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A new model of mixing energy and application to the calcium, magnesium and manganese carbonates

By

Rainer Aloys Schultz-Güttler, São Paulo

With 7 figures and 3 tables in the text

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Abstract: A new mixing energy model for binary systems showing ordered compounds of intermediate composition is presented. The model starts from disordered solid solution and incorporates the energetic effect of clustering of atoms or ions (ordering) over restricted intervals of composition. The free energy, enthalpy and chemical potential of the ordered intermediate compound are all represented as continuous functions of those depicting the properties of the constituent end members. In this respect, the new model differs from previous formulations (NAVROTSKY & LOUCKS 1977, GROVER 1980).

The passage of an ordered intermediate compound (of stoichiometric composition) to the disordered state can be represented by a first or higher order transition, each of which can be incorporated into the model.

Numerical parameters to be needed for this formulation are the interaction parameters of the end member components (for the case of the disordered solid solution) and the critical temperature of loss of order (for the case of formation of the ordered intermediate compound with a stoichiometric composition).

The application of this model to the systems $CaCO_3$-$MnCO_3$ and $CaCO_3$-$MgCO_3$ showed good correspondance between experimental data and calculated phase relations. The model predicts, for instance, a critical temperature of the solvus on the $CaCO_3$-rich side of the system $CaCO_3$-$MgCO_3$ of 1070 °C (experimentally: 1054–1074 at 8 kbar) and 1300 °C on the $MgCO_3$ rich side (1365–1410 °C at 27 kb: IRVING & WYLLIE 1975).

For the system $CaCO_3$-$MnCO_3$ it predicts, at 1 bar, 550 °C for the critical temperature of closing of the solvus on the $MnCO_3$-rich part of the phase diagram (the same temperature as found experimentally) and of 490 °C on the $CaCO_3$-rich side. The mixing energies for these systems including the formation of dolomite and kutnahorite respectively, are given by

$$\Delta G^{Mix} = RT\,(X_A \ln X_A + X_B \ln X_B) + X_A X_B\,(W_G^A X_A + W_G^B X_B) + \\ + G_{AB}^{Order} \exp\,[G_{AB}^{Order} . T^{-0.333}(0.5 - X_A)^2] \qquad (1)$$

where for the system $CaCO_3$-$MnCO_3$: A = $CaCO_3$, B = $MnCO_3$, AB = $Ca_{0.5}Mn_{0.5}CO_3$ $calmol^{-1}$, T°K

$W_G^B = 4370.4 - 1.802T$; $W_G^A = 9339.8 - 6.965T$;
$G_{AB}^{Order} = 2282 - 2.755T$; $T_{crit} = 555\ °C$;

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and for the system $CaCO_3$-$MgCO_3$: A = $CaCO_3$, B = $MgCO_3$, AB = $Ca_{0.5}Mg_{0.5}CO_3$

$$W_G^B = 7815.2 - 5.36T;\ W_G^A = 9436.7 - 1.69T;\ T_{crit} = 1210\,°C$$

$$-\quad G_{AB}^{Order} = 4084.8 - 2.755T;$$

Key words: Carbonates, mixing properties, solid solutions, stability.

Introduction

The evaluation of the free energy of mixing of disordered solid solutions is a relatively simple task today. Saxena (1973) and Grover (1980) present reviews of the methods which have been used and applied to specific cases.

These methods, however, do not deliver satisfactory answers and even fail, when the system shows ordering over restricted compositional ranges, or when an ordered compound of intermediate composition is formed, whose structure is a superstructure of the disordered solid solution (Carpenter 1980).

The schematic deductions of Carpenter (1980) serve as a basis to develop a new model of mixing energies for systems showing ordering which should avoid the pitfalls shown by previous formulations (Navrotsky & Loucks 1977, Grover 1980, 1974).

The new model allows the quantitative calculation of phase relationships including the evaluation of both spinodal and "conditional spinodal" exsolution relations (Allen & Cahn 1976).

Theoretical considerations about cation disordering and phase transitions of first or higher order

Interruptions in phase relations of solid solutions, depending on the energetic interactions between components, are mainly of three types: a) formation of non-isostructural miscibility gaps, b) isostructural solvus relations, and c) formations of intermediate compounds with concomitant change of symmetry, due to ordering of atoms or ions on specific lattice sites.

The first two processes were extensively discussed by Thompson (1967) and Saxena (1973), while the last one was reviewed by Jagodzinski (1949), and discussed in detail by Seitz (1940), Münster (1962) and Guttman (1956).

No satisfactory quantitative treatment has, as yet, been offered in the literature, especially for modelling more complex crystal structures. It is clear, also, as shown in the cited literature, that phase transitions of the first or higher order cannot be ignored when dealing with order-disorder phenomena.

Fig. 1 (modified after de Boers 1952) shows how several thermodynamic parameters of a specific compound vary, as a function of temperature, for transitions of the first and second order.

It is clearly observed that all possible variations exist, thus defining an almost continuous sequence of types of transitions, of which the pure first order and pure second order transitions are but extreme cases.

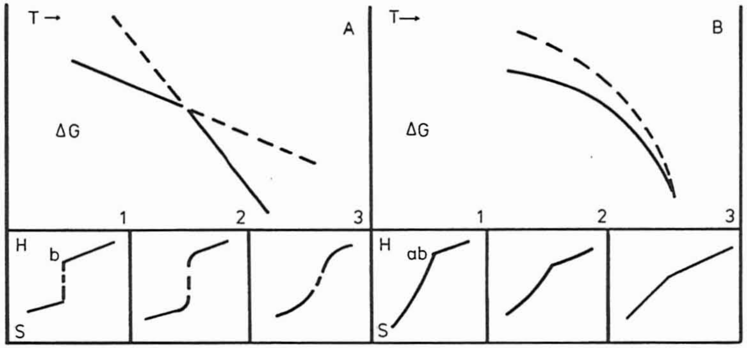

Fig. 1. Relations between Gibbs free energy G, enthalpy H and entropy S in first order (A) and second order (B) transitions as function of temperature. The deciding question whether a given transition is of type A or B is the coincidance of a and b. The examples A2, A3 and B1, B2 all may show the character of a lambda-point transition.

It is often a difficult task to decide on a model based on a first or a second order transition, even when given experimental evidences. In our model, this aspect is not considered relevant, since it applies equally well to those two cases of transitions.

Superposition of Order-Disorder and Exsolution

A system showing simultaneously order-disorder and exsolution will not only show miscibility gaps but also form an ordered intermediate compound.

Schematic free energy diagrams for such systems as function of composition and the resulting T−X diagrams of two possible cases, one with first, the second with higher order transitions, are discussed by Carpenter (1980). In both cases, the free energy of the ordered compound is a function of an non-thermodynamic "order parameter" (Guttman 1956). From the discussion about the order of transition, it can easily be deduced, that a distinction between two cases as done by Carpenter (1980), may be artificial and the need to differentiate only arises due to lack of proper characterisation of the energetic relations of the system. It may very well be possible for a system to show simultaneously different types of transitions at different composition ranges and temperatures (Burton 1983).

It is even possible to imagine composition induced phase transitions of higher order but first order transitions with respect to temperature. In both cases it depends on the slope of $\delta\Delta G/\delta\chi$ at constant temperature or $\delta\Delta G/\delta T$ at constant composition being continuous or not at the passage from the ordered to the disordered phase.

The Problem of Short-Range-Order and Long-Range-Order and the definition of intrinsic order

The definition of these two types of order, short-range order (SRO) and long-range-order (LRO), depends on the appearance or not of the so-called superstructure X-ray reflections indicating a macroscopic change in the crystalstructure of phases. With the onset of formation of superstructure reflections, LRO is said to be established, although the degree of LRO may not yet be high. This is the reason for the definition of the LRO order parameter S varying from O to 1 for perfect LRO.

