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A NEW THEORY OF MAGMA: A NATURAL CRITICAL FLUID DECOMPOSING SPINODALLY

(8 Figs.)

Abstract: On the basis of modern statistical mechanics studies and taking into account the known physico-chemical data on the vitreous state, a new theory of magma is proposed. According to this theory “magma is a naturally occurring critical melt which decomposes by spinodal mechanism”. In particular, starting from a parent hypothetical basic magma of critical density, it is possible, in the long run, to imagine it fractionates spinodally in an acidic sense as temperature decreases. In this case the phases in equilibrium are “closely related” and “one phase makes the other by continuous composition changes”. The stable equilibrium state is achieved when crystallization starts as a consequence of density fluctuations in the bulk of the magma. According to us the formation of the original rocks of the Earth involved a liquid fractionation process based on the equilibrium vapour pressure of the compounds making up the “truly primitive” magma.

Резюме: На основе современного статистического изучения механики и учитывая знакомые физико-химические данные о стекловатом состоянии была создана новая теория о магме. По этой теории магма является природной критической выплавкой которая разлагается по спиноидальному механизму. Начиная из маточной гипотетической магмы с критической плотностью возможно представлять себе что в течении времени, с понижением температуры в ней проходит спиноидальная фракционация в кислотном смысле. В этом случае равновесные фазы являются „родственными“ и „одна фаза делает другую постоянным изменением состава“. Стабильное равновесие достигается когда кристаллизация начинает как результат изменения плотности в массе магмы. По нашему мнению возникновение первичных пород на Земле произошло тоже процессом фракционации жидкостей на основе равновесно-го давления пар соединений образующих „настоящую примитивную магму“.

Key words: theory, magma, spinodal decomposition, thermodynamics, immiscibility.

Introduction

Magma is a Greek word meaning a paste; it is an old subject still unresolved. The commonest popular concept seems to be that of a “molten rock under the surface of the Earth generally at temperatures ranging from 1200 to 800 °C”. Nevertheless the flowing magma often contains bubbles of gas and crystals in suspension, and to refer to such a physically complex mixture as “molten rock” is unwarranted simplification.

In the last century knowledge of the properties and composition of magmas was gleaned almost entirely from their consolidation products, the igneous rocks. And although over the years volcanologists have succeeded in measuring magma temperatures, estimating lava viscosity, recording the changing composition of magma as the eruptive cycle of a volcano progresses, direct measurements on magma below the Earth's surface are as yet very difficult

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problems because of the adverse physical conditions, particularly the high temperatures, that are encountered in trying to work close to the vent during eruptions. So, today it is still the igneous products themselves, that provide the most complete information on the composition and diversity of magmas.

The term magma used in this paper refers to a phase having the composition of silicate melt. Furthermore, unless otherwise specified, the term "particles" will refer either to molecules and/or ions according to the context. We have drawn extensively from the General Discussion of the Faraday Society on The Vitreous State (1970), and the van der Waals Centennial Conference on Statistical Mechanics (1973).

Magma: stability, problems and constraints

A magma is defined as stable if any disturbance in its chemical composition tends to disappear spontaneously in the course of time. On the contrary, a magma in which a disturbance tends to grow is said to be unstable or metastable, according to the minimum size of the initial disturbance that will keep on growing. A magma is unstable if an infinitesimally small disturbance grows (see, for example, Lucido, 1981, 1983, 1984; Lucido-Triolo, 1983, 1984); it is metastable if only certain disturbances of finite size grows (for example an undercooled magma, i. e., a magma below its melting point). However, a given magma may at the same time be stable, with respect to one reaction (for instance, immiscibility of two liquids) and unstable with respect to another reaction (crystallization). In addition, it is worth to note that a metastable state is characterized by an affinity (De Donder-Van Rysselberghe, 1936) which is not zero, but by a zero velocity of reaction. Metastable states may thus persist over great lengths of time!

Nobody has seen a magma in a subterranean position. So, the physical and mechanical conditions to which any magma is subject are not known, although some deductions may be made from the properties of synthetic magmas made in the laboratory. From such a picture, some questions to which it's hard to answer arise: from the physico-chemical point of view just what is a magma? What is its dynamics? And its cooling behavior? From the physico-chemical point of view, magma is generally regarded as multicomponent system consisting of a liquid phase, or "melt", and of a number of solid phases such as suspended crystals of olivine, pyroxene, plagioclase, etc., along with a gas phase. Such a system is so complex and the variables so numerous that the number of possible models of behavior is embarrassingly large. However, imposing a number of constraints, we must try for suitable answers to these questions. For this purpose the following fundamental preliminary remarks are indispensable.

Firstly, it is necessary to avoid any "strict" determinism and instead rely on a "correct" probabilistic approach (see e. g. Carapezza, 1987; Philip-Watson, 1987). We must explain most of phenomena with a minority of hypotheses. In our case, for example, we can say if the magma might, or might not, behave in a specified manner. Secondly, as magma arises from the interior of the Earth, to think our planet as a whole, and fixing a reference-point to go back to its origin. Such a reference-point is, in our view, "the fluid state preceding any crystallization process"; since that time indeed the Earth has undergone a continuous cooling. Thirdly, taking into account the hypothesis of a planet rising as an homogeneous body from which successively originate nucleus, mantle and crust, to consider a magma as an initially simple and homogeneous fluid. This is possible, if we apply to natural magmas the spinodal decomposition theory, and if the starting magma (at temperatures above its liquidus temperature) is cooling in critical conditions.

