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ABSTRACT

Stability relations of siderite ($FeCO_3$) in the system Fe-C-O were determined between 500 and 2000 bars in a $CO_2 + CO$ atmosphere as a function of T, P_F ($= P_{CO_2} + P_{CO}$) and f_{O_2}, using solid-phase oxygen buffers Siderite was synthesized for the experiments by decomposition of ferrous oxalate dihydrate ($FeC_2O_4 \cdot 2H_2O$) in sealed tubes at 2000 bars P_{H_2O} and approximately 380°C During stability runs, f_{O_2} was controlled by surrounding the siderite sample with either graphite or hematite-magnetite buffer mixtures.

The stability field of siderite + gas in P_F - T - f_{O_2} space is a narrow wedge bounded by stable divariant reaction surfaces representing decomposition of siderite to (1) hematite + gas, (2) magnetite + gas, (3) magnetite + graphite + O_2. The latter reaction surface lies entirely in the condensed region below the graphite buffer and is not experimentally accessible. Reactions of siderite to form iron or wustite ($Fe_{1-x}O$) are not stable

Points along the univariant equilibrium curve siderite + hematite + magnetite + gas (SHMG) were located reversibly at $P_F = 500$ bars, $T = 363 \pm 10$°C, $\log f_{O_2} = -24.8$, $P_F = 1000$ bars, $T = 365 \pm 10$°C, $\log f_{O_2} = -24.7$ The univariant equilibrium curve siderite + magnetite + graphite + gas (SMGrG) passes through the following points $P_F = 500$ bars, $T = 455 \pm 10$°C, $\log f_{O_2} = -25.7$; $P_F = 1000$ bars, $T = 458 \pm 10$°C, $\log f_{O_2} = -25\ 2$, $P_F = 2000$ bars, $T = 465 \pm 10$°C, $\log f_{O_2} = -24.4$.

In an isobaric f_{O_2}-T section, the univariant curve siderite + hematite + gas (SHG) corresponds to low temperatures and relatively high f_{O_2} values The univariant curve siderite + magnetite + gas (SMG) is stable at higher temperatures and relatively lower f_{O_2} values. The stability of the assemblage siderite + gas is strongly dependent on T and f_{O_2}, but is practically independent of the value of $P_{CO_2} + P_{CO}$. The univariant equilibrium siderite + magnetite + graphite + gas fixes the maximum stability temperatures of siderite, 455-465°C in the range $P_F = 500$-2000 bars. In this range, siderite is not stable at f_{O_2} values above about 10^{-24} bars and decomposes to either hematite (lower T) or magnetite (higher T). The determined stability field of siderite + gas lies at f_{O_2} values above the stability field of fayalite (Fe_2SiO_4) and therefore reactions between siderite and quartz to form fayalite are not stable

The stability relations of natural iron-rich carbonates are more complex than those determined for pure siderite. The presence of other volatile species in a natural gas phase, producing a condition in which $P_{CO_2} + P_{CO} < P_F$, will produce slightly lower decomposition temperatures, and the presence of H_2O may stabilize iron hydroxide phases at lower temperatures. By contrast, the substitution of Mg^{2+}, Mn^{2+}, or Ca^{2+} for Fe^{2+} will stabilize iron-rich carbonates at higher temperatures and f_{O_2} values.

During metamorphism, natural iron-rich carbonates react with available quartz and water to produce iron-rich amphiboles (grunerite). The present experimental data, combined with geological studies of metamorphosed iron-formations, suggest that this reaction occurs at about 300-450°C. Conversely, the coexistence of siderite + quartz in many hydrothermal veins indicates temperatures below this value. Conversion of quartz-free siderite units to magnetite in contact-metamorphic aureoles requires temperatures exceeding 400-450°C.

CONTENTS

SYMBOLS AND NOTATIONS USED

Symbols used generally follow conventions of Thompson (1955) and Greenwood (1961).

T = temperature (°K).

P_s = isotropic pressure on solid phases

P_F = total pressure of the fluid (gas) phase.

P_{E_i} = "osmotic equilibrium" pressure of component i in a fluid phase (Greenwood, 1961).

P_t = total pressure in a closed experimental system where $P_t = P_F = P_s$.

P_i = partial pressure of component i in a closed experimental system where $\Sigma P_i = P_t$.

f_i = fugacity of component i in a fluid phase.

γ_i = fugacity coefficient of component i in the fluid phase, defined by $\gamma_i = f_i/P_i$.

ΔV_s = volume change of the solid phases in a reaction, defined as $\Delta V_s = \Sigma(V_s)_{\text{products}} - \Sigma(V_s)_{\text{reactants}}$.

$\Delta G_{f\ T}^{\circ}$ = standard Gibbs free energy of formation of a compound from its elements at a specified temperature and unit fugacities of gaseous components

ΔG_T° = standard Gibbs free energy of reaction, equal to $\Sigma(\Delta G_{f\ T}^{\circ})_{\text{products}} - \Sigma(\Delta G_{f,T}^{\circ})_{\text{reactants}}$.

$\Delta H_{f\ T}^{\circ}$ = standard enthalpy of formation of a compound from its elements.

ΔH_T° = standard enthalpy change in a reaction.

$K_i(T)$ = equilibrium constant of reaction i, written with fugacities of gaseous components, a function of T only.

C_p = molar heat capacity of a substance at constant pressure

ABBREVIATIONS FOR PHASES IN TABLES AND ILLUSTRATIONS

S = siderite ($FeCO_3$)

H = hematite (Fe_2O_3)

M = magnetite (Fe_3O_4)

I = iron (Fe)

Wu = wustite ($Fe_{1-x}O$)

Gr = graphite (C)

Q = quartz (SiO_2)

F = fayalite (Fe_2SiO_4)

G = gas phase in a CO_2 + CO atmosphere

G* = gas phase (O_2) in condensed region below the graphite buffer curve.

In tables of experimental results, occurrence of trace amounts of a phase are indicated by parentheses, as (S). Such occurrences are not believed to represent stable reaction products and may result from contamination or from metastable reaction. Clearly metastable products in a significant amount are indicated by an asterisk, as (S*). Small letters (m, s, h, etc.) designate phases which may be in equilibrium with the observed phases but which were not detected, e.g , the assemblage S + M + h.

STABILITY RELATIONS OF SIDERITE ($FeCO_3$), DETERMINED IN CONTROLLED-f_{O_2} ATMOSPHERES

INTRODUCTION

Iron-bearing minerals are of particular interest in petrogenetic studies, because they may participate in reactions involving oxidation and reduction (Eugster, 1959, Buddington and Lindsley, 1964). The occurrence and composition of iron-bearing minerals thus reflect in part the value of f_{O_2} in the environment during their formation. Knowledge about the stability of iron-bearing minerals is thus directly applicable to analyses of conditions of formation of iron-bearing assemblages and to discussions of the behavior of volatile components (H_2O, CO_2, O_2 et al.) during metamorphism (Mueller, 1960, Kranck, 1961, French, 1968, Klein, 1966, Butler, 1969).

Siderite ($FeCO_3$) is a common constituent of low-grade sedimentary iron formations and of some hydrothermal veins, and information about its stability is of great importance in discovering how such deposits have formed and what were the compositions of the volatile phases with which they coexisted Unlike most other carbonates, the stability of siderite is dependent on temperature, pressure, and the fugacities of both CO_2 and O_2, and exact determination of its stability requires simultaneous control of both f_{CO_2} and f_{O_2}.

Two types of decarbonation reactions exist for natural carbonate minerals (Jamieson and Goldsmith, 1959)

$$RCO_3 = RO + CO_2 \qquad (1)$$

$$aRCO_3 + \frac{1}{2} O_2 = R_aO_{a+1} + a\,CO_2 \qquad (2)$$

In reaction (1), the divalent cation (R) is not oxidized, and equilibrium is independent of the partial pressure of oxygen In reaction (2), the cation may assume different valences and form a variety of oxides at different values of P_{O_2}. The stability of a carbonate which decomposes by reactions of the second type will depend on the partial pressure of oxygen as well as on temperature and P_{CO_2}.

Most experimental studies have dealt with reactions of the first type Stability relations as a function of P_{CO_2} and T have been determined for calcite ($CaCO_3$) and magnesite ($MgCO_3$) (Harker and Tuttle, 1955a) and for smithsonite ($ZnCO_3$) (Harker and Hutta, 1956). The analogous reaction of dolomite to form calcite, periclase (MgO), and CO_2 has been determined by Harker and Tuttle (1955a)

Natural carbonates which decompose according to reaction (2) are siderite ($FeCO_3$) and rhodochrosite ($MnCO_3$). Their stability is thus a function of T, P_{CO_2}, and P_{O_2}, and these three variables must be simultaneously controlled for rigorous stability determinations Such control has been made possible by the use of solid-phase oxygen buffers in an atmosphere of CO_2 + CO (French, 1964a, French and Eugster, 1965) Preliminary data have been presented for the stability of siderite (French, 1965, French and Eugster, 1965, French and Rosenberg, 1965) and a detailed study of rhodochrosite stability has recently appeared (Huebner, 1969). Siderite decomposes stably to hematite and magnetite by oxidation reactions of the second type. The rhodochrosite stability field is bounded chiefly by analogous oxidation reactions, but rhodochrosite also decomposes stably to manganosite (MnO) over a limited range of P_{O_2} (Huebner, 1969)

DESCRIPTION OF THE CRYSTALLINE PHASES

The term siderite refers here to calcite-type carbonates in which the $FeCO_3$ end-member is dominant. In the carbonate crystal structure, complete solid solution apparently exists between Fe^{2+} and Mg^{2+} and between Fe^{2+} and Mn^{2+} (Palache et al , 1944, Goldsmith, 1959, Rosenberg, 1963a, 1963b, 1967) A wide miscibility gap exists, however, between $CaCO_3$ and $FeCO_3$. Limited solubility of Ca^{2+} in siderite is observed, the experimentally determined solubility does not exceed 10 mole percent $CaCO_3$ at temperatures as high as 550°C (Rosenberg and Harker, 1956, Rosenberg, 1963a, 1963b, 1967). Fe^{2+} is more soluble in calcite, at 550°C, calcite may contain 20 mole percent $FeCO_3$ (Rosenberg, 1963a).

Although carbonates with over 95 mole percent $FeCO_3$ have been reported (Hutchinson, 1903, Ford, 1917), most natural siderites contain significant amounts of Mn^{2+} and Mg^{2+}. Analyses of natural siderites and related carbonates have been compiled by Ford (1917), Sundius (1925a, 1925b), Schoklitsch (1935), Palache et al. (1944), Hügi (1945), Smythe and Dunham (1947) and Deer et al. (1962, p. 272-277). The composition of siderite in the Lake Superior iron formations varies between 74 and 92 mole percent $FeCO_3$ (James, 1954), and analyzed siderites from unmetamorphosed iron formation on the Mesabi Range contain between 61 and 80 mole percent $FeCO_3$, 18-31 mole percent $MgCO_3$, and 2-7 mole percent $CaCO_3$ (French, 1968).

In natural occurrences, siderite is commonly associated with iron-rich dolomite (ankerite). Siderite is most commonly found in sedimentary iron formations (James, 1954, Pettijohn, 1957, Carrozi, 1960) and in hydrothermal veins (Lindgren, 1933, Wahlstrom, 1935, Legraye, 1938, Fabian et al , 1957; Shaw, 1959) The dominant carbonates in carbonatite bodies associated with alkalic igneous rocks are generally iron-poor, but both siderite and ankerite have been reported from several localities (Pecora, 1956, Smith, 1956). Siderite has also been observed in salt-dome cap rock (Rolshausen, 1934), in a bauxite-bearing clay (Burchard, 1924), and in a tourmaline-bearing pegmatite (Simpson, 1929). Siderite is present in moderately metamorphosed iron-rich rocks, generally associated with the iron-amphibole grunerite (Tilley, 1938, Gustafson, 1933, James, 1955, Klein, 1966), but has not been reported from highly-metamorphosed rocks containing iron-rich pyroxenes (James, 1955, Gundersen and Schwartz, 1962, French, 1968, Bonnichsen, 1968).

Magnetite, Fe_3O_4, is the most commonly observed member of the spinel group. Several cations, particularly Ti, Cr, Al, and Mg, may substitute for Fe in the structure (Palache et al., 1944). Above 900°C, magnetite may depart from stoichiometry by cation deficiency (Greig et al., 1935, Darken and Gurry, 1945, 1946). Magnetite is a common accessory mineral in sedimentary, igneous, and metamorphic rocks, in hydrothermal veins, and in contact-metasomatic deposits Magnetite has also been recognized as an original constituent of sedimentary iron formations (James, 1954), and is generally present when such rocks are metamorphosed (LaBerge, 1964, French, 1968)

Hematite, α-Fe_2O_3, is a common mineral in igneous and metamorphic rocks · It is the dominant iron oxide in post-Precambrian sedimentary iron formations Hematite can contain a small amount of Al_2O_3 in solid solution (Turnock and Eugster, 1962); Ti, Mn, and other cations may also be present Other polymorphs of Fe_2O_3 (see Rooksby, 1961) were not observed in the present study

Graphite, the hexagonal crystalline form of carbon, is found in igneous rocks, in metamorphosed sediments and coals, and in vein deposits of uncertain origin Much carbonaceous material from unmetamorphosed sediments, which has been considered graphite, is probably amorphous or poorly-crystalline carbon or hydrocarbons A thorough summary of the properties of graphite and related compounds is given by Ubbelohde and Lewis (1960). Graphite may form during metamorphism from noncrystalline or poorly crystalline carbonaceous matter in sediments (Quinn and Glass, 1958, French, 1964b)

PREVIOUS STUDIES OF SIDERITE STABILITY

Instability Under Atmospheric Conditions

The instability of siderite under the conditions of low P_{co_2} and high P_{o_2} present at the surface has been demonstrated by (1) thermodynamic calculations, (2) observed alteration of natural siderite, (3) experimental oxidation of siderite at room temperature

Thermodynamic calculations of the stability of siderite, hematite, and magnetite indicate that siderite is not stable under the values of P_{o_2} (0.2 atm) characteristic of the atmosphere (Holland, 1959, 1965, Garrels, 1960) At the value of P_{co_2} in the atmosphere (3×10^{-4} atm), and at 25°C, siderite should decompose to hematite above $10^{-7\ 5}$ atm P_{o_2}

Natural siderite, exposed to the atmosphere or to ground water, commonly oxidizes to hematite, limonite, or goethite, and more rarely to magnetite (Palache et al , 1944, Pettijohn, 1957, p 145, Burchard, 1924, Smythe and Dunham, 1947, Deer et al., 1962) Silliman (1820) described the oxidation of pieces of siderite exposed for about 50 years on the mine dump at Roxbury, Connecticut, a rim of dark, oxidized material one-quarter to one-half inch thick surrounded a core of lighter unaltered siderite

Siderite oxidizes readily in laboratory experiments at room temperature A siderite sample stored at room temperature underwent progressive oxidation (Schaller and Vlisidis, 1959) over a period of 43 years, the FeO content decreased linearly from 59 42 to 0 74 percent. Jamieson and Goldsmith (1960) oxidized natural siderite to hematite by prolonged grinding at room temperature Synthetic siderite partially oxidized in air during drying at 100°C (Sharp, 1960) A kinetic study of siderite oxidation (Seguin, 1966) between 25°C and 300°C suggests that the process is a first-order reaction with an activation energy of about +10 kcal/mole

DTA Studies

Previous experimental studies of the decomposition of siderite have been carried out largely by differential thermal analysis (DTA) or by thermo-gravimetric analysis (TGA). The

DTA pattern of siderite obtained by many investigators (Cuthbert and Rowland, 1947, Kerr and Kulp, 1947, Frederickson, 1948, Rowland and Jonas, 1949, Beck, 1950, Kulp et al , 1951, Kissinger et al., 1956, Powell, 1965) consists of an exothermic peak in the range 400-650°C, followed by an endothermic peak at 750-850°C The first peak has been ascribed to the breakdown of siderite to FeO, the second to the oxidation of FeO to magnetite or hematite This interpretation is uncertain because stoichiometric FeO does not exist and the compound $Fe_{1-x}O$ (wustite) is stable only above 560°C and at low values of P_{O_2} (Darken and Gurry, 1945, 1946)

The DTA studies have been made in atmospheres in which P_{O_2} is unknown and is probably too high for equilibrium decomposition of siderite The exothermic peak may indeed represent the non-equilibrium reaction of siderite to an iron oxide (hematite, magnetite, or possibly wustite), while the higher-temperature endothermic peak may indicate complete conversion of the iron oxides to hematite (Powell, 1965)

The interpretation of the DTA results is uncertain. The partial pressure of oxygen was not controlled and is not known, it was probably much higher than the values required for equilibrium between siderite and the iron oxides. This interpretation is favored by the observed strong effects of different furnace atmospheres on reaction temperatures (Rowland and Jonas, 1949, Kissinger et al., 1956, Powell, 1965) and by the observed lowering of the temperature of the exothermic peak with decreasing heating rate (Kissinger et al , 1956)

Hydrothermal Studies

The stability relations of siderite-bearing carbonate assemblages in the subsolidus region of the system $CaCO_3$-$MgCO_3$-$FeCO_3$-$MnCO_3$ have been studied experimentally at temperatures up to 550°C and fluid pressures as high as 4 kb (Rosenberg and Harker, 1956, Rosenberg, 1963a, 1963b, 1967). Similar assemblages in the subsolidus region of the system $CaCO_3$-$MgCO_3$-$FeCO_3$ have been examined at temperatures up to 800°C at total pressures of 15 kb (Goldsmith et al., 1962). In these studies, the value of P_{CO_2} was maintained high enough to prevent dissociation of the carbonates. The value of P_{O_2} was not strictly controlled and significant alteration of siderite to magnetite was occasionally observed (Rosenberg, 1960, p 8, Goldsmith et al., 1962, p. 660).

More recent experimental studies have concentrated on the stability and decomposition of siderite itself Seguin (1968a), in a study of the complicated Fe-C-O-S-H_2O system, decomposed siderite to iron oxides by various techniques, both with and without the use of solid-phase oxygen buffers. In buffered experiments, he obtained decomposition temperatures at a total pressure of 2 kb which ranged from 296°C (HM buffer) to 438°C (MI buffer) His higher temperatures are clearly metastable with respect to the graphite buffer (French and Eugster, 1965), and interpretation of his other results is difficult because of the complexity of the system in which he worked and the lack of demonstrated reversibility in his reactions.

Johannes (1968, 1969) investigated the stability of Fe-Mg carbonates in equilibrium with Fe^{2+}- and Mg^{2+}-bearing aqueous solutions While the value of P_{O_2} was not explicity controlled in his experiments, he observed that siderite and Fe-Mg carbonates containing more than 30 mole percent $FeCO_3$ decomposed to magnetite at about 400°C

A study of siderite decomposition relations in the system Fe-C-O (Weidner and Tuttle, 1964, Weidner, 1968) was carried out using sealed tubes in a CO_2 atmosphere at pressures up to 10 kb. Temperatures determined for the equilibria siderite + hematite + magnetite + gas and siderite + magnetite + graphite + gas are higher than those determined in the present study (French, 1965, French and Rosenberg, 1965), and a break in the slope of the curve for the equilibrium siderite + magnetite + graphite + gas, located at 5 kb, was interpreted as indicating a polymorphic transition of siderite to a high-pressure phase (Weidner and Tuttle, 1964).

The present investigation of siderite stability is the first in which explicit control of the value of P_{O_2} is obtained by use of open capsules combined with solid-phase oxygen buffers (French and Eugster, 1965, Huebner, 1969). A detailed discussion of the difference in results obtained on siderite stability by different experimental methods of different investigators is given below (p 31).

THERMODYNAMIC CALCULATION OF SIDERITE STABILITY

Sufficient thermodynamic data exist for calculation of the stability field of siderite in terms of P_{CO_2}, P_{O_2}, and T (see, e g , Garrels and Christ, 1965, Holland, 1959, 1965, Mel'nik, 1964, Yui, 1966). The stability field of siderite is considered to be bounded by the following possible reactions

$$2\,FeCO_3 + \frac{1}{2}\,O_2 = Fe_2O_3 + 2\,CO_2$$

$$\text{siderite} = \text{hematite} + \text{gas}$$

$$\log K_3(T) = 2\log f_{CO_2} - \frac{1}{2}\log f_{O_2} \tag{3}$$

$$3\,FeCO_3 + \frac{1}{2}\,O_2 = Fe_3O_4 + 3\,CO_2$$

$$\text{siderite} = \text{magnetite} + \text{gas}$$

$$\log K_4(T) = 3\log f_{CO_2} - \frac{1}{2}\log f_{O_2} \tag{4}$$

$$0.947\,FeCO_3 + 0.026\,O_2 = Fe_{0.947}O + 0.947\,CO_2$$

$$\text{siderite} = \text{wustite} + \text{gas}$$

$$\log K_5(T) = 0.947\log f_{CO_2} - 0.026\log f_{O_2} \tag{5}$$

$$FeCO_3 = Fe + CO_2 + \frac{1}{2}\,O_2$$

$$\text{siderite} = \text{iron} + \text{gas}$$

$$\log K_6(T) = \log f_{CO_2} + \frac{1}{2}\log f_{O_2} \tag{6}$$

$$3\,FeCO_3 = Fe_3O_4 + 3C + \frac{5}{2}O_2$$

siderite = magnetite + graphite + gas

$$\log K_7(T) = \frac{5}{2}\log f_{O_2} \qquad (7)$$

$$FeCO_3 = Fe + C + \frac{3}{2}O_2$$

siderite = iron + graphite + gas

$$\log K_8(T) = \frac{3}{2}\log f_{O_2} \qquad (8)$$

Reactions (7) and (8) can be stable only at f_{O_2} values below that of the graphite buffer, they lie entirely within the condensed region and do not involve CO_2 or CO (French and Eugster, 1965). Calculated stability fields of siderite, bounded by reactions (3), (4), and (6), have been presented by Garrels (1960) for 298°K and by Holland (1959) for 300-600°K. Neither author considered possible reactions involving siderite and graphite.

