Settling of Immiscible Droplets: A Theoretical Model for the Missing Link Between Microscopic and Outcrop Observations

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Abstract  Liquid immiscibility is a critical mechanism to diversify magma compositions. The physical separation of exsolved melt droplets is an essential process in generating new magmas. However, little attention has been paid to this physical process. In this study, we present a new model for segregation of immiscible melt droplets in which exsolution, settling, and coalescence are all considered. The separation of immiscible droplets is similar to that of crystals in magma when the discrete melt exsolves as large (millimeter-size) droplets and/or when the magma cools slowly. However, when immiscible melt droplets are small (micrometer-size) and/or magma cools rapidly, coalescence can significantly enhance their separation. The low interfacial tension between coexisting silicate melts leads to the exsolution of extremely small melt droplets. Furthermore, the high viscosity of silica-rich melt suppresses the coalescence of droplets. Consequently, the separation of highly viscous silica-rich melt droplets is slow but could have occurred in a slowly cooling magma such as the Skaergaard intrusion. By contrast, the coalescence rate of melt droplets with low viscosity is high. Iron-rich melt droplets, which have low viscosities, could have been separated from hydrous andesitic melts to form magnetite-apatite ore deposits at El Laco and Marcona. Furthermore, the viscosities of sulfide and carbonatitic melts are low. Therefore, immiscibility between sulfide and silicate melts may lead to the formation of magmatic sulfide deposits, and immiscibility between carbonatitic and silicate melts can support periodical eruptions of carbonatitic lava.

1. Introduction

Magma diversity has been attributed to the segregation of magmatic phases with distinct chemical compositions. Liquid immiscibility is an important mechanism to generate magma diversity (Winter, 2013). This process can lead to unmixing of homogeneous silicate melt to form ferrobasaltic and andesitic-to-rhyolitic melts (hereafter referred to as “iron-rich” and “silica-rich” melts, respectively). Microscopic exsolution of immiscible silica-rich (or iron-rich) droplets has been observed in both laboratory experiments and volcanic rocks (Charlier & Grove, 2012; Dixon & Rutherford, 1979; Honour et al., 2019; Hou et al., 2018; Philpotts, 1982). This unmixing process has been proposed to have produced mafic and/or felsic plutonic outcrops, and magnetite-apatite deposits (Charlier et al., 2011; Chen et al., 2010; McBurney, 1975; Tornos et al., 2017; VanTongeren & Mathez, 2012). Melts other than iron-rich and silica-rich silicates can also be produced via liquid immiscibility in magmatic systems. The carbonatitic lava observed in the East African Rift has been suggested to have resulted from carbonate-silicate immiscibility (Jones et al., 2013, and references therein). Moreover, sulfide liquid can exsolve from mafic magma, which may ultimately lead to the formation of magmatic sulfide ore deposits (Simon & Ripley, 2011, and references therein). The geochemical evolution of liquid immiscibility has been studied extensively (Thompson et al., 2007). However, little attention has been given to the physical process of macroscopic separation between two immiscible melts, which is crucial to magmatic evolution (Chung & Mungall, 2009; Holzheid, 2010; Honour et al., 2019; Zhang, 2015). This physical process depends on how the immiscible melt droplets settle in the magma chamber.

The settling of immiscible melt droplets is to a degree similar to that of crystals in magma. The timescale of crystal settling estimated from the ratio of the magma thickness to the crystal settling velocity (Martin & Nokes, 1988, 1989) depends strongly on the crystal size according to Stokes’ law. In basaltic magma, this settling can be efficient if crystals are as large as a few millimeters, or inefficient if crystals are only a few
micrometers or even smaller (Martin & Nokes, 1988, 1989). The immiscible melt droplets exsolved in magma are often very small (micrometer size), which means that settling can be negligible within the timescale of magma cooling (Holzheid, 2010; Honour et al., 2019; Veksler et al., 2010). The settling of both crystals and melt droplets in magma may be facilitated by diffusive growth (James, 1975; Wilson, 1993; Zhang, 2008). In contrast to crystals, immiscible melt droplets could coalesce with each other to form larger droplets, thereby enhancing separation efficiency (Wang & Davis, 1995, 1996). However, it is not clear how the coalescence of melt droplets can promote the settling process in magma. The role of liquid immiscibility in large-scale magmatic differentiation therefore remains ambiguous.

In the present study, we develop a theoretical model for the evolution of immiscible melt droplets in magma that provides constraints on the role of liquid immiscibility in magmatic differentiation. A statistical approach has been used to model the evolution of the volume fraction and size distribution of melt droplets in magma. Melt exsolution, droplet coalescence, and gravitational settling are all considered in our model. We also discuss the physical mechanisms that control the separation timescale in the two different regimes. The separation of melt droplets is similar to the settling of crystals when the discrete melt exsolves as large droplets and/or magma cools slowly. On the other hand, the separation can be significantly enhanced by coalescence when immiscible melt droplets are small and/or magma cools rapidly. Our results provide insights into melt separation in natural magmas in which liquid immiscibility has occurred.

2. Model Development

This study is focused on the physical separation of immiscible melt droplets in magma. Therefore, magma is simplified to be a melt-melt mixture in which the exsolved discrete melt (hereafter referred to as “discrete melt” or “melt droplets”) disperses as droplets in the dominant continuous melt (hereafter referred to as “continuous melt”). A statistical approach is used to model the evolution of melt droplets in this two-phase mixture. The size distribution of droplets is assumed to be continuous within a control volume $\delta \Omega$. This control volume is much smaller than the whole magma body $\Omega$ in which immiscibility occurs but much larger than any individual droplet $V$, $V'$, or $V+V'$ (Figure 1). Thus, the number of droplets with volume between $V_1$ and $V_2$ in the control volume $\delta \Omega$, $\delta N(V_1, V_2, \delta \Omega)$, can be calculated as

$$\delta N(V_1, V_2, \delta \Omega) = \int_{\delta \Omega} \int_{V_1}^{V_2} n(V) dV,$$

where $n(V)$ is the droplet population density (i.e., the number of droplets per unit droplet volume per unit magma volume) with units of $m^{-6}$, and $\int_{V_1}^{V_2} n(V) dV$ is the number of droplets with volume between $V_1$ and $V_2$.
and $V_2$ per unit volume of magma with units of m$^{-3}$. All the variables in this study, as well as their definitions and units, are listed in Table 1. The volume fraction of melt droplets $\phi$ can be calculated as

$$\phi = \int_0^\infty V n(V) dV.$$  \hspace{1cm} (2)

In this study, we assume that melt droplets form continuously as the exsolution of discrete melt occurs in magma. It has been confirmed that homogeneous nucleation of melt droplets occurs in both laboratory experiments and volcanic rocks, even with the presence of crystals (e.g., Charlier & Grove, 2012; Honour et al., 2019; Philpotts, 1982). Thus, this approximation of the exsolution process is acceptable (see discussion in section 5). The discrete and the continuous melts have different densities, resulting in the gravitational settling of melt droplets in the magma. During settling, two melt droplets may encounter each other and coalesce, forming a larger droplet at the expense of the two smaller ones (Figure 1e). The evolution of droplet population density can be formulated as

$$\frac{\partial n(V)}{\partial t} + \nabla \cdot \left[ n(V) \left( \vec{U} + \vec{u}(V) \right) \right] = \Gamma_{\text{exs}}(V) + \Gamma_{\text{coal}}(V),$$  \hspace{1cm} (3)

where $t$ is the time, $\Gamma_{\text{exs}}(V)$ is the formation rate of melt droplets with volume $V$ via exsolution with units of m$^{-6}$s$^{-1}$, $\Gamma_{\text{coal}}(V)$ is the net formation rate of melt droplets with volume $V$ via droplet coalescence with units of m$^{-6}$s$^{-1}$, $\vec{U}$ is the flow velocity of the continuous melt caused by magma convection (see discussion in section 2.1), and $\vec{u}(V)$ is the gravitational settling velocity of melt droplets relative to the surrounding continuous melt (Clift et al., 2005). This last variable can be calculated as follows:

