DISTINCTION BETWEEN CALCITE AND DOLOMITE ON POLISHED SURFACES.*

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ABSTRACT. The existing methods for distinguishing calcite and dolomite on polished surfaces have been culled from the literature, tested in the laboratory, and evaluated. The most satisfactory method is staining in copper nitrate solution, followed by fixation in ammonia. This method has been carefully studied and a standard procedure suggested.

PART I. SUMMARY OF EXISTING METHODS.

DURING the laboratory study of carbonate rocks from Dutchess County, New York, in 1939, Mrs. E. B. Knopf and the writer found it desirable to distinguish between calcite and dolomite on polished surfaces. An exhaustive study of the existing staining methods was therefore undertaken. A similar study had been begun the year before by the late C. D. Cooksey, Jr., and the writer was given access to the material that he had accumulated.

Mrs. Knopf's unfailing and helpful interest during the course of the study and her generous contribution of materials is gratefully acknowledged. The writer wishes also to thank Dr. C. S. Ross of the U. S. Geological Survey and Prof. H. W. Foote of the Chemistry department of Yale University for critical reading of the manuscript.

Principle. All chemical methods for distinguishing between calcite and dolomite depend ultimately on the much greater rate of solubility of calcite in cold dilute acid. In the staining methods, in general, the salt of a strong acid and a weak base is used, giving a pH considerably less than 7; the solution therefore acts like a weak acid. The salt is chosen so that, upon attacking the calcite, the solution leaves a coating of some compound that is colored or that can be made to acquire a color.

The other rhombohedral carbonates react to weak acid in the same way as dolomite, and the orthorhombic carbonates (except cerussite) react in the same way as calcite; separation can therefore be effected between these two groups, e.g. between calcite and ankerite. In the calcite-rhodochrosite isomorphous

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series,[1] distinction can be made between pure calcite and material high in manganese.[2]

Weak acid. The oldest method of differentiation between calcite and dolomite is by etching with a cold dilute acid (acetic acid is usually used). This method is of very limited application, particularly in the study of polished surfaces, because, a: there is no color contrast, b: dolomite is also slightly attacked and loses its polish, and c: calcite and dolomite are both attacked at different rates in unlike lattice directions, so that adjoining grains of the same mineral may appear quite different.

An improvement on this method was suggested by Linck.[3] Ammonium acid phosphate is added to the acetic acid; this reacts with the dolomite to give a gelatinous precipitate of magnesium ammonium phosphate which protects the dolomite from any further attack. The other difficulties remain however.

Lemberg's hydroxide stains. The first really important work on stains to distinguish calcite from dolomite was reported by J. Lemberg[4] in a series of papers. His first satisfactory stain depends on the salt $FeCl_3$, which deposits a coat of $Fe(OH)_3$ on the surface of the calcite. Since this gives only a faint brown color, the specimen is treated with $(NH_4)_2S_x$ which converts the stain to black FeS. This stain is the one known as Lemberg's stain in Europe where it seems to be the favored one.

The solution is made up by adding 1 part of crystalline $FeCl_3.6H_2O$ to 10 parts H_2O; it is stable. The specimen is immersed not more than one minute (less if fine-grained), is very carefully and gently washed, and is dipped in $(NH_4)_2S_x$

[1] Krieger, Philip: Amer. Mineral., Vol. 15, p. 23, 1930.

[2] Ross, C. S.: U.S.G.S. Prof. Paper 179, p. 8, 1935.

[3] Linck, G.: Abhandlungen zu geologischer Spezialkarte von Elsass-Lothringen, 3, p. 1, 1884. See p. 17. This periodical is listed in American libraries under the heading: Alsace-Lorraine, Geologisches Landesanstalt.

[4] Lemberg, J.: Zeitschrift der deutschen geologischen Gesellschaft,
24, p. 187, 1872 (esp. p. 226),
28, p. 519, 1876 (esp. p. 571),
39, p. 489, 1887,
40, p. 357, 1888,
42, p. 737, 1890 (esp. p. 744),
44, p. 224, *1892* (*esp. p. 231*),
44, p. 823, 1892. The important contributions are italicized.

(strength and time unimportant). Dolomite will turn pale green if immersed too long in the iron solution.

