III)/Fe(II) ratio as reported by Soule⁴⁸ compared to the average value of 1.96 for the same ratio as determined presently.

Gas Analysis

(1) Apparatus

The complete system is shown in Figure 6. The apparatus consisted of four parts--a gas extraction chamber and induction furnace, a water vapor measuring system, a Toepler pump, and a low pressure gas analysis system--connected in series to form an integral unit. A mercury diffusion pump backed by a high vacuum Welsh oil pump maintained the basic vacuum in the entire system. Two other mercury diffusion pumps served as pumps in the system; one was used to remove the gas as it was extracted from the heated sample and to pass it into the water vapor trap while the other was used as a circulating pump in the gas analysis section.

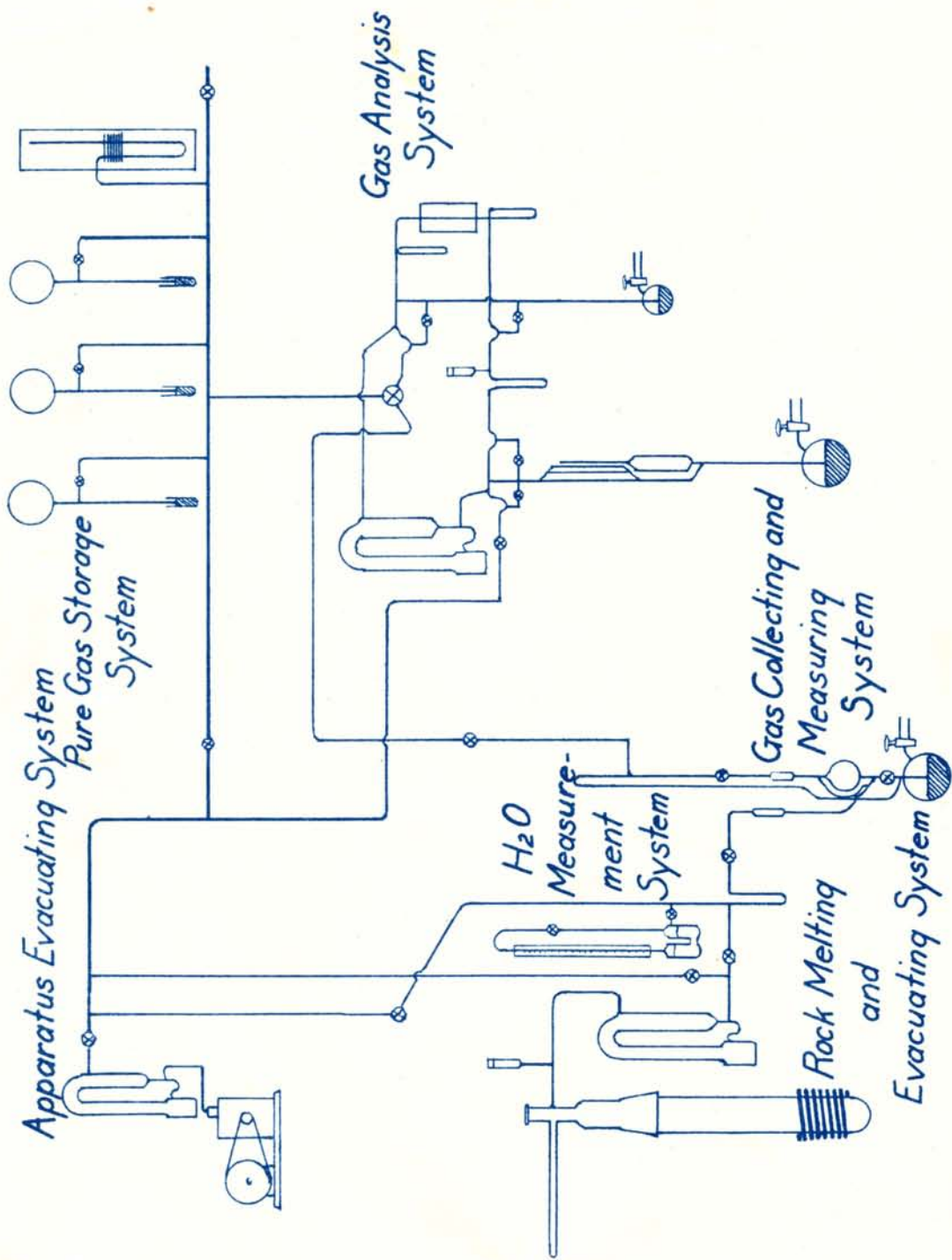


Figure 6. Schematic Diagram of System for Degassing Solid Samples and Analyzing the Extracted Gases

The gas extraction chamber (Figure 7) was transparent quartz tubing, 40 mm. in diameter, closed at one end. Connection to the system was via a water jacketed ground glass joint. Use of the ground glass joint facilitated the removal of the sample from the platinum crucible and permitted the cleaning of the evaporated platinum from the chamber with aqua regia after each determination. An induction heater which consisted of a Lepel high frequency converter and a water-cooled load coil of copper tubing was used to attain the required fusion temperatures of the samples. The platinum crucible, that was heated by acting as a secondary for the inductor, was used also as a container for the fusion and was placed on a ceramic crucible. The sample was introduced into the hot degassed platinum crucible by means of a special dumper which was made from 3 cm. of pyrex tubing, 9 mm. in diameter, sealed on one end. A rod of pure iron about the same size as the tubing was attached to the sealed end with a chain forged from copper wire. A small permanent magnet was used to move the dumper along the side-arm. Figure 7 shows the gas extraction chamber.

The water vapor measuring section is shown in Figure 8. A dry ice-acetone mixture (-78°C , vapor pressure of water-- 10^{-3} mm.) was utilized as coolant around the trap. The water

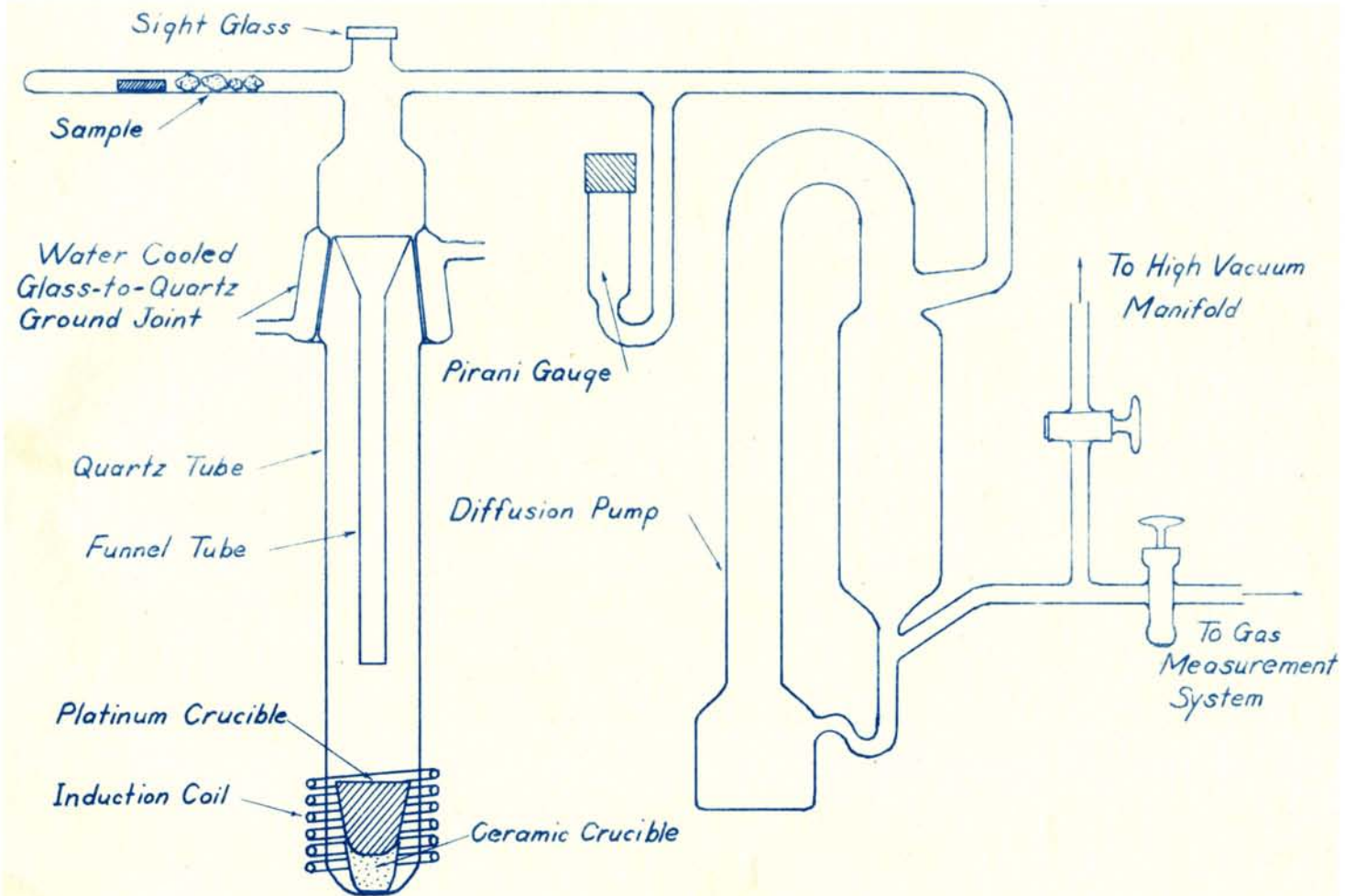


Figure 7. Gas Extraction Chamber

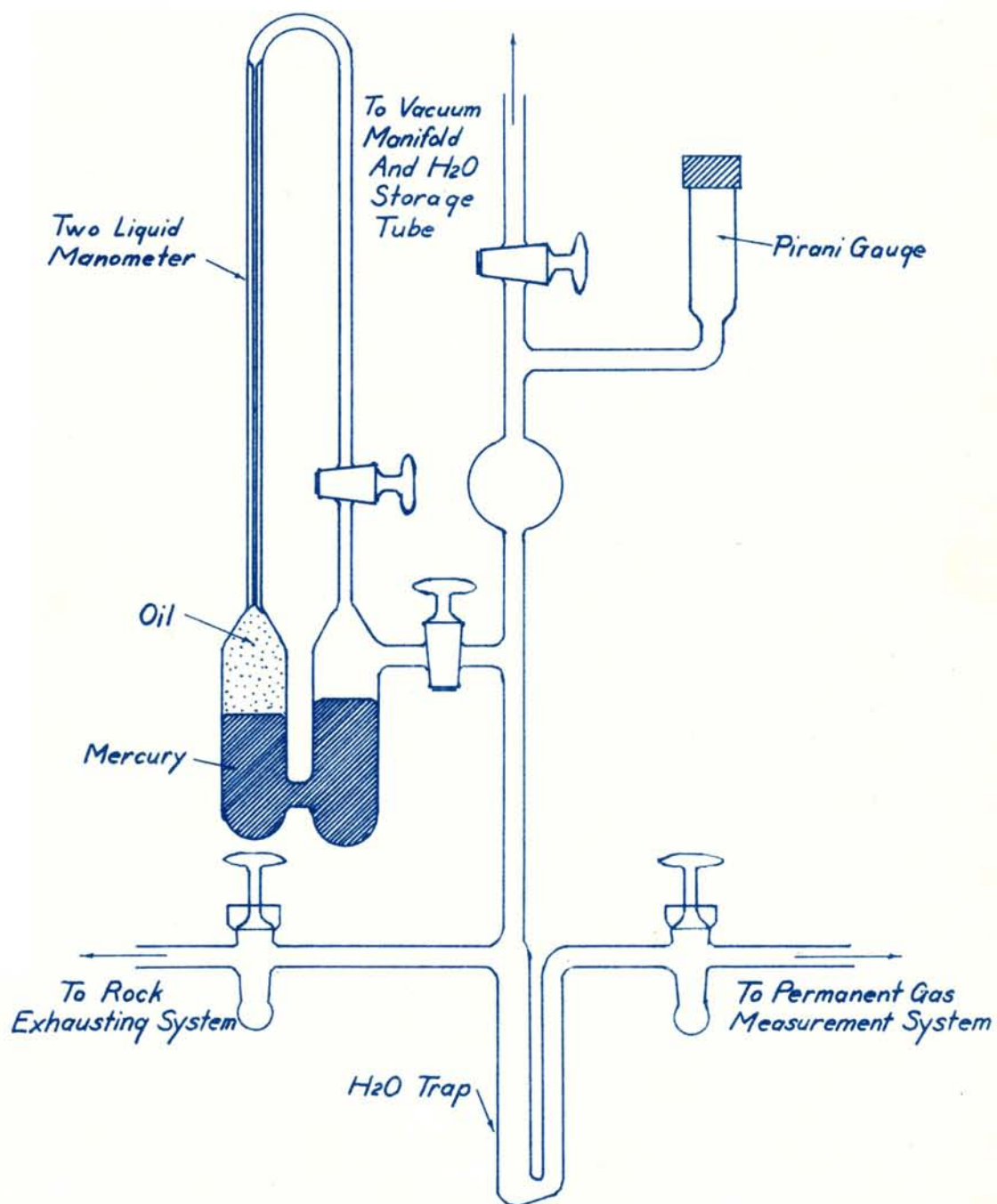


Figure 8. Water Vapor Measuring System

vapor pressure measurements were made on a special two-liquid manometer that could be used for intermediate pressures to 20 mm. Hg. The two liquids used were octoil S and mercury. The manometer was calibrated by measuring the readings produced by known weights of water introduced with capillary tubes. A value, 6.5 ± 0.1 cm./mg. was obtained, thus giving an accuracy of ± 0.015 mg. of water.

