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MI: heterogeneously entrapped bubbles

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Heterogeneously entrapped, vapor-rich melt inclusions record pre-eruptive magmatic volatile contents

Matthew Steele-MacInnis^{1*}, Rosario Esposito², Lowell R. Moore³, Margaret E. Hartley⁴

¹) Department of Geosciences, The University of Arizona, Tucson AZ 85721 USA

²) Department of Earth, Planetary and Space Sciences, University of California, Los Angeles, Los Angeles CA 90095 USA

³) Department of Geosciences, Virginia Tech, Blacksburg VA 24061 USA

⁴) School of Earth and Environmental Sciences, University of Manchester, Manchester M13 9PL UK

**Corresponding author.* Email: steelemacinnis@email.arizona.edu

Tel.: 520-621-1385

Fax: 520-621-2672

ABSTRACT

Silicate melt inclusions (MI) commonly provide the best record of pre-eruptive H₂O and CO₂ contents of subvolcanic melts, but the concentrations of CO₂ and H₂O in the melt (glass) phase within MI can be modified by partitioning into a vapor bubble after trapping. Melt inclusions may also enclose vapor bubbles together with the melt (i.e., heterogeneous entrapment), affecting the bulk volatile composition of the MI, and its post-entrapment evolution. Here, we use numerical modeling to examine the systematics of post-entrapment volatile evolution within MI containing various proportions of trapped vapor from zero to 95 volume percent. Modeling indicates that inclusions that trap only a vapor-saturated melt exhibit significant decrease in CO₂ and moderate increase in H₂O concentrations in the melt upon nucleation and growth of a vapor bubble. In contrast, inclusions that trap melt plus vapor exhibit subdued CO₂ depletion at equivalent conditions. In the extreme case of inclusions that trap mostly the vapor phase (i.e., CO₂-H₂O fluid inclusions containing trapped melt), degassing of CO₂ from the melt is negligible. In the latter scenario, the large fraction of vapor enclosed in the MI during trapping essentially serves as a buffer, preventing post-entrapment modification of volatile concentrations in the melt. Hence, the glass phase within such heterogeneously entrapped, vapor-rich MI records the volatile concentrations of the melt at the time of trapping. These numerical modeling results suggest that heterogeneously entrapped MI containing large vapor bubbles represent amenable samples for constraining pre-eruptive volatile concentrations of subvolcanic melts.

Keywords: silicate melt; melt inclusions; fluid inclusions; vapor bubbles; H₂O; CO₂; degassing

1. INTRODUCTION

Silicate melt inclusions (MI) are aliquots of melt trapped within crystals during crystal growth or fracture healing (Lowenstern 1995; Lowenstern 2003; Bodnar and Student 2006; Cannatelli et al. 2016), although Lowenstern (1995) noted that trapping secondary MI in volcanic phenocrysts may be unlikely owing to the viscosity of silicate melts. As such, MI represent samples of the melt during various stages of fractionation in an evolving magmatic system, providing a record of igneous processes which may be otherwise inaccessible. The evolution of dissolved volatiles (e.g., CO₂, H₂O, Cl, S, etc.) in the melt is one such process. Crystal-hosted melt inclusions in volcanic rocks can be analyzed to constrain the concentrations of volatile components dissolved in the melt prior to volcanic eruption and/or degassing. If the melt reached saturation with a magmatic fluid or vapor phase prior to eruption, then measured volatile concentrations can be interpreted according to solubility models (e.g., Holloway and Blank 1994; Newman and Lowenstern 2002; Papale et al. 2006; Shishkina et al., 2014) to constrain depths of magma emplacement as well as progressive degassing of an initially CO₂-enriched melt during ascent (Lowenstern 1994; Métrich and Wallace 2008).

Apparently coeval melt inclusions commonly record wide ranges of CO₂ concentrations in the glass phase (Esposito et al. 2014). Variation in volatile concentrations of MI glasses can be induced independently of magma degassing, as a result of several potential post-entrapment processes. Firstly, volatile concentrations in the melt in an inclusion can be modified by diffusive re-equilibration with the exterior carrier melt (Qin et al. 1992; Danyushevsky et al. 2000; Portnyagin et al. 2008; Mironov and Portnyagin 2011; Gaetani et al. 2012; Bucholz et al. 2013; Mironov et al. 2015; Hartley et al. 2015). This process can occur on timescales of days to hours in some cases. Secondly, volatile components within MI can be partitioned between the melt and

a vapor phase (bubble) subsequent to trapping (Anderson and Brown 1993; Steele-MacInnis et al. 2011; Hartley et al. 2014; Moore et al. 2015; Wallace et al. 2015; Tuohy et al. 2016; Aster et al. 2016). A vapor phase within an initially homogeneous melt inclusion may nucleate and grow after trapping as a result of differential thermal contraction of melt versus the host crystal (Lowenstern 2003; Moore et al. 2015), by post-entrapment crystallization (PEC; Steele-MacInnis et al. 2011) of the host mineral on the inclusion walls, or a combination of these processes. In all three scenarios, nucleation and growth of the vapor bubble results in strong depletion of CO₂ from the melt phase with concomitant minor variation in the H₂O concentration. The divergent trends in CO₂ versus H₂O concentration in the melt are a consequence of the extremely different CO₂/H₂O ratios in the melt versus the exsolving fluid phase: In general, the CO₂/H₂O ratio in the exsolving vapor is significantly greater than that in the coexisting melt (i.e., CO₂-rich vapor exsolved from a melt which is generally more enriched in H₂O), and as such the exsolution of the vapor phase drives the CO₂/H₂O ratio of the melt to lower values. Thus, several studies have used Raman spectroscopy to determine the amount of CO₂ exsolved into the bubble to constrain the bulk CO₂ content of the inclusion (e.g., Esposito et al. 2011; Moore et al. 2015; Hartley et al. 2014; Tuohy et al. 2016). The H₂O in the vapor bubble has not generally been detected during Raman spectroscopic analysis of MI vapor bubbles, but has recently been detected as a rim of H₂O-rich liquid at the glass/bubble interface in re-heated MI (Esposito et al. 2016). Like the case for CO₂, Esposito et al. (2016) suggested that depending on the initial conditions, most of the H₂O and of the S of the originally trapped melt may be stored in the bubble.