The theory presented in this paper is qualitative in nature and combines concepts from both physical and chemical contrasting viewpoints. Before we present our theory of magma, it is necessary to see the thermodynamic behaviour of a fluid in critical conditions and then go to recover the conventional metallurgical theory of spinodal decomposition.

Thermodynamics analogy between simple fluid and multicomponent fluid-mixtures near critical points

The thermodynamic properties of a pure fluid are completely determined once one knows the chemical potential μ as a function of pressure P , and temperature T . Fig. 1 shows schematically a portion of a phase diagram for a binary mixture in the space P , T , and μ_2 . The coexistence curve of a pure fluid here becomes a two-dimensional surface (represented by light lines) terminating in a line of critical points (represented by a heavy line). Two phases can coexist in equilibrium only if the thermodynamic state is represented by a point on the coexistence surface. As such a point approaches the critical line, the properties of the two coexisting phases resemble each other more and more, till finally the distinction vanishes along the critical line itself (Griffiths, 1974). A section of the phase diagram in Fig. 1, obtained by examining the P , T plane for μ_2 a constant, is qualitatively similar to that of a pure fluid. That is, the intersection of the coexistence surface with the surface $\mu_2 = \text{constant}$ is a coexistence curve which terminates in a critical point, the intersection of the line of critical points with $\mu_2 = \text{constant}$. This qualitative analogy suggests that: the thermodynamic properties near the critical point in such a section are very similar to those of a pure fluid near its critical point. It is what enables us to reduce the problem of critical point thermodynamics for a multicomponent system to that of a pure fluid (Griffiths, 1974). The two dimensional section just discussed could equally well have been formed by holding P constant, or T constant, or some linear combination of P , T , and μ_2 , or even some nonlinear combination which generates a smooth surface in the P , T , μ_2 space. In any case, however, it is essential that the two-dimensional section be formed by holding an intensive (or field) variable rather than an extensive (or density) variable fixed. Exceptional behaviour would only be expected in the accidental circumstance that the surface determining the section is parallel to the coexistence surface near the critical point of interest.

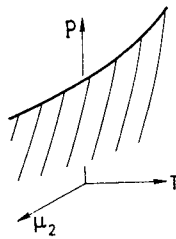


Fig. 1. Schematic phase diagram near a line of critical points in a binary mixture (Griffiths, 1974).

The generalization of the foregoing to ternary and yet more complex mixtures is straightforward, at least in principle. A ternary mixture is described by four independent fields. The coexistence hypersurface is three-dimensional, and will terminate in a two-dimensional critical surface. In general, with n independent fields the coexistence and critical

hypersurfaces are of dimension $n-1$ and $n-2$, respectively (Griffiths, 1974). Since it is difficult to visualize 3-dimensional hypersurfaces in 4-dimensional spaces, it is useful to reduce the problem, if possible, to a series of 3-dimensional sections formed by holding one of the variables constant. Provided this is a field variable and not a density variable, the result is a phase diagram qualitatively analogous to that of a simple fluid or binary mixture.

The conclusion is that, from the qualitative point of view, near the critical region the thermodynamic behaviour of a simple fluid is the same as that of a multicomponent fluid-mixture, like magma. For this reason, in the following we will consider a magma as a simple fluid or binary mixture. Evidently, the analogous theory for the liquid-vapour problem is also valid near the critical point.

On spinodal decomposition

Spinodal decomposition occurs in a simple fluid, or binary mixture, if the free energy of the state having two immiscible constituents is lower than the homogeneous state. While in a simple fluid the relevant variable is density, in a binary mixture the relevant one is composition. We will use these two variables interchangeably.

The limit between metastability and instability in a phase diagram is the spinodal, defined as the locus of points for which $\delta^2 G / \delta X^2 = 0$ (here G indicates the Gibbs free energy and X refers to composition), corresponding to the inflection points i, j of the free energy – composition curve (see, Fig. 2) (Zarzycki, 1970). In the region (I), shown on this figure, $(\delta^2 G /$

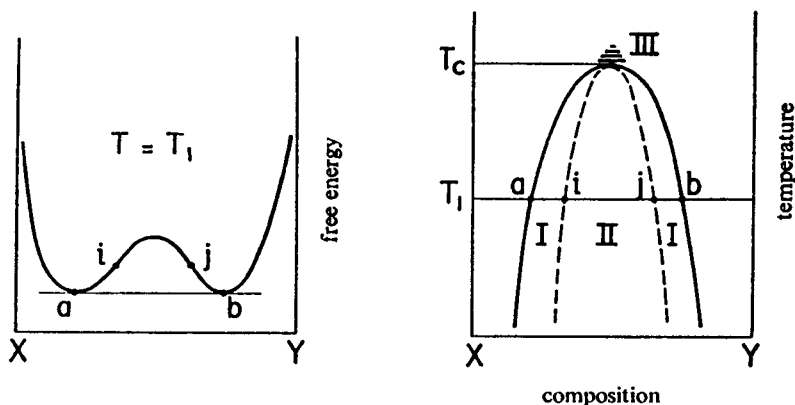


Fig. 2. Free energy – composition and temperature – composition curves illustrating the stability regions associated with a miscibility gap.

