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Experimental Control of Oxygen Fugacities
By Graphite-Gas Equilibria

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Abstract

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Control of oxygen fugacities in a CO_2 + CO atmosphere has been established experimentally by using a solid-phase buffer technique. Equilibration between the buffer and the enclosed sample is established by diffusion of the gas atmosphere through the buffer. The establishment of equilibrium by this method is indicated by the reversibility of experimental results in a study of the decomposition relations of siderite, $FeCO_3$.

Precipitation of solid graphite from a CO_2 + CO atmosphere under reducing conditions provides a method for control of f_{O_2} values through equilibrium between crystalline graphite and the oxides of carbon in the gas phase. Equilibrium values of f_{O_2} are calculated from thermodynamic data for several values of $P_{gas} = P_{co_2} + P_{co}$. For values of P_{gas} greater than 100 bars, the following approximation may be used without serious error:

$$\log f_{O_2} = -\frac{20,586}{T} - 0.044 + \log P_{gas} - 0.028\left(\frac{P_{gas} - 1}{T}\right)$$

[redacted]

These results indicate two important consequences of the presence of graphite in igneous and metamorphic rocks. First, equilibrium between graphite and gas will buffer a value of f_{O_2} which is within the stability field of magnetite for most geological environments. Secondly, this buffering will be produced regardless of the presence of other volatile components in the gas phase.

In gas phases in the system C-H-O, equilibration with graphite allows approximate calculation of such ratios as CO_2/CO, H_2O/H_2, and CH_4/H_2. A noteworthy result is that the value of CH_4/H_2 in equilibrium with graphite will be large over a wide range of geological conditions; methane will become a significant to dominant component of the gas phase under moderately reducing conditions.

Introduction

The method of using solid buffers for the control of oxygen fugacities in hydrothermal experiments at elevated pressures (Eugster, 1957; Eugster and Wones, 1962) has been applied successfully to studies of the stability of a number of iron-bearing minerals (see e.g., Turnock and Eugster, 1962; Wones, 1963a, 1963b; Ernst, 1960, 1962; Buddington and Lindsley, 1964) and to the melting relations of iron-rich liquids (Hamilton, Burnham, and Osborn, 1964).

An oxygen buffer is an assemblage of solid phases (A,B,C, etc.) related to each other by reactions of the type:

$$A = B + O_2$$

$$A + B = C + O_2$$

For such assemblages, f_{O_2} is fixed if total pressure and temperature are known; values of f_{O_2} can be calculated from thermodynamic data (Eugster and Wones, 1962). In the presence of water, oxygen buffers also define f_{H_2} and the f_{H_2O}/f_{H_2} ratio of the gas phase. Dire determinations of f_{H_2} for some buffers made by Shaw (1963) are in good agreement with the calculated data.

In hydrothermal experiments, the sample is contained in a sealed platinum or silver-palladium (Muan, 1963) tube and surrounded by the oxygen buffer. Equilibrium between the buffer and the sample is established by diffusion of hydrogen through the walls of the tube. The attainment of equilibrium is demonstrated by reversing the particular reaction under investigation. Throughout the experiment, the bulk composition of the sample does not change except for its hydrogen content.

Studies of the phase relations of carbonates pose a somewhat different problem. Decomposition reactions of divalent carbonates may be represented by two distinct equations (Jamieson and Goldsmith, 1960), in which R represents a divalent cation.

$$(1) \quad R\,CO_3 = R\,O + CO_2$$

$$(2) \quad a\,R\,CO_3 + \tfrac{1}{2}\,O_2 = R_aO_{a+1} + (a-1)\,CO_2$$

Reactions of the first type, in which oxidation does not occur, have been studied experimentally in carbon dioxide atmospheres, using samples contained in open tubes (see e.g., Harker and Tuttle, 1955; Harker and Hutta, 1956; Goldsmith and Graf, 1957).

Siderite ($FeCO_3$) and rhodochrosite ($MnCO_3$) are carbonates whose stability is governed by reactions of the second type. Such reactions must be studied under controlled fugacities of both CO_2 and CO. Since noble metal tubes are not sufficiently permeable to CO_2 and O_2, sealed tubes cannot be used for buffered experiments in a $CO_2 + CO$ atmosphere. For this reason, experimental studies on siderite (French and Eugster, 1962; French, 1964a) were carried out in unsealed silver tubes, allowing direct equilibration between the gas phase and the charge. Because of contamination problems, only those buffer assemblages could be used which are possible decomposition products of the carbonate, i.e., pairs of iron oxides for siderite and of manganese oxides for rhodochrosite.

Oxygen Fugacities in a CO_2 + CO Atmosphere

In a carbon dioxide atmosphere, the value of f_{O_2} of the oxygen buffer will also fix the value of the CO_2/CO ratio through the decomposition of CO_2 ($CO_2 = CO + \frac{1}{2}O_2$). If CO_2, CO, and O_2 are the only species in the gas phase, then the values of f_{co} and f_{co_2} may be calculated (see Eugster and Wones, 1962, p. 93, for analogous calculations for a hydrothermal atmosphere). Since data on the fugacity coefficients γ_i of CO and CO_2 in mixtures are not available, it is assumed that the values of γ_i are the same for each species in the mixture as for the pure components at the same temperature and total pressure (Lewis and Randall's Rule; see Denbigh, 1957, p. 127). Since the value of f_{O_2} at moderate temperatures is less than 10^{-10} bar, we may assume that,

$$(3) \quad P_{gas} = P_{co_2} + P_{co}$$

$$(4) \quad K_b(T) = f_{co_2}/f_{co}\,(f_{O_2})^{\frac{1}{2}}$$

Values of K_b are tabulated by Wagman et al. (1945).[1]

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[1] Wagman's tabulated values of log K_b agree to within 0.01 with values calculated from more recent standard free energy data (Coughlin, 1954, JANAF tables). Experimental measurements (Darken and Gurry, 1945, 1946) differ from these values by 3 to 4 per cent.