At a value of S = O, standard X-ray investigations do not show anymore superstructure reflections.

More detailed investigations, however, revealed very often diffuse intensity maxima in apparently disordered phases at positions of former superstructure reflections indicating a certain degree of order not observable by normal X-ray investigations. To reconcile the theory of order-disorder, a parameter σ for this type of SRO has been defined with values from 0 to 1 (Guttmann, 1956).

The total order existing in a phase is therefore a function of S and σ and any truly disordered phase must necessarily show $S = \sigma = O$. At fixed composition, the temperatures for loss of LRO and of SRO may be different, whereby the critical temperature for loss of SRO is generally higher.

As shown by Putnis (1984) under certain P, T conditions exists a continuous change from short range order to long range order, confirming the conclusion above.

This fact introduces some complications for systems showing order-disorder relations superimposed on a mixing model with miscibility gaps.

As shown above and by Carpenter (1980), the formation of a miscibility gap in a binary A–B system indicates positive excess energies of mixing. On an atomistic scale like bonds AA or BB are favored. Order relations, on the other hand, indicate preference for un-like bonds (AB) leading ultimately to the formation of ordered compounds in certain composition ranges, with negative excess energies. It is intuitively clear that the introduction of B particles in a phase composed predominantly of A will create under certain P, T and crystal structural conditions some AB bonds with the creation of local order (SRO) reducing in this way the positive excess energy applicable to the disordered mixing case. Therefore partial order may show up over larger P, T and X conditions in phases generally considered disordered. The above mentioned crystal structural conditions refer to the mechanical and energetic responses of the three dimensional lattice of A, which determines whether local order may be set up or not by the introduction of B particles and vice versa. The strong correlation between the mixing enthalpy and the octahedral distortion in the system $CaCO_3$-$MgCO_3$ (Schultz-Güttler 1984) confirms the rôle of crystal structural parameters on solid solution formation. To characterise now all states of order, this paper uses "intrinsic order" (Wagner & Schottky 1930) to indicate any P, T, X region in the phase diagram with partial order in phases showing superstructure X-ray reflections or not.

The appearance of superstructure X-ray reflections, indicating a very advanced state of ordering, may then be characterised by some special features in the ordering free energy curves versus composition as shown in Fig. 3 d of Carpenter (1980).

One such point may be the turning point, whereby $\delta\Delta G^{order}/\delta X^2 = 0$ separating stable from unstable regions in normal miscibility gaps.

Thermodynamic partial molar quantities

Despite all the work done in systems containing ordered compounds (Guttman 1956), precise data about partial molar entropies, chemical potentials, activities and activity-coefficients of the components in ordered compounds and their P–T–X dependance are hard to find in the literature.

Concerning solids, the work by Steiner & Komarek (1964) and T. B. Holland (1983) about the activity-composition relations of the compound NiAl and omphacitic pyroxene, respectively, may be mentioned. More precise data are displayed by Kleppa (1976) from work in molten salt mixtures forming anion-complexes with high degrees of order in certain composition ranges. The partial entropies in such systems show characteristic sigmoidal shaped curves, the negative mixing enthalpies display Gaussian distribution curves as function of composition, with minima at the stoichiometric composition of the anion-complex.

In all cases, large negative deviations from regular behaviour are found and, characteristically, the curves of the partial molar quantities are all continuous in the range of stability of the ordered compound or anion-complex.

The lack of more data precludes the derivation of an algebraic function relating these properties to changes in composition or temperature. On the other hand, the data discussed above and the theoretical free energy-composition relations shown by Carpenter (1980) and Allen & Cahn (1976) makes it likely that any function describing these properties may include some exponential terms in contrast to most models of mixing used in geology. This reasoning in mind, Fig. 2 then shows a theoretical chemical potential (μ)-composition (X) diagram. The dashed and full lines show the μ–X relations for disordered and a partially ordered solid solution respectively.

Fig. 3 presents the ln γ–X relations deduced from Fig. 2. The negative deviations (due to ordering) from the γ–X and ln γ–X relations for the disordered case are cleary evident. Unfortunately, no means exists to deduce the way other partial order states will show up in Fig. 2 and Fig. 3.

They may be confined between the respective curves shown or may involve larger or smaller compositional ranges, depending on the particular T–X conditions and crystal structural requirements (see above) of the ordered or disordered phases. A scan through the specialised physico-chemical literature

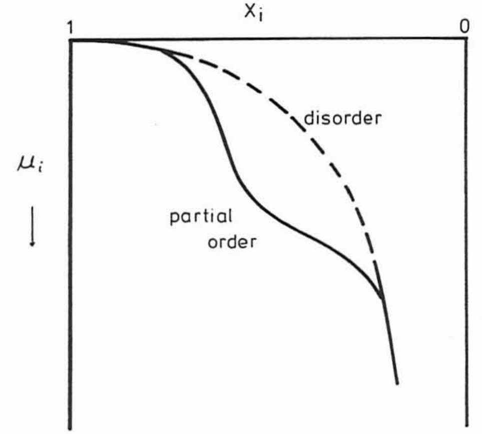

Fig. 2. Chemical potential (μ) versus composition (X_i) for disordered solid solution (d) and partially ordered solid solution (o). In case of symmetrical mixture, the $\mu - X_i$ relation for the second component is a mirror image of the above shown relations with mirror plane at $X = 0.5$.

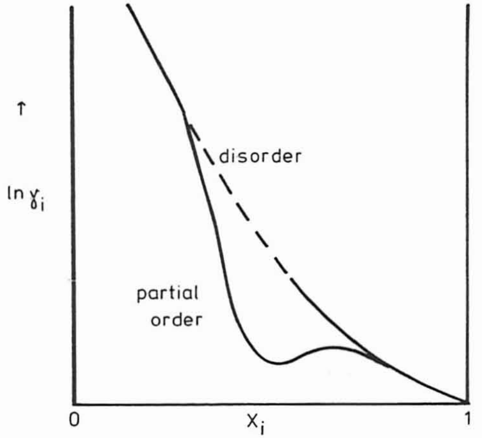

Fig. 3. Logarithm of activity coefficient ($\ln\gamma_i$) versus composition X_i for symmetric disordered solid solutions (d) and partially ordered solid solution (o). The curve of the ln $\gamma_i - X_i$ relation for the second component has the same shape, but starting at $X_i = 0$.

in search for an algebraic equation reproducing the above shown experimental results did not bring up much except the model of Wagner & Schottky (1930), which failed grossly when applied by Steiner & Komarek (1964).

Other treatments dealing with similar problems used the law of mass action and resemble in this way the thermodynamic model presented by Grover

(1980, 1974). His approach needs much energy parameters and shows some conceptual difficulties, although it is very instructive. The shortcomings of the previous models prompted now to try to find a suitable algebraic equation which reproduces the main features of thermodynamic properties in systems with order relations discussed above.

The Proposed Gaussian Distribution Function for the Ordering energy

To inquire theoretically about possible forms of the required numerical equations, the differences of the chemical potentials of the ordered and disordered case, shown in Fig. 2, have been evaluated and plotted as a function of composition for each component. These differences represent the partial chemical potentials of ordering of the components.

The equations $\Delta G^{order} = X_A d\mu_A + X_B d\mu_B$, giving the free energy of order as a sum of the partial chemical potential of order of the components, has been used to construct the curve of ΔG^{order} as function of composition. The resulting curve is very much like a Gaussian distribution curve showing a maximum at the stoichiometric composition of the ordered compound, points of inflection symmetrical to the composition axis and approaching zero at low and high values of X.