### Table 1

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V$</td>
<td>Volume of an individual melt droplet</td>
<td>m$^3$</td>
</tr>
<tr>
<td>$r(V)$</td>
<td>Radius of a droplet with volume $V$</td>
<td>m</td>
</tr>
<tr>
<td>$\delta N(V_1, V_2, \delta \Omega)$</td>
<td>Number of droplets with volume between $V_1$ and $V_2$ in the control volume $\delta \Omega$</td>
<td></td>
</tr>
<tr>
<td>$n(V)$</td>
<td>Droplet population density</td>
<td>m$^{-6}$</td>
</tr>
<tr>
<td>$\phi$</td>
<td>Volume fraction of the discrete melt</td>
<td></td>
</tr>
<tr>
<td>$\vec{U}$</td>
<td>Convective velocity of the continuous melt</td>
<td>m·s$^{-1}$</td>
</tr>
<tr>
<td>$\vec{u}(V)$</td>
<td>Stokes settling velocity of a droplet with volume $V$</td>
<td>m·s$^{-1}$</td>
</tr>
<tr>
<td>$H$</td>
<td>Thickness of the emulsified magma</td>
<td>m</td>
</tr>
<tr>
<td>$\mu$</td>
<td>Viscosity of the continuous melt</td>
<td>Pa·s</td>
</tr>
<tr>
<td>$\mu_d$</td>
<td>Viscosity of the discrete melt</td>
<td>Pa·s</td>
</tr>
<tr>
<td>$\Delta \rho$</td>
<td>Density difference between the discrete melt and the continuous melt</td>
<td>kg·m$^{-3}$</td>
</tr>
<tr>
<td>$\beta$</td>
<td>Viscosity ratio between the discrete melt and the continuous melt, $\mu_d/\mu$</td>
<td></td>
</tr>
<tr>
<td>$\Gamma_{\text{exs}}$</td>
<td>Production rate of melt droplets due to melt exsolution</td>
<td>m$^{-6}$s$^{-1}$</td>
</tr>
<tr>
<td>$\Gamma_{\text{coal}}$</td>
<td>Net production rate of melt droplets due to coalescence</td>
<td>m$^{-6}$s$^{-1}$</td>
</tr>
<tr>
<td>$R_{\text{exs}}$</td>
<td>Volume of discrete melt exsolved per unit volume and unit time</td>
<td>m$^{-1}$s$^{-1}$</td>
</tr>
<tr>
<td>$f(V)$</td>
<td>Size distribution function of newly exsolved droplets</td>
<td></td>
</tr>
<tr>
<td>$V_0$</td>
<td>Characteristic volume of newly exsolved droplets</td>
<td>m$^3$</td>
</tr>
<tr>
<td>$r_0$</td>
<td>Characteristic radius of newly exsolved droplets</td>
<td>m</td>
</tr>
<tr>
<td>K($V, V'$)</td>
<td>Collision kernel</td>
<td>m$^3$·s$^{-1}$</td>
</tr>
<tr>
<td>$e(\beta, V')$</td>
<td>Collision efficiency</td>
<td></td>
</tr>
<tr>
<td>$\lambda(V, V')$</td>
<td>Normalized collision efficiency</td>
<td></td>
</tr>
<tr>
<td>$E(\beta)$</td>
<td>Reference collision efficiency at viscosity ratio $\beta$</td>
<td></td>
</tr>
<tr>
<td>$P$</td>
<td>Dimensionless exsolution rate; $P = (H/\mu(V_0))R_{\text{exs}}$</td>
<td></td>
</tr>
<tr>
<td>$L$</td>
<td>Dimensionless magma thickness; $L = H/r_0$</td>
<td></td>
</tr>
<tr>
<td>$\gamma$</td>
<td>Dimensionless coalescence efficiency; $\gamma = E(\beta)PL$</td>
<td></td>
</tr>
<tr>
<td>$dF/dT$</td>
<td>Amount of discrete melt exsolved per decrement of temperature</td>
<td>K$^{-1}$</td>
</tr>
<tr>
<td>$dT/dt$</td>
<td>Cooling rate of magma (absolute value)</td>
<td>K·s$^{-1}$</td>
</tr>
<tr>
<td>$\phi_s$</td>
<td>Volume fraction of melt droplets at steady state</td>
<td></td>
</tr>
<tr>
<td>$\tau$</td>
<td>Residence time (separation timescale) of melt droplets</td>
<td>s</td>
</tr>
</tbody>
</table>
where $r(V) = (3V/4\pi)^{1/3}$ is the radius of a melt droplet with volume $V$, $\Delta \rho$ is the difference in density between the discrete melt (i.e., melt droplets) and the continuous melt, $\mu$ is the viscosity of the continuous melt, $\beta = \mu_d/\mu$ is the viscosity ratio between the discrete melt and the continuous melt (here, $\mu_d$ is the viscosity of the discrete melt), and $g$ is the gravitational acceleration.

### 2.1. Magma Convection and Droplet Settling

The continuous melt flows in the magma chamber because of thermal and/or compositional convection (Figure 1a). Using the divergence theorem, we obtain

$$
\int_{\Omega} \nabla \cdot [n(V)(\mathbf{U} + \bar{u}(V))] \, d\Omega = \int_{A_b} n(V)(\mathbf{U} + \bar{u}(V)) \cdot d\mathbf{A}.
$$

(5)

where $\Omega$ is the whole magma body in which immiscibility occurs (i.e., the emulsified region; Figure 1), $d\Omega$ is the volume element, $A_b$ is the domain boundary (i.e., the boundary of the emulsified region $\Omega$), and $d\mathbf{A}$ is the outward-pointing area element vector. The convective flow of the continuous melt cannot cross the domain boundary, yielding the boundary condition $\mathbf{U} \cdot d\mathbf{A} = 0$. Therefore, Equation 5 can be transformed to

$$
\int_{\Omega} \nabla \cdot [n(V)(\mathbf{U} + \bar{u}(V))] \, d\Omega = \int_{A_b} n(V) \bar{u}(V) \cdot d\mathbf{A}.
$$

(6)

Assuming that the discrete melt is denser than the continuous melt, the melt droplets near the bottom leave the emulsified region $\Omega$ and form a separate layer beneath it (Figure 1a). The melt droplets in the interior continue to settle and feed the bottom of the emulsified region. Consequently, $n(V)$ at the bottom of the emulsified region $\Omega$ is the same as that in the interior. By contrast, the droplets near the top of the emulsified region $\Omega$ sink through the continuous melt, and no droplets are fed from above. Thus, the number density of melt droplets at the top boundary can be assumed to be zero (Figure 1b). Therefore, Equation 6 can be rewritten as

$$
\int_{\Omega} \nabla \cdot [n(V)(\mathbf{U} + \bar{u}(V))] \, d\Omega = \int_{A_b} n(V) u(V) \, dA.
$$

(7)

where $u(V)$ is the magnitude of $\bar{u}(V)$ and $A_b$ is the bottom boundary of the emulsified region $\Omega$.