In the present study, $\Delta G_f{}^\circ{}_T$ data for siderite were calculated from thermodynamic data (Kelley and Anderson, 1935). Values of ΔG_T° for each reaction were calculated using values for the oxides tabulated by Coughlin (1954) The calculated values of ΔG_T° are essentially linear functions of T from 298° to 1200°K (Table 1). Uncertainties in the values were calculated from the stated uncertainties of Coughlin (1954) for the oxide data, and a 1 percent uncertainty was assumed for the siderite data, the total uncertainty in ΔG_T° is thus only a minimum value.

Table 1

Calculated Thermodynamic Data for Siderite Decomposition Reactions

Reaction	ΔG_{298}° (cal)	ΔG_T° (cal)	$\log K_i$ (T)
(3) siderite + O_2 = hematite + CO_2 $2\,FeCO_3 + 1/2\,O_2 = Fe_2O_3 + 2\,CO_2$	-43,850 ± 4,500	-26,500 - 54 29 T	+6012/T + 11 87
(4) siderite + O_2 = magnetite + CO_2 $3\,FeCO_3 + 1/2\,O_2 = Fe_3O_4 + 3\,CO_2$	-42,870 ± 6,200	-13,900 - 96 44 T	+3039/T + 21 08
(5) siderite + O_2 = wüstite + CO_2 $0\ 947\,FeCO_3 + 0\ 026\,O_2 = Fe_{0\ 947}O + 3\,CO_2$	+4,490 ± 1,800	+16,300 - 39 6 T	-3564/T + 8 66
(6) siderite = iron + CO_2 + O_2 $FeCO_3 = Fe + CO_2 + 1/2\,O_2$	+66,780 ± 1,700	+84,600 - 59 65 T	-18,495/T + 13 04
(7) siderite = magnetite + graphite + O_2 $3\,FeCO_3 = Fe_3O_4 + 3\,C + 5/2\,O_2$	+239,910 ± 6,100	+268,300 - 91 69 T	-58,656/T + 20 05
(8) siderite = iron + graphite + O_2 $FeCO_3 = Fe + C + 3/2\,O_2$	+161,040 ± 1,600	+178,700 - 58 97 T	-39,068/T + 12 89

Values of $\Delta S°$ and $\Delta H°$ for each reaction (Table 1) were calculated from the free energy data, using the relations

$$\left(\frac{\partial \Delta G°}{\partial T}\right)_P = -\Delta S° \tag{9}$$

$$\left(\frac{\partial \frac{\Delta G°}{T}}{\partial \frac{1}{T}}\right)_P = \Delta H° \tag{10}$$

(Lewis et al., 1962, p 165). $\Delta S°$ and $\Delta H°$ for all reactions are virtually independent of T over the temperature range 298-1200°K

The equilibrium constants K(T) for each reaction were calculated from the relation

$$\Delta G_T° = -2\ 303\, RT \log K(T)$$

$$\log K(T) = \frac{-\Delta G°}{2\ 303\, RT} \tag{11}$$

and are given in Table 1

Values of equilibrium f_{O_2} as a function of T can then be calculated from the equilibrium constant for any specified total pressure. In those reactions in which CO_2 also participates, it is reasonable to assume that $P_F = P_{CO_2}$ for temperatures below 600°C and f_{O_2} values above those of the graphite buffer (French and Eugster, 1965). Values of f_{CO_2} were calculated for these reactions from the relation $f_i = \gamma_i P_i$, using fugacity coefficient data tabulated by Robie (1962). The results of such calculations for $P_F = 2000$ b are shown in Figure 1 with the curves for several specified oxygen buffer assemblages

The calculated stability field of siderite thus obtained is a narrow wedge bounded by reactions (3), (4), and (7), with stable decompositions to hematite, to magnetite, and (below the graphite buffer curve) to magnetite + graphite. In a CO_2 + CO atmosphere, the breakdown of siderite to iron (reaction 6) lies in the condensed area below the graphite buffer curve where CO_2 and CO do not exist (French and Eugster, 1965). This reaction is therefore metastable, and the siderite stability field is thus much smaller than those presented by Holland (1959) and Garrels (1960). The breakdown of siderite to wüstite is also metastable, in agreement with the calculations of Muan (1958) for 1 atm total pressure The stability field of siderite does not intersect that of fayalite (Fe_2SiO_4), the upper limit of which is bounded by the quartz + fayalite + magnetite (QFM) buffer curve (Figure 1). Reaction between siderite and quartz to produce fayalite is not stable at these pressures (French and Eugster, 1962, French, 1964a).

The system Fe-C-O contains three components, from the Phase Rule, F = 5 - P Reactions (3) and (4), in which two solid phases are in equilibrium with a gas phase, are therefore divariant

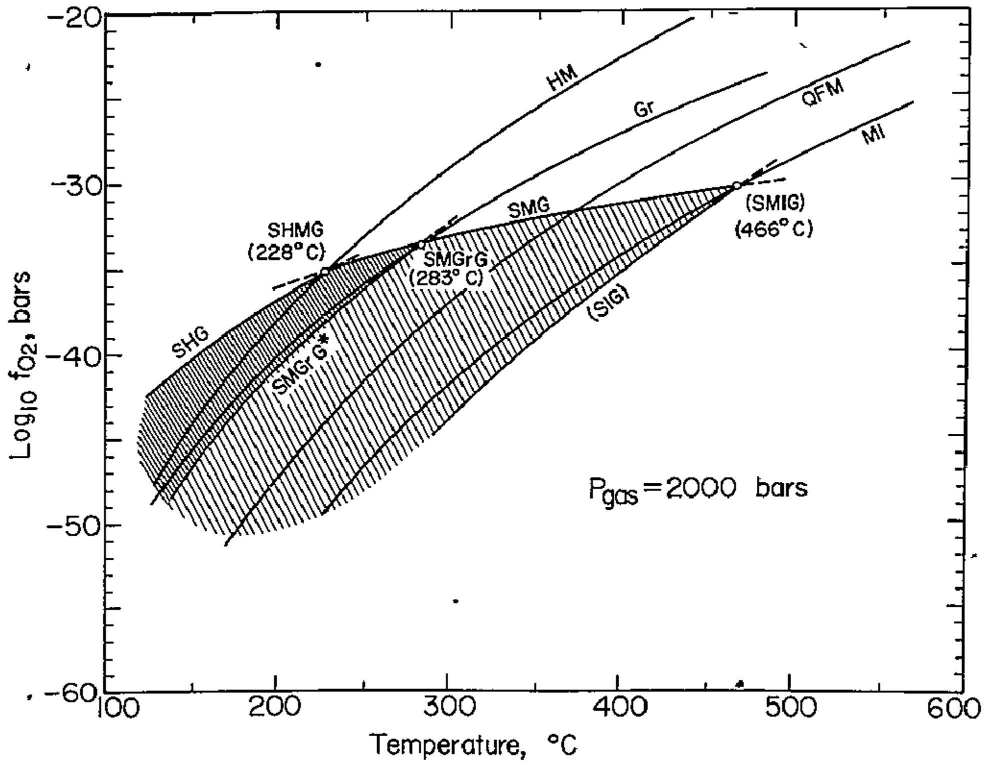


Figure 1—Isobaric section at P_F = 2000 bars, showing siderite stability relations calculated from thermodynamic data The stable field of siderite (narrow ruling) is bounded by decomposition reactions to hematite (SHG), magnetite (SMG), and magnetite + graphite (SMGrG*). The latter reaction lies entirely in the condensed region below the graphite buffer (Gr) Because of the reactions involving graphite, this field is much smaller than that calculated using reactions not involving graphite (Holland, 1959, Garrels, 1960) Other solid lines (HM, Gr, QFM, and MI) designate solid-phase oxygen buffers

reaction surfaces in P_F - f_{O_2} - T space Reaction (7), in which three solid phases and a gas coexist, is univariant and lies entirely within the region of the diagram where P_F = P_{O_2} (French and Eugster, 1965).

We may imagine addition of an inert ideal gas to the condensed region in such a manner that the value of P_F below the graphite buffer curve is always kept equal to the value of P_F = P_{CO_2} + P_{CO} above it Under these conditions, the region below the graphite buffer curve is a four-component system Fe-C-O-gas and the four-phase assemblage becomes a divariant surface in P_F - P_{O_2} - T space. The surface will have an orientation similar to that of other buffering assemblages (Eugster and Wones, 1962).

With this reservation, reaction (7) likewise becomes a divariant reaction surface in P_F - P_{O_2} -T space The three divariant surfaces of reactions (3), (4), and (7) intersect in two univariant curves The curve siderite + hematite + magnetite + gas (SHMG) is fixed by the intersection of reactions (3) and (4) with the hematite-magnetite (HM) buffer The curve siderite + magnetite + graphite + gas (SMGrG) is the mutual intersection of reactions (4) and (7) with the graphite buffer surface. This latter univariant curve is the only part of the surface of reaction (7) which is experimentally accessible. These univariant curves appear in Figure 1 as isobaric invariant points, SHMG at 228°C and SMGrG at 283°C.. (A third intersection, corresponding to a univariant curve for the equilibrium siderite + hematite + graphite + gas, is theoretically possible, but appears to be metastable under reasonable experimental conditions.)

In the system Fe-C-O, five phases must coexist at a true invariant point (four solids plus gas). The point siderite + magnetite + wüstite + iron + gas is apparently metastable, since it requires a minimum temperature of 560°C. It is uncertain if the equilibrium siderite + hematite + magnetite + graphite + gas is metastable or whether it is stable at temperatures too low to be meaningful or experimentally accessible.

These thermodynamic calculations are useful for delineating stability relations in advance of actual experimental work. However, because of the uncertainties inherent in the basic thermodynamic data, these calculated stability diagrams can be only approximations. The relative stability relations can generally serve to indicate closely the stability field determined experimentally, but great differences between calculated and experimentally determined equilibrium temperatures can be expected. The effect of such uncertainties is indicated in Figure 2, a plot of ΔG against T for reactions (3) and (4) at total pressures of 1 bar and 2 kb. Values of ΔG are calculated from the relation

$$\Delta G = \Delta G^\circ + 2.303\,RT\left(\underline{a}\log f_{CO_2} + \frac{1}{2}\log f_{O_2}\right) \qquad (12)$$

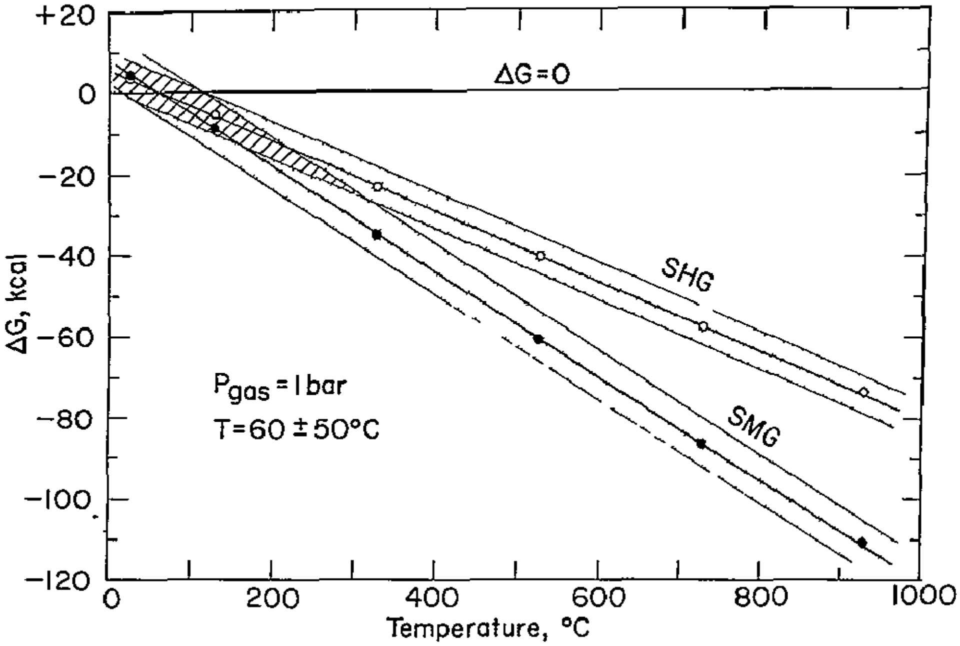
($\underline{a}$ is the coefficient of siderite in each reaction, $a = 2$ for reaction (3) and $a = 3$ for reaction (4)). Values of $\log f_{O_2}$ are those for the hematite-magnetite (HM) buffer. Ideally, the two curves for reactions (3) and (4) should intersect each other and the line $\Delta G = 0$ at the equilibrium temperature of the isobaric invariant point siderite + hematite + magnetite + gas. The estimated uncertainty in ΔG° is the sum of the uncertainties in $\Delta G_{f,T}^\circ$ for the individual phases, the values are ±4.5 kcal/mole for reaction (3) and ±6.0 kcal/mole for reaction (4). These uncertainties produce an uncertainty in the equilibrium temperature of ±50°C at $P_F = 1$ bar and ±90°C at $P_F = 2$ kb. Even these large uncertainties in equilibrium temperature are only minimum values.

EXPERIMENTAL METHOD

Introduction

In experimental studies at low pressure, control of f_{O_2} in a gas phase can be attained by using a gas mixture with a specified H_2O/H_2 or CO_2/CO ratio that corresponds to the desired value of f_{O_2}. This gas-mixing method is difficult to use at the high pressures characteristic of many dehydration and decarbonation reactions of geologic interest.

In high-pressure hydrothermal studies of oxidation-reduction reactions, control of f_{O_2} is therefore attained by surrounding the sample with an "oxygen buffer" consisting of one or more solid



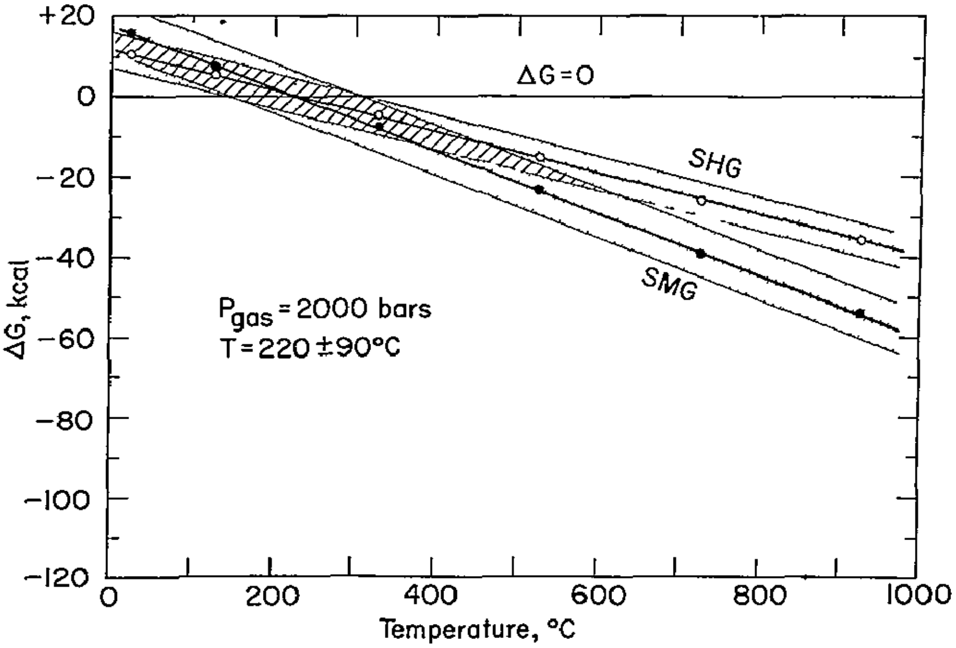


Figure 2—Plot of ΔG vs T for the reactions siderite = hematite + gas (SHG) and siderite = magnetite + gas (SMG) at total pressures of 1 bar and 2000 bars, at values of log f_{O_2} fixed by the hematite-magnetite buffer The calculated equilibrium temperature is defined by the intersection of the two curves with each other and with the ΔG = 0 line. Note that the uncertainties in ΔG (stippled areas) produce an area of uncertainty at the intersection (diamond-shaped ruled area) which corresponds to a large uncertainty in the equilibrium temperature Uncertainties are ±4 5 kcal for the SHG reaction and ±6 2 kcal for the SMG reaction (Table 1)

phases whose presence fixes the oxygen fugacity for any given temperature and total pressure (Eugster, 1957, 1959, French and Eugster, 1965). This technique has been successfully applied to hydrothermal studies of iron-bearing minerals whose stability is dependent on f_{O_2} iron-spinels and -chlorites (Turnock, 1960, Turnock and Eugster, 1962), iron-amphiboles (Ernst, 1960, 1961, 1962), and iron-biotites (Eugster and Wones, 1962, Wones and Eugster, 1965) In these studies, equilibrium in the gas phase was attained by diffusion of hydrogen through sealed platinum capsules which contain a sample surrounded by the buffer The attainment of such equilibrium was demonstrated by the consistence and reversibility of the reactions studied (Eugster and Wones, 1962, Turnock and Eugster, 1962).

The buffering principle is quite general and the techniques can be applied to any system involving solid-gas equilibria. Similar buffers have already been developed for use in CO_2 atmospheres (French and Eugster, 1965) and buffers controlling CH_4 and F have been used experimentally (Eugster and Skippen, 1968)..

The present method for studying the stability of siderite is based on the use of a $CO_2 + CO$ atmosphere, combined with solid polyphase oxygen buffers to control the value of f_{O_2} (French and Eugster, 1965, Huebner, 1969). Independent control of the two volatiles CO_2 and O_2 is thus possible, since, for a given $P_F = P_{CO_2} + P_{CO}$, the values of f_{CO_2}, f_{CO}, and f_{O_2} for any given temperature can be calculated (French, 1964a, French and Eugster, 1965). For the range of temperature and f_{O_2} values investigated in the present study, P_{CO_2} is virtually equal to P_F (French, 1964a).

In this study, values of f_{O_2} specified by the hematite-magnetite (HM) buffer are those calculated by Eugster and Wones (1962, p. 90), according to the equation

$$\log f_{O_2} = -24,912/T + 14.41 + 0.019(P_t - 1)/T \qquad (13)$$

A slightly different equation, obtained more recently for the hematite-magnetite buffer for temperatures above 750°C (Haas, 1968) produces no significant changes in f_{O_2} values calculated for the present experiments. Data for the graphite buffer have been calculated previously (French and Eugster, 1965). For values of $P_F \geq 500$ bars, the following approximation is satisfactory

$$\log f_{O_2} = -20,586/T - 0.044 + \log P_F + 0.028(P_t - 1)/T \qquad (14)$$

Experimental Procedure

The powdered samples, generally siderite, were contained in a small (3 mm O.D.) silver tube (Figure 3), this inner tube was surrounded by a buffer mixture contained in a larger silver tube (4.5 mm O.D) The ends of both tubes were crimped but not sealed. During a run, CO_2 from the surrounding atmosphere diffused through the oxygen buffer, the CO_2/CO ratio of the gas was thereby adjusted to the equilibrium f_{O_2} specified by the buffer and the run temperature.

Runs were made in Tuttle-type cold-seal "test-tube" type bombs (Tuttle, 1948, 1949) made of Haynes Stellite 25 alloy The bombs were externally heated in horizontal furnaces. Liquid CO_2

under pressure was supplied to the bomb from a commercial siphon-equipped tank by a modified Sprague pump operated by compressed air. A maximum CO_2 pressure of about 30,000 psi can be produced by the pump, operating on 80-100 psi of compressed air. During the early parts of this study, pressure was measured with several gauges calibrated against a 14-inch Heise gauge. Later, these were replaced by a self-calibrating Foxboro gauge. Recorded pressures are believed accurate to ±5 percent.

Temperatures were measured by chromel-alumel thermocouples (Figure 3), using a Leeds and Northrop potentiometer. Each furnace-bomb combination was calibrated with National Bureau of Standards samples of tin (M.P. 231.9°C) and zinc (M.P. 419.5°C), consisting of metal filings vacuum-sealed in 5.5 mm O.D. Pyrex tubes. The calibration runs indicate that the temperature error is less than ±3°C, variation in run temperature during a two-week run generally did not exceed ±4°C. The maximum temperature uncertainty is thus ±7°C, and the run temperatures are believed accurate to ±5°C.

Analytical grade Fe_3O_4 and Fe_2O_3 were used for buffers. Graphite was prepared by grinding spectrograph electrodes. The siderite used as samples was synthesized as needed (see below, p. 13) and used soon after synthesis to avoid possible oxidation during long storage at room temperature.

At the end of a run, the bomb was isolated from the line and quenched in water. Pressure and temperature fell together during the quench period of a few minutes. Since runs of about two weeks duration were required to produce detectable reaction in the charge, it is believed that no significant reaction occurred during the heating and cooling periods.

