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 $P_{E\,CO_2}$ in the coexisting gas phase. For pure siderite, 465°C is the maximum temperature of stable existence between 500 and 2000 bars $P_{CO_2} + P_{CO}$.

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 ($Fe_7Si_8O_{22}(OH)_2$) 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:

$$7\,FeCO_3 + 8\,SiO_2 + H_2O = Fe_7Si_8O_{22}(OH)_2 + 7\,CO_2. \tag{20}$$

The equilibrium depends on both f_{CO_2} and f_{H_2O} 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_{H_2O}, 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:

$$3\,FeCO_3 + \tfrac{1}{2}\,O_2 = Fe_3O_4 + 3\,CO_2 \tag{4}$$

$$7\,Fe_3O_4 + 24\,SiO_2 + 3\,H_2O = 3\,Fe_7\,Si_8O_{22}(OH)_2 + \frac{7}{2}\,O_2. \tag{21}$$

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_{H_2O}, 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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