Synthesis, characterization, and energetics of solid solution along the dolomite-ankerite join, and implications for the stability of ordered 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, O₂), 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 \(-9.29 \pm 1.97\) and \(6.98 \pm 2.08\) 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, CaFe\((\text{CO}_3)_2\) (approximately 10 kJ/mol), which may explain the nonexistence of ordered 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 FeCO₃-MgCO₃ system, whereas Fe\(^{2+}\) only partially substitutes for Mg\(^{2+}\) in dolomite to form ankerite [Ca\((\text{Fe}_{x}\text{Mg}_{1-x})\text{CO}_3\)], \(0 \leq x \leq 0.7\) (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 temperatures, ankerite is expected to undergo a disordering transition, as does dolomite, to the calcite structure. End-member ankerite, 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 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 CaFe\((\text{CO}_3)_2\) (calcite-type) phase at 845 °C and 30 kbar and suggested that ordered CaFe\((\text{CO}_3)_2\) could exist at low temperature.

Several efforts have been made to explain the nonexistence of ordered 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 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 CaMg\((\text{CO}_3)_2\) and 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 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 CaCO₃ and synthetic MgCO₃, and FeCO₃, were used as starting materials. As suggested in previous work (Rosenberg 1967, 1968), precipitated CaCO₃ was used to promote the synthesis reaction. MgCO₃ and FeCO₃ were prepared from basic magnesium carbonate and iron oxide, respectively, in a CO₂ 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 Ag₂C₂O₄ 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 Ag₂C₂O₄. The welded platinum capsule was about one-half the length of the graphite furnace. A W/3%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 ± 50 °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 Ag₂C₂O₄ 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 CaCO₃ and basic magnesium carbonate at 700 °C in CO₂ 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 CuKα 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° 2θ 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 O₂ atmosphere with the use of a Netzsch STA 409C apparatus. The flow rate of O₂ was approximately 0.5 cm³/s. The experimental temperature ranged from room temperature to 1050 °C, with a 10 °C/min heating rate. Al₂O₃ 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, 2PbO·B₂O₃). 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 Fe²⁺-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 Fe³⁺-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 Fe²⁺ in the lead borate solvent (Chai and Navrotsky 1994). A two-step calorimetric procedure was used for the Fe²⁺-bearing carbonates. The first step of oxidative decarbonation in O₂ was followed by dissolution of the Fe³⁺-containing oxide products. Once the Fe²⁺ 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 Fe²⁺ in the dolomite structure [i.e.,
TABLE 1. Composition and unit-cell parameters of the ankerite solid solutions

<table>
<thead>
<tr>
<th>Sample</th>
<th>x</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>V (Å³)</th>
<th>Figure of merit</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaMg(CO₃)₂*</td>
<td>0.00</td>
<td>4.8076(3)</td>
<td>16.007(2)</td>
<td>320.40</td>
<td>F(15) = 113</td>
</tr>
<tr>
<td>ankl</td>
<td>0.1583</td>
<td>4.8108(2)</td>
<td>16.1095(17)</td>
<td>322.88</td>
<td>F(13) = 98</td>
</tr>
<tr>
<td>ank2</td>
<td>0.4996</td>
<td>4.8131(1)</td>
<td>16.1209(9)</td>
<td>323.41</td>
<td>F(13) = 169</td>
</tr>
<tr>
<td>ank3</td>
<td>0.6480</td>
<td>4.8300(9)</td>
<td>16.210(1)</td>
<td>327.72</td>
<td>F(10) = 21</td>
</tr>
<tr>
<td>ank4</td>
<td>1.00</td>
<td>4.8291(3)</td>
<td>16.210(1)</td>
<td>327.72</td>
<td>—</td>
</tr>
<tr>
<td>CaFe(CO₃)₂**</td>
<td>1.00</td>
<td>4.8108(2)</td>
<td>16.007(2)</td>
<td>320.40</td>
<td>—</td>
</tr>
</tbody>
</table>

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(Fe₃Mg₋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 ankl with x = 0.1583 but disappear in the samples with higher Fe contents. When CuKα 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 ankl3 and ankl4 (x = 0.6480) are probably at least partially disordered. To determine the degree of disordering, Rietveld refinements were attempted for sample ankl3 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 ankl5 (x = 1.0) are consistent with those of disordered CaFe(CO₃)₂ from Davidson et al. (1993), strongly suggesting that ankl5 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 apparatus. 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). Disordering 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-
Dedicated that the decomposition products for all ankerite solid solutions are CaO, MgO, and Ca$_2$Fe$_2$O$_4$. 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 Ca$_2$Fe$_2$O$_4$).

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$_2$O 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, Ca(Fe,Mg,_,)(CO$_3$)$_2$, were calculated from enthalpies of drop solution ($\Delta H^\circ$) 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 ($\Delta H_{\text{decomp}}$), heat contents ($\Delta H_\text{m}$), and enthalpies of drop solution ($\Delta H^\circ$) 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 decomposition 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:

\[
\begin{align*}
\text{CaCO}_3 (25 \degree C, s) & \rightarrow \text{CaO} (770 \degree C, \text{soln}) \\
+ \text{CO}_2 (770 \degree C, g) & \quad \text{(1)} \\
\text{CaO} (25 \degree C, s) + \text{CO}_2 (25 \degree C, g) & \rightarrow \text{CaCO}_3 (25 \degree C, s) \quad \text{(2)} \\
\text{CO}_2 (770 \degree C, g) & \rightarrow \text{CO}_2 (25 \degree C, g). \quad \text{(3)}
\end{align*}
\]

Adding Equations 1, 2, and 3, we have

\[
\text{CaO} (25 \degree C, s) \rightarrow \text{CaO} (770 \degree C, \text{soln}). \quad \text{(4)}
\]

The enthalpy of Reaction 1 is the measured enthalpy of drop solution ($\Delta H_{\text{decomp}}$) of calcite (Table 2), the enthalpy of Reaction 2 is the heat of formation ($\Delta H_\text{f}$) of calcite, and the enthalpy of Reaction 3 is heat content ($\Delta H_\text{m}$) of CO$_2$. The latter two values are from Robie et al. (1978). The calculated enthalpy of drop solution of CaO (Reaction 4)

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**Table 2.** Calorimetric data for the ankerite solid solutions

<table>
<thead>
<tr>
<th>Sample</th>
<th>$x$</th>
<th>$\Delta H_{\text{m}}$</th>
<th>$\Delta H_\text{m}^\dagger$</th>
<th>$\Delta H_\text{m}^\ddagger$</th>
<th>$\Delta H^\circ_{\text{f}}$</th>
<th>$\Delta H^\circ_{\text{m}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dolomite</td>
<td>0.00</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>399.21 ± 0.90(6)</td>
<td>362.64 ± 3.11</td>
</tr>
<tr>
<td>ank1</td>
<td>0.1583</td>
<td>404.19 ± 2.10(4)</td>
<td>75.024</td>
<td>33.477</td>
<td>362.64 ± 3.11</td>
<td>36.33 ± 1.11</td>
</tr>
<tr>
<td>ank2</td>
<td>0.2990</td>
<td>375.54 ± 1.24(4)</td>
<td>76.974</td>
<td>42.344</td>
<td>340.91 ± 2.30</td>
<td>37.33 ± 1.11</td>
</tr>
<tr>
<td>ank3</td>
<td>0.4996</td>
<td>333.89 ± 4.44(5)</td>
<td>79.750</td>
<td>54.868</td>
<td>308.11 ± 4.88</td>
<td>40.34 ± 1.11</td>
</tr>
<tr>
<td>ank4</td>
<td>0.6482</td>
<td>306.99 ± 1.45(5)</td>
<td>81.811</td>
<td>64.340</td>
<td>289.52 ± 1.88</td>
<td>32.84 ± 1.11</td>
</tr>
<tr>
<td>ank5</td>
<td>1.00</td>
<td>253.72 ± 1.45(6)</td>
<td>86.690</td>
<td>86.525</td>
<td>253.56 ± 1.84</td>
<td>25.84 ± 1.11</td>
</tr>
<tr>
<td>Calcite</td>
<td>0.00</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>196.85 ± 0.49(6)</td>
<td>63.68 ± 0.83</td>
</tr>
<tr>
<td>Magnesite</td>
<td>0.00</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>193.07 ± 1.68(5)</td>
<td>63.68 ± 0.83</td>
</tr>
</tbody>
</table>

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

$^\dagger$ Heat contents of oxides are from Robie et al. (1978).