Figure 9 shows the manually operated Toepler pump which collected and transferred the gas into a calibrated space where the quantity of permanent gases was measured.

The gas analysis section as shown in Figure 10 consisted of a mercury diffusion pump, a Pirani gauge, freeze-out traps, a combustion furnace, and a McLeod gauge. During the analysis the system was isolated by means of strategically located mercury cut-offs. Stopcocks could not be used since the concomitant greases used absorb and give off gases in an unpredictable manner. The combustion furnace which contained platinum wire catalyst was operated at 475°C and used to oxidize carbon monoxide and hydrogen. The Pirani gauge was used to indicate the presence or complete passage of a gas.

A more detailed description of the entire gas analysis set-up is given in the thesis of K. Terada.⁴²

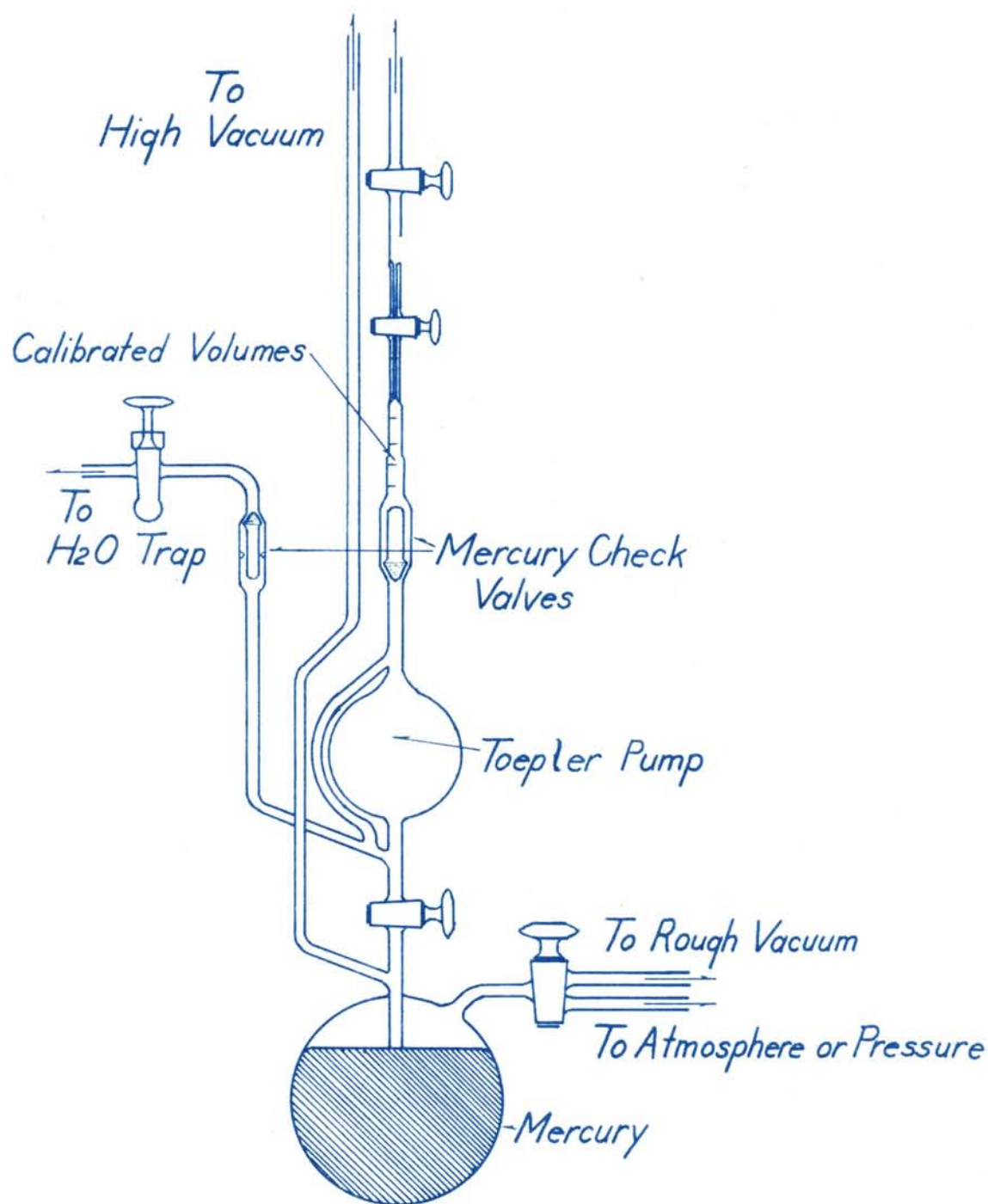


Figure 9.
Toepler Pump with System for Measuring Permanent Gases

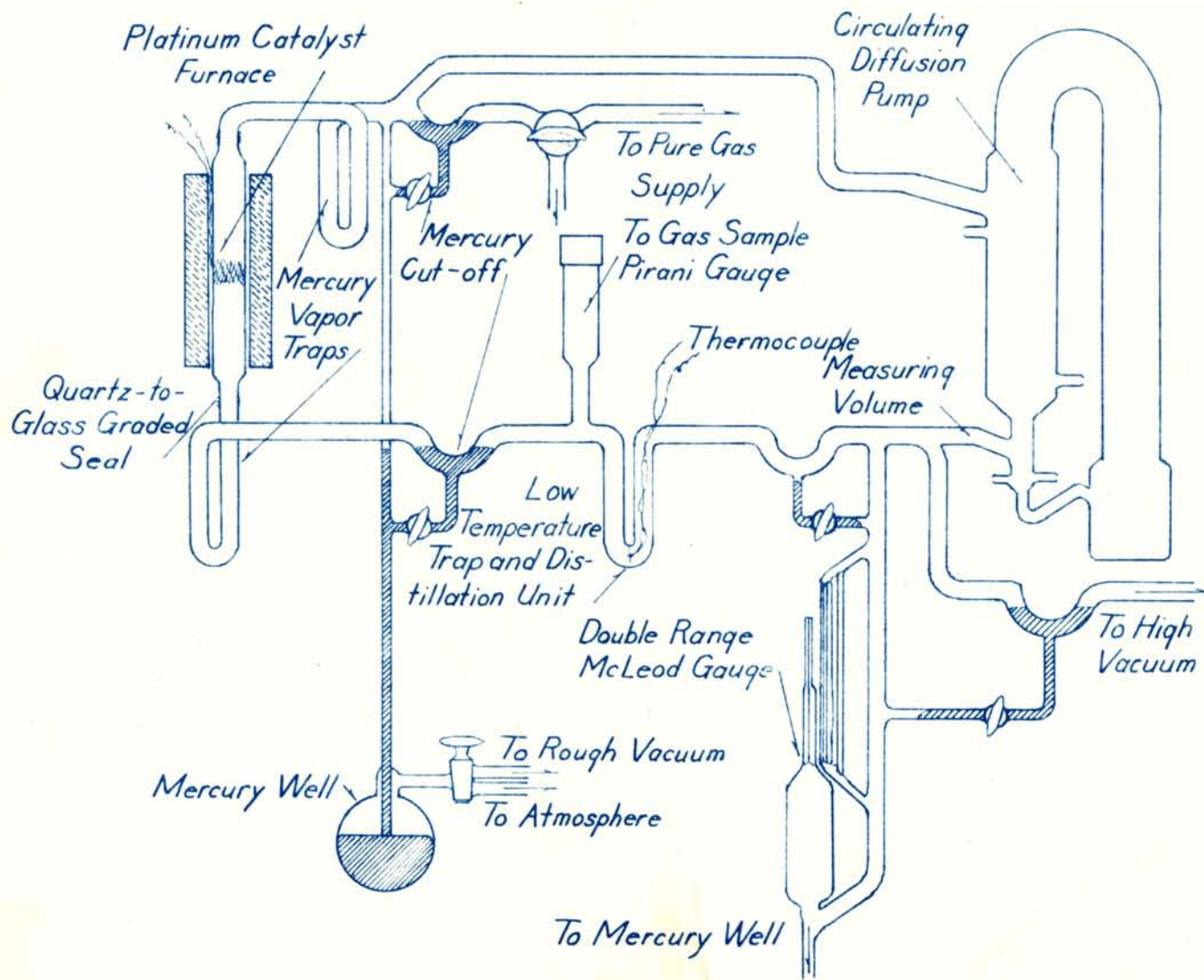


Figure 10. Low Pressure Gas Analysis System

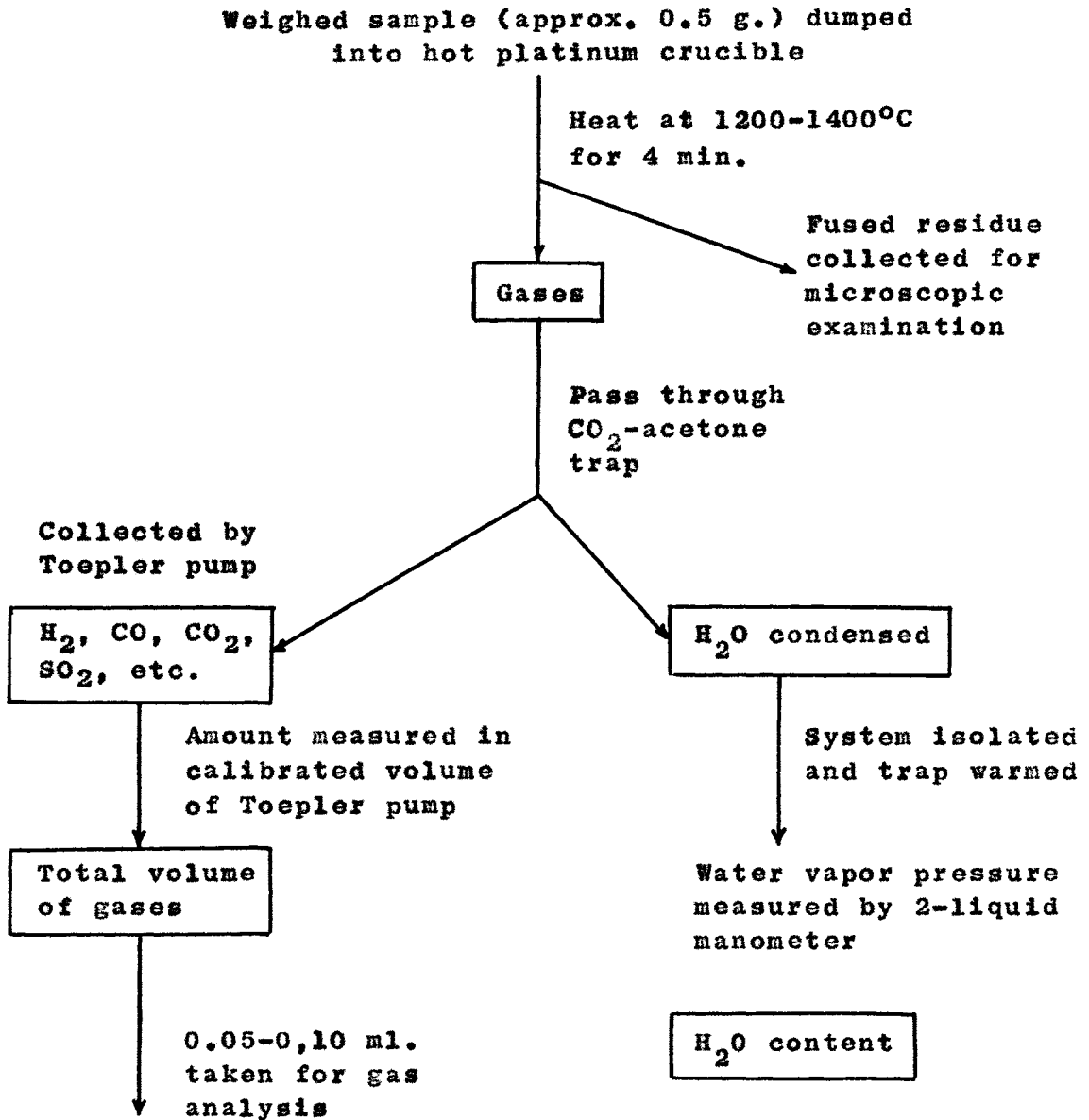
(2) Procedure

The chronological steps in the procedure are indicated on Flow Sheets I, II, III. The samples were weighed on an analytical balance and usually about 0.6 g. was used. The weighed sample was placed in the dumper and pushed into the side-arm of the combustion chamber. The side-arm was then sealed. A preliminary degassing of the gas extraction chamber included heating of the platinum crucible for three five-minute periods at one hour intervals at the temperature of the extraction. Four hours was the minimum time allowed for evacuation and often six hours were required to completely degas the system. A brush flame was used to gently warm the dumper to remove any adsorbed surface gas. When a four minute blank heating time at the temperature of the extraction showed no increase in pressure on the Pirani gauge, degassing was judged to be complete. The sample was introduced by means of a magnet manipulated to cause the dumper to pour its contents through the funnel into the hot platinum crucible. Extraction was continued for a four-minute period, the solid particles having completely melted at the end of this time. The extracted gases were pumped through the trap immersed in a dry ice-acetone mixture and collected in the calibrated space by the Toepler pump. The amount of water in the trap was determined

FLOW SHEET I

EXTRACTION OF GASES

Procedure for extraction of gases from rock samples.



