

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 $CO_2 + CO$ 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 $CO_2 + CO$ atmosphere, combined with solid polyphase oxygen buffers to control the value of f_{O_2} (French and Eugster, 1965; Huebner, 1969). Independent control of the two volatiles, CO_2 and O_2 , is thus possible, since, for a given $P_F = P_{CO_2} + P_{CO}$, the values of f_{CO_2} , f_{CO} , and f_{O_2} for any given temperature can be calculated (French, 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:

$$\log f_{O_2} = -24,912/T + 14.41 + 0.019(P_t - 1)/T \quad (12)$$

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:

$$\log f_{O_2} = -20,586/T - 0.044 + \log P_F - 0.028(P_t - 1)/T. \quad (13)$$

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

¹In this experimental system, the statement that $P_F = P_{CO_2} + P_{CO}$ 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

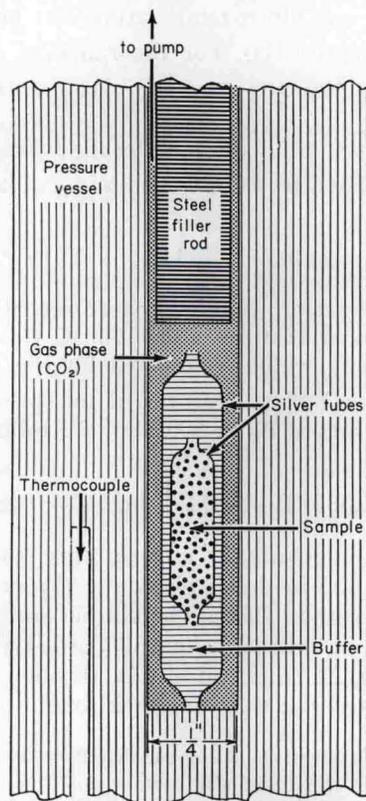


Fig. 2. Cutaway sketch of run assembly. In most runs, the sample (large dotted area) is synthetic siderite, and the buffer (horizontal ruled area) is a mixture either of hematite + magnetite or of magnetite + graphite. Buffering of the sample is established by diffusion of the gas phase (stippled area)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