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Primary aqueous fluids in rhyolitic magmas: Melt inclusion evidence for pre- and post-trapping exsolution

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Abstract

This study examines melt inclusions containing bubbles of aqueous fluid (L, V, and L + V), occurring in rhyolites from the Okataina Volcanic Centre, New Zealand, and the Río Blanco Cu–Mo deposit, Chile. We demonstrate that these aqueous fluids coexisted with silicate melts (magmas) and represent either post-trapping exsolution (in the case of Okataina), or co-trapping of phases already coexisting in the magma (in the case of Río Blanco). Microthermometry proves that some of the bubbles are a single-phase aqueous liquid, and all are shown by PIXE analysis to be metal rich saline solutions. As such, these aqueous fluids provide the closest approximation to direct testing of the proposition that cooling magmas exsolve metal-rich aqueous fluid. In the case of pre-trapping exsolution at Río Blanco we show that some inclusions record and preserve magmatic emulsions (melt + aqueous fluid) that are the first stage in the evolution of hydrothermal fluids. We demonstrate that heating experiments on volatile-rich melt inclusions can produce in-situ exsolution of hypersaline metal-rich aqueous fluid bubbles, potentially permitting magma-chamber processes to be experimentally modelled.

Keywords: Melt inclusions; Felsic magma; Fluid; Immiscibility; Magmatic emulsions; Metals

1. Introduction

Volatiles dissolved in magmas, and volatiles exsolved from magmas, have long been recognised as being of critical importance to magmatic processes such as magma ascent, crystallisation, and eruption (e.g., Bowen and Tuttle, 1950; Burnham, 1967; Candela, 1991). The occurrence (or non-occurrence) of volatile-phase exsolution (VPE) has important consequences for magma evolution and geological processes related to it, for example, exsolved volatiles (particularly H_2O and CO_2) power eruptions, in part determining if eruptions are explosive or effusive, or even whether or not magma vents to the surface (Johnson et al., 1994; Gilbert and Sparks, 1996). More pertinently for this study VPE exerts major controls on the chemistry of magmas, particularly on metal partitioning between silicate melts and aqueous fluids, (e.g., Candela and Holland, 1984; Heinrich et al., 1992; Candela and Piccoli, 1995; Williams et al., 1995).

However, important as the processes are, evidence of the details of volatile phase exsolution is fugitive. Exsolved volatile-rich phases generally have significant density and viscosity contrasts with the enclosing silicate melt, promoting separation of the newly exsolved phases under gravity and compaction (Candela, 1991; Shinohara et al., 1995; Cloos, 2001). If this separation is efficient, the residual magma can be assumed to be

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significantly depleted in volatiles and metals relative to the parental magma, and reconstructing the original metal and volatile content is extremely difficult. One approach to this problem is the use of magmatic inclusions trapped in phenocrysts, which provide the closest approximation to samples of magmatic phases (e.g., Roedder, 1992; Bodnar, 1995; Lowenstern, 1995; Frezzotti, 2001; Kamenetsky et al., 2004, and references therein). This paper demonstrates the coexistence of aqueous fluids and silicate melts using examples of volatile-rich bubbles in melt inclusions, but also shows that exsolution of aqueous fluids in melt inclusions can occur post-trapping. The approach used in this melt inclusion study allows observation of details of exsolution processes, such as formation of magmatic melt-fluid emulsions, and sequestering of metals from melt to volatile-rich phases. We also show that we can perform experiments on some melt inclusions that may mimic VPE processes in magma-chambers.

Herein we show that primary magmatic fluids can be trapped in melt inclusions, and preserved largely intact, and also provide criteria for distinguishing pre- and post-trapping aqueous fluid exsolution. Thus, aqueous fluid bubbles in melt inclusions are currently the only representation of pristine samples of magmatic aqueous fluids derived from, and coexisting with, silicate melts. As such they provide an invaluable tool in unravelling the composition and physical parameters of VPE, and processes (such as mineralisation) which may arise from it.

2. Sample descriptions

Two suites of subduction-related rhyolites are used in this study. Both suites have somewhat different origins and tectonic settings; however, in both cases melt inclusions are trapped in quartz and feldspar phenocrysts in upper-crustal rhyolitic magma chambers, and have broadly similar major-element compositions. We have selected both an un-mineralised and a mineralised suite for this study.

The un-mineralised suite consists of rhyolitic lavas from the Okataina Volcanic Centre, located in the Taupo Volcanic Zone (TVZ; Wilson et al., 1995 and references therein). The suite (22 samples representing 9 different rhyolite flows or domes) contains very fresh quartz+feldspar±biotite±hornblende phenocrysts in a glassy pumiceous groundmass, and are <65 ka in age. Detailed studies of melt inclusions, including their volatile abundances, have been reported for Okataina (Davidson, 2004) and other TVZ centres (Dunbar et al., 1989a; Dunbar and Kyle, 1993).

The mineralised suite is from the Río Blanco Cu–Mo deposit, located in the Andes in central Chile (Serrano et al., 1996). The deposit consists of a series of mineralised and barren porphyry and breccia complexes, superimposed on a porphyry Cu deposit (Warnaars et al., 1985; Serrano et al., 1996); the studied samples came from late- to post-mineral rhyolitic intrusive bodies with extrusive equivalents (La Copa Rhyolite, 4.03±0.19 Ma, Deckart et al., 2005). The samples are unaltered porphyritic breccia-textured rhyolites containing quartz, plagioclase, and biotite phenocrysts, with sparse clasts of coarse- and fine-grained volcanics. Some aspects of the Río Blanco melt inclusions, and their significance in relation to metal transport have been previously published (Davidson and Kamenetsky, 2001; Davidson et al., 2006).

3. Inclusion descriptions

3.1. Okataina

Okataina melt inclusions in quartz phenocrysts are typically rounded to negative crystal-shaped, 20–50 μm in diameter, and contain rhyolitic glass with one or more shrinkage bubbles (Fig. 1A). Commonly they have abundant daughter crystals (Fig. 1B), described herein as crystal-rich inclusions. The volume percentage of shrinkage bubbles in a given inclusion (the bubble-fraction) is usually <0.5 vol.%. Aqueous fluids are present as fine sub-micron bubbles (Fig. 1C), or as more commonly as discrete bubbles up to 10 μm diameter (Fig. 1C–F). At room temperature bubbles in Okataina melt inclusions may contain aqueous vapour, aqueous liquid, or both (Fig. 1E,F), sometimes with cubic crystalline precipitates (Fig. 1D), and opaque crystals (Fig. 1F). Single-phase aqueous bubbles occupy 0.4–0.9 vol.% of a given inclusion, 2-phase bubbles occupy a larger and more variable volume, but it appears that the liquid portion still occupies 0.4–0.9 vol.% of the inclusion (Fig. 1E, F).

