Highly explosive basaltic eruptions driven by CO₂ exsolution

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The most explosive basaltic scoria cone eruption yet documented (>20 km high plumes) occurred at Sunset Crater (Arizona) ca. 1085 AD by undetermined eruptive mechanisms. We present melt inclusion analysis, including bubble contents by Raman spectroscopy, yielding high total CO₂ (approaching 6000 ppm) and S (~2000 ppm) with moderate H₂O (~1.25 wt%). Two groups of melt inclusions are evident, classified by bubble vol%. Modeling of post-entrapment modification indicates that the group with larger bubbles formed as a result of heterogeneous entrapment of melt and exsolved CO₂ and provides evidence for an exsolved CO₂ phase at magma storage depths of ~15 km. We argue that this exsolved CO₂ phase played a critical role in driving this explosive eruption, possibly analogous to H₂O exsolution driving silicic caldera-forming eruptions. Because of their distinct gas compositions relative to silicic magmas (high S and CO₂), even modest volume explosive basaltic eruptions could impact the atmosphere.

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unset Crater, a small, monogenetic scoria cone composed of alkali basalt in northern Arizona, was the source of multiple sub-Plinian basaltic events (plumes >20 km high) ~1000 years ago (1085 AD). It has recently been documented as the most explosive scoria cone eruption identified on Earth to date, but the driving mechanism of such highly explosive basaltic eruptions is unclear. Some recent studies have focused on rapid microlite crystallization and corresponding rheology changes to explain explosive behavior in basaltic magmas. In viscous, silicic systems, large explosive eruptions can be triggered when the magmatic system becomes overpressurized by processes such as crystallization-induced volatile exsolution, new magma injection, or external changes in the pressure regime. These processes, however, may be less applicable to basaltic magmas of much lower viscosity. Nevertheless, explosive volcanic eruptions can inject ash and volatiles into the stratosphere with the potential to impact global climate. Aside from the notable exceptions of basaltic eruptions of significant volume such as Laki (Iceland) or large igneous provinces, the impact of basaltic volcanism on the global atmospheric system is largely unknown. Magmatic volatile content is an integral part of the interpretation of an eruption but is difficult to measure because volatiles exsolve and escape as magma ascends and depressurizes. The best-preserved pre-eruptive concentration of magmatic volatiles is found within melt inclusions (MIs) that are trapped inside of growing crystals at depth within the magma plumbing system. Because MIs are isolated from the surrounding magma by their crystal host, they theoretically serve as a record of pre-eruptive magma composition and volatile content at the time and location of their entrapment. MI bubbles, however, are susceptible to modification from post-entrapment crystallization and shrinkage during eruption, and quench at the surface, which often results in significant CO2 loss to a bubble within the MI (Fig. 1a). MI bubbles may not develop solely post-entrapment, however, as they can also originate as a co-entrapped exsolved phase.

One approach to determine MI bubble contents is in situ measurement by Raman spectroscopy. A number of recent studies using Raman and other methods have found up to 90% of the total MI CO2 sequestered in the bubble, demonstrating the importance of MI bubbles in calculating magmatic volatile budgets. Notably, these previous studies of MI bubbles examined samples with relatively low CO2 content in the MI glass, generally ~100–200 ppm but up to 1500 ppm in rare samples.

Here we present an investigation of the total volatile budget of the basaltic sub-Plinian eruption of Sunset Crater by MI analysis, including Raman spectroscopic measurements of MI bubbles. We model the size of MI bubbles that can develop post-entrapment and demonstrate that an exsolved CO2 phase existed in the magma at ~15 km depth. We compare magmatic volatiles at Sunset Crater to those in explosive caldera-forming silicic eruptions such as the Bishop Tuff to highlight differences in their abundance and composition. This comparison suggests that the exsolved CO2 phase is a critical pre-eruptive condition that drives highly explosive basaltic eruptions. Furthermore, we constrain the total stratospheric injection of multiple volatile species by the Sunset Crater eruption and propose that basaltic eruptions, including small scoria cones, may be an overlooked source of atmospheric aerosol loading.

