

Ternary iron, magnesium, calcium carbonates: A thermodynamic model for dolomite as an ordered derivative of calcite-structure solutions

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ABSTRACT

A ternary expansion of the generalized point approximation is the simplest model that can treat the order-disorder relations, phase equilibria, and solution enthalpy systematics for $(\text{Ca},\text{Mg},\text{Fe})\text{CO}_3$ solutions. A minimum of eight interaction parameters are needed to fit experimentally determined phase relations: two for each binary join, plus one each for asymmetry in the Ca-Fe and Ca-Mg joins. The model places limits on both the stable and metastable occurrence of dolomite-ankerite solid solution. Calculated phase relations show that the stability of ordered $\text{CaFe}(\text{CO}_3)_2$ is limited to $T < \sim 450^\circ\text{C}$ by the breakdown to calcite + siderite solid solutions. This maximum temperature rises with Mg content. Between 1000 and 1200 K, there is an isobaric singularity where tricritical calcite-dolomite-ankerite solid solution coexists with magnesite-siderite solid solution. For still higher temperatures, the stability of ordered dolomite-ankerite solid solution is limited to high Mg contents by the intersection of the order-disorder transition with the two-phase field boundaries for calcite + dolomite-ankerite solid solutions and magnesite-siderite + dolomite-ankerite solid solutions, as predicted by Goldsmith et al. (1962). The maximum temperature for metastability of ordered $\text{CaFe}(\text{CO}_3)_2$ is predicted to be 767°C , rising more than 300°C with complete Mg for Fe substitution.

INTRODUCTION

Phase relations in the $(\text{Ca},\text{Mg},\text{Fe})\text{CO}_3$ system are dominated by interactions among the disordered calcite structure solutions and the ordered, intermediate dolomite solutions. Because these two solutions are related by a high-temperature disordering transition, we have investigated the phase relations with a new thermodynamic model for ternary solutions that exhibit order-disorder and phase separation. Figure 1 shows high-pressure stability fields for the two solutions, omitting polymorphism near the CaCO_3 apex. At relatively low temperatures, the disordered phase is limited to compositions near CaCO_3 (Cc) and near $(\text{Mg},\text{Fe})\text{CO}_3$ (magnesite-siderite solid solution, or Mag-Sid). The ordered intermediates with compositions near $\text{Ca}(\text{Mg},\text{Fe})(\text{CO}_3)_2$ (dolomite-ankerite solid solution, or Dol-Ank) disorder at high temperatures to the calcite structure. At higher temperatures there is a complete solution between CaCO_3 and FeCO_3 with the calcite structure (Davidson et al., 1993). To date, attempts to synthesize an ordered ankerite of $\text{CaFe}(\text{CO}_3)_2$ composition have failed, but model calculations suggest that it may occur stably at temperatures below $\sim 720\text{ K}$ (and pressures high enough to prevent decarbonation). The simplest solution model that can account for dolomite as an ordered derivative structure of the disordered calcite

structure solution, based on a ternary extension of the generalized point approximation (GPA) given by Capobianco et al. (1987), is presented. For a fundamentally different approach to this system, based on separate free energy functions for ordering and unmixing processes, the reader is referred to the recent work of McSwiggen (1993). Calibration of eight binary interaction parameters (including two describing asymmetry in the Ca-Mg and Ca-Fe binary joins) with available experiments and new experiments in the Fe-Ca join afford quantitative agreement with phase equilibria and critical temperatures for disordering, and qualitative agreement with mixing enthalpy measurements.

MODEL FORMALISM

The simplest treatment of the order-disorder transition as a higher order transition that can also produce the low-temperature two-phase fields for coexisting Cc + Dol-Ank and Dol-Ank + Mag-Sid and positive mixing enthalpy values for disordered $\text{CaMg}(\text{CO}_3)_2$ is a ternary extension of the GPA (Capobianco et al., 1987; Burton and Davidson, 1988). Before presenting its extension to ternary systems, we review briefly the GPA as previously applied to binary carbonate solutions. The GPA is similar to the model presented by Meierjng (1963) for metallurgical systems in which magnetic ordering transitions intersect two-phase fields, except that the maximum temperature of disordering occurs near the 50:50 composition in the 1:1 layered structures as in dolomite, rather

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than at an end-member as in Meierjring's examples. In the GPA, all ordering is treated as long-range, but competing interaction energies (governed by W_{ira} , for repulsive intralayer pairs among Ca-Mg and Ca-Fe, and by W_{ier} , for attractive interlayer pairs among Ca-Mg and Ca-Fe), favor cation segregation into alternating Ca-rich layers and Mg-rich layers. The free energy of solution G_{sol} (excluding mechanical mixing contributions from disordered end-members) for the double carbonate unit in a binary join is then given by

$$G_{\text{sol}} = W_{\text{ier}}[X - X^2(1 - S^2)] + W_{\text{ira}}[X - X^2(1 + S^2)] + \sum_{i,j} RT(X_{ij} \ln X_{ij}). \quad (1)$$

