



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

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1 MI: heterogeneously entrapped bubbles

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

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**ABSTRACT**

Silicate melt inclusions (MI) commonly provide the best record of pre-eruptive H<sub>2</sub>O and CO<sub>2</sub> contents of subvolcanic melts, but the concentrations of CO<sub>2</sub> and H<sub>2</sub>O 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 CO<sub>2</sub> and moderate increase in H<sub>2</sub>O concentrations in the melt upon nucleation and growth of a vapor bubble. In contrast, inclusions that trap melt plus vapor exhibit subdued CO<sub>2</sub> depletion at equivalent conditions. In the extreme case of inclusions that trap mostly the vapor phase (i.e., CO<sub>2</sub>-H<sub>2</sub>O fluid inclusions containing trapped melt), degassing of CO<sub>2</sub> 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; H<sub>2</sub>O; CO<sub>2</sub>; 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., CO<sub>2</sub>, H<sub>2</sub>O, 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 CO<sub>2</sub>-enriched melt during ascent (Lowenstern 1994; Métrich and Wallace 2008).

Apparently coeval melt inclusions commonly record wide ranges of CO<sub>2</sub> 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



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4 66 a vapor phase (bubble) subsequent to trapping (Anderson and Brown 1993; Steele-MacInnis et  
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7 67 al. 2011; Hartley et al. 2014; Moore et al. 2015; Wallace et al. 2015; Tuohy et al. 2016; Aster et  
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9 68 al. 2016). A vapor phase within an initially homogeneous melt inclusion may nucleate and grow  
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11 69 after trapping as a result of differential thermal contraction of melt versus the host crystal  
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14 70 (Lowenstern 2003; Moore et al. 2015), by post-entrapment crystallization (PEC; Steele-MacInnis  
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16 71 et al. 2011) of the host mineral on the inclusion walls, or a combination of these processes. In all  
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19 72 three scenarios, nucleation and growth of the vapor bubble results in strong depletion of CO<sub>2</sub>  
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21 73 from the melt phase with concomitant minor variation in the H<sub>2</sub>O concentration. The divergent  
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24 74 trends in CO<sub>2</sub> versus H<sub>2</sub>O concentration in the melt are a consequence of the extremely different  
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26 75 CO<sub>2</sub>/H<sub>2</sub>O ratios in the melt versus the exsolving fluid phase: In general, the CO<sub>2</sub>/H<sub>2</sub>O ratio in the  
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29 76 exsolving vapor is significantly greater than that in the coexisting melt (i.e., CO<sub>2</sub>-rich vapor  
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31 77 exsolved from a melt which is generally more enriched in H<sub>2</sub>O), and as such the exsolution of the  
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34 78 vapor phase drives the CO<sub>2</sub>/H<sub>2</sub>O ratio of the melt to lower values. Thus, several studies have  
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36 79 used Raman spectroscopy to determine the amount of CO<sub>2</sub> exsolved into the bubble to constrain  
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39 80 the bulk CO<sub>2</sub> content of the inclusion (e.g., Esposito et al. 2011; Moore et al. 2015; Hartley et al.  
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41 81 2014; Tuohy et al. 2016). The H<sub>2</sub>O in the vapor bubble has not generally been detected during  
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44 82 Raman spectroscopic analysis of MI vapor bubbles, but has recently been detected as a rim of  
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46 83 H<sub>2</sub>O-rich liquid at the glass/bubble interface in re-heated MI (Esposito et al. 2016). Like the case  
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49 84 for CO<sub>2</sub>, Esposito et al. (2016) suggested that depending on the initial conditions, most of the  
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51 85 H<sub>2</sub>O and of the S of the originally trapped melt may be stored in the bubble.

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53 86 Heterogeneous entrapment represents an alternative origin for the vapor bubbles in some  
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56 87 MI. In this scenario, the host phenocryst encloses a multi-phase assemblage of vapor-saturated  
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58 88 melt plus vapor. Evidence for heterogeneous entrapment of melt plus magmatic fluid has been  
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4 89 reported in several studies. For example, Harris et al. (2003), Zajacz et al. (2008) and Stefanova  
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6 90 et al. (2014) described MI from high-temperature porphyry veins, containing globules of high-  
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8 91 density, high-salinity brine. In these studies, the brine globules are interpreted as trapped  
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11 92 hydrothermal fluid, which presumably exsolved from the silicate melt prior to trapping of the  
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14 93 melt inclusions. Bodnar and Student (2006) noted that in the case of heterogeneous entrapment,  
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16 94 the volume fraction of vapor would likely be variable for groups of coevally entrapped MI (or  
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19 95 melt inclusion assemblages; MIA). Moore et al. (2015) developed a numerical model to estimate  
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21 96 the maximum volume fraction of vapor expected as a result of differential thermal contraction  
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24 97 for MI hosted in various minerals, and concluded that in general, vapor bubbles of up to a few  
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26 98 percent of the MI volume are consistent with bubble nucleation and growth by this mechanism.  
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29 99 As such, vapor bubbles exceeding a few volume percent of the MI may represent trapped vapor  
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31 100 (Fig. 1). Aster et al. (2016) similarly used a numerical model to estimate the maximum volume  
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33 101 fraction of vapor expected purely from cooling, PEC and quenching of initially homogeneous  
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36 102 trapped melt, and used this information to infer which MI appeared to have trapped some portion  
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38 103 of vapor. Hartley et al. (2014) and Moore et al. (2015) reported melt inclusions containing  
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41 104 exceptionally large vapor bubbles up to several tens of volume percent, suggesting that these MI  
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43 105 trapped melt plus vapor. In the most extreme example reported by Hartley et al. (2014) and  
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45 106 Moore et al. (2015), the MI vapor bubble represented >90 vol.% of the inclusion; as such, the  
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48 107 most vapor-rich MI approach the limiting case of magmatic CO<sub>2</sub>-H<sub>2</sub>O fluid inclusions containing  
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51 108 a small proportion of trapped melt, similar to clinopyroxene-hosted fluid inclusions reported for  
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53 109 example by Belkin et al. (1985) and Belkin and De Vivo (1993); and olivine-hosted fluid  
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55 110 inclusions by Mironov and Portnyagin (2011), Zanon and Frezzotti (2013), and Zanon and  
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58 111 Pimentel (2015). Note, however, that H<sup>+</sup> diffusion out of the MI may also promote formation of  
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4 112 anomalously large vapor bubbles (Bucholz et al., 2013; Aster et al. 2016), which is not  
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7 113 considered in the present study. In addition, decrepitation and/or leakage of MI may also  
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9 114 contribute to forming anomalously large bubbles, as discussed below.