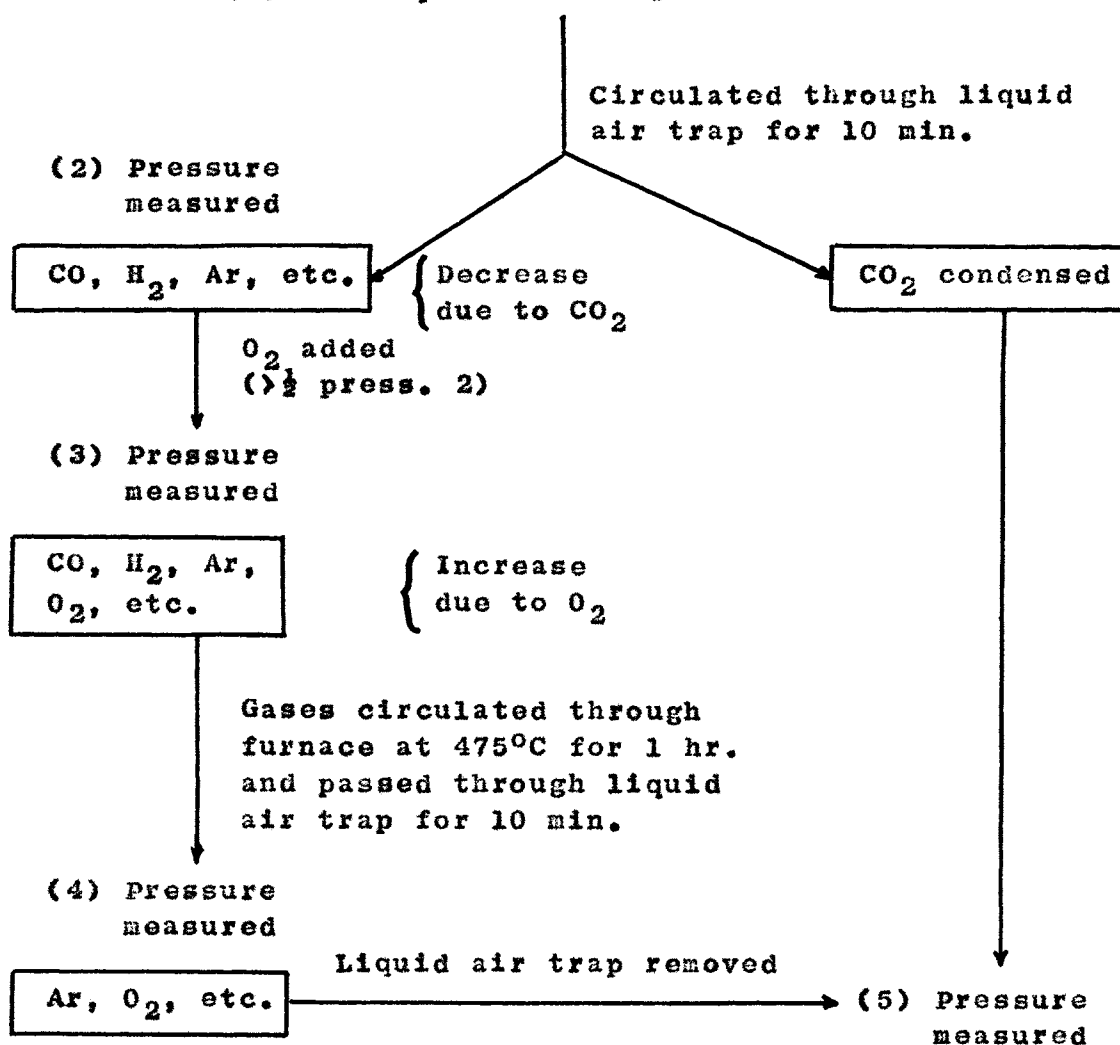
FLOW SHEET II

GAS ANALYSIS

Procedure for samples containing no SO_2 .

0.05-0.10 ml. gas sample introduced

(1) Total pressure of gases measured

Calculation:

$$\text{CO}_2: (1) - (2)$$

$$\text{CO}: [(5) - (4)] - (\text{CO}_2)$$

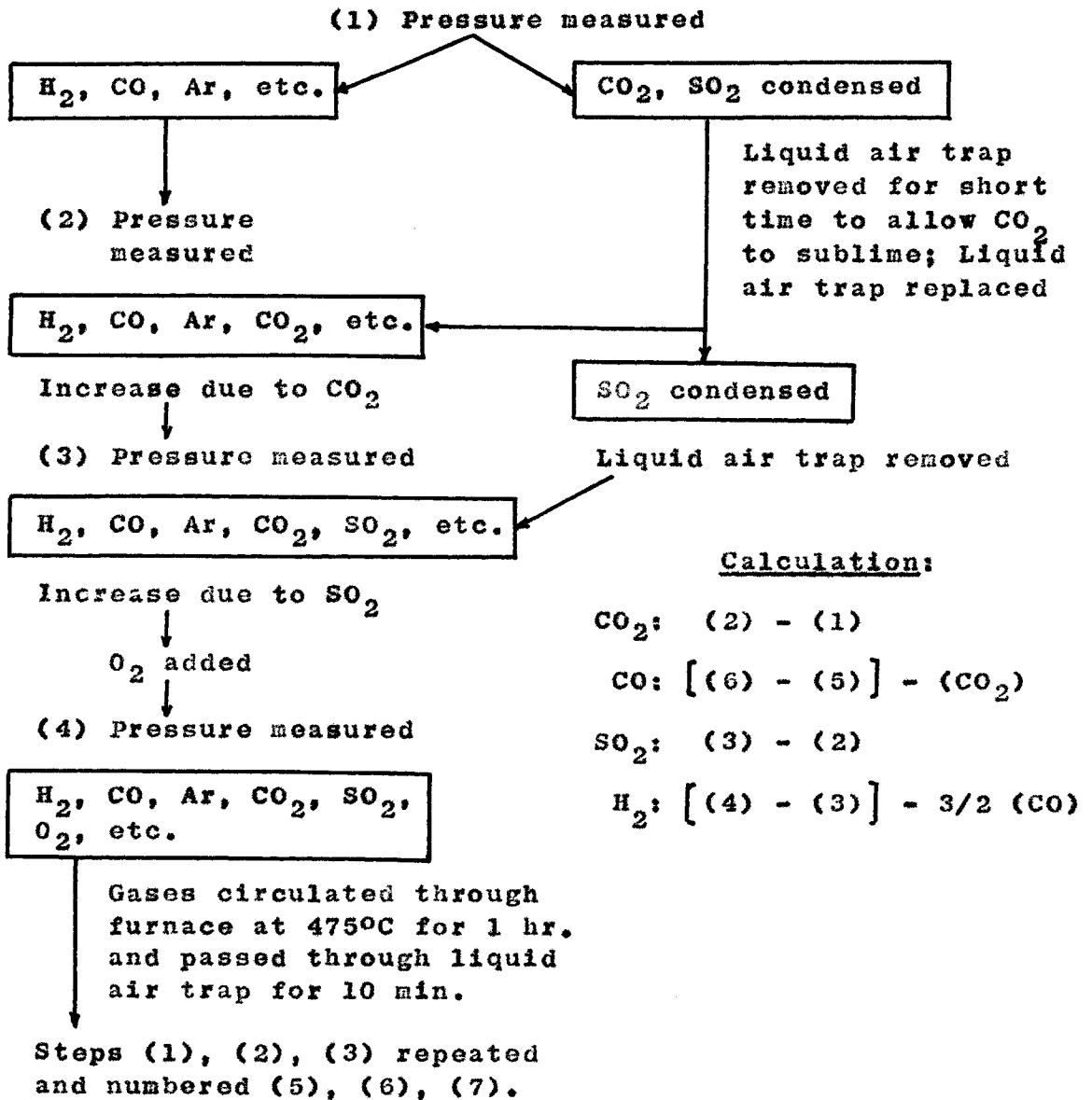
$$\text{H}_2: [(3) - (4)] - \frac{3}{2} (\text{CO})$$

FLOW SHEET III

GAS ANALYSIS

Procedure for samples containing SO_2 .

0.05-0.10 ml. gas sample introduced and circulated through liquid air trap for 10 min.



as vapor and the total quantity of permanent gases collected above the Toepler pump measured. The fused sample was removed from the platinum crucible and saved for later microscopic examination. The gas extraction tube was removed and cleaned in aqua regia after each determination. The platinum crucible was cleaned in hydrofluoric acid followed by treatment in hot concentrated hydrochloric acid after each determination.

A modified low pressure micro method was used for analyzing the gas.⁴⁹ The complete gas analysis was carried out on 0.05-0.10 ml. samples. All the pressure readings were made on a double range McLeod gauge. In all trials, successive readings which were identical were the criteria used to ascertain an acceptable reading. The carbon dioxide content was determined by freezing out this component in a trap cooled in liquid air and measuring the pressure of the gas in a constant volume before and after freeze-out. Sulfur dioxide was determined in the natural rock samples, andesine andesite and olivine basalt, by separating it from the carbon dioxide by fractional distillation from the liquid air trap. Removal of the liquid air trap for a short time caused the carbon dioxide to distill off while keeping the sulfur dioxide in the trap. After the carbon dioxide was removed completely, as indicated by the Pirani gauge returning to its initial

reading, the trap was again immersed in liquid air to prevent sulfur dioxide from distilling. No sulfur dioxide was detected in the synthetic slags and a slightly modified procedure of analysis was followed for these samples. The carbon monoxide and hydrogen were determined by introducing pure oxygen and oxidizing them in the platinum catalyst furnace at 475°C to carbon dioxide and water. The freeze-out traps before and after the furnace were immersed in dry ice-acetone mixtures and served to prevent the entrance of mercury vapor into the furnace. The required pressure readings and the various steps in the complete analysis of the gas are indicated on Flow Sheets I, II, III. The calculations to determine the relative amounts of carbon dioxide, carbon monoxide, hydrogen and sulfur dioxide are also indicated.

Known mixtures of gases have been analyzed in this system with results that are indicated in Table I.⁴² An average deviation of 0.4 for the approximate size of sample used in these determinations is obtained.

TABLE I
ANALYSIS OF A PREPARED GAS MIXTURE

Gas	Volume % Prepared	Volume % Found
Hydrogen	8.0	7.7
Carbon monoxide	15.2	15.9
Sulfur dioxide	5.4	5.5
Carbon dioxide	48.8	49.0
Oxygen	4.8	4.1
Nitrogen	18.0	17.4
	Average deviation	0.4

Microscopic Examination

To establish the presence of metallic iron, fayalite, magnetite and silica in the various samples involved in the study of the Fe-O-Si system, a microscopic technique was employed using a reflecting metallurgical microscope. Several grains of the sample were mounted in transoptic mounting powder and made into a disc, 3 cm. diameter and 1 cm. thick under a pressure of 3500-4000 p.s.i. at a temperature of 130-150°C. The disc was successively polished on "Wetordry Tri-M-Itte" paper, 320 C and 600 A, a polishing cloth covered lightly with levigated alumina, and a nappe of levigated alumina embedded in carnauba wax.

The metallic iron was detected by treating the polished, mounted sample with a dilute solution of copper sulfate. The bright orange-red color of the displaced copper was easily identified. Magnetite grains were detected by examination through the microscope using transmitted and reflected light. The magnetite is opaque and appears black to transmitted light and appears very light and metallic in reflected light. The fayalite was identified by gelatinizing it in fumes of concentrated hydrochloric acid, staining with methylene blue, followed by a microscopic examination. Silica was identified by observing its transparency and by its negative reaction to the above tests.

III. DISCUSSION AND RESULTS

Selection of a Model System

In previous work carried on at the University of Hawaii an extreme variability of the result of the analyses of gases in rocks was noted and correlation between gas composition and rock composition was poor.⁴² This, however, was to be expected because the complete history of these rocks was unknown and obviously quite complex and varied. Many factors influence the final state and composition of the rock before it is collected and analyzed. When the oxidation-reduction system is considered, the degree of exposure to air and moisture while at a relatively high temperature is a very important factor. The rate of cooling and the temperature of the original lava are factors which influence the solubilities and the composition of the gases in the final rock. In addition to these factors, which affect the final rock composition, the variables introduced by the actual analyses are important. Decomposition or volatilization of oxides, adsorbed surface gases and time at extraction temperature are factors which have to be considered.

In order to circumvent or reduce to a minimum these complicating influences, an approach through artificially prepared melts and equilibration techniques introduced by

the metallurgist was worked out. It was decided that the most feasible and simplest system for the investigation was $\text{FeO-Fe}_2\text{O}_3\text{-SiO}_2$. This model system fulfills the requirements of (1) being simple, (2) having the presence of an oxidation-reduction system, Fe(II)-Fe(III) , and (3) being a silicate. Natural rock melts are of course much more complex than the simple oxide-silica systems. The simple systems, however, may provide clues as to what actually occurs in the natural complex silicate systems.

