Coherent lamellar exsolution in ternary pyroxenes: A pseudobinary approximation

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ABSTRACT

Coherent exsolution, previously modeled for several important binary mineral systems, also occurs in ternary systems, most notably in Ca-Fe-Mg pyroxenes. We propose an approximate method to evaluate the effect of lattice coherency in such an important system when no complete thermodynamic description, in the form of a ternary equation of state, is available. In this approximation, a pair of clinopyroxene compositions coexisting in incoherent equilibrium is used to define a binary system that is collinear in composition space with that clinopyroxene pair. Chemical compositions of coherent lamellae are then assumed to lie within that binary system, and the effect of coherent elastic strain on exsolution is calculated within that subsystem.

The theory is developed for clinopyroxenes at temperatures safely above the $C2/c \leftrightarrow P2_1/c$ (pigeonite) inversion. Seven coexisting clinopyroxene pairs, chosen from the literature, define seven binary systems in which the effect of coherency is calculated. Calculation of the elastic energy term associated with coherency takes advantage of the fact that the only elastic stress required by coherency is along the b direction of the lattice.

Calculations indicate that the effect of coherency on the solvus is significant for the pure Mg-Ca binary pair (the depression of the critical point is 47 °C) but decreases and becomes virtually negligible (<2 °C) for intermediate clinopyroxenes [Fe/(Fe + Mg) ≈ 0.6].

INTRODUCTION

Cahn (1962) was the first to describe coherent exsolution, in which the crystallographic lattices of the two "exsolutes" are constrained to remain continuous across their common boundaries. Cahn pointed out that the elastic strain imposed on the coexisting phases by coherency resulted in a strain-energy term that was, in effect, a penalty against exsolution and caused a shrinkage of the two-phase field; typically, for regular solutions, it results in a lowering of the critical temperature.

Cahn's theory was restricted to binary systems with isotropic transformation strain and isotropic elasticity; it was thus applicable mostly to metallic alloys. Yund and McCallister (1970), however, pointed out that coherent exsolution should also occur in mineral systems. Indeed, on the basis of observations in transmission electron microscopy, Champness and Lorimer (1971) suggested that a lunar pyroxene exhibited coherent exsolution, and Willaime and Brown (1972), Willaime and Gandais (1972), and Willaime et al. (1973) presented evidence that coherent exsolution, and the resulting elastic strains, occurred in alkali feldspar. Shortly after, Yund (1974) experimentally produced and annealed coherent exsolution lamellae in the microcline–low albite series, and Robin (1974) developed a quantitative theory for coherent lamellar exsolution in binary systems that he applied to the monoclinic alkali feldspar solvus. Tullis and Yund (1979)

generalized Robin's binary calculations and applied them to high-temperature alkali feldspars, Fe-free clinopyroxenes, nepheline-kalsilite, and hematite-ilmenite. Coherent exsolution is now well demonstrated in natural and synthetic crystals of several mineral systems. In particular, there is abundant evidence, reviewed below, of coherent exsolution in pyroxenes.

Natural pyroxenes, however, are described by more than two chemical components. Yet, except for a report on spinodal decomposition in clinopyroxenes by Fletcher and McCallister (1974), there has been no attempt to model coherent exsolution in a mineral system of more than two components.

The purpose of the present paper is to present an approximate method to evaluate a coherent solvus in an important ternary mineral system, that of the high-temperature Ca-Mg-Fe clinopyroxenes. The pseudobinary approximation proposed is a useful method whenever there is no complete thermodynamic description of the ternary solution, as is the case for clinopyroxenes (Grover, 1980). Pyroxenes probably constitute one of the best-known multicomponent systems in mineralogy and also provide us with perhaps the best record of coherent exsolution of all mineral systems. Their importance in interpreting the petrogenesis of mafic and ultramafic rocks is clear. The results obtained here could possibly be used to refine our knowledge of exsolution in ternary pyroxenes

and to improve the methods of geothermometry-geobarometry that rely on that knowledge (e.g., Lindsley, 1983).

It is not within the scope of this paper, however, to give a complete discussion of coherent exsolution in pyroxenes. The phenomenon is complex: variations of all lattice parameters with composition, temperature, and symmetry states lead to significant effects of bulk composition and crystallization history on elastic strains. Further work is needed to clarify the topic.

Lamellar exsolution in pyroxenes

Regardless of the number of chemical components required to describe the minerals involved, we assume, following Robin (1974), that the exsolutes are coherent lamellae and that the surface energy of the coherent interfaces is negligible. Significant departures from these ideal conditions would mean that there would not be a unique, definite solvus (Robin, 1974).

The evidence for lamellar coherent exsolution in pyroxenes comes from several sources:

1. Transmission electron microscopy. Champness and Lorimer (1971) were the first to propose, on the basis of observations in TEM, that coherent exsolution might occur in pyroxenes. TEM remains the chief source of evidence for coherency (e.g., Champnesss and Lorimer, 1976; Nord et al., 1976; Buseck et al., 1980); it reveals interfaces that are free of lattice dislocations over distances of several micrometers. These observed interfaces can also be among the most truly planar features in nature.

2. X-ray crystallographic data. In order to explain X-ray data on lattice parameters and relative orientations, Robinson et al. (1971) applied a model (the "O-lattice") that implied that the lamellae were coherent (Robin, 1974, 1977; Robinson et al., 1977).

