

## A "conditional spinodal" within the peristerite miscibility gap of plagioclase feldspars.

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### Abstract

Some of the arguments over whether the peristerite miscibility gap in plagioclase feldspars is a true solvus or a binary loop can be resolved by using free energy curves and assuming that the Al/Si order/disorder transformation in albite is other than first order in character. If the disordered plagioclase solid solution behaves nearly ideally in the sodium rich range and the substitution of excess Al (in the form of the  $\text{CaAl}_2\text{Si}_2\text{O}_8$ ) in low albite is energetically highly unfavorable, then a miscibility gap appears which contains a "conditional spinodal" between ordered albite and disordered oligoclase. The thermodynamic driving force for exsolution is considered to be entirely due to the ordering of Al and Si in albite so that the miscibility gap must peak below the transformation temperature in pure albite ( $\sim 575\text{--}625^\circ\text{C}$ ). A three dimensional diagram of free energy, composition and degree of order allows a rationalization of the compositions and occurrence of coexisting albite + oligoclase in low grade metamorphic rocks based on variations in the degree of order achieved during crystal growth.

### Introduction

That there is a close relationship between cation ordering and exsolution in plagioclase feldspars has long been realized. The precise nature of interactions between the two processes, however, has so far remained enigmatic. As a consequence there is considerable uncertainty concerning the equilibrium phase diagram (Smith, 1972, 1974, 1975) and a wide variety of schematic phase relations have been published (Laves, 1960; Megaw, 1962; Gay, 1962; Smith and Ribbe, 1969; Nord et al., 1974; McConnell, 1974). Recent progress in the treatment of analogous complex metallurgical systems which show both ordering and unmixing has been achieved by using free energy diagrams to define all possible transformation pathways and mechanisms allowed under specific temperature/composition conditions. In particular, it has been recognized that the mechanisms available for exsolution can depend on whether the order/disorder reactions are thermodynamically of first or other than first order<sup>2</sup> (Allen and Cahn, 1976a,b).

Predictions of solid state behavior which are based on a given set of free energy curves may be tested experimentally for metals (*e.g.*, Allen, 1977) more readily than for silicates because of slow diffusion rates in the latter. The theory, however, is largely phenomenological and should be generally applicable. If the mechanisms of transformations in any mineral solid solution can be deduced from observations of the microstructures and compositions of naturally occurring samples, then a great deal may be inferred regarding their metastable and equilibrium phase relations, as has been shown for sodic pyroxenes (Carpenter, 1980). The purpose of the present paper is to demonstrate how such an approach leads to a clarification of some of the remaining issues concerning exsolution in the sodium rich members of the plagioclase series known as peristerites.

Previous explanations of the peristerite miscibility gap fall into two groups (Fig. 1): those favoring a "solvus" (Laves, 1960; Ribbe, 1962; Crawford, 1966; Viswanathan and Eberhard, 1968; Weber, 1972;

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<sup>2</sup>There is some doubt as to whether the classical thermodynamic description of phase transformations as being of first, second or

higher order is strictly appropriate (Thompson and Perkins, 1980). To avoid this issue, which does not affect the substance of this paper, the terms "other than first" or "non-first" order will be used to imply transformations in which the first derivatives of Gibbs free energy with respect to all intensive variables are continuous.

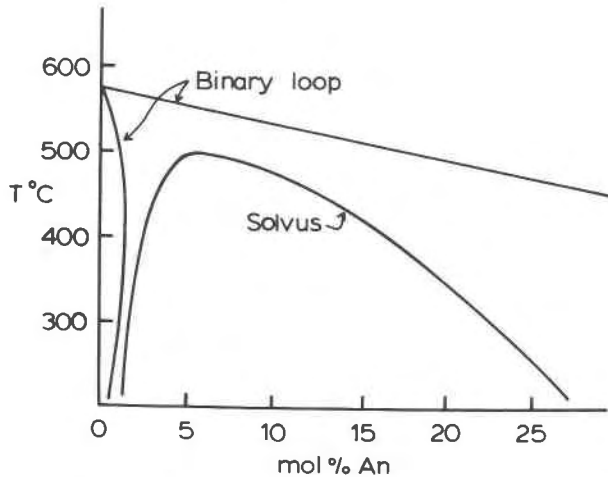


Fig. 1. Binary loop (Orville, 1974) and solvus (Crawford, 1966) models for the peristerite miscibility gap, after Nord *et al.* (1978).