The choice of a sample size of #20 -40 mesh was made for three reasons. (1) The average particle size of approximately 0.5 mm. diameter is large enough so that the adsorption of gases is kept at a minimum. Calculation shows that not more than 0.0066 ml. of a gas like carbon dioxide should be adsorbed on the surface of one gram of sample with the average particle size of 0.5 mm. diameter. (2) The size of the average particle is sufficiently small so that equilibration of the sample is completed in a reasonable length of time (6 hr.). (3) The average particle size is sufficiently small so that the samples can be dissolved in a HF-HCl mixture within a short period in the Fe(II)-Fe(III) iron determination. This short solution time is necessary for an accurate determination of the ferrous and ferric ion concentrations.

Following the study of the Fe-O-Si system, experiments on melts with calcium oxide (CaO) added were carried out to study the influence of a more alkaline condition on gas solubility and equilibrium. In this connection, the addition of alkali oxides (Na₂O and K₂O) were avoided for these are quite volatile at temperatures of the extraction. Finally, the natural rocks, olivine basalt and andesine andesite, were equilibrated and studied similarly to determine whether naturally occurring rocks are affected by varying equilibrating atmospheres in the same way as was the model system. The olivine basalt represented a relatively basic rock whereas the andesine andesite a fairly acidic one.

Volumes of Gases Extracted from Melts

The solubility of gases in silicates has been discussed previously on pp. 11-12. The extent of the solubility of the gases proved to be very slight in the present study. Table II gives the amounts of total permanent gas (approx. 0.1 ml./g.), carbon dioxide, carbon monoxide and water (0.01-0.06 mg./g.) per gram of sample. It was found that this amount of gas was sufficient for an analysis. It is believed that the extent of solubility and nature of the gases present would depend on the phases present. For example, the existence of a magnetite phase depends upon only carbon dioxide or a more

TABLE II

VOLUMES OF GASES EXTRACTED FROM EQUILIBRATED SYNTHETIC MELTS
(At pressure, 760 mm. Hg and temperature, 28°C)

Sample No.	Wt. H ₂ O (mg./g.)	Total Vol. Gas (ml./g.)	Vol. CO ₂ (ml./g.)	Vol. CO (ml./g.)
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Fe-O-Si System

1	0.00	0.098	0.018	0.014
2	0.04	0.091	0.013	0.080
3	0.03	0.112	0.011	0.053
4	0.04	0.165	0.008	0.010
5	0.00	0.159	0.047	0.060
6	0.02	0.126	0.024	0.016
7	0.04	0.127	0.033	0.018
8	0.00	0.095	0.020	0.008 ⁶
9	0.01	0.098	0.021	0.007 ⁴
10	0.03	0.130	0.025	0.008 ⁴

CaO-Fe-O-Si System

1	0.01	0.063	0.017	0.045
2	0.02	0.065	0.046	0.017
3	0.10	0.075	0.041	0.030
4	0.06	0.096	0.035	0.036
5	0.10	0.337	0.118	0.152

oxidizing gas being present in the equilibrating atmosphere. To compensate for a more reducing atmosphere some of the magnetite would necessarily have to be reduced.

It is conceivable that some of the gases may not be soluble in the phases present in a given system and that if such is the case they would not appear on analysis. Chipman and his workers have investigated the hydrogen content in steelmaking slags exposed to various atmospheres.⁵⁰ They conclude that slags do not dissolve significant amounts of hydrogen from hydrogen gas and that hydrogen in slags results from reaction of the slag with water vapor. In the present study no measurable amounts of hydrogen could be detected from the gases extracted from the iron oxide-silica samples equilibrated in the carbon dioxide-carbon monoxide or water-hydrogen atmospheres. The results thus appear to be in line with Chipman's conclusion on hydrogen solubility. It should perhaps be emphasized at this point that it is the ratio of related gases such as $\text{CO}_2\text{-CO}$ and $\text{H}_2\text{O-H}_2$ that is the controlling factor of the oxidation state of the system and that the absolute amounts of these gases is of little consequence. Silicates are known to be highly permeable to the small hydrogen molecule at even mildly elevated temperatures,⁵¹ and it is believed that it is because hydrogen is so permeable

that it readily effuses from the sample and does not appear in the analysis.

Discussion of Data Plots

The results of the study are represented by graphs of $\log \frac{\text{CO}_2}{\text{CO}}$ vs. $\frac{\text{Fe(III)}}{\text{Fe(II)}}$. The choice of these ratios as the abscissa and ordinates respectively is justified on thermodynamic grounds. The ferric and ferrous ion contents of the system is dependent on the state of oxidation of the system. The oxygen activity is equal to its partial pressure in the gas phase, which in turn is determined by the carbon dioxide-carbon monoxide ratio in the equilibrating atmosphere. It is the homogeneous gas equilibrium $\text{CO}_2 \rightleftharpoons \text{CO} + \frac{1}{2}\text{O}_2$ which controls the oxygen partial pressure. Because the carbon dioxide and carbon monoxide amounts are controlled and present in a known ratio, the oxygen partial pressure or oxygen activity may be calculated. Thus, the free energy of the oxygen in the gaseous phase is known from the equation $\Delta F_0 = RT \ln a_0$. The partial molal free energy of each component being the same in all phases at equilibrium, the free energy and therefore the activity of oxygen in the silicate system is established. The relationship between free energies and the components of a solution is given by

the Gibbs-Duhem equation. This equation is:

$$N_1 d\bar{F}_1 + N_2 d\bar{F}_2 + \dots + N_i d\bar{F}_i = 0$$

where N is the mole or atom fraction of the component and $d\bar{F}$ is the partial molal free energy change of the component in solution. In view of the equation, $d\bar{F} = RT \ln a$, the above expression may be rewritten:

$$N_1 d \ln a_1 + N_2 d \ln a_2 + \dots + N_i d \ln a_i = 0$$

If the components of the silicate system under study are taken as Fe, O, and SiO₂, their activities may be expressed in the Gibbs-Duhem equation as follows:

$$N_{Fe} d \log a_{Fe} + N_O d \log a_O + N_{SiO_2} d \log a_{SiO_2} = 0$$

For a silica saturated material such as fayalite, when some of the ferrous ion has been oxidized as in the samples used in the investigation, it may be concluded that free silica is present. This being the case, a_{SiO_2} is constant and $d \log a_{SiO_2} = 0$. Also, the equilibrium $CO_2 \rightleftharpoons CO + \frac{1}{2}O_2$ makes a_O proportional to P_{CO_2}/P_{CO} and $d \log a_O = d \log P_{CO_2}/P_{CO}$. Substituting in the modified Gibbs-Duhem equation and integrating, we have:

$$d \log a_{Fe} = - \int (N_O/N_{Fe}) d \log (P_{CO_2}/P_{CO})$$

The integration may be readily carried out graphically.⁵² The value of $\log a_{Fe}$ is found as the area under the curve of N_O/N_{Fe} plotted against $\log P_{CO_2}/P_{CO}$ between the limits of N_{Fe} existing

at the two chosen $P_{\text{CO}_2}/P_{\text{CO}}$ values. If the integration is performed from the composition in equilibrium with metallic iron to the composition under consideration, the activity thus calculated is relative to metallic iron taken as unity.

From the above considerations, it can be concluded that there is a thermodynamic justification for the plot of $\log \text{CO}_2/\text{CO}$ vs. N_0/N_{Fe} , or some related function for the latter; this permits calculation of the activities of the other components in the system. Inasmuch as the present work is concerned primarily with the relationship existing between compositional variables and gas content, the above plot is sufficient and no further calculation of the activities of each component is needed, but the form is used for convenience in future work.

The ratio N_0/N_{Fe} may be related to a number of other expressions involving Fe(II) and Fe(III).

$$\begin{aligned} (1) \quad \frac{N_0}{N_{\text{Fe}}} &= \frac{\text{Fe(II)} \nearrow \text{Fe(III)} \nearrow \frac{1}{2}\text{Fe(III)}}{\text{Fe(II)} \nearrow \text{Fe(III)}} \\ &= 1 \nearrow \frac{1}{2} \cdot \frac{\text{Fe(III)}}{\text{Fe(II)} \nearrow \text{Fe(III)}} \end{aligned}$$

$$\begin{aligned} (2) \quad \frac{N_0}{N_{\text{Fe}}} &= \frac{\text{Fe(II)} \nearrow \text{Fe(III)} \nearrow \frac{1}{2}\text{Fe(III)}}{\text{Fe(II)} \nearrow \text{Fe(III)}} \\ &= \frac{1 \cdot 2\text{Fe(II)} \nearrow 3 \text{Fe(III)}}{2 \text{Fe(II)} \nearrow \text{Fe(III)}} \end{aligned}$$

$$= \frac{1}{2} \cdot \frac{3 \text{ Fe(II)} \neq 3 \text{ Fe(III)} - \text{Fe(II)}}{\text{Fe(II)} \neq \text{Fe(III)}}$$

$$= \frac{3}{2} - \frac{1}{2} \cdot \frac{\text{Fe(II)}}{\text{Fe(II)} \neq \text{Fe(III)}}$$

Chipman used the ratio from (1), $\frac{\text{Fe(III)}}{\text{Fe(II)} \neq \text{Fe(III)}}$, which he designated as "j" values for his plot,³⁶ Darken in his work used the reciprocal of (2), $\frac{\text{Fe(II)} \neq \text{Fe(III)}}{\text{Fe(II)}}$,⁹ and we have selected $\frac{\text{Fe(III)}}{\text{Fe(II)}}$. It can be shown that plots of this latter ratio against the $\log \frac{\text{CO}_2}{\text{CO}}$ is similar and related to the above thermodynamically justified ratios (1) and (2). Since these ratios are interrelated the choice is primarily one of convenience.

Fe-O-Si System

The data from the equilibration study on the Fe-O-Si system are shown on pp. 60 and 61 as plots of the ratios of $\frac{\text{Fe(III)}}{\text{Fe(II)}}$ vs. $\log \frac{\text{CO}_2}{\text{CO}}$. A comparison of the two curves, which were plotted separately on two graphs for the sake of clarity, shows the correlation existing between the ratio of carbon dioxide to carbon monoxide in the extracted gases and the controlled ratio of carbon dioxide to carbon monoxide used in the equilibrating atmosphere. The experimental indication is that the composition of gases involved in rock systems might be controlled by the oxidation-reduction equilibrium.

TABLE III

ANALYTICAL RESULTS FOR CO_2/CO AND $\text{Fe(III)}/\text{Fe(II)}$ RATIOS--
SYNTHETIC MODEL SYSTEMS

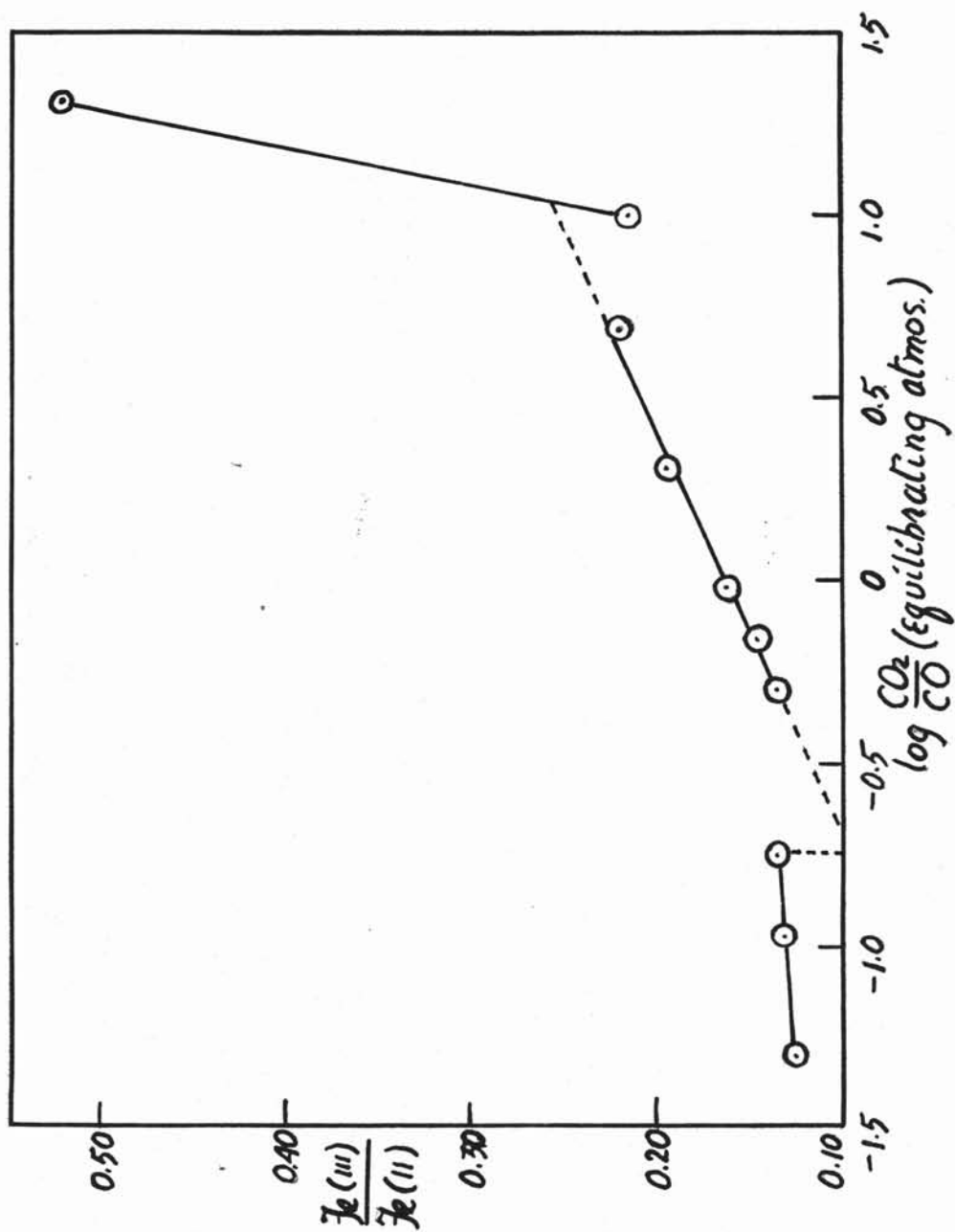
Sample No.	$\frac{\text{Fe(III)}}{\text{Fe(II)}}$	Equilibrated		Extracted	
		$\frac{\text{CO}_2}{\text{CO}}$	$\log \frac{\text{CO}_2}{\text{CO}}$	$\frac{\text{CO}_2}{\text{CO}}$	$\log \frac{\text{CO}_2}{\text{CO}}$
<u>Fe-O-Si System</u>					
1	0.14 ⁶	0.685	-0.164	1.33	0.124
2	0.12 ⁶	0.950	-1.298	0.159	-0.799
3	0.13 ⁵	0.500	-0.301	0.372	-0.429
4	0.13 ⁴	0.175	-0.757	0.374	-0.427
5	0.13 ⁰	0.106	-0.975	1.00	0.000
6	0.16 ³	0.950	-0.022	1.55	0.190
7	0.19 ⁵	2.00	0.301	1.82	0.260
8	0.21 ⁹	4.70	0.672	2.33	0.367
9	0.21 ³	10.0	1.00	2.66	0.425
10	0.52 ¹	20.0	1.30	3.00	0.477

