

Synthesis, characterization, and energetics of solid solution along the dolomite-ankerite join, and implications for the stability of ordered $\text{CaFe}(\text{CO}_3)_2$

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ABSTRACT

Samples along the dolomite-ankerite join were synthesized using a piston-cylinder apparatus and the double-capsule method. Some of the ankerite samples may be disordered. Thermal analysis and X-ray diffraction showed that all samples can be completely decomposed to uniquely defined products under calorimetric conditions (770 °C, O_2), and a well-constrained thermodynamic cycle was developed to determine the enthalpy of formation.

The energetics of ordered and disordered ankerite solid solutions were estimated using data from calorimetry, lattice-energy calculations, and phase equilibria. The enthalpies of formation of ordered dolomite and disordered end-member ankerite from binary carbonates, determined by calorimetry, are -9.29 ± 1.97 and 6.98 ± 2.08 kJ/mol, respectively. The enthalpy of formation of ordered ankerite appears to become more endothermic with increasing Fe content, whereas the enthalpy of formation of disordered ankerite becomes more exothermic with increasing Fe content. The enthalpy of disordering in dolomite (approximately 25 kJ/mol) is much larger than that in pure ankerite, $\text{CaFe}(\text{CO}_3)_2$ (approximately 10 kJ/mol), which may explain the nonexistence of ordered $\text{CaFe}(\text{CO}_3)_2$.

INTRODUCTION

Fe^{2+} and Mg^{2+} substitution is common in mineral systems. Fe^{2+} and Mg^{2+} form a complete solid solution in the FeCO_3 - MgCO_3 system, whereas Fe^{2+} only partially substitutes for Mg^{2+} in dolomite to form ankerite [$\text{Ca}(\text{Fe}_x\text{Mg}_{1-x})(\text{CO}_3)_2$, $0 \leq x \leq 0.7$] (Reeder 1983; Anovitz and Essene 1987; Reeder and Dollase 1989; Davidson et al. 1993, and references therein). As a solid solution, ankerite has the same crystal structure as dolomite, with Ca^{2+} occupying one set of cation sites and Fe^{2+} and Mg^{2+} the other (Reeder and Dollase 1989). At high temperature, ankerite is expected to undergo a disordering transition, as does dolomite, to the calcite structure. End-member ankerite, $\text{CaFe}(\text{CO}_3)_2$, has not been found as a mineral. Furthermore, phase-equilibrium studies (Goldsmith et al. 1962; Rosenberg 1963, 1967) show that the composition $\text{CaFe}(\text{CO}_3)_2$ lies in a two-phase field at temperatures between 350 and 800 °C consisting of calcite and siderite. Recently, Davidson et al. (1993) successfully synthesized a disordered $\text{CaFe}(\text{CO}_3)_2$ (calcite-type) phase at 845 °C and 30 kbar and suggested that ordered $\text{CaFe}(\text{CO}_3)_2$ could exist at low temperature.

Several efforts have been made to explain the nonexistence of ordered $\text{CaFe}(\text{CO}_3)_2$ (Rosenberg and Foit 1979; Reeder and Dollase 1989, 1991; Rosenberg 1991). Rosenberg and Foit (1979) proposed that the distortion of

the cation octahedra may be responsible for the instability of ankerite with high Fe content. Reeder and Dollase (1989) studied the crystal structures of ankerite with the use of mineral single crystals and found no obvious indication of significant distortion of the coordination polyhedra.

Study of the energetics of ankerite solid solutions may explain the apparent instability of $\text{CaFe}(\text{CO}_3)_2$. Recently, we developed calorimetric methods for Fe^{2+} -bearing carbonates (Chai and Navrotsky 1994, 1996). We used this method to determine the enthalpy of formation of synthetic ankerite. We also derived the enthalpies of formation of $\text{CaMg}(\text{CO}_3)_2$ and $\text{CaFe}(\text{CO}_3)_2$ with the use of calculated lattice energies. These results help to define the energetics of mixing of ordered and disordered $\text{Ca}(\text{Fe,Mg})(\text{CO}_3)_2$ solid solutions.

EXPERIMENTS

Synthesis

Ankerite samples were synthesized using a piston-cylinder high-pressure apparatus and the double-capsule method (Powell et al. 1984; Anderson and Crerar 1993). Precipitated CaCO_3 and synthetic MgCO_3 and FeCO_3 were used as starting materials. As suggested in previous work (Rosenberg 1967, 1968), precipitated CaCO_3 was used to promote the synthesis reaction. MgCO_3 and FeCO_3 were prepared from basic magnesium carbonate and iron oxalate, respectively, in a CO_2 atmosphere using a cold-seal vessel apparatus (Chai and Navrotsky 1993, 1994).

