MND (microlite number density) water exsolution rate meter

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1. Introduction

Since the pioneering works of Wilson and coworkers (Wilson et al., 1978, 1980), the modeling of conduit flow has undergone significant enhancement. We can now form a graphical output of the steady state ascent velocity of magma in the conduit through the Internet given the chemical composition and phenocryst contents (Martin and Chiorso, 2000). Further, the effects of the crystal content and vesiculation on the transient behavior of conduit magmas have been studied (Melnik and Sparks, 1999; Wylie et al., 1999). In addition, it has been recognized that the transition between explosive and non-explosive eruptions is controlled by the ascent velocity in the conduit and degassing from the magma column due to a permeable flow (Jaupart and Allègre, 1991; Woods and Koyaguchi, 1994). Hence, the theoretical flow behavior has been well understood during this decade, although important issues such as magma fragmentation, propagation of vesiculation, and unsteady flow problems remain unsolved. On the other hand, only Rutherford and Hill (1993) succeeded in the quantitative estimation of the flow dynamics based on the decompression-induced breakdown rim of the amphibole in the case of the 1980–1986 Mount St. Helens eruptions. The current status of the studies on conduit dynamics reveals a lack of natural evidence for theory. This suggests that modeling studies are rather predominant and direct observations or quantitative estimations of conduit flow dynamics using the erupted materials are required.

Microlites in effusive or pyroclastic rocks are possible indicators of water exsolution. In particular, the microlite number density (MND) is considered to be a function of the rate of water exsolution from melt. In this paper, we have constructed a MND water exsolution rate meter based on the recent results of theory, experiments and the natural observation of crystallization kinetics. The MND method accounts for the effects of melt composition and water content on the diffusivity of crystallizing components in melt. By using this meter, we can estimate the water exsolution rate at the microlite nucleation depth from a MND value provided the crystal phase (plagioclase or clinopyroxene) is known. We applied the meter to the case of the 1991–1995 dome eruption at Unzen and the 1986B subplinian eruption at Izu-Oshima. We obtained the water exsolution rates in the range of $6.1 \times 10^{-6}$ to $2.8 \times 10^{-5}$ (wt.%/s) approximately at 70 (MPa) for Unzen (plagioclase MND = $10^{15}$ to $10^{17}$ (m$^{-3}$)) and $1.1 \times 10^{-3}$ to $1.1 \times 10^{-1}$ (wt.%/s) for Izu-Oshima (pyroxene MND = $10^{15}$ to $10^{17}$ (m$^{-3}$)). Under the assumption of equilibrium vesiculation and steady state flow, the corresponding decompression rate and ascent velocity are calculated in the range of 240 to 1100 (Pa/s) and 0.014 to 0.068 (m/s) for Unzen and 1.2×10$^4$ to 1.3×10$^6$ (Pa/s) and 1.3 to 133 (m/s) for Izu-Oshima. This contrast in the ascent velocity at the microlite nucleation depth is closely related to the reason why Unzen and Izu-Oshima revealed the different eruption styles, namely, dome growth and explosive eruption, respectively.
High MND (microlite number density) values are a characteristic of microlites. In Fig. 1, the MND data compiled for various volcanic rocks show systematic variations with distance from the margin and the crystal phases. We observe that the MND values are in the range of $10^4$ to $10^9$ (mm$^{-3}$) or $10^{13}$ to $10^{18}$ (m$^{-3}$). For comparison, the highest crystal number density ($10^6$ mm$^{-3}$) of the groundmass at the margin (distance of 1 mm to 1 cm from the contact, just inside the chilled margin) in mafic dikes (Gray, 1970, 1978) is also shown. Since the groundmass crystal number densities of the dikes systematically vary with the distance from the margin, they reflect the cooling rate variation (Gray, 1970, 1978; Toramaru, 2001) (see later). It is evident that the groundmass crystals are formed due to cooling by the country rocks. The MND values of some basaltic anodesic and andesitic rocks are very high, as shown in Fig. 1. If we try to explain these MNDs on the basis of the cooling-induced crystallization, it appears that a higher cooling rate corresponding to a distance of less than 1 mm from the contact between the country rocks and dikes, where a chilled margin is normally formed, is required. Although the effects of the melt composition and the effective cooling rate could be offset with a more accurate examination, these high MNDs suggest that the microlites in the effusive or pyroclastic rocks are not formed by cooling. Rather, they are formed by supersaturation due to the effect of water exsolution on the increase in the liquidus temperature during the decompression and vesiculation of magmas.

In this paper, we focus on the MND as an indicator of the water exsolution or the decompression rate, and develop a new method for the quantitative estimation of the water exsolution rate from the MND. First, we demonstrate the fundamental aspects of phase diagrams by using some simple water-bearing and realistic systems to examine the microlite formation process, by emphasizing on the analogy between the cooling-induced and the decompression-induced crystallization. Second, we describe a procedure to construct a MND water exsolution rate meter, derive an equation to calculate the decompression rate and ascent velocity. Third, we address the validity and limitation of the MND method by applying it to the Izu-Oshima 1986B subplinian eruption. Lastly, we illustrate the method by using the 1991–1995 Unzen eruptions as an example.

