SUBSOLIDUS RELATIONS ON THE DOLOMITE JOIN, CaMg(CO₃)₂-CaFe(CO₃)₂-CaMn(CO₃)₂

P. E. ROSENBERG, *Department of Geology, Washington State University, Pullman, Washington.*

ABSTRACT

Subsolidus relations on the dolomite join, $CaMg(CO_3)_2$-$CaFe(CO_3)_2$-$CaMn(CO_3)_2$ and on bounding joins have been studied largely at 450°C and total pressures of 2–3 kbars using hydrothermal apparatus and cold-seal pressure vessels. Under these conditions, the dolomite join contains one single-phase, one three-phase and three two-phase areas.

Ternary relations exist only within a one-phase area which occupies most of the Mg-rich portion of the dolomite join; these solid solutions are believed to be cation-ordered. A two-phase area of disordered Mg-poor solid solutions extends almost the entire length of the join $CaFe(CO_3)_2$-$CaMn(CO_3)_2$; the hypothetical iron analog of dolomite, $CaFe(CO_3)_2$, which has neither been synthesized nor reported as a mineral, lies within this two-phase area. Two disordered solid solutions, one Ca-rich and the other Ca-poor coexist with dolomite solid solutions in a three-phase area located in the Mg-poor region and extending from the join $CaMg(CO_3)_2$-$CaFe(CO_3)_2$ to approximately 40 mole percent $CaMn(CO_3)_2$. Flanking the three-phase area and separating it from the one-phase area is a narrow two-phase area in which dolomite solid solutions coexist with disordered, Ca-poor solid solutions. The presence and extent of a third two-phase area has been inferred from subsolidus relations on the join $CaMg(CO_3)_2$-$CaMn(CO_3)_2$.

Application of phase relations on the dolomite join to natural carbonate assemblages is limited by the presence of excess $CaCO_3$ in most natural dolomites.

INTRODUCTION

The compositions of rock-forming carbonates may be adequately expressed in terms of the quaternary system $CaCO_3$-$MgCO_3$-$FeCO_3$-$MnCO_3$. Although a number of experimental studies have been devoted to bounding binary and ternary systems, phase relations in the quaternary system have not been reported in the literature to date. An experimental investigation of subsolidus relations on the dolomite join, $CaMg(CO_3)_2$-$CaFe(CO_3)_2$-$CaMn(CO_3)_2$ which divides the quaternary system into two volumes, one Ca-rich and the other Ca-poor, was undertaken as a contribution to the study of the quaternary system. The join approximates the compositions of natural dolomites and ankerites; end-members are dolomite, $CaMg(CO_3)_2$, kutnahorite, $CaMn(CO_3)_2$, and the hypothetical iron analog of dolomite, $CaFe(CO_3)_2$, which has neither been synthesized nor reported as a mineral.

Although much of the experimental data presented here are at a single temperature, 450°C, phase relations in bounding systems (Goldsmith and Graf, 1960; Goldsmith *et al.*, 1962; Rosenberg, 1967) suggest that small variations in temperature will produce only gradual changes in subsolidus relations. The results of this investigation should be applicable to a nar-

row temperature range which lies within or close to the range in which many dolomite-bearing hydrothermal deposits are believed to have formed.

<div align="center">EXPERIMENTAL DETAILS</div>

Experiments were carried out using standard hydrothermal apparatus and techniques (Harker and Tuttle, 1955). A more detailed account of experimental procedures has been given by Rosenberg (1960, 1967).

Starting compositions were prepared as mechanical mixtures of precipitated $CaCO_3$, reagent-grade MgO, $MnCO_3$, and purified $FeC_2O_4 \cdot 2H_2O$. Conversion of $MnCO_3$ to Mn_2O_4 resulted in an unexpected 4 percent weight loss which was assumed to be due to the presence of water in $MnCO_3$ (Goldsmith and Graf, 1957). Corrections in the weight, of $MnCO_3$ added to each mixture were made on this basis. Ferrous oxylate and magnesium oxide react quickly and completely to give the respective carbonates under the conditions of these experiments.

