

Supplemental Material

Supplement A: Geologic setting of the samples

All MI analyzed in this study are hosted in olivine phenocrysts ejected during eruptions of Mt. Somma-Vesuvius, Italy. The Mt. Somma-Vesuvius volcanic field is part of the Campanian Magmatic Province which in turn is part of the Plio-Quaternary volcanism of the Italian Peninsula (Peccerillo, 2005 and references therein). Three volcanic megacycles have been identified based on whole rock composition (De Vivo et al., 2010 and references therein). According to Rolandi et al. (1993), the first megacycle lasted from >33 ka to ~14 ka, the second from ~8 ka to ~2.7 ka, and the third from AD 79 to 1944 eruption. Mt. Somma-Vesuvius has not erupted since 1944, indicating that the 1944 eruption represents either the end of the third magmatic cycle or the beginning of an anomalously long repose time between eruptions within the third cycle. The degree of Si undersaturation and K enrichment increases with time from >33 ka to AD 1944. The reader is referred to Peccerillo (2005 and references therein) for more details on the geology of Mt. Somma-Vesuvius volcanic system.

The 20 bubble-bearing MI studied are hosted in olivine phenocrysts representative of both (1) Plinian: AD 1631 (AD 1631; 1 MI), Pollena (AD 472; 1 MI), Pompeian (AD 79; 8 MI), and Avellino (3.8 ka; 5 MI) and (2) inter-Plinian events: Pre-Codola lavas (>33 ka; 5 MI) (Ayuso et al., 1998 and references therein). The samples used in this study are lavas, white and grey pumices and the bulk rocks were reported by Ayuso et al. (1998). The lava samples used in this study (SCL12-SCL14) are

representative of group 1, the Avellino eruption pumice samples (LFL1-LFL2) are representative of group 2, and the youngest pumice samples (P1-P2-LM8-R6) are representative of group 3 as classified by Ayuso et al. (1998). Samples SCL4 plot at the boundary between the field of trachy-basalt and shoshonite, the samples from the Avellino eruption plot in the phonolite field, and the youngest pumice samples plot in the fields of phonotephrite, tephriphonolite, and phonolite based on the TAS diagram (Le Bas et al., 1986). The forsterite (Fo) composition of olivine separated from the studied samples span in a wide range. Olivines from lava sample SCL12 are from 71 to 73 mole% Fo, and those from lava sample SCL14 are from 68 to 78 (Redi, 2014). Olivines from sample LFL1, LFL2, and P1 show bimodal distribution, one group of olivine ranges from 71 to 81 mole% Fo and another group ranges from 82 to 90 mole% Fo (Redi, 2014). Olivines from the other samples studied (P2, LM8, and R6) show Fo mole% spanning from 79 to 91 (Redi, 2014). The olivine selected for this study varies from 68 to 90 ([Supplementary TableDR1](#)) and for two MI from the lava samples were not measure and we reported in the Supplementary TableDR1 the relative Fo range of olivine from the same sample.

Many studies on magma dynamics and depth of magma storage at Mt. Somma-Vesuvius were based on melt and fluid inclusions hosted in crystals from xenoliths and juvenile material (Klébesz et al., 2015 and references therein). These studies all point to multiple magma storages at different depths between the Moho discontinuity (~30 km) and the carbonatic sediments (~4 km) below Mt. Somma-Vesuvius (De Vivo et al., 2010 and references therein).

Supplement B: Methods

We performed 16 heating experiments at CODES, ARC Centre of Excellence in Ore Deposits and School of Earth Sciences, University of Tasmania (Tasmania, Australia) to homogenize crystal-bearing MI followed by quenching to a homogeneous glass (+/- a vapor bubble) using a Vernadsky heating stage (Sobolev et al., 1980). The accuracy of the temperature measurement is $\pm 4^{\circ}\text{C}$ at 1064°C , based on melting $\sim 50\text{ }\mu\text{m}$ gold flakes mounted on the top surface of the olivine phenocryst $\sim 100\text{ }\mu\text{m}$ from the analyzed MI.