CaO-Fe-O-Si System

1	0.13 ⁸	0.069	-1.162	0.706	-0.151
2	0.18 ⁴	1.00	0.000	2.73	0.436
3	0.16 ⁶	0.500	-0.301	1.04	0.017
4	0.15 ⁶	0.250	-0.602	0.962	-0.017
5	0.14 ⁵	0.133	-0.876	0.778	-0.109

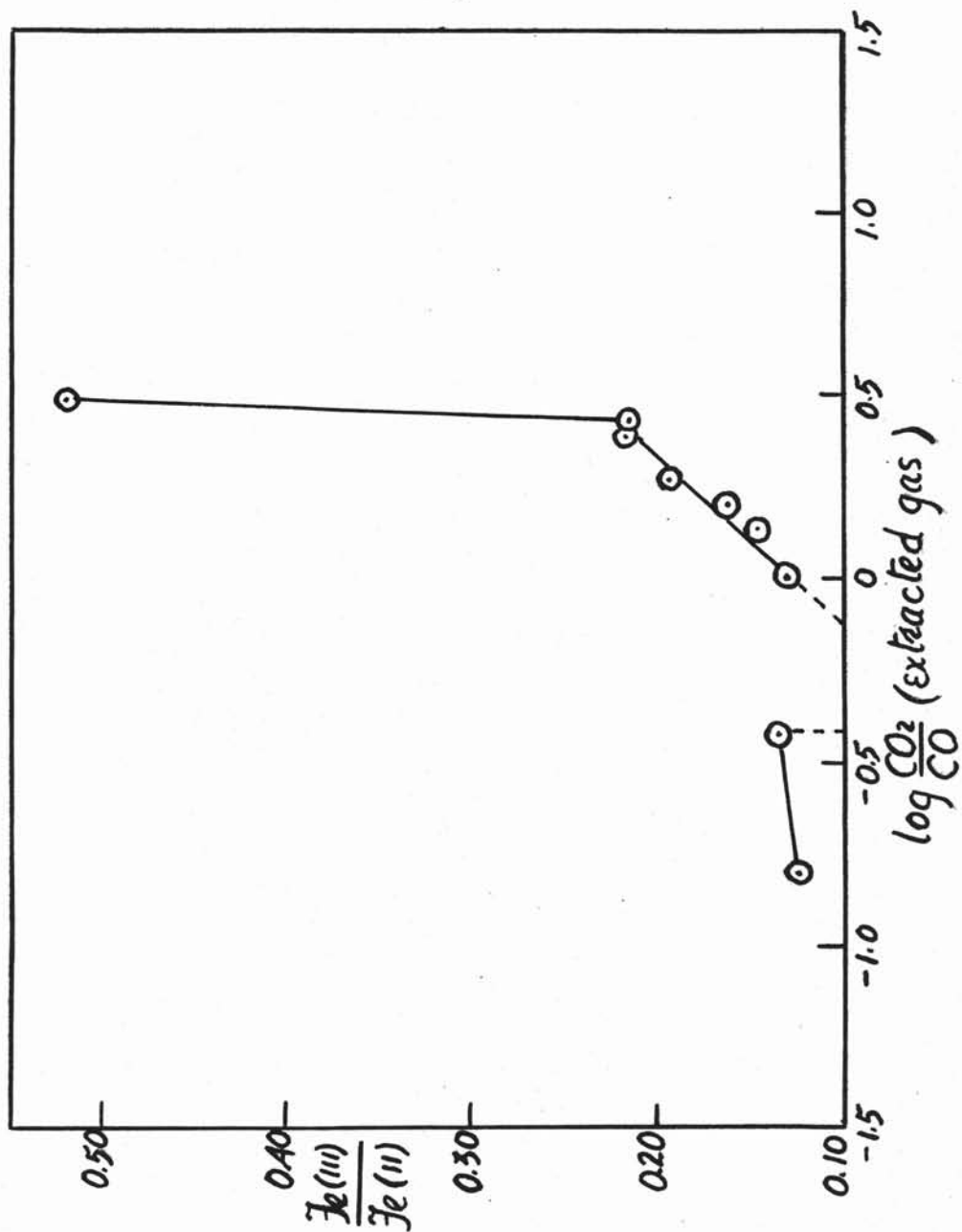
Graph 1

Fe-O-Si System

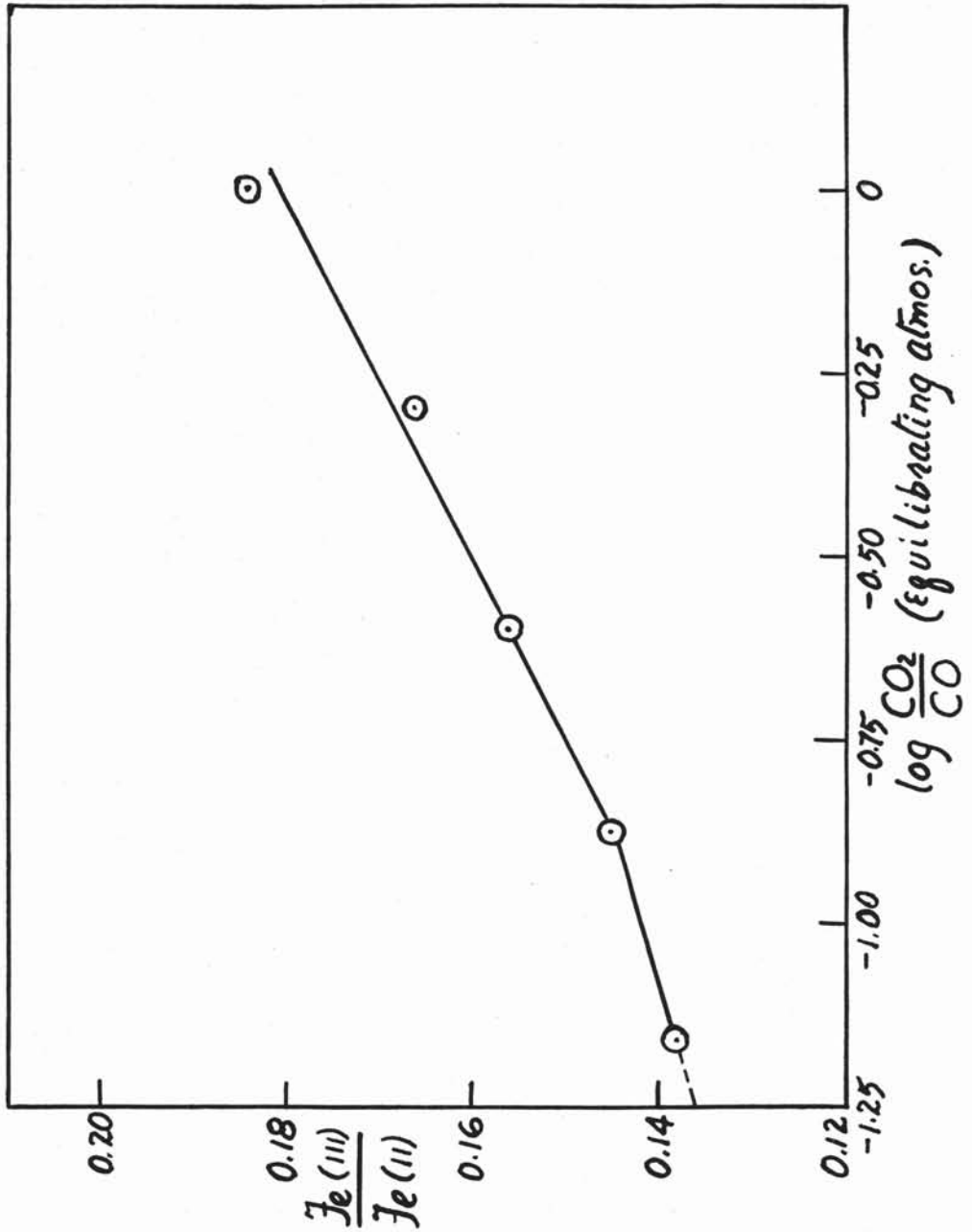


Graph 2

Fe-O-Si System

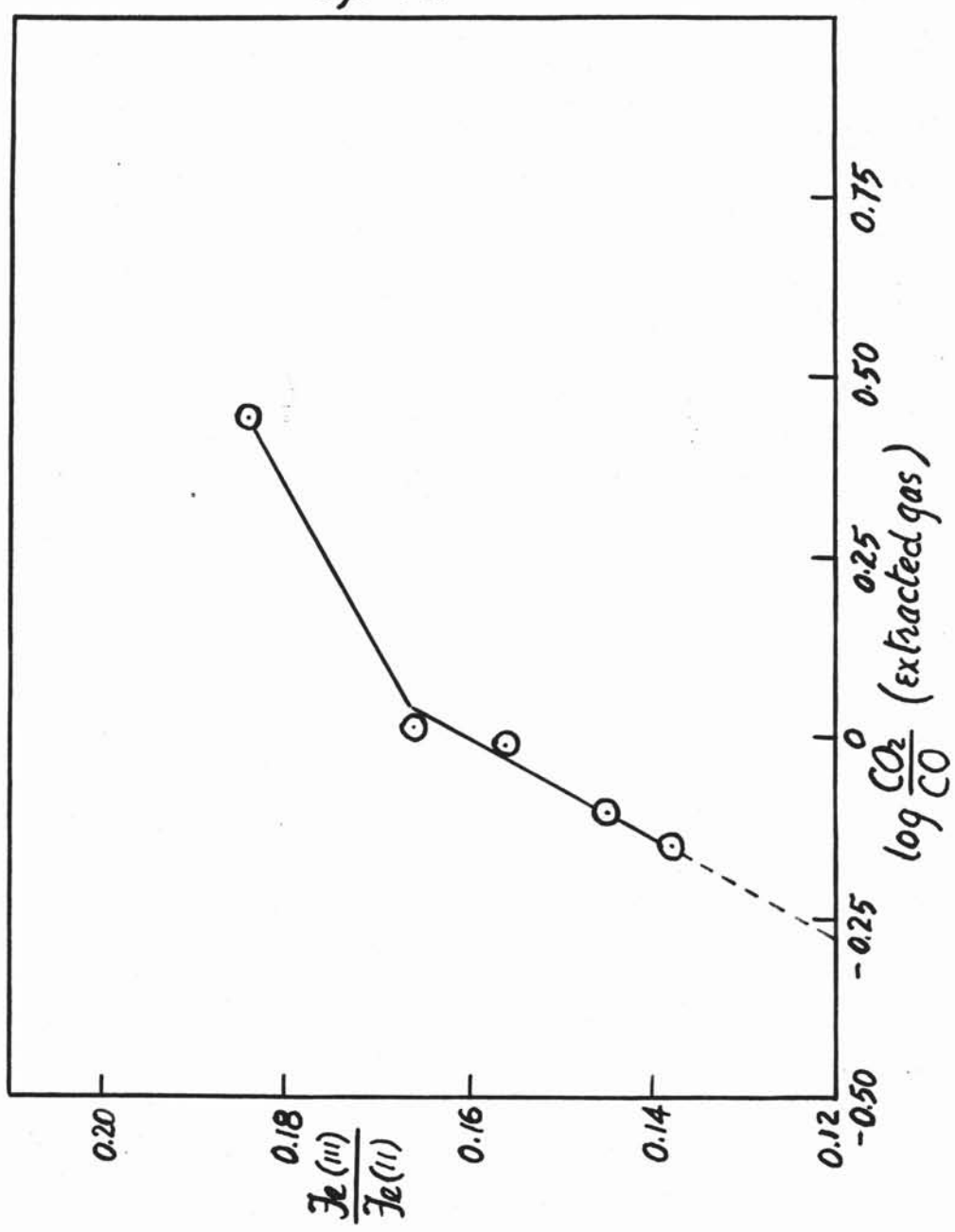


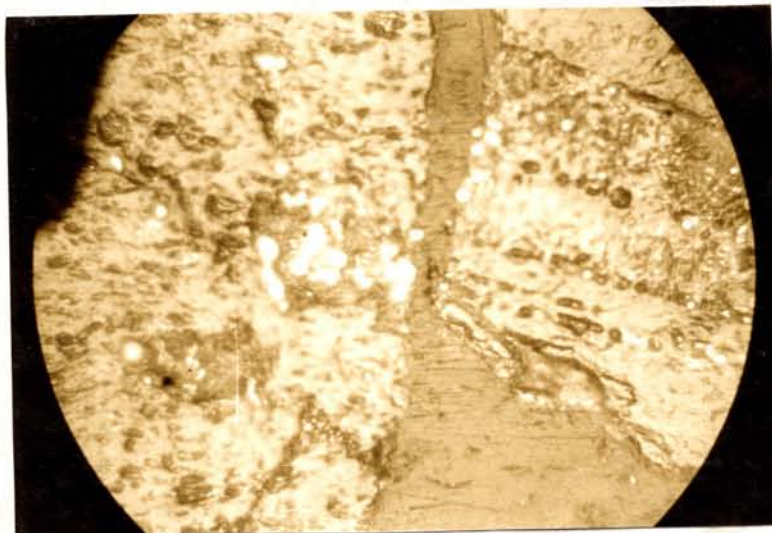
Iron oxide - silica + Calcium oxide
System