Starting materials were wrapped in gold-foil envelopes to which a drop of 0.01M Li_2CO_3 solution was added to promote reaction. The total weight of Li_2CO_3 added to each sample was never in excess of 0.1 percent (wt.). X-ray reflections attributable to lithium carbonate were not observed and no changes in spacings were detected in $CaCO_3$, $MgCO_3$ or $FeCO_3$ treated with this solution and exposed to experimental conditions.

Experimental atmospheres were pure, bone dry CO_2 containing approximately 2 percent (vol.) of CO which served to prevent the oxidation of iron. Pressures sufficient to prevent the dissociation of the carbonates were used throughout this study.

Samples were held under the desired p-T conditions for varying lengths of time and quenched by immersion of the reaction vessel in water. Products were identified by their X-ray powder diffraction patterns using, for the most part Ni-filtered Cu-radiation, although Fe-radiation was used in limited and largely unsuccessful attempts to improve the resolution of diffraction patterns. During the course of the experiments runs were quenched and samples remixed at intervals of three to five days. Equilibrium was assumed to have been attained when the (211) X-ray spacings which vary with carbonate composition (Goldsmith and Graf, 1960; Rosenberg, 1963a, 1963b, 1967) were found to be constant, within the precision of the measurements, for all phases present in a sample after two or three successive reruns. X-ray measurements were made using an internal standard, CdF_2, which has a conveniently located reflection at 28.7° CuKα. The total time necessary to approach equilibrium varied from ten to twenty days at 450°C.

X-ray reflections for all samples were relatively weak and somewhat broadened. Reasonably precise measurements were possible only for d_{211} and many weaker reflections were not observed in powder patterns. The appearance of X-ray ordering reflections was noted when observed but it was not possible to delimit the extent of ordering; detection of ordering in Mg-poor dolomites often requires single crystal photographs (Goldsmith and Graf, 1960). The precision of d_{211} measurements for most dolomites, synthesized from compositions lying within the one-phase area on the dolomite join, was ± 0.005 Å. The differences in the unit-cell dimensions of the end-members $CaMg(CO_3)_2$, $CaMn(CO_3)_2$ and hypothetical $CaFe(CO_3)_2$ (Graf, 1961) are not very large so that variations in d_{211} resulting from changes the relative amounts of Mg, Mn and Fe in dolomite are rather small and could not be determined accurately by X-ray measurements. Furthermore, precise d_{211} measurements were not possible for dolomite compositions lying in the Ca-rich portion of the quaternary system. As a consequence, no attempt was made to delineate tie-lines in two-phase fields. However, approximate d_{211} measurements were of value in the identification of phases due to the limited extent of the one-phase fields in the quaternary system. Knowledge of the number

of phases present in a sample and their approximate (211)-spacings was sufficient for qualitative phase identification throughout this study.

Phases having compositions on or near the dolomite join are believed to be cation-ordered at 450°C (Rosenberg, 1960; Goldsmith and Graf, 1960; Goldsmith *et al.*, 1962) with the possible exception of those close to the end-member kutnahorite, $CaMn(CO_3)_2$, in which disorder has been observed to begin at this temperature (Goldsmith and Graf, 1960); these phases are referred to as dolomite in this paper. Solid solutions having compositions far removed from the dolomite join are considered to be disordered (Goldsmith and Graf, 1960; Goldsmith *et al.*, 1962).

Experimental Results

The Join $CaMg(CO_3)_2$-$CaFe(CO_3)_2$—Subsolidus relations in the system $CaCO_3$-$MgCO_3$-$FeCO_3$ have been studied by Goldsmith *et al.* (1962) and, in the p-T range of this investigation (350–550°C; 2.1–2.9 kbars), by Rosenberg (1960, 1967). Experimental data for the join $CaMg(CO_3)_2$-$CaFe(CO_3)_2$ (Table 1)[1] have been extracted from the latter source.