From statistical mathematics it is well known that such curves may be formulated as follows

$$A(x) = A_o(z)\exp. - A_o'(z)\,(X_o - X)^2 \qquad (1)$$

whereby A_o indicates the value of A at the mean value, X_o indicates the mean of the distribution and $(X_o - X)$ the distance of X from the mean. A_o' is related to A_o, but not to X, and may be a function of a parameter Z.

It appears then, that the order energy may equally well be described by such numerical equations representing distribution curves. In that case, A indicates the order energy, A_o the order energy at the stoichiometric composition of the ordered compound, X the molefraction and X_o the molefraction of the stoichiometric compound.

If $X_o = 0.5$, the curve is symmetrical and bell-shaped, if $X_o \neq 0.5$ the curve is skewed to higher or lower X-values. The Z-parameter may be in this case the temperature, giving the order energy for the stoichiometric composition as function of temperature.

It is then possible to write

$$\Delta G^{order}(X) = \Delta G^{order}_{stoich.}(T)\exp \Delta G'^{order}_{stoich.}(T)\,F(T_o)\,(X_{stoich}\text{-}X)^2 \qquad (2)$$

As for equation (2), $\Delta G'^{order}_{stoich.}$ is related to $\Delta G^{order}_{stoich.}$ by the same parameter T but with a different functional relation $F(T_o)$. Equations of these types will have the exponential term in the derivatives (for instance chemical potentials, partial entropies versus composition), a fact reflected in the relations of $\mu_{ordered}$-$\mu_{disordered}$ versus composition discussed in the preceding paragraph.

The relation $\Delta G^{order}_{stoich}/\Delta G'^{\,order}_{stoich}$ gives a measure of the steepness of the resulting bell shaped curve with $\Delta G^{order}(X)$ restricted over certain composition intervals at low temperature and spreading over the whole range of X at higher temperature as one possibility or with large compositional range of order at low and shrinking regions at higher temperatures. The first case applies for increase of solubility with T for the ordered compound, the latter for reduced solubility relations at higher temperatures. Both cases can be observed in phase diagrams.

The proposed model for the energy of ordering

The deductions of the preceeding paragraphs define the following boundary conditions for any numerical quantification:

1) The process of order-disorder at certain P, T and X conditions is superimposed on the model of disordered solid solutions.

2) The passage of the ordered compound with stoichiometric composition to the disordered state as a function of temperature can be characterized by any type of phase transition. At off-stoichiometric compositions it can show transitions of first or higher order, depending on the particular P, T and X relations (Burton 1983).

3) The activities of the components of the ordered compound at a stoichiometric composition have well defined values; both, free energy of exchange ΔG°_{E} (Grover 1980) and configurational enthalpy H_c (Grover 1980) stay finite. The curve of activity versus composition is continuous when passing through the stoichiometric composition.

4) The ordering is a complex function of the chemical interactions of the involved species, of the "strain-energy" of the crystallattice and of the temperature and composition (Guttman 1956). There will be no particular distinction between short-range and long-range order, which will be defined by an "intrinsic order" of the crystal (Wagner & Schottky 1930).

5) The order-disorder energy is represented to a first approximation by a type of Gauss-Laplace equation (equation 2).

In equation (2) the term $\Delta G^{Order}_{stoichiom.}$ characterizes the free energy of order of the stoichiometric compound and is a function of temperature only. The temperature may be the temperature of the system (giving the equilibrium order) or, in states of frozen-in order, the particular order temperature (T_{Order}).

The exponential term (zero at stoichiometric composition) takes into account the combined influences from deviations in composition, temperature and effect of strain energy of the crystal lattice on the order-disorder energy. These influences define the slopes of $\delta\Delta G^{Order}/\delta X$ and especially the latter the relation between $\Delta G^{Order}_{stoichiometric}$ and $\Delta G'^{\,Order}_{stoichiom.}$ of equation (2) at constant temperature. Trial computations with equation (2) revealed the great influence of the relation $\Delta G^{Order}_{stoich.}/\Delta G'^{\,Order}_{stoich.}$ on the slope $\delta\Delta G^{Order}(X)/\delta X$ and on the compositional range of ordering.

These five conditions stated above lead to the numerical symbolism

$$G^{Mix}(X) = G^{ideal}(X) + G^{excess}(X) + G^{Order}(X) \tag{3}$$

$$\Delta G^{Order}(X) = \Delta G^{Order}_{stoichiom}\,(T_{Order}\,\exp\Delta G'^{\,Order}_{stoich.}(T_o).\ f(T_o).\ (X_{stoich.}\text{-}X)^2 \tag{4}$$

For systems, discussed below, showing binary intermediate ordered compounds of 1:1 composition, the equation for the order-disorder energy is as follows.

$$\Delta G^{Order}(X) = \Delta G^{Order}_{stoichiom}(T_o)\exp\,\Delta G^{Ord}_{stoich}(T_o)\ f(T_o)\ (0.5\text{-}X)^2 \tag{5}$$

with $f(T_o) = T_o^{-1/n}$ $(n \geqslant 3)$ for ordered compounds with increased solubility of the components at higher temperatures, as is normally observed in mineral systems. If $f(T_o)$ equals T_o $(n = -1)$, the slope of $\delta\Delta G^{Order}(X)/\delta X$ is too steep at higher temperatures, if n equal one or two, however, the slope is too small and ordering spreads over the total composition range.

The critical temperature T_c of the ordered compound is defined by the condition of random occupancy of the ions or atoms on the lattice sites, expressed as $\ln K_x = 0$. The enthalpy of order-disorder is then given by

$$\Delta H\ \text{disorder} = 2RT_c\,(X_A \ln X_A + X_B \ln X_B). \tag{6}$$

Inserting the values of $X_A = 0.5$ and $X_B = 0.5$ for the 1:1 ordered compound results in equation (7) and gives as first approximation

$$-\ \Delta H\ \text{disorder} = 2.755\ T_{critical} \tag{7}$$

The free energy of mixing of the system $CaCO_3$-$MnCO_3$

This system contains three phases, calcite, rhodochrosite and kutnahorite $CaMn(CO_3)_2$. Details about structures, physical properties and thermodynamic quantities can be found in Goldsmith (1959), Lippmann (1973), Althoff (1977), Robie et al. (1978), Helgeson et al. (1978) and Jacobs et al. (1981). Problems arising from possible anion-rotational disorder in carbonates are discussed by Salje & Viswanathan (1976), Mirwald (1976, 1979), Carlson (1980) and Reeder (1981) and will not be considered here due to lack of sufficient experimental data.

The free energy of mixing of the disordered solid solution

A first step towards calculating the effects of order-disorder superposed upon exsolution is to evaluate the mixing energy of the disordered solid solution through the calculation of the activities of all components. These figures were calculated using the decomposition relations of binary mixtures of $CaCO_3$ and $MnCO_3$ presented by Goldsmith & Graf (1957). The equilibrium temperatures of $(Ca,Mn)CO_3$ solid solutions in coexistence with pure MnO at selected compositions X_{MnCO_3} are given in Table 1.

The activities and activity coefficients of the respective components are evaluated by the relation $\log a^{Carbonate}_{MnCO_3} = \log f_{CO_2}/f^{o}_{CO_2}$ (T = const) and $\log \gamma^{Carbonate}_{MnCO_3} = \log f_{CO_2}/f^{o}_{CO_2} - \log X_{MnCO_3}$.

Table 1. Equilibrium temperatures of solid solutions of $CaCO_3$-$MnCO_3$ coexisting with MnO and CO_2. The CO_2 pressure is given in bars, the compositions in molefractions of $MnCO_3$ and the equilibrium temperatures in centrigrades. Interpolations and extrapolations of data given by GOLDSMITH & GRAF (1957).