Heterogeneous entrapment represents an alternative origin for the vapor bubbles in some MI. In this scenario, the host phenocryst encloses a multi-phase assemblage of vapor-saturated melt plus vapor. Evidence for heterogeneous entrapment of melt plus magmatic fluid has been

reported in several studies. For example, Harris et al. (2003), Zajacz et al. (2008) and Stefanova et al. (2014) described MI from high-temperature porphyry veins, containing globules of high-density, high-salinity brine. In these studies, the brine globules are interpreted as trapped hydrothermal fluid, which presumably exsolved from the silicate melt prior to trapping of the melt inclusions. Bodnar and Student (2006) noted that in the case of heterogeneous entrapment, the volume fraction of vapor would likely be variable for groups of coevally entrapped MI (or melt inclusion assemblages; MIA). Moore et al. (2015) developed a numerical model to estimate the maximum volume fraction of vapor expected as a result of differential thermal contraction for MI hosted in various minerals, and concluded that in general, vapor bubbles of up to a few percent of the MI volume are consistent with bubble nucleation and growth by this mechanism. As such, vapor bubbles exceeding a few volume percent of the MI may represent trapped vapor (Fig. 1). Aster et al. (2016) similarly used a numerical model to estimate the maximum volume fraction of vapor expected purely from cooling, PEC and quenching of initially homogeneous trapped melt, and used this information to infer which MI appeared to have trapped some portion of vapor. Hartley et al. (2014) and Moore et al. (2015) reported melt inclusions containing exceptionally large vapor bubbles up to several tens of volume percent, suggesting that these MI trapped melt plus vapor. In the most extreme example reported by Hartley et al. (2014) and Moore et al. (2015), the MI vapor bubble represented >90 vol.% of the inclusion; as such, the most vapor-rich MI approach the limiting case of magmatic CO₂-H₂O fluid inclusions containing a small proportion of trapped melt, similar to clinopyroxene-hosted fluid inclusions reported for example by Belkin et al. (1985) and Belkin and De Vivo (1993); and olivine-hosted fluid inclusions by Mironov and Portnyagin (2011), Zanon and Frezzotti (2013), and Zanon and Pimentel (2015). Note, however, that H⁺ diffusion out of the MI may also promote formation of

anomalously large vapor bubbles (Bucholz et al., 2013; Aster et al. 2016), which is not considered in the present study. In addition, decrepitation and/or leakage of MI may also contribute to forming anomalously large bubbles, as discussed below.

The occurrence of MI containing a heterogeneously trapped vapor phase raises questions as to the systematics of melt-vapor partitioning within inclusions that trapped both melt and vapor. Conceptually, coeval melt inclusions and fluid inclusions are expected to follow different temperature-pressure trajectories subsequent to trapping (Fig. 2). The pressure-temperature trajectory followed by a vapor-saturated silicate melt inclusion is a function of compressibility and expansivity of melt and vapor, the vapor solubility relations, and the evolution of PEC (Student and Bodnar 1996; Steele-MacInnis et al. 2011; Schiavi et al. 2016). In contrast, the temperature-pressure trajectory for CO₂-H₂O fluid inclusions is constrained by the isochore (pressure-temperature locus of constant density) of the CO₂-H₂O fluid phase (Sterner and Bodnar, 1991; Diamond, 2003) according to the composition and bulk density of the fluid. For example, Mironov and Portnyagin (2011) estimated the trapping temperature and pressure conditions of coeval melt and fluid inclusions hosted in olivine by intersecting the temperature estimated from MI with the isochores of the coeval CO₂-H₂O fluid inclusions. As such, the temperature-pressure trajectory followed by heterogeneously entrapped, vapor-rich MI is expected to vary between these two endmembers according to the proportion of trapped vapor (Fig. 2). Moreover, the temperature-pressure trajectory of the MI is expected to tend towards the coeval fluid-inclusion isochore at high proportions of trapped vapor. Steele-MacInnis et al. (2011) reported that evolution of CO₂ and H₂O concentrations in the melt (glass) within MI is correlated to the pressure-temperature trajectory followed by the MI after trapping. Hence, we expect that the volatile systematics of heterogeneously entrapped MI will also vary according to

the proportion of trapped vapor. Stated differently, the partitioning of volatile components between melt and vapor is sensitive to the relative proportions of phases trapped. Thus, interpreting volatile contents of MI glass, bubble, and bulk inclusion can be complicated by heterogeneous entrapment.

In this study, we build upon the earlier thermodynamic modeling of Steele-MacInnis et al. (2011) to characterize volatile evolution of MI melt (glass) and vapor during post-entrapment crystallization of heterogeneously entrapped MI. Steele-MacInnis et al. (2011) focused on MI that trapped only vapor-saturated melt (without trapped vapor), and reported contrasting behavior of CO₂-rich versus H₂O-rich melts and intermediate CO₂-H₂O-saturated melts. Here, we extend these results to heterogeneously entrapped inclusions, including end-member scenarios of homogeneously entrapped melt or vapor, and several intermediate scenarios with various relative proportions of trapped melt and vapor. In the present contribution, we do not include the effects of diffusive re-equilibration, nor the effects of bubble expansion during syn-eruptive cooling and quenching, although we recognize that these effects may be significant for many natural MI and that future studies incorporating them will be necessary. As such, the present contribution represents one endmember of the various complexities that can manifest in MI volatile systematics. The results of this analysis indicate that for inclusions that trap a large proportion of vapor, the H₂O and CO₂ concentrations in the melt (glass) phase within the inclusion are relatively insensitive to post-entrapment crystallization. These results thus suggest that heterogeneously entrapped MI may represent amenable samples for characterizing pre-eruptive dissolved volatile contents of melts.