The MI were analyzed by Raman spectroscopy at Virginia Tech using a JY Horiba LabRam HR (800 mm) Raman microprobe equipped with a 514.5 nm (green) argon laser (Laser Physics 100S-514 Ar+) to test for the presence of volatiles in vapor bubbles of MI. The output of the laser was 50 mW at the source and less than 10 mW at the sample target. The objective used for Raman analysis was 100x resulting in an approximate beam diameter of $1\text{ }\mu\text{m}$. For each MI, a first Raman spectra was obtained in the glass exposed to the surface on the top of the included bubble. After the glass spectra was obtained for reference for the analysis of the glass/bubble interface and the inner bubble, a series of Raman spectra were recorded each $\sim 2\text{ }\mu\text{m}$ from the surface to the inner part of the bubble. For each of these steps, we first recorded the spectrum from 100 to 4000 cm^{-1} to search for signals of mineral, vapor, and liquid phases. Secondly, we recorded the Raman spectra from 1000 to 1500 cm^{-1} if the CO₂ Fermi diad peaks were detected in the first step, and from 3000 to 4000 cm^{-1} if the H₂O fluid signal was detected.

The CO₂ peaks were fitted using a Gaussian+Lorentzian model after linear baseline subtraction. Only peaks defined by ≥ 4 data points above background were considered for calculating CO₂ density. For each CO₂ Raman spectrum we simultaneously collected two Ne emission lines (1031.36 cm⁻¹ and 1458.58 cm⁻¹) to constrain the position of the Fermi diad peaks Lin et al. (2007). We used the Fall et al. (2011) equation to resolve the density of the CO₂ vapor of the bubbles.

Some vapor bubbles were analyzed by Raman spectroscopy at high T (up to 150°C) to test for the presence of H₂O in the bubbles using the protocol reported by other studies (Berkesi et al., 2009; Dubessy et al., 1992; Lamadrid et al., 2014). A Linkam THSG 600 mounted on the Raman optical microscope stage was used. Previous studies have shown that, while H₂O is often not detected during analysis of CO₂-rich bubbles at room temperature, it is sometimes possible to detect H₂O if the bubble is analyzed at elevated temperature (Berkesi et al., 2009; Dubessy et al., 1992; Lamadrid et al., 2014). This occurs because, during heating, the small amount of liquid H₂O that might be present as a thin film on the inclusion walls evaporates (or dissolves) into the CO₂-rich phase, making its detection more likely.

Five freezing/heating experiments were performed on bubbles contained in MI using the Linkam THSG 600 stage at Virginia Tech. The Linkam was calibrated at the CO₂ and H₂O triple points, and the critical point of H₂O using synthetic fluid inclusions (Sterner and Bodnar, 1984) and the estimated precision and accuracy of the measurements is $\pm 0.1^\circ\text{C}$ over the temperature range investigated. During microthermometry, olivine phenocrysts were cooled to -120°C and the vapor bubble was observed during heating to 150°C.

To estimate concentrations of H₂O and CO₂ in the magmatic vapor phase, we compared the relative peak areas of H₂O and CO₂ in the spectra acquired at 150 °C

Relative Raman scattering efficiencies of H₂O-vapor and CO₂ were obtained from Burke (2001), assuming that scattering efficiencies are independent of T. The instrument factors at the peak positions of CO₂ and H₂O are ~1.

Supplement C: Petrography and microthermometric behavior of MI

The compositions of the olivine phenocrysts from this study are reported by Redi (2014) and range from Fo₆₉ to Fo₈₁ and from Fo₈₄ to Fo₉₀ (Table DR1).

Five MI were slightly crystallized and contained a bubble occupying between 2.1 and 4.6 volume % of the MI (Table DR1), suggesting that these bubbles formed by differential thermal contraction (Moore et al., 2015) and/or PEC (Steele-MacInnis et al., 2011). All of the other MI were highly crystallized and appeared dark (Fig. 1) in transmitted light.