Crystallised silicate melt inclusions are common in most of the Okataina samples and the evidence suggests that they are simply crystallised equivalents of glass inclusions (Davidson, 2004).

3.2. Río Blanco

In both the intrusive and equivalent extrusive units from Río Blanco, glass and crystallised silicate melt inclusions in quartz phenocrysts are similar in size, shape, and distribution (Fig. 2A, B) to those found at Okataina, however there are some differences (Davidson and Kamenetsky, 2001; Davidson et al., 2006). Crystal-rich inclusions are rare, and bubble-fractions in glass inclusions

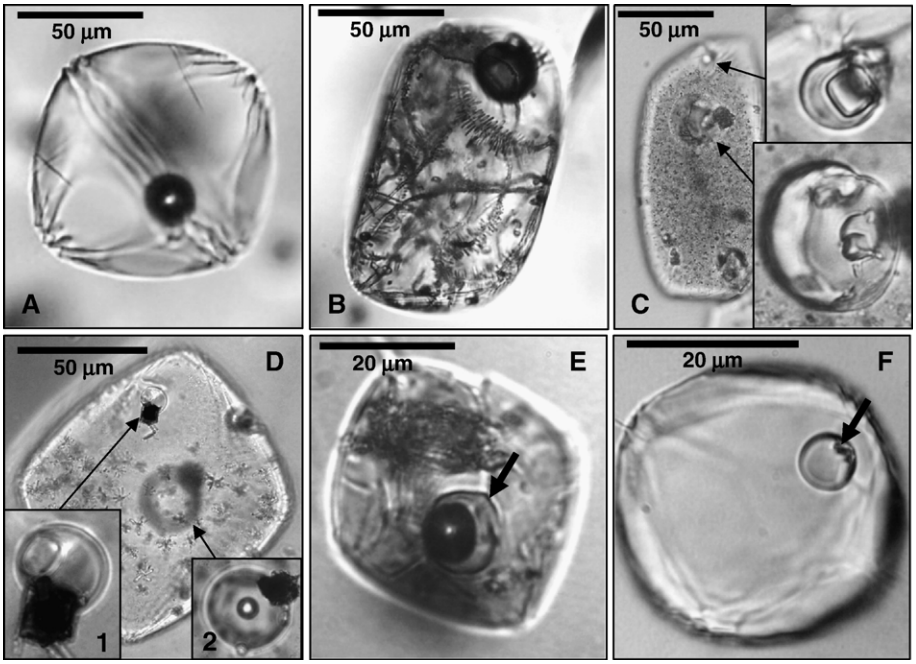


Fig. 1. Melt inclusions in quartz phenocrysts from Okataina. (A) Strongly facetted glass inclusion with a small shrinkage bubble, sample NZL3. (B) Glass inclusion showing strongly crystal-rich texture. The amphibole? daughter crystals form elaborately curved chains of short, stubby crystals, on which have nucleated acicular crystals (typically in pairs on opposite sides of the chain), sample NZL20b. (C) A granular-textured crystal-rich glass inclusion containing two large multiphase aqueous bubbles. The granular texture is composed of numerous tiny ($\ll 1$ μm) crystals and bubbles, and the large bubbles containing aqueous liquid, and one or more salt phases, but no vapour bubbles (see insets), sample NZL11. (D) Crystal-rich glass inclusion containing three initially single-phase aqueous bubbles; all have nucleated on large silicate crystals (amphiboles?). Inset 1 is a close-up of a multiphase bubble (for PIXE analysis see Fig. 8A), inset 2 shows the larger bubble after PIXE analysis, note that the initially single-phase bubble is now 2-phase, sample NZL11. (E) A crystal-rich glass inclusion with a 2-phase liquid-rich bubble (arrowed), sample NZL2d. (F) Glass inclusion containing a single-phase aqueous bubble, with traces of an opaque crystalline precipitate (arrowed). Compare the appearance of a single-phase aqueous bubble with a typical shrinkage bubble (Fig. 1A), sample NZL16b.

are very high and variable (average 6 vol.%, e.g. Fig. 2A, but with examples >50 vol.%). Crystallised silicate melt inclusions range from silicate-rich (>95 vol.%, e.g. Fig. 2C) to vapour-rich (<5 vol.% of silicate crystals).

Rare glass inclusions containing bubbles of vapour, single-phase aqueous liquid, or 2-phase liquid/vapour bubbles (Fig. 2D–I) are found only in the extrusive samples. Of these, most show multiple bubbles containing a variety of phases, in variable proportion (aqueous liquid and/or vapour, clear and opaque crystals, Fig. 2D–I). Some inclusions containing very large numbers of 1- or 2-phase aqueous bubbles are noted (e.g. Fig. 2D,E), herein described as emulsion textures. Vapour bubbles (probably shrinkage bubbles) are almost invariably spherical (e.g. Fig. 2A), however, single-phase aqueous bubbles display a wide range of shapes, even in inclusions with spherical vapour bubbles (Fig. 2H, I).

Quartz phenocrysts from Río Blanco also contain abundant primary magmatic vapour inclusions, commonly in growth planes with crystallised silicate melt inclusions (Fig. 2B). Characteristically, these are smaller than crystallised silicate melt inclusions (commonly 5–20 μm in diameter) with a rounded negative crystal shape. These inclusions usually appear black in transmitted light, but may contain a thin film of liquid water at room temperature.

In addition to abundant magmatic vapour inclusions there are also rare primary 2-phase aqueous fluid inclusions, coexisting in the same growth plane with glass and crystallised melt inclusions (Fig. 3).