**Results and discussion**

**MI and bubble compositions.** Analysis of MIs reveals pre-eruptive properties of the Sunset Crater magma. MIs are hosted in minimally normally zoned Fo ~82–85 olivine phenocrysts sampled from tephra from the first of several sub-Plinian phases of the eruption (phase 3). The MIs are largely homogeneous in major element composition corrected for 4–11% post-entrapment crystallization (see Supplementary Material). Bubbles are ubiquitous in MIs from all phases of the Sunset Crater eruption, with most MIs containing a single bubble that, in the samples analyzed here, ranges in size from 0.82 vol% to 3.26 vol% of the host MI (Fig. 1b, c). Throughout this section, we present data demonstrating that MIs should be classified into two groups based on bubble vol%. MIs with bubbles <2.5 vol% are hereafter referred to as “Group I” (black filled symbols in Figs. 2–4; example MI in Fig. 1b) and those with bubbles >2.5 vol% as “Group II” (open symbols in Figs. 2 and 3; cyan symbols in Fig. 4a, b; example MI in Fig. 1c). Total CO2 contents, accounting for both the MI bubble (from Raman spectroscopy) and MI glass (from Fourier transform infrared spectroscopy (FTIR)), encompass a wide range from 2664 to 5591 ppm, with an average value of 4268 ppm (Fig. 2a and Supplementary Material). Group II MIs (bubbles >2.5 vol%) have the highest total CO2 contents (>4000 ppm; open symbols in Fig. 2a). S and Cl contents measured for a different subset of phase 3 MIs are ~2000 and ~425 ppm, respectively, and show minimal variability across all samples (see Supplementary Material).

There are two different mechanisms that could produce a set of MIs with a wide range of volatile contents as observed in the Sunset Crater samples. One possible explanation is that the magma is volatile undersaturated, and so as crystallization proceeds, volatile elements that are incompatible in phenocryst phases will concentrate in the magma. The alternative explanation is that the MI volatiles record a degassing path as a volatile-saturated magma ascends and depressurizes. The data presented here show that the total CO2 content generally decreases with decreasing host Fo content in these samples (Fig. 2b). This relationship implies that the magma is volatile saturated when olivine is crystallizing because CO2 exsolves from the magma as crystallization proceeds and Fo content decreases. However, these

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**Fig. 1 MI bubble formation and representative Sunset Crater MIs.**

(a) Diagram showing post-entrapment formation mechanisms of MI bubbles. (b, c) Photomicrographs of example MIs; scale bar is 20 μm. (b) MI from Group I (<2.5 vol% bubble). (c) MI from Group II (>2.5 vol% bubble).
olivine data also show two roughly parallel but distinct trends: Group II MIs (>2.5 vol% bubbles) show the same decrease in CO2 with lower Fo, but offset to higher total CO2 than Group I samples (Fig. 2b). So, while the Sunset Crater magma was likely volatile saturated and degassed as it ascended, this mechanism does not explain why there are two trends in Fig. 2b nor provide justification for the highest CO2 contents being restricted to MIs with larger (>2.5 vol%) bubbles.

Further observations also support the division of MIs into two distinct groups by bubble vol%. Bubbles in Group II samples are proportionally larger by vol% than those in Group I, and they also typically have larger diameters, with average bubble diameters of 26 μm for Group II vs. 20 μm for Group I (see Supplementary Material). Additionally, Group I MIs define a relatively linear trend between CO2 concentration in the bubble and bubble vol% (Fig. 2c), while some Group II MIs deviate from this relationship. The two groups are also distinguished by the percentage of the total MI CO2 that is contained in the bubble (Fig. 2d); most Group I MIs contain <40% of their total CO2 content in their bubbles, whereas all Group II MI bubbles contain >40% of the total MI CO2. These results suggest that the bubbles in MIs from each of the two groups may have formed by different processes.

