

## STABILITY RELATIONS OF SIDERITE ( $\text{FeCO}_3$ ) IN THE SYSTEM Fe-C-O

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

The stability field of siderite + gas in  $P_F$ - $T$ - $f_{\text{O}_2}$  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 +  $\text{O}_2$ . 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 ( $\text{Fe}_{1-x}\text{O}$ ) are not stable.

Points along the univariant equilibrium curve: siderite + hematite + magnetite + gas (SHMG) were located reversibly at:  $P_F = 500$  bars,  $T = 363 \pm 10^\circ\text{C}$ ,  $\log f_{\text{O}_2} = -24.8$ ;  $P_F = 1000$  bars,  $T = 365 \pm 10^\circ\text{C}$ ,  $\log f_{\text{O}_2} = -24.7$ . The univariant equilibrium curve: siderite + magnetite + graphite + gas (SMGrG) passes through the following points:  $P_F = 500$  bars,  $T = 455 \pm 10^\circ\text{C}$ ,  $\log f_{\text{O}_2} = -25.7$ ;  $P_F = 1000$  bars,  $T = 458 \pm 10^\circ\text{C}$ ,  $\log f_{\text{O}_2} = -25.2$ ;  $P_F = 2000$  bars,  $T = 465 \pm 10^\circ\text{C}$ ,  $\log f_{\text{O}_2} = -24.4$ .

In an isobaric  $f_{\text{O}_2}$ - $T$  section, the univariant equilibrium: siderite + hematite + gas (SHG) corresponds to low temperatures and relatively high  $f_{\text{O}_2}$  values. The univariant equilibrium: siderite + magnetite + gas (SMG) is stable at higher temperatures and relatively lower  $f_{\text{O}_2}$  values. The stability of the assemblage siderite + gas is strongly dependent on  $T$  and  $f_{\text{O}_2}$  but is practically independent of the value of  $P_{\text{CO}_2} + P_{\text{CO}}$ . 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  $f_{\text{O}_2}$  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  $f_{\text{O}_2}$  values above the stability field of fayalite ( $\text{Fe}_2\text{SiO}_4$ ), 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  $P_{\text{CO}_2} + P_{\text{CO}} < P_F$  will produce lower decomposition temperatures, and the presence of  $\text{H}_2\text{O}$  may stabilize iron hydroxide phases at lower temperatures. By contrast, the substitution of  $\text{Mg}^{2+}$ ,  $\text{Mn}^{2+}$ , or  $\text{Ca}^{2+}$  for  $\text{Fe}^{2+}$  will stabilize iron-rich carbonates at higher temperatures and  $f_{\text{O}_2}$  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 ( $^\circ\text{K}$ ).

$P_s$  = 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  $\sum P_i = P_t$ .  
 $f_i$  = fugacity of component  $i$  in a fluid phase.  
 $\gamma_i$  = fugacity coefficient of component  $i$  in the fluid phase, defined by  $\gamma_i = f_i/P_i$ .  
 $\Delta V_s$  = volume change of the solid phases in a reaction, defined as  $\Delta V_s = \sum (V_s)_{\text{products}} - \sum (V_s)_{\text{reactants}}$ .  
 $\Delta G^\circ_{f,T}$  = standard Gibbs free energy of formation of a compound from its elements at a specified temperature and unit fugacities of gaseous components.  
 $\Delta G^\circ_T$  = standard Gibbs free energy of reaction, equal to  $\sum (\Delta G^\circ_{f,T})_{\text{products}} - \sum (\Delta G^\circ_{f,T})_{\text{reactants}}$ .  
 $\Delta H^\circ_{f,T}$  = standard enthalpy of formation of a compound from its elements.  
 $\Delta H^\circ_T$  = 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

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| S = siderite ( $\text{FeCO}_3$ )          | Wü = wüstite ( $\text{Fe}_{1-x}\text{O}$ ) |
| H = hematite ( $\text{Fe}_2\text{O}_3$ )  | Gr = graphite (C)                          |
| M = magnetite ( $\text{Fe}_3\text{O}_4$ ) | Q = quartz ( $\text{SiO}_2$ )              |
| I = iron (Fe)                             | F = fayalite ( $\text{Fe}_2\text{SiO}_4$ ) |
- G = gas phase in a  $\text{CO}_2 + \text{CO}$  atmosphere  
 G\* = gas phase ( $\text{O}_2$ ) 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  $f_{\text{O}_2}$  during formation but also provide information about the be-