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

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

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

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

The graphite buffer surface (GrG) forms the lower boundary of the experimentally accessible portion of the field of siderite + gas. Reactions involving siderite and CO_2 become metastable at values of log f_{O_2} below

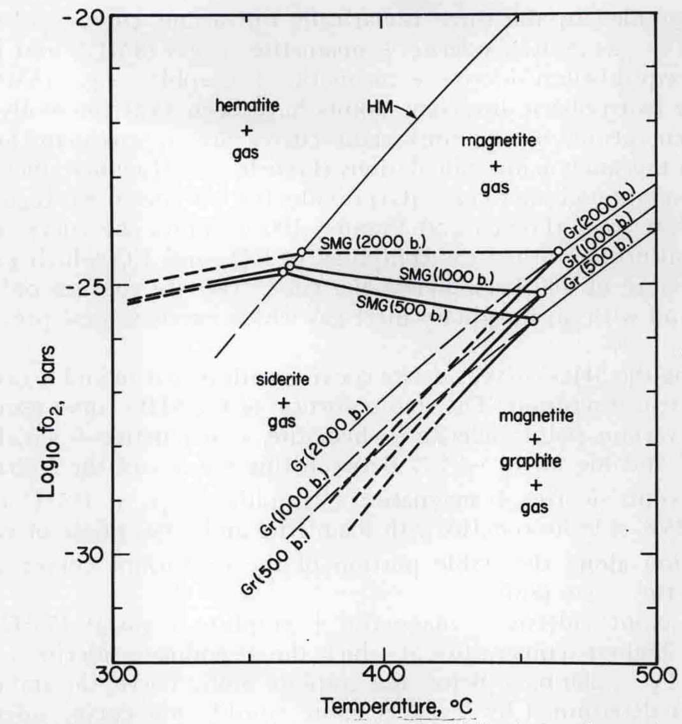

Fig. 9. Polybaric projection of the stability field of siderite + gas determined at 500, 1000, and 2000 bars $P_{CO_2} + P_{CO}$. The SHMG point at 2000 bars is extrapolated from data at lower pressures. The stability field of siderite + gas is bounded by stable decompositions to hematite + gas, to magnetite + gas, and to magnetite + graphite + gas. The size of the field of siderite + gas is only slightly affected by changing total pressure between 500 and 2000 bars; most of the effect arises from the change in location of the graphite buffer curve (Gr) with changing $P_{CO_2} + P_{CO}$.

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_F.

The assemblage siderite + gas is stable over a relatively narrow range of f_{O_2} values; below 2000 bars, siderite is not stable above 10^{-24} bars