

MINERALOGY AND PETROLOGY OF THE SYSTEM
CaO-MgO-CO₂-H₂O AT CRESTMORE, CALIFORNIA

ALDEN B. CARPENTER, *Department of Geology, University of
Missouri, Columbia, Missouri*

ABSTRACT

The metamorphosed limestones at the Crestmore mine, Riverside, California, consist of alternating layers of calcite-dolomite and calcite-dolomite-periclase rock. The calcite in both of these assemblages contains 4 to 5 mole percent MgCO₃. The periclase is low in iron (Mg_{0.94}Fe_{0.06}O) with $n=1.756$ and $a=4.216$. Most of the periclase has altered to the "onion-skin" variety of brucite. Dolomite is present as rod shaped inclusions 4 μ in diameter and 100 μ in length in calcite, as individual grains up to 20 mm in length and as partial rims up to 0.5 mm thick around periclase.

Chemical and modal analyses indicate that periclase is restricted to rocks containing more than 14 mole percent Mg/Ca+Mg. This suggests that the calcite-dolomite marbles contained only magnesian calcite at the peak of metamorphism and that the dolomite is the result of exsolution. The dolomite inclusions in calcite probably formed in this manner. The larger dolomite grains and the dolomite rims around periclase are also interpreted as exsolution phenomena on the basis of the work by Brett (1964). A minimum temperature of 760-800°C and 700 bars CO₂ pressure would have been required at the time of metamorphism if all of the dolomite in the Crestmore rocks has been produced by exsolution from magnesian calcite.

INTRODUCTION

The purpose of this report is to document the occurrence of the mineral assemblage calcite-dolomite-periclase at Crestmore, California, and to present data which can be used to provide quantitative information on the origin of this assemblage.

The Crestmore mine and quarries of the Riverside Cement Company are located four miles northwest of Riverside, California, approximately 55 miles east of Los Angeles. A description of previous work on Crestmore mineralogy with a complete chronological bibliography is available in Murdoch (1961).

GENERAL GEOLOGY

There are three major rock units in the vicinity of the limestone mine. The oldest of these is a metasedimentary rock complex consisting of feldspathic quartz-biotite gneisses and dolomitic marbles, believed to be of late Paleozoic or Triassic age. The metasediments have been intruded and metamorphosed by the Bonsall tonalite which is part of the early Cretaceous Southern California batholith. At the mine itself, the metasediments consist of two tabular masses of marble with minor amounts of hornfels and schist (Fig. 1). The upper body is known as the Sky Blue marble; the lower is known as the Chino marble. These rocks are com-

pletely engulfed by the tonalite and appear to be the remnants of a roof pendant in the batholith. The contact skarn between the tonalite and the marbles is usually less than two feet thick and consists predominantly of grossularite, diopside and wollastonite. Both the metasediments and the tonalite have been intruded by a small body of quartz monzonite porphyry. Burnham (1959) has described the igneous rocks and contact metamorphism at the mine.

MINERALOGY AND PETROGRAPHY OF THE MARBLES

The unmetasomatized marbles at the Crestmore mine have not previously been the subject of a general mineralogical and petrological

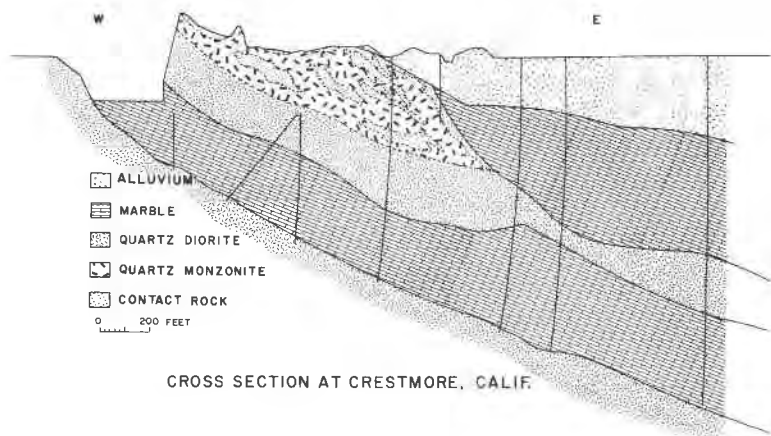


FIG. 1. Geologic cross section at Crestmore, California (courtesy of the Riverside Cement Company).

investigation. Examination of diamond drill core and mine openings by numerous investigators has shown that the chemical and gross petrographic features of both marbles are quite similar. In each case, the lower portions consist of alternating layers of predazzite¹ and coarse-grained calcite marble; the remainder consists of relatively magnesium-free marbles. The layers of predazzite are parallel to layers of graphite, spinel, phlogopite and thin zones of hornfels and it is very likely that all of these features are relicts of compositional differences in the original sediment and are parallel to the bedding. Some of the individual minerals in the marbles have been studied in detail in order to obtain data of value in interpreting the mineral textures and associations described below.

¹ Predazzite: a calcite marble containing brucite pseudomorphs after periclase.

Calcite. The widespread occurrence of calcite-dolomite intergrowths in both marbles similar to those produced by exsolution suggested that some Crestmore calcite might contain appreciable MgCO_3 in solid solution. The X-ray method used by Goldsmith, Graf, and Joensuu (1955) to determine the magnesium content of calcite from a number of geologic environments was applied to a series of marble samples from the mine. New data on the unit-cell dimensions of calcite and magnesian calcite

TABLE 1. SELECTED SPACINGS AND MAGNESIUM CONTENT OF CALCITE FROM CRESTMORE, CALIFORNIA¹

| Sample | d_{315}^2 | d_{30-12}^3 | Mole Percent MgCO_3 | | Other minerals in contact with the calcite |
|--------|-------------|---------------|------------------------------|-----------------|--|
| | | | Calculated from | Calculated from | |
| C517 | 1.040 Å | 1.0065 Å | 5.2 | 5.5 | Dolomite, periclase ⁶ |
| C518 | 1.041 | 1.0080 | 4.2 | 4.0 | Dolomite, periclase ⁶ |
| C514 | 1.041 | — | 4.1 | — | Dolomite, ⁷ periclase ⁶ |
| C516 | 1.044 | 1.0108 | 1.0 | 1.2 | Dolomite ⁷ |
| C519 | 1.0401 | 1.0074 | 4.6 | 5.1 | Dolomite |
| C520 | 1.0398 | 1.0073 | 5.4 | 4.7 | Dolomite |
| C503 | 1.0399 | 1.0070 | 5.3 | 5.0 | Dolomite, brucite |
| S504 | 1.0445 | 1.0175 | 0.5 | 0.5 | Sample consists of blue calcite containing numerous grains of monticellite and green spinel. |

¹ Data obtained using a 114.59 mm camera, line source and Fe radiation.

² *hkl* are Miller-Bravais indices; *i* is omitted. ± 0.002 Å.

³ ± 0.001 Å

⁴ $\pm 0.7\%$ MgCO_3 at 5% MgCO_3 .