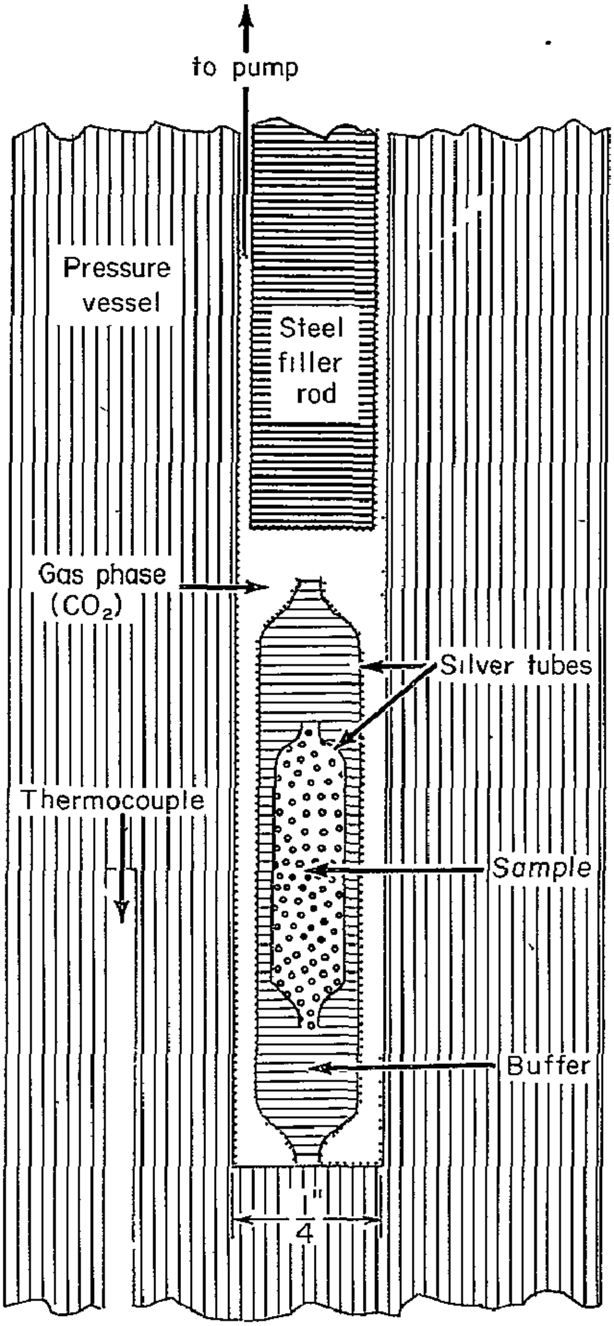


Figure 3—Cutaway sketch of run assembly. In most runs, the sample (large dotted area) was synthetic siderite, and the buffer (horizontal ruled area) was a mixture of either hematite + magnetite or of magnetite + graphite. Buffering of the sample is established by diffusion of the gas phase (stippled area) though the buffer.

In the majority of runs, the samples consisted of synthetic siderite, while the buffers were either mixtures of hematite and magnetite (HM) or of magnetite and graphite (MGr). In the latter case, the magnetite is not part of the buffer assemblage, because buffering is produced by the graphite alone (French and Eugster, 1965), but this arrangement allowed reversibility of the reaction to be demonstrated in a single run. If the run temperature was above the stability field of siderite, the siderite sample decomposed to the oxides (Plate 1B) while the buffer remained unchanged. Within the stability field of siderite, the sample remained unchanged while siderite formed from the oxides in the buffer. The addition of magnetite to the graphite buffer allowed this reverse reaction to be detected.

Because the sample is surrounded during the run by potential reaction products in the buffer, care was taken to avoid contamination. After the run, the sample tube was carefully extracted and cleaned; the ends of the sample tube were clipped and discarded. A sample of the buffer adjacent to the sample tube was examined separately from the remainder of the buffer.

Sample and buffer were examined under a binocular microscope, then studied by X-ray diffraction and oil immersion methods. In many of the runs, particularly those with the HM buffer, the amount of reaction was slight. Reaction of less than 5 percent could not be detected by X-ray diffraction. Sample decomposition in small amounts could be detected under the binocular microscope by the red or gray-black color produced by the iron oxides and by the magnetism of the sample. Under the petrographic microscope, small amounts of sample breakdown was indicated by the presence of strongly magnetic grains or of larger grains of siderite showing discoloration or opaque inclusions (Plate 1B). Buffer decomposition (growth of siderite) was indicated by the formation of white areas in the buffer and could be verified under the petrographic microscope by the presence of birefringent siderite in the otherwise opaque buffer materials. As little as 0.5 percent siderite in the buffer could be detected and identified by the high birefringence and by the "twinkle" caused by the great change in relief on rotation of the microscope stage.

SYNTHESIS OF SIDERITE

Experimental Methods

Synthetic siderite was used as the starting material in this study. Natural siderites were considered undesirable because of the common partial oxidation of the material and because of the amounts of other divalent cations generally present in solid solution.

Several investigators have previously synthesized siderite by combining compounds containing Fe^{2+} and CO_3^{2-} in solution, generally under high CO_2 pressure to prevent dissociation (Palache et al., 1944; Sharp, 1960; Graf, 1961; Powell, 1965; Johannes, 1968, 1969). Commonly used compounds are $FeCl_2$, $FeSO_4$, $CaCO_3$, and $NaHCO_3$. A second method of synthesis involving decomposition of ferrous oxalate dihydrate ($FeC_2O_4 \cdot 2H_2O$) has been independently developed by several workers (Rosenberg, 1960; French, 1964a; Weidner, 1968) after siderite was reported as an unexpected product of mixes containing ferrous oxalate (Turnock, 1960).

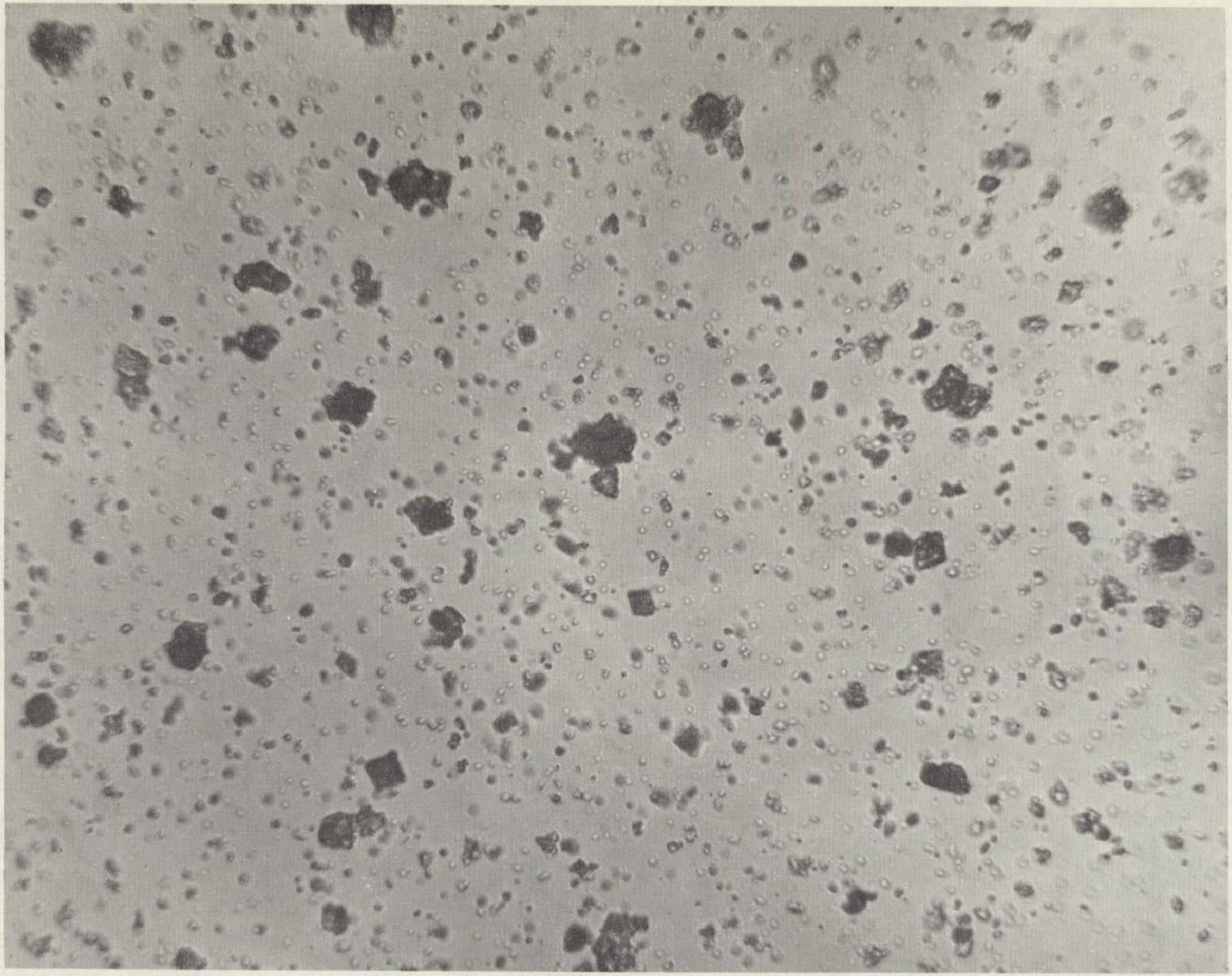


Plate 1A—Synthetic siderite formed by decomposition of ferrous oxalate dihydrate in a sealed silver tube (P_{H_2O} = 2000 bars; 374°C; 164 hrs). Plane polarized light; largest grains are about 10μm across. Many crystals are well-formed rhombohedra and show no trace of oxides.

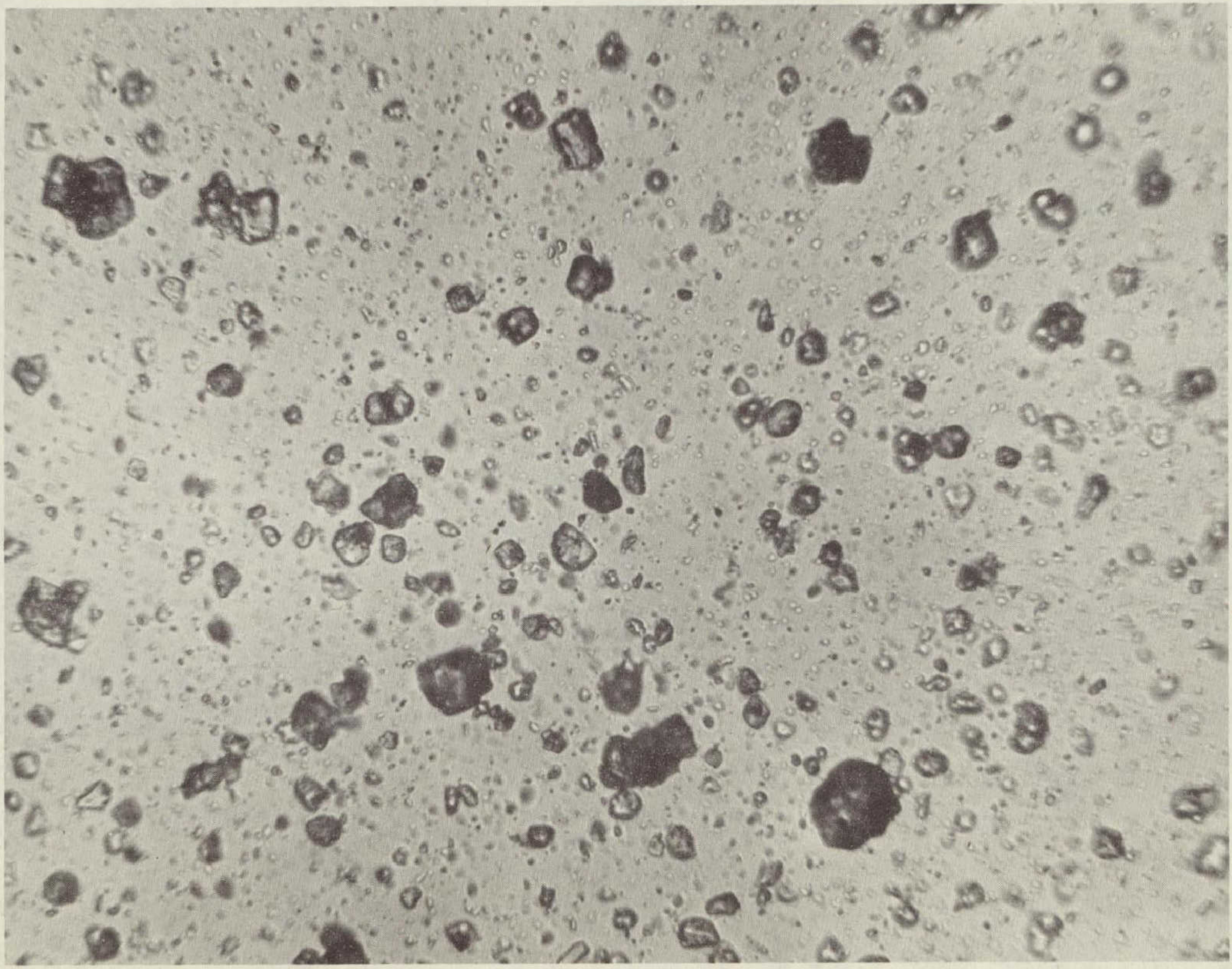


Plate 1B—Recrystallization and partial decomposition of siderite to hematite and magnetite above the equilibrium temperature (Run 125; P_F = 1000 bars; 418°C; HM buffer; log f_{O_2} = -21.5; 291 hrs). Plane polarized light; largest grains are 20–30 μm across. The siderite has recrystallized to larger grains, but numerous grains (e.g., upper and lower right) show incipient decomposition to opaques, a red color, and definite magnetism.

The siderite used in this study was synthesized by decomposition of ferrous oxalate dihydrate. In the synthesis runs, from 100 to 400 mg of reagent $FeC_2O_4 \cdot 2H_2O$ was placed in a 4.5-mm O.D. silver tube from 2 to 8 cm long. The tube was welded shut, placed in a Tuttle cold-seal bomb, and heated to between 350° and 380°C under 2 kb water pressure. Reaction times ranged between 6 and 452 hours and were generally between 40 and 115 hours. Neither reaction time nor temperature was particularly critical to the reaction, and complete conversion of the oxalate to siderite was observed in virtually all runs. In shorter runs near 350°C some unconverted oxalate occasionally remained, and in runs near 400°C the siderite was accompanied by small amounts of magnetite. The siderite used in the stability runs was entirely pure and was generally produced at about 380°C in runs of 90-120 hours duration.

The siderite produced was a gray-white crystalline powder which gradually assumed a light buff or brownish color on drying at room temperature. The material was identified as siderite by both optical and X-ray methods. The individual siderite grains are colorless to pale yellow, ranging in size from less than 1 μm to 10 μm (Plate 1A); many of the large crystals are well-developed rhombohedra. This material, which showed no traces of oxides or other impurities, was used as starting material for the stability runs. The value of n_o, determined on six samples, was 1.875 ± 0.005, in good agreement with other determinations (Winchell and Winchell, 1951; Rosenberg, 1960).

Samples of the ferrous oxalate dihydrate and synthetic siderite were analyzed through the kindness of Dr. B. F. Jones and Miss S. Rettig of the U. S. Geological Survey. The partial analyses are (in weight percent):

	Oxalate	Synthetic Siderite (S-31)	Ideal Siderite
Fe	31.25	47.5	48.2
Mn	0.00	0.05	
Na	<0.1	<0.1	
K	<0.1	<0.1	
Ca	—	0.0	
Mg	0.00	0.0	
C_2O_4	47.2	—	
Total	78.45	47.6	

These analyses show that divalent cations other than iron are not present in significant amounts in either the oxalate or the synthetic siderite.

Measurements of the d-spacings of the strong siderite (104) reflection indicated no perceptible difference in the cell dimensions between several synthetic siderites or between three siderites used in stability runs at varying temperatures and f_{O_2} values Measurements were made on an X-ray diffractometer using a CdF_2 internal standard (Haendler and Bernard, 1951, Harker and Tuttle, 1955a, 1955b, Rosenberg, 1960). Measurement of the $2\theta_{104}$ value can be made to ±0.02°. The values of d_{104} thus determined are consistent to ±0.001 A and are believed accurate to this value

It was found necessary to redetermine the value of the (111) reflection of CdF_2 used as a standard for measurements of $2\theta_{104}$ The original determination by film methods of the CdF_2 cell parameters (Haendler and Bernard, 1951) gave $a_o = 5.3880 \pm 0.0005$ A., $d_{111} = 3.103$ A ($2\theta_{111} = 28.770°$ for Cu K_α radiation). The original A.S.T.M card based on this data (5-0567) gives $d_{111} = 3.1051$ A ($2\theta_{111} = 28.750°$). Using a standard of Lake Taxaway, N. C. quartz, for which $2\theta_{211} = 26.664°$ (Lipson and Wilson, 1941, Swanson et al , 1954), a value of $2\theta_{111}$ for CdF_2 was determined as 28.701 ± 0.005° This value, which is used in the present study, is in good-agreement with a similar determination by Rosenberg (1960), in which a value of $2\theta_{111} = 28.699 \pm 0.005°$ was determined. Using additional CdF_2 reflections, a new value of $a_o = 5.3872 \pm 0.0009$ A was obtained This new value agrees, within the uncertainties, with the original value of 5.3880 ± 0.0005 (Haendler and Bernard, 1951), but the differences in the two values of $2\theta_{111}$ are greater than the error of measurement Accordingly, the value of $2\theta_{111} = 28.701°$ was used as a standard for measurement of the values of d_{104} of the synthetic siderite

The average value of d_{104} determined from four synthetic siderites is 2.7919 A, in excellent agreement with previously calculated (2.7912, Graf, 1961) and measured (2.789, Sharp, 1960) values. A similar constancy was observed in d_{104} of three synthetic siderites exposed to various temperatures and f_{O_2} values during stability runs (see Tables 2 and 3) 2.7897 A (Run 29, HM buffer, 230°C, $\log f_{O_2} = -34.8$), 2.7913 A (Run 52, HM buffer, 318°C, $\log f_{O_2} = -27.5$), 2.7908 (Run 46, MGr buffer, 493°C, $\log f_{O_2} = -23.4$). The latter sample was about 20 percent decomposed to magnetite. The average value for the three runs, 2.7906 A, is not significantly different from that of the synthetic siderites.

Similar agreement was found for d-spacings of other reflections of the synthetic siderites (French, 1964a), irrespective of whether they had been used in stability runs The data indicate that neither variations in synthesis conditions nor changes in temperature and f_{O_2} during later experimental studies have any effect on siderite cell size. The X-ray data further provide no evidence for any significant amount of Fe^{3+} in siderite as a function of f_{O_2}.

Production of Organic Compounds During Siderite Synthesis

A sharp, fetid odor, suggestive of organic compounds, was observed during the siderite synthesis runs. The odor often appeared upon opening the bombs, even before the sealed capsules containing the siderite were opened The capsules themselves were puffed, contained considerable positive pressure at room conditions, and produced a similar "organic" odor when opened A brief study of the gas phase coexisting with siderite during synthesis was undertaken to see what, if any, organic compounds might be forming during the process of siderite synthesis.

The decomposition of ferrous oxalate dihydrate to siderite may be written

$$FeC_2O_4 \quad 2\,H_2O = FeCO_3 + CO + 2\,H_2O \qquad (15)$$

In a gas phase consisting initially of H_2O and CO, equilibria will be established between the various gas species H_2O, H_2, CO_2, CO, CH_4, and O_2 (French and Eugster, 1965, French, 1966) The successful production of siderite indicates that $f_{O_2} \leq 10^{-25}$ bars (French, 1965, French and Eugster, 1965) and, if equilibrium is established with the ambient f_{O_2} of the hydrothermal bomb (approximately that of the Ni-NiO buffer), $f_{O_2} \sim 10^{-30}$ bars (Eugster and Wones, 1962, p. 95).

Under such reduced f_{O_2}, it is likely that CH_4 will be a significant component of the gas phase, together with other reduced species (French, 1966). Furthermore, an atmosphere in which $H_2O/CO = 2$ might be expected to generate additional organic species through inorganic equilibrium reactions (Dayhoff et al., 1964)

Accordingly, a brief search was made for methane and other organic species in the gas phase coexisting with siderite during synthesis Dr. T. C Hoering, of the Carnegie Institution of Washington Geophysical Laboratory, kindly analyzed a portion of the vapor from a siderite synthesis run with a mass spectrometer The sealed tube was opened in the spectrometer system. Surprisingly, the vapor consisted almost entirely of water and complex oxygenated hydrocarbons; methane and CO_2 were not present in more than trace amounts. A cursory analysis of the complex mass-spectrometer patterns suggested the presence of propionic acid (CH_3CH_2COOH) and ethyl alcohol (CH_3CH_2OH), possibly present in addition were butyric acid ($CH_3CH_2CH_2COOH$), acetic acid (CH_3COOH), and ketones. These organic compounds are undoubtedly responsible for the distinctive odor accompanying siderite synthesis.

The apparent synthesis of complex organic compounds in a gas phase in equilibrium with siderite has significant implications for such problems as the nature and evolution of planetary atmospheres and the prebiological formation of organic materials in meteorites and on the primitive earth. Numerous investigators have shown that a wide variety of organic compounds, including amino acids, can be produced inorganically by the action of diverse energy sources on low-pressure mixtures of simple gases such as CH_4, NH_3, H_2O, CO_2, CO, etc. (Miller, 1955, 1957, Miller and Urey, 1959, Oro, 1965, Abelson, 1966, Ponnamperuma and Gabel, 1970). Reactions of this nature are considered to have been necessary for producing, from chemically simple primordial atmospheres, the critical organic compounds necessary for the development of life.

The related problem of whether the organic compounds in meteorites have originated through biological activity or from abiotic synthesis has been strongly debated (see, e.g., Urey, 1966, Urey and Lewis, 1966; Studier et al , 1965). There is, however, considerable theoretical and experimental evidence to indicate that such compounds may form abiotically through near-equilibrium reactions between simple components such as H_2O, CO_2, H_2, CH_4, etc., in either a primordial solar nebula or a primitive planetary atmosphere (Dayhoff et al., 1964, Eck et al , 1966, Studier et al , 1968, Hayatsu et al , 1968). Formation of organic compounds under these conditions takes place by Fischer-Tropsch reactions (Oro, 1965, Studier et al , 1968) in which catalysis by iron-bearing phases such as Fe or Fe_3O_4 has a definite promoting effect (Storch et al , 1951, p 1-35, 222-308, Anderson, 1956).

