

SPINODAL AND NUCLEATION AS INDICATORS OF MAGMATIC CONDITIONS

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Abstract: In the initial part of the paper we attempt to summarize on a qualitative level the factors which have been found to be important in phase separation phenomena. In particular, we focus our attention on the thermodynamics and kinetics of the spinodal and nucleation mechanisms. Continuity (or connectivity) between both decay mechanisms, as one crosses the spinodal curve, is emphasized. In the second part of the paper, spinodal and nucleation mechanisms are applied to natural magmatic fluids. This application appears of great geological interest because has significant effects on the cooling and differentiation of magmas. Fluctuations give rise to the transient appearance of clusters of different sizes, compositions, and densities whose equilibrium abundance varies according to their free energy and supersaturation. The peaks and valleys resulting in the composition waves eventually become two discrete phases. Furthermore, phenomena that are too fast to be observed in magmas can be seen easily in igneous rocks, and vice-versa. In this manner, different geological conditions (particularly cooling rates) produce different final textures in the igneous rocks. Finally, considering the "truly primitive" basic magma as an initially simple and homogeneous fluid characterized by density fluctuations in critical conditions, a scheme of magma differentiation is proposed.

Key words: spinodal decomposition, nucleation, magma, cooling, differentiation, phase separation.

Introduction

The importance of spinodal and nucleation phenomena has stimulated a considerable amount of theoretical and experimental work on phase separation in alloys, glasses and liquid mixtures. However, the study of both phenomena in magmas has received very little attention in the literature. This gap is fundamentally due to the following reasons: 1 - only recently the use of the transmission and scanning electron microscopy has been extended to both synthetic and natural systems, 2 - for many years the metamict state of matter has been largely ignored by researchers, 3 - only in recent years considerable experimental progress has been achieved in physical geochemistry, and 4 - lately, computer simulations and calculations of the phase stability diagram of mixtures containing an adequate number of components have been published (Caccamo et al. 1993). Also, phase separation is probably the phenomenon which is least understood by geologists. On the contrary, the study of spinodal and nucleation in natural magmatic fluids is of great importance to both igneous geochemistry and petrology since these disciplines are concerned with differentiation phenomena which occur in magmas. If these magmas were in equilibrium to begin with, and if this equilibrium were such that it could not be disturbed by changes in conditions such as are encountered in the Earth's interior, these magmas would never undergo any differentiation process. In particular, spinodal and nucleation point out the connection between thermal conditions during the cooling history of magmas and the resulting different microstructural patterns relating to these phase transformations. To achieve this goal, however, an evaluation of the factors which

affect the thermodynamics and kinetics of phase separation phenomena is necessary. This, in turn, requires an understanding of the mechanisms by which a particular reaction occurs. In this respect, we will focus our attention on the behaviour of a magma as a non-ideal fluid changing, on cooling, from an initial homogeneous system to a heterogeneous one. Our purpose is to provide a brief but fairly comprehensive summary of the spinodal and nucleation concepts and make suggestions concerning their specific and general extensions to natural magmas.

Spinodal decomposition: general concepts

Spinodal decomposition is the spontaneous process of phase separation which can take place in a thermodynamically unstable system. A spinodal reaction implies that the phases separate by a continuous process. So, the particles increase indefinitely in size by growth, then coalesce until, in principle, only one particle is left in order to reduce the interface. Spinodal mechanism involves the time evolution of composition waves with progressively increasing wavelength and amplitude in which the overall symmetry reflects that of the parent structure. We shall look at the process from the standpoint of purely phenomenological, irreversible thermodynamics. The surface of the phase diagram representing the locus of the maximum temperatures at which phase separation occurs is called the coexistence or consolute curve and, for a simplified two-component mixture, is shown in Fig. 1. This represents the temperatures and concentrations at which the chemical potentials of the two immiscible phases are equal. In our example the critical composition of the

system is represented by the concentration of the constituents which has the highest transition temperature. Spinodal is a thermodynamic concept described as the limit beyond which a homogeneous phase is no longer metastable (Gibbs 1961). In a phase diagram, it is defined as the locus of points for which

the second derivative of the Gibbs free energy with respect to the concentration is equal to zero ($\partial^2 G / \partial X^2 = 0$). It is not a phase but a boundary corresponding to the inflection points S, S (spinodes) of the free energy - concentration curve (see Fig. 1). In order to understand why the spinodal marks the limit of metastability, let us consider a binary fluid system for which we know the Gibbs free energy as a function of composition (see Fig. 2). Let us compare the free energy of a mole of homogeneous fluid of composition X(1) with that of a mole of fluid of average composition X(2) (Cahn 1968). We see that a homogeneous phase with composition X(2) is an unstable phase. Small separations in composition about X(2) all lower the free energy. Equilibrium, the lowest free energy for X(2), is obtained by the common tangent. Vice-versa we see that X(1) represents a metastable phase. Small separations in composition all raise the free energy, but large enough composition changes in the right-hand direction can lead to decreases in free energy. In phase stability, the two independent continuous variables are size and composition difference. To reach this state by a continuous process requires the formation of regions in the fluid having so large a difference in composition that a free-energy decrease can occur. But this necessary large difference in composition leads to a new component in free energy: the interfacial free energy. An examination of this term indicates that a phase is always metastable with respect to the formation of an infinitesimal droplet with a finite composition difference if this leads to an interface with positive interfacial free energy. However, if the free energy is decreased by infinitesimal excursions in composition, large regions can change continuously and the system can always select a scale coarse enough that interface contributions are negligible and do not stabilize the unstable system (Cahn 1968).