Bubble growth modeling. The two primary mechanisms of MI bubble formation include differential shrinkage of the MI and crystal host as well as crystallization at the MI–crystal interface (Fig. 1a). Shrinkage occurs because the host crystal is relatively incompressible compared to the MI and thus the MI shrinks more than the crystal during cooling14,25, resulting in pressure loss within the MI. Post-entrapment crystallization involves diffusion of elements from the MI into a denser crystal phase, decreasing the MI volume within its cavity and thus decreasing pressure in the MI16,26.

Bubbles in MIs form and grow in two stages: in the subsurface due to small degrees of pre-eruptive cooling (early stage) and during rapid cooling upon eruption into the atmosphere until quench (late stage). The cooling rate of the magma during early-stage bubble growth is typically slow enough such that both post-entrapment crystallization and shrinkage occur. Additionally, because CO2 solubility is very strongly pressure dependent27, the decrease in pressure associated with these post-entrapment modifications will cause CO2 to exsolve into the bubble that forms. On the other hand, in late-stage (syn-eruptive) growth, especially in explosive eruptions, cooling is extremely rapid and CO2 does not have time to diffuse from the MI into the bubble15,28. In fact, cooling during late-stage growth is rapid enough that post-entrapment crystallization is also kinetically inhibited20, but the bubble volume does continue to increase syn-eruption due to the shrinkage process.

The size of MI bubbles that can be generated due to post-entrapment modification processes during early- (pre-eruption) and late-stage (syn-eruptive) cooling can be modeled from properties of the melt and host phenocryst at different temperatures20. Bubble formation during early-stage shrinkage
is a function of the difference between the temperature of the magma when the MI is trapped and its temperature just prior to eruption ($\Delta T$). The additional early-stage bubble volume generated during post-entrapment crystallization is determined by the amount of crystallization that occurs, which also depends on $\Delta T$. Modeling of late-stage shrinkage requires an estimation of the glass transition temperature ($T_g$), which varies based on total $\text{H}_2\text{O}$ content and quench rate$^{29}$.

The lines in Fig. 3a show the results of modeling the size of MI bubbles generated by both stages of post-entrapment cooling for the Sunset Crater magma. The value $\Delta T$ on the x-axis represents cooling prior to eruption and accounts for early-stage differential shrinkage and post-entrapment crystallization. The value of $T_g$ represents the post-eruptive quench temperature, while the lines represent the final bubble vol% resulting from combined early- and late-stage bubble growth for different values of $\Delta T$ and $T_g$.

The results are strongly dependent on the value of $T_g$, which has been investigated experimentally in basaltic melts at cooling rates between 5 and 20 °C/min$^{29}$. However, for a highly explosive eruption such as at Sunset Crater, the cooling of small clasts, and especially the free crystals analyzed here, is likely to occur much faster than 20 °C/min. Based on $T_g$ data$^{29}$ and the shape of the relaxation curve of a silicate liquid$^{31}$, we estimate $T_g$ for these MIs to be 675 °C (Fig. 3a, solid line). In order to illustrate the sensitivity of these estimates to $T_g$, we also plot modeled bubble volumes for values of $T_g$ at $+$/−100 °C from our preferred value (Fig. 3a, dashed lines). Based on these calculations, Group II MIs are too large to have formed from post-entrapment cooling alone.

