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

$$\left(\frac{\partial P_s}{\partial T}\right)_{P_{E_{CO_2}}} = \frac{\Delta S}{\Delta V_s} = \frac{dP_t}{dT} \times \frac{\Delta V_s + (V_{CO_2})_{P_{E_{CO_2}}}}{\Delta S} \qquad (18)$$

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

$$\left(\frac{\partial P_s}{\partial T}\right)_{P_{E_{CO_2}}} = \frac{dP_t}{dT} \times \frac{\Delta V}{\Delta V_s} \qquad (19)$$

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 $(\partial P_s/\partial T)_{P_{E_{CO_2}}}$ are approximately -40 to -80 bars/deg.

The corresponding univariant curves for fixed values of $P_{E_{CO_2}}$ will lie at temperatures below the univariant curves specified by the condition $P_t = P_{CO_2}$ (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 $P_{E_{CO_2}}$. 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 $P_{E_{CO_2}}$ and P_t.

A second effect of water in the gas phase is the potential stabilization of iron hydroxides such as goethite and lepidocrocite (FeO.OH), particularly at lower temperatures and moderate P_{H_2O} 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-be oriented at diverse angles within the envelope established by the sta-

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.
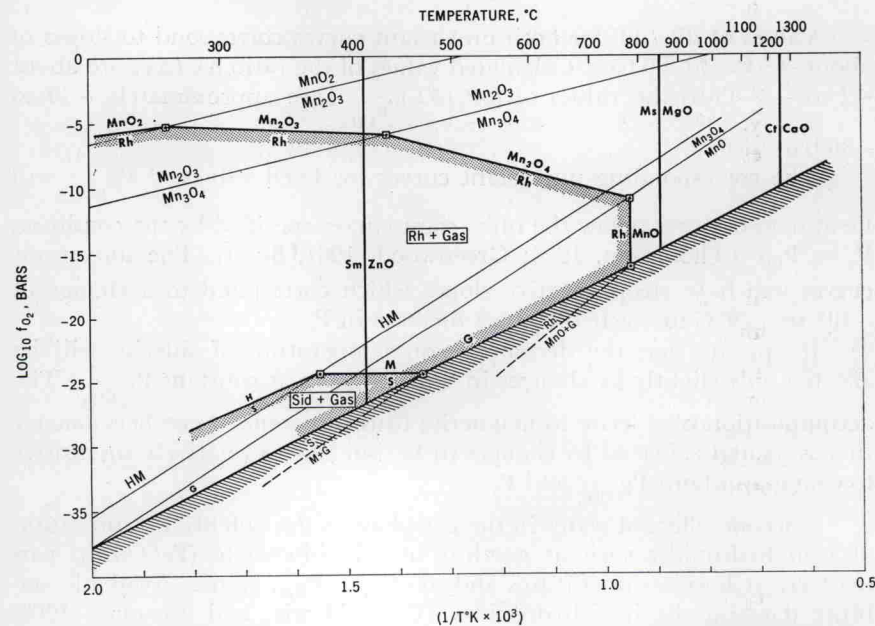

Fig. 12. Isobaric section at $P_F = P_{CO_2} + P_{CO} = 2000$ bars, showing stability relations of siderite and other carbonates as a function of log f_{O_2} and $1/T$. Heavy lines indicate carbonate decomposition reactions; light lines indicate oxygen buffer curves. The condensed region below the graphite 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 Hutta, 1956), magnesite ($MgCO_3$) (Ms) (Harker and Tuttle, 1955a), and calcite ($CaCO_3$) (Ct) (Harker and Tuttle, 1955a). The relative positions of the stability fields indicate that the introduction of Mn^{2+}, Mg^{2+}, and Ca^{2+} into siderite will stabilize the resulting Fe-rich carbonate to higher temperatures and f_{O_2} values. The effect of included Zn^{2+} will be to stabilize the carbonate at higher f_{O_2} values with only a minor change in stability temperatures.