DETERMINATION OF SMALL QUANTITIES OF DOLOMITE BY DIFFERENTIAL THERMAL ANALYSIS*

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ABSTRACT

A method which will be most useful in evaluating the product of laboratory synthesis of dolomite is described. The dolomite content of carbonate rocks can be quantitatively determined by differential thermal analysis when as little as 0.3 percent dolomite is present. Thermograms of prepared and natural mixtures containing small amounts of dolomite and calibration curves relating the area of the thermogram loops to the dolomite content are presented and compared with recast chemical analyses.

The general study of the problem of dolomites and the process of dolomitization frequently requires the determination of small quantities of the mineral dolomite in mixtures with other carbonates and other minerals. Likewise, in experimenting with different methods for the laboratory synthesis of dolomite, it is important that even a small percentage of the mineral be detected. Until now, there has been no reliable technique for this purpose. In small quantities, dolomite is most likely to be fine grained and intimately mixed with other carbonates; hence, the microscopic and staining techniques are not suitable. The recasting of chemical analyses becomes especially difficult when the magnesium content is less than 2 per cent, and, of necessity, the magnesia in the chemical analysis is assigned arbitrarily to the mineral dolomite. Frequently it is suggested in the literature that some of the magnesium may be present in the form of periclase or brucite. Dolomite in quantity less than 2 percent may not be detected by *x*-ray techniques.

In recent years the differential thermal analysis technique has been applied to the study of carbonate minerals (Cuthbert and Rowland, 1947), (Beck, 1950), (Faust, 1950), (Gruver, 1950). This technique can be used to distinguish dolomite in calcite-dolomite mixtures, both qualitatively and quantitatively. With an extremely sensitive recording apparatus and a controlled furnace atmosphere of CO_2, dolomite may be determined in prepared mixtures of dolomite and calcite when only 0.3 percent dolomite is present.

Differential thermograms of dolomite and calcite in an air atmosphere and in a CO_2 atmosphere are shown in Fig. 1. The thermogram of dolomite heated in air consists of two interfering loops. The first accompanies

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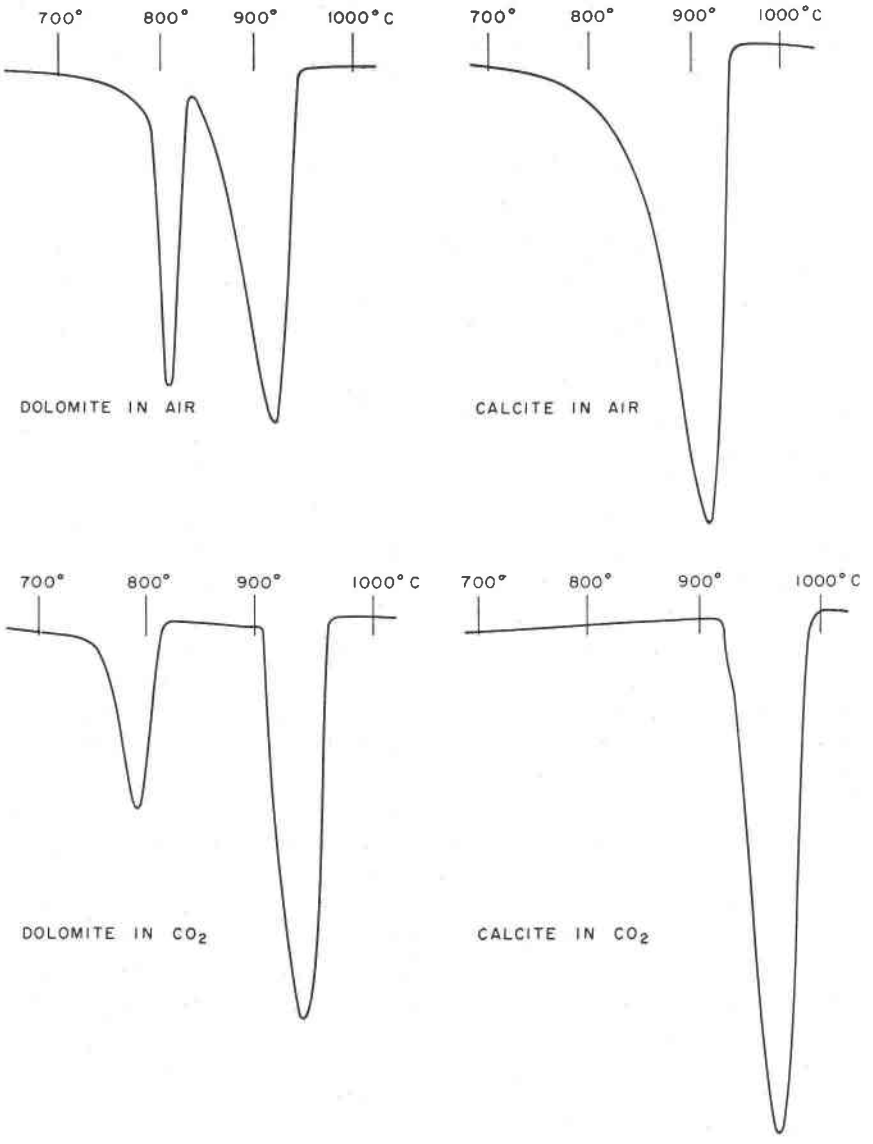