However, an alternate explanation for the different bubble trends in Group I and Group II MIs is that they experienced different cooling histories either pre- or syn-eruption. We reject this hypothesis on the basis of our interpretation of eruption dynamics and associated cooling during subsurface ascent and syn-eruptive quench. First, the data suggest that the pre-eruptive (subsurface) cooling was not significantly different between the two groups of MIs. The MI compositions (see Supplementary Material) indicate that they originated from a batch of homogeneous magma at depth that ascended rapidly without any pause at shallower depths prior to eruption. Additionally, there is no correlation between the amount of post-entrapment crystallization experienced by the MIs and the bubble size (Fig. 3b) nor is there any difference in the amount of post-entrapment crystallization between the two groups of MIs. Second, syn-eruptive quench would have been rapid in a sub-Plinian eruption (>20 km high plume). However, if the rates of syn-eruptive quench differed among crystals, the bubble CO$_2$ densities would also show differences, because during quench the bubble grows without CO$_2$ diffusion into the bubble. In other words, MIs experiencing slower syn-eruptive cooling should have larger bubbles (i.e., Group II MIs) with lower bubble CO$_2$ densities, but this is not recorded in the bubble density data (Fig. 3c).

One additional factor that can affect the size of MI bubbles is H$^+$ diffusion out of the MI during pre-eruptive (subsurface) cooling. This process results in a lower partial molar volume of the MI, which can lead to contraction of the MI and formation of a bubble$^{31}$. This process cannot be solely responsible for the differences in bubble sizes between Group I and Group II MIs given the similar H$_2$O contents of all MIs (Fig. 2a) and that samples with nearly identical H$_2$O contents have different bubble sizes. Two samples show relatively low H$_2$O contents that could indicate some minor H$^+$ diffusion, but all other Group II MIs share similar H$_2$O contents to Group I MIs and should not have been affected by H$^+$ diffusion.

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**Fig. 3 Bubble vol% vs. MI properties to illustrate variable formation mechanisms for the two groups.** Filled symbols are MIs with bubbles <2.5 vol% (Group I) and open symbols are MIs with bubbles >2.5 vol% (Group II). a Results from modeling post-entrapment bubble formation. The solid line indicates the maximum bubble size (vol%) attainable from post-entrapment crystallization and shrinkage assuming a glass transition temperature of 675 °C. b Percentage of post-entrapment crystallization experienced by each MI (see "Methods"). c Bubble CO$_2$ density (g/cm$^3$) as determined by Raman spectroscopy. Error in MI bubble vol% is 15% (i.e., 0.3 vol% error for a 2 vol% bubble); see "Methods" for details on error estimates.
Given the lack of evidence for different cooling histories or significant H⁺ diffusion, Group II MIs do have bubbles that are too large to have formed solely from post-entrapment cooling. Therefore, our favored explanation is that Group II MIs were trapped heterogeneously as two phases: liquid melt and exsolved CO₂. The Group II MIs have greater total CO₂ contents (Fig. 2a), as well as a greater percentage of the total MI CO₂ content in their bubbles (Fig. 2d), supporting the presence of an initial CO₂-rich exsolved phase.

We can estimate the original dissolved CO₂ content at entrapment for MIs with a co-entrapped exsolved phase by approximating the proportion of dissolved MI CO₂ that sequesters into Group II bubbles during post-entrapment processes. According to models, the entrapment of MIs during post-entrapment processes results in a reduction of the original CO₂ content due to the formation of bubbles. The degree of suppression of CO₂ exsolution not only depends on the initial pressure but also on the initial bubble volume fraction and magma composition. Using this model, we estimate that two MI samples of alkali basalt composition at 450 MPa, one with no initial bubble and one with a 1 vol% bubble, should lose nearly the same proportion of their original dissolved CO₂ to a bubble after 10% post-entrapment crystallization (~30 vs. 26%). Thus the proportion of originally dissolved CO₂ that exsolves into Group II bubbles should be similar to that of Group I bubbles (~35% on average) as the two groups experienced similar amounts of post-entrapment crystallization (Fig. 3b).

If we reconstruct the dissolved volatile contents at MI entrapment, assuming Group II MIs lost 35% of the originally dissolved CO₂ to a bubble, the two groups of MIs overlap in dissolved volatile content at entrapment (Fig. 4a). Note that the two Group II samples with the lowest H₂O contents could be affected by H⁺ loss via diffusion as discussed above. H⁺ loss would facilitate additional CO₂ exsolution during pre-eruptive cooling, thus the CO₂ contents at entrapment shown in Fig. 4a may be slightly underestimated for these two samples. The reconstructed CO₂ at MI entrapment also clarifies the crystallization process, yielding one primary trend with Fo that suggests simple exsolution of CO₂ from the magma as crystallization proceeds (Fig. 4b).