(I) region of nucleation and growth; (II) region of spinodal decomposition; (III) critical region (Zarzycki, 1970).

$\delta X^2 > 0$), the system is stable towards infinitesimal composition fluctuations which all raise its free energy, and metastable towards the occurrence of a phase widely differing in composition. The separation occurs by a nucleation and growth process which is controlled by a thermodynamic barrier. In the region (II), $(\delta^2 G / \delta X^2 < 0)$, the system is unstable towards all, even the smallest, composition fluctuations; the decomposition is controlled by diffusion. These composition fluctuations are particularly marked in the critical region (III) (Fig. 2) where they give rise to critical phenomena.

Cahn-Hilliard phenomenology and statistical fluctuations

The mathematical theory of spinodal decomposition developed by Cahn-Hilliard (1958), is based on a general diffusion equation containing terms relative to the gradient of concentration. To describe a two-component system in detail, let the function $c(r)$ denote the average concentration in some small region around the position r . The specific form of the coarse-grained Helmholtz free energy $F\{c\}$ which was chosen by Cahn-Hilliard (1958) is the so-called Ginzburg-Landau functional:

$$F\{c\} = \int dr \left[\frac{1}{2} K (\nabla c)^2 + f(c) \right], \quad (1)$$

where the function $f(c)$ is the free-energy density for a completely uniform state, while the gradient energy, $\frac{1}{2} K (\nabla c)^2$, is the extra energy associated with departures from uniformity. Cahn (1961, 1965) has solved this equation in a linearized form by means of a spatial Fourier transform of the concentration. However, Cahn's treatment is restricted by the fact that a linearized equation is considered and so the solution is limited to small perturbations.

The simplest way to describe the kinetics of a two-component mixture is to start with a continuity equation of the form

$$\frac{\partial c}{\partial t} = -\nabla \cdot j, \quad (2)$$

where j is a current density which describes the interdiffusion of the atomic species and is given by

$$j = -M \nabla \frac{\delta F}{\delta c(r)} = -M \nabla \left(-K \nabla^2 c + \frac{df}{dc} \right), \quad (3)$$

where $\delta F/\delta c$ is a local chemical potential and M is proportional to a mobility. That is, the current is driven by the gradient of the chemical potential. But such an analysis of the spinodal instability has two missing ingredients: the non-linear terms and the thermal fluctuations (Langer, 1975). That is to say, it is necessary to take into account the statistical fluctuations caused by the interactions between the system and its thermal reservoir. The important effect of these interactions is "an exchange of energy between the spinodal system and the reservoir"; so that, whereas F is a decreasing function of time according to the thermodynamic Cahn-Hilliard theory "it may occasionally fluctuate upward in the statistical theory".

Equations (2) and (3) constitute a generalized diffusion equation which cannot describe a thermally activated nucleation process; but the stochastic equations (4-5) to be discussed below can do so (Langer, 1975). We can introduce the heat bath formally by adding to the right-hand side of (2) a Langevin force which will represent the physical effect of lattice vibrations or any other thermal transport mechanism which is fast compared to the times required for the rearrangement of atomic positions (Langer, 1974). Then, via statistical methods, we can derive an equation of motion for a distribution-functional $\varrho\{c\}$ defined on the space of functions $c(r)$. This equation can be written as a functional continuity equation (Langer, 1971):

$$\frac{\partial \varrho\{c\}}{\partial t} = - \int dr \frac{\delta J(r)}{\delta c(r)}, \quad (4)$$

where the probability current $J(r)$ is given by

$$J(r) = -M \nabla^2 \left[\frac{\delta F}{\delta c(r)} \varrho + k_B T \frac{\delta \varrho}{\delta c(r)} \right], \quad (5)$$

in which ϱ is the density, k_B is the Boltzmann constant and T is the temperature. Together, equations (1), (4), and (5) constitute a complete statistical theory for a binary mixture. They can be solved by standard computational methods, i.e. using step-by-step calculations by electronic computers.

Now, if we apply this thermodynamic statistical theory to magmas, we see as a probabilistic approach can show the route of a conceptual plan which in the past was searched for in vain by strict determinism. In other words, it is necessary to take into account the statistical fluctuations caused by the interactions between magma and its thermal reservoir. The important effect of these interactions is "an exchange of energy between the magma and the reservoir"; so that, whereas the free energy is a decreasing function of time according to the thermodynamic Cahn-Hilliard theory "it may occasionally fluctuate upward in the statistical theory".