4. Techniques

Heating and freezing experiments were performed in order to better characterise the composition and behaviour of the inclusions and the aqueous fluid bubbles. Most heating experiments were performed on individual phenocrysts prepared as doubly-polished heating stage wafers, using a Linkam TS1500 heating stage with an Olympus model BX 60 optical microscope fitted with a CCD camera. In order to test the effects of longer heating times bulk heating techniques were utilised, in these a

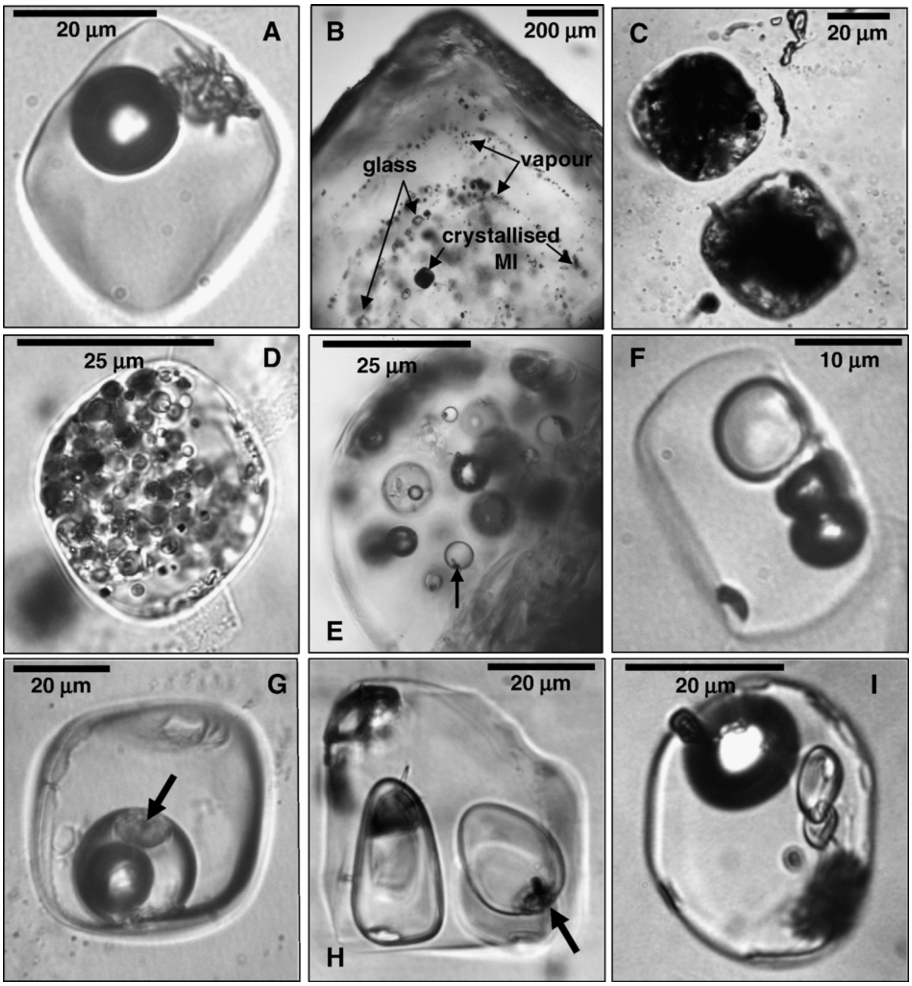


Fig. 2. Melt inclusions in quartz and feldspar phenocrysts from Río Blanco. (A) Glass inclusion in a quartz phenocryst, containing a large shrinkage bubble, and uncommonly, a cluster of silicate crystals, sample CA31. (B) Photomicrograph of a quartz phenocryst showing a typically pattern of glass and crystallised silicate melt inclusions decorating growth planes with the phenocryst, sample CA31. (C) A pair of large crystallised silicate melt inclusions in quartz, sample CA30. (D) Emulsion-textured inclusion in quartz showing an uneven distribution of bubbles. The composition of the bubbles also varies randomly, with liquid, vapour, and some 2-phase bubbles, sample CA30 (Davidson et al., 2006). (E) An emulsion-textured inclusion in quartz showing randomly distributed coexisting vapour and 1- and 2-phase liquid-rich bubbles, note that all of the single-phase aqueous bubbles contain a small opaque phase (arrowed, probably magnetite, C/F Fig. 8D), sample CA31. (F) A glass inclusion in a feldspar phenocryst, containing a single-phase aqueous bubble and two vapour-rich shrinkage bubbles, sample CA31. (G) A large multi-phase bubble in a glass inclusion in a quartz phenocryst, the bubble contains aqueous liquid, a vapour bubble and clear crystalline precipitates (arrowed), sample CA31. (H) Glass inclusion in a feldspar phenocryst, containing three globules of aqueous liquid; crystalline precipitates (some of which are silicates) are apparent on the globule walls, sample CA30. (I) In this composite inclusion in quartz two single-phase aqueous globules occur in glass with a large shrinkage bubble. The two globules are deformed in parallel, although the shrinkage bubble is not affected, sample CA30 (Davidson et al., 2006).

quantity of quartz phenocrysts were placed in a ceramic crucible in a furnace, and heated to 800 °C for 96 h. The crucible was then removed from the furnace, and the grains air-quenched.

Freezing experiments, using a Linkam THMS 600 fluid inclusion stage with liquid nitrogen cooling (effective range +600 °C to −100 °C), on 1- and 2-phase bubbles in Río Blanco melt inclusions were used to test the assumption that the clear bubbles contained aqueous fluid, and to estimate salinity. Standard microthermometric techniques were used throughout (e.g. Roedder, 1984).

Quantitative analysis of micron-sized aqueous bubbles within melt inclusions presents considerable difficulties. For this study we made use of Proton Induced X-ray Emission (PIXE) microprobe analyses, performed on the CSIRO-GEMOC Nuclear Microprobe, at North Ryde in Sydney. This technology uses a very high-energy proton beam (3 MeV), focussed to 1.3 μm diameter, to excite the

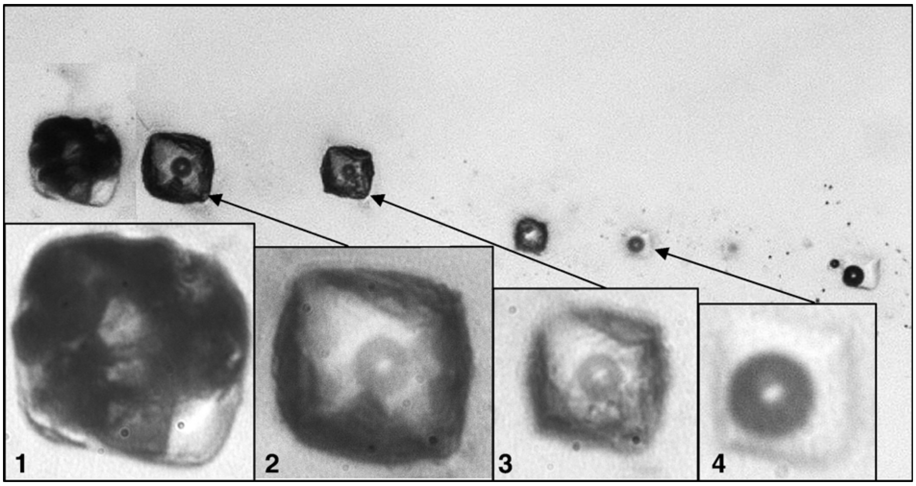


Fig. 3. Photomicrograph of a growth plane in a quartz phenocryst from Río Blanco, containing a crystallised silicate melt inclusion (inset 1), 2-phase liquid-rich fluid inclusions (insets 2 and 3) and glass inclusions (inset 4 and the remainder of the trail). The 2-phase aqueous bubbles show Brownian motion of the vapour bubbles, and freeze at low temperature, whereas the glass and crystallised silicate melt inclusions do not.

elements in a sample to emit characteristic X-rays and gamma-rays. PIXE microprobe analyses can provide both element concentration maps and bulk inclusion compositions, the process is non-destructive, can be used on unexposed inclusions, and requires no internal standard (Ryan et al., 1999).

5. Characteristics of fluid bubbles

5.1. Constraints from freezing experiments

Microthermometric experiments on 1- and 2-phase aqueous bubbles from extrusive units of the La Copa Rhyolite demonstrate that these bubbles contain an aqueous liquid, since they freeze into a mass of tiny ice crystals (Fig. 4). First ice melting temperatures for these inclusions are low but variable, on average −40 to −45 °C, but with some inclusion as high as −30 °C.

Attempts to use microthermometric techniques to establish salinities for single-phase aqueous bubbles were only partly successful due to a number of problems. Firstly, the low first ice melting temperatures suggest the presence of significant dissolved component besides NaCl. The second problem is the occurrence of metastability effects, for example positive final ice melting temperatures up to +0.8 °C were noted. Laser Raman analysis of vapour bubbles in these samples showed CO_2 concentrations to be below detection levels, so we do not consider these positive final ice melting temperatures to represent gas hydrates. In addition to positive final ice melting temperatures, another metastability effect observed was that some initially single-phase aqueous bubbles sometimes nucleated a vapour bubble after final ice melting, which disappeared at some random time later (minutes to days, see Fig. 5).

Fig. 6 is a histogram of final ice melting temperatures of 1- and some 2-phase aqueous bubbles in quartz and feldspar phenocrysts from extrusive units of the La Copa Rhyolite. We estimate the salinity in bubbles containing clear precipitates (e.g. Fig. 2G) to be ≥40 wt.% $NaCl_{equiv}$. From the final ice melting temperatures of 1- and 2-phase bubbles it appears that the salinities in some bubbles may be as low as a few wt.% $NaCl_{equiv}$. However, these high final ice melting temperatures may be compromised by metastability effects, or the presence a component such as hydrohalite.

5.2. Constraints from heating experiments

5.2.1. Okataina

During heating experiments on initially crystal-rich melt inclusions (e.g. Fig. 1B–E) the nucleation of aqueous bubbles is occasionally noted. Such bubbles contained heterogeneous 2- or 3-phase mixes of aqueous liquid, vapour bubble, and occasionally one or several salt phases (Fig. 7) occupying 0.5 to 0.9 vol.% of the inclusion. These aqueous bubbles (e.g. Fig. 7) nucleate at temperatures of 450 °C (glass transition) or higher (commonly at 573 °C, the α to β quartz transition temperature), and at similar temperatures an aqueous liquid phase may appear in originally vapour-rich bubbles. Within these bubbles clear cubic minerals (salts) crystallise upon cooling (Figs. 7B, 8B).

If heated to >630 °C the daughter crystals melt, the bubbles shrink, and in many cases disappear, resulting in a homogeneous melt at 800–820 °C. Although not

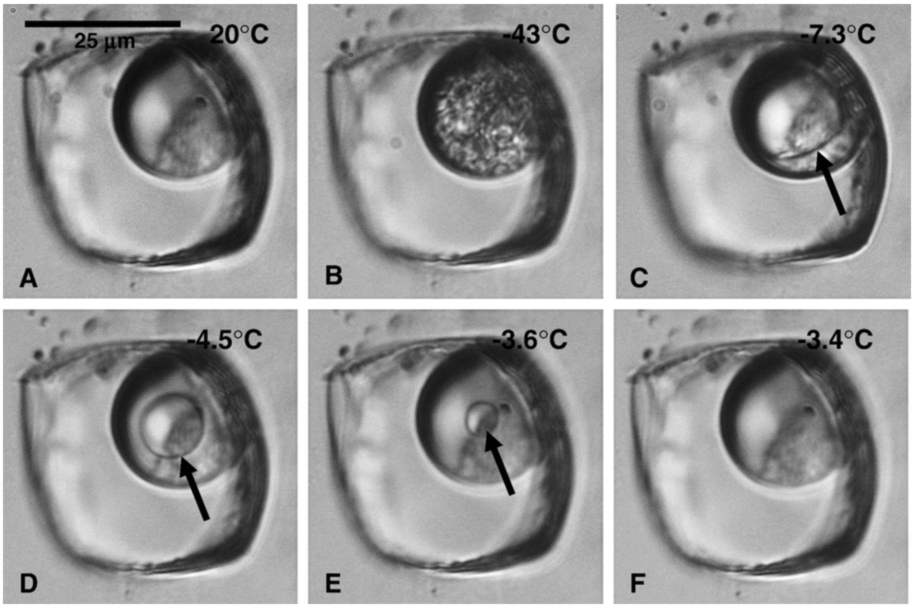


Fig. 4. Freezing experiment on a Río Blanco silicate melt inclusion in quartz containing a large, clear single-phase bubble, (A) at room temperature, (B) at −43 °C the bubble has frozen to a mass of tiny ice crystals, (C)–(F) heating progressively melts the ice (note the phase boundary marked by arrows) until the final ice melting temperature of −3.4 °C.

always possible, repeated cycling of temperature between 650 and 800 °C can produce nucleation of hypersaline fluid bubbles, and originally single-phase vapour bubbles can develop a vapour-liquid phase boundary. The bubbles with a phase boundary always homogenize into liquid, and crystallise solids upon cooling below 400 °C (Fig. 7B).

In many experimentally homogenised melt inclusions it was observed that there was a sudden vesiculation of minute bubbles near the α to β quartz transition temperature (573 °C). This appearance is similar to some unheated melt inclusions (e.g., Fig. 1C), which otherwise might be considered as being partly devitrified. In some cases large single aqueous bubbles also appeared at that point.

5.2.2. Río Blanco

During bulk heating experiments on quartz phenocrysts from Río Blanco some crystallised silicate melt inclusions melted more or less completely, cooling to glass, sometimes with residual crystals of variable feldspar compositions. Rarely, the resultant glass contained multiphase bubbles, ranging from 2-phase vapour dominated, to bubbles containing abundant clear "salts" with vapour and a small amount of liquid (Fig. 8C) resembling salt-melt inclusions (e.g., Kamenetsky et al., 2003). As crystallised silicate melt inclusions are dark and inhomogeneous in colour it is uncertain whether the salt-melt globules resulted from immiscibility triggered by heating, or simply from the agglomeration of pre-existing salt phases during melting.

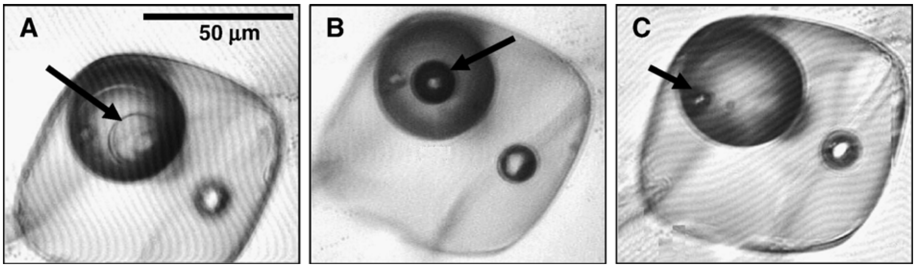


Fig. 5. Microthermometric experiments on a melt inclusion containing two initially single-phase aqueous bubbles in a quartz phenocryst from a La Copa extrusive, sample CA31. (A) inclusion at −0.5 °C, with ice still present (ice boundary arrowed), the final ice melting temperature was +0.7 °C, (B) after one freeze/thaw cycle a vapour bubble (arrowed) spontaneously appeared in the large bubble and was still present when the experiments finished, (C) one week later the experiment was resumed and it was found that the bubble had spontaneously disappeared, inclusion shown here at room temperature, the phase marked by the arrow may be a salt crystal and is present in Fig. 5A and B.

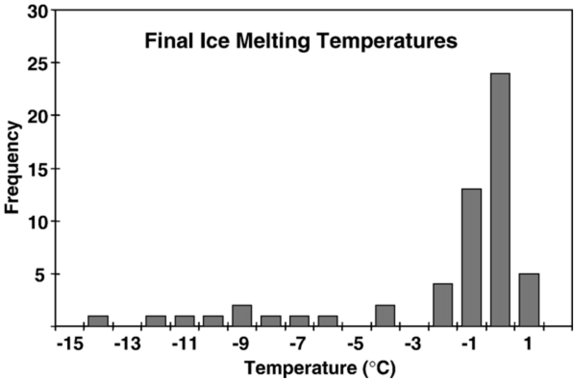


Fig. 6. Histogram of final ice melting temperatures from 1- and 2-phase aqueous bubbles in melt inclusions in quartz and feldspar from extrusive units of the La Copa Rhyolite (e.g. Fig. 5).

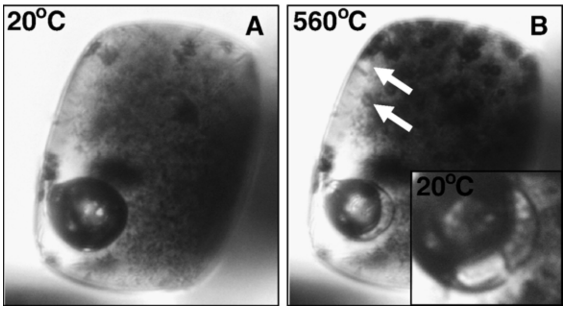


Fig. 7. Heating experiment on a crystal-rich inclusion from Okataina (A) Initially the inclusion contains a single large shrinkage bubble and very large numbers of small crystals ($\ll 1$ μm). (B) At 560 °C, a phase boundary has appeared in the shrinkage bubble, many smaller bubbles have nucleated in the inclusion (arrowed), and upon cooling (see inset) the liquid phase crystallised several salt crystals.

5.3. Constraints on bubble compositions

5.3.1. Okataina

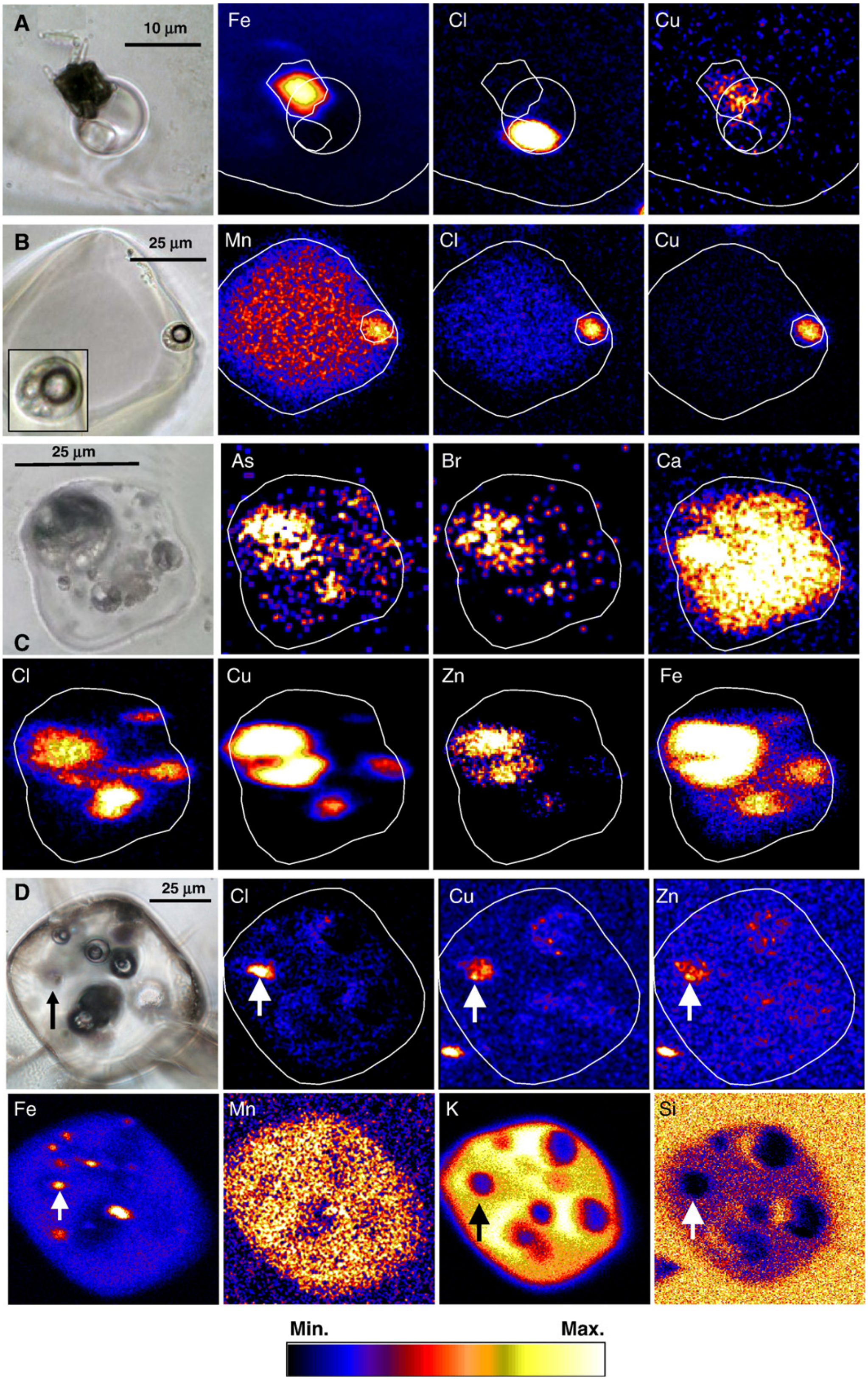
PIXE analyses of multiphase aqueous bubbles naturally occurring in pristine glass inclusions from sample NZL11 (Fig. 8A) showed high concentrations of Cl in such bubbles, indicating that the clear crystalline phases are chlorides. Metals (Cu and Zn) are also associated with these bubbles, and with amphibole crystals in the same inclusions.

Heating experiments on initially crystal-rich melt inclusions, specifically designed to force VPE within the closed system of a melt inclusion, resulted in bubble nucleation (e.g., Fig. 8B). PIXE analysis of such bubbles shows significantly elevated concentrations of metals (Cu, Zn, Fe, Mn) and volatiles (e.g., Cl, Br), relative to the inclusion glass. The recorded high Cu abundances in these hypersaline bubbles (globules) can be a result of Cu diffusion through quartz from the experimental environment (Kamenetsky and Danyushevsky, 2005), however, there is a strong similarity in Cu contents between the naturally occurring aqueous bubbles and those produced artificially.

5.3.2. Río Blanco

The locations of 1- and 2-phase bubbles in an emulsion textured inclusion is clearly shown in the element concentration maps for K and Si (Fig. 8D), which correspond in shape, size and location to those in the accompanying photomicrograph. One of the bubbles in particular contains abundant Cl, Cu and Zn, possibly present as soluble chloride complexes. However, the signal for Cl attenuates rapidly with depth, and Cu and Zn signals from deeper in the inclusion show more diffuse concentrations, but still corresponding to other bubbles. However, we have previously noted extreme heterogeneity in adjacent salt-melt globules in the same inclusion in inclusions from the Omsukchan Granite (NE Russia, Kamenetsky et al., 2004). The distribution of Fe is quite inhomogeneous; in addition to Fe in the glass, PIXE maps show small Fe bright spots which correspond to a tiny opaque phase (magnetite?) in most of the bubbles.

Fig. 8. Optical images and PIXE (proton-induced X-ray emission) element maps of fluid bubbles inside silicate glass inclusions in quartz phenocrysts. Analysis was performed by the CSIRO-GEMOC Nuclear Microprobe using a 0.6 nA beam of 3 MeV protons focussed into a 1.3 mm beam spot, and a 250 mm Be filter. The colour scale in each element image is normalised to its own maximum. The white outlines on the element maps correspond to the inclusion and phase boundaries in the photomicrograph. (A) PIXE element maps for the small hypersaline bubbles in an un-heated Okataina crystal-rich melt inclusion (Fig. 1D). The bubble is attached to a crystal of amphibole? which is indicated by the high concentration of Fe, and the clear crystal is halite. Cu is distributed between the amphibole crystal and the bubble. (B) During heating experiments on an Okataina glass inclusion, initially crystal-rich (similar to Fig. 1B) nucleation of a hypersaline fluid bubble occurred (magnified image in inset). The PIXE element map demonstrates that the bubble contained most of the Cu and Cl in the inclusion, presumably as metal-rich brine. (C) A crystallised silicate melt inclusion from Río Blanco after a heating experiment. Heating an initially dark, inhomogeneous crystallised melt inclusion (similar to Fig. 2C) to 850 °C resulted in the formation of several globules of re-crystallised salt-melt in a silicate glass. The salt-melt contains most of the metals (Cu, Fe, and Zn) as well as most of the As, Br, and Cl, in the inclusion. The glass component contains a uniform distribution of Ca corresponding to the outline of the inclusion. (D) Multiple aqueous bubbles (L, L + V, and V) in an un-heated glass inclusion from Río Blanco. Individual bubbles show most clearly as low-concentration zones in the K and Si images. Metals (Fe, Cu, and Zn) and Cl are concentrated unevenly in some of the bubbles. Note the concentrations of Cl, Cu and Zn in one of the bubbles (arrowed); Fe is concentrated in several bubbles, possibly corresponding to tiny opaque phases (magnetite?) visible in some of the bubbles.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Multiphase salt-melt globules resulting from melting of crystallised silicate melt inclusion, (Fig. 8C) show that the globules have strong concentrations of metals (Cu, Zn, and Fe), as well as Cl, Br, and As. In contrast, Ca is uniformly distributed through the inclusion, and is a proxy for the aluminosilicate glass. The much stronger signal (c/f Fig. 8D) results from the fact that the bubbles in these inclusions are salt-melts, rather than hypersaline brines.

We emphasise that in all cases the aqueous bubbles in the inclusions (heated and unheated) were significantly, if variably enriched in metals and some volatiles (including Cl, Br, and As).

6. Discussion: origin of the aqueous bubbles: pre- vs. post-trapping immiscibility

6.1. Río Blanco, pre-trapping immiscibility

The Río Blanco magmas started exsolving immiscible aqueous fluids prior to, and during, the crystallisation of quartz phenocrysts, as demonstrated by:

- Abundant primary magmatic vapour inclusions present in quartz phenocrysts (Fig. 2B), and rare examples of primary 2-phase aqueous fluid inclusions, co-trapped with silicate melt inclusions (Fig. 3);
- Phase ratios between aqueous fluid and silicate melt (now glass or crystallised silicates) are highly variable (e.g. Fig. 2H, I), which implies co-trapping of random amounts of melt and aqueous fluid (Roedder, 1984; Kamenetsky et al., 2003);
- The occurrence of deformed single-phase aqueous bubbles (Fig. 2H, I), sometimes in inclusions with spherical vapour bubbles, implies plastic deformation of the more dense bubbles with the enclosing melt. This would be consistent with pre- or syn-trapping deformation of an emulsion of silicate melt and aqueous bubbles. However, selective re-filling of deformed bubbles (the only other explanation) seems highly improbable.

6.1.1. Magmatic emulsions

In this paper we have used the term emulsion textures to describe inclusions such as those in Fig. 2D and E, in the non-genetic sense of an intimate mixture of large numbers of bubbles suspended in a medium (in this case glass). However, can we extend this term to indicate trapping of an original emulsion of aqueous fluid bubbles in a silicate melt?

- The existence of magmatic emulsions is supported by the volume of aqueous fluid in some inclusions (Fig. 2E, H), which is simply too large to have dissolved in the melt of the inclusion at the solubility of H_2O in silicate melts (Johnson et al., 1994), at any feasible pressure ($\ll$1 kbar at Río Blanco, Holmgren et al., 1988; Serrano et al., 1996).
- The large total volume of vapour bubbles in some inclusions also points to co-trapping of co-existing vapour bubbles (rather than post-trapping exsolution which would produce a constant phase relationship, as in the examples from Okataina), which is feasible, given the low trapping pressure at Río Blanco.
- The wide and random variation of composition of bubbles within a given emulsion-textured inclusion (e.g., Fig. 2D, E) implies co-trapping of existing phases. Multiple nucleation of bubbles from an H_2O-oversaturated silicate melt (due to overcooling or decrepitation) is possible, but would be expected to produce bubbles of a similar composition, and with similar phase relationships.

Although the intrusive and extrusive units are co-magmatic (Warnaars et al., 1985; Serrano et al., 1996) magmatic emulsion inclusions are absent in the La Copa Rhyolite intrusives. However, as noted crystallised silicate inclusions from the La Copa Rhyolite show an apparently continuous range from >95 to <5 vol.% silicates (the remainder being aqueous fluid, principally vapour). This is consistent with the range of the bubble/glass ratio from silicate melt inclusions, through magmatic emulsion inclusions, to primary magmatic vapour inclusions. We suggest that the crystallised silicate melt inclusions from the intrusives represent the crystallised equivalents of magmatic emulsions, or the melts from which magmatic emulsions exsolved (Davidson and Kamenetsky, 2001; Davidson et al., 2006). In contrast, crystallised silicate melt inclusions from Okataina (where VPE occurred post-trapping) are always >99 vol.% silicate, consistent with the glass inclusions.

6.2. Okataina, post-trapping immiscibility

The following evidence suggests that the Okataina magma was not volatile-saturated at the time melt inclusions were trapped:

- Primary magmatic vapour-phase inclusions in quartz are rare, and there are no examples of primary aqueous liquid inclusions (unlike Río Blanco, see Fig. 3);
- The almost constant and volumetrically low bubble fraction in the melt inclusions suggest that the bubbles are shrinkage bubbles;

- The lack of textural evidence of co-trapping of aqueous phases with a silicate melt, such as emulsion textures (Fig. 2D, E).

Thus, at the time of trapping the system was probably under-saturated in H_2O. The fact that the aqueous bubbles are present in the Okataina melt inclusions suggests that they nucleated post-trapping, during cooling and decompression during eruption. Crystallisation of quartz on the inclusion wall (resulting from cooling) increases H_2O concentration of the residual melt, ultimately driving it into saturation. In this context we note the very high H_2O concentrations (up to 7–8 wt.%) analysed in Okataina melt inclusions (Dunbar et al., 1989b; Dunbar and Kyle, 1993; Davidson, 2004; Kamenetsky and Danyushevsky, 2005).

6.3. Single-phase aqueous bubbles

Freezing experiments have shown that in both samples studied, clear bubbles in some of the melt inclusions (e.g., Figs. 1D, F, 2E, F, H,I, 3, 4) contain single-phase aqueous fluids. Other similar occurrences in rhyolites from Central Slovakia and the Tien Shan Mountains were explained by extremely high pressure (5.6–17 kbar) existing in the magma chamber (Naumov et al., 1992, 1994, 1996). However, we do not find any indication of such high pressure at Okataina (2–3 kbars, Ewart et al., 1975), and at Río Blanco ($\ll 1$ kbar, Holmgren et al., 1988) where primary magmatic vapour inclusions coexist with crystallised silicate melt inclusions, indicating a boiling regime. Rather, we would suggest that the presence of single-phase aqueous bubbles in melt inclusions is a metastability effect, in the sense of a phenomenon which would be unstable under more general conditions, but which is stable under specific and rarely met with conditions.