Based on these estimates of the original dissolved volatile content, Group II MIs were trapped with 487 to 2226 ppm of exsolved CO₂.
in a bubble. Assuming that these heterogeneously entrapped bubbles formed as a result of oversaturation in a magma at 450 MPa and 1200°C where the density of CO₂ is ~0.74 g/cm³, the bubbles would be ~9–18 μm in diameter, corresponding to 0.18–0.80 vol% of their host MI. Modeling indicates that these very small (<1 vol%) initial bubble sizes would not significantly suppress further CO₂ exsolution at these storage pressures, which validates our conclusion that both groups of MIs likely do lose a similar proportion of originally dissolved CO₂ to a bubble during early-stage (pre-eruptive) cooling.

Implications for eruption style and scale. The MI results show that the Sunset Crater magma was volatile saturated and included a CO₂-rich exsolved phase. Fluid-saturated isobars for Sunset Crater indicate MI entrapment pressures between 300 and 500 MPa, corresponding to depths between ~12 and 17 km (Fig. 4a). The MIs with a co-entrapped exsolved phase (Group II; cyan symbols in Fig. 4a) show entrapment pressures consistent with this entire magma storage region, suggesting a bubbly magma deep in the system. Figure 4c presents the interpretation of MI entrapment and bubble growth in MIs in the Sunset Crater magma. Group I and II MIs are both trapped at storage depths between 300 and 500 MPa, but Group II MIs are trapped with a pre-existing bubble. The MIs next undergo early (pre-eruptive) bubble growth with CO₂ exsolution as a result of a slight decrease in temperature, causing both post-entrainment crystallization and shrinkage. Finally, the MIs are erupted and quenched, which yields late (syn-eruptive) bubble growth due to shrinkage only, and without further CO₂ exsolution. The modifications shown in Fig. 4c are cumulative from the entrapment stage. In summary, the MIs undergo the same two stages of bubble growth, but the bubbles in Group II samples remain proportionally larger due to their initial volumes.

Even if the Group II samples could be explained without heterogeneous entrapment, we would still expect CO₂ exsolution in this deep magma storage region on the basis of the total CO₂ results (Fig. 2a). As explained previously, the olivine data (Fig. 2b) show that the magma was volatile saturated throughout the entire depth range over which the MIs were trapped because samples follow a trend of decreasing CO₂ with decreasing Fo content (i.e., CO₂ exsolves as crystallization proceeds). If the total CO₂ in Group II MIs did represent the dissolved CO₂ at MI entrapment, the MIs would be trapped over a very wide pressure range from almost 600 to 300 MPa (i.e., Fig. 2a). A volatile-saturated magma of the Sunset Crater composition ascending from 600 to 300 MPa would have to exsolve nearly 3000 ppm of CO₂ into bubbles based on volatile solubility data.

Experimental work confirms that bubbles with similar dimensions to our estimates for the heterogeneously entrapped bubbles (i.e., 10s of micrometers in diameter) can be generated in alkali basalt magma at these pressures. Bubbles with these properties (0.74 g/cm³ and ~20 μm diameter) would be coupled with the magma: bubble rise velocities would be on the order of 10⁻¹¹ m/s based on calculations of the buoyancy force balanced against gravity and viscous forces, assuming Stokes drag and a range of reasonable magma viscosities, temperatures, and densities. This pre-eruptive system at Sunset Crater with a bubbly basaltic magma could be analogous to silicic magmas that produce highly explosive eruptions such as the Bishop Tuff rhyolite.

