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Calorimetric studies of the energetics of order-disorder in the system $Mg_{1-x}Fe_xCa(CO_3)_2$

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ABSTRACT

Calorimetric studies by Chai and Navrotsky (1996) on dolomite-ankerite energetics have been extended by including two additional types of samples: a very disordered stoichiometric $MgCa(CO_3)_2$ prepared from low-temperature aqueous solution and three largely ordered natural samples of intermediate iron content.

Combining these data with previous work, we see three distinct energetic trends. These represent samples with nearly complete order, nearly complete disorder, and intermediate order. From these trends, the enthalpy of complete disordering is estimated to be 33 ± 6 kJ/mol for $MgCa(CO_3)_2$ and 18 ± 5 kJ/mol for $FeCa(CO_3)_2$.

INTRODUCTION

Substitution of Fe for Mg in dolomite, ordered $CaMg(CO_3)_2$, results in a solid solution, the more iron-rich part of which is referred to as ankerite. However, the solid solution is incomplete (Goldsmith et al. 1962; Reeder and Dollase 1989; Davidson et al. 1993), and the ordered phase $FeCa(CO_3)_2$ does not exist, although a disordered calcite-type solid solution of this composition can be made above about 650 °C (Davidson et al. 1993). Goldsmith et al. (1962) examined the dolomite-ankerite system both experimentally and by characterization of natural samples, and concluded that ordered compositions extend little more than two-thirds across the join toward $CaFe(CO_3)_2$, a limit essentially confirmed by Rosenberg (1967). Reeder and Dollase (1989) used single-crystal X-ray diffraction (XRD), Mössbauer spectroscopy, and transmission electron microscopy (TEM) to characterize the structural states of a suite of largely ordered samples over this composition range in an effort to identify a structural cause for the limited Fe-Mg substitution. However, no cause was found.

Chai and Navrotsky (1996) determined the energetics of a series of synthetic, largely disordered, solid solutions along the $MgCa(CO_3)_2$-$FeCa(CO_3)_2$ join, and Chai et al. (1995) measured the enthalpies of formation of a set of Ca-rich natural dolomites. Those studies expanded the data base for the $MgCO_3$-$FeCO_3$-$CaCO_3$ system, whose energetics are dominated by order-disorder reactions, but the work left several unanswered questions. In particular, the results suggested that the enthalpy of complete disordering of dolomite was in the 20–30 kJ/mol range. This value is much higher than the 12 kJ/mol suggested by Navrotsky and Capobianco (1987) on the basis of a calorimetric study of a dolomite that had been quenched from above its order-disorder transition but which may have undergone significant reordering upon cooling. Furthermore, because the synthetic (Mg, Fe)$Ca(CO_3)_2$ solid solutions had an increasingly disordered structural state with increasing Fe/(Fe + Mg), their energetics were difficult to interpret. The purpose of this communication is to report and interpret additional new calorimetric data relevant to the issue of order-disorder along the dolomite-ankerite join. Two types of samples were investigated in the present study: natural ankerites that are more strongly ordered than their synthetic counterparts, and a highly disordered synthetic $MgCa(CO_3)_2$ phase produced by precipitation from aqueous solution that appears to approximate a fully disordered dolomite (Siegel 1961; Brady, unpublished observations). By comparing samples of different structural state at the same composition, the systematics suggested by Chai and Navrotsky (1996) have been confirmed and made more quantitative.

EXPERIMENTAL METHODS

Sample preparation and characterization

The natural ankerites were taken from a set of samples studied by XRD, Mössbauer, and TEM techniques (Reeder and Dollase 1989). They had been analyzed with the electron microprobe in the earlier study and two calorimetric samples have been analyzed again with the microprobe (see Table 1). Of the many samples studied previously, we chose three that showed strong ordering reflections, nearly stoichiometric Ca content, and compositional homogeneity.