Continuation from the metastable into the unstable region

The free energy and its first derivatives are continuous across the critical point, so that analyses applicable to critical second-order phase transitions (e.g. Ornstein-Zernike 1926; Landau-Lifshitz, 1958; Fisher, 1964) are applicable here. This continuity suggests that the unstable composition fluctuations present below the transition temperature

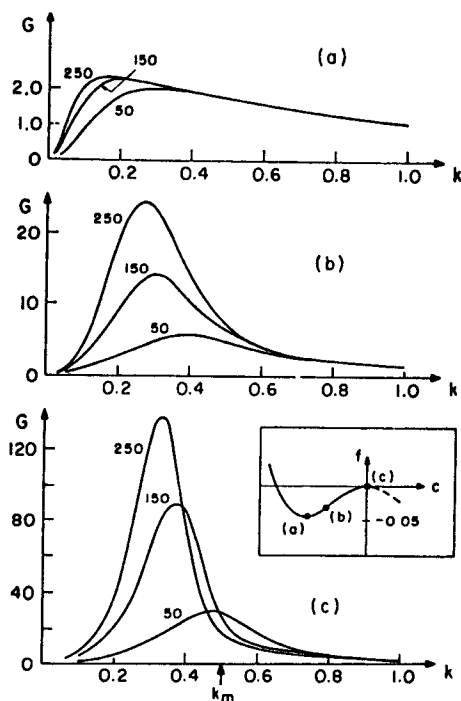


Fig. 3. Sequences of correlation functions $G_{(k)}$ for values of composition such that composition lies: (a) on the binodal line; (b) on the physical spinodal curve; (c) within the spinodal region.

Each curve is labelled by a time after quench, where time is measured in units such that the mobility M is unity. Note that the vertical scale is different in each of the three figures (Langer, 1974).

T_c are also expected to occur above T_c . These fluctuations in the supercritical state have lifetimes determined by the kinetic properties of the material and are precursor of the subcritical state. So, if for instance the diffusion coefficient is low, then the fluctuations will take time to grow to the amplitude characteristic of the thermodynamic state (Simmons et al., 1970).

In Fig. 3 there is shown a set of three different time sequences of functions $G(k)$ (here G is a quantity which is directly measurable via small-angle X-ray scattering techniques), all computed for the same Helmholtz free-energy function $f(c)$. This $f(c)$ is shown in the inset in Fig. 3. When the second derivative of the free energy with respect to the concentration is <0 , there exists a critical wavevector k_c such that, for values of $k < k_c$, $G(k)$ grows exponentially without bound. The most rapidly growing Fourier component of G occurs at $k_m = k_c/\sqrt{2}$. The first sequence, (3a), shows the development of $G(k)$ for composition into the stable region of the phase diagram. Note here that G simply approaches an Ornstein-Zernike form, with the longer wavelengths equilibrating much more slowly than the short ones. In (3c) is shown the normal spinodal decomposition which occurs for composition well into the unstable region. Here the peak rises at roughly the predicted position k_m , but moves rapidly to smaller k . Fig. (3b) illustrates what happens near the spinodal. The data shown there actually correspond to a slightly positive value of the second derivative of the free energy with respect to the concentration. A peak still seems to develop, but very much more slowly than in (3c), and at a smaller value of k . On the high- k side of the peak, $G(k)$ does not shift to the left as in (3c), but appears to approach an inverse-square law ($1/k^2$) envelope. The system exhibits critical fluctuations while undergoing phase separation (Langer, 1974). In Fig. 4, we have

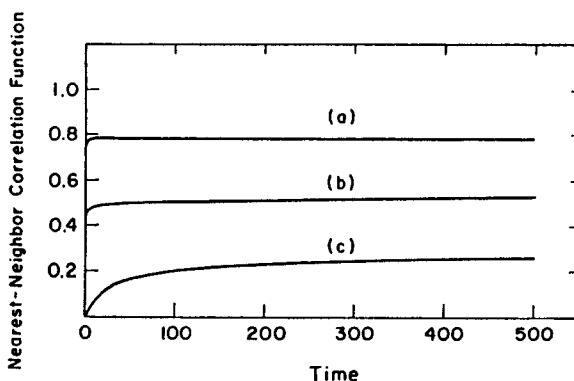


Fig. 4. Nearest-neighbor correlation function versus time for the three cases shown in Fig. 3 (Langer, 1974).

plotted nearest-neighbor correlation functions as functions of time for the three cases shown in Fig. 3. Alternatively, these graphs may be interpreted as completion curves or as the negatives of the interaction energies. The stable case, (a), equilibrates within the first ten time units, and undergoes no noticeable change thereafter. At the spinodal, the correlation function (b) at first rises slightly less rapidly than (a), but continues to increase very slowly later on. The unstable case (c) exhibits the slowest initial rise, but increases the most rapidly over long times. Taken together, Figs. 3 and 4 indicate a remarkable continuity of the decomposition mechanism across the entire miscibility gap (Langer, 1974).

In conclusion, the ideal limit of metastability is not very sharply defined. It constitutes a physical spinodal line in the sense that systems well on the metastable side decay via nucleation, and systems on the unstable side undergo spinodal decomposition. "The change from one decay mode to the other takes place slowly and continuously as a function of composition." The situation is summarized in Fig. 2.