While Sunset Crater and silicic caldera-forming systems, exemplified by the middle-erupted Bishop Tuff, both may be characterized by eruption from bubbly magma storage zones, their storage depths and volatile compositions are notably different. Magma storage depths, calculated from MI saturation pressures, were 12–17 km at Sunset Crater but just 7 km for the Bishop Tuff magma. The total dissolved H₂O and CO₂ content of the Sunset Crater magma was 4.6 mol% at the time of MI entrapment, of which 89 mol% was H₂O and 11 mol% was CO₂. In contrast, the Bishop Tuff magma contained significantly greater dissolved volatile content at MI entrapment (17 mol%), which was essentially 100 mol% H₂O. The composition of the exsolved phase in equilibrium with each magma, as calculated from fluid isopleths (ref. 30 for rhyolite and ref. 32 for basalt), is also distinct. The exsolved phase in the Sunset Crater magma had only trace H₂O (3 mol%) and was predominantly CO₂ (97 mol%). The Bishop Tuff, on the other hand, had an exsolved phase that was primarily H₂O (92 mol% H₂O) with a small amount of CO₂ (8 mol%)34,35.

Exsolved H₂O is expected to play a large role in explosive eruptions, but an exsolved CO₂ phase at the greater depths of magma storage in basaltic eruptions may also produce the conditions necessary for large explosive eruptions. The significant overpressure from exsolved CO₂ can fracture wall rocks, leading to rapid magma ascent and an explosive eruption. Given that storage zones of basaltic systems are expected to be deeper than those of silicic magmas based on neutral buoyancy considerations, and the greater solubility of H₂O compared to CO₂, high CO₂ concentrations are required for an exsolved phase to exist at expected storage depths for basalt. This exsolved CO₂ phase may be necessary to initiate a pathway to the surface via overpressure and fracturing, and to drive rapid ascent from the deeper part of the system to the shallow region, where H₂O exsolution is expected to take over the driving role. We thus propose that the exsolved CO₂ phase present at depth, as indicated by co-entrapped MI bubbles, was a necessary or critical condition that drove the sub-Plinian eruption of basalt at Sunset Crater, analogous to exsolution of H₂O-rich fluids driving caldera-forming silicic eruptions.

Rapid ascent due to an exsolved CO₂ phase at depth may be a common mechanism for mafic explosive eruptions. For example, Mt. Etna (Italy) has experienced some sub-Plinian and Plinian events and is similar in composition to Sunset Crater38–40. While some Etna MIs do contain significant dissolved CO₂41, the CO₂ in Etna MI bubbles has not yet been quantified. Stromboli (Italy) is another mafic volcano that has produced explosive paroxysms, and exsolved CO₂ at depths up to 10 km beneath the crater has been proposed as the trigger for these events based on measured crater plume emissions42. Additionally, fluid inclusions in phenocrysts from Piton de la Fournaise (Réunion Island) suggest that CO₂ exsolution begins deep in the magma plumbing system of this volcano (500 MPa)43. Based on findings presented here, we would expect that the MI bubbles from the most explosive eruptions at these volcanoes might also contain significant CO₂ and evidence of a co-entrapped exsolved CO₂ phase, suggesting bubbly magma deep in the plumbing system. MI analysis following the procedures described here, we would expect that MI bubble contents and formation would provide the data necessary to test this theory.

There are other processes, such as rapid shallow microlite crystallization and corresponding rheology changes, that have been proposed to explain explosive behavior in mafic magmas. CO₂ exsolution was proposed as the trigger for the ~456 ka Pozzolane Rosse explosive mafic eruption at Colli Albani (Italy), but the CO₂ was not magmatic in origin, and the explosive nature was controlled by increased magma viscosity as a result of extensive decompression-induced leucite crystallization. Extensive crystallization has also recently been proposed as the cause of the Masaya Triple Layer mafic Plinian eruption (2.1 ka; Nicaragua), which is relatively volatile poor45. While there is evidence in the Sunset Crater eruptive products for variable microlite crystallization in a portion of the groundmass, a significant fraction of the tephra in the sub-Plinian phases has a glassy and vesicular texture1, suggesting that rapid microlite
crystallization cannot be the only important control. We further emphasize that rapid microcrystalline crystallization is generally driven by exsolution of H₂O from the magma in the shallow subsurface, and we therefore favor the idea that a deeper mechanism, such as exsolution of CO₂, is required to explain eruption initiation and rapid magma ascent in basaltic systems whose magmas ascend from greater depths to feed explosive eruptions.

