Critical phenomena originating magmatic rocks in western Sicily

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The behaviour of a model magma in the vicinity of a critical region is in agreement with results of studies of structures in the melt in basaltic rocks from Sicily. The behaviour of ionic-non ionic fluid mixtures simulating a magma has been analysed in the light of results obtained recently with simple statistical mechanical approximations. It is suggested that the Sicilian magma is to be considered as an extremely rare natural example of two immiscible liquids having almost consolute composition.

INTRODUCTION

The term "fluid" includes both liquid and gas and it is used generally to mean a particular state of matter intermediate between the fully disordered gas state and the fully ordered ideal crystal state. Knowledge of the properties of fluids in the ranges of temperature and pressure within the earth is essential to understanding magmatic processes.

The term magma, as used by geologists, can be defined as a naturally occurring mobile liquid within the earth that may contain suspended crystals or rock fragments as well as dissolved or exsolved gases, and can form a crystalline to glassy rock, on intrusion or extrusion as a lava (YODER, 1976). From the physico-chemical point of view, any magma may be considered as a hot ionic fluid. It should then be possible to describe magmatic fluids within the McMillan-Mayer theory (MCMILLAN and MAYER, 1945; MAYER, 1950) or better within McMillan-Mayer type theories. For example, the Mean Spherical Approximation (MSA) has been used to calculate structure functions of pure and mixed molten salts (ABRAMO *et al.*, 1976, 1978; BHUIYAN *et al.*, 1977).

In this regard, TRIOLO and FLORIANO (1981) recently obtained quite good agreement between experimental or "quasi experimental" structure

functions and those obtained within the framework of the MSA, for high density ionic fluids. According to the universal concept of critical phenomena, one can expect to be able to describe any system near critical points or critical surfaces with the same critical exponents characterising the asymptotic behaviour of the correlation function (SCHNEIDER *et al.*, 1980).

In this paper we will focus attention on the behaviour of a magma as an ionic fluid at the critical point of liquid immiscibility. On the basis of some peculiar features discovered in the Sicilian rocks and considering the possibility of existence of critical or quasi critical behaviour in magmatic melts without crystals, for the first time to the authors knowledge, we propose a possible model of differentiation.

PETROGRAPHICAL OBSERVATIONS PERTAINING TO SICILIAN ROCKS

During research carried out on basaltic rocks of western Sicily, felsic ocelli were discovered in alkaline rocks (LUCIDO, 1981). These alkaline rocks form three small hillocks that crop out upon a probable erosion surface of Palaeocene, Eocene and Oligocene sediments. They generally show porphyritic texture, but panidiomorphic one is also observed. The Sicilian ocelli show structures different from those more commonly

described the world over (LUCIDO, 1981) and have a contrasting composition compared with the basaltic host-rock. They are clearly richer in silica, alumina and alkalis and are poorer in Fe, Mg, Ca, Mn, Ti and P than the enclosing basaltic rock (LUCIDO, 1981). Minerals occurring in the felsic portion are identical with those occurring in the basaltic spherules. Nevertheless the phases are varied in proportions, since leucocratic and hydrous minerals are notably concentrated in the felsic fraction. This is formed essentially by titanite, kaersutite, andesine, K-feldspar, analcite and zeolites. Previous studies (LUCIDO, 1981, 1983) argue against physical mixing of separate magmas (or other processes) for the Sicilian rocks; we report here three significant points against this process:

- 1) Several Sr isotope measurements indicate that the felsic and the basaltic rocks have initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 0.7039 and 0.7036, respectively. These very similar ratios indicate no crustal contamination and suggest that the Sicilian rocks are genetically related through a common process.
- 2) Samples showing chemical characteristics intermediate between felsic and basaltic rocks have spotted texture. This texture, inverted compared with the typical ocellar structure, is incompatible with a mixing model and largely favours liquid immiscibility. In confirmation of this, basaltic spots are often present at the margins of the felsic fractions.
- 3) There is no microscopic evidence of mixing gradients at the contact between felsic and basic rocks. Even though diffusion rates are low in silicate melts, one would expect to see some types of chemical gradients and mineralogical gradients, if the mixing model were applicable.

On the basis of chemical and textural evidence, LUCIDO (1981) suggested that they were formed by liquid immiscibility.

