X-RAY DETERMINATION OF DOLOMITE-CALCITE RATIO OF A CARBONATE ROCK

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ABSTRACT

An x-ray method has been developed for the determination of the percentage of dolomite in a carbonate rock. Such analyses may be useful in exploration work due to the association of highly dolomitized zones with locations favorable for mineral deposition.

INTRODUCTION

The meaning of the percentage of dolomite as used here is the per cent of the total carbonate, dolomite ($CaCO_3 \cdot MgCO_3$) plus calcite ($CaCO_3$), which is present as dolomite in a rock specimen. Mineral deposits are often found in dolomitized carbonate rock. Geologists believe that such dolomitization often precedes or accompanies the mineral emplacement. The dolomitization often extends from the center of mineralization for considerable distances.

From the association of dolomite and mineral deposits, it is obvious that a study of dolomitization of limestone might yield useful information on the location of such deposits, the more likely direction of concentration being in the direction of increasing dolomitization.

An x-ray method has been developed for determining the percentage of dolomitization and is here described. It should be specifically noted that the method does not give information as to whether or not the dolomite present is primary or secondary in the paragenetic sense. This information must be determined from other geological information.

EXPERIMENTAL

The procedure consists of measuring the relative intensities of the strongest powder x-ray diffraction line for calcite and for dolomite in a series of mixtures of known proportions, and applying these results to samples of unknown composition.

MATERIALS

The dolomite used for standardization was selected from a group of specimens purchased from Ward's Natural Science Establishment. It is the coarsely crystalline dolomite from Lee, Berkshire County, Massachusetts. Its purity was established by powder x-ray examination and

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chemical analysis. The analysis expressed in terms of the carbonates is as follows:

Lee Dolomite	$\begin{cases} 54.26\% \text{ CaCO}_3 \\ 45.18\% \text{ MgCO}_3 \end{cases}$
Theoretical for Dolomite	$\begin{cases} 54.27\% \text{ CaCO}_3 \\ 45.73\% \text{ MgCO}_3 \end{cases}$

The calcium carbonate used was Baker's analyzed, calcium carbonate powder. This material gave a sharp calcite powder x-ray diffraction pattern. Both materials were finely ground (-325 mesh) and dried at 100° C. and stored in a desiccator.

Sample Preparation

All samples after reduction to -325 mesh were wet ballmilled. The procedure used was an adaptation of the ideas of Ballard, Oshry, and Schrenk, 1943. The ballmills were screw top salve jars approximately $2\frac{1}{4}''$ in diameter and $1\frac{3}{4}''$ deep. The cardboard liner in the screw top was replaced with a solid rubber gasket. The mill was charged with approximately 180 grams of $\frac{1}{4}''$ diameter stainless steel balls, 2 grams of sample and 2 ml. of ethyl alcohol. Silicone stopcock grease was used on the gasket seal and the samples ground overnight (15 hours) at 24 r.p.m. Tests have shown that a grinding period of at least eight hours is essential. Klug and Alexander (1954) discuss the particle size requirements for reproducibility in x-ray spectrometer applications.

The arrangement of the drive mechanism allowed the mills to be tilted to approximately 45°. Following the grinding period in the horizontal position, the mills were inclined, the covers removed and the samples dried by allowing the alcohol to evaporate while the milling continued. The samples were recovered by emptying the mill contents onto a coarse (28 mesh) screen. The samples were given a brief hand mortar grind (one minute), and then back-packed through a screen into an aluminum cell against a plate glass surface (McCreery, 1949). This cell was then mounted in the x-ray diffractometer (North American Philips Company—high angle diffractometer).

Counting Procedure

Nickel filtered copper x-radiation was used. Before counting, a strip chart was run from 26°–34° 2θ to check for interference and to select locations for background count. The background was recorded at a 2θ position slightly larger than that for the dolomite line used and also at a 2θ position just below the 2θ position for the calcite line. The exact positions of the calcite and dolomite peaks were determined by a series of

counts through the appropriate 2θ range recording the time for various 2θ settings using fixed count operation.

The intensities were measured for the 3.03 Å calcite line and the 2.88 Å dolomite line at the 2θ positions determined, and corrected using the corresponding background value. Also, when the counting rate was high, corrections were made for the non-linear response of the Geiger counter. All intensity counts were made for 64 seconds. This procedure supplied data with which a calcite-dolomite intensity ratio could be calculated. Such a ratio is proportional to the ratio of concentration of these two materials in a given sample.