Nord *et al.*, 1978) and those preferring a binary loop associated with a first order order/disorder transformation in albite (Smith, 1972, 1974, 1975; Orville, 1974). According to the analysis outlined below it strictly is neither of these but should perhaps be described as a conditional solvus containing a "conditional spinodal" (Allen and Cahn, 1976a). The implications are that the miscibility gap exists only after some degree of order has been achieved and that the order/disorder reaction is other than first order in character.

#### Peristerite exsolution: salient features

In the interest of brevity and because extensive reviews of peristerite exsolution are available elsewhere (Smith, 1972, 1974; McLaren, 1974; Ribbe, 1975; Champness and Lorimer, 1976), only the observations which must be incorporated into any overall interpretation of the miscibility gap will be outlined here. They are:

1. Exsolution commonly occurs in crystals whose compositions lie in the range  $\sim\text{An}_2\text{-An}_{17}$ . The exsolved phases have compositions  $\sim\text{An}_{1\pm 1}$  and  $\text{An}_{25\pm 5}$ .
2. The exsolved phases differ in the degree of Al/Si order they possess; the albite is usually fully ordered but the oligoclase has only limited order (Ribbe, 1960). The An rich component usually has an albite-like reciprocal lattice, but some specimens exhibit diffuse intensity at positions of type e reflections in single crystal X-ray photographs (Bown and Gay, 1958).
3. The exsolution microstructures observed by transmission electron microscopy can often be interpreted as the products of spinodal decomposition (Christie,

1968; Korekawa *et al.*, 1970; Weber, 1972; Lorimer *et al.*, 1974; McLaren, 1974; Nord *et al.*, 1978). While a spinodal mechanism has not been proved experimentally for peristerites, the arguments in favor of it are strong (Nord *et al.*, 1978).

4. There appears to be a marked asymmetry to the miscibility gap. This is indicated both by the range of compositions showing exsolution (Ribbe, 1962) and by the compositions of coexisting crystals (albite + oligoclase) observed in metamorphic assemblages (Crawford, 1966).

5. Disordered feldspars in the composition range  $\text{An}_0\text{-An}_{50-55}$  show nearly ideal solid solution behavior at 700 and 600°C, according to the ion exchange experiments of Orville (1973, 1974).

6. There is a marked change in the kinetics of Al/Si ordering in albite within the temperature range 575–625°C (McConnell and McKie, 1960). Whether this represents a continuous (*i.e.*, other than first order) or a discontinuous (first order) transformation is the subject of debate (Smith, 1974), but there is a continuous range of equilibrium Al/Si distributions above and below it (MacKenzie, 1957; Stewart and Ribbe, 1969; Thompson *et al.*, 1974). No symmetry change is involved, however; both high and low albite have space group  $\text{C}\bar{1}$ .

7. Estimates of the peak temperature of the miscibility gap generally fall around 550°C and below (Brown, 1962; Crawford, 1966, 1970; Viswanathan and Eberhard, 1968; Smith, 1972; Nord *et al.*, 1978). Experimental data of Moody *et al.* (in preparation) suggest a slightly higher value.