In the Sicilian magma the growth mechanism is dominated by the diffusion and coalescence of previously formed clusters. It is evident that at the moment of the phase separation much of the

magmatic melt is in a state of intensive motion. In particular, upon phase separation, individual rotating cluster forms independent flow in the magmatic melt (LUCIDO, 1983). So, even though the gradient flux encourages rapid coalescence, when preference for clusters is very large the gradient flux is in the direction in which they are attracted, i.e., up the concentration gradient. A similar system is found within the spinodal (e.g., CAHN, 1968). Owing to the wave nature of the spinodal mechanism we should expect regularity of spacing between the nuclei. Moreover, in spinodal decomposition we should expect very high nucleation rate (in droplets formed per cm^3 per s) and non linear effects limiting the growth rate of nuclei. Our samples fulfill all these 3 conditions as shown in Figs. 1, 2 and 3 which are portions of hand specimen only millimetres apart.

OCELLI DIMENSIONS AND COMPARISON WITH OTHER SIMILAR OCCURRENCES

Spinodal decomposition and metastable immiscibility are phenomena of considerable importance in the glass industry (e.g., CAHN, 1968; SEWARD *et al.*, 1968; DOREMUS, 1973; TEWHEY and HESS, 1974; LAUGHLIN and CAHN, 1975; ZDANIEWSKI, 1975; ALLEN and CAHN, 1976, LAUGHLIN, 1976). However, in contradistinction to the importance in glassy systems, these phenomena are underestimated from the geo-

Fig. 1. Evident spacing regularity between felsic clusters (light spots) in the Sicilian basaltic rock. Width of Fig. 1 is 30 mm.

Fig. 2. Coarsening of felsic blobs (light spots) due to the wave nature of spinodal nucleation. The number of blobs (formed per cm^3 per s) and the relations between themselves indicate that nucleation rate proceeded at an unmeasurably rapid rate.

Fig. 3. Detail of felsic portion at late stage of its evolution. In the middle and in the right part of the figure are still evident light spots spontaneously grown until nonlinear effects limited the growth rate (spinodal ripening). Scale in millimetres.

logical point of view. For instance, in our opinion the significance of such phenomena in magmatic systems needs to be evaluated. We think that, during the evolution of a magma, the metastable immiscibility and/or spinodal decomposition may play a very important role. In our case, however, for the spinodal mechanism, a difficulty is offered by the large dimensions of the Sicilian ocelli. In preferring this mechanism and in an attempt to overcome this difficulty, we propose what follows.

Spinodal decomposition has in the past been studied only in glasses and alloys where the concentration diffusivity D is very small (e.g., HILLIARD, 1970). In fluids, however, D is much larger. According to GOLDBURG and HUANG (1975) the difference between theoretical predictions and phase separation experiments near the critical point is connected with the presence of additional hydrodynamic degrees of freedom which are available to a fluid. Furthermore, at present, there is no general theory for the time-dependence of the characteristic "droplet" size in a nucleating fluid system (LABARBE *et al.*, 1981, VENZL, 1983). BINDER and STAUFFER (1974) have given a compelling argument as to why the "droplet" size should increase as $t^{1/3}$ in a liquid. Micro-graphic phase separation measurements in a liquid mixture quenched in the spinodal region show, for example, that at a quench depth $\Delta T = 6\text{mK}$ and a time $t=20$

minutes after quench, the average zone size is roughly 45 microns (GOLDBURG and HUANG, 1975). In this way, even though on the basis of experiments spinodal ripening could produce ocelli of very small dimensions (about 0.1 mm), for the above reasons, very likely, in naturally occurring phenomena the "droplet" size can be much greater. In fact, as regards natural occurrence of liquid immiscibility in silicate melts, CAWTHORN and MCCARTHY (1977) have found ocelli up to 15 cm in diameter in the Ventersdorp Supergroup lavas (South-Africa). According to these authors, these ocelli are of an order of magnitude bigger than nearly all ocelli previously reported as evidence for liquid immiscibility. Taking into account the small differences in composition between the coexisting pairs of liquids, CAWTHORN *et al.* (1979) suggested that the Ventersdorp Supergroup original magmas must have had almost consolute composition. GÉLINAS *et al.* (1976), studying pre-eruption immiscibility in Archean tholeiites, also report lavas that contain varioles having compositions essentially the same as that of the matrix. They assume that these originated through crystallization, but, according to ROEDDER (1979), it is tempting to suggest that they might represent immiscibility with only a small compositional difference, near to consolute curve. Also in our case, some pairs of liquids show only small differences in composi-

tion. In our view, therefore, the Sicilian cooling magma entered the immiscibility solvus close to the "consolute" top of the loop. Successively, on cooling, it may be changed from the initial consolute condition having the second derivative of the free energy with respect to the concentration ($\delta^2 G / \delta C^2$) equal to 0 to a binodal one with $\delta^2 G / \delta C^2 > 0$. In corroboration of this, very recently, HENRY *et al.* (1983) found that phase separation along the Ab-Di join in the system albite-anorthite-diopside indicates immiscibility occurred by "initial" spinodal decomposition. In addition, JANTZEN (1980) suggested that a spinodal mechanism may be operative in KAlSi_3O_8 - $\text{NaAlSi}_3\text{O}_8$ quenched glasses from natural orthoclase and albite.

MODERN STATISTICAL MECHANICS CONSIDERATIONS

In recent years in connection with the studies on oil-surfactant-cosurfactant interactions in Enhanced Oil Recovery research (SHAH, 1981), critical phenomena of fluids received much attention with particular emphasis on the structure and thermodynamics of the medium. According to this new view, critical phenomena are due to change in the rate of fluctuations of many solution parameters, by approaching the critical temperature; eventually these parameters will diverge (e.g., GOLDBURG and HUANG, 1975). This type of interpretation can be generalised to complex systems like, for example, molecular and ionic fluids and, of course, their mixtures. Typical systems of this last kind are magmatic fluids.

Structure of magma as a critical ionic-fluid system In this paper, unless otherwise specified, we will use the definition of "structure" in terms of probability density functions of the position of the particles making up the magmatic fluid. This will not be purely ionic in that other non ionic species will be dissolved.

It is clear, however, that the dominant interactions which in turn will be responsible for the gross physico-chemical behaviour of this fluid will be coulombic in nature. Finally, we want to stress the fact that the discussion will be qualitative in nature.

Using the above definition of structure, for two particles (ions and/or non ions) separated by the scalar distance r , we can define a probability function $g_{ij}(r)$ (pair correlation function) giving the probability density for finding the particle j at distance r from a reference particle i . This probability function, among other things, will depend on the particle number densities ρ_i and ρ_j and the bulk number density ρ of the fluid.* In turn the structure can be defined in terms of the pair interaction potential $U_{ij}(r)$ which characterises the interaction between particle i and particle j a distance r apart. In this context the statistical mechanics is nothing else but a valuable tool which allows to calculate $g_{ij}(r)$ given an interparticle potential $U_{ij}(r)$.

The importance of $g_{ij}(r)$ is also due to the fact that while it is related to the effective pair interaction potential ($U_{ij}(r)$), it is also related to the partial structure functions $S_{ij}(k)$, where k is the momentum transfer. These functions, or linear combinations of these functions can be obtained by means of scattering experiments. The fact that the total interaction potential $U(r)$ can be written as the sum over the possible pairs (i, j) of the pair interaction potentials $U_{ij}(r)$ has an important consequence: all the properties of mixtures of particles can be derived by the knowledge of the pair correlation function $g_{ij}(r)$ once a suitable "effective" pair potential $U_{ij}(r)$ has been selected. This in turn means that the results obtained for a given pair (i, j) of particles (and hence strictly valid for a two component system) can be conceptually extended to a multicomponent system whose properties will be obtained by properly weighing the results obtained for the different pairs.

*The number density ρ_α is the number of particles α contained in a unit volume. If the distance r_{ij} is given in Å, ρ_α is given usually in number of particles per Å³.

For this reason, in what follows, we will briefly outline some basic results obtainable for a two component system.

Going back to $S_{ij}(k)$, we want to stress the fact that the partial structure functions are functions of the pair correlation functions, the number densities ρ_i and the momentum transfer k (TRIOLO and FLORIANO, 1981).

The structure functions, in their thermodynamic limit, i.e. for $k=0$, are related to the fluctuations of particle number densities. Actually new structure functions can be defined, such as the number-number structure function, S_{NN} , the concentration-concentration structure function, S_{CC} and the number-concentration structure function, S_{NC} . The theory of these functions as well as the relation between these functions and some very well defined thermodynamic properties has been developed in detail (BHATIA and THORNTON, 1970; BEEBY, 1973; BHATIA and RATTI, 1976; DAMAY and CHIEUX, 1979). We will summarize some important results with the purpose in mind of pointing out particularly the thermodynamic limit of the structure functions.

Thermodynamic limit of the partial structure functions If we indicate with $\langle N_i \rangle$ and $\langle N_j \rangle$ the fluctuation of the number density of particles i and j , respectively, it turns out that (see BEEBY, 1973):

$$S_{ij}(0) = \lim_{k \rightarrow 0} S_{ij}(k) = \frac{\langle \Delta N_i \rangle \langle \Delta N_j \rangle}{(\langle \Delta N_i \Delta N_j \rangle)^{1/2}} \quad (1)$$

Values of this limit can be obtained by calculating values of $S_{ij}(k)$ in the vicinity of $k=0$ and by extrapolating the results thus obtained to $k=0$. Calculations of this sort, even using simple approximations, can be very expensive for systems having large number of components like magmas. Because of the additivity of the pair potential it is however, instructive to limit ourselves to consider much simpler systems and extrapolate (conceptually) the results to more complicated systems.