From these relations, the individual fugacities may be determined as,

$$f_{co_2} = \frac{K_b\, P_{gas}\, \gamma_{co}\, \gamma_{co2}\, (f_{O2})^{\frac{1}{2}}}{K_b\, (f_{O_2})^{\frac{1}{2}}\, \gamma_{co} + \gamma_{co2}} \qquad (5)$$

$$f_{co} = \frac{P_{gas}\, \gamma_{co}\, \gamma_{co2}}{K_b\, (f_{O_2})^{\frac{1}{2}}\, \gamma_{co} + \gamma_{co2}} \qquad (6)$$

These expressions are analogous to those obtained for f_{H_2O} and f_{H_2} in a hydrothermal atmosphere (see Eugster and Wones, 1962, p. 93).

Values of log f_{co} as a function of temperature are given in Figure 1 for a number of oxygen buffers at total pressures of 1 bar and 2000 bars. At P_{gas} = 1 bar, the fugacities of all components are assumed equal to the partial pressures ($\gamma_i = 1.00$). Fugacity data for CO_2 are available to 1400 bars (Robie, 1962), based on Kennedy's (1954) experimental determinations of P-V-T relations. The values of γ_{co_2} for 2000 bars were estimated by extrapolation of Robie's data. Values for γ_{co} are taken from Newton (1935). The effect of the extrapolations and uncertainties on the value of f_{co} is probably less than an order of magnitude.

Derivation of the results for the "graphite buffer" (Fig. 1) is discussed in detail in the following section.

Oxygen Fugacities of the Graphite Buffer

When the oxygen fugacity of a gas phase consisting primarily of CO and CO_2 is reduced sufficiently, graphite may precipitate according to the reaction $2\ CO = C_{(gr)} + CO_2$ (see, e.g., Muan, 1958).

Equilibrium between graphite and such a gas phase is governed by two relations:

$$(7) \quad C + \tfrac{1}{2}O_2 = CO \qquad K_a(T) = f_{co}/(f_{O_2})^{\frac{1}{2}}$$

$$(8) \quad CO + \tfrac{1}{2}O_2 = CO_2 \qquad K_b(T) = f_{co_2}/f_{co}(f_{O_2})^{\frac{1}{2}}$$

Hence, for a given temperature and total pressure, the presence of graphite defines the composition of the gas phase as well as the fugacities of CO_2, CO, and O_2. In other words, the assemblage graphite + gas acts as an oxygen buffer.[2]

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[2] The same conclusions are reached by applying the Gibbs Phase Rule ($F + P = C + 2$) to the two-component system C-O. A two-phase assemblage (graphite + gas) has two degrees of freedom ($F = 2$). If both temperature and total pressure are specified, the system becomes invariant, and the composition of the gas phase is uniquely determined.

In calculating oxygen fugacities of a gas phase in equilibrium with graphite, allowance must be made for the partial pressure of CO, which becomes significant at high temperatures and low total pressures (Muan, 1958). The method of calculation used here is based on Equations (7) and (8), which we may write:

$$(7a) \qquad K_a = \gamma_{co} P_{co} (f_{O_2})^{-1/2}$$

$$(8a) \qquad K_b = \frac{\gamma_{co_2} P_{co_2}}{\gamma_{co} P_{co}} (f_{O_2})^{-1/2}$$

Eliminating f_{O_2} and combining with Equation (3), we have,

$$P_{co_2} = \frac{\gamma^2_{co}}{\gamma_{co_2}} P^2_{co} \frac{K_b}{K_a} = P_F - P_{co}$$

and (9)

$$P_{co} = \frac{-1 + \sqrt{1 + 4P_F \frac{K_b}{K_a}\left(\frac{\gamma^2_{co}}{\gamma_{co_2}}\right)}}{2\frac{K_b}{K_a}\left(\frac{\gamma^2_{co}}{\gamma_{co_2}}\right)}$$

Values of K_a and K_b are obtained from tabulations (Wagman et al., 1945). Values of P_{co} in equilibrium with graphite have been calculated from Equation (9) for total pressures of 1, 100, 500, 1000, and 2000 bars.

From these data and the fugacity coefficients of the individual gases, the value of f_{O_2} in equilibrium with graphite can be calculated from the relation in Equation (8).

$$(10) \qquad \log f_{O_2} = 2\left[\log \frac{\gamma_{CO_2}\, P_{CO_2}}{\gamma_{CO}\, P_{CO}} - \log K_b\right]$$

Results are given in Table 2 and Figure 2.

A simpler but less rigorous method of obtaining the same results consists of combining Equations (7) and (8) to obtain:

$$(11) \qquad C + O_2 = CO_2$$

$$\log K_c(T) = - \frac{\Delta G^o}{2.303\, RT} = \log f_{CO_2} - \log f_{O_2}$$

Rearranging, we obtain,

$$(12) \qquad \log f_{O_2} = \frac{\Delta G^o}{2.303\, RT} + \log f_{CO_2}$$

Equation (12) applies for a total pressure at which all compounds are in their respective standard states; this will not be significantly different from one atmosphere (Denbigh, 1957, p. 120-124, 146). An increase in total pressure will affect the free energy of reaction, ΔG, because of the volume change of graphite with pressure. The effect of this change on the value of $K_c(T)$ may be calculated (see Eugster and Wones, 1962, p. 91-92).

For the equilibrium represented by Eq. (11), at constant temperature,

$$\Delta G = \Delta G^{o} + RT\ \ell n\ K = \Delta G^{o} + RT \left[\ell n\ f_{co_2} - \ell n\ f_{O_2} \right]$$

$$d\Delta G = 0 = \Delta V_s dP_s + RT \left(\frac{\partial\ \ell n\ f_{co_2}}{\partial\ P_{gas}} \right)_T dP_{gas} - RT \left(\frac{\partial\ \ell n\ f_{O_2}}{\partial\ P_{gas}} \right) dP_{gas}$$

When rearranged and integrated, this becomes,

$$RT\ \ell n \frac{f_{O_2}\ (P_2)}{f_{O_2}\ (P_1)} = \Delta V_s\ (P_2 - P_1) + RT\ \ell n \frac{f_{co_2}\ (P_2)}{f_{co_2}\ (P_1)}$$

Setting $P_1 = 1$ atm., and substituting Eq. (12), we obtain,

$$(13) \qquad \log f_{O_2}\ (P_2) = \frac{\Delta G^{o}}{2.303RT} + \log f_{co2}\ (P_2) + \frac{\Delta V_s\ (P_2 - P_1)}{2.303RT}$$

Or,

$$(14) \qquad \log f_{O_2} = \frac{C^{o}_{T}\ \ (CO2)}{2.303\ RT} + \log f_{co2} - 0.028\ \frac{P - 1}{T}$$

The molar volume of graphite (5.30 cm.^{3}) is here assumed to be independent of pressure.

