Detection of liquid H$_2$O in vapor bubbles in reheated melt inclusions: Implications for magmatic fluid composition and volatile budgets of magmas

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**Abstract**

Fluids exsolved from mafic melts are thought to be dominantly CO$_2$-H$_2$O $\pm$ S fluids. Curiously, although CO$_2$ vapor occurs in bubbles of mafic melt inclusions (MI) at room temperature ($T$), the expected accompanying vapor and liquid H$_2$O have not been found. We reheated olivine-hosted MI from Mt. Somma-Vesuvius, Italy, and quenched the MI to a bubble-bearing glassy state. Using Raman spectroscopy, we show that the volatiles exsolved after quenching include liquid H$_2$O at room $T$ and vapor H$_2$O at 150 °C. We hypothesize that H$_2$O initially present in the MI bubbles was lost to adjacent glass during local, sub-micrometer-scale devitrification prior to sample collection. During MI heating experiments, the H$_2$O is redissolved into the vapor in the bubble, where it remains after quenching, at least on the relatively short time scales of our observations. These results indicate that (1) a significant amount of H$_2$O may be stored in the vapor bubble of bubble-bearing MI and (2) the composition of magmatic fluids directly exsolving from mafic melts at Mt. Somma-Vesuvius may contain up to 29 wt% H$_2$O.

**Keywords:** Raman spectroscopy, Mt. Somma-Vesuvius, volatile solubility, mafic melt, sulfur budget, melt inclusion, fluid inclusion, heating experiments

**Introduction**

Melt inclusions (MI) are aliquots of melt trapped in phenocrysts during crystallization of magmas. MI analyses potentially allow characterization of the volatile contents of pre-eruptive silicate melts. Typically, concentrations of volatiles such as H$_2$O, CO$_2$, and S are measured in the glass phase in quenched MI and compared to experimentally determined solubility models to deduce the composition of a coexisting vapor phase (Métrich and Wallace 2008 and references therein). However, recent studies have emphasized that, after entrapment, most of the CO$_2$ may be transferred from the melt or glass to a coexisting vapor bubble within the MI (e.g., Esposito et al. 2011), as a result of processes such as post-entrapment crystallization (Steele-MacInnis et al. 2011) or differential thermal contraction (Moore et al. 2015 and references therein). In fact, bubbles in MI may contain more CO$_2$ (by mass) than the coexisting glass phase (Anderson and Brown 1993; Esposito et al. 2011; Hartley et al. 2014; Moore et al. 2015; Wallace et al. 2015). Thus, it is necessary to understand the partitioning of volatiles between melt (or glass) and bubbles during MI cooling as part of the characterization of pre-eruptive volatile systematics (e.g., Kamenetsky et al. 2002; Lowenstern 1995).

H$_2$O may be abundant in mafic melts and should also be partitioned into any MI bubbles that form. However, reports of condensed, liquid H$_2$O are chiefly in MI hosted by quartz in felsic plutonic systems (e.g., Frezzotti 2001; Harris et al. 2003; Zajacz et al. 2008). Several studies have commented on the non-detection of H$_2$O in bubbles within felsic and mafic melt inclusions in volcanic rocks. For instance, Lowenstern et al. (1991) reported CO$_2$ vapor in the bubbles of reheated MI hosted in quartz from Pantelleria (Italy), and stated that H$_2$O was likely present in the bubble, but “the lack of a liquid phase in the bubble and negligible H$_2$O vapor peaks in the IR spectra indicated that it was subordinate to CO$_2$.” Yang and Scott (1996) and Kamenetsky et al. (2002, 2001) also found that the main volatile component of MI bubbles was CO$_2$, and echoed Lowenstern et al. (1991) in stating that although H$_2$O was likely present, it was not detected. It is important to note that Kamenetsky et al. (2002) detected H$_2$O as a component of gyspum, nahcolite, and silicate crystals found at bubble-glass interfaces. Moore et al. (2015) suggested that the “missing” H$_2$O could reflect nuances of spectroscopic detection of H$_2$O, particularly given that H$_2$O-CO$_2$ fluids would likely separate into an H$_2$O-rich liquid and CO$_2$-rich vapor at ambient conditions. Anderson (1991) suggested that H$_2$O could be present in devitrified glass surrounding bubbles.

Based on the various results and interpretations described above, H$_2$O is expected to be a major component of magmatic...