3. Experimental work. Description of the experiments by Ross et al. (1973) on homogenization of lunar pyroxenes as well as the reported crystallographic relationships between hosts and lamellae suggest that these authors were, in fact, investigating coherent behavior. More experimental work on pyroxenes, commonly combined with TEM and/or X-rays, has been done by McCallister and Yund (1977) and later workers (see Buseck et al., 1980; Brady and McCallister, 1983); it confirms the relative ease with which coherent lamellae can form or be dissolved over the time scale of laboratory experiments.

Pseudobinary approximation

In the approximation presented here, coexisting phases, whether incoherent or coherent, are treated as if they belonged to the same binary subsystem at all temperatures. In other words, it is assumed that the direction, in compositional space, of the tie line connecting the coexisting coherent pair remains fixed and is the same as that joining the compositions of two phases in incoherent equilibrium. The pseudobinary approximation amounts therefore to an artificial constraint placed on the possible variations in the chemical compositions of the lamellae. Under this constraint, coherency strains and elastic en-

ergy then depend on only one compositional parameter, and calculation of the coexisting coherent pair is done in the same manner (Robin, 1974) as for a binary system. Relaxing this constraint would require a full theory of coherent exsolution in ternary systems.

Assumptions of convenience

A number of convenient, simplifying assumptions are required to make the calculation easier and/or because we have no reason, in the present state of knowledge, to introduce complexities. As discussed further, we believe that the main results would not be significantly affected by more elaborate formulations.

1. For clinopyroxenes the exsolution can be regarded mainly as a miscibility gap on the M2 site, between Ca, on the one hand, and (Fe + Mg), on the other hand, while Fe and Mg substitute on both M1 and M2 sites. In a first approximation, then, we assume that we can describe each pseudobinary section of the ternary solvus as a binary solvus in a system

$$Ca_x(Mg,Fe)_{1-x}(Mg,Fe)(SiO_3)_2, \quad \text{with } 0 < x < 1.$$

The composition, x, is the mole fraction of the Ca end member; in effect, it is the fraction of M2 sites occupied by Ca. Mg and Fe are not necessarily partitioned equally between the two sites, and the Ca-rich clinopyroxene has a preference for Mg over Fe compared to the Ca-poor one. Given an equilibrium incoherent pair, the coexisting compositions are used to define the binary subsystem; a pseudobinary incoherent solvus is then obtained for that subsystem, using a regular solution model with two Margules parameters (e.g., see Thompson, 1967).

2. In order to use a simple Margules equation of state, we restrict our attention to high-temperature clinopyroxenes with the $C2/c$ symmetry. The effects of the transition to low-temperature pigeonite symmetry, $P2_1/c$, begin to be felt below ~1200 °C at Mg-rich compositions (Robinson et al., 1977). We therefore restrict the calculations to binary subsystems, each defined by one incoherent equilibrium pair at a pressure of 1 atm and a temperature greater than 1200 °C (1185 °C for the most Fe-rich pair).

If more data were available, one could use a model with more than two Margules parameters. On the other hand, a system may not be describable by a Margules expression: in this case, some new, appropriate form for the Gibbs energy as a function of composition along binary sections must be found. Should a complete equation of state, in the form of an expression of molar Gibbs energy as a function of two compositional parameters, be available, its value for compositions within our binary subsystem can be used. However, in such a case, one might prefer using a full ternary theory instead.

3. In clinopyroxenes, the only elastic strain required for coherency is to match the b dimensions of the coexisting lamellae (see below), at least at the time these lamellae first form. As in Robin (1974), we assume that, over the compositional range of interest, b varies linearly with composition and that these variations are not af-

fected by temperature. Transformation strains are small enough to be considered infinitesimal, allowing us to use linear elasticity. The relevant elastic constant is assumed to have a uniform value, independent of composition. Consequently, the elastic strain in a lamella is proportional to the difference between its composition and that of the bulk crystal, and the strain energy is accordingly proportional to the square of that difference (see below).

If departures from these approximations are significant, the solvus can still be calculated, but it becomes dependent on the bulk composition of the crystal (Cahn, 1962; Robin, 1974). In fact, Tullis and Yund (1979) did allow for such departures, acknowledging a slight dependence of their results on bulk composition.

SOURCE OF DATA

Huebner and Turnock (1980, Fig. 5) have presented a series of isothermal sections above 1150 °C, showing equilibria involving synthetic augite, pigeonite, orthopyroxene, and liquids. Each three-phase field involving augite, pigeonite, and another phase was considered to provide the most constrained data on coexisting augite-pigeonite pairs, and seven such pairs were read directly from Huebner and Turnock's (1980) Figure 5. Figure 1 shows the seven pairs chosen and the seven binary subsystems they defined, labeled from A to G. Huebner and Turnock (1980) obtained pair A of this data set from the literature, rather than from their own experiments; it may therefore stand somewhat apart from the other data. Table 1, columns 2, 3, 4, and 5, list the corresponding compositions of the midpoints, temperatures, and values of the pseudobinary compositional parameters, x_a and x_b, for the coexisting compositions.