⁵ $\pm 0.5\%$ MgCO_3 at 5% MgCO_3 .

⁶ periclase now altered to brucite.

⁷ dolomite present as exsolution lamellae in the calcite.

obtained by Graf (1961) and Goldsmith, Graf, and Heard (1961) were used in calculating the spacings of X-ray reflections considered to be particularly suitable for this technique. Observation has shown that the small amount of iron and manganese in the marbles, approximately 0.3 percent as (Fe, Mn)O, is present largely in the form of pyrrhotite, and may be neglected as a source of error in this procedure. Selected spacings and estimated compositions for a series of Crestmore calcites are given in Table 1.

Another method of obtaining the same kind of data is to construct a graph showing the volume percent dolomite in a rock as a function of

both the mole fraction of magnesium in the total carbonate and the magnesium content of the calcite (Fig. 2). Such a diagram may be used for the graphical determination of the magnesium content of calcite in those rocks for which the percentage of dolomite and the Mg/Ca+Mg ratio in the total carbonate is known. The Mg/Ca+Mg ratio of the bulk carbo-

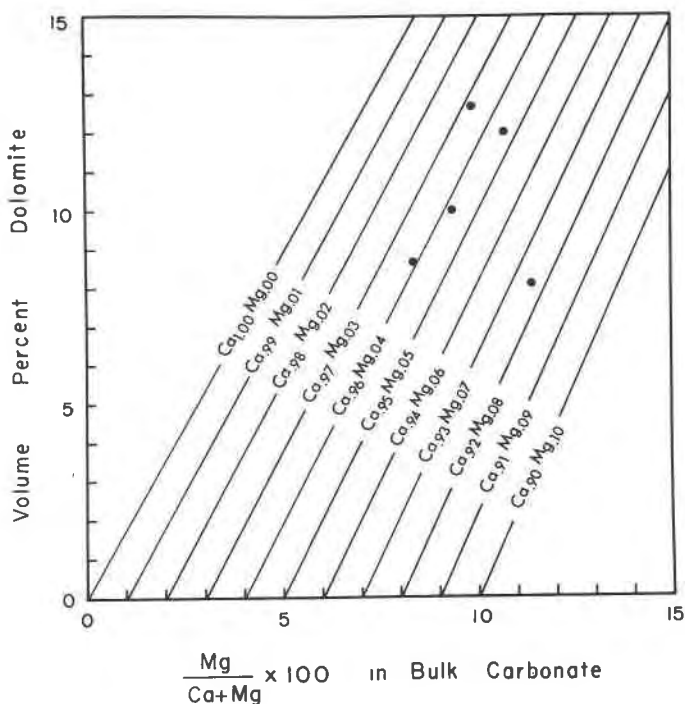


FIG. 2. Diagram showing the relationship between bulk composition, calcite composition and volume percent dolomite in calcite-dolomite rocks. This diagram can be used to estimate the composition of a magnesian calcite if the Mg/Ca+Mg ratio of the bulk carbonate and the volume percent dolomite in a sample are known. These data for six Crestmore samples have been plotted on the diagram.

nate and the volume percent dolomite in six marble samples have been plotted in Figure 2.

Although the number of samples in Table 1 and Figure 2 is small, the data indicate that the calcite in the Chino marble generally contains 4 to 5 mole percent MgCO_3 in solid solution. In addition, there does not appear to be any significant difference in the magnesium content of the calcite in those samples containing periclase as opposed to those which contain only dolomite. The calcite from the Sky Blue marble (S504) was taken

from a metasomatized zone at a contact with the quartz monzonite porphyry and not too surprisingly contains the least amount of magnesium. It is very likely that the magnesium content of the calcites is primarily related to the manner in which it was quenched after metamorphism and is not a measure of the maximum temperature of metamorphism.

Periclase. Unaltered grains of periclase 0.2 to 2 mm in diameter have been collected from four localities in the mine. These grains are invariably surrounded by a complete and relatively uniform alteration rim of brucite. A 164 mg sample of periclase containing $\frac{1}{2}$ to 1 percent inclusions of geikielite, spinel and chondrodite was analyzed, yielding the following results:

| | Sample #1 (59.6 mg) | Sample #2 (104.5 mg) |
|--------------------|------------------------|-------------------------|
| Mg as MgO | 95.1 | 95.2 |
| Fe as FeO | 5.78 | 5.78 |
| Mn as MnO | 0.03 | 0.03 |
| Insoluble (in HCl) | 0.4 | 0.8 |
| | 101.3 | 101.8 |

R. Koirtzohann, analyst; Univ. of Missouri Spectrographic Laboratory.

The chemical formula calculated from this analysis is $Mg_{0.942}Fe_{0.057}O$. Periclase in the analyzed sample had a refractive index of 1.7560 ± 0.0005 and a unit cell of $4.26 \pm 0.001 \text{ \AA}$. It is noteworthy that the refractive index for this periclase is substantially lower than 1.766 ± 0.002 obtained by interpolating data from Bowen and Schairer (1935). If the magnesio-wustites synthesized by Bowen and Schairer contained some ferric iron, this would explain why their refractive indices were higher than in natural material of the same total iron content. The refractive indices of periclase from two other localities in the mine are 1.747 ± 0.001 and 1.7500 ± 0.0005 .

Brucite. There are two distinct, morphologically different varieties of brucite at Crestmore. The overwhelmingly dominant form is the well known scaly-concentric ("onion-skin") pseudomorphs after periclase (Fig. 3a). All of the unaltered periclase that has been observed at Crestmore occurs in the cores of these brucite grains. Turner and Weiss (1965) have explained the origin of the onion-skin texture as the result of the oriented brucite crystals kinking under radially directed compressive stress. In the text below, the term periclase will be used to indicate either periclase or brucite pseudomorphs after periclase.

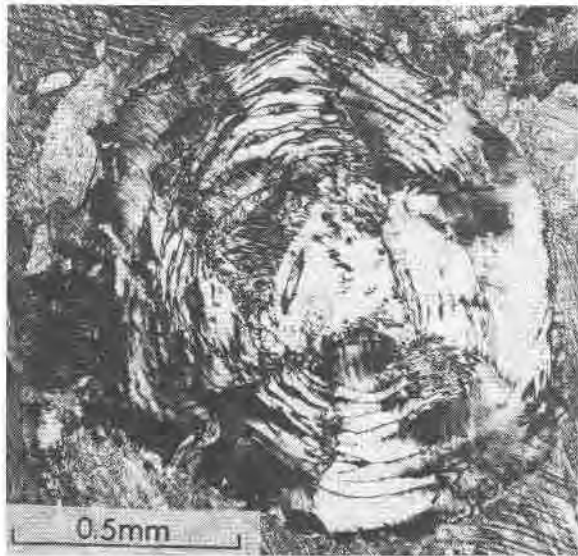


FIG. 3a. Brucite pseudomorphs after periclase. Note scaly concentric "onion-skin" texture. Crossed nicols.

