

STABILITY RELATIONS OF SIDERITE (FeCO_3) IN THE SYSTEM Fe-C-O

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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 $\text{CO}_2 + \text{CO}$ atmosphere as a function of T , $P_F (= P_{\text{CO}_2} + P_{\text{CO}})$, and f_{O_2} , using solid-phase oxygen buffers. Siderite was synthesized for the experiments by decomposition of ferrous oxalate dihydrate ($\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) in sealed tubes at 2000 bars $P_{\text{H}_2\text{O}}$ and approximately 380°C . The value of 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 wüstite (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, $T = 363 \pm 10^\circ\text{C}$, $\log f_{\text{O}_2} = -24.8$; $P_F = 1000$ bars, $T = 365 \pm 10^\circ\text{C}$, $\log f_{\text{O}_2} = -24.7$. The univariant equilibrium curve: siderite + magnetite + graphite + gas (SMGrG) passes through the following points: $P_F = 500$ bars, $T = 455 \pm 10^\circ\text{C}$, $\log f_{\text{O}_2} = -25.7$; $P_F = 1000$ bars, $T = 458 \pm 10^\circ\text{C}$, $\log f_{\text{O}_2} = -25.2$; $P_F = 2000$ bars, $T = 465 \pm 10^\circ\text{C}$, $\log f_{\text{O}_2} = -24.4$.

In an isobaric f_{O_2} - T section, the univariant equilibrium: siderite + hematite + gas (SHG) corresponds to low temperatures and relatively high f_{O_2} values. The univariant equilibrium: 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 $P_{\text{CO}_2} + P_{\text{CO}}$. The univariant equilibrium: siderite + magnetite + graphite + gas fixes the maximum stability temperatures of siderite, 455° to 465°C in the range $P_F = 500$ to 2000 bars. In this range, siderite is not stable at f_{O_2} values above about 10^{-21} 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 with $P_{\text{CO}_2} + P_{\text{CO}} < P_F$ will produce 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° to 450°C . Conversely, the coexistence of siderite + quartz in many hydrothermal veins suggests temperatures below this value. Conversion of quartz-free siderite units to magnetite in contact-metamorphic aureoles probably occurs at temperatures exceeding 400° to 450°C .

SYMBOLS AND NOTATIONS USED

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

T = temperature ($^\circ\text{K}$).

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 $\sum P_i = P_t$.
 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 $\Delta V_s = \sum (V_s)_{\text{products}} - \sum (V_s)_{\text{reactants}}$.
 $\Delta G^\circ_{f,T}$ = 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 $\sum (\Delta G^\circ_{f,T})_{\text{products}} - \sum (\Delta G^\circ_{f,T})_{\text{reactants}}$.
 $\Delta H^\circ_{f,T}$ = 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)	Wü = wüstite (Fe_{1-x}O)
H = hematite (Fe_2O_3)	Gr = graphite (C)
M = magnetite (Fe_3O_4)	Q = quartz (SiO_2)
I = iron (Fe)	F = fayalite (Fe_2SiO_4)
G = gas phase in a $\text{CO}_2 + \text{CO}$ 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 is 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, et cetera) designate phases that may be in equilibrium with the observed phases but that were not detected, for example, the assemblage $S + M + h$.

INTRODUCTION

Iron-bearing minerals are of particular interest in petrogenetic studies because they participate in reactions involving oxidation and reduction (Eugster, 1959; Buddington and Lindsley, 1964). Their occurrence, compositions, and stability relations not only reflect the values of T and f_{O_2} during formation but also provide information about the be-

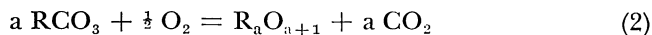
havior of other volatile components (H_2O , CO_2 , and others) (Mueller, 1960; Kranck, 1961; Klein, 1966; French, 1968; Butler, 1969).

Siderite (FeCO_3) is a common constituent of low-grade sedimentary iron formations and some hydrothermal veins. The mineral is of particular interest because, as an iron carbonate, its stability is dependent on pressure, temperature, and the fugacities of both CO_2 and O_2 . Experimental determination of siderite stability relations therefore provides useful data for estimating the values of T , f_{O_2} , and f_{CO_2} present during certain types of chemical sedimentation, low- to medium-grade metamorphism, and hydrothermal activity.

The term siderite here refers to calcite-type carbonates in which the FeCO_3 end-member is dominant. Complete solid solution apparently exists between Fe^{2+} and Mg^{2+} and between Fe^{2+} and Mn^{2+} (Palache, Berman, and Frondel, 1944; Goldsmith, 1959; Rosenberg, 1963a, 1963b, 1967), and although carbonates with over 95 mole percent FeCO_3 have been reported (Hutchinson, 1903; Ford, 1917), most natural siderites contain significant amounts of Mg^{2+} and Mn^{2+} . (For analyses, see Ford, 1917; Sundius, 1925a, 1925b; Schoklitsch, 1935; Palache, Berman, and Frondel, 1944; Hügi, 1945; Smythe and Dunham, 1947; Deer, Howie, and Zussman, 1962, p. 272-277; James, 1954; French, 1968.)

Natural siderite is commonly associated with iron-rich dolomite (ankerite) and is most commonly found in sedimentary iron formations (James, 1954; Pettijohn, 1957; Carozzi, 1960) and in hydrothermal veins (Lindgren, 1933; Wahlstrom, 1935; Lefraye, 1938; Fabian, Mueller, and Roese, 1957; Shaw, ms). (For detailed information on other occurrences, see Deer, Howie, and Zussman, 1962, p. 272-277; French, 1970). Siderite is present in moderately metamorphosed iron-rich rocks, generally associated with the iron-amphibole grunerite (Gustafson, 1933; Tilley, 1938; 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; Bonnicksen, ms).

Two types of decarbonation reactions exist for natural carbonate minerals (Jamieson and Goldsmith, 1960):



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} .

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).

Siderite (FeCO_3) and rhodochrosite (MnCO_3) decompose according to reaction (2). Their stability is a function of T , P_{CO_2} , and P_{O_2} , and these three variables must be controlled simultaneously for rigorous stability determinations (French and Eugster, 1965; Huebner, 1969).

The effect of f_{O_2} has generally not been considered in previous studies of siderite stability. Siderite is not stable under atmospheric conditions ($P_{\text{O}_2} = 0.2$ atm) as has been demonstrated by several lines of evidence (French, 1970): (1) thermodynamic calculations (Holland, 1959, 1965; Garrels, 1960); (2) conversion of natural siderite to iron oxides or hydroxides upon exposure to the atmosphere or to near-surface ground waters (Silliman, 1820; Burchard, 1924; Smythe and Dunham, 1947); (3) experimental room-temperature oxidation of siderite (Schaller and Vlisisdis, 1959; Jamieson and Goldsmith, 1960; Seguin, 1966).

The absence of f_{O_2} control in DTA (differential thermal analysis) studies of siderite decomposition makes the results difficult to interpret (for details, see French, 1970). The experiments were performed apparently under metastably high f_{O_2} values, as indicated by the strong effect of different furnace atmospheres on reaction temperature (Rowland and Jonas, 1949; Kissinger, McMurdie, and Simpson, 1956; Powell, 1965) and by the change in observed reaction temperature with changes in heating rate (Kissinger, McMurdie, and Simpson, 1956).

Subsolidus relations in the system $\text{CaCO}_3\text{--MgCO}_3\text{--MnCO}_3\text{--FeCO}_3$ have been studied hydrothermally at elevated temperatures, using values of P_{CO_2} high enough to prevent dissociation of the carbonate (Goldsmith, and others, 1962; Rosenberg and Harker, 1956; Rosenberg, 1963a, 1963b, 1967). In these studies, f_{O_2} was not controlled, and occasional oxidation of siderite to magnetite was observed (Rosenberg, ms, p. 8; Goldsmith and others, 1962, p. 660). More recent hydrothermal studies on the decomposition and stability of siderite itself (Weidner and Tuttle, 1964; Weidner, ms; Seguin, 1968; Johannes, 1968, 1969) were made also without explicit f_{O_2} control.