This stain has the following disadvantages, a: FeS is unstable and will oxidize, turning brown and crumbling; b: both FeS and $Fe(OH)_3$ contract very strongly on drying, leaving cracks all over the calcite areas; c: the stain rubs off very easily. Lemberg recognized all these difficulties and he stated that the stain is good only in a damp atmosphere and for a few minutes. He suggested the following modifications; 1: Heat the stain quickly so that it will go over to Fe_2O_3; this obviates the change with time but the shrinkage is enormous. 2: Treat with $K_3Fe'''(CN)_6$ immediately after reduction to the sulphide and before any oxidation has taken place; the result is Turnbull's blue which is stable and has less shrinkage, but still enough to be quite noticeable. However, the reagent will attack the dolomite in the specimen if it is iron-bearing. Others have suggested, 3: Treat with KCNS, without reduction to the sulphide. However, the resulting stain is very weak, for $Fe(CNS)_3$, though deep red in color, is not a precipitate. None of these modifications has found favor.

Lemberg also based a stain on the corresponding reaction with $AlCl_3$. A precipitate of $Al(OH)_3$ forms on the calcite, which is colorless but can easily be stained with a dye (logwood is the dye always used). This is the stain known in this country as Lemberg's stain, and until recently it has been used here almost to the exclusion of all others. The iron stain can conveniently be referred to as the black Lemberg stain, and the aluminum stain as the red Lemberg stain, although Lemberg invented some other stains.

Lemberg made his solution as follows: Add 4 parts of $AlCl_3$ and 6 parts of logwood chips to 60 parts of H_2O; boil for 20-25 minutes, stirring constantly and replenishing the water lost by evaporation; filter. The specimen is immersed for a period ranging from five to ten minutes. Dolomite will become speckled with faint blue spots if immersed for 20 minutes.

This stain has the following disadvantages; a: the stain is stable but the solution is not (the time limit of its stability is not given in the literature); b: the stained coating contracts very strongly and tends to spall off if thick, therefore the best

results are obtained with minimum immersion; c: the stain rubs off very easily.

Steidtmann[5] used the above formula with 6 parts of logwood extract instead of the chips; he found it necessary to dilute the very strong solution thus obtained with 1200 parts of H_2O. Fairbanks[6] obtained good results by using 0.6 part of logwood extract (haematoxylin) instead of 6 parts, adding a few drops of H_2O_2 to oxidize the dye; further dilution was unnecessary. This may be taken as a satisfactory standardization.

Lemberg's silver stains. Before he developed the hydroxide stains, Lemberg[7] had been working on a method for distinguishing calcium-bearing from magnesium-bearing minerals. Magnesium compounds decompose to the oxide at much lower temperatures than do calcium compounds; by heating the material to be studied to the proper intermediate temperature and then cooling and treating with $AgNO_3$, he obtained a black stain (of Ag_2O ?) on the magnesium compounds. He applied this to a calcite-dolomite rock and found that the dolomite stained but very irregularly, so that the result was equivocal. Meyer,[8] working on this method, found that, if the carbonates were heated below the boiling point of water in the presence of a silver solution and were then treated with a reducing agent, the calcite was stained and not the dolomite. Lemberg (op. cit.) investigated this reaction further and developed two more stains.

In each of these, the rock is immersed in ten per cent $AgNO_3$ at 60° or 70° C. for two to five minutes, depending on the depth of stain desired. The Ag_2CO_3 precipitated on the calcite is then either 1: reduced to Ag by a strong reducing agent (such as pyrogallol, 1 cgr. in 5 cc. of H_2O, prepared immediately before use[9]) or 2: converted to Ag_2CrO_4, a bright orange compound, by immersing in a solution of K_2CrO_4 for about a minute. The author had very poor results with the pyrogallol stain; it covered everything and was precipitated quite heavily

[5] Steidtmann, Edward: Geol. Soc. Amer. Bull., Vol. 28, p. 431 (see p. 434), 1917.

[6] Fairbanks, E. E.: Amer. Mineral., Vol. 10, p. 126, 1925.

[7] Lemberg, J.: First two papers cited.

[8] Meyer, Otto: Zeitschrift der deutschen geologischen Gesellschaft, Vol. 31, p. 445, 1879.

[9] Manganous salts are also suggested.

by a nearly pure dolomite rock. The chromate test, however, usually gives a very good color contrast with sharp borders, and it does not shrink. It does rub off, however, and on fine-grained rocks has a tendency to diffuse over all the grains. Perhaps future investigation can obviate the latter difficulty.