Approximately 300 mg of the starting materials with

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appropriate stoichiometry were ground together in an agate mortar with acetone for about 1 h. A portion of the mixture was then packed into a gold capsule (0.38 cm diameter and 0.8 cm long). The gold capsule was placed within a platinum capsule (0.46 cm outside diameter and 1.6 cm long) along with approximately 100 mg of $\text{Ag}_2\text{C}_2\text{O}_4$ and a small amount of graphite (as the reducing buffer materials). One end of the platinum capsule was previously sealed by arc welding. After loading the charge, the other end of the platinum capsule was welded with the part of the platinum capsule containing the charge immersed in water to prevent the decomposition of $\text{Ag}_2\text{C}_2\text{O}_4$. The welded platinum capsule was about one-half the length of the graphite furnace used in the piston cylinder. A heat-treated pyrophyllite cup was used to separate the platinum capsule from the graphite furnace. A W3%Re/W25%Re thermocouple and an Eurotherm 818 controller were used to measure temperature.

The double-capsule technique yielded about 50–80 mg of sample in each experiment. To obtain a sufficient amount of sample for characterization and thermochemical measurements, 2–3 successful experiments under similar conditions were needed. We found it was difficult to reproduce temperature among the experiments, possibly because it was difficult to control the positions of the platinum capsule and the thermocouple when the whole sample assembly was under pressure. All samples used for later experiments were produced using power control. The temperature for all experiments was approximately $850 \pm 50^\circ\text{C}$.

A typical experiment was run at 18 kbar for 24 h. At the start of each experiment, temperature and pressure were increased simultaneously to reduce the possibility of abrupt bursting of the capsule as a result of the decomposition of $\text{Ag}_2\text{C}_2\text{O}_4$ and the expansion of gas during heating.

At the end of each experiment, the power was cut to zero. The temperature dropped to about 300°C within 5 s. Pressure was then released. When the platinum capsule was opened, the release of gas indicated that the experiment was successful. The white color of the sample also indicated that the temperature was well controlled and that Fe was divalent.

The dolomite sample was made from a mechanical mixture of precipitated CaCO_3 and basic magnesium carbonate at 700°C in CO_2 atmosphere with the use of a cold-seal vessel apparatus (Chai and Navrotsky 1993).

Characterization

Samples were characterized by X-ray diffraction (XRD) with the use of a Scintag PAD-V diffractometer with a solid-state detector and $\text{CuK}\alpha$ radiation. Because of the limited amount of sample, a slurry of the sample powder with acetone was mounted on a zero-background quartz sample holder. The sample holder was spun during data collection to minimize preferred orientation. For unit-cell parameters and structure refinements, powder X-ray diffraction data were collected in a step-scan mode with a

step of $0.02^\circ 2\theta$ and a counting time of 4 s (per step). The 2θ range was usually from 10 to 90° . Si was used as an external standard. The unit-cell parameters were refined using the subroutine in the controlling software.

Simultaneous differential thermal analysis and thermogravimetric analysis (DTA/TGA) were conducted in a dynamic O_2 atmosphere with the use of a Netzsch STA 409C apparatus. The flow rate of O_2 was approximately $0.5 \text{ cm}^3/\text{s}$. The experimental temperature ranged from room temperature to 1050°C , with a $10^\circ\text{C}/\text{min}$ heating rate. Al_2O_3 crucibles were used as sample containers. The buoyancy effect was corrected using experiments with empty crucibles.

Calorimetry

All calorimetric measurements were made using a Calvet-type calorimeter operating at 770°C (Navrotsky 1977). Three types of calorimetric experiments were used: drop-solution calorimetry, solution calorimetry, and transposed-temperature-drop calorimetry. In solution calorimetry, a sample is preequilibrated at the calorimetric temperature before it is dissolved in the solvent (molten lead borate, $2\text{PbO} \cdot \text{B}_2\text{O}_3$). The measured heat effect is the enthalpy of solution. In drop-solution calorimetry, small pellets of about 20 mg of sample are dropped from room temperature into a platinum crucible containing solvent in the calorimeter. The measured heat effects consist of heat content and enthalpy of solution. In transposed-temperature-drop calorimetry, small pellets of sample are dropped from room temperature into an empty platinum crucible in the calorimeter. The heat effects in this case include heat content of the sample and any heat effects resulting from reactions (decarbonation, oxidation) in the calorimeter.

Calorimetric methods for carbonates in general and Fe^{2+} -containing carbonates in particular were described by Chai and Navrotsky (1993, 1994, 1996). Drop-solution calorimetry in a flowing gas has proved effective for calcite, magnesite, and dolomite. However, for the Fe^{2+} -bearing carbonates, direct drop-solution calorimetry could not be used because the calorimetric reaction reached an irreproducible final state, presumably because of the slow oxidation of Fe^{2+} in the lead borate solvent (Chai and Navrotsky 1994). A two-step calorimetric procedure was used for the Fe^{2+} -bearing carbonates. The first step of oxidative decarbonation in O_2 was followed by dissolution of the Fe^{3+} -containing oxide products. Once the Fe^{2+} components in both reactants and products in the ankerite-formation reaction were transformed into the same oxidation state (+3) in the solvent, the enthalpy of formation could be calculated. Detailed equations are given below.