#### Free energy-composition-order relations

Conflicting interpretations of the peristerite gap as a solvus or a binary loop arise from the observations that the disordered solid solution behaves nearly ideally at 600°C, not even showing potential for unmixing (Orville, 1974), but that exsolution in a binary loop can only be by nucleation and growth (Champness and Lorimer, 1976; Nord *et al.*, 1978). Spinodal decomposition requires that there be a continuous free energy-composition ( $G\text{-}X$ ) path between the two end member components (Cahn, 1968); this requirement can be met where one component is ordered and the second is disordered if the order/disorder transformation is other than first order in character (Allen and Cahn, 1976a,b; Carpenter, 1980). A series of  $G\text{-}X$  curves and the consequent phase relations appropriate for peristerites are shown in Figure 2. The disordered (high albite structure) solid solu-

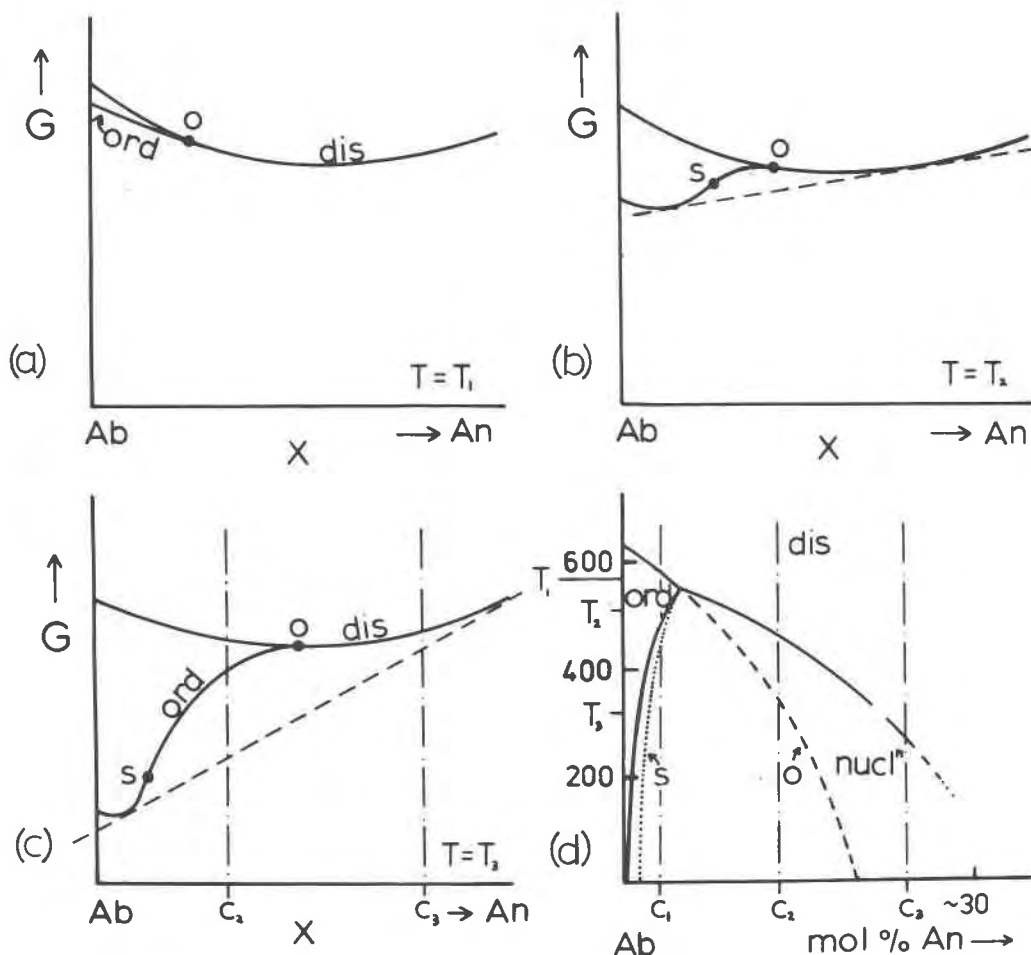


Fig. 2. Free energy ( $G$ )—composition ( $X$ ) curves for ordered albite (ord) and disordered plagioclase solid solution (dis)(a-c), and the resulting phase diagram (d). (a) At temperature  $T_1$ , the curves have the configuration of a typical non-first order transformation with  $\delta G/\delta X$  continuous. (b) At  $T_2$  the substitution of excess Al in ordered albite has become so unfavorable that a two phase field, given by the common tangent (broken line), has developed. Spinodal decomposition is possible in phases lying on the curve between the points  $o$  and  $s$ . (c) At lower temperatures the two phase field widens. (d) Within the two phase field but outside the conditional spinodal (which is delineated by the dotted and broken lines, respectively the loci of the point of convergence,  $o$ , and the point of inflection,  $s$ , in the  $G$ - $X$  curves) the exsolution mechanism is nucleation and growth. During cooling, a crystal with composition  $c_1$  will order and then exsolve disordered oligoclase by nucleation and growth or spinodal decomposition. Crystal  $c_2$  can nucleate ordered albite or exsolve into ordered and disordered components by spinodal decomposition;  $c_3$  can only nucleate ordered albite. The dis $\rightarrow$ ord transformation cannot be second order in albite since there is no symmetry change (Lifshitz, 1942); strictly speaking the line separating the single phase fields should not, therefore, be drawn in. Note that this analysis yields only the form of the phase relations for albite and disordered plagioclase and ignores the effect of "e" type ordering at low temperatures.

tion is treated as nearly ideal for the whole temperature range.