2. METHODS

The methods used here were mostly described in detail by Steele-MacInnis et al. (2011), so here we provide only an abridged overview (see Steele-MacInnis et al., 2011 for additional details). We modeled the effects of volatile exsolution during post-entrapment crystallization of an albitic ($\text{NaAlSi}_3\text{O}_8$) melt trapped in albite using constant volume (isochoric), constant composition (closed) boundary conditions. The albitic model was used primarily because this system represents a relatively simple endmember, and because the parameterization is very well constrained. In addition, we extended this model to basaltic melts trapped in olivine, because the latter system is one of the most widely studied in terms of natural MI and information relative to bubble and MI are available from the literature (e.g., Hartley et al. 2014; Moore et al., 2015). The methods used in this modeling are described below.

For the albitic melt, solubilities of H_2O and CO_2 in the melt were calculated according to the models described by Holloway and Blank (1994). Volumetric properties of albitic melt and albite were calculated using the model of Burnham and Davis (1971; 1974). To initiate the model, the composition of vapor-saturated melt in equilibrium with albite was calculated, which defined the composition of the initial melt aliquot. The volume of the melt inclusion (constant in all subsequent steps) was calculated according to the specific volume of melt and the mass of the aliquot. In each subsequent step, a portion of melt (arbitrarily set to 1% of the albitic component of the initial melt) was crystallized. Consequently, the remaining melt was enriched in CO_2 and H_2O via subtraction of $\text{NaAlSi}_3\text{O}_8$ into newly-formed albite (i.e., PEC). However, because the melt was initially vapor-saturated, enrichment in CO_2 and H_2O drives the melt towards supersaturation, and some portion of CO_2 and H_2O must be released into a free vapor phase, or bubble. In a closed system, at any given temperature and pressure the $\text{CO}_2/\text{H}_2\text{O}$ ratio of the exsolved vapor phase is constrained by the $\text{CO}_2/\text{H}_2\text{O}$ ratio in the coexisting melt, and an iterative

procedure is employed to solve for melt-vapor equilibrium. The density and volume of the exsolved vapor phase was calculated using the Redlich-Kwong equation of state (Redlich and Kwong, 1949) with the parameters of Holloway (1977). To achieve constant volume conditions, a nested iterative procedure was also employed to adjust internal pressure (with temperature constrained by the vapor-saturated liquidus surface). Note that in the latter isochoric constraint, the volume of the inclusion was defined by the sum of volumes of melt plus vapor plus albite formed during PEC (i.e., albite crystallized on the walls of the inclusion). The two constraints (mass balance and isochoricity) were solved simultaneously for each increment of PEC, to obtain a trajectory of evolving pressure-temperature-composition (melt+vapor) conditions. The calculations did not treat external pressure as a variable, nor did they account for compressibility of the host mineral.

In addition to the simulations using an albitic melt composition trapped in albite, we conducted several simulations using a basaltic melt composition trapped in olivine. The solubility model for volatile species in the basaltic melt (based on an average tholeiitic basalt composition) was from Holloway and Blank (1984). The volumetric properties of the basaltic melt, as well as the volume of fusion of olivine, were modeled based on the data of Lange and Carmichael (1990). Effect of H₂O on the olivine crystallization temperature was modeled based on the data of Almeev et al. (2007). Our model is thus somewhat simplified and does not invoke compositional changes or effects in the basaltic melt (nor host olivine) but nevertheless serves to compare and contrast the mafic system with the earlier albitic model.

Note that the recent study by Tuohy et al. (2016) reported new numerical modeling showing a greater volume fraction of vapor at equivalent degree of PEC than reported by Steele-MacInnis et al. (2011). The model described by Tuohy et al. (2016) used similar methods to

those used by Steele-MacInnis et al. (2011), but including MI of basaltic composition entrapped in olivine (rather than albitic composition entrapped in albite). The larger volume fractions of vapor predicted for olivine-hosted MI by Tuohy et al. (2016) is consistent with the numerical model of Moore et al. (2015), which also showed that the relative volume contraction during cooling of olivine-hosted MI is significantly greater than that of MI hosted in alkali feldspar (see Fig. 8a versus 8e of Moore et al. 2015). Thus, Moore et al. (2015) stated that among MI trapped in olivine, pyroxenes, feldspars and quartz, the MI trapped in alkali feldspars are expected to exhibit the smallest vapor bubbles, in terms of relative volume fractions. These same effects are reproduced by the model described here, when using the parameters appropriate for a basaltic melt and olivine host. We should note that Steele-MacInnis et al. (2011) stated that the effect of PEC in olivine-hosted MI would be less than that in albite-hosted MI according to a lesser volume of fusion of olivine compared to albite; however, this statement was incorrect because of failure to account for the different stoichiometries of one formula unit of albite versus olivine reported by Lange and Carmichael (1990). When compared at an equivalent 8-oxygen basis ($\text{NaAlSi}_3\text{O}_8$ versus $(\text{Fe,Mg})_4\text{Si}_2\text{O}_8$), olivine exhibits a greater ΔV_{fusion} than albite, which leads to a greater volume fraction of vapor produced in olivine-hosted MI at equivalent degrees of PEC (Moore et al. 2015; Tuohy et al. 2016).

The key addition to the methods described above, for the case of heterogeneously entrapped inclusions, was to set the initial conditions within the MI such that the inclusion initially contained vapor-saturated melt plus a finite volume of trapped vapor. Thus, at the initial pressure-temperature conditions, the composition of vapor in equilibrium with melt was calculated using the model of Holloway and Blank (1994), and an initial mass of H_2O and CO_2 in the vapor phase was defined according to the calculated $\text{CO}_2/\text{H}_2\text{O}$ ratio. The volume of the

resulting trapped vapor phase was calculated using the Redlich-Kwong equation of state. The combined volume of initial melt plus vapor was then used as the reference volume for constant-volume calculations in all subsequent steps.