The synthetic disordered $CaMg(CO_3)_2$ sample was grown after the method of Siegel (1961) by combining equal volumes (10 mL) of 1 *M* $MgSO_4$ and 1 *M* $CaCl_2$ to form a $CaSO_4$ gel, followed by addition of 20 mL of 1 *M* Na_2CO_3 and stirring at 70 °C. After 20 minutes of reaction, samples were filtered and washed with deionized water. Both XRD and TEM showed no ordering reflections. Chemical analysis by DCP indicated a

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TABLE 1. Natural ankerite compositions studied, normalized to two cations

	BM 1931-294	CAMB-UNK	AMNH
$CaCO_3$	1.002 ± 0.007* 0.997†	1.001 ± 0.002* 0.999	0.997†
$MgCO_3$	0.755 ± 0.030* 0.769†	0.644 ± 0.024* 0.646†	0.273†
$FeCO_3$	0.227 ± 0.027* 0.221†	0.301 ± 0.019* 0.292†	0.676†
$MnCO_3$	0.016 ± 0.002* 0.013†	0.055 ± 0.006* 0.063†	0.054†
$x = \frac{Fe+Mn}{Fe+Mn+Mg}$	0.243 ± 0.035* 0.233†	0.356 ± 0.030* 0.355†	0.730†

* Microprobe analysis on calorimetric sample. Error is standard deviation of 5–6 point analysis.

† Reeder and Dollase (1989). Samples are the same as those studied by Reeder and Dollase (1989). Sample numbering is same as that in their paper. Samples came from the British Museum (BM), Cambridge University (CAMB), and the American Museum of Natural History (AMNH).

Ca:Mg ratio of 1:1.

Thermogravimetric studies to observe weight changes corresponding to dehydration (of adsorbed water) and decarbonation in $MgCa(CO_3)_2$ were done using a Netzsch STA 409 thermal analysis system. Differential thermal analysis (DTA) scans were obtained simultaneously. Samples were run in air at a heating rate of 10 °C/min.

Calorimetry

The general methodology of oxide melt solution calorimetry of carbonates has been described previously (Chai and Navrotsky 1993, 1996; Navrotsky 1997). High-temperature oxide melt calorimetry of synthetic ankerites had been performed by a three-step method (Chai and Navrotsky 1996). In the first step, the sample was dropped into a solvent-free crucible in the calorimeter at 770 °C and oxidized and decarbonated to a mixture of Fe^{3+}-bearing phases. The heat content of the decarbonated and oxidized sample was measured in a second transposed temperature drop experiment. The third step consisted of dropping and dissolving the oxidized product in the molten $2PbO{\cdot}2B_2O_3$ solvent at 770 °C. From these three steps, the enthalpy of drop solution involving decarbonation and oxidation was calculated, and the values compared for endmembers and solid solutions to obtain heats of formation. This multistage process was required because the iron-bearing carbonates appeared to oxidize in an irreproducible fashion when introduced directly into the lead borate solvent, even when O_2 gas flowed over the surface of the melt. This three-step procedure has now been simplified to a single direct drop-solution experiment by a new technique developed in our laboratory (McHale et al. 1997), in which a gas (in this case O_2) not only is flushed above the melt but also is bubbled through the solvent by means of a small Pt capillary. This gas flow through the solvent brings the Fe^{2+}-bearing phases into much more direct contact with an oxidizing environment, speeds oxidation by minimizing need for gas diffusion through the melt, and enhances dissolution by effectively stirring the solvent. These improvements occur without disturbing the calorimetric baseline signal or changing the calibration factor. Experiments with the most iron-rich disordered synthetic ankerite sample, ANK62495, $FeCa(CO_3)_2$, from Chai and Navrotsky (1996) showed well-behaved calorimetric peaks and an enthalpy of drop solution plus oxidation of 250.08 + 1.79 kJ/mol, which is within experimental error of the value (253.56 ± 1.84 kJ/mol) obtained by Chai and Navrotsky (1996) using the three-step method (see Table 2).