The present study of siderite stability is the first in which definite control of f_{O_2} has been established by the use of open capsules surrounded by a solid-phase oxygen buffer (French and Eugster, 1965; Huebner, 1969). Preliminary data on siderite stability obtained by this method have already been presented (French, 1965; French and Eugster, 1965; French and Rosenberg, 1965).

THERMODYNAMIC CALCULATION OF SIDERITE STABILITY

Preliminary thermodynamic calculation of the stability field of siderite was undertaken to: (1) determine the general shape of the stability field and the relations between possible stable and metastable reactions; (2) allow subsequent comparison between calculated and experimentally determined stability data.

Sufficient thermodynamic data exist for calculation of the stability field of siderite in terms of P_{CO_2} , f_{O_2} , and T (see, for example, Garrels and

Christ, 1965; Holland, 1959, 1965; Mel'nik, 1964; Yui, 1966). The stability field of siderite is considered to be bounded by six possible reactions (table 1, eqs 3-8).

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° to 600°K. Neither author considered possible reactions involving siderite and graphite.

In the present study, $\Delta G^\circ_{\text{f,T}}$ data for siderite were calculated from thermodynamic data (Kelley and Anderson, 1935). Values of $\Delta G^\circ_{\text{T}}$ for each reaction were calculated using values for the oxides tabulated by Coughlin (1954). The calculated values of $\Delta G^\circ_{\text{T}}$ 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 $\Delta G^\circ_{\text{T}}$ is thus only a minimum value. Data on the other physical properties of the phases involved are summarized elsewhere (Eugster and Wones, 1962; French, ms, 1970).

Values of ΔS° and ΔH° for each reaction (table 1) were calculated from the free energy data, using the relations:

$$\left(\frac{\partial \Delta G^\circ}{\partial T} \right)_p = -\Delta S^\circ \quad (9)$$

$$\left(\frac{\partial \frac{\Delta G^\circ}{T}}{\partial \frac{1}{T}} \right)_p = \Delta H^\circ \quad (10)$$

(Lewis and others, 1961, p. 165). ΔS° and ΔH° for all reactions are virtually independent of T over the temperature range 298° to 1200°K.

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

$$\begin{aligned} \Delta G^\circ_{\text{T}} &= -2.303 RT \log K(T) \\ \log K(T) &= \frac{-\Delta G^\circ}{2.303 RT} \end{aligned} \quad (11)$$

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 $P_{\text{F}} = P_{\text{CO}_2}$ 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 cal-

TABLE 1
Calculated thermodynamic data for siderite decomposition reactions

Reaction	ΔG°_{298} (cal)	ΔG°_m (cal)	$\log K_1(T)$
3. Siderite + O ₂ = hematite + CO ₂ 2 FeCO ₃ + $\frac{3}{2}$ O ₂ = Fe ₂ O ₃ + 2 CO ₂ $\log K_3(T) = 2 \log f_{CO_2} - \frac{3}{2} \log f_{O_2}$	- 43,850 \pm 4,500	- 26,500 - 54.29 T	+ 6012/T + 11.87
4. Siderite + O ₂ = magnetite + CO ₂ 3 FeCO ₃ + $\frac{1}{2}$ O ₂ = Fe ₃ O ₄ + 3 CO ₂ $\log K_4(T) = 3 \log f_{CO_2} - \frac{1}{2} \log f_{O_2}$	- 42,870 \pm 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 + 0.947 CO ₂ $\log K_5(T) = 0.947 \log f_{CO_2} - 0.026 \log f_{O_2}$	+ 4,490 \pm 1,800	+ 16,300 - 39.6 T	- 3564/T + 8.66
6. Siderite = iron + CO ₂ + O ₂ FeCO ₃ = Fe + CO ₂ + $\frac{1}{2}$ O ₂ $\log K_6(T) = \log f_{CO_2} + \frac{1}{2} \log f_{O_2}$	+ 66,780 \pm 1,700	+ 84,600 - 59.65 T	- 18,495/T + 13.04
7. Siderite = magnetite + graphite + O ₂ 3 FeCO ₃ = Fe ₃ O ₄ + 3 C + $\frac{5}{2}$ O ₂ $\log K_7(T) = \frac{5}{2} \log f_{O_2}$	+ 239,910 \pm 6,100	+ 268,300 - 91.69 T	- 58,656/T + 20.05
8. Siderite = iron + graphite + O ₂ FeCO ₃ = Fe + C + $\frac{3}{2}$ O ₂ $\log K_8(T) = \frac{3}{2} \log f_{O_2}$	+ 161,040 \pm 1,600	+ 178,700 - 58.97 T	- 39,068/T + 12.89

culated 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 $P_F = 2000$ bars 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 $\text{CO}_2 + \text{CO}$ 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). The 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 (fig. 1). Reaction between siderite and quartz to produce fayalite is not stable at these pressures (French and Eugster, 1962; French, ms).

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 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

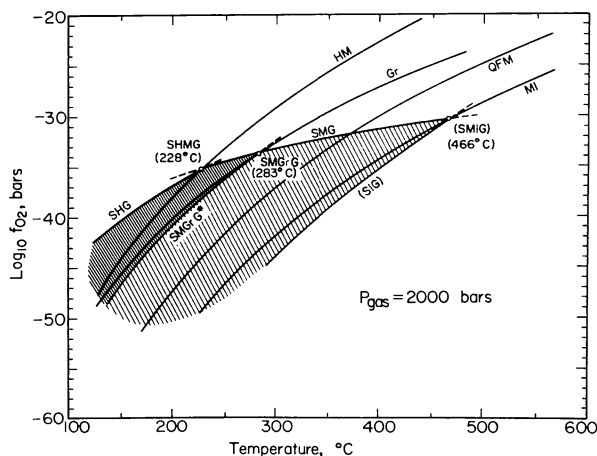


Fig. 1. Isobaric section at $P_F = 2000$ bars, showing siderite stability relations calculated from thermodynamic data. The stable field of siderite (narrow ruling) is bounded by decomposition reactions to hematite (SHG), magnetite (SMG), and magnetite + graphite (SMGrG*). The latter reaction lies entirely 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 (wide ruling) (Holland, 1959; Garrels, 1960). Other solid lines (HM, Gr, QFM, and MI) designate solid-phase oxygen buffers.

where $P_F = P_{O_2}$ (French and Eugster, 1965). The metastable reaction of siderite to iron + graphite + O_2 (reaction 8) also lies in this region and is similarly univariant.

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) that 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, assuming that a gas phase is always present, five phases (four solids plus gas) must coexist at a true invariant point. 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 (see French and Eugster, 1965).

The thermodynamic calculations are useful in predicting approximate stability relations in advance of actual experimental work. However, uncertainties in the thermodynamic data produce large uncertainties in calculated equilibrium temperatures of the invariant points. Calculations for the equilibrium point: siderite + hematite + magnetite + gas (SHMG) give *minimum* uncertainties of $\pm 50^\circ\text{C}$ at $P_F = 1$ bar and $\pm 90^\circ\text{C}$ at $P_F = 2000$ bars (for details, see French, 1970, p. 9-10). Under these conditions, significant discrepancies between calculated and experimentally determined equilibrium temperatures may reasonably be expected.