Atmospheric loading. Sunset Crater erupted a significant volume of volatile-rich magma that reached the stratosphere during its most explosive phases. The eruption produced 0.52 km³ dense-rock equivalent (DRE) (2.8 g/cm³ dense rock density) of volcaniclastic material, of which 0.22 km³ was erupted during the sub-Plinian phases. As a result of the analysis presented here, along with these previously published volcanological characteristics, we estimate that the Sunset Crater eruption released ~0.6 Mt Cl, ~6 Mt SO₂, and ~11 Mt CO₂. SO₂ released during the sub-Plinian phases of the eruption (~2.45 Mt) could reach the stratosphere and generate H₂SO₄ aerosols. Assuming that 75% of the aerosol estimate that the Sunset Crater eruption released ~0.6 Mt Cl, ~6 μm in diameter (often larger, depending on the placement of the bubble), range from ellipsoidal to negative crystal shapes. All MIs contain one bubble ranging in size from ~1 to 5 vol% in typical MIs. Rarely, multiple bubbles are present in a single MI and in some cases, there is one primary bubble with the other bubble(s) being much smaller in size. We carefully selected primary MIs that did not exhibit evidence of extensive H₂O loss or decrepitation. The only secondary modification physically apparent in the analyzed MIs was the bubble.

**CO₂ calibration.** To correct for instrument variability, any CO₂ densimeter must be adjusted using CO₂ standards analyzed using a specific Raman instrument. In this study, pure CO₂ gas was sealed in capillary tubes using a vacuum line to create a set of synthetic inclusions for use as standards. These CO₂ gas standards have densities between 0.008 to 0.133 g/cm³, which is consistent with the lower range of CO₂ densities measured in MI bubbles.

**Raman analysis.** MI bubbles were analyzed using Raman spectroscopic techniques. The Raman data were collected using a custom built Raman spectrometer in a 180° geometry at ASU in the LeRoy Eyring Center for Solid State Science (LE-CSS). The sample was excited using a 150-mW Coherent Sapphire 532nm laser with a 532-nm laser wavelength. The laser power was controlled using a neutral density filter and a linear laser power controller. The laser was focused onto the sample using a Collin 750 spectrometer on an Andor iDUS back thinned Silicon CCD cooled to ~95 °C, and a 1200 mm−1 grating was utilized to achieve optimal spectral resolution while preserving signal strength. High-quality MIs were polished to <3 μm from the MI bubble and imaged with a petrographic microscope in preparation for Raman analysis. The MIs were specifically chosen to provide a representative sample of textural features observed in the Sunset Crater eruption (e.g., variable bubble volumes, MI sizes, MI shapes). In addition to these MIs and the four CO₂ standards, calcite, quartz, enstatite, and 1.4 bis (2methylstyryl) benzene were also analyzed as Raman shift axis calibration standards during the measurement session. For each bubble, the laser power at the sample was set to 6 mW (in isolated cases where the signal was low, the power was increased to 12 mW), and five 30-s scans were accumulated.