RESULTS AND DISCUSSION

Cation disordering and structural changes

The compositions of the ankerite samples were calculated from the starting stoichiometry and are reported as the mole fraction of Fe^{2+} in the dolomite structure [i.e.,

TABLE 1. Composition and unit-cell parameters of the ankerite solid solutions

Sample	<i>x</i>	<i>a</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å ³)	Figure of merit
CaMg(CO ₃) ₂ *	0.00	4.8076(3)	16.007(2)	320.40	F(15) = 113
ank1	0.1583	4.8102(6)	16.0524(43)	321.66	F(13) = 38
ank2	0.2990	4.8108(2)	16.1095(17)	322.88	F(13) = 98
ank3	0.4996	4.8131(1)	16.1200(9)	323.41	F(13) = 169
ank4	0.6480	4.8182(8)	16.1543(5)	324.79	F(13) = 355
ank5	1.00	4.8300(9)	16.221(8)	327.72	F(10) = 21
CaFe(CO ₃) ₂ **	1.00	4.8291(3)	16.210(1)	327.38	—

Note: The numbers in parentheses in unit-cell parameters are the errors in the last decimal place.

* Eugui dolomite.

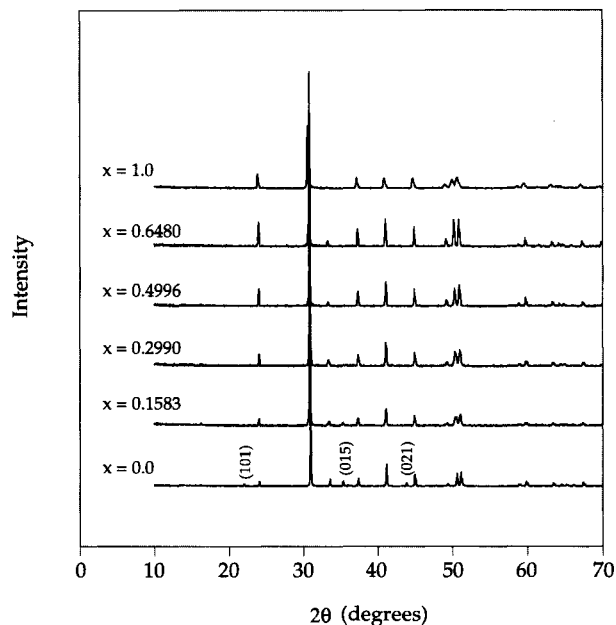
** From Davidson et al. 1993.

x in Ca(Fe_{*x*}Mg_{1-*x*})(CO₃)₂, Table 1]. X-ray diffraction patterns of the ankerite solid solutions show that the ordering reflections gradually disappear with increasing Fe content (Fig. 1). The ordering reflections (015) and (021) can still be seen in the sample ank1 with *x* = 0.1583 but disappear in the samples with higher Fe contents. When CuK α radiation is used the backgrounds of the XRD patterns of the Fe-bearing phases are usually high because of the fluorescence of Fe. To reduce the signal/noise ratio, a scan with longer counting time (10 s) was performed for ank3 with composition *x* = 0.4996. No ordering reflections were found.

Goldsmith et al. (1962) observed a wider composition range in which ordering reflections were found. Also, they found that ankerite deviated from the ideal stoichiometry (to more Ca-rich composition) with increasing Fe content. These different results may be due to the higher temperature used in this study.

The disordering temperature is expected to decrease with increasing Fe content. The disordering of CaMg(CO₃)₂ occurs at about 1150 °C (Reeder and Wenk 1983), whereas disordered CaFe(CO₃)₂ has been made at about 845 °C and 30 kbar (Davidson et al. 1993). Therefore, samples ank3 and ank4 (*x* = 0.6480) are probably at least partially disordered. To determine the degree of disordering, Rietveld refinements were attempted for sample ank3, with ordered, disordered, and partially disordered dolomite structures used as the starting structural models. Unfortunately, no structural model showed a clear advantage over the others.

In general, unit-cell parameters of synthetic and natural ankerite samples increase with Fe content (Table 1 and Fig. 2). The unit-cell parameters of ank5 (*x* = 1.0) are consistent with those of disordered CaFe(CO₃)₂ from Davidson et al. (1993), strongly suggesting that ank5 is completely disordered. The unit-cell parameters for natural ankerite and a Eugui dolomite are also included in this figure. The natural ankerite samples are ordered, with Fe²⁺ occupying the Mg²⁺ site in the dolomite structure (Reeder and Dollase 1989). Mn²⁺ contents are up to 4.7 mol% (a significant impurity) in those samples. The disordered Eugui dolomite in the study of Navrotsky and Capobianco (1987) was obtained by quenching the annealed sample from 1250 °C using a piston-cylinder ap-

**FIGURE 1.** X-ray diffraction patterns of the ankerite solid solution. Three ordering reflections in dolomite are indexed.

paratus. This sample is generally considered to be partially disordered (Navrotsky and Capobianco 1987) because of the likelihood of reordering during the quench (Reeder and Wenk 1983).

The unit cell of ankerite expands as the amount of Fe²⁺ increases because of the replacement of Mg²⁺ by the larger Fe²⁺. For a given composition, *x*, the *a* parameters of all synthetic samples (disordered) are smaller than those of natural samples (ordered), whereas there is a turnover in the *c* parameters between ordered and disordered samples. This trend is seen clearly in the volume-composition plot (Fig. 2c). Disorder in dolomite increases unit-cell volume; disordering in end-member ankerite decreases unit-cell volume. The thermochemical results, discussed in the following section, support the above interpretation of the ordering state.