FIG. 1. Dolomite and calcite in air and carbon dioxide.

the decarbonation of the $MgCO_3$ part of the dolomite; the second, the dissociation of CO_2 from the $CaCO_3$ part of the dolomite. In a CO_2 atmosphere these two loops are separated largely because the dissociation temperature of the $CaCO_3$ portion is raised and the inflections are

sharpened (Fig. 1). Therefore, thermograms of dolomite in a CO_2 atmosphere are more useful for accurate measurement of the loop areas. In mixtures of dolomite and calcite, the $CaCO_3$ loop of dolomite and the calcite loop are superimposed. With decreasing amounts of dolomite the $CaCO_3$ loop becomes larger and the $MgCO_3$ loop diminishes. When the $MgCO_3$ loop becomes so small that it cannot be measured with any degree of accuracy, the technique described in the next paragraph is employed to overcome this difficulty.

The apparatus used is a standard DTA arrangment with platinum (platinum 10 per cent, rhodium difference) thermocouples, the e.m.f. from which is measured with a Leeds and Northrup Type R galvanometer having 50 ohms shunting resistance (sensitivity, 0.5 microvolt per mm.) (Rowland, 1948). The galvanometer deflections are recorded with a Beckman Photopen. With this apparatus dolomite normally is recorded with a 110-ohm series resistor in the galvanometer circuit. During the recording of the loop between 700° C and 800° C, when small amounts of dolomite are present, a 10-ohm series resistor replaces the 110-ohm resistor in the circuit. After the completion of this loop and before the inception of the loop between 900° C and 1000° C, the series resistance is changed to 310 ohms in order to contain the second loop within the dimensions of the chart. The sample is heated in a furnace atmosphere of CO_2, according to the method described by Rowland and Lewis (1951).

The area of each loop, described by the loop and a line joining the points at which a line 45° to the base line (Fig. 2, 1st two curves) is tangent to the maximum inflexion of the beginning and ending of each loop, was measured by planimetering. The method used can be extended to cover the range of dolomite-calcite mixtures, from 100 percent dolomite to 100 percent calcite. Berg's (1945) complicated construction of a line to close the loop was found to be unnecessary.

The experimental results of six prepared mixtures of dolomite and calcite are shown in Fig. 2; and the area of the $MgCO_3$ loop, as well as the percent factor of

$$\frac{\text{Area } MgCO_3 \text{ loop} \times 100}{\text{Area } MgCO_3 \text{ loop} + \text{Area } CaCO_3 \text{ loop}}$$

is shown in Table 1. Figure 3 plots the information of Table 1. Figure 4 presents the experimental results, using the above method, for three samples of the Trenton limestone, Clinton County, Illinois. Table 2 tabulates the area of the $MgCO_3$ loop, the percent factor, and the percent dolomite as determined by each method. Table 3 gives the chemical analyses of the three limestones. All the magnesia has been assigned arbitrarily to dolomite though there is no optical, x-ray, or staining evidence to indicate the presence of dolomite.