### 2. Construction of the MND water exsolution rate meter

#### 2.1. Analogy between the decompression-induced crystallization and the cooling-induced crystallization

In this section, we address the assumption on which the water exsolution rate meter is constructed. The basic assumption is the equivalence between the decompression-induced crystallization and the cooling-induced crystallization. The liquidi of the crystallizing phases are influenced by the water content. This effect is essential for the decompression-induced crystallization of microlites. Fig. 2 shows the effects of $H_2O$ or the water-saturation pressure $P_W$ on the diopside (Di)-anorthite (An) eutectic system (Yoder, 1965; Kushiro, 1979) as a simple example of phase diagrams for minerals that are common to the groundmass of volcanic rocks such as plagioclase and pyroxene. This figure indicates that both the cooling (thick arrow from point Q) and water exsolution (arrow from the liquidus curves at $P_W$=5 kbar) by decompression have the same effect that brings the system to the supersaturated state for the crystallized mineral in a similar manner. Therefore, we can apply quantitative understanding on the crystallization kinetics by cooling to that on the decompression-induced crystallization. The difference between cooling and decomposition is that the effect of water on the liquidus depends on the phase of the mineral. For instance, it is found that the effect of the water-saturation pressure on the liquidus of anorthite is more intensive than that on the diopside one (this is clearly shown by the difference of $b$ value, see later in detail). Therefore, the eutectic composition shifts toward anorthite-rich component with an increase in $P_W$. In other words, at a low pressure $P_W$, plagioclase tends to crystallize first. Hence, the composition $C_{Di-Ab}$ and temperature $T_{Di-Ab}$ of the eutectic point $E_{Di-Ab}$ of the binary system consisting of anhydrous minerals are functions of the water content or water-saturation pressure.

The combination of an anhydrous mineral and water results in a eutectic system such as albite (another end member of plagioclase) and $H_2O$, as reported by Yoder (1976). The difference between this system and the solid–solid eutectic system is the negative slope of the phase boundary of liquid(L)/liquid+$H_2O(vapor)\cdot(L+V)$, which is due to the negative $H_2O$-exsolution heat. The composition $C_{Di-Ab}$ and temperature $T_{Di-Ab}$ of the eutectic point $E_{Di-Ab}$ of the anhydrous solid+$H_2O$ binary system are also functions of the confining pressure.

An important feature is that all the phase boundaries and eutectic or cotectic points move with a change in the confining pressure. To observe

![Fig. 2. Effects of $H_2O$ or $P_W$ on diopside (Di)-anorthite (An) eutectic system. $E_{Di-Ab}$ denotes the eutectic point at $P_W$=10 kbar. $C_{Di-Ab}$ and $T_{Di-Ab}$ indicate the composition and temperature of $E_{Di-Ab}$ (Yoder, 1965; Kushiro, 1979).](image-url)
this, in Fig. 3a, we show the eutectic temperature $T_{Eut}=\phi$ in albite–H$_2$O, anorthite–H$_2$O and diopside–H$_2$O systems as a function of pressure (Burnham and Davis, 1974; Yoder, 1965; Hodges, 1974). As a function of the increasing rate of $dT/dt$, the Plagioclase liquidus decreases with $-\Delta T/s$ for a water-saturated condition.

On the basis of the description presented in the previous section, the crystallization induced by water exsolution is equivalent to that due to simple cooling when the cooling rate $|dT/dt|$ is replaced with an increasing rate $dT/dt$ of liquidus due to water exsolution. In the case of linear cooling crystallization of a binary eutectic system, a numerical simulation (Toramaru, 1991, 2001) reveals that the MND is proportional to the $3/2$ power of the cooling rate. Therefore we can express MND or $N (\text{m}^{-3})$ as a function of the increasing rate of $dT/dt$ (K/s) as follows:

$$N = a \left(\frac{dT}{dt}\right)^{3/2},$$

where $a$ is the kinetic factor. This is expressed as $10^{3.5} \times C_0 (16a\gamma^2c^2/3k_1T_0)^{1/2} (12\psi D/4\pi K T_0)^{-1/2}$, where $C_0$, $\gamma$, $v$, $\phi_0$, $T_0$, $k_1$, and $D$ denote the number of molecules of crystallizing components per unit volume, interfacial tension between the crystallizing phase and melt, volume of the crystallizing molecule, initial volume fraction of the crystallizing phase, initial liquidus of the crystallizing phase, Boltzmann constant and effective diffusivity of the crystallizing component, respectively. The numerical factor $10^{3.5}$ depends on the shape of the assumed liquidus of the crystallized phase in the binary eutectic system in the numerical experiment (represented by a dimensionless parameter $\Delta s/k_0$; $\Delta s$ is the fusion entropy of the crystallizing phase per molecule) and the effect of latent heat release (represented by the Stefan number $\delta$). In this paper, we do not determine the value of $a$ using the data on these material

![Fig. 3](image-url)

**Fig. 3.** (a) The eutectic temperature, $T_{Eut}$, in albite–H$_2$O, anorthite–H$_2$O, and diopside–H$_2$O systems as a function of pressure (Burnham and Davis, 1974; Yoder, 1965; Hodges, 1974). (b) Comparison between the plagioclase liquidus by experiments and those by MELTS calculations for groundmass and bulk compositions of the Unzen 1991–1995 eruptions. Bulk experiment is from Holtz et al. (2005). Groundmass experiments from Sato et al. (1999). Note that curves other than PI for bulk composition have similar slopes. The experimental liquidus approximate few points of data satisfying the water-saturated condition.