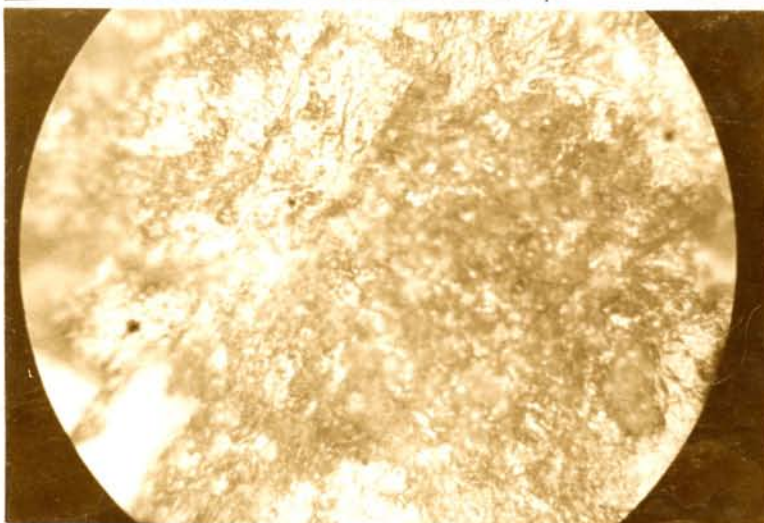
Graph 4

Iron oxide - silica + Calcium oxide System

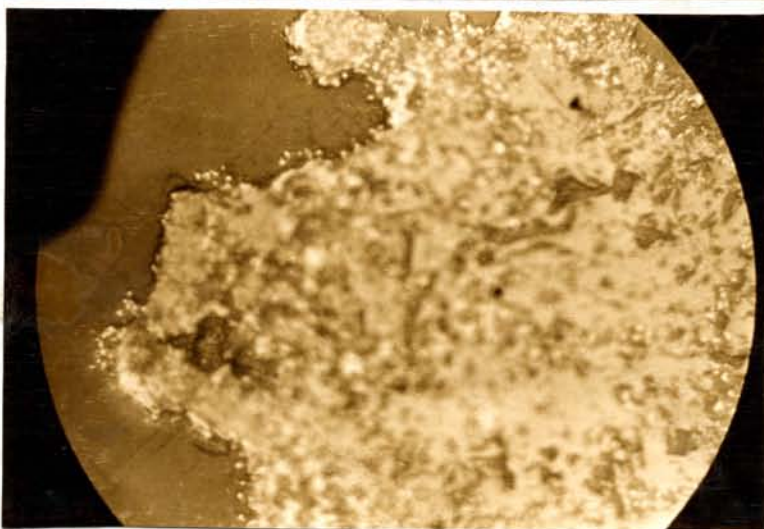




(1) Iron--
Orange-red
spots appear
white.



(2) Fayalite--
Blue dye appears
as dark shaded
areas.



(3) Magnetite--
White dendrites
bordering sample.

Figure 11.
Photomicrographs--magnification 400x

The three breaks in the curve are attributed to changes in phases in going from low $\frac{\text{CO}_2}{\text{CO}}$ ratio to higher values and correspond to shifts from metallic iron through fayalite to magnetite. Microscopic examination substantiate the three phase changes. The two points at the extreme left which correspond to samples low in the ratio $\frac{\text{Fe(III)}}{\text{Fe(II)}}$ show definitely the presence of metallic iron; the last point with the value of $\frac{\text{Fe(III)}}{\text{Fe(II)}}$ equal to 0.52 contained relatively large amounts of magnetite. The intermediate points represent samples with no metallic iron, large amounts of fayalite, and possibly slight amounts of magnetite as the $\frac{\text{CO}_2}{\text{CO}}$ ratio approached the value for the last point. Darken's work, shown in Figure 1, p. 6, and briefly discussed previously, also substantiate the three phase changes.

The oxygen partial pressure in the present study of the model system, Fe-O-Si, was controlled exclusively by the ratio of carbon dioxide to carbon monoxide in the equilibrating atmosphere. The CO_2 -CO ratio, however, is not the only factor that controls the oxygen partial pressure in natural rock gases. In magmatic gases, other combination of gases are known to exist. A. J. Ellis has discussed the chemical equilibrium in magmatic gases and made thermodynamic calculations for the theoretical compositions of some water,

sulfur, carbon dioxide gas systems.⁵³ In addition to the CO₂-CO system with which the investigation is directly concerned, natural gases would be expected to contain other related systems such as H₂O-H₂, SO₃-SO₂, COS-CO, and H₂O-S₂. The equilibrium existing between the two gases making a related pair is intimately related to the oxygen partial pressure for the whole system. In other words, the relative amounts of each gas would be dependent on the existing oxygen partial pressure. The ratio of one gas to the other that make up an oxidation-reduction couple should be a measure of the oxidation-reduction state of the system in any equilibrium situation.

When a detailed examination and comparison of $\log \frac{\text{CO}_2}{\text{CO}}$ vs. $\frac{\text{Fe(III)}}{\text{Fe(II)}}$ curves for equilibrating gases and extracted gases is made, it will be noted that for a given sample represented by the experimental points, a shift is evident in the point position for the two situations. This shift is either from high $\log \frac{\text{CO}_2}{\text{CO}}$ values to low, or vice versa, and is consistent in any one region of the plot. This becomes more evident when the two plots are superimposed as in Figure 12, curves (a) and (c). Of course it must be recognized that the significant feature of the work described is the relationship between oxidation-reduction constitution and equilibrating and

extracted gases aside from any shift that may be noted. It is, however, of interest to explore the probable reasons for this activity shift.

First, it should be noted that no change in $\frac{\text{Fe(III)}}{\text{Fe(II)}}$ could be detected in the extracted samples when compared with the equilibrated samples. The change seems to be due to some factor or factors that alter the oxygen activity (and hence the CO_2/CO ratio) in the sample from the value for the equilibrating conditions to a new value for the conditions of extraction. Two factors which can be recognized as the probable cause of this behavior, are best examined with reference to the model Fe-O-Si system. (1) The change in oxygen activity in going from the equilibration conditions at 1100°C where the silicate is a solid to the extracting conditions at $1300\text{-}1400^\circ\text{C}$ where the silicate is a liquid, and (2) the alteration produced in the $\frac{\text{CO}_2}{\text{CO}}$ ratio by the water without its oxidation-reduction companion hydrogen for a given oxygen activity. The combined effects may be best understood by referring to Figure 12.

(1) Shift due to melting--Michal and Schuhmann have investigated the partial pressures of oxygen in equilibrium with silica saturated slags in the Fe-O-Si system.³⁸ Their data is plotted as curve (b) in Figure 12. Once the molten

Fe-O-Si System

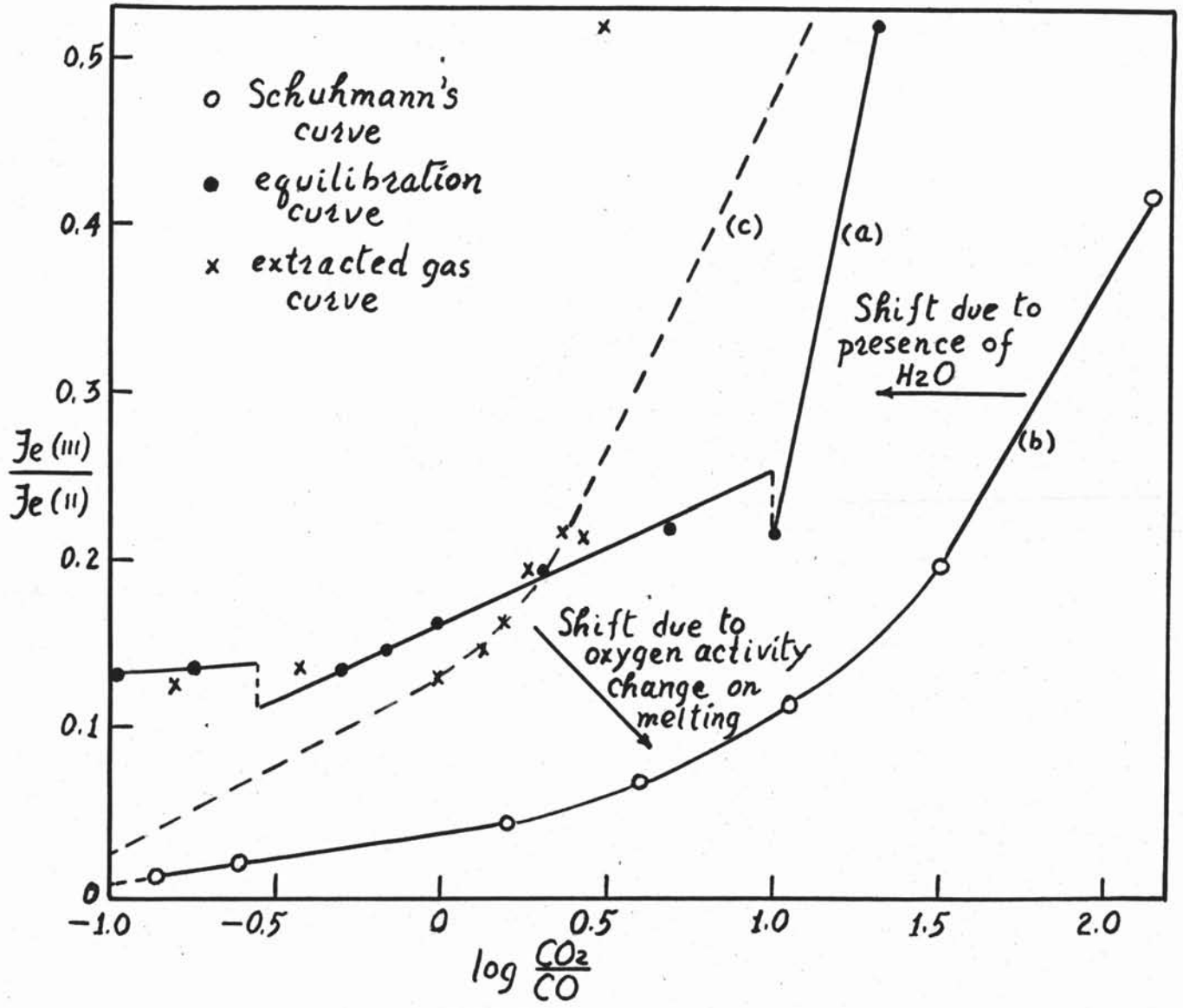


Figure 12. Combined Plots of Fe(III)/Fe(II) vs. $\log CO_2/CO$ for Data from (1) Equilibration, (2) Extraction and (3) Schumann

phase had been achieved, no temperature effect was noted within experimental error. A smooth curve was obtained since only the single liquid phase was encountered throughout their studies. In contrast, the curve representing the work reported here on the equilibrium partial pressures of oxygen in the Fe-O-Si system (curve (a)) shows discontinuities due to phase changes (iron-fayalite-magnetite), as mentioned previously, and is positionally shifted from the curve for the liquid system. On melting, then, the partial pressure of oxygen that is in equilibrium, and presumably can be extracted, will be higher for a given $\frac{\text{Fe(III)}}{\text{Fe(II)}}$ ratio. This, in turn, would be exhibited as a higher $\frac{\text{CO}_2}{\text{CO}}$ ratio.