The production of significant amounts of organic compounds in a high-pressure gas phase in equilibrium with siderite supports the conclusion that organic compounds can be produced abiotically by Fischer-Tropsch reactions The results further suggest that such syntheses can occur at high total gas pressure corresponding to moderate depths in a planetary crust where the existence of CH_4-rich phases may be favored by low f_{O_2} values controlled by equilibrium with graphite and other minerals (French, 1966) Siderite, in particular, may promote such synthesis catalytically, as the high-pressure production of hydrocarbons from reaction of H_2 with carbonate minerals strongly suggests (Giardini and Salotti, 1969)

These brief results suggest that organic compounds may form abiotically by reaction between a high-pressure gas phase and siderite, other carbonates, or other iron-bearing minerals On a planetary body, such suitable conditions might be attained by hydrothermal activity at moderate depths within the crust The organic compounds produced at depth could then be emitted to the surface, providing material for further biological development even in cases where such synthetic reactions were not possible in the planetary atmospheres or oceans themselves

EXPERIMENTAL RESULTS

The Equilibrium Siderite + Hematite + Magnetite + Gas (SHMG)

The univariant equilibrium siderite + hematite + magnetite + gas (SHMG) is the intersection of three divariant surfaces in P_F - f_{O_2} - T space, the surface, siderite + hematite + gas (SHG), the surface, siderite + magnetite + gas (SMG); and the degenerate buffer surface, hematite + magnetite + gas (HM) The location of the SHMG curve was determined at 500 and 1000 b P_F by reversing reactions in samples of siderite surrounded by hematite-magnetite buffers (Table 2, Figure 4) The values obtained are

P_F	T(±10°C)	$-\log f_{O_2}$ (±0 8)
500	363	24 7
1000	365	24 6

The greatest difficulty in determining equilibrium temperatures along the hematite-magnetite buffer was caused by the slight amount of reaction in both directions, under 5 percent. Determination of phases was necessarily made by optical study and by the detection of color changes and magnetism in the sample

Limits on the equilibrium temperature of the isobaric invariant point SHMG at 500 bars are fixed by Runs 108 (354°C) and 93 (372°C) An equilibrium temperature of 363 ± 10°C is estimated

Table 2

Experimental Data for Determination of the Equilibrium
Siderite + Hematite + Magnetite + Gas (SHMG) Along the Hematite-Magnetite Buffer

Run No.	Sample	T°C	$-\log f_{O_2}$ (bars)	Time (hrs.)	Products	
					Sample	Buffer
$P_F = P_{CO_2} + P_{CO} = 2000$ bars						
25	S	203	37.5	185	S	H + M + S
29	S	230	34.8	328	S	H + M + S
33	S	249	33.0	501	S	H + M + S
30	S	270	31.2	329	S	H + M
34	S	274	30.8	506	S	H + M + S
42	S	276	30.7	473	S + H + M	H + M + S
38	S	283	30.1	354	S + H + M	H + M + (S)
43	S	289	29.6	473	S	H + M
54	S	290	29.5	710	S + H + M	H + M + (S)
39	S	291	29.5	355	S	H + M
53	S	292	29.4	432	S	H + M
18	S	301	28.8	91	S + H + m	H + M + (S)
26	S	302	28.7	185	S + H + M	H + M
131	S	302	28.7	335	S + H + m	H + M + (S*)
52	S	318	27.5	415	S	H + M + (S)
55	S	320	27.4	710	S + H + M	H + M
132	HM	254	32.6	335	H + M + (S)	H + M + (S)
133	HM	306	28.4	331	H + M + (S)	H + M
$P_F = P_{CO_2} + P_{CO} = 1000$ bars						
44	S	241	33.9	238	S	H + M + S
45	S	280	30.5	190	S	H + M + S
58	S	294	29.4	356	S	H + M + S
70	S	303	28.6	356	S	H + M + S
71	S	325	27.1	356	S	H + M + (S)
79	S	348	25.6	567	S	H + M + S
49	S	360	24.8	531	S	H + M + S
120	S	360	24.8	372	S + h + M	H + M + S
65	S	370	24.2	373	S + H + M	H + M + (S)
124	S	380	23.6	385	S + h + (M)	H + M + (S)
121	S	389	23.1	371	S + H + M	H + M + (S)
59	S	400	22.5	356	S + h + M	H + M + (S)
125	S	418	21.5	291	S + H + M	H + M + (S*)
126	HM	349	25.5	387	H + M + (S)	H + M + (S)
127	HM	410	>22.0	289	M	M
$P_F = P_{CO_2} + P_{CO} = 500$ bars						
66	S	297	29.3	453	S + (M)	H + M + S
73	S	342	26.1	356	S	H + M
108	S	354	25.3	369	S	H + M + S
93	S	372	24.2	373	S + H + M	H + M + S
109	S	379	23.8	369	S + h + M	H + M + S
115	S	390	23.1	329	S + H + M	H + M
105	S	404	22.4	257	S + H + M	H + M + (S)
99	S	419	21.5	330	S + H + M	M
116	HM	365	24.6	327	H + M + (S)	H + M + (S)
117	HM	407	22.2	325	H + M	H + M + (S)

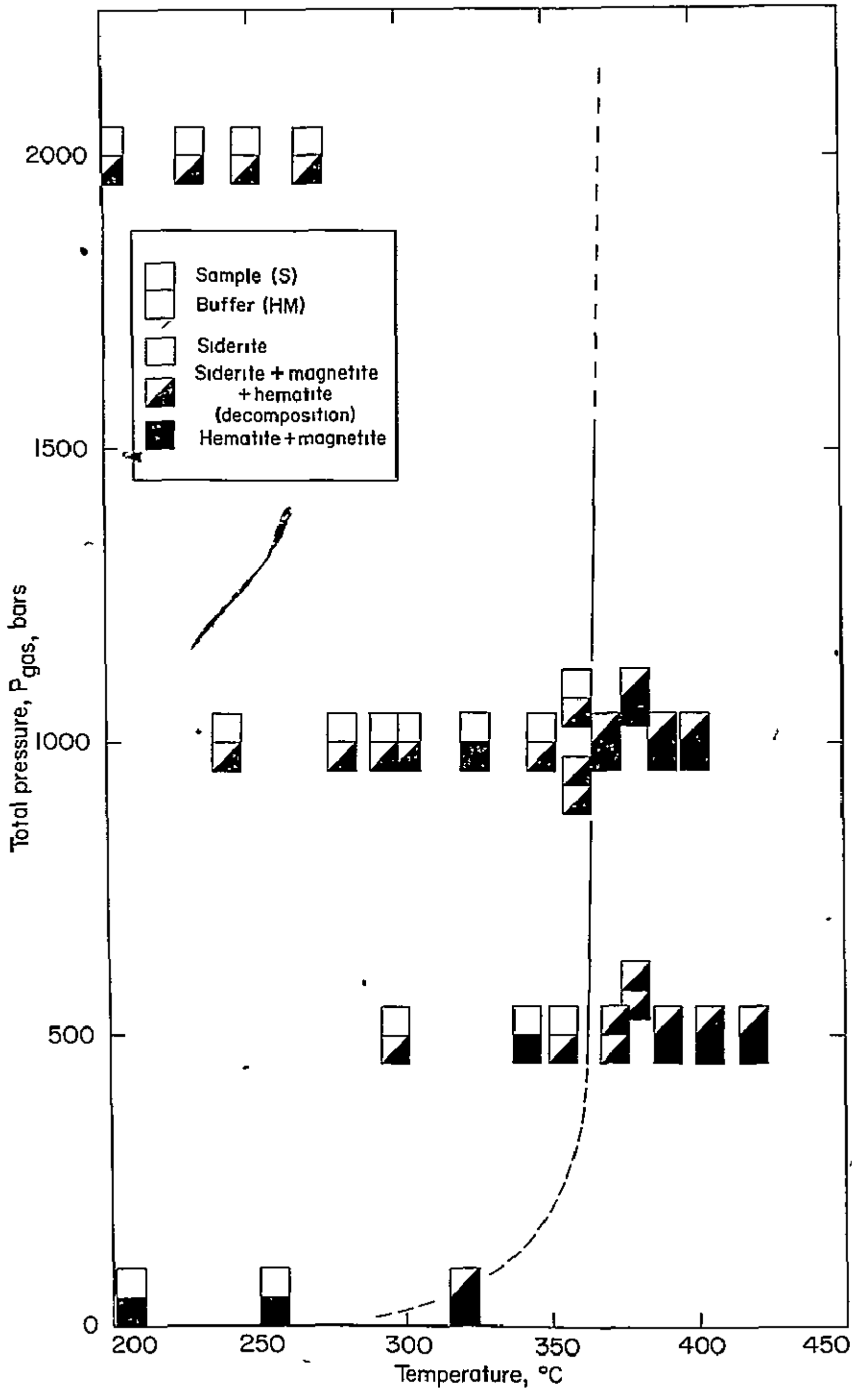


Figure 4—Plot of $P_F = P_{CO_2} + P_{CO}$ against T, showing location of the experimentally determined univariant curve siderite + hematite + magnetite + gas (SHMG). Dashed portions of the curve are extrapolated from runs made at 500 and 1000 bars. In each run symbol, upper box denotes behavior of the siderite sample, lower box denotes behavior of the buffer. Displacement of some run symbols vertically is for visibility only and does not indicate differences in run pressure. Runs near zero pressure were made at 30 psi CO_2 pressure and do not locate a definite decomposition temperature.

on the basis of these two runs The equilibrium temperature at P_F = 1000 bars is bracketed by Runs 49 (360°C) and 65 (370°C), the estimated equilibrium temperature is 365 ± 10°C, indicating that the SHMG curve is virtually vertical between 500 and 1000 bars.

The equilibrium temperature for the SHMG curve at P_F = 2000 bars was not definitely determined Definite decomposition of the HM buffer to siderite was identified at temperatures below 280°C (Table 2), but decomposition of siderite above this temperature could not be clearly established Reactions were extremely sluggish at 2000 bars, several runs held for five weeks at about 300°C showed no detectable change in either direction In several runs about 375°C, the HM buffer was completely reduced to magnetite during the experiment, while the siderite sample showed slight, but not significant, decomposition

The reason for the anomalous behavior of the runs at 2000 bars is not definitely known The combination of relatively low reaction rates with high pressures may retard reaction by inhibiting diffusion of gaseous reactants and products through the solid sample and buffer. Such a kinetic explanation for the lack of reaction at 2000 bars is favored by the observed greater degree of reaction in both direction at lower pressures. Decomposition of the HM buffer to siderite appeared particularly favored by lower total pressures.

Small amounts of siderite, estimated generally at about 0.1 percent, were observed rarely in runs made above the equilibrium temperatures at 500 and 1000 bars, in which the siderite samples themselves showed definite decomposition The small amounts of siderite in the buffers in these runs are not considered to represent stable formation of siderite at the run temperature Such siderite could have formed (1) during run-up of the bomb at temperatures within the stability field of siderite; (2) by contamination of the buffer by mechanical leakage of siderite from the sample In these runs, decomposition of the siderite sample was regarded as the true indicator of reaction direction

Siderite may, however, also develop metastably in the buffer Since buffering results from diffusion of the fluid phase through the buffer, the portion of the buffer at the extreme ends of the tube will be exposed to the f_{O_2} of the bomb, which lies below that of the hematite-magnetite buffer (Eugster and Wones, 1962). At such lower f_{O_2} values, siderite is stable at higher temperatures (Figure 1) and could thus form in the buffer at temperatures above the true equilibrium temperature of the SHMG reaction In all the experiments, however, nothing was observed to suggest that such formation of siderite did occur. No color boundary was observed in the buffer, nor was there any apparent concentration of siderite at the ends of the sample tube.

Such metastable formation of siderite is illustrated by Run 125 (P_F = 1000 bars, T = 418°C). In this run, the siderite sample recrystallized into larger single crystals 5 μm to 20 μm in size (Plate 1B), similar crystals of siderite are scattered through the buffer. Definite decomposition of the sample was indicated by a general red color and by the definite magnetism of the sample (Plate 1B).

The Equilibrium Siderite + Magnetite + Graphite + Gas (SMGrG)

The univariant equilibrium siderite + magnetite + graphite + gas (SMGrG) is defined by the intersection of three divariant surfaces: siderite + magnetite + gas (SMG), graphite + gas (the graphite buffer curve), and siderite + magnetite + graphite + O_2 (SMGrG*). The latter surface lies entirely within the condensed region below the graphite buffer (French and Eugster, 1965) and is only accessible at the univariant curve. Location of the univariant SMGrG curve was determined by the same method, samples of siderite were surrounded by a magnetite + graphite mixture, allowing reaction in both directions in a single run (Table 3; Figure 5).

Data obtained for the SMGrG curve are

P_F (bars)	T(±10°C)	$-\log f_{O_2}$ (±0 8)
500	455	25.8
1000	458	25 2
2000	465	24.4

Minor amounts of siderite decomposition were observed in all runs, even those in which significant amounts of siderite formed in the buffer. This decomposition, which did not exceed 5 percent, produced a dark gray color and definite magnetism in the sample. The amount of such decomposition appeared relatively constant with temperature and may have been produced by incomplete buffering during the early part of the run.

The direction of reaction in any run was determined from (1) the absence of siderite in the buffer; (2) a sudden sharp increase in the amount of sample decomposition as the run temperatures were increased. An approximate indicator of siderite instability was the appearance of magnetite peaks in the X-ray pattern of the sample. Above the equilibrium temperatures, the amount of sample decomposition increases rapidly (Table 3, Figure 6). Below the equilibrium temperatures buffer decompositions of 2-10 percent were observed. With one unexplained exception (Run 85), not even trace amounts of siderite were observed in the buffer above the equilibrium temperature.

At P_F = 500 bars, Run 89 (448°C) shows very slight sample decomposition combined with definite development of siderite in the buffer. By contrast, Run 100 (464°C) exhibits no siderite in the buffer, while the siderite sample was almost entirely decomposed. The equilibrium temperature lies between these runs, and the almost complete sample decomposition in Run 100 suggests that it lies closer to the lower temperature. The equilibrium temperature estimated at P_F = 500 bars is 455 ± 10°C.

The same criteria indicate that the equilibrium temperature at P_F = 1000 bars is bracketed by Runs 130 (452°C) and 122 (466°C), the estimated value is 458° ± 10°C.

At P_F = 2000 bars, the equilibrium temperature lies between Runs 92 (462°C) and 76 (469°C) and is estimated as 465 ± 10°C. Above this temperature, siderite samples were increasingly decomposed, no siderite remained in a sample run at 537°C.

Table 3

Experimental Data for Determination of the Equilibrium
Siderite + Magnetite + Graphite + Gas (SMGrG) Along the Graphite Buffer

Run No	Sample	T°C	$-\log f_{O_2}$ (bars)	Time (hrs.)	Products		
					Sample	Percent Decomposition	Buffer
$P_F = P_{CO_2} + P_{CO} = 2000$ bars							
68	S	197	41.0	429	S + M + g	2-5	M + G + S
62	S	304	32.1	353	S + M + g	5	M + G + S
63	S	348	29.6	353	S + M + g	2-4	M + G + (S)
56	S	402	27.1	355	S + M + g	2-5	M + G + S
40	S	422	26.2	263	S + M + g	5	M + G + S
41	S	441	25.4	263	S + M + g	2	M + G + S
81	S	451	25.0	371	S + M + g	2-5	M + G + S
92	S	462	24.6	407	S + M + g	2-5	M + G + S
76	S	469	24.2	355	S + M + g	10-20	M + G
57	S	470	24.2	356	S + M + g	40-60	M + G
51	S	478	23.9	478	S + M + g	90-95	M + G
46	S	493	23.4	338	S + M + g	50	M + G
77	S	537	21.9	355	M + g	100	M + G
47	S	606	19.9	331	M + G	100	M + G
$P_F = P_{CO_2} + P_{CO} = 1000$ bars							
69	S	196	41.9	426	S + M + g	3	M + G + S
61	S	298	33.0	375	S + M + g	5	M + G + S
123	S	421	26.7	372	S + M + g	2-5	M + G + S
60	S	446	25.7	356	S + M + g	5	M + G + S
130	S	452	25.5	385	S + M + g	2	M + G + S
122	S	466	24.9	372	S + M + g	30-40	M + G
87	S	479	24.4	326	S + M + g	70-80	M + G + (S)
80	S	515	23.2	475	M + G	100	M + G
128	MG	419	26.8	385	M + G + (S)	0.5	M + G + (S)
129	MG	491	24.0	385	M + G	0	M + G
$P_F = P_{CO_2} + P_{CO} = 500$ bars							
67	S	398	28.2	453	S + M + g	5	M + G + S
89	S	448	26.0	406	S + M + g	1	M + G + S
100	S	464	25.4	326	M + S + G	90	M + G
94	S	475	25.0	308	M + S + G	80	M + G
101	S	485	24.6	326	M + (S) + g	98	M + G
85	S	498	24.1	302	M + S + g	80-90	M + G + (S*)
95	S	525	23.2	307	M + g	100	M + G
90	S	548	22.5	405	M + g	100	M + G
118	MG	439	26.4	325	M + G + (S)	0.5-1	M + G + S
119	MG	470	25.2	325	M + G	0	M + G

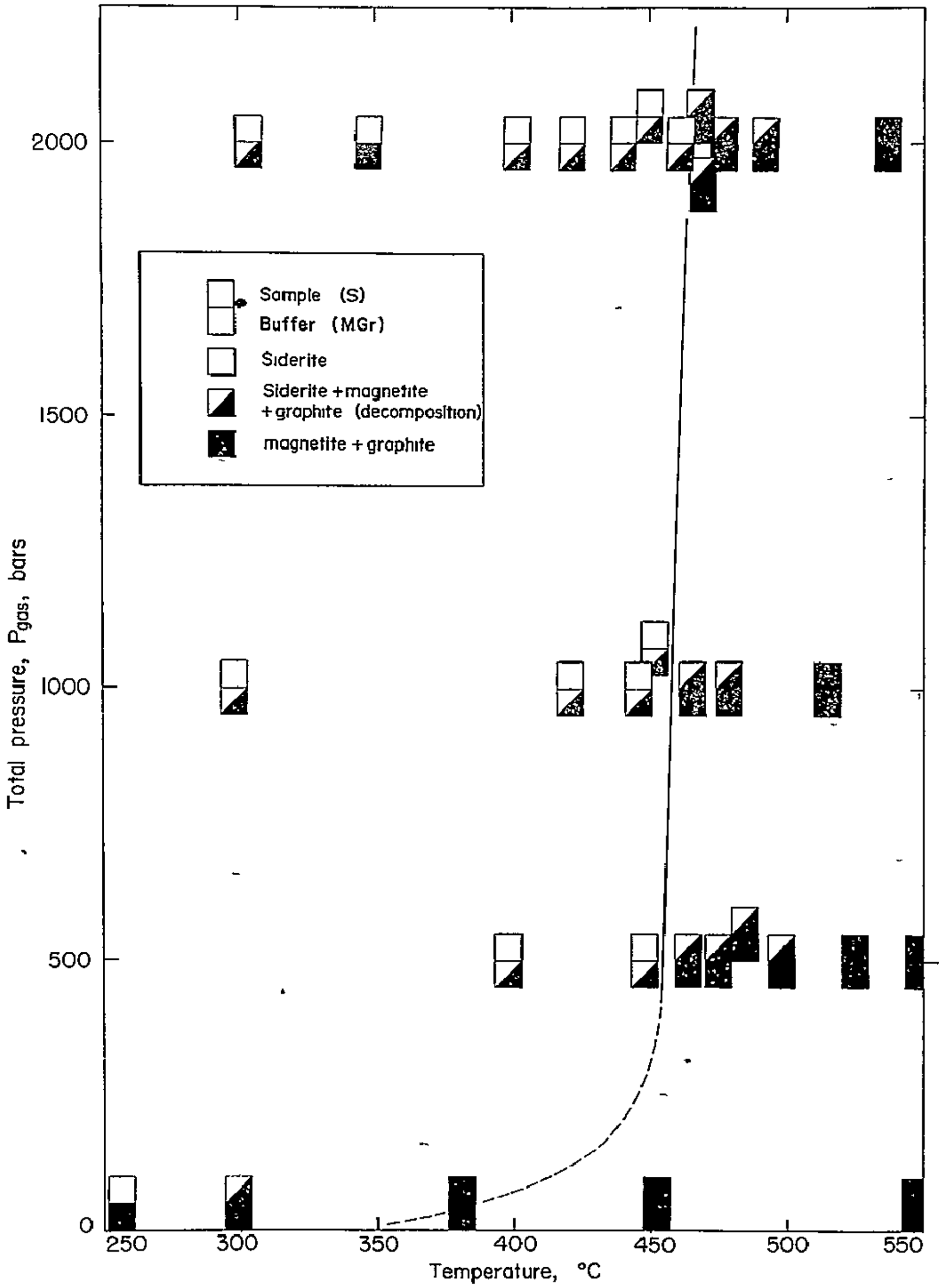


Figure 5—Plot of $P_F = P_{CO_2} + P_{CO}$ against T, showing location of the experimentally determined univariant curve siderite + magnetite + graphite + gas (SMGrG). In each run symbol, the upper box denotes behavior of the siderite sample, the lower box denotes behavior of the buffer. Slight vertical displacements of run symbols have been made for visibility and do not indicate differences in run pressure. The dashed portion of the curve is extrapolated. The runs near zero pressure were made at 30 psi CO_2 pressure and do not indicate a definite equilibrium decomposition temperature.

