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A STUDY OF IMMISCIBILITY IN THE CARBONATES FROM THE METAMORPHIC ROCKS OF SOUTHEASTERN VERMONT

BY

RALPH DALE COTTER

A

THESIS

submitted to the faculty of the

SCHOOL OF MINES AND METALLURGY OF THE UNIVERSITY OF MISSOURI

in partial fulfillment of the work required for the

Degree of

MASTER OF SCIENCE, GEOLOGY MAJOR

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1953

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Approved by - John L. Rosenfeld
Assistant Professor of Geology

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ABSTRACT

This problem is an attempt to correlate grade of metamorphism (normally assumed to be temperature dependent) with the shape and dimensions of a solid miscibility gap. Such a correlation might permit mapping of a continuously variable function of metamorphism. The system, calcite and dolomite-ankerite, was chosen for study because of its relative simplicity. Samples of quartz-carbonate granulite were collected from the Waits River formation in southeastern Vermont through a range of metamorphic grades.

Refractive index, "molecular" volume, manganese content, and density were determined for the carbonates of four of these samples. These values are plotted on a compositional diagram to show the proportions of the miscibility gap for different grades of metamorphism. No measurable narrowing of the gap is demonstrated.

A progressive increase with metamorphic grade in the refractive indices of calcite and ankerite was noted, and an attempt is made to explain it. Other unpredicted relations are mentioned, and a promising single crystal X-ray technique is described. Recommendations are made for further study of this problem.

STATEMENT OF THE PROBLEM

The problem was designed to determine the probable presence of a linear relationship between the width of solid miscibility gaps and grade of metamorphism. It is well known that miscibility gaps tend to narrow with rising temperature, and it is believed that increasing temperature accounts for the chief mineralogic changes observable in rocks of any given metamorphic terrain, i.e. rise in metamorphic grade. It is therefore believed that there should be a reciprocal relationship between the width of miscibility gap(s) and increase in grade of metamorphism.

Preliminary investigation indicated that, in the area of southeastern Vermont where the writer was to work, the rhombohedral carbonates of calcium, magnesium and iron should be suitable for this study. This same investigation indicated that optical, X-ray, and quantitative chemical tests would be useful in delineating the miscibility gap.

THEORETICAL CONSIDERATIONS

Concepts of Metamorphism

Degree of metamorphism of rocks is expressed in terms of "grade" (Barrow, 1893, p. 353) or by metamorphic facies (Eskola, 1915, p. 114). Passing from rocks of low metamorphic grade through rocks of successively higher metamorphic grade, the first appearances of certain index minerals mark the lower grade boundaries of metamorphic zones. The boundary is a line of equal metamorphism which is called an isograd. The index mineral characterizes both the zone and its lower grade boundary, or isograd (e.g. garnet isograd, garnet zone). The rocks selected for mapping grade of metamorphism must be of constant, or approximately constant, composition for the appearance of new mineral phases to have any significance. According to current concepts, a rise in grade of metamorphism implies a rise in the temperature at the time of metamorphism (Turner and Verhoogen, 1951, p. 429).

The concept of metamorphic facies is more general in its application since it is not restricted to rocks of the same composition. "An individual metamorphic facies includes all rocks, of any chemical composition, and hence of widely varying mineralogical composition, which have reached chemical equilibrium during metamorphism under a particular set of physical conditions." (Turner and Verhoogen, 1951, p. 428)

It would be desirable to be able to detect infinitesimal increments in the degree of metamorphism. The purpose of this problem is to determine whether a continuously variable function of grade of metamorphism can be determined by relating the grade of metamorphism to the width of the miscibility gap between calcite and the system, dolomite-ankerite.

If this can be done, it might eventually lead to contouring of the extent of metamorphism on a large scale.

A three component schematic diagram showing a narrowing of its miscibility gap with rising temperature is shown in Figure 3a (p.21).

Solid Solutions

The rocks chosen for this work contain the two rhombohedral carbonates, calcite and ankerite (an iron-rich dolomite). The calcite and dolomite structures permit other cations to proxy for their respective cations. Hence, in calcite, according to Palache and others (1951, p.142), Ca" may be replaced in any proportions by Mn", forming a complete solid solution series from calcite to rhodochrosite. Substitution of Fe" for Ca" up to twelve molecular percent takes place between calcite and siderite (Winchell, 1951, p. 105), and calcite may take up limited amounts of Zn" and Mg" and minor amounts of Pb", Ba" and Sr".

The double carbonate of calcium and magnesium is structurally similar to calcite except that layers of calcium ions and layers of magnesium ions alternate in the direction of the trigonal axis (Bragg, 1937, p. 116). The lack of a continuous series from calcite to dolomite is probably due to the large difference between the ionic radii of Ca" and Mg". According to Evans (1948, p. 171) these radii, in sixfold coordination, are 1.06 Å for Ca" and 0.78 Å for Mg". In the dolomite structure, considerable Fe" and lesser amounts of Mn", Zn", Co" and Pb" can occupy Mg" positions, and Fe" and Mn" may substitute for a small number of the Ca" ions. Ca" and Mg" may replace each other to a limited extent (Palache, et al., 1951, p. 211).

From these data we see that a large number of metallic ions may enter into the calcite and dolomite structures. In the average metamorphic rock, however, only the more common elements, iron and manganese, are found to proxy for the calcium and magnesium of these carbonates.

Assumptions

In dealing with a system on the basis of miscibility gap widths, certain assumptions must be made. The system of minerals delineating the miscibility gap must be assumed to have been in equilibrium at the time of metamorphism. If equilibrium was not attained, the compositions of the phases would have no easily discerned interrelationship, and would certainly not delineate their miscibility gap. Examples of possible disequilibrium conditions in carbonate rocks would be represented by secondary vein fillings of calcite in a dolomite rock, or late stage hydrothermal alteration of a calcite rock with partial alteration to dolomite. The rocks must be checked petrographically for evidence of vein filling. From independent evidence, only a very small portion of the rock, of the order of one cubic inch, may be assumed to have been in equilibrium at the time of formation. The latter restriction is due to the generally accepted belief that the fluid phase which facilitates equilibrium between the mineral phases in a rock is not compositionally uniform within a larger volume than this.

It is assumed that the chief mineralogical changes observed in rocks of any given metamorphic terrain, other than changes due to differences in rock composition, are due to differences in the temperatures of formation of these minerals. Since miscibility gaps are known generally to close with rising temperature, there should be a causal relationship between the shape and dimensions of the miscibility gap and the grade of metamorphism.

It is necessary that changes in mineralogical composition, if present, must be measurable by available methods. Of course, it would be desirable to deal with a system in which a relatively slight change in temperature would have been accompanied by a large change in composition.

APPROACH TO THE PROBLEM

Selection of Area for Study

The area chosen for this study is located northwest of the town of Rockingham in southeastern Vermont (Fig. 2, p. 9). It is about four miles long in an east-west direction, and borders the Rutland Railroad over most of this distance. The Waits River formation, from which the examined rocks were collected, outcrops over much of this area. This formation contains beds of quartz-sericite schist, graphite-sericite schist and quartz-carbonate granulite. Rosenfeld (1953, unpublished data) tentatively dates the Waits River formation as Middle Ordovician. In this area it is underlain by the Shaw Mountain formation which consists of interbedded black quartzite and amphibolite.