P_{CO_2}	82.8	200.1	552.0	1028.1	2070.0
X_{MnCO_3}			$T_{equilibrium}$		
1.0	555	604	667	715	777
0.9	555	605	668	717	780
0.8	555	606	672	721	785
0.7	556	607	676	725	792
0.6	557	610	682	732	800
0.5	560	615	690	740	811
0.4	563	621	702	752	826
0.3	570	630	716	768	847
0.2	585	644	738	797	–
0.15	597	655	752	814	–
0.10	610	675	768	834	–
0.05	650	710	795	–	–

The term f_{CO_2} indicates the fugacity of CO_2 at the given composition X_{MnCO_3} of the solid solution, $f^{\circ}_{CO_2}$ the fugacity of CO_2 for the decomposition of pure $MnCO_3$ at the same temperature.

The latter, a fit of experimental data, is given by equation (8)

$$\log F^{\circ}_{CO_2} = 8.888 - 5759.97/T + 0.0944(P-1)/T \ (R^2 = -0.99997) \qquad (8)$$

using the CO_2-pressures and equilibrium temperatures cited by GOLDSMITH & GRAF (1957); the molar volumes of solids were taken from ROBIE et al. (1978) and the activity coefficients of CO_2 from PERCHUK (1977). With the further assumption of an ideal mixing volume, the activities of $MnCO_3$ were determined as a function of temperature (Table 2). A fit of the activity coefficients $\gamma^{Carbonate}_{MnCO_3}$ and $\gamma^{Carbonate}_{CaCO_3}$ (derived by use of the Gibbs-Duhem relation) to the asymmetric mixing model of THOMPSON (1967) permitted the evaluation of the interaction parameters $W_G^{CaCO_3}$ and $W_G^{MnCO_3}$ as a function of temperature.

The mixing energy of the disordered solid solution (Ca,Mn)CO_3 is then given by equation (9)

$$\Delta G^{Mix}_{CaCO_3\text{-}MnCO_3} = RT\,(X_{CaCO_3}\ln X_{CaCO_3} + X_{MnCO_3}\ln X_{MnCO_3}) + \\ + X_{CaCO_3}X_{MnCO_3}\,[(4370.4 - 1.803T)X_{CaCO_3} + (9339.8 - 6.965T)X_{MnCO_3}] \qquad (9) \\ \text{(cal,mol, °K)}$$

From equation (9), maximum values of ΔH^{excess}_{Mix} and ΔS^{excess}_{Mix}, respectively 1.764 kcal/mol and 1.176 $calmol^{-1}k^{-1}$, are found at $X_{CaCO_3} = 0.4$. These values compare well with those determined and estimated from calorimetric results (1.5 kcal/mol and 0.9 $calmol^{-1}K^{-1}$ respectively) by CAPOBIANCO & NAVROTSKY (1983).

The formation of kutnahorite $CaMn(CO_3)_2$

Equation (9) represents an asymmetric type of mixing energy allowing only a single solvus between the end members $CaCO_3$ and $MnCO_3$. Neglecting decomposition relations, the critical point of the solvus is found to be near $X_{CaCO_3} = 0.4$ and T = 550 °C.

Table 2. Coefficients A and B of the equation $\log a^{Carbonate}_{MnCO_3} = A + B/T$ to calculate the activities of $MnCO_3$ in solid solutions of $CaCO_3$-$MnCO_3$. The compositions are given in molefractions of $MnCO_3$, T in °K. R^2 = square of the coefficient of correlation of least squares fitting.

X_{MnCO_3}	A	B	R^2
0.1	−1.4741	925.28	−0.999926
0.15	−1.39122	936.73	−0.99899
0.20	−1.36744	973.66	−0.99916
0.30	−1.00893	737.824	−0.99925
0.40	−0.819112	619.88	−0.99929
0.60	−0.4697	373.15	−0.99983
0.80	−0.1923	157.2	−0.99993
0.90	−0.06934	56.47	−0.99997

The formation of an intermediate compound $CaMn(CO_3)_2$, due to ordering, will split this extensive solvus into two miscibility gaps, one at the $CaCO_3$-rich side of the diagram, the other between $CaMn(CO_3)_2$ and $MnCO_3$. It is therefore necessary to introduce into equation (9) a term characterizing the free energy of order-disorder of the ordered compound $CaMn(CO_3)_2$.

As stated before, the critical temperature of loss of order (T_{cr}) and the condition that at T_{cr} the order-disorder energy approaches zero are sufficient to define $\Delta G^{Order}(X)$ in equation (5).

As for kutnahorite, GOLDSMITH & GRAF (1957) only state that the order reflections begin to weaken at about 450 °C. On the other hand, only slightest evidences of order were observed at about 555 °C (the lowest temperature used for activity computations, cf. Table 1) and none is reported at 600 °C in the experiments of CAPOBIANCO & NAVROTSKY (1983). Thus the disordering temperature of $CaMn(CO_3)_2$ is constrained between 450° and 555 °C.

Systematic trends of phase relations in the systems $CdCO_3$-$MgCO_3$ and $CaCO_3$-$MgCO_3$ show the disorder temperature of the ordered compound being slightly below the maximum temperature of the miscibility gaps and the disorder process taking place over a temperature interval of about 200 °C for $CaMg(CO_3)_2$ (GOLDSMITH & HEARD 1959) and about 150 °C for $CdMg(CO_3)_2$ (GOLDSMITH 1972).

The minimum temperature above which only continuous solid solutions exist in the system $CaCO_3$-$MnCO_3$ is about 550 °C (GOLDSMITH & GRAF 1957). This temperature, then, is taken as the one defining the loss of order of $CaMn(CO_3)_2$, giving thus a maximum critical temperature for disordering.

This maximum temperature estimate leads to a disordering interval of about 100 °C, which is considered reasonable when the ionic radii of Ca−Mg, Cd−Mg and Ca−Mn are compared.

Using equation (7), a figure of-2281 cal/mole is calculated for the disordering enthalpy of $CaMn(CO_3)_2$.

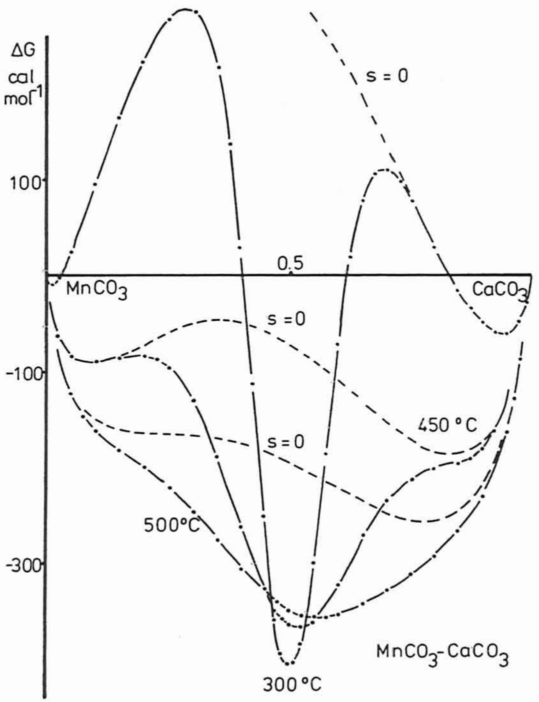

Fig. 4. The free energy of mixing of the $CaCO_3$-$MnCO_3$ system calculated by equation (11) – full lines – and by equation (9) – broken lines – at 300 °C, 450 °C and 500 °C. Equation (11) gives the values of the free energy of mixing with formation of $CaMn(CO_3)_2$, equation 9 those for the disordered case. Important are the small values of the free energy and the small energy differences for the ordered and disordered case, leading to metastable results in experimental work. The form of the curves correspond exactly to those shown by Carpenter (1980).