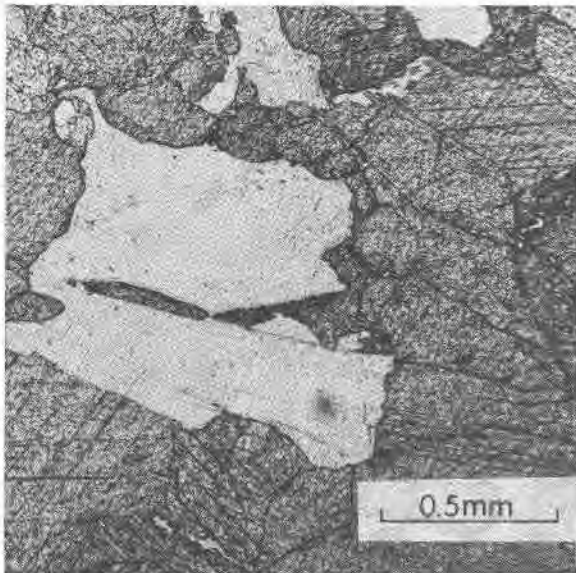


FIG. 3b. Platy crystals of brucite in the Sky Blue marble. This variety of brucite is not pseudomorphous after periclase. Plain light.

At one restricted area in the Commercial quarry micaceous plates of brucite 2 mm in diameter and 0.2 mm thick occur in a coarse-grained calcite-dolomite marble (Fig. 3b). This occurrence lies 10 to 20 feet from a potash feldspar-wollastonite-ludwigite pegmatite, derived from the quartz-monzonite porphyry, which has intruded the marble. The field relations and the habit of the brucite suggest that the brucite in these rocks has formed directly from the decomposition of dolomite without periclase as an intermediate step (Carpenter, 1963; Turner, 1965).

Dolomite. Very nearly all of the magnesian marbles at Crestmore contain dolomite in amounts ranging up to 12 percent by volume. In these rocks there are three textural varieties of dolomite which may be summarized as follows:

Fine-grained dolomite. This term is used here to designate clusters of subparallel dolomite rods approximately 10 to 40 microns in diameter and up to 1 mm in length which are present as inclusions in magnesian calcite (Fig. 4a). In the most commonly observed situation, the dolomite rods are inclined to the plane of the thin section and thus appear as cigar-shaped inclusions or even as dots. In a number of samples, the rods are curved and a very few examples of hook-shaped rods have been observed. The dolomite rods and the host calcite have a common extinction position under crossed nicols (indicating a common orientation for the c axis) in only half of the occurrences studied. In the cases where the dolomite and host do not have a common orientation, the dolomite rods usually extinguish simultaneously with one of the adjacent calcite grains. Crystallographically oriented dolomite in calcite and nonoriented dolomite in calcite are always present together in thin section and may occur as adjoining grains. The fine-grained dolomite may be found with either of the other two textural varieties of dolomite.

Coarse-grained dolomite. This term is used here to designate generally equant grains of dolomite which are usually 0.1 to 1.5 mm in diameter (Fig. 4b). Many grains have intricate globular forms with numerous reentrants and hook shapes. Other grains are elongate with maximum dimensions of 1.8 mm in diameter and 20 mm in length. The minimum diameter of the globular dolomite is approximately 50 microns. Although there is a gradation between the fine-grained rods and blebs of dolomite and the coarse-grained globular dolomite it is usually easy to assign any given sample to one category or the other on the basis of shape and size.

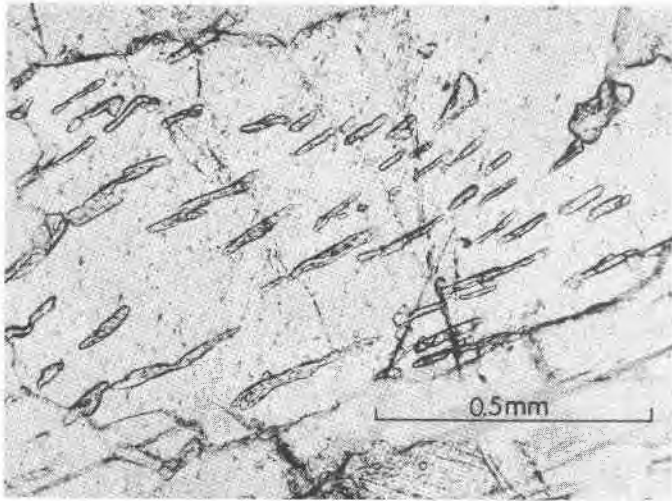


FIG. 4a. Rods and blebs of "fine-grained" dolomite in calcite. This dolomite has probably been exsolved from magnesian calcite.

Dolomite rims around periclase. In most of the marble which contains periclase the periclase grains are partially rimmed by dolomite. Variations in the dimensions and shapes of these rims can be correlated with the presence or absence of fine-grained dolomite. Samples containing

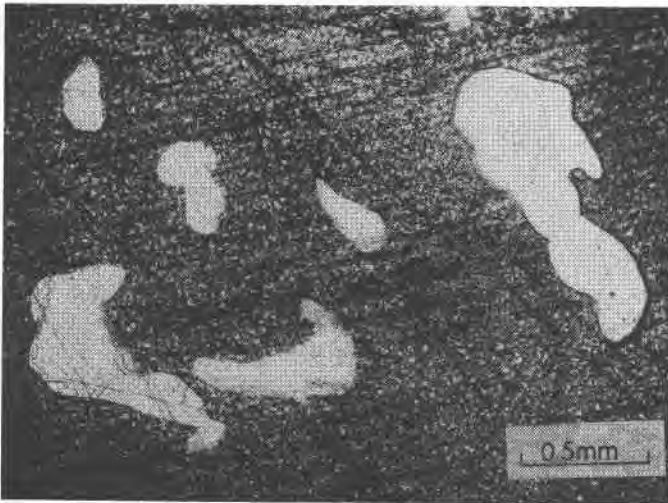


FIG. 4b. Globular masses of "coarse-grained" dolomite in calcite (stained with cupric nitrate). This variety of dolomite is probably the result of the coalescence and spheroidization of rods and blebs of dolomite similar to those illustrated in Figure 4a.