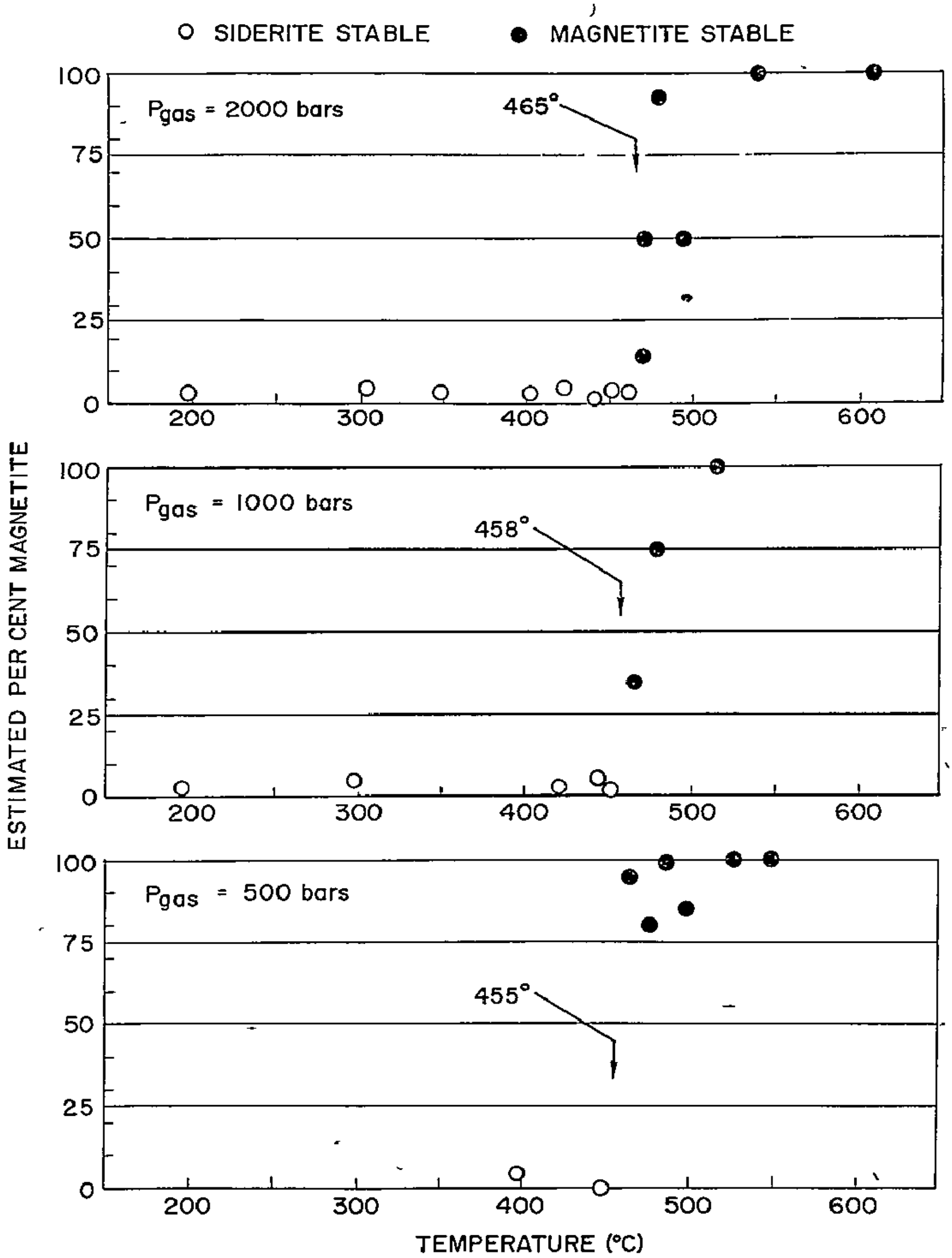


Figure 6—Plot of estimated percentage of siderite sample decomposition as a function of temperature for runs used to locate the univariant curve siderite + magnetite + graphite + gas (SMGrG). The equilibrium temperature (455–465°C) are located by the sharp increase in decomposition with increasing temperature. Decomposition below this temperature is relatively constant and does not exceed 5 percent, but decomposition is virtually complete in several runs located above the equilibrium temperature and below 500°C

There was no observable effect of total pressure on the amount of reaction along the SMGrG curve, in general, virtually complete decomposition of siderite was observed in all samples run at 30° to 50°C above the equilibrium temperature at all pressures (Table 3; Figure 6)

Runs made with a magnetite-graphite mixture in the sample position showed traces of siderite developing below the estimated equilibrium temperatures No siderite was observed to form in these runs above the equilibrium temperatures, and these runs are thus consistent with the equilibrium temperatures determined from runs using siderite samples

The temperatures obtained for the SMGrG curve in this study are supported by independent studies of siderite decomposition carried out by Rosenberg (1963a). In his experiments, siderite was decomposed under pressure in sealed gold tubes, buffering at f_{O_2} values at or close to those of the graphite buffer was apparently established by precipitation of graphite or amorphous carbon from the gas phase in the tube during the run (French and Rosenberg, 1965). The temperatures at which a sudden increase in production of magnetite from siderite was observed are virtually identical to those determined by the open-tube method used in this study (Figure 7) (French and Rosenberg, 1965). This agreement between results obtained by two different experimental methods strengthens the conclusion that the temperatures obtained do correspond to the stable equilibrium temperatures for the isobaric invariant points for the equilibrium siderite + magnetite + graphite + gas

DISCUSSION OF EXPERIMENTAL RESULTS

Buffering and Metastability in a CO_2 + CO Gas Phase

It was not possible in the present study to measure directly the CO_2/CO ratio in the gas phase coexisting with the sample during an experiment, and indirect evidence must be used to indicate whether the buffer assemblage does in fact control the f_{O_2} value imposed on the sample in a CO_2 + CO atmosphere In earlier experiments in hydrothermal ($H_2O + H_2$) atmospheres, buffering was carried out by osmotic diffusion of hydrogen through sealed platinum capsules (Eugster, 1959, Shaw, 1963) The success of this method has been demonstrated by the reversibility of reactions and by the consistently varying compositions of iron-bearing solid solutions synthesized at various f_{O_2} values (Turnock and Eugster, 1962, Eugster and Wones, 1962, Wones and Eugster, 1965). The successful operation of the buffering mechanism has also been verified by direct measurement of f_{H_2} values inside the sample tube (Shaw, 1963, 1968).

In contrast, buffering in a CO_2 + CO atmosphere such as that used in the present study involves mechanical diffusion of all gas species through the solid buffer and the open tubes and thus requires that the necessary solid-gas equilibration reactions take place in times that are short compared to run duration If these conditions are not met at the relatively low reaction temperatures involved (250-500°C), then equilibrium will not be attained and the determinations will not correspond to equilibrium siderite decomposition temperatures

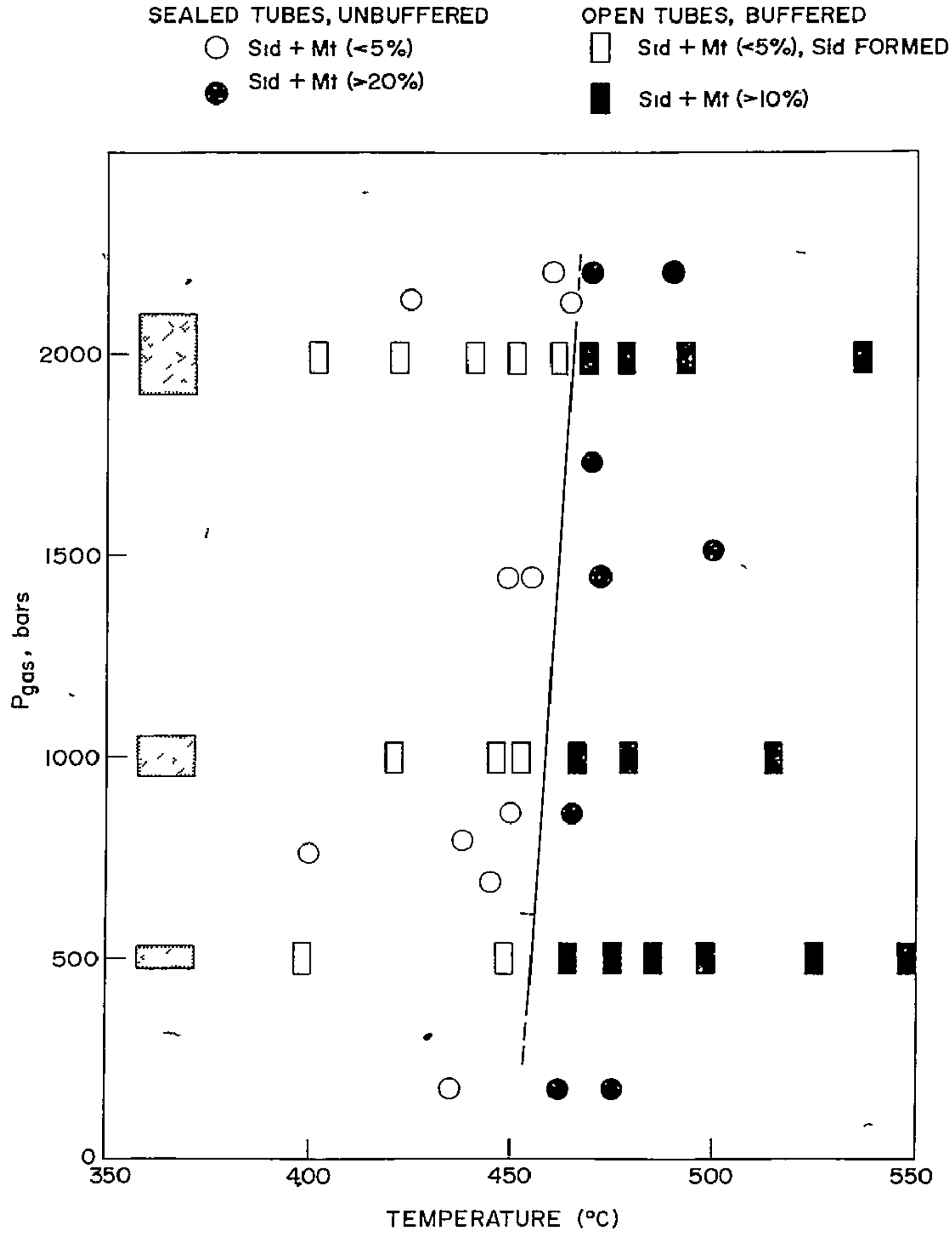


Figure 7—Location of the univariant equilibrium siderite + magnetite + graphite + gas, as determined by open-tube buffered runs (French, 1964a, rectangles) and by sealed-tube experiments (Rosenberg; circles) (from French and Rosenberg, 1965). The solid line indicates the univariant curve established from the open-tube buffered experiments, the sealed-tube experiments correspond to virtually the same curve. Stippled rectangles at left indicate the experimental uncertainty, ±7°C in run temperature and ±5 percent in total pressure.

Successful buffering at low temperatures by the hematite-magnetite (HM) buffer is indicated by several observations

(1) Reduction of the buffer entirely to magnetite occurred during long runs at temperatures near 400°C, indicating that the amount of reaction between the solid buffer and the gas phase under these conditions is sufficient to convert the original buffer to a more reduced assemblage characteristic of the lower ambient f_{O_2}. It is reasonable to assume that buffering of the sample is maintained by the solid phases until the hematite is used up.

(2) Distinctly different equilibrium decomposition temperatures for siderite are obtained, depending on whether the hematite-magnetite (HM) or the magnetite-graphite (MGr) buffering assemblages are used If the hematite-magnetite pair did not function as a buffer, the f_{O_2} on the sample would have been that of the bomb, and no more than a small difference in observed decomposition temperatures would have been expected . Because the f_{O_2} values of the graphite buffer are close to those of the pressure vessels at these temperatures (French and Eugster, 1965), similar decomposition temperatures would have been observed regardless of whether the magnetite-graphite assemblage functioned as a buffer. The large spread in decomposition temperatures for the two buffer assemblages, nearly 100°C, indicates that the hematite-magnetite assemblage provided a distinctly different f_{O_2} value to the samples.

(3) Both hematite and magnetite are observed as decomposition products of siderite samples surrounded by a hematite-magnetite mixture, although the amount of reaction is slight. Had the buffer not functioned, only magnetite would have been expected as a decomposition product.

The problem of reaction and buffering by the magnetite-graphite mixture is more complex. Considerable experimental evidence indicates that metastably low values of the CO_2/CO ratio may be preserved for significant periods, even at elevated temperatures, without precipitation of graphite (Muan, 1958, Bank et al , 1961, Bank and Verdurmen, 1963), although there is little knowledge about reaction rates under the high temperatures and pressures of the present experiments.

There is little information on the rates of equilibration of $CO_2 + CO$ atmospheres when graphite is originally present in the system The reactions are sluggish and disequilibrium may persist for hours or even days at low temperatures At higher temperatures, equilibration is attained or approached more quickly (Bradner and Urey, 1945, see also Mellor, 1924, Remy, 1956, for summaries), but catalysis may be required to promote reaction even at temperatures of 500-600°C

The present experimental conditions, involving relatively high temperatures (400-600°C), long reaction times (generally two weeks), and the presence of siderite, iron oxides, and an iron alloy reaction vessel as potential catalytic agents, offer optimum conditions for equilibration of the gas phase with the graphite buffer The following observations indicate that such buffering does in fact occur

(1) Either graphite or amorphous carbon is observed to precipitate from the gas phase This precipitation implies that metastably low CO_2/CO values are not maintained and that reaction between graphite and the gas phase does establish an equilibrium f_{O_2} value The carbon is observed

outside the capsule in the bomb, but also appears in sealed capsules of siderite run under similar conditions (Rosenberg, 1963a, French and Rosenberg, 1965).

(2) Similar graphite or carbon is observed with magnetite in samples of siderite decomposed above the equilibrium temperatures The material was detected by dissolving the sample in HF, a process which removed the finely-divided siderite and magnetite and left the carbon as a residue However, not enough of the carbon phase could be isolated for X-ray determination of its exact character.

(3) The behavior of unbuffered siderite samples exposed to the ambient bomb f_{O_2} was slightly but significantly different from siderite samples enclosed in the buffer, even when the same furnace and bomb were used Only a few unbuffered runs were made At 2000 bars, an unbuffered sample was stable at 474°C, while a buffered sample decomposed at 438°C. At P_F = 500 bars, by contrast, an unbuffered sample decomposed at 438°C, while a buffered sample was stable at 448°C These results cannot be considered definitive because of uncertainties in the actual f_{O_2} of the bombs and because of the progressive change in bomb f_{O_2} with continued use (Eugster and Wones, 1962, p 95) The results do imply, however, that the decomposition temperatures of siderite differ when a graphite buffer is employed, and the unbuffered runs provide further evidence that the graphite buffer does in fact operate under the experimental conditions Because of the similarity in f_{O_2} values for the bombs and for the graphite buffer (French and Eugster, 1965), large differences in behavior between buffered and unbuffered runs would not be expected

It is possible that precipitation of carbon during runs will alter the walls of the reaction vessels after long use, either by coating them with carbon or by producing carbon-bearing alloys or carbides in the metal. Such processes, particularly armoring the bomb by carbon, will cause the ambient bomb f_{O_2} to be fixed close to that of the graphite buffer itself, thus requiring only minimal reaction between the atmosphere and the graphite surrounding the sample to attain the specified f_{O_2} If the carbon which precipitates from the gas phase is not pure crystalline graphite, the f_{O_2} produced in the bomb will be slightly different from that calculated for the graphite buffer (see Zen, 1963, p 934)

These experimental observations indicate that, in a CO_2 + CO atmosphere, reaction between the gas phase and the solid-phase buffers is sufficient, even at relatively low temperatures, to establish f_{O_2} buffering in the sample. The temperatures determined for siderite decomposition are thus equilibrium temperatures for the reactions indicated, a conclusion strengthened by the demonstration of reversibility at each equilibrium point Reversibility was best demonstrated at the higher temperatures of the siderite + magnetite + graphite + gas curve, and these points are in good agreement with results from another experimental study which involved buffering by precipitated graphite (French and Rosenberg, 1965). Finally, the success of this buffering method and of the graphite buffer in particular has been well demonstrated in subsequent experimental studies, particularly in the determination of the rhodochrosite stability field (Huebner, 1969) and in investigations of complex metamorphic reactions involving C-H-O gas phases (Eugster and Skippen, 1968)

Comparison With Other Investigators

Johannes (1968, 1969) studied the stability relations between Fe-Mg carbonates and aqueous solutions under conditions in which f_{O_2} and other volatile pressures were not specifically controlled Because oxalic acid was often added to his system to stabilize the carbonates, the conditions of his experiments are probably most comparable to the siderite synthesis runs made in the present study In both sets of experiments, both siderite and Fe-rich carbonate showed decomposition to magnetite at temperatures above about 400°C No precipitation of graphite was observed either by Johannes or in the present syntheses, and the decomposition temperatures observed may represent equilibrium breakdown at values of f_{O_2} intermediate between the hematite-magnetite and graphite buffers

Seguin (1968a, 1968b) carried out studies in the system Fe-C-O-S-H_2O involving siderite decomposition under a variety of experimental methods and conditions. Because of the greater complexity of his system and the presence of other volatile species, it is not possible to make direct comparisons between his results and those of the present study, even for his experiments in which oxygen buffers were used. In general, his decomposition temperatures are lower than those observed in the present study and are likewise virtually independent of total pressure Interpretation of his results is complicated by a number of experimental problems Reactions were not reversed, only the decomposition of siderite being noted, and many of his curves are based on relatively few runs. Second, his use of oxygen buffering by osmotic hydrogen diffusion is uncertain, partly because the diffusion rates at temperatures of 250-500°C may not be sufficient to establish equilibrium (Eugster and Wones, 1962, p 94, Shaw, 1968), and partly because, with a C-H-O gas phase in the sample, equilibration of f_{H_2} will produce different values of f_{O_2} in the sample and the surrounding buffer (Eugster and Skippen, 1968, p. 503-504). Finally, some of the buffer assemblages which he used (e g., magnetite-iron) are clearly metastable with respect to the graphite buffer.

Even if Seguin's (1968a, 1968b) results do represent equilibrium decomposition of siderite, the experiments were performed under conditions where, because of the other components in the system, $P_{CO_2} + P_{CO} < P_F$ and the exact values of f_{CO_2}, f_{CO}, and f_{O_2} are not known It is therefore not possible to compare his temperatures with those obtained in the present study under conditions where $P_{CO_2} + P_{CO} = P_F$ and f_{O_2} is specified

The experiments of Weidner (Weidner and Tuttle, 1964, Weidner, 1968) are more comparable with the present investigation because they were performed in an atmosphere of CO_2 + CO, using sealed gold tubes containing siderite samples Explicit control of f_{O_2} was not attempted, and the observed decomposition of siderite between 500 bars and 10 kb was used to locate two reactions (1) siderite + hematite = magnetite + gas, (2) siderite = magnetite + graphite + gas The two reactions should, ideally, correspond to the SHMG and SMGrG curves, respectively, determined here In addition, a few open-tube buffered experiments similar to those in the present study were made

Decomposition temperatures determined in the sealed-tube experiments (Weidner and Tuttle, 1964, Weidner, 1968) are significantly higher than those observed for analogous reactions in the present study (French, 1965; French and Rosenberg, 1965) (Figure 8). Because of slow reaction

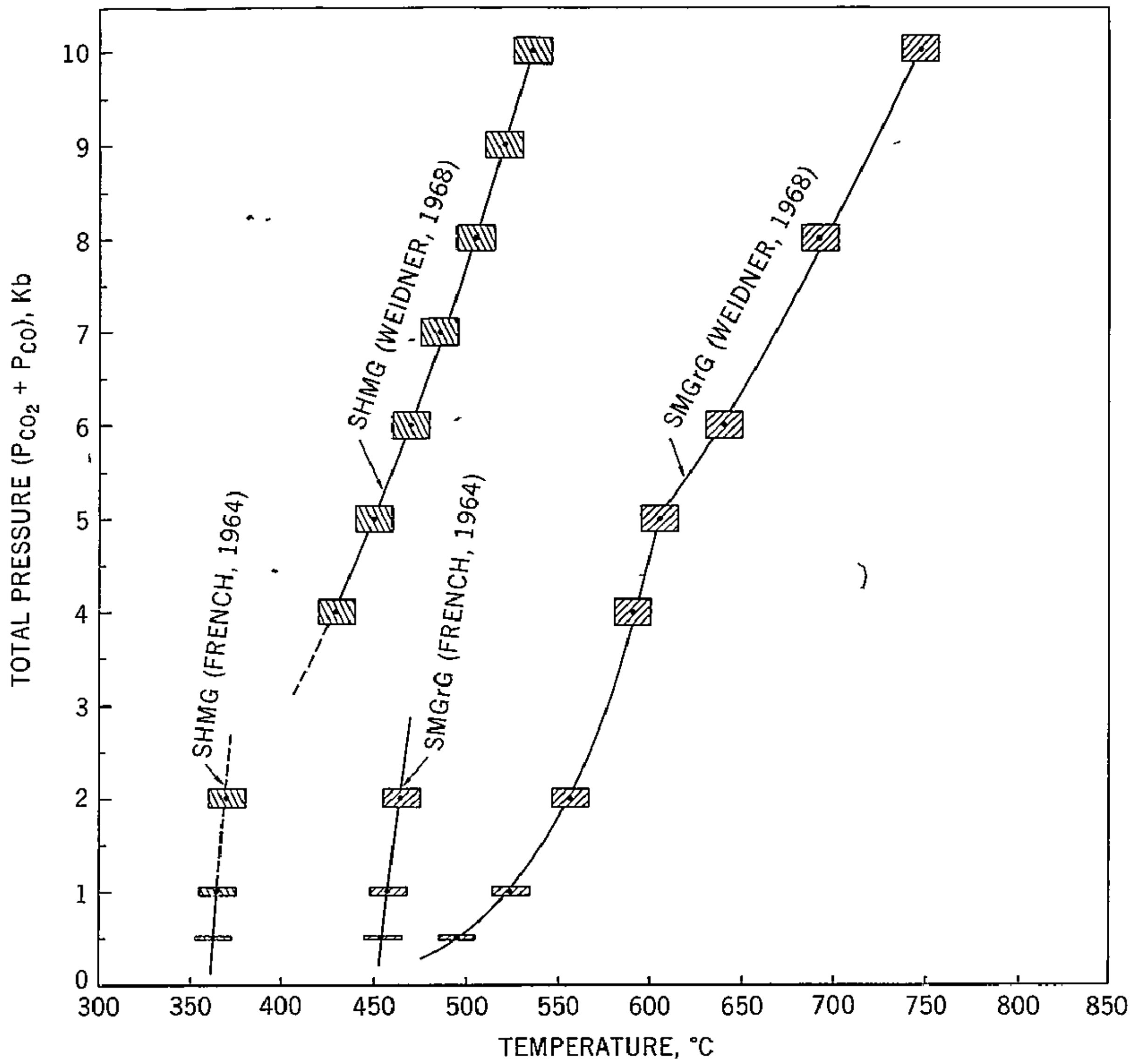


Figure 8—Location of the two univariant curves siderite + hematite + magnetite + gas (SHMG) and siderite + magnetite + graphite + gas (SMGrG) as determined by open-tube buffered experiments (French, 1964a) and by sealed-tube experiments (Weidner and Tuttle, 1964; Weidner, 1968). The greatest discrepancy is for the SMGrG curve, for which Weidner's determined equilibrium temperatures below 2000 bars are 50-90°C higher than those determined here. The break in slope of Weidner's SMGrG curve has been interpreted as indicating a polymorphic transition in siderite (Weidner and Tuttle, 1964), but no corresponding break is evident in the SHMG curve.