CALIBRATION

The procedure was calibrated by preparing known mixtures of calcite and dolomite from the materials described. These were prepared by the sample preparation procedure described and then a calcite-dolomite x-ray line intensity ratio was determined for each standard sample.

The following synthetic mixtures were used:

Weight per cent dolomite	Grams	
	Mass dolomite	Mass calcite
10	0.200	1.800
20	0.400	1.600
40	0.800	1.200
60	1.200	0.800
80	1.600	0.400
90	1.800	0.200

A calibration curve was then established by plotting the calcite/dolomite intensity ratio as determined against the known per cent dolomite. (See Fig. 1.)

TEST SAMPLES

Eight samples were used to check the x-ray method. These were field samples collected in connection with a geological study. The per cent of dolomite in each sample was determined using the x-ray method. Also, suitable chemical analyses of the samples were obtained so that the per cent of dolomite could be calculated. For the chemical determination Mg, Ca, and carbonate were determined on each sample. The Mg and Ca data are sufficient to calculate per cent dolomite and the equivalent amount of carbonate. The carbonate analysis serves as a check on the determination.

In Table 1 the per cent dolomite as determined by the two methods is listed for each sample.
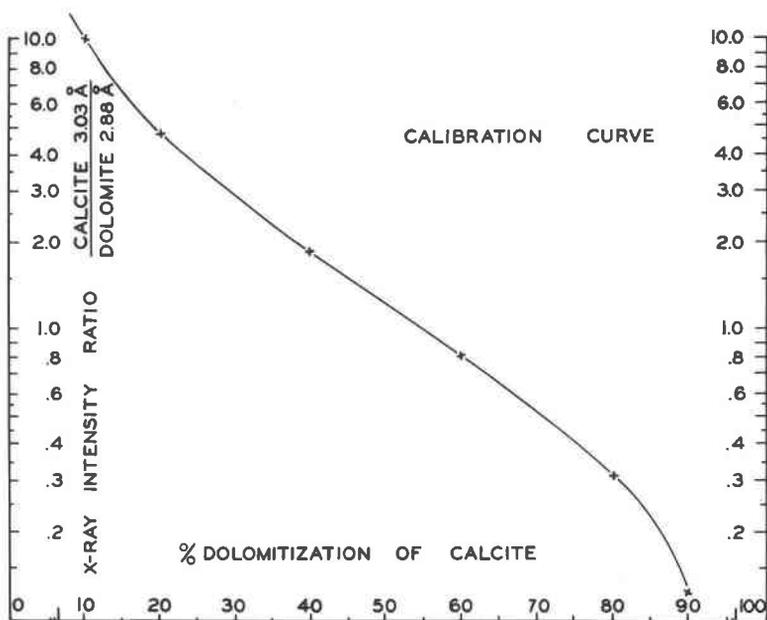
Fig. 1

TABLE 1

Sample No.	Chemical results per cent dolomite[1]	X-ray results per cent dolomite[1]
1	49.1	48
2	98.8	>90
3	50.2	50
4	84.0	86
5	44.8	44
6	11.5	<10
7	10.8	<10
8	34.3	35

[1] Per cent dolomite is determined from the ratio in weight of dolomite to that of dolomite plus calcite in the sample.

Table 2 lists the complete chemical data obtained on the samples.

The agreement of the x-ray and chemical analyses of per cent dolomite in Table 1 is very satisfactory for the application intended. In these particular samples (see Table 2) the carbonate analyses checked well with the carbonate results obtained from the calcium and magnesium analyses

calculated to their carbonate equivalents as $CaCO_3$ and $CaCO_3 \cdot MgCO_3$. Rock specimens containing other carbonates or other calcium or magnesium-bearing minerals in addition to calcite and dolomite would not agree in this fashion. Under such conditions proper calculation of per cent dolomite from chemical analysis alone would become difficult if not impossible. In the x-ray method which is based on the crystal phases

TABLE 2

Sample No.	Weight per cent calcite[1]	Weight per cent dolomite[1]	Weight per cent CO_3[2]	Per cent CO_3 calculated from metal results[1]	Per cent dolomite[3]
1	47.20	45.5	57.7	57.91	49.1
2	1.20	97.0	63.8	63.85	98.8
3	48.87	49.3	61.8	61.38	50.2
4	15.76	82.6	63.0	63.21	84.0
5	55.09	44.7	61.2	62.12	44.8
6	87.95	11.4	59.6	60.15	11.5
7	87.63	10.6	58.6	59.44	10.8
8	64.03	33.4	59.4	60.13	34.3

[1] Values calculated from chemical determination of Mg and Ca content of samples.

