Fig. 1. Experimental results on siderite decomposition to magnetite + graphite. Sealed-tube runs (Rosenberg) shown by circles; buffered open-tube runs (French) shown by rectangles. The solid line indicates the univariant curve for the assemblage, siderite + magnetite + graphite + gas, obtained from the open-tube experiments; virtually the same curve is obtained from the sealed-tube experiments (Table 1). The large rectangles at the left-hand side indicate the experimental uncertainty, ± 7°C and ± 5 percent of the total pressure.

rium could then be demonstrated by two reactions in a single run, either by decomposition of the siderite sample or by growth of siderite from magnetite in the buffer mixture. Equilibrium temperatures were located by (i) production of siderite throughout the entire buffer below the equilibrium temperature, and (ii) production of large amounts of magnetite (in excess of 10 percent of the volume) above the decomposition temperature. The two criteria yielded consistent equilibrium temperatures.

The equilibrium temperatures obtained are compared in Table 1; Fig. 1 shows the experimental data. The temperature uncertainty for each experimental point is probably ±7°C. Agreement between the two sets of data is excellent, particularly above 860 bars, where sufficient data are available. At lower pressures, the apparent close agreement may be conditioned by the small number of sealed-tube experiments.

The agreement between decomposition temperatures determined by two different experimental methods indicates (i) that the temperatures determined do in fact represent equilibrium decomposition of siderite to magnetite and graphite, and (ii) that buffering of f_{O_2} during the sealed-tube experiments is established by precipitation of graphite or carbon from the gas phase.

The equilibrium, siderite + magnetite + graphite + gas, specifies the maximum temperature for stable existence of siderite in an atmosphere of CO_2 + CO (*8*); higher values of f_{O_2} produce lower decomposition temperatures. If graphite is absent, the assemblage, siderite + magnetite + gas, may exist over a temperature interval in excess of 100°C (*8*); this interval may be increased if gas compositions metastable with respect to graphite can be preserved. Therefore, the decomposition of siderite to magnetite cannot be used as an accurate geothermometer unless the value of f_{O_2} is specified independently in some manner, for example, by the presence of additional phases such as graphite.

Studies of metamorphosed sedimentary iron formations (*8, 10, 11*) indicate that original siderite in such rocks disappears by reaction with available silica and water to form the iron-amphibole grunerite, $Fe_7Si_8O_{22}(OH)_2$. Temperatures for this reaction must be below those for the decomposition of siderite itself, but they are dependent on the fugacities of both H_2O and CO_2 and have not been experimentally determined. Approximate temperatures of 300° to 400°C have been estimated for the formation of grunerite from geological evidence (*8, 11*); the estimates are consistent with the upper limit of siderite stability established in this study.

BEVAN M. FRENCH*
Department of Geology, Johns Hopkins University, Baltimore, Maryland
P. E. ROSENBERG
Department of Geology, Washington State University, Pullman

References and Notes

1. J. C. Jamieson and J. R. Goldsmith, *Am. Mineralogist* **45**, 818 (1960).
2. R. I. Harker and O. F. Tuttle, *Am. J. Sci.* **253**, 209 (1955).
3. R. I. Harker and J. J. Hutta, *Econ. Geol.* **51**, 375 ((1956); J. R. Goldsmith, in *Researches in Geochemistry*, P. H. Abelson, Ed. (Wiley, New York, 1959), pp. 336–358. The nonoxidizing decomposition of rhodochrosite ($MnCO_3$) to manganosite (MnO) has been studied by J. R. Goldsmith and D. L. Graf, *Geochim. Cosmochim. Acta* **11**, 310 (1957).
4. A. Muan, *Am. J. Sci.* **256**, 171 (1958).
5. B. M. French and H. P. Eugster, *J. Geophys. Res.*, in press.
6. P. E. Rosenberg, *Am. J. Sci* **261**, 683 (1963); additional unpublished data.
7. J. R. Goldsmith and H. C. Heard, *J. Geol.* **69**, 45 (1961).
8. B. M. French and H. P. Eugster, *Geol. Soc. Am. Spec. Papers 73* (1962), p. 155 (abstr.); B. M. French, thesis, Johns Hopkins University (1964).
9. H. P. Eugster and D. R. Wones, *J. Petrol.* **3**, 82 (1962).
10. R. D. Irving and C. R. Van Hise, *U.S. Geol. Surv. Monogr.* No. 19 (1892); C. R. Van Hise and W. S. Bayley, *U.S. Geol. Surv. Monogr.* No. 38 (1897); R. C. Allen and L. P. Barrett, *Mich. Dept. Conserv. Geol. Surv. Div. Publ.* No. 18 (1915); J. K. Gustafson, *Econ. Geol.* **28**, 132 (1933); B. R. Rao, *Bull. Mysore Geol. Dept.* **15**, 1 (1934); C. E. Tilley, *Geol. Mag.* **75**, 76 (1938).
11. H. L. James, *Bull. Geol. Soc. Am.* **66**, 1455 (1955).
12. Both studies supported in part by grants from the National Science Foundation. French's study is part of a thesis, Johns Hopkins University; we thank H. P. Eugster and D. R. Wones for their supervision and assistance; H. D. Holland and O. F. Tuttle for their interest in, and support of, Rosenberg's work; and H. P. Eugster for a critical review of the manuscript.
* Present address: Theoretical Division, Goddard Space Flight Center, NASA, Greenbelt, Maryland.

12 January 1965