The free energy of order can then be expressed by

$$-\Delta G^{\text{Order}}_{\text{stoichiom}} = 2281.8 - 2.755T \qquad (\text{cal, } T°K) \tag{10}$$

With equation (10), all parameters for the description of the mixing behaviour in the system CaCO-$MnCO_3$ are known, including those related with the formation of the ordered compound $CaMn(CO_3)_2$:

$$\begin{aligned}\Delta G^{\text{Mix}}_{CaCO_3\text{-}MnCO_3} = {} & RT\,(X_{CaCO_3}\ln X_{CaCO_3} + X_{MnCO_3}\ln X_{MnCO_3}) \\ & + X_{CaCO_3}X_{MnCO_3}\,[(4370.4 - 1.803T)X_{CaCO_3} + \\ & + (9339.8 - 6.965T)X_{MnCO_3}] - (2282 - 2.755T_o) \\ & \exp\,[-(2282 - 2.755T_o).T_o^{-0.333}.\,(0.5 - X_{CaCO_3})^2]\end{aligned} \tag{11}$$

This equation (11) permits the calculation of the free energy of mixing for the system $CaCO_3$-$MnCO_3$ over the temperature range of stability of $CaMn(CO_3)_2$ (T_o max = 550 °C). At higher temperatures T_o stays at a value of 550 °C, the temperature of loss of order.

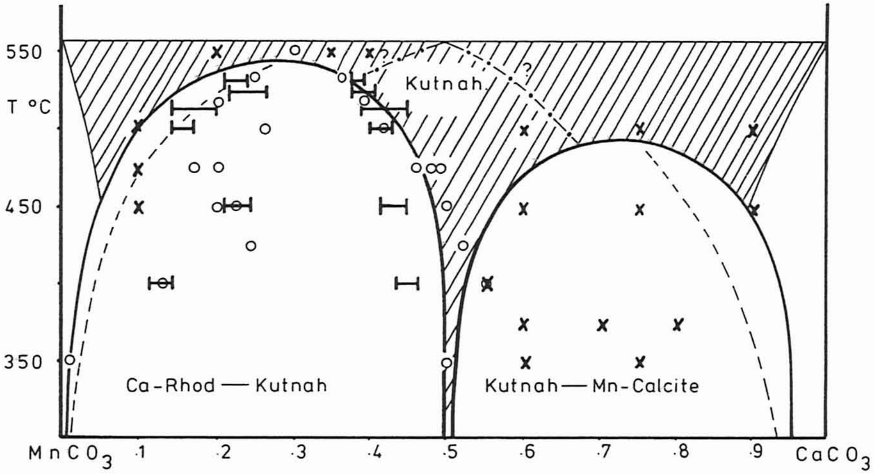

Fig. 5. Subsolidus phase diagram of the $CaCO_3$-$MnCO_3$ system. Full lines indicate the mutual solubilities with formation of $CaMn(CO_3)_2$, broken lines those for the disordered case. Shown by symbols are experimental results: ├──┤ de Capitani & Peters (1981), ○ Goldsmith & Graf (1957) two phases coexisting, × one homogeneous phase. The dot-dash line with question mark indicates the field of superstructure reflections of $CaMn(CO_3)_2$ that may be observed by powder diffraction (Goldsmith & Graf 1960). The shaded field encloses the region of thermodynamic "intrinsic order", which may be observable or not (cf. Fig. 4) by x-ray diffraction.

Fig. 4 shows the form of the ΔG^{Mix} curves calculated with equation (11) at various temperatures. Stippled lines indicate the (metastable) regions of the free energy of mixing for the disordered case ($\alpha \sim s = o$) and full lines indicate the free energy of mixing in the presence of the ordered compound $CaMn(CO_3)_2$ in its stable state of intrinsic order.

Tangents drawn on the $CaCO_3$-rich side define two coexisting phases, a manganese-bearing calcite and a kutnahorite with $CaCO_3$ in solid solutions. Tangents on the $MnCO_3$-rich side define likewise a kutnahorite with $MnCO_3$ in solid solution and a calcite-bearing rhodochrosite.

The calculated phase diagram of the system $CaCO_3$-$MnCO_3$

With the help of equation (11), as put forward in the preceeding sections, a phase diagram for the system $CaCO_3$-$MnCO_3$ was calculated. The results are shown in Fig. 5. In this figure, stippled lines represent the mutual solubilities for the disordered solutions, while full lines show the case where ordering and the formation of kutnahorite occurs.

For comparative purposes, the experimental solvus is also shown (GOLDSMITH & GRAF 1957, DE CAPITANI & PETERS 1981). The calculated phase diagram indicates a peak temperature of about 490 °C for the solvus between manganese-bearing calcites and kutnahorite solid solution, while the one between rhodochrosite solid solution and kutnahorite reaches about 550 °C, in good agreement with the experimental results.

On the other hand, our calculated results and the irregular distribution of the experimental points in Fig. 5 suggest most of the determined solubilities are not equilibrium values.

Considerations about spinodal exsolution, especially in systems with formation of ordered compounds (CARPENTER 1980, ALLEN & CAHN 1976) combined with the energetic relations shown in Fig. 4 give strong evidence that most experimental data lie in regions of metastability possibly caused by lack of complete equilibrium order of the dolomitic compound or due to kinetic problems influenced by the small energy differences between stable and metastable states in this system (cf. discussion in the next section on the system $CaCO_3$-$MgCO_3$). The lack of experimental evidence for a miscibility gap on the $CaCO_3$-rich side of the phase diagram, pointed out by crosses in Fig. 5, is certainly caused by the same problems as discussed above (metastability).

On the other hand, there is strong evidence for the opening of a miscibility gap on the calcite-rich side of the phase diagram at temperatures below 500 °C, as indicated by the work of GOLDSMITH & GRAF (1960).

The high value of the ΔH^{excess} determined by CAPOBIANCO & NAVROTSKY (1983) may give also some indication about metastability of the experimental results.

The free energy of mixing of the system $CaCO_3$-$MgCO_3$

Given its greater geological significance, plenty of experimental work was performed on this system (GRAF & GOLDSMITH 1955, 1958, GOLDSMITH & GRAF 1958, GOLDSMITH 1959, GOLDSMITH & NEWTON 1969, GOLDSMITH 1980, HARKER & TUTTLE 1955, IRVING & WYLLIE 1975, BYRNES & WYLLIE 1981).

The phase relations are in general similar to those of the system $CaCO_3$-$MnCO_3$ and $CdCO_3$-$MgCO_3$, with the difference, however, of much higher temperatures of closing of the miscibility gaps and disordering of dolomite [$T_{critical}$ of dolomite ~1200 °C, $T_{critical}$ of solvus between calcite$_{ss}$ and dolomite$_{ss}$ 1054–1074 °C at 8 kb (GOLDSMITH & HEARD 1961); about 1365–1410 °C, at 27 kb, $T_{critical}$ of solvus between magnesite$_{ss}$ and dolomite$_{ss}$ (IRVING & WYLLIE 1975].

Very few experimental data are available to evaluate the interaction parameters for the completely disordered solid solution. We are therefore forced to estimate these parameters from experimental data, combining the results of GOLDSMITH & NEWTON (1969), GOLDSMITH & HEARD (1961) and HARKER & TUTTLE (1955).