The areal geology of the Saxtons River quadrangle (Rosenfeld, 1953, unpublished data) shows the Northwest Rockingham Area to lie on the east limb of the Chester dome, a large anticline which is an axis of relatively intense metamorphism. Figure 1 shows the Chester dome which is delineated by the base of the Chester amphibolite. It also indicates the trends of the garnet isograd and the staurolite-kyanite isograd both of which indicate the progressive increase in metamorphic grade towards the axis of the Chester dome.

This area was selected because it had previously been mapped and was known to contain the two carbonate system desired for this study. The area contains rocks which have undergone progressive metamorphism. The Rutland Railroad cut afforded fresh exposures for collecting.

The carbonate system, calcite-ankerite, was chosen because of the immiscible nature of the two minerals and their relative simplicity, in

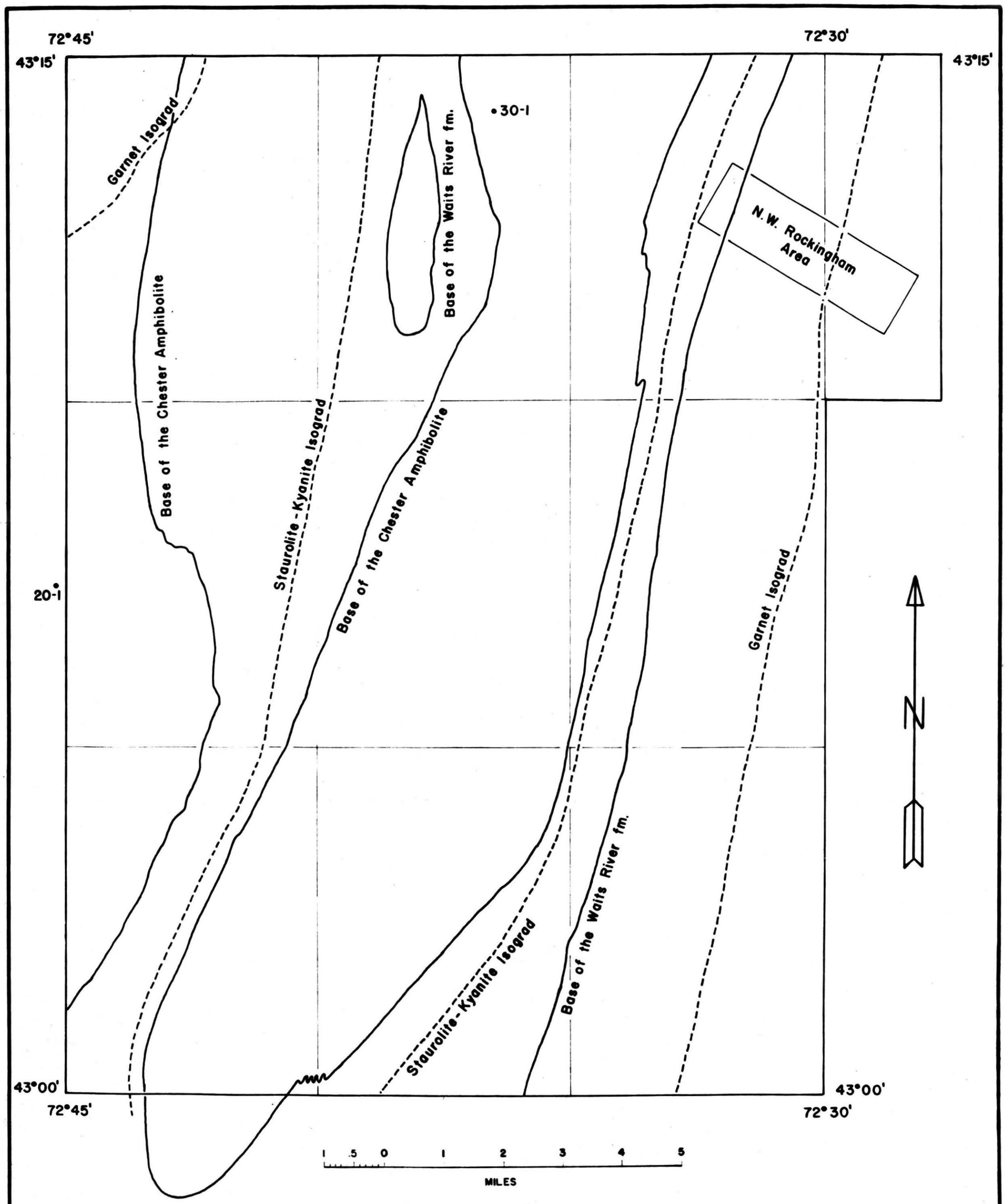

FIG. I

MAP OF THE SAXTONS RIVER QUADRANGLE, VERMONT

SHOWING THE LOCATION OF FORMATIONAL BOUNDARIES, ISOGRADS, AND THE NORTHWEST ROCKINGHAM AREA

From the unpublished thesis of J.L. Rosenfeld

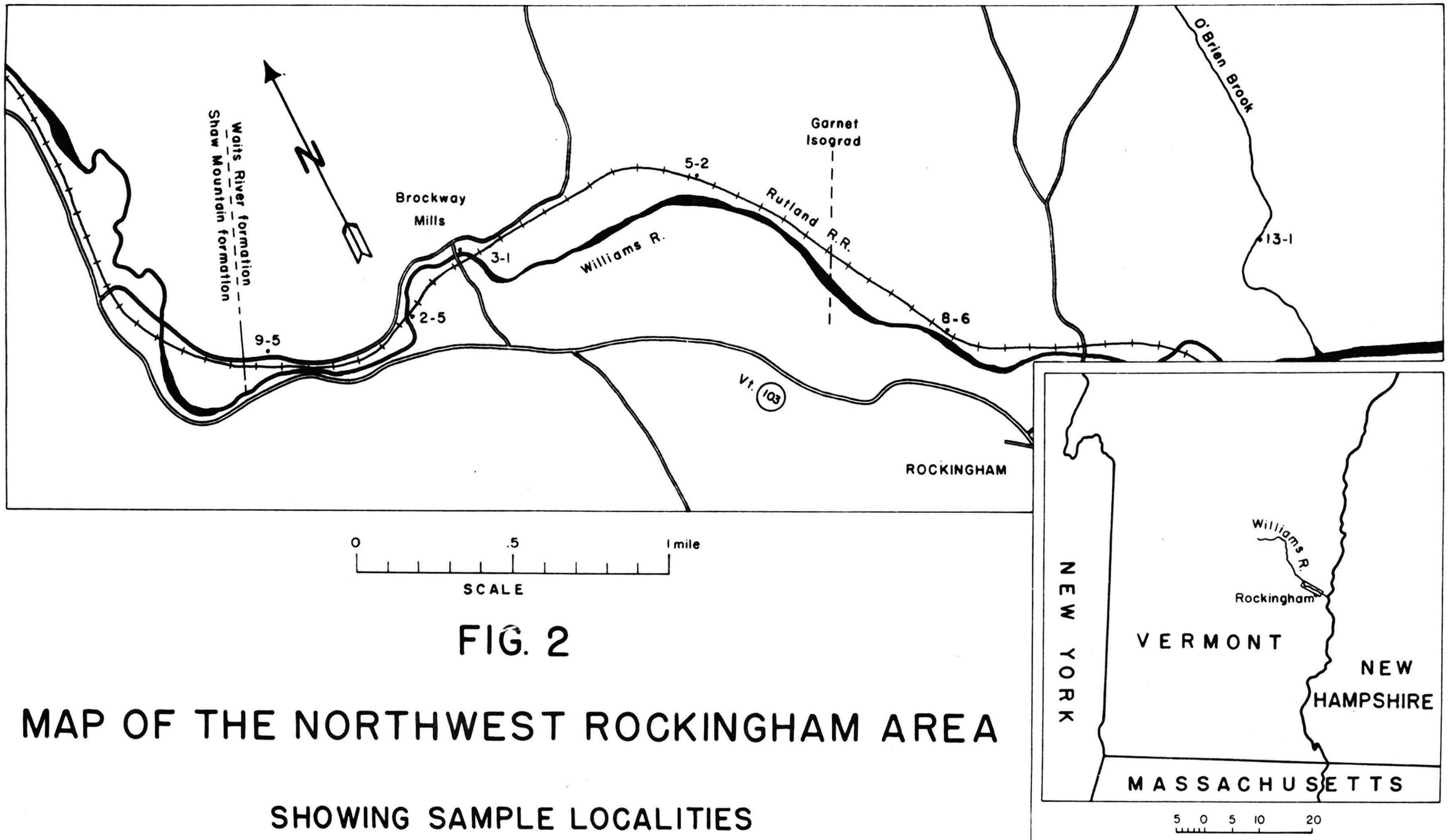

FIG. 2

MAP OF THE NORTHWEST ROCKINGHAM AREA

SHOWING SAMPLE LOCALITIES

Tracing of areal photographs from the U.S. Soil Conservation Service

INDEX MAP
SHOWING LOCATION OF THE
NORTHWEST ROCKINGHAM AREA

that few common cations enter into their structures. Most rock-forming minerals suitable for this study take a large number of common and abundant elements into their structures. A system consisting of immiscible phases of complicated composition would be very difficult to work with because of the unknown effect of the numerous elements in either "bridging" or "unbridging" the miscibility gap.

Since the system calcite-dolomite possesses a broad zone of immiscibility, the measurable effect on closure of the gap in relatively "high grade" rocks would probably tend to be small. It was for this reason that the ankerite-calcite system was chosen. Ferrous iron, which enters into both structures, should produce some closure of the gap by bringing their compositions closer together.

Field Procedure

The samples were collected on a compass and pace traverse which was begun one mile west of Brockway Mills on the Rutland Railroad track. Azimuth readings taken along the railroad track were measured from a tangent to the railroad track with a protractor because of the effect of the tracks on the compass. Wherever possible, collecting was done in railroad cuts and the bed of the Williams River where the rocks are only slightly weathered. Collecting from weathered outcrops was rather difficult because the rocks had been altered to form a rusty, "punky" crust up to one foot thick.

The carbonate rocks collected varied in their quartz content from 30% to 80%. Specimens were examined evenings while in the field using the immersion method to determine the presence of both carbonates in each sample. It was found that the low quartz rocks consistently contain both carbonates while ankerite was observed in only a few of the quartz-rich rocks. Further collecting was carried on only in the carbonate-rich bands.

The first appearance of garnets in the argillaceous rocks was noted, and recorded on Figure 2 (p. 9) as the garnet isograd. In the carbonate rocks garnets were first seen at locality 3-1 at Brockway Mills, indicating that garnets appear at a higher grade of metamorphism in the calcareous rocks than in the argillaceous rocks.

Laboratory Procedure