At a temperature  $T_1$  just below the Al/Si ordering transformation temperature for pure end member albite the  $G$ - $X$  curves for the ordered and disordered phases converge, with the configuration of a typical non-first order phase transformation (Fig. 2a), ( $\delta G/\delta X$  is continuous). The ordered and disordered fields in the equilibrium phase diagram are separated by the locus of the point of convergence,  $o$ . If, as the

temperature is reduced, the ordered albite becomes increasingly stable relative to the disordered phase but cannot accept significant excess Al substitution for Si (in the form of  $\text{CaAl}_2\text{Si}_2\text{O}_8$ ), then a miscibility gap appears (Fig. 2b,c,d). The ordered  $G$ - $X$  curve must develop a kink and a "conditional spinodal" (Allen and Cahn, 1976a) appears, delineated by the loci of  $o$  and the point of inflection,  $s$ . Outside the spinodal, the only mechanism for exsolution, as normal, will be nucleation and growth. Figure 2d, an

equilibrium phase diagram which includes the conditional spinodal, can be used to predict transformation mechanisms and sequences in crystals of selected compositions.

During continuous cooling a crystal with composition  $c_1$  would order first and then, at a lower temperature, exsolve disordered oligoclase by nucleation and growth or by spinodal decomposition, depending principally on the cooling rate. A disordered crystal with composition  $c_2$  would first pass through a field of nucleation of ordered albite. On entering the spinodal region, ordering could metastably precede, or occur concurrently with, spinodal decomposition. Crystal  $c_3$  could only precipitate ordered albite by nucleation and growth.

The reaction sequence in crystals grown metastably within the two phase field can also be predicted. For example, given sufficient time, crystal  $c_2$  grown metastably disordered at  $T_3$  would probably order first and then decompose by a spinodal mechanism since ordering requires only short range diffusion and should therefore be faster.

Asymmetry in the limbs of the two phase field and in the composition range of each exsolution mechanism arises from the relative curvature of the  $G-X$  curves for the two phases. If the ordered phase experiences a steep increase in free energy when its composition departs from the pure end member and the disordered curve is shallow, common tangents relating equilibrium compositions at different temperatures should meet the ordered curve over a narrow range but will vary widely along the disordered one. This argument is exactly that of Christie (1968) except that he did not specify the role of order/disorder in producing the  $G-X$  asymmetry.