### 2.2. Relationship between MND and increasing rate of liquidus

<table>
<thead>
<tr>
<th>Table 1</th>
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<tr>
<td>Water-free melt compositions assumed for Unzen dacite and Izu-Oshima basaltic andesite</td>
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<table>
<thead>
<tr>
<th>Component</th>
<th>Unzen*</th>
<th>Izu-Oshima**</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>68.14</td>
<td>54.62</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>0.57</td>
<td>1.27</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>15.08</td>
<td>14.55</td>
</tr>
<tr>
<td>FeO</td>
<td>3.78</td>
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<tr>
<td>MgO</td>
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<td>CaO</td>
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<tr>
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<td>0.47</td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
<td>0.14</td>
<td>0.10</td>
</tr>
<tr>
<td>Total</td>
<td>100.0</td>
<td>100.0</td>
</tr>
</tbody>
</table>

*Data from Nakada and Motomura (1999).  **Data from Fujii et al. (1988).
properties (e.g., γ or ν) and the value of the numerical factor calculated in the numerical experiment. The reasons for this are as follows: (1) γ at the nucleation stage is not well constrained in the experiments; (2) ν is a hypothetical quantity, but not a property with the reality determined by experiments; (3) the numerical factor 10^{1.5} depends on the detailed shape of the liquidus curve in the cooling-induced crystallization, and it is still unclear how this value is influenced by the decomposition-induced crystallization; (4) the numerical factor includes the uncertainty by the numerical solution. Despite the ambiguity of these values, we can understand the dependences of these properties on MND and use the knowledge of them in constructing the MND rate meter.

It is significant that only the diffusivity of the crystallizing component in melt has a remarkable dependence on the composition of melt including H₂O, and that other properties such as γ and ν have no evident dependence on the composition and are effectively almost canceled arithmetically. Therefore, we consider a as an adjustable constant except for the SiO₂ dependence of the diffusivity of the crystallizing component. In addition, we must note here that we use the equivalence between the cooling-induced crystallization and the decomposition-induced crystallization. In other words, the value of a that is determined for the cooling-induced crystallization can be applied to the decomposition-induced crystallization. According to this, in the next subsection, we determine the value of a using dike data from the natural experiment of the cooling-induced crystallization.

The physics behind Eq. (1) can be interpreted by expressing the nucleation rate as a function of the degree of supersaturation. Generally, we consider that the nucleation rate responds nonlinearly to the degree of supersaturation, as shown in Fig. 4. An increase in liquidus ΔT_l raises the degree of supersaturation ΔS. In this figure, the instantaneous nucleation rate is determined for a certain value of ΔS. In the case of a continuous change in temperature (cooling-induced) or liquidus (decomposition-induced), the maximum nucleation rate J_{max} can be achieved during the entire history of crystallization determines the MND. More importantly, J_{max} should be different from the apparent maximum rate of nucleation J_0 which is determined by constant ΔS experiments. In fact, J_{max} is determined by the interplay between the increase in ΔS due to the rising of liquidus and the decrease in ΔS due to the depletion of the crystallizing component resulting from the growth of nucleated crystals. It is known that J_{max} is proportional to the increasing rate of supersaturation, specifically, to the 5/2 power of dT_l/dt, J_{max} ∝ (dT_l/dt)^{5/2}. The power of 5/2 originates from the classical theory of homogeneous nucleation and the diffusion-limited growth in the nucleation stage. The MND is determined by the product of J_{max} and nucleation duration 6τ; N = J_{max} × 6τ. J_{max} is proportional to the time scale of supersaturation or inversely proportional to dT_l/dt. Hence, the MND is proportional to the 3/2 power of dT_l/dt. The power 3/2 is related to the diffusion-controlled growth law which is proportional to the square root of time. A more detailed illustration is given in Toramaru (2001).

2.3. Determination of a

The constant a can be determined by fitting the model prediction under the assumption of conductive cooling (Toramaru, 2001), i.e., |dT_l|/dt ∝ γ^{-2}, where γ denotes the distance from the contact of the dikes, to the natural data on solidified mafic dikes. Fig. 5 compiles the data obtained by Gray (1970, 1978) together with the model prediction lines. The model lines for plagioclase, pyroxene, and oxide are drawn with the following control point: MND = 5 mm^3 for plagioclase, pyroxene and oxide at a distance of 10^3 mm. For 50 wt.% SiO₂, which represents the compositions of these mafic dikes (normally negligible water content C_w = 0 wt.% can be assumed), the value of a is derived as 3 × 10^{15} ± 1 for plagioclase, pyroxene and oxide. The bound ±1 accounts for data dispersion.

It should be noted that a depends on SiO₂ and the water concentration in the melt and temperature only through the diffusivity of the crystallizing component a as a = D_{CI}^{1/2}, as argued in the last section. In this case, we consider that the crystallization components can be represented by Si. Si diffusion is the slowest among the diffusivities of major species in silicate melts such as Ca and Al (Baker, 1992; Liang et al., 1996a), and is controlled by the melt polymerization. The diffusivity of Si in silicate melts is related to the viscosity of the melt γ as a measure of melt polymerization, by the following equation: D_{CI} ∝ γ^{-0.8} (Liang et al., 1996a). The viscosity of the silicate melt is constrained effectively as a function of the silica concentration C_{Si}, water content C_w, and temperature T as γ = exp[0.46(C_{Si} - 72) - 1.25C_{w} + 2 × 10^{11}/T] (Toramaru, 1995). Furthermore, the temperature of magmas is correlated with C_{Si} as T = 10^{7}/(0.16 + 0.01C_{Si}) (Toramaru, 1995). Finally, from these relationships, it is found that the diffusivity of Si in silicate melts depends on C_{Si} and C_w, i.e., D_{CI} = exp(-0.53C_{Si} + C_w) (direct measurement by Baker (1991) shows the dependence on H₂O by the term exp(0.77C_{w})). By considering the SiO₂ and water dependence of diffusivity, we obtain

\[
a = 3 \times 10^{15} ± 1 \times 10^{15} \times \frac{0.34S_{C_{Si}} - 0.65S_{C_{w}}}{\delta}
\]

for plagioclase, pyroxene and oxide, where ΔC_{Si} = C_{Si} - 50, and C_{Si} and C_{w} in wt.%. Then, we can plot the MND as a function of the effective cooling rate, C_{Si} and C_{w} from Eqs. (1) and (2), as shown in Fig. 6. We can estimate the increasing rate of the liquidus from the MND value as follows:

\[
\frac{dT_l}{dt} = \left( \frac{N}{a} \right)^{2/3}
\]