Decomposition products

It is essential to understand the composition change during the decomposition and the behavior of the decomposition products at the calorimetric temperature and at room temperature to interpret calorimetric data. The two-step calorimetric approach is based on the assumption that the energy state of the decomposition products after the first step does not change before they are dissolved in the solvent in the second step. This may be a reasonable assumption because the decarbonation of ankerite and the oxidation of Fe²⁺ component are usually rapid and complete in the first step. Several experiments were performed to understand the behavior of the intermediate products.

DTA/TGA showed that all samples decomposed below 800 °C in O₂. XRD of the products after DTA/TGA in-

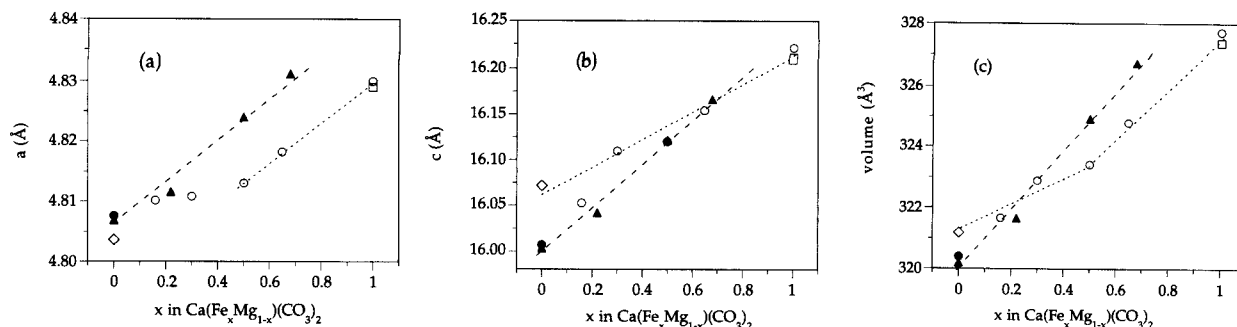


FIGURE 2. Unit-cell parameters of synthetic and natural ankerite samples. The circles are from this work, the triangles are from Reeder and Dollase (1989), the squares are from Davidson et al. (1993), and the diamonds are from Navrotsky and Capobianco (1987). The dashed lines are the proposed changes for ordered samples, and the dotted lines are for disordered samples.

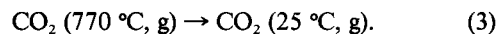
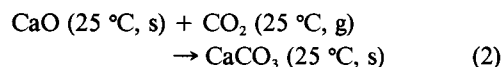
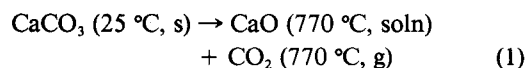
indicated that the decomposition products for all ankerite solid solutions are CaO, MgO, and $\text{Ca}_2\text{Fe}_2\text{O}_5$. The sample weight change was monitored during calorimetry. XRD and weight changes confirmed that all samples, prepared as pellets, completely decomposed under the calorimetric conditions to form oxide mixtures (CaO, MgO, and $\text{Ca}_2\text{Fe}_2\text{O}_5$).

Weight changes of the decomposition products at room temperature in air were also monitored. The reactions of the decomposition products in air (presumably of CaO and MgO with H_2O and CO_2) were slow and continuous. This made direct calorimetric measurements of the decomposition products difficult.

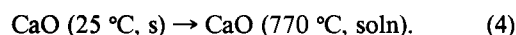
Energetics of ankerite solid solutions

The enthalpies of formation of ankerite solid solution, $\text{Ca}(\text{Fe}_x\text{Mg}_{1-x})(\text{CO}_3)_2$, were calculated from enthalpies of drop solution (ΔH_{ds}^*) of ankerite, calcite, magnesite, and siderite (Table 2). The enthalpies of drop solution of calcite, magnesite, and dolomite were measured directly, whereas the enthalpies of drop solution of ankerite and siderite were calculated from enthalpies of decomposition (ΔH_{dec}), heat contents (ΔH_{hc}), and enthalpies of drop solution (ΔH_{ds}) of the decomposition products. Enthalpies of decomposition of ankerite solid solutions were determined by transposed-temperature-drop calorimetry. Heat contents and enthalpies of drop solution of the decom-

position products were not measured directly because of the reactivity of CaO and MgO in the decomposition products (mentioned above). The heat contents were calculated from the individual oxide values of Robie et al. (1978). The enthalpies of drop solution of the decomposition products were also calculated from individual oxide values rather than from data for the decomposition samples themselves. The enthalpies of drop solution of CaO and MgO were derived from the measured enthalpies of drop solution of the corresponding carbonates as follows:



Adding Equations 1, 2, and 3, we have



The enthalpy of Reaction 1 is the measured enthalpy of drop solution (ΔH_{ds}) of calcite (Table 2), the enthalpy of Reaction 2 is the heat of formation (ΔH_f) of calcite, and the enthalpy of Reaction 3 is heat content (ΔH_{hc}) of CO_2 . The latter two values are from Robie et al. (1978). The calculated enthalpy of drop solution of CaO (Reaction 4)