According to this model the peristerite gap is neither a conventional solvus nor a simple binary loop. It might be described as a non-first order binary loop or a conditional solvus since its existence depends on the development of ordering. It can only appear at temperatures below which substantial Al/Si ordering occurs in pure albite. An order dependent spinodal was anticipated, at least qualitatively, by McConnell (1974, 1975) in his analysis of the Huttenlocher miscibility gap.

### Discussion

The free energy-composition-order analysis correctly predicts all the salient features of peristerite exsolution observed in natural specimens as listed above. Several of the assumptions and implications should be examined more closely, however. First, the

model requires that the order/disorder transformation in pure albite at 575–625°C is other than first order. This is at odds with the suggestion of McConnell and McKie (1960) that the transformation is "smeared", involves the stable coexistence of two phases (of identical composition but different Al/Si order) and thus has first order properties. As pointed out by Smith (1974), though, the kinetic data can be interpreted in terms of a non-first order transformation, as can the range of equilibrium Al/Si distributions deduced by Stewart and Ribbe (1969). According to Orville (1974) the thermochemical measurements of Holm and Kleppa (1968) are consistent with either a first or a second order transformation at  $575 \pm 50^\circ\text{C}$ . Group theoretical arguments, however, preclude a second order character since there is no symmetry change (Lifshitz, 1942). Thompson et al. (1974) and Thompson and Hovis (1979) have disputed that there is any discontinuity and show that a continuous equilibrium ordering function can be defined which merely shows a relatively rapid change between  $\sim 550$  and  $\sim 650^\circ\text{C}$ . There are instances where a rapid change in physical properties without discontinuities can be associated with a two phase region, a possible analogy being a binary liquid/vapor system just above the critical point of one component (J. B. Thompson, Jr., personal communication; Ricci, 1951, p. 56). Another analogy, that with magnetic ordering problems, is used by Mazo (1977) and Anderson and Mazo (1980) in devising statistical mechanical models of albite which also show no discontinuity in the Al/Si ordering behavior. The form of the  $G-X$  curves for these alternative non-first order possibilities would be essentially the same as for ideal second order behavior though the order/disorder transformation should not, strictly speaking, be shown as a line on the equilibrium phase diagram.

Second, it is implied that the thermodynamic driving force for exsolution comes entirely from the ordering of Al and Si in albite. This is not a new idea, nor does it appear to be controversial (Ribbe, 1962; McConnell, 1974; Ribbe, 1975); it is in strict accordance with the conclusion of Orville (1974) that the disordered solid solution is nearly ideal in the appropriate composition range, at least down to  $600^\circ\text{C}$ . In the interpretation of McConnell (1974) the disordered phase is "passive" during exsolution as it does not contribute to the overall free energy reduction, indeed its free energy may actually increase as it becomes richer in An component.

Third, the cause of the miscibility gap is consid-

ered to be the energetic unfavorability of substituting excess Al for Si in low albite. As has been pointed out on a number of occasions (Megaw, 1962; Smith and Ribbe, 1969; Orville, 1974), additional Al cannot be added to ordered albite without causing two Al's to be bonded to the same oxygen. Such a circumstance is considered to be highly unfavorable in an ordered crystal, as is amply demonstrated by the fact that the sodic component of peristerite exsolution is typically close to, if not exactly,  $An_0$  and that exsolution occurs even in crystals with composition  $An_{2-3}$  (Brown, 1960; McLaren, 1974). With increasing temperature the equilibrium state of order involves some degree of disorder (MacKenzie, 1957; Stewart and Ribbe, 1969) and excess Al substitutions should become more favorable. The miscibility gap is then expected to peak just below the transformation temperature of pure albite at an An content which corresponds to the maximum equilibrium extent of solid solution achieved by the ordered structure.

The peristerite gap has been treated here as being between ordered albite and a disordered An rich component, ignoring any possible Al/Si ordering in the latter. This is not unreasonable since it is widely held (Smith and Ribbe, 1969; Smith, 1972, 1974, 1975; McConnell, 1974) that the ordered intermediate plagioclase structure is metastable and appears only at low temperatures as an alternative to the more stable assemblage of ordered albite + ordered anorthite. The main effect of "e" type ordering would be restricted to temperatures below the miscibility gap peak and would consist of stabilizing the oligoclase, thereby limiting the degree of An enrichment it is likely to achieve.