For the CaCO_3 - MgCO_3 join, X_{ij} is the mole fraction i of Ca and Mg on the j site, dolomite layers A (Ca-rich) and B (Mg-rich); $X = X(\text{CaCO}_3)$; and the ordering parameter S is defined such that $X_{\text{Ca,A}} = X + XS$. Then the enthalpy of solution (again excluding mechanical mixing contributions) is given by

$$H_{\text{sol}} = (X - X^2)[W_{\text{ier}} + W_{\text{ira}}] + (X^2 S^2)[W_{\text{ier}} - W_{\text{ira}}]. \quad (2)$$

As Burton and Davidson discussed for systems in which W_{ira} is positive, W_{ier} is negative, and $[W_{\text{ier}} + W_{\text{ira}}]$ is positive, phase separation is possible, and enthalpy of mixing values can be positive for the disordered solution ($S = 0$) but negative for the ordered intermediate phase ($S = 1$)—the only possibility allowed by the original Bragg-Williams disordering model.

For ternary systems, the model can be derived from the addition of configurational entropy contributions of the form $RT(X_{ij} \ln X_{ij})$ and pairwise energy terms, $Z_{kl} X_k X_l E_{kl}$, where Z_{kl} is the coordination number for pairs of atoms k and l , E_{kl} is their interaction energy, and their pair probability is approximated by the product of site fractions X_k and X_l representing, for example, Ca on the A layer and Mg on the B layer. In terms of the binary interaction parameters shown above, we can express G_{sol} for the $(\text{Ca,Mg,Fe})(\text{CO}_3)$ system as

$$\begin{aligned} G_{\text{sol}} = & X_{\text{Ca}} X_{\text{Fe}} [2W_{\text{ira}}(\text{Fe-Ca}) + W_{\text{ier}}(\text{Fe-Ca})] \\ & + X_{\text{Ca}}^2 S^2 W_{\text{ier}}(\text{Fe-Ca}) \\ & + X_{\text{Mg}} X_{\text{Fe}} [2W_{\text{ira}}(\text{Fe-Mg}) + W_{\text{ier}}(\text{Fe-Mg})] \\ & + X_{\text{Mg}}^2 V^2 W_{\text{ier}}(\text{Fe-Mg}) \\ & + X_{\text{Ca}} X_{\text{Mg}} [2W_{\text{ira}}(\text{Mg-Ca}) + W_{\text{ier}}(\text{Mg-Ca})] \\ & + X_{\text{Ca}} X_{\text{Mg}} SV [W_{\text{ier}}(\text{Mg-Ca}) - W_{\text{ier}}(\text{Mg-Fe}) \\ & \quad - W_{\text{ier}}(\text{Fe-Ca})] \\ & - X_{\text{Ca}} X_{\text{Mg}} (1 + SV) \\ & \cdot [W_{\text{ira}}(\text{Mg-Ca}) - W_{\text{ira}}(\text{Mg-Fe}) - W_{\text{ira}}(\text{Fe-Ca})] \\ & - W_{\text{ira}}(\text{Fe-Ca}) [X_{\text{Ca}}(1 - X_{\text{Ca}}) + X_{\text{Ca}}^2 S^2] \\ & - W_{\text{ira}}(\text{Fe-Mg}) [X_{\text{Mg}}(1 - X_{\text{Mg}}) + X_{\text{Mg}}^2 V^2] \\ & + RT[X_{\text{Ca,A}} \ln(X_{\text{Ca,A}}) + X_{\text{Ca,B}} \ln(X_{\text{Ca,B}}) \\ & \quad + X_{\text{Mg,A}} \ln(X_{\text{Mg,A}}) + X_{\text{Mg,B}} \ln(X_{\text{Mg,B}}) \\ & \quad + X_{\text{Fe,A}} \ln(X_{\text{Fe,A}}) + X_{\text{Fe,B}} \ln(X_{\text{Fe,B}})] \end{aligned} \quad (3)$$

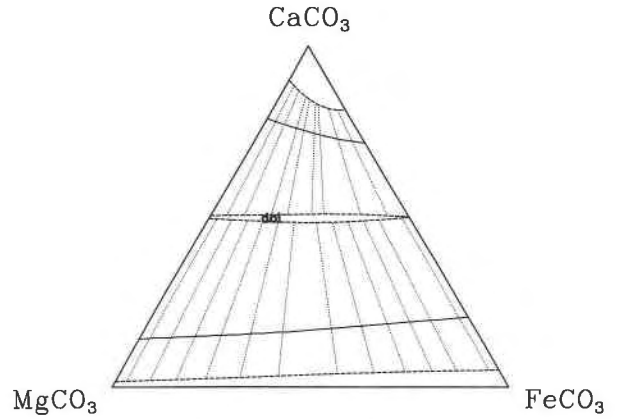


Fig. 1. Stability fields for the principal solid solutions in the system CaCO_3 - MgCO_3 - FeCO_3 . Note that the stability field for Dol-Ank includes the hypothetical Mg-free end-member, which may be stable at low temperatures. The solid curves indicate the disordering spinodal, inside which the disordered solution is unstable with respect to assemblages that include the ordered intermediate.