Convection occurs in cooling magma due to the density contrast resulting from thermal and/or compositional fluctuations. The thermal Rayleigh number of typical magma chamber ranges from $10^8$ to $10^{10}$ ($10^8$ to $10^{12}$ for granitic and $10^{12}$ to $10^{16}$ for basaltic magmas) and the compositional Rayleigh number is typically several orders of magnitude larger (Martin et al., 1987). The Rayleigh number of magma chamber indicates that convection is likely unsteady/time-dependent (Martin et al., 1987) and convective velocities are much larger than the settling velocities of millimeter-size melt droplets (Martin & Nokes, 1988, 1989). Hence, the convective magma flow can homogenize the spatial distribution of melt droplets in the emulsified region $\Omega$ (Martin & Nokes, 1988, 1989). Therefore, $n(V)$ can be assumed to be independent of the position of the melt droplet. The integration of Equation 3 leads to

$$
|\Omega| \left[ \frac{\partial n(V)}{\partial t} - \Gamma_{\text{exs}}(V) - \Gamma_{\text{coal}}(V) \right] = -|A_b| n(V) u(V).
$$

(8)

where $|A_b|$ is the area of the bottom boundary $A_b$ and $|\Omega|$ is the volume of the emulsified region $\Omega$. The average thickness of the emulsified region $\Omega$ is calculated as $H = |\Omega| / |A_b|$ and taken as constant (see discussion in section 5). Hence, Equation 8 can be transformed to

$$
\frac{\partial n(V)}{\partial t} = -\frac{u(V)}{H} n(V) + \Gamma_{\text{exs}}(V) + \Gamma_{\text{coal}}(V).
$$

(9)
2.2. Melt Exsolution

The exsolution of immiscible melt occurs through different processes. New melt droplets form when nuclei overcome the free energy barrier to nucleation. On the other hand, preexisting melt droplets grow as species of the discrete melt diffuse into the droplets from the continuous melt to increase the discrete melt fraction or from smaller melt droplets through the continuous melt to reduce total interface energy (James, 1975; Zhang, 2008).

In this study, we assume that exsolution results only in the formation of new melt droplets and does not lead to the growth of preexisting melt droplets (Figure 1f). Furthermore, most newly exsolved melt droplets are assumed to be around a characteristic size. This characteristic size can be considered as a typical size that melt droplets can grow to through diffusion in the separation timescale. It has been demonstrated that the diffusive growth is the most significant for the smallest droplets (James, 1975; Zhang, 2008) while coalescence proceeds more rapidly for larger droplets (Wang & Davis, 1993). Therefore, it is reasonable to assume that diffusive growth occurs only for droplets which volumes are smaller than this characteristic volume while coalescence occurs between larger droplets. The production rate of melt droplets due to melt exsolution $\Gamma_{\text{exs}}(V)$ can be calculated as

$$\Gamma_{\text{exs}}(V) = R_{\text{exs}}(V),$$  \hspace{1cm} (10)

where $R_{\text{exs}}$ is the exsolution rate of the discrete melt (i.e., the volume of discrete melt exsolved per unit volume and time) with units of s$^{-1}$ and $f(V)$ is the size distribution function of the newly formed melt droplets with units of m$^{-3}$. Although the droplet characteristic size strongly affects the settling and coalescence processes, the specific formula adopted for the size distribution function is not essential and has only a slight influence (Martin & Nokes, 1988; Wang & Davis, 1993). An exponential distribution is used for the size distribution function:

$$f(V) = \frac{1}{V_0} e^{-(V/V_0)},$$  \hspace{1cm} (11)

where $V_0 = 4\pi r_0^3/3$ is the characteristic volume of newly exsolved melt droplets and $r_0$ is the characteristic radius of newly exsolved melt droplets. The factor $1/V_0^2$ is used so that $\int_0^\infty f(V) dV = 1$.

2.3. Droplet Coalescence

Coalescence can produce or consume melt droplets with a specific volume. The coalescence between two droplets with volumes $V'$ and $V - V'$ leads to the formation of a droplet with volume $V$. On the other hand, the coalescence between a droplet with volume $V$ and any other droplet results in the loss of this droplet with volume $V$ (Figure 1e). Therefore, the net production rate of melt droplets due to coalescence, $\Gamma_{\text{coal}}(V)$, is calculated as

$$\Gamma_{\text{coal}}(V) = \frac{1}{2} \int_0^V n(V') n(V - V') K(V - V', V') dV' - \int_0^V n(V') K(V, V') dV',$$  \hspace{1cm} (12)

where $K(V, V')$ is the collision kernel with units of m$^3$·s$^{-1}$ (Rogers & Davis, 1990; Wang & Davis, 1993). This collision kernel can be calculated as

$$K(V, V') = \pi \left[ r(V) + r(V') \right]^3 u(V') - u(V) \left| e(\beta, V, V') \right|,$$  \hspace{1cm} (13)

where $e(\beta, V, V')$ is the collision efficiency (Wang & Davis, 1993). The collision efficiency of two melt droplets with volumes $V$ and $V'$ depends on both the viscosity ratio $\beta$ and the volumes of the two melt droplets. We separate the dependence of collision efficiency on the viscosity ratio $\beta$ and the volumes of the melt droplets as

$$e(\beta, V, V') = E(\beta) \hat{\lambda}(V, V'),$$  \hspace{1cm} (14)

where $E(\beta)$, a function of the viscosity ratio $\beta$, is the reference collision efficiency of two encountering droplets with radii of 10 $\mu$m and $\hat{\lambda}(V, V')$, a function of $V$ and $V'$, is the normalized collision efficiency. The
collision efficiency is typically on the order of 0.1 when $\beta < 0.1$ (Manga & Stone, 1994; Zhang & Davis, 1991) and on the order of $10^{-4}$ or smaller when $\beta > 10^3$ (Rother et al., 1997; Zhang & Davis, 1991). It is extremely difficult to obtain an accurate value for $\lambda(V, V')$ (Rother et al., 1997). However, some approximations can still be made. If the volume ratio of the two encountering droplets is close to zero, the normalized collision efficiency $\lambda(V, V')$ becomes zero as well. The very small melt droplet simply follows the streamline surrounding the large one and passes by without collision and coalescence (Manga & Stone, 1994; Zhang & Davis, 1991). If droplet deformation and van der Waals attraction are neglected, $\lambda(V, V')$ is positively correlated to the radius ratio of the smaller droplet to the larger one and reaches a maximum when the volumes of two droplets are the same (Manga & Stone, 1994; Zhang & Davis, 1991). The effects of droplet deformation and interdroplet attraction are not significant in our model (see discussion in section 5). Therefore, an approximation can be obtained using

$$\lambda(V, V') = \min(r(V), r(V')) / \max(r(V), r(V')).$$

(15)

Under different geologic conditions, $E(\beta)$ can vary by several orders of magnitude (see section 6), which makes minimizing the uncertainty of $\lambda(V, V')$ nonessential. Therefore, this approximation of $\lambda(V, V')$ can be used to assess the droplet coalescence process.

