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GEOCHEMISTRY

Kinetic Approach to the Crystallization of Magmatic Melts

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Igneous rocks exposed at the day surface are dominated by two groups: gabbro–basalt and granite–rhyolite. This is typically explained in the following way: the melting of the Earth's mantle and crustal materials primarily generates the lowest temperature melts with the eutectic-type composition: (i) pyroxene–plagioclase (gabbro–basalt group); (ii) quartz–plagioclase–alkali feldspar (K-Fsp) ± eutectic mafic mineral (granite–rhyolite group). The melt evolves during its ascent from the magma generation area to the crystallization site. Consequently, the melt composition becomes closer to eutectic at the beginning of its crystallization within the Earth's crust or on its surface. Therefore, the crystallization of such melts is typically analyzed using phase state–temperature equilibrium diagrams [1, 2, and others], which indicate that cooling of the eutectic melt depending on heat loss should yield either glassy (vitrophyric) or equigranular rock. Noneutectic melts produce a unequigranular or porphyritic texture with (or without) the glass. The diagrams also show that the number of phenocrysts must always be one unit less than the number of components. In these diagrams, the composition of crystallizing minerals is accepted to be constant.

The term "equilibrium crystallization" must be applied only if we postulate that the system is characterized by continuous and instantaneous attainment of equilibrium over the entire volume of both liquid and crystalline phases. In other words, the diffusion rate of all components in the melt must be infinitely large or it is necessary to accept that the process of crystallization continues for an indefinitely large period. In the case of infinitely slow cooling of silicate and aluminosilicate melts (equilibrium crystallization), the distribution of internal energy and enthalpy by the degree of freedom of the system can follow the cooling rate $q = dT/dt$. If the attainment rate of a new equilibrium state in the system at an infinitely small temperature drop becomes lower than the cooling rate, the system is characterized by a lag, because its equilibrium parameters have not had enough time to follow the cooling rate.

The processes of crystal nucleation and growth (disequilibrium processes) are described in several works [3, 4, and others]. It was established that crystal nuclei are surrounded by the melt zone (crystallization front melt, CFM). Its chemical composition and temperature differ from those of the main volume of the melt (Fig. 1), because the composition of the growing mineral always differs from that of the magmatic melt. It was experimentally established that the content of incompatible components (impurities) in the CFM has an inverse correlation with the crystallization temperature (Fig. 1). The diffusion rate of incompatible components from CFM into the main volume of the melt and that of compatible elements in the opposite direction are determined by the melt viscosity, which depends on the composition and temperature of the melt and the size of diffusing particles. Figure 1 shows that the content of incompatible components in the CFM changes exponentially with distance from the growing crystal.

The nucleus (crystallization center) can appear only under conditions of supercooling (ΔT) in its crystallization field. This is related, in particular, to the fact that the formation of the melt–crystal phase boundary is an energy-consuming process. The value of supercooling for silicate and aluminosilciate nuclei varies for different minerals from 50 to 350°C [5]. Homogenous nucleation is typical of melt supercooling [6] near the growing crystal relative to the temperature of the main melt volume (Fig. 2). The figure also demonstrates that the supercooling has a direct correlation with the melt viscosity. As the supercooling increases, the homogeneous nucleation (HNR) and crystal growth (CGR) rates first increase, reach the maximum, and then decrease. The maximums of HNR and CGR do not coincide, and the corresponding curves can be overlapped or not overlapped.

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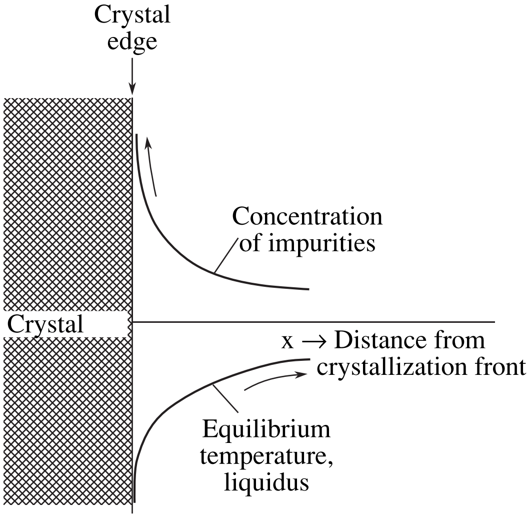

Fig. 1. Change in concentrations of impurities (incompatible components) and temperature in the CFM at the crystallization front of the growing crystal facet.