where site occupancies $X_{\text{Ca,A}}$, $X_{\text{Ca,B}}$, $X_{\text{Mg,A}}$, $X_{\text{Mg,B}}$, $X_{\text{Fe,A}}$, and $X_{\text{Fe,B}}$ are related to bulk composition variables X_{Ca} , X_{Mg} , and X_{Fe} and the two order parameters S and V as follows:

$$\begin{aligned} X_{\text{Ca,A}} &= X_{\text{Ca}} + X_{\text{Ca}} S \\ X_{\text{Mg,A}} &= X_{\text{Mg}} - X_{\text{Mg}} V \\ X_{\text{Fe,A}} &= 1 - X_{\text{Ca}} - X_{\text{Ca}} S - X_{\text{Mg}} + X_{\text{Mg}} V \\ X_{\text{Ca,B}} &= X_{\text{Ca}} - X_{\text{Ca}} S \\ X_{\text{Mg,B}} &= X_{\text{Mg}} + X_{\text{Mg}} V \\ X_{\text{Fe,B}} &= 1 - X_{\text{Ca}} + X_{\text{Ca}} S - X_{\text{Mg}} - X_{\text{Mg}} V. \end{aligned}$$

Equilibrium values of the order parameters are found by simultaneously minimizing G_{sol} with respect to S and V , so that $G_S = 0$ and $G_V = 0$, while the determinant of the Hessian matrix of second derivatives with respect to the ordering variables ($G_{SS} G_{VV} - G_{SV}^2$) is positive. The disordering transition surface is found as the locus of points $(T, X_{\text{Ca}}, X_{\text{Mg}})$ for which this determinant is zero, with $S = 0$ and $V = 0$.

Examples of G_{sol} as a function of X_{Ca} and X_{Mg} for idealized systems are given in Figures 2 and 3. Figure 2 illustrates the case where one binary join exhibits phase separation and a disordering transition, but the other two binary joins exhibit ideal mixing. The regions of instability that flank the ordered-phase stability field vanish at tricritical points in the ternary compositional system, much as they do in binary T - X sections, where two-phase fields for coexisting ordered + disordered solutions are replaced above tricritical temperatures by a higher order transition line. The idealized example of a dolomite-an-

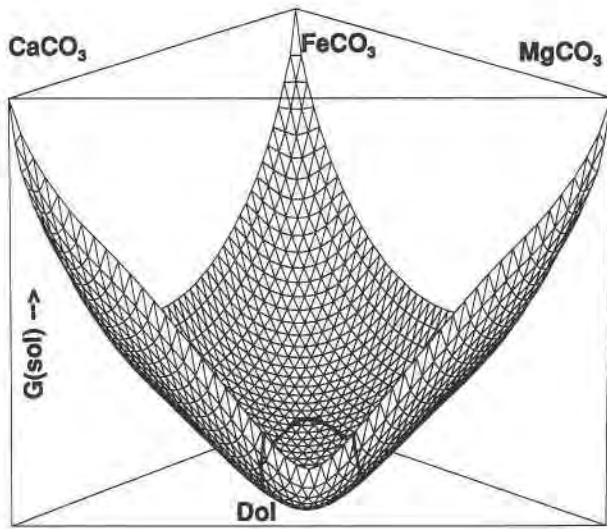


Fig. 2. Idealized ternary $G_{\text{sol}}-X$ surface; one binary join shows tricritical phase relations, whereas the remaining two are ideal solutions. The heavy line indicates the ordering spinodal, inside which the disordered solution is unstable.

kerite solid solution is illustrated in Figure 3, where two binaries exhibit ordered-phase stability fields with flanking two-phase regions, and the third binary is an ideal solution. In this case, the ordered-phase stability field extends across the ternary system for compositions near $X_{\text{Ca}} = 0.5$ and X_{Mg} from 0 to 0.5, where magnesite-siderite is the ideally mixing binary join. For the system $(\text{Ca},\text{Mg},\text{Fe})\text{CO}_3$, the model must include asymmetry in both Ca-bearing binaries; work by Goldsmith and co-workers (Goldsmith and Heard, 1961; Goldsmith et al., 1962) showing that the field for coexisting disordered carbonates is skewed toward the Ca-free end has been extensively corroborated [e.g., Davidson et al., 1993, for $(\text{Fe},\text{Ca})\text{CO}_3$; Irving and Wyllie, 1975, for $(\text{Mg},\text{Ca})\text{CO}_3$]. Also, the Fe end-member of Dol-Ank has never been found naturally and has eluded synthesis to date, implying that it is much less stable than Fe-free dolomite; therefore, it is clear that models for the Ca-Mg and the Ca-Fe joins cannot be identical or even topologically equivalent. However, since the GPA can produce the various phase diagram topologies involving stability fields for the calcite-structure and dolomite-structure solutions reviewed by Goldsmith (1983), we can proceed with this model as a general expression for ternary solutions with ordered, intermediate phases. [See for example, the possibilities shown by Davidson and Burton (1987) for a topologically equivalent case, that of omphacitic pyroxenes.]

