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SUBSOLIDUS RELATIONS IN THE SYSTEM $CaCO_3$-$MgCO_3$-$FeCO_3$ BETWEEN 350° AND 550°C

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ABSTRACT

Subsolidus relations in the system $CaCO_3$-$MgCO_3$-$FeCO_3$ have been studied in the temperature range 350–550°C at total pressures largely between 2 and 3 kilobars, using "hydrothermal" apparatus and cold seal pressure vessels.

Under these conditions, the system contains one three-phase, three two-phase and three one-phase areas. Two one-phase areas of disordered, ternary solid solutions occupy a small field close to the $CaCO_3$ end-member and a narrow region along the binary join $MgCO_3$-$FeCO_3$. A third one-phase area of cation-ordered solid solutions extends from dolomite along the join $CaMg(CO_3)_2$-$CaFe(CO_3)_2$, departs from this join after traversing approximately two-thirds of its length and terminates in the $CaCO_3$-rich portion of the system without reaching the binary join $CaCO_3$-$FeCO_3$. Two disordered solid solutions coexist with a cation-ordered dolomite solid solution in a three-phase area, located in the Mg-poor portion of the system. With increasing temperature the field of dolomite solid solution extends further toward the composition $CaFe(CO_3)_2$ and the three-phase area is displaced toward the binary join $CaCO_3$-$FeCO_3$. The iron analog of dolomite, the compound $CaFe(CO_3)_2$, which has not been reported as a mineral, lies in a two-phase area in the temperature range of this study.

The $FeCO_3$ content of dolomites synthesized from bulk compositions lying within the three-phase area approach the maximum $FeCO_3$ content observed in natural dolomites ($\sim$35 mole %). Potential applications of the $FeCO_3$ content of natural dolomite to geothermometry are suggested.

INTRODUCTION

To a first approximation, the compositions of rock-forming carbonates may be considered to lie close to the system $CaCO_3$-$MgCO_3$-$FeCO_3$, since the proportion of the fourth significant component, $MnCO_3$, is very often low. Mineral compositions in the system $CaCO_3$-$MgCO_3$-$FeCO_3$ are members of three ternary solid solution series which are well known from analytical studies of mineral samples and previous experimental investigations. These solid solutions include two disordered series; calcite solid solutions and siderite-magnesite[1] solid solutions, and one cation-ordered series; dolomite solid solutions (ferroan dolomites and ankerites).

The present investigation has been confined to temperatures between 350° and 550°C, which are significantly higher than those encountered in

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[1] Refers to members of the complete binary solid solution series between siderite and magnesite.

sedimentary environments but lie within or close to the temperature range in which many carbonate-bearing hydrothermal deposits are believed to have formed. Subsolidus relations reported in this paper are applicable to the interpretation of carbonate assemblages in these deposits and may provide some insight into assemblages formed at lower temperatures.

Previous Investigations

Although the system $CaCO_3$-$MgCO_3$ has been studied most recently by Goldsmith and Heard (1961), the limits of the dolomite-calcite and dolomite-magnesite miscibility gaps were taken from an earlier study by Harker and Tuttle (1955*b*) which provides data in the *P-T* range of the present investigation. A complete series of solid solutions exists in the system $MgCO_3$-$FeCO_3$ at temperatures at least as low as 295°C (Rosenberg, 1963*b*). The position of the solvus in the system $CaCO_3$-$FeCO_3$ has been determined by Goldsmith, *et al.* (1962) and, in the temperature range of this study, by Rosenberg (1963*a*). The iron analog of dolomite, $CaFe(CO_3)_2$, has not been synthesized to date nor has it been reported as a mineral; the 1:1 composition in the system $CaCO_3$-$FeCO_3$ lies in a two-phase area between 300°C and 800°C (Goldsmith, *et al.*, 1962; Rosenberg, 1963*a*).

Subsolidus relations in the system $CaCO_3$-$MgCO_3$-$FeCO_3$ have been studied in the temperature range 600–800°C at pressures of 10–15 kilobars (Goldsmith, *et al.*, 1962). Experimental data for the ternary system heretofore unpublished (Rosenberg, 1960) are in general accord with those of the above study; significant differences in the results of these investigations will be considered in a later section of this paper.

