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# A Method for Determining the Relative Abundance and Composition of Calcite and Dolomite in Carbonate Rocks

CARL L. HILTROP and JOHN LEMISH<sup>1</sup>

*Abstract.* The problem of determining the molar calcite to dolomite ratio in a carbonate rock arose as a result of investigations of concrete aggregate. A method for that determination is proposed, based on a combination of wet chemistry and X-ray techniques. Two carbonate rocks were analyzed and calcite to dolomite ratios were determined, basing the computations on two different assumptions. Those results are compared and suggestions made for further work.

The problem of determining the relative proportions of calcite and dolomite in a rock arises naturally when one considers a carbonate rock's suitability for use as concrete aggregate. This is a problem which has also long concerned the sedimentary petrologist.

Calcite and dolomite are quite similar optically and, at best, only a fair approximation can be obtained by a thin-section traverse, even though careful etching and counting procedures are employed (Belyankin, *et al.*, 1940). Furthermore, the two minerals are quite similar in their chemical properties and, thus, it has remained, to date, impossible to separate them quantitatively. Slight differences in their rates of solution in acid media have been reported, however (Weyl, 1957, 1958). That difference is the basis upon which staining procedures have been formulated which purport to give estimates of calcite-dolomite ratios in carbonate rocks (Weissmann and Diehl, 1953; Lawson, 1950).

Staining procedures take advantage of the fact that calcite goes into solution at a slightly faster rate than does dolomite and will impart a characteristic color to a prepared dyestuff more quickly than will an equivalent amount of dolomite. Obviously, in such a procedure, sample preparation will be critical. Rate of solution of both calcite and dolomite is surely a function of surface area exposed to solvent and, therefore, particle size is a critical factor.

Another variable upon which rate of solution of both calcite and dolomite will surely depend is composition—that is, the amount of excess calcium, or magnesium, above the ideal one to one ratio in dolomite, or the amount of magnesium ion in solid solution in calcite. These are factors which as yet have not been investigated, and their

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influence on staining techniques has not been evaluated. It is believed that answers to such problems are forthcoming, however, as is evidenced by the careful work of Weyl (1957, 1958) on the solution kinetics of calcite.

Tennant and Berger (1957) proposed an X-ray method which, according to those authors, has the advantage of giving results proportional to the total amount of material present having the calcite and dolomite structure types. Those authors state that a correction would be necessary in the X-ray calibration if the sample showed a variation from the ideal calcite ( $\text{CaCO}_3$ ) or dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ) composition. Their method consists of measuring the relative intensities of the strongest X-ray diffraction line for calcite and for dolomite in a series of mixtures of known proportions and applying those results to samples of unknown composition. That series of mixtures of known compositions gave rise to the smooth calibration curve illustrated in Figure 1.