(2) Shift due to high water vapor concentration--In contrast to the effect of melting there is the countering effect of a high concentration of water vapor in the extracted gases tending to produce a lower $\frac{\text{CO}_2}{\text{CO}}$ ratio for a given activity. The water vapor, in effect, takes the place of part of the carbon dioxide. Whereas it is possible to control and eliminate the water vapor in an equilibrating atmosphere, water vapor seems to be rather generally found in the extracted gases and is not subject to control with the present understanding of these systems. It does enter into the oxidation-reduction systems of the silicates, and with the escape of

hydrogen that is the normal reduced form in the oxidation-reduction couple, it would exert an oxidizing influence. It is difficult to estimate quantitatively what the effect of the water vapor would be on the $\frac{\text{CO}_2}{\text{CO}}$ ratio, since the accuracy in the determination of water was poor. If a constant correction is applied to the liquid silicate equilibrium curve (b) (Figure 12), we could draw the hypothetical curve (c) representing the $\frac{\text{CO}_2}{\text{CO}}$ equilibrium with a correction for water vapor. In sum, the oxygen activity of a silica saturated silicate melt as measured by the $\frac{\text{CO}_2}{\text{CO}}$ ratio in the Fe-O-Si system as a function of the $\frac{\text{Fe(III)}}{\text{Fe(II)}}$ ratio is given by curve (c) (Figure 12), and represents the composition of extracted gases. It will be noted that agreement in accounting for the shift is good for the middle six points representing the fayalite region, and less so for the magnetite and iron containing samples. Similar considerations are undoubtedly involved in the shifts noted in the other natural and artificial systems studied, but equilibrium phase relationships have not been worked out, and no comprehensive discussion can be given.

CaO-Fe-O-Si System

The addition of calcium oxide to the simple iron oxide-silica system increased the general gas solubility. This may be seen by examining Table II. The fact that increases in

basicity increases the carbon dioxide solubility has been demonstrated by E. E. Schumacher in his investigation of silicates involved in glasses.²⁶ Chipman and Larson in their extensive work on the effect of basicity on "j-values", the ratio $\frac{\text{Fe(III)}}{\text{Fe(II)} + \text{Fe(III)}}$, showed that increases in basicity were accompanied by increases in "j-values".³⁷ Comparison of the plots of $\frac{\text{Fe(III)}}{\text{Fe(II)}}$ vs. $\log \frac{\text{CO}_2}{\text{CO}}$ on pp. 62 and 63 reveals this same effect in the present study.

Natural Rock Systems--Andesine Andesite and Olivine Basalt

Chemical analyses for andesine andesite and olivine basalt samples of Mauna Kea and Mauna Loa on the island of Hawaii are summarized in Table IV. These analyses by H. S. Washington are typical for the two rock types, and serve to point out the differences that exist in their chemical compositions.⁵⁴

The data obtained for the natural rocks equilibrated in varying $\frac{\text{CO}_2}{\text{CO}}$ atmospheres at 1100°C are plotted on pp. 75-78. Andesine andesite which represents a relatively acidic rock type, and olivine basalt, a relatively basic type, are represented by curves similar to those obtained for the model system, Fe-O-Si. Table V shows that the water content of andesine andesite is practically zero, whereas it averages 0.03 mg./g. for the olivine basalt samples. The total volumes

TABLE IV
 CHEMICAL COMPOSITIONS OF NATURAL ROCKS⁵⁴

<u>Constituent</u>	<u>Percentages</u>	
	<u>Olivine Basalt</u> <u>Mauna Loa</u>	<u>Andesine Andesite</u> <u>Mauna Kea</u>
SiO ₂	52.30	50.68
Al ₂ O ₃	11.84	16.42
Fe ₂ O ₃	2.06	5.79
FeO	9.03	6.22
MgO	7.15	4.25
CaO	10.60	6.47
Na ₂ O	2.47	4.70
K ₂ O	0.49	2.16
H ₂ O ^f	0.15	0.23
H ₂ O ⁻	0.03	0.19
TiO ₂	3.98	2.64
P ₂ O ₅	0.28	0.17
MnO	0.10	0.22
Total	100.48	100.14

TABLE V

VOLUMES OF GASES EXTRACTED FROM EQUILIBRATED NATURAL ROCKS
(At pressure, 760 mm. Hg and temperature, 28°C)

Sample No.	Wt. H ₂ O (mg./g.)	Total Vol. Gas (ml./g.)	Vol. CO ₂ (ml./g.)	Vol. CO (ml./g.)	Vol. SO ₂ (ml./g.)
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Andesine-andesite System

1	0.01	0.135	0.018	0.027	0.000
2	0.01	0.072	0.009	0.018	0.000
3	0.01	0.153	0.006	0.015	0.002
4	0.00	0.051	0.004	0.009	0.000
5	0.00	0.328	0.007	0.010	0.010
6	0.00	0.108	0.007	0.038	0.000

Olivine Basalt System

1	0.01	0.134	0.014	0.011	0.000
2	0.02	0.175	0.009	0.018	0.002
3	0.05	0.353	0.008	0.111	0.000
4	0.03	0.268	0.010	0.030	0.003
5	0.03	0.157	0.010	0.024	0.002

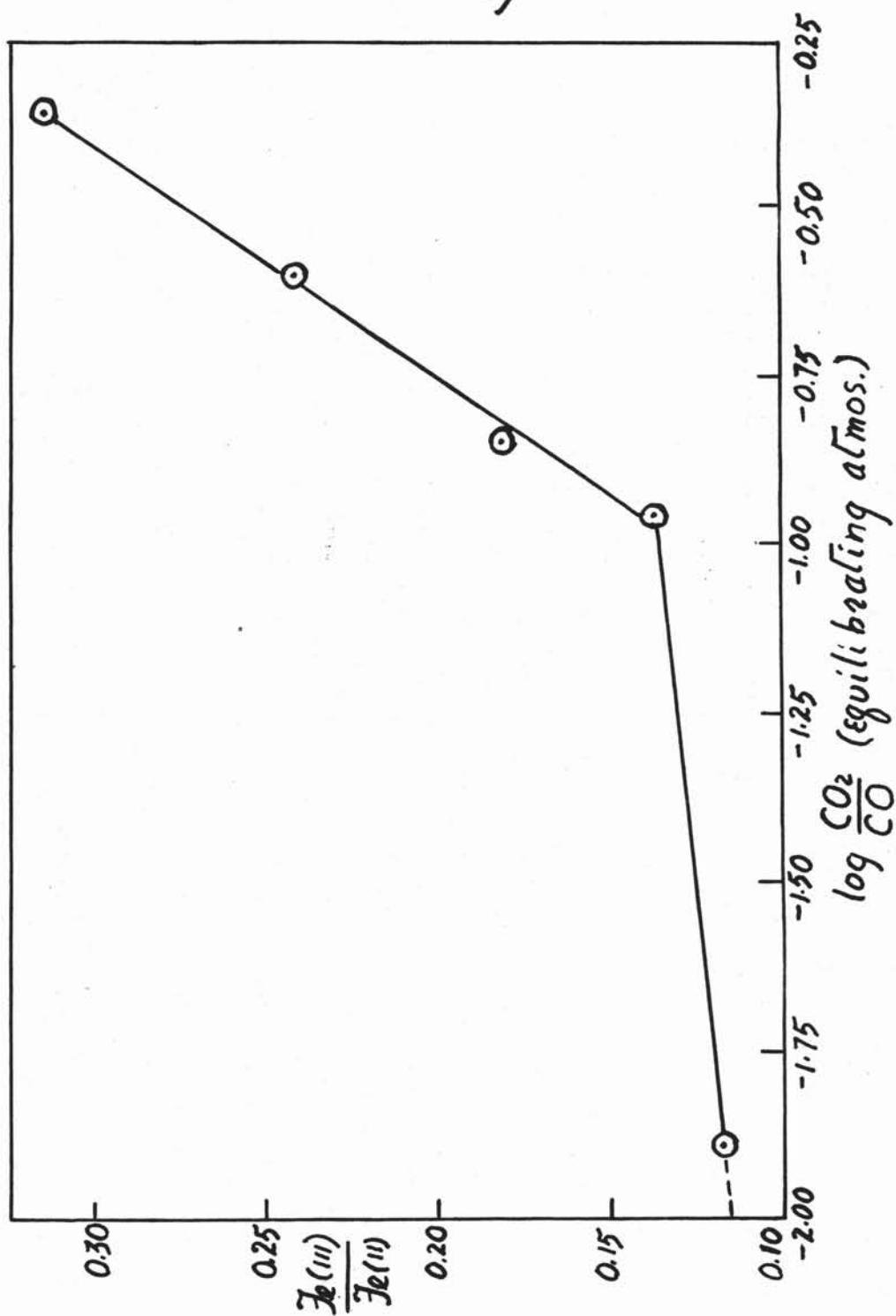
TABLE VI

ANALYTICAL RESULTS FOR CO₂/CO AND Fe(III)/Fe(II) RATIOS--
NATURAL ROCK SYSTEMS

Sample No.	$\frac{\text{Fe(III)}}{\text{Fe(II)}}$	<u>Equilibrated</u>		<u>Extracted</u>	
		$\frac{\text{CO}_2}{\text{CO}}$	$\log \frac{\text{CO}_2}{\text{CO}}$	$\frac{\text{CO}_2}{\text{CO}}$	$\log \frac{\text{CO}_2}{\text{CO}}$
<u>Andesine-andesite System</u>					
1	0.31 ³	0.435	-0.361	0.665	-0.177
2	0.24 ¹	0.250	-0.602	0.500	-0.301
3	0.18 ¹	0.141	-0.851	0.375	-0.426
4	0.20 ²	--	--	0.429	-0.367
5	0.13 ⁶	0.109	-0.963	0.332	-0.479
6	0.11 ⁷	0.013	-1.89	0.192	-0.717
<u>Clivine Basalt System</u>					
1	0.36 ¹	1.22	0.086	0.665	-0.177
2	0.32 ⁵	0.545	-0.264	0.500	-0.301
3	0.23 ⁴	0.051	-1.29	0.068	-1.16
4	0.27 ²	0.100	-1.00	0.332	-0.479
5	0.29 ⁸	0.198	-0.703	0.416	-0.381