The behaviour of aqueous fluids in very small containers, where the surface tension effects can form a significant part of the total energy budget of the inclusion, can produce very unusual behaviours (see ch. 10, Roedder, 1979). In particular fluids can "stretch", that is, the fluids may increase their average inter-atomic distances, rather than nucleate a bubble. Roedder (1984) states "*As the surface tension varies inversely with the radius of the bubble …, but the internal tension is independent of volume, there is a bubble volume (and, hence, an inclusion volume for a given composition and total density) below which the fluid will remain stretched indefinitely (i.e., without nucleation of a bubble), as the stable configuration*". We stress that this is true only for very small aqueous bubbles, and for specific compositions and densities, however, it does explain the otherwise puzzling existence of primary magmatic single-phase aqueous fluids. Moreover, we have noted the nucleation of metastable vapour bubbles during heating and freezing experiments on initially single-phase bubbles. This implies that the bubble can be temporarily forced into a more stable configuration (Fig. 5), but the fact that in some cases these bubbles spontaneously return to a single-phased means that under *these specific conditions* the "metastable" configuration is actually more stable. We note that other, possibly related, metastability effects may occur in these bubbles, including positive final ice melting temperatures (as high as +0.8 °C).

The fact that single-phase aqueous bubbles are found in situations of both pre- and post-trapping exsolution suggests that this phenomenon is related to the physical characteristics of aqueous bubbles in melt inclusions, not the means by which the bubbles were created.

One potential difficulty with the study of single-phase aqueous bubbles is that without microthermometry it can be difficult to recognise such inclusions. Visually, the only difference is that a shrinkage bubble in a melt inclusion typically has a shiny black appearance, typically with a "bulls-eye" effect due to internal reflection (e.g., Figs. 1A and 2A). In contrast, single-phase aqueous bubbles have a translucent grey appearance typically without the "bulls-eye" effect (e.g., Figs. 1F and 2H). Although the differences are small, once seen, they are sufficient to reliably detect single-phase aqueous bubbles, and microthermometry can be used for confirmation. Two-phase aqueous bubbles are easy to recognise if the phase-boundary is distinctive. When 2-phase aqueous bubbles are present then a search for single-phase aqueous bubbles may be productive. That single-phase aqueous bubbles have been observed in a number of occasions (Naumov et al., 1992, 1994, 1996; Davidson, 2004; Davidson et al., 2006) suggests that they should be looked for in other instances.

6.4. Implications

Having demonstrated that primary magmatic aqueous fluids co-existed in the Río Blanco melt as emulsions of silicate melt and aqueous liquid and vapour, and were formed post-trapping at Okataina, and that both can be preserved, there are several areas in which such inclusions may be of use.

One consistent problem in trying to establish the composition of magmatic fluids is the problem of contamination and interaction of fluids with wall rocks, and their chemical fractionation due to boiling, mixing, crystallisation and chromatographic effects. Typically, any samples of geofluids trapped as fluid inclusions in the hydrothermal quartz will have been evolved from magmatic precursors, and been contaminated by interaction with wall rocks and possibly cool groundwaters, but to an unknown extent. The results of our study offer an opportunity to look at a direct snapshot of the pristine magmatic aqueous fluids that exsolved either during, or shortly prior to crystallisation of the magma. Importantly, while such exsolution is probably ubiquitous, such a snapshot is only preserved as inclusions of fluid in magmatic phenocrysts. In these case studies we have dealt with aqueous fluids in felsic magmas, however, we note that a similar approach can be exercised in the case of fluid and magmas of different composition, for example, CO_2 fluids exsolving from basaltic magmas (Kamenetsky et al., 2002).

Importantly, melt inclusion and phenocryst hosted fluid phases represent very small aliquots of the fluid just exsolved, and prior to the processes that can change the original compositions (e.g., coalescence, reactive transport, mixing, crystallisation). Our study also shows that the aqueous fluids, although pristine, are carrying significant, but varying amounts of metals and chlorine. We present observations and experimental evidence (Fig. 8) that metals are sequestered from the silicate melt to the aqueous fluids, and that compositional diversity of exsolved fluids can occur at very fine scales. Aqueous fluids trapped in melt inclusions and phenocrysts are the closest approximation of naturally exsolved volatiles, and thus they make possible quantification of partitioning of metals and volatiles.

Being a mineralised system, Río Blanco also demonstrates that aqueous fluid bubbles in melt inclusions provide the starting point on the path from silicate melts to ore bodies (Davidson and Kamenetsky, 2001; Davidson, 2004; Davidson et al., 2006). In other words, the study of such bubbles can be used to ascertain whether the magmatic fluid composition governs mineralisation.

The insights gained from this study may be extended to other systems, and the techniques used may prove significant. We note that, in effect, the heating experiments have triggered volatile phase exsolution within a trapped sample of a parental melt, and, if problems of trace element mobility can be satisfactorily dealt with (Kamenetsky and Danyushevsky, 2005), may provide proxies for magma chamber processes.

7. Conclusions

In this study we have shown that aqueous bubbles in melt inclusions represent primary magmatic aqueous fluids. As such, they offer researchers an unrivalled opportunity to sample such fluids. We have demonstrated both pre-trapping (Río Blanco) and post-trapping (Okataina) origin (exsolution) of such primary aqueous liquids. In both cases we have demonstrated high, but variable metals concentrations in these fluids.

In the case of pre-trapping exsolution all of the phases co-existing with a silicate melt can be co-trapped in melt inclusions, and under favourable conditions preserved against subsequent alteration and contamination.

In cases where post-trapping exsolution did not occur in nature (common in Okataina crystal-rich inclusions), heating experiments can accentuate nucleation of aqueous fluid bubbles, and thus mimics VPE in magma chamber conditions.

Single-phase aqueous bubbles in melt inclusions (which sample pristine magmatic fluids) are rarely reported in the literature, but we suggest that single-phase aqueous bubbles may not be uncommon, simply unrecognised. Given the existence of samples closely approximating primary magmatic fluids researchers now have a technique for directly examining the sequestering of metals and volatiles from silicate melts to coexisting aqueous fluids, and the evolution of hydrothermal fluids.

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