checked by optical and x-ray methods are necessary before the presence and limits of such a mineral series can definitely be established.

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SYNTHETIC SOLID SOLUTIONS IN THE SYSTEMS $MgCO_3$-$FeCO_3$ AND $MnCO_3$-$FeCO_3$

P. E. ROSENBERG, *Department of Geology, Washington State University, Pullman, Washington.*

INTRODUCTION

Complete series of solid solutions have long been predicted in the systems $MgCO_3$-$FeCO_3$ and $MnCO_3$-$FeCO_3$ on the basis of mineral analyses (Palache *et al.*, 1951) but experimental studies of these systems have not been reported in the literature. On theoretical grounds, considerable solid solubility might be expected, even at relatively low temperatures, since the ionic radii of divalent Mg, Mn, and Fe do not differ widely (Goldsmith, 1959). Subsolidus relations in the above binary systems were studied experimentally in order to substantiate the predicted relations at moderate temperatures and pressures.

EXPERIMENTAL DETAILS

Standard "hydrothermal" apparatus and techniques (Harker and Tuttle, 1955) were employed in this investigation. Starting materials were prepared as mechanical mixtures of reagent-grade MgO, $MnCO_3$ and purified $FeC_2O_4 \cdot 2H_2O$ (recrystallized). Conversion of $MnCO_3$ to Mn_3O_4 resulted in an unexpected 4 per cent weight-loss which was assumed to be due to the presence of water (Goldsmith and Graf, 1957) and therefore corrections in the weight of $MnCO_3$ added to each mixture were made on this basis. Ferrous oxylate and magnesium oxide react completely under the conditions of the experiments to give the respective carbonates.

Starting materials were wrapped in gold foil, sealed in a pressure vessel and brought to temperature in an atmosphere of CO_2 containing in addition approximately 2 per cent by volume of CO which served to prevent the oxidation of iron. Pressures sufficient to prevent the dissociation of the carbonates were employed throughout this study. In order to promote reaction, a drop of distilled water was added to samples in the system $MgCO_3$-$FeCO_3$ while in the system $MnCO_3$-$FeCO_3$ a drop of an .01M Li_2CO_3 solution was added for this purpose. Runs were quenched by immersion of the pressure vessels in water and the charges were examined by means of an *x*-ray powder diffractometer.

X-ray measurements were made using an internal standard, CdF_2, having a convenient reflection at 28.70° ($CuK\alpha$) which was carefully calibrated with an internal quartz standard. Progressive displacements of the carbonate (211) reflections with composition were observed for solid solutions in both systems and the angular distances ($\Delta 2\theta$) between these reflections and the CdF_2 reflection were measured and recorded. The precision of the $\Delta 2\theta$ values, based on measurements of four *x*-ray diffraction patterns per sample, are believed to be within $.01° 2\theta$. Cu-radiation was more readily available and was used throughout this study. Equilibrium was assumed to have been reached when experiments of longer duration produced no further change in $\Delta 2\theta$.

THE SYSTEM $MgCO_3$-$FeCO_3$

Subsolidus relations have been studied in the temperature range between 295° and 500° C. and at pressures of $CO_2(+CO)$ from 20,000 to 60,000 psi. The duration of the experiments was between 24 and 72 hours. A complete series of solid solutions was observed over the entire

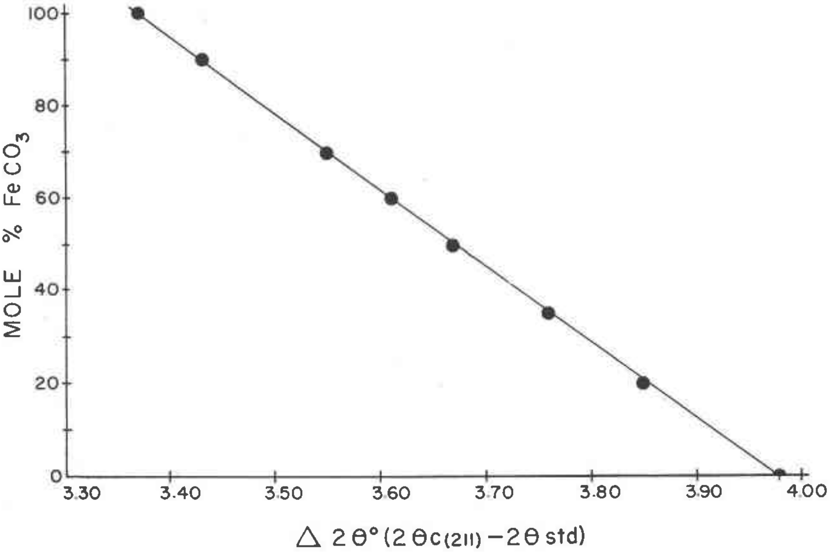

FIG. 1. Variation of $\Delta 2\theta$ with composition in the system $MgCO_3$-$FeCO_3$. Diameter of dots indicates approximate precision of $\Delta 2\theta$ measurements. Straight line is drawn between $\Delta 2\theta$ values of end-members. C(211) denotes carbonate (211) reflection.

temperature range of this study, the $\Delta 2\theta$ values for solid solutions varying linearly with composition and lying close to the straight line formed by joining the $\Delta 2\theta$ values of the end-members (Fig. 1). No significant variations in these measurements with temperature were observed. Critical data at 450° C., including refractive indices (ω) of the synthetic solid solutions, are summarized in Table 1. Narrow ranges were observed in the

TABLE 1. EXPERIMENTAL DATA FOR THE SYSTEM $MgCO_3$-$FeCO_3$ AT 450° C.