Calorimetric measurements for the synthetic disordered dolomite were also performed at 770 °C using molten $2PbO{\cdot}B_2O_3$ as the solvent. Because oxidation is not required, the experiments were not performed with bubbling gas through the solvent, but flowing gas over the melt was used to insure that the CO_2 released during solution was removed from the calorimeter (Navrotsky et al. 1994). Initial experiments were performed without drying the sample. The enthalpy of drop solution appeared more endothermic than that for ordered dolomite. This would suggest an enthalpy of formation more exothermic than that for ordered dolomite, which is not consistent with observations that ordered dolomite is the energetically favored low-temperature phase. We then realized that the disordered dolomite contained water. The sample was subsequently dried for 12 h at 120 °C and immediately placed in an Ar-filled glove box to ensure that the sample did not rehydrate. Drop-solution experiments performed with the dried sample yielded a value of 366.49 ± 4.04 kJ/mol, which is less endothermic than that of ordered dolomite and consistent with ordered dolomite being the energetically favored phase at low temperatures.

Realizing the hygroscopic nature of the sample, we performed weight loss experiments with both samples of disordered dolomite used for calorimetry. The "dried" sample contained 0.85 weight percent H_2O, and the "as received" sample contained 11.7 wt% H_2O. The enthalpies of drop solution given in Table 2 have been corrected for each observed H_2O content assuming the water is physisorbed and has an enthalpy equivalent to that of pure water [$H_{770\ °C,gas} - H_{25\ °C,liquid}$ = 74.28 kJ/mol (Robie and Hemingway 1995)]. The observation that most of the water is readily removed at 120 °C is consistent with it being physisorbed rather than strongly held in the structure.

RESULTS AND DISCUSSION

Synthetic disordered dolomite

Figure 1 shows the XRD pattern of the synthetic dolomite, confirming its crystalline but largely disordered nature. This pattern is very similar to that published by Siegel (1961) for the material originally prepared using this synthetic route.

The sample was analyzed using TGA-DTA techniques to evaluate both the H_2O content and decarbonation behavior. The sample was heated to a maximum temperature of 1200 °C and two major endothermic reactions (near 450 and 780 °C) were observed (see Fig. 2). These were followed by a diffuse endotherm at 800–1100 °C. These three endotherms also correspond to regions of weight loss in the TGA. To evaluate the nature of the decarbonation reactions, the sample was heated to a temperature just above the endotherm, quenched, and an XRD pattern taken. The peak temperature of the first endotherm is ~450 °C, which is ~300 °C lower than is generally associated with the onset of decarbonation of dolomite. The XRD pattern indicates that the assemblage formed during heating is calcite + huntite [$CaMg_3(CO_3)_4$] + periclase. The next endotherm occurs

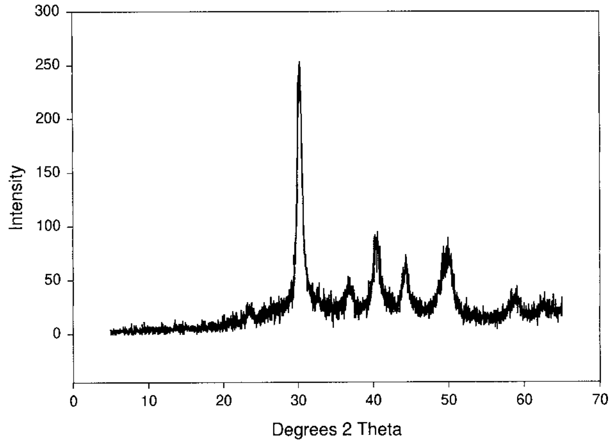

FIGURE 1. XRD pattern of synthetic disordered dolomite (obtained using Cu*K*α radiation).

