# DEDOLOMITIZATION, AND ITS RELATION TO A POSSIBLE DERIVATION OF A MAGNESIUM-RICH HYDROTHERMAL SOLUTION*

GEORGE T. FAUST, *U. S. Geological Survey, Washington, D. C.*

## CONTENTS

## ABSTRACT

This paper presents an interpretation, based on physical-chemical principles and data, of the phenomena arising in the aureole of metamorphism, resulting from the intrusion of a magma into dolomitic rocks. It is assumed that dedolomitization takes place in those beds closest to the magma. It also suggests a mechanism by which hydrothermal solutions passing through the zone of dedolomitized rocks may become rich in magnesium. A summary is given of the available data on the system $MgO$-$CaO$-$CO_2$-$H_2O$ and its subsidiary systems. Probable phase equilibrium diagrams have been drawn for the systems $MgO$-$CO_2$-$H_2O$ and $CaO$-$CO_2$-$H_2O$. The course of the reactions, involved in hydrothermal dolomitization of limestones, and the special conditions necessary for the formation of magnesite, are discussed.

## INTRODUCTION

A fundamental object in geochemistry is the development of theories to explain the origin of rocks formed or altered by hydrothermal solu-

---

* Published by permission of the Director of the U. S. Geological Survey.

tions. Such theories should minimize the use of unusual constituents whose former presence cannot be established by a study of the rocks and minerals of the deposit and the associated rocks. The hydrothermally formed brucite, dolomite, and magnesite deposits constitute a typical group of such rocks and have been under study by the writer for the past six years. The hydrothermal solutions which formed the carbonate deposits were rich in magnesium and carbon dioxide.

Hydrothermal dolomitization of limestones in the aureole of mineralization in ore deposits has been recognized for many years. An especially fine contribution by Hewett (1928) has refocussed attention upon this phenomenon. Hewett made a field study of the association of dolomitized limestones and ore deposits of zinc and lead both in this country and in Europe, and he emphasizes the frequency of this relationship. He also points out that in some deposits there is zoning among the carbonates and in others, particularly at Iglesias in Sardinia, islands of unreacted limestone are contained within the dolomite. Concerning magnesite he writes (page 856):

> Magnesite is uncommon, if not very rare, near zinc and lead deposits, and similarly zinc and lead minerals are rare or unknown near the larger replacement magnesite deposits. Viewed broadly, such magnesite deposits are very uncommon, whereas dolomitized limestone near the zinc and lead deposits is rather common.

Hewett concludes his paper with a discussion of the possible sources of the magnesium.

A great many interesting geochemical problems are posed by these phenomena. In this study we are particularly concerned with (*a*) a mechanism or mechanisms by which hydrothermal solutions rich in magnesium and carbon dioxide may be derived, and (*b*) the manner in which these solutions will react with the preexisting limestones which they traverse.

In a study of the magnesite deposits of Currant Creek, Nev., Faust and Callaghan (1948) proposed a mechanism for the derivation of solutions, rich in magnesium and carbon dioxide, namely through the attack of hydrothermal solutions charged with carbon dioxide upon dolomitic rocks. The derivation proposed in that paper was one that seemed to fit best the geological relationships of the area. In addition, through a correlation of the physical chemistry, the observed mineralogical character and the texture and structure of the deposits, an explanation was offered for the formation of the dolomite, zoning, the presence of relicts of calcite (limestone), and the formation of magnesite. The comparative rarity of magnesite with respect to dolomitized limestone was also explained.

The present paper goes beyond the limitations imposed by the geology at Currant Creek, Nev., and proposes another mechanism for the derivation of solutions rich in magnesium and carbon dioxide.

The hydrothermal solutions which accomplished these reactions must have contained significant quantities of magnesium and carbon dioxide because, first, these substances are essential constituents of dolomite and magnesite and were introduced into the system; and second, from considerations of the phase rule, carbon dioxide is present both in the liquid and vapor phases whenever carbonates are precipitated from solutions.

The term carbon dioxide is used in this discussion for the sake of simplicity. In a solution of carbon dioxide in water, the following equilibria exist (1)

$$[H_2O + CO_2 \rightleftarrows H_2CO_3 \rightleftarrows H^+ + HCO_3^- \rightleftarrows 2H^+ + CO_3^{--}]. \tag{1}$$

In addition carbon dioxide is present as a gas dissolved in the solution.

The purpose of this paper is to show how magnesium-rich solutions may also be derived from the attack of hydrothermal solutions upon dolomites thermally metamorphosed by intrusives. Such dedolomitized rocks have been called predazzite, pencatite, and brucite marble. Harker (1904) has defined these rocks as follows:

> It is most in accordance with the original usage to employ the name pencatite for an aggregate of calcite and brucite in equal molecular proportions, i.e. with the percentage composition of 63.3 calcite to 36.7 brucite, reserving the predazzite for varieties richer in calcite.

Periclase, MgO, was the magnesium mineral present in these rocks after thermal metamorphism. Brucite, $Mg(OH)_2$, belongs to a later period in the genesis of the rock.

The structure, texture, and mineralogy of these metamorphic rocks will influence the character and rate of the reactions with the later hydrothermal solutions which traverse them.

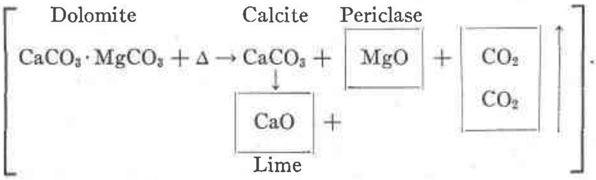
## THERMAL DISSOCIATION OF DOLOMITE

In order to gain an understanding of the origin of these dedolomitized rocks, the physical chemistry of the dissociation of dolomite is considered here.

The dissociation of dolomite may take place in two stages as is shown in the following equations:

At temperatures sufficient to cause the complete decarbonatization of the dolomite the over-all reaction will give the products outlined in boxes:

(2)



$$\left[\begin{array}{ccccccc} \text{Dolomite} & & \text{Calcite} & & \text{Periclase} & & \\ CaCO_3\cdot MgCO_3 + \Delta \rightarrow & & CaCO_3 & + & \boxed{MgO} & + & \boxed{\begin{array}{c} CO_2 \\ CO_2 \end{array}} \uparrow \\ & & \downarrow & & & & \\ & & \boxed{CaO} & + & & & \\ & & \text{Lime} & & & & \end{array}\right]. \tag{2}$$

At somewhat lower temperatures, incomplete dissociation occurs:

$$\left[\overset{\text{Dolomite}}{CaCO_3\cdot MgCO_3} + \Delta \rightarrow \overset{\text{Calcite}}{\boxed{CaCO_3}} + \overset{\text{Periclase}}{\boxed{MgO}} + \boxed{CO_2}\uparrow\right] \tag{3}$$

The dissociation of dolomite may be therefore either partial or complete and the heat necessary to bring about the reactions is quite different.

The course of these two reactions may be followed by means of the method of thermal analysis. A study of many thermal curves prepared in the petrology laboratory of the U. S. Geological Survey [Faust (1944–48)] demonstrates that the temperatures at which dolomite dissociates into calcite and periclase and at which calcite subsequently decomposes to form CaO are somewhat variable, and depend chiefly upon the grain size and the rate of heating.

Typical thermal analysis curves for calcite, magnesite, and dolomite obtained in this laboratory are given in Fig. 1. Reactions (2) and (3), as given above are irreversible in an open system because the system loses $CO_2$. Some studies have been made under conditions which are essentially reversible. Thus Smyth and Adams (1923) present equilibrium data for the reversible dissociation of calcite, as expressed in equation (4) (double arrow).

$$\left[CaCO_3 + \Delta \rightleftarrows CaO + CO_2\right]. \tag{4}$$

In the natural process of thermal metamorphism of dolomite (or a magnesian limestone), the following factors will affect the process: grain size, rate of heating, pressure, closure of system, and associated minerals.

Laboratory studies indicate that the finer the grain size of dolomite, the lower will be the temperature of dissociation. The data suggest that a similar condition may hold under natural conditions of metamorphism and that this may explain the failure of some dolomites to undergo dissociation while other beds nearby are changed into new rock types.

The rate of heating of the carbonate rocks is difficult to evaluate. Aside from the heat transmitted by conduction through the solid rock, it is necessary to consider the thermal energy transported by the emanations, chiefly water vapor, from the cooling magma, and also that contributed to the advancing heat front by the $CO_2$ arising from the dissociation of the dolomite. This subject is discussed more fully below.

Hydrostatic pressure alone may influence the dissociation of dolomite so much as to prevent its decomposition. Halla (1936) has calculated the effect of pressure on the stability of dolomite. A translation of his views follows:

> From the values of $\Delta F°$ and the "means" of the known molecular volumes of dolomite, magnesite, and calcite, the conclusion is allowed that increased pressure (Gebirgsdrucke an der Erdoberfläche) has the effect of stabilizing dolomite.

The difference between the reaction studied by Halla, equation (5)

$$(5)\quad \left[\begin{matrix}\text{Dolomite} \\ CaCO_3\cdot MgCO_3\end{matrix} \rightarrow \begin{matrix}\text{Calcite}\\ CaCO_3\end{matrix} + \begin{matrix}\text{Magnesite}\\ MgCO_3\end{matrix}\right] \text{system closed, } P=\text{very high}$$

and equations (2) and (3) should be noted. Bowen (1940) has treated the more complicated effect of pressure on the thermal metamorphism of siliceous limestone and dolomite, and has given the phase assemblages stable at various temperatures and pressures.

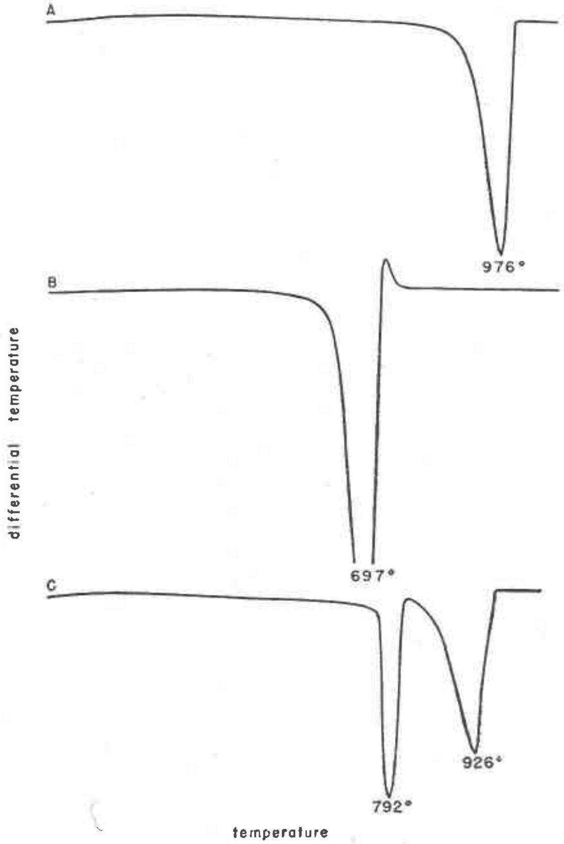


FIG. 1. Thermal analysis curves of calcite, magnesite, and dolomite. (A, calcite, Joplin, Missouri, analyzed sample—pure, resistance in series with galvanometer 999.9 ohms. Record C-89. (B, magnesite, Currant Creek, Nevada, analyzed sample—pure, resistance in series with galvanometer 999.9 ohms. Record C-79. (C, dolomite, Millville, West Virginia, analyzed sample, resistance in series with galvanometer 900 ohms. Record F-3.