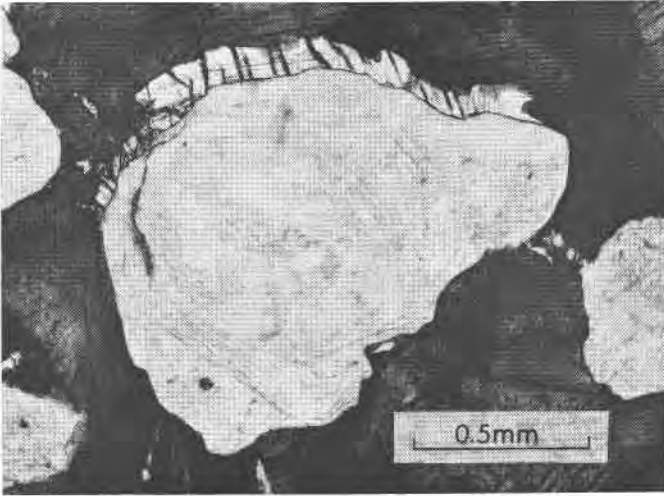


FIG. 5a. Relatively thin partial rim of dolomite around periclase (now altered to brucite) in calcite (stained dark by alizarine red S). This partial rim is probably due to the exsolution of dolomite from magnesian calcite along calcite-periclase grain boundaries. The presence of fine-grained rods and blebs of dolomite in the calcite of periclase-bearing rocks appears to be largely restricted to those samples which contain thin dolomite rims around periclase. Plain light.

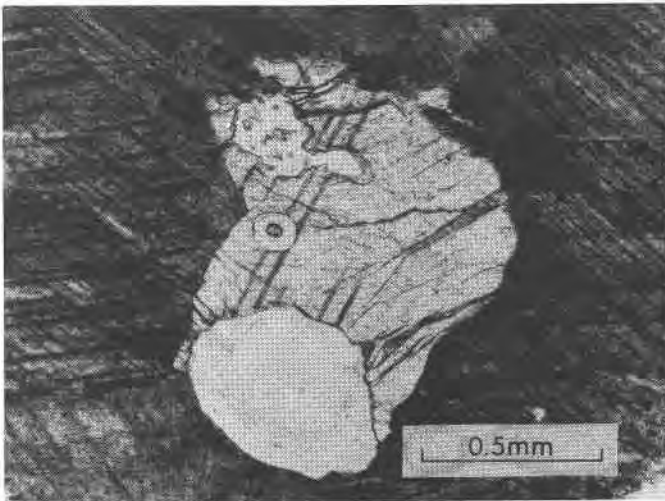


FIG. 5b. Partial rim of dolomite around periclase (now altered to brucite) in calcite (stained dark by alizarine red S). This partial rim is probably due to the exsolution of dolomite from magnesian calcite along calcite-periclase grain boundaries. Note the uniform alteration halo of hydrocalcite (?) around the spinel inclusion in the dolomite. Plain light.

fine-grained dolomite generally have thin distinct partial rims up to 60 microns thick (Fig. 5a). The rims in samples which are free of fine-grained dolomite are larger and range up to 0.5 mm in thickness (Fig. 5b). The coarse-grained globular variety of dolomite appears to be relatively rare in the periclase-bearing rocks.

Accessory minerals. Small amounts, usually less than two percent in total, of pale lavender spinel ($n = 1.724 \pm 0.001$; $a = 8.091 \pm 0.001 \text{ \AA}$), apatite

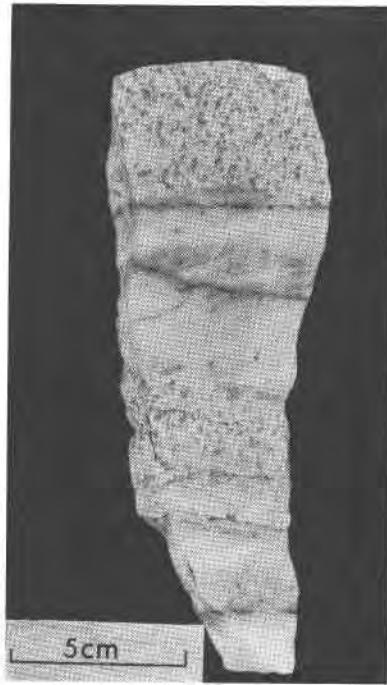


FIG. 6a. Alternating beds of predazzite (mottled) and dolomitic marble. Specimen M3. Chemical and petrographic data for this specimen are given in Table 2.

(variety wilkieite), pyrrhotite, geikielite, and colorless chondrodite and clinohumite are disseminated throughout the marbles. Each of these minerals has been confirmed by X-ray diffraction.

PETROGRAPHY OF THE LAYERED ROCKS

The marbles studied most extensively during this investigation are from the lower portion of the Chino marble where the interlayering of the calcite-dolomite-periclase rocks and the calcite-dolomite-marbles is especially well developed. Even casual study of the mine walls shows that

these two rock types are more or less regularly and evenly interbedded. The thickness of the periclase-bearing layers ranges from one-half inch to as much as thirty inches whereas the beds of calcite-dolomite marble range from one-half inch to five or six feet. In the upper portion of the Chino marble, periclase beds are rare and usually occur as one-half inch layers separated by 50 to 80 feet of low magnesium marble. Two examples of interlayered predazzite and marble are illustrated in Figure 6. Chemical and mineralogical data for these rocks are presented in Table 2.



FIG. 6b. Alternating beds of predazzite (mottled) and dolomitic marble. Specimen M4. Chemical and petrographic data for this specimen are given in Table 2.

Thirty-nine specimens of dolomitic marble and predazzite which were found to be homogeneous, with less than one percent in total accessory minerals and free from alteration by ground water were selected for detailed study. Twenty-six of these were diamond drill core samples taken from throughout the marble deposit; the others were obtained from the central portion of each layer of five large banded marble blocks removed from the mine walls. A thin-section, modal analysis and partial chemical analysis were obtained for each sample. The chemical analyses were made by digesting the samples in hydrochloric acid and determining Si (silico-molybdate method), Ca (EDTA) and Mg (atomic adsorption). The mole fraction of magnesium, $Mg/Ca + Mg$, in the carbonate

TABLE 2. CHEMICAL AND MINERALOGICAL DATA FOR INDIVIDUAL LAYERS IN BANDED PREDAZZITES

| Layer | wt. % MgO | $\frac{\text{Mg}}{\text{Ca}+\text{Mg}} \times 100$ | vol. % periclase ¹ | vol. % dolomite |
|-----------------------|-----------|--|-------------------------------|-------------------|
| Sample M3 (Figure 6a) | | | | |
| 1 | 18.7 | 39.8 | 30.2 | 9.7 |
| 2 | 3.94 | 9.4 | none | 10.0 |
| 3 | 21.1 | 43.9 | 27.2 | 10.8 |
| 4 | | | none | n.d. ² |
| Sample M4 (Figure 6b) | | | | |
| 1 | 15.1 | 32.9 | 14.4 | 10.2 |
| 2 | 4.88 | 10.7 | none | 11.9 |
| 3 | 14.2 | 31.0 | 16.3 | 11.9 |
| 4 | | | none | n.d. |

¹ All of the brucite is pseudomorphous after periclase.

² Present but not determined.

plus periclase portion of each sample was calculated after making a magnesium correction for chondrodite based on the amount of Si reported in the analysis. These data are presented in Figure 7.

