Kinetics and dynamics of mineral formation

Agoshkov V.M. Modeling of crystal growth from the magmatic melt in the open system

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Study of modeling of an interaction of melt (magma)–growing crystal under the specific physical and hydrodynamic conditions of mass and heat exchange, viscosity, diffusion and crystal motion in a magma is very interesting for understanding of the processes of crystallization and differentiation. Precipitation of minerals from the magmatic melt is, in fact, a non-equilibrium process, since growth and increase of mineral mass occurs with a finite limited rate only at a finite departure from equilibrium. A major stage of magmatic crystallization occurs under stationary conditions, then overcooling and a rate of temperature drop are constant during long time. A stationary state in the open thermodynamic system plays the same role as the thermodynamic equilibrium for the isolated systems in the equilibrium thermodynamics.

Consider the major physical and hydrodynamic features of magmatic crystallization as an example of the stationary process.

Density of a silicate melt $\rho^*$ and concentration of ions $(C_i)$ as a function of composition, temperature and pressure can be calculated with an accuracy of $\pm 1-2\%$ within the range 950-1400°C and 1-10000 bars [1]; density of rock-forming minerals $\rho^*$ are also known.

The dynamic viscosity $\mu$ of silicate melts is investigated in the wide range of $T$, $P$, and $C$ in dry and water-bearing systems [1, 2]. The effective viscosity below liquidus is defined not only by the activation energy and temperature, but also by an amount of crystals in the melt. As portion of crystals in the liquid increases, the effective viscosity notably increases as well. There are empirical equations describing the effective viscosity of melts as a function of the liquid/crystal ratio [3].

The dependence of ionic diffusivities $(D_i)$ on $T$ and $P$ is studied precisely for diverse magmatic melts [3].

The mutual movements of crystals and the melt includes a movement of growing crystal faces toward the liquid and a free movement of crystals in the liquid by the Archimedes’ force. The latter is possible if a crystal is not attached to a fixed wall or is not in the cumulate substratum. The maximal velocity of the freely moved crystal with respect to the melt $U$ is determined by the Stokes’s low and depends of differences in densities of the melt and the solid phase, as well as on the crystal size. An increase of a portion of suspended crystals results in an increase of the effective viscosity and lowers the velocity of mutual displacement of the liquid and the solid phases.

In hydrodynamics and in the theories of mass and heat transfer, the dimensionless ratios of sizes and characteristic physical parameters of the given phenomenon are widely used. These values are called as criteria, or numbers, of similarity [4].

The Reynolds criterion for magmas $(Re \sim 10^4-10^5)$ shows that motion of crystals occurs in the laminar regime. Diffusion Peclet $(Pe_\varphi \sim 10^{-10^{-2}})$ and Prandtl $(Pr_\varphi \sim 10^7-10^8)$ numbers define an influence of molecular diffusion, viscosity, and velocity of crystal motion in the melt on the transfer of components (ions) and support a leading role of a liquid flow.

Owing to the frictions of the liquid against the crystal surface and the internal friction (viscosity) in the melt, the hydrodynamic, or viscous, boundary layer forms between the phases. In this boundary layer, velocity of the liquid motion decreases down to zero at the surface of the crystal, as well melt viscosity increases by leap perpendicular to the interphase surface. The thickness of the viscous layer $(\delta)$ for the crystal with the mean linear size $l \sim 10^{-3}$ cm, moving in the melt by the Archimedes force with velocity $U$ is $\delta \sim (\rho \delta U)^{1/2} \sim 10^{-2}$ cm. Within this boundary layer, the melt viscosity increases by 2-3 orders of magnitude, and at the surface of the crystal, it is $10^5-10^6$ Poise. Such high value of viscosity in the boundary layer prevents from separation of crystals and the thin $(\sim 10 \mu)$ film of the residue liquid at any accelerations of crystal shifts with respect to the melt.