Stains with Turnbull's Blue. $K_3Fe''(CN)_6$ will precipitate a permanent stain of Turnbull's blue with the slightest trace of ferrous iron. As noted above, Lemberg used this to fix FeS. Later Krech,[10] using a freshly prepared solution of $K_3Fe''(CN)_6$, acidified with a few drops of HCl, was able to reveal slight traces of Fe'' in dolomite. He found that sometimes dolomite would stain while calcite did not. Heeger[11] combined this effect with that of a weak acid, adding a few drops of $K_3Fe''(CN)_6$ to a dilute solution of HCl, and watching the reaction under the microscope. He found that, as the acid attacked the carbonates, any Fe'' present produced a blue precipitate, whose strength varied rather with the rate of attack by acid than with the percentage of Fe'' in the mineral grain. Thus calcite stained more quickly than dolomite, and dolomite than ankerite. Moreover, delicate zoning and other structures were revealed by variations in Fe'' content. Heeger believed that most calcite would stain (as well as most dolomite, if given time enough), but Steidtmann (op. cit.) used a similar solution and claimed that dolomite invariably stained and primary calcite (but not vein calcite) invariably remained unstained. The author has stained the ankerite of a calcite-ankerite rock with this solution, obtaining clear distinction and very sharp boundaries, but a marble known to be a mixture of calcite and dolomite failed to stain at all. Obviously a stain that depends not on the inherent properties of calcite and dolomite but on their Fe'' content cannot be safe. The stain is very valuable, however, in detecting ankerite.

Henbest[12] has standardized the solution as follows: 2 parts of conc. HCl in 88 parts of H_2O, 10 parts of $K_3Fe''(CN)_6$ (preferably of a concentrated solution) added just before use. The solution is unstable, giving off HCN.

Copper stain. Two decades after Lemberg's work, Hin-

[10] Krech: Jahrbuch der königlichen preussischen geologischen Landesanstalt, I, p. 59 (esp. p. 68), 1909.

[11] Heeger: Centralblatt für Min. Geol., und Paläont., p. 44, 1913.

[12] Henbest, L. G.: Jour. Paleo., 5, p. 355 (see p. 362), 1931.

den[13] reported on an investigation of the effects of salts of several weak bases on powders of the carbonates. He paid no attention to Lemberg's publications but announced that $FeCl_3$ gave calcite a satisfactory stain, $CuSO_4$ a fair one, $Pb(C_2H_3O_2)_2$ and $HgCl_2$ none at all. As the major conclusion was that the iron salt gives the best stain, a conclusion already accepted in Germany, his paper provoked nothing but a rebuke for overlooking Lemberg's work.

Mahler[14] and Spangenberg[15] investigated solutions of iron and copper salts in a search for some solvent that would remove only the calcite from a powdered mixture of carbonates; acetic acid had not been selective enough. $FeCl_3$ was not satisfactory, but solutions of $CuSO_4$ and $Cu(NO_3)_2$, when heated to boiling, were found to dissolve calcite readily, dolomite slightly, and magnesite not at all. The use of a boiling solution of copper nitrate was introduced to the English literature by Holmes.[16]

Ross (loc. cit.) appears to have been the first to stain calcite by immersing specimens in a cold solution of $Cu(NO_3)_2$ for several hours. The faint blue-green stain so obtained is washed in NH_4OH, producing a deep-blue stain of $Cu(NH_3)_4(OH)_2$ on the calcite. This stain has several advantages over the others described; a: it is as delicate as any of the others, b: it does not shrink or crack, c: it is usually very uniform, d: it does not rub off, e: the solutions are easily prepared and are stable. Photographs of this stain are reproduced in Plates 19-22 of U. S. Geol. Surv. Prof. Paper 179. As shown there, the blue stain photographs as white and contrasts well with gray quartz.

For work that requires the contrast between calcite (stained blue) and dolomite (white) the author of the present paper made an effort to increase the color contrast.

The first method tried was immersion of the stained specimen in $(NH_4)_2S_x$, converting the stain into black CuS. The method has several disadvantages; a: the stain will form only

[13] Hinden, E.: Verhandlungen der naturforschenden Gesellschaft in Basel, 15, p. 201, 1904.

[14] Mahler, O.: Doctorate dissertation at Freiburg, 1906. The writer has not had access to this paper, but it is quoted freely by Spangenberg.

[15] Spangenberg, K.: Zeitschrift für Kryst., 52, p. 529 (esp. p. 546), 1913.