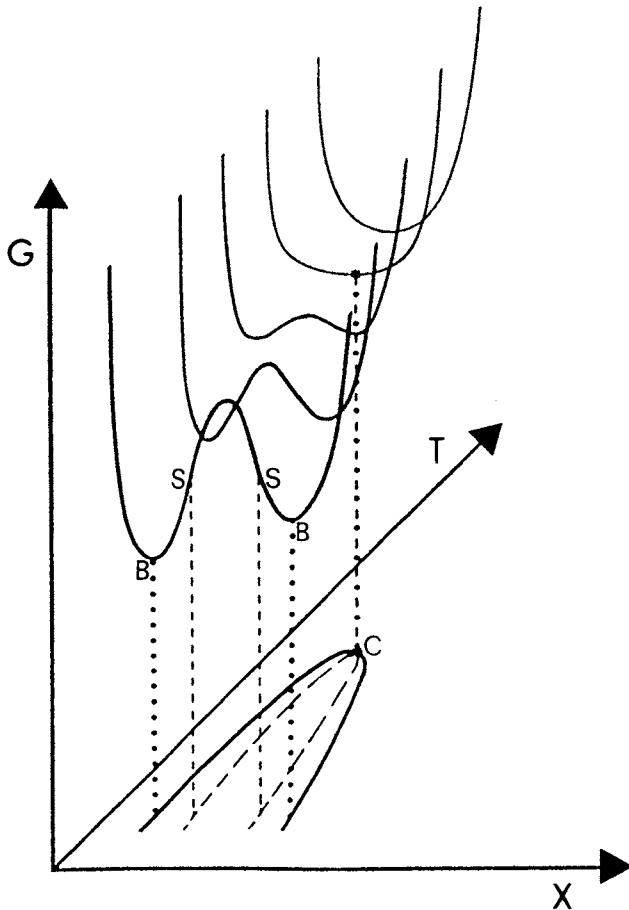


Fig. 1 - Gibbs free energy - concentration - temperature relations in a binary system (or simple fluid) showing spinodes (S, S), binodes (B, B) and the critical point (C).

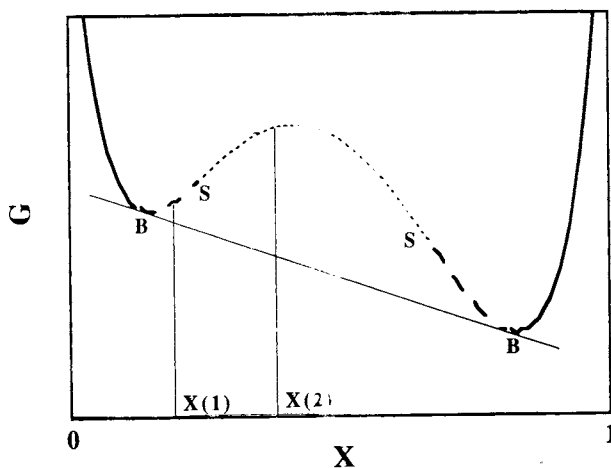


Fig. 2 - Gibbs free energy versus composition for a two-component fluid illustrating the change in free energy due to continuous fluctuations around two compositions X(1) and X(2). Full curve - stable; dashed curve - metastable; dotted curve - unstable.

Nucleation: general concepts

The nucleation event involves the formation of a particle of the separated phase of a sufficient size that it can grow with a decrease in free energy. The free energy change accompanying separation, ΔG_{total} , is composed of three terms: $\Delta G_{total} = \Delta G_v + \Delta G_s + \Delta G_r$. ΔG_v is the volume free energy difference between the homogeneous mixture and separated phases; this is the driving force for the reaction. ΔG_s is the free energy increase accompanying the creation of the interface between the matrix and the new phase and ΔG_r is the strain energy due to the difference in volume between the separated phase and the matrix (Champness & Lorimer 1976). Both ΔG_s and ΔG_r are positive terms and oppose the nucleation event. Fig. 3 shows the variation in ΔG_{total} with the size of nucleus, r . At the critical nucleus size, r^* , growth of the nucleus can proceed with a decrease in free energy; the value of $\Delta G_{total} = \Delta G^*$ is the activation-energy barrier for the nucleation process. The values of r^* and, hence ΔG^* , in any system are sensitive functions of the extent of undercooling below the solvus (see Fig. 3). If $\Delta T = 0$, the critical nucleus is infinitely large and the nucleation rate I^* is zero. As the undercooling, ΔT is increased, ΔG_v becomes larger and r^* becomes smaller. When r^* is sufficiently small that, by random short-range fluctuations in composition over a sensible period of time, it is possible to form a critically-sized nucleus, then the nucleation rate I^* increases rapidly (see Fig. 4). It is important to note that a major degree of undercooling is required for homogeneous nucleation to occur than heterogeneous nucleation. If the elastic misfit between the matrix and the new phase is more