### 2.4. Nondimensionalization

The number of independent parameters in the governing equations used to model the evolution of the droplet population density in the region $\Omega$, that is, Equations 9–15, can be minimized by nondimensionalization using the following dimensionless variables:

$$\tilde{V} = V/V_0, \quad \tilde{r} = r/r_0, \quad \tilde{f}(\tilde{V}) = V_0^2 f(V), \quad \tilde{u}(\tilde{V}) = u(V)/u(V_0) = \tilde{r}^2,$$

$$\tilde{K}(\tilde{V}, \tilde{V'}) = K(V, V')/\pi r_0^2 u(V_0) E(\beta)] = \left[\tilde{r}(\tilde{V}) + \tilde{r}(\tilde{V'})\right]^2 \tilde{r}(\tilde{V})^2 - \tilde{r}(\tilde{V'})^2 \tilde{\lambda}(V, V'),$$

$$\tilde{n}(\tilde{V}) = n(V)V_0^2 \sqrt{E(\beta)L/P}, \quad \text{and} \quad \tilde{t} = [tu(V_0)/H] \sqrt{E(\beta)L/P},$$

where the hatted variables are dimensionless, $P$ is the dimensionless exsolution rate (or the characteristic droplet fraction if coalescence is negligible in the emulsified region) defined as

$$P = (H/u(V_0)) R_{\text{exs}},$$

(16)

and $L$ is the dimensionless magma thickness defined as

$$L = H/r_0.$$

(17)

Thus, the governing equation can be transformed into a dimensionless equation as follows:

$$\frac{\partial \tilde{n}(\tilde{V})}{\partial \tilde{t}} = - \frac{\tilde{r}^2}{\gamma} \tilde{n}(\tilde{V}) + \tilde{f}(\tilde{V}) + \tilde{\gamma}_{\text{coal}}(\tilde{V}),$$

(18)

where $\gamma = E(\beta) PL$ is the dimensionless coalescence efficiency that quantifies the contribution of coalescence during melt droplet settling and $\tilde{\gamma}_{\text{coal}}(\tilde{V})$ can be calculated as

$$\tilde{\gamma}_{\text{coal}}(\tilde{V}) = \frac{3}{4} \int_0^1 \tilde{V} \tilde{n}(\tilde{V}) n(\tilde{V} - \tilde{V'}) \tilde{K}(\tilde{V} - \tilde{V'}, \tilde{V'}) d\tilde{V'} - \tilde{n}(\tilde{V}) \int_0^\infty \tilde{V} \tilde{n}(\tilde{V}) \tilde{K}(\tilde{V}, \tilde{V'}) d\tilde{V'},$$

(19)

As the only dimensionless parameter in Equation 18, $\gamma = E(\beta) PL$ controls the separation process of immiscible melt droplets. When no coalescence occurs in magma, the characteristic timescale of droplet settling is $H/u(V_0)$, and the volume fraction of immiscible melt droplets suspended in the emulsified region $\Omega$ is approximately $R_{\text{exs}}[H/u(V_0)]$ (Martin & Nokes, 1989). The characteristic timescale of
coalescence in magma with droplet volume fraction $\phi$ is roughly $r_0/\sqrt{\phi E(\beta)L/P}$ (Wang & Davis, 1993). The dimensionless coalescence efficiency $\gamma$ can be considered as the ratio between the characteristic coalescence timescale $H/u(V_0)$ and the characteristic coalescence timescale $r_0/\sqrt{\phi E(\beta)L/P}$ when $\phi = R_{ex}(H/u(V_0))$. If $\gamma \ll 1$, a melt droplet is unlikely to coalesce with any other droplet in the emulsified magma region $\Omega$; thus, coalescence is negligible in this separation process. In contrast, if $\gamma \gg 1$, a droplet is likely to continuously coalesce with other droplets until leaving region $\Omega$. Thus, coalescence plays an important role in the separation process.

Using the dimensionless droplet volume $\tilde{V} = V/V_0$ and dimensionless droplet population density $\tilde{n}(\tilde{V}) = n(V)\sqrt{E(\beta)L/P}$, Equation 2 can be transformed to

$$\int_{0}^{\infty} \tilde{V} \tilde{n}(\tilde{V}) d\tilde{V} = \frac{n(V)}{2} \sqrt{\frac{E(\beta)L/P}{V}} \tilde{V}^{\frac{1}{2}} = \phi \sqrt{\frac{E(\beta)L/P}{V}}. \quad (20)$$

This equation indicates that the droplet volume fraction $\phi$ can be normalized by a scale $\left(\frac{E(\beta)L/P}{V}\right)^{-1}$. This normalization scale is the characteristic droplet volume fraction when $\gamma \gg 1$ (see discussion in section 4). In the following discussion, we use the normalized droplet volume fraction, instead of the absolute droplet volume fraction, because it is more compatible with other variables in the nondimensionalized system.

### 3. Results

We solve Equation 18 using a finite difference scheme similar to that used by Wang and Davis (1993). Here, we set the initial condition to be $\tilde{n}(\tilde{V}) = 0$ (i.e., no preexisting immiscible melt droplets at $\tilde{t} = 0$). The temporal evolution path of normalized droplet volume fraction $\phi \sqrt{E(\beta)L/P}$ varies systematically with $\gamma$ (Figure 2). If $\gamma < 1$, the normalized volume fraction $\phi \sqrt{E(\beta)L/P}$ of suspended melt droplets decreases monotonically with time until reaching a steady state (Figure 2). By contrast, if $\gamma > 10$, the normalized volume fraction $\phi \sqrt{E(\beta)L/P}$ of the suspended melt droplets first increases with time at a nearly constant rate until $\tilde{t} \approx 2$ and then oscillates with decreasing amplitude until reaching a steady-state value. This evolution path is further discussed in Appendix A.

For all $\gamma$, when $\tilde{t} > 6$, a steady state is achieved (Figure 2) at which the volume fraction of melt droplets in the emulsified region $\Omega$ is constant: that is, the formation rate of new droplets is equal to the loss rate of droplets that continuously leave region $\Omega$ (Figure 1). Therefore, the residence time $\tau$ and the dimensionless residence time $\tilde{\tau}$ of droplets in the emulsified region $\Omega$ can be defined as

$$\tau = \phi_s / R_{ex}, \quad (21)$$

$$\tilde{\tau} = \tau u(V_0) / H \sqrt{E(\beta)L/P} = \phi_s \sqrt{E(\beta)L/P}. \quad (22)$$

where $\phi_s$ is the volume fraction of immiscible melt droplets in the emulsified region $\Omega$ at the steady state. This residence time can also be considered to be the separation timescale of the discrete melt from the continuous melt. Using the numerical results from Equation 18, a correlation can be established between the dimensionless residence time $\tilde{\tau}$ and the dimensionless coalescence efficiency $\gamma$ (Figure 3). This correlation indicates that there are two distinct regimes for $\tilde{\tau}$ (Figure 3). The dimensionless residence time $\tilde{\tau}$ is proportional to $\sqrt{\gamma}$ if $\gamma < 1$. However, the dimensionless residence time $\tilde{\tau}$ becomes a constant of about 1.5 if $\gamma > 10$. In general, the numerical results of Equation 18 at the steady state of both regimes can be well fitted using a simple formula:
Figure 3. Variation of the dimensionless residence time $\tilde{\tau}$ of melt droplets in magma with the dimensionless coalescence efficiency $\gamma$. Each circle represents a numerical result of Equation 18 at steady state. The solid line represents the fitting curve of Equation 23.

\[
\tilde{\tau} \approx \frac{-b + \sqrt{b^2 + 4a\gamma}}{2a\sqrt{\gamma}},
\]

with $a = 0.4$ and $b = 1.2$ (Figure 3), the derivation of which is given in Appendix B.