It is important to recognize that the ternary solvus is not very well known: compare, for example, the 1200 °C, 1-atm isothermal sections of Huebner and Turnock (1980, Fig. 5), with the same authors' comparable sections for natural pyroxenes (Huebner and Turnock, 1980, Fig. 10) and with the sections by Lindsley and Andersen (1983, Fig. 6). These latter authors estimated the accuracy of their isotherms to correspond to an uncertainty of ±30 °C. For the present purpose, however, which is to present a method and to give approximate results, it is sufficient, and preferable for consistency, to use one data set. The
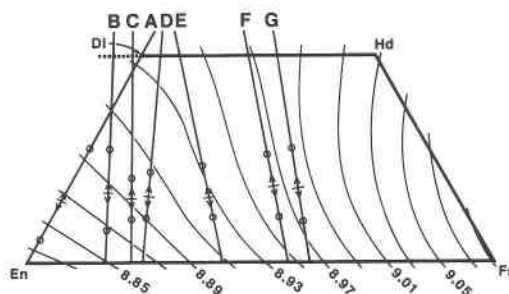

Fig. 1. The Mg-Ca-Fe pyroxene quadrangle. Curved lines: contours for the b parameters of clinopyroxenes (from Turnock et al., 1973, Fig. 2). Straight lines marked A to G: seven binary sections, each defined by two coexisting clinopyroxene compositions (shown by little circles) chosen from Huebner and Turnock (1980). The "anticline" sign indicates the critical composition calculated for each pseudobinary system.

data of Huebner and Turnock (1980) were originally chosen because they were for higher temperatures and we were concerned with avoiding possible effects of the $C2/c$ to $P2_1/c$ transition in the pigeonite.

ELASTIC STRAIN AND STRAIN ENERGY IN COHERENT CLINOPYROXENES

Strain

Robinson et al. (1971), Robin (1977), and Robinson et al. (1977) pointed out that the repeat distances of crystal lattices of coexisting clinopyroxenes, whether coherent or not, can always be matched along two directions in the a-c plane without requiring any stress. Figure 2 illustrates this point. The directions of the lamellar boundaries are indeed observed to be parallel to the b direction; thus the only elastic strain required for a coherent match is along the b axis. In order to evaluate the elastic strain in a lamella of composition x, we must know the stress-free compositional strain η_2, i.e., the relative variation of b under no stress.

Once a set of lamellae is formed and its crystallographic orientation within the host crystal is set, stresses other than that along b may arise during further cooling; the corresponding elastic energy should also affect the exso-

TABLE 1. Parameters and results calculated from coexisting pairs for pseudobinary sections A to G

| 1	2 $\frac{Fe}{Fe + Mg}$	3 T_{pair} (°C)	4 x_a	5 x_b	6 W_1 (kJ/mol)	7 W_2 (kJ/mol)	8 x_i	9 T_i (°C)	10 $d\eta_2/dX$ (× 10^{-2})	11 k (kJ/mol)	12 x_c	13 T_c (°C)	14 $T_i - T_c$ (°C)
A	0.0000	1300.0	0.541	0.105	9.401	33.850	0.293	1561.0	1.4797	0.9477	0.290	1513.9	47.1
B	0.0994	1250.0	0.539	0.159	15.102	31.113	0.330	1390.1	1.0718	0.4971	0.328	1363.7	26.4
C	0.1768	1330.0	0.407	0.209	10.299	30.589	0.302	1374.6	0.8830	0.3374	0.301	1357.5	17.1
D	0.2182	1300.0	0.437	0.209	12.587	30.359	0.316	1353.4	0.8600	0.3201	0.315	1336.7	16.7
E	0.3674	1250.0	0.457	0.229	15.087	29.339	0.337	1295.3	0.4263	0.0786	0.336	1291.0	4.3
F	0.5345	1200.0	0.531	0.219	17.937	28.746	0.365	1272.3	0.2641	0.0302	0.364	1270.6	1.7
G	0.5994	1185.0	0.554	0.192	17.488	29.074	0.358	1286.8	0.2839	0.0349	0.358	1284.9	1.9

Note: Column numbers are referred to in text.
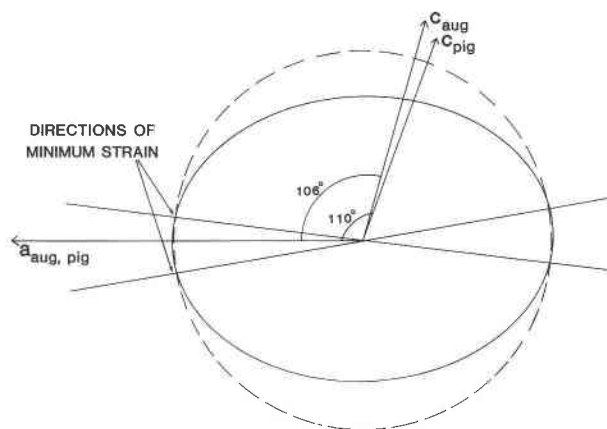
Fig. 2. The change in lattice parameters associated with the difference in composition of the two crystals is a strain, called the compositional strain. The compositional strain within the *a-c* plane is represented here by a strain ellipse, with the augite lattice taken as the reference state (i.e., unstrained by definition) and thus shown as a circle. For the purpose of illustration, the strain ellipse, representing the lattice of the pigeonite, is greatly exaggerated. The crystallographic lattices of an augite and a pigeonite coexisting in equilibrium can always be matched without strain along two directions within their *a-c* plane: the *c* parameter of the pigeonite is smaller than that of the augite but *a* and *β* are larger and there are therefore two directions of no strain in the *a-c* plane. For the three-dimensional lattices, however, the *b* dimensions are not identical under no stress; coherency therefore imposes an elastic strain along *b*. A plane defined by the *b* axis and one of the two directions in the figure is therefore a *direction of minimum strain*.

lution process (Robin, 1977). These effects are ignored in the present paper.