Experimental Details

Experiments were carried out using cold-seal pressure vessels and "hydrothermal" apparatus essentially identical to that described by Harker and Tuttle (1955*a*).

Starting compositions were prepared as mechanical mixtures of precipitated $CaCO_3$, which proved to be more reactive than the reagent-grade material, reagent-grade MgO and purified $FeC_2O_4 \cdot 2H_2O$. $CaCO_3$ was precipitated from nitrate solutions by Na_2CO_3; the precipitate was washed five times with hot water and dried carefully, along with the other starting materials, before weighings were made. MgO and $FeC_2O_4 \cdot 2H_2O$ react quickly and completely to give the respective carbonates under the conditions of these experiments.

Early in the study it was found that the addition of small quantities of dilute alkali carbonate solutions to samples promoted reaction appreciably. Initially, 0.1M Na_2CO_3 and Li_2CO_3 solutions were used but later 0.01M solutions were substituted in experiments involving almost all compositions in order to keep the alkali content of the samples to a minimum. The more dilute solutions proved to be highly effective except for a few ternary compositions close to the binary join $MgCO_3$-$FeCO_3$. The total weight of alkali carbonate added to each sample was never in excess of 1 weight percent. X-ray reflections attributable to alkali carbonates were not observed and no changes in d were detected in end-member carbonates treated with alkali carbonate solutions and exposed to experimental conditions.

Starting materials were wrapped in gold-foil envelopes to which a drop of an alkali carbonate solution was added. Pure, bone-dry CO_2 and CO were used to provide the experimental atmosphere, the function of the CO being to prevent the oxidation of iron. The procedure for admitting the experimental atmosphere into the pressure vessel has been described previously (Rosenberg, 1963*a*). Pressures of CO_2 [$+\sim 2\%$ (vol.) CO] sufficient to prevent the dissociation of the carbonates were used throughout these experiments. Samples were held under the desired P-T conditions for varying lengths of time and quenched at pressure by immersion of the reaction vessel in water. Products were identified by their X-ray powder diffraction patterns using Ni-filtered, Cu-radiation which was more readily available than Fe-radiation.

During the course of the study, it was found that, if runs were quenched and samples remixed at intervals of 3 to 5 days, the total time necessary to approach equilibrium was considerably reduced. This procedure was adopted for all experiments reported in this paper. Equilibrium was assumed to have been attained when d_{211}, which varies with carbonate composition (Rosenberg, 1960, 1963*a*; Goldsmith and Graf, 1960), was found to be constant ($\pm 0.01° 2\theta$) for all phases present in a sample after two successive reruns. X-ray measurements were made using an internal standard, CdF_2, which has a conveniently located reflection at 28.70° CuK_α. The total time necessary to approach equilibrium varied from two days at 550°C, to one month at 350°C.

EXPERIMENTAL RESULTS

Ternary relations at 450°C.—An isothermal section at 450°C. based on experimental data is shown in Figure 1[1]. Phase boundaries were deter-

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[1] A table completely summarizing the experimental data has been deposited as Document 9423 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D. C. 20242. Copies may be secured by citing the Document number and remitting in advance $1.25 for photoprints or $1.25 for microfilm.

mined within 1–2 mole percent by the presence or absence of phases in experiments with different bulk compositions. The limits of the field of dolomite solid solution were scrutinized more closely than other phase boundaries and are believed to be known within 1 mole percent. X-ray ordering reflections were observed in all members of the dolomite solid solution series (Rosenberg, 1960).