From these observations and equations (2 and 3) it is evident that thermal dissociation of dolomite is also dependent on the state of closure of the system. If the system is closed so that $CO_2$ cannot escape, then the effects of thermal metamorphism will consist largely of recrystallization of the dolomite to a dolomite marble, marmorization. Griggs (1946) recrystallized the Yule marble to a new texture in the presence of $H_2O$ and $CO_2$ at a high confining pressure and at a temperature of only 150° C. If the system is open and $CO_2$ can escape, then periclase can form and the dolomite will be dedolomitized.

This reaction of dissociation is also dependent upon the kind and amount of the associated minerals in the original dolomite. Bowen (1940) has treated these relations for siliceous dolomites and has shown the effect in producing new phase assemblages at given temperatures and pressures.

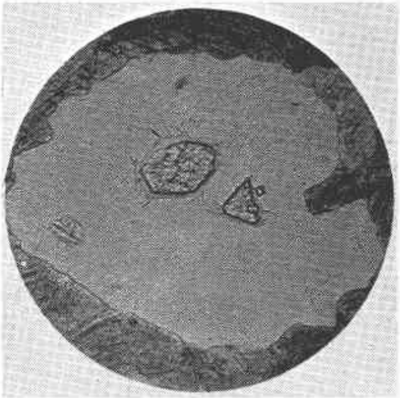


FIG. 2. Unaltered cores of periclase enclosed within brucite Pencatite from the Organ Mountains, New Mexico. Plane-polarized light. Mag. 70×.

In summary of the data of thermal dissociation studies and their application to thermal metamorphism, it is evident that natural metamorphic processes introduce factors difficult to assess and do not permit the direct use of such data as fixed points in geological thermometry. Thermal analysis data do show, however, how minerals break down at higher temperatures. They indicate an upper limit to the temperature of dissociation and they furnish in a general way the range of temperatures at which the process may occur.

The thermal dissociation of dolomite is accompanied by a change in volume. If reaction (3) goes to completion, the volume change is a decrease of 22 per cent. The change in volume accompanying reaction (2) is 38 per cent. As both of these reactions result in a diminution in volume, hydrostatic pressure will favor the thermal dissociation of dolomite *if*

$CO_2$ can escape, according to the principle of LeChatelier and Braun [see Rivett (1923)]. An examination of thin sections of predazzite and pencatite, which contain unaltered cores of periclase (see Fig. 2), shows this mineral to be present in dense form. Periclase, formed by the thermal dissociation of magnesite in the laboratory, is a pseudomorph after magnesite (see Fig. 3). Faust (1944) has studied these pseudomorphs and found that, following thermal dissociation, the resulting periclase consists of a skeletal boxwork inheriting the rhombohedral form of magnesite. This aggregate is composed of crystallites of periclase and air-filled spaces. Upon longer heating, this unstable structure collapses.

FIG. 3. Optically anomalous periclase resulting from the conversion of magnesite grains (−150+200 mesh) to the oxide by heating. Crossed nicols. Mag. about 75×.

Thermal metamorphism under geologic conditions would not permit an unstable structure, such as described above, to exist; for the hydrostatic pressure and the continuous passage of heat would jointly serve to produce a dense form of periclase.

## OCCURRENCE OF THERMALLY METAMORPHOSED DOLOMITES

Thermal analysis data show that contact metamorphism of dolomites can produce two types of rocks. If the temperature and the thermal

TABLE 1. FIELD RELATIONSHIPS OF THE OCCURRENCES OF PREDAZZITE AND PENCATITE

| Locality | Intrusive rock responsible for thermal metamorphism | Name given to metamorphosed dolomites | Characteristics of the original carbonate rock | Reference |
|---|---|---|---|---|
| Near heads of Big Cottonwood and Little Cottonwood Creeks, S.E. of Salt Lake City, Utah. | Granodiorite and quartz diorite. | Metamorphosed dolomite. | Dolomitic beds in the Maxfield (Cambrian) Jefferson (?) (Devonian) and Deseret (Mississippian) limestones. | Calkins, F. C., and Butler, B. S., Geology and ore deposits of the Cottonwood-American Fork Area, Utah: *U.S. Geol. Survey, Prof. Paper* **201** (1943). Also Calkins, F. C., Oral Communication, Dec. 1946. |
| Philipsburg Quadrangle, Montana. | Granodiorite (?) | Metamorphosed dolomite. | Dolomite of the Hasmark formation (Cambrian) | Emmons, W. H., and Calkins, F. C., Geology and ore deposits of the Philipsburg Quadrangle, Montana: *U.S. Geol. Survey, Prob. paper* **78** (1913). Also Calkins, F. C., Oral Communication, Dec. 1946. |
| Organ Mountains, New Mexico. | Quartz monzonite. | Pencatite, predazzite. | Dolomites of lower Paleozoic age. | Dunham, C. K., The Geology of the Organ Mts.: *New Mexico School of Mines, Bull.* **11** (1935).<br>Hunt, W. F. and Faust, G. T., Pencatite from the Organ Mts., New Mexico: *Am. Mineral.*, **22,** 1151–1160 (1937). |
| Crestmore, near Riverside, California. | Porphyritic quartz monzonite.<br>The predazzite occurs as a roof pendant. | Predazzite. | Magnesian limestone of upper Paleozoic age. | Rogers, A. F., Periclase from Crestmore near Riverside, California, with a list of minerals from this locality: *Am. Mineral.*, **14,** 462–469 (1929).<br>Woodford, A. O., Crestmore minerals: *California Jour. Mines and Geology*, 333–365 (1943). |
| Near Wakefield, Quebec, Canada. | Hastingsite syenite. The brucitic limestone occurs as roof pendants in a batholith. | Brucitic limestone. | Dolomites of pre-Cambrian age (Grenville). | Ambrose, J. W., Brucitic limestones and hastingsite syenite near Wakefield, Quebec: *Royal Soc. Canada, Proc. and Trans.*, 3rd Ser., **37,** 9–22 (1943). |
| Near Wilkinson, Ontario, Canada. | Granites or syenites. The brucite limestone occurs as roof pendants in a batholith. | Brucite limestone. | Magnesian limestones. | Brown, I. C., Brucite in limestone near Wilkinson, Ontario; *Econ. Geology*, **38,** 408–419 (1943). |
| Assynt district, Sutherland, Scotland. | Loch Borolan granite, syenites. | Marbles. | Cambrian dolomites and limestones. | Teall, J. J. H., *Mem. Geol. Survey, United Kingdom*, 453–462 (1907). |
| Island of Skye, Scotland. | "In the area of extreme metamorphism next the granite." | Predazzite. Pencatite. | Dolomitic limestones of Cambrian age. | Harker, A., The tertiary igneous rocks of Skye: *Mem. Geol. Survey, United Kingdom*, 144–151, especially p. 150 (1904). |
| Predazzo, Tyrol, Province of Veneto, Italy. | Monzonite. | Predazzite.<br>Pencatite. | {Triassic Kalken {Mendelund-Latemar-Kalk.<br>{Unteren {Muschelkalks. | Klebelsberg, R. von., Geologie von Tirol: Gebrüder Borntraeger, Berlin, p. 354 (1935). |
| Nantei mine, Suian, Tyôsen (Korea). | Granodiorite. A small batholith. | Brucite marble (predazzite). | Pre-Cambrian dolomites and slates | Watanabe, Takeo, On the brucite-marble (Predazzite) from the Nantei Mine, Suian, Tyôsen, (Korea): *Jour. Fac. Sci. Hokkaidô Imp. Univ.*, 4th Ser., **3,** No. 1, 49–59 (1935). |

energy are sufficient to dissociate dolomite completely, the resulting minerals would be lime (CaO) and periclase (MgO). No geologic occurrence of a completely dissociated dolomite which contains lime is known. Only one occurrence of lime as a mineral has so far been reported. Zambonini (1935) has listed lime as a mineral occurring in the blocks of calcareous rock enclosed within lava at Vesuvius. Such highly dissociated rocks, if they exist, are stable only when protected from solutions and water vapor and presumably at some depth within the earth's crust.

The partly calcined dolomites called predazzite and pencatite, on the other hand, have been observed in many places. Rogers (1918, 1929) has summarized their distribution in California, Utah, and Montana. Hunt and Faust (1937) and Dunham (1935) have described them from New Mexico.

Recently, Goudge (1939), Ambrose (1943), and Brown (1943) have described brucitic limestones from Canada.

An interesting relationship exists between the metamorphic rocks, predazzite and pencatite, and the type of intrusive rocks which are responsible for their metamorphism. Table 1 shows this relationship. The intrusive rocks are chiefly granites, granodiorites, and less commonly, quartz diorites. These rocks are predominantly the siliceous types and their close association with the dedolomitized rocks suggests that the composition of the intrusive rock is a factor in determining the degree of metamorphism of the dolomite. The reasons for this interrelation are developed in the following section on the source of heat for metamorphism.

The association of certain types of mineralization with certain types of rocks has long been observed by geologists. A comprehensive review of this association has been given by Buddington (1933) and the reader is referred to his paper.

## Source of Heat for Metamorphism

It is assumed in this paper that a magma supplied the heat necessary for metamorphism.

A study of the conduction of heat through rocks by Birch and Clark (1940) shows that the chemical composition of the magma is a relatively unimportant factor, for at depths of about 10 to 20 km., and at elevated temperatures, the differences in the constants of thermal conductivity are very small. The thermal characteristics of the magma type are thus not important factors in determining the degree of thermal metamorphism of the intruded rocks.

The conductivity of rocks is so low and the resultant rate of conduction of heat is so low that additional sources of heat are required for the thermal energy necessary to bring about the remarkable changes produced in the process of dedolomitization.

Intensive studies of contact-metamorphic ore deposits and of the aureole of metamorphism associated with igneous intrusion have been made during the last three decades. These studies have shown that the contact zones are not all alike in character nor are the resultant effects indicative of an equality in intensity. The effects produced depend upon many factors of which the following are very important: size of the intrusive; structural relation of the complex assemblage; amount of cover and the closure of the system; composition and texture of the country rock; and the abundance of gaseous and hydrothermal emanations. The importance of emanations from a magma to the process of contact metamorphism is now gaining wide acceptance. Ross (1928) has commented on the importance of emanations as follows (p. 873):

> The almost complete absence of recognizable contact-metamorphic effects in the wall rock of even the relatively hot magmas that have formed basalt dikes or diabase sills is noteworthy. Hypabyssal intrusive magmas, even those that are known to have had high temperatures, were in general able to exert little effect on most enclosing rocks by means of their heat energy unassisted by hydrothermal or gaseous emanations, and without doubt vein-forming materials are cooler than basalt magma.

The relative quantity of gaseous and hydrothermal emanations associated with "basic" and "acid" magmas has been discussed by many geologists and petrologists, and Bowen (1933) in particular has considered this relationship with respect to the differentiation of magma:

> Page 113, In a full differentiation sequence from basic types to acid types, there will be a natural tendency to this greater concentration of hyperfusibles in the acid types.

and again,

> Page 115, Generally speaking it is in the granitic and related magmas that the greater concentration of the hyperfusibles come into being.

Buddington (1933) likewise writes:

> Page 354, The percentage and the kinds of volatiles may vary widely with different kinds of magma, and this must affect the resultant mineralization. It is generally accepted that the percentage of $H_2O$ and other volatiles is usually considerably greater in siliceous magmas than in basic varieties.

Gaseous and hydrothermal emanations are responsible for the transportation of and transfer of heat into the country rock. It is generally conceded that the principal constituents of emanations are chiefly $H_2O$ and $CO_2$, with the former more abundant. The emanations from a magma have a very low viscosity and hence are very mobile. This mobility permits the gases and solutions to move out into the country rock, and accordingly is an important factor in the transfer of heat from the magma to the country rock by the emanations. In addition, the heat capacities of the gaseous and hydrothermal emanations are significantly larger than that of a molten magma itself. The heat capacities of ($H_2O$) vapor, ($H_2O$) liquid, ($CO_2$) vapor, together with those of molten magma, and of several types of granitic rocks are given in Table 2, and in Fig. 4.

TABLE 2. HEAT CAPACITY OF GASES, WATER (LIQUID), AND ROCKS AT HIGH TEMPERATURES. HEAT CAPACITY, CP IN JOULES PER GRAM[1]

| Substance | Temperature in degrees centigrade | | | | | | |
|---|---|---|---|---|---|---|---|
| | 0° | 200° | 220° | 400° | 600° | 800° | 1200° |
| $CO_2$ (gas)[2] | 0.82 | | | 1.12 | | | 1.32 |
| $H_2O$ (gas)[2] | 1.847 | | | 2.052 | | | 2.478 |
| $H_2O$ (liquid)[3] | 4.219 | 4.341 | 4.376 | | | | |
| Granite[2] | 0.65 | 0.95 | | 1.07 | | 1.13 | |
| Granodiorite[2] | 0.70 | 0.97 | | $1.08_5$ | | $1.17_5$ | |
| Diorite[2] | 0.71 | 0.99 | | 1.09 | | 1.18 | |
| Molten magma[4] | | | | 0.8 | | | 1.2 |

[1] One joule is equivalent to 0.23895 gram calorie at 15°C.

[2] Data from: Birch, F., Schairer, J. F., and Spicer, H. C., Handbook of Physical Constants: *Geol. Soc. Am., Special Paper* no. **36** (1942).

[3] Data from: Kaye, G. W. C., and Laby, T. H., Tables of Physical and Chemical Constants and Some Mathematical Functions. London, Longmans, Green and Co., 8th ed., p. 59. 1935.

[4] Data from: Barus, Carl, High Temperature Work in Igneous Fusion and Ebullition Chiefly in Relation to Pressure: *U. S. Geol. Survey, Bull.* **103,** 53–54 (1893). An estimated curve is sketched in figure 4 based on Barus' data.

The contribution of heat transferred by the gases $CO_2$ and, to a very minor extent $H_2O$, released by the heating and thermal dissociation of dolomite rock, is also significant. These gases may be released: (*a*) by the ingestion of masses of dolomite or limestone entrapped within the magma as it stopes its way upward. Evidence for such relations is found at some of the localities in the form of xenoliths of predazzite, Dunham (1936); (*b*) by the transmission of heat to the dolomite directly in contact with the magma. The gases when released are at a high temperature and have a relatively high specific heat. They can escape into the country rock or move along the contact and mingle with the gaseous emanations of the magma and then escape into the country rock. As more and more dolomite is dissociated, they continue to be released and are available for transmitting heat. As long as dolomite is being dissociated, there will be $CO_2$ gas available for thermal metamorphic processes.

The available thermal energy for metamorphism is the sum of the heat

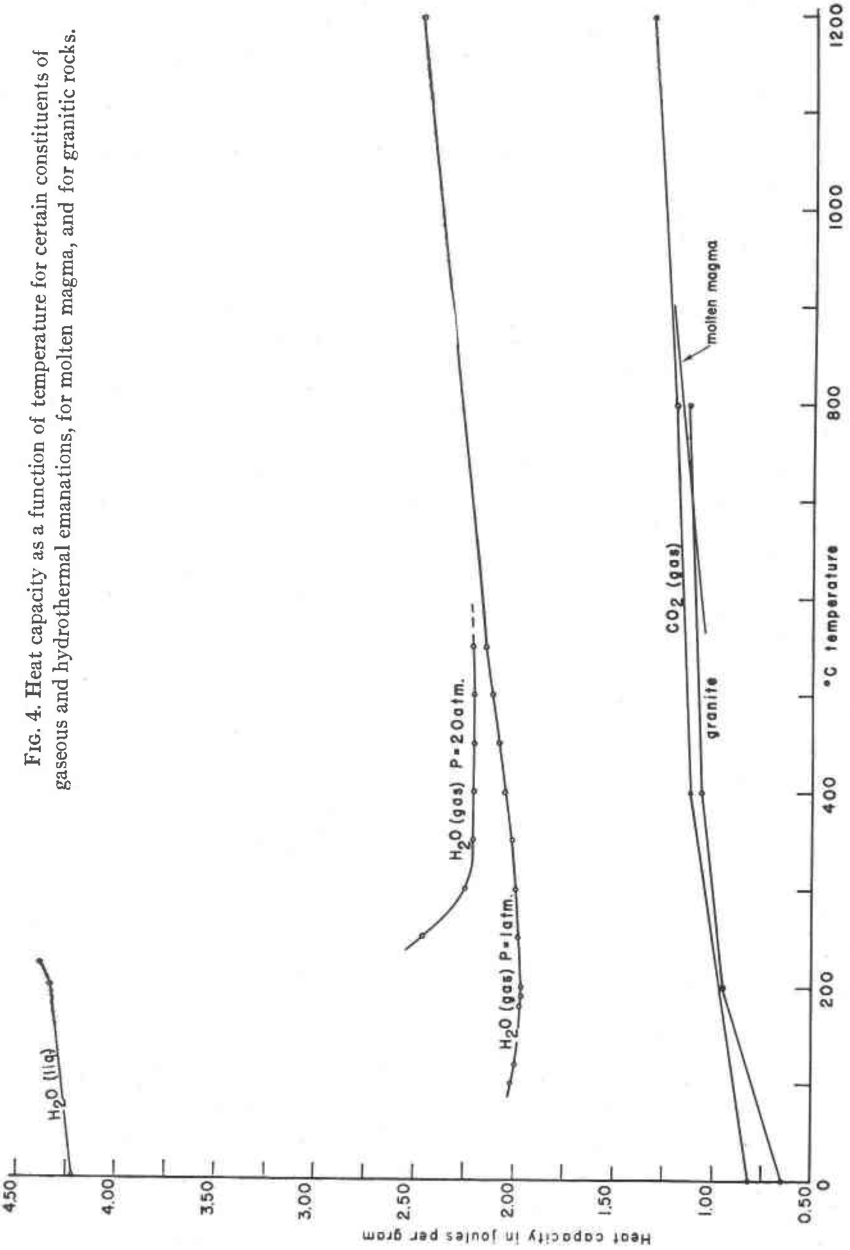


FIG. 4. Heat capacity as a function of temperature for certain constituents of gaseous and hydrothermal emanations, for molten magma, and for granitic rocks.

transmitted by conduction through the magma, the heat contributed by the emanations from the magma, the heat carried by the $CO_2$ gas resulting from the dissociation of dolomite; and the heat contributed by miscellaneous processes such as radiation, radioactivity, etc. For present purposes, the miscellaneous contributions may be neglected because of their small effect. The quantity of heat transmitted by conduction through the country rock is generally expressed as follows:

$$\left[Q = k\frac{(\theta_1 - \theta_2)At}{X}\right] \tag{6}$$

in which $k$ is the thermal conductivity; $\theta_1$ is the temperature of the magma and $\theta_2$ that of the country rock; $X$ the distance; $A$ the area; and $t$ the time. This equation implies a continuous function, as the time $t$ is included. In other words, heat flow is a continuous process. A more complete statement of the problem requires the use of the diffusivity $h$, defined as, $h^2 = k/c\rho$, in connection with equation (6). In the definition of the diffusivity $h$, $c$, and $\rho$ represent the specific heat and density respectively.

In order to simplify the presentation, we will treat the relations as an instantaneous matter and express $Q_i$ as the maximum heat available, assuming that all the heat is given up to the pencatite or predazzite. The quantity of heat, $Q_i$, available at the earliest stage of metamorphism when the gaseous constituents are the dominant part of the emanations, is:

$$\left[Q_i = \underbrace{C_p(T_m - T_{cr})M_m}_{\substack{\text{Heat available for}\\ \text{transmission by}\\ \text{conduction.}}} + \underbrace{C_p{}^1(T_m - T_{cr})M_e}_{\substack{\text{Heat available for}\\ \text{transportation by}\\ \text{the gaseous ema-}\\ \text{nations.}}}\right] \tag{7}$$

where $C_p$, $C_p'$ are the specific heats of the magma and the gaseous emanations, and $T_m$, $T_{cr}$ are the temperatures of the magma and country rock and $M_m$ and $M_e$ the masses of the magma and emanations, respectively.

The heat contributed by the gaseous phase for the same weight in grams, is two to three times as large as that available from the magma. The relative masses of magma and emanations are, however, greatly different. At the earliest stage of intrusion of magma, the emanations are at a minimum; as time passes and the magma crystallizes and cools, the amount of emanations increases. At a still later stage in the history of the magma when the magmatic solution contains a preponderance of $H_2O$, the amount of emanation reaches its maximum. An exception to these relations occurs when a magma that has intruded or entrapped xenoliths of a carbonate-rich rock, such as dolomite or limestone, is hot enough and has sufficient heat content to dissociate these carbonate rocks, liberating hot gaseous carbon dioxide and thus bringing about a local enrichment of the emanations.

The available heat conducted into the dolomite, if the temperature is sufficient to dissociate dolomite, will be consumed in raising the temperature of the dolomite to the dissociation temperature, dissociating the dolomite, and then finally spent in raising the temperature of the periclase, calcite, and the gaseous carbon dioxide.

The heat content of the first-formed pencatite or predazzite is as follows:

$$
\begin{aligned}
Q_D = {} & \left[C_p^{\mathrm{II}}\left(\frac{T_m - T_{cr}}{2}\right) \mathrm{M}_{\mathrm{MgO}}\right] + \left[C_p^{\mathrm{III}}\left(\frac{T_m - T_{cr}}{2}\right) \mathrm{M}_{\mathrm{CO_2}}\right] \\
& + \left[C_p^{\mathrm{IV}}\left(\frac{T_m - T_{cr}}{2}\right) \mathrm{M}_{\mathrm{Calcite}}\right]
\end{aligned}
\tag{8}
$$

in which $C_p^{\mathrm{II}}$, $C_p^{\mathrm{III}}$, $C_p^{\mathrm{IV}}$, are the specific heats respectively of periclase, carbon dioxide (gas), and calcite; and $\mathrm{M}_{\mathrm{MgO}}$, $\mathrm{M}_{\mathrm{CO_2}}$, $\mathrm{M}_{\mathrm{Calcite}}$) are the respective masses of periclase, carbon dioxide (gas), and calcite. An examination of the physical meaning of the mathematical statements in the three members of this equation shows that the heat content of the solid phases expressed in the first and third terms of equation (8) may be dissipated by conduction; whereas the heat content of the gaseous phase, $CO_2$, given in the second term, is available for thermal processes because the gaseous phase is mobile and can transfer its heat content elsewhere. When mixed with the emanations from the magma its temperature may be raised. It is this phenomenon of the release of $CO_2$ gas by carbonate rocks that undergo dissociation that modifies a straightforward mathematical treatment of heat conduction such as can be used for most country rock that is essentially thermally inert.