### 4. Separation Timescale of Melt Droplets in Magma

The dimensionless residence time can be dimensionalized to provide scaling relations correlating with the parameters that control the separation timescale $\tau \propto \mu H / (r_0^2 \Delta \rho g)$ when $\gamma < 1$ and the separation timescale $\tau \propto [\mu(\rho_0 \Delta \rho g R_{\text{ex}} E(\beta))]^{1/2}$ when $\gamma > 10$ (Figure 3). In the two different $\gamma$ regimes, the scaling relations are very different, as are the temporal evolution paths of the volume fraction of melt droplets (Figure 2). This difference indicates that the separation timescale of melt droplets is controlled by different mechanisms in the two regimes, which is illustrated by the steady-state size distributions of melt droplets suspended in $\varphi_{\text{sus}}$ and separated from $\varphi_{\text{set}}$ the emulsified region $\Omega$, calculated as follows:

\[
\varphi_{\text{sus}} = \frac{\bar{u}(\bar{V})}{\bar{\bar{u}}(\bar{V})} \frac{d\bar{V}}{d(\log_{10}(\bar{\bar{V}}))},
\]

\[
\varphi_{\text{set}} = \frac{\bar{\bar{u}}(\bar{V})}{\bar{\bar{u}}(\bar{V})} \frac{d\bar{V}}{d(\log_{10}(\bar{\bar{V}}))}.
\]

The difference between the size distributions of melt droplets ($\varphi_{\text{sus}}$ and $\varphi_{\text{set}}$) with different values of $\gamma$ is significant (Figure 4). The distributions $\varphi_{\text{sus}}$ and $\varphi_{\text{set}}$ are nearly equal when $\gamma$ is small (Figures 4a and 4b). This similarity indicates that the melt droplets rarely coalesce with each other before leaving the emulsified region $\Omega$. In this regime, the separation mechanism of immiscible melt droplets is very similar to that of crystals (Martin & Nokes, 1988). The separation timescale is therefore given as

\[
\tau \approx \frac{H}{u(V_0)} \propto \frac{\mu H}{r_0^2 \Delta \rho g},
\]

However, when $\gamma$ is relatively large (i.e., $\gamma > 10$), $\varphi_{\text{sus}}$ and $\varphi_{\text{set}}$ are very different (Figures 4c and 4d). The suspended discrete melt occurs mainly as droplets with volumes on the order of $V_0$, similar to volumes of newly exsolved melt droplets. By contrast, the discrete melt leaving the emulsified region $\Omega$ mainly consists of much larger melt droplets (i.e., $V \gg V_0$). This volume difference indicates that the newly exsolved droplets coalesce to form larger droplets before leaving region $\Omega$. Furthermore, the coalesced large melt droplets leave region $\Omega$ very rapidly. Therefore, the separation timescale in this regime is controlled by the coalescence of small droplets. For melt droplets with volumes on the order of $V_0$, the population density $n$ is on the order of $\phi_s/V_0$. The coalescence rate $\Gamma_{\text{coal}}$ is on the order of $n^2 r_0^4 \Delta \rho g E(\beta)/\mu$, and the exsolution rate $\Gamma_{\text{exs}}$ is on the order of $R_{\text{exs}}/V_0$. The settling of droplets with volumes close to $V_0$ is negligible. Hence, the equilibrium of formation and consumption of melt droplets with volumes near $V_0$ leads to

\[
\left( \frac{\phi_s}{V_0} \right)^2 r_0^4 \Delta \rho g E(\beta) / \mu \propto \frac{R_{\text{exs}}}{V_0}.
\]

This formula gives the scale of the steady-state droplet volume fraction in the emulsified region $\Omega$ as $\phi_s \propto [\mu R_{\text{exs}} / (r_0^4 \Delta \rho g E(\beta))]^{1/2}$, or equivalently, $\phi_s \propto [P(E(\beta) L)]^{1/2}$. The latter formula gives the normalization scale of the droplet volume fraction. The residence time $\tau = \phi_s / R_{\text{exs}}$ can thus be scaled as
There are two different evolution paths during the settling of immiscible melt droplets that depend on the value of γ. Two different mechanisms are needed to explain the two distinct temporal evolution paths of droplet volume fraction in the emulsified region Ω (Figure 2). The coalescence of melt droplets in magma with small γ is negligible. Therefore, the term of coalescence (Γ_{coal}) in the governing equation (Equation 18) can be neglected, that is to say, \( \partial n / \partial \tilde{t} \approx -\tilde{r}^2 \sqrt{\tilde{r}} \). This finding suggests that the segregation rate is nonnegligible from the very beginning. By contrast, in a magma with large γ, the newly exsolved melt droplets are too small to leave the emulsified region Ω. Coalescence can produce larger melt droplets at the expense of smaller ones, and the large droplets can be rapidly separated from region Ω. However, producing large droplets via coalescence takes time. Therefore, the segregation rate at the very beginning of the process (when \( \tilde{t} < 2 \)) is nearly zero (see Appendix A for further discussion).

5. Model Limitations and Validations

Some assumptions have been made in our model development to simplify the setup of this model. On the other hand, the assumptions could potentially limit the applications of this model. Therefore, it is important to discuss both the model limitations due to these assumptions and validations of the model.

The system in this model is a melt-melt mixture, in which crystals are not included. In natural magma, liquid immiscibility usually occurs during crystallization. The suspended crystals can affect the magma rheology.
Figure 5. Variation of the residence time $\tau$ with average radius $r_0$ for silica-rich melt droplets. The dashed line represents the residence time of melt droplets without coalescence. The solid lines represent the residence times of melt droplets with different values of $E(\beta) = 10^{-8}$ (blue), $10^{-6}$ (red), and $10^{-4}$ (orange). The parameters used in the calculations are $E(\beta) = 10^{-8}$, $10^{-6}$, and $10^{-4}$, $dF/dT = 10^{-3}$ K yr$^{-1}$, $dF/dT = 0.2$ vol$\%$ K$^{-1}$, $H = 1$ km, $\mu = 100$ Pa s, and $\Delta \rho = 400$ kg m$^{-3}$.

Melt droplets in the continuous melt can break into smaller ones due to the droplet deformation (Ichikawa et al., 2010). The breakup occurs mostly to droplets larger than a maximum stable size, which imposes an upper limit for the droplet size spectrum in the continuous melt (Ichikawa et al., 2010; Samuel, 2012). Our model results suggest that the separation timescale is controlled by the coalescence of small droplets in magma with large $\gamma$ and the large droplets produced by coalescence settle very rapidly. If the settling timescale of droplets with the maximum stable size is shorter than the predicted residence time, droplet breakup in magma does not affect our model. If the settling timescale of droplets with the maximum stable size is comparable or longer than the predicted residence time, melt separation timescale is likely controlled by the settling of droplets with the maximum stable size. This scenario has been suggested to occur during the segregation of liquid metal to form the Earth’s core from the terrestrial magma ocean (e.g., Ichikawa et al., 2010; Samuel, 2012). Therefore, we suggest that neglecting droplet breakup does not limit the application of our model in natural magma.

The van der Waals attraction and droplet deformation can affect the droplet collision efficiency. These effects are not considered in the normalized collision efficiency $\lambda(V,V')$, which is considered as a function of only the ratio of the droplet radii (Zhang & Davis, 1991). If droplets are much more viscous than the continuous melt (i.e., $\beta \gg 1$), it is difficult to evaluate the overall effect of van der Waals attraction and droplet deformation. The van der Waals attraction may increase the collision efficiency to $10^{-3}$ for droplets with radii of a few tens of micrometers (Zhang & Davis, 1991). The droplet deformation caused by the lubrication resistance between colliding droplets may decrease the collision efficiency, especially for droplets larger than a few tens of micrometers (Rother et al., 1997). It has been implied that deformation may reduce the collision efficiency to almost zero for droplets larger than a certain size (Rother et al., 1997). This effect essentially imposes an upper limit for the droplet size, similar to the droplet breakup. Therefore, the model on settling of droplets with large viscosity ratios (e.g., silica-rich droplets exsolved in iron-rich silicate melt) can have large uncertainties, especially when coalescence is important during melt separation. However, the model could still be reliable for the highly viscous droplets that settle efficiently without significant coalescence (i.e., small dimensionless coalescence efficiency $\gamma$). If the droplets are much less viscous than the continuous melt (i.e., $\beta \ll 1$), the effect of van der Waals attraction is very minor (Zhang & Davis, 1991) and the...
deformation may increase the collision efficiency of melt droplets due to the enhanced droplet alignment and reduced lubrication resistance (Manga & Stone, 1994; Rother et al., 1997). The deformation effect is not important for droplets smaller than a few millimeters (Manga & Stone, 1994). The separation timescale in our model is controlled by the coalescence between droplets around the initial exsolution size, which is usually a few to a few tens of micrometers. This size difference suggests that the deformation effect does not change the separation timescale much. Therefore, the overall effect of droplet deformation and van der Waals attraction is not important for droplets with low viscosity ratios (e.g., iron-rich silicate droplets exsolved in silica-rich melt, sulfide droplets exsolved in basaltic melt, and carbonate droplets exsolved in nephelinitic melt).