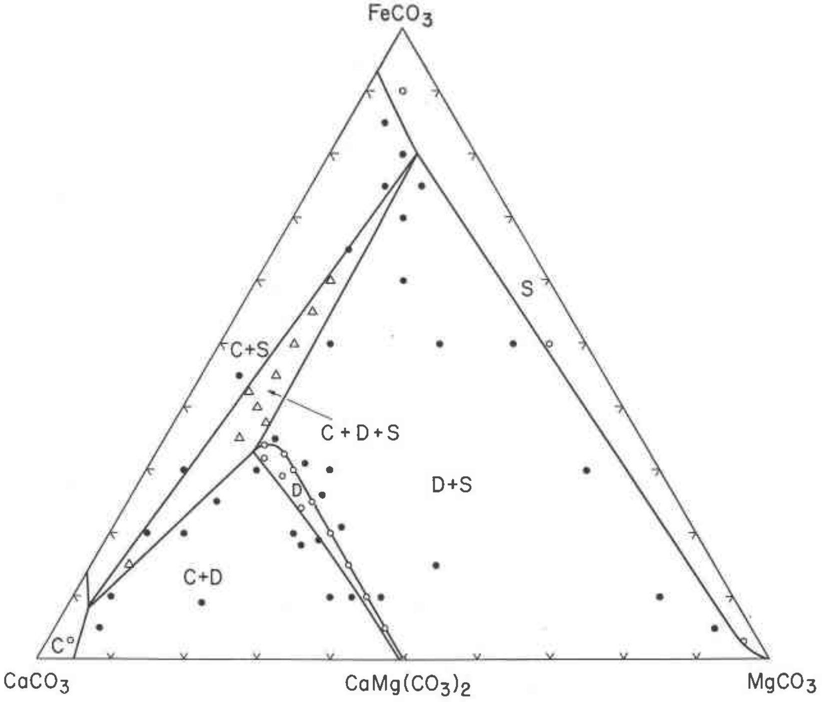

FIG. 1. Subsolidus relations in the system $CaCO_3$-$MgCO_3$-$FeCO_3$ at 450°C. D—dolomite solid solution; C—calcite solid solution; S—siderite-magnesite solid solution. Open circles, one-phase; filled circles, two-phase; and triangles, three-phase assemblages.

The ternary system (Fig. 1) contains one three-phase, three two-phase and three one-phase areas. Two one-phase areas of disordered solid solutions include a small field close to the end-member $CaCO_3$ and a narrow region along the binary join $MgCO_3$-$FeCO_3$. A third one-phase area of cation-ordered solid solutions extends from dolomite along the join $CaMg(CO_3)_2$-$CaFe(CO_3)_2$, but departs from the join after traversing approximately two-thirds of its length and terminates in the $CaCO_3$-rich portion of the system. The three two-phase areas are extensions into the ternary system of miscibility gaps observed in the systems $CaCO_3$-

$MgCO_3$ (Harker and Tuttle, 1955*b*) and $CaCO_3$-$FeCO_3$ (Rosenberg, 1963*a*). One ordered and two disordered solid solutions of fixed composition[1] coexist in a three-phase triangle located in the magnesium-poor portion of the system. In accord with previous investigations, the 1:1 composition in the system $CaCO_3$-$FeCO_3$ lies in a two-phase area in the present study.

Measurement of the angular distance ($\Delta 2\theta$) between the dolomite (211) X-ray reflection and that of internal standard CdF_2 yields values which vary linearly with the composition of dolomites synthesized from mixtures lying on the join $CaMg(CO_3)_2$-$CaFe(CO_3)_2$ within the one-phase area (Fig. 2). The $\Delta 2\theta$ values of dolomites synthesized from compositions on the above join but beyond the one-phase area are lower than those predicted by the linear relationship (Fig. 2) suggesting that the field of dolomite solid solution terminates in the $CaCO_3$-rich portion of the system (Rosenberg, 1960). The field of dolomite solid solution described by Goldsmith, *et al.*, (1962) at temperatures above 600°C also terminates in the $CaCO_3$-rich portion of the system.

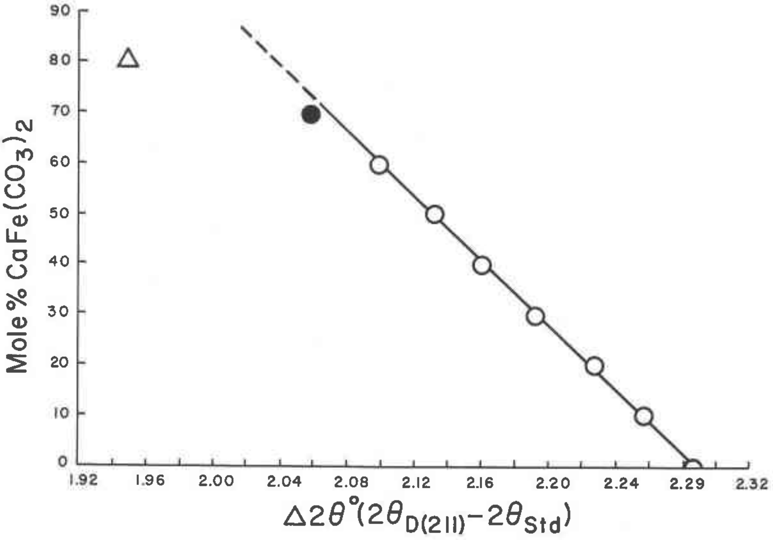

FIG. 2. $\Delta 2\theta$ ($2\theta_{D(211)}$-$2\theta_{std.}$) of dolomites synthesized from compositions on the join $CaMg(CO_3)_2$-$CaFe(CO_3)_2$ at 450°C. Symbols as in Fig. 1.