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12 115         The occurrence of MI containing a heterogeneously trapped vapor phase raises questions  
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14 116 as to the systematics of melt-vapor partitioning within inclusions that trapped both melt and  
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16 117 vapor. Conceptually, coeval melt inclusions and fluid inclusions are expected to follow different  
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18 118 temperature-pressure trajectories subsequent to trapping (Fig. 2). The pressure-temperature  
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20 119 trajectory followed by a vapor-saturated silicate melt inclusion is a function of compressibility  
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22 120 and expansivity of melt and vapor, the vapor solubility relations, and the evolution of PEC  
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24 121 (Student and Bodnar 1996; Steele-MacInnis et al. 2011; Schiavi et al. 2016). In contrast, the  
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26 122 temperature-pressure trajectory for CO<sub>2</sub>-H<sub>2</sub>O fluid inclusions is constrained by the isochore  
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28 123 (pressure-temperature locus of constant density) of the CO<sub>2</sub>-H<sub>2</sub>O fluid phase (Sterner and  
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30 124 Bodnar, 1991; Diamond, 2003) according to the composition and bulk density of the fluid. For  
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32 125 example, Mironov and Portnyagin (2011) estimated the trapping temperature and pressure  
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34 126 conditions of coeval melt and fluid inclusions hosted in olivine by intersecting the temperature  
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36 127 estimated from MI with the isochores of the coeval CO<sub>2</sub>-H<sub>2</sub>O fluid inclusions. As such, the  
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38 128 temperature-pressure trajectory followed by heterogeneously entrapped, vapor-rich MI is  
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40 129 expected to vary between these two endmembers according to the proportion of trapped vapor  
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42 130 (Fig. 2). Moreover, the temperature-pressure trajectory of the MI is expected to tend towards the  
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44 131 coeval fluid-inclusion isochore at high proportions of trapped vapor. Steele-MacInnis et al.  
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46 132 (2011) reported that evolution of CO<sub>2</sub> and H<sub>2</sub>O concentrations in the melt (glass) within MI is  
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48 133 correlated to the pressure-temperature trajectory followed by the MI after trapping. Hence, we  
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50 134 expect that the volatile systematics of heterogeneously entrapped MI will also vary according to  
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4 135 the proportion of trapped vapor. Stated differently, the partitioning of volatile components  
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7 136 between melt and vapor is sensitive to the relative proportions of phases trapped. Thus,  
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9 137 interpreting volatile contents of MI glass, bubble, and bulk inclusion can be complicated by  
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11 138 heterogeneous entrapment.

14 139 In this study, we build upon the earlier thermodynamic modeling of Steele-MacInnis et  
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16 140 al. (2011) to characterize volatile evolution of MI melt (glass) and vapor during post-entrapment  
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19 141 crystallization of heterogeneously entrapped MI. Steele-MacInnis et al. (2011) focused on MI  
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21 142 that trapped only vapor-saturated melt (without trapped vapor), and reported contrasting behavior  
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24 143 of CO<sub>2</sub>-rich versus H<sub>2</sub>O-rich melts and intermediate CO<sub>2</sub>-H<sub>2</sub>O-saturated melts. Here, we extend  
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26 144 these results to heterogeneously entrapped inclusions, including end-member scenarios of  
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29 145 homogeneously entrapped melt or vapor, and several intermediate scenarios with various relative  
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31 146 proportions of trapped melt and vapor. In the present contribution, we do not include the effects  
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34 147 of diffusive re-equilibration, nor the effects of bubble expansion during syn-eruptive cooling and  
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36 148 quenching, although we recognize that these effects may be significant for many natural MI and  
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38 149 that future studies incorporating them will be necessary. As such, the present contribution  
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41 150 represents one endmember of the various complexities that can manifest in MI volatile  
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43 151 systematics. The results of this analysis indicate that for inclusions that trap a large proportion of  
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46 152 vapor, the H<sub>2</sub>O and CO<sub>2</sub> concentrations in the melt (glass) phase within the inclusion are  
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48 153 relatively insensitive to post-entrapment crystallization. These results thus suggest that  
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51 154 heterogeneously entrapped MI may represent amenable samples for characterizing pre-eruptive  
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53 155 dissolved volatile contents of melts.

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## 58 157 2. METHODS

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4 158           The methods used here were mostly described in detail by Steele-MacInnis et al. (2011),  
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6 159           so here we provide only an abridged overview (see Steele-MacInnis et al., 2011 for additional  
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9 160           details). We modeled the effects of volatile exsolution during post-entrapment crystallization of  
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11 161           an albitic ( $\text{NaAlSi}_3\text{O}_8$ ) melt trapped in albite using constant volume (isochoric), constant  
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13 162           composition (closed) boundary conditions. The albitic model was used primarily because this  
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15 163           system represents a relatively simple endmember, and because the parameterization is very well  
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17 164           constrained. In addition, we extended this model to basaltic melts trapped in olivine, because the  
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19 165           latter system is one of the most widely studied in terms of natural MI and information relative to  
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21 166           bubble and MI are available from the literature (e.g., Hartley et al. 2014; Moore et al., 2015). The  
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23 167           methods used in this modeling are described below.

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26 168           For the albitic melt, solubilities of  $\text{H}_2\text{O}$  and  $\text{CO}_2$  in the melt were calculated according to  
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28 169           the models described by Holloway and Blank (1994). Volumetric properties of albitic melt and  
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30 170           albite were calculated using the model of Burnham and Davis (1971; 1974). To initiate the  
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32 171           model, the composition of vapor-saturated melt in equilibrium with albite was calculated, which  
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34 172           defined the composition of the initial melt aliquot. The volume of the melt inclusion (constant in  
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36 173           all subsequent steps) was calculated according to the specific volume of melt and the mass of the  
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38 174           aliquot. In each subsequent step, a portion of melt (arbitrarily set to 1% of the albitic component  
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40 175           of the initial melt) was crystallized. Consequently, the remaining melt was enriched in  $\text{CO}_2$  and  
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42 176            $\text{H}_2\text{O}$  via subtraction of  $\text{NaAlSi}_3\text{O}_8$  into newly-formed albite (i.e., PEC). However, because the  
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44 177           melt was initially vapor-saturated, enrichment in  $\text{CO}_2$  and  $\text{H}_2\text{O}$  drives the melt towards  
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46 178           supersaturation, and some portion of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  must be released into a free vapor phase, or  
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48 179           bubble. In a closed system, at any given temperature and pressure the  $\text{CO}_2/\text{H}_2\text{O}$  ratio of the  
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50 180           exsolved vapor phase is constrained by the  $\text{CO}_2/\text{H}_2\text{O}$  ratio in the coexisting melt, and an iterative  
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4 181 procedure is employed to solve for melt-vapor equilibrium. The density and volume of the  
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6 182 exsolved vapor phase was calculated using the Redlich-Kwong equation of state (Redlich and  
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9 183 Kwong, 1949) with the parameters of Holloway (1977). To achieve constant volume conditions,  
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11 184 a nested iterative procedure was also employed to adjust internal pressure (with temperature  
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14 185 constrained by the vapor-saturated liquidus surface). Note that in the latter isochoric constraint,  
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16 186 the volume of the inclusion was defined by the sum of volumes of melt plus vapor plus albite  
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19 187 formed during PEC (i.e., albite crystallized on the walls of the inclusion). The two constraints  
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21 188 (mass balance and isochoricity) were solved simultaneously for each increment of PEC, to obtain  
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24 189 a trajectory of evolving pressure-temperature-composition (melt+vapor) conditions. The  
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26 190 calculations did not treat external pressure as a variable, nor did they account for compressibility  
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29 191 of the host mineral.

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31 192 In addition to the simulations using an albitic melt composition trapped in albite, we  
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33 193 conducted several simulations using a basaltic melt composition trapped in olivine. The  
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36 194 solubility model for volatile species in the basaltic melt (based on an average tholeiitic basalt  
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38 195 composition) was from Holloway and Blank (1984). The volumetric properties of the basaltic  
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41 196 melt, as well as the volume of fusion of olivine, were modeled based on the data of Lange and  
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43 197 Carmichael (1990). Effect of H<sub>2</sub>O on the olivine crystallization temperature was modeled based  
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46 198 on the data of Almeev et al. (2007). Our model is thus somewhat simplified and does not invoke  
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48 199 compositional changes or effects in the basaltic melt (nor host olivine) but nevertheless serves to  
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51 200 compare and contrast the mafic system with the earlier albitic model.

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53 201 Note that the recent study by Tuohy et al. (2016) reported new numerical modeling  
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55 202 showing a greater volume fraction of vapor at equivalent degree of PEC than reported by Steele-  
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58 203 MacInnis et al. (2011). The model described by Tuohy et al. (2016) used similar methods to

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

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

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4 227 resulting trapped vapor phase was calculated using the Redlich-Kwong equation of state. The  
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7 228 combined volume of initial melt plus vapor was then used as the reference volume for constant-  
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9 229 volume calculations in all subsequent steps.