The dependence of the MND on distance (Fig. 5) can be explained by the cooling-induced crystallization and not by the decomposition-induced crystallization since the cooling rate because the decomposition rate does not systematically changes with the distance from the margin of the dikes. The model lines of pyroxene and oxide can successfully account for the trend exhibited by most of the observational data. On the other hand, the model line for plagioclase disagrees with this approximate trend. However we think that this discrepancy is not important for the decomposition-induced crystallization by the following reason. This discrepancy implies that the plagioclase nucleation in cooling dikes is controlled by a nucleation style that is different from that of a simple homogeneous nucleation, which is assumed to generate the model prediction lines. The difference in the nucleation styles is possibly related to the pre-nucleation condition. Normally, the initial water content of the mafic magmas that form the dikes is very low and these magmas vesiculate at shallower depths, resulting in a very small degree of supersaturation for liquidus phase microcline nucleation (the
The supercooling required for nucleation is estimated to be approximately 80 °C for the plagioclase of the Unzen 1991–1995 dacite: see the application section for details. The normative compositions of all the dikes reveal that plagioclase is the liquidus phase (Fig. 7). On the other hand, pyroxene and oxide represent the second and third crystallizing phases, respectively, which are initially above their liquidi. Initially, in the mafic dikes, plagioclase is slightly below the liquidus; however, it does not crystallize and forms molecular clusters. Thus, in comparison with the pre-existing cluster-free condition which is expected for the decompression-induced crystallization, the number density of groundmass plagioclase and the related crystal morphology formed by the cooling-induced nucleation with preexisting clusters are significantly insensitive to the cooling rate (Grove, 1990; Sato, 1995). This explains the

Fig. 6. MND of plagioclase as a function of SiO₂ content for various effective cooling rates. (a) Cw = 0 wt.%. (b) Cw = 3.5 wt.%. Hatched area covers MND range in natural samples in Fig. 1.

Fig. 7. Normative plots on the diopside–anorthite–albite ternary diagram for mafic dikes reported by Gray (1978). The solid curve represents the cotectic line at 1 bar.
reason for the difference between the distance dependences of plagioclase MNDs and those of pyroxene and oxide in the cooling mafic dikes. In the case of the decompression-induced crystallization in extrusive rocks, we believe that plagioclase, pyroxene, and oxide microlites start to crystallize under super- or on-liquidus condition. In conclusion, for plagioclase, pyroxene, and oxide, we can assume the same dependence of the MND on the increasing rate of the liquid (i.e., the exponent 3/2).

2.4. Relationship between the increasing rate of liquidus and the water exsolution rate

We determine the relationship between $\frac{dT_L}{dt}$ (K/s) and $\frac{dC_{W}}{dt}$ (wt.%/s) from the phase diagrams of the water-bearing systems presented in the previous section. We assume the following linear relationship:

$$\frac{dT_L}{dt} = b \frac{dC_{W}}{dT}$$

(4)

where $b$ is the thermodynamic factor defined by $\frac{dT_L}{dC_w}$. Fig. 8 gives the plot of the liquidus of plagioclase and clinopyroxene as functions of $C_{W}$ (wt.%), which is calculated by MELTS. The linearity of $T_L(C_w)$ in Fig. 8 suggests that the assumption of Eq. (4) is valid in the margin of error (see the later discussion). From this figure, $b$ is calculated as follows:

$$b = 40$$

(5a)

for plagioclase in the Unzen dacite and Izu-Oshima basaltic andesite and

$$b = 17$$

(5b)

for the clinopyroxene in the Izu-Oshima basaltic andesite. The dependence of $b$ on the melt composition for plagioclase seems to be negligible judging from the curve for Unzen and Izu-Oshima in Fig. 8. The $b$ value and stability for pyroxene seems to depend on the melt composition; hence, the precise value of $b$ should be determined by experiments using natural samples. However, experiments (e.g. Moore and Carmichael, 1998) at lower pressures – up to 3 kbar – cannot provide a detailed shape of the liquidus curve because of the paucity of experimental conditions in the $P_{w}-T$ space, although the value of $b$ is similar to that of Eq. (5b).

We have to address the thermodynamic definition of $b$. According to Burnham model of water-bearing albite system (Burnham, 1979), we can write the liquidus of albite $T_L(C_w)$ as a function of water content $C_w$ at the water saturated state or eutectic temperature with water as follows.