[2] Values calculated from chemical determination of carbonate content of samples.

[3] (Weight per cent dolomite) : (weight per cent dolomite plus weight per cent calcite).

dolomite and calcite, the ratio of calcite-to-dolomite is determined independently of other Mg, Ca and carbonate-bearing materials.

DISCUSSION

The x-ray method has the advatage of giving results proportional to the total amount of material present having the calcite and dolomite structure types. A correction would be necessary in the x-ray calibration if samples showed major substitution of other cations for Ca^{++} and Mg^{++}. However, it seems most likely that the x-ray results would be affected less by small variation in chemical make up than would a method based on chemical analysis.

Harker and Tuttle (1955) and Graf and Goldsmith (1955) indicate that Mg can substitute for Ca in calcite to an appreciable per cent only at high temperature. Harker and Tuttle (1955) conclude from the ease of exsolution observed in their equilibrium studies that it is unlikely that in nature carbonate rocks would usually be quenched sufficiently rapidly from high temperatures to prevent unmixing on cooling.

We have examined the calcite samples referred to in this report by the

procedure of Harker and Tuttle for lattice variations which might indicate Mg^{++} content. The lattice variations for all samples fall in a range between pure calcite and calcite with a $MgCO_3$ content of less than four weight per cent.

Goldsmith, Graf and Joensuu (1955) list measurements on a large group of natural calcites in which variations in magnesium content were measured by x-ray. Their results indicate that small amounts of $MgCO_3$, typically in the 4 weight per cent range, occur in solution in calcite.

Chave (1952) has noted that larger variations in magnesium content in calcite are observed in materials formed from living organisms. However, he recognizes their lack of stability and reports that the magnesium content falls to 1 or 2 per cent often within a few tens of millions of years.

The small $MgCO_3$ contents reported would not appreciably affect results of our x-ray analysis. Harker and Tuttle's data on solution of $CaCO_3$ and $MgCO_3$ in dolomite and Graf and Goldsmith's data on solution of $CaCO_3$ in dolomite indicate that there is no complication whatsoever as regards to solid solution of these phases.

Other divalent elements are known to substitute in calcite and dolomite and some to a large extent. Numerous examples of such substitutions can be obtained in most descriptive mineralogy texts. However, the general consensus of opinion is that such substitutions occur rarely in natural occurring calcite and dolomite.

The above considerations indicate that complications from solid solution of the phases involved and from substitution should be minor but nevertheless kept in mind and checked for in given applications of this method.

Faust and Callaghan (1948) report studies of calcite deposits which have reacted with Mg^{++}-bearing solutions. In a later paper, Faust (1949) treated the subject in more detail. The products of such reaction are calcite plus dolomite or magnesite ($MgCO_3$) plus dolomite. The combination of calcite plus magnesite does not occur in nature. These observations are in agreement with equilibrium laboratory studies of the system CaO-MgO-CO_2. The studies show that the combination magnesite-calcite does not occur but either one of these minerals can exist in equilibrium with dolomite.

The diffraction peaks we are using in this work are calcite 3.03 Å and dolomite 2.88 Å. The corresponding magnesite peak is at 2.73 Å, thus illustrating the continuing decrease in lattice dimension as the smaller Mg^{++} replaces Ca^{++}. As the above figures indicate, the magnesite peak falls on the opposite side of the dolomite peak from the calcite peak. The separation of the calcite and dolomite peaks is of the same order as the separation of the magnesite and dolomite peaks. With these condi-

tions there would be no line interference due to magnestite and its occurrence could readily be detected. In our work we checked for the presence of magnesite whenever a per cent dolomite determination occurs in the 90–100% range.

If magnesite does occur in samples and information on its concentration is desired, it appears that a further application of the experimental techniques described above would readily permit determinations of magnesite-dolomite ratios by a procedure identical to that described here for the calcite-dolomite ratios.

Acknowledgment

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