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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_2O contents of deep, primitive melts in subduction settings may reach up to >15 wt% H_2O (e.g., Krawczynski et al., 2012). But curiously, mafic glasses preserved in melt inclusions – commonly the best available tool to analyze H_2O 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_2O 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_2O concentrations, and that mafic melts exceeding ~9 wt% H_2O 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_2O 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_2O 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_2O contents of melts are widely used to evaluate depths of magmatic

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plumbing systems, based on the thermodynamic relationship between pressure and solubility of volatiles (Audétat and Lowenstern, 2014, and references therein). However, the H_2O contents of pre-eruptive melts are also elusive parameters. Experimentally calibrated proxies have been developed to estimate H_2O contents of melts based on mineral equilibria (e.g., Krawczynski et al., 2012), but commonly, the only available tool to directly quantify the H_2O (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_2O (Esposito et al., 2016), and that H_2O 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_2O (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_2O 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_2O 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_2O is likely partitioned into bubbles (Esposito et al., 2016), such partitioning is unlikely to have such a dramatic effect on the measured H_2O 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_2O across the breadth of thousands of reported analyses, which is moreover so far below experimental predictions. What then limits melt inclusion H_2O 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_2O 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_2O 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_2O 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_2O concentrations up to ~6 wt% consistently quench to form optically clear glass. Melts containing from ~6 to ~9 wt% H_2O are somewhat difficult to quench, and consistently form crystallites in addition to glass. Melts exceeding 9 wt% H_2O 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_2O 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_2O 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_2O 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_2O and CO_2 in melt inclusions. Similarly, Esposito et al. (2016) argued that H_2O 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_2O 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_2O contents of arc magmas—instead, indicating that the elusive, H_2O-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_2O-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.

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