The temporal variations of model parameters (e.g., viscosity, exsolution rate, and magma thickness) are not considered in this model. In natural magma, these parameters change with time, depending on temperature (i.e., cooling) and composition (i.e., crystallization and immiscibility). Here we discuss cooling-induced variation because compositional change is related to magma cooling. The parameters do not change much if the decrease of temperature is small (a few to a few tens of degrees) over the melt droplet residence time. The model is reliable and the melt separation can be efficient. By contrast, if the decrease of temperature is large (e.g., over 100 K) over the droplet residence time, the chemical composition of melt can change significantly due to crystallization. It has been demonstrated that the compositional change caused by fractional crystallization can even drive the melt out of the two-liquid immiscibility field (Charlier et al., 2013). In this case, droplets that cannot settle rapidly may dissolve in the continuous melt, and the model is not applicable anymore. Therefore, this model can be applied to magmas that experience a temperature decrease of a few to a few tens of degrees.

Figure 6. Correlation between the residence time of silica-rich melt droplets and the viscosity of continuous iron-rich silicate melt. (a–c) Residence time τ; (d–f) temperature decrease of magma within one residence time τ · dT/dt. The average radii of newly exsolved melt droplets are assumed to be 500, 50, and 5 μm. The dashed lines represent the residence times of melt droplets without coalescence. The solid lines represent residence times calculated using Equation 23 with cooling rates of $10^{-3}$, $10^{-2}$, $10^{-1}$, and 1 K·yr$^{-1}$, respectively. $\beta(\beta) = 10^{-4}$ and $H = 1$ km.
6. Geological Implications

We have demonstrated that Equation 23 can fit the numerical results of Equation 18 with different γ (Figure 3). Thus, Equation 23 can be used to estimate the separation timescale, that is to say, the residence time of melt droplets. In this section, we use the estimated timescale to discuss the separation of immiscible melt droplets in natural magma undergoing liquid immiscibility.

The exsolution rate ($R_{exs}$) of immiscible melt droplets was previously considered to be an independent parameter. In natural magma, melt exsolution is driven thermodynamically and occurs as kinetic processes (see section 2.2). The kinetic processes are complicated and not very well understood (James, 1975; Zhang, 2008). In this study, we assume that these kinetic processes are rapid enough to keep magma close to equilibrium. Thus, the exsolution rate is controlled by the magma cooling rate as follows:

\[
R_{exs} = \left( \frac{dF}{dT} \right) \left( \frac{dT}{dt} \right),
\]

where $F$ is the “solubility” of the discrete melt (expressed with the volume fraction) in the magma and $T$ is the temperature. $dF/dT$ quantifies the amount of melt droplets produced in the magma with decreasing temperature, and $dT/dt$ is the cooling rate. In this section, $dF/dT$ and $dT/dt$ represent their absolute values.

6.1. Exsolution of Silica-Rich Melt

Liquid immiscibility can lead to unmixing of iron-rich and silica-rich silicate melts. The timing and extent of immiscibility in natural magma remain unsolved (McBirney, 2008; Morse, 2008; Philpotts, 2008; Veksler...
Figure 8. Variation of residence time $\tau$ with average initial radius $r_0$ of sulfide droplets in continuous basaltic melt. The dashed line represents the residence time of sulfide melt droplets without coalescence. The solid curves show residence times of sulfide melt droplets in basaltic magma with cooling rates of $10^{-3}$, $10^{-2}$, $10^{-1}$, and $1$ K·yr$^{-1}$; $\mu = 100$ Pa·s, $\Delta \varphi = 1,290$ kg·m$^{-3}$ (Kress et al., 2008), $dF/dT = 2 \times 10^{-4}$ vol%·K$^{-1}$ (Li & Ripley, 2009), and $H = 1$ km.

Cooling-induced crystallization can change magma composition and thereby affect (or even terminate) liquid immiscibility (Charlier et al., 2013). The extent of crystallization and magma composition change are controlled by temperature. Therefore, using $\tau (dT/dt)$—rather than $\tau$—to represent the efficiency of separation of immiscible melt droplets from the continuous melt is preferable. The model results suggest that, when the silica-rich melt exsolves as droplets with a characteristic radius $r_0 = 0.5$ mm, the separation timescale is not significantly different from that given by Equation 26, in which droplet coalescence is not considered (Figure 6a). The residence time of large melt droplets could be short enough for sufficient separation to occur in cooling magma (Figure 6d). However, according to the kinetic theory, the low interfacial tension between coexisting silicate melts (Veksler et al., 2010) could result in a high nucleation rate for exsolution and low Ostwald ripening rate of the melt droplets, forming numerous miniscule melt droplets in the magma during a period of silicate liquid immiscibility (James, 1975; Zhang, 2008). Thus, the exsolved silica-rich melt droplets could be very small, a few to a few tens of micrometers (e.g., Honour et al., 2019; Philpotts, 1982). The coalescence of melt droplets with small radii (smaller than a few tens of micrometers) becomes significant because such coalescence can greatly enhance the separation of immiscible silica-rich melt from the continuous iron-rich silicate melt (Figures 6e and 6f). However, even with the coalescence of melt droplets, in a small temperature range, a cooling rate of $\sim 1$ K·yr$^{-1}$ may be too high to efficiently separate immiscible silica-rich melt droplets from the continuous iron-rich silicate melt with viscosity of $\sim 100$ Pa·s. Note that these estimations could have large uncertainties because collision efficiency cannot be accurately determined (see discussion in section 5). Furthermore, the onset temperature of silicate liquid immiscibility is likely only several tens of degrees above the solidus (Charlier & Grove, 2012; Dixon & Rutherford, 1979). A complete separation of immiscible silica-rich melt may not occur in a fast-cooling magma.

It has been suggested that the exsolution of immiscible silica-rich melt droplets has occurred in the Skaergaard intrusion (Jakobsen et al., 2005, 2011; McBirney, 1975). The cooling rate of the Skaergaard magma at a temperature of silicate liquid immiscibility has been estimated to be on the order of $10^{-3}$ K·yr$^{-1}$ (Norton & Taylor, 1979), and the viscosity of the continuous iron-rich silicate melt has been estimated to be $\sim 100$ Pa·s (McBirney, 1975). Immiscible silica-rich melt droplets preserved in quenched volcanic rocks can be as small as $\sim 5$ mm (Philpotts, 1982), but the exsolved melt droplets in the slowly cooling Skaergaard magma may be larger. The separation timescale of silica-rich melt droplets with initial radii of 5–50 $\mu$m can be a few thousand years. Therefore, macroscopic separation of silica-rich melt droplets could have been achieved in the Skaergaard intrusion. This inference is consistent with the observation of et al., 2007). In a magma, silica-rich melt can exsolve as melt droplets (the discrete melt), resulting in an iron-rich silicate melt as the continuous melt (Charlier & Grove, 2012). The viscosity of the silica-rich melt is typically much higher than that of the coexisting iron-rich melt (Charlier & Grove, 2012; Hui & Zhang, 2007; Shaw, 1972). We assume that the characteristic collision efficiency $E(\beta)$ of the silica-rich melt droplets is $10^{-3}$ when viscosity ratio $\beta$ is $10^3$ (Zhang & Davis, 1991). The model results with such characteristic collision efficiency indicate that coalescence plays an important role in the separation of melt droplets with initial radii smaller than a few tens of micrometers (Figure 5). Note that the slight deformation of encountering melt droplets can make $E(\beta)$ even smaller (Rother et al., 1997), leading to an even longer residence time for melt droplets (Figure 5). Furthermore, the residence time of immiscible silica-rich melt droplets in the continuous iron-rich silicate melt depends on certain properties of the magma (Figures 6a–6c). The residence time increases with increasing viscosity ($\mu$) of the continuous melt and decreasing average radius $(r_0)$ of melt droplets. Rapid cooling of magma decreases the residence time. However, the decrease of residence time due to rapid cooling does not mean that the separation of melt droplets is more difficult in a slowly cooling magma (see below).
outcrop-scale felsic bodies in the upper zone of the Skaergaard intrusion (Jakobsen et al., 2011; Mc Birney, 1975).