We conducted simulations for an albitic melt composition hosted in albite using a trapping temperature and pressure of 930 °C and 200 MPa (equivalent to the model shown in Fig. 10 of Steele-MacInnis et al. 2011), for 12 starting volume fractions of vapor: 0, 5, 10, 15, 20, 40, 60, 80, 85, 90 and 95 vol.% vapor. We conducted additional simulations for a basaltic melt composition hosted in olivine using a trapping temperature and pressure of 1200 °C and 120 MPa, for six starting volume fractions of vapor: 0, 5, 10, 15, 20 and 40 vol.% vapor. In each simulation, we traced the evolution of H₂O and CO₂ concentrations in the melt, as well as temperature and internal pressure, during PEC up to 10% (by mass) of the silicate (albitic or basaltic) component of the melt. We modeled up to 10% PEC because greater degrees of PEC than this are rarely reported in literature (Steele-MacInnis et al. 2011).

3. RESULTS

Results of our simulations are shown in Figs. 3 and 4. For the homogeneously entrapped vapor-saturated melt (0 vol.% vapor), the results for the albitic melt are equivalent to those reported by Steele-MacInnis et al. (2011). The basaltic melt hosted in olivine shows a similar trajectory, although the decrease in internal pressure as well as CO₂ concentration in the glass is somewhat greater for basaltic MI compared to albitic MI, at equivalent degrees of PEC (Figs. 3B and 4B). Figure 3 also shows heterogeneously entrapped MI with 5-20 vol.% trapped vapor, and Fig. 4 shows heterogeneously entrapped MI with 5-40 vol.% trapped vapor. Figures 3 and 4 do not show the heterogeneously entrapped MI with higher volume fractions of trapped vapor (up to

95% vol.%) because the data points and trend lines at these high volume fractions of trapped vapor all overlap.

Figure 3 shows that as the volume fraction of trapped vapor increases, an equivalent degree of PEC is achieved at lower degree of cooling. Stated differently, if a group of MI are all trapped at the same temperature but initially contain various proportions of trapped vapor, those containing more trapped vapor are predicted to undergo more post-entrapment crystallization during the same interval of cooling. We should note that this latter prediction depends upon the assumption of thermodynamic equilibrium, and does not account for potentially differing cooling rates, nor differing glass-transition behavior discussed below. Figure 3 also shows that with increasing volume fraction of trapped vapor, the decrease in internal pressure within an MI concomitant with decreasing temperature/increasing PEC is reduced. Thus, at 10% PEC (by mass), the albitic inclusion that trapped no vapor has undergone an internal pressure decrease of ~50 MPa, whereas the albitic inclusion that trapped 10 vol.% vapor has undergone only ~5 MPa of pressure decrease. For the albitic inclusion that trapped 20 vol.% vapor, the pressure decrease at 10% PEC is only ~1 MPa, and the pressure-temperature trajectory is essentially equivalent to that of the CO₂-H₂O fluid isochore corresponding to the composition and density of the trapped vapor. Analogous trends are evident in the models for basaltic MI hosted in olivine (Fig. 3B).

As PEC, cooling and decompression progress, the silicate melt within the MI gradually exsolves H₂O and CO₂ into the vapor bubble (Steele-MacInnis et al. 2011). However, the concentrations of these volatiles in the remaining melt (glass) phase diverge owing to the order-of-magnitude difference in their solubilities in the melt, versus their relative concentrations in the conjugate vapor phase (Steele-MacInnis et al. 2011). Hence, for the albitic MI that trapped no vapor, after 10% PEC the CO₂ concentration in the melt decreases from 520 to 230 ppm,

whereas the H₂O concentration in the melt increases from 3.8 to 4.2 wt.% (Fig. 4). With increasing volume fraction of trapped vapor, these effects are more subdued (Fig. 4). For example, for the albitic MI that traps 10 vol.% of vapor, at 10% PEC the CO₂ concentration in the melt has decreased from 520 to 450 ppm, and the H₂O concentration in the melt has increased from 3.8 to 4.0 wt.%. At $\geq 60\%$ trapped vapor, both the CO₂ concentration and the H₂O concentration in the melt remain essentially constant (~ 520 ppm and ~ 3.8 wt.%, respectively) up to 10% PEC. Again, analogous trends are evident for the basaltic MI trapped in olivine (Fig. 4B).

4. DISCUSSION

As expected, as the volume fraction of trapped vapor in the melt inclusion increases, the pressure-temperature trajectory followed by the MI during PEC and cooling approaches that of a coeval CO₂-H₂O fluid-inclusion isochore (Fig. 3). Indeed, at volume fractions of trapped vapor greater than ~ 20 vol.% for the albitic melt, and ~ 40 vol.% for the basaltic melt, the pressure-temperature trajectory of the MI is indistinguishable from a coeval fluid-inclusion isochore. Consequently, the internal pressure decreases more gradually in inclusions containing more trapped vapor, and thus degassing of CO₂ and H₂O into the vapor bubble is more subdued. Hence, the volatile concentrations in the melt show less change from the initial composition at equivalent degrees of PEC, in inclusions containing more trapped vapor. In the extreme case of >60 vol.% trapped vapor, the concentrations of CO₂ and H₂O in the melt (and thus, in the glass in quenched MI) are predicted to be equal within the uncertainty of standard analytical techniques to those in the originally trapped melt.

As the volume fraction of trapped vapor increases, we also see a decrease in the degree of cooling required to achieve an equivalent degree of PEC (Fig. 3). This phenomenon is a result of

mass-balance constraints on the vapor-saturated solidus temperature of the MI. According to Burnham and Davis (1974), the solidus temperature of a vapor-saturated albitic melt is a function of the ratio of H₂O to CO₂ in the vapor phase. In a melt inclusion which traps only vapor-saturated melt (with no trapped vapor), the composition of the vapor phase becomes increasingly enriched in H₂O during cooling and PEC (i.e., the composition of each aliquot of exsolved vapor is more H₂O-rich at each increment of PEC). Because this inclusion traps only a vapor-saturated melt, and because the H₂O concentration in such a melt is commonly an order of magnitude greater than the CO₂ concentration, the inclusion is able to achieve a very H₂O-rich vapor bubble at the later stages of degassing of H₂O. As such, as cooling and PEC occur, the vapor-saturated solidus temperature is increasingly depressed, allowing PEC to proceed towards the H₂O-saturated solidus (Burnham and Davis 1974). In contrast, melt inclusions that trap a vapor bubble have their volatile budgets buffered by the composition of the trapped vapor, which is commonly significantly more CO₂-rich than the corresponding melt phase. Inclusions that trap a large proportion of vapor thus have higher vapor-saturated solidus temperatures, and may undergo an equivalent degree of PEC in a smaller temperature interval. In the extreme case of an inclusion that traps ≥ 60 vol.% vapor, the vapor-saturated solidus temperature is approximately equal to the trapping temperature, and the melt may undergo some amount of PEC nearly isothermally. Notably, this process may induce variation in the measured major-element composition of the glass phase within MI containing different proportions of trapped vapor.