$$T_L(C_w) = \frac{T_0 + K(C_w) \Delta v}{\Delta s - k_0 \ln(1 - \frac{C_w}{C_w^o})}$$

where $T_0$ is the melting temperature of the pure crystallizing phase; $C_w^o$=12, the scale of water content (mole fraction of water 0.5 corresponds to 6 wt.% at 200 MPa); $\Delta s$ is the entropy of fusion per molecule; $\Delta v$, the volume change (per molecule) of the crystallizing substance during melting; $K$, the solubility constant for $P=K(C_w/C_w^o)^{2}$; and $k_0=8 \times 10^8$ with $C_w=6$ wt.% at $P=200$ MPa (Burnham, 1975); $b$ is represented by $2k_0 T_0/(C_w \Delta s)$ as a first order approximation. So the difference in $b$ is primarily caused by the difference in $T_0/\Delta s$, which leads to $b=26.9$ for diopside ($\Delta s=-(enthalpy of fusion, 34$ kcal/mol)/$T_{298}=1.43 \times 10^{-22}$ (J/molecule) with $T_{298}=1665$ K), $b=55.1$ for anorthite ($\Delta s=-(enthalpy of fusion, 20$ kcal/mol)/$T_{298}=7.63 \times 10^{-23}$ (J/molecule) with $T_{298}=1830$ K), and $b=42.5$ for albite ($\Delta s=-(enthalpy of fusion, 15$ kcal/mol)/$T_{298}=7.53 \times 10^{-23}$ (J/molecule) with $T_{298}=1391$ K) (representative data from Well et al. (1980)). The difference of these values between pyroxene and plagioclase in simple systems are consistent with the MELTS calculations. Here, we adopt the values from MELTS because the multicomponent effect is taken into account by more relevant way.

The second order term of $T_L(C_w)$ is $(\Delta s/4k_0 T_0^2) - 1 + 4k_0/\Delta s)$, or $T_0(\Delta s/C_w^o)$. Normally this value is negligibly smaller than the first order term by one or two orders of magnitude (~0.29 for diopside, ~1.2 for anorthite and ~1.4 for albite with $\Delta s=1.5 \times 10^{-7}/6 \times 10^{-23}$ (m$^3$)). Thus, the linear approximation in Eq. (4) is valid.

2.5. Derivation of the MND water exsolution rate meter

The substitution of Eq. (4) in Eq. (1) results in the expression of the MND as a function of the water content

$$N = a \left| \frac{dC_w}{dt} \right|^{2/3}$$

Further, we obtain the water exsolution rate as a function of the MND:

$$\left| \frac{dC_w}{dt} \right| = k N^{2/3}$$

(6)

where $k$ is defined by $1/(a^{2/3})$; then,

$$k = 1.2 \times 10^{-12} - 0.23 \times C_w^{0.43}$$

(7a)

for plagioclase, and

$$k = 2.8 \times 10^{-12} - 0.23 \times C_w^{0.43}$$

(7b)

for pyroxene and oxide. These equations represent the MND water exsolution rate meter proposed in this paper.

2.6. Derivation of the MND decompression rate meter

By assuming that the water exsolution is at equilibrium, we can estimate the decompression rates from the water solubility relation $P_{w}=5.6 \times 10^5 \times C_w^2$ (5.6 $\times 10^6$ is derived by $K/C_w^o$ (Toramaru, 2006)) as follows:

$$\left| \frac{dP_w}{dt} \right| = c \left| \frac{dC_w}{dt} \right|$$

(8)

where $dP_w/dt$ is in Pa/s and $c$ is defined by $dP_w/dC_w$ as follows

$$c = 11.2 \times 10^6 \times C_w$$

(9)

By using Eq. (8) and Eq. (6), we obtain the relationship between the decompression rate and the MND:

$$\left| \frac{dP_w}{dt} \right| = c \left( \frac{N}{a} \right)^{2/3}$$

(10)
The decompression rate derived from this equation is the Lagrangian quantity attached with the material ascending within the conduit (Toramaru, 2006). Furthermore, when the decompression process is in the steady state, the decompression rate at the microlite nucleation depth \( z_n \) is expressed as follows:

\[
\left| \frac{dP}{dt} \right|_{z=z_n} = \left| \frac{dP}{dz} \right|_{z=z_n} = V_n \left| \frac{dP}{dz} \right|_{z=z_n}
\]

(11)

where \( V_n \) denotes the ascent velocity at the microlite nucleation along the vertical axis; \( \left| \frac{dP}{dz} \right|_{z=z_n} \), represents the pressure gradient at the nucleation depth; and \( \left| \frac{dP}{dz} \right|_{z=z_n} = \rho_g \left| \frac{dP}{dz} \right|_{z=z_n} \); \( \rho \) denotes the bulk density of the vesiculated magma at the nucleation depth and \( g \) denotes the gravity acceleration. This argument is valid for the case that the velocity gradient is negligible or as long as the microlite nucleation does not occur at the fragmentation level (Toramaru, 2006). Thus, from the decompression rate, we can estimate the ascent velocity at the nucleation depth as follows:

\[
V_n = \frac{1}{\rho_g} \left| \frac{dP}{dz} \right|_{z=z_n}
\]

(12)

3. Applicability and limitation of the MND rate meter

3.1. Water exsolution rate vs. decompression rate

The MND rate meter developed in the previous section exhibits some problems, which result from the disequilibrium characteristics included in the crystallization and vesiculation processes. It has been advocated that the vesiculation proceeds at disequilibrium (Larsen and Gardner, 2004; Mangan and Sisson, 2000). Since we neglect such a disequilibrium vesiculation, the present method is based on the assumption that the water exsolution proceeds at the equilibrium rate in response to the change in pressure. Nevertheless, the water exsolution rate is a true value as long as the MND is controlled by water exsolution and not by decompression, irrespective of whether the vesiculation proceeds at the equilibrium. On the other hand, the decompression rate estimated by the present method provides the minimum value because the decompression rate should be higher for the same value of MNDs observed in natural samples if the vesiculation is at disequilibrium.

It is likely that the equilibrium vesiculation occurs more efficiently in effusive eruptions than in explosive eruptions because the accelerated ascent of magma in explosive eruptions facilitates the disequilibrium exsolution of \( H_2O \) from melt. Therefore the application to the Unzen dome-forming eruptions seems to be valid for both the water exsolution rate and the decompression rate. In Section 3.3, we provide independent evidence to support the estimation by the MND meter is also reasonable also for the explosive eruption of andesitic magmas.

The MND water exsolution rate meter assumes an idealistic crystallization in which microlite nucleation occurs as a single event during decompression-induced crystallization and finishes until the surface. Further in this crystallization, the heterogeneous nucleation is not dominated and other expected realistic processes such as continuous nucleation until the surface or extraordinarily retarded nucleation do not occur. However, in natural eruptions, it is likely that such idealistic situations can be realized only for limited conditions. In fact we are sometimes able to observe pumice containing no microlites. Although the origin of extraordinarily microlite-poor vesiculated samples has not yet been understood by experiments or theories, we can suggest two possibilities. (1) The degree of disequilibrium between the pressure and water content in the melt is maintained at a high value so that the degree of supersaturation is insufficient for microlite nucleation (disequilibrium vesiculation). (2) Microlite nucleation or growth is effectively hindered by the high diffusivity or viscosity of the melt due to water depletion (glass formation). In both cases, we cannot apply the MND method to such extraordinarily microlite-poor samples.

![Fig. 9. Comparison of the MND vs. the decompression rate between experiments and MND decompression rate meter developed in the present paper. (a) Solid squares indicate 3D MND calculated by (Nakamura, 2006) for MDE experiments by (Couch et al., 2003b). Solid line is the model prediction assuming \( C_w = 71 \text{ wt.\%} \) and \( C_v = 5 \text{ wt.\%} \). (b) The experimental decompression rate vs. the calculated decompression rate given experimental MND.](image)

3.2. Comparison with experiments

Recently, several studies on the decompression-induced crystallization kinetics (Couch et al., 2003a,b; Hammer and Rutherford, 2002), Couch et al. (2003b) carried out two series of decompression experiments: SDE (single step decompression) and MDE (multi-step decompression). The MND data for MDE experiments was compiled by Nakamura (2006) who recalculated the 3D MND from the 2D original data, and correlated the 3D with the integrated decompression rate; these experiments replicated the continuous decompression with constant rates. In Fig. 9a, we plot the 3D MND data versus the decompression rate with the line indicating the relationship predicted by the MND decompression rate meter. Fig. 9b shows the comparison between the experimental decompression rate and the calculated rate for the given MND in the experiments. This figure shows that the present MND model can successfully explain the experimental MND by first order approximation. Thus the MND rate meter presented in this paper has some amount of experimental basis for reliability within some error.

3.3. Application to the Izu-Oshima 1986B subplinian eruptions

It is important to compare other independent estimations or proxies for decompression rates with those given by the present MND
rate meter. We provide the preliminary MND data for the Izu-Oshima 1986B subplinian eruption for which eruption column height data as a function of time by direct observation are available. Here, we performed a chronological comparison of the MND decompression rate and the observed column height as an indicator of the exit velocities, and argue that the MND method can be applied to explosive as well as effusive eruptions.

The Izu-Oshima 1986B subplinian eruption was documented for its geophysical (e.g. Okubo and Watanabe, 1989; Hashimoto and Tada, 1990), petrological (e.g. Fuji et al., 1988), and geochemical (e.g. Hirabayashi et al., 1988) aspects. Fig. 10a shows the change in the height of the column with time (Abe and Takahashi, 1987). The groundmass compositions of scoria (rare phenocrysts) produced by the eruption are classified into andesite with SiO$_2$ = 54.5 to 58.5 wt.% (preliminary data by EPMA). The vesicle texture varies from sample to sample; from spherical bubbles to coalesced vesicles with irregular interfaces. Tentative BNDs (bubble number density) are around $10^{10}$ to $10^{13}$ (m$^{-3}$). The microlite texture can be classified into two types: A-type (microlite-poor (not extraordinarily poor) and low MND) and B-type (microlite-rich and high MND) (Fig. 11). The transition between these two types is continuous; therefore the classification is both qualitative and tentative. General A-type scoria has a higher vesicularity with spherical bubbles whereas B-type scoria has a lower vesicularity with vesicles that are irregular in shape. The proportion of microlite textural types indicates the dominant decompression process; A-type: lower decompression rate, and B-type: higher decompression rate. Fig. 10b and c show the chronological variation of the proportion of each type in the scoria samples with approximately the same size (10 mm in diameter). From Fig. 10, we can recognize that the temporal change in texture which indicates a low-high-low variation in the decompression rate with time correlates with the low-high-low variation in the column height, which suggests that the magmas producing a higher column ascent with a higher decompression rate and ascent velocity at the microlite nucleation depth. An important fact is that the microlite texture also correlates with the groundmass composition: A-type scoria has a higher in SiO$_2$ content up to 58 wt.% whereas B-type scoria has a relatively low SiO$_2$ content — around 55 wt.%.

For quantitative estimation, we derive the value of $k$ for the MND water-exsolution rate using $C_{\text{HSi}} = 8$ wt.% for A-type and $C_{\text{HSi}} = 5$ wt.% for B-type with the same water content ($C_w = 1$ wt.%: this is a hypothetical value); and then,

$$k_{\text{pyA}} = 1.1 \times 10^{-13}$$

for pyroxene microlite in A-type scoria, and

$$k_{\text{pyB}} = 5.4 \times 10^{-13}$$

for pyroxene microlite in B-type scoria. Typical MND values of A-type and B-type are $10^{15}$ and $10^{17}$ (m$^{-1}$), respectively. These values and Eqs. (6), (13a,b) and (10) lead to water exsolution rates of 0.001 wt.%/s for A-type scoria and 0.12 wt.%/s for B-type scoria and corresponding decompression rates of $1.2 \times 10^{5}$ Pa/s for A-type and $1.3 \times 10^{6}$ Pa/s at the pyroxene microlite nucleation depth. These values are higher than those obtained for the Unzen dome eruption estimated in the next section, by around one to three orders of magnitude. Further, using Eq. (12), we estimate the ascent velocity to be 1.3 (m/s) for A-type scoria and 133 (m/s) for B-type scoria with a bulk density of 1000 (kg/m$^3$). Finally, it should be noted that A-type and B-type scoriae (with similar sizes) are found with varying proportions within the same stratigraphic height in the deposits at the same locality for unknown reasons.


