(1) Diamond Synthesis
(2) Siderite
(3) Geology

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Siderite ($FeCO_3$): Thermal Decomposition in Equilibrium with Graphite

Abstract. *The thermal stability of siderite ($FeCO_3$) was studied by two independent methods in which the oxygen fugacity of the gas phase was controlled by equilibration with graphite. Both series of experiments indicate that siderite decomposes stably to magnetite + graphite between 455° and 465°C at 500 to 2000 bars* $P_{CO_2} + P_{CO}$.

The thermal decomposition of divalent carbonates may be expressed by two distinct types of reactions (*1*), where R represents the cation.

$$R\ CO_3 = RO + CO_2 \qquad (1)$$

$$a\ RCO_3 + 1/2\ O_2 = R_aO_{a+1} + a\ CO_2 \qquad (2)$$

The stabilities of such minerals as calcite ($CaCO_3$), magnesite ($MgCO_3$), and smithsonite ($ZnCO_3$), whose cations do not oxidize during reaction, have been determined (*2*, *3*). However, the carbonates siderite ($FeCO_3$) and rhodochrosite ($MnCO_3$) may decompose by reactions of the second type, in which a variety of oxides may form. For this reason, the oxygen fugacity, f_{O_2}, must be controlled in studying decomposition of these carbonates.

We describe here the results of two independent sets of experiments, one performed by each of us, on the stability and decomposition relations of siderite ($FeCO_3$), in which the value of f_{O_2} was controlled by equilibration of the gas phase, composed of CO_2 and CO, with graphite (*4*, *5*).

In both series of experiments, siderite samples were contained in externally heated Tuttle-type cold-seal pressure vessels; carbon dioxide was supplied by an external pumping system (*2*). In the earlier experiments of Rosenberg (*6*), samples of synthetic siderite were contained in small sealed gold capsules; during heating, the siderite decomposed slightly, producing an internal pressure equal to that applied on the tube by the external atmosphere (*7*). In French's later study of siderite stability (*8*), decomposition relations were determined at values of f_{O_2} controlled by solid-phase oxygen buffer assemblages (*5*, *9*). Synthetic siderite samples contained in open silver tubes were surrounded by the solid buffer; diffusion of the gas phase through the buffer established equilibrium, and the value of f_{O_2} could be calculated directly.

The two types of experiments were carried out independently; comparison of results did not occur until the later study (*8*) had been completed. In both experiments, siderite was synthesized by decomposition of ferrous oxalate dihydrate ($FeC_2O_4 \cdot 2H_2O$) to siderite and gas at total pressures of 2000 bars and temperatures from 350° to 380°C.

In the sealed-tube experiments (*6*) there was no intrinsic method for control of oxygen fugacity. However, oxygen buffering was apparently established by the precipitation of graphite or amorphous carbon from the gas phase in the sealed tubes during the experiments. The duration of individual runs varied from 2 to 10 days.

The decomposition of siderite to magnetite within a sealed tube proceeds as follows:

$$3\ FeCO_3 = Fe_3O_4 + 2\ CO_2 + CO \qquad (3)$$

Ideally, the gas phase produced would have a CO_2 to CO ratio of 2; however, such a ratio is metastable with respect to the formation of graphite between 400° and 600°C (*4*). Thus, graphite would precipitate from the gas phase by the reaction

$$2\ CO = C_{(gr)} + CO_2 \qquad (4)$$

Small but significant amounts of black carbonaceous material formed within the sealed tubes during the experiments (*6*). The exact nature and degree of crystallinity of the material could not be determined because of its scarcity. However, x-ray diffraction studies of similar material precipitated within the pressure vessel in subsequent studies (*8*) indicate disordered graphite.

Production of graphite within the sealed tube will produce internal buffering of f_{O_2} by equilibria established between graphite and the gas phase (*4*, *5*). At a fixed value of P_{gas} (that is, $P_{CO_2} + P_{CO}$) the temperature at which siderite decomposes will correspond to that of the four-phase assemblage, siderite + magnetite + graphite + gas. In the three-component system, Fe-C-O, the phase rule indicates that this assemblage will be isobarically univariant. The decomposition of siderite to magnetite therefore defines a unique equilibrium temperature if, and only if, graphite is also present in the assemblage. However, reversibility of the reaction (that is, formation of siderite from magnetite) was not directly demonstrated by the sealed-tube method.