An additional consequence of the different predicted solidus temperatures of MI containing different proportions of trapped vapor is potentially differing glass-transition behavior. As noted above, our numerical model assumes thermodynamic equilibrium, and thus the glass transition is not included explicitly in our results. Nevertheless, we can make some

qualitative predictions based on our results and experimental data on glass transition temperatures. According to Giordano et al. (2008), the glass transition temperature of silicate liquids is depressed by increasing concentrations of H₂O. In our results, MI that contain no trapped vapor experience increasing concentration of H₂O in the melt during cooling and PEC. Consequently, these trends suggest that the glass transition temperature of such MI may be progressively depressed during cooling and PEC, inhibiting vitrification. In contrast, MI that contain trapped vapor undergo less H₂O enrichment in the melt. In particular, for MI in which the proportion of trapped vapor exceeds 40 vol.%, the H₂O concentration in the melt remains nearly constant during PEC for both albitic and basaltic MI (Fig. 4). Thus, the glass transition temperature of such MI will not be depressed during cooling and PEC, suggesting that MI that trap vapor may be more readily quenched to glass. Note that at present this possibility is speculative, and further work is required to assess the glass-forming tendency of MI with different contents of trapped vapor.

The key consequence of trapping some portion of vapor within MI is the potential for preservation of the original volatile concentrations of the melt, or glass, irrespective of cooling and PEC. Preservation of the volatile concentrations in the glass is achieved via reducing the depressurization at equivalent degrees of cooling, and in effect buffering the H₂O and CO₂ concentrations in the melt by fixing the corresponding vapor composition. Moreover, the vapor phase within such heterogeneously trapped MI is also buffered in terms of composition and density, as the MI evolves along the vapor isochore, and thus the properties of the trapped magmatic fluid phase are also preserved in such MI.

The simulations described here involving an albitic melt hosted in albite all used equivalent initial conditions to those of Steele-MacInnis et al. (2011) of 930 °C, 200 MPa, and

initial volatile concentrations of 3.8 wt.% H₂O and 520 ppm CO₂. The basaltic melt simulations used initial conditions of 1200 °C, 120 MPa, and initial volatile concentrations of 0.95 wt.% H₂O and 535 ppm CO₂. One interesting question to consider is how the predicted trends in PEC and volatile evolution within the MI may vary with different initial conditions. Steele-MacInnis et al. (2011) reported that CO₂-absent MI containing only dissolved H₂O undergo immediate and sustained pressure increase with decreasing temperature and PEC, tracking the H₂O-saturated albitic solidus. Conversely, H₂O-absent, CO₂-bearing MI undergo pressure decrease during cooling and PEC, tracking the CO₂-saturated albitic solidus. Inclusions that trap a melt containing dissolved H₂O plus CO₂ follow trends that are initially more similar to the CO₂-endmember, and evolve towards more H₂O-dominated trends as PEC and cooling progress (Steele-MacInnis et al. 2011). We expect that the results of simulations included here, for MI that trap vapor along with the melt, can be extended to other initial conditions, with the only major difference being the initial trajectory of MI which trap little or no vapor. Regardless of the initial conditions and initial H₂O-CO₂ concentrations of the trapped melt±vapor, inclusions trapping a high proportion of vapor are expected to conform to a *P-T* trajectory resembling the isochore of the vapor phase. However, it must be stressed that additional processes such as diffusive reequilibration or decrepitation, which are not modeled here, may cause deviation from this model *P-T* trajectory. Some of these factors are discussed briefly below.

Examples of photomicrographs showing MI with anomalously large (>10 vol.%) bubbles are fairly common in the literature, but it should be stressed that based on photomicrographs alone it is commonly impossible to differentiate large bubbles generated by heterogeneous entrapment versus other processes, such as diffusive reequilibration (Gaetani et al. 2012; Bucholz et al. 2013) or stretching, leakage and/or decrepitation (MacLennan, 2017). In addition,

based on photomicrographs alone it is impossible to determine the volume of glass polished away during sample preparation, as well as if any additional bubble(s) was polished away to exposed the MI at the sample surface. Moreover, photomicrographs are sometimes unrevealing in terms of whether MI exposed by polishing were originally fully enclosed, or rather connected to the exterior ("hourglass inclusions") – in the latter scenario, bubble formation can accompany evacuation of some of the melt to the exterior during decompression (Anderson 1991). Thus, we advocate an approach using coeval assemblages of melt inclusions (Fig. 1A), and using additional petrologic indicators to test for timing and post-entrapment modifications of MI (e.g., Hartley et al. 2015). In the following section, we evaluate evidence for heterogeneous entrapment in the two datasets of Hartley et al. (2014) and Moore et al. (2015).

Few analytical data are available in literature on the H₂O and CO₂ concentrations of the glass phase within inclusions containing significant trapped vapor. This probably reflects to some extent that such inclusions are deliberately not targeted for microanalysis because of their anomalously large bubbles. Moreover, analysis of glass in such inclusions may be difficult because of the small analytical volume, for instance in melt-bearing "fluid inclusions" with only a thin film of silicate glass. Our comparison with existing analytical data is therefore limited to vapor bubble CO₂ densities from Hartley et al. (2014) and Moore et al. (2015). Both these studies characterized the CO₂ density within MI vapor bubbles using Raman spectroscopy. The MI described in these two studies are shown in Fig. 5, in terms of inclusion volume versus bubble volume (based on the diagrams of Moore et al. 2015 and Aster et al. 2016). Key observations from Fig. 5 are that both datasets include several inclusions with anomalously large vapor bubbles (>10 vol.%), and that there is no obvious relationship between MI size and bubble

size (see also Fig. 1A). This latter point is consistent with heterogeneous entrapment of vapor in some of the MI, if it is assumed that MI were formed at the same time.