6.2. Exsolution of Iron-Rich Melt

Iron-rich silicate (or iron oxide) melt can also exsolve from silica-rich melt as dispersed melt droplets in silicate magma (Charlier & Grove, 2012; Honour et al., 2019; Hou et al., 2018). The viscosity of the iron-rich melt is much lower than that of the continuous silica-rich melt (Charlier & Grove, 2012; Hou et al., 2018; Hui & Zhang, 2007; Shaw, 1972). Thus, the collision efficiency of less viscous droplets is likely high (Zhang & Davis, 1991) and the melt separation can be enhanced significantly by droplet coalescence (Figure 7). This type of immiscibility has been proposed to explain the formation of magnetite-apatite ore deposits at El Laco volcano in Chile (Tornos et al., 2017) and Marcona in Peru (Chen et al., 2010). The continuous melt in El Laco magma has been suggested to have a composition similar to the bulk magma, that is, hydrous andesite (Tornos et al., 2017). Experimental studies have shown that water preferentially partitions into the silica-rich melt, which can contain up to ~4 wt% water (Hou et al., 2018). Thus, during liquid immiscibility, the viscosity of the continuous andesitic melt containing 1–3 wt% water could be ~10⁻³–10⁻² Pa·s (Hui & Zhang, 2007). If the cooling rate is lower than ~0.1 K·yr⁻¹, millimeter-size crystals could settle rapidly to keep the crystal fraction below a few percent (Martin & Nokes, 1989). The iron-rich melt could be separated within a temperature decrease of less than ~10 K even if the initial droplet size is as small as ~5 μm (Figure 7). Therefore, our model suggests that the separation of iron-rich melt can be rapid enough to form magnetite-apatite ore deposits at El Laco (Tornos et al., 2017), as well as Marcona in Peru (Chen et al., 2010).

The exsolution of iron-rich melt from silicate melt has also been used to explain the gabbrons observed in the Critical Zone of the Sept Iles intrusion (Charlier et al., 2011) and in the upper zone of the Bushveld Complex.
Figure 10. Variation of the residence time of carbonatitic melt droplets with the viscosity of host nephelinitic melt. The average radii of newly exsolved carbonatitic melt droplets are assumed to be 50 (orange) and 500 (blue) μm. The dashed lines represent the residence times of carbonatitic melt droplets without coalescence. The shaded region shows the time interval between two carbonatitic eruptions (Dawson et al., 1968). The intervals between eruptions vary from several years to several decades (Dawson et al., 1968). The generation of carbonatitic lavas has been attributed to the exsolution of 2–20% of carbonatitic melt from nephelinitic magma (Pyle et al., 1991; Williams et al., 1986). The eruption frequency indicates that the magnitude of the exsolution rate of carbonatitic melt is much lower than that of basaltic melt (Dobson et al., 2000). The viscosity ratio between sulfide and silicate melts leads to $E(\beta) \approx 0.2$ (Zhang & Davis, 1991).

The separation timescale estimated using Equation 23 indicates that the effect of coalescence between sulfide melt droplets is negligible when the droplets exsolved in basaltic magma are relatively large (Figure 8). By contrast, coalescence can play an important role in the residence time of discrete sulfide melt in a fast-cooling magma, particularly for small melt droplets (Figure 8). Even if newly exsolved sulfide melt droplets are extremely small, the separation timescale is much less than 100 years for a basaltic magma with a cooling rate of $\sim 1$ K·yr$^{-1}$ (Figure 8). Laboratory experiments suggest that sulfide melt typically exsolves as minute droplets in the micrometer size range, which has been used to argue that segregation of small sulfide melt droplets may be difficult in natural magma (Holzheid, 2010). However, our calculations suggest that separation could be efficient even for droplets as small as a few micrometers in diameter (Figure 9). Two sequential steps have been proposed to form massive magmatic sulfide deposits: the settling of sulfide droplets in the basaltic melt and the migration of separated sulfide melt within the crystal mush (Chung & Mungall, 2009). Our model results suggest that settling of sulfide droplets in basaltic magma is sufficiently rapid. Therefore, the formation of massive magmatic sulfide deposits is likely controlled by migration of sulfide melt within the crystal mush (i.e., the second step).

6.3. Sulfide-Silicate Immiscibility

Mafic magma may be sulfide oversaturated and exsolve immiscible sulfide melt droplets in continuous silicate melt (Zhang, 2015). For a basaltic magma body during sulfide-silicate separation, the viscosity of sulfide liquid is much lower than that of basaltic melt (Dobson et al., 2000). The viscosity ratio between sulfide and silicate melts leads to $E(\beta) \approx 0.2$ (Zhang & Davis, 1991).

The separation timescale estimated using Equation 23 indicates that the effect of coalescence between sulfide melt droplets is negligible when the droplets exsolved in basaltic magma are relatively large (Figure 8). By contrast, coalescence can play an important role in the residence time of discrete sulfide melt in a fast-cooling magma, particularly for small melt droplets (Figure 8). Even if newly exsolved sulfide melt droplets are extremely small, the separation timescale is much less than 100 years for a basaltic magma with a cooling rate of $\sim 1$ K·yr$^{-1}$ (Figure 8). Laboratory experiments suggest that sulfide melt typically exsolves as minute droplets in the micrometer size range, which has been used to argue that segregation of small sulfide melt droplets may be difficult in natural magma (Holzheid, 2010). However, our calculations suggest that separation could be efficient even for droplets as small as a few micrometers in diameter (Figure 9). Two sequential steps have been proposed to form massive magmatic sulfide deposits: the settling of sulfide droplets in the basaltic melt and the migration of separated sulfide melt within the crystal mush (Chung & Mungall, 2009). Our model results suggest that settling of sulfide droplets in basaltic magma is sufficiently rapid. Therefore, the formation of massive magmatic sulfide deposits is likely controlled by migration of sulfide melt within the crystal mush (i.e., the second step).

6.4. Carbonate-Silicate Immiscibility

Periodical eruptions of carbonatitic lavas have occurred at Oldoinyo Lengai volcano since the 1880s (Dawson et al., 1968). The intervals between eruptions vary from several years to several decades (Dawson et al., 1968). The generation of carbonatitic lavas has been attributed to the exsolution of 2–20% of carbonatitic melt from nephelinitic magma (Pyle et al., 1991; Williams et al., 1986). The eruption frequency indicates that the magnitude of the exsolution rate of carbonatitic melt $R_{ex}$ is on the order of 1 vol%·yr$^{-1}$. The viscosity of carbonatitic melt is much lower than that of nephelinitic melt (Dobson et al., 1996). The viscosity ratio of these two melts leads to $E(\beta) \approx 0.2$ (Zhang & Davis, 1991). The separation timescale estimated using Equation 23 indicates that coalescence of carbonatitic melt droplets can significantly increase the efficiency of separating exsolved carbonatitic melt from nephelinitic melt (Figure 10). Therefore, the separation timescale of immiscible carbonatitic melt droplets is quite brief, even if the exsolved carbonatitic melt droplets are very small ($\sim 50$ μm) and the viscosity of the nephelinitic melt is very high ($\sim 10^8$ Pa·s). The rapid separation of the carbonatitic melt is consistent with the periodical carbonatite eruptions at Oldoinyo Lengai volcano (Figure 10).