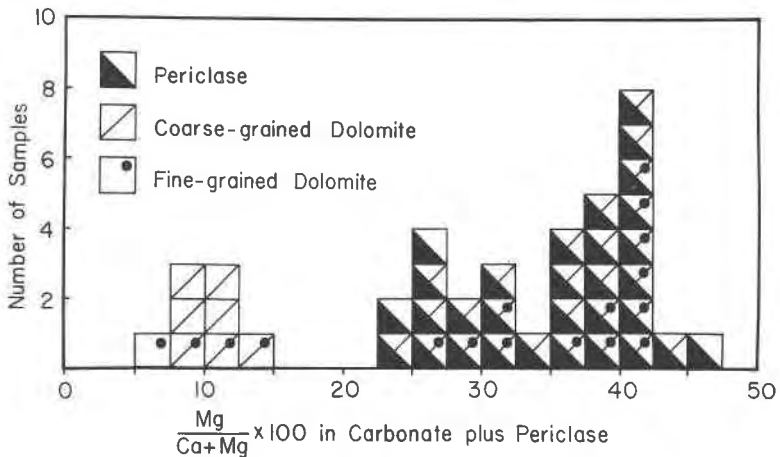
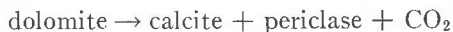


FIG. 7. Histogram showing the relationship between bulk composition and mineralogy in Crestmore marbles. Note that periclase is restricted to rocks containing more than 14 mole percent magnesium. All of the samples consist predominantly of calcite.

The data in Figure 7 strongly suggest that the presence or absence of periclase in the rocks is related to the amount of magnesium in the rock and that samples which assay less than six percent MgO do not contain periclase. The field relations, many tens of interlayered beds of predaz-zite and dolomitic marble extending over hundreds of feet, also indicate that the presence of periclase in selected beds is controlled by some aspect of rock composition rather than thermal, pressure or chemical gradients.

DISCUSSION

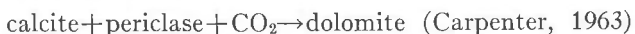
The metamorphic reaction



has been described by Bowen (1940) and studied experimentally by Graf and Goldsmith (1955) and Harker and Tuttle (1955). Since the assemblage calcite-dolomite-periclase-CO₂ is univariant (with respect to temperature and CO₂ pressure) the occurrence of interbanded predaz-zites and dolomitic marbles at Crestmore may be regarded as unexpected. Earlier papers on the mineralogy of the Crestmore limestone deposit have dealt with this problem to some extent and various explanations as to the origin of the dolomite in these rocks have been suggested. These are as follows:

1. Exsolution from magnesian calcite. The fine-grained rods and blebs of dolomite are the result of exsolution from a high-magnesian calcite which was present at the time of high grade metamorphism (Carpenter, 1963; van der Veen, 1965).

2. Back reaction. The dolomite rims around periclase (or brucite) are the result of retrograde metamorphism corresponding to the reactions:



3. Incomplete reaction. The coarse-grained dolomite is the remnant of dolomite which was originally present in the limestone and which failed to decompose during metamorphism. The shape of the grains is the result of the partial dissolution of dolomite in calcite during thermal metamorphism (Carpenter, 1963).

4. Replacement of calcite. van der Veen (1965) has described an unusual calcite-dolomite texture from Crestmore and has attributed it to the partial replacement of calcite by dolomite. However, this dolomite texture appears to be rare and is the only texture at Crestmore which has been attributed to replacement.

A brief review of recent experimental work on the system MgO-CaO-

CO_2 is an important step in attempting to evaluate these hypotheses. Figure 8 shows the magnesium content of calcite in equilibrium with dolomite or periclase for a range of temperatures at 700 bars CO_2 pressure. This diagram indicates that under conditions of high grade metamorphism calcite in equilibrium with dolomite will become highly mag-

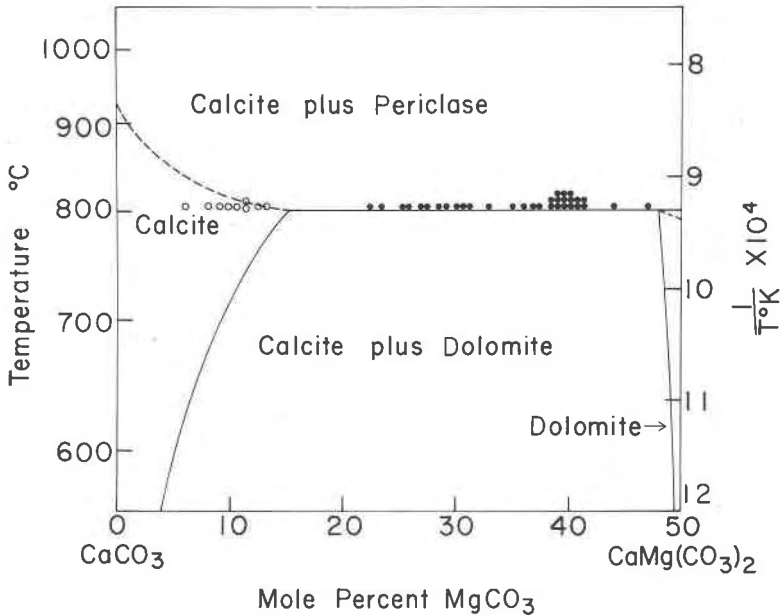


FIG. 8. Subsolidus diagram for a portion of the system CaO-MgO-CO_2 at $p_{\text{CO}_2} = 700$ bars; after Graf and Goldsmith (1955) and Goldsmith and Heard (1961). Above 800°C at this pressure dolomite decomposes to periclase plus a highly magnesian calcite. The open circles represent the bulk composition of the Crestmore calcite-dolomite rocks which appear to have been homogeneous magnesian calcite rocks at the time of metamorphism. The solid circles represent the bulk composition of periclase-bearing rocks. A minimum temperature of 760°C and a minimum CO_2 pressure of 630 bars would have been required to produce homogeneous carbonate rocks from dolomitic limestones of the compositions indicated by the open circles.

nesian. Goldsmith (1960) has studied the exsolution of dolomite from magnesian calcite and his data indicate that this reaction readily takes place in the laboratory at temperatures above approximately 600°C but that equilibrium unmixing is apparently not attained at lower temperatures. All of these data are consistent with the hypothesis that the fine-grained dolomite is the result of exsolution from a high magnesian calcite. The presence of 4 to 5 mole percent MgCO_3 in Crestmore calcite is in good agreement with Goldsmith's observation that "a number of

metamorphic calcites retain approximately 5 mole percent MgCO_3 in solid solution even in association with exsolved dolomite." According to the data in Figure 8, all of these rocks have been essentially "quenched" from 600°C . This figure is in good agreement with the temperature determined by Goldsmith as the lower limit of rapid exsolution of dolomite from magnesian calcite.