Laboratory investigation of the rocks was carried out on the two specimens which were collected the greatest distance apart (samples 13-1 and 9-5, see Fig. 2). These specimens would be expected to show the largest differences in physical properties for the carbonate minerals, if such differences could be detected. In addition to these samples, two dolomitic marble samples, specimens 20-1 and 30-1, and corresponding thin sections were obtained from J. Rosenfeld. The rock at the location of 20-1 is described by Dale (1915, p. 41). These rocks were examined to determine the behavior of a system relatively deficient in iron. As may be seen in Figure 1, these rocks are from the same general area and represent two different grades of metamorphism. Sample 20-1 was collected from the garnet zone and sample 30-1 from the staurolite-kyanite zone within the Chester dome.

Thin Sections. Thin sections of specimens 9-5 and 13-1 were ground to study their mineralogy and texture (see estimated modes, Appendix I). Textures also determined the sizing to be used in the separation. In both rocks occasional ankerite grains may be distinguished from the calcite by their "rusty" appearance. Sample 13-1 has a schistose appearance due to the alignment of the mica grains and the parallel elongation of the carbonate minerals. Aside from its carbonate content, sample 13-1 contains a large proportion of quartz and minor amounts of graphite, sericite (non-pleochroic mica), rutile, and zoisite. The carbonate grains range from 0.05 to 0.12 millimeters in diameter. Sample 9-5 is coarser grained than 13-1. The diameters of the carbonate grains range from 0.08 to 0.3 millimeters. The schistose texture brought about by aligned mineral grains is not evident in the hand specimen. The higher grade sample, 9-5, shows the development of several mineral phases not seen in sample 13-1. These are pyrite, ilmenite, garnet, oligoclase, chlorite and hematite. Oligoclase may have been present in sample 13-1 but not seen because of the fine-grained nature of this rock. The chlorite and hematite in sample 9-5 are retrograde minerals. The chlorite is present as reaction rims around the garnet porphyroblasts and the hematite occurs as an oxidation product on the pyrite. The garnet porphyroblasts are poikiloblastic, containing abundant quartz grains. Some are merely lacy outlines of garnet with bodies of the grains made up of quartz and carbonate.

Thin section 20-1, which is representative of a lower grade of metamorphism than sample 30-1, is simple in its mineralogy. It consists largely of calcite and dolomite grains varying from 0.05 to 0.1 millimeters in diameter. A few carbonate porphyroblasts up to 1 millimeter in diameter are present, along with small amounts of green, pleochroic biotite, quartz, and hematite.

Sample 30-1 shows evidence of higher grade in that the quartz has reacted with the dolomite to form tremolite and calcite. It is coarser grained with the carbonates ranging from 0.2 to 1.0 millimeters in diameter. It also contains minor amounts of green biotite but does not contain any hematite.

Separation Technique. A heavy liquid separation of the carbonate minerals was attempted in order to simplify the physical and chemical measurements which were to be made. The rocks were crushed and sized to pass through a seventy mesh screen and catch on a two hundred mesh screen. A float and sink method of separation was performed using acetelyne tetrabromide diluted with benzene. Two separations were made on each sample. The first separation was to float the quartz and sink the carbonates and heavy minerals, and the second was to float the calcite and sink the dolomite-ankerite and heavy minerals. Due to the fine-grained nature of material and the variable density of the carbonates caused by "rusty" grains, this method yielded only about seventy percent purity. Because of the difficulty in separation, and the heterogeneity of the resulting material, physical methods of analysis were used wherever possible.

