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## CALCITE STAINING: SEMIQUANTITATIVE DETERMINATION OF FERROUS IRON<sup>1</sup>

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### ABSTRACT

Calcite phases with different amounts of ferrous iron (determined by microprobe analysis) are distinguishable by study of stained thin sections and stained acetate peels. We have defined four such phases, they are (a) non-ferroan calcite (0.0% FeO; red stain), (b) ferroan calcite I (0.5% to 1.5% FeO; red-purple stain), (c) ferroan calcite II (1.5% to 2.5% FeO; purple stain), and (d) ferroan calcite III (2.5% to 3.5% FeO; purple-blue stain). Several factors, including acidity and temperature of staining solution, affect the color (hue) of the stain, indicating that a standard procedure must be followed if colorimetric techniques are to be used in the determination of ferrous iron content in calcite.

### INTRODUCTION

Calcite containing small amounts of FeO is called ferroan calcite (Palache and others, 1951, p. 154). Staining techniques to distinguish iron-free calcite and ferroan calcite in thin section are described in several recent papers (Friedman, 1959; Evamy, 1963; Dickson, 1965). This procedure has been expanded so that the stains from the surface of a rock also can be transferred to an acetate peel (Katz and Friedman, 1965; Davies and Till, 1968). Stained peels are less time consuming to prepare than thin sections, but show details of zoning with less clarity.

The commonly used stains act independently. Alizarin red-S stains calcite red, whereas potassium ferricyanide reacts with ferrous iron to form a blue stain. When these dyes are combined, they stain ferroan calcite a color composed of red and blue. Evamy (1963) suggested that as iron content increases the stain would shift from red to mauve to purple.

The value of differentiating iron-free and ferroan calcite has been demonstrated in several studies of limestones (Evamy, 1969; Evamy and Shearman, 1965; Davies and Till, 1968; Knewton and Hubert, 1969). For example, obscure diagenetic features such as sequences of pore-filling calcite are readily apparent when iron-free and ferroan calcites are differentiated.

To date, there has been little attempt to quantitatively determine the amount of FeO in ferroan calcite by staining. This is in part due to

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the fabric of the rocks studied. In calcarenite, iron-free and ferroan calcites often occur in sparry cement as layers only a few microns thick, thus precluding standard analytic techniques. Data can be obtained only with an electron microprobe, and then with considerable difficulty.

### METHODS

The present work was done on calcite-filled veins in septarian concretions. This calcite contains a wide range of iron values and occurs in bands that are thick enough so that petrographic and microprobe analyses can be compared, something that is not generally possible in limestones. Using a standard color reference we have compared the color of stains of both thin sections and peels with the iron content of the stained thin sections as determined with the microprobe. For this reason accurate recognition of colors is essential. Terminology used follows the Munsell system.<sup>2</sup> This system was used because (a) the Munsell colors are very consistent, (b) the colors are quite close to those of the stains, and (c) because most geologists are familiar with the Munsell system which is used in the Rock-Color Chart (Goddard and others, 1948).

Color is determined by several factors. *Hue* refers to the attribute which determines the

<sup>2</sup>Munsell Book of Color obtainable from Munsell Color Co. (2441 N. Calvert St., Baltimore, Md. 21218). In addition a color chart has been specially prepared for use in determining FeO content by color of stains. For information write "Color Chart," P.O. Box 10111, Alexandria, Virginia 22310.

name in everyday speech. Ten major hues are recognized and each is divided into ten numerical divisions. The major hues used in this paper are red (R), red-purple (RP), purple (P), and purple-blue (PB). Color *value* indicates the lightness or darkness of a color in relation to a neutral gray scale, which extends from absolute black to absolute white. The value symbol 0/ is used for absolute black; the symbol 10/ is used for absolute white. Values used in this work are 6/ and 7/. *Chroma* indicates the degree of departure of a given hue from a neutral gray of the same value. The scale of chroma extends from /0 (neutral gray) to /14 or further as strength (saturation) increases. Chroma values used in this work range between /6 and /12. Each color has elements of hue, value and chroma, and is described by a notation composed of three numbers and a letter.