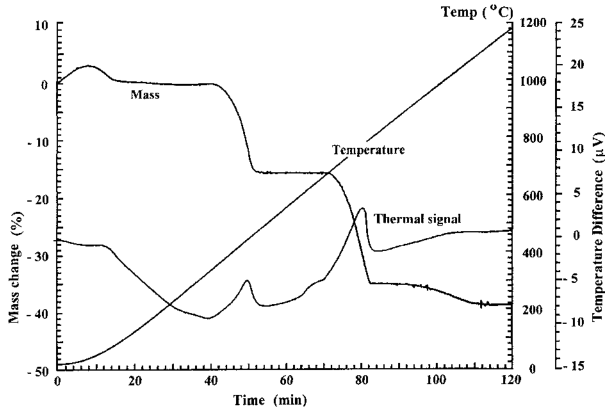

FIGURE 2. Thermal analysis scan of synthetic disordered $MgCa(CO_3)_2$. Sample run in air at heating rate of 10 °C/min. DTA signal reported as a temperature difference measured in mV, mass change in percentages. Note slightly nonlinear temperature change with time below 100 °C.

at a peak temperature of 780 °C and corresponds to the formation of CaO, but the carbonate phases huntite and calcite are still present. Complete decarbonation does not occur until 1100 °C, above which the assemblage is lime + periclase. The Eugui natural ordered dolomite, on the other hand, shows two decarbonation events that are relatively close in peak temperature (820 and 860 °C). Above 860 °C the products are MgO and CaO. The main difference between the samples is the much lower temperature for the first decarbonation peak of the synthetic disordered sample. This may reflect three factors: (1) smaller grain size, which shortens diffusion paths and enhances decomposition kinetics; (2) water content, which may also enhance reaction rates; and (3) much diminished thermodynamic stability. The diminished stability, though largely arising from Ca-Mg disorder, may also include small contributions from surface energy, from defects other than disorder, and from poorer crystallinity than that of natural ordered dolomite. However, these other terms cannot be assessed quantitatively. The formation of huntite rather than of $CaCO_3$ and MgO also suggests a difference in both thermodynamic driving force and kinetic pathway. The calorimetry (see below) confirms the energetic instability of the disordered dolomite.

The drop-solution calorimetric data (see Table 2) also suggest that this disordered $CaMg(CO_3)_2$ is energetically very different from normal ordered dolomite, with an enthalpy of disordering of 35.7 ± 3.9 kJ/mol (dried sample) and 30.6 ± 2.6 kJ/mol (initial sample) compared to Eugui dolomite. This is consistent with an extent of disordering that is much greater than that of the heat-treated and quenched sample described by Navrotsky and Capobianco (1987), which is energetically only 12 ± 1 kJ/mol above ordered dolomite.

Although the synthetic material is fine-grained (~1 μm), it is not nanophase and its XRD peaks are fairly sharp (see Fig. 1). Thus we believe that the contribution of surface energy to the energetics is relatively small (<4 kJ/mol). We attempted to order the synthetic sample, without coarsening it, with the goal of separating the energetics related to ordering and to grain size. The DSC experiments described above and several other heating studies showed, instead, that the disordered dolomite decomposed to an $MgCO_3$-rich phase [huntite, $CaMg_3(CO_3)_4$] and a Ca-rich phase [nonstoichiometric dolomite, $(Ca_{0.5+x}Mg_{0.5-x})_2(CO_3)_2$], even before any decarbonation occurred. The complexity of powder XRD patterns of these partially decomposed samples (a mixture of three phases) did not allow an assessment of the extent of ordering (identification of superstructure reflections) of the Ca-rich phase. The presence of huntite was clearly indicated, however.