EXPERIMENTAL METHODS

In high-pressure hydrothermal studies of oxidation-reduction reactions, control of f_{O_2} is attained by surrounding the sample with an "oxygen buffer" consisting of one or more solid phases whose presence fixes the oxygen fugacity for any given temperature and total pressure (Eugster,

1957, 1959). This technique has been successfully applied in hydrothermal studies of iron-bearing minerals whose stabilities are dependent on f_{O_2} (Turnock and Eugster, 1962; Ernst, 1962; Eugster and Wones, 1962; Buddington and Lindsley, 1964; Wones and Eugster, 1965). The attainment of equilibrium in these experiments was demonstrated by the consistency and reversibility of the reactions studied (Eugster and Wones, 1962; Turnock and Eugster, 1962). The principle of buffering can be applied to any system involving solid-gas equilibria. Similar buffers can be used in $\text{CO}_2 + \text{CO}$ atmospheres (French and Eugster, 1965; Huebner, 1969), 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 $\text{CO}_2 + \text{CO}$ 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 $P_F = P_{\text{CO}_2} + P_{\text{CO}}$, the values of f_{CO_2} , f_{CO} , and f_{O_2} for any given temperature can be calculated (French, ms; 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, ms).¹

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:

$$\log f_{\text{O}_2} = -24,912/T + 14.41 + 0.019(P_t - 1)/T \quad (12)$$

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

$$\log f_{\text{O}_2} = -20,586/T - 0.044 + \log P_F - 0.028(P_t - 1)/T. \quad (13)$$

The experimental techniques used in this study are conventional and have been described in detail elsewhere (French, ms, 1970; French and Eugster, 1965; Huebner, 1969). The sample and buffer, in open silver tubes, were contained in externally-heated Tuttle-type cold-seal bombs in a CO_2 atmosphere (fig. 2). Diffusion of CO_2 through the buffer surrounding the sample adjusted the CO_2/CO ratio of the gas to correspond to

¹ In this experimental system, the statement that $P_F = P_{\text{CO}_2} + P_{\text{CO}}$ is not rigorously correct, because the gas phase will also contain small amounts of dissolved species from the solid products and from the reaction vessel itself. The effects of such species on P_F is negligible, particularly at the relatively low reaction temperatures studied here, but it must be remembered that all results and conclusions are based on a system in which solution equilibrium between the gas phase and the solids is present (see Eugster, 1959, p. 398).

the f_{O_2} value specified by the buffer assemblage and the run temperature. Under the experimental conditions, only a few percent reaction was sufficient for equilibration (French and Eugster, 1965). Measured values of P_F are believed accurate to ± 5 percent and run temperatures to $\pm 5^\circ\text{C}$.

Analytical grade Fe_3O_4 and Fe_2O_3 were used for buffer materials (for details, see French, ms, p. 140-142). Graphite was obtained by grinding spectrograph electrodes. The siderite used as samples was synthesized as needed (see below) and used soon after synthesis to avoid possible oxidation during long storage at room temperature.

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 was 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

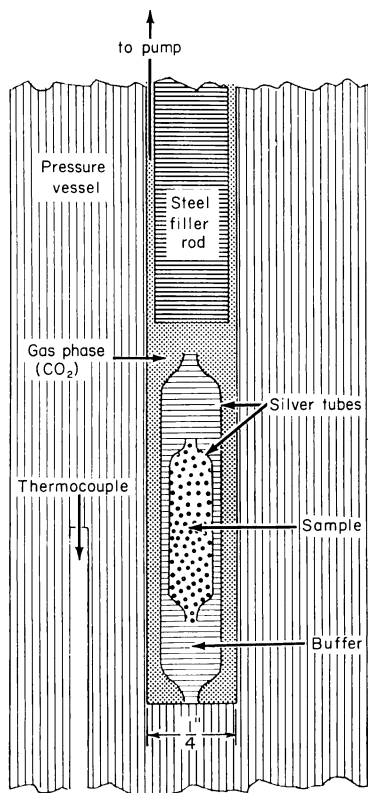


Fig. 2. Cutaway sketch of run assembly. In most runs, the sample (large dotted area) is synthetic siderite, and the buffer (horizontal ruled area) is a mixture either of hematite + magnetite or of magnetite + graphite. Buffering of the sample is established by diffusion of the gas phase (stippled area) through the buffer.

the run temperature was above the stability field of siderite, the siderite sample decomposed to the oxides 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.

After a run, sample and buffer were examined initially under a binocular microscope and 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, however, 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 were indicated by the presence of strongly magnetic grains or of larger grains of siderite showing discoloration or opaque inclusions. 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

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, Berman, and Frondel, 1944; Sharp, 1960; Graf, 1961; Powell, 1965; Johannes, 1968, 1969). A second method of synthesis involving decomposition of ferrous oxalate dihydrate ($\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) has been developed independently by several workers (Rosenberg, ms; French, ms; Weidner, ms).

The siderite used in this study was synthesized by decomposition of ferrous oxalate dihydrate. Between 100 and 400 mg of reagent grade $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ was placed in a sealed silver tube and heated to between 350° and 380°C under 2 kb water pressure. Run times ranged between 6 and 452 hours and were generally between 40 and 115 hours. Neither reaction time nor temperature were 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 to 120 hours duration.

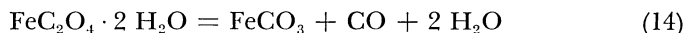
The siderite produced was a gray-white crystalline powder which gradually assumed a light buff or brownish color on drying at room temperature. The material was identified as siderite by both optical and X-ray methods. The individual siderite grains are colorless to pale yellow, ranging in size from less than 1 μm to 10 μm ; 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, ms). A partial analysis of the oxalate and a synthetic siderite, obtained through the kindness of Dr. B. F. Jones and Miss S. Rettig of the U.S. Geological Survey, indicated that divalent cations other than iron are not present in significant amounts either in the oxalate or the synthetic siderite (French, 1970, p. 16).

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, ms), for which the value of $2\theta_{111}$ was redetermined as 28.701° for CuK_α radiation, using a quartz standard (Lake Toxaway, N.C.) (French, 1970, p. 17). Measurement of the $2\theta_{104}$ value can be made to $\pm 0.02^\circ$. The values of d_{104} thus determined are consistent to ± 0.001 Å and are believed accurate to this value.

The average value of d_{104} determined from four synthetic siderites is 2.7919 Å, 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 Å (run 29, HM buffer, 230°C ; $\log f_{O_2} = -34.8$); 2.7913 Å (run 52, HM buffer, 318°C , $\log f_{O_2} = -27.5$); 2.7908 Å (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 Å, 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, ms), 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 synthesis of siderite from ferrous oxalate dihydrate may be written:



Formation of siderite in these experiments was accompanied by production of a number of complex oxygenated organic compounds (acids, alcohols, and possibly ketones) in the gas phase inside the sample tube

(French, ms, p. 65-68; 1970, p. 17-19). These compounds could be detected by the distinctive odor produced on opening the reaction vessels and sample tube after synthesis, and their complex character was qualitatively identified by a cursory mass-spectrometric analysis kindly performed by Dr. T. C. Hoering of the Carnegie Institution of Washington Geophysical Laboratory.

The production of such organic compounds appears to be an integral part of the formation of siderite by this method. Such formation is probably promoted by: (1) the reducing character of the gases produced by decomposition of $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (see French and Eugster, 1965; French, 1966); (2) the low f_{O_2} established by the hydrothermal vessel (approximately the Ni-NiO buffer, or $\log f_{\text{O}_2} \cong -30$ at 400°C ; Eugster and Wones, 1962); (3) catalysis promoted by the iron-bearing solid phases or the pressure vessel.

Similar inorganic reactions may also have produced the organic compounds now found in meteorites (for detailed references, see French, 1970). These results also suggest that formation of organic compounds can occur at elevated temperatures and high gas pressures which correspond to moderate depths in a planetary crust, where the existence of a reduced gas phase may be favored by low f_{O_2} values controlled by equilibrium between graphite or other minerals (French, 1966, 1970). Organic compounds formed during hydrothermal activity at moderate depth could then be released to the surface, providing material for 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 $P_{\text{F}}-f_{\text{O}_2}-T$ 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 bars P_{F} by reversing reactions in samples of siderite surrounded by hematite-magnetite buffers (table 2; fig. 3). The values obtained are:

P_{F}	$T(\pm 10^\circ\text{C})$	$-\log f_{\text{O}_2} (\pm 0.8)$
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 made necessarily 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).