TABLE 2. Calorimetric data for the ankerite solid solutions

Sample	x	ΔH_{dec}	$\Delta H_{\text{hc}}^\dagger$	$\Delta H_{\text{ds}}^\ddagger$	ΔH_{ds}^*	ΔH_f
Dolomite	0.00	—	—	—	$399.21 \pm 0.90(6)$	-9.29 ± 1.97
ank1	0.1583	$404.19 \pm 2.10(4)$	75.024	33.477	362.64 ± 3.11	6.80 ± 3.45
ank2	0.2990	$375.54 \pm 1.24(4)$	76.974	42.344	340.91 ± 2.30	10.36 ± 2.64
ank3	0.4996	$333.89 \pm 4.44(5)$	79.750	54.968	309.11 ± 4.68	16.21 ± 4.80
ank4	0.6482	$306.99 \pm 1.45(5)$	81.811	64.340	289.52 ± 1.88	16.54 ± 2.10
ank5	1.00	$253.72 \pm 1.45(6)$	86.690	86.525	253.56 ± 1.84	6.98 ± 2.08
Calcite					$196.85 \pm 0.49(6)$	
Magnesite					$193.07 \pm 1.68(5)$	
Siderite§					63.69 ± 0.83	

Note: Unit is kilojoules per mole. Errors are two standard deviations of the mean. The number in parentheses is the number of experiments.

† Heat contents of oxides are from Robie et al. (1978).

‡ Calculated from data of the individual oxides (see text).

§ From Chai and Navrotsky (1996).

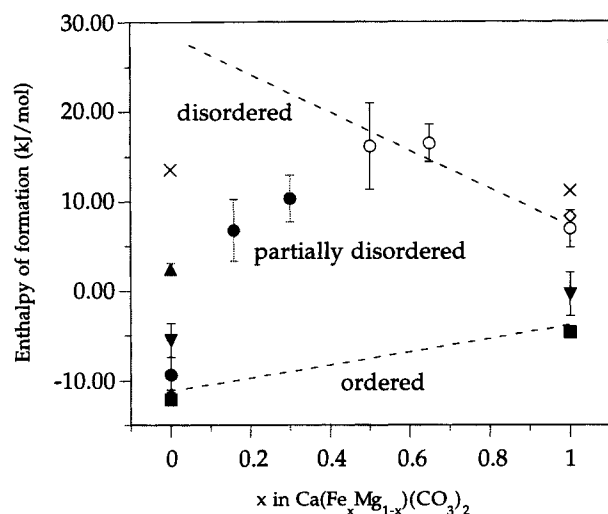


FIGURE 3. Enthalpy of formation of the ankerite solid solution. The circles are from calorimetry in this work, the squares are from lattice-energy calculations, the triangle is from Navrotsky and Capobianco (1987), the inverted triangles are from Holland and Powell (1990), and the diamond is calculated from the solvus (see text). The Xs are for disordered phases calculated from solid-solution-mixing parameter obtained from Davies and Navrotsky (1983). The darkness of the symbols indicates the degree of ordering: Solid symbols indicate complete order; open symbols, complete disorder; and shaded symbols, partial disorder.

from the above reactions is -16.28 ± 1.19 kJ/mol. The enthalpy of drop solution of MgO (39.78 ± 2.44 kJ/mol) can be derived from similar thermochemical analysis. The enthalpy of drop solution of $\text{Ca}_2\text{Fe}_2\text{O}_5$ (86.525 ± 1.33 kJ/mol for $0.5\text{Ca}_2\text{Fe}_2\text{O}_5$) was determined by drop solution of the decomposition product of ank5 with composition $\text{CaFe}(\text{CO}_3)_2$ (Table 2). The heat content of $\text{Ca}_2\text{Fe}_2\text{O}_5$ was also measured using the decomposition product of ank5. The resulting value (86.51 ± 0.68 kJ/mol for $0.5\text{Ca}_2\text{Fe}_2\text{O}_5$) from this work is in good agreement with that (86.69 kJ/mol) from Robie et al. (1978).

The total enthalpy of drop solution of ankerite $[\text{Ca}(\text{Fe}_x\text{Mg}_{1-x})(\text{CO}_3)_2]$ can then be calculated as $\Delta H_{\text{ds}}^* = \Delta H_{\text{dec}} + \Delta H_{\text{ds}} - \Delta H_{\text{hc}}$.

The enthalpy of formation of ankerite $[\text{Ca}(\text{Fe}_x\text{Mg}_{1-x})(\text{CO}_3)_2]$ from calcite, magnesite, and siderite may be calculated as $\Delta H_f(\text{ank}) = \Delta H_{\text{ds}}^*(\text{cal}) + (1-x)\Delta H_{\text{ds}}^*(\text{mag}) + x\Delta H_{\text{ds}}^*(\text{sid}) - \Delta H_{\text{ds}}^*(\text{ank})$, where $\Delta H_{\text{ds}}^*(\text{cal})$, $\Delta H_{\text{ds}}^*(\text{mag})$, and $\Delta H_{\text{ds}}^*(\text{sid})$ are the enthalpies of drop solution of calcite, magnesite, and siderite, respectively (Table 2 and Fig. 3).