Since the application of the MND rate meter to the Unzen 1991–1995 dome eruptions is extensively described in Noguchi et al. (2008–this issue), here, we briefly address the summary of its application. In order to apply the MND water-exsolution rate meter (Eq. (5)) to the plagioclase microlites of samples collected from the Unzen dome eruptions of 1991–1995, we substitute $\Delta C_{\text{Si}} = 18$ and $\Delta C_w = 3.5$ (see below) in Eqs. (6) and (7a). Then, we have

$$\frac{dC_w}{dt} = 2.8 \times 10^{-15} N^{2/3}_{\text{pl}}$$

For the MND data obtained in the range of $10^{14}$ to $10^{15}$ (m$^{-3}$) (Noguchi et al., 2008–this issue), this equation yields 6.1$ \times 10^{-16}$ and 2.8$ \times 10^{-15}$ (wt.%)/s as the water exsolution rates. The bound of $a_1 \pm 1$, in Eq. (2a) (or $\pm 2/3$ in $k$ (Eq. (7a))) yields a lower bound multiplied by 0.2 and an upper bound multiplied by 4.6 for the estimation.

In order to apply the MND decompression rate meter (Eq. (10) to the plagioclase microlites, we require the water content at the microlite
nucleation for the determination of $c$ (Eq. (9)). We use the anorthite content of the plagioclase microlites as an indicator of the water content at the nucleation. The anorthite content at the plagioclase nucleation depends on the melt composition and water content, as shown experimentally (e.g., Housh and Luhr, 1991; Couch et al., 2003a; Takagi et al., 2005). Based on this feature of the plagioclase composition, we estimate the water content at the plagioclase nucleation. At present, there is no experiment using the Unzen samples, in which An content data are systematically provided, so we estimate the anorthite content of plagioclase by experiments for Soufriere Hills Volcano, Montserrat, carried out by Couch et al. (2003a). Fig. 12 shows the anorthite content of plagioclase at the liquidus estimated by the experiment and the MELTS in which most of the important thermodynamic data on the phase equilibria for various compositions of melts are taken into account. From this figure, it can be recognized that the MELTS gives systematically high An content of liquidus plagioclase relative to experiments, though the composition of starting material in experiments is slightly different from the Unzen composition (see Noguchi et al., 2008–this issue). This discrepancy is not significant for the MND rate meter itself (the liquidus slope is essential), but it becomes important in estimating the water content at the nucleation of plagioclase microlite by the An content as a function of the water content. Here we consult the experimental data by Couch et al. (2003a,b) for An content. From this figure and data of the An content of plagioclase microlites (An=45 for smaller microlites which control the MND), we obtain $C_w=3.5$(wt.%), which corresponds to a saturation pressure of 70 MPa (see Fig. 12).

Then, the MND decompression rate meter can be written as follows:

$$\frac{dP_W}{dt} = 1.1 \times 10^{-7} N_{pl}^{2/3}$$

(15)

By applying this equation to the MND data of the Unzen 1991–1995 eruptions, we obtain the decompression rates ranging from 240 to 1100 (Pa/s). The estimated value has the bound (the lower and upper bounds are multiplied by 0.2 and 4.6, respectively).

Further, Eq. (12) yields the ascent velocities in the conduit as 0.015 to 0.068 (m/s) for $\rho=1684$ (kg/m$^3$) of the vesiculated magma in a closed system (melt density is assumed to be 2500(kg/m$^3$)). By assuming a
completely degassed magma (open system), i.e., \( \rho = 2500 \text{kg/m}^3 \), \( V_n \) is estimated to be 0.01–0.046 (m/s). The implication of these estimated values of the water-exsolution rate, decompression rates, and ascent velocities is discussed in greater detail in Noguchi et al. (2008–this issue).

5. Discussions

We address some issues related to the use of the MND water exsolution rate meter and the problems involved in the assumptions and method. First, in the case of Eq. (1), it is assumed that microlite nucleation occurs as a single event in a closed system. Although it is difficult to verify this assumption from the textural evidence of the eruption products, we can examine the applicability of this assumption to the samples from the crystal size distribution (CSD). The exponential distribution is considered to result from the nucleation and growth processes in a batch system (Marsh, 1998). On the other hand, the power–law–type distribution is related to multiple events of nucleation or magmatic mixing (locally open system). Most of the Unzen samples used in the present study exhibit exponential distributions in lower size ranges where the size of microlites is chemically confirmed to be formed due to the decompression-induced crystallization (Noguchi et al., 2008–this issue).

It is well known that some of the open systems in chemical engineering produce an exponential distribution. However, it is unlikely that microlites with sizes less than several tens of \( \mu \text{m} \) can cause a fluid dynamic size segregation in such highly viscous magmas. Thus, we believe that a single event of microlite nucleation occurred in the Unzen samples used in the present analysis.