We determine a *coefficient of compositional strain*[1] (Robin, 1974),

$$\frac{d\eta_2}{dx} = \frac{1}{b}\frac{db}{dx}, \tag{1}$$

quantifying the changes in *b* with composition *x,* for each of our seven binary subsystems. This is done by calculating the variation of *b* along the binary section defined by each pair, using the room-temperature values for lattice parameters presented by Turnock et al. (1973). Appendix A explains the procedure. The values calculated are shown in Table 1, column 10. We note that $d\eta_2/dx$ decreases as the bulk Fe content increases, down to a very low value for sections F and G. This decrease stems mainly from the fact that, as can be seen in Figure 1, the angle between the binary joins and the lines of constant *b* decreases and, therefore, the strain required to maintain coherency becomes smaller. For assemblages still more Fe-rich, the absolute value of that angle would become zero and then increase again and, therefore, so would the value of *k*.

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[1] The "matrix notation" (e.g., Nye, 1957) is used for stresses, strains, and elastic constants.

Elastic strain energy

It can be shown (Robin, 1974) that, within the linear assumptions discussed above, the Helmholtz elastic strain energy per mole in a lamella constrained to be coherent within a crystal of composition (i.e., mole fraction of the Ca end member) x_0 is

$$\bar{F} = k(x - x_0)^2, \tag{2}$$

where (App. B)

$$k = (\bar{V}/2s_{22})(d\eta_2/dx)^2, \tag{3}$$

in which $\bar{V}$ is the molar volume and s_{22} is the normal elastic compliance along the *b* direction. The value taken by the parameter *k,* which could be called an elastic energy coefficient, determines the size of the effect of coherency on exsolution (Robin, 1974; Tullis and Yund, 1979).

For the molar volume we use an average value of

$$\bar{V} = 0.647 \times 10^{-4} \text{ m}^3\cdot\text{mol}^{-1},$$

and we take

$$s_{22} = 0.7474 \times 10^{-11} \text{ Pa}^{-1}(0.7474 \text{ Mbar}^{-1})$$

for the elastic constant along the *b* direction (Frisillo and Barsch, 1972, Table 6). Table 1, column 11, shows the values of *k* calculated for the seven chosen subsystems: it ranges from less than 1 kJ·mol^{-1} on the Mg-rich end to less than 50 J·mol^{-1} for binary join G, the most Fe-rich subsystem. These values can be compared to the 2.5 to 2.95 kJ·mol^{-1} (600 to 700 cal·mol^{-1}) that Robin (1974) found for high-temperature alkali feldspar. We can therefore anticipate that coherency will lower the solvus less for clinopyroxenes than the 79 ± 7 °C depression of the critical temperature in alkali feldspars.

THE PSEUDOBINARY COHERENT SOLVI

For our pseudobinary approximation, we take the molar Gibbs energy $\bar{G}$ of a pyroxene along the binary joint to be given by a two-parameter Margules expansion for binary systems (Thompson, 1967):

$$\bar{G} = x\mu_1^0 + (1 - x)\mu_2^0 + RT[x \ln(x) + (1 - x)\ln(1 - x)] + [W_1(1 - x) + W_2x]x(1 - x), \tag{4}$$

where W_1 and W_2 are the Margules parameters. Values for the parameters W_1 and W_2 are calculated from the two coexisting compositions and the temperature at which they coexist (e.g., see Thompson, 1967). Table 1 gives the critical compositions (x_c, col. 8) and critical temperatures (T_c, col. 9) calculated from the resulting Gibbs energies.