The energetics of decomposition of disordered dolomite to huntite plus Ca-rich dolomite can be assessed as follows. Low-temperature natural $Ca_{1+x}Mg_{1-x}CO_3$ dolomites show excess Ca up to x = 0.06 (Goldsmith and Graf 1958; Reeder and Sheppard 1984). The energetics of a suite of natural Ca-rich dolomites have been determined (Chai et al. 1995), and the enthalpy of formation from the binary carbonates of the most Ca-rich dolomite studied $(Ca_{0.56}Mg_{0.44})_2(CO_3)_2$ is about +10.0 kJ/mol. That of huntite, written as $(Mg_{0.75}Ca_{0.25})_2(CO_3)_2$ is +8.9 kJ/mol, taken from the thermochemical data of Robie and Hemingway (1995). Thus for the reaction:

$$CaMg(CO_3)_2\ (\text{disordered}) = 0.81(Ca_{0.56}Mg_{0.44})_2(CO_3)_2 + 0.19(Ca_{0.25}Mg_{0.75})_2(CO_3)_2 \quad (1)$$

$\Delta H = 0.81\ (\Delta H_f$, Ca-rich dolomite$) + 0.19\ \Delta H_f$ (huntite) $- \Delta H_f$ (disordered dolomite) $= 0.81(10.0) + 0.19(8.9) - 23.9 = -14.1$ kJ/mol. This enthalpy is indeed exothermic, but not as exothermic as that associated with complete ordering (about −33 kJ/mol). The ordering enthalpy used in these calculations represents the average of the two determinations for Eugui dolomite and for disordered dolomite shown in Table 2.

Thus the decomposition of disordered dolomite follows the "Ostwald step rule" with huntite + nonstoichiometric dolomite energetically intermediate between the disordered and ordered

TABLE 2. Calorimetric data for dolomite and ankerite samples (kJ/mol)

Sample	x	Ordering state	ΔH_{ds}	ΔH_f
Eugui dolomite*	0	ordered	399.21 ± 0.90(6)	–9.29 ± 1.97
Eugui dolomite	0	ordered	398.19 ± 2.88 (10)	–8.27 ± 3.47
Synthetic, dried dolomite†	0	disordered	363.50 ± 3.80(6)	26.42 ± 4.44
Synthetic, not dried dolomite‡	0	disordered	368.59 ± 2.43(6)	21.32 ± 3.34
BM1931-294 (natural)	0.24 ± 0.03	ordered	362.12 ± 1.42(13)	–1.29 ± 2.32
Camb/Unk (natural)	0.36 ± 0.03	ordered	352.04 ± 3.36(9)	–2.88 ± 4.06
AMNH8059 ± (natural)	0.73 ± 0.03	ordered	304.98 ± 1.80(13)	–8.37 ± 2.91
ANK62495* (synthetic)	1	disordered	253.56 ± 1.84 (6)	6.98 ± 2.08
ANK62495§ (synthetic)	1	disordered	250.08 ± 1.79(3)	10.51 ± 2.76
$CaCO_3$*			196.85 ± 0.49(6)	
$MgCO_3$*			193.07 ± 1.68(5)	
$FeCO_3$*			63.69 ± 0.83 (6)	
$MnCO_3$			141.60 ± 0.89(8)	

Note: Errors are 2 standard deviations of the mean. The numbers in parentheses are the number of experiments, ds = drop solution, f = formation from simple carbonates.

* Data and sample from Chai and Navrotsky (1996).

† ΔH_{ds} corrected for 0.85 ± 0.05% adsorbed H_2O, see text.

‡ ΔH_{ds} corrected for 11.7 ± 0.7% adsorbed H_2O, see text.

§ Gas bubbling through melt, on same sample as used by Chai and Navrotsky (1996), see text.

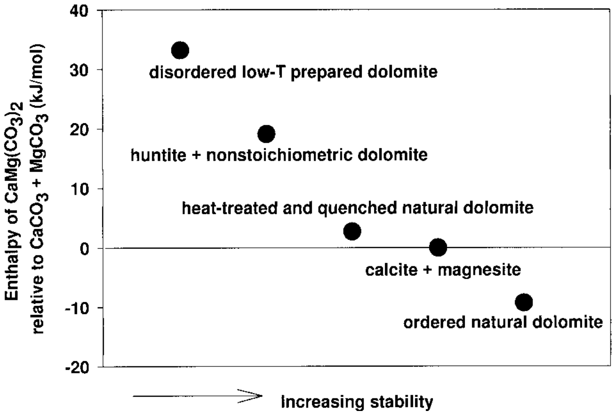

FIGURE 3. Enthalpy, relative to $CaCO_3 + MgCO_3$, of several phase assemblages of $CaMg(CO_3)_2$ composition. In this relative energy level diagram, the x axis is used only to emphasize the trend in energies.