rates at lower temperatures and pressures, Weidner did not determine the SHMG curve below about 3 kb Extrapolating his determined curve to the lower pressures attained in the present study (Figure 8) gives approximately similar decomposition temperatures, although the slopes of the two curves are distinctly different

The disagreement in the two investigations is most severe for the reaction siderite + magnetite + graphite + gas (Figure 8). The temperatures determined by Weidner are from 60° to 90°C higher than those determined here The interpretation of the break in slope of Weidner's curve at 5 kb as the result of a polymorphic transition of siderite (Weidner and Tuttle, 1964) may not be correct His experimental points with their uncertainties can be fitted reasonably to a single smooth curve, and no similar break in slope is evident in his other curve (Figure 8) The exact causes of the large temperature differences in the two investigations are not clear. Nor is it obvious why the results of Weidner's sealed-tube experiments differ so greatly from the apparently similar sealed-tube experiments of Rosenberg (French and Rosenberg, 1965)

The sealed-tube technique itself involves a number of experimental problems that complicate interpretation of the results

(1) There is no direct control of f_{O_2}, and it must be assumed that f_{O_2} is buffered during reaction as the necessary phases are produced in the sample tube This assumption is probably more justified for the graphite buffer, because formation of graphite in the charge is commonly observed (French and Rosenberg, 1965, Weidner, 1968, p 23) However, metastably low values of f_{O_2} can be produced by the dissociation of siderite, since the resulting CO_2/CO ratio will be 2 or 3 depending on the decomposition product. Such ratios correspond to values of f_{O_2} that are metastably low with respect to the graphite buffer (French and Eugster, 1965), and if these values are maintained, siderite will appear stable at temperatures above the true equilibrium temperature (see Figure 1)

(2) The reactions are not reversed, and only the decomposition of siderite is used to locate the equilibrium temperature

(3) Reaction rates may be reduced as a result of compaction of the sample tube and charge during pressurization.

(4) Decomposition of the siderite sample during run-up below the equilibrium decomposition temperature is necessary to produce internal gas pressure in the sample tube. The potential presence of decomposition products in *all* runs makes it more difficult to recognize the true equilibrium temperature by the amount of sample decomposition Further, it must be assumed that the external pressure is in fact equalized by internal gas pressure throughout the entire sample, a condition that may not exist if some external pressure is supported by the compacted sample itself.

The last two effects appear to have been important in Weidner's experiments and may account for much of the difference between his results and the results reported here for the SMGrG curve Reaction rates in Weidner's study appear generally lower than those observed in the open-tube investigations, as indicated by the negligible amount of reaction on the SHMG curve below about 3 kb. Furthermore, the sample geometry apparently influenced his results, larger amount of reaction products were observed to form when larger-diameter sample tubes were used (Weidner, 1968, p. 24-25, 38).

A crucial point in evaluating the sealed-tube experiments is the value selected by the investigator for the amount of sample decomposition produced during run-up Observed decomposition above this amount indicates that the equilibrium temperature has been exceeded, and one of the disadvantages of the sealed-tube technique is that the apparent equilibrium temperature can be a function of the limit selected. French and Rosenberg (1965) regarded more than 5 percent decomposition as indicating that the equilibrium temperature had been exceeded (Figure 6). Weidner (1968, p. 26) generally interpreted more than 10 percent magnetite as indicating stable decomposition, although, in some experiments (Weidner, 1968, p 39-44), the formation of about 30 percent magnetite at 540°C was interpreted as indicating that siderite was stable. The higher cutoff limit used by Weidner, combined with possible reduction of reaction rates by sample compaction, would combine to produce apparent decomposition temperatures in excess of the true equilibrium values.

Weidner also performed some open-tube graphite-buffered experiments that were similar in sample geometry to those used here (Figure 3). Their results, however, were interpreted by him as supporting the higher temperature values Some of these runs were made in an atmosphere containing 30-40 percent CO, a value much higher than permitted by the graphite buffer and corresponding to a metastably low f_{O_2}. Equilibration of such a reduced atmosphere with the graphite buffer requires that the gas reaction $2\ CO = CO_2 + 1/2\ O_2$ be promoted. The reaction rate may be slow enough at moderate temperatures to allow metastably low f_{O_2} values to be preserved during the experiment In such an environment, siderite will exhibit metastably high decomposition temperatures

Equilibration of a pure CO_2 atmosphere with a graphite buffer, the method used here and in some of Weidner's buffered experiments, is a more desirable technique The composition in equilibrium with the graphite buffer at these temperatures is more than 97 percent CO_2 (French and Eugster, 1965), and equilibration in this case can be established with only a small amount of the heterogeneous reaction $CO_2 + C = 2\ CO$. Such equilibration is much more likely during the course of an experiment. Weidner's buffered experiments in a CO_2 atmosphere were made at 2000 bars. At 540°C, the siderite sample showed extensive decomposition (about 55 percent magnetite). At 500°C, the siderite sample remained stable and siderite formed in the buffer Conventional interpretation of these results would place the true equilibrium temperature between these values and not at the value of 556°C determined from the sealed-tube experiments. The apparent stability of siderite at 500°C is an unexplained anomaly, since extensive decomposition of siderite was observed at even lower temperatures in the present study (Figure 6).

Although the causes of the differences between Weidner's results and the present determinations are not definitely established, it seems likely that much of the difference arises from difficulties in experiment and interpretation caused by the nature of the sealed-tube method itself. Specific effects probably include slower reaction rates resulting from sample compaction and also problems in interpretation caused by the necessary production of decomposition products below the true equilibrium temperature Both effects would tend to produce apparent equilibrium temperatures higher than the true values.

It is believed that the open-tube buffered methods used in the present study (French, 1965, French and Eugster, 1965; French and Rosenberg, 1965) are superior to the sealed-tube technique for determining stability relations of carbonates which involve oxidation reactions The open-tube technique permits direct control and estimation of f_{O_2} Further, the open tubes remove problems arising from sample compaction and also allow extensive equilibration and reaction by mechanical diffusion of the gas phase through the charge. Most importantly, using the open-tube method, sample decomposition below the equilibrium temperature is negligible and the true decomposition temperatures can be more precisely estimated.

Accordingly, the temperatures obtained in the present study are believed to correspond to the true equilibrium temperatures for the reactions studied. This conclusion is strengthened by the agreement between the results of both open-tube and sealed-tube experiments along the graphite buffer (French and Rosenberg, 1965). Weidner's results for the same equilibrium apparently represent maximum temperatures, and more study on the problems of interpretation and kinetic factors in sealed-tube experiments will be needed before the differences can be fully resolved.

SIDERITE STABILITY IN P_F-f_{O_2}-T SPACE

Data for the two univariant equilibria siderite + hematite + magnetite + gas (SHMG) and siderite + magnetite + graphite + gas (SMGrG), determined in the present study, are shown in Table 4. The experimentally determined temperatures are higher than those calculated from thermodynamic data (see Figure 1).

The stability field of siderite in P_F-f_{O_2}-T space can be constructed from the experimentally determined positions of the two univariant curves and is conveniently presented in an isobaric plot of log f_{O_2} against T. At P_F = 500 bars (Figure 9), the siderite + gas field occupies a narrow wedge bounded by the three isobarically univariant curves siderite + hematite + gas (SHG), siderite + magnetite + gas (SMG), and the degenerate equilibrium siderite + magnetite + graphite + gas (SMGrG*). Only the two isobaric invariant points have been experimentally determined, curvatures of the univariant curves are approximate and are based on thermodynamic calculations (French, 1964a, Hubner, 1969).

The graphite buffer curve (GV) divides the siderite + gas region into two distinct parts (French and Eugster, 1965). Above the curve, siderite is in equilibrium with a gas composed of CO_2 and CO which exerts a total pressure of 500 bars. Below the curve, siderite coexists only with oxygen and with an imaginary inert gas which exerts a total pressure of 500 bars.

Along the SHG curve, siderite coexists with hematite and a gas phase of variable composition, the stable portion of the SHG curve terminates in the invariant point siderite + hematite + magnetite + gas, located at 363°C and log f_{O_2} = -24.7. Between this point and the isobaric invariant point siderite + magnetite + graphite + gas at 455°C and log f_{O_2} = -25.8, siderite coexists with magnetite and a gas phase of variable composition along the stable portion of the univariant curve siderite + magnetite + gas (SMG).

The point siderite + magnetite + graphite + gas at 455°C represents the highest temperature at which the assemblage siderite + gas is stable at P_F = 500 bars. Below the graphite buffer curve, the stability of siderite is determined by the degenerate equilibrium curve siderite + magnetite + graphite + O_2 (SMGrG*), which is not experimentally accessible.

Table 4

Temperature and Gas Composition Data for Equilibrium Points Determined on the Univariant Curves, With Thermodynamic Data for the Reaction 3 Siderite + O_2 = Magnetite + 3 CO_2 at These Points

P_F	T°C (calc)	T°C (exp.)	– log f_{O_2} (bars)	f_{CO} (bars)	f_{CO_2} (bars)	log K_4 (T) (calc)	$\Delta G_T°$ (kcal) (calc)	log K_4 (T) (exper)	$\Delta G_T°$ (kcal) (exper)
Siderite + Hematite + Magnetite + Gas (SHMG)									
500	212	363	24 8	3 4 × 10^{-4}	535	+26 23	-75 7	+20 58 ± 1 0	-59 9
1000	223	365	24 7	8 8 × 10^{-4}	1230	+26 42	-75 9	+21 62	-63 1
2000	244	370*	24 4	1 3 × 10^{-3}	3600	+26 78	-76 4	+22 87	-67 3
Siderite + Magnetite + Graphite + Gas (SMGrG)									
500	234	455	25 7	1.3	570	+25 60	-84 7	+21 12 ± 1 0	-70 3
1000	277	458	25 2	2 1	1310	+25 76	-84 9	+21 95	-73 4
2000	301	465	24 2	3 5	3840	+26 07	-85 6	+22 95	-77 4

*Estimated temperature based on extrapolation from lower pressures

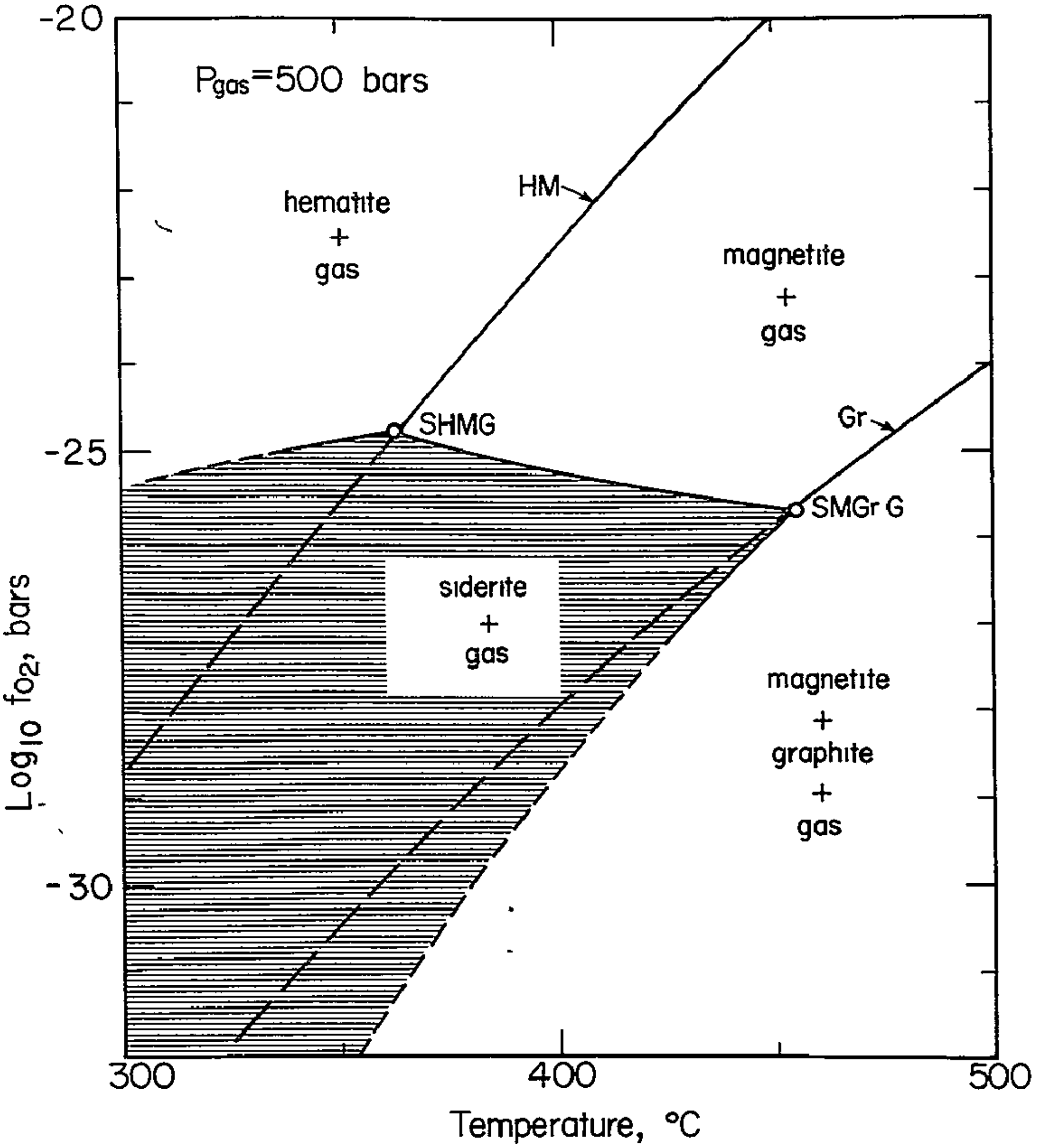


Figure 9—Isobaric section at P_F = 500 bars, showing the stability field of siderite + gas as a function of T and log f_{O_2}. The stability field is based on the experimentally determined isobaric invariant points siderite + hematite + magnetite + gas (SHMG) (363°C, log f_{O_2} = -24.8) and siderite + magnetite + graphite + gas (SMGrG) (455°C, log f_{O_2} = -25.7). Only the part of the stability field above the graphite buffer curve (Gr) is experimentally accessible.

The stability relations of siderite at total pressures of 1000 bars and 2000 bars are virtually identical to those at 500 bars, as the polybaric projection (Figure 10) indicates, except for the slightly higher temperatures of the invariant points at higher pressures The chief effect of increasing total pressure is the significant shift of the graphite + gas buffer curve toward higher values of f_{O_2} as the result of increasing P_{CO_2}

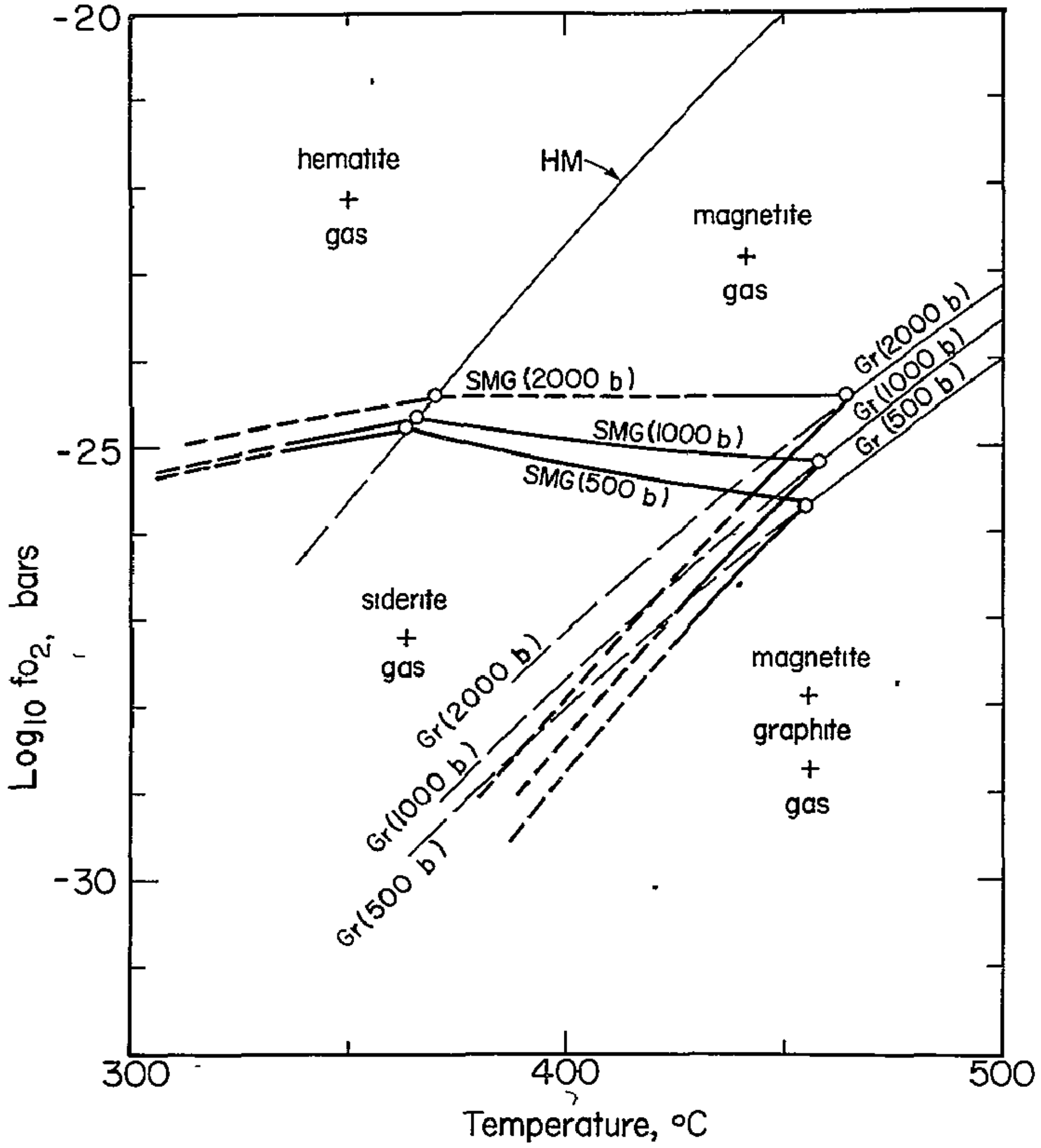


Figure 10—Polybaric projection of the stability field of siderite + gas determined at 500, 1000, and 2000 bars $P_{CO_2} + P_{CO}$. The SHMG point at 2000 bars is extrapolated from data at lower pressures. The stability field of siderite + gas is bounded by stable decompositions to hematite + gas, to magnetite + gas, and to magnetite + graphite + gas. The size of the field of siderite + gas is only slightly affected by changing total pressure between 500 and 2000 bars, most of the effect arises from the change in location of the graphite buffer curve (Gr) with changing $P_{CO_2} + P_{CO}$.

The section at P_F = 2000 bars is incomplete. The SMGrG point lies at 465°C and log f_{O_2} = -24.4. The SHMG point was not determined, but extrapolation of the SHMG curve from lower pressures suggests that the equilibrium temperature at 2000 bars is approximately 370°C, which corresponds to log f_{O_2} = -24.2 The isobaric invariant SMG curve between these points is nearly horizontal

The stability field of siderite + gas, plotted in three dimensions in P_F - log f_{O_2} - T space (Figure 11), occupies a narrow wedge bounded by the three divariant reaction surfaces siderite + hematite + gas (SHG), siderite + magnetite + gas (SMG), and siderite + magnetite + graphite + O_2 (SMGrG*).