The enthalpy of formation of disordered $\text{CaFe}(\text{CO}_3)_2$ can be estimated from the solvus of the CaCO_3 - FeCO_3 system (Davies and Navrotsky 1983; Davidson et al. 1993). This value (8.35 kJ/mol) agrees with the measurement from this study (6.98 ± 2.08 kJ/mol).

An empirical approach was applied using the WMIN program (Busing 1981) to calculate the lattice energies of carbonates in the CaCO_3 - MgCO_3 - FeCO_3 system (Chai

TABLE 3. Lattice energy of carbonates in the calcite-siderite-magnesite system

Phase	Formula	Lattice energy (kJ/mol)
Calcite	CaCO_3	-3163.5
Siderite	FeCO_3	-3412.1
Magnesite	MgCO_3	-3425.2
Dolomite	$\text{CaMg}(\text{CO}_3)_2$	-6600.8
Pure ankerite	$\text{CaFe}(\text{CO}_3)_2$	-6580.2

1995). A three-term Born equation (Coulomb interaction, repulsion, and van der Waals force) was used for the ion-pair potentials, and the parameters in the potentials were obtained by minimization of total lattice energy with the use of crystal-structure data of calcite, magnesite, dolomite, and siderite. The structural data for ordered $\text{CaFe}(\text{CO}_3)_2$ were derived by extrapolation from natural ankerite (Reeder and Dollase 1989). The calculated lattice energies (ΔH_L ; Table 3) were used to obtain the enthalpy of formation of dolomite and ankerite (Fig. 3): $\Delta H_f(\text{dol}) = \Delta H_L(\text{dol}) - \Delta H_L(\text{cal}) - \Delta H_L(\text{mag}) = -12.1$ kJ/mol, and $\Delta H_f(\text{ank}) = \Delta H_L(\text{ank}) - \Delta H_L(\text{cal}) - \Delta H_L(\text{sid}) = -4.6$ kJ/mol. This estimate of the enthalpy of formation of dolomite is in very good agreement with values determined from experiments (-11.5 ± 0.5 kJ/mol, Navrotsky and Capobianco 1987; -11.1 ± 2.5 kJ/mol, Chai and Navrotsky 1993). Therefore, the value derived from lattice energies (-4.6 kJ/mol) may give a reliable estimate of the enthalpy of formation of ordered $\text{CaFe}(\text{CO}_3)_2$, which has not been determined experimentally. This result indicates that pure ankerite is energetically less stable than dolomite relative to binary carbonates.

The measured enthalpy of formation of disordered dolomite (Navrotsky and Capobianco 1987) and the enthalpies of formation of $\text{CaMg}(\text{CO}_3)_2$ and ordered $\text{CaFe}(\text{CO}_3)_2$ from the Holland and Powell (1990) data set provide additional constraints on the energetics of mixing and disordering in the ankerite solid solution (Fig. 3). The enthalpy of formation of ordered $\text{CaFe}(\text{CO}_3)_2$ from Holland and Powell (1990) was derived from the data of Fe^{2+} - Mg^{2+} partitioning in carbonates and carbonate-silicate equilibria.

If the quenched sample from Navrotsky and Capobianco (1987) is completely disordered, then the calorimetric data from this study may define the enthalpy of mixing of disordered ankerite (Fig. 3). When a regular solution model is used, a curve fit to these data results in a regular solution parameter of 34.52 ± 4.89 kJ/mol. This implies a critical temperature of approximately 1800°C , which contradicts the experimental results (only a single phase was found in our synthesis conditions at $850 \pm 50^\circ\text{C}$). An alternative explanation is that the sample from Navrotsky and Capobianco (1987) is indeed partially disordered, and their measured enthalpy of disordering provides a lower limit to the enthalpy of disordered dolomite.

Davies and Navrotsky (1983) systematically studied the relationship of energetics and volume mismatch in some solid solutions. They found that regular solution param-

eters of the solid-solution models (W) have a linear relationship with the difference in volume of the end-members (ΔV), $W = 100.8\Delta V - 0.4$ (kJ/mol). Recently, we determined the energetics of solid solution in the system FeCO_3 - MgCO_3 (Chai and Navrotsky 1996) and found that the regular solution parameter from the calorimetric data, using a regular solution model, was in good agreement with that calculated from the above relationship. The solid solution in the system FeCO_3 - MgCO_3 crystallizes in the calcite structure, which is the same as that of disordered ankerite. Therefore, the energetics of mixing of ankerite solid solutions may be estimated from the above relationship.