Subsystem $(\text{Fe},\text{Ca})\text{CO}_3$

Experiments of Goldsmith et al. (1962), Rosenberg (1963), and Davidson et al. (1993) were fitted to a binary GPA model with the additional constraint that the assemblages of coexisting disordered solutions be stable,

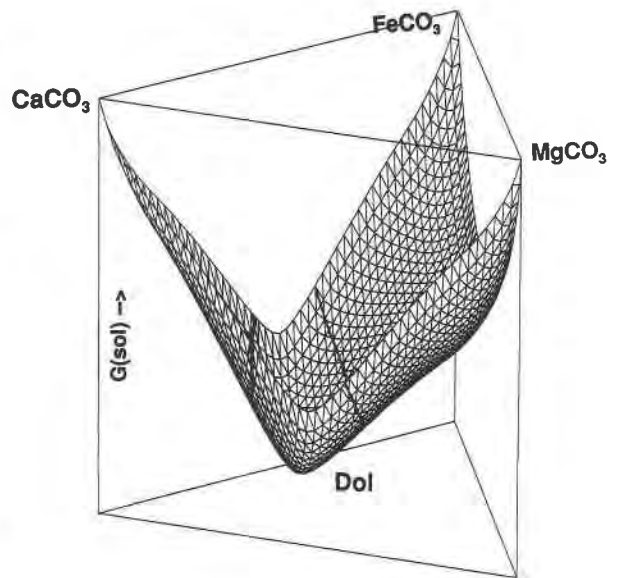


Fig. 3. Idealized $G_{\text{sol}}-X$ surface for the system CaCO_3 - MgCO_3 - FeCO_3 ; two binary joins show identical tricritical phase relations and the third is an ideal solution. The heavy lines represent the ordering spinodals, indicating that the ordered intermediate is stable for all Mg-Fe ratios.

rather than metastable, from consolute conditions down to temperatures below 600 °C. We interpret the Goldsmith results, which are from synthesis experiments, to mean that the ordered phase is less stable than assemblages of two coexisting disordered solutions. Figure 4 shows the resulting model phase relations; values for W_{ier} and W_{ira} are listed in Table 1. Notice the predicted maximum temperature for ankerite stability of 710–720 K (~450 °C); the disordering spinodal (light line) is always metastable, as in the topology of Burton's phase diagram for the system $(\text{Ca},\text{Zn})\text{CO}_3$ (1987, his Fig. 4). Experiments to synthesize ordered $\text{CaFe}(\text{CO}_3)_2$ have not succeeded to date, and so the prediction remains untested.

Subsystem $(\text{Mg},\text{Ca})\text{CO}_3$

Because this join is geologically the most important, it has been extensively studied. The general topology shown by Goldsmith (1983) still leaves some uncertainty in the compositions of coexisting Cc + Dol, as well as compositions of disordered and ordered Dol + Mag. For a discussion of early phase equilibrium studies, the reader is referred to Anovitz and Essene (1987). The recent work of Gottschalk and Metz (1992) provides new information on the maximum Ca contents of Cc coexisting with Dol, but, as they point out on p. 41–42, there are few exsolving experiments to reverse compositions for Cc + Dol. Experimental problems include slow subsolidus reaction rates (noted also by Powell et al., 1984) and potential disequilibrium in the state of order of dolomite, discussed by Schulz-Güttler (1986).

The critical temperature for dolomite disordering is known with greater precision. Reeder and Nakajima

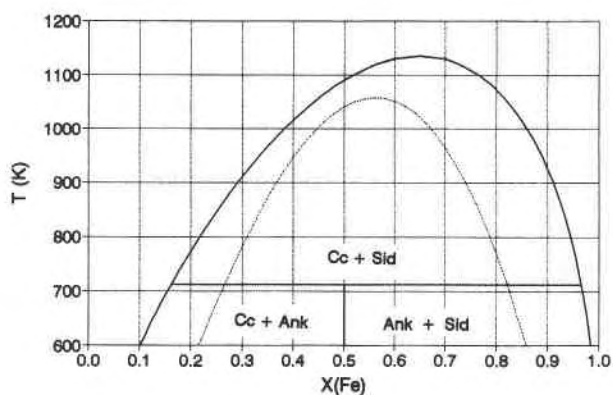
CaCO₃ - FeCO₃

Fig. 4. Phase relations for the join CaCO₃-FeCO₃. Model curves are calculated with the parameters given in Table 1. The metastable disordering spinodal is shown by the light curve; ordered ankerite stability is restricted to compositions very near CaFe(CO₃)₂ and temperatures below 720 K. After Davidson et al. (1993).

(1982) located the temperature for a natural dolomite, at 1100–1150 °C. The compositional dependence of the disordering temperature is not well known, owing to experimental problems, including rapid ordering rates that interfere in quenching the disordered state (Reeder, personal communication) and difficulties in detecting the low Bragg intensities unique to the ordered dolomite structure, especially for specimens that have only weak long-range order. Goldsmith's (1983) careful interpretation of the experimental data on variation of disordering temperature with composition shows that it does not change substantially over the range of Mg contents for dolomite stability, based on the highest temperatures of ordered Dol coexisting with Mag. This provides further support for compositional asymmetry in this join, although the exact variation of disordering temperature as a function of temperature is unknown. (Precision of the measurements of disordering temperatures is limited to ~50°, which is similar to expected changes with composition for dolomite.)