**Dissolved volatile analysis**. The total contribution of CO₂ from the MI bubble was calculated from the Raman data using a mass balance approach. In addition to the CO₂ bubble density, which is determined by the Raman analysis, this calculation requires density of the MI glass and the CO₂ concentration of the glass, as well as the volume fraction of the MI glass and bubble. CO₂ content of the MI bubble was determined by FTIR, which is described in the “Dissolved volatile analysis” section below. The densities of the MI glasses were determined from major element composition and H₂O content, and this calculation is also described in the “Dissolved volatile analysis” section below. Volumes were determined from photomicrographs of the MIs, first using ImageJ to trace the area of the MI, and then using a Shameck 750 spectrometer from Andor black thinned Silicon CCD cooled to ~95 °C, and a 1200 mm−1 grating was utilized to achieve optimal spectral resolution while preserving signal strength.

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Dissolved volatile analysis. H2O and CO2 contents of the MI glasses were determined by FTIR. MIs were doubly intersected and polished in preparation for transmission FTIR analysis. FTIR analyses were performed using a Nicolet iN10 MX instrument at the United States Geological Survey in Menlo Park. Spectra were collected between 5500 and 1000 cm^-1 wavenumber for 45 s (128 scans) with high spectral resolution, and a background was collected before analyzing each sample. The aperture was carefully maximized for each inclusion according to the size of the doubly exposed spot on the inclusion to obtain an optimal spectrum. H2O and CO2 contents were calculated using the Beer–Lambert Law:

\[ C = \frac{MW}{\rho \cdot \lambda} \]

where \( C \) is concentration in wt%, \( MW \) is the molecular weight of the absorbing species, \( \rho \) is the density of the sample in g/cm\(^3\), and \( \lambda \) is a molar absorption coefficient in L/mol-cm. Absorbances (\( \varepsilon \)) were measured after subtraction of Black curve baselines drawn beneath each peak to reproduce the spectra of volatile-free samples. Thicknesses were determined using a Zygo ZeScope optical profilometer in the LE-CSSS, which allowed for precise thickness across the FTIR aperture to be determined. Density was calculated for each MI using the method detailed in ref. 56 wherein partial molar volume contributions are totaled for a dry glass and density is adjusted according to ref. 59, with an average value of \( \approx 320 \) L/mol-cm. The ref. 59 relationship was specifically calibrated for all-alkali rich magmas such as Sunset Crater, and so we estimate \( \approx 5\% \) uncertainty for CO2 content, while the uncertainty in H2O content is \( \approx 10\% \).

Volatile contents were also corrected for olivine growth at the rim of the MI (post-entrapment crystallization) using the results of the major element corrections. H2O, CO2, and K2O display incompatible behavior with olivine crystallization. After calculation of volatile contents from FTIR spectra using Eq. 1, the ratio of analyzed and corrected K2O contents was used to adjust the volatile components for post-entrapment modification. FTIR results are listed in Supplementary Table 1.

Bubble growth model. We model post-entrapment MI bubble formation and growth following the method of ref. 50, employing differences in density to determine maximum bubble volumes. The pre-eruptive bubble volume is controlled by the difference in the temperature of the melt at the time of MI entrapment compared to its temperature just before the onset of eruption. This temperature difference is assessed during calculations of post-entrapment crystallization using Petrolog353. The final bubble volume after the crystal and MI are quenched during eruption is calculated using the volume at ambient temperature of 43.95 cm\(^3\)/mol from ref. 59 and adjusted for temperature by thermal expansion coefficients from ref. 61. Finally, the maximum bubble size that can form during eruption (\( q_{\text{max}} \)) is calculated. The bubble grows only from the shrinkage process during quench, and so the final melt volume is determined solely from the melt density at the glass transition temperature. The shrinkage of the olivine host is accounted for at this stage as described above. The bubble sizes calculated for both the pre-eruption and eruption stages are added together, and a linear fit is determined for the data to display the relationship between bubble size fraction and \( AT \) (Fig. 3a). An example calculation of the model is shown in Supplementary Table 3.

Data availability

All data acquired for this study are included in Supplementary Tables.

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**Author contributions**

All the authors conceptualized the project, interpreted the results, and wrote the paper. C.M.A. performed the analyses and bubble volume model calculations.

**Competing interests**

The authors declare no competing interests.

**Additional information**

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