The composition of dolomite solid solution in equilibrium with two dis-

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[1] Fig. 1 may be considered to be isobaric since subsolidus relations are relatively insensitive to variations in pressure and experiments were conducted over a narrow pressure range.

ordered solid solutions was estimated using the $\Delta 2\theta$ values of these dolomites (1.95° at 450°C, Fig. 2) and the position of the phase boundary representing the maximum miscibility of $CaCO_3$ in dolomite. By interpolation between the $\Delta 2\theta$ values for the end-member pairs $CaCO_3$-$CaMg(CO_3)_2$ and $CaCO_3$-$CaFe(CO_3)_2$,[1] compositions along each join at which hypothetical, ideal solid solutions would have $\Delta 2\theta$ values of 1.95° were determined and a straight line drawn between these compositions on a ternary diagram (Fig. 3). The composition of the dolomite end-member of the three-phase triangle should lie close to this line. An extrapolation of the phase boundary representing the maximum miscibility of $CaCO_3$ in dolomite, which is known to within 1 mole percent, intersects the $\Delta 2\theta = 1.95°$ line at a composition (mole %) of 54 $CaCO_3$, 33 $FeCO_3$, 13 $MgCO_3$ (Fig. 3). This composition is believed to closely approximate the composition of the dolomite end-member of the three-phase triangle at 450°C. A

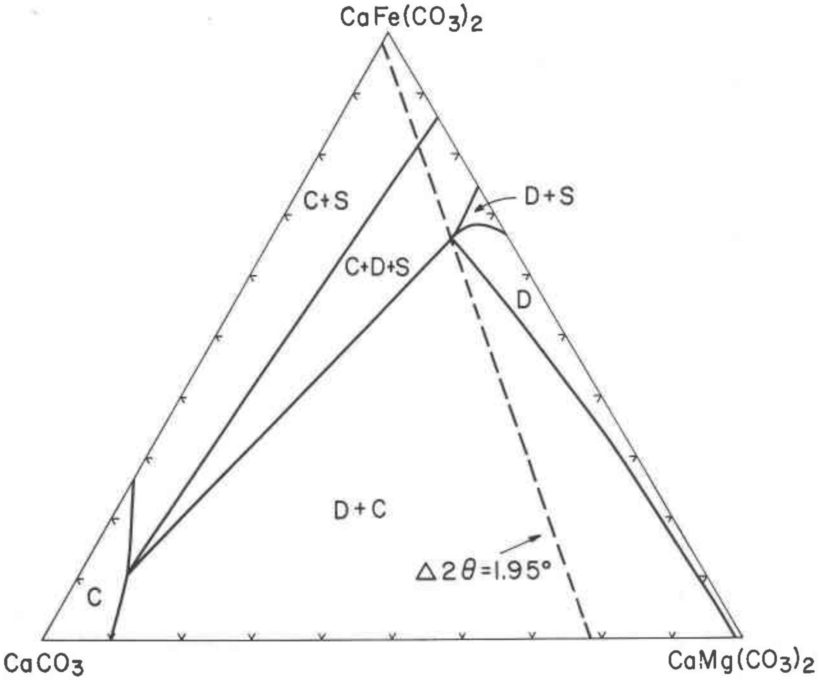

FIG. 3. Composition of dolomite coexisting with calcite and siderite solid solutions at 450°C. Symbols as in Fig. 1.

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[1] The $\Delta 2\theta$ of hypothetical $CaFe(CO_3)_2$ was assumed to lie midway between those of the two end-members, $CaCO_3$ and $FeCO_3$, perhaps introducing a small error (Goldsmith, *et al.*, 1962).

more detailed discussion of this procedure and its application to analogous dolomite solid solutions at 400°, 500° and 550°C has been given by Rosenberg (1960).