Discussion

At the critical (or consolute) composition of a fluid, it is thermodynamically possible for the spinodal decomposition and nucleation — growth mechanisms to occur below the transition temperature. What is happening at the spinodal boundary is easier to see by considering what happens as one approaches this boundary from the metastable rather than from the unstable side. As before mentioned, spinodal decomposition occurs following large-scale fluctuations in the composition of a fluid. The minimum size of these fluctuations decreases as the temperature goes further below the critical. Thus, near T_c , large migrations of the various constituents are necessary to set up the required fluctuations. If the diffusion coefficient is low, such large-scale migrations take a long time and nucleation which requires only small displacements of the constituents is likely to prevail. As a result, the kinetic properties of the fluid favour nucleation when the temperature is close to T_c (Simmons et al., 1970). So that just inside the miscibility gap, we are in a region where phase separation can occur only via a statistically very rare, thermally activated process, specifically, the nucleation event.

As one approaches the spinodal, the critical droplet becomes more and more diffuse and its activation energy decreases (Cahn — Hilliard, 1959). When this activation energy is as small as a few $k_B T$ (k_B is the Boltzmann constant and T is the temperature), then the droplet-like, finite-amplitude fluctuations against which the fluid is unstable are simply part of the spectrum of statistically significant thermal fluctuations, and the system must behave unstably even though the perfectly uniform state is thermodynamically metastable. This process is intrinsically non-linear because thermal fluctuations of finite amplitude are required for the onset of instability. In the vicinity of the spinodal, this non-linear process will remain the dominant one. Such true instabilities as there are will be of very long wavelength and will thus be extremely slow to develop. Finite-amplitude fluctuations of smaller spatial extent will occur much more rapidly. One could ask why, in the spinodal region, the interfacial free energy does not stabilize the fluid. This is due to the fact that the free energy may be decreased by infinitesimal variations in composition and large regions can continuously change their composition. The fluid then tends to adopt a scale large enough to minimize the contribution of the (diffuse) interface.

In conclusion, the spinodal decomposition is not the only mechanism possible in the region (II) of Fig. 2; even though the average composition lies inside the spinodal, there can be local regions present due to fluctuations which can decompose by a nucleation and growth process (Zarzycki, 1970). Let us now see what happens if we apply to natural magmas the spinodal decomposition mechanism.

The theory

In the light of the thermodynamic behaviour of a fluid near the critical region, assuming the Earth as a whole and the "truly primitive" magma as a simple fluid, taking into account the statistical fluctuations caused by the interactions between magma and its thermal reservoir, and considering the above — documented information on phase distributions, the following theory of magma is proposed.

Magma cooling: prediction of spinodal behaviour

Phase separation experiments and textural characters of magmatic rocks give valuable clues as to the possible behaviour of natural magmas. The particular mechanism operating will in general depend on the original composition, the cooling rate, and exact juxtaposition of the free energy versus composition curves.

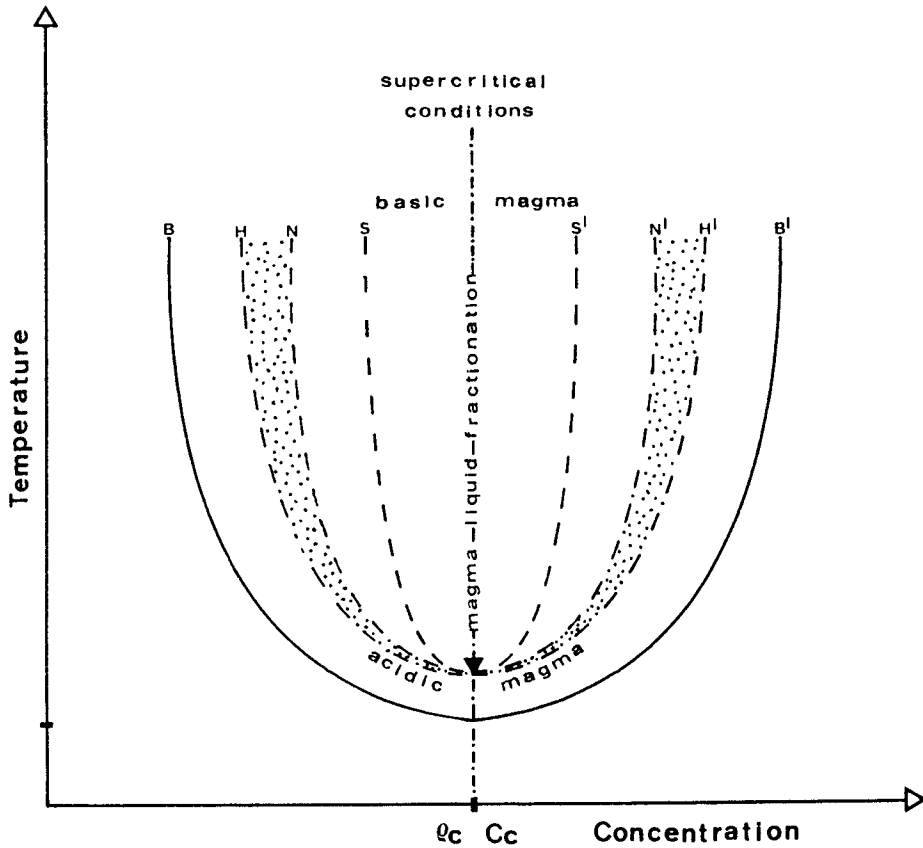


Fig. 5. Schematic phase diagram showing differentiation of an hypothetical spinodal basic magma having critical or almost critical composition into an acidic magma by liquid fractionation.