In principle, calculating a whole binary solvus from just one pair of coexisting compositions is not recommended. Our excuses for doing so anyway are several: (1) The temperature range of coexisting clinopyroxenes for a given bulk composition is rather narrow. Extrapolations are therefore never very far in temperature from the actual data pair; data on more coexisting pairs, if they existed, might provide more scatter than constraints. (2) The depression in temperature of the solvus associated with
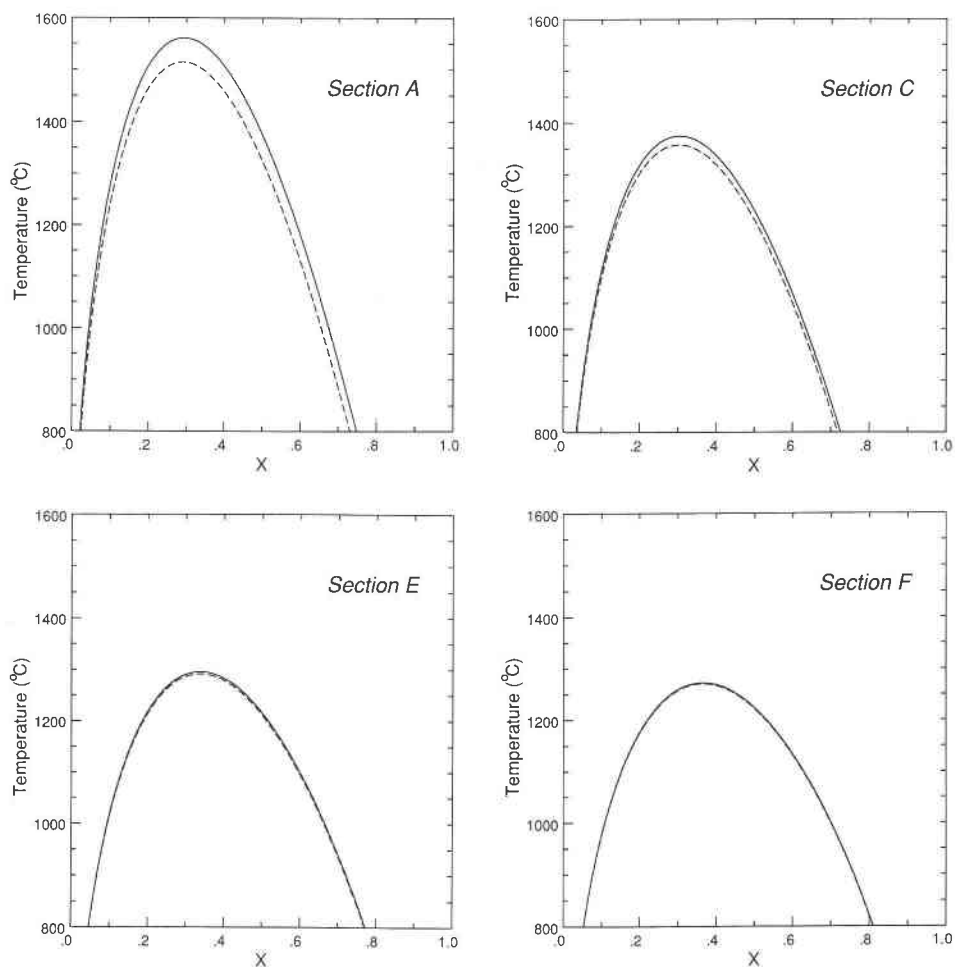
Fig. 3. The calculated incoherent (solid lines) and coherent (dashed lines) solvi for four of the coexisting pairs: A, C, E, and F. As the Fe content increases, the critical temperature decreases, as well as the difference between incoherent and coherent solvi. To within a fraction of one percent in composition, coherent and incoherent solvi for a given binary section can be superposed on each other by a translation of $T_i - T_c$ (Table 1, column 14) over the temperature range plotted here. The lower parts of the solvi shown are metastable since in reality the pigeonite would undergo the $C2/c \rightarrow P2_1/c$ transition and/or orthopyroxene would become stable.

coherency—which it is the purpose of this paper to calculate—appears not to depend strongly on the exact values of the Margules parameters (see Discussion). (3) The result is sufficient to demonstrate the method of calculation that we present.

To take the strain energy of the coherent lamellae into account, Robin (1974) showed that the sum of the Gibbs energy with the elastic energy term define the *Cahn energy*,

$$\bar{\phi} = \bar{G} + k(x - x_0)^2, \qquad (5)$$

which can be used to calculate the coherent solvus, in the same manner as $\bar{G}$ is used to calculate the incoherent one.

Figure 3 shows individual incoherent (i) and coherent (c) solvi for four different binary sections and Table 1, Columns 12, 13, and 14, summarizes the results. The last column in Table 1 gives the lowering of the critical temperature, $T_i - T_c$. As anticipated, this lowering decreases as the Fe content increases. Ranging from 47 °C on the Mg end to less than 2 °C on pseudobinary sections F and

G, we note that this effect of coherency is smaller than the uncertainty on our very knowledge of the incoherent solvus for most of the binary sections.

The shape of the coherent solvus is very similar to that of the incoherent one. In fact, over the range of temper-

TABLE 2. Parameters and results calculated from smoothed Margules parameters for pseudobinary sections A to G

1	6 W_1 (kJ/mol)	7 W_2 (kJ/mol)	8 x_i	9 T_i (°C)	12 x_c	13 T_c (°C)	14 $T_i - T_c$ (°C)
A	10.401	32.389	0.300	1474.0	0.297	1426.3	47.7
B	11.650	31.709	0.307	1430.7	0.306	1405.3	25.4
C	12.624	31.179	0.314	1398.2	0.313	1380.7	17.5
D	13.145	30.896	0.318	1381.3	0.317	1364.6	16.7
E	15.021	29.875	0.334	1323.9	0.334	1319.6	4.3
F	17.123	28.732	0.357	1267.9	0.357	1266.2	1.7
G	18.018	28.288	0.367	1249.3	0.367	1247.3	2.0

Note: Column numbers are referred to in text and correspond to like columns in Table 1.
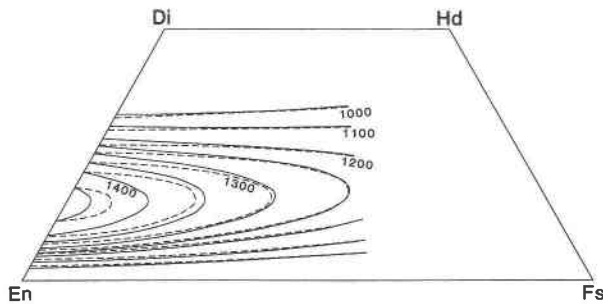
Fig. 4. The ternary incoherent (solid lines) and coherent solvi (dashed lines). These surfaces were drawn using recalculated solvi for which the Margules parameters are linear functions of the Fe content of the critical composition (approximately, see text). The temperatures are given in °C.

atures shown, the coherent solvus could be drawn by merely translating the incoherent one by $(T_i - T_c)$ parallel to the temperature axis: nowhere would the error exceed a small fraction of a percent in composition.