7. Conclusions

We have developed a model for the separation of immiscible melt droplets from emulsified magma. Both exsolution of new melt droplets and coalescence of existing melt droplets have been considered in the
model. A dimensionless parameter $\gamma$ has been proposed to assess the contribution of coalescence of exsolved melt droplets during the separation of immiscible discrete melt. The coalescence of melt droplets is negligible when $\gamma$ is small; thus, the separation timescale of the discrete melt $\tau \propto \mu H / (r_0^2 \Delta \rho g)$. However, when $\gamma$ is large, droplet coalescence is the rate-controlling process during melt separation, and the separation timescale $\tau \propto [\mu / (r_0 \Delta \rho g R_{\text{ex}}E(\beta))]^{1/2}$.

The proposed model can be applied to natural magma, which experiences liquid immiscibility. Our results suggest that separation of immiscible silica-rich melt droplets is likely in a slowly cooling large magma body, such as the Skærgaard intrusion, but can be difficult in a rapidly cooling magma. The separation of iron-rich melt droplets from the continuous hydrous intermediate silicate melt can be efficient. This is consistent with the formation of magnetite-apatite ore deposits at El Laco and Marcona. The separation of exsolved sulfide melt droplets is relatively rapid in typical basaltic magma. Therefore, the settling of sulfide melt droplets in basaltic magma may not be the critical step to control the formation of massive magmatic sulfide ore deposits. Finally, the separation of exsolved carbonatitic melt droplets is sufficiently rapid to support the periodical carbonatitic lava eruptions at Oldoinyo Lengai volcano.

**Appendix A: Temporal Evolution of Droplet Volume Fraction**

The numerical results from simulations with $\gamma \gg 1$ show that the normalized volume fraction $\phi \sqrt{E(\beta) L / P}$ of the suspended melt droplets first increases with time at a nearly constant rate until $t \approx 2$ and then oscillates with decreasing amplitude until reaching a steady-state value (Figure 2). This temporal evolution path is briefly discussed using the simulation with $\gamma = 10^3$ as a typical example (Figure A1). Note that the simulation results are obtained in a nondimensionalized system.

Three new variables are used to show the simulation results (Figure A1), defined as follows:

$$\tilde{R}_{\text{set}} = \frac{1}{\sqrt{\gamma}} \int_0^\infty \tilde{u}(\tilde{v}) \tilde{a}(\tilde{v}) \tilde{V} d\tilde{V},$$

(A1)

$$\mathcal{N}_{\text{set}} = \phi_{\text{set}} \left[ \sqrt{E(\beta) L / P} \right],$$

(A2)

$$\mathcal{N}_{\text{set}} = \phi_{\text{set}} \tilde{R}_{\text{set}},$$

(A3)

where $\tilde{R}_{\text{set}}$ is the dimensionless separation rate of melt droplets, $\mathcal{N}_{\text{set}}$ is the contribution of droplets with different sizes to the volume of droplets suspended in the emulsified region $\Omega$, and $\mathcal{N}_{\text{set}}$ is the contribution of droplets with different sizes to the separation rate of discrete melt. The droplet volume fraction increases initially due to exsolution. However, separation at this stage in the emulsified region $\Omega$ is very low (Figure A1c) because the droplets are very small (the blue curve in Figure A1a). Consequently, the droplet volume fraction increases almost linearly and eventually exceeds the steady state (Figure 2). As exsolution proceeds in the emulsified region $\Omega$, larger droplets form through coalescence (the orange and yellow curves in Figure A1a), leading to an increasing separation rate (Figures A1b and A1c). Thus, the droplet volume fraction starts to decrease rapidly (Figure 2). As the large droplets settle, the droplet size distribution (the purple curve in Figure A1a) approaches the steady state (the green curve in Figure A1a), as do the droplet volume fraction and separation rate (Figures A1b and A1c). The droplet volume fraction oscillates around the steady-state value with a decreasing amplitude (Figures 2 and A1c). It is difficult to obtain the characteristic timescales of the attenuated oscillation due to nonlinear nature of the coalescence term. However, all the evolution paths with $\gamma \gg 1$ are similar in the dimensionless coordinates (Figure 1), indicating that the characteristic timescales are likely controlled by coalescence. This evolution path has been demonstrated both theoretically (Wang & Davis, 1995) and experimentally (Wang & Davis, 1996).

**Appendix B: Derivation of Equation 23**

Two different mechanisms have been identified when emulsified magma reaches a steady state, which ultimately lead to two different scaling laws (Equations 26 and 27) for the separation timescale (the residence time). In this appendix, the two mechanisms are combined, and a general formula (Equation 23) for the residence time is derived.
The discrete melt suspended in the magma primarily consists of droplets with volume of approximately $V_0$ (Figure 4); thus, we only need to consider the formation and consumption of these droplets to calculate the volume fraction of the suspended discrete melt. The consumption rate of melt droplets with volume of approximately $V_0$ due to settling is approximately proportional to $\dot{\phi} u(V_0)/H$, and this rate, in a dimensionless form, is proportional to $\dot{\phi}/\sqrt{\gamma}$, where $\dot{\phi}=\sqrt{E(\beta)L/P}$. In contrast, the consumption rate of droplets with volume of approximately $V_0$ due to coalescence is roughly proportional to $\dot{\phi}^2 r_0^2 u(V_0)E(\beta)/V_0$ (see Equation 27) and thus to $\dot{\phi}^2$ in a dimensionless form. The dimensionless exsolution (i.e., formation) rate of immiscible melt droplets is unity. Therefore, the volume fraction of melt droplets in emulsified magma at steady state can be described as

$$a\dot{\phi}^2 + \frac{b}{\sqrt{\gamma}} \dot{\phi} = 1,$$

(A4)

where $a = 0.4$ obtained via calculating $1/\dot{\phi}^2$ when $\gamma \gg 1$ and $b = 1.2$ obtained via calculating $\sqrt{\gamma}/\dot{\phi}$ when $\gamma \ll 1$. Solving Equation A4 leads to Equation 23 as $\dot{\gamma} = \dot{\gamma}_s$ at steady state. In theory, both $a$ and $b$ depend on the droplet size distribution, and thus on $\gamma$. However, Equation 23 can fit all the numerical results for different $\gamma$ explored in our numerical experiments (Figure 3), suggesting that in practice, $a$ and $b$ do not change substantially with $\gamma$.

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### References


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**Figure A1.** Nondimensionalized temporal evolution of melt droplet in the emulsified region $\Omega$ with $\gamma = 10^3$. (a) The contribution of droplets with different sizes to the volume fraction of suspended droplets $\phi_{\text{em}}$ at different dimensionless time. (b) The contribution of droplets with different sizes to the separation rate $\phi_{\text{se}}$ at different dimensionless time. (c) The trajectory of the evolution of normalized droplet volume fraction $\phi\sqrt{E(\beta)L/P}$ and dimensionless separation rate $\dot{\rho}_{\text{se}}$. The circles on the trajectory with different colors correspond to the normalized droplet volume fraction and dimensionless separation rate at different dimensionless time, the same as those in (a) and (b).