Figure 6A shows the results of the present modeling of an albitic MI, plotted in terms of the density of the vapor bubble versus the vapor volume fraction, for trapped vapor fractions ranging from zero to 95 vol.%. At low volume fractions of trapped vapor, the density of the vapor bubble decreases abruptly with relatively low degrees of PEC. In contrast, at higher volume fractions of trapped vapor, PEC up to 10% has essentially no effect on the density of the vapor phase. The grey-shaded field on Fig. 6A thus delimits a distribution of bubble density versus volume fraction, corresponding to MI that trap various proportions of vapor and undergo various degrees of PEC up to 10%, with the assumption that all MI were trapped at the same pressure-temperature conditions and with the same H₂O and CO₂ concentrations in the trapped melt.

Figures 6B shows the data of Hartley et al. (2014), on MI bubbles hosted in olivine from the AD 1783-1784 Laki eruption, southeast Iceland. Figure 6C shows the data of Moore et al. (2015) on MI bubbles hosted in olivine from the 1959 Kilauea Iki and 1960 Kapoho eruptions, Hawaii. Both of these datasets show a similar distribution: Most of the data are clustered towards relatively low volume fractions of vapor up to ~5-10 vol.%, and within this range the vapor densities show a wide range of variability. However, a small number of MI show much higher volume fraction of vapor up to ~100 vol.%, and these MI also show variable, but generally higher densities. For example, the majority of the MI measured by Hartley et al. (2014) contain <10 vol.% vapor and have vapor densities range from <50 to ~250 kg/m³. In contrast, among the MI with >10 vol.% vapor, densities range from ~100 to ~300 kg/m³. Notice also that the lowest vapor density occurs at low volume fraction of vapor, whereas the highest vapor density occurs

at the highest volume fraction of vapor. The data of Moore et al. (2015) similarly show a greater variation in vapor density at low volume fractions of vapor, compared to generally more consistent vapor densities at volume fractions >10 vol.%. Moreover, the densities of vapor bubbles that comprise >10 vol.% in the data of Moore et al. (2015) cluster around ~130 kg/m³, which is around the maximum of the low-volume fraction cluster of data. The grey-shaded regions in Figs. 6B and 6C were constructed using the same numerical methods described above, assuming a basaltic melt composition hosted in olivine. Initial conditions for the modeling in Fig. 6B were 1210 °C and 85 MPa, whereas the initial conditions for the modeling in Fig. 6C were 1210 °C and 45 MPa. In both cases, the initial (trapping) pressures are less than those constrained by H₂O-CO₂ solubility calculations (Hartley et al. 2014; Moore et al. 2015) in order to match the relatively low density of the vapor bubbles. Stated differently, these initial pressures were selected according to the pressure on the relevant CO₂-H₂O isochore at the presumed trapping temperature of 1210°C. The discrepancy in modeled initial pressure versus inferred trapping pressure for the studied MI likely reflects expansion (and concomitant decrease in density) of the vapor bubble during quenching of the glass (Esposito et al., 2011), or vapor loss by decrepitation (MacLennan, 2017). Nevertheless, in both cases the predicted trends for MI that trapped some fraction of vapor and subsequently underwent various degrees of PEC are broadly consistent with the analytical data. Certainly, these results do not provide definitive evidence of a role of heterogeneous trapping and PEC in the distribution of data from Laki, Kilauea Iki and Kapoho, but the results are at least consonant with this general model. However, we stress once again that this interpretation relies on the assumption that the MI shown in Figs. 6B or 6C were trapped coevally, whereas we lack petrographic information to test this assumption.

The recent study of Aster et al. (2016) provides another dataset on MI vapor bubble densities and volume fractions from four cinder cones: two in the Cascade Arc and two in the Trans-Mexico volcanic belt. Aster et al. (2016) only report vapor bubbles occupying up to 15 vol.% of the MI. The densities of vapor bubbles measured by Aster et al. (2016) do not show any systematic relationship with bubble volume fraction. They inferred heterogeneous entrapment of some of the vapor bubbles by calculating the maximum expected volume fraction of vapor produced by cooling, PEC and quenching of the MI, and determined that most of the bubbles could have formed by these processes alone (i.e., without heterogeneous trapping of vapor). These results by Aster et al. (2016) indicate that the predictions made in the present study do not always apply to olivine-hosted MI, such as in the case when only bubbles up to ~15 vol.% are observed. Nevertheless, the comparison with the datasets of Hartley et al. (2014) and Moore et al. (2015) indicate that bubbles with larger volume fractions (up to ~100 vol.%) occur in olivine-hosted MI from volcanic systems, and MI hosting such bubbles may be amenable for analysis of pre-eruptive volatile concentrations.

