## Stability relations of siderite (FeCO<sub>s</sub>) in the system Fe-C-O 53

method; samples of siderite were surrounded by a magnetite + graphite mixture, allowing reaction in both directions in a single run (table 3; fig. 4). Data obtained for the SMGrG curve are:

$P_{\rm F}$ (bars)	$T(\pm 10^{\circ}C)$	$-\log f_{0_{o}}(\pm 0.8)$		
500	455	25.8		
1000	458	25.2		
2000	465	24.4		

Minor amounts of siderite decomposition were observed in all runs, even those in which significant amounts of siderite formed in the buffer. This decomposition, which did not exceed 5 percent, produced a dark gray color and definite magnetism in the sample. The amount of such decomposition appeared relatively constant with temperature and may have been produced by incomplete buffering during the early part of the run.

The direction of reaction in any run was determined from: (1) the absence of siderite in the buffer; (2) a sudden sharp increase in the amount of sample decomposition as the run temperatures were increased. An approximate indicator of siderite instability was the appearance of magnetite peaks in the X-ray pattern of the sample. Above the equilibrium temperatures, the amount of sample decomposition increases rapidly (table 3; fig. 5). Below the equilibrium temperatures buffer decompositions of 2 to 10 percent were observed. With one unexplained exception (run 85), not even trace amounts of siderite were observed in the buffer above the equilibrium temperature.

At  $P_F = 500$  bars, run 89 (448°C) shows very slight sample decomposition combined with definite development of siderite in the buffer. By contrast, run 100 (464°C) exhibits no siderite in the buffer, while the siderite sample was almost entirely decomposed. The equilibrium temperature lies between these runs, and the almost complete sample decomposition in run 100 suggests that it lies closer to the lower temperature. The equilibrium temperature estimated at  $P_F = 500$  bars is 455  $\pm 10^{\circ}$ C.

The same criteria indicate that the equilibrium temperature at  $P_F = 1000$  bars is bracketed by runs 130 (452°C) and 122 (466°C); the estimated value is 458°  $\pm$  10°C.

At  $P_F = 2000$  bars, the equilibrium temperature lies between runs 92 (462°C) and 76 (469°C) and is estimated as 465  $\pm$  10°C. Above this temperature, siderite samples were increasingly decomposed; no siderite remained in a sample run at 537°C.

There was no observable effect of total pressure on the amount of reaction along the SMGrG curve; in general, virtually complete decomposition of siderite was observed in all samples run at 30° to 50°C above the equilibrium temperature at all pressures (table 3; fig. 5).

Runs made with a magnetite-graphite mixture in the sample position showed traces of siderite developing below the estimated equilibrium temperatures. No siderite was observed to form in these runs above the Bevan M. French

TABLE 3 Experimental data for determination of the equilibrium: siderite + magnetite + graphite + gas (SMGrG) along the graphite buffer

Run no.	Sample	T°C	—log f <sub>02</sub> (bars)	Time (hrs)	Sample	Products Percent decom- position	Buffer
$P_F = P_{CO}$	$_2 + P_{co} =$	2000 b	ars				
68	S	197	41.0	429	S + M + g	2-5	M+G+S
62	S	304	32.1	353	S + M + g	5	M + G + S
63	S	348	29.6	353	S + M + g	2-4	M + G + (S)
56	S	402	27.1	355	S + M + g	2-5	$M + G + \dot{S}$
40	S	422	26.2	263	S + M + g	5	M + G + S
41	S	441	25.4	263	S + M + g	2	M + G + S
81	S	451	25.0	371	S + M + g	2-5	M + G + S
92	S	462	24.6	407	S + M + g	2-5	M + G + S
76	S	469	24.2	355	S + M + g	10-20	M+G
57	S	470	24.2	356	S + M + g	40-60	M + G
51	S	478	23.9	478	S + M + g	90-95	M + G
46	S	493	23.4	338	S + M + g	50	M + G
77	S	537	21.9	355	M+g	100	M + G
47	S	606	19.9	331	M + G	100	M + G
	$P_2 + P_{co} =$				no to no entre	10.00	erregi orte de la
69	S	196	41.9	426	S + M + g	3	M + G + S
61	S	298	33.0	375	S + M + g	5	M + G + S
123	S	421	26.7	372	S + M + g	2-5	M + G + S
60	S	446	25.7	356	S + M + g	5	M+G+S
130	S	452	25.5	385	S + M + g	2	M + G + S
122	S	466	24.9	372	S + M + g	30-40	M + G
87	S S	479	24.4	326	S + M + g	70-80	M + G + (S)
80	S	515	23.2	475	M + G	100	M+G
128	MG	419	26.8	385	M + G + (S)	0.5	M + G + (S)
129	MG	491	24.0	385	M + G	0	M+G
$\mathbf{P}_{\mathbf{F}} = \mathbf{P}_{\mathbf{CC}}$	$P_{2} + P_{co} =$	= 500 ba	rs				
67	S	398	28.2	453	S + M + g	5	M + G + S
89	S	448	26.0	406	S + M + g	1	M + G + S
100	S	464	25.4	326	M + S + G	90	M+G
94	S	475	25.0	308	M + S + G	80	M+G
101	S	485	24.6	326	M + (S) + g	98	M + G
85	S	498	24.1	302	M + S + g	80-90	$M+G+(S^*)$
95	S	525	23.2	307	M + g	100	M+G
90	S	548	22.5	405	M + g	100	M + G
118	MG	439	26.4	325	M + G + (S)	0.5-1	M + G + S
119	MG	470	25.2	325	M + G	0	M + G

equilibrium temperatures, and these runs are thus consistent with the equilibrium temperatures determined from runs using siderite samples.

The temperatures obtained for the SMGrG curve in this study are supported by independent studies of siderite decomposition carried out by Rosenberg (1963a). In his experiments, siderite was decomposed under pressure in sealed gold tubes; buffering at  $f_{0_2}$  values at or close to those of the graphite buffer was apparently established by precipitation of graphite or amorphous carbon from the gas phase in the tube during the

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