Finally, the lack of exsolution in crystals with compositions in the range  $An_{17}-An_{25}$ , the nucleation only region of the miscibility gap (Nord *et al.*, 1978, and here), is not surprising. In sodic pyroxenes a spinodal mechanism for exsolution seems to be favored also (Carpenter, 1978, 1980) reflecting the extremely slow rates of nucleation at low temperatures, particularly where the nuclei have to attain a different state of order from their host. In low grade metamorphic rocks mineral transformations are likely to proceed by continuous mechanisms wherever possible and if a reaction can only take place by nucleation and growth, it may never occur.

#### Order/disorder and crystal growth

It is often not possible to show directly if minerals which formed under natural conditions at temperatures below their equilibrium ordering temperature

grew fully ordered, metastably disordered or with some intermediate degree of order. In laboratory syntheses albite typically grows disordered (MacKenzie, 1957). Both Brown (1962) and Orville (1974) have suggested that the relative kinetics of crystal growth and Al/Si ordering determine whether a single homogeneous sodium rich plagioclase or two coexisting feldspars (albite + oligoclase) are formed at low metamorphic grades. Two feldspar assemblages have been found in kyanite/sillimanite series of metamorphism and single feldspars in contact or andalusite/sillimanite type regional metamorphism (Brown, 1962). The problem may be rationalized in the following way.

The G-X curves shown in Figure 2 are, of course, projections along an ordering axis. Effects of varying the degree of order ( $\eta$ ) achieved during crystal growth are illustrated on the full three dimensional diagram, G-X- $\eta$  (Fig. 3a). For a particular temperature and bulk composition within the miscibility gap, metastable equilibria between partially ordered albite and disordered oligoclase are given by common tangents. In the event of maximum ordering during growth ( $\eta_1$ ), albite and oligoclase will crystallize together. If the growing albite has only partial order ( $\eta_2$ ), the coexisting crystals would be of an albite with higher anorthite content and a more albite-rich oligoclase, showing textural equilibrium but indicating an apparently narrower miscibility gap (Fig. 3b). The miscibility gap does not exist in disordered crystals ( $\eta_3$ ) so that a complete range of homogeneous phases is possible when disordered growth occurs. Inconsistencies in the compositions of coexisting albite and oligoclase in apparent equilibrium with each other (Crawford, 1966, 1970) could thus be explained by variations in ordering during growth. In assemblages of pure albite + oligoclase the albite must have grown substantially ordered. Low temperatures should favor disordered states since the rate of ordering is likely to be extremely small relative to the rate of crystal growth. The range of compositions between  $An_0$  and  $An_{25}$  found in low temperature plagioclases by Nord *et al.* (1978), according to the above arguments, implies that these crystals grew with essentially disordered Al/Si distributions.

It is interesting to note that Brown (1960) used petrographic observations on crystals with composition  $An_{10}-An_{15}$  in low grade metamorphic rocks to interpret a sequence of metastable growth followed by ordering followed by exsolution which is identical to the sequence predicted for composition  $c_2$  at temperature  $T_3$  using Figures 2c, d, 3a.