The comparison of our model predictions with these literature data from Hartley et al. (2014) and Moore et al. (2015) are not unequivocal, partly because of sparseness and scatter in the data, and likely also because various factors affect the vapor densities of olivine-hosted MI. For example, MI may have been trapped at various depths, and certainly re-equilibration of volatile constituents is likely to play a role. Hartley et al. (2015) used the H₂O/Ce ratios of some of the same MI discussed here, to evaluate the degree of H₂O loss or gain by diffusion. This type of analysis could in principle be used to help constrain the degree of re-equilibration of MI containing anomalously large bubbles, but such inclusions were not analyzed by Hartley et al. (2015). An additional complication is that MI that trap relatively small volume fractions of vapor

may not exhibit anomalously large vapor bubbles (Aster et al. 2016). In some cases, trapping of vapor may be only distinguishable by calculating the volume fraction of vapor formed via pre-eruptive cooling coupled with the effects of cooling and quenching to the glass transition temperature (Aster et al. 2016). Nevertheless, the data shown in Figs. 5 and 6 are broadly consistent with the prediction that MI which trapped significant proportions of vapor can maintain a relatively high vapor density at room temperature, compared to inclusions that trapped little to no vapor. A corollary of this prediction is that the glass phase in such inclusions is expected to retain concentrations of H₂O and CO₂ that reflect the composition of the melt at the time of trapping. As such, these data and model predictions suggest that microanalysis of the glass phase within MI containing trapped vapor may be an amenable method to directly sample the H₂O and CO₂ concentrations of the trapped melt, independently of PEC. Moreover, analysis of the CO₂ and H₂O concentrations in the corresponding (heterogeneously entrapped) vapor bubble using the methods developed by Esposito et al. (2016) may be an amenable and complementary method to determine the composition of the coeval, equilibrium magmatic vapor phase.

In interpreting the patterns in vapor density versus volume fraction in Fig. 6, we must emphasize that the available data do not permit us to evaluate whether the MI record coeval entrapment. As such, it is not currently possible to verify whether the MI in Fig. 6 record similar physical and chemical conditions of trapping. The best method to constrain the relative timing of MI trapping would be to study MI in the context of coeval assemblages (Esposito et al. 2014). In the case of melt inclusions from a single eruptive event in which suitable assemblages are absent, an alternative method would be to categorize MI based on the forsterite content of the immediately adjacent host olivine, or the major element composition of the MI, or some

combination of these parameters. Such procedures may allow us to better define the trends of melt-volatile composition with trapped vapor fraction. Similarly, direct analysis of the CO₂ and H₂O concentrations in the glass phase of MI containing anomalously large bubbles would be extremely beneficial to assess the model predictions described here. Unfortunately, the available data do not allow us to assess these various potential indicators for coeval trapping (as well as for potential diffusive reequilibration, etc.) – we hope that future studies will provide additional constraints to evaluate these various factors.

Another potential issue that may influence trends such as those shown in Fig. 5B and 5C is the precipitation of carbonate at the glass/bubble interface (e.g., Kamenetsky et al. 2001; Moore et al. 2015; Esposito et al. 2016), which will lower the CO₂ density measured in the bubble. It is important to note that Kamenetsky et al. (2001) showed a positive correlation between the relative volume fraction of the vapor bubble and the amount of precipitates at the glass/bubble interface.

A final caveat that must be addressed is the possibility of forming large vapor bubbles within MI by processes other than heterogeneous entrapment, namely bubble growth as a result of H⁺ diffusion or following stretching, leakage and/or decrepitation. Hydrogen diffusion will result in an increased density (decreased molar volume) of the melt phase, which can result in formation of a bubble by contraction of the melt. Similarly, stretching, leakage and/or decrepitation may effectively reduce the *bulk* density (increase the bulk molar volume) of the inclusion, thereby favoring the subsequent production of large bubbles. Regarding H⁺ diffusion, we calculated the volume fraction of vapor that would be expected in a basaltic melt inclusion with a starting H₂O concentration of 5 wt.%, assuming different proportions of H₂O loss, according to the effect of H₂O on the density of the silicate glass (Lange and Carmichael 1987;

1990; Ochs and Lange 1999; Iacovino 2014). Our calculation was based on a basaltic melt trapped at 100 MPa and 1100 °C. In this example, if the H₂O concentration is reduced to 4 wt.% by diffusive reequilibration, then the expected volume fraction of vapor would be ~2 vol.%. In the extreme case where all H₂O was lost (resulting in an anhydrous glass) then the maximum volume fraction of the shrinkage bubble would be ~9 vol.%. As such, bubbles exceeding 2-9 vol.% vapor (e.g., Figs. 5 and 6) suggest additional factors besides diffusive reequilibration. We note that H₂O/Ce data (e.g., Hartley et al. 2015) and hydrogen isotopic analyses of MI glasses may add constraints to evaluate the extent of diffusive reequilibration in future studies.

Stretching, leakage and decrepitation (SLD) may all be induced by internal overpressure within the inclusion during exhumation and cooling (MacLennan, 2017), analogous to the same phenomena in aqueous fluid inclusions (Bodnar et al. 1989). In some cases in which SLD occurs as a result of brittle deformation (cracking) of the mineral host, it may be possible to identify signs of fluid loss from melt inclusions based on the presence of annealed cracks or decrepitation halos (e.g., Fig. 3b in Cannatelli et al., 2015). Although we did not consider or account for stretching, leakage or decrepitation in this study, we do not mean to suggest that *all* large bubbles in inclusions are generated by heterogeneous trapping, and indeed we expect that some MI containing large bubbles may reflect SLD. In particular, MI trapped at high pressures (which thus exsolve a high-density CO₂-H₂O fluid phase during PEC and cooling) may be particularly susceptible to SLD because of the potential for internal overpressure of the high-density, CO₂-rich fluid (MacLennan, 2017). Again, this suggestion is based on the experience of high-density, CO₂-bearing fluid inclusions, which are susceptible to high internal pressures and, thus, decrepitation (Diamond, 2001). Importantly, the trends expected from such processes would differ from those predicted in the case of heterogeneous entrapment. Specifically, the density of