Determination of Indices of Refraction. Measurements of the index of refraction for the ordinary ray in each of the carbonate minerals proved to be the most compositionally sensitive physical property obtained. Because only the two end samples of the Northwest Rockingham area were examined in detail, the indices of four intermediate carbonates were determined to see whether a progressive change was evident. The indices for the ordinary ray were determined by the immersion method. Using sodium light, the index oils were mixed to match the mineral, and the index of the mixed oil was checked directly on an Abbe Refractometer without amici prisms. Temperature control was not available, so the measurements were made after allowing all of the equipment to reach a constant temperature in the same room.

Two measurements were made on each mineral and they differed by a maximum of 0.0008 (see Table 1, p. 20). Samples 9-5, 13-1, 30-1, and 20-1 were measured four times and the average error was found to be ±0.0007 based on a 90% confidence interval (Youden, 1951, p. 19).

X-ray Measurements. X-ray measurements were performed on samples 9-5, 13-1, 30-1, and 20-1 to determine another physical constant which is related to mineral composition. A great deal of difficulty was encountered in obtaining sharp lines for the carbonates in the back reflection region. These minerals seem to have an inherent tendency to give broad diffuse lines on X-ray photographs. Possibly this/is due to twinning on a molecular scale and is a product of crushing.

The "powder wedge" method was tried first using a General Electric Debye-Scherrer camera with iron radiation. This method produced back reflection lines, but all of the lines were broad and could not be measured very precisely. Since part of the breadth of the lines is due to the sample size, a series of photographs was taken using rolled collodion filaments containing the mineral powder. With this decrease in sample size, long exposures, of the order of sixteen hours, were necessary. The results produced by this approach were little better than those obtained in the preceding method. This was due to the difficulty in rolling uniform collodion spindles and the tendency for these thin spindles to warp during the long period of exposure. The writer overcame this difficulty by coating a thin grease covered glass filament with the mineral powder. This method had the disadvantages of exposing too little material to the X-ray beam resulting in faint and hollow lines on the film. This last effect was produced as a result of the X-ray beam traversing the central glass section of the filament without encountering any scattering material.

Further investigation is deserved for a single crystal technique which the writer tried. It involves using Rosenfeld's method for orienting small grains under the microscope (Rosenfeld, 1950, p. 903), and transferring the oriented grain to a hollow glass fiber. This method is described in Appendix III. The fiber is then rotated in the X-ray beam to give a series of small diffraction dots on the photograph. These may be measured and indexed using the tangent formula (Buerger, 1942, p. 97). The advantage of this method lies in the fact that it gives very small back reflection dots which can be measured accurately. It was abandoned because of the prohibitive exposure times necessary, using iron radiation, for photographing the very small grains which were obtained from sample 13-1.

The finally accepted photographs were obtained using a fragment of a rolled collodion filament mounted on the end of a glass tube. The best results were obtained when the mineral grains were crushed between two glass plates. This gives a non-uniform grain size resulting in slightly "grainy" lines on the photographs. These dots due to the coarser grains help to delineate the weaker lines. The crushed powder was mixed with diamond powder in a proportion of about two to one. The diamond powder, which was used as an internal standard, was obtained through the generosity of Dr. M. E. Straumanis. A drop of collodion was added to the mixed powder to form a paste, and this was rolled between the fingers to form short fibers. The collodion stub was cemented to the end of the tube with water glass. A slender glass tube was placed against the collodion stub and a drop of water glass placed at the upper end of the tube. The water glass moved through the tube by capillarity and adhered to the collodion at the far end. It was discovered that the coating of water glass on the collodion rod gave it considerable support. This, and the shortened length of the collodion section of the mount prevented its warping during exposure.

The films were measured with a millimeter scale and a travelling microscope. A glass plate with a fine line ruled on it was used as a slider on the scale. It was placed on the film over the desired line with the aid of a magnifying glass. The millimeters were read directly off the scale and the decimal parts of millimeters were measured with the travelling microscope. This is accomplished by measuring from a millimeter line on the scale several units away, to the ruled line on the glass plate. This method tends to decrease any error due to unequal spacings of millimeters on the ruled scale. The distances measured with the travelling microscope were estimated in reading to two thousandths of a millimeter. The physical constants used in calculating "d" spacings and the camera radii from the diamond lines were obtained from Straumanis (1951, p. 843) and Barrett (1952, p. 151, 640, & 644).

Indexing of the calcite lines was done by comparison with the results of Andrews (1950, p. 86). The dolomite lines were indexed in accordance with the correlation made by Schoklitsch (1935, p. 442) between calcite and dolomite. On comparison, the values of various corresponding interplanar spacings of calcite and dolomite were found not to vary uniformly. Therefore, the "molecular" volume was chosen to represent differences between the minerals. The interplanar spacings of (00012) and (30$\bar{3}$0) were chosen for this purpose. On the basis of these values, the volume of one third of the hexagonal prism was calculated by simple trigonometry:

$$\text{Volume of 1/3 hexagonal prism} = \frac{3(d_{(30\bar{3}0)})^2}{.86602} \times 12 \times d_{(00012)}$$

This was reduced by a factor of one sixth to arrive at the "molecular" volume based on three oxygen atoms. This is not a true molecular volume, since the coordination of the ions in these minerals does not produce molecules in the chemical sense.

The precision of these measurements and calculations is based on a ninety percent confidence interval (Youden, 1951, pp. 12-19). In other words, ninety times out of one hundred the value will fall within this interval. Four measurements were made on each film and the standard deviation computed by the following formula:

$$\text{Standard Deviation} = \sqrt{\frac{\sum (x_1 - \bar{x})^2 + (x_2 - \bar{x})^2 + (x_3 - \bar{x})^2 + \ldots\ldots}{N - 1}}$$

where $(x_1 - \bar{x})$, $(x_2 - \bar{x})$, $(x_3 - \bar{x})$, ... are deviations from the mean, and N is the number of measurements. The standard deviation is multiplied by a constant which is determined by the number of measurements and the desired confidence interval. For the case of four measurements and a ninety percent confidence interval the factor is 2.35. This precision was carried through the volume calculations which are on the same basis.

Using a ninety percent confidence interval, the error in the volume based on three oxygen atoms has an average value of ± 0.21 Å^3.

<u>Density Measurements</u>. It was thought that a determination of the molecular weight of the carbonate minerals would place a strong restriction on their position in a three component diagram by allowing only one degree of freedom. It was determined from a combination of density measurements and "molecular" volume calculations.

The densities were measured by mixing heavy liquids which would suspend the mineral, and measuring the index of refraction of the liquid. Mixtures of acetylene tetrachloride and acetylene tetrabromide were found to manifest a straight line relationship between index of refraction and density. The densities were gained from the indices of refraction through this relationship. A full account of the method used is listed in Appendix II (p.30). The error in this method was determined by finding the range of liquids through which the minerals would remain suspended. It was found to correspond to an average density difference of ±0.023. The method appears to be capable of better precision than this. It is thought that the large error is due to the difficulty in obtaining grains which are not "rusty", and to the slow settling rate where the density of the mineral is very near the density of the liquid. The molecular weight was calculated by the following formula:

M.W. = Avogadro's number x "molecular" volume x density x 2

The factor, 2, is introduced to put the molecular weight on the basis of six oxygen atoms for plotting on Figure 3b (p. 22). Due to the relatively large errors in both the "molecular" volume and density, the resulting molecular weight values have a precision of ±2.4.

Manganese Determination. Iron and manganese are the only common elements which proxy for the calcium and magnesium of calcite and dolomite. The manganese content was determined to see whether it is significant.

A sodium carbonate bead test indicated the presence of manganese in the minerals. This was followed by a quantitative test using the periodate method based on the permanganous ion which is stabilized in acid solution by an excess of periodate (Snell and Snell, 1926, pp.339-341). Quantitative results were obtained using a Beckmann photometer.

These values were recalculated to take into account the insoluble quartz residue which was present because of incomplete separation methods. The percent manganese metal was recalculated to percent manganese carbonate which is the form most easily considered for the mineral. The amounts present were of the order of 0.15% $MnCO_3$ by weight.

TABLE I

TABULATION OF DATA

determined for the carbonates of the Northwest Rockingham area
and the area of the Chester dome (see Figs. 1 & 2)

Specimen No.	ω ±0.0005	wt.% $MnCO_3$	Density ±0.023	Molecular* wt. ±2.4	d(00012) in Å ±0.002 (90% Conf.)	d(30$\bar{3}$0) in Å ±0.002 (90% Conf.)	"Molecular"** volume in Å^3 ±0.21 (90% Conf.)
30-1 Calcite	1.6621		2.718	198.0	1.412	1.435	60.47
30-1 Dolomite	1.6855		2.878	185.8	1.336	1.388	53.61
20-1 Calcite	1.6591		2.680	195.2	1.413	1.435	60.47
20-1 Dolomite	1.6822		2.855	184.1	1.336	1.388	53.61
9-5 Calcite	1.6689	0.171	2.766	200.4	1.409	1.433	60.15
9-5 Ankerite	1.7057	0.100			1.342	1.389	53.85
2-5 Calcite	1.6686						
2-5 Ankerite	1.7045						
3-1 Calcite	1.6678						
3-1 Ankerite	1.7026						
5-2 Calcite	1.6677						
5-2 Ankerite	1.7045						
8-6 Calcite	1.6672						
8-6 Ankerite	1.7005						
13-1 Calcite	1.6605	0.145	2.690	197.0	1.417	1.436	60.77
13-1 Ankerite	1.6994	0.210			1.340	1.390	53.85

* Molecular weight is based on 6 oxygen atoms.
** "Molecular" volume is based on 3 oxygen atoms.

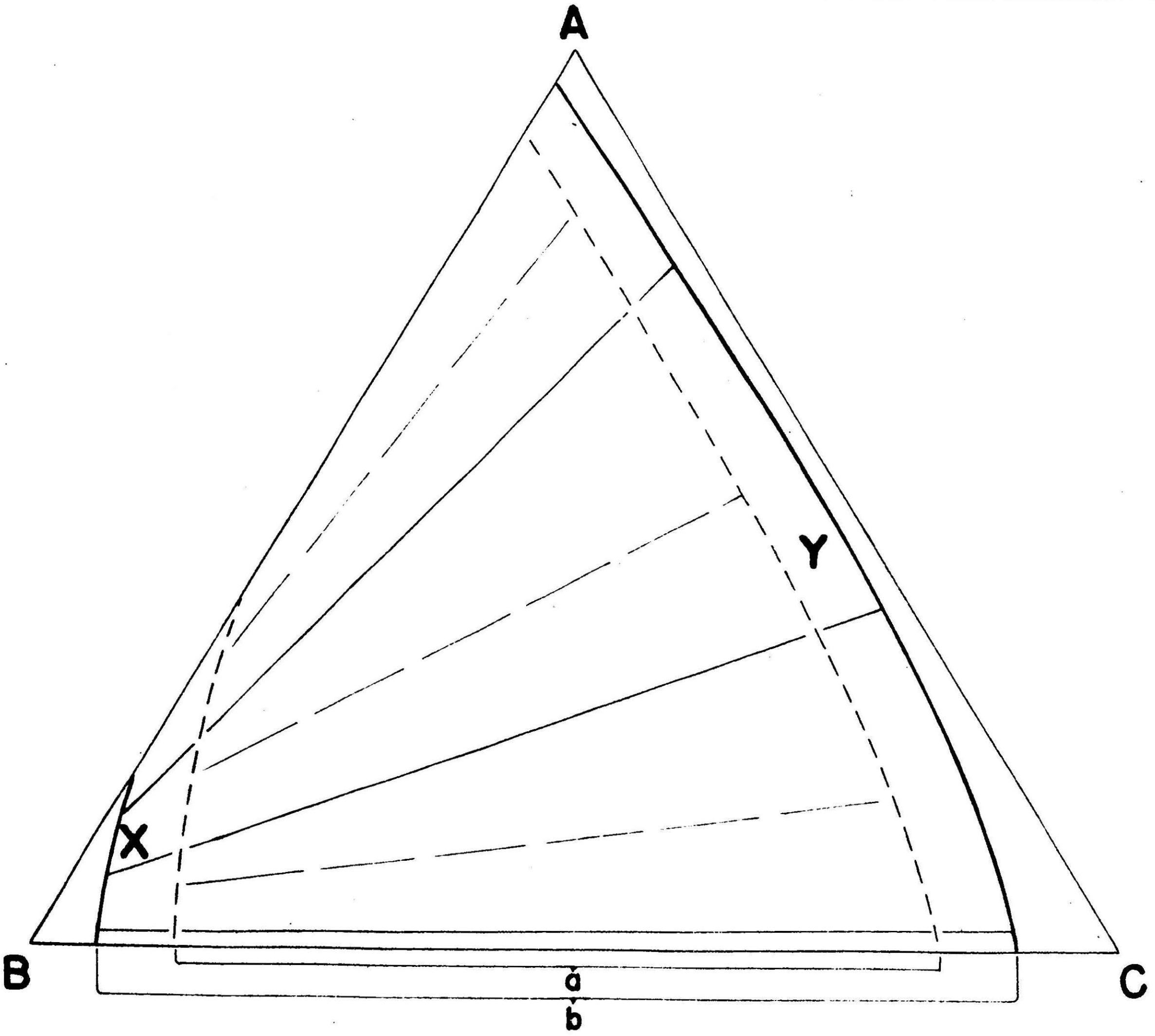

FIG. 3a

SCHEMATIC DIAGRAM OF A THREE COMPONENT SYSTEM

Showing an area of immiscibility between solid solutions X and Y

a= area of immiscibility at temperature 1
b= area of immiscibility at temperature 2
where temperature 1 is greater than temperature 2

modified after Ricci, 1951, p. 214

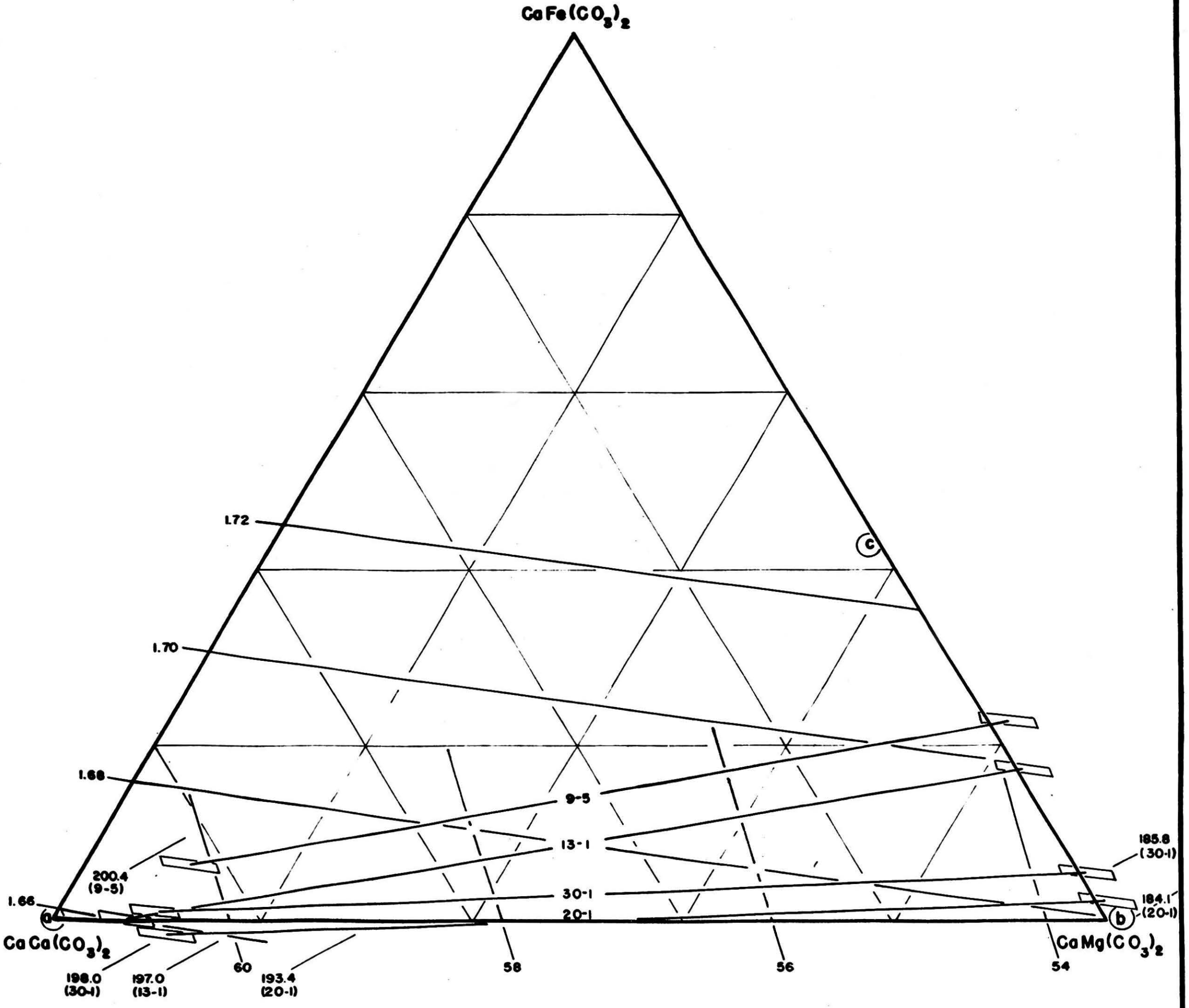

FIG. 3b

CALCITE-DOLOMITE-ANKERITE DIAGRAM

SHOWING RELATIVE POSITIONS OF EXAMINED MINERALS

EXPLANATION

9-5	Tie lines connecting the two carbonate minerals from each rock
60	Molecular volume
1.68	Index of refraction (o)
192.4 (20-1)	Calculated "Molecular" weight

The above data is plotted on the basis of values of:

- ⓐ Calcite, from Andrews (1950), p. 86, and Winchell (1951), p. 106
- ⓑ Dolomite, from Winchell (1951), p. 114 after Koller (1918)
- ⓒ Ankerite, from Schoklitsch (1935), pp. 434, 441

SYNTHESIS

Presentation of Data

The physical constants determined in the preceding section are listed in Table 1 (p. 20). "Molecular" volumes are plotted against indices of refraction in Figure 3b to show the relative positions of the samples on the three component diagram of $CaCa(CO_3)_2$, $CaMg(CO_3)_2$ and $CaFe(CO_3)_2$. The molecular weight is also plotted on this diagram. The basis for plotting these values is drawn from analyses of a calcite, a dolomite and an ankerite selected from the literature (Fig. 3b, p. 22). A grid was constructed assuming a straight line relationship between the physical constants of these minerals; and the writer's values of molecular weight, molecular volume and index of refraction were plotted on it. The error parallelograms in Figure 3b (p. 22) represent a ninety percent confidence interval for indices (±.0007) and volumes (±.21 $Å^3$). The molecular weight values have a precision of ±2.4.

Interpretation of Data

The two systems of carbonates (9-5 and 13-1, and 30-1 and 20-1), as plotted on Figure 3b, show no significant closure of the miscibility gap with rise in metamorphic grade. The closure, if any, would probably show up with a decrease in the error of the "molecular" volume. However, several features which the writer believes worthy of mention are discussed below.

An interesting fact which was noted is the progressive increase of refractive index with metamorphic grade of the six calcites and, with one exception , the six ankerites from the Northwest Rockingham area. This simple relationship might be used in the immediate

Northwest Rockingham area to determine relative grades of metamorphism for rocks of appropriate composition. In the two thin sections ground on samples 13-1 and 9-5, 9-5 shows considerable amounts of pyrite and garnet, whereas 13-1 shows no iron bearing minerals other than the carbonates. Since the amount of iron needed in the formation of the pyrite and garnet could not have been freed from a low iron rock such as 13-1, a difference in initial composition is indicated. Further petrographic work on the intermediate rocks is needed to check this idea.

The writer believes that the progressive increase in the iron content of the carbonate minerals might also be a function of grade of metamorphism in the rocks of the Waits River formation. Possibly a reaction similar to the conversion of ilmenite to rutile takes place with the released iron entering into garnet and the carbonates. J. Rosenfeld suggests that a metamorphic reaction of the following general type may take place in the rocks of the Northwest Rockingham area:

$$\underset{\text{muscovite}}{3KAl_3(Si_3O_{10})(OH)_2} + \underset{\text{ankerite}}{Ca_{16}Mg_{14}Fe_2(CO_3)_{32}} + \underset{\text{quartz}}{6SiO_2} + \underset{\text{water}}{H_2O}$$

$$\rightarrow \underset{\text{phlogopite}}{3KMg_3Al(Si_3O_{10})(OH)_2} + \underset{\text{zoisite}}{2Ca_2Al_3(SiO_4)_3(OH)} + \underset{\text{calcite}}{Ca_6Fe(CO_3)_7}$$

$$+ \underset{\text{ankerite}}{Ca_6Mg_5Fe(CO_3)_{12}} + \underset{\text{carbon dioxide}}{13CO_2}$$

This reaction would tend to increase the iron content in the carbonate minerals. It would presumably take place only when the Fe" to Mg" ratio in these minerals drops below a certain critical value, and would tend to restore the proportion to this value. The absence of phlogopite in these rocks might be explained by the proportions of Fe" to Mg" being above the critical value. The difference in iron content in the carbonates 20-1 and 30-1 might be due to the reduction of Fe"' in hematite to Fe" which entered into the carbonates of 30-1.

The ankerites and dolomites plotted in Figure 3b show a tendency towards non-stoichiometric compositions. Although their error parallelograms overlap the stoichiometric calcite-ankerite line, the four minerals show an approximate parallelism to this line, but are slightly offset towards the magnesite-siderite composition. This indicates that not only is Fe" proxying for Mg", but that Mg" and Fe" are entering into Ca" positions. Since the double carbonate is probably in equilibrium with calcite, any departure from stoichiometry might be expected to take place in the direction of calcite and not towards magnesite-siderite. This apparently anomalous compositional behavior of the dolomite and ankerite may be due to the relatively greater ease of entry of a small ion into a large "hole" as opposed to the entry of a large ion into a small "hole" in the dolomite structure.

Another feature which may be seen in Figure 3b is the approximate parallelism of the tie lines 13-1 and 9-5, and of 20-1 and 30-1, with a fanning between the two sets of tie lines towards $CaFe(CO)_2$. This might indicate that a fanning due to composition, as illustrated in Figure 3a, is dominant over the smaller effect which would be produced by changes in metamorphic grade.

SUGGESTIONS FOR FURTHER WORK

Although this problem was approached from an empirical standpoint in order to see whether a measurable closure of the miscibility gap was present, extended research on the subject would involve a thorough understanding of the basic principles of crystal chemistry, order-disorder theory, thermodynamics, and statistical mechanics. Suggested references on these subjects are: Evans' "Crystal Chemistry", Stillwell's "Crystal Chemistry", Slater's "Introduction to Chemical Physics", and Gurney's "Introduction to Statistical Mechanics".

No significant narrowing of the miscibility gap was shown by this work, mainly because of the large error in the "molecular" volume measurements. It is in this direction that any closure would show up when plotted on the same basis as Figure 3b (p. 22). If the X-ray photographs could be measured more precisely, a significant closure might be observed. The best prospect for accomplishing this end would involve using the single crystal technique described in Appendix III (p. 32). This method was abandoned by the writer during this project because of prohibitive exposure times due to the small size of the mineral grains. Exposure times could be shortened by using a shorter wave length radiation and by applying higher voltages to the target of the X-ray tube.

The density measurements yielded rather poor results. It may be that the apparent breadth of densities which will suspend the mineral grains is due to the slow rate of movement of the grains when the densities of the mineral and the liquid are nearly equal. Perhaps sufficient time was not allowed for the system to reach equilibrium. It might be possible to speed up this process by centrifuging the immersion cell. An improvement of the precision for both density and "molecular" volume measurements would give more significance to the molecular weight determination. The molecular weight determination would then serve as a good check for plotting the mineral compositions, although it still leaves one degree of freedom for mineral composition. The basis for plotting compositions (index of refraction and "molecular" volume) should give results consistent with the molecular weight.

To give a valid test of the postulated narrowing of the miscibility gap with grade of metamorphism, it would be necessary to make a study of a large scale collection of samples and relate the results to the local structure. The analyses of carbonate samples from rocks of appropriate composition should be plotted on a map of the area as lines of equal composition. If these lines were to have the same trend as the regional isograds, the method would probably be applicable for contouring grade of metamorphism. Chemical analyses should be run on a few samples to check the validity of plotting mineral compositions on the basis of the physical properties used in this work.

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APPENDIX I

Estimated Modes of Thin Sections

Mineral	Percent
Specimen 9-5	
Calcite	40
Ankerite	
Quartz	35
Pyrite	5
Graphite	5
Garnet	5
Plagioclase	3
Rutile	3
Sericite (non-pleochroic mica)	3
Zoisite	--
Biotite	--
Hematite	--
Specimen 30-1	
Calcite	85
Dolomite	
Biotite	15
Tremolite	--

Mineral	Percent
Specimen 13-1	
Calcite	70
Ankerite	
Quartz	20
Sericite (non-pleochroic mica)	5
Graphite	5
Rutile	--
Zoisite	--
Specimen 20-1	
Calcite	80
Dolomite	
Biotite	10
Quartz	5
Hematite	5

APPENDIX II

Description of Density Determination Technique

Since the material studied consisted of a mixture of minerals, the density could not be determined by the Berman balance or the pycnometer without hand picking a large number of grains. The two carbonates would have to be separated optically if this method were to be used.

A small scale sink and float method was developed in which the mineral grains were suspended in a heavy liquid of the same density. Acetylene tetrachloride and acetylene tetrabromide were chosen for mixing because the density-refractive index curve for this system is a straight line for all practical purposes and has a desirable slope (see Fig. 4, p.31). The curve was drawn on the basis of densities determined by pycnometer weighings and index of refraction determinations made with an Abbe refractometer using sodium light. These measurements were made at a constant temperature of 25°C.

A flotation cell was constructed by cementing a small glass ring to a microscope slide using water glass. A few mineral grains are placed in this cell, a heavy liquid dropped in, and a cover glass placed over the top. The mineral grains are observed under the microscope to either sink or float. Successive mixtures of acetylene tetrachloride and acetylene tetrabromide are made until the mineral grains are suspended in the liquid. The index of refraction of this liquid is measured and the density obtained from the graph in Figure 4 (p. 31).

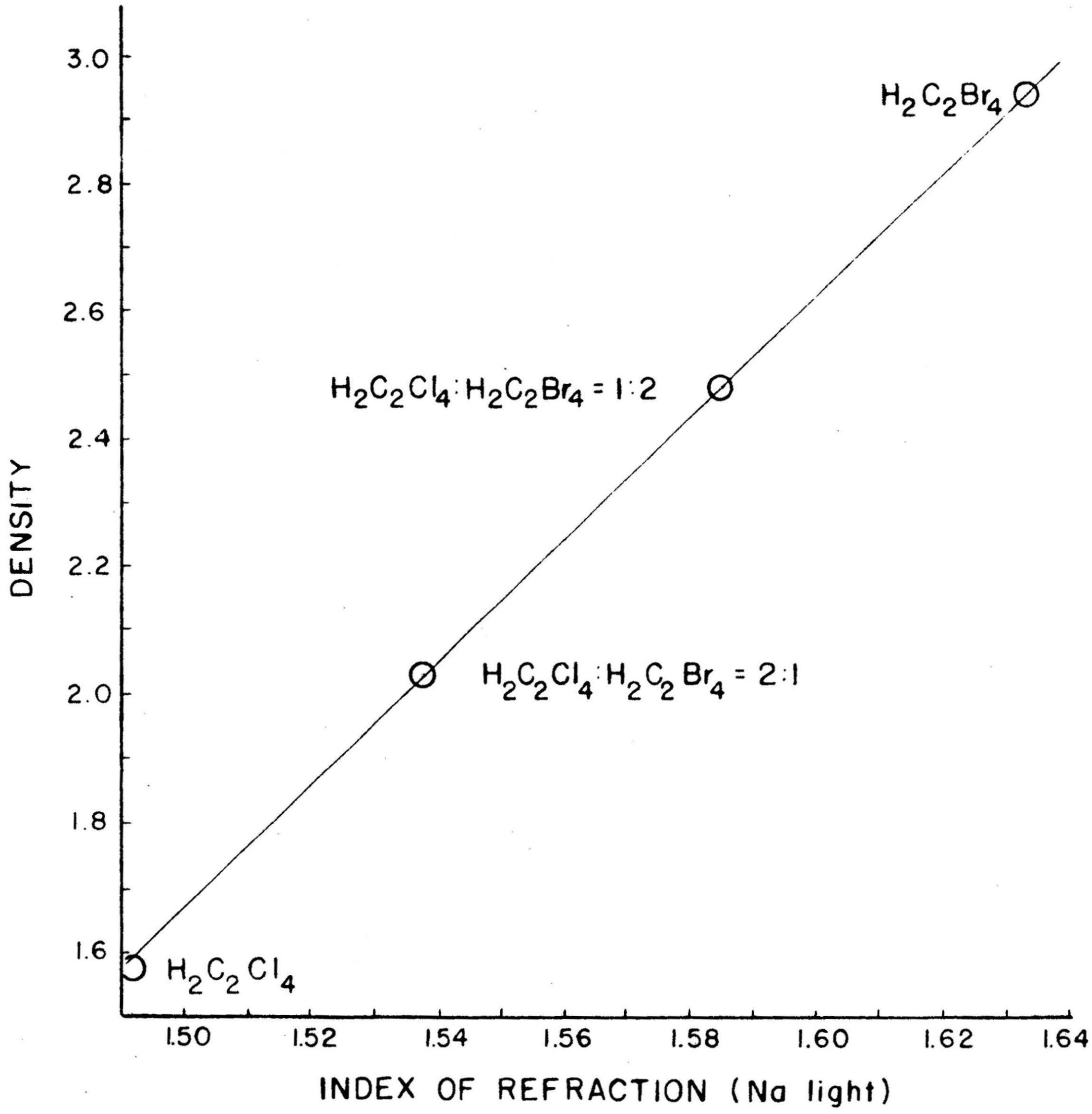

FIG. 4

GRAPH OF DENSITY VS. INDEX OF REFRACTION OF $H_2C_2Cl_4$, $H_2C_2Br_4$, AND MIXTURES at 25°C.

APPENDIX III

Description of the Single Crystal X-ray Technique

A single crystal method, which was tried during this project, is a very promising method for obtaining sharply defined X-ray diffraction photographs of the carbonate minerals. It involves mounting a grain, oriented by means of a petrographic microscope, on a glass rod and making a rotation photograph. In this way desired interplanar spacings may be determined (Buerger, 1942, p. 97). The method has the advantage of allowing the use of very small grains with or without crystal faces.

Using Rosenfeld's device and method for orienting and measuring the principal indices of refraction of difficultly oriented minerals (Rosenfeld, 1950), any recognizable linear direction of the mineral can be oriented under the microscope.

The procedure involves mounting an hatpin on a glass slide and stabilizing it by cementing small glass wedges against it (see Fig. 5, p. 34). The mineral grain is cemented to the end of the needle by touching the hot needle to a chip of glycol pthalate and quickly touching this to the hot mineral grain. The needle is inserted into its mount on the glass slide, and the grain is oriented under the polarizing microscope. The device is then clamped down and the stage fixed in this position. A fine hollow glass fiber is fastened to a second glass slide and this latter slide is carefully moved into position against the oriented grain (see Fig. 5, p. 34). A drop of diluted water glass is dropped on the far end of the glass tube, and it moves down the tube into contact with the mineral grain by capillarity. After the water glass has dried, the glycol pthalate is dissolved with acetone and the glass rod, with the attached oriented grain, is drawn away. The grain is now mounted so that the desired rotation axis is parallel to the glass rod. It is a simple matter to orient the glass rod parallel to the rotational axis of the X-ray camera.

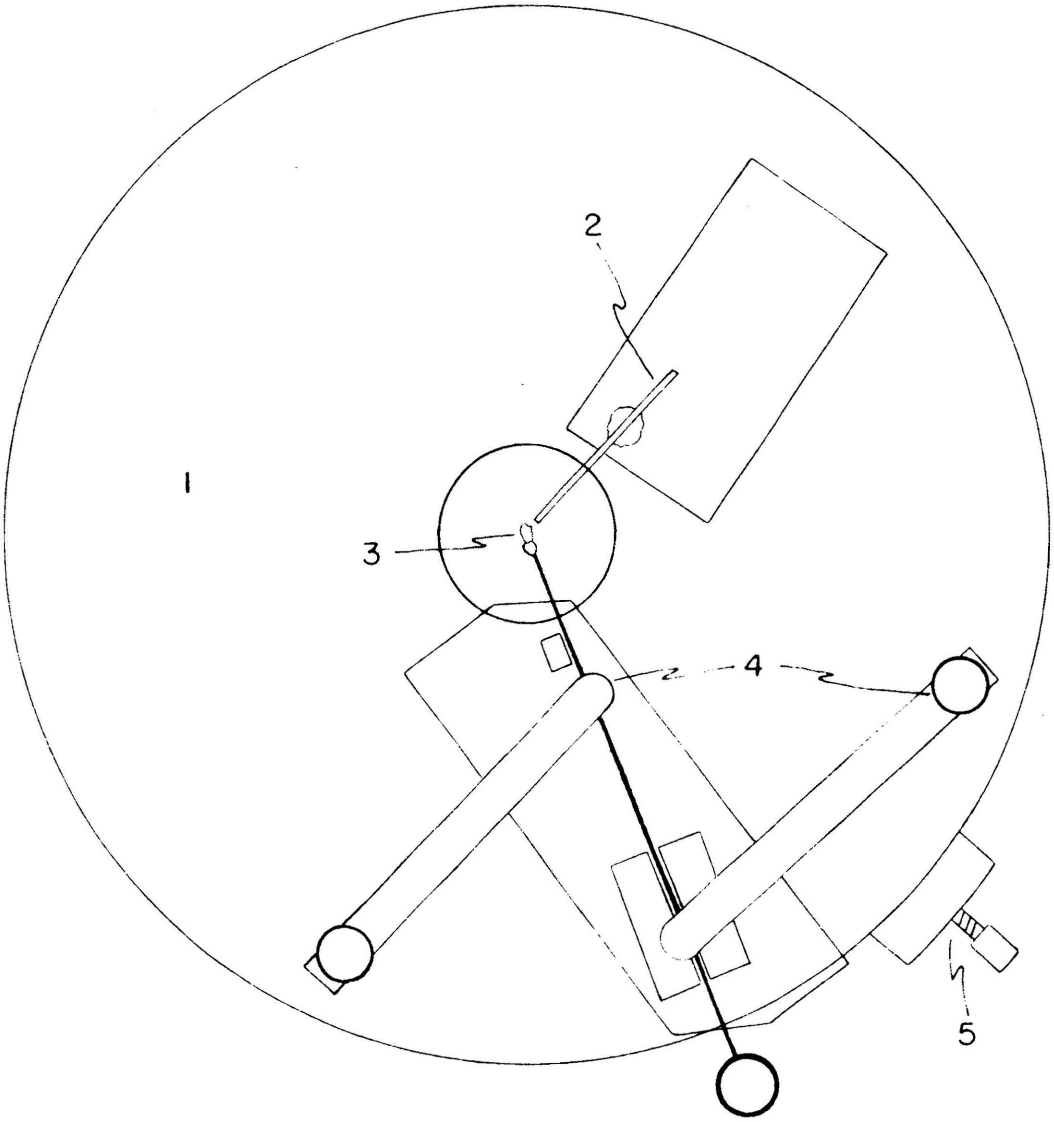

FIG. 5

DIAGRAMATIC SKETCH OF DEVICE
FOR ORIENTING MINERAL GRAINS

1. Microscope Stage
2. Glass Tube
3. Mineral Grain
4. Stage Clips
5. Stage Lock

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