$^\ddagger$ Calculated from data of the individual oxides (see text).

$^\text{§}$ From Chai and Navrotsky (1996).
...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 CaFeCO₃ was determined by drop solution of ankerite [Ca(Fe,Mg)₂CO₃] can then be calculated as \( \Delta H_{\text{alk}} = \Delta H_{\text{alk}} + \Delta H_{\text{m}} \). The enthalpy of formation of ankerite [Ca(Fe,Mg)₂CO₃] from calcite, magnesite, and siderite may be calculated as \( \Delta H_{\text{alk}} = \Delta H_{\text{alk}} + \Delta H_{\text{m}} \), where \( \Delta H_{\text{alk}} \) (cal), \( \Delta H_{\text{alk}} \) (mag), and \( \Delta H_{\text{alk}} \) (sid) are the enthalpies of drop solution of calcite, magnesite, and siderite, respectively (Table 2 and Fig. 3).

The enthalpy of formation of disordered CaFeCO₃ was derived by extrapolation from natural ankerite (Reeder and Dollase 1989). The calculated lattice energies (-4.6 kJ/mol) may give a reliable estimate of the enthalpy of formation of ordered CaFeCO₃, 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 CaMg(CO₃)₂ and ordered CaFe(CO₃)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 CaFe(CO₃)₂ from Holland and Powell (1990) was derived from the data of Fe²⁺-Mg²⁺ 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 ± 50 °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 $(\Delta V)$, $W = 100.826V - 0.4$ (kJ/mol). Recently, we determined the energetics of solid solution in the system FeCO₃-MgCO₃ (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 FeCO₃-MgCO₃ 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 Ca(Fe₉,Mg₄)₂(CO₃)₃]. 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 CaCO₃ (s) + FeCO₃ (s) → CaFe(CO₃)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 CaCO₃ (s) + MgCO₃ (s) → CaMg(CO₃)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 enthalpy 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 CaFe(CO₃)₂**

The above estimations may explain the nonexistence of pure ankerite. The enthalpy difference of disordering in dolomite is much larger than that in CaFe(CO₃)₂. In other words, there is insufficient energy gain on ordering of CaFe(CO₃)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 CaFe(CO₃)₂ from calcite and siderite is approximately the same, then the less negative enthalpy of formation of CaFe(CO₃)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 CaFe(CO₃)₂ could be made only at low temperature, but kinetic barriers may prevent its formation.

The enthalpy of disordering of CaFe(CO₃)₂ can be estimated (about 10 kJ/mol) from the data shown in Figure 3. The configurational entropy of complete disordering of CaFe(CO₃)₂, $\Delta S = 2R \ln 2 = 11.53$ J/(mol·K). Therefore, the temperature of disordering of CaFe(CO₃)₂, treated as a hypothetical first-order transition, would be 594 °C. This is below the solvus (approximately 829 °C) of the system CaCO₃-FeCO₃ at the composition of CaFe(CO₃)₂ (Davidson et al. 1993). This result, again, shows that ordered CaFe(CO₃)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, Mn²⁺. 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 CaMg(CO₃)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


Holland, T.J.B., and Powell, R. (1990) An enlarged and updated internally consistent thermodynamic dataset with uncertainties and correlations: The system K$_2$O-Na$_2$O-CaO-MgO-MnO-FeO-Fe$_2$O$_3$-Al$_2$O$_3$-Ti$_2$O$_3$-SiO$_2$-C-H$_2$O$_2$. Journal of Metamorphic Geology, 8, 89-124.


—— (1967) Subsolidus relations in the system CaCO$_3$-MgCO$_3$-FeCO$_3$ between 350 °C and 550 °C. American Mineralogist, 52, 787-796.

—— (1968) Subsolidus relations on the dolomite join, CaMg(CO$_3$)$_2$-CaFe(CO$_3$)$_2$-CaMn(CO$_3$)$_2$. American Mineralogist, 53, 880-889.


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