the vapor bubble would be expected to decrease in response to SLD, owing to the overall increase in the bulk molar volume. Thus, large bubbles produced by SLD processes would be expected to exhibit relatively low density compared to bubbles of modest volume fraction within unmodified inclusions. Thus, Figs. 5 and 6 provide some basis for comparing heterogeneous entrapment versus SLD. Heterogeneous entrapment is expected to yield larger bubbles containing vapor of relatively high density compared to the smaller vapor bubbles in the same sample. In contrast, SLD are expected to yield larger vapor bubbles of relatively low density compared to the smaller bubbles in the same sample. Figure 6 shows that in the samples from Laki, Kilauea Iki and Kapoho, the majority of the anomalously large bubbles exhibit relatively high densities suggesting heterogeneous entrapment. Nevertheless, some of the larger vapor bubbles (e.g., the bubble at ~56 vol.% in the Kapoho samples; Fig. 6C) show relatively low densities and may reflect SLD. Figure 5 also allows some qualitative estimation of the expected effects of diffusive reequilibration as well as SLD processes, because both would be expected to yield systematic relationships between MI and bubble size: In the case of diffusive H⁺ loss, smaller inclusions would be more severely affected (Qin et al. 1992; Bucholz et al. 2013), whereas larger inclusions are more susceptible to SLD processes (Bodnar et al. 1989). The results shown in Figure 5 indicate no particular relationship between inclusion size and bubble volume, which is at least broadly consistent with heterogeneous trapping, although this inference relies on the assumption that the MI were trapped at the same time (see also Fig. 1A). Nevertheless, ultimately a combined model accounting for heterogeneous entrapment, PEC and the effects of SLD will be required to assess these mutually interacting processes.

5. CONCLUSIONS

The predictions described above are testable, and future studies aimed at microanalysis of the glass phase within vapor-rich MI should be conducted to determine the variability of melt volatile contents. Based on the numerical modeling described herein, we suggest that MI containing high volume fractions of vapor (>10 vol.%) probably originate by trapping of magmatic vapor along with the silicate melt, and that the compositions of both the melt and vapor phases in such inclusions are preserved in their original (trapping) states as a result of this process. As such, MI containing trapped vapor probably should not be ignored or deliberately omitted from microanalysis, but rather should be targeted in order to estimate the original melt-volatile composition. We hope that this insight will provide an additional tool in the arsenal applied to melt inclusion volatiles in volcanic systems.

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Figure Captions:

Fig 1 Assemblages of heterogeneously trapped inclusions of melt plus magmatic vapor exhibit a wide range in the relative volume of vapor bubbles including anomalously high (>5 vol.%) volume fractions of vapor. The transmitted light photomicrographs show: (A) An assemblage and (B) a group of olivine-hosted of silicate melt inclusions from the 1959 eruption of Kilauea Iki, Hawaii (Moore et al., 2015); (C) olivine-hosted MI from the 1783-84 Laki eruption, Iceland (Hartley et al., 2014); (D) an assemblage and (E) a group of plagioclase-hosted MI from the 1783-84 Laki eruption, Iceland. Arrows in panels A, B, C and E indicate inclusions with different volume fractions of vapor (labelled). Notice the variable proportions of vapor, including anomalously large bubbles, in the assemblage shown in (A) suggesting heterogeneous entrapment. The color differences between MI in (C) probably reflect variations in light scattering between inclusions of different size

Fig. 2 Heterogeneously trapped inclusions of melt plus magmatic vapor follow pressure-temperature trajectories intermediate between those of coeval vapor-saturated melt inclusions and magmatic CO₂-H₂O fluid inclusions. The pressure-temperature phase diagram shows the vapor-saturated solidus-liquidus of albitic melt contoured by activity of H₂O (Burnham and Davis 1974) and the liquid-vapor solvus and isochores of a CO₂-H₂O fluid of 40 mol.% CO₂ (Connolly and Bodnar 1983). This fluid composition corresponds to the vapor in equilibrium with albitic melt at the trapping condition of 930 °C and 200 MPa, indicated by the star. Path "a" represents the isochore of a CO₂-H₂O fluid inclusion trapped at this condition, whereas path "b" represents the pressure-temperature trajectory followed by a melt inclusion which trapped only vapor-saturated melt during cooling and PEC. Heterogeneously trapped melt+vapor inclusions are expected to follow a pressure-temperature trajectory intermediate between these two endmembers, exemplified by path "c." Shaded box expanded in Fig. 3A

Fig. 3 Melt inclusions that trap vapor undergo subdued decompression during cooling and PEC. Model results for (A) an albitic melt trapped in albite at 930 °C and 200 MPa, and (B) a basaltic melt trapped in olivine at 1200 °C and 120 MPa. The results of our numerical model show that with increasing volume fraction of trapped vapor, the pressure-temperature pathway followed by the MI approaches that of the coeval CO₂-H₂O fluid inclusion (indicated by 100 vol.% vapor, and corresponding to the fluid-inclusion isochore). At ≥20 vol.% trapped vapor, the pressure-temperature path for the albitic MI is virtually indistinguishable from the fluid-inclusion isochore. Symbols on each curve represent 1% increments of PEC

Fig. 4 CO₂-H₂O systematics of vapor-saturated MI during PEC vary with the proportion of trapped vapor. Model results for (A) an albitic melt trapped in albite at 930 °C and 200 MPa, and (B) a basaltic melt trapped in olivine at 1200 °C and 120 MPa. The inclusions that trapped only vapor-saturated melt (0% trapped vapor) undergo the most significant decrease in CO₂ content in the melt, whereas MI that trapped more vapor experience less CO₂ loss from the melt, for both albitic and basaltic MI. Symbols on each curve represent 1% increments of PEC

Fig. 4 Volumes of vapor bubbles versus volumes of melt inclusions from (a) the AD 1783-84 Laki eruption, Iceland (Hartley et al. 2014), and (b) the 1959 Kilauea Iki and 1960 Kapoho eruptions, Hawaii (Moore et al. 2015).

Fig. 6 Densities of MI vapor bubbles vary systematically with the proportion of trapped vapor. (a) Results of our numerical model. (B) MI from the AD 1783-84 Laki eruption, Iceland (Hartley et al. 2014). (C) MI from the 1959 Kilauea Iki and 1960 Kapoho eruptions, Hawaii (Moore et al. 2015). The dashed vertical line in (B) and (C) corresponds to 5 vol.% vapor, representing the cutoff applied by both Hartley et al. (2014) and Moore et al. (2015) to differentiate MI vapor bubbles likely generated by differential thermal contraction and/or PEC (<5 vol.%) versus bubbles potentially indicating heterogeneous trapping (>5 vol.%). The light shaded regions in (B) and (C) were calculated as described in the text