The procedure for staining acetate peels that

we have followed is a modification of that used by Evamy (1963) and Katz and Friedman (1965). The solution is prepared by dissolving 1 gm alizarin red-S and 5 gm potassium ferricyanide in one liter of 0.2% HCl (998 ml distilled water containing 2 ml concentrated HCl). A slab of rock is cut and one surface ground with carborundum powder to at least 800 grit. The polished surface is etched in 2% HCl (98 ml distilled water containing 2 ml concentrated HCl) for about 20 seconds, and then immersed in the staining solution at room temperature for 4 minutes. The slab is removed from the solution and washed with distilled water making sure the surface is not hit by a direct flow of water or touched by fingers. The sample is allowed to drain, but *not* become dry. This is quite important. If the sample is too wet the acetone on the rock surface is diluted and a good peel can not be obtained; if too dry the stain will not

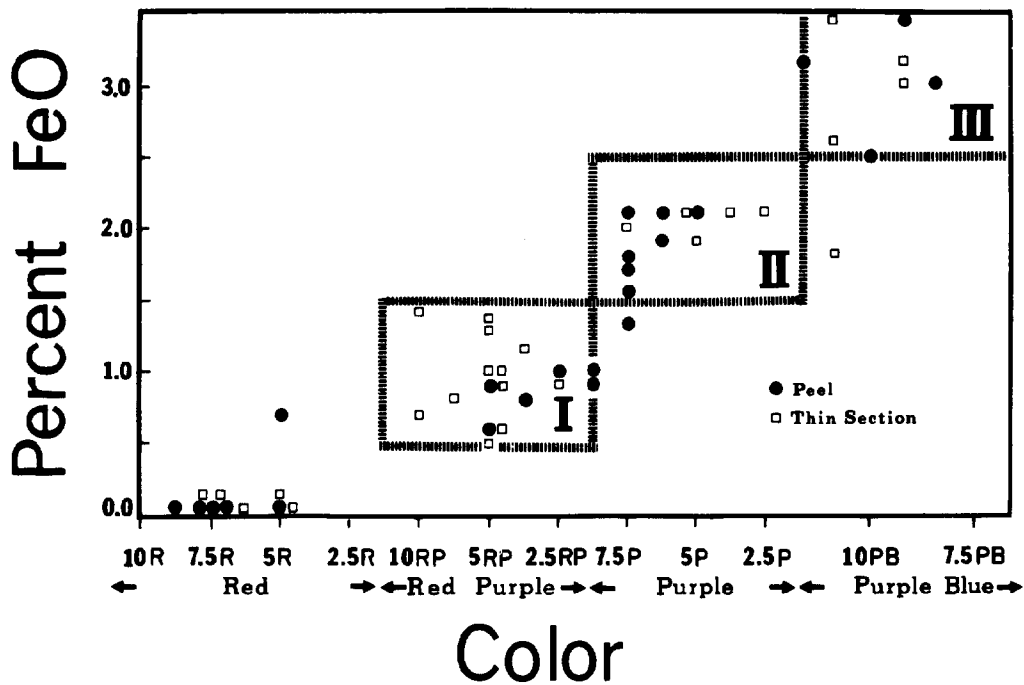


FIG. 1.—Ferrous-iron content plotted against stain color of thin sections and peels.

Calcite Phase	Percent FeO	Color of Stain
Non-ferroan calcite	0.0	Red (10R 6/12 to 2.5R 6/12)
Ferroan calcite I	0.5 to 1.5	Red-purple (10RP 6/12 to 2.5RP 6/10)
Ferroan calcite II	1.5 to 2.5	Purple (7.5P 6/10 to 2.5P 6/8)
Ferroan calcite III	2.5 to 3.5	Purple-blue (10PB 6/8 to 7.5PB 6/10)

TABLE 1.—*Factors that affect color of stain*

Factor Analysed	Results
Acidity of staining solution	High concentrations (0.4–0.8% HCl) increase color intensity and shift color toward a more blue hue. Lower acidity (0.05% HCl) has the opposite effect.
Temperature of staining solution	Warm solutions (40°C.) produce more bluish hues, as well as more intense and less uniform colors than solutions at room temperature (23°–25° C.).
Dilution of staining solution by use	250 ml of solution stains 30 square inches of rock surface without significant changes in color. Further use results in less intense colors.
Length of time rock surface is left in staining solution	Immersion times between 3 and 6 minutes produces similar colors. Shorter times (less than 3 minutes) result in reduction of color intensity, whereas longer times (greater than 6 minutes) result in more intense colors and excessively thick stains which tend to crack on drying.
Shelf life of solution	Solutions start to decompose within several days.

transfer to the peel. The nearly dried surface is immersed in acetone and immediately pressed down on a sheet of 1/16 inch acetate lying on a paper towel to absorb excess acetone and keep it from flowing on the undersurface of the acetate. The slab is pressed firmly onto the acetate without sliding it over the smooth surface. The sample is then tilted to pour off excess acetone and pressure is applied for an additional 10 seconds. After several minutes the peel can be stripped from the rock.