The increase of viscosity and decrease of the velocity of melt motion in the viscous boundary layer results in changing in the diffusion Peclet $(Pe_\varphi)$ and Prandtl $(Pr_\varphi)$ criteria, and diffusion becomes a major agent of component transfer in the melt. That results in formation of the boundary concentrational (diffusion) layer $\delta_\varphi$ (crystallization halo) at the interphase boundary, and $\delta_\varphi > \delta$. In the multi-component system, a composition of the solid phase does not coincide with the melt composition because of coefficients of component (ion) distribution $K_i = C_i/C^*$, is not equal to 1. Following to the existence of the boundary diffusion layer, the liquid can be divided into two portions: a) a portion of a constant concentration of $i$-ion in the melt $C_i$ away from the surface of heterogeneous reaction of crystallization; b) a portion, where in the thin liquid layer concentrations of $i$-ion rapidly change from $C_i$ up to $C_i$ on the front of crystallization. If $K_i < 1$, than ions $i$ are accumulated in the diffusion boundary layer and $C_i > C_i$ (piling up). If $K_i > 1$, than the boundary layer is depleted in $i$ ions $C_i < C_i$ (drained out).

Equation for the thickness of the diffusion boundary layer for the crystal moving in the melt was analytically deduced by V.G. Levich [5]. Calculations by this equation show that the thickness of the diffusion boundary layers on olivine crystal sinking into the olivine-normative basalt melt are $\sim 28 \mu$ for Mg$^{2+}$, $\sim 32 \mu$ for Fe$^{3+}$ (depletion); $\sim 30 \mu$ for Ca$^{2+}$, $\sim 42 \mu$ for Na$^+$, and $\sim 8 \mu$ for Si$^{4+}$ (enrichment).

If the velocity of crystal motion by the Archimedes’ force $U = 0$, than the thickness of the diffusion layer depends on a free convection of the melt. The convection is caused by a difference in temperatures of magma $(\nabla T)$ and crystal surface $(T)$, i.e. by overcooling of the melt $(\Delta T)$, as well as by difference in compositions of the liquid phase in the diffusion boundary layer and in the whole melt volume. Consider, how the convection caused by these phenomena influences on the crystal growth rate and thickness of the diffusion boundary layers.

The mineral growth from the melt is accompanied by release of the latent heat. A quantity of the released heat $(q)$ is equal to the surplus of crystal mass $(m)$ multiplied by the heat $(L)$ of crystallization: $q = mL$. The thermal heat transfer into the magmatic melt occurs by thermal conductivity and by free convection.
Coefficients of thermal conductivity $\lambda$ of rock-forming minerals and magmatic melts are known, and, as a rule, $\lambda$ insignificantly varies with temperature and does not depend on pressure [6, 7]. Density of a heat flux ($\varphi$) from the crystal into the melt transferred by “pure” thermal conductivity is $\varphi = \lambda / L$.

Both for the diffusion substance transfer and the heat transfer, dimensionless criteria are used. Thermal Peclet ($Pe_{q} \approx 10^{-2} - 10^{-4}$) and Prandtl ($Pr_{q} \approx 10^{-5} - 10^{-6}$) criteria define the relation between thermal conductivity of magmatic melts and convection during the heat transfer. These criteria show that heat influx into the melt at fixed crystals ($U = 0$) occurs mostly by thermal conductivity rather than convection.

Thermal transfer at free (natural) convection in nonmetallic liquids with $Pr_{q} \geq 0.6$ is characterized by that the variations of $\Delta T$ is concentrated in the thin liquid layer (δ) adjusted to the surface of growing crystal. Similar to the viscous and diffusion boundary layers, this layer of the magmatic melt can be called as thermal boundary layer, and $\delta = \delta$. Density of the heat flux transferred from the growing crystal into the melt by means of thermal conductivity and convection in stationary conditions, i.e. coefficient of thermal exchange, ($\alpha$) is equal to the amount of the released heat ($\varphi$) divided by the stationary overcooling $\Delta T$, time of heat releasing ($\tau$), and surface area of the crystal ($S$): $\alpha q / \Delta T S = m/L \Delta T S$.