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12 230 We conducted simulations for an albitic melt composition hosted in albite using a  
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14 231 trapping temperature and pressure of 930 °C and 200 MPa (equivalent to the model shown in  
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16 232 Fig. 10 of Steele-MacInnis et al. 2011), for 12 starting volume fractions of vapor: 0, 5, 10, 15,  
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19 233 20, 40, 60, 80, 85, 90 and 95 vol.% vapor. We conducted additional simulations for a basaltic  
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21 234 melt composition hosted in olivine using a trapping temperature and pressure of 1200 °C and 120  
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24 235 MPa, for six starting volume fractions of vapor: 0, 5, 10, 15, 20 and 40 vol.% vapor. In each  
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26 236 simulation, we traced the evolution of H<sub>2</sub>O and CO<sub>2</sub> concentrations in the melt, as well as  
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29 237 temperature and internal pressure, during PEC up to 10% (by mass) of the silicate (albitic or  
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31 238 basaltic) component of the melt. We modeled up to 10% PEC because greater degrees of PEC  
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33 239 than this are rarely reported in literature (Steele-MacInnis et al. 2011).

### 38 241 3. RESULTS

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41 242 Results of our simulations are shown in Figs. 3 and 4. For the homogeneously entrapped vapor-  
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43 243 saturated melt (0 vol.% vapor), the results for the albitic melt are equivalent to those reported by  
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45 244 Steele-MacInnis et al. (2011). The basaltic melt hosted in olivine shows a similar trajectory,  
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48 245 although the decrease in internal pressure as well as CO<sub>2</sub> concentration in the glass is somewhat  
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50 246 greater for basaltic MI compared to albitic MI, at equivalent degrees of PEC (Figs. 3B and 4B).  
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53 247 Figure 3 also shows heterogeneously entrapped MI with 5-20 vol.% trapped vapor, and Fig. 4  
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55 248 shows heterogeneously entrapped MI with 5-40 vol.% trapped vapor. Figures 3 and 4 do not  
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58 249 show the heterogeneously entrapped MI with higher volume fractions of trapped vapor (up to  
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250 95% vol.%) because the data points and trend lines at these high volume fractions of trapped  
251 vapor all overlap.

252 Figure 3 shows that as the volume fraction of trapped vapor increases, an equivalent  
253 degree of PEC is achieved at lower degree of cooling. Stated differently, if a group of MI are all  
254 trapped at the same temperature but initially contain various proportions of trapped vapor, those  
255 containing more trapped vapor are predicted to undergo more post-entrapment crystallization  
256 during the same interval of cooling. We should note that this latter prediction depends upon the  
257 assumption of thermodynamic equilibrium, and does not account for potentially differing cooling  
258 rates, nor differing glass-transition behavior discussed below. Figure 3 also shows that with  
259 increasing volume fraction of trapped vapor, the decrease in internal pressure within an MI  
260 concomitant with decreasing temperature/increasing PEC is reduced. Thus, at 10% PEC (by  
261 mass), the albitic inclusion that trapped no vapor has undergone an internal pressure decrease of  
262 ~50 MPa, whereas the albitic inclusion that trapped 10 vol.% vapor has undergone only ~5 MPa  
263 of pressure decrease. For the albitic inclusion that trapped 20 vol.% vapor, the pressure decrease  
264 at 10% PEC is only ~1 MPa, and the pressure-temperature trajectory is essentially equivalent to  
265 that of the CO<sub>2</sub>-H<sub>2</sub>O fluid isochore corresponding to the composition and density of the trapped  
266 vapor. Analogous trends are evident in the models for basaltic MI hosted in olivine (Fig. 3B).

267 As PEC, cooling and decompression progress, the silicate melt within the MI gradually  
268 exsolves H<sub>2</sub>O and CO<sub>2</sub> into the vapor bubble (Steele-MacInnis et al. 2011). However, the  
269 concentrations of these volatiles in the remaining melt (glass) phase diverge owing to the order-  
270 of-magnitude difference in their solubilities in the melt, versus their relative concentrations in the  
271 conjugate vapor phase (Steele-MacInnis et al. 2011). Hence, for the albitic MI that trapped no  
272 vapor, after 10% PEC the CO<sub>2</sub> concentration in the melt decreases from 520 to 230 ppm,

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4 273 whereas the H<sub>2</sub>O concentration in the melt increases from 3.8 to 4.2 wt.% (Fig. 4). With  
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7 274 increasing volume fraction of trapped vapor, these effects are more subdued (Fig. 4). For  
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9 275 example, for the albitic MI that traps 10 vol.% of vapor, at 10% PEC the CO<sub>2</sub> concentration in  
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11 276 the melt has decreased from 520 to 450 ppm, and the H<sub>2</sub>O concentration in the melt has  
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14 277 increased from 3.8 to 4.0 wt.%. At  $\geq 60\%$  trapped vapor, both the CO<sub>2</sub> concentration and the H<sub>2</sub>O  
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16 278 concentration in the melt remain essentially constant ( $\sim 520$  ppm and  $\sim 3.8$  wt.%, respectively) up  
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19 279 to 10% PEC. Again, analogous trends are evident for the basaltic MI trapped in olivine (Fig. 4B).

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#### 22 23 24 281 4. DISCUSSION

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26 282 As expected, as the volume fraction of trapped vapor in the melt inclusion increases, the  
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29 283 pressure-temperature trajectory followed by the MI during PEC and cooling approaches that of a  
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31 284 coeval CO<sub>2</sub>-H<sub>2</sub>O fluid-inclusion isochore (Fig. 3). Indeed, at volume fractions of trapped vapor  
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33 285 greater than  $\sim 20$  vol.% for the albitic melt, and  $\sim 40$  vol.% for the basaltic melt, the pressure-  
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36 286 temperature trajectory of the MI is indistinguishable from a coeval fluid-inclusion isochore.  
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38 287 Consequently, the internal pressure decreases more gradually in inclusions containing more  
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41 288 trapped vapor, and thus degassing of CO<sub>2</sub> and H<sub>2</sub>O into the vapor bubble is more subdued.  
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43 289 Hence, the volatile concentrations in the melt show less change from the initial composition at  
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46 290 equivalent degrees of PEC, in inclusions containing more trapped vapor. In the extreme case of  
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48 291  $>60$  vol.% trapped vapor, the concentrations of CO<sub>2</sub> and H<sub>2</sub>O in the melt (and thus, in the glass  
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51 292 in quenched MI) are predicted to be equal within the uncertainty of standard analytical  
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53 293 techniques to those in the originally trapped melt.