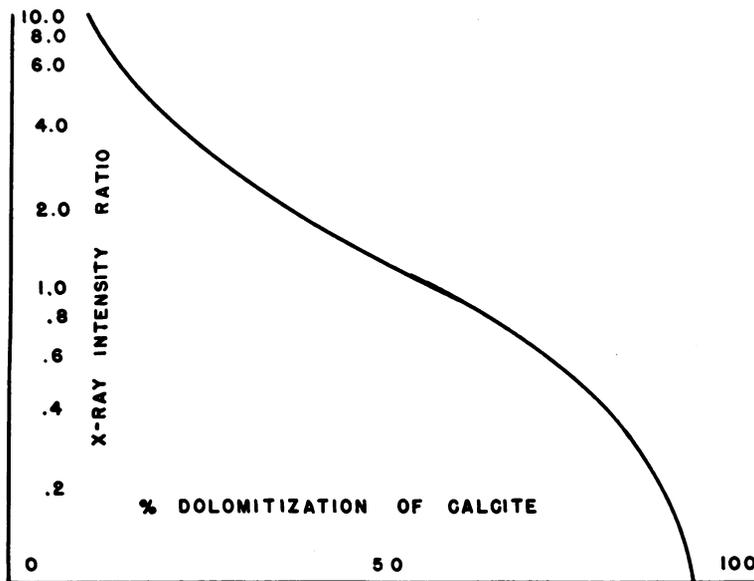


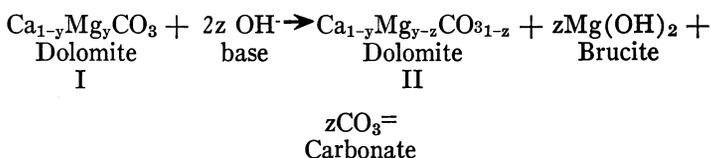
Figure 1. Calibration Curve. (After Tennant and Berger, 1957)

Those authors found, when attempting to reproduce points on the calibration curve, that preparation of sample was most critical. The samples were reduced to -325 mesh and subsequently wet ball-milled for 15 hours in the presence of ethyl alcohol. Tests showed that a grinding period of at least eight hours is essential.

Hiltrop (1958) attempted to delineate those characteristics of a carbonate rock which determine whether or not it will satisfactorily

serve as aggregate for concrete highway construction. He presented a method, based on conditional probabilities, whereby the effect of the various characteristics of a carbonate rock on serviceability could be evaluated. His probabilities indicated that high illitic clay content and low calcium to magnesium ratio (high dolomite content) correlated well with "poor" service record.

More recently, other investigators have called on a dedolomitization reaction (Swenson, 1960; Feldman, 1960; Hadley, 1960; Chaiken, 1959) in an attempt to explain the deleterious role played by some carbonate aggregates in concrete. Dedolomitization is depicted as involving the following reaction.



Dedolomitization, according to the above authors, is accompanied by weakening of the aggregate and/or of the cement paste.

Reports such as that of Hiltrop (1958) and of Swenson *et al.* (1960) lead one, once again, to consider the problem of determining calcite-dolomite ratio in a carbonate rock. A method is proposed here which employs a combination of wet chemistry and X-ray techniques. Final results are obtained by the solution of a pair of simultaneous equations.

#### PROCEDURE

Consider a hypothetical carbonate rock which is composed of the two minerals, calcite and dolomite. Assume that the average composition of the calcite is  $\text{Ca}_{1-x}\text{Mg}_x\text{CO}_3$  and the average composition of the dolomite is  $\text{Ca}_{1-y}\text{Mg}_y\text{CO}_3$ . The value of  $x$  will lie on the closed interval where  $0 \leq x \leq .22$  and  $y$  will lie on the closed interval where  $.44 \leq y \leq .51$ .

Graf and Goldsmith (1955) investigated the dolomite-magnesian calcite relations at elevated temperatures and pressures. They obtained equilibrium diagrams for those minerals. Their curves show that calcites and dolomites whose compositions vary from the ideal are unstable at normal atmospheric temperatures and pressures. Other investigators have reported the existence of such metastable phases in nature, however.

Goldsmith, Graf, and Joensuu (1955) have demonstrated the existence of calcites in which the mole per cent  $\text{Mg}^{++}$  in solid solution in the calcite can be as high as 20.8 per cent. Alderman (1959) has found dolomitic sediments being deposited in shallow

oceanic lagoons. The deposits contain magnesian calcites which have up to 22 per cent  $\text{MgCO}_3$  in solid solution. Also calcian dolomites are present in the sediments having up to 5 per cent excess  $\text{Ca}^{++}$  ion. Goldsmith (1959), has formed synthetic dolomites which have about one per cent excess  $\text{Mg}^{++}$  ion above the ideal 1:1 ratio.

Thus, even though such solid solutions are unstable, it is apparent that they do exist, and our choice of values for  $x$  and  $y$  seems reasonable in the light of present knowledge.

