

the run temperature was above the stability field of siderite, the siderite sample decomposed to the oxides while the buffer remained unchanged. Within the stability field of siderite, the sample remained unchanged while siderite formed from the oxides in the buffer. The addition of magnetite to the graphite buffer allowed this reverse reaction to be detected.

After a run, sample and buffer were examined initially under a binocular microscope and then studied by X-ray diffraction and oil immersion methods. In many of the runs, particularly those with the HM buffer, the amount of reaction was slight. Reaction of less than 5 percent could not be detected by X-ray diffraction. Sample decomposition in small amounts could, however, be detected under the binocular microscope by the red or gray-black color produced by the iron oxides and by the magnetism of the sample. Under the petrographic microscope, small amounts of sample breakdown were indicated by the presence of strongly magnetic grains or of larger grains of siderite showing discoloration or opaque inclusions. Buffer decomposition (growth of siderite) was indicated by the formation of white areas in the buffer and could be verified under the petrographic microscope by the presence of birefringent siderite in the otherwise opaque buffer materials. As little as 0.5 percent siderite in the buffer could be detected and identified by the high birefringence and by the "twinkle" caused by the great change in relief on rotation of the microscope stage.

SYNTHESIS OF SIDERITE

Synthetic siderite was used as the starting material in this study. Natural siderites were considered undesirable because of the common partial oxidation of the material and because of the amounts of other divalent cations generally present in solid solution.

Several investigators have previously synthesized siderite by combining compounds containing Fe^{2+} and CO_3^{2-} in solution, generally under high CO_2 pressure to prevent dissociation (Palache, Berman, and Frondel, 1944; Sharp, 1960; Graf, 1961; Powell, 1965; Johannes, 1968, 1969). A second method of synthesis involving decomposition of ferrous oxalate dihydrate ($\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) has been developed independently by several workers (Rosenberg, ms; French, ms; Weidner, ms).

The siderite used in this study was synthesized by decomposition of ferrous oxalate dihydrate. Between 100 and 400 mg of reagent grade $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ was placed in a sealed silver tube and heated to between 350° and 380°C under 2 kb water pressure. Run times ranged between 6 and 452 hours and were generally between 40 and 115 hours. Neither reaction time nor temperature were particularly critical to the reaction, and complete conversion of the oxalate to siderite was observed in virtually all runs. In shorter runs near 350°C some unconverted oxalate occasionally remained, and in runs near 400°C the siderite was accompanied by small amounts of magnetite. The siderite used in the stability runs was entirely pure and was generally produced at about 380°C in runs of 90 to 120 hours duration.

The siderite produced was a gray-white crystalline powder which gradually assumed a light buff or brownish color on drying at room temperature. The material was identified as siderite by both optical and X-ray methods. The individual siderite grains are colorless to pale yellow, ranging in size from less than 1 μm to 10 μm ; many of the large crystals are well-developed rhombohedra. This material, which showed no traces of oxides or other impurities, was used as starting material for the stability runs. The value of n_o , determined on six samples, was 1.875 ± 0.005 , in good agreement with other determinations (Winchell and Winchell, 1951; Rosenberg, ms). A partial analysis of the oxalate and a synthetic siderite, obtained through the kindness of Dr. B. F. Jones and Miss S. Rettig of the U.S. Geological Survey, indicated that divalent cations other than iron are not present in significant amounts either in the oxalate or the synthetic siderite (French, 1970, p. 16).

Measurements of the d-spacings of the strong siderite (104) reflection indicated no perceptible difference in the cell dimensions between several synthetic siderites or between three siderites used in stability runs at varying temperatures and f_{O_2} values. Measurements were made on an X-ray diffractometer using a CdF_2 internal standard (Haendler and Bernard, 1951; Harker and Tuttle, 1955a, 1955b; Rosenberg, ms), for which the value of $2\theta_{111}$ was redetermined as 28.701° for CuK_α radiation, using a quartz standard (Lake Toxaway, N.C.) (French, 1970, p. 17). Measurement of the $2\theta_{104}$ value can be made to $\pm 0.02^\circ$. The values of d_{104} thus determined are consistent to $\pm 0.001 \text{ \AA}$ and are believed accurate to this value.

The average value of d_{104} determined from four synthetic siderites is 2.7919 \AA , in excellent agreement with previously calculated (2.7912; Graf, 1961) and measured (2.789; Sharp, 1960) values. A similar constancy was observed in d_{104} of three synthetic siderites exposed to various temperatures and f_{O_2} values during stability runs (see tables 2 and 3): 2.7897 \AA (run 29, HM buffer, 230°C; $\log f_{O_2} = -34.8$); 2.7913 \AA (run 52, HM buffer, 318°C, $\log f_{O_2} = -27.5$); 2.7908 \AA (run 46; MGr buffer, 493°C, $\log f_{O_2} = -23.4$). The latter sample was about 20 percent decomposed to magnetite. The average value for the three runs, 2.7906 \AA , is not significantly different from that of the synthetic siderites.

Similar agreement was found for d-spacings of other reflections of the synthetic siderites (French, ms), irrespective of whether they had been used in stability runs. The data indicate that neither variations in synthesis conditions nor changes in temperature and f_{O_2} during later experimental studies have any effect on siderite cell size.

The synthesis of siderite from ferrous oxalate dihydrate may be written:



Formation of siderite in these experiments was accompanied by production of a number of complex oxygenated organic compounds (acids, alcohols, and possibly ketones) in the gas phase inside the sample tube