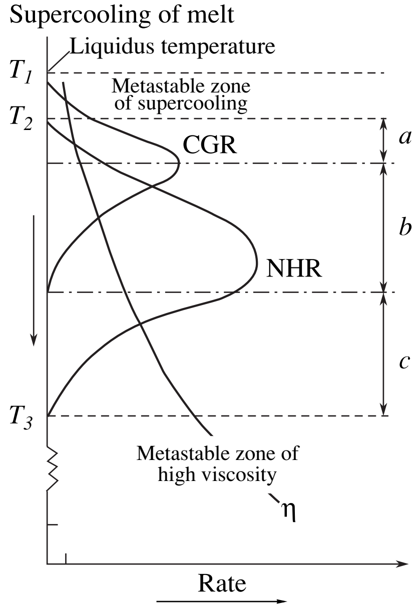

Fig. 2. Changes in crystal growth rate (CGR), homogenous nucleation rate (HNR), and viscosity (η) depending on supercooling. *T* is the temperature [after 6].

The nucleation of crystals in a certain point of the system is a probabilistic process [7] that requires supercritical concentration of the matter and the essential degree of supercooling. Such conditions can be attained owing to continuous fluctuations of temperature and energetic parameters in the melt [8].

Independent formation of mineral nuclei of both similar and different chemical compositions is seen distinctly in the rocks of different chemical compositions with phenocrysts embedded in the glassy or granular groundmass. The phenocrysts grow independent of each other during a significant period of melt cooling. Consequently, the common system of crystallizing melt consists of a great number of subsystems: grains of growing minerals and the surrounding CFM. Therefore, the crystallizing system is characterized simultaneously by the temperature of entire system and by the CFM temperature near each growing mineral grain. This feature is typical of the crystallization of a eutectic melt. It should be noted that fluctuations of temperature and composition within the entire volume of the eutectic melt can promote the asynchronous formation of stable and viable nuclei, thus providing the growth of phenocrysts. This can be seen clearly in thin sections (Fig. 3). The rock (rhyolite) has eutectic composition, but it contains two phenocryst generations of different minerals. Thus, the melt crystallized in at least three stages: (1) formation and growth of phenocrysts of the first generation (phenocryst I); (2) continuation of the growth of phenocrysts I accompanied by nucleation and growth of phenocrysts of the second generation (phenocryst II); and (3) continuation of the growth of phenocrysts I and II and formation of the groundmass minerals. The phenocrysts grew without any contact with each other during the entire crystallization stage. Each phenocryst and surrounding melt (CFM) represented an independent system. Each phenocryst grew at different compositions of the CFM and, correspondingly, different degrees of supercooling.

Let us consider the crystallization of the melt in stable conditions based on Fig. 2. It is seen that homogenous nucleation takes place only at supercooling above T_2. Some nuclei form in field *a* (insignificant supercooling). Their growth rate increases and reaches a maximum with an increase in supercooling. Therefore, stable conditions are favorable for the formation of sufficiently equigranular textures. The grain size of minerals depends on the growth rate, which varies from a small value (coarse-grained texture) to the maximum value (medium-grained texture) in field *a.* In the latter

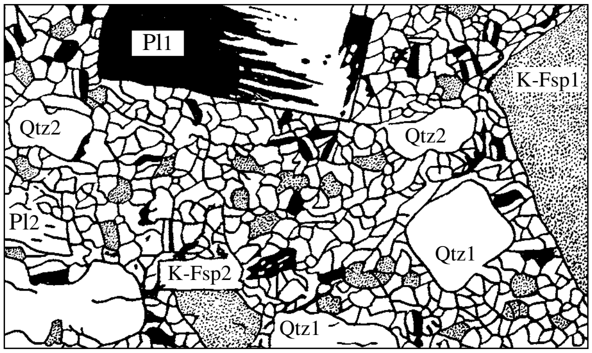

Fig. 3. Rhyolite. The rock consists of phenocrysts of plagioclase (Pl), alkaline feldspar (K-Fsp), and quartz (Qtz). All phenocrysts form two generations. The groundmass consists of the same minerals. Crossed nicols (image width 3 mm).