At a later stage in the cooling of the intrusive, when the temperatures are lower and the emanations from the magma are chiefly hydrothermal solutions, the last term in equation (7) must be modified to take into account the very much greater value of the specific heat of water (liquid), which is about four times larger than that of a crystallizing intrusive. The volume of hydrothermal solution may be very large, and these solutions are very important agents in the process of contact metamorphism.

Adams (1924) has pointed out another type of thermal effect which for liquids is always a heating effect and for gases is either a heating or cooling effect. This effect, termed the "porous-plug expansion," applies to the escape of gases and solutions through capillary and subcapillary openings, and along intergrain boundaries. As it is difficult to evaluate, it is only mentioned here, but it is recognized that because such escape of gases will take place in metamorphic processes, this effect may affect the heat content of the system.

There are thus three factors which make magmatic emanations important in contact metamorphism: their greater specific heat; their mobility, which transports the heat quickly to the country rock; their ability to enter into reaction with the country rock while at elevated temperatures. These characteristics contrast markedly with the slow, short-distance effects of heat conduction.

A unique reaction, involving one of the major components of the rock which undergoes decomposition to yield a gaseous phase, differentiates dedolomitization from simpler thermal metamorphism. The complete miscibility relations existing among gases permits the hot, released $CO_2$ to mix with gaseous emanations of the magma and to undergo an increase in temperature. Such a mixture of gases is a powerful agent in metamorphism.

From the foregoing discussion of the field relations of the aureoles of metamorphism associated with granitic rocks, it is here believed that the association of granitic or related types of rocks with the dedolomitized rocks, predazzite and pencatite, is not a fortuitous one. It is further held that most of the heat necessary for dedolomitization is transported by emanations from the magma.

## PHYSICAL CHEMICAL DATA ON THE SYSTEM $MgO\text{-}CaO\text{-}CO_2\text{-}H_2O$ AND RELATED SYSTEMS

As described above, the complete or selective dissociation of dolomite gives rise to definite assemblages of the following solid phases: lime, periclase, and calcite. These substances can react with carbonate-rich, hot solutions in various ways depending upon the variables: temperature, pressure of carbon dioxide in the system, total pressure on the system, and the presence of other ions in the solutions. A discussion of the pertinent physico-chemical relations applying to the above-mentioned system is given herewith.

Data are available on the systems $MgO\text{-}H_2O$; $H_2O\text{-}CO_2$; $CaO\text{-}CO_2\text{-}H_2O$; and $MgO\text{-}CO_2\text{-}H_2O$, which are parts of the quaternary system. However, to define completely the relationships in the complex natural system, we would require the data for the water-rich portions of the multicomponent system $MgO\text{-}CaO\text{-}CO_2\text{-}H_2O\text{-}Cl\text{-}SO_4\text{-}Na_2O\text{-}K_2O$. In the absence of such complete information, it is necessary to consider the available data on the subsystems mentioned above and to evaluate the effects of the Cl, $SO_4$, Na, and K content from existing studies on the solubilities of carbonates in salt solutions.

### *The system $MgO$-$H_2O$*

One of the sides of the tetrahedron of the quaternary system $MgO$-$CaO$-$CO_2$-$H_2O$ is the subsystem $MgO$-$H_2O$. Complete equilibrium relations in the system $MgO$-$H_2O$ are not available at present. Considerable data are, however, to be found in the literature for the phases in this system, periclase, brucite, and water in its various forms. Complete data on the equilibrium thermal relations have been determined for periclase and the various phases of $H_2O$. The equilibrium-dissociation relations for brucite have just been published by Bowen and Tuttle (1949), who found that brucite is remarkably stable thermally, dissociating into periclase at a temperature of approximately 880° C. at a pressure of about 1,000 pounds per square inch (68 atmospheres) and at about 910° at a pressure of 32,000 pounds per square inch (2,176 atmospheres). The latter pressure corresponds to a depth of 5 miles in the earth (density of the rock assumed to be 2.7).

The statement of the equilibrium dissociation of brucite is given in equation (9)

$$[Mg(OH)_2 \rightleftarrows MgO + H_2O]. \tag{9}$$

This reaction is driven to the right by temperature and to the left by the pressure of $H_2O$.

These data suggest the view that dedolomitization of dolomite, in nature, at high temperatures (above the dissociation temperature of brucite) with the formation of periclase ($MgO$) may take place in the presence of vapors composed largely of $H_2O$.

As the temperature of the natural system consisting of the magma, the dedolomitized zone, and the emanations drop and the proportion of liquid phase increases, the stability of periclase ($MgO$) decreases rapidly, and it is converted into brucite ($Mg(OH)_2$).

### *The system: $H_2O$-$CO_2$; the solubility of carbon dioxide in water*

When carbon dioxide gas is introduced into water the following equilibrium relations exist:

$$[CO_2 + H_2O \rightleftarrows H_2CO_3 \rightleftarrows H^+ + HCO_3^- \rightleftarrows 2H^+ + CO_3^{--}]. \tag{11}$$

In addition ($CO_2$) gas is dissolved as such in the solution. The solubility of carbon dioxide in pure water at high pressures and various temperatures has been measured by Wiebe and Gaddy (1939, 1940). These studies were made at pressures as high as 700 atmospheres and at temperatures of 12° to 100° C. More recently these data have been extended to 120° C. with pressures to 700 atmospheres by Prutton and Savage (1945). The solubility relations of carbon dioxide in water are shown graphically in Fig. 7. The unit of concentration should be carefully noted;

it is expressed as the number of cubic centimeters of carbon dioxide, at standard temperature (273° K = 0° C.) and pressure (1 atmosphere), contained in *one gram* of water. One cubic centimeter of carbon dioxide at (S.T.P.) weighs 0.00198 gram. Thus at 100° C. and at a *total pressure* of 25 atmospheres (pressure of $CO_2$ in the vapor phase plus the pressure of $H_2O$ in the vapor phase), 5.365 cc. of carbon dioxide (S.T.P.) are dissolved in *one gram* of water. This is equivalent to 0.0106 gram of carbon dioxide per gram of water or approximately 10.62 grams of carbon dioxide per liter.

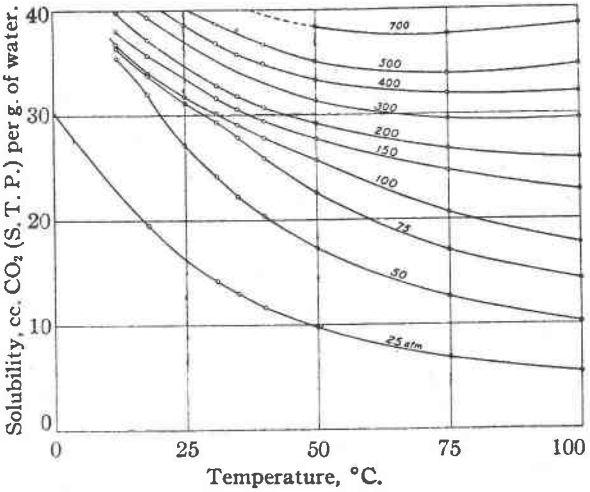


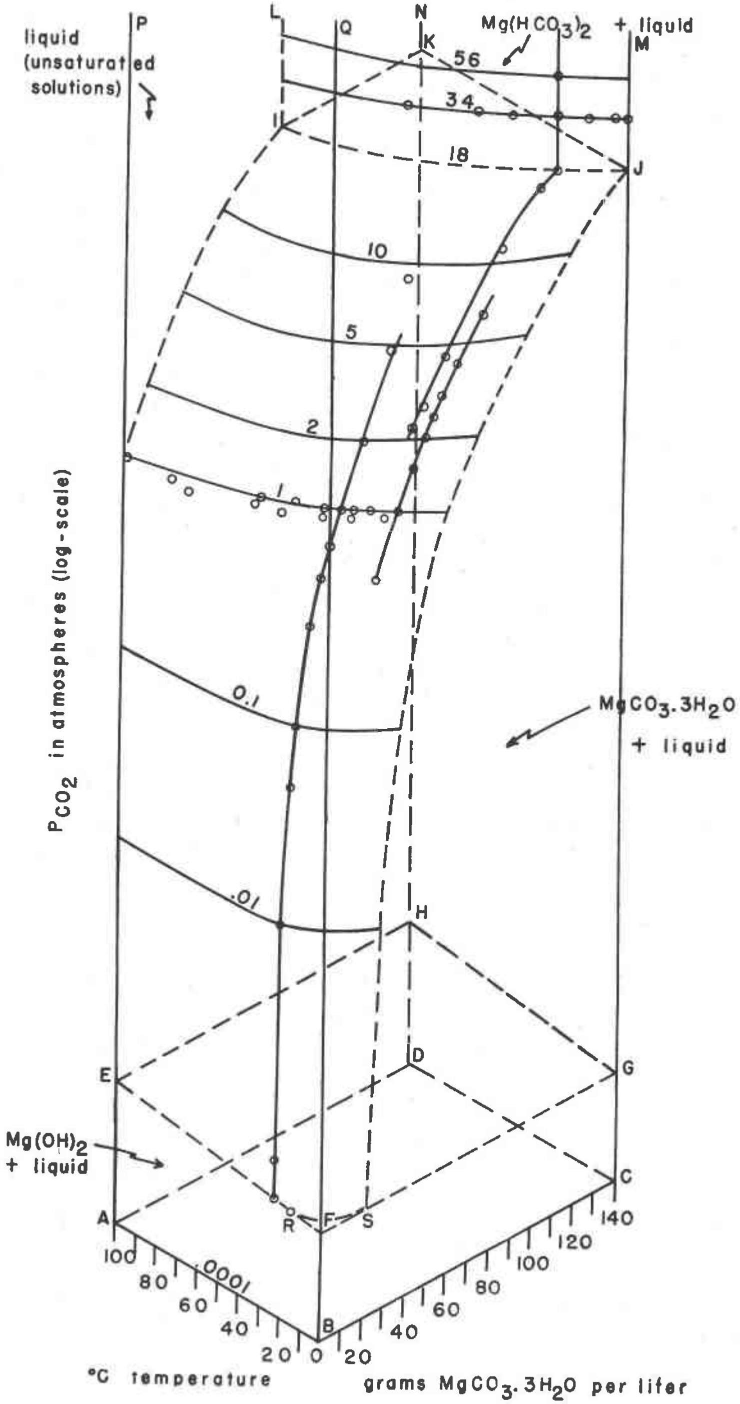
FIG. 5. The solubility of carbon dioxide, in cubic centimeters, (S.T.P.) per gram of water as a function of temperature and pressure. Wiebe and Gaddy (1939, 1940).

The solubility data for $CO_2$ in water as shown in Fig. 5 apply to pure water as the solvent. Prutton and Savage (1945) have studied the solubility of $CO_2$ in calcium chloride solutions and find that the solubility of the gas decreases as the concentration of the calcium chloride increases.

### *The system: $MgO$-$CO_2$-$H_2O$*

The information available for this system consists of (*a*) the solubility data of magnesium carbonate trihydrate in water at various pressures of carbon dioxide, (*b*) the solubility data of magnesium carbonate (magnesite) in water at various pressures of carbon dioxide, and (*c*) some observations on the reaction relations betweeen magnesium oxide and solutions of carbon dioxide in water.