Equation (1) tells us that if the fluctuations

are strong, then the values of $S_{ij}(k)$ will be high. Conversely small values of $S_{ij}(0)$ will correspond to small values of the density fluctuations; and the smaller $S_{ij}(0)$ is, the smaller will be the fluctuations.

For a two component system (identified by the subscripts 1 and 2) there will be 3 partial structure functions (S_{11} , S_{22} , S_{12}) which will generate three more functions (S_{NN} , S_{CC} , S_{NC}) according to the following equations (TRIOLO and FLORIANO, 1981):

$$S_{NN}(k) = \omega_1 S_{11}(k) + 2(\omega_1 \omega_2)^{1/2} S_{12}(k) + \omega_2 S_{22}(k) \quad (2)$$

$$S_{CC}(k) = \omega_1 S_{11}(k) - 2(\omega_1 \omega_2)^{1/2} S_{12}(k) + \omega_2 S_{22}(k) \quad (3)$$

$$S_{NC}(k) = (S_{11}(k) - S_{22}(k))/2 \quad (4)$$

where ω_1 and ω_2 are composition dependent weighting factors. The thermodynamic limit of the above functions (DAMAY and CHIEUX, 1979) is:

$$S_{NN}(0) = \rho K_B T K_T + \rho^2 (\Delta \bar{V})^2 S_{CC}(0) \quad (5)$$

$$S_{CC}(0) = N K_B T / (\delta^2 G / \delta C_2^2)_{TPN} \quad (6)$$

$$S_{NC}(0) = -\rho \Delta \bar{V} S_{CC}(0) \quad (7)$$

where ρ is the particle number density and is equal to $N/\bar{V}$, K_B is the Boltzman constant, K_T is the isotherm compressibility at temperature T , $\Delta \bar{V}$ is the difference between the partial molar volumes of the two components and $(\delta^2 G / \delta C_2^2)_{TPN}$ is the second derivative of the free energy with respect to the concentration.

Interaction potentials By approaching (from below) the critical temperature, the term S_{NN} will diverge and so will S_{CC} although more strongly. As both S_{NN} and S_{CC} are linear combinations of $S_{ij}(k)$'s which in turn are related to the fluctuations of the particles i and j , it is clear that the fluctuations in the system will be

stronger. However, we must not forget that in ionic systems, in order to promote fluctuations one must work against the coulombic forces. This is not all the story because also the term containing $\Delta \bar{V}$ can eventually compensate the electrostatic term. To show the effect of these contributions we shall now consider two different interaction potentials which can model real systems like magmas.

a) Hard core + long range coulombic interactions

This potential has been used to model simple ionic fluids (TRIOLO and FLORIANO, 1981). The hard core potential is defined by means of the following equations:

$$U_{ij}(r) = 0 \quad \text{for } r > d_{ij} \quad (8)$$

$$U_{ij}(r) = \infty \quad \text{for } r < d_{ij} \quad (9)$$

where $d_{ij} = (d_i + d_j)/2$ is the minimum distance of approach between particles i and j of diameters d_i and d_j , respectively. The coulombic potential between the particles of charges $Z_i e$ and $Z_j e$ at a distance r_{ij} imbedded in a medium of dielectric constant ϵ is:

$$U_{ij}(r_{ij}) = Z_i Z_j e^2 / \epsilon r_{ij} \quad (10)$$

By using these potentials and by solving the Ornstein-Zernicke equation with the closure typical of MSA (see TRIOLO and FLORIANO, 1981) one can calculate values of $S_{ij}(k)$ as function of Z_i and Z_j for fixed values of d_i and d_j (which amounts to calculate values of $S_{ij}(k)$ as a function of the charge density). One finds that the difference between values of $S_{ij}(k)$ for different charge densities are negligible in all the k range except in the long wavelength limit ($K \rightarrow 0$). From this model calculations we can then conclude that for purely ionic fluids the higher is the charge density, the lower is the thermodynamic limit of $S_{ij}(k)$.

b) Hard core + long range coulombic terms + short range attractive tail

The introduction of a short range attractive tail (which in the case of magmas corresponds to

non coulombic effects like the ones leading to formation of polymeric networks and/or polynuclear complexes) has the main effect of increasing substantially the probability of contact between the particles i, j compared to the case with only hard core + long range coulombic terms. This, in turn, has the effect of increasing the thermodynamic limit of $S_{ij}(k)$ owing to the fact that

$$S_{ij}(0) = \int_{-\infty}^{\infty} g_{ij}(r) dr \quad (11)$$

Consequently we can expect that in such system it will be "easier" to induce fluctuations as apposite to the case described in a). At this point it is useful to apply the concepts so far outlined to the Sicilian magma.

