

1 Highlights and Breakthroughs

2 **Bubbles do matter!**

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7 **Abstract**

8 Silicate melt inclusions (SMIs) are a very reliable tool for reconstructing the composition of magma (silicate
9 melt + volatiles) and tracing its evolution from mantle depths to the Earth's surface. Although the scientific
10 community already knew about the ability of shrinkage bubbles in SMIs to trap a significant fraction of CO₂,
11 quantitative estimates were still lacking. In the article "Melt Inclusion CO₂ contents, pressures of olivine
12 crystallization, and the problem of shrinkage bubbles" by Wallace et al (2015) included in the special
13 collection "Glasses, melts, and fluids, as tools for understanding volcanic processes and hazards", the
14 authors provide a numerical estimate of the amount of initial CO₂ dissolved in the melt that is lost to
15 shrinkage bubbles and a computational method to estimate such an amount in absence of experimental
16 studies and direct measurements by micro Raman spectroscopy.

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18 **Keywords** melt inclusion; shrinkage bubble; carbon dioxide; volatile content

19 Silicate melt inclusions (SMIs) are small droplets of silicate melt (usually 1-100 μm) that are trapped in
20 microcavities and imperfections of minerals during their growth in a magma body (Sorby, 1858). Upon
21 trapping a melt enriched in volatile species', as a result of crystallization and thermal contraction, the
22 pressure inside the melt inclusions decreases and leads to the formation of a shrinkage bubble (e.g.
23 Roedder, 1979; Lowenstern, 1995, 2003; Métrich and Wallace, 2008); SMIs then start to behave as closed
24 and isolated systems, evolving independently from their host crystal as the magma rises and erupts at the
25 surface. For this reason, the study of SMIs represents a unique opportunity to reconstruct the chemical
26 composition of the trapped magma, including its dissolved volatile content (e.g. H₂O, CO₂, Cl, S and F) which
27 is of critical importance for determining the eruptive style and magma evolution of volcanic systems, since
28 degassing is usually one of the major phenomena that occurs before and during an eruption.

29 In the last few years, several studies have focused on the role of shrinkage bubbles in controlling the
30 volatile content of melt inclusions by taking into account mechanisms such as isochoric cooling, post-
31 entrapment crystallization and rapid H⁺ diffusion as promoters of volatile exsolution and bubble nucleation.
32 If post-entrapment degassing occurs, CO₂ is trapped preferentially into the bubble as a vapor phase
33 because its solubility in basaltic melts is much lower than that of H₂O. The determination of the pre-
34 eruptive CO₂ content in melt inclusions with shrinkage bubbles then requires the adding of the mass of CO₂
35 in the bubble back into the inclusion.

36 In a recent issue of American Mineralogist, Wallace et al (2015) have developed an innovative experimental
37 method to estimate the CO₂ content of bubbles. They have selected olivine-hosted SMIs from a scoria of
38 Mauna Loa, both naturally quenched and reheated, and analyzed them by FTIR spectroscopy and electron
39 microprobe. With the application of an appropriate correction for the H₂O and CO₂ contents determined for
40 re-heated and naturally quenched SMIs, the authors have demonstrated that most of the CO₂ is lost to
41 shrinkage bubbles that form after the entrapment. The comparison between the average CO₂ content of
42 heated inclusions and unheated inclusions indicates that 40-90% of the initial CO₂ dissolved in the melt
43 inclusions was lost to shrinkage bubbles, with an average loss of 75%.

44 Wallace and co-authors have also developed a computational method to estimate the amount of CO₂ in
45 shrinkage bubbles in SMI when there is a lack of experimental heating studies or direct measurements of
46 CO₂ density by micro-Raman spectroscopy. Following the work of Riker (2005), the application of phase
47 equilibrium calculations was coupled with volume and thermal expansion data for silicate melts allowing
48 Wallace and co-authors to correlate the volume of the bubble with the difference between trapping and
49 eruption temperatures. The results obtained by this computational method show that trapping pressures
50 for heated melt inclusions are significantly higher than pressures calculated based only on the dissolved
51 CO₂ in the naturally quenched inclusions, and agree very well with pre-eruptive bubble volume for SMI
52 calculated by Riker (2005) and the estimate of the fraction of initial CO₂ lost to the shrinkage bubbles based
53 on heating experiments. They also created a closed-system degassing model to simulate the effect of post-
54 entrapment decompression in a SMI; the mass and volume of CO₂ exsolved from the melt and the mole
55 fractions of CO₂ and H₂O in the vapor phase were calculated by applying the Redlich-Kwong equation. To
56 calculate the original concentration of CO₂ in the melt at the time of trapping, the authors added the
57 estimated mass CO₂ back into each inclusion.

58 In their paper, Wallace and co-authors conclude that for tholeiitic magmas, such as those represented by
59 SMI compositions from Mauna Loa picrites, the trapping pressure together with the difference between
60 trapping and eruption temperature, and the initial content of H₂O and CO₂ in the melt, are all controlling
61 the fraction of original CO₂ that can be lost to the shrinkage bubbles or any subsequently formed
62 carbonate. The key implication of such findings is that we need to accurately quantify the CO₂ in shrinkage
63 bubbles and add it back into the melt, in order to determine pressures of trapping and correctly track
64 magma degassing behavior during ascent.

65 In conclusion, this paper provides numerical evidence that suggests an average of 75% of the CO₂ in a
66 bubble-bearing SMI is contained in the bubble. If we do not account for this fraction of CO₂, we significantly
67 underestimate the total amount of CO₂ in the SMIs, with the risk of potential errors in the determination of
68 trapping pressure, and thus depths of magma storage and “false” magma degassing paths. Furthermore,
69 this paper proves once again the reliability of melt inclusions in determining the pre-eruptive volatile
70 content of magma and reconstructing its chemical composition during its evolution from formation in the
71 mantle to its ascent and eruption at the surface.

72 **References**

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