

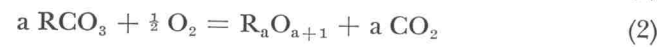
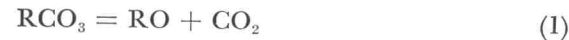
havior of other volatile components (H_2O , CO_2 , and others) (Mueller, 1960; Kranck, 1961; Klein, 1966; French, 1968; Butler, 1969).

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; Legraye, 1938; Fabian, Mueller, and Roesse, 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 Vlisidis, 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