Navrotsky and Capobianco (1987) measured the enthalpy of solution for a series of synthetic disordered Cc and for (ordered) Eugui dolomite that was subsequently annealed at high temperatures and quenched to yield a value of solution enthalpy for the disordered phase, of composition $X(\text{MgCO}_3) = 0.5$. They fitted their measurements (Fig. 5) for disordered phases with a curve for solution enthalpy H_{sol} , or for mixing enthalpy minus mechanical mixing contributions, that in my notation (Eq. 2) yields $W_{\text{ier}} + W_{\text{ira}} = 125.7 (\pm 11.8) - 177 (\pm 99.4)X_{\text{Mg}}$ kJ/mol (Ca,Mg)₂(CO₃)₂. Note the doubling of the formula unit relative to that used by Navrotsky and Capobianco. If we combine this with enthalpy of disordering, $\Delta H_{\text{dis}} = X_{\text{Ca}}^2(W_{\text{ier}} - W_{\text{ira}})$, given by the measured change in solution enthalpy for Eugui dolomite from ordered ($S \sim 1$)

TABLE 1. Model values for energy parameters

Indices	Mg-Ca	Mg-Fe	Fe-Ca
W_{ier}	-2.0	5.0	-0.6
W_{ira}	$56.17 - 22.825X_{\text{Ca}}$	10.0	$43.0 - 18.0X_{\text{Ca}}$

Note: (Ca,Mg,Fe)₂(CO₃)₂ solutions; units are kilo-Joules per mole.

to disordered ($S = 0$) of 13.94 ± 1.14 kJ/mol (CO₃)₂ unit, we can predict the critical temperature for dolomite: (from setting $G_{\text{ss}} = 0$ for $S = 0$ and $X_{\text{Ca}} = 0.5$) $T_c = (W_{\text{ira}} - W_{\text{ier}})/(4R) = \Delta H_{\text{dis}}/R = 1677 \pm 137$ K. The minimum value for T_c , 1540 K, is still greater than the maximum allowed by Reeder and Nakajima (1982), of 1423 K. This is a failure of the simple point approximation to account for short-range order and its contributions to enthalpy, particularly above the critical temperature, as discussed by Burton and Davidson (1988, p. 81–82). They showed for the analogous (Cd,Mg)(CO₃)₂ system that the effect of including short-range ordering contributions is to reduce the predicted ΔH_{dis} . However, they also concluded that the improvement afforded with the tetrahedral cluster is not great enough to suggest that a higher order CVM approximation would reduce ΔH_{dis} enough to produce quantitative agreement.

Unfortunately, that requires that the GPA fit either the enthalpy of mixing data, or T_c , but not both. For the objective of modeling phase relations in this system, we fitted T_c and phase equilibria and maintained qualitative agreement with H_{sol} for CaMg(CO₃)₂. In fitting phase equilibria, we are forced to destabilize compositions of Cc with more than a few mole percent Mg(CO₃); otherwise, predicted phase compositions are too Mg rich. The destabilization of Mg-rich Cc in turn produces H_{sol} values for the disordered phase that are positive for all compositions, rather than negative for compositions near CaCO₃, but that increase to positive values between $X(\text{MgCO}_3) = 0.12$ and 0.5, as observed. Figure 5 compares measured values of H_{sol} with those calculated for two models. One model is optimized only for phase equilibria, whereas the other model is fitted to H_{sol} values, T_c , and as much as possible to phase equilibrium data. However, the latter model predicts compositions of Cc (saturated with Dol) of $X(\text{MgCO}_3) > 0.2$, for temperatures above 350 °C. Thus we have elected to use the former model for predictions of ternary phase equilibria.

Figure 6 shows our preferred model for phase relations, along with experimental data for coexisting Cc + Dol of Gottschalk and Metz (1992) and earlier works compiled by them (Harker and Tuttle, 1955; Graf and Goldsmith, 1955, 1958; Goldsmith and Heard, 1961; Goldsmith and Newton, 1969; Byrnes and Wyllie, 1981; Fanelli and Wyllie, 1983; Gordon and Greenwood, 1970; and Puhau, 1978). Experiments for Dol + Mag (Goldsmith and Heard, 1961; Irving and Wyllie, 1975; Byrnes and Wyllie, 1981) are also shown. Although Gottschalk and Metz used a similar approach for fitting the binary phase relations, they developed a symmetric solution model, and so they