A clue to understanding the origin of the coarse-grained dolomite may be obtained by noting the relationship between the bulk composition and the mineralogy of the marbles (Figure 7). The absence of periclase in dolomitic rocks containing less than approximately 14 mole percent MgCO_3 and the presence of periclase in all rocks higher in magnesium than this amount suggests that at the time of metamorphism periclase was in equilibrium with calcite of the composition $\text{Ca}_{0.86}\text{Mg}_{0.14}\text{CO}_3$. This hypothesis implies that the coarse-grained dolomite is an exsolution phenomenon and avoids the difficulties which arise in postulating that this material is "original" dolomite which survived the period of metamorphism without change. The minimum temperature which would have been required to produce the magnesian calcite-periclase assemblage specified above may be estimated by combining the mineralogical and experimental data as in Figure 8. This figure indicates that a minimum temperature of 800°C and 700 bars CO_2 pressure would be required to maintain a 14 mole percent MgCO_3 calcite in equilibrium with periclase.

If the hypothesis outlined above is valid, it follows that all of the periclase-bearing rocks should contain visible dolomite. As the magnesian calcite-periclase rocks cooled, a set of conditions would be attained under which dolomite and low magnesium calcite would again constitute a stable assemblage. At still lower temperatures, dolomite would exsolve from the high magnesium calcite until this process was halted by slow reaction rates, presumably at approximately 500 – 600°C . Calculations based on the assumption that Crestmore calcite contains 5 mole percent MgCO_3 indicate that the amount of dolomite produced in the predazzites by this process should range between 10 and 18 percent by volume depending upon the bulk composition of the rock. Modal analyses of the predazzites reveal that the dolomite content ranges from 0 to 19 percent by volume.

The interpretation of the dolomite textures in the Crestmore rocks has been greatly facilitated by the experimental work of Brett (1964) on the effect of bulk composition and cooling rates on exsolution textures. Table 3 illustrates Brett's summary of the general relationships between the duration of annealing and the type of exsolution texture produced. The Crestmore dolomite texture types and the accompanying data on bulk composition and associated minerals appear to correspond closely

with the data for the synthetic exsolution textures. This correspondence suggests that the dolomite textures may be interpreted by analogy with the experimental textures.

Calcite-dolomite rocks. These rocks contain fine-grained dolomite, coarse-grained dolomite or both varieties simultaneously. The fine-grained dolomite texture such as that illustrated in Figure 3a is apparently the result of coherent exsolution. The fact that this texture appears to be unaccompanied by any other form of dolomite only in low magnesium rocks agrees with Brett's observation that this texture may be correlated in part with a low degree of supersaturation in the host mineral. The

TABLE 3. IDEALIZED SEQUENCE OF EXSOLUTION (FROM BRETT, 1964)

| |
|--|
| A. Initial exsolution to grain boundaries, twin planes, etc. |
| Time |
| B. Coherent exsolution lamellae, lattice works, etc. |
| Time |
| C. Noncoherent exsolution, segregation to grain boundaries, granular texture, sea and island texture, spheroidization and coalescence. |
| Time |
| D. Possible coherent secondary exsolution. Texture of C preserved with lamellae forming the recrystallized host. |

coarse-grained dolomite (Fig. 4b) is here interpreted as being the result of "spheroidization" and coalescence of the fine-grained dolomite. The coarse-grained dolomite is thus interpreted as being a noncoherent exsolution phenomenon. Rocks containing both varieties of dolomite have apparently undergone the exsolution sequence:

- B Coherent exsolution
 ↓ Time
 C Noncoherent exsolution
 ↓ Time
 D Noncoherent exsolution with secondary coherent exsolution.

This combination of textures is illustrated in Figure 9 which appears quite analogous to the synthetic example illustrated by Brett (Brett, 1964; Fig. 7).

Calcite-dolomite-periclase rocks. It has been noted above that the hypothesis of a highly magnesian calcite in contact with periclase at the time of metamorphism implies that the predazzites should contain an appreciable amount of dolomite as the result of exsolution during cooling. Since the arrangement of ions in the Mg layers in dolomite is similar to that in the Mg layers parallel to $\{111\}$ in periclase one would expect the dolomite in the predazzites to exsolve as oriented overgrowths on the periclase grains. Judging from the rarity of dolomite in these rocks, other than as overgrowths on periclase, it seems reasonable to suppose that

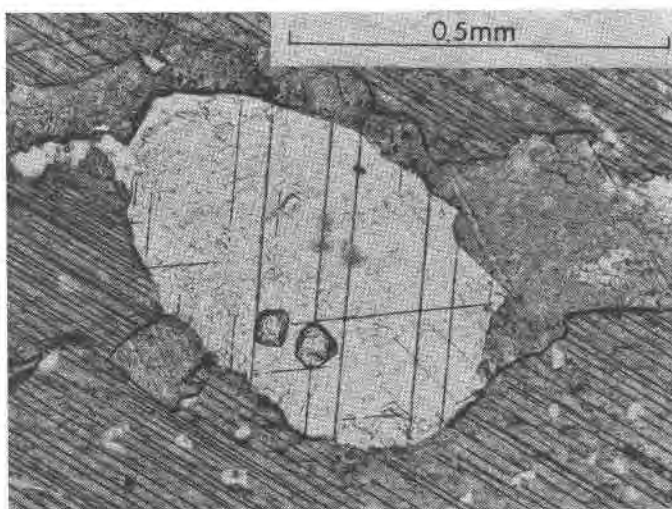


FIG. 9. Fine-grained blebs of dolomite in proximity to a crystal of coarse-grained dolomite. The coarse-grained dolomite is interpreted as being a noncoherent exsolution phenomenon produced by the coalescence of an early-formed fine-grained exsolved dolomite. The fine-grained dolomite in the illustration is believed to be the result of a secondary period of coherent dolomite exsolution. The two inclusions in the large dolomite grain are spinel; the calcite matrix has been stained with alizarin red S. Plain light.

most of the dolomite did exsolve in this manner. However, it should be noted that the presence of oriented dolomite overgrowths may not be regarded as proof of origin by exsolution since other processes such as back reaction could reasonably be expected to produce the same phenomenon. The small amount of fine-grained dolomite which has been observed in predazzite usually coincides with the occurrence of unusually thin dolomite rims around the periclase. This fine-grained dolomite is probably the result of coherent secondary exsolution analogous to that in the calcite-dolomite rocks. The sequence of dolomite exsolution phenomena in these rocks may be summarized using Brett's terminology as follows:

- A. Initial dolomite exsolution to (periclase) grain boundaries.
- ↓ Time
- D. Secondary coherent exsolution.

The relative merits of exsolution as opposed to back reaction as the explanation of the presence of dolomite in the predazzites is difficult to assess quantitatively; however, a number of lines of evidence suggest that exsolution is the more important. The basis for the back reaction hypothesis rests essentially on textural evidence. Turner (1965) states, "... there is clear evidence of yet a later reaction



The brucite pseudomorphs after periclase are rimmed with clear dolomite which also occurs elsewhere as patches and veinlets cutting the dusty looking calcite." However, this texture is not in fact similar to the uniform and entirely complete rims of brucite around periclase or hydrotalcite(?) around spinel which occur in these same rocks. In thin section, only approximately 5 percent of the dolomite "rims" completely encircle the brucite grains and in many cases the rim continues for only half or less than half of the grain circumference (Fig. 5). Since reactions characteristic of retrograde metamorphism tend to produce uniform and complete alteration rims, such as "kelyphite" rims around almandine in pelitic rocks, it is likely that "partial rim" dolomite texture is largely the result of some phenomenon other than back reaction.