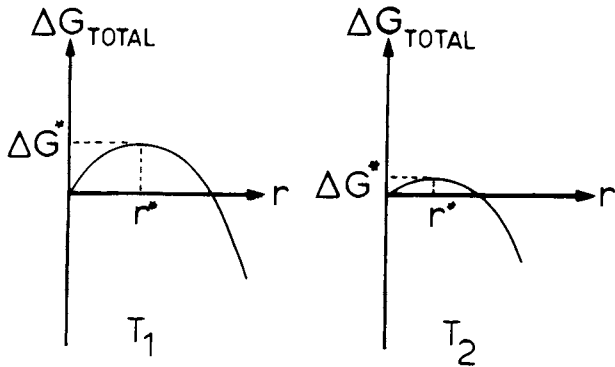


Fig. 3 - Change in free energy (ΔG) with the radius of compositional fluctuations (r) for two values of undercooling, T_1 and T_2 , where $T_1 > T_2$. ΔG^* is the activation barrier to nucleation (Champness & Lorimer 1976).

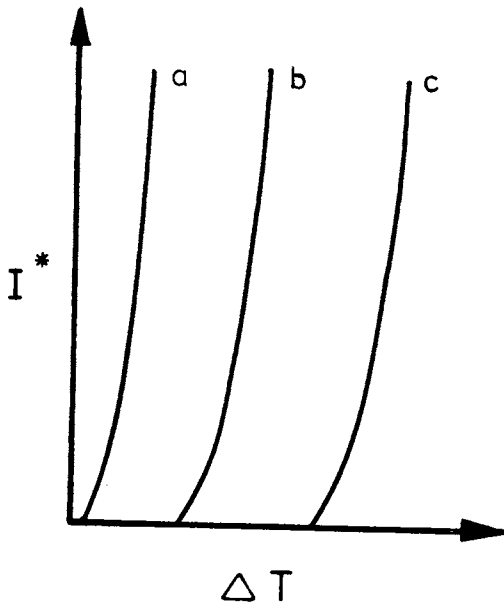


Fig. 4 - Schematic variation in nucleation rate I^* as a function of undercooling ΔT for: a - heterogeneous nucleation at grain boundaries, b - heterogeneous nucleation at dislocations, c - homogeneous nucleation (Champness & Lorimer 1976).

than about 2% (Nicholson 1970) ΔG_r (and hence r^*) will be so large that it will be impossible to form a critically-sized nucleus of the equilibrium phase, even at very large undercoolings, and homogeneous nucleation will not be observed. One way of overcoming this prohibitively high energy barrier is by heterogeneous nucleation at either planar or linear defects. Another way by which the large free energy barrier opposing the nucleation of the equilibrium phase can be circumvented is by formation of a transitional (intermediate) phase which is structurally more similar to the matrix than the equilibrium phase. If this transitional phase is structurally fully coherent with the matrix, i.e. the lattice planes are continuous across the interface, then homogeneous nucleation of the intermediate phase may occur. When the misfit can no longer be accompanied by elastic strain, dislocations are inserted at the boundary and the precipitate/matrix interface is structurally semi-coherent. At low temperatures, coherent precipitates become first semi-

coherent and after incoherent during growth originating an interconnected structure (e.g. Zarzycki 1970; Simmons et al. 1970; Champness & Lorimer 1976); finally, at even lower temperatures, crystallization starts.

Continuity between the spinodal and nucleation mechanisms

We have insofar treated spinodal decomposition and nucleation mechanism as two independent processes. However, these processes are only extreme cases and, for compositions near the coherent spinodal, the properties of the composition fluctuation are intermediate. At a low degree of supersaturation the stable nucleus is closely approximated by the classical theory of nucleation. As the degree of supersaturation increases, the interface with the matrix becomes more diffuse and the nucleus is no longer homogeneous. The classical model predicts that the radius of the critical nucleus is infinite at the solvus and decreases as the degree of supersaturation increases. However, the critical radius passes through a minimum and becomes infinite again at the coherent spinodal. Nevertheless, and most important, the work required to form the nucleus decreases continuously to zero as the coherent spinodal is approached from the low supersaturation side. Thus there is no discontinuous change in the kinetics at the coherent spinodal. Near and within the coherent spinodal the system is unstable and the barrier to nucleation is low or zero provided that the nucleus is large in extent (Yund & McCallister 1970).