Engel and Ville (1881) measured the solubility of magnesium carbonate in water charged with carbon dioxide at temperatures from 13.4°


liquid
(unsaturated solutions)
P
L
Q
N
K
Mg(HCO$_3$)$_2$ + liquid
M
56
34
I
18
J
10
5
2
1
0.1
.01
.0001
H
MgCO$_3$.3H$_2$O
+ liquid
E
D
G
Mg(OH)$_2$
+ liquid
C
A
R
F
S
B
100
80
60
40
20
0
20
40
60
80
100
120
140
P$_{CO_2}$ in atmospheres (log-scale)
°C temperature
grams MgCO$_3$.3H$_2$O per liter

to 100° C. and pressures from 1 to 9 atmospheres. Mitchell (1923) measured the solubility at 20° C. and at pressures of 6 to 21 atmospheres. Haehnel (1924) made measurements in the range to 0 to 60° C. and at pressures up to 56 atmospheres. Kline (1929) gives solubility data at 25° C. for pressures from 0.001 atmosphere to 15 atmospheres pressure of carbon dioxide. Bär (1932) has added to these data and summarized the results. Doerner, Holbrook, and Fortner (1946) have determined the solubility relations over the temperature range of 10° to 100° C. at a pressure of carbon dioxide of 700 millimeters (0.92 atmosphere). These data are given in Fig. 6, and the graphs show that the solubility of magnesium carbonate in a solution containing carbon dioxide increases rapidly with increasing $CO_2$ pressure for a given temperature. For a given pressure the solubility decreases with an increase in temperature.

The data of Haehnel show that the solubility becomes constant at 18 atmospheres and for a temperature of 18° C. and remains so, as far as he studied the relations, up to 56 atmospheres pressure of $CO_2$. This constancy in solubility means that a new solid phase has formed and Haehnel concludes this phase is magnesium bicarbonate, $Mg(HCO_3)_2$.

The probable phase relationships existing in the system $MgO\text{-}CO_2\text{-}H_2O$ from 0° C. to 100° C., and at pressures of $CO_2$ ranging from $1 \times 10^{-4}$ atmospheres to 56 atmospheres have been sketched in Fig. 6. These phase boundaries have been drawn based on (*a*) the solubility data of magnesium carbonate trihydrate (nesquehonite), (*b*) the data on the transition of nesquehonite to brucite as related to the pressure of $CO_2$, (*c*) the stability relationships for magnesium bicarbonate. The field of magnesite lies at higher temperatures than those given here. The relationships at very low temperatures between nesquehonite ($MgCO_3 \cdot 3H_2O$) and lansfordite ($MgCO_3 \cdot 5H_2O$) have been ignored.

The presence of other ions in the solution also affects the solubility relations of magnesium carbonates in water that contains carbon dioxide. Cameron and his associates (1903, pp. 578–590; 1907, pp. 577–580) have studied qualitatively the solubility of magnesium carbonate and calcium carbonates in various aqueous solutions containing ions commonly present in natural waters. In general, the solubilities of these

---

FIG. 6. The solubility of magnesium carbonate in water as a function of temperature and pressure based on the data of Otto Haehnel, Kline, Engel and Ville, and Doerner, Holbrook and Fortner. The figure also portrays the probable phase relationships existing in the system $MgO\text{-}CO_2\text{-}H_2O$, within the temperature range of 0° C. and 100° C., and pressures of $CO_2$ ranging from $1 \times 10^{-4}$ atmospheres to 56 atmospheres. The stability field of magnesite is situated at higher temperatures than those shown here. The stability relations of lansfordite $MgCO_3 \cdot 5H_2O$, at very low temperatures, have been ignored.

carbonates increase, with increasing quantities of the salts in the aqueous solutions, to a maximum, beyond which the solubility of the carbonates decreases. For solutions containing 100 grams of the salt per liter, sodium sulfate at 23° C. caused a four-fold increase in the solubility of magnesium carbonate while sodium chloride approximately doubled the solubility over that in pure water. These experiments were conducted in an atmosphere free of carbon dioxide. A notable exception is the solubility of magnesium carbonate in the presence of sodium carbonate which—for the same range of concentration as the other salts—shows a continuously rising curve of solubility.

The solubilities referred to above concern the relations for magnesium carbonate trihydrate (nesquehonite), and magnesium bicarbonate in equilibrium with solutions having definite carbon dioxide pressures above them. Haehnel (1924) found no difference in his solubility experiments whether he used artificial nesquehonite, magnesite from Snarum, Norway, or magnesium oxide as starting materials.

In the reaction between the dedolomitized rock and hydrothermal solutions charged with carbon dioxide, we are interested in the reaction between MgO (periclase) and a solution of water containing carbon dioxide. Doerner, Holbrook, and Fortner (1946) give the following two equations (12) and (13) to represent the conditions:

$$[MgO + 2CO_2 + H_2O \rightleftarrows Mg(HCO_3)_2] \tag{12}$$

or in two steps:

$$\left[\begin{array}{l} MgO + CO_2 + H_2O \rightleftarrows Mg(CO_3)(H_2O)_x \\ Mg(CO_3)(H_2O)_x + CO_2 \rightleftarrows Mg(HCO_3)_2 + (x-1)H_2O \end{array}\right] \tag{13}$$

they state further:

> Reaction (12) can be carried out in two steps (13) and no conclusive evidence that it occurs in a single step has been found.

According to these investigators, the result of the solution of MgO (periclase) in water charged with $CO_2$ is the production of a solution of magnesium bicarbonate. The proportion of MgO (periclase) converted to bicarbonate depends on the volume of the solution, amount of periclase, temperature, and the pressure of $CO_2$ in the system.

Terada (1928) made a study of the reaction of MgO and $Mg(OH)_2$ with waters saturated with $CO_2$, and on page 41 of the English abstract he writes:

> When MgO or $Mg(OH)_2$ is used as the sample, the water is charged with $CO_2$ gas so that it remains always at saturation, they dissolve very quickly, and soon attain a state of supersaturation, forming a meta-stable solution of $Mg(HCO_3)_2$.
>
> $MgCO_3 \cdot 3H_2O$, in the same condition as above stated, dissolves slowly; and only the stable saturated solution is obtained, forming no meta-stable solution.

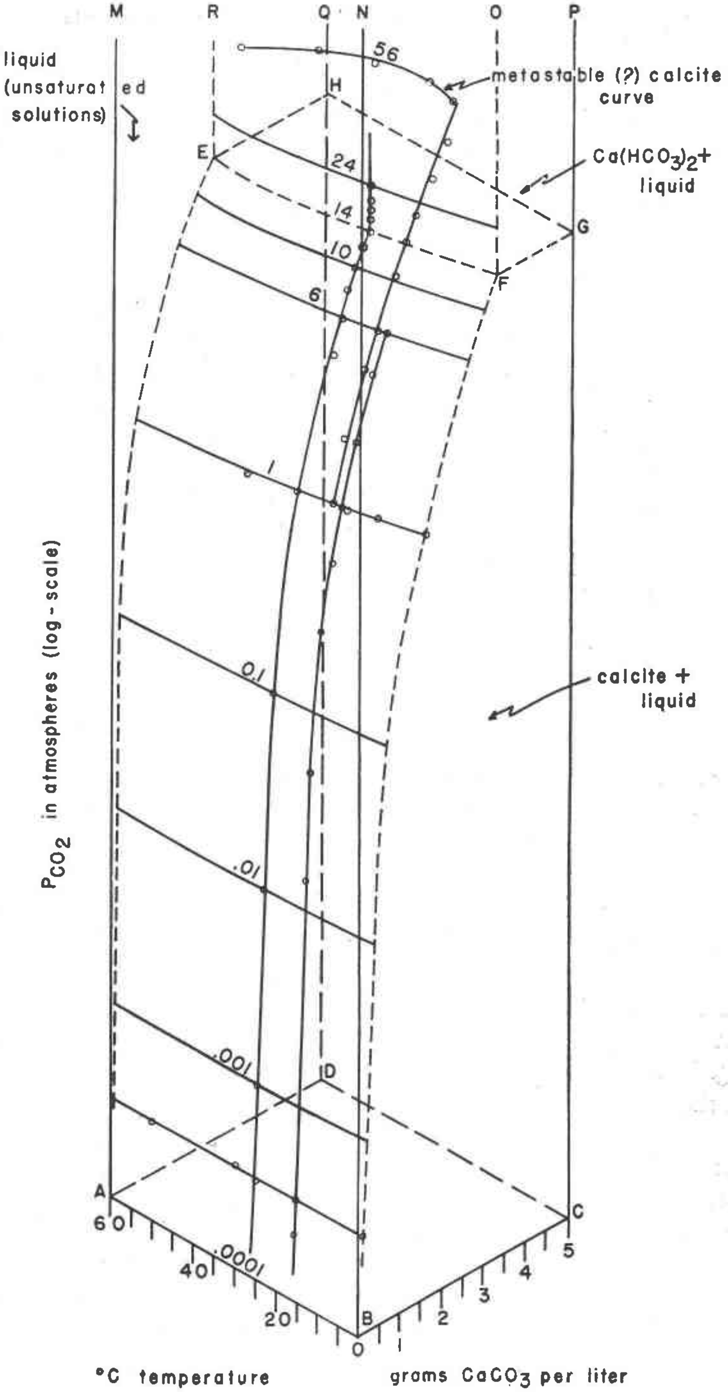
He further found that the metastable solution decomposes just on standing and that the addition of a small quantity of magnesium carbonate crystals will destroy the metastability, causing $CO_2$ gas to escape and precipitating an undetermined solid phase.

It appears from the comprehensive studies of Terada that irrespective of the original starting materials, the resulting solution will stabilize itself and end as a solution of magnesium carbonate. Haehnel (1924) also found his solubility studies for $MgCO_3 \cdot 3H_2O$ to be independent of the starting materials.

*The system: $CaO$-$CO_2$-$H_2O$*

This system has been studied in considerable detail at relatively low temperatures by Johnston and his coworkers. Frear and Johnston (1929) have given a list of the reliable solubility determinations for calcite and have prepared a table of solubilities for 25° C. and for $CO_2$ pressures ranging from $3.2 \times 10^{-4}$ to 10 atmospheres, based on the data of all workers (Fig. 7). Haehnel (1924) has measured the solubility of calcium carbonate between 10 and 56 atmospheres pressure of $CO_2$ at 18° C. and at temperatures from 18° to 55° C. at a constant pressure of $CO_2$ of 56 atmospheres.

The great difference in the solubility of calcium carbonate (calcite) and magnesium carbonate trihydrate (nesquehonite) is easily seen on comparing Figs. 6 and 7. In comparing these two diagrams, it should be observed that the scales along the axis representing the pressure of carbon dioxide are identical in both figures but that the scales along the other two axes are not the same. In Fig. 6, the temperature axis covers the range of 0° C. to 100° C. while the corresponding axis in Fig. 7 covers the range of 0° C. to 60° C. The scale representing composition in Fig. 6 covers the range of 0 to 140 grams per liter of $MgCO_3 \cdot 3H_2O$ while the same distance in Fig. 7 covers the range in composition of 0 to 5 grams per liter of $CaCO_3$. In other words the diagram for the solubility relations of calcite is greatly magnified in comparison with that of magnesium carbonate. This disproportionate solubility of the carbonates in water charged with carbon dioxide will permit the separation of one carbonate from the other. Thus at a pressure of carbon dioxide of 1 atmosphere and at a temperature of 19.5° C., magnesium carbonate trihydrate is soluble to the extent of 42.3 grams per liter of water, whereas calcium carbonate will only dissolve to the extent of 1.08 grams per liter at 18° C. At 10 atmospheres pressure of $CO_2$ and 18° C., calcium carbonate is soluble to the extent of 2.56 grams per liter, whereas magnesium carbonate trihydrate at 10 atmospheres pressure of carbon dioxide and at a temperature of 18° C. dissolves to the extent of 96.8 grams per liter.