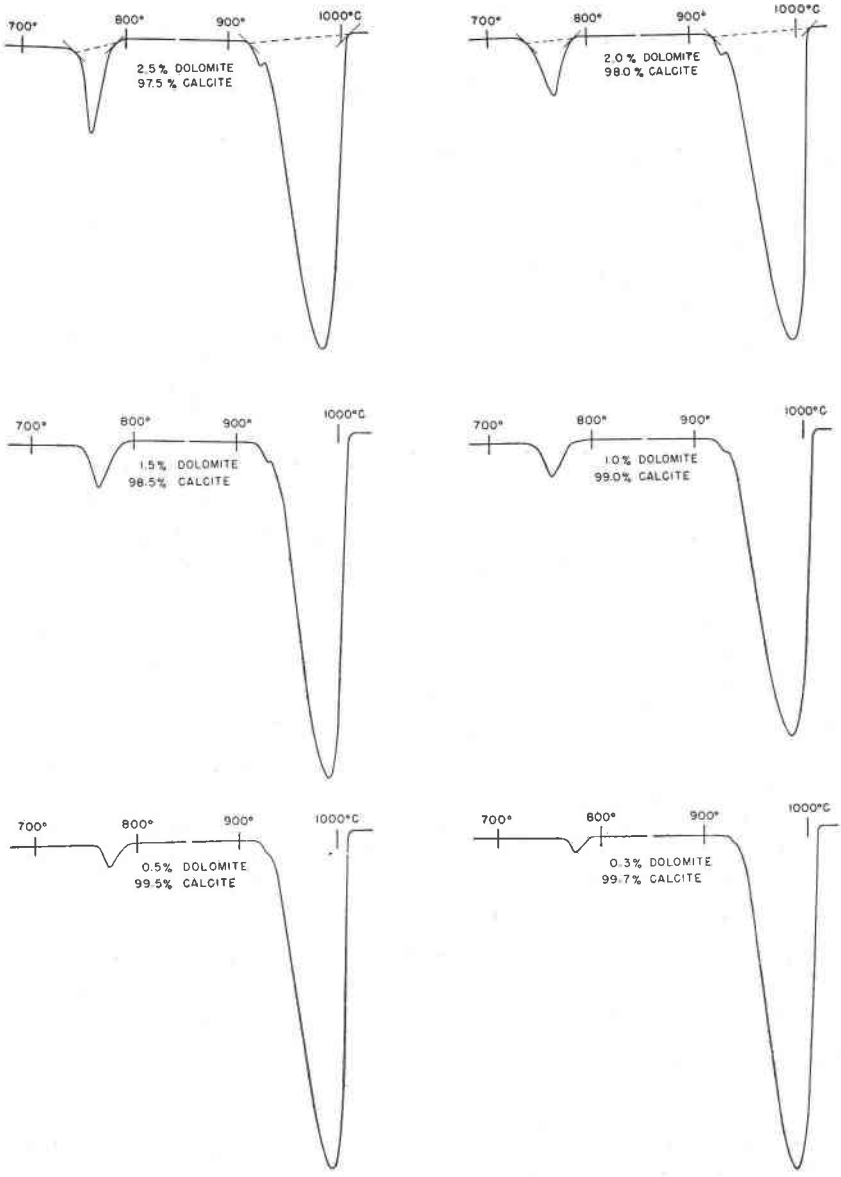


FIG. 2. DTA Calibration Curves of Small Percentages of Bureau of Standards Dolomite and Iceland Spar Calcite—10 Ohms and 310 Ohms. Undiluted.