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 _{O₂} (bars)	Time (hrs)	Products	
					Sample	Buffer
P _F = P _{CO₂} + 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 _{CO₂} + 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 _{CO₂} + 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)

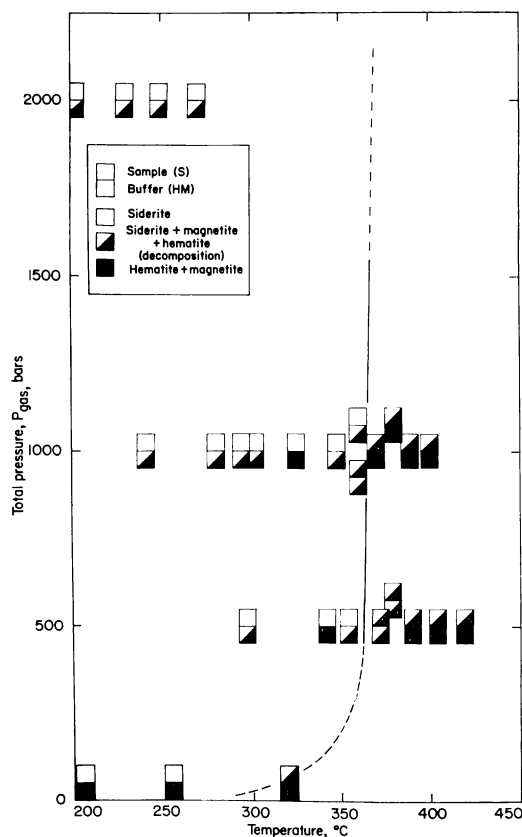


Fig. 3. Plot of $P_F = P_{\text{CO}_2} + P_{\text{CO}}$ against T , showing location of the experimentally determined univariant curve: siderite + hematite + magnetite + gas (SHMG). Dashed portions of the curve are extrapolated from runs made at 500 and 1000 bars. In each run symbol, upper box denotes 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.

An equilibrium temperature of $363 \pm 10^\circ\text{C}$ is estimated 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 $365 \pm 10^\circ\text{C}$, 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 established clearly. Reactions were extremely sluggish at 2000 bars; several runs held for 5 weeks at about 300°C showed no detectable change in

either direction. In several runs at 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 high pressures may inhibit diffusion of gaseous reactants and products through the solid sample and buffer, thus producing a drastic reduction in reaction rates that are slow even at lower pressures. Such a kinetic explanation for the lack of reaction at 2000 bars is favored by the observed greater degree of reaction in both directions 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 (fig. 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, $T = 418^\circ\text{C}$). In this run, the siderite sample recrystallized into larger single crystals 5 μm to 20 μm in size; 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.

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; fig. 4). Data obtained for the SMGrG curve are:

P_F (bars)	$T(\pm 10^\circ\text{C})$	$-\log f_{\text{O}_2} (\pm 0.8)$
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; fig. 5). Below the equilibrium temperatures buffer decompositions of 2 to 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 $455 \pm 10^\circ\text{C}$.

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 $458^\circ \pm 10^\circ\text{C}$.

At $P_F = 2000$ bars, the equilibrium temperature lies between runs 92 (462°C) and 76 (469°C) and is estimated as $465 \pm 10^\circ\text{C}$. Above this temperature, siderite samples were increasingly decomposed; no siderite remained in a sample run at 537°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; fig. 5).

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

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)	Sample	Products Percent decom- position	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

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

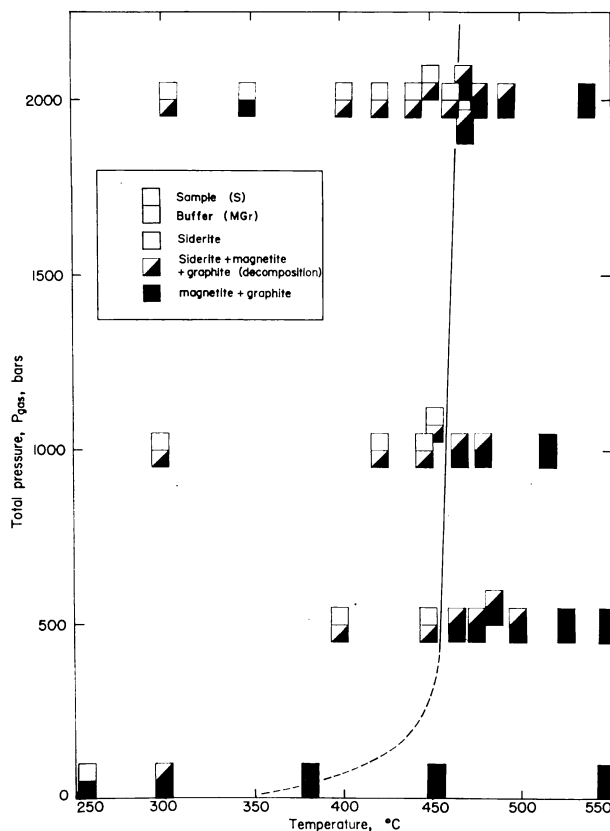


Fig. 4. Plot of $P_F = P_{\text{CO}_2} + P_{\text{CO}}$ against T , showing location of the experimentally determined univariant curve: siderite + magnetite + graphite + gas (SMGrG). In each run symbol, the upper box denotes behavior of the siderite sample, the lower box denotes behavior of the buffer. 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.

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 (fig. 6) (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 $\text{CO}_2 + \text{CO}$ gas phase.—Buffering in a $\text{CO}_2 + \text{CO}$ atmosphere involves mechanical diffusion of gas species

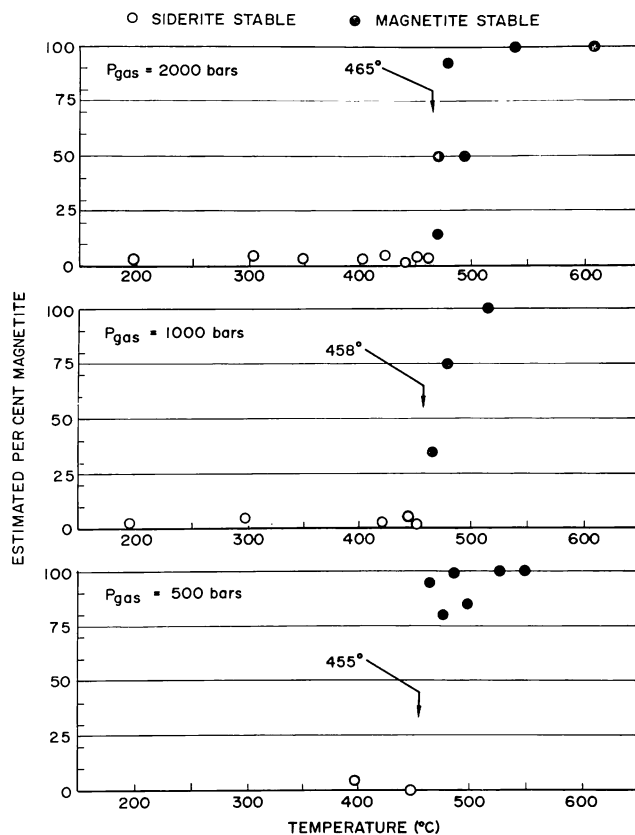


Fig. 5. Plot of estimated percentage of siderite sample decomposition as a function of temperature for runs used to locate the univariant curve: siderite + magnetite + graphite + gas (SMGrG). The equilibrium temperatures (455°-465°C) are located by the sharp increase in decomposition with increasing 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.

through the solid buffer and requires that the necessary solid-gas equilibration reactions take place in times that are short compared to run duration (French and Eugster, 1965). If these conditions are not met at the reaction temperatures involved (300°-500°C), then equilibrium will not be attained, and the determinations will not correspond to equilibrium siderite decomposition temperatures.