While Equation (14) is a rigorous expression, approximate values of log f_{O_2} may be conveniently obtained by introducing the following simplifying assumptions: (a) that, at total pressures in excess of 100 bars, $\log f_{co_2} = \log P_{gas}$; (b) that $G_T^o\ (CO_2) = - 94,200 - 0.2\ T$ cal./mole (Kubaschewski and Evans, 1958). Substituting in Equation (14), we obtain the approximate expression:

$$(15) \qquad \log f_{O_2} \simeq - \frac{20,586}{T} - 0.044 + \log P_{gas} - 0.028\ \frac{P_{gas} - 1}{T}$$

A comparison of values of $\log f_{O_2}$ calculated from Equation (15) and Equation (10) indicates that at temperatures above 500°K and total pressures in excess of 100 bars, the approximations used do not introduce serious errors (Table 2). The calculated values of $\log f_{O_2}$ for the graphite buffer at various total pressures (Table 2 and Figure 2) are believed accurate to at least ± 0.5.

Figure 2 shows that, for each value of $P_{gas} = P_{co_2} + P_{co}$, there is specified an isobarically univariant graphite + gas buffer curve. The family of such curves for different values of P_{gas} forms a surface in $P_{gas} - P_{O_2} - T$ space. The surface has a shape and orientation similar to those of other buffering surfaces (Eugster and Wones, 1962); higher temperatures and higher total pressures correspond to higher values of $\log f_{O_2}$. However, the effect of changes in total pressure on f_{O_2} is much more pronounced for the graphite buffer, particularly at lower pressures. At 700°C, for instance, f_{O_2} of the graphite buffer lies within the iron stability field at 1 bar pressure, but lies above the fayalite + magnetite +

quartz buffer curve at 2000 bars. By contrast, increasing temperature makes the graphite buffer more reducing with respect to the iron oxide buffers.

An important difference between the graphite buffer and other oxygen buffers is a consequence of the fact that the graphite buffer contains only one solid phase and that its buffering characteristic is due to the assemblage graphite + gas.[3] Therefore, the graphite buffer curves divide P_{gas}-P_{O_2}-T space into two distinctly different regions, a region above the graphite + gas curve, which represents the existence of a CO_2-rich gas (graphite absent) and a region below the graphite buffer curve, which is condensed.

Consider, for instance, a fixed value of P_{gas}, e.g., 2000 bars (Fig. 2), and a value of f_{O_2} and T above that of the 2000 bar graphite + gas buffer curve. Under these conditions, any bulk composition in the system C-O is represented by a gas phase consisting essentially of CO_2 and CO, the CO_2/CO ratio of which is defined by the quantities P_{gas}, T, and f_{O_2}. If the value of f_{O_2} in the gas

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[3] The presence of a gas is not necessary to define the oxygen fugacity of, e.g., an Fe_3O_4-Fe_2O_3 buffer for a specific temperature and total pressure. The gas phase is necessary only for the buffer to function, since the values of P_{O_2} specified are vanishingly small. By contrast, a gas phase (CO_2) enters directly into the buffering reaction for the graphite buffer.

is decreased until the graphite buffer curve at 2000 bars is reached, reduction of CO_2 and CO occurs and graphite is precipitated (Muan, 1958). The value of f_{O_2} will remain fixed on the curve until all the oxides have been converted to graphite.

In the two-component system C-O, values of f_{O_2} below the graphite-gas curve therefore represent a system in which all carbon is present as graphite and the gas phase may contain only oxygen (the vapor pressure of graphite is neglected). The value of P_{gas} below the graphite + gas curve is no longer 2000 bars, but has become equal to P_{O_2}, or 10^{-20} to 10^{-30} bars. Hence, no gas can be present in the region below the curve, unless voids remain while the solid graphite supports a pressure of 2000 bars ($P_{gas} \ll P_s$). The region below the graphite + gas curve is thus condensed in the sense that carbon oxides must be absent from the gas phase.

It is very important to realize that, as long as graphite is present it is not possible to produce equilibrium values of f_{O_2} within the condensed region by the addition of other volatile components (e.g. hydrogen or a hydrogen-water mixture). To illustrate this point, consider a graphite-vapor assemblage in equilibrium at $P_{gas} = 2000$ bars (Fig. 2). At constant total pressure, if f_{O_2} is suddenly reduced to a value below the graphite + gas curve by addition of a proper hydrogen + water mixture, then a situation is produced in which $P_{gas} = 2000 \text{ bars} > P_{CO_2} + P_{CO}$. To re-establish equilibrium, graphite will precipitate from the gas, reducing the value of $P_{co_2} + P_{co}$ to that value which corresponds to the particular graphite + gas curve which passes through the specified value of f_{O_2}. Regardless of the value of log f_{O_2} originally established by the new mixture, equilibrium between graphite and gas will be maintained, although, under strongly reducing conditions, the value of $P_{co_2} + P_{co}$ may become very small.

By contrast, if the value of f_{O_2} is fixed above the original graphite + gas curve, the graphite will oxidize, increasing the value of $P_{co_2} + P_{co}$ until a new graphite + gas curve through the value of f_{O_2} is reached. If the graphite is completely oxidized before this value is attained, a divariant one-phase gas assemblage is produced.