One single-phase, two two-phase and one three-phase areas are present along the join (Fig. 1) which is binary only within the one-phase area of dolomite solid solutions. The one-phase area extends from $CaMg(CO_3)_2$ across approximately 2/3 the length of the join, terminating in a narrow two-phase area of dolomite solid solutions and disordered Ca-poor solid solutions. Compositions richer in $CaFe(CO_3)_2$ lie in a three-phase area of dolomite solid solutions plus two disordered solid solutions, one Ca-rich and the other Ca-poor. A two-phase area of disordered Ca-rich and Ca-poor solid solutions occupies the high $CaFe(CO_3)_2$ portion of the join. The compositions of all phases within two and three-phase areas are ternary including the dolomite solid solutions which lie in the $CaCO_3$-rich portion of the ternary system (Rosenberg, 1967).

Above 350°C, with increasing temperature (Fig. 1) the three-phase area and the two-phase area separating it from the one-phase area are displaced toward $CaFe(CO_3)_2$ composition with the result that the field of dolomite solid solution extends further toward the $CaFe(CO_3)_2$ end-member. The increment of this displacement decreases with increasing temperature suggesting that the displacement is approaching a maximum at 550°C.

In accord with previous experimental studies neither the iron analog of dolomite, $CaFe(CO_3)_2$, nor the solid solution of this composition were synthesized in the present investigation. X-ray measurements ($2\theta_{d(211)}$-$2\theta_{std.}$) for dolomite solid solutions vary linearly with composition within

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[1] Tables 1–4 summarizing all experimental data reported in this paper have been deposited as Document No. 9897 with the ADI, Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington D.C. 20540. Copies may be secured by citing the document number and remitting in advance $1.25 for photoprints or $1.25 for microfilm, payable to Chief, Photoduplication Service, Library of Congress.
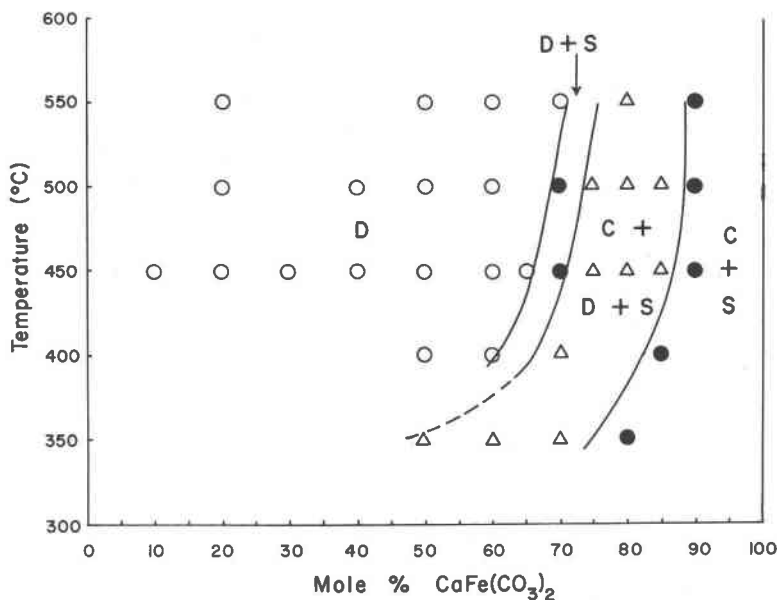
Fig. 1. Subsolidus relations on the join $CaMg(CO_3)_2$-$CaFe(CO_3)_2$. D—dolomite solid solutions; C—Ca-rich solid solutions; S—Ca-poor solid solutions. Open circles, one-phase; filled circles, two-phase; and triangles, three-phase assemblages.

the one-phase area but depart from this relationship within the two and three-phase areas where dolomite compositions contain excess $CaCO_3$ (Rosenberg, 1960, 1967). X-ray ordering reflections were observed in all members of the dolomite solid solution series (Rosenberg, 1960).