The problem of reaction and buffering by graphite is especially important. 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 and others, 1961; Bank and Verdurmen, 1963), although

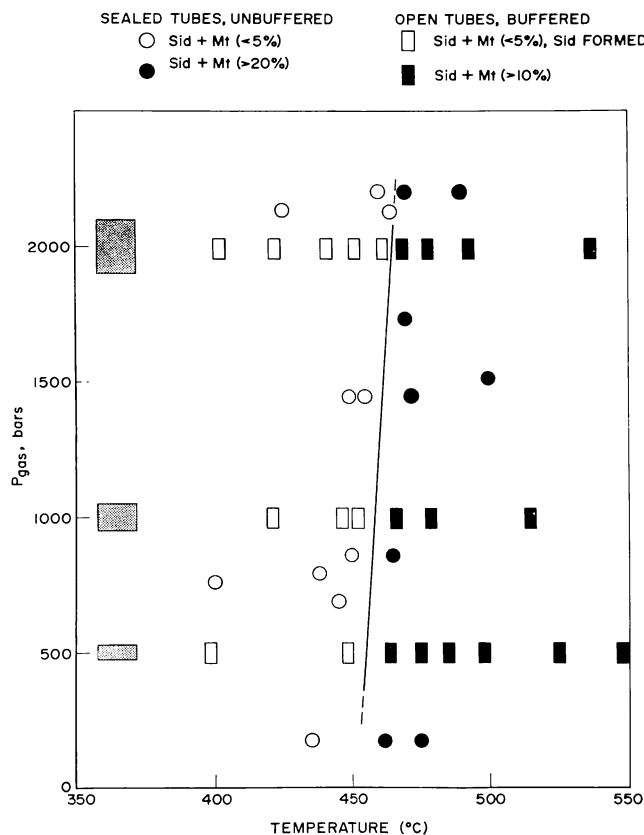


Fig. 6. Location of the univariant equilibrium: siderite + magnetite + graphite + gas, as determined by open-tube buffered runs (French, ms; rectangles) and by sealed-tube experiments (Rosenberg; circles) (from French and Rosenberg, 1965). The solid line indicates the univariant curve established from the open-tube buffered experiments; the sealed-tube experiments correspond virtually to the same curve. Stippled rectangles at left indicate the experimental uncertainty, $\pm 7^\circ\text{C}$ in run temperature and ± 5 percent in total pressure.

there is little information about reaction rates at the high temperatures and pressures of the present experiments.

There is also little information about the rates of equilibration of $\text{CO}_2 + \text{CO}$ atmospheres when graphite is present originally 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° to 600°C .

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 a run, but indirect evidence indicates that the buffer assemblage does in fact control

the f_{O_2} value imposed on the sample (French, 1970). The experimental conditions, involving relatively high temperatures (300°-500°C), long reaction times (generally two weeks), and the presence of siderite, iron oxides, and an Ni-Co alloy reaction vessel as potential catalytic agents, offer optimum conditions for equilibration of the gas phase with the buffer. The following observations indicated that such buffering did in fact occur:

1. Complete reduction of the hematite-magnetite buffer to magnetite occurred during long runs near 400°C, indicating that extensive reaction does occur between the gas phase and buffer at these temperatures.

2. Distinctly different equilibrium decomposition temperatures are obtained, depending on whether the hematite-magnetite (HM) or magnetite-graphite (MGr) buffer assemblages are used.

3. Both hematite and magnetite are observed as decomposition products of siderite samples surrounded by a hematite-magnetite buffer.

4. In runs with the graphite buffer, graphite (or amorphous carbon) is observed to precipitate from the gas phase, indicating that metastably low CO_2/CO ratios are not maintained in the gas phase and that reaction between graphite and the gas does establish an equilibrium f_{O_2} (Rosenberg, 1963a; French and Rosenberg, 1965). A similar carbon phase occurs with magnetite in samples of siderite decomposed above the equilibrium temperature.

The temperatures determined for siderite decomposition are therefore believed to be 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.—Studies of siderite stability using hydrothermal techniques (Weidner and Tuttle, 1964; Weidner, ms; Johannes, 1968, 1969; Seguin, 1968) cannot be rigorously compared with the present investigations (for detailed discussion, see French, 1970, p. 31-35). In none of the studies was f_{O_2} explicitly controlled, and the values of f_{O_2} during the experiments are not known. Further, some investigations were carried out with a gas phase containing H_2O (Johannes, 1968, 1969; Seguin, 1968). In such cases, only the total pressures are specified, and the partial pressures of individual species, particularly CO_2 and CO , are unknown.

The experiments of Weidner (Weidner and Tuttle, 1964; Weidner, ms) are more comparable with the present study because they were performed in an atmosphere of $\text{CO}_2 + \text{CO}$, but they were carried out in sealed tubes without external buffers. In Weidner's experiments, the 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. Ideally, these reactions should correspond, respectively, to the SHMG and SMGrG curves determined in the present study.

Decomposition temperatures determined in these experiments (Weidner and Tuttle, 1964; Weidner, ms) are significantly higher than those observed for analogous reactions in the present study (French, 1965; French and Rosenberg, 1965) (fig. 7). Because of slow reaction 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 (fig. 7) gives approximately similar decomposition temperatures, although the slopes of the two curves are

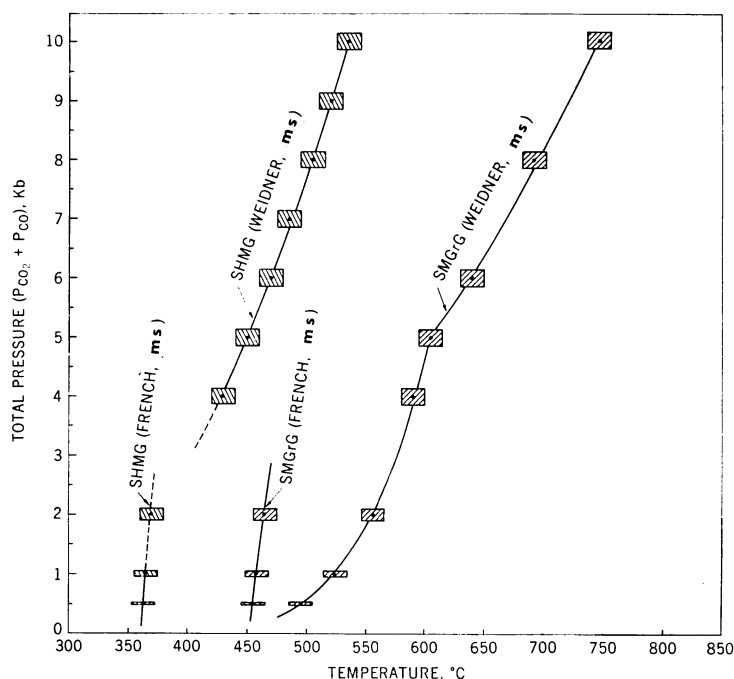


Fig. 7. Location of the two univariant curves: siderite + hematite + magnetite + gas (SHMG) and siderite + magnetite + graphite + gas (SMGrG) as determined by open-tube buffered experiments (French, ms) and by sealed-tube experiments (Weidner and Tuttle, 1964; Weidner, ms). The greatest discrepancy is for the SMGrG curve, for which Weidner's determined equilibrium temperatures below 2000 bars are 50° to 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.

distinctly different. The disagreement is more severe for the reaction: siderite + magnetite + graphite + gas (fig. 7). The temperatures determined by Weidner are from 60° to 90°C higher than those determined here.

The exact causes of the large temperature difference in the two investigations are not clear. Nor is it obvious why the results of Weidner's sealed-tube experiments also differ greatly from the apparently similar sealed-tube experiments of Rosenberg (French and Rosenberg, 1965).

The sealed-tube technique differs from the present experimental method in several ways that may affect the interpretation of the results (for details, see French, 1970):

1. There is no direct control of f_{O_2} , and it must be assumed that f_{O_2} is buffered during the run as the necessary phases are produced by reaction. However, the decomposition of siderite to magnetite or hematite produces a gas phase with high contents of CO which correspond to f_{O_2} values that are metastably low with respect to the graphite buffer (French and Eugster, 1965; French, 1970). At metastably low values of f_{O_2} , the decomposition of siderite to magnetite will take place at temperatures above the true equilibrium temperature (see fig. 1).

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

3. Compaction of the sample tube and charge occurs during pressurization. This effect may reduce reaction rates by restricting the removal of volatile products produced in the solid sample. Further, during run-up, part of the external pressure is supported by the solid sample. These effects produce a complex and uncertain pressure-temperature history in the sample until sufficient decomposition has occurred to equalize the internal and external gas pressures.