Table 3. Temperatures (°C) and selected compositions, given in molefractions, of magnesian calcites and magnesites containing $CaCO_3$ in solution used to calculate the interaction parameters $W_G^{CaCO_3}$ and $W_G^{MgCO_3}$ (cal/mol).
Data are compiled from GOLDSMITH & NEWTON (1969), GOLDSMITH & HEARD (1961) and HARKER & TUTTLE (1955).

	$X_{MgCO_3}^{Calcite}$	$X_{CaCO_3}^{Magnesite}$	W_{CaCO_3}	W_{MgCO_3}
400 °C	0.022	0.001	9234	5155
450 °C	0.032	0.0016	9245	5003
500 °C	0.042	0.0025	9204	4903
550 °C	0.055	0.0035	9253	4817
600 °C	0.069	0.0050	9207	4722
650 °C	0.089	0.0067	9199	4494
700 °C	0.111	0.0086	9214	4257
720 °C	0.117	0.0095	9215	4244
780 °C	0.152	0.0127	9156	3827
900 °C	0.245	0.0210	8934	2544

Neglecting, at first, the presence of the phase dolomite, it is possible to treat Mg-calcites and calcian magnesites (as a first approximation) as defining an isostructural single solvus and to calculate interaction parameters $W_G^{CaCO_3}$ and $W_G^{MgCO_3}$ with equations given by BLENCOE (1977) or THOMPSON (1967).

The results are presented in Table 3, which lists the temperatures (°C), the compositions of the phases (mol %) and the first estimate of interaction parameters (calmol^{-1}).

These latter values have now to be corrected for the energetic influence of the presence of dolomite.

As a first assumption, it is supposed that the interaction parameters are only slightly affected by the energetic effects of the dolomite in the temperature interval from 400 to 650 °C. A fit of these values, selected from Table 3, as function of temperature is represented by equation (12) and (13):

$$W_G^{CaCO_3} = 9362.7 - 0.1647T \tag{12}$$

and

$$W_G^{MgCO_3} = 6759.2 - 2.393T \ (\text{calmol}^{-1}, \text{T°K}) \tag{13}$$

The interaction parameters of equation (12) and (13) will still have to be modified, and adapted, once more, due to the not yet predictable energetic influence of the dolomite phase on the mutual solubilities of $MgCO_3$ in calcite and $CaCO_3$ in magnesite.

The influence of dolomite on the interaction parameters

A wealth of experimental data allows some important deductions about the influence of dolomite showing varying degrees of order on the mutual solubilities between Mg-calcites and calcian magnesites. To clarify this point, Fig. 6 shows schematically the curves of the free energy of mixing, at constant P and T conditions, for different degrees of order of dolomite (S = 0 disordered, S_e = equil. order, $0 < S < S_e$ = partially ordered).

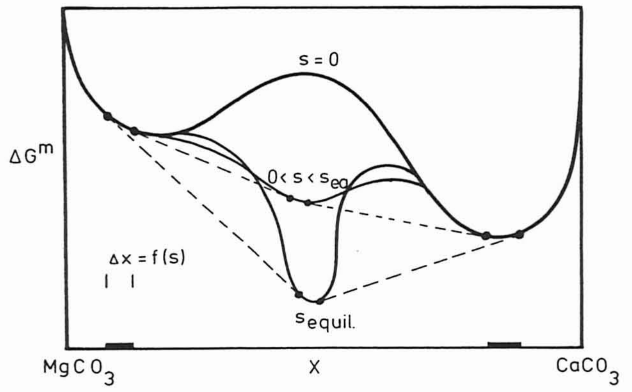

Fig. 6. The free energies of mixing at constant temperature showing the curves for complete disorder (S = 0), for intermediate ordered states of dolomite ($0 < S < S_{equilibrium}$) and for the equilibrium state of order of dolomite ($S_{equilibrium}$).

The mutual solubility of the components is different for each curve (shown by tangents and at the composition abcissa). This is a continuous process, exsolution and ordering acting simultaneous.

The composition of the coexisting phases, defined by tangents, vary as function of the degree of order.

The analysis of Fig. 6 shows two important conclusions:

1) The degree of order of dolomite influences strongly the composition of coexisting calcite solid solutions and magnesite solid solutions. Mutual solubilities are highest for the disordered solid solution.

2) At low degrees of order of dolomite, two carbonate phases can be metastably associated with dolomite.

Supporting evidence for these statements can be found in all experimental work dealing with carbonates, especially those carried out at low temperature as shown in a review by Lippmann (1973).

Even at higher temperatures, experimental work has clearly shown that the Mg-content in Mg-calcites decreases apparently as a function of the degree of order of coexisting dolomite.

Harker & Tuttle (1955) found, for instance, a decrease of X_{MgCO_3} in $calcite_{ss}$ of up to 20 % as longer run times (which went from 14 to 576 hours at 600 °C) allowed for a better ordering of dolomite. Similarly, the Mg-content in Mg-calcite decreased up to 50 % at 450 °C as run times went from 4 to 1008 hours (Harker & Tuttle 1955, Goldsmith & Newton 1969).

These facts call then for a revision of the values estimated for the interaction parameters.

Thus, the true solubility of $MgCO_3$ in calcite and that of $CaCO_3$ in magnesite are much higher than the ones given in Table 2, possibly by a factor of two. Judging from the 50 % decrease in solubility at 450 °C as a function of greater order of dolomite, all compositions of Table 2 have been doubled in amount to represent the limiting solubilities for disordered solid solution.

These new values of solubilities have been used to calculate the following interaction parameters as function of temperature (450 to 650 °C):

$$W_G^{CaCO_3} = 9436.7 - 1.69T \tag{14}$$

$$W_G^{MgCO_3} = 7815.25 - 5.36T \, (calmol^{-1}, T°K) \tag{15}$$

A comparison with the values of the first estimate show a slight increase in the interaction enthalpy, but a marked one for the excess entropy. This increase is as expected, since high excess entropies are to be predicted equally well for solid solutions in the system $CaCO_3$-$MgCO_3$ as also shown by the excess entropy value of the similiar system $CaCO_3$-$MnCO_3$ by Capobianco & Navrotsky (1983).

It appears then, that equations (14) and (15) represents values of the interaction parameters quite near the true values which could not been evaluated exactly.

The calculated phase diagram for the system $CaCO_3$-$MgCO_3$

An equation can now be set up, using the following auxiliary values or parameters: 1) estimates of the interaction parameters, as represented by values given in equations (14) and (15); 2) a dolomite order-disorder enthalpy parameter of −4084 calmol⁻¹, computed for a critical temperature of 1210 °C (Goldsmith & Heard 1961); 3) the condition that $\Delta G^{Order}_{dolomite} = 0$ at $T = T_{critical}$ for LRO and SRO.

Equation (16) incorporates the above mentioned parameters and represents the free energy of mixing of the system $CaCO_3$-$MgCO_3$, including the formation of dolomite.

$$\begin{aligned}\Delta G^{Mix}_{CaCO_3\text{-}MgCO_3} = {} & RT\,(X_{CaCO_3} \ln X_{CaCO_3} + X_{MgCO_3} \ln X_{MgCO_3}) + X_{CaCO_3} X_{MgCO_3} \\ & [(9436.7 - 1.69T) X_{MgCO_3} + (7815.2 - 5.36T) X_{CaCO_3}] - \\ & - (4084.8 - 2.755T_o) \exp - [(4084.8 - 2.755T_o).\ T_o^{-0.331} \\ & 0.5 - X_{CaCO_3})^2]\ (calmol^{-1}, °K)\end{aligned} \tag{16}$$

Equation (16) is valid up to the critical temperature of stoichiometric dolomite; at higher temperatures, T_o remains fixed at $T_{critical}$ (1210 °C) Fig. 7 shows the phase diagram for the system $CaCO_3$-$MgCO_3$ calculated by use of equation (16).