stoichiometric phases (Fig. 3). The observation of such decomposition, not possible for ordered $CaMg(CO_3)_2$, supports our finding that this precipitated material is indeed disordered and of much higher energy than the ordered phase.

The calorimetric data for nonstoichiometric dolomites used in the calculation above were obtained from a set of natural samples. These tend to show complex ordering and domain structures that might make them energetically somewhat different from the decomposition products of the synthetic sample. It is possible that such features would make the natural sample energetically somewhat more stable than the nonstoichiometric decomposition product of disordered dolomite, but the extent of such a difference cannot be ascertained. If such a difference exists, then the decomposition products might be somewhat closer to the starting material (disordered dolomite) in enthalpy, but are very unlikely to lie above the starting material. Thus the Ostwald step rule relationship described above will be maintained. Similarly, if the nonstoichiometric Ca-rich phase has a somewhat different composition, then the relative proportions of Ca-rich dolomite and huntite in the decomposition products will change, and the energetics will be slightly different, but the qualitative conclusions above are unlikely to be altered.

We note that the enthalpy of formation of huntite from calcite and magnesite reported in Robie and Hemingway (1995) is positive. This may reflect a possible problem in the enthalpy and free energy of either huntite itself or of magnesite, for which Robie and Hemingway (1995) give a somewhat more negative value than other tabulations. This issue deserves further study but does not affect the argument above, since the assemblage of huntite plus nonstoichiometric dolomite will lie energetically between disordered and ordered dolomite in any case.

Comparison of dolomite-ankerite solid solutions of different degrees of order

Calorimetric data for the natural dolomite-ankerite series are presented in Table 2, the last column of which gives the enthalpy of formation from the binary carbonates according to the reaction:

$$aFeCO_3 + bMnCO_3 + cMgCO_3 + (2\text{-}a\text{-}b\text{-}c)CaCO_3 = Fe_aMn_bMg_cCa_{(2\text{-}a\text{-}b\text{-}c)}(CO_3)_2 \qquad (2)$$

The effect of the variable but amounts of manganese on the heat of formation is accounted for in this reaction. To project these data onto the $Fe_xMg_{1-x}Ca(CO_3)_2$, binary, we make the following assumptions. We take the heats of formation shown in Table 2 and assume that (1) the effect of the very slight deviation from Ca stoichiometry in the samples chosen can be neglected, and (2) Mn can be counted with Fe. Thus we calculate a value, x = (Fe + Mn)/(Fe + Mn + Mg), which is the compositional parameter chosen to compare natural and synthetic samples.

Using the data in this study and data from previous work (Chai and Navrotsky 1996; Navrotsky and Capobianco 1987), we classify the samples studied into three categories (Fig. 4). The first group contains well-ordered samples (Eugui dolomite and the natural ankerites in this study). The second group contains samples showing no ordering reflections and having, pre-

