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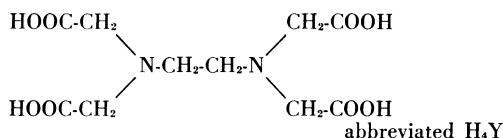
A New Method Utilizing Versene for Determination of the Calcite-Dolomite Ratio in Carbonate Rocks

By ROBERT C. WEISSMANN AND HARVEY DIEHL

The sedimentary petrologists have long been concerned with the determination of the calcite-dolomite ratio of carbonate rocks. The ratio is difficult to determine in thin section with any accuracy; the minerals are very similar optically and at best only a fair approximation can be obtained by a thin section traverse. The Lemberg staining procedure, which utilizes a silver nitrate-potassium chromate reagent, is rather involved and not too reliable. The differential thermal analysis and thermoluminescence methods are fairly rapid and accurate but involve elaborate equipment.

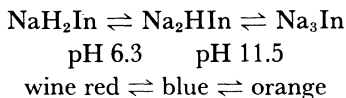
We are now reporting a relatively simple chemical method of differentiating calcite and dolomite which is inexpensive and can be used in the field. With a little care, semiquantitative results can be obtained. The test is based on a difference in the rate at which calcite and dolomite dissolve in ethylenediaminetetraacetic acid. This acid is the same as that used for the determination of the hardness of water (1) and as in the hardness determination, the organic dyestuff, eriochromeschwartz T, is used as indicator.

Ethylenediaminetetraacetic acid (Versene) forms a series of



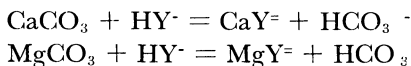
salts on neutralization, the disodium salt, $\text{Na}_2\text{H}_2\text{Y} \cdot 2\text{H}_2\text{O}$, being used to prepare the reagent solution for the test. Ethylenediaminetetraacetic acid reacts with the ions of calcium and magnesium to form the complex ions $\text{CaY}^{=}$ and $\text{MgY}^{=}$, in which the calcium and magnesium are very tightly bound. Both of these are slightly dissociated to yield calcium and magnesium ions, the complex magnesium ion being somewhat more dissociated than the calcium one; but the extent of this dissociation is so slight that solutions containing sodium ethylenediaminetetraacetate at pH 7 or higher dissolve practically all of the compounds of the alkali metals, even attacking glass and silicates slowly. In the test, the sodium ethylenediaminetetraacetate is used in conjunction with a hydroxy, azo dyestuff

known as eriochromeschwartz T or F 241. F 241 is itself a tribasic acid which functions as an acid-base indicator with two color changes.

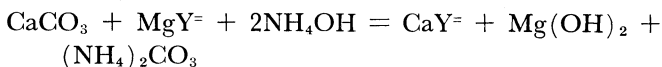


The most alkaline form of the indicator combines with magnesium to form a non-dissociated magnesium derivative, MgIn , which is red in color. Magnesium, however, unites with ethylenediaminetetraacetate in preference to F241, so that in the presence of ethylenediaminetetraacetate F241 retains its own color, wine-red, blue, or orange, depending on the pH. At a pH of 10, the indicator is in the blue form but if magnesium ions are present in amounts greater than those required to balance the ethylenediaminetetraacetate, the F241 will change to the red, MgIn form.

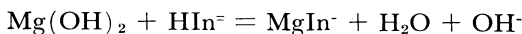
In the test, a solution containing both ethylenediaminetetraacetate and F241 is used. The ethylenediaminetetraacetate attacks the carbonate rock taking into solution both calcium and magnesium. The substances involved are HY^- (the form which the acid has at pH 10), HIn^- , Ca, and Mg and the various ions formed. Calcium combines with ethylenediaminetetraacetate more firmly than does magnesium. Both combine with ethylenediaminetetraacetate more firmly than with F241. On the other hand magnesium combines with F241 more firmly than does calcium. The test then involves the following sequence of reactions: at the start, solid sample plus excess ethylenediaminetetraacetate, pH 10.



toward the end, as the amounts of calcium and magnesium become equivalent to the ethylenediaminetetraacetate



and finally



Starting with a limited amount of sodium ethylenediaminetetraacetate then, sufficient rock is dissolved so that all of the calcium ties up the ethylenediaminetetraacetate and the magnesium then changes the color of the indicator from blue to red. The magnesium does not change the indicator earlier in the process because it is tied up with the ethylenediaminetetraacetate until the calcium is present in sufficient amount to displace the magnesium.

RECOMMENDED PROCEDURE

Reagent. A single reagent solution is prepared by mixing the proper volumes of three solutions: a solution of sodium ethylenediaminetetraacetate, a buffer solution, and an indicator solution. To prepare the sodium ethylenediaminetetraacetic acid solution, dissolve 4.0 g. of disodium dihydrogen ethylenediaminetetraacetate dihydrate¹, $\text{Na}_2\text{H}_2\text{Y} \cdot 2\text{H}_2\text{O}$, in 750 ml. of distilled water. To prepare the buffer solution, mix 6.75 g. of ammonium chloride and 57.0 ml. of concentrated ammonium hydroxide and dilute to 100 ml. with distilled water. The pH of this solution is just over 10. To prepare indicator solution, dissolve 1.0 g. of eriochromeschwartz T (F241)¹ in 100 ml. of methyl alcohol. To prepare the final reagent solution, mix 50 ml. of the sodium ethylenediaminetetraacetate solution, diluted with 50 ml. of distilled H_2O , 12.5 ml. of the buffer solution and 0.25 ml. of the indicator solution.