The volume differences between disordered and ordered dolomite samples and pure ankerite are small. Thus, the predicted enthalpies of mixing are nearly ideal [approximately <1 kJ/mol for $\text{Ca}(\text{Fe}_{0.5}\text{Mg}_{0.5})(\text{CO}_3)_2$]. Therefore, it may be reasonable to treat the enthalpies of formation as linear with Fe content. With this assumption, the calorimetric data of ank3, ank4, and ank5, combined with the solvus data for pure ankerite (Davies and Navrotsky 1983; Davidson et al. 1993), define the energetics of disordered ankerite (upper dashed line, Fig. 3). The calorimetric data, combined with lattice-energy calculations for dolomite and ankerite, give the best estimate of the energetics of ordered ankerite (lower dashed line, Fig. 3). The calorimetric data, then, for $x = 0.158$ and 0.299 represent partially ordered samples. The intercept at $x = 0$ of the upper line represents the extrapolated enthalpy of formation of a totally disordered dolomite, implying an enthalpy of complete disordering that is at least twice that measured by Navrotsky and Capobianco (1987). From Figure 3 it can be seen that the enthalpy of formation of ordered ankerite becomes more endothermic with increasing Fe content, whereas disordered ankerite becomes more exothermic with increasing Fe content.

The correlation between volume mismatch and mixing energetics of Davies and Navrotsky (1983) may also be used to estimate the enthalpies of formation of disordered ankerite and disordered dolomite from the mixing of two binary carbonates. For the reaction CaCO_3 (s) + FeCO_3 (s) $\rightarrow$ $\text{CaFe}(\text{CO}_3)_2$ (s) (disordered), the enthalpy is estimated to be 11.3 kJ/mol (the volume-mismatch parameter of calcite and siderite is 0.2257), in reasonable agreement with the measured value of 7.0 ± 2.1 kJ/mol. For the reaction CaCO_3 (s) + MgCO_3 (s) $\rightarrow$ $\text{CaMg}(\text{CO}_3)_2$ (s) (disordered), the enthalpy is estimated to be 13.6 kJ/mol (the volume-mismatch parameter of calcite and magnesite is 0.2742). Because the enthalpy of formation of ordered dolomite from calcite and magnesite is -11.3 kJ/mol, this calculation yields an enthalpy of disordering of 24.9 kJ/mol, in the general range found by extrapolation of the calorimetric studies and significantly higher than the value of about 13 kJ/mol estimated by Navrotsky and Capobianco (1987), again suggesting that their sample had partially ordered upon quench.

The above arguments placed limits on the enthalpies of disordering of dolomite and pure ankerite. The en-

thalpy of disordering is 20–30 kJ/mol for dolomite but only about 10 kJ/mol for iron dolomite. It should be emphasized that the uncertainty of the above estimation for the energetics of disordered dolomite is relatively large.

Implications for the stability of ordered $\text{CaFe}(\text{CO}_3)_2$

The above estimations may explain the nonexistence of pure ankerite. The enthalpy difference of disordering in dolomite is much larger than that in $\text{CaFe}(\text{CO}_3)_2$. In other words, there is insufficient energy gain on ordering of $\text{CaFe}(\text{CO}_3)_2$ to stabilize it relative to a two-phase mixture of siderite and calcite.

The entropy of formation of dolomite from calcite and magnesite is -1.6 J/(mol·K) (Robie et al. 1978). If the entropy of formation of ordered $\text{CaFe}(\text{CO}_3)_2$ from calcite and siderite is approximately the same, then the less negative enthalpy of formation of $\text{CaFe}(\text{CO}_3)_2$ is the reason for the instability of this phase. The $-T\Delta S$ term is always positive and increases at high temperature, which is not favorable for the formation of ordered ankerite. The disordered phase, on the other hand, is increasingly stabilized at high temperature by its large positive configurational entropy. Thus, ordered $\text{CaFe}(\text{CO}_3)_2$ could be made only at low temperature, but kinetic barriers may prevent its formation.

The enthalpy of disordering of $\text{CaFe}(\text{CO}_3)_2$ can be estimated (about 10 kJ/mol) from the data shown in Figure 3. The configurational entropy of complete disordering of $\text{CaFe}(\text{CO}_3)_2$ is $\Delta S = 2R \ln 2 = 11.53$ J/(mol·K). Therefore, the temperature of disordering of $\text{CaFe}(\text{CO}_3)_2$, treated as a hypothetical first-order transition, would be 594 °C. This is below the solvus (approximately 829 °C) of the system CaCO_3 - FeCO_3 at the composition of $\text{CaFe}(\text{CO}_3)_2$ (Davidson et al. 1993). This result, again, shows that ordered $\text{CaFe}(\text{CO}_3)_2$ could exist only at low temperature, if at all, which is consistent with the prediction by Davidson et al. (1993).

It is also interesting that our data suggest that the volumes of disordered synthetic samples are smaller than those of more ordered natural samples in the range of high Fe content, although a complication is that the latter contain a few mole percent of the larger cation, Mn^{2+} . This may suggest a negative volume of disordering (as suggested by Davidson et al. 1993) and reflects the expansion of the c axis in the more disordered structure. This behavior is opposite that of $\text{CaMg}(\text{CO}_3)_2$ and again points to the conclusion that the alternate stacking of Fe and Ca layers does not appear to be favorable, either structurally or energetically. This negative volume change in ordering of pure ankerite indicates that higher pressure is not favorable for the formation of the ordered ankerite.