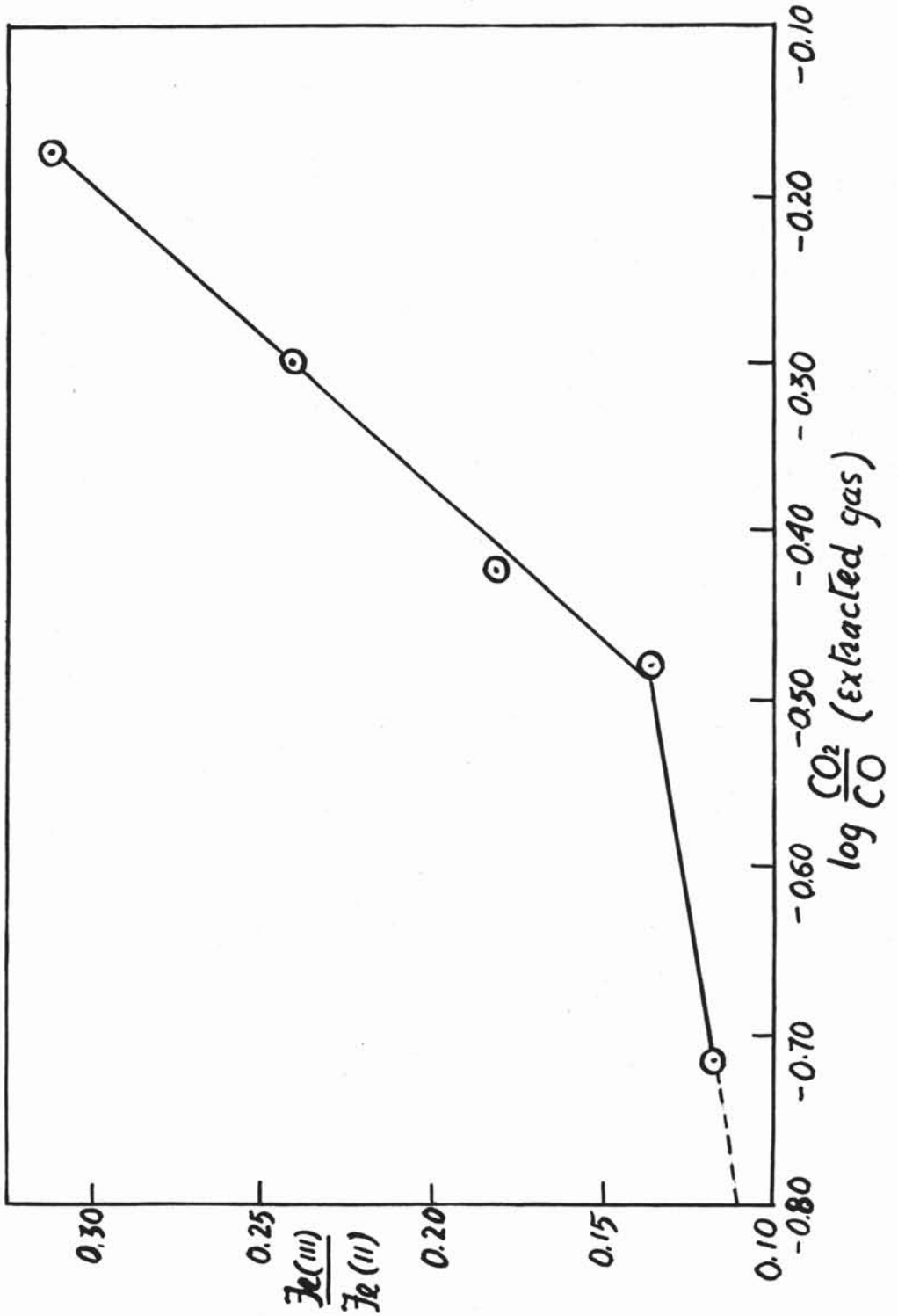
Graph 5

Andesine-andesite System



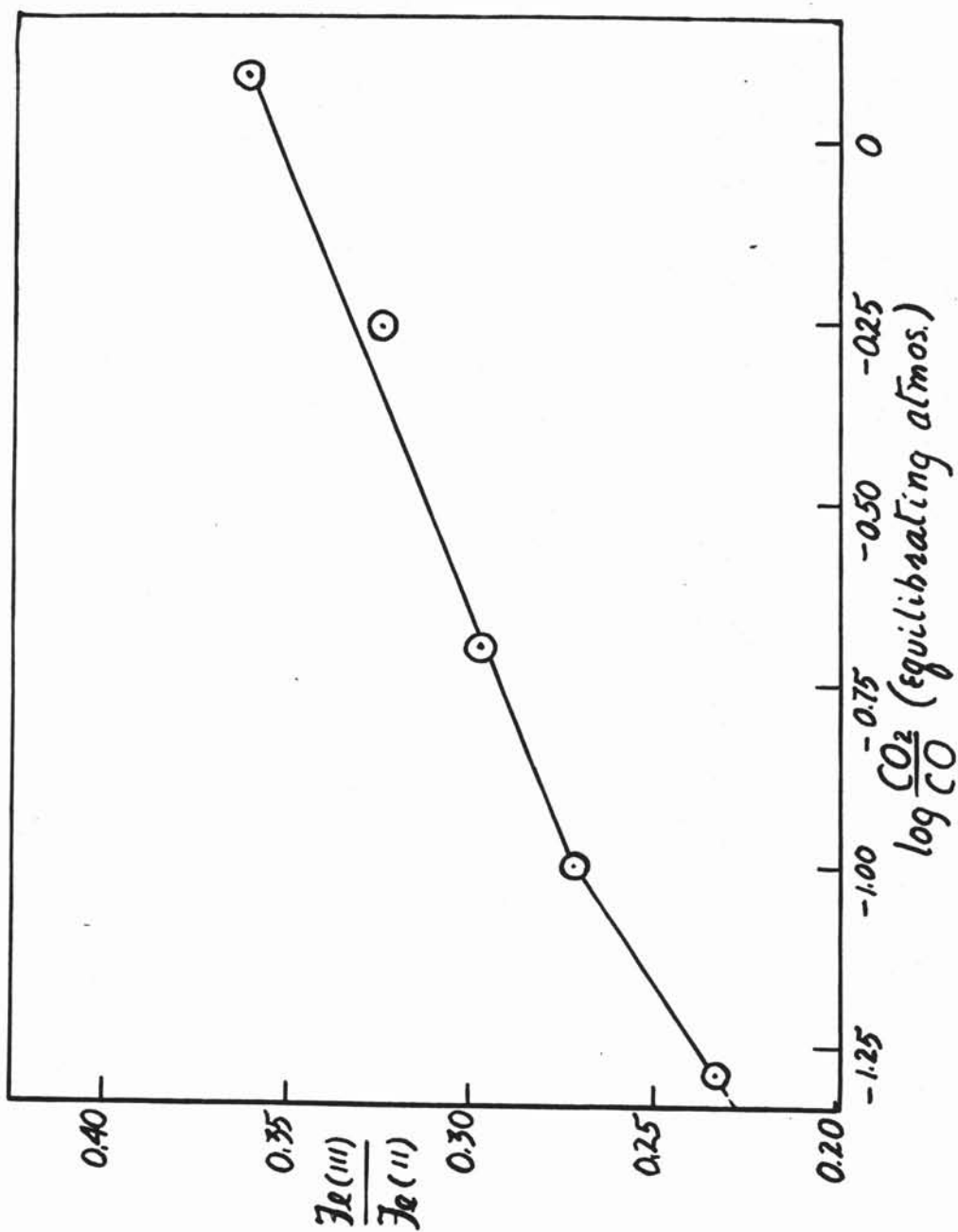
Graph 6

Andesine-andesite System

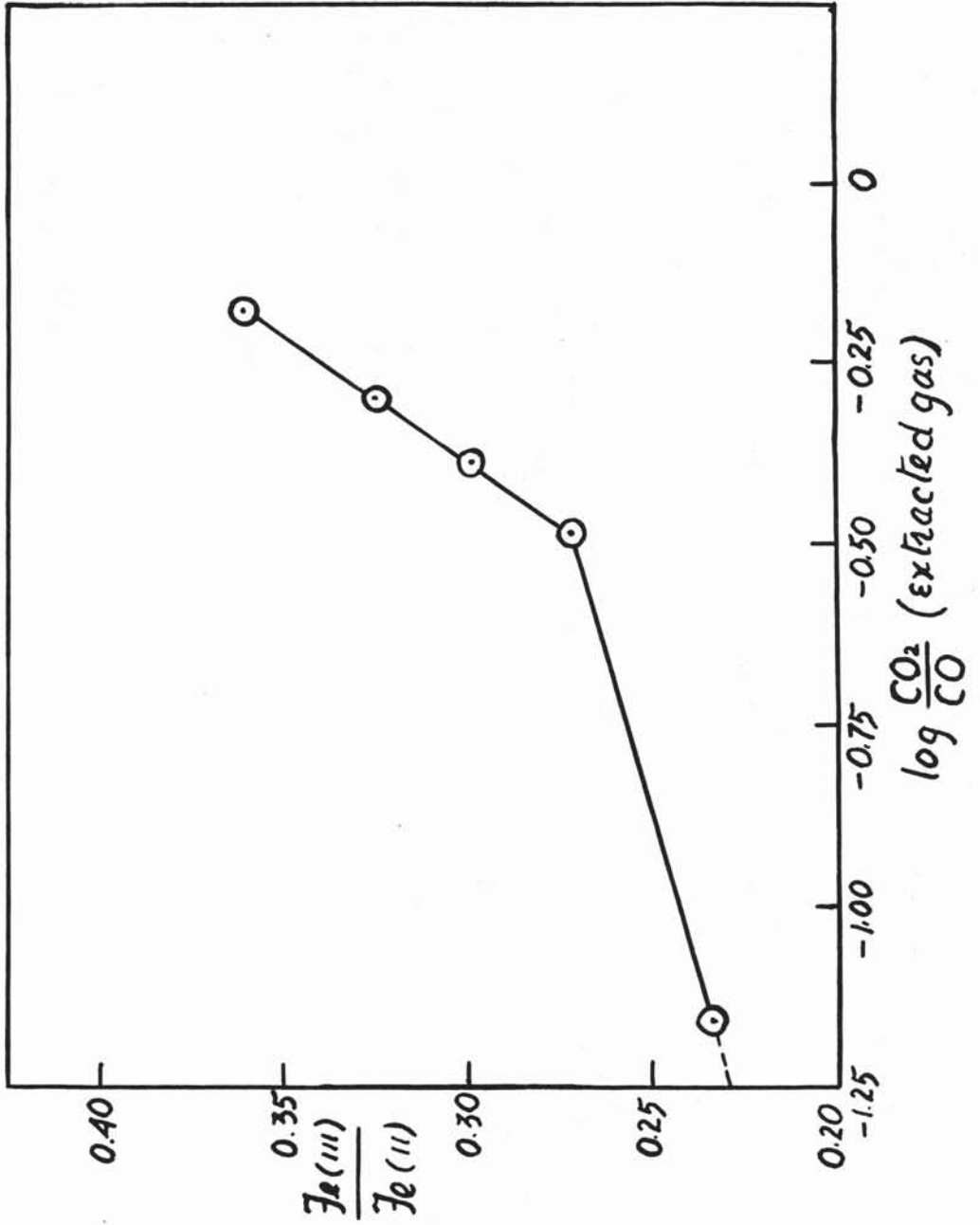


Graph 7

Olivine basalt System



Graph 8

Olivine basalt System

of gases extracted from the natural rocks samples were generally greater than those for the synthetic model system.

The correlations between the curves representing the extracted and equilibrated gases should be noted. Just as in the case in the Fe-O-Si system, the experimental results indicate that the composition of gases in natural rock systems is controlled by the oxidation-reduction equilibrium in the rocks. The added complexity of the situation does not seem to destroy the correlations.

No attempt was made to analyze the $\frac{\text{CO}_2}{\text{CO}}$ and $\frac{\text{Fe(III)}}{\text{Fe(II)}}$ ratios existing in unequilibrated natural rocks and to compare these with data obtained for the equilibrated rocks. In view of the analytical experience gained in this work in both the ferrous-ferric iron analysis and gas analysis, it would be desirable that the older results be re-examined. It has, however, been noted that equilibration of a rock or a silicate in a gaseous atmosphere is relatively easy and rapid at elevated temperatures. Thus, the question arises as to the significance of attempts to relate rock composition to gas content in rocks that have been sampled without regard to contact at elevated temperatures with air, steam or other disturbing oxidation-reduction changes. In this respect work with pumice, clinker or "aa" lava would be particularly questionable.

IV. CONCLUSIONS

The exploratory nature of the research and the extreme difficulty of the analytical techniques on which the conclusions are based should be emphasized. The solution of silicates without alteration of the ferrous ion content--a problem which has beset analytical chemists for years, and the extraction of gases from the rock samples and analysis of a few tenths of a cubic centimeter or less are problems which had to be solved prior to exploring the possibility of the existence of oxidation-reduction correlations in rock systems.

The work shows that a definite correlation exists between the composition of the gases extracted from rocks and their composition with respect to oxidizable and reducible components. In addition, it is demonstrated that the phases present have a considerable influence, for it appears that they markedly alter the activity or effective concentration of the oxide ion and hence influence the gaseous composition. The conditions of gas extraction contribute some modifications to the gaseous composition, which again may be related to changes in oxide ion activity. The low hydrogen content of synthetic model silicates after equilibration in hydrogen-water vapor atmospheres was noted, confirming the work of

Chipman on slags, but additional unknown components were deduced to be present in natural rocks that retain hydrogen much as certain metals do. Equilibration with gaseous atmospheres were found to occur in relatively short time at elevated temperatures, being completed within a six-hour period for small samples at 1100°C.

The results and conclusions point out precautions and factors that must be considered in working with gases extracted from natural rock systems, or associated with such systems as we have in fumaroles or sulfatara. The importance of rock sampling with a careful consideration of atmospheric factors is emphasized. The petrographic variations that may be produced in a rock or silicate through exposure to atmospheres of different oxidation potential even to the appearance of new phases is noteworthy. Knowledge of the temperature and pressure conditions of extraction of a gas from a rock is important in relating the gas composition to the petrographic and chemical composition of the rock. With changes in temperature and pressure in silicate systems containing petrographically important oxidizable and reducible phases, it may be possible in the future to deduce the thermal and pressure history of a rock by analysis of its gas content and its chemical and petrographic composition.

IV. SUMMARY

Although there has been much speculation concerning the correlation of gas composition and rock composition, no experimental work has shown the existence of any consistent relationships. A good avenue of attacking the problem was through an oxidation-reduction system of the rock and because iron oxide is a common rock constituent, the Fe(II)-Fe(III) couple was the oxidation-reduction system chosen for the condensed phase. The object of the present work is to establish any existing relationship between the composition of gases extracted from the rock samples, the equilibrating atmosphere that controls the oxidation-reduction state, and the composition of the rocks.

The model system, Fe-O-Si, was chosen for study and synthetically prepared samples were exposed to atmospheres of known oxygen partial pressures (known ratios of CO₂:CO) until equilibria were reached. The effect of increasing basicity of the model system was studied. Finally the effect on the composition of rock systems that occur naturally when exposed to varying oxidizing atmospheres was investigated.

The problem of solubilizing silicate rock samples without altering the Fe(III) and Fe(II) ion contents which has troubled analysts for many years was solved by using a

HF-HCl mixture under a protective carbon dioxide blanket. A spectrophotometric method of analysis employing the Fe(III) and Fe(II) ion complexes of 1,10-phenanthroline, which was both rapid and accurate, was used. The difficulties of gas extraction and analysis were overcome and a standardized procedure established.

The following conclusions may be reached from the results of the present research:

(1) There is a definite correlation between the composition of gases extracted from the melt and the composition of the equilibrating atmosphere for the model system, Fe-O-Si. The Fe(III)/Fe(II) ratio in the condensed phase of the Fe-O-Si system is related linearly to the $\log \text{CO}_2/\text{CO}$ ratio of the extracted gases. Shifts in correlations can be accounted for by the different conditions encountered in extraction of gases when compared to the equilibrating conditions.

(2) The addition of calcium oxide to the Fe-O-Si system does not alter the above conclusions; the increase in basicity increases the general gas solubility.

(3) The natural rocks when exposed to controlled CO_2/CO atmospheres, also behave similarly to the synthetic Fe-O-Si system and the correlations between the Fe(III)/Fe(II) ratios and the $\log \text{CO}_2/\text{CO}$ ratios of the extracted gases and the equilibrating atmospheres are comparable to the simple model systems.

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