In summary, all displacements from the equilibrium graphite + gas surface in $P_{gas} - P_{O_2} - T$ space will produce changes in gas composition and in the magnitudes of P_{co_2}, P_{co}, and f_{O_2} which tend to return to a new equilibrium position on the same surface. If graphite is removed by oxidation before equilibrium is attained, a one-phase gas assemblage is produced.

Experimental Determination of Carbonate Stabilities Using Oxygen Buffers

The techniques of using solid-phase buffers in a CO_2 + CO atmosphere to control f_{O_2} were applied to a study of the stability relations of siderite ($FeCO_3$) (French, 1964a; French and Eugster, 1965).

Values of f_{O_2} along most of the solid-phase buffers used in earlier studies (Eugster and Wones, 1962) are metastable with respect to graphite. The two buffers used in the siderite study were graphite and hematite-magnetite mixtures.

The experimental arrangement is shown in Figure 3. The sample (usually synthetic siderite) is contained in a small (0.120 in. O.D.) silver tube; this inner tube is surrounded by a buffer mixture contained in a larger (0.173 in. O.D.) silver tube. Since neither CO_2 nor CO will diffuse through silver, the ends of both tubes are crimped but left unsealed, in contrast to the method of preparation of samples run in a hydrothermal atmosphere. The charge is then placed in a Tuttle "test-tube" type bomb, into which CO_2 is supplied by an external pumping system. Temperature control and measurement are carried out in the same manner as earlier hydrothermal experiments.

During the run, CO_2 from the atmosphere diffuses through the buffer; the CO_2/CO ratio to which the sample is subjected is thereby adjusted to the value specified by the f_{O_2} of the buffer. The attainment of equilibrium by this method was indicated by the consistency and reversibility of runs.

In these experiments, magnetite (Fe_3O_4) is added to the graphite buffer, so that, with both buffer mixtures, a single run will indicate the location of the reversible equilibrium with respect to run temperature by two reactions. If the run temperature lies within the stability field of siderite, the sample is unchanged while siderite forms in the buffer ($Fe_2O_3 + Fe_3O_4$ or $Fe_3O_4 + C_{(gr)}$); if the run temperature lies above the stability field of siderite, the buffer remains unaffected while the sample decomposes to the respective buffer assemblages. (It must be emphasized that magnetite plays no part in buffering f_{O_2} when graphite is also present, and thus it is not correct to speak of a "magnetite-graphite" buffer.)

Figure 4 presents stability data for siderite at a gas pressure of 1000 bars, as determined by French (1964*a*). Only the two isobaric invariant points, siderite + hematite + magnetite + gas and siderite + magnetite + graphite + gas, are accessible by this method; the curves bounding the stability field of siderite + gas have been calculated approximately from thermodynamic data.

It is possible that rates of equilibration between graphite and gas (represented by Equations (7), (8), and (11)) are slow enough so that a gas phase with metastably low CO_2/CO ratios could be maintained without precipitation of graphite, particularly at low temperatures (Muan, 1958; Rosenberg, 1962, unpublished data). However, the experimental data (French, 1964a; Rosenberg and French, 1964; French and Eugster, 1965) indicate that equilibrium is attained through precipitation of graphite during runs of long (two weeks) duration.

In other studies of siderite stability carried out in sealed unbuffered tubes, the bulk composition is constant ($FeCO_3$). Some decomposition of the sample to oxides is necessary to produce gas pressure within the sample tube. However, f_{O_2} is neither constant nor exactly known for such decompositions, and magnetite or hematite may be in equilibrium with siderite over a wide range of T and f_{O_2} (see Fig. 4). Unless f_{O_2} is known, the results of such experiments must be treated with caution.

Graphite as an Oxygen Buffer In Igneous and Metamorphic Rocks

The control of oxygen fugacities in a vapor phase through equilibration with graphite has great significance in the study of mineral assemblages produced by igneous or metamorphic processes. Recent studies of the behavior of oxygen in rocks (Chinner, 1960; Mueller, 1960; Kranck, 1961; Zen, 1963) have concentrated on iron-bearing minerals whose composition and stability relations are influenced by the f_{O_2} of the vapor phase with which they coexist (Eugster, 1959). One difficulty with such assemblages is that equilibrium between two or more solid phases is generally required to specify the value of f_{O_2} present; such equilibrium may often be difficult to demonstrate texturally (Zen, 1963). Moreover, if the assemblages contain carbonates or hydrous silicates, the f_{O_2} will be influenced by the fugacities of additional gas components such as H_2O and CO_2.

More recently, several researchers have called attention to the possible role of graphite and related carbonaceous matter in controlling the value of f_{O_2} in such diverse mineral assemblages as metamorphosed sediments (Miyashiro, 1964; Mueller and Condie, 1964) and meteorites (Mueller, 1964). Approximate calculations of the f_{O_2}

values permitted by graphite for total pressures of 10 bars and 10 kilobars were carried out by Miyashiro (1964), assuming ideal behavior for all gas components.

The importance of graphite in natural assemblages is that only a single solid phase is required to control the value of f_{O_2} in a CO_2 + CO atmosphere. Furthermore, since the buffering reaction occurs only in the system C-O, the effect of graphite upon f_{O_2} will be independent of the presence of other solid phases or gases. Introduction of other volatile components will create a situation in which $P_{gas} > P_{co_2} + P_{co}$.

The presence of graphite in a mineral assemblage therefore defines a relationship between the three parameters, T, f_{O_2}, and $(P_{co_2} + P_{co})$ whereby, if any two are known, the third is completely determined without regard to other components in the system or other phases in the mineral assemblage. Because of the low gram-molecular weight of graphite, even trace amounts of graphite will exert a very large buffering effect with respect to changes in the composition of the gas phase.

For a fairly wide range of values of $P_{co_2} + P_{co}$, the occurrence of graphite in a mineral assemblage formed at moderate temperatures indicates a value of f_{O_2} within the stability field of magnetite. This feature has been proposed as an explanation of the apparent reduction during metamorphism and of the preservation of steep gradients in f_{O_2} over relatively short distances (Zen, 1963; Miyashiro, 1964).