EFFECT OF COHERENCY ON ISOTHERMAL SECTIONS OF THE TERNARY SOLVUS

Whereas a binary solvus is commonly represented in a temperature-composition diagram, a ternary solvus is more commonly displayed as isothermal contours in ternary-composition coordinates. If we try, in such a ternary representation, to join points at the same temperature on the seven independent pseudobinary solvi calculated above, we obtain rather ragged isothermal contours; this is because of the rather large errors involved in estimating pairs of Margules parameters from a single, uncertain, pair of coexisting compositions. In order to visualize the effect of coherency in such a representation, we need more-likely-looking isothermal sections: that is, we need to smooth out the variations of the Margules parameters from section to section. To this end, the Margules parameters W_1 and W_2 found from each binary pair were linearly correlated against the Fe/(Fe + Mg) ratio of the corresponding critical points. By replacing W_1 and W_2 found above for each binary join by new values calculated from the linear-regression equation, new solvi—both coherent and incoherent—are obtained for each binary section (Table 2).

The worst difference in calculated critical temperature between these new solvi and the original set is found for binary joint A, for which the difference is about 87 °C; it is less than 45 °C for all other sections. As noted earlier, the uncertainty on the solvus is of that same order. Figure 4 is then obtained by joining points at the same temperature on the different solvi. Note that the effect of coherency is still small compared to the uncertainty in the incoherent data themselves.

DISCUSSION

Value of k

An important result of the present analysis is the relatively small size of the elastic energy coefficient k, the parameter describing the elastic effect of coherency on the thermodynamics of exsolution; in fact, k becomes negligible as the Fe content increases. The direct consequence of the small k values is that the coherent solvus lies below but close to the incoherent one.

The values of k could be notably different if they were calculated with other values for η_2; that is, in effect, with other data on the b lattice dimensions. Even for the room-temperature data we used, the coefficient of compositional strain depends significantly on how Turnock et al. (1973) drew the contours of b, shown in Figure 1 and Appendix Figure A1 and on the orientations of the tie lines joining binary pairs, also shown in Figure 1 and Appendix Figure A1. For the Fe-rich binary joins F and G, in particular, we see that a slightly different partition of Fe and Mg between the two clinopyroxenes, for example, could lead to no coherency strain (i.e., to $\alpha = 0$ in App. Fig. A1) and therefore to $k = 0$. Ideally, one would want data at high temperatures; Tullis and Yund (1979) found, in the case of exsolution on the Mg-Ca join, that high-temperature data on b appear to yield a still smaller k than Turnock et al.'s (1973) b data (20 cal·mol^{-1} instead of 200 cal·mol^{-1}). It is our judgment that more accurate b values would not lead to significantly higher values of k for ternary compositions, but complete resolution of this matter would require further investigation.

Thus the uncertainty on k, in relative terms, could be quite large. It is important to remember however that k is small in any case and that the error, in absolute terms, remains small.

Other equations of state

Similarly, we believe that other values of the Margules parameters, or even other equations of state may change the solvi calculated but would not change $T_i - T_c$ very much.

For one example, we can compare the two sets of solvi (Tables 1 and 2) for which the effects of coherency were calculated above: although the solvi were different (different W values, hence different critical T and x), $(T_i - T_c)$ stayed essentially unchanged.

For another example, we note that our calculation for binary section A (the pure Ca-Mg join) is directly comparable to Tullis and Yund's (1979) calculation for curve b of their Figure 4, for which they have also used Turnock et al.'s (1973) room-temperature lattice-parameter data. Tullis and Yund, however, have used a different equation of state; yet, our calculated $(T_i - T_c)$ agrees with theirs to within 1 °C. Finally, similar calculations carried out with the data of Lindsley and Andersen (1983) give different solvi but the predicted depressions of the critical temperature due to coherency are again very similar.

The "robustness" of the present conclusions is further supported by a comparison with the results of Fletcher and McCallister (1974). Fletcher and McCallister were concerned with coherent spinodal fluctuations, which they modeled theoretically as variations in Ca while keeping

Fe/(Fe + Mg) constant. These authors were not explicitly concerned with coherent solvi but with the "undercooling to the coherent spinodal," ΔT, which they calculated is nevertheless comparable to our quantity $(T_i - T_c)$. In the formulation of the present paper, Fletcher and McCallister's calculation corresponds to (1) taking pseudobinary sections with constant Fe/(Fe + Mg) ratio (i.e., colinear with the Wo corner) and (2) assuming a strictly regular, symmetric solution (e.g., Thompson, 1967). The "undercooling" found by Fletcher and McCallister ranges from 110 °C on the Mg join, decreases down to 0 °C for Fe/(Fe + Mg) ≈ 0.70, and increases again toward the Fe join. For the critical composition that Fletcher and McCallister assumed, the Fe content for which $\Delta T = 0$ corresponds to where the lines of constant b (Fig. 1) are parallel to lines of constant Fe/(Fe + Mg). The differences between the results of Fletcher and McCallister and ours are probably the result of using different variations of b with composition, but the essential conclusion is the same.