The width of the transition regime between nucleation and spinodal decomposition can be estimated and interpreted in terms of the generalized Ginzburg (1960) criterion. This criterion is the following condition: the mean-square fluctuation of the order parameter (Φ in Figs. 5 and 6) in a volume region of linear dimension L , over which we average, must be small in comparison with the order parameter square itself. This criterion is invoked to conclude that mean-field theory is accurate if the correlation length has a large prefactor (see e.g. de Gennes 1977, 1979; Joanny 1978; Binder 1983). Figs. 5 and 6 show various cross-overs between different types of nucleation. In the unstable regime, the linear theory of spinodal decomposition holds initially. The ultimate limit of metastability is reached when the nucleation barrier is no longer small, $\Delta F^*/T_c$ (ΔF^* is the nucleation Helmholtz free energy barrier and T_c the critical temperature) of order unity (Binder 1984). There one then observes a smearing of the transition between nucleation and spinodal decomposition over a finite regime rather than occurring at a well-defined sharp line. Again it is seen that the smearing of the spinodal is small in the mean-field critical regime, but it becomes large, of order unity, when one reaches the crossover region to the non-mean-field critical regime. In this non trivial critical regime, the regime of "spinodal" nucleation, as studied by Klein & Unger (1983), and the gradual transition from nucleation to spinodal decomposition are no longer clearly distinguished (Binder 1984). Moreover, the regime between classical and spinodal nucleation (in between the two broken curves in Fig. 6) in the mean-field critical region is characterized by very high nucleation barriers and a treatment along the lines of Cahn & Hilliard (1959) is valid. In fact, one expects a smooth interpolation between classical and spinodal nucleation in this crossover regime (Fig. 5 a). Finally, very close to T_c we have the non-mean-field critical region. In this

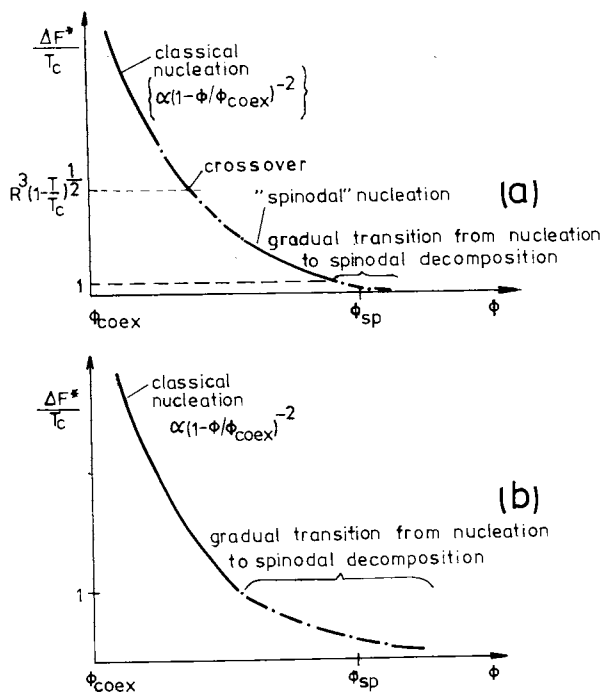


Fig. 5 - Schematic plot of the free energy barrier against homogeneous nucleation as a function of volume fraction for: **a** - the mean-field critical region, i.e., $R^3(1 - T/T_c)^{1/2} \ll 1$; **b** - the non-mean-field critical region, i.e., $R^3(1 - T/T_c)^{1/2} \gg 1$; R represents the range of interaction and Φ is the order parameter (volume fraction of one component); the labels *coex*, *sp* and *crit* identify the values of Φ at the binode, spinode and at the critical point, respectively) (Binder, 1984).

region neither spinodal nucleation nor "linear" spinodal decomposition occur. Here spinodal decomposition is highly nonlinear already in its earliest stages. Binder (1984) concludes that for a time smaller than the crossover time ($t < t_{cr}$) very weak fluctuations will grow, but the wavelength does not change during this time, i.e., the fluctuations "compactify" (see Heermann & Klein 1983a), but do not coarsen, while for $t > t_{cr}$ one enters a basically nonlinear regime where the inhomogeneous structure coarsens. A behaviour very similar to this has been observed by Heermann & Klein (1983b), but rather on the nucleation side of the spinodal line where "ramified clusters" first compactify and only afterwards start to grow. In conclusion, what above-mentioned is consistent with a rather smooth crossover between both decay mechanisms as one crosses the spinodal curve.