During heating experiments, slightly crystallized MI showed nucleation of dark micrometer-scale phases between 579-800 °C and the MI became progressively darker with increasing temperature (Table DR1). All of the studied MI showed melting that moved progressively inward from the olivine/MI interface starting between 815 and 1082°C, as described by Esposito et al. (2012). The recognition of first melting was roughly correlated with the MI size (smaller ones started first). There was no correlation between the Fo content of the olivine and first melting or quenching T, suggesting that the H₂O content of these MI is variable (Fig. C2), as previously suggested [2.3-4.9 wt%, Marianelli et al. (2005); 0.9-2.7 wt%, Belkin et al. (1998); <0.3-5 wt%, Webster et al. (2001)]. As T increased, several micron-sized spherical vapor bubbles were observed,

and these coalesced into a single bubble with continued heating. The bubbles did not contain any visible solids at high T. As T increased, the bubble size decreased.

Supplement D: H₂O-liquid and Volatile budget calculations

Calculation of the H₂O rim thickness

Webster et al. (2001) studied cumulate sub-effusive nodules from the 3.8 ka Avellino, AD 79 Pompei, and AD 472 Pollena eruptions. Belkin and De Vivo (1993) reported many CO₂-H₂O fluid inclusions that were coeval with melt inclusions hosted in clinopyroxene crystals. The mole fraction of H₂O in the inclusions ranged from ~0.3 to ~0.6 based on CO₂ density (estimated by microthermometry) and on H₂O volume/total volume estimated optically (Belkin and De Vivo, 1993). Similarly, Marianelli et al. (2005) estimated that the fluid in equilibrium with the melt associated with recent Mt. Somma-Vesuvius eruptions (from AD 1794 to AD 1944) contains between 0.2 and 0.6 mole fraction H₂O, based on H₂O and CO₂ contents of glass in MI and experimental melt-fluid partitioning data (Fig. C2). If we assume that the reheated bubble-bearing MI of this study are similar to those reported by Marianelli et al. (2005), the number of moles of H₂O present in the bubble of our MI can be estimated. In fact, the number of moles of CO₂ is known based on the density of the CO₂ vapor (determined from the splitting of the diad Fermi peaks) and the volume of the vapor bubble in reheated MI of this study. We can calculate the number of moles of H₂O based on the range in mole fraction H₂O estimated by Marianelli et al. (2005) and Belkin and De Vivo (1993). Finally, we can estimate the volume occupied by H₂O liquid in the bubble at room T based on the calculated number of moles of H₂O. Finally, the thickness of the H₂O rim at the

glass/bubble interface can be estimated by volume difference assuming that the bubble is a sphere (TableDR2).

TableDR2 caption

Estimation of the H₂O rim thickness at the glass/bubble interface and of the maximum H₂O vapor content for bubbles showing Raman signals of C-O-H-S species.

Calculation of volatile budget of bubble in MI reported in Table 1

For calculations showed in Table 1, we considered only bubbles showing Raman signals for native sulfur and/or calcite or gypsum, H₂O, and CO₂. We assumed that the shape of dark solids at the glass/bubble interface is cylindrical with heights of 1 and 2 μm . We assumed that the dark solids are uniformly distributed through all the glass/bubble interfaces (only the upper part of the bubble is visible under the microscope). Bubbles are spheres, and the dark solids are mixtures of calcite crystals and native S crystals. We calculate the volatile contents of the bubbles assuming that the fraction native S in the crystal mixture varies from 0.1 to 0.9. Dark crystals of P1-D49-2-7 are 100% gypsum, and H₂O of P1-D49-2-7 is only from gypsum. Finally, We consider different H₂O/CO₂ molar ratios ranges from 1.5 to 0.2, and the density of glass of MI is 2.75 g/cm³. Excel spreadsheets for the calculations are available upon request to R.E.