M
R
Q
N
O
P
liquid (unsaturated solutions)
metastable (?) calcite curve
Ca(HCO$_3$)$_2$+ liquid
calcite + liquid
H
E
G
F
D
A
B
C
56
24
14
10
6
1
0.1
.01
.001
.0001
$P_{CO_2}$ in atmospheres (log-scale)
60
40
20
0
1
2
3
4
5
°C temperature
grams CaCO$_3$ per liter

According to Mitchell (1923) and others, at carbon dioxide pressures of 15 atmospheres and greater, the solid phase in equilibrium with the solution is calcium bicarbonate. Haehnel (1924), working at high pressures and temperatures, did not, according to his interpretation, find the solid phase calcium bicarbonate, but actually observed a decrease in the solubility of calcite. If this is the correct interpretation, it may be that Haehnel actually followed the metastable solubility curve of calcite in this region.

The phase relationships existing in the system $CaO$-$CO_2$-$H_2O$, from 0° C. to 100° C. and at pressures of $CO_2$ ranging from $1\times10^{-4}$ atmospheres to 56 atmospheres, have been sketched in Fig. 7. These boundaries have been drawn based on (*a*) the solubility data of calcite, and (*b*) on the stability relations of calcium bicarbonate. The stability relationships of $CaCO_3\cdot 6H_2O$ are not too well known and so have been ignored. They would not affect the thesis of this paper.

In the reaction between dedolomitized rock and hydrothermal solutions charged with carbon dioxide, we are concerned with the solubility of calcite in such solutions. According to Tillmans and Heublein (1912) this proceeds as follows:

$$[CaCO_3 + H_2O + nCO_2 \rightleftarrows Ca(HCO_3)_2 + (n-1)CO_2] \qquad (14)$$

the reaction taking place in aqueous solution and at a definite pressure of carbon dioxide in equilibrium with the solution. The aforementioned data on the solubility of calcite show that although the solubility of calcite is low at low pressures of carbon dioxide it does increase somewhat with an increase in pressure of $CO_2$ and such an increase would drive the reaction, expressed in equation 14, to the right. The increase in solubility of calcite, however, does not compare with that of magnesium carbonate trihydrate.

The solubility of calcite generally increases in the presence of other ions and this has been studied by Frear and Johnston (1929), who give data for the solubility of calcite in solutions of NaCl and $CaSO_4\cdot 2H_2O$. They found the solubility of calcite in one molal sodium chloride to be practically double that in the absence of the salt. Calcium sulfate slightly decreases the solubility of calcite.

### *The system: $MgO$-$CaO$-$CO_2$-$H_2O$*

The data previously given are for the two ternary and two binary systems that belong to the quarternary system. Very little systematic data are available for the quarternary system and these data concern

---

FIG. 7. The solubility of calcium carbonate in water and in equilibrium with various carbon dioxide pressures. Based on data summarized by Frear and Johnston and the determinations of Haehnel. The field of stability of $CaCO_3\cdot 6H_2O$ has been ignored.

the solubility of dolomite, a relationship not pertinent to this discussion.

A considerable amount of information on this system has been determined in connection with the recovery of magnesium compounds from calcined dolomite. The assemblage of phases in such calcined dolomites, particularly the partially calcined dolomite, corresponds closely to those present in the naturally occurring dedolomitized rocks. From the previous discussion we note (1) that calcite is much less soluble than magnesium carbonate in water containing carbon dioxide; (2) that MgO forms a highly soluble carbonate when it reacts with a solution rich in carbon dioxide. As a result of these relationships, a mixture of MgO and $CaCO_3$ will react with a solution of water rich in carbon dioxide, with the transference of most of the magnesium but with only a minor amount of the calcium into the liquid phase.

Experimental evidence supporting these conclusions is furnished by the work of Doerner, Holbrook, and Fortner (1946). These workers studied means of removing the magnesium from dolomite. They calcined dolomite selectively so that only the magnesium carbonate was dissociated and the resulting product consisted of MgO (periclase) and $CaCO_3$ (calcite). Their calcination studies were carried out under various conditions: (*a*) in the presence of $CO_2$; (*b*) in vacuo; (*c*) in air. Their experiments on the calcination of dolomite in the presence of $CO_2$ suggest parallelism with the conditions prevailing in the natural process of dedolomitization and so only these results are considered here.

Their procedure was as follows: dolomite was calcined selectively in a $CO_2$ atmosphere to give a mixture of MgO (periclase) and $CaCO_3$ (calcite), and this calcine was leached in a solution of water saturated with carbon dioxide at 20° C. The resulting solution was analyzed. They found that a dolomite calcined so that 47.8 per cent of it was dissociated gave up 90.8 per cent of its MgO in 40 minutes when leached by a solution of carbon dioxide in water at 20° C. The resulting solution contained *only 0.0008 gram of calcium oxide per liter.* The leaching reaction evolves heat. These authors also measured the pH of saturated solutions of the various components and these are given in Table 3.

TABLE 3. pH OF SATURATED SOLUTIONS OF THE VARIOUS COMPONENTS AT 20° C. DATA OF DOERNER, HOLBROOK, AND FORTNER (1946)

| Saturated solution | pH |
|---|---|
| Carbon dioxide in water | 5.0 |
| MgO in water | 10.6 |
| $Mg(HCO_3)_2$ in water | 7.5 |
| CaO in water | 13.0 |
| $Ca(HCO_3)_2$ in water | 6.35 |

They state further:

> A batch of calcine in water has a pH between 10.6 and 13.0. When it is charged with $CO_2$, the pH gradually drops to 7.5 as the concentration of MgO in the solution approaches the "saturation value" (10.0 grams per liter at 20° C.) and remains constant at 7.5 when supersaturation is attained. Since the pH of $Ca(HCO_3)_2$ is less than 7.5, the solubility of the lime is low in a saturated $Mg(HCO_3)_2$ solution.

Evidence that some of the reactions outlined above take place on a large scale is afforded in a brief description of a commercial chemical plant operation. The physical chemical relationships in the preparation of magnesium from dolomite at the Austin plant of the International Minerals and Chemical Corporation have been described by Manning and Kirkpatrick (1944). In this process dolomite is completely calcined to a mixture of CaO (lime) and MgO (periclase), and its mixture of oxides is slaked in water resulting in the formation of hydroxides and some unreacted oxides. The slurry so prepared is carbonated by the introduction of carbon dioxide gas under pressure. Calcium carbonate is precipitated as a finely divided solid and the magnesium is retained in the solution.

In summary of the foregoing chemical data on the system MgO-CaO-$CO_2$-$H_2O$, we find that dolomite which has been dissociated to a mixture of lime (CaO) and periclase (MgO) will react with a solution of water charged with carbon dioxide to yield a precipitate (or reaction product) of calcite and a solution containing magnesium carbonate and a disproportionately smaller amount of calcium bicarbonate. If such a solution is aerated or some of the carbon dioxide can escape in another way, much of the remaining calcium bicarbonate will be precipitated as calcite, and a still purer magnesium-rich carbonated solution will be formed. If, on the other hand, dolomite is partially dissociated to a mixture of calcite ($CaCO_3$) and periclase (MgO) and this is reacted with a solution of water charged with carbon dioxide, the periclase will be converted to magnesium carbonate and remain in the solution, whereas the calcite is only slightly dissolved and a relatively small amount enters into the solution. The relationships observed for the partially dissociated dolomite are of considerable interest in this discussion for they provide a mechanism for the derivation of magnesium-rich solutions from the brucite marbles (predazzite and pencatite).

The solubility data for magnesium carbonate trihydrate show that as the temperature is raised, the solubility is decreased and that an increase in the pressure of carbon dioxide offsets this decrease. A decrease in the solubility at higher temperatures changes the quantitative relations in that larger volumes of water charged with carbon dioxide will be needed to leach an equivalent amount of periclase in comparison with that reacted at lower temperatures.

It must be emphasized here that the reactions between a partially dissociated dolomite, consisting of periclase and calcite, and a hydrothermal solution charged with carbon dioxide and considered in this discussion, are entirely different from the relationships involved in the attack of the same solutions on the rock dolomite. Dolomite is another phase in the quaternary system $MgO$-$CaO$-$CO_2$-$H_2O$ and its solubility relationships have been discussed elsewhere by Faust and Callaghan (1948).

## THE PROCESS OF DEDOLOMITIZATION

The process of dedolomitization may be considered to take place in the following manner. After the magma has been emplaced and has started to cool, heat will be conducted from it to the country rock and some of the vapor phase associated with the magma will try to escape at the periphery of the intrusive mass. This vapor phase will escape into the fracture system of the country rock, along intergrain boundaries, and through capillary and subcapillary openings in the rocks. At the contact with the dolomite, it will be joined by $CO_2$ liberated from xenoliths and $CO_2$ liberated by reaction with the wall rock. The resulting mixed-gas phase is no longer in equilibrium with the magma and is most certainly not in equilibrium with the country rock. The chemical species which make up the gaseous phase are dominantly $H_2O$ and $CO_2$. In addition, minor amounts of B, Cl, S, etc., are present. In such an environment as this, the stability of the various phases will depend on temperature and pressure conditions. It is possible for anhydrous phases to exist in equilibrium with $H_2O$, most of which is in the gaseous phase. In this stage, periclase may form as a stable mineral. It is noteworthy also that the zone containing periclase is, as Harker (1904) remarks, closest to the intrusive mass. As the magma crystallizes, the proportion of emanations derived from the magma will increase in amount and at some later stage, the magmatic solution will be composed largely of water together with the residual constituents, "the hyperfusibles of Bowen." This fluid phase will migrate from the cooling rock and become the hydrothermal solution. As this solution and its accompanying vapor phase move into the country rock, they will react with the earlier formed periclase to produce brucite. This reaction, as judged from the texture of the brucite whorls, does not take place over a whole crystal of periclase at once, but rather is the result of successive stages of hydration (see Fig. 8). The periclase now present in these rocks was protected by an armor of brucite. As these hydrothermal solutions move through the country rock, they will dissolve some of the brucite.

The hydrothermal solutions which formed the brucite did not contain much $CO_2$, for brucite is unstable in contact with $CO_2$-bearing solutions except for very low concentrations. Kline (1929) states:

> For with decreasing partial pressure of carbon dioxide there corresponds an increase in the ratio $[(OH^-)/(CO_3^=)]$ and, owing to the fact that magnesium hydroxide is much less soluble than the carbonate there is a pressure below which the hydroxide becomes the stable solid phase. . . .

Many of those who have studied brucite marble, predazzite, and pencatite, both in the field and the laboratory, agree that the first stage in dedolomitization is the dissociation of dolomite to periclase and calcite. Keith (1946) believes that for the deposits studied by him, the brucite was formed by the action of superheated steam on dolomite. The absence of periclase in his rocks leads him to believe that it may never have been present.

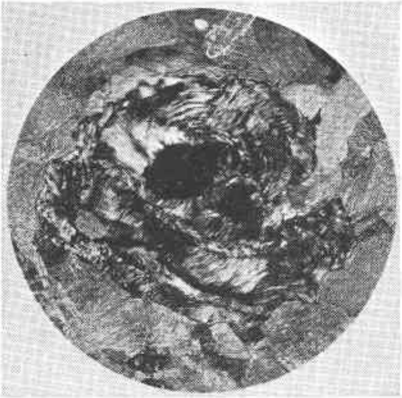


FIG. 8. Whorls of brucite surrounding periclase. Note that the oriented foliae in each whorl are not related to those in the adjacent whorls. This is a photograph of the same area recorded in Fig. 2, made with crossed nicols. Mag. 75×. Brucite and periclase in pencatite from the Organ Mountains, New Mexico.