Application of spinodal and nucleation to magmas

Spinodal and nucleation mechanisms give valuable clues as to magma cooling and its relative differentiation process. In this respect, very recently, Lucido (1990) proposed a new theory of magma behaviour. According to this theory magma is a natural critical fluid decomposing spinodally. The theory is based on the fact that near the critical zone the thermodynamic properties of a simple fluid are qualitatively the same as those of a multicomponent fluid-mixture, like magma. On this ground, in the follow-

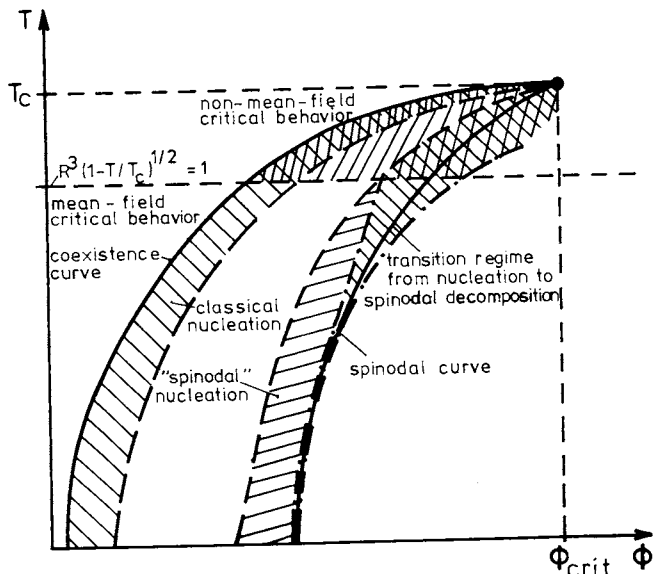


Fig. 6 - Phase diagram showing various regimes in the temperature - concentration plane near T_c (only concentrations $\Phi < \Phi_{crit}$ are shown). The regime inside the two dashed-dotted lines is the regime where a gradual transition from nucleation to spinodal decomposition occurs. The regime between coexistence curve and the left of the two broken lines is described by classical nucleation theory. In this regime, a further (smooth) crossover from mean-field-like critical behaviour to non-mean-field behaviour occurs. The regime between the right broken curve and the left dashed-dotted curve is the regime of "spinodal nucleation": it exists only in the regime of mean-field critical behaviour (Binder 1984).

ing we will treat magma as a simple fluid or binary mixture. Here, considering the "truly primitive" basic magma as an initially simple and homogeneous fluid characterized by density fluctuations in critical conditions, let us first see what in general is magma behaviour on cooling, and subsequently, what are the factors responsible for magmatic differentiation.

Magma cooling

The TTT diagram

The temperature-time-transformation diagram, usually referred as the TTT diagram, is useful for understanding and interpreting thermal histories of magmas. The TTT diagram, developed as a guide for the treatment of steels (Davenport & Bain 1930), may illustrate the extent of transformation of a magma. It is constructed by calculating the extent of isothermal transformations as a function of log (time) at a number of temperatures, and then contouring the transformations (Fig. 7). Each contour goes through a minimum of log (time), and asymptotically approaches the temperature at which the extent of transformation is at equilibrium (Ganguly & Saxena 1987). To illustrate this diagram let us assume that X_0, X_1, X_2, X_3 etc. represent progressive degrees of ordering in a magma. X_0 represents the equilibrium ordering at the temperature T_0 . Let us also assume that the dashed curve represents the cooling path of a magma. As the magma cools, it passes through the ordering

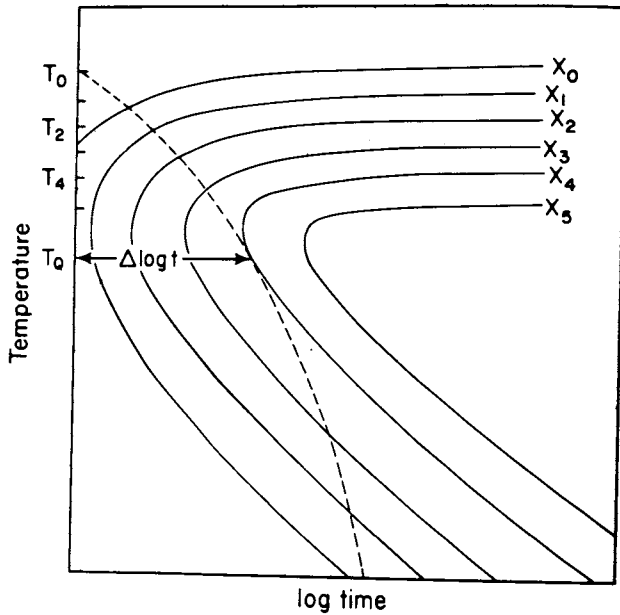


Fig. 7 - Hypothetical TTT plot of a magma. X_1, X_2 etc. represent various extents of transformations. Dashed curve is an arbitrary cooling path (after Ganguly 1982).