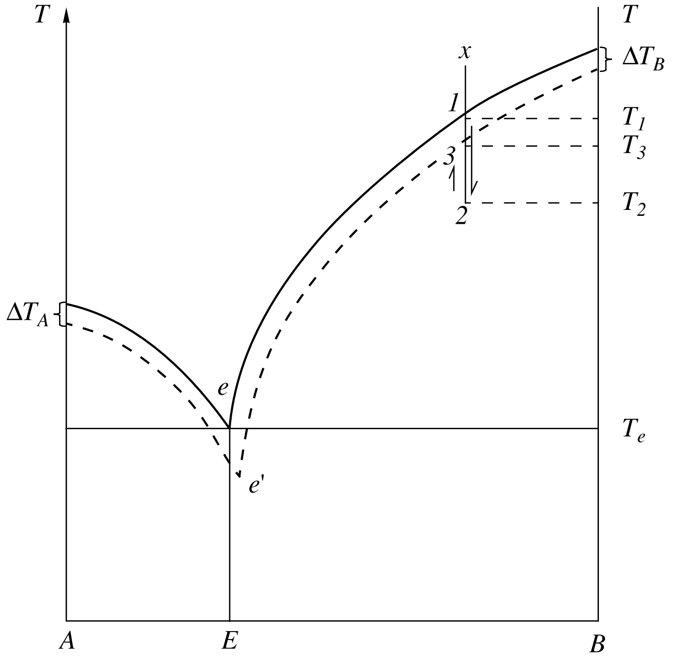

Fig. 4. Disequilibrium two-component diagram *AB*. (*A*, *B*) Components; (T) temperature; (ΔT) supercooling; (T_2) nucleation temperature; (T_3) CFM temperature; (T_1) thermodynamic crystallization temperature; (*e*) eutectic composition of melt of the entire system; (*e*') CFM composition common for nearly contiguous and jointly growing mineral edges.

case, a medium-grained texture is formed. In field *b* (higher supercooling), the CGR decreases to minimum values, while the HNR value reaches the maximum. Such conditions foster the formation of a fine-grained equigranular texture. In field *c*, the CGR tends to an infinitely small value, while the CMF value decreases and a coarse-grained texture is formed. If supercooling exceeds T_3, the melt is solidified into glass. Unstable conditions existing in fields *a* and *b* promote the formation of unequigranular and porphyritic textures.

Figure 3 shows that phenocrysts are represented by several generations, which are not in contact with each other. Such a texture is formed under unstable conditions: crystallization began in field *a* after the formation of phenocrysts I. With increasing supercooling, phenocrysts I continued to grow in field *b*. This was accompanied by nucleation and growth of phenocrysts II. Phenocrysts I and II continued to grow, and minerals of the groundmass formed under conditions of maximum supercooling (field *c*).

Figure 4 demonstrates the liquidus temperature of the entire system (solid lines), formation temperature of phase *B* nucleus (point *2*, temperature T_2), and variation in CFM temperature (dashed line) near the growing grains of phases *A* and *B*. It should be noted that no stable and viable nuclei of phase *B* are formed at temperature T_1 (the temperature at which the data point is plotted in the liquidus of the entire system), i.e., the thermodynamic crystallization temperature. At this temperature, the number of newly forming nuclei is equal to that of dissolved nuclei. Only supercooling conditions can provide the formation of stable and viable nuclei. The higher the radius of the newly formed nucleus, the less supercooling is required for its stability [9]. The dashed lines (CFM_A and CFM_B) are intersected below the eutectic temperature of entire system: the intersection point of CFM_A and CFM_B (*e*') is below point *e* (temperature T_e). Its position depends on the melting temperature of pure phases *A* and *B* and on the value of CFM supercooling near the growing grains *A* and *B* (ΔT_A and ΔT_B, respectively). Therefore, this point can be located in the crystallization field of phase *A* (or *B*) or correspond to the eutectic composition of the entire system (*E*). Data point *e*' corresponds to conditions of eutectic crystallization of almost contiguous grains of phases *A* and *B*.

Thus, nuclei of different minerals are formed independently in different points of the melt. Mineral grains grow at the expense of the CFM matter, which is supplied by diffusion from the main volume of the melt. The diffusion rate of compatible components from the main melt volume into the CFM and the diffusion rate of incompatible elements in the opposite direction govern the growth rate of the crystal facet. The structure of the rock begins to form when the growing grains begin to come into contact and disturb mutual growth. Eutectic crystallization takes place when minerals of different chemical compositions from the common CFM are almost adjoined.

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