Supplement E: Calculations of potential H₂O-loss by diffusion

It is possible that H₂O loss from the melt inclusions can be induced by diffusion during heating experiments (Bucholz et al., 2013; Gaetani et al., 2012). Therefore to quantify the degree of H₂O loss that may have been induced during our heating experiments, we

computed diffusive H₂O-loss time series trajectories using the numerical model described by Qin et al. (1992), using the same protocols and parameters described by Bucholz et al. (2013). We assumed a starting H₂O concentration in the inclusion of 4 wt% H₂O, and an external environment 0 wt% H₂O. The MI radius was 50 μm and the olivine radius 450 μm . The olivine-melt partition coefficient for hydrogen was set to 0.0015 (Hauri et al., 2006). On average, the heating experiments lasted ~17 minutes, but the majority of this time period was spent heating the sample towards the melting temperature; the majority of experiments spent ~9 minutes at the melting temperature (<1100°C), and ~3 minutes at the maximum temperature of the experiment (<1250°C). As such, for the diffusion modeling (diffusion rate positively correlated with T), we assumed a temperature of 1250°C to estimate a maximum amount of H₂O loss. After 9 minutes, the melt inclusion (initially 4 wt% H₂O) contains ~3.9 wt% H₂O, for a total H₂O loss of ~0.1 wt% H₂O. After 17 minutes at 1250°C, the inclusion would contain ~3.7 wt% H₂O (representing H₂O loss of ~0.3 wt% H₂O); note, however, that the latter value is based on a significantly longer timespan at the maximum temperature than in our experiments. Thus, we infer that the amount of H₂O loss from the inclusions during our experiments is ≤ 0.1 wt% H₂O (and likely significantly less than this amount).

References Cited

Ayuso, R. A., De Vivo, B., Rolandi, G., Seal II, R. R., and Paone, A., 1998, Geochemical and isotopic (Nd–Pb–Sr–O) variations bearing on the genesis of volcanic rocks from Vesuvius, Italy: *Journal of Volcanology and Geothermal Research*, v. 82, p. 53-78.

- Belkin, H. E., and De Vivo, B., 1993, Fluid inclusion studies of ejected nodules from plinian eruptions of Mt. Somma-Vesuvius: *Journal of Volcanology and Geothermal Research*, v. 58, p. 89-100.
- Belkin, H. E., De Vivo, B., Török, K., and Webster, J. D., 1998, Pre-eruptive volatile content, melt-inclusion chemistry, and microthermometry of interplinian Vesuvius lavas (pre-A.D. 1631): *Journal of Volcanology and Geothermal Research*, v. 82, no. 1-4, p. 79-95.
- Berkesi, M., Hidas, K., Guzmics, T., Dubessy, J., Bodnar, R. J., Szabó, C., Vajna, B., and Tsunogae, T., 2009, Detection of small amounts of H₂O in CO₂-rich fluid inclusions using Raman spectroscopy: *Journal of Raman Spectroscopy*, v. 40, no. 11, p. 1461-1463.
- Bucholz, C. E., Gaetani, G. A., Behn, M. D., and Shimizu, N., 2013, Post-entrapment modification of volatiles and oxygen fugacity in olivine-hosted melt inclusions: *Earth and Planetary Science Letters*, v. 374, p. 145-155.
- Burke, E. A., 2001, Raman microspectrometry of fluid inclusions: *Lithos*, v. 55, no. 1, p. 139-158.
- De Vivo, B., Petrosino, P., Lima, A., Rolandi, G., and Belkin, H., 2010, Research progress in volcanology in the Neapolitan area, southern Italy: a review and some alternative views: *Mineralogy and Petrology*, v. 99, no. 1, p. 1-28.
- Dubessy, J., Boiron, M.-C., Moissette, A., Monnin, C., and Sretenskaya, N., 1992, Determinations of water, hydrates and pH in fluid inclusions by micro-Raman spectrometry: *European Journal of Mineralogy*, v. 4, no. 5, p. 885-894.
- Esposito, R., Klebesz, R., Bartoli, O., Klyukin, Y. I., Moncada, D., Doherty, A. L., and Bodnar, R. J., 2012, Application of the Linkam TS1400XY heating stage to melt inclusion studies: *Central European Journal of Geosciences*, v. 4, no. 2, p. 208-218.
- Fall, A., Tattitch, B., and Bodnar, R. J., 2011, Combined microthermometric and Raman spectroscopic technique to determine the salinity of H₂O-CO₂-NaCl fluid inclusions based on clathrate melting: *Geochimica et Cosmochimica Acta*, v. 75, no. 4, p. 951-964.
- Gaetani, G. A., O'Leary, J. A., Shimizu, N., Bucholz, C. E., and Newville, M., 2012, Rapid reequilibration of H₂O and oxygen fugacity in olivine-hosted melt inclusions: *Geology*, v. 40, no. 10, p. 915-918.
- Hauri, E. H., Gaetani, G. A., and Green, T. H., 2006, Partitioning of water during melting of the Earth's upper mantle at H₂O-undersaturated conditions: *Earth and Planetary Science Letters*, v. 248, p. 715-734.
- Klébesz, R., Esposito, R., De Vivo, B., and Bodnar, R. J., 2015, Constraints on the origin of sub-effusive nodules from the Sarno (Pomici di Base) eruption of Mt. Somma-Vesuvius (Italy) based on compositions of silicate-melt inclusions and clinopyroxene: *American Mineralogist*, v. 100, no. 4, p. 760-773.
- Lamadrid, H. M., Lamb, W. M., Santosh, M., and Bodnar, R. J., 2014, Raman spectroscopic characterization of H₂O in CO₂-rich fluid inclusions in granulite facies metamorphic rocks: *Gondwana Research*, v. 26, no. 1, p. 301-310.
- Le Bas, M. J., Le Maitre, R. W., Streckeisen, A., and Zanettin, B. A., 1986, Chemical classification of volcanic rocks based on the total alkali-silica diagram: *Journal of Petrology*, v. 27, no. 3, p. 745-750.