## LATER STAGES OF HYDROTHERMAL ACTIVITY AND THE DEVELOPMENT OF MAGNESIUM-RICH SOLUTIONS

### (*a*) *Leaching of dedolomitized rocks by hydrothermal solutions poor in carbon dioxide.*

The more or less continuous migration of successive surges of hydrothermal solutions through the aureole of metamorphism in the carbonate rocks may dissolve some of the brucite. The amount dissolved will depend on the temperature, the ions present, and the volume of the hydrothermal solutions which traverse the rocks. Long-continued leaching by dilute solutions poor in carbon dioxide can remove appreciable quantities of brucite. Keith (1946) has observed a cellular limestone in the Rutherglen District, Ontario, which he attributes to the leaching of the brucite by dilute magmatic solutions. In some deposits the amount of leaching has been small, for in pencatite the ratio of magnesium to calcium is that required by the composition of dolomite. Analyses of several brucite marbles, the predazzites, show, on the other hand, less magnesium than the theoretical ratio. Some of these rocks may be metamorphosed magnesian limestones, whereas others may represent brucite marbles leached of part of their brucite. Evidence for the movement of brucite is given by Keith (1946), who noted that the ratio of magnesium to calcium in some rocks studied by him exceeded the theoretical values for dolomite. This certainly indicates that successive waves of hydrothermal solutions reworked the brucite. Some calcite may also have been reworked by these later solutions.

It is possible thus by reworking brucite and periclase, formed at an earlier stage, to derive a hydrothermal solution which will be able to deposit brucite. These relations probably account for the formation of brucite in and near some magnesite deposits and they also offer a mechanism for the migration of brucite in magnesite deposits.

### (*b*) *Reaction of dedolomitized rocks with hydrothermal solutions rich in carbon dioxide.*

The passage of a hydrothermal solution rich in carbon dioxide over a completely dissociated dolomite will convert the lime to calcite and dissolve the periclase and yield a solution which will be rich in magnesium and poor in calcium. Calcium bicarbonate is much less stable than magnesium carbonate in such a solution and it tends to precipitate out as calcite. This process is similar to the industrial process at Austin, Texas, mentioned previously.

Where the hydrothermal solutions rich in carbon dioxide seek egress through partially dissociated dolomite, the reaction is still simpler. Calcite will be only slightly soluble while the periclase will be dissolved. The resulting hydrothermal solution will be rich in magnesium and carbon dioxide and relatively poor in calcium. The analogous chemical process has been studied at lower temperatures than those of hydrothermal solutions by Doerner, Holbrook, and Fortner (1946). Hydrothermal solutions rich in carbon dioxide which traverse predazzite and pencatite may react with the brucite and residual periclase to form a solution of magnesium carbonate. Some calcite may also dissolve but, as mentioned before, the concentration of calcium bicarbonate is not likely to be significant.

The mechanisms here proposed for deriving hydrothermal solutions, rich in magnesium and carbon dioxide and relatively poor in calcium, through the selective reaction of a hydrothermal solution rich in carbon dioxide upon dedolomitized rocks are simple, straightforward chemical processes which require no unusual chemical constituents.

(*c*) *Subsequent reactions of hydrothermal solutions rich in magnesium and carbon dioxide with the country rock.*

If the proposed mechanism produces, in nature, hydrothermal solutions rich in magnesium and carbon dioxide, the question arises as to the probable ways by which these hydrothermal solutions will give up their mineralizing constituents. If we assume that the solutions continue to migrate away from the zone of higher temperatures into the cooler country rock, these hydrothermal solutions will become cooler. If they enter zones of greater porosity, they may lose some of their carbon dioxide to the country rocks. Either, or both, of these changes may bring about the approach to saturation conditions for magnesium carbonate, (magnesite). The structural relationships of the country rock, its texture, and chemical and mineralogical character will determine the manner in which the magnesium and carbon dioxide will be removed from the solutions.

If the country rock is chemically inert with respect to the solutions, they will pass through the fracture systems, deposit magnesite in veins or fillings. However, they may continue and possibly move into the upper levels of the crust, mingle with cooler meteoric waters, and eventually emerge as springs at the earth's surface, where they may deposit hydromagnesite, $3MgCO_3 \cdot Mg(OH)_2 \cdot 3H_2O$, in "sinter" form.

In areas where hydrothermal solutions rich in magnesium and carbon dioxide enter limestone, dolomitization takes place. Armoring of the calcite by dolomite will protect larger masses of limestone from reaction. This phenomenon is well illustrated by the description and figures in Hewett (1928) concerning the islands of limestone in dolomite at Iglesias in Sardinia. Zoning, by dolomitization, about the fracture system, or between limestone and an inert rock may yield channelways along which the hydrothermal solutions can migrate without further reaction with the limestone. These magnesium-rich solutions, because of their failure to react with limestone protected by armoring or zoning, may deposit magnesite in the fracture system. Magnesite may form in direct contact with dolomite with which it is in equilibrium. Bain (1924) and Hewett (1928) have both pointed out examples of zoning. Hewett (1928) writes:

> Where magnesite appears to replace limestone near its contact with intrusive igneous rocks, especially in Styria, Austria; Stevens County, Washington; and Argenteuil County,

Quebec, there is a zone of dolomite between the limestone and the magnesite which lies next to the intrusive rock.

An examination of the literature on dedolomitized dolomites shows that in the vicinity of some of these rocks magnesite has been found, whereas in others it is lacking.

In the Organ Mountains in New Mexico, Dunham (1935) describes the presence of lenticular masses of magnesite as much as 5 feet in thickness. Concerning their origin he writes (p. 36):

> Metamorphism of the dolomite xenoliths by the quartz-monzonite converted them into periclase marbles, consisting essentially of periclase and calcite . . . at a later stage periclase and forsterite were in part converted into brucite and serpentine. Later still, the xenoliths were invaded by solutions, probably rich in carbon dioxide which were able to convert the marble into magnesite.

And again on page 104, Dunham writes:

> The further change of brucite marble into magnesite probably belongs to a much later stage in the history of the rock, but, as it is difficult to decide definitely the time of this change it will be considered here. The nature of the change is shown by the analyses. . . . There is a decrease in lime and an increase in magnesia and carbon dioxide; the reaction also involves the removal of water:
>
> $$[Mg(OH)_2 + CO_2 = MgCO_3 + H_2O].$$
>
> It is suggested that waters charged with carbon dioxide would be capable of effecting this reaction. The lime would be removed as calcium bicarbonate and the magnesia precipitated as the carbonate magnesite, which if the process is to work, must be supposed to be less soluble in carbonated water than calcium carbonate. Temperature may have been a controlling factor. A very porous rock was produced.

Magnesite has been reported from the 910-foot level of the Commercial quarry at Crestmore, Calif., by Woodford, Crippen, and Garner (1941).

Magnesite has not been found at Wakefield, Wilkinson, or Rutherglen in Ontario; in the Cottonwood-American Fork area, Utah; Philipsburg, Mont.; nor at the deposits of Korea. The chemical analyses of some of the specimens from the localities in Ontario suggest that magnesite may be present, Keith (1946). The author believes that the absence of magnesite at these localities arises from the reaction relationship pointed out previously. That is, any hydrothermal solution rich in magnesium and carbon dioxide was consumed in the process of dolomitizing the neighboring limestone rocks. Dolomitization of the limestones is recognized at the Cottonwood-American Forks area, Utah, and at Philipsburg, Mont.

Brown (1943) has noted that the chief constituents of the brucite-bearing lenses at Wilkinson, Ontario, are calcite, dolomite, and brucite; and that the proportions of these minerals vary from place to place. He states also that (page 410).

Calcite and dolomite (in the brucitic limestone) form a mosaic of closely interlocking grains traversed by tiny stringers of dolomite, which also cuts through the spherules of brucite. In places this later carbonate forms areas with micrographic texture, which are probably due to replacement of the older carbonate by later ones.

Dolomite is also present in the brucitic limestones at Rutherglen (Keith).

## SUMMARY OF THE DOLOMITE RELATIONSHIPS

A summary of the dolomite relationships as given in the paper by Faust and Callaghan (1948) is presented here for purposes of comparison of the two proposed mechanisms.

The solubility of dolomite in solutions rich in carbon dioxide has been studied by several investigators and at present the following views are held:

(*a*) Dolomite is congruently soluble in carbon dioxide rich waters—that is, dolomite dissolves completely without the separation of a solid phase. Faust and Callaghan (1948) reasoned that the congruent solubility of dolomite might be the normal relationship and, by the use of the existing experimental data on the attempts at synthesis of dolomite, proposed a mechanism for deriving a magnesium- and carbon dioxide-rich solution. A solution of magnesium and calcium in the proportions necessary to form dolomite, and containing carbon dioxide may, under conditions of metastability, precipitate calcite, and leave a solution rich in magnesium and carbon dioxide. If these constituents are left together they will react to form dolomite, but if they can be separated, a magnesium-rich solution will result. It is necessary that there be sufficient $CO_2$ in the system to keep the magnesium in solution. Thus a hydrothermal solution rich in carbon dioxide may attack dolomite and dissolve it congruently. As the solutions move on, they may later precipitate their calcium content as calcite; the remaining solution will then be rich in magnesium and carbon dioxide. These solutions will dolomitize the calcite if left in contact with it, but if they move on, they can dolomitize other calcareous rocks.

(*b*) Dolomite is incongruently soluble in carbon dioxide-rich waters, that is, it dissolves to yield a solution and a solid phase other than dolomite. Two possibilities must be considered in this relationship. Incongruent solubility of dolomite may give rise, either (1) to a solution rich in magnesium with the separation of the solid-phase calcite, or, (2) to a solution rich in calcium with the separation of the solid-phase magnesite. If the solubility of dolomite takes place according to (1), the solution will be magnesium rich. After migration away from its source to areas of different porosity and temperature, the solution may deposit magnesite or react with limestones to form dolomite. If solubility of dolomite takes place according to (2), an insoluble residue of magnesite will result. A later surge of hydrothermal solutions may dissolve this residue, which thus will produce magnesium-rich solutions.

(*c*) Dolomite exhibits both congruent and incongruent solubility depending on the variables—temperature, pressure of carbon dioxide, or the concentration of other ions in solution. All these possibilities can be used to derive magnesium-rich solutions either by the selective leaching of magnesium or by the removal first of the calcium by leaching followed by the subsequent attack on a magnesium carbonate residue.

It should be re-emphasized that the two proposed mechanisms are not identical. The earlier mechanism proposed by Faust and Callaghan (1948) involves the attack of hydrothermal solutions rich in carbon dioxide upon dolomite. The phase relationships concerning this mechanism are referred to the quaternary system $MgCO_3$-$CaCO_3$-$H_2O$-$CO_2$. The second mechanism proposed by Faust, in this paper, involves the attack of hydrothermal solutions rich in carbon dioxide upon previously dedolomitized dolomites. They consist of periclase ($MgO$) and/or brucite ($Mg(OH)_2$) with calcite; and the phase relationships are referred to the quaternary system $CaO$-$MgO$-$CO_2$-$H_2O$.