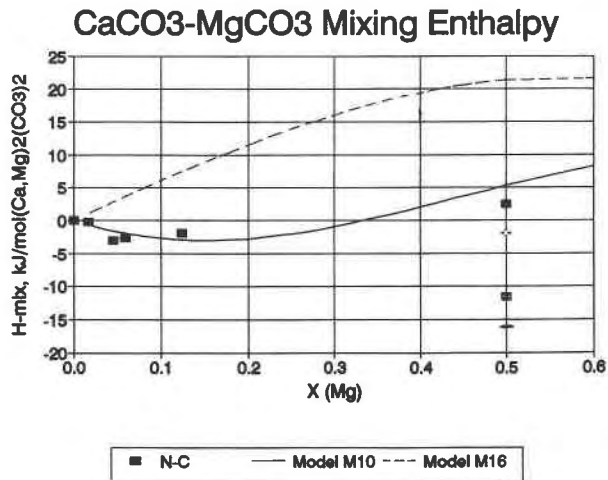


Fig. 5. Solution enthalpy for the join $\text{CaCO}_3\text{-MgCO}_3$. Measurements by Navrotsky and Capobianco (1987) for the disordered solution are shown by solid squares and for ordered dolomite by the boxed \times . Model M10 is a fit to their data, which is equivalent within error to the asymmetric fit they gave in their Eq. 4; model M16 is preferred for fitting phase equilibrium experiments. Calculated values for ordered dolomite, $X = 0.5$, are also shown by the solid line for M10 and by the dashed line for M16.

were unable to include the Mg-rich experiments. They were also unable to fit simultaneously the Ca-rich phase relations and Navrotsky and Capobianco's (1987) H_{sol} measurements (see their discussion, p. 48), because their model for H_{sol} (p. 47, Eq. 49) would yield positive values for the disordered solution near CaCO_3 composition. As does the model adopted here, Gottschalk and Metz's preferred model for phase relations leads to values for H_{sol} that are too positive (destabilizing) for the disordered phase, relative to that required by phase relations. Incorporating temperature-dependence in the energy parameters would allow a more precise fit to half-brackets in the $\text{CaCO}_3\text{-MgCO}_3$, which are predicted to show more mutual solubility than the dissolving half-brackets generally show; however, there is no theoretical justification for that. Nor can the fit be improved by including an elastic energy term (entirely independent of the state of order) to G_{sol} , which can increase model flexibility in higher order CVM approximations (Burton, 1989); for the GPA the inclusion of such a term is equivalent to modifying the combination $W_{\text{ier}} + W_{\text{ira}}$ in Equation 1.

Subsystem (Mg,Fe) CO_3

Unlike the Ca-Mg and Ca-Fe binary systems, where phase equilibrium experiments are available for calibration of energy parameters, the simpler (Mg,Fe) CO_3 join shows complete miscibility, and so of course phase relations within the binary join give no information as to its solution properties. New data from exchange equilibrium experiments with Dol-Ank (Symmes, in preparation) and calorimetric measurements of solution enthalpy (Chai and Navrotsky, in preparation) will provide the necessary in-

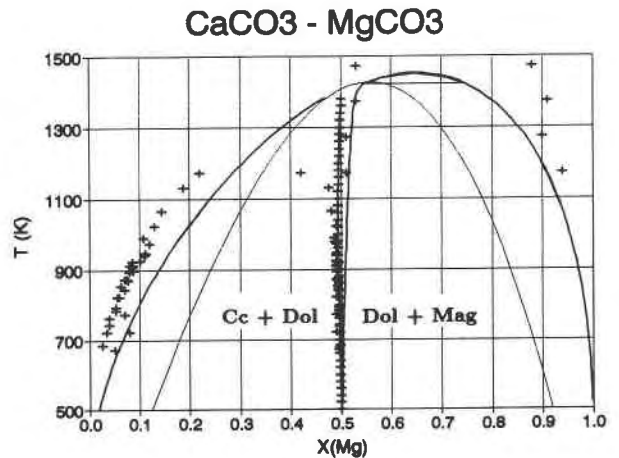


Fig. 6. Phase relations for the join $\text{CaCO}_3\text{-MgCO}_3$. Model curves are calculated with the parameters given in Table 1. Experiments cited in the text are plotted as plus signs. The ordering spinodal is indicated by the light line; phase boundaries are shown as heavier lines.

formation. Until studies such as these are done, we are forced to rely, as were Anovitz and Essene (1987), on analyses of naturally equilibrated pairs and the sparse information on compositions of coexisting Dol + Cc + Mag-Sid from the syntheses of Goldsmith et al. (1962) and Rosenberg (1967). If we assume (Mg,Fe) CO_3 to be an ideal solution, then tie lines between Cc and Dol-Ank, as well as between Dol-Ank and Mag-Sid, radiate from the CaCO_3 apex (Fe-Mg ratios in coexisting phases are identical). However, the experimentally synthesized compositions in the three-phase assemblages are not collinear, nor do naturally coexisting pairs exhibit identical FeMg ratios. As Anovitz and Essene's analysis demonstrates, the Fe-Mg ratio is greater for Mag-Sid than for coexisting Dol-Ank in natural pairs. Assumption of relatively small, but positive values of the solution parameters $W_{\text{ira}}(\text{Fe-Mg})$ and $W_{\text{ier}}(\text{Fe-Mg})$ (given in Table 1) yields Fe-enriched Mag-Sid relative to coexisting Dol-Ank.