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55 294 As the volume fraction of trapped vapor increases, we also see a decrease in the degree of  
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58 295 cooling required to achieve an equivalent degree of PEC (Fig. 3). This phenomenon is a result of  
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4 296 mass-balance constraints on the vapor-saturated solidus temperature of the MI. According to  
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7 297 Burnham and Davis (1974), the solidus temperature of a vapor-saturated albitic melt is a function  
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9 298 of the ratio of H<sub>2</sub>O to CO<sub>2</sub> in the vapor phase. In a melt inclusion which traps only vapor-  
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11 299 saturated melt (with no trapped vapor), the composition of the vapor phase becomes increasingly  
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14 300 enriched in H<sub>2</sub>O during cooling and PEC (i.e., the composition of each aliquot of exsolved vapor  
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16 301 is more H<sub>2</sub>O-rich at each increment of PEC). Because this inclusion traps only a vapor-saturated  
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19 302 melt, and because the H<sub>2</sub>O concentration in such a melt is commonly an order of magnitude  
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21 303 greater than the CO<sub>2</sub> concentration, the inclusion is able to achieve a very H<sub>2</sub>O-rich vapor bubble  
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24 304 at the later stages of degassing of H<sub>2</sub>O. As such, as cooling and PEC occur, the vapor-saturated  
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26 305 solidus temperature is increasingly depressed, allowing PEC to proceed towards the H<sub>2</sub>O-  
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29 306 saturated solidus (Burnham and Davis 1974). In contrast, melt inclusions that trap a vapor bubble  
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31 307 have their volatile budgets buffered by the composition of the trapped vapor, which is commonly  
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33 308 significantly more CO<sub>2</sub>-rich than the corresponding melt phase. Inclusions that trap a large  
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36 309 proportion of vapor thus have higher vapor-saturated solidus temperatures, and may undergo an  
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38 310 equivalent degree of PEC in a smaller temperature interval. In the extreme case of an inclusion  
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41 311 that traps  $\geq 60$  vol.% vapor, the vapor-saturated solidus temperature is approximately equal to the  
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43 312 trapping temperature, and the melt may undergo some amount of PEC nearly isothermally.  
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46 313 Notably, this process may induce variation in the measured major-element composition of the  
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48 314 glass phase within MI containing different proportions of trapped vapor.

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50 315 An additional consequence of the different predicted solidus temperatures of MI  
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53 316 containing different proportions of trapped vapor is potentially differing glass-transition  
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55 317 behavior. As noted above, our numerical model assumes thermodynamic equilibrium, and thus  
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58 318 the glass transition is not included explicitly in our results. Nevertheless, we can make some  
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4 319 qualitative predictions based on our results and experimental data on glass transition  
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6 320 temperatures. According to Giordano et al. (2008), the glass transition temperature of silicate  
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9 321 liquids is depressed by increasing concentrations of H<sub>2</sub>O. In our results, MI that contain no  
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11 322 trapped vapor experience increasing concentration of H<sub>2</sub>O in the melt during cooling and PEC.  
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14 323 Consequently, these trends suggest that the glass transition temperature of such MI may be  
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16 324 progressively depressed during cooling and PEC, inhibiting vitrification. In contrast, MI that  
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19 325 contain trapped vapor undergo less H<sub>2</sub>O enrichment in the melt. In particular, for MI in which  
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21 326 the proportion of trapped vapor exceeds 40 vol.%, the H<sub>2</sub>O concentration in the melt remains  
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24 327 nearly constant during PEC for both albitic and basaltic MI (Fig. 4). Thus, the glass transition  
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26 328 temperature of such MI will not be depressed during cooling and PEC, suggesting that MI that  
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29 329 trap vapor may be more readily quenched to glass. Note that at present this possibility is  
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31 330 speculative, and further work is required to assess the glass-forming tendency of MI with  
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34 331 different contents of trapped vapor.

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36 332 The key consequence of trapping some portion of vapor within MI is the potential for  
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38 333 preservation of the original volatile concentrations of the melt, or glass, irrespective of cooling  
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41 334 and PEC. Preservation of the volatile concentrations in the glass is achieved via reducing the  
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43 335 depressurization at equivalent degrees of cooling, and in effect buffering the H<sub>2</sub>O and CO<sub>2</sub>  
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46 336 concentrations in the melt by fixing the corresponding vapor composition. Moreover, the vapor  
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48 337 phase within such heterogeneously trapped MI is also buffered in terms of composition and  
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51 338 density, as the MI evolves along the vapor isochore, and thus the properties of the trapped  
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53 339 magmatic fluid phase are also preserved in such MI.

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55 340 The simulations described here involving an albitic melt hosted in albite all used  
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58 341 equivalent initial conditions to those of Steele-MacInnis et al. (2011) of 930 °C, 200 MPa, and  
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4 342 initial volatile concentrations of 3.8 wt.% H<sub>2</sub>O and 520 ppm CO<sub>2</sub>. The basaltic melt simulations  
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6 343 used initial conditions of 1200 °C, 120 MPa, and initial volatile concentrations of 0.95 wt.% H<sub>2</sub>O  
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9 344 and 535 ppm CO<sub>2</sub>. One interesting question to consider is how the predicted trends in PEC and  
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11 345 volatile evolution within the MI may vary with different initial conditions. Steele-MacInnis et al.  
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14 346 (2011) reported that CO<sub>2</sub>-absent MI containing only dissolved H<sub>2</sub>O undergo immediate and  
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16 347 sustained pressure increase with decreasing temperature and PEC, tracking the H<sub>2</sub>O-saturated  
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19 348 albitic solidus. Conversely, H<sub>2</sub>O-absent, CO<sub>2</sub>-bearing MI undergo pressure decrease during  
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21 349 cooling and PEC, tracking the CO<sub>2</sub>-saturated albitic solidus. Inclusions that trap a melt  
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24 350 containing dissolved H<sub>2</sub>O plus CO<sub>2</sub> follow trends that are initially more similar to the CO<sub>2</sub>-  
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26 351 endmember, and evolve towards more H<sub>2</sub>O-dominated trends as PEC and cooling progress  
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29 352 (Steele-MacInnis et al. 2011). We expect that the results of simulations included here, for MI that  
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31 353 trap vapor along with the melt, can be extended to other initial conditions, with the only major  
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33 354 difference being the initial trajectory of MI which trap little or no vapor. Regardless of the initial  
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36 355 conditions and initial H<sub>2</sub>O-CO<sub>2</sub> concentrations of the trapped melt±vapor, inclusions trapping a  
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38 356 high proportion of vapor are expected to conform to a *P-T* trajectory resembling the isochore of  
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41 357 the vapor phase. However, it must be stressed that additional processes such as diffusive  
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43 358 reequilibration or decrepitation, which are not modeled here, may cause deviation from this  
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46 359 model *P-T* trajectory. Some of these factors are discussed briefly below.

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48 360       Examples of photomicrographs showing MI with anomalously large (>10 vol.%) bubbles  
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50 361 are fairly common in the literature, but it should be stressed that based on photomicrographs  
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53 362 alone it is commonly impossible to differentiate large bubbles generated by heterogeneous  
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55 363 entrapment versus other processes, such as diffusive reequilibration (Gaetani et al. 2012;  
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58 364 Bucholz et al. 2013) or stretching, leakage and/or decrepitation (MacLennan, 2017). In addition,  
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4 365 based on photomicrographs alone it is impossible to determine the volume of glass polished  
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6 366 away during sample preparation, as well as if any additional bubble(s) was polished away to  
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9 367 exposed the MI at the sample surface. Moreover, photomicrographs are sometimes unrevealing  
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11 368 in terms of whether MI exposed by polishing were originally fully enclosed, or rather connected  
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14 369 to the exterior ("hourglass inclusions") – in the latter scenario, bubble formation can accompany  
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16 370 evacuation of some of the melt to the exterior during decompression (Anderson 1991). Thus, we  
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19 371 advocate an approach using coeval assemblages of melt inclusions (Fig. 1A), and using  
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21 372 additional petrologic indicators to test for timing and post-entrapment modifications of MI (e.g.,  
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24 373 Hartley et al. 2015). In the following section, we evaluate evidence for heterogeneous  
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26 374 entrapment in the two datasets of Hartley et al. (2014) and Moore et al. (2015).

