STABILITY RELATIONS OF SIDERITE (FeCO$_3$) IN THE SYSTEM Fe–C–O

BEVAN M. FRENCH

Planetology Branch, Goddard Space Flight Center, Greenbelt, Maryland 20771

ABSTRACT. Stability relations of siderite (FeCO$_3$) in the system Fe–C–O were determined between 500 and 2000 bars in a CO$_2$ + CO atmosphere as a function of T, P_F (= P_{CO_2} + P_{CO}), and f_{O_2}, using solid-phase oxygen buffers. Siderite was synthesized for the experiments by decomposition of ferrous oxalate dihydrate (FeC$_2$O$_4$. 2H$_2$O) in sealed tubes at 2000 bars P_{H_2O} and approximately 380°C. The value of f_{O_2} was controlled by surrounding the siderite sample with either graphite or hematite-magnetite buffer mixtures.

The stability field of siderite + gas in P_F–T–f_{O_2} space is a narrow wedge bounded by stable divariant reaction surfaces representing decomposition of siderite to: (1) hematite + gas, (2) magnetite + gas, (3) magnetite + graphite + O$_2$. The latter reaction surface lies entirely in the condensed region below the graphite buffer and is not experimentally accessible. Reactions of siderite to form iron or wüstite (Fe$_{1-x}$O) are not stable.

Points along the univariant equilibrium curve: siderite + hematite + magnetite + gas (SHMG) were located reversibly at: P_F = 500 bars, T = 363 ± 10°C, log f_{O_2} = −24.8; P_F = 1000 bars, T = 365 ± 10°C, log f_{O_2} = −24.7. The univariant equilibrium curve: siderite + magnetite + graphite + gas (SMGrG) passes through the following points: P_F = 500 bars, T = 455 ± 10°C, log f_{O_2} = −25.7; P_F = 1000 bars, T = 458 ± 10°C, log f_{O_2} = −25.2; P_F = 2000 bars, T = 465 ± 10°C, log f_{O_2} = −24.4.

In an isobaric f_{O_2}–T section, the univariant equilibrium: siderite + hematite + gas (SHG) corresponds to low temperatures and relatively high f_{O_2} values. The univariant equilibrium: siderite + magnetite + gas (SMG) is stable at higher temperatures and relatively lower f_{O_2} values. The stability of the assemblage siderite + gas is strongly dependent on T and f_{O_2} but is practically independent of the value of P_{CO_2} + P_{CO}. The univariant equilibrium: siderite + magnetite + graphite + gas fixes the maximum stability temperatures of siderite, 455° to 465°C in the range P_F = 500 to 2000 bars. In this range, siderite is not stable at f_{O_2} values above about 10^{-24} bars and decomposes to either hematite (lower T) or magnetite (higher T). The determined stability field of siderite + gas lies at f_{O_2} values above the stability field of fayalite (Fe$_2$SiO$_4$), and therefore reactions between siderite and quartz to form fayalite are not stable.

The stability relations of natural iron-rich carbonates are more complex than those determined for pure siderite. The presence of other volatile species in a natural gas phase with P_{CO_2} + P_{CO} < P_F will produce lower decomposition temperatures, and the presence of H$_2$O may stabilize iron hydroxide phases at lower temperatures. By contrast, the substitution of Mg^{2+}, Mn^{2+}, or Ca^{2+} for Fe^{2+} will stabilize iron-rich carbonates at higher temperatures and f_{O_2} values.

During metamorphism, natural iron-rich carbonates react with available quartz and water to produce iron-rich amphiboles (grunerite). The present experimental data, combined with geological studies of metamorphosed iron-formations, suggest that this reaction occurs at about 300° to 450°C. Conversely, the coexistence of siderite + quartz in many hydrothermal veins suggests temperatures below this value. Conversion of quartz-free siderite units to magnetite in contact-metamorphic aureoles probably occurs at temperatures exceeding 400° to 450°C.

SYMBOLS AND NOTATIONS USED

Symbols used generally follow conventions of Thompson (1955) and Greenwood (1961).

T = temperature (°K).

P_s = isotropic pressure on solid phases.

P_F = total pressure of the fluid (gas) phase.

P_{E_i} = "osmotic equilibrium" pressure of component i in a fluid phase (Greenwood, 1961).

P_t = total pressure in a closed experimental system where $P_t = P_F = P_s$.

P_i = partial pressure of component i in a closed experimental system where $\Sigma P_i = P_t$.

f_i = fugacity of component i in a fluid phase.

γ_i = fugacity coefficient of component i in the fluid phase, defined by $\gamma_i = f_i/P_i$.

ΔV_s = volume change of the solid phases in a reaction, defined as $\Delta V_s = \Sigma(V_s)_{products} - \Sigma(V_s)_{reactants}$.

$\Delta G^\circ_{f,T}$ = standard Gibbs free energy of formation of a compound from its elements at a specified temperature and unit fugacities of gaseous components.

ΔG°_T = standard Gibbs free energy of reaction, equal to $\Sigma(\Delta G^\circ_{f,T})_{products} - \Sigma(\Delta G^\circ_{f,T})_{reactants}$

$\Delta H^\circ_{f,T}$ = standard enthalpy of formation of a compound from its elements.

ΔH°_T = standard enthalpy change in a reaction.

$K_i(T)$ = equilibrium constant of reaction i, written with fugacities of gaseous components; a function of T only.

C_P = molar heat capacity of a substance at constant pressure.

ABBREVIATIONS FOR PHASES IN TABLES AND ILLUSTRATIONS

S = siderite ($FeCO_3$)	Wü = wüstite ($Fe_{1-x}O$)
H = hematite (Fe_2O_3)	Gr = graphite (C)
M = magnetite (Fe_3O_4)	Q = quartz (SiO_2)
I = iron (Fe)	F = fayalite (Fe_2SiO_4)

G = gas phase in a $CO_2 + CO$ atmosphere

G* = gas phase (O_2) in condensed region below the graphite buffer curve.

In tables of experimental results, occurrence of trace amounts of a phase is indicated by parentheses, as (S). Such occurrences are not believed to represent stable reaction products and may result from contamination or from metastable reaction. Clearly metastable products in a significant amount are indicated by an asterisk, as (S*). Small letters (m, s, h, et cetera) designate phases that may be in equilibrium with the observed phases but that were not detected, for example, the assemblage S + M + h.

INTRODUCTION

Iron-bearing minerals are of particular interest in petrogenetic studies because they participate in reactions involving oxidation and reduction (Eugster, 1959; Buddington and Lindsley, 1964). Their occurrence, compositions, and stability relations not only reflect the values of T and f_{O_2} during formation but also provide information about the be-