On the other hand, a considerable amount of magnesium must have exsolved as dolomite from magnesian calcite in the Crestmore marbles. Abundant evidence exists for highly magnesian calcite in association with periclase at the time of metamorphism. Goldsmith (1960), shows that dolomite exsolves relatively rapidly from supersaturated magnesian calcites at temperatures above 600°C. The exsolution hypothesis may be tested by constructing a diagram which shows the calculated volume percent brucite as a function of Mg/Ca+Mg in the rock and the bulk composition of the coexisting carbonate phase or phases (Fig. 10). In effect, the coexisting carbonate is treated as though it were the homogeneous material which would have existed at the time of metamorphism although at the present time this matrix contains both calcite and dolomite. The points on this diagram (with one exception) indicate that the carbonate matrix of the predazzites contains up to 15 mole percent MgCO₃ which is in good agreement with the maximum MgCO₃ content noted for the dolomitic marbles. Thus, the dolomite in *both* the predazzites and the dolomitic marbles can be interpreted as the result of exsolution.

Theoretically, if all the periclase were in equilibrium with the same

high-magnesium calcite at the time of metamorphism, all of the points should lie along one line of constant content of MgCO_3 in calcite. The scatter in Figure 10 suggests that a simple relationship does not exist between bulk composition and periclase content in predazzite samples collected at random throughout the mine. However, local variations in the physicochemical environment during metamorphism may be respon-

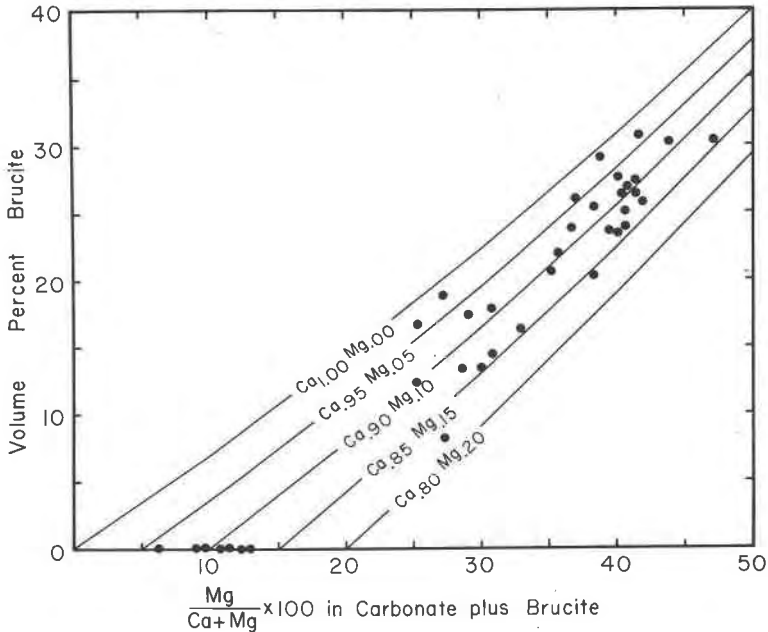


FIG. 10. Diagram showing the relationship between bulk composition, calcite composition and volume percent brucite in Crestmore marbles. This diagram indicates that magnesian calcite in the composition range $\text{Ca}_{0.95}\text{Mg}_{0.05}$ - $\text{Ca}_{0.85}\text{Mg}_{0.15}$ coexisted with periclase at the time of metamorphism. The dolomite in these rocks is probably the result of exsolution from this magnesian calcite.

sible for these deviations. The magnesium content of the carbonate matrix in predazzite layers becomes progressively lower toward the monticellite-bearing rocks at the contacts with quartz monzonite porphyry. These monticellite-bearing rocks have been subjected to higher temperatures or lower CO_2 pressure environments (or both) during metamorphism than the interior of the marble body. Consequently, the magnesium content of the carbonate matrix in predazzites adjacent to contacts should be unusually low.

The mineralogical data for individual layers in five marble blocks

containing alternating dolomitic and predazzite bands are presented in Figure 11. It is interesting to note that in two of these five samples the carbonate matrix of the predazzite is lower in magnesium than the bulk carbonate of the adjacent dolomitic layer. Since the carbonate in the predazzite should always be saturated with magnesium during metamorphism one would expect the magnesium content of the carbonate

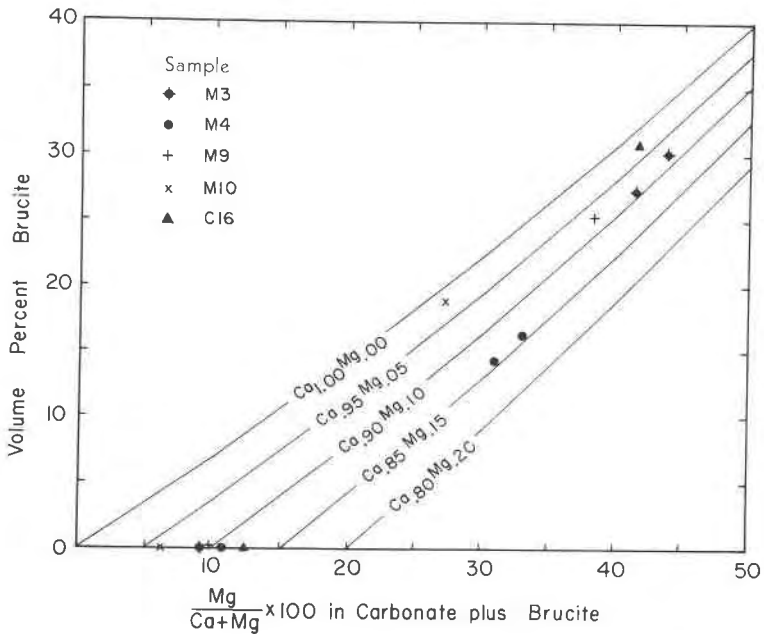


FIG. 11. Diagram showing the relationship between bulk composition, calcite composition and volume percent brucite samples from alternating predazzite and dolomitic layers in banded marble. The dolomitic layer in samples C16 and M9 are higher in total MgCO_3 than the matrix of the adjacent predazzite. This may be due to differences in the decarbonation rates of homogeneous magnesian calcite rocks and periclase-bearing rocks.