[16] Holmes, Arthur: Petrographic Methods and Calculations. London, p. 267, 1921.

if the original stain is wet and preferably before ammonia fixation, b: it is not very uniform, c: it is easily rubbed off (less so if first allowed to dry), d: the dolomite becomes a pale green which greatly lessens the effective contrast. It is doubtful if this stain will ever be satisfactory.

A somewhat better method involves the conversion of the blue stain into $Cu_2Fe''(CN)_6$, a red precipitate. After the original stain has been fixed with ammonia and (preferably) dried, the specimen is carefully rubbed to remove any excess Cu, and is then immersed for five minutes in a strong solution of $K_4Fe''(CN)_6$; the blue stain is converted into a deep red which will not easily rub off unless immersion has been for too short a time. The stain will not crack and is quite uniform on the calcite. However, since the faintest trace of Cu causes reaction, the dolomite often becomes pink where no trace of color could be seen before. In particular, the boundaries between grains of dolomite are outlined in pink, but this is often a real advantage in the study of coarse-grained rocks. On the other hand boundaries between calcite and dolomite grains become blurred, especially if the specimen was left too long in either the nitrate or the ferrocyanide solution; underexposure to the nitrate is definitely to be preferred. The stain will be of little use for fine-grained rocks, but may be of value where the grain-size is 1 mm. or over.

After the author had completed his laboratory work, he learned from Charles F. Park of the U. S. Geological Survey that calcite can be stained by solutions of nickel or of cobalt nitrate. Doctor Ross[17] has made some experiments on these stains and has kindly permitted the writer to make use of his results. The nickel salt requires two to three days' inmersion over a steam bath, and the stain, which is bright green, never seems to be sufficiently uniform; it is therefore inferior to the copper stain. Cobalt nitrate will stain calcite in about six hours[18] over a steam bath, producing a uniform lavender stain

[17] Personal communication.

[18] Cobalt nitrate stains aragonite in polished section in about twenty minutes over a steam bath (Meigen's reaction). Holmes (loc. cit.) states that the contrast between calcite and aragonite in the same specimen is not good nor selective to fine grain, and suggests treatment in $(NH_4)_2S_x$, converting the stain to black CoS. For calcite vs. dolomite, however, the selection is very sharp.

which for some purposes may be preferable to the copper stain, despite the necessity for long immersion at high temperature.

PART II. SUGGESTED EXPERIMENTAL PROCEDURE IN THE USE OF THE $Cu(NO_3)_2$ STAIN.

Variables. The following variables have been considered in relation to this stain: Time, concentration, acid radical, temperature, percentage of calcite in specimen.

Time and Concentration. If a suite of specimens of the same rock which have been immersed in a given solution of $Cu(NO_3)_2$ for differing lengths of time are examined, the staining is seen to progress as follows: The calcite first acquires a light coat with considerable speckling, which at first indicates unstained areas. As the coat deepens, this irregularity becomes less and less, and finally the whole grain becomes coated with a deep uniform coat of blue. The dolomite remains uncolored for a considerable period but it is attacked, as can be seen from its loss of the original polish, contrasting very well with quartz, chert, or other insoluble material. After a time, a faint green haze develops on the dolomite. This slowly becomes a green speckling, and at the same time the boundaries between calcite and dolomite, which have been very sharp, become blurred. However, during the time of observation (up to 24 hours) the dolomite never acquires a stain at all like that on the calcite, so that the general relations remain quite clear.

Optimum conditions therefore are those under which the calcite stain becomes deep and uniform, but the dolomite has not begun to stain or the borders to become blurred. Some lack of uniformity in the coating on the calcite is to be preferred to lack of distinction in the boundaries.

The results of staining a rock predominately dolomite in solutions of varying strength for varying times are tabulated below:

Solution—¼ mol per liter.
- 6 hours—calcite stain not complete.
- 9 hours—calcite stain complete, but still a little irregular.
- 12 hours—calcite stain satisfactory, dolomite beginning to stain.

Solution—½ mol per liter.
- 6 hours—calcite stain not uniform.
- 9 hours—calcite stain fairly satisfactory.
- 12 hours—calcite stain satisfactory, dolomite beginning to stain.

Solution—1 mol per liter.

3 hours—calcite stain not uniform.
4 hours—calcite stain fairly satisfactory.
5 hours—calcite stain satisfactory.
6 hours—calcite stain satisfactory.
7 hours—vague stain on dolomite.
8 hours—distinct stain on dolomite.

Solution—2 mols per liter.

3 hours—calcite stain not entirely uniform.
4 hours—calcite stain (on any one grain) uniform.
5 hours—calcite stain uniform.
6 hours—dolomite beginning to stain.