4. Decomposition of the sample during run-up is necessary to produce internal gas pressure in the sample tube. The potential presence of decomposition products in *all* runs makes it difficult to recognize the true equilibrium temperature from the amount of sample decomposition. The estimated equilibrium temperature is thus a function of the value chosen for the amount of sample decomposition during run-up (French and Rosenberg, 1965), and, if this value is too high, the resulting equilibrium temperatures determined will also be too high.

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 the stability relations of carbonates which involve oxidation reactions. The open-tube method permits direct calculation and control of f_{O_2} . Further, the open tubes minimize any kinetic problems that may arise 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

TABLE 4

Temperature and gas composition data for equilibrium points determined on the univariant curves, with thermodynamic data for the reaction: $3 \text{ siderite} + \frac{1}{2} \text{O}_2 = \text{magnetite} + 3 \text{CO}_2$ at these points

P_F (bars)	$T^\circ\text{C}$ (calc)	$T^\circ\text{C}$ (expt.)	$-\log f_{\text{O}_2}$ (bars)	f_{CO} (bars)	f_{CO_2} (bars)	$\log K_1(T)$ (calc)	ΔG°_r (kcal) (calc)	$\log K_1(T)$ (expt.)	ΔG°_r (kcal) (expt.)
Siderite + hematite + magnetite + gas (SHMG)									
500	212	363	24.8	3.4×10^{-4}	535	+26.23	-75.7	$+20.58 \pm 1.0$	-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	$+21.12 \pm 1.0$	-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.

can be more precisely estimated, particularly in the case of the SMGrG equilibrium (fig. 5). Accordingly, the temperatures obtained in the present study are believed to be the true equilibrium temperatures for the reactions studied.

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 fig. 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 (fig. 8), the siderite + gas field occupies a narrow

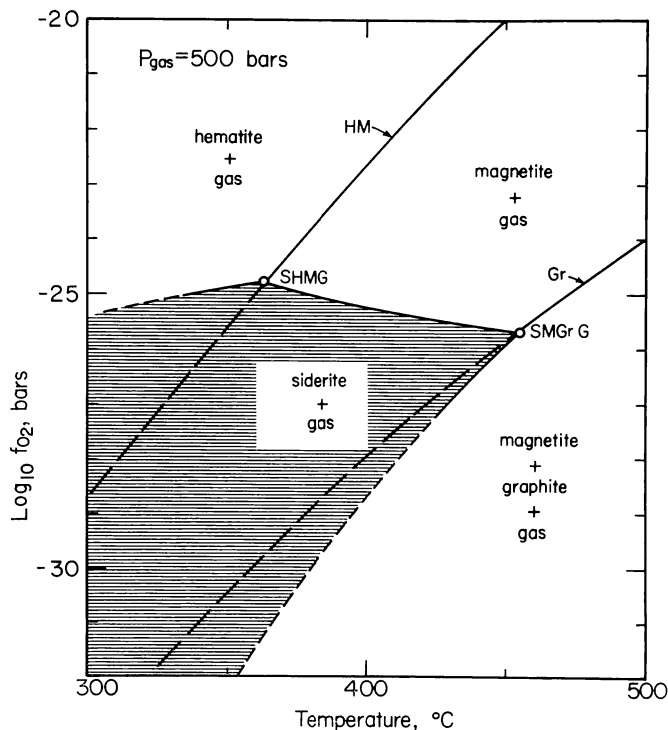


Fig. 8. Isobaric section at $P_F = 500$ bars, showing the stability field of siderite + gas as a function of T and $\log f_{O_2}$. The stability field is based on the experimentally determined isobaric invariant points; siderite + hematite + magnetite + gas (SHMG) (363°C ; $\log f_{O_2} = -24.8$) and 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.

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, ms; Huebner, 1969).

The graphite buffer curve (Gr) 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 $\log f_{\text{O}_2} = -24.7$. Between this point and the isobaric invariant point: siderite + magnetite + graphite + gas at 455°C and $\log f_{\text{O}_2} = -25.8$, 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.

The stability relations of siderite at total pressures of 1000 and 2000 bars are virtually identical to those at 500 bars, as a polybaric projection (fig. 9) 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} .

The section at $P_F = 2000$ bars is incomplete. The SMGrG point lies at 465°C and $\log f_{\text{O}_2} = -24.4$. 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 $\log f_{\text{O}_2} = -24.2$. The isobaric univariant SMG curve between these points is nearly horizontal.

The stability field of siderite + gas, plotted in three dimensions in P_F - $\log f_{\text{O}_2}$ - T space, 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 $\log f_{\text{O}_2}$ below

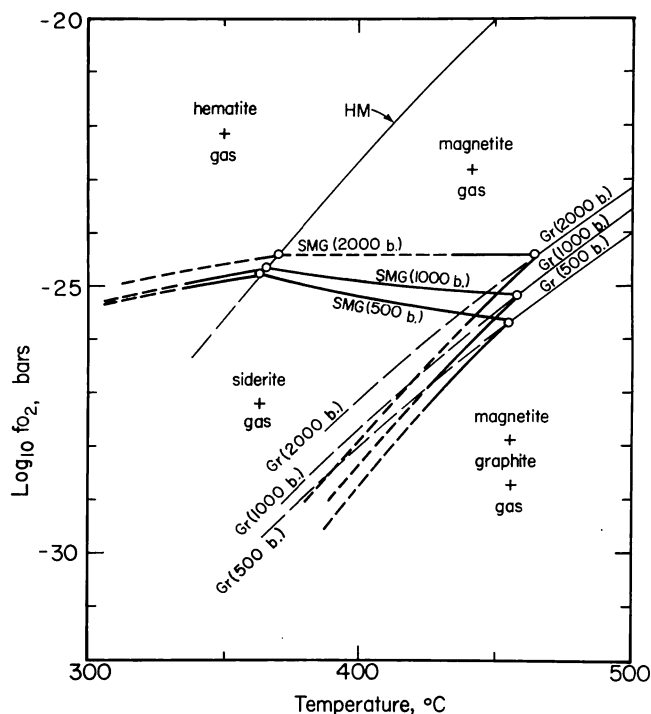


Fig. 9. Polybaric projection of the stability field of siderite + gas determined at 500, 1000, and 2000 bars $P_{\text{CO}_2} + P_{\text{CO}}$. The SHMG point at 2000 bars is extrapolated from data at lower pressures. The stability field of siderite + gas is bounded by stable decompositions to hematite + 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 $P_{\text{CO}_2} + P_{\text{CO}}$.

this surface. For this reason, the stability field of siderite + gas determined here 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 10; 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_T .