The Join $CaMg(CO_3)_2$-$CaMn(CO_3)_2$.—Subsolidus relations in the system $CaCO_3$-$MgCO_3$-$MnCO_3$ have been studied by Goldsmith and Graf (1960) in the temperature range 500–800°C and at total pressures of 10 kbars. Although the present investigation was confined to the join $CaMg(CO_3)_2$-$CaMn(CO_3)_2$ and to temperatures of 450 and 500°C, experimental techniques and pressures (2.1–2.5 kbars) were significantly different than those of the above study and, therefore, it is of interest to compare results.

All experiments (Table 2)[1] resulted in the synthesis of a single phase indicating a complete series of solid solutions at temperatures at least as low as 450°C. X-ray ordering reflections were observed for compositions from $CaMg(CO_3)_2$ to 40 mole percent $CaMn(CO_3)_2$.

At 500°C, Goldsmith and Graf (1960) found that a two-phase area en-
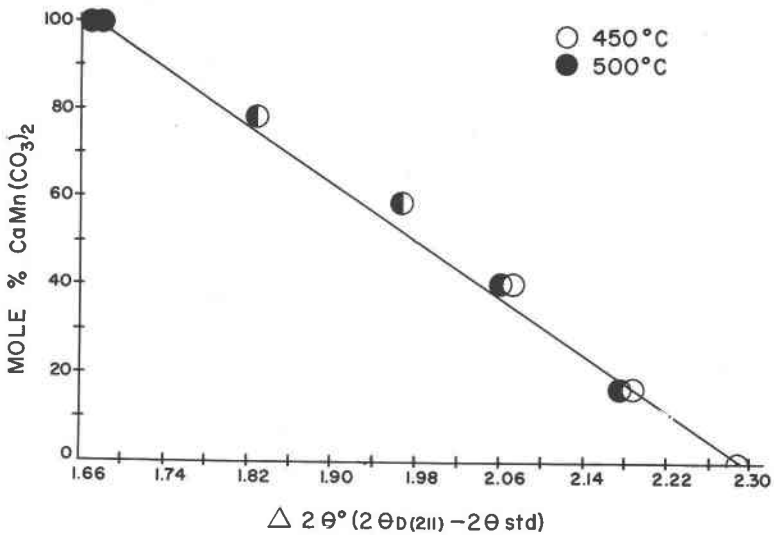
[1] Refer to footnote, page 882.

Fig. 2. $\Delta 2\theta (2\theta_{d(211)}-2\theta_{std.})$ of dolomites synthesized from compositions on the join $CaMg(CO_3)_2$-$CaMn(CO_3)_2$.

croaches slightly on the $CaMg(CO_3)_2$-rich portion of the join. It is interesting to note that the $\triangle 2\theta$ values $(2\theta_{d(211)}-2\theta_{std.})$ of synthetic solid solutions (Fig. 2) depart slightly from the linear variation with composition observed on the join $CaMg(CO_3)_2$-$CaFe(CO_3)_2$ (Roesnberg, 1967). $\triangle 2\theta$ values of intermediate solid solutions lie above those predicted by the line drawn between the $\triangle 2\theta$ values of the end-members (Fig. 2). This small deviation is in accord with the displacement of dolomite compositions from the join into the $MnCO_3$-rich portion of the ternary system observed by Goldsmith and Graf (1960). Thus, it appears that part of the join may lie just within a two-phase area and that small undetected quantities of a Ca-rich solid solution were probably present in the products of some experiments.