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REFERENCES CITED

- Anderson, G.M., and Crerar, D.A. (1993) *Thermodynamics in geochemistry, the equilibrium model*, 342 p. Oxford University Press, New York.
- Anovitz, L.M., and Essene, E.J. (1987) Phase equilibria in the system $\text{CaCO}_3\text{-MgCO}_3\text{-FeCO}_3$. *Journal of Petrology*, 23, 389-414.
- Busing, W.R. (1981) WMIN, a computer program to model molecules and crystals in terms of potential energy functions. Oak Ridge National Laboratory Report, ORNL-5747.
- Chai, L. (1995) Synthesis, characterization, and energetics of carbonates in the $\text{CaCO}_3\text{-MgCO}_3\text{-FeCO}_3$ system. Ph.D. thesis, Princeton University, Princeton, New Jersey.
- Chai, L., and Navrotsky, A. (1993) Thermochemistry of carbonate-pyroxene equilibria. *Contributions to Mineralogy and Petrology*, 114, 139-147.
- (1994) Enthalpy of formation of siderite and its application in phase equilibrium calculation. *American Mineralogist*, 79, 921-929.
- (1996) Synthesis, characterization, and enthalpy of mixing of the $(\text{Fe,Mg})\text{CO}_3$ solid solution. *Geochimica et Cosmochimica Acta*, in press.
- Davidson, P.M., Symmes, G.H., Cohen, B.A., Reeder, R.J., and Lindsley, D.H. (1993) Synthesis of the new compound $\text{CaFe}(\text{CO}_3)_2$ and experimental constraints on the $(\text{Ca,Fe})\text{CO}_3$ join. *Geochimica et Cosmochimica Acta*, 57, 5105-5109.
- Davies, P.K., and Navrotsky, A. (1983) Quantitative correlations of deviations from ideality in binary and pseudobinary solid solutions. *Journal of Solid State Chemistry*, 46, 1-22.
- Goldsmith, J.R., Graf, D.L., Witters, J., and Northrop, D.A. (1962) Studies in the system $\text{CaCO}_3\text{-MgCO}_3\text{-FeCO}_3$: 1. Phase relations; 2. A method from major-element spectrochemical analysis; 3. Compositions of some ferroan dolomites. *Journal of Geology*, 70, 659-688.
- Holland, T.J.B., and Powell, R. (1990) An enlarged and updated internally consistent thermodynamic dataset with uncertainties and correlations: The system $\text{K}_2\text{O-Na}_2\text{O-CaO-MgO-MnO-FeO-Fe}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-TiO}_2\text{-SiO}_2\text{-C-H}_2\text{-O}_2$. *Journal of Metamorphic Geology*, 8, 89-124.
- Navrotsky, A. (1977) Progress and new directions in high temperature calorimetry. *Physics and Chemistry of Minerals*, 2, 89-104.
- Navrotsky, A., and Capobianco, C. (1987) Enthalpies of formation of dolomite and of magnesian calcites. *American Mineralogist*, 72, 782-787.
- Powell, R., Condoliffe, D.M., and Condoliffe, E. (1984) Calcite-dolomite geothermometry in the system $\text{CaCO}_3\text{-MgCO}_3\text{-FeCO}_3$: An experimental study. *Journal of Metamorphic Geology*, 2, 33-41.
- Reeder, R.J. (1983) Crystal chemistry of the rhombohedral carbonates. In *Mineralogical Society of America Reviews in Mineralogy*, 11, 394 p.
- Reeder, R.J., and Wenk, H.-R. (1983) Structure refinements of some thermally disordered dolomites. *American Mineralogist*, 68, 769-776.
- Reeder, R.J., and Dollase, W.A. (1989) Structural variation in the dolomite-ankerite solid-solution series: An X-ray, Mössbauer and TEM study. *American Mineralogist*, 74, 1159-1167.
- (1991) Structural variation in the dolomite-ankerite solid-solution series: An X-ray, Mössbauer, and TEM study—Reply. *American Mineralogist*, 76, 661-662.
- Robie, R., Hemingway, B.S., and Fisher, J.R. (1978) *Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar (10^5 pascals) pressure and at higher temperatures*. U.S. Geological Survey Bulletin 1452.
- Rosenberg, P.E. (1963) Subsolidus relations in the system $\text{CaCO}_3\text{-FeCO}_3$. *American Journal of Science*, 261, 683-690.
- (1967) Subsolidus relations in the system $\text{CaCO}_3\text{-MgCO}_3\text{-FeCO}_3$ between 350 °C and 550 °C. *American Mineralogist*, 52, 787-796.
- (1968) Subsolidus relations on the dolomite join, $\text{CaMg}(\text{CO}_3)_2\text{-CaFe}(\text{CO}_3)_2\text{-CaMn}(\text{CO}_3)_2$. *American Mineralogist*, 53, 880-889.
- (1991) Structural variation in the dolomite-ankerite solid-solution series: An X-ray, Mössbauer, and TEM study—Discussion. *American Mineralogist*, 76, 659-660.
- Rosenberg, P.E., and Foit, F.F., Jr. (1979) The stability of transition metal dolomites in carbonate system: A discussion. *Geochimica et Cosmochimica Acta*, 43, 951-955.

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