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

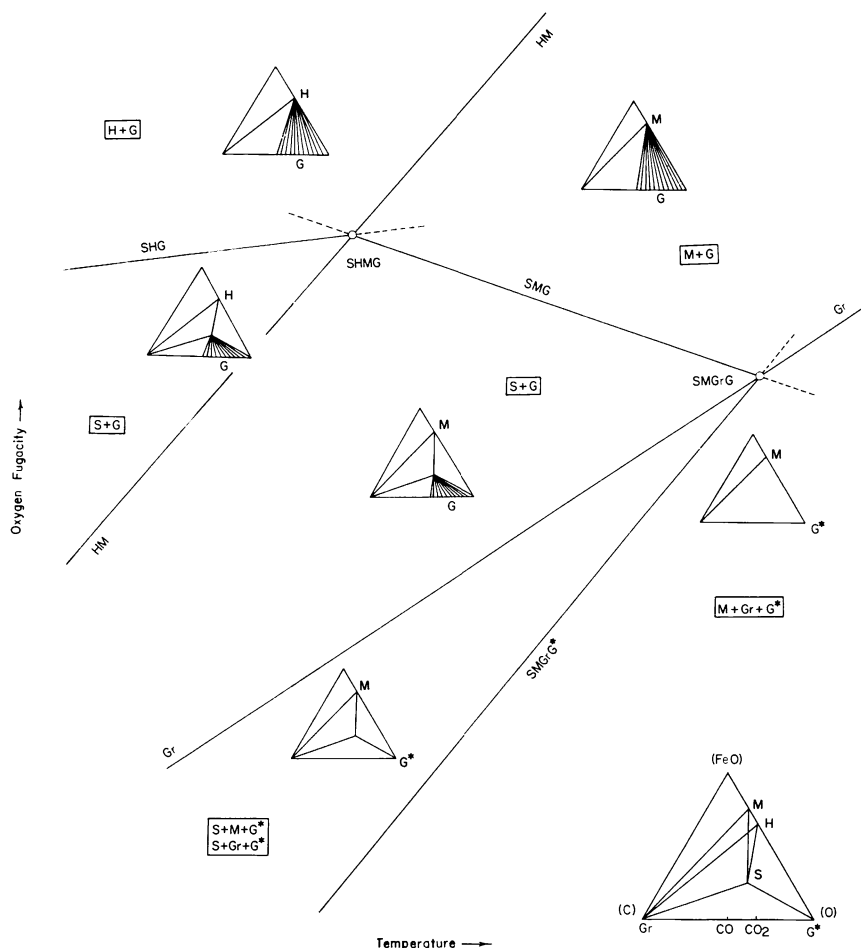


Fig. 10. Schematic isobaric section through the system Fe-C-O , showing stable assemblages as a function of $\log f_{\text{O}_2}$ and T . All solid phases coexist with a gas phase. Stable univariant equilibria are shown by solid lines; metastable extensions are dashed. Boxes indicate assemblages stable in each region. Above the graphite buffer curve (Gr), $P_F = P_{\text{CO}_2} + P_{\text{CO}}$, the gas phase is variable in composition, and an assemblage of one solid + gas is divariant. Below the graphite buffer curve, $P_F = P_{\text{O}_2}$, and two solids + gas form a divariant assemblage.

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.²

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 $\log f_{\text{O}_2}$. For example, at 500 bars, a change in $\log f_{\text{O}_2}$ 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.

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, fig. 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 (eq 4) by computing values for

$$\log K_4 = 3 \log f_{\text{CO}_2} - \frac{1}{2} \log f_{\text{O}_2} \quad (4)$$

and applying the relationships:

$$\Delta H^\circ = -2.303R(d \log K/d(1/T)) \quad (15)$$

$$\Delta G^\circ = -2.303R T \log K. \quad (16)$$

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 $\Delta G^\circ_{f,T}$

² Recently redetermined values for f_{O_2} along the quartz-fayalite-magnetite buffer (Wones and Gilbert, 1969) are slightly more positive than those used here (Eugster and Wones, 1962). These new values extend the fayalite stability field to slightly higher f_{O_2} values and bring it closer to the siderite stability field (see fig. 1). However, calculations based on the new data do not indicate that there is any intersection or overlap of the two fields.

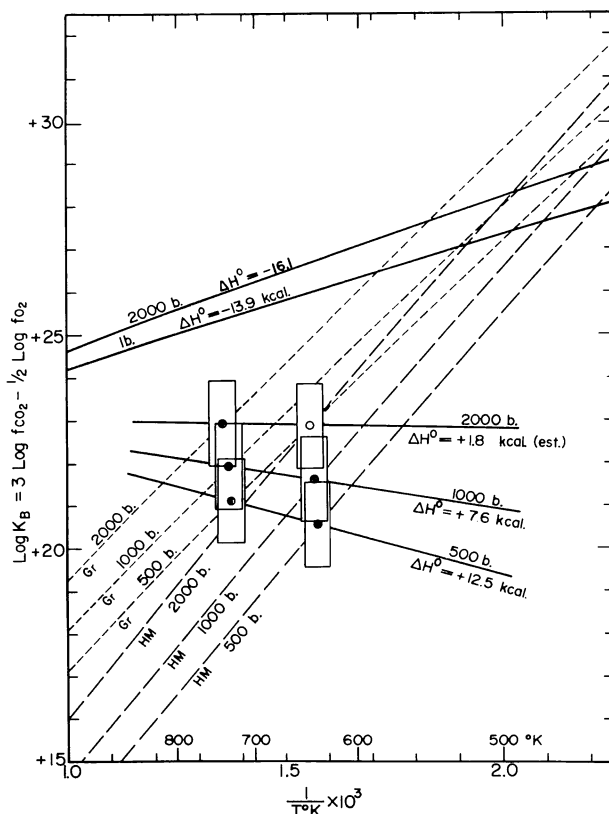


Fig. 11. Comparison of calculated and experimentally determined values of ΔH° for the reaction: $3 \text{ siderite} + 1/2 \text{ O}_2 = \text{magnetite} + 3 \text{ CO}_2$ (eq 4), derived from plotting the equilibrium constant against $1/T$. Values of $\log K_4(T)$ ($\equiv \log K_B$) derived from thermodynamic data are shown by solid lines for $P_r = 1$ bar and 2000 bars. Dashed lines indicate values of the quantity: $3 \log f_{\text{CO}_2} - 1/2 \log f_{\text{O}_2}$ 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 $\log K_4$ ($\equiv \log K_B$) 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 ($\log K_4 \pm 1.0$; $1/T \times 10^3 \pm 0.03$). 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 $\log K_4$ suggests that the derived values of ΔH° may not be meaningful.

for siderite. Eugster and Wones (1962) applied the same method to calculate thermodynamic data for the iron-biotite, annite.

Experimentally determined values of $\log K_4$ (table 4; fig. 11) are quite closely grouped and are considerably smaller than values calculated from ΔG° for 1 bar and 2000 bars. The lines that connect each pair of experimental points at the same total pressure have high negative slopes

which become more negative at lower pressures, in contrast to the positive slopes of the calculated lines (fig. 11).

Values of ΔH° calculated 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 from thermodynamic data (fig. 11). 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 between calculated and experimental values of ΔG° (table 4); the experimental results are about 10 kcal/mole more positive. Assuming that ΔS° is constant with temperature, the experimental results yield a value of $\Delta S^\circ = +111$ cal/mole-deg, in contrast to a calculated value of about +96 cal/mole-deg (table 1).

Using the relationship:

$$\Delta G^\circ_{298^\circ\text{K}} = \Delta G^\circ_{\text{T}} + \Delta S^\circ (\text{T} - 298) \quad (17)$$

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

Approximate values of ΔG° and ΔH° can be calculated from Weidner's (ms) data by assuming that $f_{\text{CO}_2} = P_{\text{F}}$ (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 (ms) data yield values of $\Delta G^\circ_{298} = -29.1$ kcal/mole, $\Delta H^\circ = -1.4$ kcal/mole, $\Delta S^\circ = +93$ cal/mole-deg (table 6).

Thermodynamic data for the decomposition of siderite to magnetite (eq 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 reaction. 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 in-

TABLE 5
Calculated and experimentally determined values of ΔH° for the
reaction: 3 siderite + $\frac{1}{2}$ O₂ = magnetite + 3 CO₂

P_{F} (bars)	ΔH° (kcal)	
	calc	expt.
1	-13.9 \pm 7.0	—
500	—	+12.5
1000	—	+7.6
2000	-16.1 \pm 7.0	+1.8(*)

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

licate 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° (eq 15) involves the quotient of two small difference terms, and even reasonable estimates of experimental uncertainty ($T_{\text{eq}} \pm 10^\circ\text{C}$; $\log K_4 \pm 1.0$) produce uncertainties as large as several hundred percent in the derived value of ΔH° .

The corresponding values of ΔG° are less affected; the stated experimental uncertainties produce an uncertainty in ΔG° of about 5 to 8 percent or about ± 5 kcal/mole, comparable to the uncertainty in the value of ΔG° derived from thermodynamic data (table 1). However, the subtractions and other operations necessary to derive values for ΔG°_{298} (eq 17) multiply this uncertainty to the point where the calculated value of ΔG°_{298} has a minimum uncertainty of about 100 percent.

Because of the large uncertainties, the differences between the various calculated and experimental values in table 6 are probably not significant. The difficulty of using the experimental data to evaluate the experiments themselves is further indicated by the fact that the strongly divergent experimental results of French (ms) and Weidner (ms) give comparable values for the thermodynamic parameters at 298°K .