The Join $CaFe(CO_3)_2$-$CaMn(CO_3)_2$.—No previous studies of this join have been reported in the literature. The present investigation was limited to the temperature range 400–500°C and to pressures of 2.1–2.6 kbars (Table 3).[1]

The join contains a small one-phase area of dolomite solid solutions close to the end-member $CaMn(CO_3)_2$ and a large two-phase area of disordered Ca-rich and Ca-poor solid solutions extending from $CaFe(CO_3)_2$ to approximately 97 mole percent $CaMn(CO_3)_2$ (Fig. 3). Binary relations

[1] Refer to footnote, page 882.

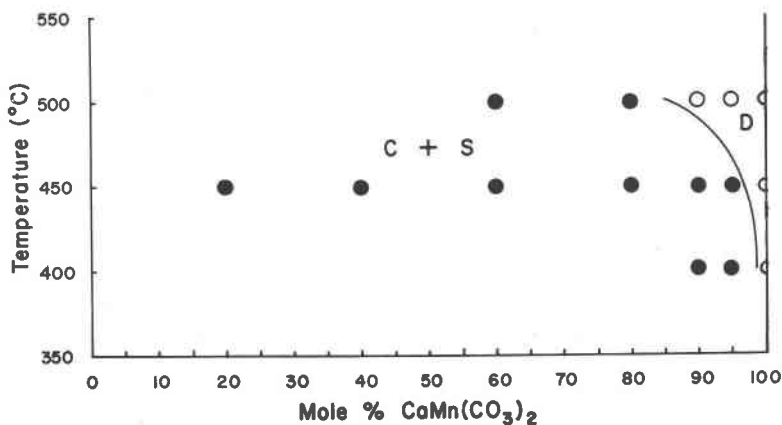FIG. 3. Subsolidus relations on the join $CaFe(CO_3)_2$-$CaMn(CO_3)_2$. Symbols as in Fig. 1.

exist only within the one-phase area which expands rapidly with increasing temperature. X-ray ordering reflections were not observed in dolomites synthesized from compositions lying on this join.

The Join $CaMg(CO_3)_2$-$CaFe(CO_3)_2$-$CaMn(CO_3)_2$.—Subsolidus relations on the dolomite join, $CaMg(CO_3)_2$-$CaFe(CO_3)_2$-$CaMn(CO_3)_2$, have been studies at a single temperature, 450°C, and at pressures between 2.1 and 2.6 kbars (Table 4).[1] Phase relations based on experimental data given in Tables 1–4[1] are shown in an isothermal and essentially isobaric diagram (Fig. 4).

The dolomite join contains five stability fields including one single-phase, one three-phase, and three two-phase areas. Ternary relations exist only within the one-phase area of dolomite solid solutions which occupies most of the Mg-rich portion of the join. X-ray ordering reflections were not observed in dolomites synthesized from compositions on the join. A two-phase area of disordered Mg-poor solid solutions occupies almost the entire length of the join $CaFe(CO_3)_2$-$CaMn(CO_3)_2$; the hypothetical iron analog of dolomite, $CaFe(CO_3)_2$, which has neither been synthesized nor reported as a mineral lies within this two-phase area. Two disordered solid solutions, one Ca-rich and the other Ca-poor, coexist with dolomite solid solutions in a three-phase area located in the Mg-poor region and extending from the join $CaMg(CO_3)_2$-$CaFe(CO_3)_2$ to approximately 40 mole percent $CaMn(CO_3)_2$. Flanking the three-phase area and separating it from the one-phase area is a narrow two-phase area in which dolomite solid solutions coexist with disordered Ca-poor solutions. The
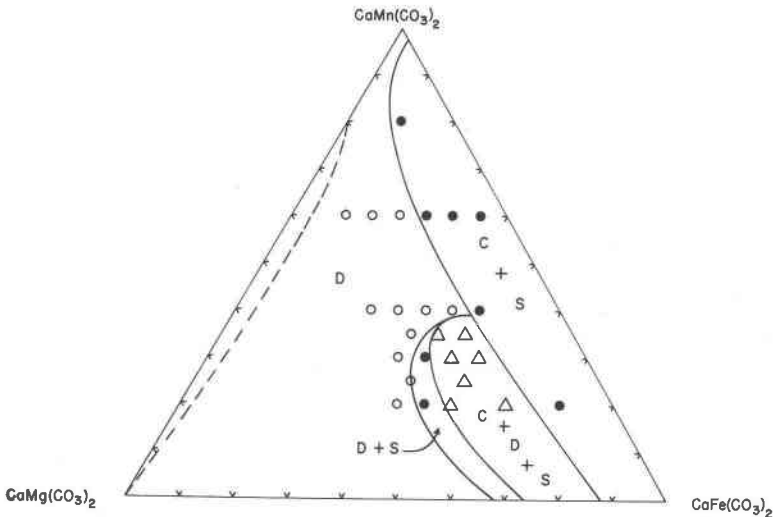
[1] Refer to footnote, page 882.