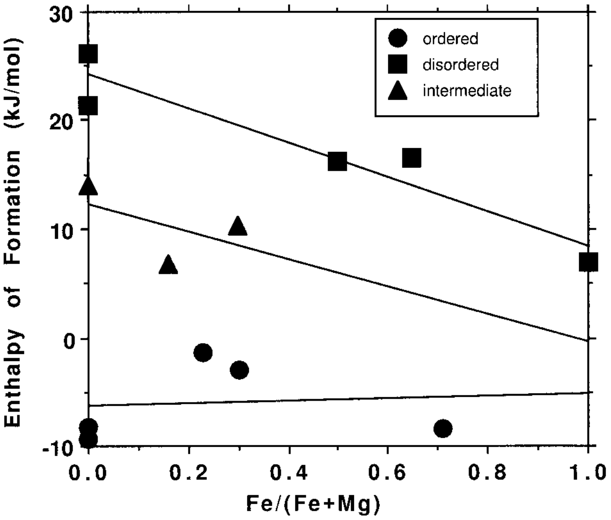

FIGURE 4. Enthalpy of formation from the binary carbonates of phases projected along the $MgCa(CO_3)_2$-$FeCa(CO_3)_2$ join, as discussed in text. Solid circles represent ordered dolomite and largely ordered natural samples. Squares represent the largely disordered synthetic $MgCa(CO_3)_2$ described in this work and the synthetic samples showing no superstructure reflections measured by Chai and Navrotsky (1996). Triangles represent partly ordered samples, the quenched heat-treated Eugui dolomite of Navrotsky and Capobianco (1987) and the synthetic samples with weak superstructure reflections measured by Chai and Navrotsky (1996). The lines, though least-squares fits, are presented as aids to the eye in emphasizing the three distinct trends. The exact degree of order of each sample differs and this may account for the scatter about these trends.

sumably, nearly complete disorder (the disordered dolomite studied in this work and the more iron-rich synthetic ankerites of Chai et al. (1995). The third group contains samples with possible weak ordering reflections and partial order (heat treated Eugui dolomite and Mg-rich synthetic ankerites). It is clear that the trends defined by the ordered and disordered samples are different, with the partially ordered samples intermediate. The straight lines drawn in Figure 4 for ordered and disordered samples are least-squares fits. The scatter in the data from these trends probably results from compositional heterogeneity, differing Mn contents, and the uncertainty and variability in the degree of order in the "ordered" natural samples (Reeder and Dollase 1989). Nevertheless, these trends allow fairly compelling conclusions to be drawn. (1) The degree of disorder has a marked effect on the enthalpy of formation, with negative enthalpies of formation from the binary carbonates for strongly ordered samples and positive enthalpies of formation for strongly disordered samples. This is consistent with negative (stabilizing) interlayer interactions competing with positive (destabilizing) intralayer interactions at all Fe/(Fe + Mg) ratios. (2) The intercepts of the lines for ordered and disordered phases (see Fig. 4) give an estimate of the enthalpy of complete disordering. For $MgCa(CO_3)_2$, this value is about 32 ± 5 kJ/mol, or about three times the value initially suggested by Navrotsky and Capobianco (1987). This value is consistent with that obtained from calorimetry on the two samples of disordered $MgCa(CO_3)_2$ (35.7 ± 3.9 and 30.6 ± 2.6 kJ/mol), as discussed above. The trends shown suggest that the heat treated and quenched Eugui dolomite that Navrotsky and Capobianco used indeed suffered considerable reordering on cooling and falls on the trend of partially ordered samples. This is consistent with the findings of Reeder and Wenk (1983), who were unable to recover a fully disordered dolomite by quenching from above the critical disordering temperature. For $FeCa(CaCO_3)_2$, the enthalpy of disordering is about 18 ± 5 kJ/mol. The much smaller value for $FeCa(CaCO_3)_2$ than for $MgCa(CO_3)_2$ is consistent with the absence of fully ordered iron-rich phases on the $MgCa(CO_3)_2$-$FeCa(CO_3)_2$ join. If the critical temperature for disordering scales with the enthalpy of disordering, and that for $MgCa(CO_3)_2$ is about 1423 K (Reeder and Wenk 1983), then the disordering temperature for $FeCa(CO_3)_2$ would be about 800 K (527 °C). Such a low ordering temperature would make it difficult, kinetically, to make ordered $FeCa(CO_3)_2$ because the thermodynamic driving for ordering even at lower temperatures (100–400 °C) would be small, and the kinetics would be slow.

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