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29 375         Few analytical data are available in literature on the H<sub>2</sub>O and CO<sub>2</sub> concentrations of the  
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31 376 glass phase within inclusions containing significant trapped vapor. This probably reflects to  
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33 377 some extent that such inclusions are deliberately not targeted for microanalysis because of their  
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36 378 anomalously large bubbles. Moreover, analysis of glass in such inclusions may be difficult  
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38 379 because of the small analytical volume, for instance in melt-bearing "fluid inclusions" with only  
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41 380 a thin film of silicate glass. Our comparison with existing analytical data is therefore limited to  
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43 381 vapor bubble CO<sub>2</sub> densities from Hartley et al. (2014) and Moore et al. (2015). Both these  
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46 382 studies characterized the CO<sub>2</sub> density within MI vapor bubbles using Raman spectroscopy. The  
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48 383 MI described in these two studies are shown in Fig. 5, in terms of inclusion volume versus  
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51 384 bubble volume (based on the diagrams of Moore et al. 2015 and Aster et al. 2016). Key  
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53 385 observations from Fig. 5 are that both datasets include several inclusions with anomalously large  
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55 386 vapor bubbles (>10 vol.%), and that there is no obvious relationship between MI size and bubble

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

389 Figure 6A shows the results of the present modeling of an albitic MI, plotted in terms of  
390 the density of the vapor bubble versus the vapor volume fraction, for trapped vapor fractions  
391 ranging from zero to 95 vol.%. At low volume fractions of trapped vapor, the density of the  
392 vapor bubble decreases abruptly with relatively low degrees of PEC. In contrast, at higher  
393 volume fractions of trapped vapor, PEC up to 10% has essentially no effect on the density of the  
394 vapor phase. The grey-shaded field on Fig. 6A thus delimits a distribution of bubble density  
395 versus volume fraction, corresponding to MI that trap various proportions of vapor and undergo  
396 various degrees of PEC up to 10%, with the assumption that all MI were trapped at the same  
397 pressure-temperature conditions and with the same H<sub>2</sub>O and CO<sub>2</sub> concentrations in the trapped  
398 melt.

399 Figures 6B shows the data of Hartley et al. (2014), on MI bubbles hosted in olivine from  
400 the AD 1783-1784 Laki eruption, southeast Iceland. Figure 6C shows the data of Moore et al.  
401 (2015) on MI bubbles hosted in olivine from the 1959 Kilauea Iki and 1960 Kapoho eruptions,  
402 Hawaii. Both of these datasets show a similar distribution: Most of the data are clustered towards  
403 relatively low volume fractions of vapor up to ~5-10 vol.%, and within this range the vapor  
404 densities show a wide range of variability. However, a small number of MI show much higher  
405 volume fraction of vapor up to ~100 vol.%, and these MI also show variable, but generally  
406 higher densities. For example, the majority of the MI measured by Hartley et al. (2014) contain  
407 <10 vol.% vapor and have vapor densities range from <50 to ~250 kg/m<sup>3</sup>. In contrast, among the  
408 MI with >10 vol.% vapor, densities range from ~100 to ~300 kg/m<sup>3</sup>. Notice also that the lowest  
409 vapor density occurs at low volume fraction of vapor, whereas the highest vapor density occurs

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4 410 at the highest volume fraction of vapor. The data of Moore et al. (2015) similarly show a greater  
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6 411 variation in vapor density at low volume fractions of vapor, compared to generally more  
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9 412 consistent vapor densities at volume fractions >10 vol.%. Moreover, the densities of vapor  
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11 413 bubbles that comprise >10 vol.% in the data of Moore et al. (2015) cluster around  $\sim 130 \text{ kg/m}^3$ ,  
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14 414 which is around the maximum of the low-volume fraction cluster of data. The grey-shaded  
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16 415 regions in Figs. 6B and 6C were constructed using the same numerical methods described above,  
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19 416 assuming a basaltic melt composition hosted in olivine. Initial conditions for the modeling in Fig.  
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21 417 6B were 1210 °C and 85 MPa, whereas the initial conditions for the modeling in Fig. 6C were  
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24 418 1210 °C and 45 MPa. In both cases, the initial (trapping) pressures are less than those  
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26 419 constrained by H<sub>2</sub>O-CO<sub>2</sub> solubility calculations (Hartley et al. 2014; Moore et al. 2015) in order  
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29 420 to match the relatively low density of the vapor bubbles. Stated differently, these initial pressures  
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31 421 were selected according to the pressure on the relevant CO<sub>2</sub>-H<sub>2</sub>O isochore at the presumed  
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33 422 trapping temperature of 1210°C. The discrepancy in modeled initial pressure versus inferred  
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36 423 trapping pressure for the studied MI likely reflects expansion (and concomitant decrease in  
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38 424 density) of the vapor bubble during quenching of the glass (Esposito et al., 2011), or vapor loss  
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41 425 by decrepitation (Maclennan, 2017). Nevertheless, in both cases the predicted trends for MI that  
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43 426 trapped some fraction of vapor and subsequently underwent various degrees of PEC are broadly  
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46 427 consistent with the analytical data. Certainly, these results do not provide definitive evidence of a  
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48 428 role of heterogeneous trapping and PEC in the distribution of data from Laki, Kilauea Iki and  
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51 429 Kapoho, but the results are at least consonant with this general model. However, we stress once  
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53 430 again that this interpretation relies on the assumption that the MI shown in Figs. 6B or 6C were  
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55 431 trapped coevally, whereas we lack petrographic information to test this assumption.  
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4 432 The recent study of Aster et al. (2016) provides another dataset on MI vapor bubble  
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6 433 densities and volume fractions from four cinder cones: two in the Cascade Arc and two in the  
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9 434 Trans-Mexico volcanic belt. Aster et al. (2016) only report vapor bubbles occupying up to 15  
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11 435 vol.% of the MI. The densities of vapor bubbles measured by Aster et al. (2016) do not show any  
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14 436 systematic relationship with bubble volume fraction. They inferred heterogeneous entrapment of  
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16 437 some of the vapor bubbles by calculating the maximum expected volume fraction of vapor  
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19 438 produced by cooling, PEC and quenching of the MI, and determined that most of the bubbles  
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21 439 could have formed by these processes alone (i.e., without heterogeneous trapping of vapor).  
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24 440 These results by Aster et al. (2016) indicate that the predictions made in the present study do not  
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26 441 always apply to olivine-hosted MI, such as in the case when only bubbles up to ~15 vol.% are  
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29 442 observed. Nevertheless, the comparison with the datasets of Hartley et al. (2014) and Moore et  
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31 443 al. (2015) indicate that bubbles with larger volume fractions (up to ~100 vol.%) occur in olivine-  
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33 444 hosted MI from volcanic systems, and MI hosting such bubbles may be amenable for analysis of  
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36 445 pre-eruptive volatile concentrations.

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38 446 The comparison of our model predictions with these literature data from Hartley et al.  
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41 447 (2014) and Moore et al. (2015) are not unequivocal, partly because of sparseness and scatter in  
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43 448 the data, and likely also because various factors affect the vapor densities of olivine-hosted MI.  
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46 449 For example, MI may have been trapped at various depths, and certainly re-equilibration of  
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48 450 volatile constituents is likely to play a role. Hartley et al. (2015) used the H<sub>2</sub>O/Ce ratios of some  
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51 451 of the same MI discussed here, to evaluate the degree of H<sub>2</sub>O loss or gain by diffusion. This type  
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53 452 of analysis could in principle be used to help constrain the degree of re-equilibration of MI  
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55 453 containing anomalously large bubbles, but such inclusions were not analyzed by Hartley et al.  
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58 454 (2015). An additional complication is that MI that trap relatively small volume fractions of vapor  
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4 455 may not exhibit anomalously large vapor bubbles (Aster et al. 2016). In some cases, trapping of  
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6 456 vapor may be only distinguishable by calculating the volume fraction of vapor formed via pre-  
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9 457 eruptive cooling coupled with the effects of cooling and quenching to the glass transition  
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11 458 temperature (Aster et al. 2016). Nevertheless, the data shown in Figs. 5 and 6 are broadly  
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14 459 consistent with the prediction that MI which trapped significant proportions of vapor can  
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16 460 maintain a relatively high vapor density at room temperature, compared to inclusions that  
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19 461 trapped little to no vapor. A corollary of this prediction is that the glass phase in such inclusions  
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21 462 is expected to retain concentrations of H<sub>2</sub>O and CO<sub>2</sub> that reflect the composition of the melt at  
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24 463 the time of trapping. As such, these data and model predictions suggest that microanalysis of the  
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26 464 glass phase within MI containing trapped vapor may be an amenable method to directly sample  
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29 465 the H<sub>2</sub>O and CO<sub>2</sub> concentrations of the trapped melt, independently of PEC. Moreover, analysis  
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31 466 of the CO<sub>2</sub> and H<sub>2</sub>O concentrations in the corresponding (heterogeneously entrapped) vapor  
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33 467 bubble using the methods developed by Esposito et al. (2016) may be an amenable and  
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36 468 complementary method to determine the composition of the coeval, equilibrium magmatic vapor  
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38 469 phase.