Determination of decomposition temperatures by the sealed-tube method was hampered in that some siderite decomposes below the true equilibrium temperature, producing the necessary internal pressure. Traces of magnetite (less than 5 percent of the sample volume) were attributed to such decomposition within the siderite stability field, while production of relatively large amounts of magnetite (more than 20 percent) was evidence that the decomposition temperature of siderite had been exceeded (*6*).

In subsequent experiments with buffered siderite samples in open tubes (*8*) for an independent determination of the decomposition temperatures, the buffer mixture consisted of graphite to which magnetite had been added; buffering was accomplished by the graphite alone. Reversibility of the equilib-

Table 1. Estimated decomposition temperatures for siderite in equilibration with graphite. $P_{gas} = P_{CO_2} + P_{CO}$.

P_{gas} (bars)	Sealed tubes (*6*)		Open tubes, buffered (*8*)	
	T (°C)	$-\log f_{O_2}$*	T (°C)	$-\log f_{O_2}$
500	452	25.9	455	25.7
1000	454	25.4	458	25.2
2000	463	24.5	465	24.4

* Values of log f_{O_2} calculated for the graphite + gas buffer (*5*), corrected for the effect of pressure on the solid phase.

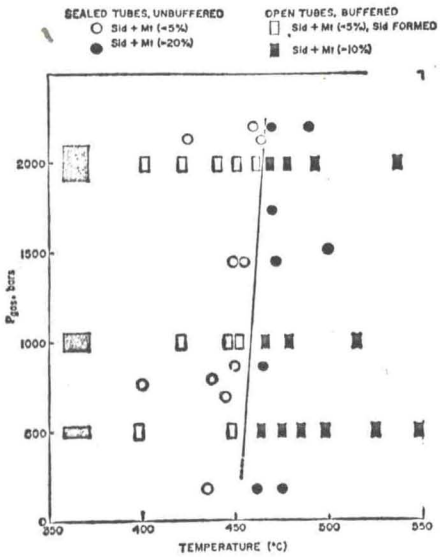

Fig. 1. Experimental results on siderite decomposition to magnetite + graphite. Sealed-tube runs (Rosenberg) shown by circles; buffered open-tube runs (French) shown by rectangles. The solid line indicates the univariant curve for the assemblage, siderite + magnetite + graphite + gas, obtained from the open-tube experiments; virtually the same curve is obtained from the sealed-tube experiments (Table 1). The large rectangles at the left-hand side indicate the experimental uncertainty, ± 7°C and ± 5 percent of the total pressure.

rium could then be demonstrated by two reactions in a single run, either by decomposition of the siderite sample or by growth of siderite from magnetite in the buffer mixture. Equilibrium temperatures were located by (i) production of siderite throughout the entire buffer below the equilibrium temperature, and (ii) production of large amounts of magnetite (in excess of 10 percent of the volume) above the decomposition temperature. The two criteria yielded consistent equilibrium temperatures.

The equilibrium temperatures obtained are compared in Table 1; Fig. 1 shows the experimental data. The temperature uncertainty for each experimental point is probably ±7°C. Agreement between the two sets of data is excellent, particularly above 860 bars, where sufficient data are available. At lower pressures, the apparent close agreement may be conditioned by the small number of sealed-tube experiments.

The agreement between decomposition temperatures determined by two different experimental methods indicates (i) that the temperatures determined do in fact represent equilibrium decomposition of siderite to magnetite and graphite, and (ii) that buffering of f_{O_2} during the sealed-tube experiments is established by precipitation of graphite or carbon from the gas phase.

The equilibrium, siderite + magnetite + graphite + gas, specifies the maximum temperature for stable existence of siderite in an atmosphere of CO_2 + CO (*8*); higher values of f_{O_2} produce lower decomposition temperatures. If graphite is absent, the assemblage, siderite + magnetite + gas, may exist over a temperature interval in excess of 100°C (*8*); this interval may be increased if gas compositions metastable with respect to graphite can be preserved. Therefore, the decomposition of siderite to magnetite cannot be used as an accurate geothermometer unless the value of f_{O_2} is specified independently in some manner, for example, by the presence of additional phases such as graphite.

Studies of metamorphosed sedimentary iron formations (*8, 10, 11*) indicate that original siderite in such rocks disappears by reaction with available silica and water to form the iron-amphibole grunerite, $Fe_7Si_8O_{22}(OH)_2$. Temperatures for this reaction must be below those for the decomposition of siderite itself, but they are dependent on the fugacities of both H_2O and CO_2 and have not been experimentally determined. Approximate temperatures of 300° to 400°C have been estimated for the formation of grunerite from geological evidence (*8, 11*); the estimates are consistent with the upper limit of siderite stability established in this study.

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