The stippled lines indicate the mutual solubilities of the components for the hypothetical case of disordered solid solution, while the full lines show the equilibrium diagram for the coexistence of Mg-calcites and dolomites and calcian magnesites and dolomites, respectively. Plotted with appropriate symbols are also the experimental results obtained by Graf & Goldsmith (1955), Goldsmith & Newton (1969), Harker & Tuttle (1955), Goldsmith & Heard (1961) and Irving & Wyllie (1975).

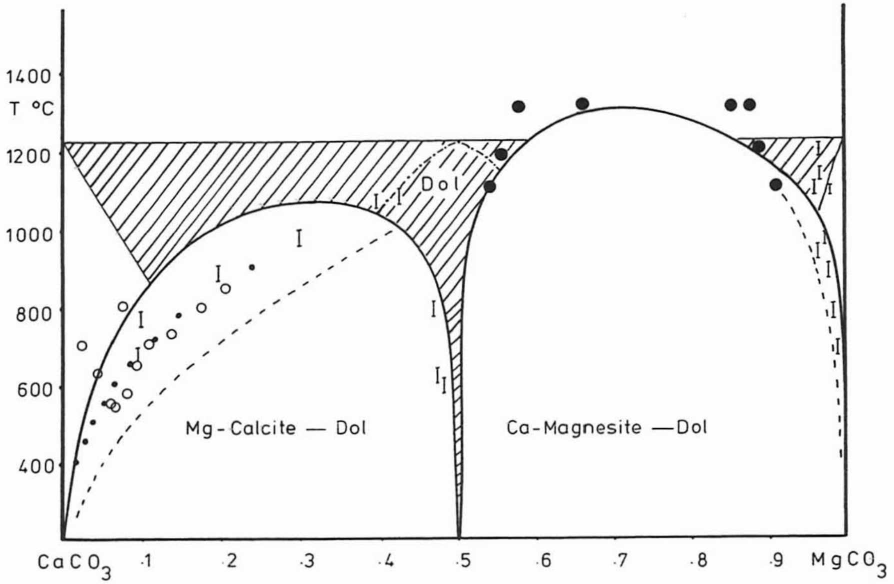

Fig. 7. The calculated subsolidus phase diagram of the $CaCO_3$-$MgCO_3$ system. Full lines indicate phase boundaries for the coexistence of dolomite in its state of equilibrium order. Broken lines, the completely disordered case. Experimental results are shown by symbols: ○ Graf & Goldsmith (1955) ⊤ Goldsmith & Heard (1961) ● Goldsmith & Newton (1969) ● Irving & Wyllie (1975). The dot-dash line indicates the appearance of superstructure reflections as determined experimentally. The shaded field encloses the region of thermodynamic "intrinsic order".

The calculated temperature for the closing of the miscibility gap in the $CaCO_3$-rich part of the system is at 1070 °C which compares very favorable with 1055 – 1074 °C, the experimental result at 8 kb as obtained by Goldsmith & Heard (1961).

The corresponding temperature in the $MgCO_3$-rich part of the system is 1300 °C at 1 atm, neglecting decomposition. Comparing this temperature and the calculated miscibility gap with the experimental results of Irving & Wyllie (1975), the agreement is very satisfactory, notwithstanding the approximations that had to be made and the limited temperature interval of 400 – 650 °C used to calculate the interaction parameters.

The solubilities of $CaCO_3$ in magnesite and of $MgCO_3$ in dolomite (or its disordered equivalent at $T > 1210$ °C) shown by Irving & Wyllie (1975) can well be nearer the calculated compositions if one takes into account the very short run times (about 2 to 5 minutes at $T > 1200$ °C) and the high applied pressure.

The calculated phase diagram is very similar to the one of the system $CdCO_3$-$MgCO_3$ (Goldsmith 1972). This latter system shows two, rather symmetrical, miscibility gaps with critical compositions near the ones calculated for the system $CaCO_3$-$MgCO_3$. The experimentally determined difference of the critical temperatures of the two "solvi" in the system $CdCO_3$-$MgCO_3$ is about 175 °C, while the calculated difference for the system $CaCO_3$-$MgCO_3$ is about 230 °C.

The calculated phase diagram of this work shows one solvus closing below the temperature of loss of order of dolomite and the other one above this temperature as confirmed by experimental results. This is in contrast to calculations of phase relationships of the same system by Navrotsky & Loucks (1977) showing the closing of both "solvi" below the critical temperature of dolomite.

The calculated solubilities of the components $CaCO_3$ and $MgCO_3$ in dolomite correspond satisfactorily with experimental data (higher X_{CaCO_3} in dolomite on the $CaCO_3$-rich side and lower X_{MgCO_3} on the $MgCO_3$-rich side of the phase diagram at the same temperature). Trial computations were performed with changed values of interaction parameters and ΔG^{Order} to increase the calculated solubilities of $MgCO_3$ in calcite, but the results only increased the discrepancy to experimental data.

If there are no other processes acting in the system (anion rotational disorder, for instance) increasing the $MgCO_3$-content of the calcites, calculations with varying degree of order of dolomites give perfect agreement between experimental solubilities and calculated ones. At 800 °C, for instance, a frozen-in disorder of dolomite (corresponding to $T_{order} = 1000$ °C) doubles the solubility from 8 to 16 mol % $MgCO_3$ in calcite and increases the one of $CaCO_3$ in dolomite from 2.5 to 3.5 mol %, in excellent agreement with data of Goldsmith & Newton (1969).

In our model, two extreme curves of solubilities can be calculated: one assuming dolomite formation (equil.order) and thus showing the smallest mutual solubilities of the components, and the other which allows for complete disorder and the largest possible values of solubility. Most experimental points fit within the two extreme values obtained by our calculations, thus strongly suggesting non-equilibrium order-disorder relations of dolomites in the experimental runs.

Considerations about the influence of pressure

As for the influence of pressure on solubilities, only qualitative statements can be put forward, since very little is known about partial molar volumes and expansion or compressibility coefficients of the solid solutions and ordered phases.

The solubility of $MgCO_3$ in calcite increases with pressure (Goldsmith & Newton 1969) and the critical temperature of closing of the miscibility gap on the $CaCO_3$-rich side decreases. On the other hand, due to the great size difference between Mg and Ca, the temperature of closing of the miscibility gap on the $MgCO_3$-rich side may increase (Irving & Wyllie 1975, Brey et al. 1983).

Comparison with other mixing models applied to the system $CaCO_3$-$MgCO_3$

The only other mixing models applied to the system $CaCO_3$-$MgCO_3$ are based on a more conventional treatment. The model of Navrotsky & Loucks (1977), a Bragg-Williams type of order-disorder relation, used more energy parameter than the present work, but was not able to reproduce the solubility relations over the whole composition range. Typical for this conventional treatment is the result that the critical temperature for loss of order of the ordered phase is always above the temperatures of the closing of the miscibility gaps. It is well known, that the Bragg-William treatment is a quite poor approximation (Guttmann 1956) and it is therefore not surprising that the authors did not succeed with this approach.

A more sophisticated model, based on the cluster variation method, has been applied by Burton & Kikuchi (1984). Although this method gives good results for simpler systems (Kikuchi 1974), it shows, when applied to the system $CaCO_3$-$MgCO_3$, a phase diagram alike the one presented by Navrotsky & Loucks (1977).

Both models fail to reproduce the experimental findings, namely that the temperatures for loss of order of dolomite lies between the temperatures of closing of the miscibility gaps and that this system shows, at the $MgCO_3$-rich side, a miscibility gap between two $R\bar{3}C$ (disordered) carbonates above T critical of dolomite. This $R\bar{3}C$ miscibility gap is the piercing of the disordered mixing model in P–T–X regions where dolomite is not any more stable.