Composition, $FeCO_3$	Mole % $MgCO_3$	Products	$\Delta 2\theta$ ±.01°	2θ° CuKα	d(211) Å	ω	Index Range
100	—	Siderite	3.37	32.07	2.791	1.875[1]	
90	10	Sid-Mag.S.S.	3.43	32.13	2.786	1.856	±.003
70	30	Sid-Mag.S.S.	3.55	32.25	2.776	1.820	±.005
60	40	Sid-Mag.S.S.	3.61	32.31	2.771	1.810	±.002
50	50	Sid-Mag.S.S.	3.67	32.37	2.766	1.790	±.002
35	65	Sid-Mag.S.S.	3.76	32.46	2.758	1.758	±.003
20	80	Sid-Mag.S.S.	3.85	32.55	2.751	1.736	±.002
—	100	Magnesite	3.98	32.68	2.740	1.700	±.001

[1] Palache *et al.* (1951).

TABLE 2. EXPERIMENTAL DATA FOR THE SYSTEM $MnCO_3$-$FeCO_3$

Composition $FeCO_3$	Mole % $MnCO_3$	Time Hrs.	Products	$\Delta 2\theta$ $\pm .01°$	$2\theta°$ CuKα
—	100	—	Rhodochrosite	2.74	31.44
10.4	89.6	144	Rh.-Sid.S.S.	2.80	31.50
20.8	79.2	144	Rh.-Sid.S.S.	2.88	31.58
30.9	69.1	144	Rh.-Sid.S.S.	2.95	31.65
41.0	59.0	144	Rh.-Sid.S.S.	3.00	31.70
51.0	49.0	144	Rh.-Sid.S.S.	3.08	31.78
60.9	38.9	144	Rh.-Sid.S.S.	3.15	31.85
70.8	29.2	600	Rh.-Sid.S.S.	3.22	31.92
80.6	20.4	600	Rh.-Sid.S.S.	3.27	31.97
90.4	9.6	600	Rh.-Sid.S.S.	3.32	32.02
100	—	—	Siderite	3.37	32.07

indices of refraction of all samples reflecting small variations in crystal composition which indicate that complete equilibrium was not attained.

THE SYSTEM $MnCO_3$-$FeCO_3$

Experimental data, summarized in Table 2, indicate complete solid miscibility at 450° C. and pressures of $CO_2(+CO)$ between 30,000 and 37,000 psi. Compositions in the Fe-rich portion of the system were slow to react at 450° C. and complete equilibrium was probably not attained even in the runs of greatest duration. However, in series of successively longer runs at 450° C., the measured $\Delta 2\theta$ values gradually approached the straight line representing a linear relationship between $\Delta 2\theta$ and composition (Fig. 2) and it seems likely that experiments of even longer duration would justify the linear relationship indicated in Fig. 2. Several solid solutions synthesized at 500° C. support this conclusion, giving $\Delta 2\theta$ values which, within the limits of measurement, lie on the straight line in Fig. 2.

SUMMARY AND CONCLUSIONS

1. Predicted solid miscibilities in the systems $MgCO_3$-$FeCO_3$ and $MNCO_3$-$FeCO_3$ have been confirmed experimentally by the preparation of complete series of solid solutions at 450° C.

2. In the system $MgCO_3$-$FeCO_3$, no indication of the presence of a solvus has been found at 295° C., the minimum experimental temperature.

3. In both systems, linear or nearly linear relationships exist between $\Delta 2\theta°$ $(2\theta_{c(211)}-2\theta_{std.})$ and composition.

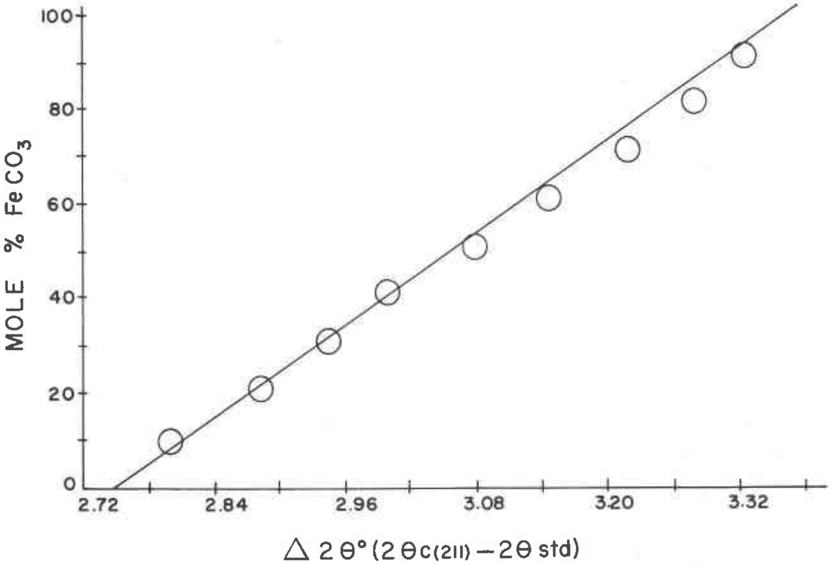

FIG. 2. Variation of $\Delta 2\theta$ with composition in the system $MnCO_3$-$FeCO_3$. Diameter o circles indicates approximate precision of $\Delta 2\theta$ measurements. Straight line is drawn between $\Delta 2\theta$ values of end-members. C(211) denotes carbonate (211) reflection.

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