- Lin, F., Sum, A. K., and Bodnar, R. J., 2007, Correlation of methane Raman v1 band position with fluid density and interactions at the molecular level: *Journal of Raman Spectroscopy*, v. 38, no. 11, p. 1510-1515.
- Marianelli, P., Sbrana, A., Métrich, N., and Cecchetti, A., 2005, The deep feeding system of Vesuvius involved in recent violent strombolian eruptions: *Geophysical Research Letters*, v. 32, p. L02306.
- Moore, L., Gazel, E., Tuohy, R., Lloyd, A., Esposito R., Steele-MacInnis, M. J., Hauri, E. H., Wallace, P., Plank, T., and Bodnar, R. J., 2015, Bubbles matter: An assessment of the contribution of vapor bubbles to melt inclusion volatile budgets *American Mineralogist*, v. 100, p. 806-823.
- Peccerillo, A., 2005, Plio-Quaternary Volcanism in Italy: *Petrology, Geochemistry, Geodynamics*, Heidelberg
- Qin, Z., Lu, F., and Anderson, A. T., 1992, Diffusive reequilibration of melt and fluid inclusions: *American Mineralogist*, v. 77, p. 565-576.
- Redi, D., 2014, Pyroxene and olivine chemistry as an indicator of melt evolution. A contribution to the understanding of Somma-Vesuvius eruptive behaviour [PhD: University of Tasmania and University of Napoli Federico II.
- Rolandi, G., Barrella, A. M., and Borrelli, A., 1993, The 1631 eruption of Vesuvius: *Journal of Volcanology and Geothermal Research*, v. 58, no. 1-4, p. 183-201.
- Sobolev, A. V., Dmitriev, L. V., Barsukov, V. L., Nevzorov, V. N., and Slutsky, A. B., 1980, The formation conditions of the high magnesium olivines from the monomineralic fraction of Luna 24 regolith: *Proceedings of the Lunar and Planetary Science Conference*, v. 11, p. 105-116.
- Steele-MacInnis, M. J., Esposito, R., and Bodnar, R. J., 2011, Thermodynamic model for the effect of post-entrapment crystallization on the H₂O-CO₂ systematics of volatile saturated silicate melt inclusions: *Journal of Petrology*, v. 52, p. 2461-2482.
- Sterner, S. M., and Bodnar, R. J., 1984, Synthetic fluid inclusions in natural quartz I. Compositional types synthesized and applications to experimental geochemistry: *Geochimica et Cosmochimica Acta*, v. 48, no. 12, p. 2659-2668.
- Webster, J., Raia, F., De Vivo, B., and Rolandi, G., 2001, The behavior of chlorine and sulfur during differentiation of the Mt. Somma-Vesuvius magmatic system: *Mineralogy and Petrology*, v. 73, p. 177-200.