System (Ca,Mg,Fe)(CO_3)

Combining the binary models for Ca-Mg and Ca-Fe joins with estimates of the Fe-Mg interaction energies allows us to predict ternary phase relations, including critical temperatures for disordering and maximum stability temperatures for the Dol-Ank, relative to assemblages of coexisting disordered solutions. We have calculated phase relations at several temperatures (Fig. 7) and T_c contours shown in Figure 8. These diagrams are calculated from our model, with energy parameters given in Table 1. Notice that above a singular temperature (1040.4 K) the limit of metastability for ordered Dol-Ank is within the ternary system; no Mg-free ordered $\text{CaFe}(\text{CO}_3)_2$ is even metastable. Also, the transition from the topology at 1000 K to that at 1300 K requires an isobarically singular temperature where a Ca-rich tricritical phase (between Dol-Ank and Cc) coexists with Mag-Sid. This is reflected in calculated stability relations for

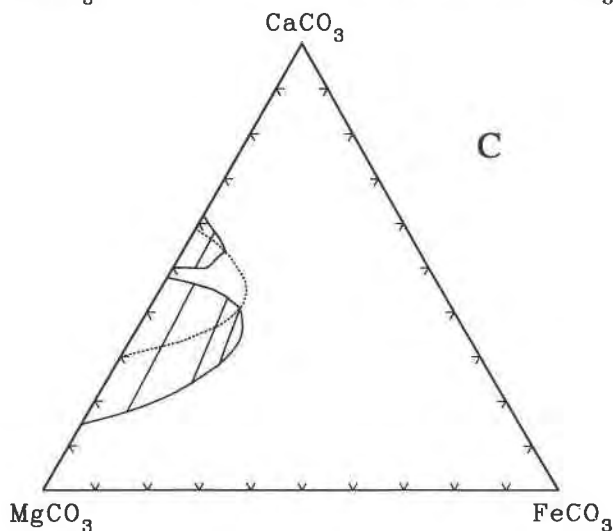
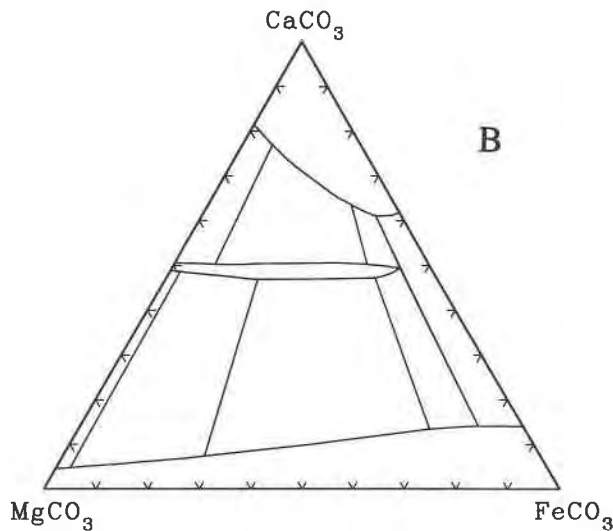
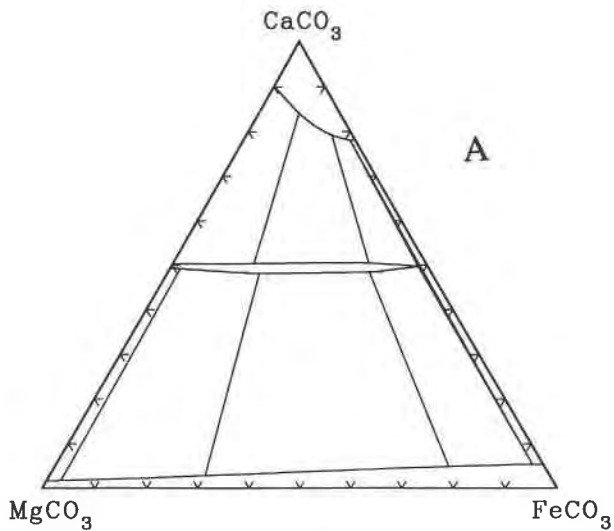


Fig. 7. Calculated phase relations for the system CaCO_3 - MgCO_3 - FeCO_3 for several temperatures, with representative tie lines. (A) 800 K. (B) 1000 K. (C) 1300 K. Note the ordering spinodal indicated by the dotted line and the presence of a small region for coexisting disordered Dol-Ank + Sid-Mag.