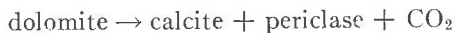
matrix in the predazzites to be equal to or higher than the magnesium content of the carbonate matrix in the adjacent dolomitic bands. The unexpectedly high magnesium content in the two dolomitic samples may be the result of differences in the rate of decarbonation of dolomite and high magnesium calcite at high temperature. The similarity of magnesium ion arrangement in the $\{111\}$ plane of periclase and the $\{0001\}$ plane of dolomite facilitates the formation of periclase crystals in dolomite which has been heated above the decarbonation temperature. Periclase formed in this manner would act as seed crystals and promote

the decomposition of high magnesium calcite, produced by the destruction of dolomite, to low magnesium calcite plus periclase at still higher temperatures. In contrast to dolomite, magnesian calcite does not contain cation layers preferentially enriched in magnesium. Consequently, it must be more difficult to nucleate periclase in homogeneous magnesian calcite rocks than in dolomites. A major difference in the ease of periclase crystal growth must affect the rates of decarbonation reactions and would tend to produce some dolomitic marbles with a higher magnesium content than the matrix of adjacent predazzite beds.

CONCLUSIONS

The metamorphosed limestones at Crestmore, California, consist of alternating layers of calcite-dolomite and calcite-dolomite-periclase rock. The composition of the calcite in both of these assemblages has been estimated by X-ray methods and from chemical and modal analyses of the marbles. The results indicate that most of the calcite contains 4 to 5 mole percent $MgCO_3$. The iron content of the periclase is sufficiently low (6 mole percent) that experimental work involving this mineral may be applied to the interpretation of Crestmore rocks with little chance of serious error. Although most of the periclase has hydrated to brucite, the unique onion-skin texture which develops during the alteration process makes it possible to recognize those rocks which contained periclase at the time of metamorphism. There are three textural varieties of dolomite in the marbles. There are: (1) rods and blebs of dolomite up to 10 microns in diameter and 100 microns in length which are present as inclusions in magnesian calcite, (2) grains of dolomite up to 20 mm in length, and (3) partial rims of dolomite up to 60 microns thick around grains of periclase.

There is strong evidence that the dolomite in the dolomitic marbles is the result of exsolution from magnesian calcite. The reaction



is univariant and consequently the mineral assemblage dolomite-periclase should not ordinarily be found in metamorphosed magnesian limestones. In addition, chemical and modal analyses of the dolomitic marble and the predazzites indicate that periclase is restricted to rocks containing more than 14 mole percent $Mg/(Ca+Mg)$. These facts suggest that the calcite-dolomite marbles contained only magnesian calcite at the time of metamorphism and that the dolomite is the result of exsolution. This hypothesis implies that the predazzites should also contain exsolved dolomite since the magnesian calcites in these rocks should have been fully saturated with magnesium at the time of meta-

morphism. The modal analyses show that the predazzites contain up to 19 volume percent dolomite which is very close to the maximum amount which would be predicted by a quantitative application of the exsolution hypothesis. A minimum temperature of 760–800°C and 700 bars CO₂ pressure would have been required during metamorphism in order to produce a magnesian calcite in association with periclase capable of exsolving this amount of dolomite during cooling.

The dolomite textures in the Crestmore rocks are interpreted on the basis of the experimental work of Brett (1964). The tiny rod-like inclusions of dolomite in calcite are regarded as the result of coherent exsolution from the calcite. The coarser-grained dolomite is thought to be a noncoherent exsolution phenomenon which has been produced by the coalescence of the earlier exsolved dolomite rods. The partial rims of dolomite around periclase is most likely also the result of noncoherent exsolution. The general scarcity of complete rims around the periclase is textural evidence that this dolomite has not formed as the result of a retrograde metamorphic reaction.

ACKNOWLEDGEMENTS

The author wishes to thank Dr. Walter D. Keller and Jerome B. Krause for reviewing the manuscript and suggesting a number of improvements. The modal analyses of drill core samples were kindly made available by Mr. Krause (Krause, 1966). The chemical analyses of core samples were performed by Mr. Krause and Ronald Hutson; the analyses of samples from the banded marble blocks were carried out by Dr. Roy Koirtyohann of the University of Missouri Spectrographic Laboratory. The author also wishes to thank the Riverside Cement Company of Riverside, California, for their very generous financial support and for the assistance of the many company employees who helped with the related field work. Additional financial support was provided by the University of Missouri Research Council and the Society of the Sigma Xi.

REFERENCES

- BOWEN, N. L. (1940) Progressive metamorphism of siliceous limestone and dolomite. *J. Geol.* **68**, 225–274.
- AND J. F. SCHAIRER (1935) The system FeO-MgO-SiO₂. *Amer. J. Sci.* **229**, 194–284.
- BRETT, R. (1964) Experimental data on the system Cu-Fe-S and their bearing on exsolution textures in ores. *Econ. Geol.* **59**, 1241–1269.
- BURNHAM, C. W. (1959) Contact metamorphism of magnesian limestones at Crestmore, California. *Geol. Soc. Amer. Bull.* **70**, 879–920.
- CARPENTER, A. B. (1963) *Mineralogy of the system CaO-MgO-H₂O-CO₂ at Crestmore, California*. Ph.D. Diss., Harvard University.
- GOLDSMITH, J. R. (1960) Exsolution of dolomite from calcite. *J. Geol.* **68**, 103–109.
- , D. L. GRAF and H. C. HEARD (1961) Lattice constants of the calcium-magnesium carbonates. *Amer. Mineral.* **46**, 453–457.
- , AND O. I. JOENSUU (1955) The occurrence of magnesian calcites in nature. *Geochim. Cosmochim. Acta* **7**, 212–230.
- , AND H. C. HEARD (1961) Subsolidus relations in the system CaCO₃-MgCO₃. *J. Geol.* **69**, 45–74.

- GRAF, D. L. (1961) Crystallographic tables for the rhombohedral carbonates. *Amer. Mineral.* **46**, 1283-1316.
- AND J. R. GOLDSMITH (1955) Dolomite-magnesian calcite relations at elevated temperatures and CO₂ pressures. *Geochim. Cosmochim. Acta* **7**, 109-128.
- HARKER, R. K. AND O. F. TUTTLE (1955) Studies in the system CaO-MgO-CO₂: Part 2. Limits of solid solution along the join CaCO₃-MgCO₃. *Amer. J. Sci.* **253**, 274-282.
- KRAUSE, J. B. (1966) *Thermal metamorphism of dolomitic limestones at Crestmore, California*. M. A. Thesis, Univ. of Missouri.
- MURDOCH, J. (1961) Crestmore, past and present. *Amer. Mineral.* **46**, 245-257.
- TURNER, F. J. (1965) Note on the genesis of brucite in contact metamorphism of dolomite. *Beitr. Mineral. Petrogr.* **11**, 393-397.
- AND L. E. WEISS (1965) Deformational kinks in brucite and gypsum. *Proc. Nat. Acad. Sci. U. S.* **54**, 359-364.
- VAN DER VEEN, A. H. (1965) Calcite-dolomite intergrowths in high temperature carbonate rocks. *Amer. Mineral.* **50**, 2070-2076.

Manuscript received, January 24, 1967; accepted for publication, July 3, 1967.