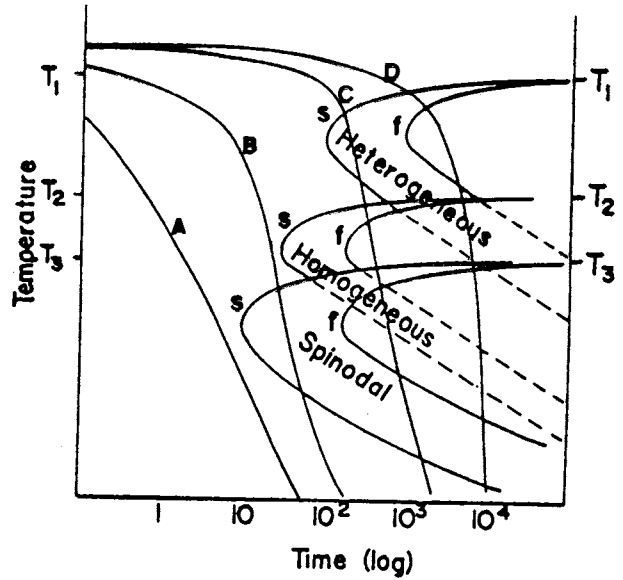


Fig. 8 - Time-temperature-transformation plot for composition X_2 within the spinodal (Fig. 9) showing the start (S) and finish (f) curves for: spinodal decomposition, homogeneous nucleation and growth, and heterogeneous nucleation and growth. The temperatures T_1, T_2, T_3 refer to the maximum temperatures at which the three mechanisms can operate. A, B, C and D refer to various cooling curves (after Buseck et al. 1980).

states X_1, X_2, X_3 , and finally quenches in the state X_4 , since otherwise there has to be a reversal of the sense of transformation with further cooling. To obtain the cooling rate from an observed quenched ordering state of a magma, one constructs several cooling paths on the TTT diagram from an initial temperature according to a certain cooling law, and selects the one that is tangential to the contour of the observed ordering state. Thus, if X_4 is the observed ordering state, then the cooling rate represented by the dashed line is the appropriate cooling rate for the magma (Ganguly & Saxena 1987). However, the use of the TTT diagram yields the time for isothermal ordering at $\sim T_0$, and not that for ordering by continuous cooling. Thus, the cooling rates obtained by the TTT method can be treated as first approximations of those obtainable from continuous cooling models (CCT diagrams), and represent a lower bound to the latter.

Different cooling paths

Fig. 8 is a TTT plot schematically showing three different transformation mechanisms. Each of these mechanisms is represented as C-shaped "start" and "finish" curves on the diagram (Buseck et al. 1980). The start curve indicates the time at which a transformation is first detectable for a particular temperature, whereas the finish curve indicates the time necessary for the transformation to go to completion at a particular temperature. In the case of nucleation, the C-shape is due to a rapidly increasing nucleation rate as undercooling increases and then a decreasing diffusion rate as temperature decreases. In spinodal decomposition there is no nucleation event but the extent of the transformation follows a similar C-shaped curve. This is because, as the temperature is reduced below the temperature of the spinodal, the longest wavelength decreases and, in turn, this decreases the diffusion distance necessary for growth of the microstructure and so does the reaction rate. As the temperature is reduced further, the decreasing diffusion rate requires longer times for the start and finish of the transformation (Buseck et al. 1980). Competition between decreasing diffusion dis-

tance and rate results in a transformation curve with a maximum (the nose). The three regions shown on the TTT diagram in Fig. 8 illustrate the transformation kinetics for a composition close to the critical one (X_2 in Fig. 9). These regions correspond to heterogeneous nucleation and growth (below T_1 , on the strain-free solvus, Fig. 9), homogeneous nucleation and growth (below T_2 , on the coherent solvus, Fig. 9), and spinodal decom-

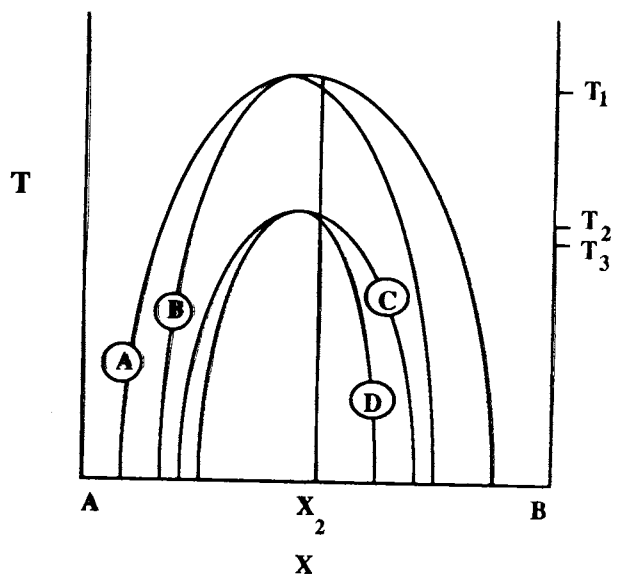


Fig. 9 - Temperature versus composition diagram showing coherent and strain-free (or chemical) solvi and spinodals in a binary mixture. A - strain-free solvus; B - strain-free spinodal curve; C - coherent solvus; D - coherent spinodal curve. T_1, T_2 and T_3 are the temperatures used in reference to Fig. 8.

position (below T_3 on the coherent spinodal, Fig. 9). A, B, C, and D refer to various schematic cooling curves. Curve A corresponds to the extremely rapidly chilled melts; no decomposition takes place. Curve B intersects the start curve for spinodal decomposition, but not the finish curve, indicating that decomposition was not complete. Curve C intersects the heterogeneous nucleation start-curve and then enters the homogeneous nucleation field. Cooling along curve C therefore would produce an heterogeneously nucleated phase in a matrix containing a finer phase. Finally, at very slow cooling rates, curve D passes through the field of heterogeneous nucleation and growth.