Most geological considerations have assumed a gas phase composed dominantly of H_2O and CO_2. However, if such a phase is equilibrated with graphite, two buffering reactions, involving both oxygen and hydrogen, are established. The equilibria involved in the system C-H-O may be described by the following four independent reactions, which involve methane (CH_4) as well as the other components of the gas phase:

(16) $C + O_2 = CO_2$

(17) $C + 2H_2 = CH_4$

(18) $CO_2 = CO + \frac{1}{2}O_2$

(19) $H_2O = H_2 + \frac{1}{2}O_2$

In the three-component system C-H-O, the assemblage graphite + gas will have three degrees of freedom. At a fixed temperature and total gas pressure, the system therefore becomes univariant. Thus, the fugacities of all volatile components in the gas may be specified uniquely in terms of one fugacity, e.g., f_{O_2}.

Detailed calculations of the equilibria in this system have been carried out for a variety of temperatures and total pressures (French, 1964 b). Preliminary results indicate that methane will be a significant component of the gas phase over a wide range of geologically reasonable conditions; at temperatures below about 800°C, the ratio f_{CH_4}/f_{H_2} will be greater than unity. Further, it appears that methane will become dominant in a gas phase coexisting with graphite at values of f_{O_2} corresponding to the lower part of the magnetite stability field where fayalite (Fe_2SiO_4) may become a stable phase (Eugster, 1959). Such calculations do, however, neglect the possibility of polymerization of methane in the vapor phase to produce more complex paraffin-group hydrocarbons or other organic materials (see, e.g., Mueller, 1964).

The great potential significance of graphite in natural mineral assemblages indicates that more detailed identification and study of the carbonaceous matter in sediments and metamorphic rocks is required. In such studies, an exact distinction must be made between crystalline graphite and amorphous organic matter with which it is often confused and from which it may develop by metamorphism (French, 1964 *c*). The calculations here apply only to crystalline graphite; they are not rigorously applicable to organic matter of uncertain character, although such material may be significant in producing and maintaining reducing values of f_{O_2} during metamorphism.

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Table 1. Terms and symbols used in equations

T	Temperature in degrees Kelvin.
P_s	Isotropic pressure on solid phases.
P_{gas}	Total pressure of the gas phase. The unqualified term "total pressure" refers to closed experimental systems in which $P_s = P_{gas}$.
P_i	Partial pressure of component *i* in the gas phase.
f_i	Fugacity of component *i* in the gas phase.
γ_i	Fugacity coefficient of component *i* in the gas phase, defined by $\gamma_i = f_i/P_i$.
G_T^o	Standard Gibbs free energy of formation of a compound from its elements at a specified temperature and unit fugacities of components occurring in the gaseous state.
ΔG^o	Standard Gibbs free energy change in a reaction, equal to $\Sigma\, (G_T^o)_{products} - \Sigma\, (G_T^o)_{reactants}$.
$K(T)$	Equilibrium constant of a reaction, written using fugacities of gaseous components; a function of T only.
$\log N$	Logarithm of N to the base 10.
$\ln N$	Logarithm of N to the base *e*.

Table 2. Calculated values of P_{co} and log f_{O_2} in equilibrium with graphite for various values of P_{gas} (= $P_{co_2} + P_{co}$) (*approximate values from Eq. 15)

T°K	T°C	P_{co}	$-\log f_{O_2}$	$-\log f_{O_2}$(*)
P_{gas} = 1 bar				
400	127	2.3×10^{-7}	51.53	51.51
500	227	4.2×10^{-5}	41.26	41.22
600	327	1.4×10^{-3}	34.40	34.35
700	427	0.016	29.51	29.45
800	527	0.099	25.89	25.78
900	627	0.35	23.16	22.92
1000	727	0.72	21.24	20.63
1100	827	0.93	19.95	18.76
1200	927	0.98	19.01	17.20
P_{gas} = 100 bars				
400	127	2.0×10^{-6}	49.62	49.51
500	227	3.9×10^{-4}	39.29	39.22
600	327	0.013	32.40	32.36
700	427	0.16	27.49	27.46
800	527	1.0	23.82	23.78
900	627	4.3	20.97	20.92
1000	727	12.9	18.73	18.63
1100	827	29.4	16.93	16.76
1200	927	52.8	15.55	15.20

Table 2. Continued

T°K	T°C	P_{co}	$-\log f_{O_2}$	$-\log f_{O_2}(*)$
P_{gas} = 500 bars				
400	127	3.1×10^{-6}	49.07	48.84
500	227	6.8×10^{-4}	38.62	38.55
600	327	0.025	31.69	31.68
700	427	0.31	26.75	26.87
800	527	2.0	23.03	23.10
900	627	8.6	20.20	20.23
1000	727	27.0	17.93	17.90
1100	827	66.9	16.09	16.07
1200	927	135	14.60	14.51
P_{gas} = 1000 bars				
400	127	3.0×10^{-6}	48.73	48.58
500	227	7.2×10^{-4}	38.26	38.27
600	327	0.028	31.44	31.40
700	427	0.36	26.39	26.49
800	527	2.4	22.62	22.81
900	627	10.6	19.83	19.95
1000	727	34.6	17.56	17.66
1100	827	86.8	15.70	15.79
1200	927	182	14.20	14.22
P_{gas} = 2000 bars				
400	127	3.0×10^{-6}	48.19	48.35
500	227	7.2×10^{-4}	37.75	38.03
600	327	0.026	30.85	31.15
700	427	0.36	25.90	26.23
800	527	2.6	22.24	22.55
900	627	11.8	19.38	19.68
1000	727	39.8	17.10	17.39
1100	827	104	15.24	15.51
1200	927	228	13.72	13.95

FIGURE CAPTIONS

1. Values of f_{co} as a function of temperature in a CO_2 + CO atmosphere for several oxygen buffer assemblages. Data for graphite buffer calculated in this paper; other data from Eugster and Wones, 1962. Abbreviations: G, graphite; HM, hematite + magnetite; MI, magnetite + iron; MW, magnetite + wüstite; WI, wüstite + iron; QFM, quartz + fayalite + magnetite.

