HIGHLIGHTS AND BREAKTHROUGHS

Seeking the most hydrous, primitive arc melts: The glass is half full

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Experimental studies and petrologic constraints suggest that H\textsubscript{2}O contents of deep, primitive melts in subduction settings may reach up to >15 wt\% H\textsubscript{2}O (e.g., Krawczynski et al., 2012). But curiously, mafic glasses preserved in melt inclusions – commonly the best available tool to analyze H\textsubscript{2}O contents of melts – seem to be limited to much lower values, mostly <6 wt\% (Plank et al., 2013). This apparent conundrum suggests that empirical results defy predictions, and challenges our view of H\textsubscript{2}O in subduction-related magmatism. To address this issue, Gravilenko et al. (2019) experimentally tested the quenching behavior of hydrous, mafic melts. Their results demonstrate that quenching to glass becomes difficult at high H\textsubscript{2}O concentrations, and that mafic melts exceeding ~9 wt\% H\textsubscript{2}O are essentially unquenchable at realistic cooling rates. This implies that glasses preserved in melt inclusions provide only a partial record of the volatile contents of deep-seated melts, and are incapable of recording the deepest, most hydrous melts. This work thus elegantly reconciles what previously appeared to be a stark contradiction between prediction and observation, and adds a key piece to our evolving understanding of how to analyze and interpret melt inclusions.

The H\textsubscript{2}O concentrations of melts exert a strong control on properties such as buoyancy (Ochs and Lange, 1999), viscosity (Schulze et al., 1996), chemical diffusivity (Watson, 1994) and explosivity (Sparks, 1978), as well as the ore-forming potential of arc magmas (Hedenquist and Lowenstern, 1994). The H\textsubscript{2}O contents of arc magmas are also central to quantifying and interpreting global geochemical cycling between Earth’s surface and deep interior (Bodnar et al., 2013). Moreover, H\textsubscript{2}O contents of melts are widely used to evaluate depths of magmatic
plumbing systems, based on the thermodynamic relationship between pressure and solubility of volatiles (Audétat and Lowenstern, 2014, and references therein). However, the H$_2$O contents of pre-eruptive melts are also elusive parameters. Experimentally calibrated proxies have been developed to estimate H$_2$O contents of melts based on mineral equilibria (e.g., Krawczynski et al., 2012), but commonly, the only available tool to directly quantify the H$_2$O (and other volatile) contents of pre-eruptive melts is by analysis of melt inclusions (Audétat and Lowenstern, 2014). In recent years, a growing body of theoretical, experimental and analytical studies has contributed new insights into the systematics of volatiles in melt inclusions, and how to best analyze and interpret them. It is now widely recognized that bubbles within melt inclusions can host a preponderance of the bulk CO$_2$ (Moore et al., 2015) and H$_2$O (Esposito et al., 2016), and that H$_2$O concentrations can be rapidly modified by diffusive reequilibration (Gaetani et al., 2012). Careful attention to these phenomena has helped elucidate the record of pre-eruptive volatiles and degassing. Yet even in light of these developments, still the growing body of analytical data presents some enigmatic results.

One of the crucial and fundamental questions that has confounded our view of volatiles in subduction-related melt inclusions arises from the growing recognition that H$_2$O (as well as CO$_2$) contents of glasses preserved in melt inclusions seem to show an unexpectedly restricted range. Specifically, mafic glasses in melt inclusions from arc settings seem to be limited to H$_2$O contents mostly less than ~6 wt%, and never exceeding ~9 wt% (Plank et al., 2013). In contrast, experimental phase equilibria consistently predict much higher H$_2$O contents, up to >15 wt% (Krawczynski et al., 2012). This apparent contradiction fundamentally challenges our view of either the fidelity of melt inclusions, or how well our experiments reproduce nature, or both.