These results emphasize the extreme difficulty of integrating available thermodynamic data with experimental results in this particular system. The uncertainties in available thermodynamic data make it difficult to calculate equilibrium decomposition temperatures with any pre-

TABLE 6
Calculated thermodynamic data for siderite formation and decomposition to magnetite at 298°K

1. Reaction: $3 \text{FeCO}_3 + 1/2 \text{O}_2 = \text{Fe}_3\text{O}_4 + 3 \text{CO}_2$			
	ΔG°_{298} (kcal)	ΔH°_{298} (kcal)	ΔS°_{298} (cal/mole-deg)
Calculated (French, ms and this study) (table 1)	-42.87	-13.90	+ 96.4
Experimental (French, ms and this study)	-25.49	- 7.60	+ 111.1
Weidner (ms)	-29.10	- 1.39	+ 93.0
Holland (1965)*	-22.12	+ 7.43	+ 99.3
Yui (1966)*	-29.7	- 0.14	+ 99.3
2. Reaction: $\text{Fe} + \text{C} + 3/2 \text{O}_2 = \text{FeCO}_3$			
	$\Delta G^\circ_{f,298}$ (kcal/mole)	$\Delta H^\circ_{f,298}$ (kcal/mole)	$S^\circ_{298}(\text{siderite})$ (cal/mole-deg)
Calculated (Robie, 1966)	-161.06	-178.20	23.9
Experimental (French, ms and this study)	-166.6	-185.4	17.7

* Recalculated from author's original values for the analogous reaction: $3 \text{FeCO}_3 = \text{Fe}_3\text{O}_4 + 2 \text{CO}_2 + \text{CO}$.

cision (see above, and French, 1970, p. 9-10). Conversely, uncertainties in the experimental stability determinations are sufficient to prevent precise calculation of the thermodynamic properties of siderite from the experimental results, and values so calculated may not be any more accurate than the original data.

New values of thermodynamic parameters of siderite were, however, calculated from the experimental data on the assumptions that the differences between calculated and experimentally derived values of ΔG°_{298} , ΔH°_{298} , and ΔS°_{298} for reaction (4) were real and were due entirely to the thermodynamic data for siderite. With these assumptions, 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° to 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 produce 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° to 700°K than are values determined by direct measurement (Moore, 1943) and that similar differences are observed in values of $\Delta G^\circ_{f,T}$ 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 $P_{\text{CO}_2} + P_{\text{CO}} < P_F$. These effects must be considered in estimating the decomposition temperatures for natural siderite.

The effect of conditions where $P_F \neq P_{\text{CO}_2}$ may be approximately calculated for the SHMG and SMGrG univariant curves from the relation:

$$\left(\frac{\partial P_s}{\partial T}\right)_{P_{\text{FeCO}_2}} = \frac{\Delta S}{\Delta V_s} = \frac{dP_t}{dT} \times \frac{\Delta V_s + (V_{\text{CO}_2})_{P_{\text{FeCO}_2}}}{\Delta S} \quad (18)$$

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

$$\left(\frac{\partial P_s}{\partial T}\right)_{P_{\text{FeCO}_2}} = \frac{dP_t}{dT} \times \frac{\Delta V}{\Delta V_s} \quad (19)$$

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 $(\partial P_s/\partial T)_{P_{\text{FeCO}_2}}$ are approximately -40 to -80 bars/deg.

The corresponding univariant curves for fixed values of P_{FeCO_2} will lie at temperatures below the univariant curves specified by the condition $P_t = P_{\text{CO}_2}$ (Thompson, 1955; Greenwood, 1961, fig. 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_{FeCO_2} . The decomposition of siderite to magnetite thus represents a geothermometer that is strongly affected by changes in f_{O_2} but that is relatively insensitive to changes in both P_{FeCO_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 and moderate $P_{\text{H}_2\text{O}}$ values. Available stability data on the iron hydroxides (Deer, Howie, and Zussman, 1962, p. 118-127; Berner, 1969) 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 (fig. 12) 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 de-

bility relations of the pure end-members (fig. 12; 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.

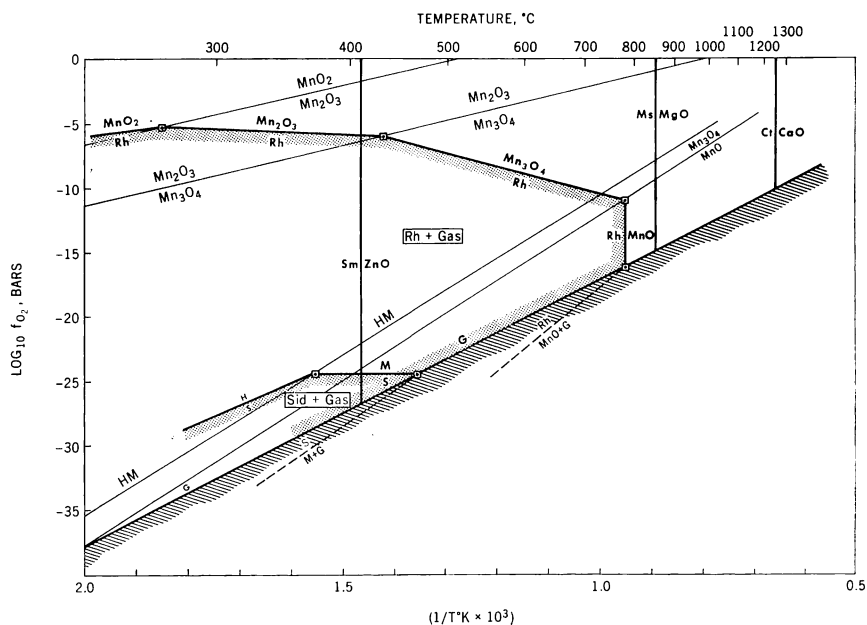
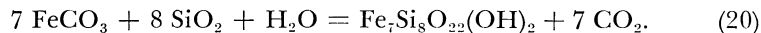


Fig. 12. Isobaric section at $P_F = P_{CO_2} + P_{CO} = 2000$ bars, showing stability relations of siderite and other carbonates as a function of $\log f_{O_2}$ and $1/T$. Heavy lines indicate carbonate decomposition reactions; light lines indicate oxygen buffer curves. The condensed region below the 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 Tuttle, 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.

Siderite-hematite assemblages (presumably primary) are occasionally found in sedimentary iron formation (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_{FeCO_2} in the coexisting gas phase. For pure siderite, 465°C is the maximum temperature of stable existence between 500 and 2000 bars $P_{\text{CO}_2} + P_{\text{CO}}$.

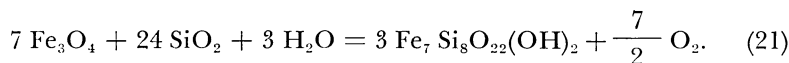
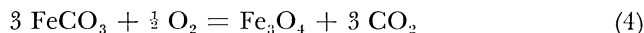
Geological studies of metamorphosed iron formations indicate that iron-rich siderites generally do not decompose directly to magnetite. Instead, they react with the available quartz and water to produce amphiboles rich in the grunerite ($\text{Fe}_7\text{Si}_8\text{O}_{22}(\text{OH})_2$) end-member. Such reaction has been 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:



The equilibrium depends on both f_{CO_2} and $f_{\text{H}_2\text{O}}$ but is independent of f_{O_2} for a purely ferrous grunerite. On a plot of f_{O_2} versus T , for specified f_{CO_2} and $f_{\text{H}_2\text{O}}$, 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:



Formation of grunerite in magnetite-quartz assemblages (eq 21) is observed in iron formations at the same level of metamorphism (Miles, 1943, 1946; James, 1955; Marmo, 1956, fig. 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} , $f_{\text{H}_2\text{O}}$, 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, for example, Lindgren, 1933; Shaw, ms). The well-known siderite-rich vein at Roxbury, Conn. (Silliman, 1820) contains siderite and quartz without grunerite, suggesting a temperature of formation below 300° to 400°C. The rocks that 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.

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