Wetting Agent. Dissolve 0.1 g. of Aerosol in 100 ml. of water.

Sampling Spoon. The sampling spoon used in this study is made of brass. The spoon bowl is $\frac{1}{4}$ " in diameter, $\frac{1}{16}$ " deep and highly polished to prevent adhering of mineral grains. It was designed to have a minimum of rim area in order to allow more consistent measuring of samples. The samples measured weighed 0.0147 g. Anyone wishing to use the accompanying time factors should have a spoon made which has exactly the same weight capacity. For the procedure outlined below, any sampling device with a weight capacity of 0.010 to 0.015 g. can be used, for which an independent set of time factors can be determined.

Procedure. Crush the specimen completely so that it all passes through a 100 mesh Tyler sieve; retain on the pan. Measure out a sample of the powdered specimen using a suitable sampling spoon; level off the sample by sliding a straight edge across the spoon. Transfer the sample to a white evaporating dish, 6 cm. in diameter. Wet the sample with one drop of Aerosol solution. Pipet 3.0 ml. of the versenate solution into the dish and note as zero time the instant when the last drop leaves the pipet. Stir the mixture vigorously with a small glass stirring rod. Note the time when the color changes definitely from blue to a purple-pink (10.0 B 6/4 to 10.0 PB 6/6, Munsell)³. Repeat the procedure three times. From the average value for the observed time, obtain the calcite-dolomite ratio using the data of Table I or similar data obtained personally from tests on known materials.

¹Disodium dihydrogen ethylenediaminetetraacetate and eriochromeschwartz T can be obtained from the Hach Chemical Company, Ames, Iowa.

Notes on Reagent and Procedure. The magnesium chloride needed to make the indicator function properly is added to the standard solution of sodium versenate as prepared for the hardness titration. Such magnesium has been intentionally omitted in the reagents used in this test. All calcite used contained sufficient magnesium to serve with the indicator.

The color change at the calcitic end is rather sharp and can be determined easily within two or three seconds. However, at the extreme dolomitic end, the color change becomes slower and requires a minute or more to become definite. It is best noted by actually observing the grains, which turn a definite pinkish color while the solution is still a rather indefinite purplish-blue. This transition time does not introduce a significant error in that the time differences at the dolomitic end are widely spaced.

The pH of 10 obtained with the buffer solution specified is a satisfactory value. At lower pH the test fails.

The quantities of reagents specified for the preparation of the reagent are those found best from a series of studies; the amounts taken should not vary appreciably from those specified.

The reagent solution must be freshly prepared in order to obtain consistent results. The constituents of the reagent solution are believed to keep indefinitely; but once they are mixed, slow decomposition takes place. It is advised that the reagent solution not be used after 24 hours standing. A polyethelene flask is found to be the most suitable container for the reagent.

EXPERIMENTAL CONFIRMATION OF THE METHOD

Results with Standard Calcite-Dolomite Mixtures. Crystalline calcite and crystalline dolomite were ground separately to pass a 100 mesh Tyler sieve. Samples ranging from pure calcite to pure dolomite in increments of 10 per cent were prepared by mixing weighed quantities of each component.

The test was applied to each of these eleven standard mixtures. The time at which the change in color occurred for each is given in Table I. The spread in time is sufficiently great that there was no difficulty in differentiating adjacent mixtures of the series.

Tests on Carbonate Rocks From the Field. Specimens of carbonate rock from (a) Fort Dodge, Iowa, (b) Iowa Falls, Iowa, and (c) Alden, Iowa, were subjected to the test. The carbonate rocks from these localities exhibit a wide range in calcite-dolomite ratio.

The rocks were examined in thin section and the ratio estimated.

The test was applied as described above. The results agreed in each case but one.

One point of difference in reaction time between the standards and the rock samples occurred at the calcite end of the range. The 100% calcite standard required 64 seconds in order to enact a color change, a pure limestone sample required but 44 seconds. This difference is probably due to the fact that the limestone powders more upon crushing than does the crystalline calcite, and dissolves in the versene solution more rapidly. This slight difference in relative solubility would be sufficient to cause the difference in time noted. It is believed that this is insignificant in that the remainder of the standards and actual rock samples checked out very well.

As a further check, the test was applied to a series of carbonate rocks whose calcite-dolomite ratios had previously been determined by the silver nitrate-potassium carbonate method (Lawson 1951). The result of the two methods agreed in each case within 10%.

Table 1
Time to Produce Change in Color of Regent in Dissolving
Calcite-Dolomite Mixtures

Standards	Ave. Time Minutes: seconds
Pure Calcite	1:04
9 cal 1 dol	1:14
8 cal 2 dol	1:29
7 cal 3 dol	1:42
6 cal 4 dol	2:07
5 cal 5 dol	2:30
4 cal 6 dol	3:24
3 cal 7 dol	4:37
2 cal 8 dol	7:00
1 cal 9 dol	12:10
Pure Dolomite	30:00+

References

- (1) Diehl and Smith, *Quantitative Analysis*, John Wiley and Sons, Inc., New York, 1952, Page 340.
- (2) Lawson, Ralph W., *Determination of Calcite-Dolomite Ratios in Carbonate Rocks*. Iowa Academy of Science, Proc., Vol. 57, 1950, page 263-266.
- (3) *Munsell Book of Color*, Munsell Color Company Inc., Baltimore, Maryland, Vol. 1, 1942.

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