Magma differentiation

Metastable and unstable fluctuations

On a microscopic scale, the composition of a magma is in a state of continuous fluctuations around the average macroscopic composition. As mentioned before, when a magmatic fluid has composition $X(1)$ between the spinodal and the solvus or composition $X(2)$ close to the critical one (see Fig. 2), the spinodal curve plays a special role in the differentiation process. Fig. 10 schematically shows the free energy changes of such a magmatic fluid having compositions $X(1)$ and $X(2)$ due to fluctuations. Unlike those around $X(2)$, the fluctuations for $X(1)$ lead to a maximum of the free energy of the system. When the fluctuations suddenly or discontinuously exceed the ΔX value corresponding to the maximum in G , these become stable and continue to grow, since further growth of these fluctuations leads to a lowering of the free energy of the fluid; the opposite holds for the fluctuations smaller than ΔX . The stable fluctuations constitute the nuclei of the new phase. The stable compositions of the immiscible phases for both $X(1)$ and $X(2)$ must, of course, be the same, and are defined by the binodes. The radius of compositional fluctuation corresponding to the maximum in G is the critical radius of nucleation, r^* . As mentioned above, the formation of stable nuclei by just discontinuous fluctuations is due to homogeneous nucleation. The essential difference between metastable and unstable states is that in the latter infinitesimal fluctuations may lead to the formation of a small portion of the phase with lower free energy, which will therefore tend to grow; whereas in the metastable state much larger fluctuations would be required. Such large fluctuations are, however, exceedingly rare, and the chances that a non-ad-

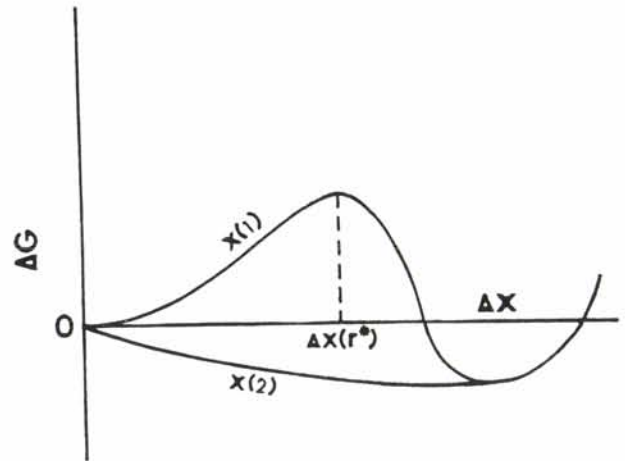


Fig. 10 - The change in free energy due to compositional fluctuations around $X(1)$ and $X(2)$ in Fig. 2 $\Delta G = G(\Delta X) - G(\Delta X = 0)$. $\Delta X(r^*)$ = compositional fluctuation corresponding to critical radius of nucleation (after Ganguly & Saxena 1987).

jacent phase might form are therefore small. A classical example of a metastable magma is an undercooled magma, i.e., a magma below its melting point, which is stable with respect to all other magmatic liquids (adjacent phases) differing only infinitesimally from it, but which is unstable with respect to a certain solid phase which has a different entropy, different volume, etc. If a disturbance originates germs of this solid phase, these germs will grow in the course of time. If the magma were originally above its melting point these germs would disappear by melting. An example of an unstable magma is that of the Sicilian basaltic magma (see Lucido 1981, 1983, 1984; Lucido & Triolo 1983, 1984). Very small changes in the conditions caused the magma to split into two liquids of different composition.

Dynamics of clustering

Fig. 11 schematically illustrates the dynamics of clustering or phase separation in magmas by spinodal mechanism and by nucleation and growth. In the early stage (stage 1), the clusters produced by fluctuations grow both in amplitude and wavelength by uphill diffusion of species toward their respective clusters. Thus, in this stage of growth, textures produced by spinodal decomposition have a modulated structure without sharply