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41 470 In interpreting the patterns in vapor density versus volume fraction in Fig. 6, we must  
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43 471 emphasize that the available data do not permit us to evaluate whether the MI record coeval  
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46 472 entrapment. As such, it is not currently possible to verify whether the MI in Fig. 6 record similar  
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48 473 physical and chemical conditions of trapping. The best method to constrain the relative timing of  
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51 474 MI trapping would be to study MI in the context of coeval assemblages (Esposito et al. 2014). In  
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53 475 the case of melt inclusions from a single eruptive event in which suitable assemblages are absent,  
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55 476 an alternative method would be to categorize MI based on the forsterite content of the  
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58 477 immediately adjacent host olivine, or the major element composition of the MI, or some  
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4 478 combination of these parameters. Such procedures may allow us to better define the trends of  
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7 479 melt-volatile composition with trapped vapor fraction. Similarly, direct analysis of the CO<sub>2</sub> and  
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9 480 H<sub>2</sub>O concentrations in the glass phase of MI containing anomalously large bubbles would be  
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11 481 extremely beneficial to assess the model predictions described here. Unfortunately, the available  
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14 482 data do not allow us to assess these various potential indicators for coeval trapping (as well as for  
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16 483 potential diffusive reequilibration, etc.) – we hope that future studies will provide additional  
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19 484 constraints to evaluate these various factors.

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21 485         Another potential issue that may influence trends such as those shown in Fig. 5B and 5C  
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24 486 is the precipitation of carbonate at the glass/bubble interface (e.g., Kamenetsky et al. 2001;  
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26 487 Moore et al. 2015; Esposito et al. 2016), which will lower the CO<sub>2</sub> density measured in the  
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29 488 bubble. It is important to note that Kamenetsky et al. (2001) showed a positive correlation  
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31 489 between the relative volume fraction of the vapor bubble and the amount of precipitates at the  
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33 490 glass/bubble interface.

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36 491         A final caveat that must be addressed is the possibility of forming large vapor bubbles  
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38 492 within MI by processes other than heterogeneous entrapment, namely bubble growth as a result  
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41 493 of H<sup>+</sup> diffusion or following stretching, leakage and/or decrepitation. Hydrogen diffusion will  
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43 494 result in an increased density (decreased molar volume) of the melt phase, which can result in  
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46 495 formation of a bubble by contraction of the melt. Similarly, stretching, leakage and/or  
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48 496 decrepitation may effectively reduce the *bulk* density (increase the bulk molar volume) of the  
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51 497 inclusion, thereby favoring the subsequent production of large bubbles. Regarding H<sup>+</sup> diffusion,  
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53 498 we calculated the volume fraction of vapor that would be expected in a basaltic melt inclusion  
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55 499 with a starting H<sub>2</sub>O concentration of 5 wt.%, assuming different proportions of H<sub>2</sub>O loss,  
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58 500 according to the effect of H<sub>2</sub>O on the density of the silicate glass (Lange and Carmichael 1987;  
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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 H<sub>2</sub>O 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 H<sub>2</sub>O 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 H<sub>2</sub>O/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 CO<sub>2</sub>-H<sub>2</sub>O fluid phase during PEC and cooling) may be particularly susceptible to SLD because of the potential for internal overpressure of the high-density, CO<sub>2</sub>-rich fluid (MacLennan, 2017). Again, this suggestion is based on the experience of high-density, CO<sub>2</sub>-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

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4 524 the vapor bubble would be expected to decrease in response to SLD, owing to the overall  
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6 525 increase in the bulk molar volume. Thus, large bubbles produced by SLD processes would be  
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9 526 expected to exhibit relatively low density compared to bubbles of modest volume fraction within  
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11 527 unmodified inclusions. Thus, Figs. 5 and 6 provide some basis for comparing heterogeneous  
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14 528 entrapment versus SLD. Heterogeneous entrapment is expected to yield larger bubbles  
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16 529 containing vapor of relatively high density compared to the smaller vapor bubbles in the same  
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19 530 sample. In contrast, SLD are expected to yield larger vapor bubbles of relatively low density  
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21 531 compared to the smaller bubbles in the same sample. Figure 6 shows that in the samples from  
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24 532 Laki, Kilauea Iki and Kapoho, the majority of the anomalously large bubbles exhibit relatively  
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26 533 high densities suggesting heterogeneous entrapment. Nevertheless, some of the larger vapor  
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29 534 bubbles (e.g., the bubble at ~56 vol.% in the Kapoho samples; Fig. 6C) show relatively low  
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31 535 densities and may reflect SLD. Figure 5 also allows some qualitative estimation of the expected  
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33 536 effects of diffusive reequilibration as well as SLD processes, because both would be expected to  
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36 537 yield systematic relationships between MI and bubble size: In the case of diffusive H<sup>+</sup> loss,  
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38 538 smaller inclusions would be more severely affected (Qin et al. 1992; Bucholz et al. 2013),  
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41 539 whereas larger inclusions are more susceptible to SLD processes (Bodnar et al. 1989). The  
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43 540 results shown in Figure 5 indicate no particular relationship between inclusion size and bubble  
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45 541 volume, which is at least broadly consistent with heterogeneous trapping, although this inference  
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48 542 relies on the assumption that the MI were trapped at the same time (see also Fig. 1A).  
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51 543 Nevertheless, ultimately a combined model accounting for heterogeneous entrapment, PEC *and*  
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53 544 the effects of SLD will be required to assess these mutually interacting processes.  
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## 546 5. CONCLUSIONS

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4 547           The predictions described above are testable, and future studies aimed at microanalysis of  
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6 548 the glass phase within vapor-rich MI should be conducted to determine the variability of melt  
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9 549 volatile contents. Based on the numerical modeling described herein, we suggest that MI  
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11 550 containing high volume fractions of vapor (>10 vol.%) probably originate by trapping of  
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14 551 magmatic vapor along with the silicate melt, and that the compositions of both the melt and  
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16 552 vapor phases in such inclusions are preserved in their original (trapping) states as a result of this  
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19 553 process. As such, MI containing trapped vapor probably should not be ignored or deliberately  
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21 554 omitted from microanalysis, but rather should be targeted in order to estimate the original melt-  
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24 555 volatile composition. We hope that this insight will provide an additional tool in the arsenal  
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26 556 applied to melt inclusion volatiles in volcanic systems.