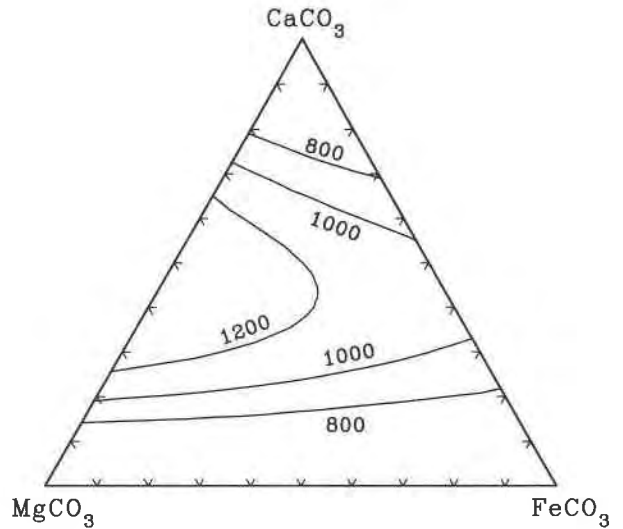


Fig. 8. Contours of the ordering spinodal. T_c (K) values are indicated next to the curves.

the join $\text{CaMg}(\text{CO}_3)_2$ - $\text{CaFe}(\text{CO}_3)_2$ (Fig. 9) that show the stability of Dol-Ank as being limited at high Fe contents by the assemblage Cc + Mag-Sid, but at high Mg contents by the higher order transition to the disordered phase. The singularity for coexisting tricritical phase + Mag-Sid would be at the juncture of the lines for T_c and Ank = Cc + Sid, or approximately 1070 K. Of course, this phase diagram topology was predicted by Goldsmith et al. (1962).

Calculated stability relations of $(\text{Mg,Fe})\text{Ca}(\text{CO}_3)_2$ (Fig. 9) predict that Dol-Ank may persist to higher Fe contents than the early studies by Goldsmith et al. (1962) and Rosenberg (1967) suggest. Experiments in progress (G. Symmes, personal communication) to explore the maximum Fe content of ordered Dol-Ank will serve as a test of these predictions.

The effect of pressure on solution properties and phase relations has not been explored here because the range of pressures (2–30 kbar) represented by the data is not sufficient to change phase diagram topologies, so long as polymorphism in CaCO_3 and decarbonation reactions are ignored. Yet some pressure effect on compositions of coexisting phases, if small, has been observed. Goldsmith and Newton (1969) reported a shift of up to ~ 1.5 mol%/kbar for the binary CaCO_3 - MgCO_3 , as did Gottschalk and Metz (1992), although it is within the precision of determination of phase compositions. Also, volumes of mixing show slight negative deviations from ideality in the binary joins CaCO_3 - FeCO_3 (Davidson et al., 1993) and CaCO_3 - MgCO_3 (as determined from unit-cell data in Table 1 of Navrotsky and Capobianco, 1987), indicating pressure dependence in G_{sol} and phase relations. Furthermore, if pressure strongly influences the relative stabilities of ordered vs. disordered Dol-Ank, increasing pressure would appear to stabilize disordered $\text{CaFe}(\text{CO}_3)_2$ (Davidson et al., 1993). When reversed phase equilibrium data within the ternary system as a function of pres-

STABILITY OF DOLOMITE-ANKERITE SS

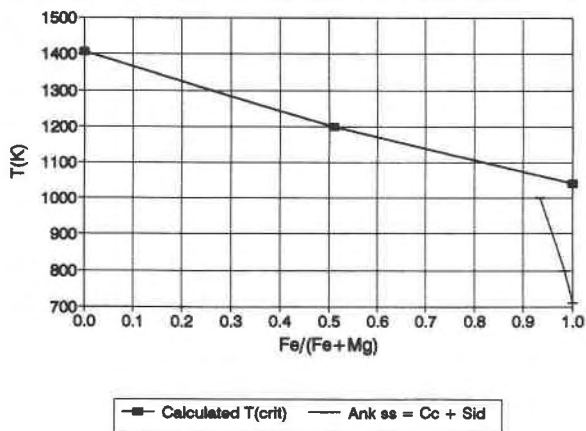


Fig. 9. Calculated stability relations for the join $(\text{Ca,Mg})(\text{CO}_3)_2$ - $(\text{Ca,Fe})(\text{CO}_3)_2$.

sure become available, assessing pressure dependence of energy parameters can readily be accomplished.

CONCLUSIONS

A ternary expansion of the GPA is the simplest model that can treat the order-disorder relations, phase equilibria, and solution enthalpy systematics for $(\text{Ca,Mg,Fe})\text{CO}_3$ solutions. A minimum of eight interaction parameters are needed to produce quantitative agreement with experimentally determined phase relations: two for each binary join plus one each for symmetry in the Ca-Fe and Ca-Mg joins.

The model places limits on both the stable and the metastable occurrence of Dol-Ank. Calculated phase relations show that the stability of ordered $\text{CaFe}(\text{CO}_3)_2$ is limited to $T < \sim 450^\circ\text{C}$ by the breakdown to Cc + Sid. This maximum temperature rises with Mg content. Between 1000 and 1200 K, there is an isobaric singularity where tritritical Cc-Dol-Ank coexists with Mag-Sid. For still higher temperatures, the stability of ordered Dol-Ank is limited to high-Mg contents by the intersection of the order-disorder transition with the two-phase field boundaries for Cc + Dol-Ank and Mag-Sid + Dol-Ank, as predicted by Goldsmith et al. (1962). The maximum temperature for metastability of ordered $\text{CaFe}(\text{CO}_3)_2$ is predicted to be 767°C , rising more than 300°C with complete Mg for Fe substitution.

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