It is apparent that if one were simply to dissolve our hypothetical carbonate rock and analyze for  $\text{Ca}^{++}$  and  $\text{Mg}^{++}$  in solution, he could possibly arrive at quite erroneous results by assigning the composition  $\text{CaCO}_3$  to calcite and  $\text{CaMg}(\text{CO}_3)_2$  to dolomite. That is the procedure which has been followed in the past and is the difficulty which this proposed method hopes to circumvent.

Consider a small chip of hypothetical rock which is composed of  $N_c$  moles of calcite and  $N_d$  moles of dolomite having the compositions  $\text{Ca}_{1-x}\text{Mg}_x\text{CO}_3$  and  $\text{Ca}_{1-y}\text{Mg}_y\text{CO}_3$ , respectively. The problem is to determine experimentally  $x$ ,  $y$ ,  $N_c$ , and  $N_d$ .

Since it is generally agreed that calcite dissolves more rapidly than does dolomite, it seems that it would be possible to collect pure dolomite by leaching away all the calcite. Such a possibility seems even more promising in the case of those rocks which are composed of relatively coarse dolomite rhombs distributed throughout a matrix composed of very fine calcite grains. Such a leaching procedure was accomplished, and X-ray diffraction curves of the dolomite concentrate indicate the absence of calcite.

The method used to collect the dolomite fraction is as follows: About 50 grams of rock are pulverized to  $-\frac{1}{8}$  inch and placed in a beaker of 30 per cent acetic acid. Leaching is allowed to continue for several days, and then the undissolved portion is washed through a series of sieves. In the case of the two rocks examined here, that fraction passing the number 270 sieve, but remaining on the number 325, was found to give no X-ray diffraction peaks indicative of the presence of calcite. In such a leaching procedure, one assumes that all the calcite has been removed as well as some of the dolomite. Pure dolomite has been collected, but a quantitative separation has not been accomplished. This results in the necessity of solving a set of simultaneous equations.

Once pure dolomite has been collected, the calcium to magnesium ratio in the mineral can be determined by titration with versenate as described by Cheng *et al.* (1952). The results of these determinations are presented in Table 1.

With the publication of data which show the relationship between carbonate lattice constants and calcium-magnesium composition (Goldsmith and Graf, 1958) an alternative method for determining calcium to magnesium composition in dolomite has become available. A comparison of the results of these two methods is also presented in Table 1.

Table 1  
Table of Experimental Results

Specimen	Burlington Limestone	RL - 40
Chemical Dtrm. Dolomite	$\text{Ca}_{.50}\text{Mg}_{.44}\text{CO}_3$	$\text{Ca}_{.54}\text{Mg}_{.46}\text{CO}_3$
2 $\theta$ Dolomite		
10 $\bar{1}$ 12	70.15°	70.50°
2 $\theta$ Calcite		
10 $\bar{1}$ 12	65.77°	65.60°
C <sub>o</sub>		
Dolomite	16.0848	16.0152
C <sub>o</sub>		
Calcite	17.0332	17.0628
X-ray Dtrm. Dolomite	$\text{Ca}_{.54}\text{Mg}_{.46}\text{CO}_3$	$\text{Ca}_{.51}\text{Mg}_{.49}\text{CO}_3$
X-ray Dtrm. Calcite	$\text{Ca}_{.99}\text{Mg}_{.01}\text{CO}_3$	$\text{CaCO}_3$
Ca <sub>s</sub> ++	0.0079	0.0091
Mg <sub>s</sub> ++	0.0058	0.0052
Mole % Calcite Based on Chem.	3.7%	21.0%
Dtrm. of Dolomite		
Mole % Calcite Based on X-ray Dtrm. of Dolomite	8.0%	25.9%