The procedure for staining thin sections is essentially the same as that for preparation of stained peels. The thin section is etched and then immersed in the staining solution. After four minutes the thin section is removed from the staining solution and the surface rinsed with distilled water. The wet thin section is examined under plane-polarized light with a petrographic microscope. The slide should be periodically immersed in distilled water, because when dry, the color of the stain is difficult to determine accurately. The colors of corresponding areas of stained thin sections and stained peels are very similar with no systematic variations.

Colors of stains are determined by visual comparison with a standard reference. The stains are examined in plane-polarized light

(with blue filter) with the substage condenser in and diaphragm open so that cleavage and crystal outlines are barely visible. This allows more light than is normally used to pass through the microscope and is necessary to reduce surface effects caused by irregularities on the thin section or peel. For consistent results the external light source on the color reference must be standardized. We have used one 250 watt, 3,200° K General Electric lamp, placed 3 feet above the color reference. Natural and overhead light are eliminated.

The microprobe analyses were conducted on stained thin sections with an ARL-EMX-SM electron microprobe. The crystal detectors used were LIF, ADP and RAP. All analyses were carried out at 15 kv acceleration potential and 0.1  $\mu$ a sample current. The beam current was integrated against time in order to reduce the effects of beam drift. Chemically analyzed carbonates were used as standards. The elements sought were Fe, Si, Mg, Sr, Mn, and Al. At least twenty five 10-second counts were taken on each phase. Background corrections were applied to the raw data. Accuracy should be better than  $\pm 10\%$  of the amount present.

#### RESULTS

Several factors, other than iron content, affect the color of stains. Factors related to technique were analyzed separately using a sample containing three distinctly different and relatively homogeneous calcite phases. The results summarized in Table 1, show some factors (e.g., high acidity and high temperatures) change the hue of the stain, while others (e.g., low acidity, prolonged use of solution, and too short immersion times) reduce the intensity (chroma) to a point where hue is difficult to determine. Both results are undesirable, indicating that the technique we have outlined should be followed closely if one wishes to use our color references to estimate FeO content in ferroan calcite.

The orientation of calcite crystals with respect to the stained surface and the presence of elements other than iron were also considered. Orientation does not seem to have any significant effect on the hue of the stain, although it does alter the intensity slightly. Manganese is the only element analysed with the microprobe which might affect the hue. It was absent or present in trace amounts and does not seem to be a factor in determining the color of the stain.

When iron content and stain color of both thin sections and corresponding areas on peels are plotted on a scatter diagram (fig. 1) there is an obvious trend such that higher iron values are associated with more bluish hues. There is

some deviation from a simple straight-line relationship. This is in part due to our inability to exactly match areas analyzed by the microprobe with areas analyzed by the petrographic microscope. This problem is complicated by gradational changes in iron content from one area to another and zoned (with respect to iron content) calcite crystals. Another difficulty is in the observers' inability to differentiate clearly between colors of slightly different hues.

Despite these problems we find it useful to suggest a division into four different calcite phases (fig. 1). They are (1) non-ferroan calcite (0.0% FeO), (2) ferroan calcite I (0.5% to 1.5% FeO), (3) ferroan calcite II (1.5% to 2.5% FeO), and (4) ferroan calcite III (2.5% to 3.5% FeO). Roman numerals designating the various ferroan phases refer to the mean FeO value. Any more formal nomenclature would be

premature and would only add confusion to the literature. No values of FeO greater than 3.5% were observed. The difficulties involved in differentiating the color of stains preclude a further breakdown of the different types of calcite with respect to color and FeO content.

Regardless of the terminology we conclude that if proper care is taken during preparation of stained thin sections or peels, the color can be used for semiquantitative determination of the FeO content of the calcite.

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### A USEFUL VOLUMETER<sup>1</sup>

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#### ABSTRACT

A micrometer caliper, modified by the addition of a needle-tipped extension rod and removal of part of the frame, is the basis of a simply constructed, useful volumeter. Different tubes may easily be used, allowing each particle of a wide range of sizes to be measured with the same pre-specified precision.

#### INTRODUCTION

When it was necessary to find the individual volumes of many particles which were too large

to fit into the cup of an air comparison pycnometer on hand, the simple volumeter described below was constructed and found to be very useful. At first an overflow volumeter similar to that described by Schurecht (1920) was constructed and used, but the very slow draining needed for

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