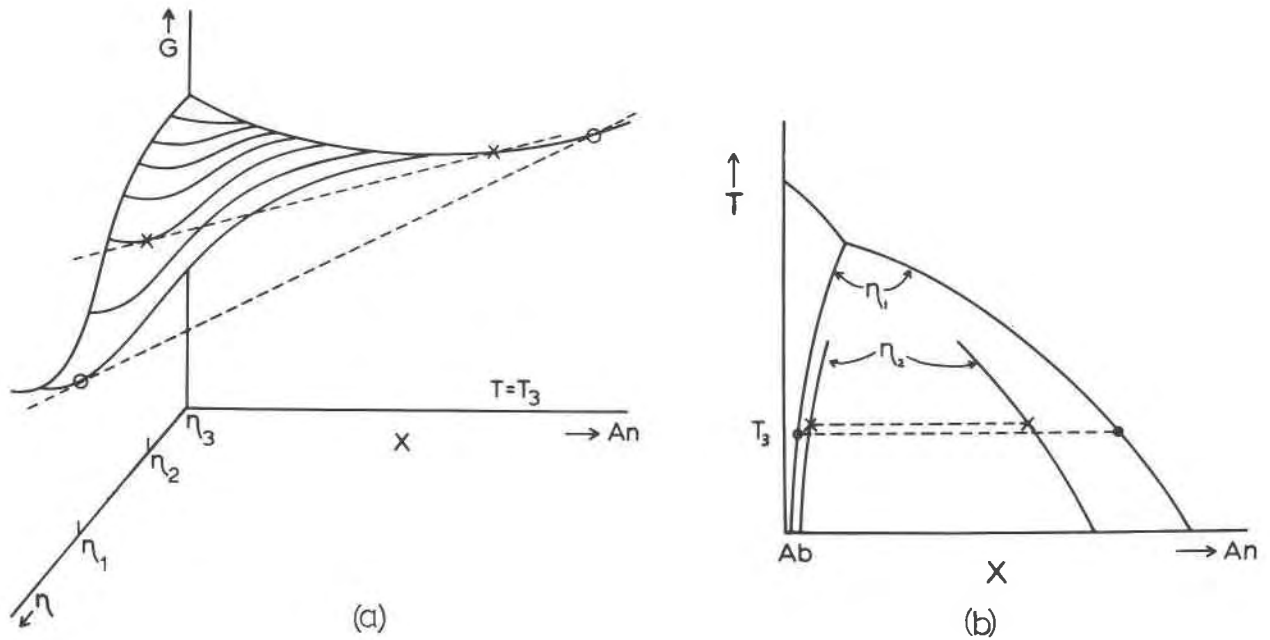


Fig. 3. The effect of varying the degree of order achieved during crystal growth. (a) A schematic plot of free energy ( $G$ ), composition ( $X$ ) and degree of order ( $\eta$ ) at temperature  $T_3$ . Compositions of coexisting albite and oligoclase are given by the common tangents (broken lines) for maximum order during growth ( $\eta_1$ ) and partial order ( $\eta_2$ ). These compositions are shown by tie lines in the phase diagram (b). The miscibility gap is effectively diminished if less than full Al/Si order develops in the albite during crystallization. In the event of disordered growth ( $\eta_3$ ) a single homogeneous plagioclase will form.

### Conclusion

Some of the differences between the conflicting solvus and binary loop models of the peristerite miscibility gap can be resolved if the Al/Si order/disorder transformation in albite is other than first order in character. The approach of using  $G$ - $X$ - $\eta$  diagrams, as opposed to simply assessing equilibrium phase relations, has the distinct advantage that possible transformation sequences and mechanisms, particularly for metastable conditions, can be predicted and then compared with interpretations of natural specimens. Similar analysis of the Huttenlocher miscibility gap leads almost to a mirror image of the peristerite topology since a spinodal mechanism appears to be available for decomposition into ordered and disordered components (Heuer *et al.*, 1972; Nord *et al.*, 1974; McLaren, 1974; McConnell, 1974, 1975). The ideal subsolidus phase diagram which results, allowing for the higher ordering temperature in anorthite and for its wider solid solution range, would be rather different from the previous suggestions which assume first order ordering relations (Smith, 1972, 1974, 1975). The value of such equilibrium diagrams for any assessment of the transformation behavior of natural intermediate plagioclases, however, is se-

verely limited since much of that behavior appears to be metastable. A complete analysis may be achieved if the free energy relations between the different ordered structures can be defined.

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