Relaxing the pseudobinary constraint

It was noted above that the pseudobinary approximation amounted to an artificial constraint on possible compositions of coherent exsolutes. Relaxing it means that the coherent exsolutes are no longer constrained to lie in the same binary subsystem as an incoherent equilibrium pair. In such a case, we anticipate that their composition would shift in such a way that the tie line joining them would rotate toward the line of constant stress-free b value for the bulk composition of the crystal, since this would lead to a decrease in strain energy. To that lower strain energy would correspond a lower coherency effect and, therefore, a still lower $(T_i - T_c)$ than calculated here. However, preliminary calculations, based on the assumption of ideal Fe-Mg solution within both coexisting pyroxenes, suggest that the tie-line rotation and the corresponding decrease in the strain-energy term would be small.

Conclusions

1. The pseudobinary approximation presented here allows an evaluation of the effect of coherency stresses on exsolution in mineral systems that require three chemical components to describe their compositions. It is useful when no complete ternary equation of state is available or reliable. The method is relatively simple for clinopyroxenes because we can get a reasonable expression of $\bar{G}$ along a binary section. The method is applicable, however, any time an expression of $\bar{G}(x)$, of any form, can be found along a binary section.

2. When applied to high-temperature ($C2/c$) Mg-Fe-Ca clinopyroxenes, it is found that coherency causes a drop in critical temperature that is less than 50 °C for Mg-rich compositions and becomes less than 2 °C for intermediate compositions. This drop in critical temperature due to coherency is expected to increase again, after dropping to zero, as bulk compositions move farther toward the Fe join. A 50 °C drop is comparable to our uncertainty concerning the solvus itself, while a 2 °C drop is negligible. Experimental work on coherent exsolution could therefore yield useful data on the incoherent solvus.

References cited

Brady, J.B., and McCallister, R.H. (1983) Diffusion data for clinopyroxenes from homogenization and self-diffusion experiments. American Mineralogist, 68, 95–105.

Buseck, P.R., Nord, N.L., Jr., and Veblen, D.R. (1980) Subsolidus phenomena in pyroxenes. Mineralogical Society of America Reviews in Mineralogy, 7, 117–204.

Cahn, J.W. (1962) Coherent fluctuations and nucleation in isotropic solids. Acta Metallurgica, 10, 907–913.

Champness, P.E., and Lorimer, G.W. (1971) An electron microscopic study of a lunar pyroxene. Contributions to Mineralogy and Petrology, 33, 171–183.

——— (1976) Exsolution in silicates. In Electron microscopy in mineralogy. Springer-Verlag, Berlin.

Fletcher, R.C., and McCallister, R.H. (1974) Spinoidal decomposition as a possible mechanism in the exsolution of clinopyroxene. Carnegie Institution of Washington, Annual Report of the Director, Geophysical Laboratory, 1973–1974, 396–399.

Frisillo, A.L., and Barsch, G.A. (1972) Measurement of single-crystal elastic constants of bronzite as a function of pressure and temperature. Journal of Geophysical Research, 77, 6360–6384.

Grover, J.E. (1980) Thermodynamics of pyroxenes. Mineralogical Society of America Reviews in Mineralogy, 7, 341–373.

Huebner, J.S., and Turnock, A.C. (1980) The melting relations at 1 bar of pyroxenes composed largely of Ca-, Mg-, and Fe-bearing components. American Mineralogist, 65, 225–271.

Lindsley, D.H. (1983) Pyroxene thermometry. American Mineralogist, 68, 477–493.

Lindsley, D.H., and Andersen, D.J. (1983) A two-pyroxene thermometer. Proceedings of the Thirteenth Lunar and Planetary Science Conference, Part 2. Journal of Geophysical Research, 88, Supplement, A887–A906.

McCallister, R.H., and Yund, R.A. (1977) Coherent exsolution in Fe-free pyroxenes. American Mineralogist, 62, 721–726.

Nord, G.L., Jr., Heuer, A.H., and Lally, J.S. (1976) Pigeonite exsolution from augite. In Electron microscopy in mineralogy. Springer-Verlag, Berlin.

Nye, J.F. (1957) Physical properties of crystals. Oxford University Press, London.

Robin, P.-Y.F. (1974) Stress and strain in cryptoperthite lamellae and the coherent solvus of alkali feldspars. American Mineralogist, 59, 1299–1318.

——— (1977) Angular relationships between host and exsolution lamellae and the use of the Mohr circle. American Mineralogist, 62, 127–131.

Robinson, Peter, Jaffe, H.W., Ross, M., and Klein, C., Jr. (1971) Orientation of exsolution lamellae in clinopyroxenes and clinoamphiboles: Consideration of optimal phase boundaries. American Mineralogist, 56, 909–939.