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41 562 ideas towards interpretation of MI-volatile data, and helped significantly improve this  
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## REFERENCES

- 565  
566 Aster EM, Wallace PJ, Moore LR, Watkins J, Gazel E, Bodnar RJ (2016) Reconstructing CO<sub>2</sub>  
567 concentrations in basaltic melt inclusions using Raman analysis of vapor bubbles. *J*  
568 *Volcanol Geoth Res* 323:148-162
- 569 Almeev RR, Holtz F, Koepke J, Parat F, Botcharnikov RE (2007) The effect of H<sub>2</sub>O on olivine  
570 crystallization in MORB: Experimental calibration at 200 MPa. *Am Mineral* 92: 670-674
- 571 Anderson AT (1991) Hourglass inclusions: Theory and application to the Bishop Rhyolitic Tuff.  
572 *Am Mineral* 76:530-547
- 573 Anderson AT, Brown GG (1993) CO<sub>2</sub> contents and formation pressures of some Kilauean melt  
574 inclusions. *Am Mineral* 78:794-803
- 575 Belkin HE, De Vivo B, Roedder E, Cortini M (1985) Fluid inclusion geobarometry from ejected  
576 Mt. Somma-Vesuvius nodules. *Am Mineral* 70:288-303
- 577 Belkin HE, De Vivo B (1993) Fluid inclusion studies of ejected nodules from plinian eruptions  
578 of Mt. Somma-Vesuvius. *J Volcanol Geoth Res* 58:89-100
- 579 Bodnar RJ, Binns PR, Hall DL (1989) Synthetic fluid inclusions – VI. Quantitative evaluation of  
580 the decrepitation behaviour of fluid inclusions in quartz at one atmosphere confining  
581 pressure. *J Metamorphic Geol* 7:229-242
- 582 Bodnar RJ, Student JJ (2006) Melt inclusions in plutonic rocks: Petrography and  
583 microthermometry. In: Webster JD (ed) *Melt Inclusions in Plutonic Rocks*, Mineralogical  
584 Association of Canada Short Course Series Volume 36. pp 1-26
- 585 Bucholz CE, Gaetani GA, Behn MD, Shimizu N (2013) Post-entrapment modification of  
586 volatiles and oxygen fugacity in olivine-hosted melt inclusions. *Earth Planet Sci Lett*  
587 374:145-155
- 588 Burnham CW, Davis NF (1971) The role of H<sub>2</sub>O in silicate melts: I. P-V-T relations in the  
589 system NaAlSi<sub>3</sub>O<sub>8</sub>-H<sub>2</sub>O to 10 kilobars and 1000°C. *Am J Sci* 270:54-79
- 590 Burnham CW, Davis NF (1974) The role of H<sub>2</sub>O in silicate melts: II. Thermodynamic and phase  
591 relations in the system NaAlSi<sub>3</sub>O<sub>8</sub>-H<sub>2</sub>O to 10 kilobars, 700° to 1100°C. *Am J Sci*  
592 274:902-940
- 593 Cannatelli C, Doherty AL, Esposito R, Lima A, De Vivo B (2016) Understanding a volcano  
594 through a droplet: A melt inclusion approach. *J Geochem Explor* 171:4-19
- 595 Connolly JAD, Bodnar RJ (1983) A modified Redlich-Kwong equation of state for H<sub>2</sub>O-CO<sub>2</sub>  
596 mixtures: Application to fluid inclusion studies. *EOS Transactions* 64:350
- 597 Danyushevsky LV, Della Pasqua FN, Sokolov S (2000) Re-equilibration of melt inclusions  
598 trapped by magnesian olivine phenocrysts from subduction-related magmas; petrological  
599 implications. *Contrib Mineral Petr* 138:68-83
- 600 Diamond LW (2003) Introduction to gas-bearing, aqueous fluid inclusions. In: Samson I,  
601 Anderson A, Marshall D (eds) *Fluid Inclusions Analysis and Interpretation*,  
602 Mineralogical Association of Canada Short Course Series Volume 32. pp 101-158
- 603 Esposito R, Bodnar RJ, Danyushevsky LV, De Vivo B, Fedele L, Hunter J, Lima A, Shimizu N,  
604 (2011) Volatile evolution of magma associated with the Solchiaro eruption in the  
605 Phlegrean Volcanic District (Italy). *J Petrol* 52:2431-2460
- 606 Esposito R, Hunter J, Schiffbauer JD, Shimizu N, Bodnar RJ (2014) An assessment of the  
607 reliability of melt inclusions as recorders of the pre-eruptive volatile content of magmas.  
608 *Am Mineral* 99:976-998
- 609 Esposito R, Lamadrid HM, Redi D, Steele-MacInnis M, Bodnar RJ, Manning CE, De Vivo B,  
610 Cannatelli C, Lima A (2016) Detection of liquid H<sub>2</sub>O in vapor bubbles in reheated melt

- 611 inclusions: implications for magmatic fluid composition and volatile budgets of magmas.  
612 Am Mineral 101:1691-1695
- 613 Gaetani GA, O'Leary JA, Shimizu N, Bucholz CE, Newville M (2012) Rapid reequilibration of  
614 H<sub>2</sub>O and oxygen fugacity in olivine-hosted melt inclusions. *Geology* 40:915-918
- 615 Giordano D, Potuzak M, Romano C, Dingwell DB, Nowak M (2008) Viscosity and glass  
616 transition temperature of hydrous melts in the system CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>-CaMgSi<sub>2</sub>O<sub>6</sub>. *Chem*  
617 *Geol* 256:203-215
- 618 Harris AC, Kamenetsky VS, White NC, van Achterbergh E, Ryan CG (2003) Melt inclusions in  
619 veins: Linking magmas and porphyry Cu deposits. *Science* 302:2109-2111
- 620 Hartley ME, Maclennan J, Edmonds M, Thordarson T (2014) Reconstructing the deep CO<sub>2</sub>  
621 degassing behaviour of large basaltic fissure eruptions. *Earth Planet Sci Lett* 393:120-131
- 622 Hartley ME, Neave DA, Maclennan J, Edmonds M, Thordarson T (2015) Diffusive over-  
623 hydration of olivine-hosted melt inclusions. *Earth Planet Sci Lett* 425:168-178
- 624 Holloway JR (1977) Fugacity and activity of molecular species in supercritical fluids. In: Fraser  
625 DG (ed) *Thermodynamics in Geology*. Reidel, Dordrecht. pp 161-181.
- 626 Holloway JR (1987) Igneous fluids. *Rev Mineral* 17:211-233
- 627 Holloway JR, Blank JG (1994) Application of experimental results to C-O-H species in natural  
628 melts. *Rev Mineral* 30:187-230
- 629 Iacovino K (2014) Glass Density Calc v.3.0. [http://www.kaylaiacovino.com/tools-for-](http://www.kaylaiacovino.com/tools-for-petrologists/)  
630 [petrologists/](http://www.kaylaiacovino.com/tools-for-petrologists/). Accessed 28 January 2017.
- 631 Kamenetsky VS, Binns RA, Gemmell JB, Crawford AJ, Mernagh TP, Maas R, Steele D (2001)  
632 Parental basaltic melts and fluids in eastern Manus backarc Basin: implications for  
633 hydrothermal mineralisation. *Earth Planet Sci Lett* 184:685-702
- 634 Lange RL, Carmichael ISE (1987) Densities of Na<sub>2</sub>O-K<sub>2</sub>O-CaO-MgO-FeO-Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub>-SiO<sub>2</sub>  
635 liquids: new measurements and derived partial molar volumes. *Geochim Cosmochim*  
636 *Acta* 53:2195-2946
- 637 Lange RL, Carmichael ISE (1990) Thermodynamic properties of silicate liquids with emphasis  
638 on density, thermal expansion and compressibility. *Rev Mineral* 24:25-64
- 639 Lowenstern JB (1994) Dissolved volatile concentrations in an ore-forming magma. *Geology*  
640 22:893-896
- 641 Lowenstern JB (1995) Applications of silicate-melt inclusions to the study of magmatic volatiles.  
642 In: Thompson JFH (ed) *Magmas, fluids and ore deposition*, Mineralogical Association of  
643 Canada Short Course Series Volume 23. pp 71-99
- 644 Lowenstern JB (2003) Melt inclusions come of age; volatiles, volcanoes, and Sorby's legacy. In:  
645 De Vivo B, Bodnar RJ (eds) *Melt Inclusions in Volcanic Systems: Methods, Applications*  
646 *and Problems*. Elsevier, Amsterdam. pp 1-21
- 647 Maclennan, J (2017) Bubble formation and decrepitation control the CO<sub>2</sub> content of olivine-  
648 hosted melt inclusions. *Geochem, Geophys, Geosyst* (in press)  
649 doi:10.1002/2016GC006633
- 650 Métrich N, Wallace PJ (2008) Volatile abundances in basaltic magmas and their degassing paths  
651 tracked by melt inclusions. *Rev Mineral Geochem* 69:363-402
- 652 Mironov N, Portnyagin M (2011) H<sub>2</sub>O and CO<sub>2</sub> in parental magmas of Kliuchevskoi volcano  
653 inferred from study of melt and fluid inclusions in olivine. *Russ Geol Geophys* 52:1353-  
654 1367
- 655 Mironov N, Portnyagin M, Botcharnikov R, Gurenko A, Hoernle K, Holtz F (2015)  
656 Quantification of the CO<sub>2</sub> budget and H<sub>2</sub>O-CO<sub>2</sub> systematics in subduction-zone magmas