Both mechanisms, however, do yield solutions rich in magnesium and carbon dioxide. It must not be concluded that the author believes that these are the only methods by which solutions may become enriched in magnesium and carbon dioxide. It is his belief that these two mechanisms offer a satisfactory explanation for the widespread dolomitization associated with ore deposition. The common association of magnesite and serpentinized peridotites and dunites requires another mechanism, and Bowen and Tuttle (1949) have proposed one. If the hydrothermal solutions rich in magnesium and carbon dioxide and derived from such intrusives migrate into the country rock and encounter limestone, the ensuing reactions between the hydrothermal solutions and the limestone will be governed by the same principles given in this paper and the paper by Faust and Callaghan (1948).

## SUMMARY AND CONCLUSIONS

This paper describes a mechanism for the derivation of a magnesium-rich solution through the attack of hydrothermal solutions, rich in carbon dioxide, upon metamorphosed dolomites such as predazzite, pencatite, and brucite marble.

In order to gain an understanding of the origin of these dedolomitized rocks, the physical chemistry of the dissociation of dolomite is examined. Thermal analysis data show that contact metamorphism of dolomites can produce two types of rocks. The complete dissociation of dolomite results in the formation of lime and periclase. No geologic occurrence of a completely dissociated dolomite which contains lime is known. The partial dissociation of dolomite results in the formation of periclase and calcite, and rocks containing these minerals are well known. Periclase is quite unstable and alters to brucite.

From a study of the heat exchange relations between the hot magma, which supplied the heat necessary for metamorphism, and the country rock, it is concluded that heat conduction from solid to solid will not alone suffice to explain the relations in the process of dedolomitization. It is proposed, here, that the magmatic emanations and the carbon dioxide liberated in the process of dedolomitization served as important agents in the transfer of heat. Three factors which make the magmatic emanations important in contact metamorphism are (1) their greater specific heat (heat capacity); (2) their mobility, which serves to transport the heat quickly to the country rock; and (3) their ability to enter into reactions with the country rock while at elevated temperatures.

The physical-chemical data concerning the system $MgO$-$CaO$-$CO_2$-$H_2O$ allow the following conclusions to be drawn: (1) that calcite is much less soluble than magnesium carbonate in water containing carbon dioxide; (2) that $MgO$ forms a highly soluble carbonate when it reacts with a solution rich in carbon dioxide. As a result of these relationships, a dedolomitized dolomite, consisting of $MgO$ (periclase) and $CaCO_3$ (calcite) will react with a solution of water rich in carbon dioxide, with the transfer of most of the magnesium but with only a minimum amount of calcium into the liquid phase. This is the mechanism proposed for the derivation of a magnesium-rich hydrothermal solution.

## ACKNOWLEDGMENTS

I wish to thank Professor Eugene Callaghan, formerly in charge of the geologic studies on magnesium minerals and rocks for the U. S. Geological Survey and now of Indiana University, for his kind interest and continuous encouragement in this work. I have derived much from him in many discussions, both in the field and in the laboratory, on the probable nature and relationships of the hydrothermal solutions which served as agents for the formation of magnesite and brucite deposits.

I am indebted to Drs. Michael Fleischer, Clarence S. Ross, and Earl Ingerson for a critical reading of the paper. Likewise, I wish to thank my colleague, H. Cecil Spicer, for a careful reading of the sections on the heat relations.

Professor W. F. Hunt, Editor, *The American Mineralogist*, and Professor Alan M. Bateman, Editor, *Economic Geology*, kindly loaned the

cuts for figures 2 and 8, and figure 3, respectively. Professor W. H. Parsons, Editor, *Journal of the American Chemical Society* granted permission to reproduce figure 5.

## Bibliography

Adams, L. H. (1924), A physical source of heat in springs: *Jour. Geology*, **32,** 191–194.

Ambrose, J. W. (1943), Brucitic limestones and hastingsite syenite near Wakefield, Quebec: *Royal Soc. Canada Proc. and Trans.*, 3rd Ser. **37,** 9–22.

Bain, G. W. (1924), Types of magnesite deposits and their origin: *Econ. Geol.*, **19,** 412–434.

Bär, Otto (1932), Beitrag zum Thema Dolomitenstehung: *Centralbl. Mineral.* Abt. A., 46–62.

Birch, F., and Clark, Harry (1940), The thermal conductivity of rocks and its dependence upon temperature and composition: *Am. Jour. Sci.*, **238,** 529–558 and 613–635.

Bowen, N. L. (1933), The broader story of magmatic differentiation briefly told; in Ore Deposits of the Western States (Lindgren Volume): *Am. Inst. Min. Met. Eng.*, Part 2, Chapter 3, 106–128.

Bowen, N. L. (1940), Progressive metamorphism of siliceous limestone and dolomite: *Jour. Geology*, **48,** No. 3, 225–274.

Bowen, N. L., and Tuttle, O. F. (1949), The system $MgO\text{-}SiO_2\text{-}H_2O$: *Bull. Geol. Soc. Am.*, **60,** 439–460.

Brown, I. C. (1943), Brucite in limestone near Wilkinson, Ontario: *Econ. Geology*, **38,** 408–419.

Buddington, A. F. (1933), Correlation of kinds of igneous rocks with kinds of mineralization: in Ore Deposits of the Western States (Lindgren Volume): *Am. Inst. Min. Met. Eng.*, 350–385.

Cameron, F. K., and Seidell, A. (1903), The solubility of magnesium carbonate in aqueous solutions of certain electrolytes: *Jour. Physical Chem.*, **7,** No. 8, 578–590.

Cameron, F. K., and Robinson, W. O. (1907), The solubility of calcium carbonate in aqueous solutions of potassium chloride and potassium sulfate at 25°: *Jour. Physical Chem.*, **11,** No. 8, 577–580.

Doerner, H. A., Holbrook, W. F., and Fortner, O. W. (1946), The bicarbonate process for the production of magnesium oxide: *U. S. Bur. Mines, Tech. Paper* **684,** 48 pp.

Dunham, K. C. (1935), The geology of the Organ Mountains: *New Mexico School of Mines, Bulletin* **11.**

Dunham, K. C. (1936), Xenoliths in the Organ batholith, New Mexico: *Am. Mineral.*, **21,** 312–320.

Engel, P., and Ville, J. (1881), Sur la solubilité du carbonate de magnésie dans l'eau chargée d'acide carbonique: *Compt. rend.*, **93,** 340–341.

Faust, G. T. (1944), The differentiation of magnesite from dolomite in concentrates and tailings: *Econ. Geology*, **39,** 142–151.

Faust, G. T. (1944–48), Thermal analysis studies: Unpublished work.

Faust, G. T., and Callaghan, Eugene (1948), The mineralogy and petrology of the Currant Creek magnesite deposits and associated rocks of Nevada: *Bull. Geol. Soc. America*, **59,** 11–74.

Frear, G. L., and Johnston, J. (1929), The solubility of calcium carbonate (calcite) in certain aqueous solutions at 25° C: *Jour. Am. Chem. Soc.*, **51,** 2082–2093.

Goudge, M. F. (1939), A preliminary report on brucite deposits in Ontario and Quebec and their commercial possibilities: *Ontario Dept. Mines, Rept. Ser. No.* **75.**

Griggs, David (1946), in Knopf, E. B., Study of experimentally deformed rocks: *Science, New Ser.* **103,** No. 2665, p. 103.

Haehnel, Otto (1924), Über die Löslichkeit des Magnesiumcarbonats in kohlensäurehaltigem Wasser unter höheren Kohlendioxyddrucken und über die Eigenschaften solcher Magnesiumbicarbonatlösungen: *Jour. prakt. Chemie,* **108,** 61–74.

Haehnel, Otto (1924), Über die Löslichkeit des Calciumcarbonats in kohlensäurehaltigem Wasser unter hohen Drucken und die Eigenschaften solcher Lösungen: *Jour. prakt. Chemie,* **107,** 165–176.

Halla, Franz (1936), Über die freie Energie bei der Dolomitbildung: *Min. pet. Mitt., Band* **48,** 275–278.

Harker, A. (1904), The Tertiary igneous rocks of Skye: *Great Britain Geol. Survey Mem.,* 144–151 (with definition on p. 150).

Hewett, D. F. (1928), Dolomitization and ore deposition: *Econ. Geology,* **23,** No. 8, 821–863.

Hunt, W. F., and Faust, G. T. (1937), Pencatite from the Organ Mountains, New Mexico: *Am. Mineral.,* **22,** 1151–1160.

Keith, M. L. (1946), Brucite deposits in the Rutherglen district, Ontario: *Bull. Geol. Soc. Am.,* **57,** 967–984.

Kline, W. D., (1929), The solubility of magnesium carbonate (nesquehonite) in water at 25° C. and pressures of carbon dioxide up to one atmosphere: *Jour. Am. Chem. Soc.,* **51,** 2093–2097.

Manning, P. D. V., and Kirkpatrick, J. D. (1944), Better utilization of mineral resources through new chemical technology: *Chem. Met. Eng.,* **51,** 92–96.

Mitchell, A. E. (1923), Studies on the dolomite system—part 2: *Jour. Chem. Soc. London,* **123,** 1887–1904.

Prutton, C. F., and Savage, R. L. (1945), The solubility of carbon dioxide in calcium chloride-water solutions at 75, 100, 120° and high pressures: *Jour. Am. Chem. Soc.,* **67,** 1550–1554.

Rivett, A. C. D. (1923), The phase rule and the study of heterogenous equilibria, Chapter 2, The Principle of Le Chatelier-Braun: Oxford University Press, Oxford

Rogers, A. F. (1918), An American occurrence of periclase and its bearing on the origin and history of calcite-brucite rocks: *Am. Jour. Sci.,* **46,** 581–586.

Rogers, A. F. (1929), Periclase from Crestmore near Riverside, California, with a list of minerals from this locality: *Am. Mineral.,* **14,** 462–469.

Ross, Clarence S. (1928), Physico-chemical factors controlling magmatic differentiation and vein formation: *Econ. Geology,* **23,** No. 8, 864–886.

Smyth, F. H., and Adams, L. H. (1923), The system calcium oxide-carbon dioxide: *Jour. Am. Chem. Soc.,* **45,** 1167–1184.

Terada, Kiyomatsu (1928), On the solubility of magnesium carbonate in aqueous solutions charged with $CO_2$: *Inst. Physical Chem. Research, Tokyo, Bull.* **7,** 452–465. (In Japanese). See also: Abstracts—*Inst. Physical Chem. Research, Tokyo, Bull.,* **1,** No. 4, 41–42, 1928 (In English).

Tillmans, J., and Heublein, O. (1912), Über die kohlensäuren kalk angreifende Kohlensäure der natürlichen Wässer: *Gesundheits-Ing. Jahrg.,* **35,** No. 34, 669–677.

Wiebe, R., and Gaddy, V. L., (1939), The solubility in water of carbon dioxide at 50°, 75° and 100° at pressures to 700 atmospheres: *Jour. Am. Chem. Soc.,* **61,** 315–318.

Wiebe, R., and Gaddy, V. L. (1940), The solubility of carbon dioxide in water at various temperatures from 12° to 40° and at pressures to 500 atmospheres. Critical Phenomena. *Jour. Am. Chem. Soc.,* **62,** 815–817.

Woodford, A. O., Crippen, R. A., and Garner, K. B. (1941), Section across commercial quarry, Crestmore, California: *Am. Mineral.,* **26,** 351–381.

Zambonini, F., and Quercigh, E. (1935), Mineralogia Vesuviano: Second Edition, Naples, p. 58.