In order to estimate the kinetic factor \( a \) or \( k \), we use the crystallization data on the water-poor mafic dikes. The effect of the bulk composition of melts on the diffusivities is considered in the estimation. \( a \) includes the effects of the latent heat release and the shape of liquidus curves of plagioclase and pyroxene in the anhydrous composition-temperature space (as shown in Fig. 2). However these effects are parametrically taken into account by the kinetica factor \( a \) from the numerical study (Toramaru, 2001).

Actually, melts, plagioclase, and other microlite minerals such as pyroxene form a multicomponent system. However, the growth rate of such solid solution minerals is influenced only by the diffusion of the slowest species in the melt and not by the (coupled) diffusion process within the crystal. Muncill and Lasaga (1987, 1988) attempted to solve this diffusion effect in the melt by incorporating it into the viscosity term of the growth rate by assuming a reaction–limited mechanism. The most accurate method is to solve the multicomponent diffusion in the melt surrounding a growing crystal and then include this effect into the MND formulation. However, this procedure does not appear to be successful because the nature of multicomponent diffusion still requires understanding, as shown recently by many related articles (Chakraborty et al., 1995a,b; Liang et al., 1996a,b, 1997; Richter et al., 1998; Mungall et al., 1998; Mungall, 2002), and because the growth rate of a solid-solution nucleus with a critical size has not been formulated thus far. Therefore, to avoid the ambiguity and uncertainty induced by the inclusion of this complex process, we selected a method in which the diffusion effect is taken into account solely by the Si diffusion, which is the slowest species in common melts. This method was based on the result of Baker (1992) and Liang et al. (1996a) that silicon diffusion is the slowest process in dacite and rhyolite. Si diffusion was incorporated into the model through the viscosity, similar to Muncill and Lasaga; but the Stokes–Einstein relation is broken in the relation used in the present model which may be more realistic as pointed out by Muncill and Lasaga (1988). Thus, we believe that the simplification adopted in the present paper allows readers to realize the influence of the composition on the MND rate meter through the physical properties more clearly.

A recent experiment (Hammer, 2004) suggests that the interfacial energy of the crystal/melt interface is effectively reduced by the addition of water. The effect of the water content on the interfacial energy is not taken into account in the evaluation of \( a \). In addition, the chemical composition of crystals and melts may affect the interfacial energy. In this study, we consider that \( y \) has no strong systematic dependence on composition, and the bound of \( a \) involves these uncertainties. However in the future, we should aim to determine \( a \) accurately from the precise values of physical properties and laboratory experiments, and to confirm Eq. (1).

A key factor in the estimation of the water exsolution rate is the evaluation of the liquidus curve as a function of the water concentration in the melt. Hence, we recommend, if possible, that the value of slope \( \left( \frac{dT_f}{dC_w} \right) \) should be determined from experiments using natural samples of a target eruption, although in the present paper, we have used MELTS for the estimation. The thermodynamic meaning of the slope is discussed in the Section 2.4.

It is important to determine the water content at the microlite nucleation or the pressure for the calculation of \( k \). With this regards, we consulted the experimental results using the different composition rather than the MELTS calculation. The MELTS provides the reasonable slopes of phase boundaries owing to the thermodynamic data on which it is based. However in estimating the water content from the anorthite content of plagioclase microlite, the absolute value estimated for anorthite content appears to have some ambiguity. Thus the experiments is highly desired to determine the anorthite content as function of the water content at the water-saturated state for the target eruption. With regards to pyroxene, we also need to carry out experiments for nucleation condition because of no manner to estimate the nucleation condition (pressure or water content).

The coupling between the vesiculation and crystallization can be expected because the vesiculation makes the system supersaturated for the crystallizing components, which in turn makes the system supersaturated for the volatile components. The vesiculation that is enhanced by crystallization accelerates the crystallization. The supersaturated and disequilibrium state for both crystallization and vesiculation continues until the crystallization and water exsolution are completed. However, such an achievement of the reaction is not accomplished in natural products by effusive and explosive eruptions. Thus, a precise interpretation of the texture of volcanic rocks requires a rigorous understanding of the coupling of vesiculation and crystallization during the later stages.

We now comment on the relation between the decompression rate estimated using the BND (bubble number density) decompression rate meter (Toramaru, 2006) and the MND meter. The BND estimates the decompression rate at the bubble nucleation depth, whereas the MND estimates it at the microlite nucleation depth. Hence, the BND estimates the decompression rate in a deeper part of the conduit. Thus, we can describe the change in the decompression rate along the magma ascent in the conduit using both the BND and MND decompression rate meters.

6. Conclusions

We have developed a method using the MND (microlite number density) to quantitatively estimate the water exsolution rate, decompression rate, and ascent velocity at the microlite nucleation depth. This method assumes the equivalence between the cooling-induced crystallization and the decompression-induced crystallization. On the basis of this assumption, we have determined the kinetic factor controlling the relationship between the MND and the water exsolution rate by observing the natural experiment of crystallization in mafic dikes. In order to incorporate the effect of the melts composition we take into account the diffusivity in the melt as a function of the viscosity, which depends on the melt composition. The thermodynamic factor controlling the relation between the liquidus and dissolved water content is examined in order to develop the MND water exsolution rate meter. The validity of this method is supported by a comparison with the experiments and the independent evidence.
from the chronologically well documented Izu-Oshima 1986 sub-plinian eruption. In the MND decomposition rate meter, certain limitations arise with regard to the disequilibrium vesiculation and in the determination of the kinetic constant; these limitations have been addressed. The application of this method to the Unzen 1991–1995 dome forming eruptions is briefly summarized.

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References


Cashman, K.V., Blundy, J., 2000. Degassing and crystallization of ascending andesite and dacite forming eruptions is brie