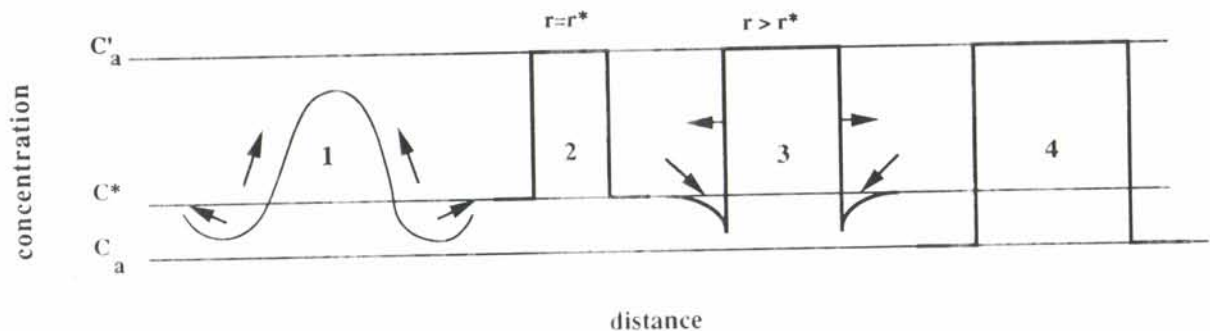


Fig. 11 - Schematic evolution of concentration profiles to illustrate phase separation in magmas. The diagram shows the evolution with time (from left to right) for: (stage 1) spinodal decomposition, (stage 2) nucleus origin, (stage 3), coarsening process, (stage 4) final compositions, C_a and C_a' , on the coherent solvus. Particles of a radius smaller than the critical radius r^* dissolve and feed those with a radius greater than r^* ; c^* is the original bulk composition.

| MAGMA TYPE | COURSE OF EVENTS | REACTION | EQUILIBRIUM | STRUCTURE |
|-----------------------------|-----------------------------|--------------------------|-------------|-------------|
| BASIC | PHASE SEPARATION | SPINODAL | UNSTABLE | FINE |
| ↓ | ↓ | ↓ | ↓ | ↓ |
| ACIDIC AND BASIC UNMIXED | METASTABLE IMMISCIBILITY | NUCLEATION AND GROWTH | METASTABLE | BIDISPERSED |
| ↓ | ↓ | ↓ | ↓ | ↓ |
| ACIDIC | AGGREGATION | COARSENING | STABLE | COARSE |

Fig. 12 - Scheme of the differentiation characteristics of a hypothetical basic magma having critical or almost critical composition into an acidic magma by liquid fractionation. The arrows indicate the direction and the continuous transition from one stage of the fractionation to the other as temperature decreases.

defined interfaces. However, as the phase separation proceeds, the diffuse interface progressively sharpens. The spinodal thus marks the limit not only between stability regions but between modes of initial clustering. When the attraction for like species is insufficient to cause a flux up the concentration gradient but strong enough for a large cluster to retain the particles, the formation of a nucleus (stage 2) occurs: it is due to a composition fluctuation. In the vicinity of a growing nucleus the matrix concentration is reduced and feeding of the nucleus occurs by normal diffusion down the concentration gradient (stage 3). The fluid tends to reduce its interface by a coarsening process. The final stage (stage 4) shows the compositions of the exsolved phases on the coherent solvus. The composition fluctuation grows continuously in time and nonlinear effects become important. In fact, in this late stage, the amplitude of the composition fluctuation is no longer distinguishable from its equilibrium value determined by the coexistence curve.

In summary, if we consider the starting magma as an unstable simple basic fluid originating acidic portions by critical density fluctuations, the scheme of the magmatic differentiation is that shown in Fig. 12.

Conclusions

Phase separation in magmas, driven by free energy minimization, occurs by diffusion. It is initiated by spinodal decomposition and may proceed by homogeneous nucleation and growth followed by heterogeneous nucleation and growth. Cooling at high rates of bulk compositions near the solvus critical composition will favour spinodal decomposition because the magma is cooled in less time than it takes for the cluster distribution to form. In particular, if the cooling rate of magma is fast compared to diffusion, the wavelength of the composition fluctuation is essentially independent of time and remains nearly constant. In this case the resulting magmatic rocks fundamentally are extrusive lithotypes. Vice-versa, cooling at low rates of bulk compositions away from the consolute curve on the solvus will favour nucleation and growth because the magmatic fluid will spend a long period between coherent solvus and spinodal. In particular, if the cooling rate is slow compared to diffusion, the wavelength of the composition fluctuation depends on the cooling rate and there will be a much broader distribution of wavelengths around the one receiving maximum amplification. Under the circumstances, the resulting rocks are those characterizing the plutonic environment, namely, they essentially are intrusive terms. Clearly, magmatic conditions intermediate between these two extremes will originate igneous rocks having intermediate char-

acteristics. For a slight degree of undercooling, only large nuclei are stable, and the probability of a large fluctuation in the melt is small. The number of nuclei increases with increasing undercooling, but when the undercooling becomes large, that is when the temperature drops noticeably, the rate of diffusion in the magma decreases rapidly. In such a case, the rate of growth of each nucleus is small and crystallization is slow, in spite of the large number of nuclei present at that stage. Supporting our view, a very great number of microstructures consistent with spinodal decomposition have been observed in pyroxenes, amphiboles, alkali feldspars, plagioclases and many other minerals (see, e.g. Wenk 1976). In addition, studies of lunar pyroxenes indicate that spinodal decomposition is the dominant mechanism in rapidly cooled clinopyroxenes, whereas nucleation and growth dominate the composition of more slowly cooled clinopyroxenes (Buseck et al. 1980). Finally, both spinodal decomposition and nucleation and growth mechanisms followed by coarsening have also been suggested (see Nord et al. 1976; Buseck et al. 1980).

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