

HIGHLIGHTS AND BREAKTHROUGHS

Bursting the bubble of melt inclusions†

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Abstract: Most silicate melt inclusions (MI) contain bubbles, whose significance has been alternately calculated, pondered, and ignored, but rarely if ever directly explored. Moore et al. (2015) analyze the bubbles, as well as their host glasses, and conclude that they often hold the preponderance of CO₂ in the MI. Their findings entreat future researchers to account for the presence of bubbles in MI when calculating volatile budgets, saturation pressures, and eruptive flux. **Keywords:** Melt inclusion, glass inclusion, bubble, volatile, CO₂

On page 806, of this issue, Lowell Moore and colleagues contribute an exciting, scholarly, and admirably thorough treatise on the importance of vapor bubbles to the budget of CO₂ in melt inclusions (MI). The paper offers a clear resolution to an oft-debated question in MI-petrology: can I ignore those little bubbles? The answer: *No*.

Melt inclusions (MI) are small blebs of silicate melt, typically 1 to 200 μm across, trapped during crystal growth in magmatic systems. Some MI are glassy, representing relatively rapid quenching of the host rock, or pyroclast, though others may be entirely crystalline. In volcanic rocks, because MI may be trapped long prior to eruption, they can record changes in melt chemistry in the magma reservoir or during transport toward the surface. For volatile species such as H₂O, CO₂, Cl, and S, which readily degas during eruption, MI offer the best empirical data on the initial concentrations of magmatic volatiles dissolved in melt. They are therefore used for studies of explosive volcanism, magmatic degassing, ore deposits, geothermal systems, and a host of other topics within the field of igneous petrology and geochemistry (Roedder 1979; DeVivo and Bodnar 2003; Kamenetsky and Kamenetsky 2009; Audétat and Lowenstern 2014). One critical application of MI is to calculate a saturation pressure (Anderson et al. 1989), the minimum pressure at which a melt could have been trapped without being fluid-saturated. Once the inclusion is trapped in a crystal “pressure vessel,” the volatile-rich melt composition can be preserved during depressurization and can yield information about the depth of crystallization.

MI represent a special subcategory of fluid inclusions (FI), in which the trapped *fluid* is quenched to glass, or depending on cooling rate and melt composition, can crystallize to form a mass of microcrystalline solids. Most FI and MI contain bubbles: the bubbles typically form during cooling and decompression along an isochore within the near-constant-volume inclusion. In essence, the different thermal expansion properties of the host


crystal and trapped liquid create conditions that strongly favor creation of a low-density phase. In studies of FI, the bubbles are studied intensively (Samson et al. 2003). Experimental heating and homogenization provide insight into the temperature of entrapment and the conditions of formation. Raman spectroscopy and other techniques can provide quantitative information on gas species within bubbles.

Surprisingly, little has been done to analyze the bubbles within MI—perhaps partly because of interference from the surrounding glass greatly complicates spectroscopic and other analytical methods. Many authors recognize that bubbles can contain a significant percentage of the volatiles in an inclusion, particularly for those with low solubility in the melt such as CO₂ (Anderson and Brown 1993). But there is little consensus on how to account for the presence of bubbles. Part of the problem is that bubbles can exist for different reasons: (1) as discussed, they can be an inevitable result of slow cooling; (2) a pre-existing bubble can be trapped along with the melt in a volatile-saturated system and therefore represents an extra aliquot of volatiles (Kamenetsky and Kamenetsky 2009); or, (3) they can form during leakage, by vesiculation of inclusions connected by fine capillaries to the crystal exterior, or during decrepitation (rupture) of the host crystal (Lowenstern 1995).

There have been several approaches utilized by researchers with respect to bubbles. Some avoid bubble-bearing inclusions and only study the most rapidly quenched MI, which lack bubbles. Such MI are often present in deposits of explosive eruptions but are much less common in pyroclastic flows, lavas, and subvolcanic intrusions (Lowenstern 1995). Others have ignored the bubbles, or assumed their presence negligible in terms of the mass balance of volatiles. And yet others have developed protocols to homogenize the bubbles back into the melt by rapidly heating the host crystal back to magmatic temperatures and then rapidly cooling the sample to prevent re-formation of the bubble. Unfortunately, additional controversy exists regarding leakage of volatiles during any experiment by diffusion through the host crystal toward a volatile-free (or volatile-saturated) external atmosphere (Gaetani et al. 2012). Petrologists are left with a conundrum: Do I leave the MI in their natural (bubble-bearing) state or re-homogenize them and risk creating unintended changes to the inclusions?

Notwithstanding such controversies, Moore et al. (2015) clearly document that bubbles can contain substantial fractions of the total CO₂ located within MI. Part of the elegance of the study stems from their careful attention to sample selection, focusing only on those inclusions where the volume fraction of bubble was consistent with post-entrapment bubble formation during cooling, and not due to leakage or entrapment of pre-existing vapor. They then applied Raman spectroscopy to measure the densities of CO₂ in the bubbles. Combined with CO₂ analysis

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of the glass, as well as measurements of bubble and inclusion volume, the authors were able to constrain the proportion of CO₂ in bubbles from scores of MI in volcanic systems from Kilauea Iki and Kapoho (Hawaii, U.S.A.), Fuego (Guatemala), and Seguam Island (Alaska, U.S.A.). They found that bubbles most often contained 40 to 90% of the total CO₂ in the MI, requiring that some inclusions were trapped >10 km deeper than would be calculated ignoring the bubble! Similar conclusions were drawn in a recent study on melt inclusions from the 1783–1784 Laki eruption (Hartley et al. 2014).

Several other useful topics are discussed within the paper. The authors provide protocols for estimating minimum CO₂ concentrations of MI analyzed solely by Raman analysis of the bubble. The research demonstrates that additional CO₂ can be sequestered in small (generally <<10 μm) carbonate crystals that presumably form at high temperature when CO₂ reacts with the melt/glass wall (see also Kamenetsky and Kamensky 2009). Another interesting aspect is a discussion of the likely size of bubbles given different host minerals and melt compositions. Finally, the authors evaluate some of the kinetic factors that control when and why vapor bubbles may accumulate significant proportions of the CO₂ content of the MI.

Some rhyolitic and other magmatic systems are CO₂-depleted, so not every bubble need contain significant CO₂. However, if the magma is CO₂-bearing, the bubbles may be important. If one ignores CO₂ in the bubble, and analyzes solely the host glass, spurious geochemical trends can result that reflect post-entrapment fractionation of CO₂ within the MI, rather than pre-eruptive degassing reflected in a series of MI trapped at different times. With this new research, it is now apparent that if one cannot find bubble-free MI in a sample, additional work must be undertaken

to analyze the bubbles, to homogenize them, or to recognize that volatile concentrations and calculated formation pressures are most certainly minima.

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