Although some H$_2$O is likely partitioned into bubbles (Esposito et al., 2016), such partitioning is unlikely to have such a dramatic effect on the measured H$_2$O concentration in the glass (Steele-MacInnis et al., 2011). Diffusive reequilibration also likely plays a role in reducing water contents in melt inclusions (Gaetani et al., 2012). But neither process is not expected to yield such a consistent threshold of H$_2$O across the breadth of thousands of reported analyses, which is moreover so far below experimental predictions. What then limits melt inclusion H$_2$O contents? Could it be that magmas related to subduction have only half the amount of water implied by experimental studies?
On page XXXX of this issue, Gravilenko et al. (2019) test an alternative hypothesis, that the upper limit of H$_2$O contents of glasses preserved in melt inclusions reflects a quench control. Specifically, Gravilenko et al. (2019) hypothesize that wetter melts are more difficult to quench, and that the wettest melts simply cannot be quenched. This hypothesis is rooted in the well-known relationships between H$_2$O concentration, viscosity and the glass transition (Mysen and Richet, 2005): Wetter melts are less viscous, and less viscous melts are less easily quenched, requiring either greater degrees of undercooling or faster cooling rates in order to be quenched as glass. Gravilenko et al. (2019) test this hypothesis by conducting rapid-quench experiments on mafic melts over a wide range of H$_2$O contents. Importantly, the cooling rates achieved in their experiments (20-90 K/s) are consistent with best estimates for cooling rates during eruption (maximum ~22 K/s; Lloyd et al., 2013). The results are remarkable. Melts that contain modest H$_2$O concentrations up to ~6 wt% consistently quench to form optically clear glass. Melts containing from ~6 to ~9 wt% H$_2$O are somewhat difficult to quench, and consistently form crystallites in addition to glass. Melts exceeding 9 wt% H$_2$O do not quench to glass, and instead form friable aggregates of crystallites, vapor bubbles, and material resembling devitrified glass. And compellingly, the limiting values of H$_2$O concentrations align perfectly with the empirical results from melt inclusions.

The results by Gravilenko et al. (2019) strongly indicate that an apparent upper limit on the H$_2$O contents of mafic melts is a consequence of the inability of wetter melts to form glassy inclusions. Recently, Maclennan (2017) used numerical modeling to investigate an apparent upper limit of CO$_2$ contents of melt inclusions from low-H$_2$O settings, and concluded that high CO$_2$ concentrations (resulting from high trapping pressures) give rise to intense overpressure and inevitable decrepitation during magma ascent. These two studies, Maclennan (2017) and Gravilenko et al. (2019), indicate complementary phenomena that control and restrict the observed ranges of both H$_2$O and CO$_2$ in melt inclusions. Similarly, Esposito et al. (2016) argued that H$_2$O exsolved into vapor bubbles in melt inclusions rapidly reacts with the surrounding glass causing devitrification, which would further obscure bulk volatile concentrations. It seems likely that the quench control could work in tandem with exsolution of vapor, devitrification, overpressure and decrepitation, as well as diffusive reequilibration, all conspiring to prevent preservation of the most volatile-rich glasses in melt inclusions.
The major implication of the results by Gravilenko et al. (2019) is that wetter melts are unlikely to form glassy melt inclusions, which in turn implies that glassy inclusions are incapable of preserving a complete record of the deepest, wettest melts. On the one hand, this is a sobering message. But on the other hand, this work illuminates a fundamental control, and by understanding this phenomenon we stand a better chance of obtaining robust interpretations of water contents of melts. This conclusion underscores the need to analyze melt inclusions in the context of robust petrographic and geochemical constraints on timing of trapping and post-entrapment processes (Esposito et al., 2014), and provides impetus for development and application of complementary techniques that are not reliant on glassy inclusions. In any case, previous empirical observations showing a restricted range of H$_2$O contents can be viewed as a natural consequence of "quenchability." This result neatly reconciles the observations with experimental predictions, without undermining the fidelity of glassy melt inclusions or predicted H$_2$O contents of arc magmas—instead, indicating that the elusive, H$_2$O-rich primitive arc melts may simply be missing from the record of glassy melt inclusions. Interestingly, this does not necessarily preclude the possibility of more H$_2$O-rich, non-glassy melt inclusions, which would appear as being partially crystallized or devitrified. Such inclusions may be easily overlooked or discarded, but future workers seeking wet, primitive melts may be wise to search for and specifically target such inclusions.

REFERENCE CITED