The present model appears to show more agreement with the experimental results (Fig. 7) and even allows to calculate metastable phase relations, sometimes to be found by experimental work (Harker & Tuttle 1955), by fixing a type of frozen-in temperature for dolomite, which may be different from the system temperature. In that way, the solubility relations may be calculated showing different degrees of order of dolomite. Comparing the energetic relations of the present model with those of Burton & Kikuchi (1984) one notes that $\Delta H^{Mix}_{disordered}$ and $\Delta H^{Mix}_{ordered}$ at $X_{CaCO_3} = 0.5$ obey all the constraints on the intra- and intersublattice energies given by Burton & Kikuchi (1984).

The enthalpy of stabilization of dolomite, as calculated in the present work, amounts to about -1.9 kcal/mol, nearly the value of the cluster-variation method for E ira/E eir = 0.5, which can be compared with the relation $H^{Mix}_{diss}/H^{Mix}_{order} = 0.54$ as presented in this model.

Furthermore, the compositions of the closing of the miscibility gaps in this system, as calculated by Burton & Kikuchi (1984) coincides with the compositions deduced by the present model ($X_{MgCO_3} \cong 0.3$ and $X_{MgCO_3} \cong 0.72$). It may be, from these coincidences, that the use of better energy values in the cluster variation method may give better approximations on the experimental facts, but surely with much more energy constants than in the present model, which needs only the usual mixing model for disordered solid solutions, the critical temperature of loss of the ordered compound and a Gaussian free energy of order equation.

Summary

The energetic characterisation of mineral system showing the formation of intermediate compounds due to the simultaneous process of exsolution and ordering is one of the most difficult task to solve numerically. A schematic treatment, however, may be set up easily, as shown by discussions of Carpenter (1980) and Allen & Cahn (1976).

In this first part of a series of papers dealing with the same topic, an empirical mathematical model is presented to calculate quantitatively phase diagrams for such systems.

The model starts from the disordered real solid solution and takes into account the energetic effect of ordering, leading to the formation of a distinct phase, but related to the disordered solid solution by a superstructure.

The mathematical form of the model needs only a minimum amount of parameters, depending on the complexity of the representation of the free energy of the disordered solid solution and on the number of intermediate ordered compounds.

In the case of a symmetric model for the free energy of mixing of the disordered solid solution, given the formation of one intermediate ordered commpound, only two parameters (W^G and ΔG^{Order}) are necessary to characterize the free energy of mixing of the system. For an asymmetric model and one ordered compound, only three parameters are sufficient (W^A_G, W^B_G and ΔG^{Order}). Additional ordered compounds can be easily incorporated into the proposed equations, since each new compound only adds one more parameter (ΔG^{Order}). The application of this model to the binary systems $CaCO_3$-$MnCO_3$ and $CaCO_3$-$MgCO_3$ showed very good correspondance between the experimentally determined phase relations and the calculated ones. The model reproduced the phase relations quantitatively, in contrast to other formulations (Navrotsky & Loucks 1977) and avoids inconsistencies in thermodynamic properties (Grover 1980).

The interaction parameters calculated for the system $CaCO_3$-$MnCO_3$ were verified by calorimetric work (Capobianco & Navrotsky 1983) and the high excess enthalpy and excess entropy strongly suggest, that the $CaCO_3$-rich part of this system must have a miscibility gap; the experimental results of Goldsmith & Graf (1957) thus probably show metastable relations.

The interaction parameters of the system $CaCO_3$-$MgCO_3$, although estimated, predict likewise high excess entropies.

This prediction is in accordance with the energetic effect of elongated thermal ellipsoids for Mg-ions in Mg-calcites (Althoff 1977). The model, as proposed here, implies a phase transition for stoichiometric dolomite apparently of first order, a likely result as shown by theoretical analysis (Burton 1983) and experimental data (Goldsmith 1980, Brey et al. 1983), at least with respect of temperature. Experimental problems (Irving & Wyllie 1975, Byrnes & Wyllie 1981), however, may not allow to trace exactly the disorder relations near the critical temperature.

For both carbonate systems, the model predicts "intrinsic order" spread over larger composition intervals at higher temperatures or higher degrees of disorder at lower temperatures, apparently in contrast to powder diffraction evidences. Single crystal diffraction may be a better means to detect order-disorder phenomena (Guttman 1956) and the experimental results may be an artifact of the powder method. On the other hand,

the enlarged compositional range of ordering is a necessary feature to permit the closing of the solvi in accordance with experimental phase relations.

To derive the necessary parameters for the calculation of the phase relations, no other experimental data of the ordered compound except the critical temperature of loss of order has been used and the only curve-fitting was applied to evaluate the interaction parameters for the disordered solid solutions.

The resulting calculated quantitative phase relations showing the mutual solubilities of components in calcites$_{ss}$, magnesites$_{ss}$, rhodochrosites$_{ss}$, dolomites$_{ss}$ and kutnahorites$_{ss}$ are therefore the result only of the characterisation of the order-disorder energy proposed in this work. Studies to show and to test the applicability of this model to other systems (binary and ternary) are in preparation or progress (Schultz-Güttler 1982).

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Author's address:

Rainer Aloys Schultz-Güttler, Universidade de São Paulo, Instituto de Geociências, Caixa Postal 20899, Brasil.

Presently: Institut für Mineralogie und Petrographie, Universität Bern, Baltzerstr. 1, CH-3012 Bern, Switzerland.

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Mica-chlorite intergrowths in very low-grade metamorphosed sedimentary rocks from Norway

By

Sadoon Morad, Uppsala, Sweden

With 12 figures and 3 tables in the text

Morad, S.: Mica-chlorite intergrowths in very low-grade metamorphosed sedimentary rocks from Norway. – Neues Jahrbuch Miner. Abh. **154:** 271–287; Stuttgart 1986.

Abstract: Grains composed of chlorite-mica (biotite and/or phengite) intergrowths are common in very low-grade metamorphosed shales, siltstones and sandstones of the Brøttum Formation (Upper Proterozoic; the Sparagmite region of southern Norway). Mineralogical and chemical evidence indicate that chlorite-phengite intergrowths in the rocks studied and most probably in similar rocks elsewhere result from differential alteration of detrital biotite during late diagenesis-early metamorphism.

Key words: Mica-chlorite, intergrowths, low-grade metamorphism, clastic sedimentary rocks, biotite, alteration; Norway.

Introduction

Significant textural, mineralogical and crystal chemical changes occur in clastic sedimentary rocks during progressive transition from diagenesis to low-grade metamorphism. One of the commonly reported mineral textural features formed during late diagenesis-early metamorphism is grains showing chlorite-illite/muscovite intergrowths (Voll 1960; Kossovskaya & Shutov 1970; Williams 1972; Holeywell & Tullis 1975; Beutner 1978; White & Knipe 1978; Craig et al. 1982). Several terms were suggested for such grains (see review by van der Plujm & Kaars-Sijpesteijn 1984). These authors have suggested different origins for the intergrowths (for details, see review by Craig et al. 1982), which are: 1) strain-controlled growth of chlorite in openings along cleavage planes of detrital muscovite (e.g. Voll 1960; van der Plujim 1984), 2) detrital (Beutner 1978), 3) strain-controlled synkinematic growth of chlorite-white mica intergrowths (Weber 1980, quoted in Craig et al. 1982) and 4) pre-tectonic replacement of clay minerals (montmorillonite) during burial (Craig et al. 1982).

In the present paper, an origin related to alteration of detrital biotite is suggested (see also White et al. 1985) based on a detailed textural and chemical

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