- 1  
2  
3  
4 657 through the experimental hydration of melt inclusions in olivine at high H<sub>2</sub>O pressure.  
5 658 Earth Planet Sci Lett 425:1-11  
6  
7 659 Moore LR, Gazel E, Tuohy R, Lloyd AS, Esposito R, Steele-MacInnis M, Hauri EH, Wallace PJ,  
8 660 Plank T, Bodnar RJ (2015) Bubbles matter: An assessment of the contribution of vapor  
9 661 bubbles to melt inclusion volatile budgets. Am Mineral 100:806-823  
10 662 Newman S, Lowenstern JB (2002) VOLATILECALC: A silicate melt-H<sub>2</sub>O-CO<sub>2</sub> solution model  
11 663 written in Visual Basic for excel. Chem Geol 28:597-604  
12 664 Ochs FA, Lange RA (1999) The density of hydrous magmatic liquids. Science 283:1314-1317  
13 665 Papale P, Moretti R, Barbato D (2006) The compositional dependence of the saturation surface  
14 666 of H<sub>2</sub>O+CO<sub>2</sub> fluids in silicate melts. Chem Geol 229:78-95  
15 667 Portnyagin M, Almeev R, Matveev S, Holtz F (2008) Experimental evidence for rapid water  
16 668 exchange between melt inclusions in olivine and host magma. Earth Planet Sci Lett  
17 669 272:541-552  
18 670 Qin Z, Lu F, Anderson AT (1992) Diffusive reequilibration of melt and fluid inclusions. Am  
19 671 Mineral 77:565-576  
20 672 Redlich O, Kwong JNS (1949) On the thermodynamics of solutions. Chem Rev 44:233-244  
21 673 Schiavi F, Provost A, Schiano P, Cluzel N (2016) P-V-T-X evolution of olivine-hosted melt  
22 674 inclusions during high-temperature homogenization treatment. Geochim Cosmochim  
23 675 Acta 172:1-21  
24 676 Shishkina TA, Botcharnikov RE, Holtz F, Almeev R, Jazwa AM, Jakubiak AA (2014)  
25 677 Compositional and pressure effects on the solubility of H<sub>2</sub>O and CO<sub>2</sub> in mafic melts.  
26 678 Chem Geol 388:112-129  
27 679 Steele-MacInnis M, Esposito R, Bodnar RJ (2011) Thermodynamic model for the effect of post-  
28 680 entrapment crystallization on the H<sub>2</sub>O-CO<sub>2</sub> systematics of vapor-saturated, silicate melt  
29 681 inclusions. J Petrol 52:2461-2482  
30 682 Stefanova E, Driesner T, Zajacz Z, Heinrich CA, Petrov P, Vasilev Z (2014) Melt and fluid  
31 683 inclusions in hydrothermal veins: The magmatic to hydrothermal evolution of the Elatsite  
32 684 porphyry Cu-Au deposit, Bulgaria. Econ Geol 109:1359-1381  
33 685 Sterner SM, Bodnar RJ (1991) Synthetic fluid inclusions. X: Experimental determination of P-V-  
34 686 T-X properties in the CO<sub>2</sub>-H<sub>2</sub>O system to 6 kb and 700°C. Am J Sci 291:1-54  
35 687 Student JJ, Bodnar RJ (1996) Melt inclusion microthermometry; petrologic constraints from the  
36 688 H<sub>2</sub>O-saturated haplogranite system. Petrology 4:291-306  
37 689 Student JJ, Bodnar RJ (2004) Silicate melt inclusions in porphyry copper deposits; identification  
38 690 and homogenization behavior. Can Mineral 42:1583-1599  
39 691 Tuohy, RM, Wallace PJ, Loewen MW, Swanson DA, Kent AJR (2016) Magma transport and  
40 692 olivine crystallization depths in Kīlauea's east rift zone inferred from experimentally  
41 693 rehomogenized melt inclusions. Geochim Cosmochim Acta 185:232-250  
42 694 Wallace PJ, Kamenetsky VS, Cervantes P (2015) Melt inclusion CO<sub>2</sub> contents, pressures of  
43 695 olivine crystallization, and the problem of shrinkage bubbles. Am Mineral 100:787-794  
44 696 Zajacz Z, Halter WE, Pettke T, Guillong M (2008) Determination of fluid/melt partition  
45 697 coefficients by LA-ICPMS analysis of co-existing fluid and silicate melt inclusions:  
46 698 Controls on element partitioning. Geochim Cosmochim Acta 72:2169-2197  
47 699 Zanon V, Frezzotti ML (2013) Magma storage and ascent conditions beneath Pico and Faial  
48 700 islands (Azores archipelago): A study on fluid inclusions. Geochem Geophys Geosyst  
49 701 14:3494-3514  
50  
51  
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62  
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Zanon V, Pimentel A (2015) Spatio-temporal constraints on magma storage and ascent conditions in a transtensional setting: The case of Terceira Island (Azores). *Am Mineral* 100:795-805

**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 CO<sub>2</sub>-H<sub>2</sub>O fluid inclusions. The pressure-temperature phase diagram shows the vapor-saturated solidus-liquidus of albitic melt contoured by activity of H<sub>2</sub>O (Burnham and Davis 1974) and the liquid-vapor solvus and isochores of a CO<sub>2</sub>-H<sub>2</sub>O fluid of 40 mol.% CO<sub>2</sub> (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 CO<sub>2</sub>-H<sub>2</sub>O 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 CO<sub>2</sub>-H<sub>2</sub>O 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** CO<sub>2</sub>-H<sub>2</sub>O 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 CO<sub>2</sub> content in the melt, whereas MI that trapped more vapor experience less CO<sub>2</sub> 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).

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6 **Fig. 6** Densities of MI vapor bubbles vary systematically with the proportion of trapped vapor.  
7 (a) Results of our numerical model. (B) MI from the AD 1783-84 Laki eruption, Iceland (Hartley  
8 et al. 2014). (C) MI from the 1959 Kilauea Iki and 1960 Kapoho eruptions, Hawaii (Moore et al.  
9 2015). The dashed vertical line in (B) and (C) corresponds to 5 vol.% vapor, representing the  
10 cutoff applied by both Hartley et al. (2014) and Moore et al. (2015) to differentiate MI vapor  
11 bubbles likely generated by differential thermal contraction and/or PEC (<5 vol.%) versus  
12 bubbles potentially indicating heterogeneous trapping (>5 vol.%). The light shaded regions in  
13 (B) and (C) were calculated as described in the text  
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