Fig. 4. Subsolidus relations on the dolomite join, $CaMg(CO_3)_2$-$CaFe(CO_3)_2$-
$CaMn(CO_3)_2$. Symbols as in Fig. 1.

presence and extent of a third two-phase area has been inferred (Fig. 4, broken line) from phase relations in the system $CaCO_3$-$MgCO_3$-$MnCO_3$ (Goldsmith and Graf, 1960) and on the join $CaMg(CO_3)_2$-$CaMn(CO_3)_2$ (this paper). The compositions of all phases within two and three-phase areas are quaternary and have not been determined in this study.

DISCUSSION OF THE QUATERNARY SYSTEM

The compositions of the large majority of natural carbonates and carbonate assemblages lie in the Ca-rich portion of the quaternary system. Experiments in this region proved fruitless due to reaction problems similar to those encountered in the systems $CaCO_3$-$MgCO_3$-$MnCO_3$ (Goldsmith and Graf, 1960) and $CaCO_3$-$MgCO_3$-$FeCO_3$ (Goldsmith et al., 1962). However, phase relations on bounding planes provide some insight into quaternary relations.

Subsolidus relations in the Ca-rich portions of the systems $CaCO_3$-$MgCO_3$-$FeCO_3$ and $CaCO_3$-$MgCO_3$-$MnCO_3$ and on the dolomite join are sketched in a tetrahedral diagram (Fig. 5). In order to make use of data available for the dolomite join and for the system $CaCO_3$-$MgCO_3$-$FeCO_3$ (Rosenberg, 1967), the diagram has been drawn for a temperature of 450°C. Subsolidus relations on the plane $CaCO_3$-$CaMg(CO_3)_2$-$CaMn(CO_3)_2$ (Fig. 5) are estimated from data at 500°C and 10 kbars for the ternary system $CaCO_3$-$MgCO_3$-$MnCO_3$ (Goldsmith and Graf, 1960) and from data for the join $CaMg(CO_3)_2$-$CaMn(CO_3)_2$ (this paper).
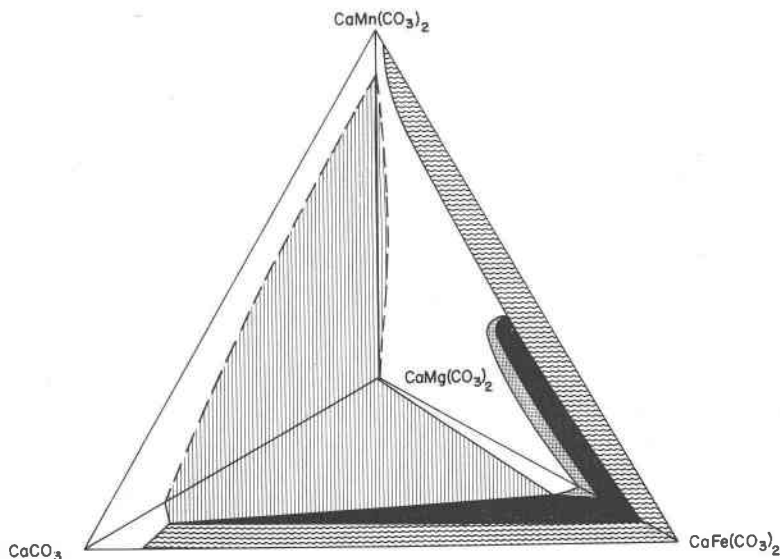
Fig. 5. A sketch illustrating subsolidus relations on planes bounding the Ca-rich portion of the quaternary system $CaCO_3$-$MgCO_3$-$MnCO_3$ at 450°C; $CaCO_3$-$CaMg(CO_3)_2$-$CaFe(CO_3)_2$, Rosenberg (1967); $CaCO_3$-$CaMg(CO_3)_2$-$CaMn(CO_3)_2$, Goldsmith and Graf (1960) and this paper; $CaMg(CO_3)_2$-$CaFe(CO_3)_2$-$CaMn(CO_3)_2$, this paper.