Effect of temperature. In addition to an isothermal section at 450°, Rosenberg (1960) shows sections at 400° and 500°C which are quite similar to that at 450°C (Fig. 1). Critical data for these sections are given in the table[1] along with limited data at 350°C and 550°C.

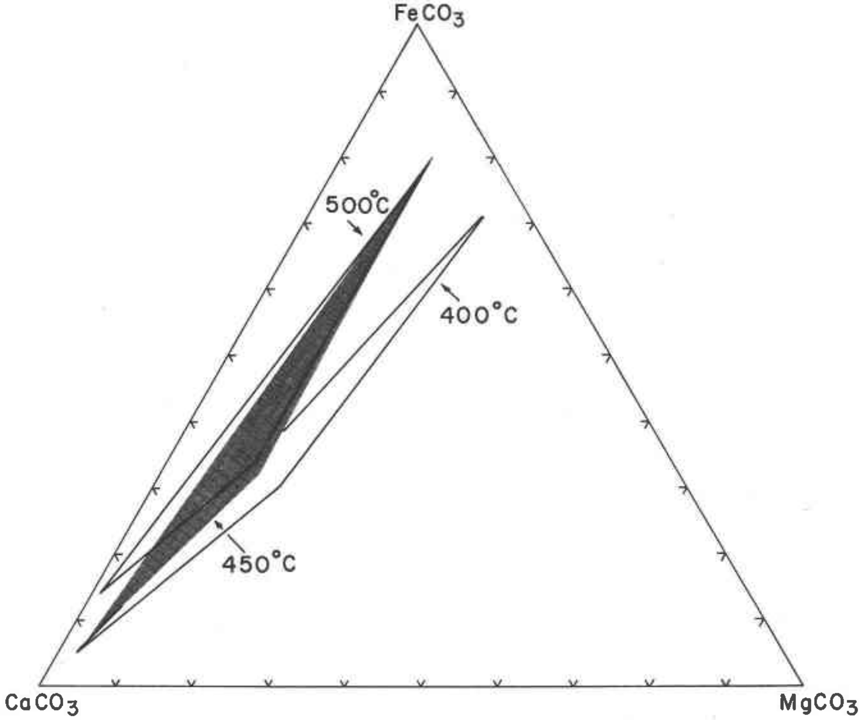

FIG. 4. Three-phase triangles for temperatures of 400°C, 450°C (shaded), and 500°C shown superimposed.

The most significant change in subsolidus relations with increasing temperature is in the position of the three-phase triangle and the extent of the field of dolomite solid solutions toward the composition $CaFe(CO_3)_2$. The effect of variations in temperature on ternary subsolidus relations is illustrated in Fig. 4 in which the positions of the three-phase triangles at 400°, 450° and 500°C are shown superimposed. Estimated compositions of dolomite end-members of the three-phase area between 350°

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[1] See footnote, p. 789.

and 550°C are given in Table 1. At temperatures of 400°C and above, dolomite compositions are based on $\Delta 2\theta$ measurements and on the positions of ternary phase boundaries; these compositions are believed to be known to within approximately 1 mole percent. At 350°C precise $\Delta 2\theta$ measurements were not possible and the data available provide only an upper limit for the maximum $FeCO_3$ content of end-member dolomite.

With increasing temperature, the maximum $FeCO_3$ content of dolomite increases (Table 1) and the entire three-phase triangle is displaced toward the binary join $CaCO_3$-$FeCO_3$ (Fig. 4). The increment of this displacement appears to be progressively smaller at higher temperatures suggesting that the field of dolomite solid solution is approaching a maximum in its extent toward the composition $CaFe(CO_3)_2$.

TABLE 1. ESTIMATED COMPOSITIONS OF DOLOMITE END-MEMBERS OF THREE-PHASE AREAS

Temp (°C)	$\Delta 2\theta$ $[2\theta_{(211)} - 2\theta_{std.}]$	Composition (mole %)		
		$FeCO_3$	$MgCO_3$	$CaCO_3$
350	not measured	<25	—	—
400	2.03 ±0.01	30	16.5	53.5
450	1.950±0.005	33	13	54
500	1.934±0.005	34	11.5	54.5
550	1.890±0.01	36	9	55

Goldsmith, *et al.*, (1962) describe three-phase triangles at 600° and 650°C which are broader and closer to $CaMg(CO_3)_2$ composition than those reported here. As a result, their one-phase areas of dolomite solid solution do not extend as far toward $CaFe(CO_3)_2$ composition at 600° and 650°C as do the fields observed in the present study at lower temperatures. However, the effect of pressure on ternary phase relations has not been evaluated and the difference in the ranges of total pressures used in these investigations (1.9–3.9 kilobars vs. 10–15 kilobars) may account for this discrepancy (Goldsmith, *et al.*, 1962).