Robinson, Peter, Ross, M., Nord, G.L., Jr., Smyth, J.R., and Jaffe, H.W. (1977) Exsolution lamellae in augite and pigeonite: Fossil indicators of lattice parameters at high temperature and pressure. American Mineralogist, 62, 857–873.

Ross, M., Huebner, J.S., and Dowty, E. (1973) Delineation of the one atmosphere augite-pigeonite miscibility gap for pyroxenes from lunar basalt 12021. American Mineralogist, 58, 619–635.

Thompson, J.B., Jr. (1967) Thermodynamic properties of simple solutions. In P. H. Abelson, Ed., Researches in geochemistry, vol. 2, p. 340–361. Wiley, New York.

Tullis, J., and Yund, R.A. (1979) Calculation of coherent solvi for alkali feldspar, iron-free clinopyroxene, nepheline-kalsilite, and hematite-ilmenite. American Mineralogist, 64, 1063–1074.

Turnock, A.C., Lindsley, D.H., and Grover, J.E. (1973) Synthesis and unit cell parameters of Ca-Mg-Fe pyroxenes. American Mineralogist, 58, 50–59.

Willaime, C., and Brown, W.L. (1972) Explication de l'orientation des interfaces dans les exsolutions des feldspaths, par un calcul d'énergie élastique. Comptes Rendus à l'Académie des Sciences de Paris, 275, 627–629.

Willaime, C., and Gandais, M. (1972) Study of exsolution in alkali feldspars. Calculation of elastic stresses inducing periodic twins. Physica Status Solidii, A9, 529–539.

Willaime, C., Brown, W.L., and Gandais, M. (1973) An electron-microscopic and X-ray study of complex exsolution textures in a cryptoperthitic alkali feldspar. Journal of Materials Science, 8, 461–466.

Yund, R.A. (1974) Coherent exsolution in the alkali feldspars. In Geochemical transport and kinetics. Carnegie Institution of Washington Publication 634, 173–183.

Yund, R.A., and McCallister, R.H. (1970) Kinetics and mechanisms of exsolution. Chemical Geology, 6, 5–30.

## Appendix A. Determination of the Compositional Strain Coefficient

Appendix Figure A1 shows an example of a binary subsystem, $A'B'$. The coefficient of compositional strain sought is that along the binary section $A'B'$ at the critical point. However, since this point is generally not known ahead of time, we measure the coefficient at the half-way point, Z, between the two coexisting compositions; thus, it is assumed that this half-way point is close enough to the critical composition.

While db/dx could be read directly from the intersections (i.e., points A and B) of the binary line with contour lines of constant b, the error introduced by the curvature and lack of parallelism of these contours can be quite significant in some cases. Instead, db/dx is calculated from the gradient of the $b(x,y)$ surface at Z and from the angle that the binary section makes with the constant-b contour lines. The formula used is, in effect, the same as that which gives the apparent dip of a plane on a vertical cross section (our binary section) from the true dip (the gradient) of that plane.

A line EF is drawn through Z as tangent to a contour line of constant b. Its orientation is interpolated from the orientations of the two nearest contour lines drawn by Turnock et al. (1973). The gradient of b is measured along CD, orthogonal to EF: it is $\delta b/\overline{CD}$, in which δb is the change of b between the two actual
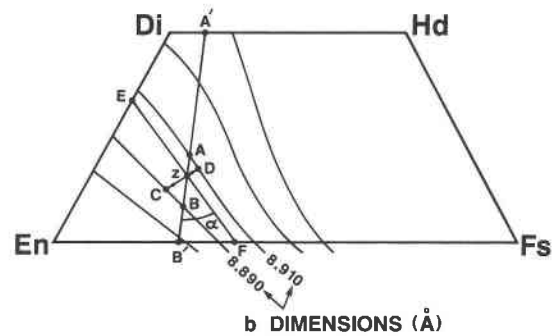
App. Fig. A1.   A binary section $A'B'$, such as in Fig. 1, superimposed on the lattice-parameter data for b in clinopyroxenes (from Turnock et al., 1973).

contour lines. The angle α is that between lines EF and $A'B'$. The value of db/dx along the line $A'B'$ is calculated by

$$db/dx = \overline{A'B'}(\delta b/\overline{CD})\sin \alpha. \tag{A1}$$

This value is then inserted in Equation 1.

Appendix B. Strain-Energy Density in Clinopyroxene Lamellae

Under the linear assumptions discussed, the elastic strain, e_2, required to compel a lamella, of composition x, to be coherent within a crystal of bulk composition x_0 is

$$e_2 = -\eta_2(x) + \eta_2(x_0) = (d\eta_2/dx)(x - x_0). \tag{B1}$$

The only nonzero stress being σ_2, the tension or compression along the b direction, Hooke's law of linear elasticity is expressed by

$$e_2 = s_{22}\sigma_2, \tag{B2}$$

where s_{22} is the isothermal normal elastic compliance along the b direction. The Helmholtz elastic strain energy per mole in a lamella is

$$\bar{F} = (\bar{V}/2)\sigma_2 e_2 = (\bar{V}/2)(e_2/s_{22})e_2. \tag{B3}$$

Using Equation B1, Equation B3 becomes

$$\bar{F} = k(x - x_0)^2, \tag{2}$$

where

$$k = (\bar{V}/2s_{22})(d\eta_2/dx)^2. \tag{3}$$