2. Values of f_{O_2} for the graphite + gas buffer as a function of temperature for selected values of $P_{gas} = P_{co_2} + P_{co}$. Graphite + gas curves shown in solid lines; values of P_{gas} given in parentheses. The dashed lines indicate values of f_{O_2} for other buffering assemblages (Eugster and Wones, 1962) calculated for P_{gas} = 1 bar; The effect of total pressure on this group of buffers is slight. Abbreviations: HM, hematite + magnetite; NNO, nickel + bunsenite; QFM, quartz + fayalite + magnetite; MI, magnetite + iron; MW, magnetite + wüstite; WI, wüstite + iron.

3. Cutaway sketch of experimental run assembly. The sample (heavy dots) is enclosed in a solid-phase buffer (horizontal ruling). Buffering of the sample is established by diffusion of the CO_2-rich gas phase through the buffer.

4. Isobaric section through the stability field of siderite + gas at P_{gas} = 1000 bars. Only the two isobaric invariant points, siderite + hematite + magnetite + gas (SHM) and siderite + magnetite + graphite + gas (SMG) were determined. The stability field of the assemblage, siderite + gas (horizontal ruling) is bounded by the three univariant curves, siderite + hematite + gas, siderite + magnetite + gas, and siderite + magnetite + graphite + gas. The latter curve lies entirely within the condensed region below the graphite + gas buffer curve (slanted dashed area). HM designates the hematite-magnetite buffer and G the graphite + gas buffer for this value of P_{gas}.

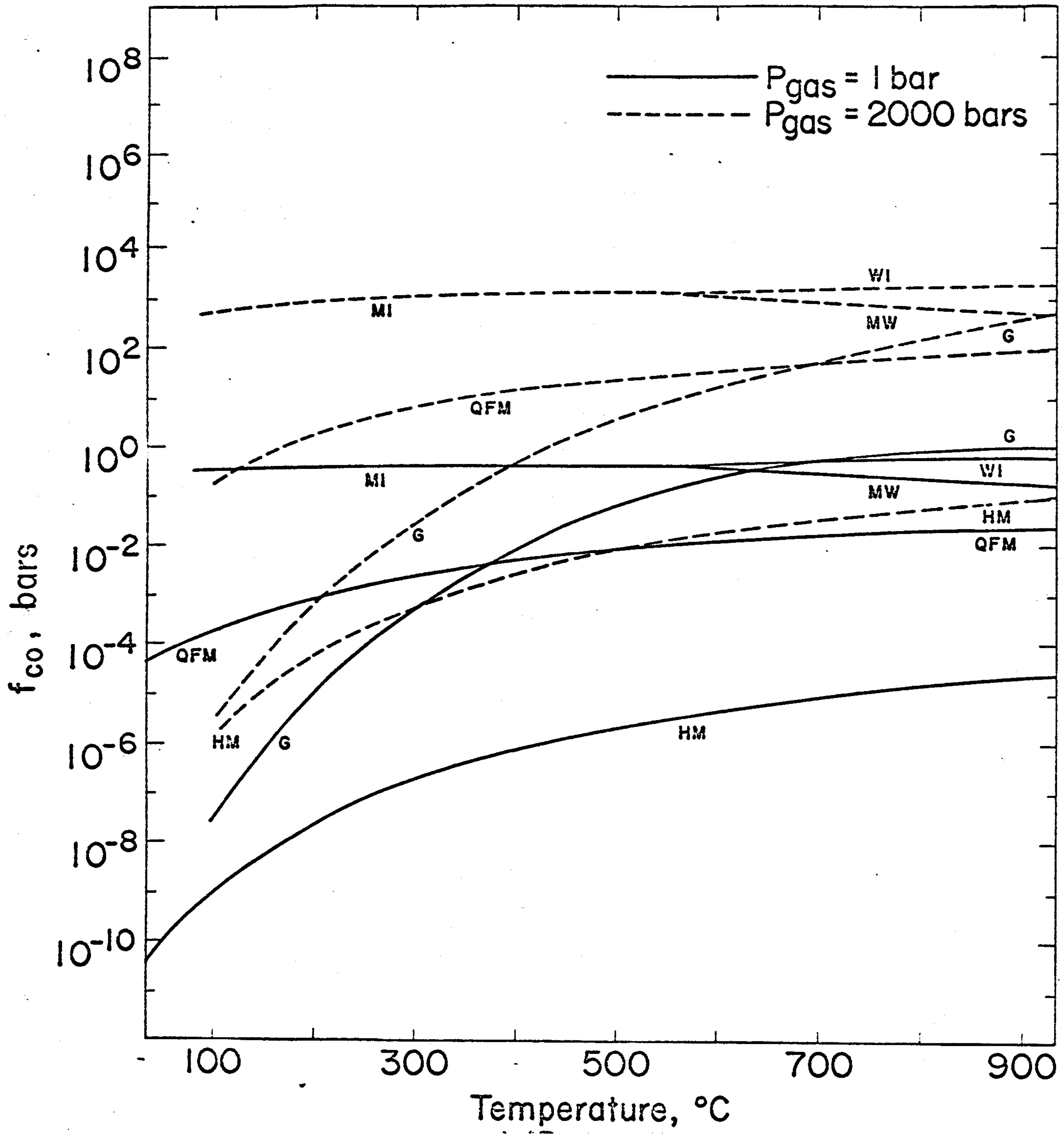
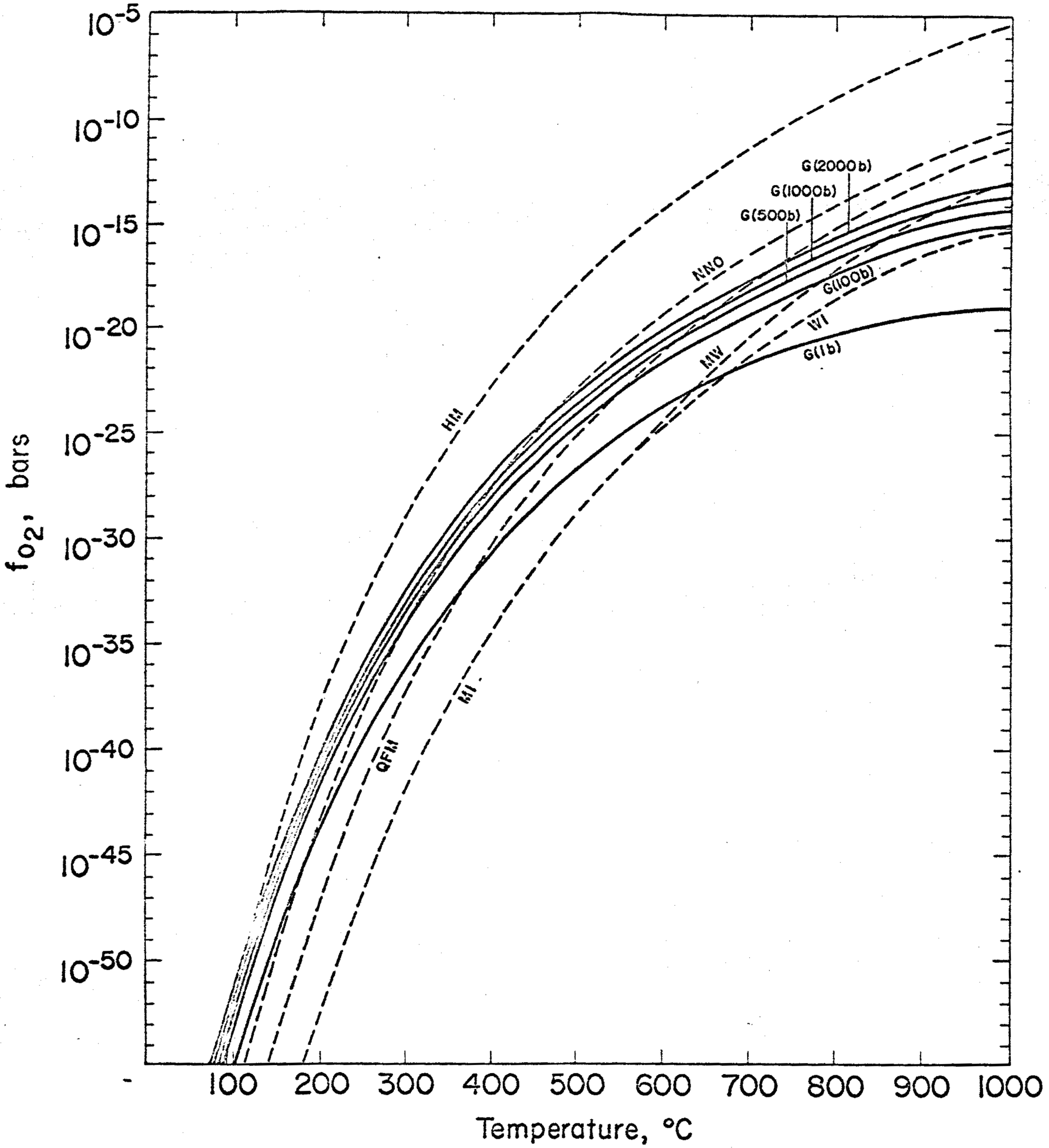