RELATION TO NATURAL CARBONATES

Compositions of natural Fe-rich carbonates have been studied in a number of previous investigations. Although analyses of members of all three solid solution series have been reported (e.g. Smythe and Dunham, 1947; Shaw, 1959; Rosenberg, 1960), particular attention has been given to ferroan dolomites and ankerites. On the basis of mineral analyses, Smythe and Dunham (1947) concluded that the series of dolomite solid solutions extends from $CaMg(CO_3)_2$ to 70±5 mole percent $CaFe(CO_3)_2$. Shaw (1959) found a maximum $FeCO_3$ content of 35 mole percent in ankerites containing 50–56 mole percent $CaCO_3$. Estimated compositions of natural dolomites (Fe/Mn $>$ 5) based on $\Delta 2\theta$ and refractive index measurements (Rosenberg, 1960 and unpublished data) also contained up to 35 mole percent $FeCO_3$. Goldsmith, *et al.* (1962), observed a maximum $FeCO_3$ content of 31.3 mole percent in natural dolomites. Although Fe-rich carbonates undoubtedly form under a wide range of environmental conditions, compositions approaching the system $CaCO_3$-$MgCO_3$-$FeCO_3$ lie close to the experimentally determined one-phase areas described in this paper (Rosenberg, 1960).

Compositions of natural and synthetic dolomites cannot be compared in detail due to the presence of small, but significant, quantities of $MnCO_3$ in solid solution in the natural minerals. However, the tendency of dolomite to contain $CaCO_3$ in excess of 50 mole percent (Goldsmith and Graf, 1958) has been observed to extend to the ferroan varieties in both natural and synthetic materials (Rosenberg, 1960; Goldsmith, *et al.*, 1962). It is of interest to note that the maximum $FeCO_3$ content observed in natural dolomite ($\sim$35 mole percent) is close to that of synthetic materials prepared between 500° and 550°C in the present investigation. In the study by Goldsmith, *et al.* (1962), temperatures of approximately 800°C were required to synthesize dolomite compositions approaching the maximum $FeCO_3$ content observed in natural samples; at 600°C the maximum $FeCO_3$ content of synthetic dolomite was only about 23 mole percent. Temperatures of formation suggested by these data are significantly higher than those to be expected in natural environments. In order to account for this discrepancy, which seems to imply greater solubility of $FeCO_3$ in natural than in synthetic materials, Goldsmith, *et al.* (1962), suggest metastable solubility of $FeCO_3$ in the natural materials or a reversal in $FeCO_3$ solubility with increasing temperature. Since the present investigation provides no information on equilibrium compositions above 550°C, a reversal in $FeCO_3$ solubility in dolomite at higher temperatures is a definite possibility. Although metastable solubility of $FeCO_3$ in natural dolomites cannot be ruled out, synthesis of dolomites, approaching natural compositions at geologically reasonable temperatures in the present study, does not suggest such metastability.

Since the maximum $FeCO_3$ content of synthetic dolomite is temperature dependent and, to a first approximation, isothermally invariant, applications to geothermometry are possible. For natural compositions lying within the ternary system, the $FeCO_3$ content of dolomite might provide an approximate formation temperature for three-phase carbonate assemblages and a minimum formation temperature for one- and two-phase carbonate assemblages. However, these temperature estimates will be highly imprecise, even where the $MnCO_3$ content of the carbonates is negligible, due to the small increase in the maximum $FeCO_3$ content of dolomite above 450°C and the limited data available below 450°C. The ubiquitous presence of $MnCO_3$ in solid solution places further limitations on applications to geothermometry, at present. When more data are available at lower temperatures and when the effect of $MnCO_3$ content on the position of ternary phase boundaries is known, useful temperature estimates may be possible.

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