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The Determination of Calcium-magnesium Ratios in Sedimentary Rocks

By DONALD C. BOARDMAN

INTRODUCTION

The study of clastic sediments has been basic work for most geologists. Field descriptions tell the kind of rock, its color, its texture, how it is bedded, and its mineral and organic content. In the laboratory more exact mechanical and mineralogical analyses are made to add to the statistics. Among the laboratory analyses insoluble residue studies have been a valuable tool in research on the clastic sediments and the analysis of samples to determine the insoluble percentages has been systematized so that highly skilled technicians are not required to perform most of the work. As a result many thousands of samples are processed each year. The insoluble portion is often also analyzed to compute grain size, sorting, and mineral content. Unfortunately the soluble portion of the rocks has been largely neglected because of the time required in making chemical analyses.

Pettijohn (1949, p. 313) has classified carbonate rocks on the ratios of calcite to dolomite in the carbonate fraction. It is suggested that a statistical analysis of the soluble portions of sandstone should be made using a modification of this classification and that a study of the cement of these clastic sediments would be an important key in the problem of the origin of dolomites which has so long been perplexing geologists.

The proposed classification would have the following five divisions:

1. *Limestone* cement containing over 95% calcium carbonate and less than 5% magnesium carbonate.
2. *Magnesian limestone* cement containing from 90% to 95% calcium carbonate and 5% to 10% magnesium carbonate.
3. *Dolomitic limestone* cement containing from 50% to 90% calcium carbonate and 50% to 10% magnesium carbonate.
4. *Calcitic dolomite* cement containing from 50% to 10% calcium carbonate and 50% to 90% magnesium carbonate.
5. *Dolomite* cement containing less than 10% calcium carbonate and more than 90% magnesium carbonate.

METHOD

With the help of Dr. Harold Fiess of the department of chemis-

try of Wheaton College, Illinois a procedure has been worked out that makes the determination of the magnesium and calcium carbonate content of the soluble portion of a sediment a comparatively simple process. It is carried out as part of the regular insoluble residue analysis.

Samples are crushed and treated with hydrochloric acid by the standard method described by McQueen (1931, p. 104-107). After thorough washing with distilled water, the solution and all wash water, amounting to about 300 milliliters, is treated by adding about ten grams of ammonium chloride and then made basic by the addition of ammonium hydroxide, causing the iron to precipitate. The ammonium chloride supplies ammonium ions which prevent the precipitation of the magnesium present. The iron precipitate is removed by filtering. The remaining solution is diluted to one liter and a twenty-five milliliter portion removed. The total calcium and magnesium carbonate is determined by titrating this portion using a modification of the Schwarzenbach method as worked out by Diehl, Goetz, and Hach (1950). Indicators for this process have been perfected under the trade names of UniVer and TitraVer by the Hach Chemical Company, Ames, Iowa and are used in this determination.

A second twenty-five milliliter portion is titrated with CalVer indicator, also marketed by the Hach Chemical Company, to determine the amount of calcium carbonate. The amount of magnesium carbonate is then computed by subtraction. The indicators used are calibrated to indicate the parts per million of calcium carbonate and magnesium carbonate in the solution so it is a simple mathematical calculation to compute either the total weight of the calcium carbonate and magnesium carbonate in the sample or the ratios of these two compounds. In practice the ratios have been used to classify the cement as indicated above.

EXAMPLE

A number of samples of Jordan and Madison sandstones of Cambrian age collected in the region of the Wisconsin Arch near Madison, Wisconsin were treated as described. The following results were obtained:

1. The Madison sandstone which is a very fine grained sandstone and siltstone and occurs east of the Wisconsin Arch has an average ratio of 62% calcium carbonate to 38% magnesium carbonate which would make it, according to the proposed classification, a *dolomitic limestone* cement.

2. The Jordan sandstone, a fine sand, has an average ratio of 73.5% calcium carbonate and 26.5% magnesium carbonate east of the crest of the structure. This cement is also a *dolomitic limestone*.

3. On the west side of the structure the Jordan sandstone varies in texture from medium sand to silt. In all samples analyzed, however, the cement is found to be extremely high in calcium carbonate, averaging 98% calcium carbonate to 2% magnesium carbonate. Thus, this is a *limestone* cement.

RESULTS

It is believed that this preliminary study shows that the Wisconsin Arch has had a bearing on the chemical composition of the cement of the sandstones laid down around it and that the composition of the cementing material is independent of the grain size.

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