TABLE 1. DATA FROM DTA CURVES OF SYNTHETIC MIXTURES OF BUREAU OF STANDARDS DOLOMITE AND ICELAND SPAR CALCITE

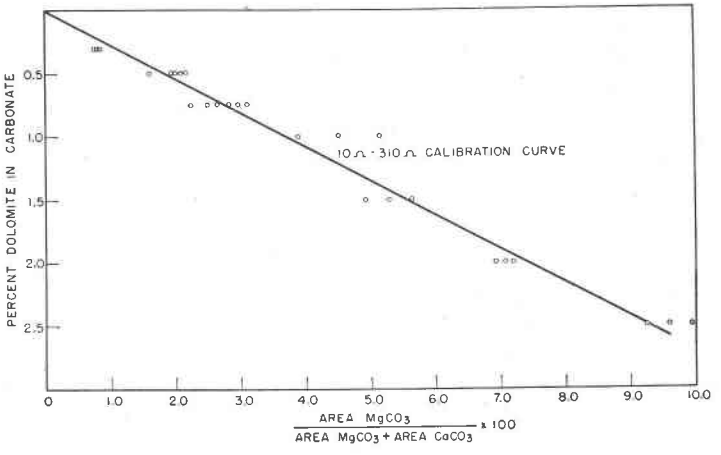
Percent Dolomite	Percent Factor	Area $MgCO_3$ Loop
2.5	8.58	68
2.0	6.90	54
1.5	5.04	39
1.0	3.27	25
0.5	1.85	14
0.3	0.93	7

TABLE 2. DATA FROM TRENTON LIMESTONE, CLINTON COUNTY, ILLINOIS

Depth	Percent Factor	Percent Dolomite from Percent Factor	Area $MgCO_3$ Loop	Percent Dolomite from Area $MgCO_3$ Loop
3496	2.38	0.64	15	0.70
3951	0.39	0.11	3	0.14
3960	1.98	0.55	14	0.67

TABLE 3. CHEMICAL ANALYSIS OF TRENTON LIMESTONE SAMPLES, CLINTON COUNTY, ILLINOIS

	Sample Number		
	3946	3951	3960
CaO	50.60%	54.00%	54.70%
MgO	0.64	0.65	0.04
CO_2	40.40	43.10	43.00
R_2O_3	1.20	0.44	0.27
−105° C	0.05	0.07	0.07
−1050° C	40.60	42.80	43.30
Recast percent dolomite	1.76	1.67	0.10



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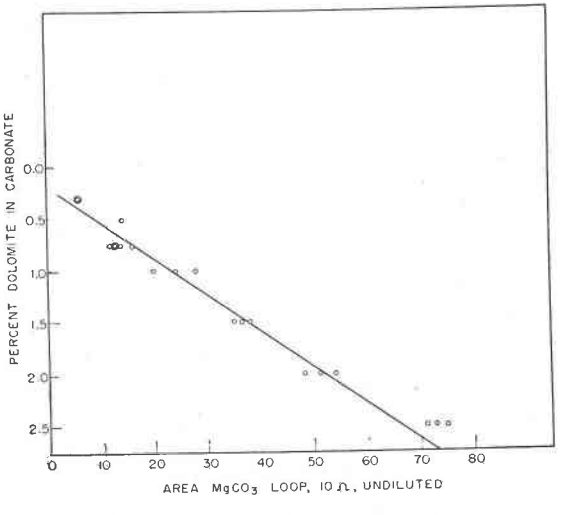

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FIG. 3. Calibration Curves of Small Quantities of Dolomite Plotted (*a*) Percent Factor vs. Percent Dolomite in Carbonate, and (*b*) Area $MgCO_3$ vs. Percent Dolomite in Carbonate.

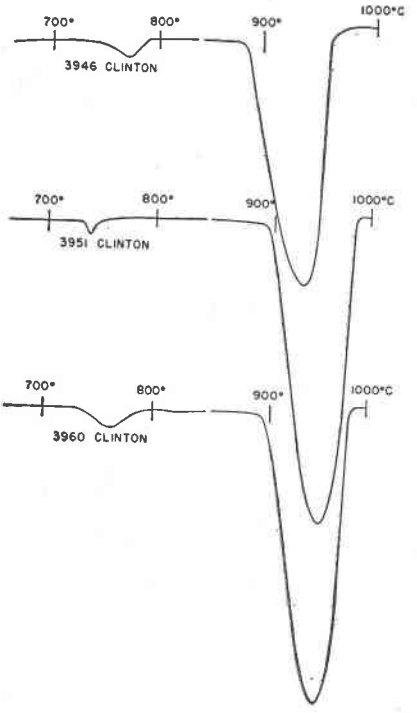

FIG. 4. DTA Curves of Three Samples from Trenton Limestone, Clinton County, Illinois.

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