P_{gas} = 1 bar
P_{gas} = 2000 bars
10^8
10^6
10^4
10^2
10^0
10^{-2}
10^{-4}
10^{-6}
10^{-8}
10^{-10}
f_{co}, bars
100
300
500
700
900
Temperature, °C
WI
MI
MW
G
QFM
G
WI
MI
MW
HM
G
QFM
QFM
HM
G
HM

FIGURE I



10^{-5}
10^{-10}
10^{-15}
10^{-20}
10^{-25}
10^{-30}
10^{-35}
10^{-40}
10^{-45}
10^{-50}
f_{O_2}, bars
HM
G(2000b)
G(1000b)
G(500b)
NNO
G(100b)
WI
MW
G(1b)
QFM
MI
100
200
300
400
500
600
700
800
900
1000
Temperature, °C

FIGURE 2

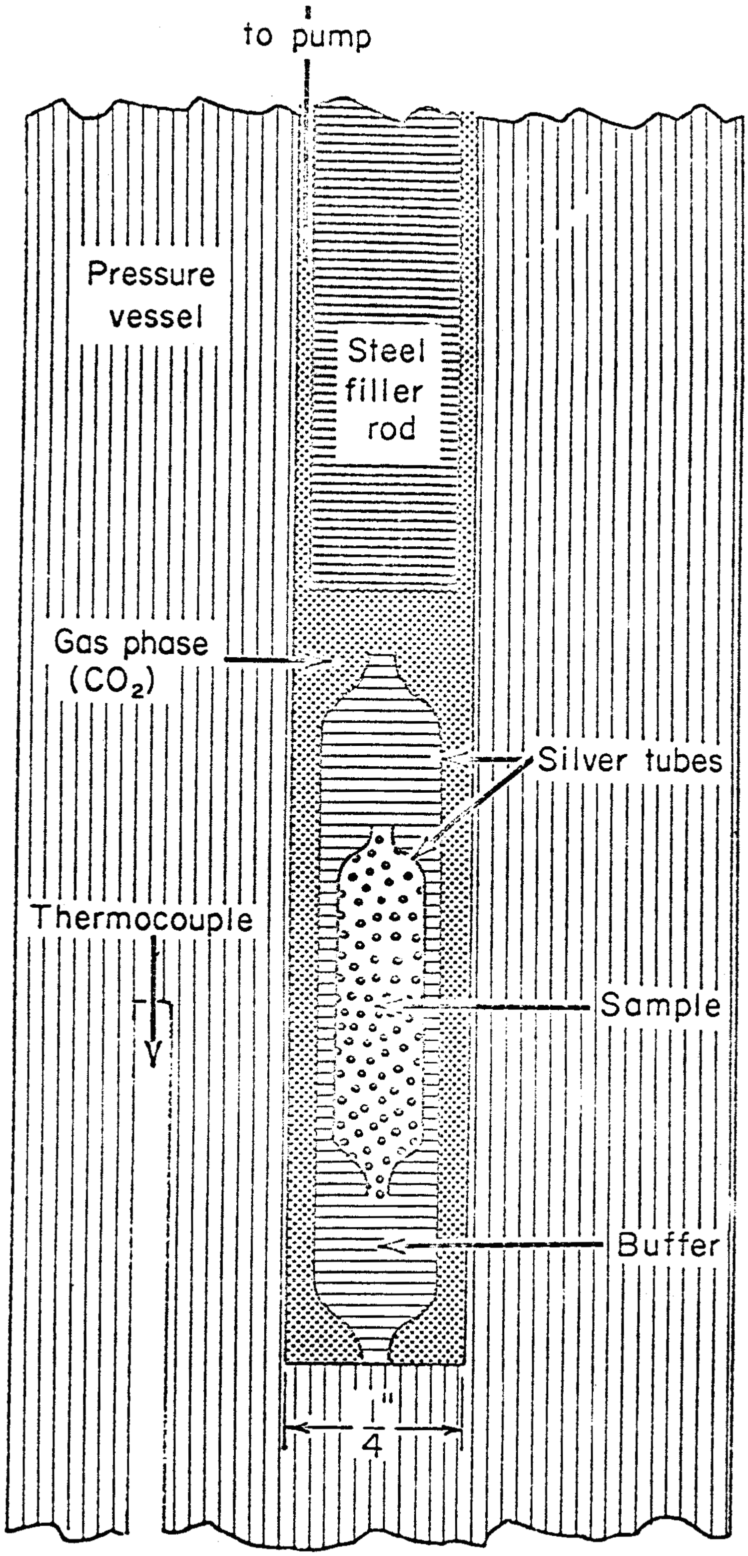

to pump
Pressure vessel
Steel filler rod
Gas phase (CO_2)
Silver tubes
Thermocouple
Sample
Buffer
1"
4

FIGURE 3

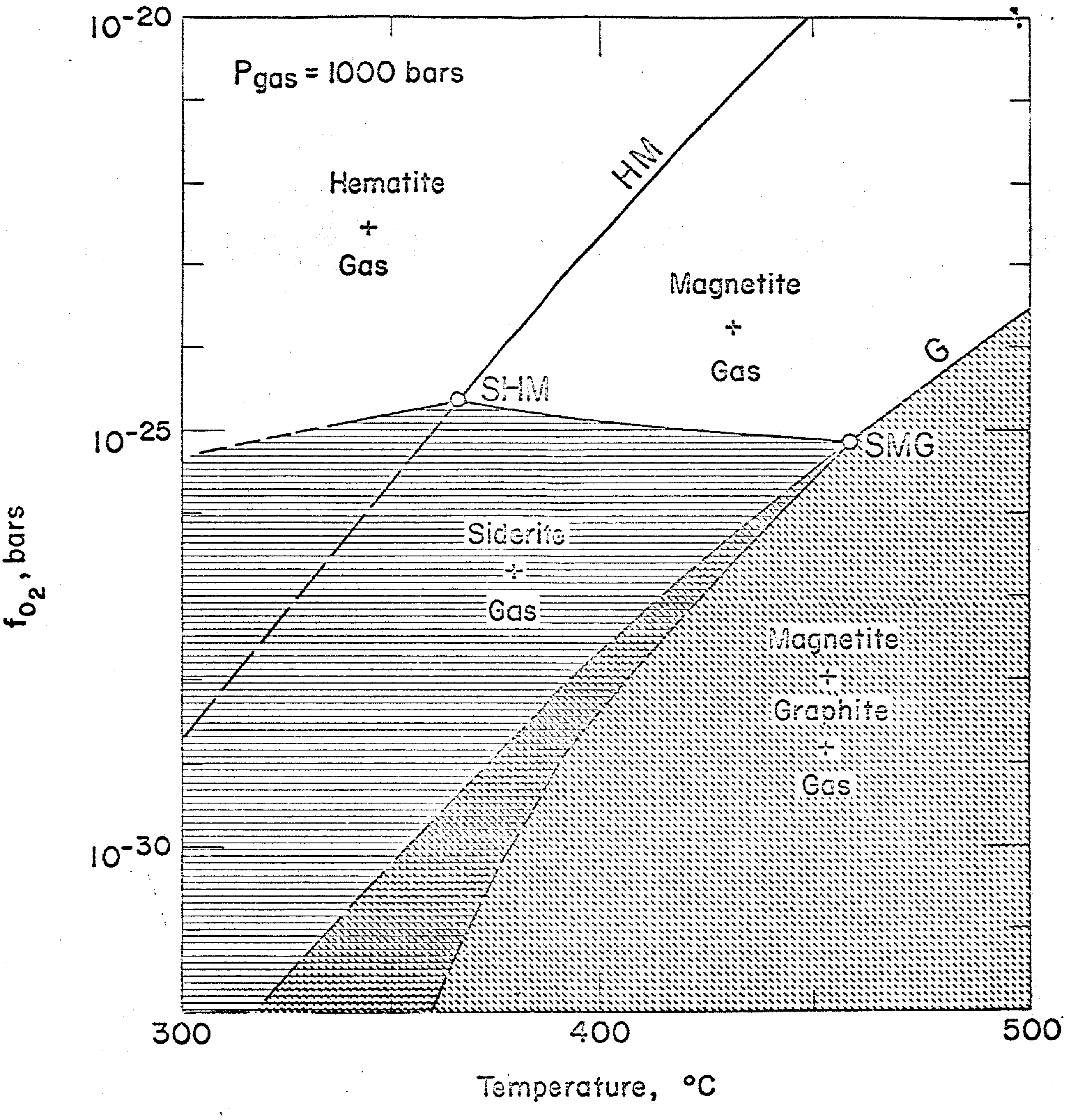

10^{-20}
P_{gas} = 1000 bars
Hematite + Gas
HM
Magnetite + Gas
G
SHM
SMG
10^{-25}
f_{O_2}, bars
Siderite + Gas
Magnetite + Graphite + Gas
10^{-30}
300
400
500
Temperature, °C

FIGURE 4