

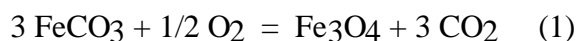
EXPERIMENTAL DETERMINATION OF SIDERITE (IRON CARBONATE) STABILITY UNDER MODERATE PRESSURE-TEMPERATURE CONDITIONS, AND APPLICATION TO MARTIAN CARBONATE PARAGENESES. Andrea M. Koziol. Department of Geology, The University of Dayton, 300 College Park, Dayton, OH 45469-2364, USA; e-mail: koziol@neelix.udayton.edu.

Introduction: Siderite (FeCO_3) occurs in metamorphosed iron formations, altered igneous rocks, and as a solid solution component in Fe-Mg carbonates that are found in carbonatites [1, 2]. Its stability is controlled in part by O_2 fugacity and CO_2 fugacity. Siderite therefore is of interest as a monitor phase of these parameters.

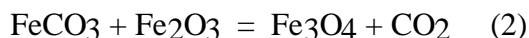
An unusual extraterrestrial occurrence of carbonate has also focused attention on siderite and Fe-Mg carbonates. The carbonate globules in ALH84001 that have intrigued the scientific community are magnesite-siderite solid solutions with variable Ca content [3 - 5]. Compositional zoning generally varies from Ca-rich cores, to magnesite-rich rims. In some samples there is an iron-rich (siderite-rich) zone outside the magnesite rims.

Although some experimental data on magnesite has recently become available [6] the data on siderite stability are limited and contradictory [7, 8] and experimental data on ternary carbonates are also contradictory [9, 10]. While it is probable that non-equilibrium processes related to variable fluid composition, low temperatures or impact processes have operated on Martian rocks, it is important to have an understanding of the equilibrium properties of siderite and other carbonate components, especially under changing temperature, pressure, oxygen fugacity, and CO_2 fugacity conditions.

The reaction of siderite with oxygen is



(Fe_3O_4 : magnetite). An easier way of performing experiments on siderite in such a system is to use an appropriate mineral phase to deliver the oxygen component:



(Fe_2O_3 : hematite). Through the presence of hematite and magnetite in the experimental charge, and the addition of hematite and magnetite surrounding the charge, the oxygen

fugacity of the experiments is defined to be on the hematite-magnetite buffer at that pressure and temperature. This is an appropriate f_{O_2} value for application of the results to Earth parageneses as well as Martian carbonates.

Experimental Method: Experiments on reaction (2) were made in a piston-cylinder apparatus, using procedures similar to those described in [6]. Samples consisted of homogenized powders of synthetic siderite, hematite, and a natural magnetite, sealed in 1 mm diameter Pt tube segments with weighed amounts of silver oxalate ($\text{Ag}_2\text{C}_2\text{O}_4$) as the CO_2 source. These piston-cylinder experiments were performed with the samples buffered with hematite + magnetite mixtures. The buffer lasted throughout the length of the experiment and weight loss data indicates all gas in the samples was CO_2 . Two methods were used to monitor reaction direction. Powder X-ray diffractometer scans of the same solid charges obtained before and after the experiments were compared. In addition weight loss upon puncturing of the sample capsule was recorded. A CO_2 yield at least 15% larger than expected from the $\text{Ag}_2\text{C}_2\text{O}_4$ decomposition indicated reaction to magnetite + CO_2 ; a CO_2 yield 15% smaller than expected signified siderite and hematite growth.

Results: Experiments on reaction 2 are shown in Figure 1. These include all experiments in which inner and outer capsules maintained their integrity. In most experiments X-ray analysis confirmed the weight-loss data. Experiments where change in volatile content or X-ray reflection intensity was not significant are considered as "no reaction". No new phases were detected in the experimental charges.

Discussion: Chai and Navrotsky [11] show that calculated decarbonation curves for siderite are shifted by 70 to 100° C (at 7 to 10 kbar), depending on the value used for H_f° of siderite. This adds greatly to uncertainties in thermobarometric calculations for metamorphosed iron formations, carbonatites, and other parageneses.

A value of the enthalpy of formation (H°_f) of siderite of -760.6 kJ (kilojoules) was derived from the present reversal data. The data set of Holland and Powell [12] version 2.3 was used for values of entropy, heat capacity, volumes of all phases and for the enthalpies of hematite and magnetite.

Work is underway to examine the reaction products of such experiments to see if textural relations involving voids or minute magnetite grains are similar to those observed in ALH 84001 [13 - 15]. Brearley [14] has hypothesized that thermal decomposition of Fe-rich carbonate produced the concentration of tiny magnetite particles seen by McKay et al [15] and no biological hypothesis is necessary.

This study can provide a framework of what equilibrium thermodynamics predicts for carbonates of this range of compositions coexisting with orthopyroxene and small grains of magnetite and SiO_2 , as is seen in ALH84001 [4, 15]. It is possible that the chemical zoning seen in these carbonates can be interpreted as changes in temperature, CO_2 or oxygen fugacity in the vicinity of the carbonate globules.

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Figure: Pressure-temperature diagram showing experimental determination of the reaction siderite + hematite = magnetite + CO_2 . Open symbols: siderite + hematite stable. Filled symbols: magnetite + CO_2 stable. Also shown is the calculated curve using the dataset of Holland and Powell (12).