Goldsmith and Graf hypothesized that lattice spacings in calcite should be a linear function of the amount of magnesium in solid solution. The upper line in Figure 2 is a straight line connecting C<sub>o</sub> (d<sub>10 $\bar{1}$ 12</sub>) for calcite with C<sub>o</sub> for magnesite. Small circles indicate experimentally determined points. It can be seen that the four calcites examined by Goldsmith and Graf determine a straight line which lies slightly below the first line. This lower line was employed to determine the amount of magnesium in solid solution in calcite. Goldsmith and Graf also examined four dolomites and found their compositions and lattice spacings to plot as indicated by the three small circles on the graph. (Two of the experimental points coincide.) If a straight line is drawn through these three points and extended to the value for pure calcite, one has a means of experimentally estimating the calcium to magnesium ratio in a dolomite. A segment of such a line is shown in Figure 2 extending from 40 mole per cent MgCO<sub>3</sub> to 60 mole per cent MgCO<sub>3</sub>. By making use of this straight line and X-ray determined C<sub>o</sub> spacings, one has an

alternative method for estimating the composition of dolomite. That is, there are two independent methods to estimate  $y$  in the original problem.

Now, take a chip of the original rock and completely dissolve it in hydrochloric acid. The number of moles of calcium ion in solution,  $\text{Ca}_s^{++}$ , and the number of moles of magnesium ion in solution,  $\text{Mg}_s^{++}$ , can be determined by the versenate method. Once this is done, one can set down the following pair of simultaneous equations.

$$\text{Ca}_s^{++} = (1-x)N_c + (1-y)N_d \tag{1}$$

$$\text{Mg}_s^{++} = xN_c + yN_d \tag{2}$$

where  $y$  has been determined by either of the methods discussed above. Equations (1) and (2) form a pair of independent simultaneous equations in three unknowns. In order to solve for the unknowns, there must be either another independent equation supplied or one of the unknowns must be determined by independent means. The latter method is employed here. The variable quantity  $x$  is obtained by determining  $C_o$  spacings and referring to Goldsmith and Graf's straight line function (Figure 2). When that has been done, equations (1) and (2) reduce to a pair of simultaneous equations in two unknowns and can be solved for  $N_c$  and  $N_d$ . This, then, is equivalent to determining the molar ratio of calcite to dolomite in the original rock.

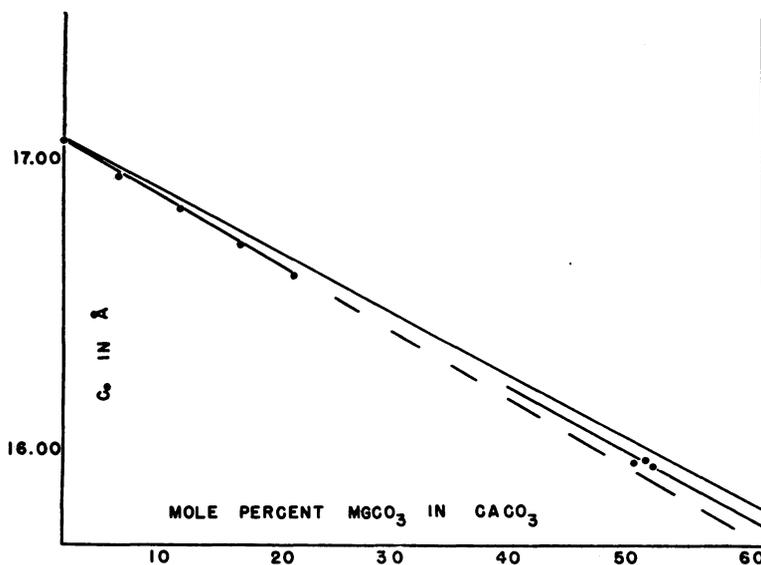


Figure 2. Variation of  $C_o$  for the Ca-Mg Carbonates. (After Goldsmith and Graf, 1958)

## EXPERIMENTAL RESULTS

The mole per cent calcite, relative to total carbonate present, was determined in two rocks. Those two rocks are designated in this paper as Burlington limestone and RL-40. Pertinent data concerning that determination, as well as the final results, are presented in Table 1.