Blank area, one phase, disordered or cation-ordered (dolomite) solid solution. Shaded areas, two phases; straight lines, Ca-rich solid solution and dolomite solid solution; wavy lines, Ca-poor and Ca-rich solid solutions; stippled area, dolomite solid solution and Ca-poor solid solution. Filled area, three phases, Ca-rich solid solution, Ca-poor solid solution, and dolomite solid solution.

Extension of phase areas from the bounding planes into the tetrahedron suggests that the Ca-rich portion of the quaternary system (Fig. 5) contains one single-phase, one three-phase and three two-phase volumes; all of these phase volumes are represented on the dolomite join. The one-phase volume includes disordered and cation-ordered solid solutions; no attempt has been made to delimit the extent of ordering. These subsolidus relations are merely inferred and remain to be established in future studies of the quaternary system.

RELATION TO NATURAL DOLOMITES

A detailed comparison of synthetic and natural dolomites is difficult because almost all natural compositions are quaternary solid solutions and few lie precisely on the dolomite join. Excess $CaCO_3$, although very often present in dolomites, rarely amounts to more than 10 mole percent and frequently is less than 5 mole percent (Smythe and Dunham, 1947;

Goldsmith *et al.*, 1962). The dolomite join, therefore, does provide a close approach to the compositions of many natural dolomites.

The mineral dolomite commonly contains small amount of $MnCO_3$ usually not exceeding 10 mole percent $CaMn(CO_3)_2$ (Smythe and Dunham, 1947; Goldsmith *et al.*, 1962). Rosenberg (1960) noted that the compositions of natural Fe(Mn)-bearing dolomites lie close to the one-phase area in the system $CaCO_3$-$MgCO_3$-$FeCO_3$ at 500°C suggesting that no drastic change in subsolidus relations takes place with the addition of small amounts of $MnCO_3$ to the ternary system. This observation is confirmed by experimental results obtained for the dolomite join.

The presence of $MnCO_3$ does affect the position of phase boundaries in the system $CaCO_3$-$MgCO_3$-$FeCO_3$ to an extent which is significant if the maximum $FeCO_3$ content of dolomite is to find application in geothermometry (Rosenberg, 1967). Neglecting excess $CaCO_3$, it appears that for the large majority of natural dolomites, failure to consider $MnCO_3$ content will result in lower apparent temperatures of formation. Although the extent of displacement of phase boundaries is known for compositions lying on the dolomite join at 450°C, the limited data available and the presence of excess $CaCO_3$ in natural dolomites prohibit quantitative evaluation for natural compositions. When the positions of phase boundaries in the Ca-rich portion of the quaternary system (Fig. 5) are established over a suitable temperature range and the effect of the presence of $MnCO_3$ and excess $CaCO_3$ on the maximum $FeCO_3$ content of dolomite can be evaluated simultaneously, useful temperature estimates may be possible.

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