The graphite buffer surface (GrG) forms the lower boundary of the experimentally accessible portion of the field of siderite + gas. Reactions involving siderite and CO_2 become metastable at values of log f_{O_2} below this surface. For this reason, the stability field of siderite + gas shown in Figure 11 is much smaller than that calculated in similar diagrams (Holland, 1959, Garrels and Christ, 1965), in which reactions involving graphite are not considered.

A schematic isobaric section is shown in Figure 12; all the stable assemblages coexist with gas Above the graphite + gas curve, solid phases coexist with a gas phase composed of CO_2 and CO. Below the curve, the solid phases coexist with O_2 and with an imaginary inert gas that is added to exert the specified total pressure The presence of the additional (imaginary) component allows divariant assemblages below the curve to have one more solid phase than do divariant assemblages above the curve The point siderite + magnetite + graphite + gas (SMGrG) represents the maximum temperature of stable existence of the assemblage siderite + gas at this value of P_F.

The assemblage siderite + gas is stable over a relatively narrow range of f_{O_2} values, below 2000 bars, siderite is not stable above 10^{-24} bars f_{O_2}, and most of the siderite + gas field occupies an area between 10^{-24} and 10^{-30} bars. The quartz-fayalite-magnetite buffer curve, which is the upper limit of stability of fayalite (Fe_2SiO_4), lies entirely in the condensed region below the graphite buffer curve over the entire temperature range for which siderite is stable (Eugster and Wones, 1962, French and Eugster, 1965) Accordingly, the stability fields of siderite + gas and of fayalite + gas do not intersect, and the possible reaction of siderite + quartz to form fayalite is not stable.

Changes in the value of P_{CO_2} appear to have only a slight effect on the stability of siderite between 500 and 2000 bars, the equilibrium temperatures of the two univariant curves vary less than 10°C in that interval. By contrast, siderite stability is strongly affected by changes in the value of log f_{O_2} For example, at 500 bars, a change in log f_{O_2} of 1 0 will change the equilibrium temperature of the assemblage siderite + magnetite + gas by more than 50°C. This effect is more striking at higher total pressures, where the SMG curve becomes flatter Small changes in f_{O_2} will produce similarly large temperature variations in the assemblage, siderite + hematite + gas.

The isobaric sections demonstrate that, regardless of total pressure, an increase in f_{O_2} at constant temperature favors the decomposition of siderite to hematite or magnetite. The attitude of the SHG surface indicates that a temperature increase at constant P_F and f_{O_2} promotes the formation of siderite from hematite However, because of the negative slope of the SMG curve at constant P_F, an increase in temperature under the same conditions will promote decomposition of siderite to magnetite. The SMG curve appears to be an exception to the general observation that an increase in temperature at constant f_{O_2} favors formation of the more reduced of two equivalent assemblages (Eugster, 1959, Eugster and Wones, 1962) Some of the analogous decomposition curves for rhodochrosite at constant P_F have similar orientations (Huebner, 1969, Figures 8-9)

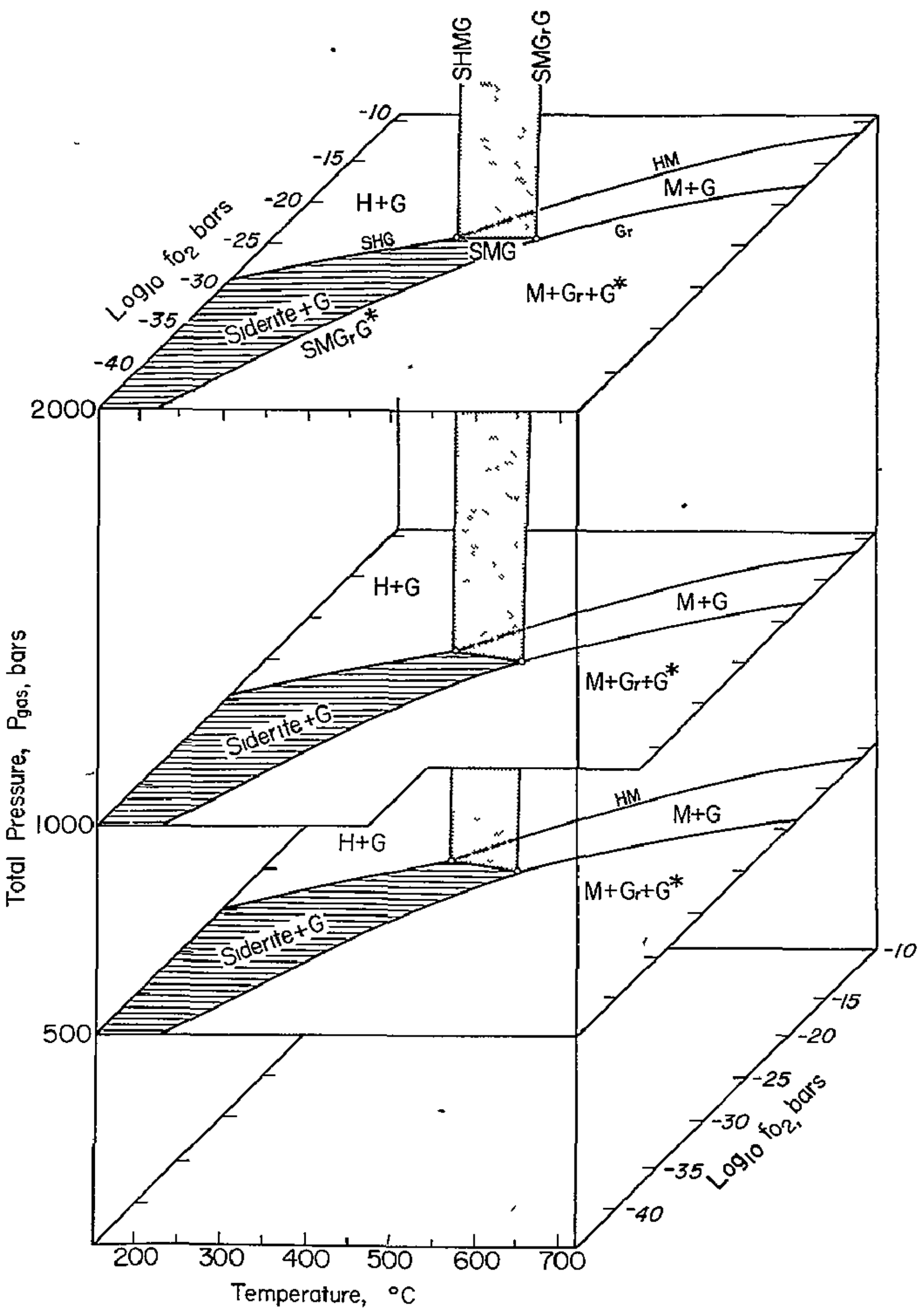


Figure 11—Block diagram in P_F – log f_{O_2} – T space showing the stability field of siderite + gas and its stability relations. The stability field of siderite + gas (ruled areas on sections) is a narrow prism bounded by divariant reaction surfaces (shown only as univariant curves on sections) involving decompositions to hematite + gas (SHG), magnetite + gas (SMG), and magnetite + graphite + gas (SMGrG*). The equilibrium surface siderite + magnetite + gas (stippled) is bounded by the two univariant curves determined experimentally. Stable mineral assemblages outside of the siderite stability field are indicated by larger lettering, smaller letters (HM, Gr) indicate buffer curves.

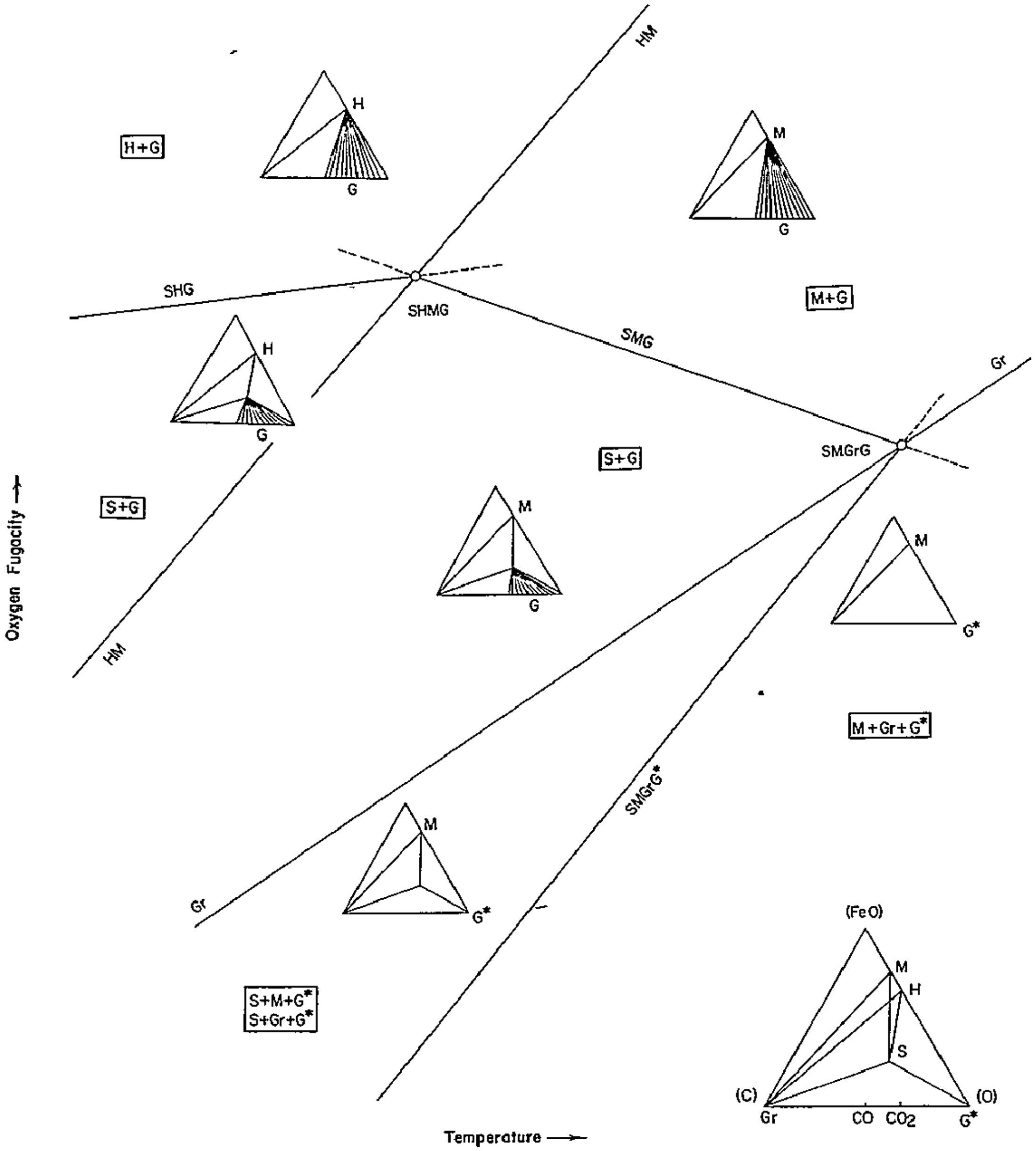


Figure 12—Schematic isobaric section through the system Fe-C-O, showing stable assemblages as a function of log f_{O_2} and T. All solid phases coexist with a gas phase. Stable univariant equilibria are shown by solid lines, metastable extensions are dashed. Boxes indicate the assemblages stable in each region. Above the graphite buffer curve (Gr), $P_F = P_{CO_2} + P_{CO}$, the gas phase is variable in composition, and an assemblage of one solid + gas is divariant. Below the graphite buffer curve, $P_F = P_{O_2}$, and two solids + gas form a divariant assemblage.

COMPARISON OF EXPERIMENTAL RESULTS WITH THERMODYNAMIC CALCULATIONS

The experimentally determined univariant curves generally lie about 150°C above curves calculated from thermodynamic data (Table 4). The experimental curves have considerably steeper slopes (higher values of dP_F/dT) than do their calculated counterparts This difference may reflect in part the uncertainty in the equilibrium temperature. When the curves are steep, small uncertainties in the temperature determinations produce disproportionate uncertainties in the calculated slopes (see Burnham and Jahns, 1962, Figure 7).

Because all the experimentally determined isobaric invariant points lie on the divariant reaction surface. siderite + magnetite + gas, the experimental data may be used to calculate values of ΔH° and ΔG° for the decomposition of siderite to magnetite (Equation 4) by computing values for

$$\log K_4 = 3 \log f_{CO_2} - \frac{1}{2} \log f_{O_2} \tag{4}$$

and applying the relationships.

$$\Delta H^\circ = -2.303 R(d \log K/d(1/T)) \tag{16}$$

$$\Delta G^\circ = -2.303 R T \log K \tag{17}$$

In theory, such experimentally determined values of ΔH° and ΔG° would allow a more accurate determination of the values of $\Delta H^\circ_{f\,T}$ and $\Delta G^\circ_{f\,T}$ for siderite. Eugster and Wones (1962) applied the same method to calculate thermodynamic data for the iron-biotite, annite.

Calculated and experimentally determined values of log K_4 (Table 4) are presented in Figure 13, together with values of the quantity (3 log f_{CO_2} - 1/2 log f_{O_2}) specified by the hematite-magnetite and graphite buffers as a function of temperature. The experimental values of log K_4 are quite closely grouped and are considerably smaller than values calculated from ΔG° for 1 bar and 2000 bars. The lines which connect the experimental points at the same total pressure have high negative slopes which become more negative at lower pressures. This behavior contrasts with the positive slopes of the calculated lines. The negative slopes observed for the lines through the experimental points imply that the value of ΔH° is positive. Positive values of ΔH° for the experimental data are also suggested by the negative slope of the SMG curve in the isobaric sections (Figures 9 and 10), since the value of $(\partial \log f_{O_2}/\partial T)_{P_F}$ will tend to have a sign opposite to that of ΔH° (French, 1964a, p. 48).

Values of ΔH° derived from the experimental results are positive and range from +7 to +12 kcal/mole between 500 and 2000 bars, in sharp contrast to the values of -13 to -16 kcal/mole derived for these total pressures from thermodynamic data (Figure 13). These differences are too great to be caused by the effect of changing total pressure on ΔH° (see Orville and Greenwood, 1965), because the differences exist between calculated and experimental data for the same total pressure, and because the effect of total pressure on this reaction can be calculated to be only about -2 kcal/mole between 1 bar and 2000 bars.

Similar differences exist in values of ΔG° calculated from the experimental results. The values of ΔG° calculated from thermodynamic data (Table 1) are about -75 kcal/mole on the hematite-magnetite buffer and about -85 kcal/mole on the magnetite-graphite buffer (Table 4). The experimental results are about 10 kcal/mole more positive. about -64 kcal/mole (SHMG) and -74 kcal/mole (SMGrG). Assuming that ΔS° is constant with temperature, the experimental results yield a value of ΔS° = 111 cal/mole-deg, in contrast to a calculated value of about +96 cal/mole-deg.

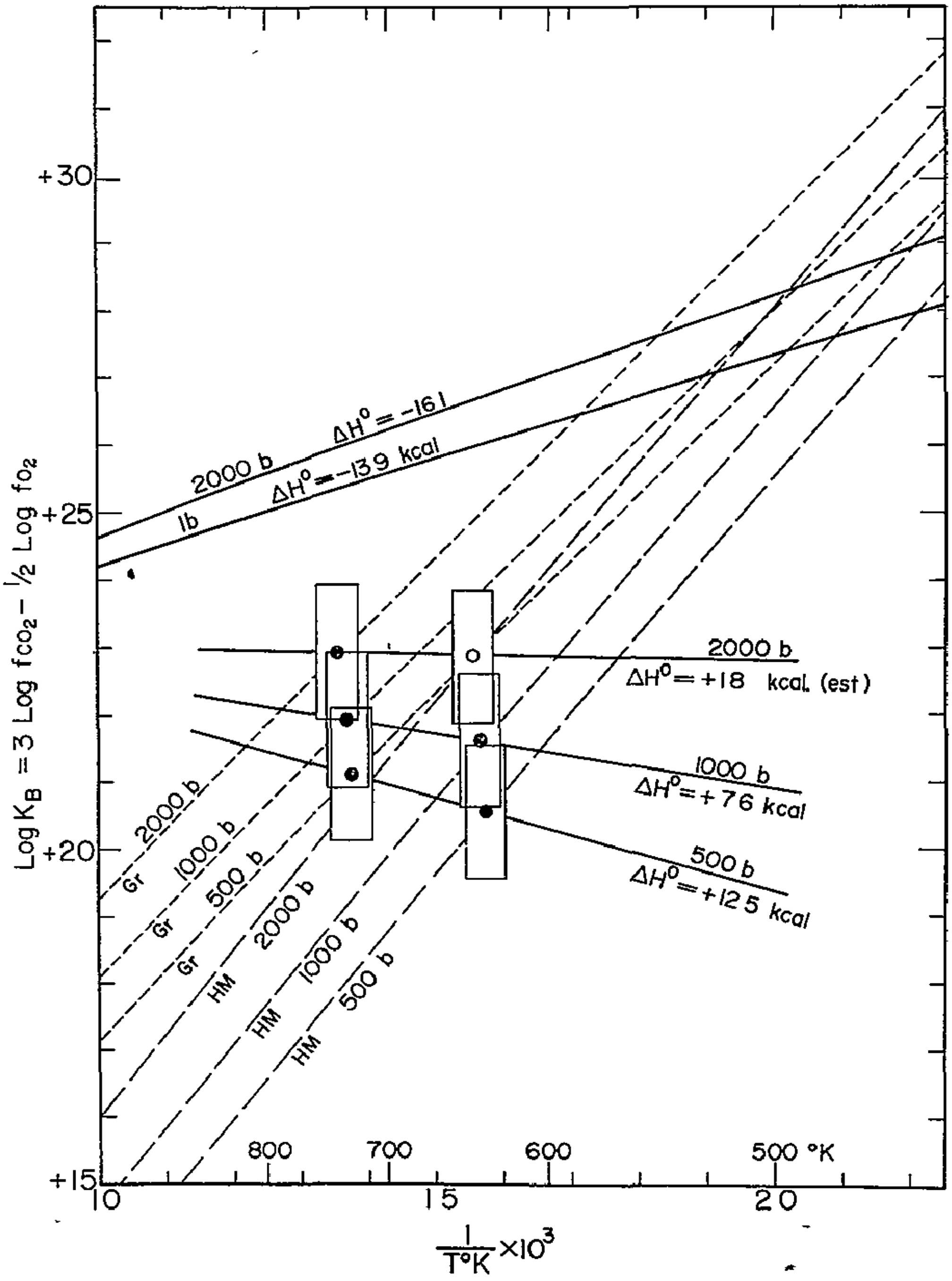


Figure 13—Comparison of calculated and experimentally determined values of ΔH° for the reaction: 3 siderite + 1/2 O_2 = magnetite + 3 CO_2 (Equation 4), derived from plotting the equilibrium constant against 1/T. Values of log K_4 (T) (= log K_B) derived from thermodynamic data are shown by solid lines for P_F = 1 bar and 2000 bars. Dashed lines indicate values of the quantity 3 log f_{CO_2} − 1/2 log f_{O_2} as a function of temperature, using f_{O_2} values along the hematite-magnetite (HM) (long dashes) and graphite (Gr) (short dashes) buffers. Intersections of the dashed lines with the solid lines correspond to calculated equilibrium temperatures for a particular pressure.

Values of log K_4 (= log K_B) calculated from experimental results (Table 4) are plotted as solid circles (the open circle indicates an extrapolated value for the SHMG point at 2000 bars). Boxes around the points indicate the estimated uncertainty (log $K_4 \pm 1.0$; 1/T x 10^3 = 0.03). Values of ΔH° obtained from the experimental equilibrium constants by connecting points at the same total pressures differ significantly from the calculated values and are opposite in sign. However, the fact that the error boxes overlap the entire range of variation in log K4 suggests that the derived values of ΔH° may not be meaningful.

Using the relationship

$$\Delta G^\circ_{298^\circ K} = \Delta G^\circ_T + \Delta S^\circ (T - 298) \tag{18}$$

the experimental data yield a value of $\Delta G^\circ_{298^\circ K}$ = -25.5 kcal/mole and ΔH° = +7.6 kcal/mole, in contrast to the calculated values of -42.9 kcal/mole and -13.9 kcal/mole, respectively (Table 5)

Weidner (1968) did not calculate thermodynamic data from his experimental results. Approximate values of ΔG° and ΔH° can be calculated from his data by assuming that $f_{CO_2} = P_F$ (French and Eugster, 1965) and neglecting the change in f_{O_2} of the buffers with changing P_F (Eugster and Wones, 1962) The errors introduced by these two effects are opposite in sign and will probably not produce uncertainties greater than those in the experimental data themselves. With these assumptions, Weidner's (1968) data yield values of ΔG°_{298} = -29.1 kcal/mole, ΔH° = -1.4 kcal/mole, ΔS° = +93 cal/mole-deg (Table 6).

Values of the thermodynamic quantities for the decomposition of siderite to magnetite (Equation 4) derived from these two experimental studies are given in Table 6, together with values calculated by other workers (Holland, 1965, Yui, 1966) for the same decomposition The latter two values are not completely independent, having been based on the earlier results of French and Rosenberg (1965). The results calculated from experimental data appear to indicate a higher value of ΔS°_{298} and correspondingly more positive values of ΔG°_{298} and ΔH°_{298} than are obtained directly from the thermodynamic data themselves.

Because of the large effect of experimental uncertainties on the calculation of the thermodynamic quantities from the experimental results, it is doubtful whether the differences obtained are meaningful or whether these calculations can be used to evaluate the experimental data themselves The operation of calculating ΔH° (Equation 16) involves the quotient of two small difference terms and even reasonable estimates of experimental uncertainty (T_{eq} ± 10°C, log K_4 ± 1.0) produce uncertainties as large as several hundred percent in the derived value of ΔH°.