Solutions of 4 and 6 mols per liter were also tested but the results were rather erratic; it seems that the NH_4OH did not give uniform fixation over the surface of the specimen at these higher concentrations. Even with the 2 molar solution, staining was poor where the edges of the specimen were in contact with only a thin film of solution.

High concentrations incline therefore to be erratic; low concentrations give best results with about ten hours' exposure, but staining on the dolomite tends to set in before complete uniformity is reached on the calcite. Optimum conditions seem to be obtained with a molar solution and an immersion of five to six hours, with underexposure to be preferred to overexposure. Further modifications will appear below.

Acid radical. Specimens were left for equal periods of time in molar solutions of $Cu(NO_3)_2$, $CuCl_2$, and $CuSO_4$. Practically no stain developed on the specimens in the sulphate even after 12 hours. Perhaps a protective coating of $CaSO_4$ prevented the reaction. The calcite in the chloride solution was attacked more deeply than that in the nitrate, and it became a bright green on fixation with NH_4OH. However, the stained material was loosened from the specimen and much of it fell off the surface of the specimen while still in the solution, leaving merely a deeply pitted surface. Thus $Cu(NO_3)_2$ gave the only satisfactory stain.

No attempt was made to study the difference in action of solutions of varying pH.

Temperature. Specimens were stained in $Cu(NO_3)_2$ at boiling temperatures and slightly below. The time necessary to produce a good stain was about 15 minutes, but the results

were rather erratic. Some parts of a single surface would show an excellent stain, whereas others would hardly be stained at all. No intermediate temperatures were tried; as room temperatures give satisfactory results, heating is not considered desirable.

Percentage of calcite in specimen. It was observed that specimens consisting largely of calcite became coated so deeply that structural details failed to show through. Specimens largely of calcite were therefore stained for various periods in a molar solution of $Cu(NO_3)_2$. Staining of the dolomite does not set in any earlier, but complete uniformity on the calcite is reached at four hours. Even here the stain is so deep that for some purposes less time is desirable. After two hours' exposure, there is practically no unstained calcite; two and one-half to three hours is therefore a satisfactory period for those rocks on which a deep coat would interfere with study.

Grain-size. No experiments bearing directly on the effect of grain-size were made. Dolomite of course reacts much more quickly when powdered, and scratches across the polished surface of the dolomite take a stain long before the rest of the grain. A porous area such as a badly weathered edge will often soak up the solution and will react with the NH_4OH whatever the mineral composition. Similarly porous dolomites will stain without reference to the presence of calcite; for these some other staining method will be necessary. The copper stain can only be trusted on well-polished surfaces of compact rocks (such as the Appalachian dolomites); scratches need cause no confusion if not numerous. Experience shows that the stain is selective down to extremely fine-grain, but whether a shorter exposure to the copper solution would heighten the contrast is not known.

Suggested standard technique. The molar solution of $Cu(NO_3)_2$ is prepared by adding 188 gms. $Cu(NO_3)_2$,

255 gms. $Cu(NO_3)_2.3H_2O$,

or 332 gms. $Cu(NO_3)_2.6H_2O$ to

1000 gms. of H_2O. A strong solution of NH_4OH is also necessary. The specimen is immersed in the nitrate solution in such a way that the polished surface is not against the floor of the vessel. This can be done in a petrie dish with one corner of the specimen resting on a small glass plate; it is best to cover

the dish to prevent evaporation. Care should be taken that no air bubbles adhere to the polished surface. Immersion should be for five to six hours at room temperature unless there is an excess of calcite. For specimens high in calcite, two and one-half to four hours is sufficient, depending on the purpose of study. When the specimen is removed from the nitrate solution, it is immersed *without washing and before drying* in the NH_4OH. A few seconds is enough, more does no harm. It is then washed and rubbed before drying, to remove the excess precipitate. The specimen is then ready for study.

It is important not to rub or even violently wash the specimen before it is immersed in the ammonia, as the light-green stain acquired in the nitrate solution will quickly come off; the specimen may, if desired, be dipped gently into standing water. After the ammonia treatment, however, the stain is permanent; even a gentle buffing will not remove it.

The solutions are not affected by standing unused. They can be used over and over for a considerable period, but it is well to filter them occasionally. The ammonia solution quickly turns a deep blue but can be used as long as it smells strongly of ammonia. Shortly before exhaustion, it produces a paler (though equally accurate) stain; it should then be replaced.

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