## DISCUSSION

It is not claimed that the above procedure for determining calcite-dolomite ratios is the "last word" on the subject. Not at all. What is claimed is that this is an alternative method for such a determination. Several specimens should be examined for calcite/dolomite by this method and by the method of Tennant and Berger (1957), and the results compared. Furthermore, this method claims to give only average values for  $x$  and  $y$ . In some rocks, at least, it would seem probable that the composition of both the calcite and the dolomite would vary from place to place within the rock. Tennant and Berger are aware of this fact and admit that the effect of such a variation on intensity of X-ray reflection has not been investigated.

Another simplification which has been made, in order to outline the method as briefly and straightforwardly as possible, is to consider dolomite to be composed of only calcium and magnesium. It is known that it may contain a significant proportion of iron and manganese as well. This is a factor which other workers may wish to take into consideration. It is possible that such a consideration may lead to a third independent equation which, in turn, will allow the evaluation of  $x$ ,  $N_c$ , and  $N_d$ . For example, if it is found that the dolomite, once having been collected, has the formula  $Ca_{1-y-w}Mg_yFe_wCO_3$ , and if it can be shown that all the iron which goes into solution is from the dolomite, then a third independent equation will have become available. That is, the number of moles of iron in solution,  $Fe_s^{++}$ , is equal to the number of moles of dolomite,  $N_d$ , which went into solution, multiplied by  $w$ .

$$Fe_s^{++} = wN_d. \quad (3)$$

Another interesting avenue of research is made apparent when one considers equations (1) and (2). Addition of equations (1) and (2) gives

$$Ca_s^{++} + Mg_s^{-} = N_c + N_d. \quad (4)$$

Now, if the assumption is made that the method of Tennant and Berger gives reliable information concerning the calcite to dolomite ratio in a rock, a new method becomes available for determination

of  $x$  and  $y$ . For if a value for  $\frac{N_d}{N_d + N_c}$  is obtained (as it is in the Tennant and Berger method), that is equivalent to adding a third independent equation to our original pair of simultaneous equations (i.e., equations 1 and 2).

For example, if

$$\frac{N_d}{N_d + N_c} = K, \tag{5}$$

then,

$$N_d = \frac{KN_c}{1 - K}.$$

Substitution of this quantity for  $N_d$  in (4) allows the evaluation of  $N_d$  and  $N_c$ . Then equations (1) and (2) can be solved for  $x$  and  $y$ .

Results obtained in that way could be compared with those obtained by Goldsmith and Graf's X-ray method.

Another interesting approach to the evaluation of  $x$  is afforded by the work of Harker and Tuttle (1955). They showed that the weight per cent  $MgCO_3$  in solid solution in calcite is a straight line function of the change in position of the  $29.3^\circ 2\theta$  X-ray diffraction peak of calcite. In order to measure accurately the change in  $2\theta$  a convenient standard was added to the unknown. The material which was chosen for a standard was cadmium fluoride. That standard was found to have its strongest peak at an angle of  $0.72^\circ 2\theta$  below that of pure calcite. Using such a standard peak for reference, it was possible to measure the angular shift in the position of the strongest peak of calcite with an accuracy of  $\pm 0.01^\circ$ .

#### APPLICATION TO THE CONCRETE AGGREGATE PROBLEM

Calcite-dolomite ratios, as well as the compositions of calcite and dolomite, could be determined for those rocks discussed by Hiltrop and Lemish (1959). In that report an attempt was made to relate various rock properties (including calcium to magnesium ratio) with serviceability. From the recent arguments put forth by the proponents of a deleterious "dedolomitization" reaction, calcite-dolomite ratios as well as calcite and dolomite composition would appear more critical than simply total  $Ca^{++}$  ion and  $Mg^{++}$  ion composition.

An attempt could be made to bring about dedolomitization of a

rock in the laboratory. The quantities  $x$ ,  $y$ , and  $\frac{N_d}{N_c + N_d}$  should

be determined as accurately as possible before and after dedolomitization has taken place. Investigations in this direction may lead to a better understanding of the reaction, its extent, its rate and degree to which it is harmful to concrete.

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