The corresponding values of ΔG° are less affected and the stated experimental uncertainties produce an uncertainty in ΔG° of about 5-8 percent or about ±5 kcal/mole, comparable to the uncertainty in the value of ΔG° derived from thermodynamic data (Table 1). Even this moderate undertainty can produce large differences in calculated equilibrium temperatures (see Figure 2) However, the subtractions and other operations necessary to derive values for ΔG°_{298} (Equation 18) multiply this uncertainty to the point where the calculated value of ΔG°_{298} has a minimum uncertainty of about 100 percent.

Table 5

Calculated and Experimentally Determined Values of ΔH° for the Reaction Siderite + O_2 = Magnetite + 3 CO_2

P_F (bars)	ΔH° (kcal)	
	Calculated	Experimental
1	-13.9 ± 7.0	—
500	—	+12.5
1000	—	+7.6
2000	-16.1 ± 7.0	+1.8*

*Based on estimated temperature of 370°C for the SHMG curve at 2000 bars

Because of the large uncertainties, the differences between the values in Table 5 is probably not significant. The difficulty of using the experimental data to evaluate the experiments themselves is indicated further by the fact that

Table 6

Calculated Thermodynamic Data for Siderite Formation and Decomposition to Magnetite at 298°K.

(1) Reaction $3\ FeCO_3 + 1/2\ O_2 = Fe_3O_4 + 3\ CO_2$			
	ΔG°_{298} (kcal)	ΔH°_{298} (kcal)	ΔS°_{298} (cal/mole-deg)
calculated (French, 1964a and this study) (Table 1)	-42.87	-13.90	+93.0
experimental (French, 1964a and this study)	-25.49	-7.60	+111.1
Weidner (1968)	-29.10	-1.39	+93.0
Holland (1965)*	-22.12	+7.43	+99.3
Yui (1966)*	-29.7	-0.14	+99.3

(2) Reaction $Fe + C + 3/2\ O_2 = Fe\ CO_3$			
	$\Delta G^\circ_{f\ 298}$ (kcal/mole)	$\Delta H^\circ_{f\ 298}$ (kcal/mole)	ΔS°_{298} (siderite) (cal/mole-deg)
calculated (Robie, 1966)	-161.06	-178.20	23.9
experimental (French, 1964a and this study)	-166.6	-185.4	17.7

*Recalculated from author's original values for the analogous reaction $3\ FeCO_3 = Fe_3O_4 + 2\ CO_2 + CO$

the strongly divergent experimental results of French (1964a) and Weidner (1968) give comparable values for the thermodynamic parameters at 298°K

The large uncertainties in thermodynamic values obtained from the experimental data indicate that any new thermodynamic data for siderite calculated from the experimental results will probably not be meaningful If the data in Table 6 are, however, taken at face value, then the differences between experimentally derived thermodynamic quantities and those calculated from original thermodynamic data arise from differences in the thermodynamic quantities of one or more of the participating phases The uncertainty in $\Delta G^\circ_{f,298}$ for magnetite and CO_2 is probably less than ±2 kcal (Coughlin, 1954) If the entire difference is assigned to the thermodynamic data for siderite, a change of about +7 kcal/mole in $\Delta H^\circ_{f\ 298}$ and of about +5 kcal/mole in $\Delta G^\circ_{f\ 298}$ at 600-700°K would bring the experimental and calculated values into agreement (Table 6). This would correspond to a change of about +4 percent in the present values (Kelley and Anderson, 1935, Robie, 1962).

Thermodynamic data for siderite at elevated temperatures (600-700°K) are not definite enough to exclude a difference of this magnitude. Current heat-capacity data (Kelley, 1960) are based on studies between 50° and 300°K of a natural siderite containing only 90 percent $FeCO_3$ (Anderson, 1934), values of C_p were corrected by Anderson for the additional components $CaCO_3$, $MgCO_3$, and $MnCO_3$ in the sample Extrapolation of these data to higher temperatures could result in the indicated difference.

High-temperature heat-capacity data on pure siderite will probably be needed to resolve the question entirely It should be noted that estimated values of C_p for rhodochrosite ($MnCO_3$) based on Anderson's data (Kelley and Anderson, 1935) are 5 to 10 percent lower in the range 500-700°K than are values determined by direct measurement (Moore, 1943), and that similar differences are observed in values of $\Delta G_f^\circ{}_T$ for rhodochrosite determined from experimental stability data (Huebner, 1969). It is very likely that a similar difference could exist in the thermodynamic data for siderite.

GEOLOGICAL APPLICATIONS

Data on the stability of siderite may be applied to estimate conditions present during the metamorphism of iron formations (French, 1968) and the emplacement of siderite-bearing hydrothermal veins. The experimental results determined here are in a simpler system than present in nature, and application of the experimental data to natural processes is limited by the additional components present in the natural environment.

(1) Water is undoubtedly present in significant amounts in any gas phase coexisting with natural siderite. Introduction of water into the gas makes possible the formation of H_2 and CH_4 (French, 1966) and produces a situation in which $P_{CO_2} + P_{CO} < P_F$. These effects must be considered in estimating the decomposition temperatures for natural siderite.

The effect of conditions where $P_F \neq P_{CO_2}$ may be approximately calculated for the SHMG and SMGrG univariant curves from the relation

$$\left(\frac{\partial P_s}{\partial T}\right)_{P_{E_{CO_2}}} = \frac{\Delta S}{\Delta V_s} = \frac{dP_t}{dT} \times \frac{\Delta V_s + \left(V_{CO_2}\right)_{P_{E_{CO_2}}}}{\Delta S} \tag{19}$$

(Thompson, 1955; Greenwood, 1961, p. 3924-3925). Applying this relation to the univariant curves gives

$$\left(\frac{\partial P_s}{\partial T}\right)_{P_{E_{CO_2}}} = \frac{dP_t}{dT} \times \frac{\Delta V}{\Delta V_s} \tag{20}$$

Values of dP_t/dT for both univariant curves correspond to slopes of about +5 deg/1000 bars. Calculated values of the ratio $\Delta V/\Delta V_s$ are about -2 to -4. Thus the values of $(\partial P_s/\partial T)_{P_{E_{CO_2}}}$ are approximately -40 to -80 bars/deg

The corresponding univariant curves for fixed values of $P_{E_{CO_2}}$ will lie at temperatures below the univariant curves which are specified by the condition $P_t = P_{CO_2}$ (Thompson, 1955, Greenwood, 1961, Figure 1). The univariant curves will have steep negative slopes which correspond to a change of -10° to -20°C for each 1000 bars increase in P_s

It appears that the decomposition temperature of siderite will be affected only slightly by changes in total pressure at constant $P_{E_{CO_2}}$. The decomposition of siderite to magnetite thus represents a geothermometer which is strongly affected by changes in f_{O_2} but which is relatively insensitive to changes in both $P_{E_{CO_2}}$ and P_t.

A second effect of water in the gas phase is the potential stabilization of iron hydroxides such as goethite and lepidocrocite (FeO·OH), particularly at lower temperatures. Available stability data on the hydroxides (Deer et al., 1962, v. 5, p 118-127) are not sufficient to evaluate this effect in detail

(2) Natural siderites commonly contain 10 to 20 mole percent of other components, chiefly $MgCO_3$ and $MnCO_3$, in solid solution. The decomposition curve for pure magnesite ($MgCO_3$) lies at 750° to 850°C for values of P_{CO_2} between 500 and 2000 bars (Harker and Tuttle, 1955a) and is virtually independent of f_{O_2}, while the stability field of rhodochrosite ($MnCO_3$) extends to higher temperatures and f_{O_2} values than does the field of siderite (Huebner, 1969). The stability relations of the various carbonate minerals whose components can substitute in siderite (Figure 14) indicate that the stability of siderite will be extended to higher temperatures and f_{O_2} values by the addition of Mg^{2+}, Mn^{2+}, or Ca^{2+}. The decomposition curves for various intermediate carbonate compositions will be oriented at diverse angles within the envelope established by the stability relations of the pure end-members (Figure 14, also see Huebner, 1969, p 477, Wones and Eugster, 1965, p. 1254).

Despite these limitations, the present experimental data may be applied to natural occurrences of siderite.

The stability of siderite is strongly dependent on the value of f_{O_2}. Siderite is in stable equilibrium with gas over a narrow range of f_{O_2} and is not stable above 10^{-24} bars f_{O_2} below $P_F = P_{CO_2} + P_{CO} = 2000$ bars Siderite coexists stably with magnetite and gas over a very narrow interval of f_{O_2} values which correspond to gas compositions in which the values of P_{CO_2}/P_{CO} exceed 500. The formation of oxides from siderite at constant $P_{CO_2} + P_{CO}$ may occur either through increasing temperature or through increasing f_{O_2} values in the environment

Siderite-hematite assemblages (presumably primary) are occasionally found in sedimentary iron formations (Gruner, 1946, p. 31, French, 1968, p. 29-30). Metamorphism of iron formations, however, apparently occurs at T and f_{O_2} values within the magnetite stability field, and thus the assemblage siderite + magnetite + gas assumes major importance in evaluating such rocks For experimental conditions, which cover the values of P_{CO_2} in most geological environments at moderate depth, the decomposition of siderite to magnetite may occur between 363° and 465°C, depending on the values of both f_{O_2} and $P_{E_{CO_2}}$ in the coexisting gas phase. For pure siderite, 465°C is the maximum temperature of stable existence between 500 and 2000 bars $P_{CO_2} + P_{CO}$.

Geological studies of metamorphosed iron formations indicate that iron-rich siderites generally do not decompose directly to magnetite Instead, they react with the available quartz and water to produce amphiboles rich in the grunerite ($Fe_7Si_8O_{22}(OH)_2$) end-member. Such reaction has been

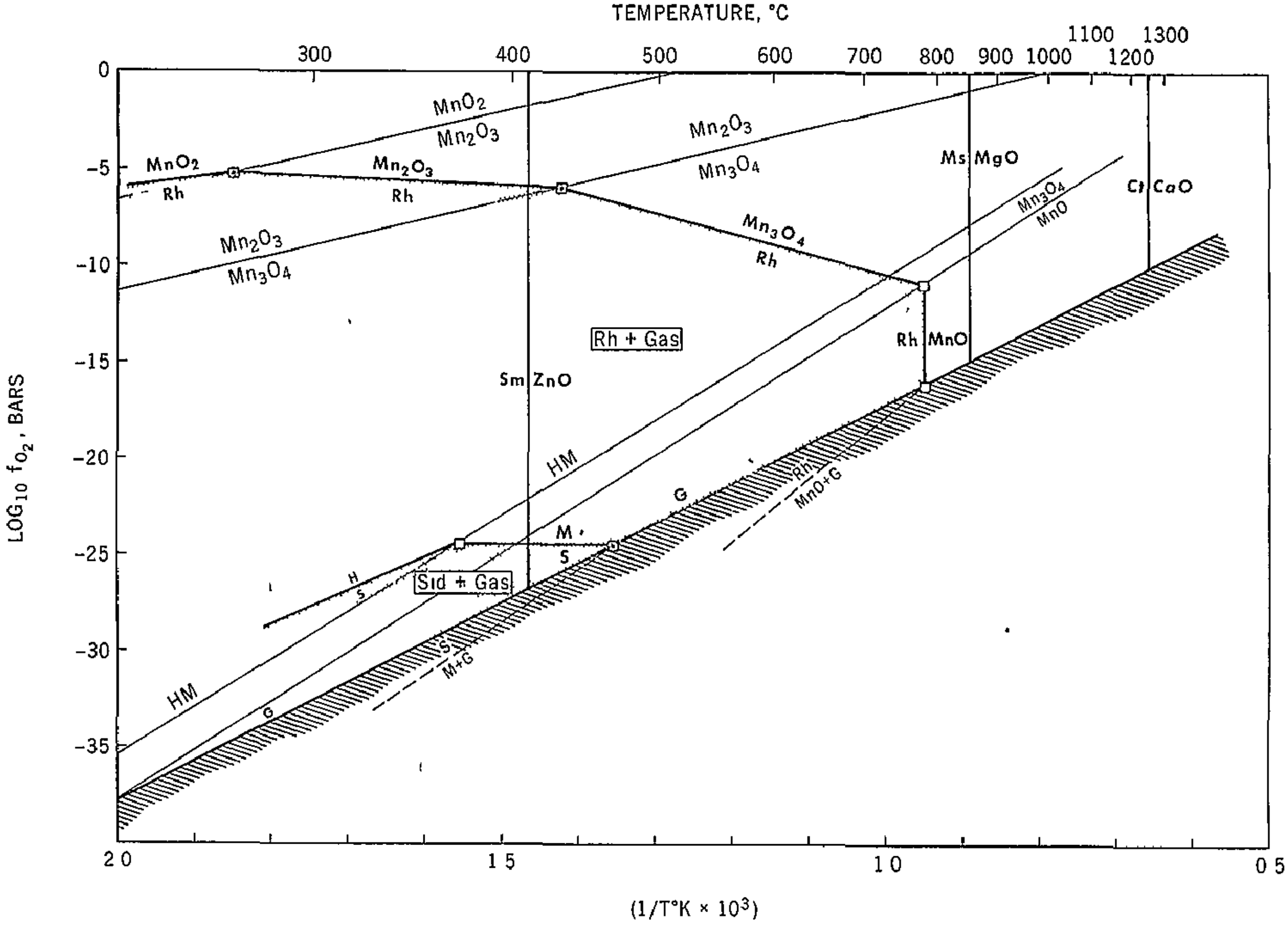


Figure 14—Isobaric section at $P_F = P_{CO_2} + P_{CO} = 2000$ bars, showing stability relations of siderite and other carbonates as a function of log f_{O_2} and 1/T. Heavy lines indicate carbonate decomposition reactions, light lines indicate oxygen buffer curves. The condensed region below the graphite buffer curve is indicated by ruling. The stability field of rhodochrosite ($MnCO_3$) (Rh) + gas (Huebner, 1969) is circumscribed by decompositions to several Mn oxides and extends to higher temperatures and f_{O_2} values than does the stability field of siderite (Sid) + gas. The vertical lines indicate decomposition temperatures for carbonates whose decomposition forms only the 1 1 oxide and are therefore independent of f_{O_2} smithsonite ($ZnCO_3$) (Sm) (Harker and Hutta, 1956), magnesite ($MgCO_3$) (Ms) (Harker and Tuttle, 1955a), and calcite ($CaCO_3$) (Ct) (Harker and Tuttle, 1955a). The relative positions of the stability fields indicate that the introduction of Mn^{2+}, Mg^{2+}, and Ca^{2+} into siderite will stabilize the resulting Fe-rich carbonate to higher temperatures and f_{O_2} values. The effect of included Zn^{2+} will be to stabilize the carbonate at higher f_{O_2} values with only a minor change in stability temperatures

observed in many regions the Lake Superior district (Van Hise and Bayley, 1897, p. 368, Irving and Van Hise, 1892, Allen and Barrett, 1915, James, 1955, French, 1968), South Dakota (Gustafson, 1933), India (Rao, 1934), and Britain (Tilley, 1938).

Formation of grunerite from siderite and quartz may be written

$$7\,FeCO_3 + 8\,SiO_2 + H_2O = Fe_7Si_8O_{22}(OH)_2 + 7\,CO_2 \qquad (21)$$

The equilibrium depends on both f_{CO_2} and f_{H_2O}, but is independent of f_{O_2} for a purely ferrous grunerite. On a plot of f_{O_2} vs T, for specified f_{CO_2} and f_{H_2O}, the reaction would appear as a line parallel to the f_{O_2} axis, intersecting the siderite stability field at some temperature below that of maximum stability.

Magnetite is a commonly associated mineral in such rocks, suggesting that two other related reactions are possible under the same conditions

$$3\,FeCO_3 + \frac{1}{2}\,O_2 = Fe_3O_4 + 3\,CO_2 \qquad (4)$$

$$7\,Fe_3O_4 + 24\,SiO_2 + 3\,H_2O + 3\,Fe,\,Si_8O_{22}(OH)_2 + \frac{7}{2}\,O_2 \qquad (22)$$

Formation of grunerite in magnetite-quartz assemblages (Equation 22) is observed in iron formations at the same level of metamorphism (Miles, 1943, 1946, James, 1955, Marmo, 1956, Figure 2).

The present experimental data on siderite stability indicate that siderite is not stable above 465°C, on this basis, an approximate temperature of about 300° to 400°C is estimated for the formation of grunerite from iron carbonates These temperatures correspond approximately to the equilibrium between siderite and magnetite under the experimental conditions, and they will vary slightly in the natural environment, depending on f_{CO_2}, f_{H_2O}, and the amounts of other cations present in the carbonate These estimates are consistent with geological observations. James (1955) observed that grunerite develops in iron formations approximately coincident with the appearance of garnet in associated pelitic rocks, he estimates a temperature of about 300°C for the garnet isograd in this region.

Grunerite is invariably produced by metamorphism of siderite-quartz assemblages, indicating that water is generally available. No occurrence of fayalite produced anhydrously from the reaction of siderite + quartz has been recognized. As mentioned earlier, the stability fields of pure siderite and fayalite do not intersect under the experimental conditions, and, in the absence of water, a siderite + quartz assemblage would be converted to magnetite + quartz, which could then react to form fayalite at sufficiently low values of f_{O_2} (Yoder, 1957, Gundersen and Schwartz, 1962, French, 1968). These conclusions apply rigorously only to pure siderite and fayalite. Intermediate Mg-Fe carbonates (Huebner, 1969) and olivines (Fisher, 1967) will be stable at higher values of f_{O_2} Reactions between intermediate Mg-Fe carbonates and quartz to form Mg-Fe olivines may be stable at

f_{O_2} values above the quartz-fayalite-magnetite buffer curve. Such reactions may explain the occasional occurrences of siderite-olivine assemblages in metamorphosed iron-rich rocks (Tilley, 1936, Klein, 1966)

In localities where quartz is absent from siderite-bearing rocks, magnetite is produced by metamorphism. Goodwin (1962) has described magnetite-rich aureoles produced in a pure siderite bed by a diabase dike at Michipicoten, Ontario A minor amount of grunerite is also found in the aureole, associated with magnetite and quartz in the non-carbonate iron formation. Temperatures above 400°C at this locality are likely on both geological and mineralogical grounds.

Hydrothermal veins commonly contain siderite as a late-stage mineral (see e.g., Lindgren, 1933, Shaw, 1959). The well-known siderite-rich vein at Roxbury, Connecticut (Silliman, 1820) contains siderite and quartz without grunerite, suggesting a temperature of formation below 300-400°C. The rocks which enclose the vein have been metamorphosed to the sillimanite grade (Gates, 1959), suggesting that the vein was emplaced after the main period of metamorphism. Similar temperatures for formation of siderite-bearing veins have been estimated from other experimental data on the stability of Fe-Mg carbonates themselves (Johannes, 1968, 1969) on the basis of the instability of siderite and Fe-rich carbonates above about 400°C in aqueous solutions

SUMMARY AND CONCLUSIONS

The stability of siderite, $FeCO_3$, depends on the value of f_{O_2} as well as on P_{CO_2} and T. Determinations of siderite stability were carried out in an atmosphere of CO_2 + CO, using solid-phase buffer assemblages to control f_{O_2}.

The stability field of siderite + gas is circumscribed by stable decompositions to (1) hematite, (2) magnetite, (3) magnetite + graphite The latter reaction lies in a condensed region below the graphite buffer curve which is not experimentally accessible Reactions of siderite to form iron and wüstite are metastable.

The univariant equilibrium curve siderite + hematite + magnetite + gas (SHMG) passes through the points 363°C at P_F = 500 bars, and 365°C at P_F = 1000 bars. The univariant equilibrium curve siderite + magnetite + graphite + gas (SMGrG) passes through the points 455°C (500 bars), 458°C (1000 bars), and 465°C (2000 bars). The experimental curves lie at considerably higher temperatures than do those calculated from available thermodynamic data. Temperatures for the same equilibria derived from sealed-tube experiments (Weidner and Tuttle, 1964, Weidner, 1968) lie at even higher temperatures Thermodynamic analysis of the experimental data indicates that these differences could result entirely from experimental uncertainties The differences could also be produced if the value of $\Delta G^\circ_{f\,T}$ for siderite at elevated temperatures is about 4 percent more positive than the presently accepted value. The quality of the available thermodynamic data for siderite indicates that such a difference is quite possible

Under the experimental conditions of the present study, the stability field of siderite + gas is entirely separated from the stability field of fayalite, and reactions between siderite and quartz to produce fayalite are metastable. This observation agrees with the apparent absence of natural siderite-fayalite assemblages The addition of SiO_2 to the system Fe-C-O thus has no effect on the stability field of siderite + gas beyond the addition of quartz to all assemblages

Geological application of the experimental results is complicated by the fact that (1) natural siderites generally contain other elements in solid solution, and (2) natural gas phases during metamorphism contain considerable H_2O, so that $P_{CO_2} + P_{CO} < P_F$ Maximum stability temperatures for pure siderite between 500 and 2000 bars $P_{CO_2} + P_{CO}$ are established by the univariant curve siderite + magnetite + graphite + gas, which passes through the interval 455-465°C. The effects of conditions where $P_{CO_2} + P_{CO} < P_F$ will be to lower these temperatures slightly The stability of siderite is strongly dependent upon f_{O_2}, slight variations in this quantity will stabilize the assemblage siderite + magnetite + gas over a temperature interval of about 100°C

Studies of metamorphosed iron formation indicate that siderite in these rocks reacts with available quartz and water to form grunerite-rich amphiboles The reaction probably occurs at temperatures between 300° and 400°C Coexistence of siderite and quartz (as in many hydrothermal veins) indicates probable temperatures of formation below these values Formation of magnetite during contact metamorphism of quartz-free siderite-rich iron formations probably occurs at temperatures above 400°C

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