The arrow indicates the direction and the continuous transition from one stage of the fractionation to the other (originating intermediates magmas) as temperature decreases.

Fig. 5 represents a schematic phase diagram appropriate to a simple magmatic fluid (or binary mixture). It can be used to illustrate many of the phase transformations which occur in magmas. This diagram has an inverted binodal curve (BB') with a lower critical point defined by T_c , q_c (simple fluid) or T_c , C_c (mixture). The curves SS' and NN' are respectively the coherent spinodal and coherent solvus; both are heightened above the equilibrium binodal

curve due to strain (see, e. g., Simmons et al., 1970; Zarzycki, 1970; Champness – Lorimer, 1976). The area between the two SS' and BB' curves is the metastable region. Spinodal decomposition can occur in the unstable region (which lies above the spinodal line SS'), homogeneous nucleation and growth in the dotted area, and heterogeneous nucleation and growth in the area between the two HH' and BB' curves. Finally, the dashed-dotted line indicates the critical composition of the magmatic fluid. Now, keeping in mind that real systems, particularly magmas, are generally characterized by a range of composition, let us see what happens on cooling a magma having such a critical composition, or better a composition close to the critical one.

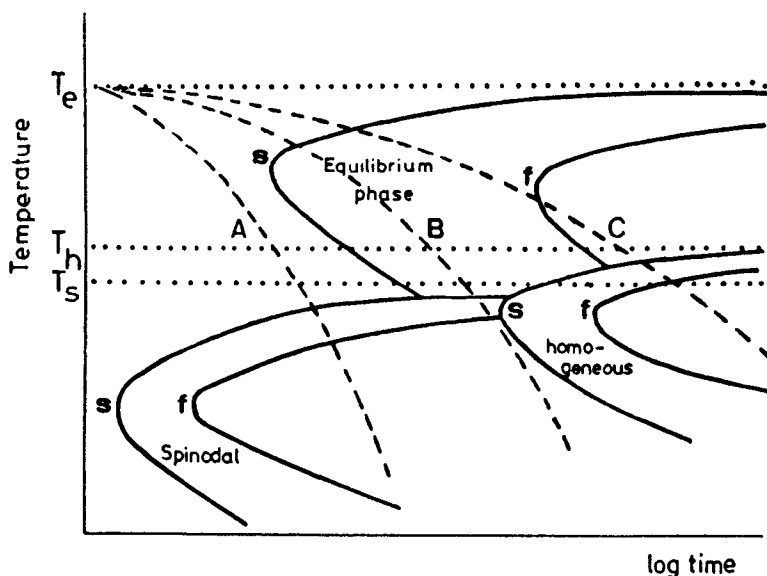


Fig. 6. Time-temperature-transformation diagram for a magmatic fluid of an almost critical composition illustrating the start (S) and finish (f) curves for three mechanisms: heterogeneous nucleation and growth, homogeneous nucleation and growth, and spinodal decomposition.

The temperatures T_e , T_h , T_s refer to the maximum temperatures at which the three transformation mechanisms can operate. The curves A, B and C correspond to fast, intermediate and slow geological cooling rates (after Champness – Lorimer, 1976).

Information concerning prediction of magma cooling can be illustrated on Time-Temperature-Transformation (TTT) diagrams (see, for example, Chadwick, 1972) where the times for a given fraction of a reaction to proceed are plotted as a function of temperature. Fig. 6 is a schematic TTT diagram for a system having a composition close to the critical composition in which heterogeneous nucleation and growth, spinodal decomposition, and homogeneous nucleation and growth can occur, depending on the cooling rate (Champness – Lorimer, 1976). Three cooling curves have been superimposed on the TTT diagram. For rapid cooling

rates, A in Fig. 6, separation of the equilibrium phase will not take place at a detectable rate and splitting will proceed completely by a spinodal mechanism. At slow cooling rates, C in Fig. 6, heterogeneous nucleation of the equilibrium phase will occur when the cooling curve crosses the start line. Growth of the equilibrium phase will continue as the temperature falls until the cooling curve crosses the finish line for the equilibrium phase. At an intermediate cooling rate, B in Fig. 6, nucleation of the equilibrium phase will occur at a high temperature, but only a proportion of the reaction will have occurred before the start of the spinodal reaction is crossed. For homogeneous nucleation the strain and surface-energy terms, together with the larger diffusion distances involved, leads to a lower rate of transformation compared with spinodal decomposition (Chapness-Lorimer, 1976). This is reflected in the relative positions of the noses of the two curves. Consequently, homogeneous nucleation of the equilibrium phase is only expected for a narrow range of intermediate cooling rates.

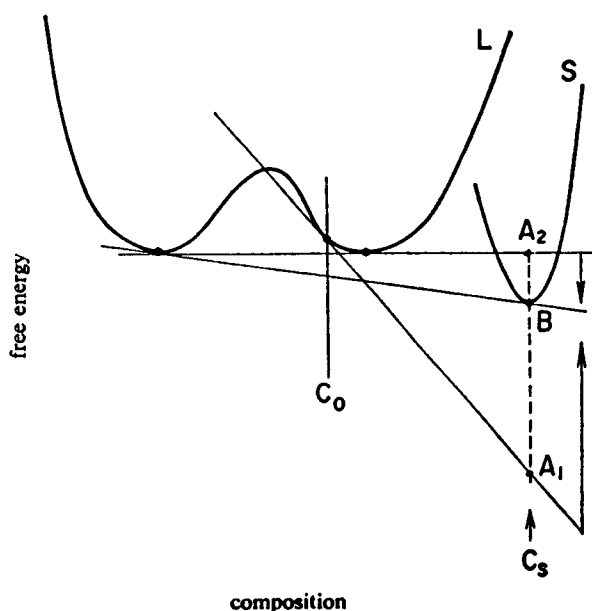


Fig. 7. Free-energy versus composition diagram showing the thermodynamic blocking of a stable phase (Zarzycki, 1970).

From such a picture, a number of interesting conclusions can be drawn for magmatic rocks. Firstly, suppressing prior nucleation, quenching textures originate in the ejected materials during volcanic explosions. That is, the magma is cooled in less time that it takes for the cluster distribution to form. Secondly, in lavas or in small intrusions the cooling is slower and fine textures are found. These textures are consistent with spinodal decomposition without coarsening of the differentiated clusters. Thirdly, in large intrusions the cooling time is much longer and coarser nuclei can form. Between these two latter extremes, clearly there is an

optimum degree of undercooling at which the transformation rate is a maximum. In our view, this maximum corresponds to the metastable immiscibility originating a bidispersed texture. Composition changes brought about by phase-separation, and/or the extensive interface thus created, might promote crystal nucleation. However, as has been suggested by *Cahn* (1969), immiscibility is a precursor reaction; crystallization may be blocked, for thermodynamic reasons, until phase separation takes place (see Fig. 7). The stable crystalline phase S of composition C_S cannot precipitate from the metastable phase L of composition C_0 as this would require an increase of the free energy (path $A_1 B$) until the liquid has undergone immiscibility. The precipitation then corresponds to a decrease of free energy (path $A_2 B$). More exactly, in order that the thermodynamic blocking as proposed by *Cahn* (1969) be effective, the bottom, B , of the free energy curve of the stable phase C_S must be situated above A_1 (Fig. 7). Even if the segment $A_2 A_1$ is very reduced and point B much below, the possibility of finding B between A_2 and A_1 increases when the composition C_S shifts to the right, i. e., differs more from the limiting composition of the separating liquid phases (*Zarzycki*, 1970). Thus, this mechanism might be more likely to apply to the cases when "the crystalline phase is distinctly different in composition from that of the closest metastable branch of the coexistence curve". According to us, this circumstance is exactly the case of a basic magma originating a crystalline phase critically differentiated in an acidic sense with time.

Density fluctuations and liquid fractionation

Near the critical region the coherence length, ξ , of density (ρ) fluctuations, is large compared to the mean distance $\rho^{-1/3}$ between neighboring particles. One may therefore define a mean local density ρ' by averaging over regions that are of large volume compared to ρ^{-1} and hence contain, on average, many particles and yet are of small volume compared to ξ^3 (*Widom*, 1974). This local density ρ' fluctuates (both in time and space) about the overall mean density ρ . Fig. 8 shows, schematically, what the geometrical surface on which ρ'

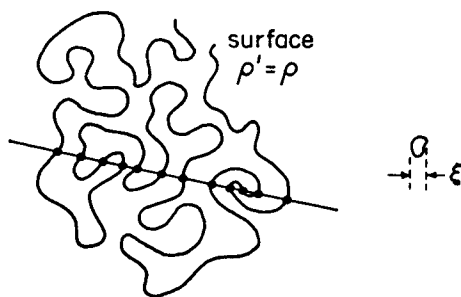


Fig. 8. The surface on which the mean local density ρ' , equals the overall mean density ρ , and an arbitrary line intersecting the surface at the points shown as dots. Also shown is a "droplet" of linear dimension ξ equal to the mean distance between those intersections (*Widom*, 1974).

$= \rho$ might look like at any instant: it is a complex and sponge-like surface. Any straight line, such as that shown in Fig. 8, makes many intersections with it, and the mean distance between those intersections is a measure of the coherence length ξ . Because such intersections with mean spacing of order ξ occur whatever the direction of the line, it is convenient to think of the

regions $\varrho' < \varrho$ and $\varrho' > \varrho$ as each consisting of many small, independent volume elements ("droplets") of linear dimension ξ (see Fig. 8). The view presented in this paper is that "magma is thought of as consisting of such droplets produced by density fluctuations. These space and time dependent fluctuations are small for temperatures far above the critical, $T \gg T_c$, and grow in size near T_c ". The fundamental reason for the appearance of embryos or nuclei of a new phase in a homogeneous magma is the existence of these fluctuations. However, a new phase never forms at exactly the temperature and pressure at which it is in equilibrium with the parent phase; there must be a certain amount of undercooling (see Jaeger, 1957 a, 1957 b, 1968; Babčan – Zatkalíková, 1988) into the region of the parent phase. Let us first see what in general is the chemical behaviour of a spinodal magma on cooling, and secondly, what are the involvements due to different degree of undercooling. As before mentioned, within the spinodal the second derivative of the free energy with respect to the concentration ($\delta^2 G / \delta X^2$) is < 0 . Now if the molar free energy curve remains continuous with continuous first derivatives, we have a spinodal in such a magma at all temperatures above the critical consolution temperature. In such a case the two phases in equilibrium are "closely related" and "one phase makes the other by continuous composition changes" (Cahn, 1968). Above the monotectic temperature (see Fig. 5) the two-liquid equilibrium and the spinodal have a "metastable continuation" and thus we have a spinodal reaction leading to two related metastable phases (see Chan – Goldburg, 1987) in a "liquidus plus solid portion of the diagram". That is, there is a closely related new phase in the melt corresponding to a liquid in density or nearest neighbor distance. Starting from a parent hypothetic basic magma in the critical condition, as temperature decreases, a second liquid phase at different density initially separates on a submicroscopic scale, and then, coalescing, collects into larger silicic clusters that are first tiny globules (Lucido, 1989). In other words, in time, as temperature of magma decreases, a continuous "liquid fractionation" in an acidic sense occurs along the dashed-dotted line (see arrow) of Fig 5. Such a continuous process is characterized by the production of intermediate magmas ranging from basic compositions to acidic ones.

Now, if a magma is very rapidly quenched along the dashed-dotted line (Fig. 5), the system will pass directly into the solvus without crossing through the metastable states which lie between BB' and SS' . However, because real systems, particularly magmas, are generally characterized by a range of composition, it is possible that a magma is supercooled to a point lying just below the spinodal line SS' , where the nucleation rate proceeds at a noticeably rapid rate. Such a magma may remain an astronomically long time before a fluctuation initiates homogeneous nucleation. In this case it is necessary to take into account the above statistical fluctuations due to the interactions between the magma and its thermal reservoir. In fact, only over a sensible period of time, when the magma will have a quench depth such that the dotted area will be attained, homogeneous nucleation will take place. On further cooling, between the two HH' and BB' curves heterogeneous nucleation occurs. The adjustments of the lattices at and near coherent or semi-coherent interfaces create elastic strain, and thus a positive contribution to the energy of the magma. The stable equilibrium state is achieved when the exsolved compositions shift from the coherent to chemical solvus by removing the coherency strain through a process such as the formation of "discrete grains". In this manner, crystallization starts (Walton, 1969; Reiss, 1976; Ganguly – Saxena, 1987) as a result of fluctuations in the bulk of the magma!

It is clearly apparent that the above phase separation is characterized by several time scales. More specifically we observe a crossover from a rapid, quench-depth dependent, rate of zone growth to a slower one. Although this separation is continuous, it can occur in a number of successive steps, each of which takes place with a different velocity in response to temperature

– pressure (P-T) gradients. The initial magma may then either ascend to the surface of the Earth without any fractionation or it may undergo one or several stages of liquid fractionation. In this way at any stage during its development the composition of the magma is controlled by the phase relations and the P-T conditions. The P-T conditions are governed by the dynamic processes, and it is, therefore, the dynamic processes which exert the ultimate control on the composition of magmas.

Final remarks

The processes which control phase separation in magmas are characterized by the interplay of thermodynamic and kinetic properties of the melts. In our view, along the cooling path (represented in Fig. 5 by the dashed-dotted line), the thermodynamic properties fit really well the kinetic properties of a magma. In particular, in the proximity of the metastable zone (region of immiscibility) the flux up the concentration gradient is damped owing to the lower value of the diffusion coefficient of the component species and the thermodynamic blocking of the previous crystallized phase. In such a condition, the magma is at the same time stable with respect to immiscibility and unstable with respect to crystallization. When the metastable zone is approached through the spinodal region (see Fig. 5), a new phase with a distinct density appears when the metastable zone is reached; and the principle that was initially stated now explains how the magma “knows” what shall be the density of the newly appearing phase: it shall be that density that the original homogeneous magma had been practicing making in its spontaneous density fluctuations.

According to us, although such a magma is an hypothetic one, it is of great petrologic and geochemical significance. In the light of modern knowledge, in fact, our theory re-proposes the century-old idea that also-called igneous rocks had congealed from a molten magma. We think that the formation of the original solid rocks of the Earth involved such a liquid fractionation process based on the equilibrium vapour pressure of the compounds making up the “truly primitive” magmatic fluid. If this be the case, the entropy of the Earth is decreasing with time. Of course, there is a prospect of an end; every magmatic episode transfers a quantity of heat from the interior of the Earth to the surface in a non-recoverable way; but as with a spring-driven clock, the Earth goes through innumerable episodes before the originally stored energy is all spent out.

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