PETROLOGICAL APPLICATION

The assumption used in this paper is that liquid phase splitting precedes any crystallization process. By applying the above considerations, now we shall devote our attention to some processes which occur in nature. In particular, focussing on a basaltic magma of the type found in western Sicily (LUCIDO, 1981), let us see what happens on approaching the critical conditions.

Among the various properties that tend to diverge on approaching the critical surface is the "correlation length" ξ . In a sense this quantity is an indication of the distance over which the position as well as the dynamics of the particles are correlated: it represents the spatial scale of a fluctuation. For a magmatic fluid very much away from the critical region, ξ is of the order of a few molecular diameters. By approaching the critical region the correlation length ξ will increase up to several hundred molecular diameters and hence the magmatic fluid will actually behave in a peculiar way, in a sense will act like an unstable system with high compressibility and long range correlation between the particles. From a physico-chemical standpoint this amounts to a magmatic fluid in which the behaviour of any portion of the whole fluid is strictly related to the behaviour of any other

portion of the fluid itself. This means that by approaching the critical surface liquid phases will behave less and less as liquid and more and more like a mixture of liquid and gas phases, owing to the increase of ξ .

Let us now see what happens on leaving the critical conditions by cooling the magmatic fluid. The effect of decreasing the temperature is also to decrease the fluctuations characterising the critical behaviour. In particular, the above correlation length will decrease and the magma will behave more like a fluid with short range correlation (liquid). Of course again, the fluctuations involving high surface charge ions will be more effectively damped than the others, and so there might be a tendency of the fluid to split into two immiscible liquids, one enriched in high charge ions and the other enriched in low charge ions. In this way, the magmatic fluid will tend to separate into two immiscible liquid fractions, one enriched in elements like iron, magnesium, calcium, titanium etc., and the other enriched in low charge density ions and elements having the tendency to form polymeric networks. Furthermore either one or both melt phases can solidify forming crystal phases, whose composition depends on the original composition as well as other factors including the time elapsed between the immiscible liquids splitting and the crystallization. So, as a consequence of the hypothesized mechanism we should expect to find small almost spherical drops of dark (Fe rich) phase dispersed in a clearer phase richer in elements forming framework structures or vice versa. In our opinion the petrographical observations pertaining to magmatic rocks from Sicily verify this view. In particular, synthesizing the foregoing evidence, our model is supported by the fact that:

- 1) the Sicilian ocelli are clearly richer in Si, Al, K and Na and are poorer in iron, magnesium, calcium, manganese, titanium and phosphorus than the enclosing basaltic rock (see LUCIDO, 1981).
- 2) at the moment of immiscibility much of the Sicilian magma was in a state of intensive

motion (an unstable melt) (see LUCIDO, 1983).

- 3) the Sicilian rock-samples exhibit regularity of spacing between the felsic clusters (Fig. 1).
- 4) Coarsening of the clusters occurred at a very high nucleation rate (Fig. 2).
- 5) non linear effects limited the growth rate of the Sicilian felsic nuclei (Fig. 3).

CONCLUSIONS

The use of concepts developed for ionic and non ionic fluids by using modern statistical mechanical approximations has been found useful to interpret the mechanism of phase separation in magmas.

In our view, this mechanism finds a verification in some peculiar structures discovered in basaltic rocks from Sicily. We think that the two Sicilian magmas had almost identical compositions at first, but on cooling gradually diverged from critical (consolute) curve along curving paths on the solvus. Subsequently, very likely, they contacted the liquidus surface simultaneously, at points on a tieline on that surface. Then, crystallization of mineral phases along binodal curve may cause continuous change in the compositions and amounts of the two magmatic melts. In our view, therefore, the Sicilian magma must be considered as a quite rare case of two immiscible liquids having almost consolute composition. So, the textural features showing inhomogeneity in the chemical and mineralogic composition are interpreted by us as evidence for critical phenomena in the Sicilian basaltic magma. Concluding we suggest that the application of modern statistical mechanics theories to magmas is a very useful tool for future igneous geochemistry.

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