The Archimedes ($Ar \approx 10^{-6} - 10^{-7}$) and Grashof ($Gr \approx 10^{-6} - 10^{-7}$) criteria for the magmatic melt characterize an influence of liquid density on work against the viscosity and thermal expansion of the melt in the heat boundary layer.

If both phenomena take place, the total Grashof number ($Gr$) is equal to module of an algebraic sum of $Ar$ and $Gr$: $Gr = Ar + Gr$. The number $Gr$ defines the heat transfer during the convective heat exchange for the free convection.

The heat transfer in the stationary conditions of the free convection are defined by the thermal Nusselt number ($Nu_{q}$), which is a function of $Gr$ and $Pr_{q}$: $Nu_{q} = C(Gr^{n}Pr_{q})^{3}$; where constants $C$ and $n$ are shown in Table 1:

<table>
<thead>
<tr>
<th>Product $Gr\cdot Pr_{q}$</th>
<th>$C$</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^{-3} &lt; Gr \cdot Pr_{q}$</td>
<td>0.45</td>
<td>0</td>
</tr>
<tr>
<td>$10^{-2} &lt; Gr \cdot Pr_{q} &lt; 10^{-1}$</td>
<td>1.18</td>
<td>0.125</td>
</tr>
<tr>
<td>$10^{-1} &lt; Gr \cdot Pr_{q} &lt; 2 \times 10^{-1}$</td>
<td>0.54</td>
<td>0.250</td>
</tr>
<tr>
<td>$2 \times 10^{-1} &lt; Gr \cdot Pr_{q}$</td>
<td>0.135</td>
<td>0.333</td>
</tr>
</tbody>
</table>

The Nusselt number ($Nu_{q}$) is a ratio of the density of the stationary heat flux defined by the coefficient of heat exchange ($\alpha$) and the density of the heat flux, which would be in the case of “pure thermal conductivity” without convection: $Nu_{q} = \alpha / \varphi = \alpha / (\lambda / L) = mL / \Delta TS \lambda$. Thus, $m / St = Nu_{q} \Delta T / L$. The value $m / St$ is density of a total stationary mass flux ($j$) toward the surface of the growing crystal, i.e. a rate of mass accretion on the unit surface area: $j = m / St = Nu_{q} \Delta T / L$. Division of the density of mass flux by the crystal density $\rho$ gives a linear rate of crystal growth: $v = j \rho = m / St \rho = Nu_{q} \Delta T / L \rho$. Thus, the crystal growth rate is expressed by physical properties of the melt, the heat of crystallization, and overcooling. The density of mass flux for the i-ion in the melt ($j_{i}$) is equal to the density of the total mass flux ($j$) multiplied by mass fraction ($pi$) of the i-ion in the crystal: $j_{i} = j p_{i}$. The thickness of the diffusion boundary layer ($\delta_{i}$) for the i-ion in the melt at the growing crystal is $\delta_{i} = j_{i} / D_{i}$. Concentration $C_{i}$ in the stationary conditions at the front of crystallization is a complex function of $K$, $v$, and $\delta$.

On the basis of the above equations and relations, an algorithm of programs in the Windows software (VB language) is worked out. The programs allow to visually estimate the thickness of the boundary layers, distribution of ions within them, growth rate for rock-forming minerals from the magmatic melts in dependence on overcooling and the velocity of crystal displacement in the magma under real physico-chemical conditions.

Conclusions

1. Mineral crystallization from the magmatic melt occurs in the open non-equilibrium thermodynamic system.

2. Chemical composition and physical properties of the melt at the surface of the growing crystal (front of crystallization) notably differ from composition and properties of the magma as a whole.

3. An existence of the viscous boundary layer predetermines the melt volume, which can be separated from the crystals during their mutual displacement in the gravity field.

References: