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A new methodology for the study of the magmatic-hydrothermal transition in felsic magmas: applications to barren and mineralised systems

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Okataina Case Study

Chapter 9: Local and Regional Geology

Introduction

 The Okataina case study is based on samples from rhyolitic lavas from the Okataina Volcanic Centre, in the Taupo Volcanic Zone (TVZ), North Island, New Zealand (Fig. 9-1), generously provided by Dr. Sharon Allen. The TVZ is the largest and most active rhyolitic system on Earth (Houghton et al., 1995; Sutton et al., 2000), having produced at least $15{\text -}20{,}000 \text{ km}^3$ of dominantly rhyolitic, calc-alkaline rocks during the 2 Ma during which it has been active. The Okataina Volcanic Centre (OVC) is one of the two potentially active volcanic centres of the TVZ, and has produced one major historic eruption, Tarawera in 1886.

 The Okataina case study follows the plan of the Río Blanco study, beginning with a review of the regional geology and tectonics of the TVZ, then the local geology of the Okataina Volcanic Centre, finishing with sample descriptions. Twenty samples were selected as suitable for study, all are fresh, unaltered rhyolitic lavas containing melt inclusions, and the following chapter describes those inclusions. Chapter 11 details the heating stage experiments performed on a representative sub-set of the Okataina samples, and chapter 12 describes the geochemistry. Chapter 13 concludes this case study with a discussion and the conclusions.

Regional Geology of the Taupo Volcanic Zone

Introduction

 The Taupo Volcanic Zone (TVZ) is located in the North Island of New Zealand, \approx 100 km inboard of the Australian / Pacific plate boundary (Fig. 9-1). Wilson et al. (1995) defined the TVZ as being the zone defined by a line drawn around all caldera structural margins, and individual vent sites, associated with the NNE-SSW oriented Kermadec subduction zone, and active during the ≈ 2 Ma life of the zone (Fig. 9-2). Wilson et al. (1995) subdivided the TVZ by age into:

• Old TVZ: all units from the beginning of activity in the TVZ (\approx 2Ma) up to the extremely voluminous Whakamaru-group eruptions (0.34 Ma) that buried much of their predecessors. Primarily the Old TVZ outcrops on the NW margin of the TVZ.

Fig 9-1 Map of the North Island of New Zealand, and the Taupo Volcanic Zone (TVZ), in tectonic context. The TVZ is stippled, coarse stippling is the young TVZ (< 0.34 Ma). The continental shelf, and the Kermadec ridge, are outlined by the 2000 m isobath. Also shown is the Vening Meinesz Fracture Zone (VMFZ). Diamonds mark the lines of the modern rifting axes for the Havre Trough, and the TVZ; note the offset where the rifting axis crosses the VNFZ

Fig 9-2 Map of the TVZ showing the structural margins of all caldera structures, from Sutton et al. (2000).

Young TVZ: all units erupted between 0.34 Ma and the present, and bounded by the unequivocally dated caldera margins and vent sites.

• Modern TVZ: all centres active between the 65 ka Rotoiti eruption from the Okataina Volcanic Centre, and the present. This period is considered by Wilson et al. (1995) to be representative of current activity in the TVZ

The TVZ is a thick $(2.0 \text{ to } >2.5 \text{ km})$, dominantly rhyolitic sequence of explosive, to effusive volcanics, deposited in a deep graben (The Taupo Graben (Stern and Davey, 1987)), which extends 200 km from Okakune to the Bay of Plenty, and is 10-60 km wide. Strong segmentation is a feature of the TVZ (e.g. Graham et al., 1992; Wilson et al., 1995). Andesitic volcanism dominates both ends of the TVZ, with the Tongariro-Ruapehu complex in the southern, and Whale $&$ White Islands in the Bay of Plenty in the northern sections. The Okataina Volcanic Centre is located in the central TVZ, where rhyolites dominate (> 95%), over minor andesites (\approx 5%) and trivial amounts basalts and dacites $\ll 1\%$). Activity in the central TVZ is mainly caldera-forming ignimbrite eruptions, with volumes between 30 and $>$ 300 km³ DRE (Dense Rock Equivalent). Pre- and post-caldera pyroclastic eruptions are also significant, ranging from plinian to sub-plinian, with volumes typically $\leq 10 \text{ km}^3 \text{ DRE}$, and dome-building eruptions with minor pyroclastics, both pre- and post-caldera, also typically $\leq 10 \text{ km}^3$ DRE. The $>15,000 \text{ km}^3$ of rhyolites show almost no major compositional changes across the rhyolite-dominated central TVZ, and throughout most of its existence (1.6 Ma - present) (Dunbar and Kyle, 1989; Wilson et al., 1995).

 The TVZ differs from other volcanic arcs in having probably the highest geothermal heatflow on Earth (Wilson et al., 1995), in the region of 4200 ± 500 MW. The TVZ also differs from other arc-related silicic systems in the huge volume of rhyolite magmas. It differs from other non-arc-related silicic systems in the high eruption rates, wide spectrum of coexisting magma types (rhyolites to basalts), and very limited compositional variation either across the TVZ, or within a given magma chamber. Houghton et al. (1995) demonstrated that the TVZ is producing smaller, and more frequent rhyolitic eruptions than any equivalent rhyolitic centre (e.g. Yellowstone), and that this trend within the TVZ increases with decreasing age.

Tectonics and Geology

 The location of the pole of rotation between the Australian, and Pacific plates, produces relative convergence rates of ≈ 50 mm a⁻¹, but with a pronounced change in the obliqueness of subduction along the length of North Island (Fig. 9-1). It has been proposed (Wilson et al., 1995) that the TVZ is a tectonic rift, propagating southward

into the North Island of New Zealand, related to subduction on the Australian / Pacific plate margin. Wilson et al. (1995) noted good geodetic evidence of widening of the TVZ, and measured spreading rates over the last several decades range from 7 mm a⁻¹ in the Bay of Plenty, to 18 mm a^{-1} in the region of Lake Taupo. Figure 9-3 is a proposed section across the TVZ as proposed by Stern and Davey (1987), based on geophysical evidence. Similar, but more detailed results for shallower levels (<10km) are reported in Sherburn et al. (2003).

Fig 9-3 A combined geological-geophysical model for a profile A- A' (see inset) across the North Island. From Stern & Davey (1987).

 The following is a summary genetic model of the TVZ, based largely on the work of Cole (1979), Stern and Davey (1987), McCulloch et al. (1994), Graham et al. (1995), and Wilson et al. (1995):

- Mantle melting in a rifted arc setting produces parental high-alumina basalts.
- Fractionation of HAB's produces silica-rich melts, and as yet undiscovered cumulates (possibly the "anomalous mantle" described by Stern and Davey (1987), detected seismically at depths below 15 km under the TVZ, with $V_p = 7.4 - 7.5$ km/s).
- Contamination of silica-rich melts by AFC processes, which may go on to produce the andesites in the thicker crust beneath the northern, and southern ends of the TVZ.
- Possible mixing with crustal melts from either greywacke basement, or earlier intrusives in the central TVZ, assisting in the formation of rhyolitic melts.
- Whether by AFC or mixing with crustal melts (or both), modelling of rhyolites requires up to 25% by volume of crustal material, suggesting significant and progressive consumption of the already rifting-thinned sub-TVZ crust.
- Rifting and plastic deformation of the crust provides much of the heat to drive the magmatic processes, and so weakens the crust that large magma chambers cannot form.
- Rifting also produces a strong extensional environment that, combined with strong density contrasts with basalts, and to a lesser degree diorites and andesites, acts as a filter favouring the eruption of rhyolites in the central TVZ (almost to the exclusion of anything else).

The Okataina Volcanic Centre

Introduction

 The Okataina Volcanic Centre (OVC) is the most northerly rhyolitic centre in the central TVZ (Fig. 9-2). Mt Edgecumbe, a young (3.5-5.5 ka) andesitic stratovolcano, lies 5 km from the OVC, and the Bay of Plenty is 20 km away. The OVC is one of the two active rhyolitic centres in the TVZ, the other being the Taupo Volcanic Centre at the southern end of the central TVZ. The OVC has been episodically active from 280 ka to present, and although dominantly rhyolitic, does contain some minor basaltic units.

 As usually defined, the OVC includes all vents in, and adjacent to, the Haroharo Caldera (Fig. 9-4), plus the associated rhyolite domes & flows (e.g. Nairn, 1992). Surviving distal ignimbrite flows may extend a further 20-30 km beyond the OVC boundary. Strictly speaking, the Haroharo Caldera is a caldera complex, as it contains a number overlapping collapse structures, and consists of a broad shallow depression filled with pyroclastic debris, currently hosting several lakes (Fig. 9-4). The Haroharo Caldera is 16 by 28 km, is coincident with a 40 mGal residual gravity low, and it is modelled as a 2 km deep depression filled with low-density volcanic deposits (Bailey and Carr, 1994).

 Volcanism in the OVC is primarily concentrated along two northeast-trending lineaments, the Haroharo and Tarawera vent zones (Bailey and Carr, 1994). Eruptions along the Haroharo vent zone have been largely rhyolitic, the Tarawera vent zone, although dominantly rhyolitic, has produced occasional basaltic eruptions (Fig. 9-4).

Fig 9-4 Okataina caldera complex, showing the positions of the Haroharo and Tarawera vent zones, from Burt et al. (1998). Sample locations as per this study.

The Tarawera vent zone has been the most active in the past few thousand years, producing the most recent rhyolitic eruption, the Kaharoa eruption in 1336, and the most recent basaltic eruption, Tarawera in 1883.

Geological history of the Okataina Volcanic Centre

 The OVC appears to have begun with the 280 ka Matahina ignimbrite eruption leading to the collapse of the Haroharo Caldera. Infilling of the Haroharo Caldera by subsequent eruptions has obscured much of the evidence of events prior to the 65 ka Rotoiti eruptions. The Rotoiti eruptions are estimated to have produced $\approx 50 \text{ km}^3 \text{ DRE}$ of magma (Nairn, 1992). Two subsequent ignimbrite eruptive episodes extended or modified the Haroharo Caldera, the Mangaone subgroup at 32 ka ($\approx 22 \text{ km}^3 \text{ DRE}$) (Jurado-Chichay and Walker, 2000) and the 21 ka Te Rere episode ($\approx 13 \text{ km}^3 \text{ DRE}$) (Nairn, 1992).

 Each major ignimbrite eruption tended to bury much of the evidence of its predecessors. However, since the 21 ka Te Rere episode there is good preservation. In the 21 ka since the Te Rere eruptions 11 distinct eruption episodes have occurred, from 40 vents, each episode represents only a brief period compared to the > 1000 year breaks that separate them (Nairn, 1992).

Rhyolite domes from the Okataina Volcanic Centre

 The samples used for this study are taken from the numerous rhyolite lavas and domes that postdate (and may on occasion predate) major pyroclastic eruptions. Stevenson et al. (1994) noted that the OVC contains some of the youngest (21-0.8 ka) and largest rhyolitic lavas in the TVZ (up to 8 km long). Typically, rhyolite lavas or domes have a concentrically layered structure (Stevenson et al., 1994). The core of the flow is a tabular body of rhyolite with a crystalline groundmass, surrounded by a chilled, glassy carapace. Due to the upward movement of volatiles during emplacement, the outermost part of this carapace is finely vesicular pumice, which may grade into glassy obsidian close to the crystalline core. Due to their high viscosity, rhyolitic lavas typically have steep fronts, and avalanching of loose material tends to build up a talus slope at the advancing flow front. Some of this talus and chilled pumice carapace may subsequently be mechanically re-incorporated into the lower part of the advancing flow. Mathematical modelling by Stevenson et al. (1994), of two rhyolite flows in the OVC, Haumingi (average ≈ 125 m high, 2.5 km long), and Waiti, (average ≈ 100 m high, 3.0 km long), suggested emplacement times in the range of 0.6 - 1.6 years. Cooling time to

glass transition temperature (670°C) for the upper 20 m of the flow was estimated at \approx 3 years, and >30 years for the crystalline core.

Petrology of the Okataina rhyolites

 Rhyolites across the whole central TVZ show surprisingly little difference in major element composition (e.g. Dunbar and Kyle, 1989, 1993). This is true of the Okataina Volcanic Centre, but minor variations in trace elements have been used by Hochstein et al. (1993) to identify distinct batches of magma. These magma batches produced both single eruptions, and multiple eruption events, over 10^3 - 10^4 year time scales. It has been suggested that these variations imply the emplacement of multiple small batches of similar magma, rather than the presence of large, long-lived magma chambers.

Isotopically, Okataina magmas have ${}^{87}Sr/{}^{86}Sr$ values of 0.7054 - 0.7056, and δ 18O values of 7.0 - 7.3‰ (Blattner et al., 1996), which are about mid-range for the TVZ (TVZ range ${}^{87}Sr/{}^{86}Sr$ 0.7048 - 0.7060, δ18O 6.8 - 8.0 (Blattner et al., 1996)).

 Most Okataina rhyolites are porphyritic (like TVZ rhyolites generally), plagioclase is the dominant and ubiquitous phenocryst phase, quartz is usually subordinate, and titanomagnetite and ilmenite are minor but ubiquitous. The minor compositional variations between lavas in the OVC are expressed as variations in the assemblage of mafic silicates and opaques. Rare alkali feldspars and fayalitic olivine are occasionally observed, and apatite and zircon are common accessory phases (Graham et al., 1995). Ewart et al. (1975) described four different mafic phenocryst assemblages at Okataina:

- 1. cummingtonite + calcic hornblende \pm orthopyroxene (725-765 °C)
- 2. calcic hornblende + orthopyroxene \pm augite (750-825°C)
- 3. biotite + calcic hornblende \pm cummingtonite \pm orthopyroxene (720-765^oC)
- 4. orthopyroxene \pm augite (860-915°C)

The temperatures in brackets is the Fe-Ti oxide equilibration temperature range from Ewart et al. (1975) which are similar to estimates from Dunbar and Kyle (1989). The calculated phenocryst equilibration pressure for these assemblages averages 2.2 Kbar (ie. depth \approx 7-8 km (Ewart et al., 1975)), and crystallisation is demonstrated to have been at H₂O saturation (≥ 6 wt% H₂O). Since cummingtonite is unstable above 750 °C it seems that the cummingtonite-absent rhyolites that dominate the TVZ may represent higher-temperature sources (Ewart et al., 1975).

 The presence of cummingtonite in some units from the Haroharo Vent Zone is unique in the TVZ (Cole, 1979). Experimental crystallisation studies by Nicholls et al. (1992) on contrasting metaluminous and peraluminous Okataina rhyolites confirm that cummingtonite could have crystallised only at pressures of 3 kb (ie. depth ≈ 10 km), probably in the roof zone of a shallow crustal magma chamber. These results are consistent with the findings of Ewart et al. (1975).

Sample selection and descriptions

 Samples used in this study were selected from fresh, unaltered rhyolite lavas, carrying identifiable melt inclusions. Most are from the Okataina Volcanic Centre, and erupted from the Tarawera or Haroharo vent zones. Two additional samples (NZL22 and NZL 27b) were selected from the Central Maroa sub-centre of the Mokai Ring Structure, an adjacent, but probably age-equivalent centre. As the intention of this study is an understanding of late-magmatic processes, rather than the geology of the Okataina Volcanic Centre *per se*, selection was based simply on sampling magma batches, rather than unravelling the evolution of the Okataina Volcanic Centre.

 Dr Sharon Allen collected the samples used in this study from several rhyolite lavas and domes in the OVC. Samples from different domes have individual numbers (e.g. NZL1, NZL2, etc.), and multiple samples taken from different stratigraphic positions within some domes have different suffix letters, **a** signifies a sample from the crystalline core of a dome (e.g. NZL1a), **b** is a sample from the inner carapace near to the crystalline core (e.g. NZL1b), **c** is a sample from the outer pumiceous carapace of a dome (e.g. NZL1c).

 All samples used in this study are pale- to mid-grey plagioclase- and quartzphyric rhyolites. Most also contain minor pyroxenes and hornblende, and more rarely biotite. All samples contain accessory Fe and Ti oxides, apatite, and zircon. Plagioclase crystals are generally well formed euhedra, although sieve-textures are observed in some samples. Quartz phenocrysts tend to be rounded euhedra, commonly embayed, and always containing bubble-rich glass in the embayments.

 Phenocrysts in the Okataina samples are predominantly set in a glass matrix. Characteristically, the matrix glass comes in two forms, a pale, finely vesicular glass, and dense, massive obsidian. The finely vesicular glass is commonly clear, although a few examples of darker brown/black obsidian exist, and one sample (NZL17b) shows an intermixing of a dominant brown glass with clear glass on a mm scale. The massive glass commonly shows a "ropy" lamellar flow banded texture, commonly with more or less elongate bubbles aligned along the flow laminations.

Most samples are inhomogeneous on a mm scale, with irregular bundles of "ropy" textured glass, mixed with vesicular glass masses and randomly distributed phenocrysts of feldspars, quartz, hornblende, apatite and magnetite.

 Alteration is, at most, minor, rare patchy sericite alteration of the feldspar, and patchy chlorite alteration of the pyroxenes in some samples, although most samples are pristine. Evidence of uneven re-hydration of the glass is observed, such as perlitic cracking, and this has been confirmed by electron microprobe analysis. Spherulitic alteration of the glass is variable; in some it is intense, although in most samples it ranges from minor to absent.

Chapter 10: Inclusion Descriptions

Introduction

 Having described the tectonic and geological setting of the Okataina rhyolites, and the samples used, in the previous chapter, this chapter examines the inclusions, and the ways in which they occur. The Okataina rhyolites have a diverse range of inclusion varieties, but they are still dominated by glass and inhomogeneous crystalline silicate inclusions (CSMI's); however, there is also a very wide range of glass inclusions containing abundant and diverse daughter phases (e.g. Figs. 10-1, -2, -3).

 The following two chapters discuss the experimental, and analytical results from the Okataina inclusions respectively. This case study finishes with a discussion of issues raised by the Okataina inclusions, and the conclusions that can be drawn from them.

Patterns of inclusion occurrence

 In all, some 24 samples representing 19 distinct flows or domes in 4 volcanic complexes, mostly within the Okataina Volcanic Centre, were examined for this case study (Table 10-1). Although each sample had its own specific populations of inclusions, overall, some reasonably consistent patterns can be observed in the occurrence of inclusions at Okataina.

- Inclusions generally occur as isolated large individuals; growth planes in Okataina phenocrysts are usually indicated by wide zones of thinly spaced negative-crystal shaped inclusions with aligned axes (Fig. 10-1).

- Primary magmatic 1- or 2-phase liquid/vapour inclusions, and hypersaline fluid inclusions are rare.

- Decrepitation haloes of small vapour-rich inclusions surrounding large crystalline silicate melt inclusions are not common, with the exception of sample NZL10b.

Inclusion descriptions

Glass inclusions

 Okataina samples contain abundant clear glass inclusions (Fig. 10-4), with shrinkage bubbles and occasional daughter crystals (Fig. 10-5).

Table 10-1 Table of sample locations and melt inclusion populations; blank entries indicate that the inclusion type is absent, or very rare (< 1%). Note: the age of Central Maroa dacite is poorly constrained, it is younger than 140 Ka, but older than 20 Ka.

Many inclusions have a rounded negative-crystal shape (Fig. 10-4), but facetted glass inclusions (Fig. 10-6) are common, and more unusual shapes are observed (Fig. 10-5). Faceted glass inclusions are negative-crystal shaped, with flat faces and sharp edges, giving a "facetted" appearance. Commonly, the edges of facets have a distinct Mshaped ridge-valley-ridge margin with the adjacent facet (Fig. 10-7). In general, the more strongly facetted inclusions are smaller than the rounded forms.

 Glass inclusions typically contain clear glass, but examples in which the glass inclusions have a brownish appearance have been observed (Fig. 10-8). This "brown" glass is typically granular, but rare examples occur in which the colouration is quite uniform.

Figure 10-1. Growth plane of crystal-rich & granular-textured glass inclusions in a quartz phenocryst from the Okataina Volcanic Centre. Note the characteristically widely spaced inclusions, and the 120° bend which demonstrates that this is a growth plane.

NZL4a. 50µm scalebar

Figure. 10-2. Glass inclusions showing typical crystal-rich texture. The amphibole? daughter crystals form elaborately curved chains of short, stubby crystals, from which spring acicular crystals (typically in pairs on opposite sides of the chain) NZL20b. 50µm scalebar

Figure 10-3. Glass inclusions showing typical granular texture. This inclusion has two obvious shrinkage bubbles, a typically brown colour, and fine, granular texture. The granularity in this example is too small to be resolved by optical microscope. NZL1f. 50µm scalebar

Figure 10-4. A typical large-bubble glass inclusion from Okataina; such inclusions do not homogenise. NZL1g. 25µm scalebar

Figure 10-5. An atypical example of an Okataina glass inclusion, showing an elongate form, two shrinkage bubbles, and minor fine-scale daughter crystals along both edges. NZL8. 50µm scalebar

NZ1-0024 NZ1-0089

Figure 10-6. Facetted glass inclusion, with typical flat negative-crystal faces, and sharp edges. The shrinkage bubble is relatively large, and this inclusion would also be unlikely to homogenise. NZL22. 50µm scalebar

Figure 10-7. Ribbed-and-facetted glass inclusion, showing the characteristic M-shaped ridge-valley-ridge join between the negative-crystal faces (C/F fig 10-6). This inclusion has a small shrinkage bubble, and would probably homogenise. NZL3. 50µm scalebar

Figure 10-8. Glass inclusion with an unusually uniform brown colour; more commonly brown coloured glass is seen in granular textured glass inclusions (eg fig 10-3) NZL1g. 50µm scalebar

Figure 10-9. Multiple-bubble glass inclusion with numerous, very small shrinkage bubbles. NZLk1d. 25µm scalebar

Figure 10-10. Glass inclusion with no shrinkage bubble; such inclusions are restricted to Okataina samples with the smallest average bubble-fraction. NZL27b. 25µm scalebar

Figure 10-11. Bubble-free glass inclusion showing a granular texture, which is unusual for bubble-free glass inclusions NZL27b. 50µm scalebar

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Brown colouration is typical of partial devitrification of glass; however, it is shown experimentally (see chapter 11) that this colouration may be primary, having formed at the moment the melt cooled, and passed the glass transition temperature. Many glass inclusions (as well as CSMI's) in all Okataina samples show trapped microphenocrysts, most commonly apatite, zircon, biotite, and Fe-Ti oxides.

 Okataina glass inclusions typically have only a single shrinkage bubble, although examples of multiple bubble glass inclusions are reasonably common (Figs. 10-5, -9), and some samples contain rare glass inclusions with no bubble at all (Figs. 10- 10, -11). Bubbles in the Okataina samples are generally small, but show a wide range. Sample NZL3 has a typical average bubble fraction of 2.56 ± 0.66 vol% (1 σ), and a range of 0.97 - 9.85 vol% (Fig. 10-7). In contrast, sample NZL27b has the smallest average bubble fraction of any Okataina sample, with an average of 0.44 ± 0.24 vol⁹% (1σ) , but has a range of 0.16 - 8.41 vol%. In general, samples dominated by glass inclusions have small average bubble-fractions, and the only Okataina samples with bubble-free glass inclusions (NZL16b, and NZL27b) also have the smallest average bubble-fractions. The occasional presence of very large bubbles is probably a sign of inhomogeneous trapping of a vapour phase (eg. Lowenstern, 1995, 2002). Inclusions with no bubbles probably represent a quenching phenomenon, consistent with all Okataina samples being extrusives, the inclusions in question are, in effect, naturally homogenised. For the purposes of this study, I define inclusions with "large" shrinkage bubbles as having a bubble-fraction > 0.5 vol%. By this definition, NZL3 has only large shrinkage bubbles, and NZL27b has generally small shrinkage bubbles, but with significant exceptions. This may seem somewhat arbitrary; however, homogenisation experiments (see chapter 11) show that inclusions with large shrinkage bubbles do not homogenise.

 Figure 10-12 shows an electron photomicrograph of a typical glass inclusion, with a smooth-walled shrinkage bubble in a uniform glass matrix. A tendency observed in Okataina inclusions is for the glass to have shrunk away from the host phenocryst, presumable during cooling (Figs. 10-13a, b, and c). Close examination of the border between the inclusion and the host shows a discontinuous parting between them. Another glass inclusion (figure 10-14) is most notable because of the crystalline material in the bubble. The EDS spectra show this to be an alumina-rich silicate (alumina \approx silica) with minor K and significant Fe; the spectra also show a pronounced oxygen peak.

Crystal-rich and granular-textured glass inclusions

 A characteristic feature of Okataina magmatic inclusions is the existence of a wide range of glass inclusions containing abundant daughter phases.

Glass inclusions show a variety of textures, typically granular (e.g. Fig. 10-3) and/or crystal-rich (e.g. Fig. 10-2). In this study, crystal-rich and granular-textured glass inclusions will be referred to collectively as $C R & G T$ glass inclusions, where it is necessary to distinguish them from clear, crystal-free glass inclusions (such as Figs. 10- 4 to -7).

 Crystal-rich glass inclusions typically contain abundant euhedral, acicular greenish crystals (Figs. 10-2, -15, and -16). Laser Raman microprobe analysis show the columnar green crystals in NZL10b to be a pyroxene (e.g. Fig. $10-17$), and microprobe analysis of the green crystals in some other samples suggests they are amphiboles (e.g. 10-18). Crystal-rich glass inclusions always have a shrinkage bubble, and commonly, crystals are observed to have neucleated on them (Fig. 10-18).

 In some glass inclusions the daughter crystals are present as trichites, ie very fine, curved, hair-like fibres randomly arranged within the inclusion (Figs. 10-19, - 20). Trichites are crystallites of clino- or orthopyroxene, more rarely amphiboles, and are interpreted to result from high degrees of overcooling (Ross, 1962; Sharp et al., 1996). Similar features can be found in the matrix glass (Fig. 10-21).

 More commonly, crystal-rich glass inclusions host short, stubby pyroxene or amphibole crystals arranged end-to-end; from these, one or two elongate acicular green crystals grow outwards on either side, usually in the same plane (Figs. 10-2, -22). In a viscous silicate melt the growing crystals are likely to cause local depletion of some elements required for further crystal growth, due to slow diffusion rates in the melt. Crystal growth may thus be directed by diffusion gradients from distant parts of the inclusion undepleted in those elements.

 Granular textures are also common in glass inclusions. Typically, such inclusions contain a shrinkage bubble(s), and abundant fine "granularity", mostly below optical resolution (Figs. 10-23, -24). With very few exceptions, granular inclusions have smooth rounded sides, commonly producing an almost globular shape. Strongly facetted granular inclusions are rare, and ribbed and facetted granular inclusions have not been observed. The glass in the majority of granular inclusions is brown (Fig. 10- 24), although a few inclusions contain clear glass (Fig. 10-23). Typically, granular glass inclusions contain a shrinkage bubble, but rare examples are observed with none (Fig. 10-11). Melt inclusions similar to granular-textured glass inclusions have been noted in the Bishop Tuff, USA (Anderson et al., 2000; Wallace et al., 2003), and in the Altiplano-Puna, Chile (Schmidt, 2001).

 Granular textured glass inclusions characteristically contain abundant, very fine particles in the glass (Fig. 10-23). These rarely exceed 1 µm and are typically 2 to 4 orders of magnitude smaller than the shrinkage bubble in the same inclusion.

Figure 10-12. Electron photomicrograph of a glass inclusion in a quartz phenocryst. A parting is just visible between the inclusion and the host quartz, which has permitted the inclusion to separate from the host when the phenocryst broke. Note the smooth bubble wall, the small silicate particles appear to be dust introduced during sample preparation. NZL1g. 50µm scalebar

Figure 10-13. Electron photomicrograph of a glass inclusion; arrows point to the areas in the close-ups (b, c) showing the parting between the inclusion and the host phenocryst. Note the "bubbly" texture covering the inclusion and extending into the bubble. The parting wraps around irregularities in the inclusion wall (b), and there are "trails" of bubbles in the glass (c). The shrinkage bubble appears to open into the parting, with no sign of a meniscus. The unusual texture suggests that a carpet of fine bubbles formed on the inclusion wall during cooling. NZL4a. scalebars (a) 10μ m, (b), (c) 2.5μ m

Figure 10-14. Glass inclusion in quartz phenocryst from the Kapenga Rhyolite. Note the abundant aluminosilicate crystals growing in the shrinkage bubble. This was common in the La Copa Rhyolite, but not at Okataina. IN24. 50µm scalebar

Figure 10-15. Glass inclusion with a crystal-rich texture; a tube-like growth of daughter crystals nucleated on the shrinkage bubble, and terminates in a spray of acicular crystals. Several similar formations have been observed in other samples. NZL2d. 50µm scalebar

Figure 10-16. A more common texture for Okataina crystal-rich glass inclusions; large green (pyroxene?) crystals nucleated on the shrinkage bubble. Note the beginning of brownish "devitrification" in the glass. NZL2d. 50µm scalebar

Figure 10-17. The large, tabular green crystal has the laser Raman signature for pyroxene. Although the crystal appears to protrude slightly from the inclusion, similar inclusions in the same sample show similar crystals with the same phase ratio, suggesting these are daughter phases. NZL10b. 50µm scalebar

Figure 10-18. A pair of CR& GT glass inclusions in a growth plane, and in both a similarly shaped cluster of daughter crystals has nucleated on the shrinkage bubbles. NZLk1b. 50µm scalebar

Figure 10-19. Glass inclusion containing trichites, fine hair-like crystallites of pyroxene, probably resulting from high degrees of overcooling (see Ross (1962)). NZL18. 25µm scalebar

Figure 10-20. Densely packed trichites in a glass inclusion; compare this with the forms found in some CR> glass inclusions, eg figure 10-3 or 10-30. NZL22. 25µm scalebar

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Figure 10-21. An example of trichites occurring in matrix glass. NZL12. 50µm scalebar

Figure 10-22. Glass inclusion with a crystal-rich texture; the small red hexagonal crystals (arrowed) are probably hematite. NZL13b. 50µm scalebar

Figure 10-23. Granular textured glass inclusion (exposed by polishing) with a closeup (b) showing the fine-scale granularity. NZL1g. scalebars 25 µm

Figure 10-24. A similar granular textured glass inclusion (exposed by polishing) with a closeup (b) showing the fine-scale granularity. In this case the granularity is coarse enough to determine it is composed of minute bubbles, some of which show phase boundaries.

NZL1g. scalebars (a) 50µm, (b) 10 µm

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Figure 10-25. A similar granular textured glass inclusion, also showing phase boundaries in the minute bubbles NZL1g. scalebars (a) $50 \mu m$, (b) 10 μ m

Figure 10-26. Granular textured glass inclusion; this example shows the more common situation, in which the granularity can be seen to be minute daughter crystals. NZL22. scalebars (a) $50 \mu m$, (b) 10 μm

Figure 10-27. CR> glass inclusion showing a bi-modal distribution of crystals; most are sub-µm granularity, but there are some larger crystals, including a clear cube nucleated on the shrinkage bubble. NZL2d. 50µm scalebar

Figure 10-28. Another example of bi-modal distribution of crystals, showing a common tendency for crystals to nucleate (or at least accumulate) on the shrinkage bubble. NZLk1b. 25µm scalebar

However, a very wide range both in absolute size, and in the size range in a given inclusion, is observed. Generally, particles in most granular CSMI's are below the limit of optical resolution, but in some examples they are much larger, and can be identified as minute bubbles (Figs. 10-24, -25), or crystals (Fig. 10-26). In some examples with minute bubbles, phase boundaries can be observed. Crystals in granular textured glass inclusions commonly have a bi-modal size distribution, with abundant $\leq 1 \text{ µm}$ "granularity" and a smaller number of > 5 µm crystals, typically clear (Fig. 10-27) or green pyroxene/amphibole (Fig. 10-28). Mixed examples with $\leq 1 \mu m$ bubbles, and crystals of various sizes are observed. Due to the generally small size of the "granularity", difficulties arise in determining its composition, however:

- Granular inclusions homogenise completely at 850-880°C.
- Homogenised granular glass inclusions have similar compositions to unhomogenised glass inclusions

Thus, the granularity, whatever the form, is composed of daughter phases, although not necessarily daughter crystals.

 Conventionally, magmatic inclusions with this brown granular appearance are described as "devitrified" or "partly devitrified" (e.g. Wallace et al., 2003). Devitrification, sensu stricto, is the sub-solidus re-crystallisation of glass, and implies that the inclusion was, at some stage, clear glass, and further implies that the process was sub-solidus and secondary. However, heating experiments (chapter 11) show that the same appearance can be generated at temperatures above the glass transition temperature, when the inclusion still contains silicate melt. Thus, I have chosen to use the strictly descriptive "brown" or "granular", rather than "devitrified" or "partly devitrified" to avoid genetic implications, particularly the implication that brown granularity is secondary.

 Figure 10-29 is an electron photomicrograph of a typical brown granular glass inclusion hosted in a quartz phenocryst. The inclusion has a distinct conchoidal fracture, the fracture planes are generally smooth, and the glass shows little sign of granularity. The shrinkage bubble contains columnar aluminosilicate crystals, and has an almost botryoidal surface, densely studded with 1-0.5 µm crystals which appear to be embedded in the bubble wall. The EDS spectra of these crystals suggest a Fe-rich phase, possibly magnetite. Along parts of the lower margin, platy crystals projecting into the inclusion can be seen (Fig. 10-29f), which have a K-rich aluminosilicate EDS spectra, and are probably mica. Small globular cavities mostly $> 1 \mu m$ in diameter are randomly distributed throughout the glass (Figs. 10-29, -30). Figure 10-40 shows a very similar brown granular inclusion with more globular cavities, and a mass of aluminosilicates, possibly amorphous, in the shrinkage bubble. The μ m-scale globular cavities correspond to the minute bubbles in figures 10-24, -25.

 In contrast, the surface of the inclusion in Figure 10-31 shows granularity in the 1-2 µm range, although rare micro-bubbles in a similar size range have been observed. EDS spectra of glass and embedded crystals show similar compositions (Na-Kaluminosilicates). The shrinkage bubble shows smooth glassy walls with rosettes of an unknown Fe-rich mineral 3-4 µm in diameter (Fig. 10-31d). The bubble wall is puckered in around the rosette, giving a strong implication that the rosette was solid while the glass was still molten; ie the rosette was floating in the meniscus of the glass bubble prior to final solidification. Composition of the rosette is Fe-rich, with a high oxygen peak, possibly Fe-oxides or hydroxides. The presence of oxide phases in shrinkage bubbles, with evidence that they formed while the inclusion was still molten, is similar to observations in Kamenetsky et al. (2002a). Evidence presented by Kamenetsky et al. (2002a) demonstrates that such phases are precipitates from a metalrich vapour.

Crystalline silicate melt inclusions

 A characteristic feature of Okataina magmatic inclusions is the existence of a wide range of completely crystalline silicate melt inclusions (Figs. 10-32, -33), indistinguishable from Río Blanco CSMI's. Okataina CSMI's are dark, completely crystalline silicate inclusions, showing clear areas separated by dark patches and films, although shrinkage bubbles are not present. There is a wide variety within this inclusion type, from very dark (mainly black in transmitted light (Fig. 10-34)), to pale (Fig. 10- 35). In some samples (particularly NZL17b) CSMI's can be difficult to assign to either CG> glass inclusions or CSMI's. CSMI's also demonstrate a wide variety in the density and uniformity of colour, with a number of distinctly bi-modal crystalline inclusions (Fig. 10-36). When exposed, Okataina CSMI's always contain numerous very small cavities rather than a single large cavity.

 In the darkest inclusions, short decrepitation cracks parallel to the inclusion caxis are common (Fig. 10-33), as are haloes of small liquid+vapour inclusions. Some samples (e.g. NZL10b) contain only very dark CSMI's with abundant short decrepitation cracks and decrepitation haloes of small 2-phase fluid inclusions (Figs. 10- 37). Generally, pale CSMI's rarely show these decrepitation features.

 Electron microphotograph of exposed CSMI's from Okataina always show < 10% open space (compared with numerous inclusions from Rio Blanco that were >90% cavity). Figure 10-38 shows a typical example of a CSMI, which contains a mass of well-formed euhedral silicate crystals. The crystal shapes suggest feldspars, which is supported by the EDS spectra, indicating aluminosilicates with varying alkali concentrations. Ragged platy crystals may be micas.

Figure 10-29. Granular textured glass inclusion (c) with closeups of the bubble (a, b, d), and the glass(e, f). Arrows on (c) show locations of closeups. The bubble contains several large silicate crystals (a, b) and has a botryoidal texture studded with minute Feoxide crystals (d). The glass shows numbers of minute bubbles (e) c/f fig 10-33, and silicates, presumably mica, line the inclusion walls (f) NZL1g. scalebars (c) 50µm, (a, b, e, f) 10 µm, (d) 2.5 µm

Figure 10-30. Electron photomicrograph of a CR> glass inclusion, inclusion outline overlaid on (a), closeup of the glass (b) showing apparent phase boundaries inside the exposed micro-bubble.

NZL1g. scalebars (a) $50 \mu m$, (b) 10 μ m

Figure 10-31. Granular textured glass inclusion, possibly corresponding to figure 10-34. The glass in the closeup (b) shows a μ m-scale granularity, but not micro-bubbles. EDS spectra for the crystallites show Ca, Mg, Si, and Al, but are not dissimilar to the glass. The shrinkage bubble shows a meniscus, suggesting the merging of two shrinkage bubbles while still molten (c), and a small rosette of a Fe-rich mineral located on, and in, the bubble wall, suggesting it floated in the bubble while the glass was still a silicate melt.

NZL1g. scalebars (a) 50μ m, (c) 10 μ m, (b, d) 2.5 μ m

Figure 10-32. Completely crystalline silicate melt inclusion, with typically dark, inhomogeneous appearance in transmitted light. NZL19. 50µm scalebar

Figure 10-33. A dark and very inhomogeneous CSMI with well-developed decrepitation cracks parallel to the inclusion axis, and abundant, very fine vapour-rich fluid inclusions (similar to sweat haloes described in Audetat (1999)) NZL2. 50µm scalebar

Figure 10-34. Dark CSMI in a plane of large vapour-rich 2-phase fluid inclusions. NZL10b. 25µm scalebar

Figure 10-35. Pale CSMI, still containing glass, but with the dark, inhomogeneous appearance typical of other CSMI's. NZL17b. 25µm scalebar

Figure 10-36. Bi-modal CSMI's; both ends have the typical dark, inhomogeneous appearance, but there is a band of clear glass, containing acicular crystals across the middle of the inclusion. NZL10b. 25µm scalebar

Figure 10-37. A plane of large 2-phase fluid inclusions centred on a CSMI. Such pronounced decrepitation features are found only in sample NZL10b. NZL10b. 50µm scalebar

Figure 10-33

Figure 10-38. (a) Electron photomicrograph of a CSMI in a quartz phenocryst; arrows mark the inclusion boundary, (b) closeup of the large silicate crystal in the lower left of the inclusion.

NZL4a. scalebars (a) 50µm, (b) 10 µm

Figure 10-39. Bi-modal CSMI, similar to figure 10-19, showing (b) the inclusion wall,

(c), (d) the euhedral silicate crystals filling much of the inclusion.

NZL11. scalebars (a) 50μm, (b, c, d) 10 μm

Figure 10-40. Brown, granular-textured glass inclusion with a large cluster of unidentified crystals dominating the shrinkage bubble. NZL1g. 50µm scalebar

Figure 10-41. Pyroxene microphenocrysts, linked by a glass inclusion. NZL22. 25µm scalebar

Figure 10-42. Pyroxene microphenocryst without associated glass inclusions. NZL4. 50µm scalebar

Figure 10-43. A large glass inclusion in a feldspar phenocryst, containing multiple shrinkage bubbles, and tabular zircon, and acicular apatite microphenocrysts. NZL22. 50µm scalebar

Figure 10-44. Reticulated, skeletal titanomagnetite microphenocryst NZL10b. 25µm scalebar

Figure 10-45. Skeletal titanomagnetite microphenocryst, showing abundant Ti-rich exsolution lamellae.

NZL10b. 50µm scalebar

Figure 10-46. Apatite microphenocryst containing a silicate glass inclusion. NZL3. 50µm scalebar

Figure 10-47. Facetted and ribbed glass inclusion containing a single-phase aqueous globule, with traces of a crystalline precipitate. Typically, inclusions with single-phase aqueous globules have no shrinkage bubble. NZL16b. 50µm scalebar

Figure 10-48. Glass inclusion with a large 2-phase vapour-rich globule; characteristically, 2-phase globules that are as large as this example are vapourdominated. NZL9. 50µm scalebar

Figure 10-49. A similar 2-phase aqueous globule, in this case in distinctly brown glass NZL10b. 50µm scalebar

Figure 10-50. Granular textured glass inclusion containing a small, liquid-rich 2-phase globule. In general, small 2-phase globules are liquid-rich, large 2-phase globules are vapour-rich.

NZL4a. 50µm scalebar

Figure 10-51. Glass inclusion with a crystal-rich texture, and a vapour-rich 2-phase globule.

NZL2d. 25µm scalebar

Figure 10-39 shows an apparently bi-modal CSMI, which has a band of glassy material extending across the middle of the inclusion, as also observed in the inclusion in figure 10-36. This solid band of glass across the inclusion shows no micro-bubbles. Well formed silicate euhedra fill most of the remainder of the inclusion (Figs. 10-39b, c) and a sharp contact with the host can be observed (Fig. 10-39d).

Microphenocryst inclusions

 All Okataina samples contain a varied population of inclusions of pyroxene? amphibole? (Figs. 10-41, -42), apatite, zircon (Fig. 10-43), hematite, and titanomagnetite (commonly skeletal, Figs. 10-44, -45). Microphenocrysts can be found attached to, or embedded in glass inclusions. Rarely, microphenocrysts may even contain glass inclusions (Fig. 10-46).

Aqueous globules in Okataina inclusions

 Glass inclusions containing 1- or 2-phase aqueous globules in clear (Figs. 10- 47, -48), brown (Fig. 10-49), and brown granular (Fig. 10-50) or crystal-rich inclusions (Fig. 10-51) have been observed in most Okataina samples. Some single-phase liquid globules also show traces of crystalline precipitate (Fig. 10-47). Aqueous globules (1 and 2-phase) from Okataina are always spherical, as are the shrinkage bubbles. Singlephase globules form a relatively constant proportion of inclusions they are found in (\approx 2) vol%). Two-phase globules from Okataina have more variable proportions, but a correlation is observed between large globules with a high percentage of vapour phase (e.g. Figs. 10-48, -49), and small 2-phase globules with a small proportion of vapour phase (e.g. Figs. 10-47, 50). Although it is impossible to accurately quantify, it is possible that the 2-phase globules represent a shrinkage bubble (of various sizes) that has coalesced with a single-phase globule (of a fixed size, relative to the inclusion). Additionally, the following chapter shows that aqueous globules can be absorbed back into the glass when such inclusions are homogenised. Thus, it appears that the globules are daughter phases, having exsolved post-trapping, and do not represent inhomogeneous trapping of a coexisting aqueous phase.

Chapter 11: Experimental Results

Introduction

 Homogenisation experiments were performed on melt inclusions from selected Okataina samples for a number of reasons:

- to test whether inclusions would homogenise, thus discriminating uncompromised from compromised inclusions
- to establish T_h , and by inference, $T_{tranning}$
- to homogenise crystal-rich, and granular-textured $(CR>)$ glass inclusions for analysis.

As described in chapter 10, and listed in table 10-1, each of the 19 samples selected for this study has distinctive melt inclusion populations. However, there are some general groupings that can be defined, which have significance when considering the experimental and analytical results.

The majority of samples have mixed populations of CSMI's, with CR>, and clear glass inclusions coexisting in the same phenocrysts. In these samples, all clear glass inclusions have large shrinkage bubbles (bubble-fraction > 0.5 vol%). Coexisting CR> glass inclusions generally have small (or at least smaller) shrinkage bubbles. In some of these samples, petrographic examination shows a gradation from granulartextured glass inclusions to CSMI's (Figs. 11-1, -2), and it may be difficult to separate the two. Decrepitation features are rare in these samples, even associated with CSMI's.

 Several samples are dominated by clear glass inclusions, with CSMI's and CR> glass inclusions rare or absent. Where CSMI's are present, they do not generally coexist with glass inclusions in the same phenocrysts. Coexistence in the same sample, but not the same phenocryst, could represent mechanical incorporation of material from the flow carapace, as described in chapter 9 (page 152). Samples dominated by clear glass inclusions can be further sub-divided into samples with generally large-shrinkage bubbles, or small-shrinkage bubbles.

 A few samples were dominated by CSMI's, and have only minor co-existing $C R & G T$ glass inclusions, and large-bubble clear glass inclusions (e.g. NZL10b). Decrepitation features, rare in other Okataina samples, are common in these samples. In summary, the Okataina samples can be divided into samples dominated by:

- mixed CSMI's and glass inclusions
	- predominantly crystal-rich glass inclusions (NZL2d, NZL11)
	- predominantly granular-textured glass inclusions (NZL1g, NZL4d)
- clear glass inclusions
	- with large shrinkage bubble (NZL3)
	- with small shrinkage bubbles (NZL16b, NZL27b)
- CSMI's (NZL10b)

Homogenisation of Okataina inclusions

 The division of Okataina samples on the basis of melt inclusion populations is important in describing the results of heating experiments, as homogenisation behaviour varies with inclusion type, and sample. This, in turn, has driven the selection of samples for experiments and detailed analysis.

 Some inclusions in most Okataina samples could be homogenised. CSMI's were the exceptions, as they would not homogenise at any temperature, in any sample. Homogenisation occurred in glass inclusions of all sizes, but only in inclusions with small shrinkage bubbles $(< 0.5 \text{ vol\%})$. A slight tendency for the smaller inclusions in a given sample to homogenise is observed, however this correlation was poor, and far less consistent than the correlation with bubble-fraction.

 Experimental conditions used for the Okataina heating experiments were similar to those employed in the Río Blanco experiments (chapter 7, page 100). Heating to 600°C typically occupied ≈ 10 minutes, then ≈ 10 minutes to heat to 50°C below the expected T_h , and 5-10 minutes to reach T_h . As a test, a number of inclusions were held below the expected T_h for 3-4 hours, but showed only minor reduction in T_h (0-10°C, c/f heating stage calibration error of \pm 5°C). The longer heating times did promote melting in some CR> glass inclusions, but they still did not homogenise after 4 hours. Homogenisation temperatures were always tested by cooling until the bubble renucleated, then re-homogenising. If T_h varied by more than 5°C, the inclusion was cycled over 100 $^{\circ}$ C until a consistent T_h was achieved. Heating was occasionally continued to 1200°C, to verify maximum homogenisation temperatures; however, T_h 's between 1000-1200°C were rare, and in practice, heating was usually discontinued at 1000°C.

 In addition, bulk heating was used to produce large numbers of homogenised inclusions for microprobe analysis. Given the homogenisation temperatures observed in single-grain experiments, NZL1g was heated to 890°C over 2 hours, and NZL2d was heated to 950°C over 3 hours; both were air-quenched. These parameters were selected

to approximate conditions used in single-grain experiments, although heating rates were slower, and there was no cycling of temperatures above and below homogenisation temperature.

 In all samples except NZL3, most inclusions that could be homogenised at \leq 1200°C homogenised within a tight range (10-15°C). The same minimum homogenisation temperature range was observed in different phenocrysts from the same sample, and different types of inclusions in the same phenocryst, although different samples have different minimum temperatures. However, all samples contained a few inclusions that homogenised at a temperature between the narrow minimum temperature range and 1200° C. Given the wide temperature range of this group (300-400 $^{\circ}$ C), and the fact that these inclusions were randomly mixed with inclusions that homogenised within the minimum range, or not at all, it is reasonable to assume that these inclusions had decrepitated and degassed to a variable degree. Inclusions of this third group usually have a bubble-fraction intermediate between inclusions that would not homogenise (generally > 1 vol%), and those that homogenised at the minimum temperature (0.5 vol %). Thus, where a T_h is quoted, it is the minimum value for that sample, and within 10 \degree C of the majority of T_h's. This minimum homogenisation temperature is inferred to represent the trapping temperature $(T_{trapping})$. Sample NZL3 is an exception, as few inclusions homogenised, and those that did, homogenised between 900-1200°C with no distinct grouping of T_h 's near 900°C. The possibility exists therefore, that all inclusions in that sample were decrepitated and degassed, and that the minimum T_h simply represents the least decrepitated and degassed inclusion.

 In all samples, many inclusions would not homogenise at temperatures below 1200° C (the highest temperature used in these heating experiments). CR> glass inclusions which failed to homogenise commonly melted partially (Figs. 11-3, -4, -5), but bubble-disappearance did not occur. Failure of an inclusion to homogenise was invariably associated with abnormally large, or abnormally numerous shrinkage bubbles. Co-trapping of a vapour bubble would result in an inclusion that could not be homogenised at a reasonable temperature. Such co-trapping should be a random, and presumably rare event; however, large-bubble inclusions that would not homogenise formed 50-90% of the inclusions present in a given sample. Likewise, co-trapping of vapour bubbles should produce an approximately even spread of bubble-fractions from 1-100 vol%. Variations in bubble-fractions were observed; however, they were in the range 1-10 vol%; inclusions with bubble-fractions between 10-100 vol% were not observed at Okataina. This absence implies that co-trapping of melt and vapour bubbles did not occur at Okataina.

Fig 11-1 CSMI from Okataina, exposed during polishing; (a) reflected light, (b) transmitted light. The inclusion has the inhomogeneous texture in transmitted light typical of CSMI's, and is clearly crystallised, but large irregular cavities (typical of Río Blanco CSMI's) are absent. NZL17b. 25µm scalebar

Fig 11-2 Melt inclusion from Okataina, showing a texture intermediate between CSMI's (eg fig 11-1) and granular-textured glass inclusions. NZL17b. 50µm scalebar

Fig 11-3 Partly melted crystal-rich melt inclusion (15 min ω 950°C); all of the daughter phases have dissolved, but the abundant vapour bubbles have neither homogenised nor completely coalesced.

NZL1g. 50µm scalebar

Fig 11-4 Typical partly-melted granular-textured glass inclusion (15 min ω 950°C); note the large and abundant shrinkage bubbles, and the largely un-melted daughter phases.

NZL1g. 50µm scalebar

Fig 11-5 Typical partly-melted crystal-rich glass inclusion; shrinkage bubbles are large and abundant, and un-melted daughter crystals remain.

NZL1g. 50µm scalebar

Thus, it seems most probable that the failure to homogenise is a result of decrepitation and degassing, even where other petrographic evidence is lacking. The absence of bubble-fractions between 10-100 vol% has the further implication that a vapour phase did not coexist with the Okataina magma.

Large-bubble glass inclusions

 Clear glass inclusions can be divided into inclusions with large, or small shrinkage bubbles (> 0.5 or < 0.5 vol% respectively). In all samples with mixed populations of CSMI's, and CR> and clear glass inclusions, the clear glass inclusions have large shrinkage bubbles, and do not homogenise. By comparison, > 30% of granular and crystal-rich glass inclusions in the same samples homogenised at temperatures of 850-860°C or 880-890°C respectively. Thus, I conclude that all glass inclusions in these samples have, to some degree, decrepitated and degassed.

 In sample NZL3, chosen as it only contained clear glass inclusions with largebubble fractions, only a small proportion of inclusions homogenised, between 920°C and 1190 $^{\circ}$ C, and very few of those had a T_h between 920 $^{\circ}$ C and 930 $^{\circ}$ C. Thus, it is debatable if even 920° C represents the trapping temperature, particularly since CR> glass inclusions from the same eruptive centre (Haroharo) have $T_h = 854$ °C. I conclude that the trapping temperature was $\leq 920^{\circ}$ C (probably < 920°C), and that most (if not all) glass inclusions have decrepitated and degassed.

Small-bubble clear glass inclusions

 Sample NZL27b (Central Maroa Rhyolites) was selected for heating experiments because it was dominated by glass inclusions with the smallest shrinkage bubbles (average bubble fraction 0.44 ± 0.24 vol% (1σ)), some inclusions having no shrinkage bubbles at all. Glass inclusions in NZL27b have an average T_h of 784 $^{\circ}$ C; however a small number of inclusions have a T_h between 820°C and 1100°C and many could not be homogenised at all. It was generally observed that glass inclusions in NZL27b which had shrinkage bubbles with a large volume fraction $(> 2 \text{ vol\%})$, did not homogenise. Inclusions with T_h values between 820°C and 1100°C appeared to have larger shrinkage bubbles than those in the range of 784° C \pm 11^oC, and inclusions with $T_h < 800$ °C had the smallest shrinkage bubbles of all.

 Similar results were obtained from sample NZL16b, also from the Haroharo eruptive centre, and also with typically small shrinkage bubbles. NZL16b had a T_h of 780 $^{\circ}$ C, and a similar correlation between bubble-fraction and T_h.

When glass inclusions from NZL27b were heated above 573°C (the α to β quartz transition temperature), sudden vesiculation occurred in the glass over an interval of <5°C. This vesiculation resulted in a brownish colouration, and a granular appearance (Figs. 11-6, -7), identical to the appearance of unheated granular-textured glass inclusions (e.g. Fig. 10-3). This effect occurs simultaneously in almost all the inclusions in a given phenocryst, and the vesiculation was identical in appearance, and temperature interval, to those observed in heating experiments on $C R \& G T$ glass inclusions.

Crystal-rich and granular-textured glass inclusions

 Samples selected for heating experiments were NZL1g, NZL4, and NZL19 representative of granular-textured glass inclusions, and samples NZL2d and NZL11, representative of crystal-rich glass inclusions. In both samples from the Tarawera rhyolite centre (NZL1g, and NZL19), granular-textured glass inclusions have a T_h of 880 $^{\circ}$ C, and sample NZL4, from the Haroharo rhyolite centre has a T_h of 854 $^{\circ}$ C. At temperatures above 600°C granular inclusions began to lose their granular appearance (Figs. 11-6b, -6c), and homogenised at \geq 850°C or 880°C (depending on the sample). The granular texture appeared to dissolve progressively, beginning with the finest particles, and leaving only the larger bubbles $(0.5 \mu m)$, with no obvious coalescence. These larger bubbles only disappeared at homogenisation temperature. In some cases, when cooled, homogenised inclusions suddenly took on a brownish, granular texture, similar to their unheated state (Fig. 11-6j). This typically occurred in < 30 sec, and at \approx 750°C, similar to the speed and temperature range of re-nucleation of shrinkage bubbles. However, on cooling below 575-600°C, the granular texture abruptly disappeared in all cases. Such inclusions, when heated back above the α to β quartz transition temperature (575°C), sometimes experienced a sudden return of granular texture, and in other cases nucleated one large, or numerous small (1-5 μ m) shrinkage bubbles. Cycling the temperature between 550-850°C sometimes resulted in alternating between granular texture and multiple small-bubbles on successive cycles. However, granular texture rarely reappeared after nucleation of multiple bubbles.

At the α to β quartz transition temperature (573°C) the quartz host of the inclusion increase in volume by $\approx 1\%$ with a consequent sudden reduction in pressure for inclusions trapped in the phenocryst. From the similarity in temperature and pressure of the appearance of granular texture, and re-nucleation of shrinkage bubbles, and the appearance of granular texture at the α to β quartz transition temperature, I infer that the granular texture observed during heating (e.g. Fig. 11-6j) is simply vesiculation. This is consistent with the observation of tiny $(< 1 \mu m)$ bubbles in electron photomicrographs of exposed granular glass inclusions (Figs. 10-34, -37, -39).

Fig 11-6 Heating experiment on a granular-textured glass inclusion that nucleated on an apatite microphenocryst; (**A**) inclusion at room temperature, note that the hollow apatite microphenocryst contains a silicate glass inclusion, (**B**) 740°C beginning of melting, (**C**) 850°C melting becoming pronounced, (**D**) held at 850°C for 10 minutes, melting is approaching completion. The inclusion homogenised at 880°C (**E**), note the protrusion on the inclusion wall (arrowed) which marks the position of one shrinkage bubble prior to homogenisation, (**F**) cooled to 717°C, the shrinkage bubbles have re-nucleated, (**G**) heated back to 880°C where the inclusion re-homogenised, (**H**) cooled to 592°C, shrinkage bubbles re-nucleated at 730°C and began shrinking rapidly at 650°C, (**I**) cooled to 575°C vesiculation suddenly occurred, (**J**) heating resumed 600°C vesiculation now well developed, (**K**) 729°C vesiculation beginning to disappear, (**L**) 850°C vesiculation has disappeared and the bubbles have shrunk, homogenisation occurred at 875°C.

NZL1g. 50µm scalebar

Figure 11-6

Figure 11-7 Heating experiment on a crystal-rich glass inclusion; (**A**) photomicrograph of the inclusion at room temperature before heating, (**B**) same inclusion different focus, (**C**) 900°C, (**D**) 950°C, note there appears to be a phase boundary in the bubble, (**E**) inclusion cooled to room temperature, the bubble now contains liquid, a vapour bubble, and a clear cubic crystal. Experiment resumed (**F**) 380°C, (**G**) 535°C, (**H**) 569°C, (**I**) 593, note changes in the bubble as seen in the close up. Moments after the previous photomicrograph the inclusion suddenly vesiculated. Cooling below 575°C caused the vesiculation to disappear suddenly, heating caused it to re-appear between ~ 590-600°C. (J) 800°C brown granularity still present but disappeared progressively between 800- 850°C.

(Continued over page)

Figure 11-7

Figure 11-7 (continued)

(**K**) 625°C vesiculation has disappeared, and only 2 shrinkage bubbles present. Cooling continued to 550°C, then two heating/cooling cycles between 550-800°C; on the final cycle multiple small shrinkage bubbles appeared at \sim 590-600°C rather than granularity, (**L**) 632°C, after 1 hr at this temperature (**M**) traces of granularity appeared and the two bubbles merged. The bubbles contracted during cooling (**N**) 440°C, (**O**) 100°C, leaving a deformed globule (**P**) cooled to room temperature, note the changed size and contents of the bubble (C/F 11-7**E**). Resumed heating/cooling (**Q**) 680°C vesiculation reoccurred at 580°C, however, when cooled to room temperature (**R**) after the last cycle, the "salt" crystal had disappeared, and amphibole? crystals have grown adjacent to the bubble.

NZL2d. 25 µm scalebars, insets are 2x and 3x magnification.

Figure 11-7 (continued)

Vesiculation was not observed in large-bubble clear glass inclusions.

 It was not possible to preserve the vesiculation below 575°C, which may be a function of cooling rates. In this series of experiments, cooling was not extended beyond 4 hr on any heating/cooling cycle (usually much less), whereas Stevenson et al. (1994) suggests that cooling times for the cores of rhyolite flows at Okataina may be on the order of 30 years.

Crystal-rich glass inclusions

 In NZL2d the green crystals in crystal-rich inclusions begin to show signs of melting at $\approx 750^{\circ}$ C, becoming significant above 850 $^{\circ}$ C; complete melting only occurs at the homogenisation temperature, 950°C (Fig. 11-7d). Extended heating (2-3 hours) was required to melt the final crystals, but did not noticeably decrease homogenisation temperatures. In the case of crystal-rich glass inclusions from NZL11, the same processes occurred, but at correspondingly lower temperatures, for NZL11 T_h is 820 $^{\circ}$ C. The reason for the difference in T_h for NZL2d (Haroharo) and NZL11 (Tarawera) is uncertain, but analysis (see page 196) suggests that in some samples the green crystals are pyroxenes, in others, the green crystals are amphiboles.

Experimentally induced in-situ immiscibility

 In a small number of crystal-rich inclusions in samples NZL2d, and NZL11, a single multi-phase bubble remained when the last crystal had melted (Fig. 11-7d). If the inclusion was then cooled, the bubble began a complex series of phase changes down to 148°C. In the case of NZL2d, repeated heating cycles up to 950°C eventually caused the bubble to disappear, but if heating did not exceed this, the hypersaline bubble remained for up to a dozen heating/cooling cycles. During a typical cooling or heating cycle the bubble expanded, contracted, and phase boundaries disappeared and re-formed between 100°-950°C, sometimes in successive cycles. Likewise, crystals grew, melted, and new crystals grew in their place. The complex sequence of phase changes varied from inclusion to inclusion, and even during successive heating/cooling cycles, the temperature at which particular phase changes occurred varied, generally decreasing a few degrees on successive cycles. In some heating/cooling cycles the glass vesiculated (Figs. 11-7j, -7m). Photomicrographs of bubbles at room temperature show one or more crystals (Fig. 11-7e), with aqueous vapour or liquid phases. The complex series of phase changes is not consistent with a simple NaCl+H2O system, and suggests the presence of multiple chloride $(\pm$ sulphate?) species. PIXE data from such an inclusion in NZL11 shows the complex composition of those bubbles (chapter 12, page 210). The progressive reduction in the temperature of some phase changes, observed over repeated heating/cooling cycles, may be the result of progressive exchange of elements with the melt, or the environment. For example, Cl exchange between globules and melt, or hydrogen diffusion out of the inclusion.

Fluid inclusion microthermometry

 Microthermometric experiments were performed on 2-phase vapour-liquid fluid inclusions in decrepitation haloes surrounding CSMI's in sample NZL10b (eg. Fig. 11- 9), in order to determine their salinity and trapping temperature. The final ice melting temperatures for these inclusions were between -3.9°C to -4.5°C with good repeatibilty. Using the freezing point depression tables in Bodnar and Vityk (1994) the final ice melting temperatures indicate salinities between 6.3 and 7.2 wt% $NaCl_{equiv}$.

 Two types of homogenisation behaviour were observed in different phenocrysts from sample NZL10b, homogenisation by slow disappearance of the bubble rim (possibly critical behaviour), and homogenisation by liquid disappearance. Homogenisation is by slow disappearance of the bubble rim, and showed good repeatability and a tight range $(T_h 442.5 \pm 2.5^{\circ}C)$. Homogenisation by liquid disappearance showed good repeatability but a wider range $(T_h 457 \pm 19^{\circ}C)$.

Summary of heating experiments

 Heating experiments on glass inclusions from Okataina show that in the samples with mixed populations of CSMI's, and CR> and clear glass inclusions, all clear glass inclusions are decrepitated and degassed. Granular-textured glass inclusions from the Tarawera rhyolite centre (NZL1g, and NZL19) have a T_h of 880 $^{\circ}$ C, and from the Haroharo rhyolite centre (NZL4) a T_h of 854 $^{\circ}$ C. Crystal-rich glass inclusions have much more varied homogenisation temperatures, 950°C in the case of NZL2d, but only 820°C in NZL11

Figure 11-8, -9, -10

(**a**) Decrepitation halo's of large 2-phase fluid inclusions surrounding CSMI's (**b**) close

up of one of the fluid inclusions (location arrowed in (a).

NZL10b. scalebars 50μm (inset 10 μm)

 In samples dominated by small-bubble clear glass inclusions (NZL16b and NZL27b), the clear glass inclusions have, in contrast, generally not decrepitated, and have T_h's of 784°C, the lowest of any Okataina inclusion recorded in this study.

 The single sample dominated by large-bubble clear glass inclusions (NZL3), and without coexisting CSMI's or CR> glass inclusions, demonstrated that all clear glass inclusions in this sample had decrepitated. This confirms that the glass inclusions, regardless of appearance, will homogenise, provided they have small shrinkage bubbles. The appearance (clear or granular-textured glass) in un-decrepitated and un-degassed inclusions is a function of trapping temperature. The cause of crystal-rich inclusions is less certain, although trapping temperature may be a factor.

Chapter 12: Analytical Results

Sample analyses

 Characteristically, the matrix glass of the Okataina samples comes in two forms, a pale, rather pumiceous fine-grained glass (Fig. 12-1), and a denser, more solid glass that grades into obsidian.

Fig 12-1 Photomicrograph of sample NZL16b, showing phenocrysts of feldspar, quartz, and biotite in a matrix of rhyolitic glass. The matrix shows typical laminar-textured glass; note the relatively solid cores, which develop distinct laminations towards the ends (arrowed). Field of view 2mm across

The glass commonly shows a lamellar flow texture, commonly with more or less elongate bubbles aligned along the flow laminations. Most samples are inhomogeneous on a millimetre scale, with irregular bundles of laminar-textured glass, mixed with porous glass fragments and jumbled phenocrysts of quartz, feldspars, apatite, biotite and magnetite (Fig. 12-1). Commonly, the glass grains are elongate with a central solid

core, which feathers out at one or both ends into a bundle of fine tails. Glass commonly shows varying degrees of rehydration, and perlitic cracking is abundant. FTIR spectroscopy shows that the coarse glass cores have low water contents, typically 0.15 - 0.25 wt% $\mathrm{H}_{2}\mathrm{O}$; however, there is a very consistent pattern of increasing water contents with increasing proximity to cracks or flow lamellae, typically up to 0.70 - 0.90 wt% H2O on the edge of such features. The curved slivers of glass between perlitic cracks have the highest water content, typically $1.00 - 1.50$ wt % H_2O . The water content of the glass falls off consistently with distance from cracks, fractures or any other type of porosity, and it is observed that the youngest samples (\sim 700 years old) are the least hydrated. Together these provide strong evidence that the rehydration is due to postemplacement infiltration of meteoric water. Given that there is evidence of considerable rehydration, it is impossible to be certain that any of the glass is completely pristine with regard to water content. However, the inner solid glass cores show low water contents around $0.15 - 0.25$ wt% $H₂O$, and I suggest that these represent the water content at the time of emplacement.

 As the petrographic evidence suggested that the samples were a mix of phenocrysts (predominantly feldspar \pm minor quartz, biotite, and cummingtonite) in a glass matrix, XRF analyses were performed on handpicked glass samples, with a few whole-rock samples as a control. As widespread but variable rehydration has been demonstrated, the whole rock and matrix glass XRF analyses have been recalculated to 100 wt% (table 12-1, -2). Figure 12-1 shows that the matrix glass separates fall within the spread of whole rock analyses (as expected); however, there is still evidence of contamination of the glass separates by feldspar. Most glass separates trend towards feldspar compositions, and with only one exception, the whole rock analyses have the highest $SiO₂$ concentrations. This is probably because the quartz was less likely to fragment when the samples were crushed, prior to handpicking the glass separates. This is consistent with the lack of a trend in $SiO₂$ vs $P₂O₅$ (Fig. 12-2b), or any other element incompatible with feldspar. However, selective fractionation of quartz or feldspar in the parental melt cannot be ruled out. The samples show no other consistent variations. The overall similarity of samples of different ages, from different eruptive sub-centres is a common feature of igneous rocks from the Taupo Volcanic Zone (Ewart, 1968; Ewart et al., 1975).

Table 12-1

Table 12-2

Analyses of samples from the Tarawera (Table 12-1) and the Haroharo eruptive centres (Table 12-2), whole rock analyses and matrix glass, recalculated to 100 wt%; whole rock analyses by XRF, matrix glasses by electron microprobe. All analyses in wt%, and performed at the University of Tasmania.

Fig. 12-2a

Fig. 12-2b

Fig. 12-2 Okataina whole rock and matrix glass analyses; Al₂O₃ vs SiO₂ (a), P₂O₅ vs **SiO2 (b). All analyses by XRF, performed at the University of Tasmania.**

Inclusion Analysis

Introduction

 Given the time limits placed upon this study, it was necessary to restrict detailed analysis and experiments to a small representative sub-set of the samples. However, during initial sample preparation, a sufficient number of magmatic inclusions were exposed in 8 samples, and were subjected to microprobe analysis to provide some baseline compositional data on un-homogenised magmatic inclusions (Figs. 12-3, -4).

Fig. 12-3 Raw microprobe analyses of inclusions from 8 Okataina samples. Solid symbols are clear glasses, other symbols are granular-textured (bg) and crystalrich (cr) glass inclusions.

 Given the similarity of the matrix glass compositions for all samples, and the analyses of magmatic inclusions, it seems probable that the major element composition of the melt from which the inclusions were trapped was also similar, excepting trends related to the apparent feldspar fractionation. For this reason, eruption age or locations were not used to select samples for intensive analysis; rather, samples were selected which contained large, abundant, crystal-rich or granular-textured (CR>) glass inclusions.

 One inevitable problem in comparing the composition of unheated and heated (homogenised) inclusions is that unheated magmatic inclusions exposed for microprobe analysis cannot subsequently be homogenised. Thus the analyses of heated and unheated inclusions must inevitably be on different inclusions. Where possible, a

number of inclusions have been analysed and the data given either as an average, and one standard deviation from that average (1σ) , or as plots of all the data, to show the range and distribution of data.

 Figures 12-3 and 12-4 show inter-element plots for the 8 baseline samples, and several features are immediately apparent.

- Clear glass inclusions (sample NZL16b excepted) form a tight grouping, with a consistently high total wt%. The deficit (from 100 wt%) is 0-4 wt%, average 2 wt%, and in this study, the deficit is taken as a fair approximation of the H_2O concentration (see techniques chapter, page 18).

- CR> glass inclusions form a more widely dispersed, but still distinctive field, with a similar slope and an almost complete overlap between granular-textured and crystalrich glass inclusions. These inclusions typically have low total wt%, and by implication have $H₂O$ concentrations from 6-12 wt% (average 8 wt% $H₂O$).

- Clear glass inclusions from sample NZL16b overlap the granular and crystal-rich inclusions, but not the clear glass inclusions from other samples.

- From CR> to clear glass inclusions (NZL16b excepted) there is an average \approx 5 wt% increase in silica, for an average \approx 5 wt% increase in total wt%, and by implication a 5 wt% decrease in $H₂O$ (Fig. 12-3). This suggests a simple degassing trend.

 Experimental evidence has shown that all large-bubble clear glass inclusions and some $C R & G T$ inclusions are decrepitated and degassed. If the only difference between these inclusions was a loss of H_2O , then one could expect that recalculation of microprobe totals to 100 wt% (ie anhydrous compositions) would cause the degassed and un-degassed populations to coincide. Figure 12-5 demonstrates that this is not always the case, and more so for some elements pairs (e.g. Fig. 12-5b) than others (e.g. Fig. 12-5a). In most Okataina samples, discrimination between crystal-rich and granular-textured glass inclusions can be difficult, as many granular-textured inclusions contain significant amount of larger crystals (e.g. Figs. 12-6, to -9). This observation is supported by plots of microprobe analyses of un-homogenised glass from $C R \& G T$ inclusions (Figs. 12-3, -4), which show the respective fields for crystal-rich, and granular-textured glass inclusions generally overlap. For these reasons, $CR>$ inclusions are grouped together as "glass" inclusions, and considered as distinct from large-bubble clear glass inclusions.

 Typically, the composition of matrix glasses, and glass inclusions (Figs. 12-10a, b, table 12-3) have well defined, partly overlapping ranges, with the matrix glasses located at the high-SiO₂, low-Al₂O₃ end of the SiO₂ vs Al₂O₃ trend for magmatic inclusions.

Figure 12-4 Microprobe analyses of melt inclusions from the 8 Okataina baseline samples. Solid symbols are clear glasses, other symbols are granular-textured (bg) and crystal-rich (cr) glass inclusions.

Figure 12-5 Microprobe analyses, recalculated to 100 wt%, for melt inclusions from 8 baseline Okataina samples. Solid symbols are clear glasses, other symbols are granular-textured (bg) and crystal-rich (cr) glass inclusions. Compare with figure 12-4 for un-recalculated data.

Table 12-3 Analyses of melt inclusions from selected Okataina samples; an average of the 8 baseline samples, NZL1g, NZL2b, NZL41, and the matrix glasses, with 1 standard deviation (1σ). All analyses by electron microprobe, in wt%, performed at the University of Tasmania

Detailed analytical studies

 On the basis of homogenisation behaviour of glass inclusions, two groups of samples were selected for detailed analysis. NZL1g and NZL2d are dominated by $C R & GT$ glass inclusions, some of which can be homogenised; they also have small populations of CSMI's and clear glass inclusions (characterised by large shrinkage bubbles), none of which homogenise. The second group of samples, NZL16b and NZL27b, is dominated by glass inclusions characterised by small (or no) shrinkage

bubbles, and which show homogenisation behaviour similar to $C R \& G T$ glass inclusions, except that T_h is < 800°C. Table 12-3 gives the compositions (average, and 1 standard deviation (1σ)) of inclusions from the chosen samples.

NZL1g and NZL2d

The microprobe beam used for these analyses had a diameter of 5 μ m, which could potentially produce analytical artefacts, since samples NZL1g and NZL2d are inhomogeneous on a micron scale, with micron- to sub-micron bubbles or crystals (Figs. 12-6 to -9). Table 12-4 gives the analyses of the points shown in figures 12-8 and 12-9, and it is apparent that analyses of exposed crystals (e.g. GM106-b9-1a, -1d), are significantly different to analyses which do not (e.g. GM106-b9-1c, -1b). Additionally, the later resemble the average glass inclusion in the same sample. Although analyses of crystals may be subject to some edge-effects, the data suggest an amphibole, with a

composition similar to hornblende or actinolite (Deer et al., 1992).

Table 12-4 Spot microprobe analyses of melt inclusions in sample NZL2d, in wt%, location of analyses are shown on figures 12-5, and 12-6. Also included in the table is the average NZL2d glass inclusion, with 1 standard deviation. All analyses by electron microprobe, performed at the University of Tasmania.

 However, inclusions in both samples could be homogenised, and this permits a comparison between the homogenised and un-homogenised inclusions.

Figures 12-11a, b plot total wt% against $SiO₂$; both show that the homogenised inclusions plot in two groups; high-total homogenised inclusions (> 95 wt%) correspond to the un-homogenised clear glass inclusions, and the low-total homogenised inclusions $(< 95 \text{ wt\%})$ correspond to the CR> glass inclusions. However, there is a distinct trend to higher $SiO₂$ values in both groups of homogenised inclusions, which can be explained by re-melting of quartz crystallised on the inclusion wall after trapping. Similar grouping are observed in total alkalis vs SiO_2 , and Al_2O_3 vs SiO_2 . Fig. 11a

Given the relative H₂O concentrations homogenised inclusions with total < 95 wt% probable represent homogenised CR> glass inclusions, so are given solid **symbols. All analyses by electron microprobe.**

 Analysis of un-homogenised granular-textured glass inclusions shows lower levels of Cl than un-homogenised clear glass inclusions (Figs. 12-12a, b). This might seem unexpected, as electron photomicrographs (Figs. 10-38, -39) show that some granular texture consists of ≤ 1 µm vesicles, probably filled with brine and vapour. However, Cl concentrations in all homogenised inclusions are as high as unhomogenised clear glass inclusions, and the apparent low concentrations of Cl are probably an analytical artefact. When such an inclusion is exposed by polishing, any vesicles at the surface will be breached and lose their liquid, vapour, and soluble crystalline components. Thus a layer a few μ m thick at the surface is depleted in those lost contents, and as the electron microprobe only analyses to a depth of a few μ m, there is a consistent under-analysis of H_2O , NaCl, and any soluble sulphates (if present).

 Figures (12-11a, b) and table 12-3 show that homogenised inclusions in NZL1g and NZL2d have, on average, lower inferred $H₂O$ concentrations than un-homogenised inclusions from the same samples. There is an increase of $1-2$ wt% $H₂O$, between unhomogenised and homogenised inclusions in both samples. The increased SiO2 can account for some of this in dilution previously noted. However, the inferred loss of H_2O is too great to be completely accounted for by melting of the host, and a small experimental H_2O loss is implied. This is observed even though conditions for bulk heating experiments on Okataina samples were much less severe than for Río Blanco (1- 2 hours at \geq 850°C, rather than 96 hours at 850°C).

 Allowing for both re-melting of the inclusion walls, and some experimentally induced H₂O loss, the trend observed for CR& GT glass inclusions in Figure 12-11 could be interpreted either as a degassing trend, or fractionation of $H₂O$. In either case, a parental magma would have had a H_2O concentration between 8-10 wt% for NZL1g and NZL2d. If the observed trend is a degassing trend (as implied by the homogenisation behaviour of $C R \& G T$ glass inclusions), then the average may have been closer to 10 wt%. However, it should be noted that felsic melts typically have H_2O concentrations between 2-6 wt% (e.g. Johnson et al. (1994)), and only rarely as high as 8 wt% (e.g. Lowenstern, 1994). This apparent anomaly needs to be considered in light of degassing trends.

Evidence of degassing

 Given the experimental evidence for the presence of decrepitated and degassed inclusions in NZL1g and NZL2d, the analytical results may provide a means of quantifying the extent, and consequences of degassing. Figures 12-13, -14, and -15 plot the composition of homogenised glass and CR> inclusions recalculated to 100 wt% (ie. \approx recalculated to anhydrous).

Fig 12-6 A CR> glass inclusion exposed by polishing, containing both large daughter crystals, apparently nucleated on the shrinkage bubble, and sub-µm granularity; (a) transmitted light, (b) reflected light. Note the crystals exposed on the right hand side of the inclusion. NZL2d. 50µm scalebar

Fig 12-7 A glass inclusion showing a combination of crystal-rich and granular-textured glass.

NZL4a. 50µm scalebar

Fig 12-8 A crystal-rich glass inclusion exposed by polishing. Several groups of daughter crystals are exposed in this inclusion; the labelled circles are the positions of individual electron microprobe analyses, given in table 12-4. NZL2d. 50µm scalebar

Fig 12-9 Crystal-rich glass inclusion exposed by polishing; (a) transmitted light, (b) reflected light; showing the locations of electron microprobe analyses given in table 12- 4.

NZL2d. 50µm scalebar

homogenised (triangles) and unheated SiO₂ wt% inclusions (diamonds), (a) NZL1g, **(b) NZL2d. Inclusions are grouped as per Fig. 12-11**

Fig. 14

Melt inclusion compositions re-calculated to $100 \text{ wt\%}; \text{ Al}_2\text{O}_3 \text{ vs } \text{SiO}_2(\text{Fig. 12-13}),$ **K2O vs Na2O (Fig. 12-14). Homogenised glass inclusions, NZL1g (circles), NZL2d (squares). Solid symbols have total < 95 wt% (corresponding to homogenised CR>** inclusions, hollow symbols have total > 95 wt% (corresponding to **homogenised clear glass inclusions)**

Fig 12-15 Melt inclusion analyses, recalculated to 100 wt%; CaO vs MgO, homogenised glass inclusions, NZL1g (circles), NZL2d (squares). Solid symbols have total < 95 wt% (corresponding to homogenised CR> inclusions), hollow **symbols have total > 95 wt% (corresponding to homogenised clear glass inclusion**s)

If degassing only affected the H_2O concentration, one would expect the fields for glass and $C R \& G T$ inclusions to overlap. However, this is not the case, although there is some overlap among the minor components (Ti, Fe, Mg, Mn, and Ca, e.g. Figs. 12-15). Glass inclusions (recalculated to 100 wt%) are, in general, enriched in alkalis relative to CR> inclusions, and show distinct SiO_2 : Al₂O₃ ratios. However, there is considerable variation, and to examine this, figure 12-16 shows the change in composition between average, homogenised, $C R & G T$ glass inclusions, and clear glass inclusions for NZL1g and NZL2d. Figure 12-17 shows the data as a percentage of the same components in the homogenised CR> glass inclusions. In percentage terms the most notable change is an apparent increase in $Na₂O$ and $K₂O$ concentrations. As previously noted, the petrographic evidence suggests that $CR>$ and clear glass inclusions coexist in the same trapping planes, and are presumed to have trapped the same melt, differing only in that large-bubble clear glass inclusions are decrepitated and degassed. If the melts were the same, and there has not been a massive influx of Na and K during decrepitation, the only feasible explanation is a loss of other components, with the apparent increase in alkalis being an artefact caused by selective loss. Figure 12-18 shows the results of mass balance calculations (based on the techniques of MacLean and Barrett (1993), in gms/100gms) between average CR& GT glass inclusions, and clear glass inclusions. The calculation assumes that the alkali levels represent the precursor composition.

Change in composition between average homogenised CR> glass inclusions, **and average homogenised clear glass inclusions (in gm/100 gms), for samples NZL1g and NZL2d**

Percentage change in composition between average homogenised CR> and **clear glass inclusions, for samples NZL1g and NZL2d**

equation, using the techniques of MacLean and Barrett (1993), for NZL1g and NZL2d; assuming K and Na concentrations represent the precursor composition $(K = 0, and Na = 0, respectively).$

As there is some discrepancy between the results for $Na₂O$ and $K₂O$, results are shown which assume $Na₂O$, and then $K₂O$, represent the precursor concentration. Table 12-5 shows the averages of these two scenarios, and indicates significant loss of $SiO₂$, $Al₂O₃$, and H_2O . SiO₂ loss is 3-4 times the H_2O loss, but there are only minor changes in the other elements. I explain this apparent loss of $SiO₂$, not solely in terms of material lost from the inclusion (which would explain the $H₂O$ loss), but rather in terms of quartz crystallised on the inclusion wall, and not re-melted during homogenisation. H_2O in a silicate melt acts as a flux, and its loss during degassing would increase the solidus temperature, and the viscosity of a silicate melt. CR> glass inclusions (which have little or no H_2O loss), show significant apparent increase in SiO_2 after homogenisation, clear glass inclusions do not. Figure 12-14 provides some support for this, as the fields for homogenised clear glass inclusions, and the field for homogenised $C R & G T$ inclusions (totals > 95 wt% and < 95 wt% respectively) converge towards the origin of the graph (0 wt% Na₂O and K₂O, or 100 wt% SiO₂). This is the pattern that might be expected if an approximately fixed concentration of alkalis is diluted by $SiO₂$. It appears that bulk heating experiments performed on samples NZL1g and NZL2d, which homogenised the CR> glass inclusions, did not fully melt the large-bubble clear glass inclusions. However, even the relatively mild conditions used, resulted in a small but measurable H₂O loss (\leq 1 wt% H₂O) in the CR> inclusions.

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Table 12-5 Mass balance calculations (in gms/100gms) between average CR> **glass inclusions, and clear glass inclusions, assuming the alkali levels represent the** precursor composition. Results are shown assuming $Na₂O$, and then $K₂O$, **represent the precursor concentration, then the averages of these two scenarios. Calculation based on the techniques of MacLean and Barrett (1993),**

 Table 12-6 gives the trace element compositions of nine Okataina melt inclusions, four of which were homogenised, and four representative matrix glasses; figure 12-19 presents this data normalised to the primitive mantle (Sun and McDonough, 1989). The data confirms the similarity between melt inclusion and matrix glasses, and the negative Eu anomaly in the average matrix glass data is consistent with feldspar fractionation, proposed on the basis of alkali distribution. The depletion of heavy-REE relative to the light-REE concentrations, and the low Nb values are is typical of lower continental crust (Rollinson, 1993). This is consistent with the current model of the TVZ, as a rifted arc, with magma generated by fractionation of crustal melts, with a large input of melted basement sediments (dominantly greywackes) (Graham et al., 1992; McCulloch et al., 1994; Graham et al., 1995; Sherburn et al., 2003).

NZL16b and NZL27b

 Both samples are dominated by clear glass inclusions, predominantly smallbubble, and bubble-free. Since the inclusions were homogeneous, and bulk heating had demonstrated slight experimentally induced H2O loss, the analyses were principally performed on un-homogenised inclusions. However, a few inclusions from single-grain experiments on NZL27b were also analysed, as a check, and these are included in plots of NZL27b.

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Table 12-6 Ion microprobe analyses of Okataina melt inclusions and matrix glass (in ppm). Columns 3-6 heated melt inclusions, 1, 2, 7, 8 unheated melt inclusions, 9-12 matrix glasses. Analyses by Cameca IMS 4f ion microprobe (Institute of Microelectronics, Yaroslavl', Russia), except Rb, analysed by laser ablation ICPMS (RSES Australian National University, Canberra, Australia)

element plot for average Okataina melt inclusions and matrix glasses. Data from table 12-6 normalised to the primitive mantle (Sun and

McDonough, 1989)

NZL16b, (b) NZL27b, includes homogenised inclusions (squares) from the same sample. All analyses by electron microprobe.

As with samples having mixed inclusion populations (CSMI's, CR>, and large-bubble clear glass inclusions), both NZL16b and NZL27b, shows regular variation in $SiO₂$ vs total wt% (Figs. 12-20a, b), also consistent with progressive H₂O loss. Figure 12-21 shows consistent trends converging towards the origin (100 wt% $SiO₂$), as in Fig. 12-14 this is consistent with variable partial melting of the host quartz, ie a mixing trend between an original alkali concentration and variable quartz. No other consistent trends are observed.

Fig 12-21 K₂O vs Na₂O for unheated clear glass inclusions; NZL16b and NZL27b. **All analyses by electron microprobe.**

Comparisons between NZL1g and NZL2d, and NZL16b and NZL27b

Although NZL1g and NZL2d (dominated by $C R & G T$ glass inclusions) and NZL16b and NZL27b (dominated by small-bubble clear glass inclusions) come from different eruptive centres with different ages, several similarities exist. Unheated inclusions from NZL16b and NZL27b show a considerable overlap with homogenised glass inclusions from NZL1g, and NZL2d. In contrast, the unheated inclusions from NZL1g and NZL2d diverge strongly in parallel trends orthogonal to the trend in the unheated inclusions, this divergence is probably a consequence of incomplete melting of quartz crystallised on the inclusion wall, as well as elements locked up in the daughter phases. Consistent variation is observed in alkali concentrations between these samples, probably consistent with the variable Na/K fractionation across the whole Okataina system (noted on page 188); however, there is no other consistent variation. Analyses are consistent with the heating experiment data that suggest small-bubble clear glass inclusions and CR> glass inclusions crystallised from the same melt.

Experimentally induced in-situ immiscibility

 In some heating experiments on crystal-rich glass inclusions, heating to just below the homogenisation temperature resulted in the formation of complex multiphase hypersaline globules. Prolonged heating dissolved these globules back into the melt, at the T_h of other inclusions in the same phenocryst, suggesting that the globules are daughter phases, produced by post-trapping immiscibility. Since the relative proportions of globules and glass can be measured, and their compositions analysed, such inclusions provide the possibility of using them to observe (and measure) in miniature, processes that may also have occurred at magma chamber scale.

 Table 12-7 and figure 12-23 show the results of PIXE analyses of multiphase hypersaline globules, produced during heating experiments on crystal-rich inclusions from NZL11. Table 12-8 gives the compositions for NZL11 unheated, and homogenised and quenched crystal-rich glass inclusions, and matrix glasses. A comparison between globules and glass shows massive enrichment of globules in some elements. The Cl concentration of globules ranges from 8-45 wt%, in sharp contrast to homogenised glass inclusions that average 0.22 wt%. Copper concentration of globules range from 2814-33,464 ppm, homogenised glass inclusions average 58 ppm. Pb and Zn likewise show strong enrichment in the globules.

Table 12-7 PIXE analyses of selected hypersaline globules produced during heating experiments on granular and crystal-rich inclusions Columns 1-6 -globules exsolved in situ during heating experiments with melt inclusions; 7 and 8 - globules in a natural CR> glass inclusion. All inclusions are from sample NZL11, n.d. = **no data, typically because the element was below the PIXE detection limit. Other elements (e.g., Na, K, Fe, and Mn) are present, but not quantified.**

Figure 12-22a

Figure 12-22 Optical images and PIXE (proton-induced X-ray emission) element maps of immiscible fluid globules inside silicate glass inclusions. Analysis was performed by the CSIRO-GEMOC Nuclear Microprobe (North Ryde, Australia) 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. Scale bars shown on optical images are 30 µm.

Table 12-8 Compositions, as averages, with one standard deviation (1σ), for unheated and homogenised glass inclusions, and matrix glasses, from sample NZL11 Column 1. - CR> glass inclusions; 2. - CR> glass inclusions, after heating at 850°C for 6 hours and quenching; 3. - matrix glasses. Major elements and Cl (in wt%) analysed by a Cameca SX50 electron microprobe (University of Tasmania, Hobart, Australia), H2O (in wt%) analysed by a Cameca IMS 4f ion probe (Institute of Microelectronics, Yaroslavl', Russia), trace elements (in ppm) analysed by laser ablation ICPMS (RSES, Australian National University, Canberra, Australia).

Table 12-9 Mass balance calculation, giving bulk compositions of two glass inclusions containing hypersaline globules. Two melt inclusions; column A (Fig. 12-22a) and B (Fig. 11-22b) were used in this calculation. Row 1. - globule composition (PIXE analysis); 2. - glass composition (LA-ICPMS analysis); 3. -bulk compositions of melt inclusions, calculated using estimated volume of globules (0.31 and 0.96 vol%, respectively) and inferred densities of 1.0 g/cm³ (globule) and 2.5 g/ **cm3 (glass). 4. - maximum concentrations in homogenised melt inclusions in the same sample; 5. - calculated partitioning coefficients**

As the globules can be dissolved back into the melt near the T_h for the sample, it seems likely that these globules have exsolved from the melt within the inclusion. To test this possibility, a mass balance calculation performed in conjunction with

Dr. Kamenetsky, is presented Table 12-9. Two magmatic inclusions are used, for which PIXE analyses of the globules, and Ion probe analyses of the glass are available. Using the estimated bubble-fraction $(A = 0.31$ and $B = 0.96$ vol%), and the assumed densities (globule 1.0 gm/cm³, and glass 2.5 gm/cm³), a bulk concentration of Cu, Zn, Pb, Ba, and Cl for the whole inclusion was calculated. For the purpose of comparison, the maximum measured concentration of the same element, in homogenised inclusions from the same sample, is provided. Considerable variation is present in these concentrations, probably due to the partial degassing implied from the homogenisation behaviour, so the maximum value is more likely to be representative. Cu, Zn, and Cl show the greatest variability, and it is probable that these were preferentially partitioned into (and lost with) an aqueous phase. Table 12-8 shows that the calculated bulk concentrations of Cu, Zn, Pb, Ba, and Cl are within the measured range for homogenised inclusions (from the same sample). This supports the contention that the contents of the globules have exsolved (post-trapping) from their enclosing glass. It should be noted that this involved only a minor exsolution of H_2O from the glass, which explains the extremely high salinity of the globules. The mass balance calculation also provides calculated K_d 's for natural systems, which can be compared to K_d 's obtained experimentally.

 Although metal concentrations recorded in the heating experiment globules are high, there are examples from other systems, which approach these values. Dietrich et al. (1999, 2000) reported Cu concentrations between 100-7000 ppm in homogenised inclusions from a Bolivian tin porphyry, and Lowenstern et al. (1991) reported high Cu concentrations in melt inclusions from the Valley of Ten Thousand Smokes, Alaska. In both cases the evidence suggested the Cu was preferentially partitioned into the coexisting vapour phase.

Microthermometry

 PIXE analyses of 2-phase vapour-liquid fluid inclusions, occurring in decrepitation haloes surrounding type-2 inclusions in sample NZL10b (e.g. Fig. 10-8) are given below. Three inclusions were analysed, and the images show only low concentrations of those elements above the background level (Fig. 12-24). Cl and K are both present in the inclusions, which is consistent with the inclusions being NaCl and KCl brine. Cu is the only metal to show any presence on the PIXE images and that only slightly, despite high calculated concentrations. The calculated element concentrations are given in table 12-10 for those elements that have values above background. The secondary X-rays generated by Cl tend to attenuate badly in quartz, and the salinities estimated from the PIXE data are lower than the 6.3 and 7.2 wt% NaCl_{equiv} estimated by

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microthermometry for similar inclusions. For this reason the Cl concentrations from the PIXE analyses are probably underestimated. However, the concentrations for the other elements should not be affected.

 Compared to the heating experiment hypersaline globules exsolved from NZL11, NZL16b and NZL27b, the naturally occurring fluid inclusions have very low salinity. It should be noted that the exsolution of hypersaline globules reduced the $H₂O$ concentration of the glass by only a small amount. Complete degassing would have removed 6-8 wt% H_2O , so the low salinity in the NZL10b fluid inclusions, and the implied low salinity in naturally occurring 1- and 2-phase aqueous globules, is consistent with extensive degassing of the melt.

Table 12-10 PIXE analyses of decrepitation-related fluid inclusions in quartz from sample NZL10b

Summary of analytical results

 Analyses of whole rock, matrix glass, and melt inclusion compositions has shown that un-decrepitated and un-degassed melt inclusions are representative of Okataina magma compositions. Matrix glasses have similar compositions, although degassed, and subsequently partly re-hydrated. Current whole rock compositions can be explained as mixing trends between melt and Na- or K-feldspars.

 Variation between whole rock, matrix glass, and melt inclusion analyses for samples across the whole spatial and temporal range observed at Okataina, show little consistent variation, and that which is observed appears to reflect variation in Na-/Kfeldspar ratios. These observations are consistent with observations across the whole of the TVZ.

 The compositional effects of decrepitation and degassing are complex, and simply re-calculating the composition of decrepitated and degassed melt inclusions to 100 wt% does not remove the degassing effects. Likewise, homogenisation under the minimum conditions of temperature and duration necessary to homogenise an inclusion, does not result in complete melting, but still produces minor diffusive H_2O loss.

Figure 12-23 PIXE maps of decrepitation-related fluid inclusions, BM11, -13, and - 14b, from sample NZL10b. Analysis was performed by the CSIRO-GEMOC Nuclear

Chapter 13: Discussion and Conclusions

Melts represented by Okataina melt inclusions

 Combining the inclusion descriptions with the experimental and analytical data, it is apparent that the Okataina samples contain three distinct melt inclusion populations:

1. Large-bubble clear glass inclusions, none of which homogenise.

2. Crystal-rich and granular-textured glass inclusions (and small-bubble clear glass inclusions in NZL16b and 27b), some of which homogenise, others homogenise, but at unrealistic temperatures, and some of which do not homogenise at all.

3. Crystalline silicate melt inclusions (CSMI's), none of which homogenise.

All three groups coexist in various combinations in different samples, and each group shows distinctly different compositions, with separate (although sometimes parallel) trends. There are two possible explanations for this; they could represent different melts, or very different degassing trends. Three lines of evidence argue against the suggestion that these represent different original melts:

- 1. At least two of the three groups of melt inclusions coexist intimately and randomly in the same growth planes in each sample, commonly within a few 10's of microns.
- 2. Oxide/oxide plots (e.g. Figs. 12-3, -4) show no overlap between groups, and nothing that could be interpreted as a mixing trend.
- 3. No inclusions have been observed that suggest immiscible coexistence of two discrete melts.

No analytical data exists for CSMI's, but it seems unlikely that that the first two populations represent coexisting melts, and there is no evidence that CSMI's represent a separate melt. This leaves the suggestion that they represent two separate degassing trends:

- Oxide/oxide plots for CR> glass inclusions (and clear glass inclusions from NZL16b and 27b) show increasing total wt% at approximately constant ratios of $SiO₂$, $Al₂O₃$, $Fe₂O₃$, and MgO. Such inclusions show a range from homogenising to non-homogenising inclusions, implying that the high-H2O compositions represent the un-degassed end of a degassing trend.

 - In contrast, the compositions of large-bubble clear glass inclusions can only be reconciled with homogenisable glass inclusions if there was a loss of H_2O , and extensive failure of $SiO₂$ to melt during heating.

 - CSMI's may represent a third distinct inclusion population, and degassing trend, but they do not homogenise, and are too inhomogeneous to analyses, so no data is available.

Decrepitation of crystalline silicate melt inclusions

 Two compositional trends (and possibly three, the CSMI's) have been described above, with different homogenisation behaviours and compositions. Some, but not all inclusions have decrepitated and degassed, so can the differing compositions be explained in terms of decrepitation? One might speculate that if an inclusion decrepitates at high temperature it could be fluid enough to exsolve, and lose, a significant percentage of its H_2O , and may also lose H_2O soluble components, and degas down to volatile-depleted glass. Likewise, a melt inclusion that decrepitates at, or below, the glass transition temperature may simply be too viscous to lose much H_2O . External pressure may also be a factor. If a still-melted inclusion decrepitates close to its original trapping pressure, there is only a small pressure gradient to force out volatiles. If the same inclusion decrepitates at much less than its trapping pressure, the strong pressure gradient would be available to power large-scale degassing, and might result in volatile-depleted glass.

Implications of degassing

Simple degassing, as observed in the CR& GT and small-bubble clear glass inclusions, has little impact on the inter-element ratios, tending to remove only volatiles $(H₂O, CO₂)$, and any other gaseous species), and the more readily soluble species (e.g. chlorides, and some sulphates) if present. The effects on metal concentrations are uncertain, and would depend on whether they existed as soluble chloride complexes (in liquid- or vapour-phases), or as sulphides or oxides.

 The situation is quite different for large-bubble clear glass inclusions, which, at Okataina, have compositions significantly different from inclusions that homogenise, and by inference, different from their own parental melts. This difference is largely due to incomplete re-melting of quartz crystallised on the inclusion wall. Extended heating may melt this, but produces an intractable problem of knowing when to stop. Extended heating will begin to melt the host quartz, and there is no obvious visual indication when re-melting of epitaxial "daughter" quartz is complete.

 If this is true at other deposits, then any conclusions drawn from large-bubble, non-homogenising clear glass inclusions must be suspect, if such inclusions are assumed to be representative of parental melts. Such a paper was presented by Grancea et al. (2002), in which large-bubble, non-homogenising clear glass inclusions were used in this way.

Inferences from homogenisation temperatures

Samples containing $CR>$ and clear glass inclusions that can be homogenised, are not restricted to any eruptive centre or eruption age. Likewise, there is no evidence from the matrix glass or whole rock analyses (Table 12-1, Fig. 12-1) of any correlation between magma composition and inclusion type. However, there is some degree of correlation between T_h (and by implication $T_{trapping}$) and inclusion type. Glass inclusions that can be homogenised have low T_h values (NZL16b T_h = 775°C, NZL27b T_h = 784°C). Granular inclusions have a wider range (T_h = 880°C for Tarawera, $T_h = 850^{\circ}$ C for Haroharo). However, there is an apparent problem with crystal-rich inclusions. The homogenisation temperature for NZL2d is 950°C and 825° C for NZL11, which are respectively higher and lower than the T_h for granular inclusions from the same eruptive centres. This could be a kinetic function, related to the type of daughter crystals present (pyroxene or amphibole), since melting was promoted by prolonged heating. However, given the small size of individual daughter crystals (typically ≤ 1 µm dia.), the composition of each crystal cannot be confirmed. Nevertheless, it remains apparent that there is a correlation between T_h and inclusion type, which implies that the trapping temperature of an inclusion is the dominant factor in determining the physical form of cooled inclusions.

Did aqueous fluids coexist with silicate melt at Okataina?

 Inclusions have been observed in most Okataina samples, containing 1- or 2 phase aqueous globules, in clear (Figs. 10-47, -48), brown (Fig. 10-49), or brown granular glass (Fig. 10-50). However, the aqueous globules from Okataina are always spherical, and show none of the plastic deformation common to globules in Río Blanco composite inclusions. Single-phase globules form a relatively constant proportion of the inclusions in which they are found (≈ 1 vol%), unlike single-phase globules from Río Blanco. Two-phase globules from Okataina show more variable proportions, but there is a correlation between the globule size, and the proportion of vapour phase. In the large 2-phase globules (e.g. Figs. 10-48, -49), the vapour phase forms a much larger proportion of the globule (commonly $> 70\%$). Although it is impossible to accurately quantify, it is possible that the 2-phase globules represent a shrinkage bubble (of various sizes) that has coalesced with a single-phase globule, of a fixed size, relative to the inclusion.

 The requirement of Roedder's test for immiscibility (Roedder, 1984), that the phase ratios of the two supposed immiscible phases is variable, is not met for the singlephase globules, and may not be met for the 2-phase globules, if, in fact they are conucleated single-phase globules and shrinkage bubbles. Thus, it appears that Okataina inclusions (glass, granular, and crystal-rich) which contain 1- or 2-phase aqueous globules are not composite inclusions of glass+aqueous liquid, of the type observed at Río Blanco. Rather, the globules are daughter phases, having exsolved post-trapping, and lacking the deformed shapes, and probably the variable phase-ratios, characteristic of composite inclusions of glass+aqueous liquid.

 ESEM images (Figs. 10-29, -30), and apparent Cl deficiencies in microprobe analyses of un-homogenised granular-textured glass inclusions, show that the "granularity" commonly consists of minute $\ll 1 \mu m$) hypersaline brine-filled vesicles. However, heating experiments suggest this was a post- rather than pre-trapping phenomenon. Thus, it appears that there is no strong evidence for the coexistence of silicate melt, and aqueous fluid, in the Okataina magma at the time the magmatic inclusions were trapped, but very good evidence for post-trapping immiscibility.

 Okataina phenocrysts do not contain primary liquid- or vapour-rich fluid inclusions, or vapour-rich CSMI's, that are abundant at Río Blanco. The explanation for this significant difference is that the phenocrysts at Okataina probably formed at a much greater depth (and consequently pressure) than the phenocrysts at Río Blanco. Estimates of phenocryst equilibration pressure for a suite of Okataina samples (Ewart et al., 1975) average 2.2 kbars (7-8 km paleo-depth, assuming typical lithostatic pressures). Geological reconstructions, and fluid inclusions from Río Blanco, suggest probable paleo-depths for crystallisation for phenocrysts from that study, of ≤ 1 km and possibly < 0.5 km (Holmgren et al., 1988; Serrano et al., 1996; Vargas et al., 1999). Based on modelling in a paper by Shinohara (1994), it is reasonable to suppose that if any volatiles had exsolved at Okataina they would have done so as supercritical fluids; those which did exsolve at Río Blanco did so as sub-critical fluids (ie unmixed liquid and vapour phases). However, there is little evidence to suggest any exsolution prior to the trapping of Okataina inclusions.

In-situ immiscibility

 During the heating experiments on crystal-rich inclusions in samples NZL2d and NZL11, at temperatures lower than homogenisation temperature, hypersaline globules were produced. When cooled, these inclusions crystallised large halite crystals in a 2-phase aqueous liquid/vapour (Fig. 11-7e). Subsequent electron microprobe analyses confirmed that these glass inclusions had H_2O concentrations similar to $CR>$ glass inclusions. Calculations (page 213) show that the salt and metal concentrations of experimentally produced globules could have been sequestered from

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the melt filling the rest of the inclusion, without requiring the initial melt to have been unreasonably salt- or metal-rich. Moreover, the salt-rich globules have a constant phase-ratio with their inclusion, and the globules completely homogenise at the same temperature as glass inclusions. All of these factors appear to confirm that the globules are products of post-trapping experimentally induced, immiscible separation of an aqueous phase.

Given the compositional similarity of all Okataina samples (eg. Figs. 12-3, -4), it seems reasonable to assume that such behaviour is common to (at least) the Okataina crystal-rich glass inclusions. The development of both vesiculation, and hypersaline globules in homogenised inclusions, demonstrate volatile exsolution occurring within a magmatic inclusion, so it may be asked whether exsolution within an inclusion can be used as a proxy for exsolution within the magma chamber as a whole? Magmatic inclusions that homogenise are assumed in this study to represent trapped samples of their parental magma. If these experimentally produced globules can be used as a proxy for chamber-scale exsolution/immiscibility processes, then they could provide an important new tool for petrogenetic and metallogenic studies.

 That said, there are some potential limitations to be considered. One possible limitation is the extent to which the composition of the inclusions in question is representative of the composition of the chamber as a whole. On the scale of these inclusions, volatile exsolution may not be homogeneous. There is also the possibility of localised volatile enhancement in the boundary layer immediately adjacent to a growing phenocryst; however, evidence (see discussion in chapter 2) suggests that boundary layer effects are negligible.

 A second potential limitation is that, during the experiments, the temperature of certain phase transitions decrease systematically during repeated heating/cooling cycles. This implies systematic modification of the globule composition, presumably by migration of volatiles into, or out of, the globule. If so, the volatile concentrations in the globule reflect, in part, the precise heating/cooling regime employed, since these would affect the viscosity of the melted inclusion and diffusion rates. The observed systematic decrease of phase transitions temperatures was not large (1-2°C per heating/cooling cycle), but it may point to measurable experimental error.

 Aqueous globules in unheated glass inclusions from Okataina also appear to have resulted from post-trapping exsolution, rather than by co-trapping of aqueous phases coexisting in the Okataina magma. Such globules usually only contain a small proportion of crystalline precipitates. However, experimentally produced globules contain \approx 50 % halite when cooled. The analyses of these heating experiment globules (table 12-8) show that only a small fraction of the $H₂O$ exsolved. If double the quantity of H_2O had exsolved, it would not have greatly reduced the H_2O concentration of the glass, but it would have produced the apparent salinities observed in single-phase aqueous inclusions in unheated melt inclusions.

Implications of in-situ immiscibility

 One intractable problem in ore-deposit genetic studies is the actual amount of metals and volatiles extracted from a given volume of source rock. Whole rock analyses show only the residue after degassing. Fluid inclusions only give the concentration in the fluid, after an unknown amount of mixing, wall rock interactions, and other contamination, but give no clue to the actual volumes, or the concentrations at the time of exsolution. Magmatic inclusions can tell us how much metal and volatiles were in the melt (if the inclusions were trapped before exsolution) or how much was left in the residual melt (if the inclusions were trapped after exsolution). However, none show how much was extracted, rather than how much could have been. Hypersaline globules from the heating experiments in this study provide actual data on the amounts of metals, and volatiles, exsolved from a given volume of melt during cooling. Hypersaline globules have been observed in some other studies (Kamenetsky et al., 2002b, 2003b), but the potential of this technique remains to be exploited.

 The mass balance equations on the heating experiment globules (page 213) showed strong partitioning of metals into immiscible magmatic-derived fluids. For the sake of calculation, we might assume that the compositions of the studied melt inclusions are representative of un-degassed TVZ rhyolitic magmas crystallising at >3 kb, $(8 \text{ wt\% H}_2O \text{ and } 0.22 \text{ wt\% Cl})$. Further, we might assume that the partitioning of Cu during degassing (e.g. 80-90 ppm in melt inclusions down to 1.3 ppm in matrix glasses) is also typical. If so, it follows that the $>15,000$ km³ of the TVZ rhyolites erupted over the \approx 1.6 Ma life of the young TVZ (Wilson et al., 1995), could have released a total of $3x10^9$ tonnes of Cu, or \approx 5,000 kg/day (\approx 1800 tons/year). This estimate assumes 100% efficient extraction from the melt, and is the total amount degassed by all methods. Using these same assumptions, the calculated NaCl and Cu contents of the average exsolved aqueous fluid will be \sim 1 wt% and \sim 1,000 ppm, respectively, and 1 km³ of magma could have produced something in the order of 2×10^8 tons of such fluids, containing 2×10^5 tons of Cu. The potential for other metals is similar, but not to the same extent.

Degassing of the TVZ can proceed by two main routes:

Transport into the wall-rocks as hydrothermal fluids

Venting to the atmosphere as

explosive degassing, during eruptions

quiescent degassing, via fumaroles, hot springs, etc.

The history of the TVZ demonstrates large-scale examples of both explosive and quiescent degassing, ranging from caldera-forming eruptions to individual fumaroles and hot springs. Le Cloarec et al. (1992) has calculated that quiescent degassing on White Island is producing Cu at the rate $\approx 300 \text{kg/day}$ ($\approx 110 \text{ tons/year}$) (see Barclay et al. (1996) for estimates of pre-eruptive volatile concentrations). Current degassing of the whole TVZ includes two semi-active volcanoes (White Island and Mt Ruapehu), extensive hydrothermal fields across the central TVZ, and an averaged yearly contribution from periodic explosive degassing. The suggestion that White Island is producing $\approx 6\%$ of Cu degassed from the TVZ may be feasible. If so, the estimation of net degassing based on the heating experiments may be sound.

 Estimates for the worldwide metal emissions due to quiescent degassing are subject to some debate. Published estimates range from 15,000 tons/year (Lambert et al., 1988), based on element degassing efficiencies, to 9,000 tons/year (Nriagu, 1989) and 1035 tons/year (Hinkley et al., 1999), both based on field observation. The 1,800 tons/year estimated from this study is total degassing, so it would seem broadly consistent with Lambert et al. (1988) and Nriagu (1989), but, if correct, the 1035 tons/ year estimate of Hinkley et al. (1999) is inconsistent with my estimate for the TVZ. This is also true in regard to the estimated Cu/Zn ratio, which would be consistent with Lambert et al. (1988) and Nriagu (1989), but inconsistent with Hinkley et al. (1999). No reliable worldwide estimates for metal-flux from explosive degassing are available.

The estimate of $3x10^9$ tonnes of Cu potentially extracted from the TVZ magmas is sufficient to form a dozen supergiant porphyry Cu deposits, providing that suitable trapping and precipitation conditions existed. Although volcanic outgassing of the TVZ magmas will have lost a substantial portion of economic metals, some was presumably captured as deep-seated hydrothermal fluids, and possibly deposited. Any estimate of the potential for mineralisation in the TVZ is entirely speculative; however, we conclude that, if scale-dependent effects are properly considered, the study of melt inclusions can in fact, put a magma chamber "under the microscope".

Conclusions

 During the crystallisation of the Okataina magmas, growing phenocrysts trapped a volatile-rich silicate melt (> 6 wt% H₂O). Volatile-poor inclusions (< 6 wt% H₂O) have decrepitated and degassed from the same volatile-rich silicate melts. Degassing

has effects other than simple loss of volatiles, such as changes to the glass transition temperature and fusibility of silicate-melts, and re-calculation of an un-homogenised inclusion to 100 wt% does not remove the effects of degassing.

 Experimental evidence and observation from inclusions of volatile-rich melt show that post-trapping volatile-phase exsolution (ie, vesiculation and the formation of brine globules) and/or the crystallisation of hydrous daughter phases (amphiboles) was ubiquitous in volatile-rich magmatic inclusions with $T_{trapping} > 800^{\circ}$ C. Glass inclusions (un-decrepitated, un-degassed, and capable of being homogenised) formed from melts trapped at lower temperatures

 The vapour-rich fluid inclusions, and vapour-rich crystalline silicate inclusions, although common in the Río Blanco samples, are essentially absent from Okataina, due to the greater depth of crystallisation at Okataina (\approx 2 kbars). The coexistence of supercritical aqueous fluids with the Okataina magma is not supported by the melt inclusions. Rather, the evidence suggests post-trapping immiscibility as the source of 1 and 2-phase aqueous globules in glass inclusions. Heating experiments can produce similar effects, except that the resultant hypersaline fluids are typically more concentrated.

 Data from heating experiments show that post-trapping immiscibility, which produced the hypersaline globules, strongly fractionated melt-incompatible elements into the volatile phase. This unmixing produced a hypersaline metal-rich aqueous phase immiscible with respect to the melt. The Okataina phenocrysts give no clues as to the subsequent fate of these primary magmatic fluids, but their composition would seem to be a good candidate for evolution into the kinds of hydrothermal fluids responsible, in other circumstances, for mineralisation.

Chapter 14: Methodological implications of this study

Introduction

 Having completed the Río Blanco and Okataina case studies, it is appropriate to re-examine the conclusions already reached with a view to drawing together any common threads. In the introduction to this thesis I proposed, as secondary aims, investigation of factors affecting the methodology of melt inclusion studies, particularly the potential of less than perfect melt inclusions. I propose here to discuss the observations made on such inclusions, and what information can, and cannot reliably be gained from them. It has been my contention throughout this study that magmatic inclusions sample, and to a degree preserve, parental melts, and both Río Blanco and Okataina provide evidence of that. However, even decrepitated and degassed inclusions have yielded useful information.

Coexistence of volatile-poor and volatile-rich melts

 In all rocks in which both glass and CSMI's occur, Río Blanco, Okataina, and the Omsukchan Granite (Kamenetsky et al., 2003b), it is observed that they coexist in the same phenocrysts, and in the same growth planes, with random distributions. In these rocks, glass inclusions have low $H₂O$ concentrations, and CSMI's have high measured or inferred H₂O concentrations, which could imply the coexistence of volatilerich and volatile-poor melts. However, at Okataina the evidence would not support that view, but rather, evidence suggests a consistently volatile-rich melt, and any coexisting, large-bubble glass inclusions are simply decrepitated and degassed.

 In the case of Río Blanco, some evidence is equivocal. All glass inclusions, and most CSMI's are decrepitated and degassed, as shown by their failure to homogenise, so current H₂O concentrations provide no evidence for their original values. However, composite (glass + crystalline silicate melt) inclusions show variable proportions of volatile-poor glass (\approx 2.5 wt% H₂O) and crystallised silicate melt in the same inclusion. The boundaries between the phases are sharp and clearly defined, and provide evidence for immiscibility according to the test proposed by Roedder (1984) (chapter 8, page 124).

 Additional evidence for the existence of volatile-poor melts at Río Blanco may be provided by crystallised glass inclusions (e.g. Figs. 5-23, -27) as observed in the La Copa samples. These inclusions have low $H₂O$ totals (as per microprobe) and contain crystallised silicate glass, but without the dark, inhomogeneous appearance of CSMI's. Both of these may represent a volatile-poor melt, although they may also represent

variations in cooling and crystallisation paths. Therefore, the coexistence of two silicate melt phases in the Río Blanco magma is possible. However, given that Río Blanco inclusions are almost invariably decrepitated and degassed, the original volatile concentrations in the immiscible phases remains undetermined.

Inclusions that cannot be homogenised

 At Okataina, no CSMI, and no large-bubble glass inclusion, regardless of size, could be homogenised, and both can be shown to have decrepitated and degassed from the same melt. At Río Blanco, glass inclusion, and CSMI's $> 10 \mu m$ (and most that were smaller) could not be homogenised, so it is not possible to even estimate their initial $H₂O$ concentration. Evidence favours a single parental melt, but cannot rule out coexisting volatile-rich and volatile-poor melts. In both suites, large-bubble glass inclusions show intimate and random coexistence with CSMI's. So, at both Río Blanco and Okataina two distinct types of decrepitated and degassed inclusions coexist (glass and crystalline silicate melt), that at least in the case of Okataina originally trapped the same melt. How can these differences be explained?

 Solidus and glass transition temperatures of silicate melts increase with decreasing H2O concentration (e.g. Bowen and Tuttle, 1950; Dingwell, 1998; Moore et al., 1998). Therefore, the effect of removing H_2O from a melt (ie degassing) increases both temperatures, so a given melt composition would have a particular solidus temperature with > 6 wt% H_2O (for convenience, its wet solidus), and a higher solidus with \leq 2.5 wt% H₂O (for convenience, its dry solidus). From experimental evidence the wet solidus of a silicate melt must be less than the dry solidus. Thus, if an inclusion decrepitated below its dry melting temperature, but still above its wet melting temperature, it would (in effect) experience \approx instantaneous supercooling. Supercooling induces crystallisation, and the inclusion may crystallise, rather than cool to glass. In contrast, if an inclusion decrepitated above its dry solidus, no supercooling should occur, and no impediment to quenching to glass (below the glass transition temperature). For example:

In the second case, the inclusion experiences an \approx instantaneous supercooling, and is now below its solidus, although in the first case the inclusion is still above its new liquidus. Actual wet and dry solidus temperatures would depend on melt composition, H2O concentration, and pressure. However, the wet solidus must be below the trapping temperatures of inclusions, and experimental evidence suggests that the dry solidus could be 10's to 100's of degrees higher.

 With this explanation in mind, note that the Don Luis Porphyry has CSMI's but no coexisting glass inclusions. It can now be suggested that all Don Luis Porphyry melt inclusions simply decrepitated at (relatively) low temperature, ie below the dry solidus, but still above the wet solidus.

 A further case is possible, decrepitation near or below the glass transition temperature. In this case the inclusion would be \approx solid, and degassing is severely impeded. Such inclusions may partly degas, with the result that the T_h would be raised above the $T_{trapping}$, but at least in some cases one would expect that homogenisation would still be possible at < 1000°C. CSMI's with T_h values above the $T_{transing}$ for that sample, but < 1000°C were noted in all Okataina heating experiments on samples containing CSMI's.

 One final issue is the abundance of decrepitation cracks and decrepitationrelated fluid inclusions associated with CSMI's (at Río Blanco and Okataina), and their near absence from glass inclusions. CSMI's have clearly decrepitated and degassed, but it could be suggested that glass inclusions degassed by diffusive-reequilibration. However, glass and CSMI's are in intimate and random coexistence; although diffusivereequilibration is possible, one would expect that it would affect adjacent inclusions more or less uniformly. The most likely explanation is that decrepitation to glass occurs at sufficiently high temperatures to "heal" any decrepitation crack, possibly by thermal annealing.

Experimental work by Bakker and Jansen (1991) on $H₂O$ loss from melt inclusions during extended heating, showed H_2O loss with no obvious signs of decrepitation. In that study the preferred mode of $H₂O$ transport was via structural dislocations and nanochannels. Viti and Frezzotti (2000) noted reequilibration of CO₂rich fluid inclusions in olivine crystals, associated with trails of minute fluid inclusions $($0.15\mu m$), undetectable by optical microscopy. Fluid loss in this case is shown to have$ favoured crystal structure dislocations, without leaving visible sign of its passage.

Inclusions that can be homogenised

The best test that a melt inclusion is not decrepitated and degassed is its ability

to homogenise it at a temperature likely to represent its trapping temperature. By this criterion, some small CSMI's at Río Blanco, and most glass inclusions at Okataina (characteristically with small shrinkage bubbles), are not decrepitated or degassed. Microprobe analyses shows little consistent difference in inclusion compositions between the Okataina samples. The most consistent difference appears to be the trapping temperature, as deduced from the homogenisation temperature. Inclusions with $T_{trapping}$ below 800°C cooled to small-bubble glass inclusions and $T_{trapping} > 825$ °C produced CSMI's. Specifically, a $T_{trapping}$ of 850°C (NZL4) or 880°C (NZL1g, NZL19) produced granular inclusions, and a $T_{trapping}$ of 825°C (NZL11) or 950°C (NZL22) produced crystal-rich inclusions.

Summary

Inclusions that homogenise:

- are representative of compositions of the magmas from which they were trapped
- the degree to which they crystalise daughter phases is dependent primarily on trapping temperature, rather than composition.

Inclusions that do not homogenise (at $\leq 1000^{\circ}$ C):

- have decrepitated and degassed,
- however, they may still retain co-trapped phases (e.g. composite inclusions), even if textures may have been destroyed by decrepitation-induced crystallisation (vapourrich CSMI's)
- the physical appearance of such melt inclusion depends on the conditions of decrepitation, ie. both CSMI's and large-bubble glass inclusions probably represent the same melt, both have decrepitated and degassed, but under different conditions. Several effects are associated with decrepitation, principally:
	- \bullet loss of H₂O and other volatile phases
	- changes to the solidus temperatures of inclusions, which causes an apparent increase in the alkali concentrations (due to non-melting of daughter quartz crystal)
- recalculation to 100 wt% does not reverse the compositional effects of decrepitation.
- attempting to reverse the effects by heating further depletes the $H₂O$ concentrations, and is made problematic by the lack of visual evidence for the point of complete melting of epitaxial daughter quartz.
- mass balance calculations may be useful, but require proof that there has been no alkali input during decrepitation, and data from other locations to test general

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validity.
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Chapter 15: Discussion and Conclusions

Discussion

Introduction

 Río Blanco melt inclusions provide convincing evidence for the coexistence of primary magmatic fluids with silicate melts, and Okataina melt inclusions demonstrate the post-trapping exsolution of such fluids. I show that both have implications for the study of the exsolution of volatile phases from melts, and the derivation of hydrothermal fluids from newly exsolved primary magmatic fluids. The implications of volatile phase exsolution on the processes of metal sequestration and transport are considered, before I list in summary the conclusions that can be drawn from this study.

Immiscibility in the Río Blanco magmas

Melt/melt immiscibility

 In considering the coexistence of primary magmatic fluids and silicate-melts there are extensive experimental studies that examine these coexistences at various pressures and temperatures (eg. Kennedy et al., 1962; Anderson and Burnham, 1965; Boettcher and Wyllie, 1969; Eggler, 1987; Paillat et al., 1992; Bureau and Keppler, 1999; Stalder et al., 2000; Stalder et al., 2001). At low pressures there exists a discrete solidus temperature (for a given composition and pressure) below which aqueous liquids and solid silicates coexist (ie the solidus shown in fig 15-1). Above the solidus there is a temperature (again for a given composition and pressure) at which melt and fluid exist as a single phase, referred to as the critical temperature (point b in fig 15-1). With increasing pressure the critical point approaches the solidus, and eventually crosses it at a point referred to as the second critical end-point (d in fig 15-2). At any higher pressure there is no solidus phase boundary, since the first critical point is now at a lower temperature. Under such conditions silicate melt and aqueous fluids are completely miscible in any proportion, and the resultant phase is defined as critical aqueous-silicic fluid (Stalder et al., 2000).

 The pressure required to achieve the second critical end-point is dependent on the composition of the silicate-fluid system involved. Several of these have been experimentally determined:

 1080° C and 10 kbars for the system $SiO₂-H₂O$ (Kennedy et al., 1962; Anderson and Burnham, 1965)

Fig. 15-1 Chart showing phase relationships during melting of a typical silicate melt. Solid lines represent the low pressure case (P1), in which solid silicate and fluids coexist below the solidus. Above the solidus, solid, melt, and fluid can coexist in various combination depending on temperature and percentage of fluid. At high temperatures and fluid concentrations aqueous fluid and melt coexist over a narrowing interval, as temperature increases, until at the first critical pressure (**b**) melt and fluid become completely miscible.

Dotted lines represent the case at a higher pressure (P2), at which the solidus has been decreased by the higher pressure, and the critical point now intersects the new solidus. The pressure at which the two intersect is called the second critical endpoint (2.CP). Above this pressure the critical point is now below where the solidus sould be, there is no true solidus, and silicate melt and aqueous fluid are completely miscible, the resultant phase being defined as critical aqueous silicic fluid.

Figure reproduced from Stalder et al., 2000.

Fig. 15-2 A representation of the above solvus diagram in isometric projection, showing the merging of the first critical point (**b**) with the solidus at the second critical end-point (**d**). At pressures greater than P2 the critical point is below the nominal solidus. Figure reproduced from Stalder et al., 2000.

- 700 $^{\circ}$ C and 20 kbars for the system NaAlSi₃O₈- H₂O (Paillat et al., 1992; Stalder et al., 2000)
- 515°C and 32.5 kbars for the system CaO-SiO₂-CO₂-H₂O (Boettcher and Wyllie, 1969)
- $>1000^{\circ}$ C and 120-130 kbars (estimated) for the system MgO-SiO₂-H₂O (Stalder et al., 2001)

Estimates of 35 to 60 kbars have been made for more complex systems, such as diopside-H₂O, peridotite-H₂O, Ca-bearing granites-H₂O, haplogranite-H₂O, Jadeite-H₂O and nepheline- H_2O , systems that might be found in various typical lower mantle compositions, and are consistent with lower mantle temperatures (Eggler and Rosenhauer, 1978; Bureau and Keppler, 1999; Mysen and Shang, 2003). The second critical end-point has also been demonstrated in exotic boron-rich melts at pressures as low as 4 kbar (Sowerby and Keppler, 2002). Somewhat controversially (see Sowerby and Keppler, 2002), Thomas et al., (2000), and Thomas and Foster, (2003) demonstrated that complete miscibility did occur in a fluorine-, boron-, and phosphorus-rich pegmatites at \sim 1 kbar and at 712 $^{\circ}$ C, possibly as a consequence of the multiple fluxing elements (several wt% each of F, B and P).

 For temperatures and pressures below the second critical end-point the solidus for melting is an isothermal phase transition and the solubility of H_2O in a silicate melt is no more than a few wt%, and the amount of silicate in an aqueous fluid (even if the fluid contains NaCl or $CO₂$) is even less (eg. Kennedy et al., 1962; Anderson and Burnham, 1965). However, at temperatures and pressures above the second critical endpoint there is no isothermal phase transition, thus melt and aqueous fluids would completely miscible in any proportion, from an aqueous fluid, to a silicate melt, and any composition in between.

 Early in the course of this research, before the Río Blanco extrusive samples became available, and before I completed the Okataina case study, I proposed a model (Davidson and Kamenetsky, 2001) which suggested that the miscibility gap at Río Blanco closed at the temperature and pressure inferred for the Río Blanco magmas. Thus H2O and silicate melt were completely miscible in all proportions, at a temperature not much greater than 850°C (the trapping temperature of Río Blanco melt inclusion), and near the pressure of phenocryst crystallisation (probably 0.5 kbar) ie. the Río Blanco magma was above its second critical end-point. Thus, the approximately continuous range of melt inclusion types at Río Blanco, from glass (Fig. 15-3a), through vapourpoor (Fig. 15-3b) to vapour-rich CSMI's, to hypersaline fluid inclusions (Fig. 15-3d), represented conjugate melt fractions evolving from melts with very high initial H₂O

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concentrations.

the inclusion types found in the La Copa intrusives. Melt (star) existing as a completely miscible melt/aqueous fluid cools until it reaches the immiscibility solvus, where it separates into conjugate melts. Since the melt is assumed to be completely miscible, there is no restriction in the possible H2O concentration. Composite inclusions represent co-trapping of immiscible volatile-poor (L1) and volatile-rich melt (L₂)

These initial H_2O concentrations would have been far too high, and too variable (10-90) wt% H_2O) for a sub-critical melt (max 6-8 wt% H_2O). Additionally, composite inclusions could occur which co-trapped everything from volatile-poor glass (Fig. 15- 3c), through increasingly volatile-rich melts, to magmatic vapour. This suggestion was based, in part, on an analogy with heating experiments on magmatic emulsions from a pegmatite in Germany, in which Thomas et al. (2000), and Thomas and Foster (2003) showed complete miscibility did occur in a fluorine-, boron-, and phosphorus-rich pegmatitic melt at \sim 1 kbar and at 712°C. As already noted, complete miscibility has been demonstrated at >10 kbars in haplogranitic melts (Bureau and Keppler, 1999; Stalder et al., 2000), and in boron-rich melts at pressures as low as 4 kbar (Sowerby and Keppler, 2002). If complete miscibility had occurred in the Río Blanco magma, reasonably close to the trapping temperature, then it would neatly explain the observed inclusions. No subsequent experimental work has demonstrated such a possibility, but absence of evidence is not evidence of absence

Melt/vapour immiscibility, via magmatic emulsions

In light of my subsequent research, I would now propose an alternative scenario,
which explains the observed inclusions at least as well as the old model (Davidson and Kamenetsky, 2001). I would suggest that vapour-rich CSMI's (that is, CSMI's with a large percentage of crystal-lined cavities (eg. Figs. 15-4, -5)) represent trapping of magmatic melt/vapour emulsions, rather than a single melt phase (ie a critical aqueoussilicic fluid, above its second critical end-point). Thus, the continuum between the vapour-poor and vapour-rich inclusions (e.g. Figs. 15-3a to -3b) may result from trapping of emulsions containing varying proportions of melt and magmatic vapour. Instead of a single continuous melt phase, I would suggest the existence of magmatic emulsions, which have some properties of a single phase, in particular, magmatic emulsions can contain variable proportions of the continuous phase (in this case melt) and dispersed phase (in this case magmatic vapour), without requiring complete miscibility at relatively low pressures (less than 10 kbars (Bureau and Keppler, 1999)). In this scenario there is homogeneous trapping of a of a magmatic emulsion below the second critical end-point, in which the emulsion may subsequently (during cooling) coalesce into separate melt and vapour bodies, and crystallisation of the melt commonly occurs.

 Inclusions (e.g. Fig. 15-7) noted in the Río Blanco extrusives demonstrated the trapping of a bubbly magmatic emulsion of aqueous liquid and vapour globules in a silicate melt. Their preservation in the extrusives is probably a quenching effect, as the complete crystallisation normally observed in Río Blanco CSMI's would have destroyed these textures. CSMI's with a small proportion of silicates (e.g. Fig. 15-5) would, therefore correspond to magmatic emulsions, and thus would be composite (crystalline silicate melt $+$ vapour) inclusions.

 Studies by Proussevitch et al. (1993) demonstrated that magmatic emulsions posses a degree of stability, and modelling by Shinohara (1994) and Shinohara et al. (1995) suggests that under conditions feasible for Río Blanco, magmatic emulsions could be stable for > 1 year. This is geologically brief, but it may be sufficient to permit trapping in quartz phenocrysts, given the estimated maximum growth rates for quartz phenocrysts of 3 mm/year (Swanson and Fenn, 1986).

 By the test proposed by Roedder (1984), composite inclusions of glass + crystalline silicate melt provide strong evidence for immiscibility. However, they may, in fact, trap globules of melt/vapour bubble emulsion, rather than two discrete silicate melts (one volatile-rich, the other volatile-poor). That is, the composite inclusions are showing immiscibility, but melt/vapour immiscibility (specifically an emulsion of vapour bubbles in melt), rather than melt/melt immiscibility.

Exsolution of aqueous phases

The maximum solubility of H_2O in silicate melts varies with temperature, pressure, and melt composition, but is shown experimentally to be \approx 6 wt% H₂O in a rhyolitic melt, at 2 kbars, and 850°C (Moore et al., 1998). On this basis, CSMI's at Okataina trapped melts that were at, or above H2O saturation, and probably so at Río Blanco. Thus, if magma can exsolve H_2O , it should be generated from these volatilerich melts, represented by CSMI's, and in fact evidence shows that primary magmatic fluids have been exsolved at both Río Blanco and Okataina:

- The existence of 1- and 2-phase aqueous globules $(\pm$ crystalline precipitates) in melt inclusions, vapour-rich at Río Blanco, liquid-rich at Okataina
- The magmatic emulsion inclusions in the Río Blanco extrusives, containing globules of 1-phase vapour or liquid, and/or 2-phase liquids, \pm crystalline precipitates

However, it is necessary to show that these aqueous fluids are primary magmatic fluids coexisting with silicate melts, rather than secondary refilling of shrinkage bubbles. As evidence for this:

- Vesiculation commonly occurs in previously homogenised glass inclusions from Okataina (shown to be volatile-rich) at, or just above, the α to β quartz transition temperature (573°C).
- Primary, aqueous fluid-only magmatic inclusions (liquid and vapour) in the Río Blanco phenocrysts imply an independent aqueous fluid phase in the magma.
- The elevated salinities of fluid globules, some of which contain clear crystalline precipitates, imply magmatic, rather than meteoric origin.
- Aqueous globules, particularly in the Río Blanco extrusives (Fig. 15-8), sometimes show signs of plastic deformation; shrinkage bubbles in the same inclusions do not. This implies different origins for globules and shrinkage bubbles, disproving refilling of shrinkage bubbles.

It seems probable, therefore, that both Río Blanco and Okataina exsolved aqueous phases. Moreover, the exsolved phases included vapour, and low- and high-salinity liquids.

The composition of exsolved primary magmatic fluids

 Microthermometry on a selection of La Copa 1-and 2-phase liquid-filled globules (Fig 5-85) has shown they typically have salinities in the range of $1 - 15$ wt% NaCl_{equiv}. Some Río Blanco inclusions contain globules with small amounts of clear crystalline precipitates (Fig. 5-79), and rare examples with a greater proportion of precipitates (Fig. 5-87) many have salinities \geq 50 wt% NaCl_{equiv}. Heating experiments Fig. 15-4 Electron photomicrograph showing a close up of a crystal-lined cavity in a CSMI; hosted in a quartz phenocryst, from an intrusive unit of the La Copa Rhyolite. Scalebar = $50 \mu m$

Fig. 15-5 Electron photomicrograph of a vapour-rich CSMI in a quartz phenocryst from an intrusive unit of the La Copa Rhyolite. The inclusion contains a small amount of silicates and a single halite crystal, growing directly on the host quartz. Scalebar = $50 \mu m$

Fig. 15-6 Composite inclusion containing glass and crystalline silicate melt, in a quartz phenocryst from an intrusive unit of the La Copa Rhyolite. Scalebar = $50 \mu m$

Fig. 15-7 Melt inclusion that trapped magmatic emulsion, in a quartz phenocryst from an intrusive unit of the La Copa Rhyolite. Scalebar = $25 \mu m$

Fig. 15-8 Composite inclusion containing glass, a shrinkage bubble, and two globules containing aqueous liquid. Note the parallel deformation in the aqueous globules, but not in the shrinkage bubble. Inclusions hosted in a quartz phenocryst from an extrusive unit of the La Copa Rhyolite.

Scalebar = $25 \mu m$

Fig. 15-9 Partly homogenised CSMI in a quartz phenocryst from the Don Luis Porphyry. The phenocryst was heated to 850°C for 48 hrs. Note the numerous salt-melt globules of various sizes in the homogenised glass. Scalebar = $25 \mu m$

on CSMI's from the Don Luis Porphyry have revealed very high-salinity brines, up to globules that can be considered salt-melts (Fig. 15-9), with salinities > 55 wt% NaClequiv.

At Okataina, 1-and 2-phase liquid-filled globules \pm volumetrically minor crystalline precipitates are noted (Fig. 10-47), suggesting salinities up to ≈ 40 wt% NaCl_{equiv}, given that salt crystals are present, but do not form a large fraction of any globule. The Okataina heating experiments created a range of globules, from singlephase vapour-rich inclusions with presumably very low salinities, to salt-melt globules with salinities > 55 wt% NaCl_{equiv}. PIXE analyses of these fluid-filled globules show a very wide range of compositions. The very high-salinity salt-melt globules noted from Río Blanco and Okataina are comparable with salt-melt globules from the Omsukchan Granite (Kamenetsky et al., 2003b), and salt-melt globules generated in other studies (Kamenetsky et al., 2003a).

 In summary, both Río Blanco and Okataina show exsolved fluids with salinities ranging from ≈ 1 to > 50 wt% NaCl_{equiv} in different primary inclusions. Fluid inclusions from the Don Luis Porphyry show a similar range. How can these variable salinities and compositions be explained? If the Okataina analyses of homogenised glass inclusions and matrix glasses are used as the start- and end-points of degassing, then the Okataina magma could theoretically lose 7.7 wt% H₂O, 0.04 wt% Cl, and 80 ppm of Cu (Table 12-7), with full degassing. This gives a fluid with a calculated salinity of approximately 0.86 wt% NaCl_{equiv} and a Cu concentration of \approx 1000 ppm. These figures are comparable with some precipitate-free aqueous fluid globules from the Río Blanco extrusives. However, PIXE analysis of salt-melt globules in homogenised glass inclusions shows 8-45 wt% Cl, and 2,800-33,400 ppm of Cu, which are comparable with hypersaline globules from the Omsukchan Granite, and with high-temperature fluid inclusions from quartz phenocrysts in the Don Luis Porphyry.

 To account for this apparent anomaly, I note that volatile phase exsolution can occur at various times during the cooling of magma, whenever the local concentration of any one volatile phase rises above saturation. The experimental exsolution of Cu-rich hypersaline globules (\approx salt-melt) is accompanied by only a slight reduction in H₂O content. Since H_2O saturation is a function of temperature, pressure, and melt composition, it is to be expected that the composition of volatile phases exsolved at (for example) high pressure would be different to those exsolved at low pressure. This has been demonstrated experimentally by Webster (1997, 2002), and Webster and Rebbert (2001). Thus the various combinations of temperature, pressure, and melt compositions should produce wide variations in the composition of exsolved phases. The range of compositions from unheated inclusions, and the experimental and resulting calculated

values are comparable, and mixing between the high- and low-salinity endmembers could produce values over the entire observed range.

 To this, I further note the heterogeneity observed in the study on the Omsukchan Granite (Kamenetsky et al., 2003b). Exsolution at various times during the cooling of a magma would produce volatile-rich phases with varying compositions, even if the processes were at equilibrium over the whole magma chamber, provided only that the exsolved phases did not re-equilibrate (which is consistent with the findings from Kamenetsky et al. (2002b). In Kamenetsky et al. (2003b), we showed that very smallscale heterogeneity was possible, down to different globules in the same melt inclusion. We proposed that this heterogeneity could be a function of timing of exsolution and finite diffusion rates. The exsolution and growth of a volatile phase globule would deplete a small volume of melt in those elements that preferentially partitioned into it, and would be "locked up" against re-diffusing into the melt. Any subsequent volatile phase globule that exsolved in that immediate vicinity, would only be in contact with a variably depleted melt, provided that convective mixing was not rapid enough to smooth out these locally depleted zones.

 Thus, both chamber- and very small-scale processes would tend to produce compositional heterogeneity, consistent with the extreme heterogeneity actually observed at Río Blanco and Okataina, and in our studies on the Omsukchan Granite (Kamenetsky et al. 2002b; 2003b).

When did exsolution occur?

 In the case of Río Blanco, the phase ratios between aqueous globules and melt are very variable, multiple globules occur in many inclusions, and many composite inclusions contain too much aqueous fluid for it to have exsolved post-trapping, without requiring pressure far in excess of those experience at Río Blanco. This implies inhomogeneous trapping, and by inference, that exsolution occurred pre-trapping.

 In the case of Okataina, phase ratios are fairly constant, melt inclusions only contain a single globule, and the volume of fluid globules in a given inclusion is not excessive relative to the volume of the inclusion. Although not sufficient to exclude the possibility of pre-trapping exsolution, the evidence suggests homogeneous trapping of a single melt, followed by post-trapping volatile phase exsolution.

VPE at Río Blanco and Okataina: summary models

 By way of a summary, I present models of the derivation of primary magmatic fluids from volatile-rich melts, from both Río Blanco and Okataina, and show how these relate to general late-stage magma chamber processes in felsic magmas.

Fig 15-10 Immiscibility solvus diagram representing conditions at Río Blanco. Melt **α** represents a silicate melt with > 6 wt% H_2O that exsolves conjugate melt and aqueous phases (**a** and **b**) upon crossing the immiscibility solvus. Melt **β** represents a volatilepoor melt (\approx 2.5 wt% H₂O) the existence of which may be implied by volatile-poor glass in composite inclusions of glass and crystalline silicate melt. Melt **β** does not cross the immiscibility solvus, and does not exsolve an aqueous phase. The fact that all Río Blanco glass inclusions currently have low H₂O concentrations (\approx similar to β ["]) is a function of decrepitation (probably at high temperature, see chapter 14), rather than reflecting original compositions.

Fig 15-11 Immiscibility solvus diagram representing conditions at Okataina. Melt **α** exsolves conjugate melt and aqueous phases (**a** and **b**) upon crossing the immiscibility solvus; note that this occurs below the trapping interval. The bulk composition of **α**'' is similar to **α**, and this is reflected in the analyses of most Okataina melt inclusions, which can be shown to be un-decrepitated by their ability to be homogenised. Inclusions trapped under these conditions may contain two phases (**a** and **b**), either as discrete globules of aqueous fluid (e.g. figs 10-47 to 10-51), or vesiculation (e.g. figs 10-24, - 25), or the aqueous phase may be represented by hydrous daughter crystals (e.g. figs 10- 15 to 10-18).

The models are based on data from homogenisable melt inclusions, which have been shown to be representative of Río Blanco and Okataina magmas. Application of the model to Río Blanco is complicated by the endemic decrepitation; thus meaningful H_2O concentrations are not available, so some parameters from Okataina are used in figure 15-10, simply by way of illustration. The inclusion trapping interval is 825-850°C, based on the range of $T_{h(min)}$ values, and measured H_2O concentrations for Okataina inclusions indicate melts average $6-8$ wt% $H₂O$. A probable immiscibility solvus boundary is included in figures 15-10, -11; that is, the temperature/volatile concentration limit (for a given pressure) at which silicate melt and H2O become immiscible. Since most Okataina melt inclusions show trapping of a single melt phase (ie no immiscibility at the trapping temperature), the solvus boundary must be > 6 wt% H_2O in the trapping interval, and may be as high as 8 wt\% H_2O . Therefore, the hypothetical solvus boundary is shown within these limits, and with slopes such that the trapping occurs on the solvus, in the case of Río Blanco, and above the solvus at Okataina. The end of the immiscibility boundary is uncertain, but it presumably ends near the glass transition temperature, when the melt is too viscous to exsolve a fluid phase. However, as the following discussion shows, the existence of an immiscibility gap is important, but the exact position of the boundaries (within limits) is not.

Río Blanco

 The starting point for this model is a volatile-rich magma, in which crystallisation of anhydrous silicate phenocrysts progressively enriches the melt in volatiles and incompatible elements. A volatile-rich melt (**α,** Fig. 15-10), presumed to contain > 6 wt% H₂O, crosses the immiscibility gap, and is forced to exsolve conjugate melt and an aqueous volatile-rich phase (a and b, Fig. 15-10). By exsolving aqueous fluid as needed, the melt composition evolved down the immiscibility solvus during continued cooling. Within the trapping interval volatile-rich melts could be trapped as melt inclusions (α') , and cooled to the glass transition temperature to form a glass inclusion (**α**''), which would have had high volatile concentrations, if decrepitation had not occurred.

 The existence of composite inclusions containing glass and crystalline silicate melt with 2 wt% H_2O in the glass suggests that volatile-poor melts may have existed at Río Blanco, possibly as the result of local exsolution of aqueous phases in the melt. Such melts are represented (Fig. 15-10) by volatile-poor melt (**β**), and trapped (**β**'), and cooled to the glass transition temperature to form a glass inclusion (**β**''). In this case the inclusions would have a low $H₂O$ concentration without the effects of decrepitation.

 Inclusions trapped at Río Blanco could sample any phase or phases coexisting over the trapping interval, ie. volatile-rich silicate melts, primary magmatic vapour, rare aqueous liquids, and volatile-poor melts (if present), and possibly emulsions of these as well. The combinations of these give rise to the range of composite inclusions observed in the La Copa Rhyolite. Examples of trapped magmatic emulsions in the La Copa extrusives are well-preserved (Fig. 15-7). In the La Copa intrusives, these textures have been destroyed by crystallisation, but are probably represented by vapour-rich CSMI's (e.g. Fig. 15-5).

 We have shown that magmatic emulsions may have sufficient stability to survive on the timescales of quartz phenocryst growth, so there is also the possibility of trapping melt containing a globule of magmatic emulsions. In the La Copa extrusives this may be represented by inclusions such as figure 15-12. In the intrusives, the rare examples of composite inclusions containing glass and crystalline silicate melt may represent the same occurrence, with the melt cooled to glass, and the globule of magmatic emulsions now crystallised to a CSMI (Fig. 15-6).

Fig. 15-12 Magmatic emulsions inclusion; showing preferential segregation of emulsion to one side of the inclusion. This could be interpreted as a "globule" of magmatic emulsions in bubble-free melt. CA30. 25µm scalebar

Okataina

For illustration purposes, melt with an initial H_2O concentration of 6-8 wt% H2O is proposed (**α**, Fig. 15-11), which cools towards the glass transition temperature, crossing the solvus (which pushes inclusion towards $H₂O$ saturation) as it does so. Within the trapping interval, a volatile-rich melt fraction could be trapped as a melt inclusion (α') above the immiscibility gap. The melt continues cooling, and eventually crosses the immiscibility solvus, and exsolves conjugate melt/aqueous phases in response.

 This occurs both inside any trapped melt inclusions, and in the magma chamber at large. Within the inclusion, the reduction in the H_2O saturation level may be expressed in one of three ways:

- 1. The sudden vesiculation of previously homogenised glass inclusions at the **α** to **β** quartz transition temperature (573°C, as observed in some Okataina heating experiments). Granularity is common in many Okataina inclusions, and has exactly the same appearance as experimentally induced vesiculation, suggesting that this is a common response to an inclusion crossing the immiscibility gap.
- 2. The high $H₂O$ concentration in volatile-rich melts may promote crystallisation of hydrous minerals, either as crystal-rich inclusions (Fig. 10-2) or as the dust-like green crystals noted in some glass inclusions (Fig. 10-31). These two possibilities are not mutually exclusive, so vesiculation and crystallisation of daughter phases is common.
- 3. If sufficient H_2O exsolved in the inclusions, aqueous globules may be formed.

The responses of trapped melt inclusions, therefore, mimic those occurring within the magma chamber. The trapped melt should continue exsolving conjugate melt and aqueous volatile phases as it cools to the glass transition temperature, but the bulk composition is the same as that sampled at **α**, or **α**'. Likewise, the amount and composition of the exsolved phase (b, on Fig. 15-11) should be a proxy for the fluids released during volatile phase exsolution over the same interval.

Cooling magmas and the derivation of hydrothermal fluids

 Melt inclusions from Río Blanco and Okataina demonstrate the existence of volatile-rich melt fractions during the crystallisation of quartz and feldspar phenocrysts, in both magmas. Further, magmatic emulsion inclusions (represented by various types of composite inclusions) provide a snapshot of the moment of exsolution of aqueous volatile-rich phases, and of their heterogeneous compositions. From the moment of exsolution, the composition of primary magmatic fluids is heterogeneous. My research has shown a progression from:

- volatile-rich melts (with no independent fluid phase),
- to emulsions of melt and primary magmatic fluids,
- to primary aqueous magmatic fluids.

This last phase coexists with the largely crystallised magma, in the almost solid carapace (represented by the Don Luis Porphyry inclusions). The primary magmatic fluids are hypersaline metal-rich brines, which by any definition constitute hydrothermal fluids.

My research stops at the carapace of a magma chamber, but there are abundant examples in the literature, which trace the progressions from hydrothermal fluids streaming out of a pluton, and into orebodies.

Conclusions

 Conclusions have already been drawn for Río Blanco (chapter 8) and Okataina (chapter 12), for those issues specific to each, and it is not intended to duplicate them here. Rather I intend to draw general conclusions using evidence from both studies. Although both studies use rocks from very different tectonic environments, many similarities are noted between their melt inclusion populations. Both trap populations of coexisting glass and CSMI's, and both show evidence of the exsolution (and trapping) of an aqueous phase. There appear to be only two main sources of difference:

- 1. Phenocryst crystallisation pressures: volatiles exsolved at Río Blanco $(< 0.5$ kbars) did so as sub-critical, vapour-dominated 2-phase fluid, at Okataina (2-3 kbars) they would have done so as single-phase supercritical fluids.
- 2. Timing of exsolution: evidence shows that fluids began exsolving at Río Blanco prior to trapping of melt inclusions, at Okataina the evidence favours exsolution after trapping.

Conclusions may be drawn from the melt inclusions regarding the exsolution of volatile phases, from silicate melts, via exsolution as magmatic emulsions, to hypersaline hydrothermal fluids. Conclusions regarding melt inclusion studies generally were summarised in chapter 14.

Exsolution of volatile phases

 At both Río Blanco and Okataina I have shown the progression from volatilerich melts, through the exsolution of aqueous volatile-rich fluid phases (involving a magmatic emulsion stage at Río Blanco), to discrete melt and aqueous fluid fractions. These fluid fractions are metal-rich, having sequestered metals from the melt, and at least at Río Blanco may have produced mineralisation. In addition to demonstrating the processes, melt inclusions at Río Blanco and Okataina sample all the phases evolved during this process. Conclusions regarding the process of volatile phase exsolution can be grouped under three headings.

- 1. Melts: which covers the "raw material" for exsolution
- 2. Magmatic emulsions: which, at Río Blanco, sample exsolution as it was occurring
- 3. Primary magmatic fluids: which considers the actual aqueous, metal-rich fluids exsolved

Melts

- CSMI's and large-bubble glass inclusions coexist at both Río Blanco and Okataina. At Okataina it can be demonstrated that both types of inclusions trapped the same volatile-rich melt (> 6 wt% H₂O), at Río Blanco this is probable, but not certain.
- At Río Blanco and Okataina inclusions that homogenise sample un-degassed melts, and represent the original melt compositions.
- Heating experiments on some Okataina melt inclusions were able to reproduce the exsolution of aqueous phases from volatile-rich melts, enabling quantification of volatile phase exsolution.

Magmatic emulsions

- Magmatic emulsions are trapped in melt inclusions in the La Copa intrusives, and are probably represented by vapour-rich CSMI's in the intrusives.
- Magmatic emulsions represent the moment of exsolution at Río Blanco, and provide samples of all phases during the process of exsolution.
- Magmatic emulsions may act (briefly) as an independent melt fraction, and therefore may need to be considered in magma dynamics / fractionation.
- In inclusions which trap magmatic emulsions, the size of the dispersed phase (globules) is roughly the same as their size in the original melt, and is a real indication of the size scale of products of immiscibility at the point of exsolution.
- The dispersed phases in magmatic emulsions show very pronounced compositional heterogeneity; even to the extent of globules in the same melt inclusion. The compositional heterogeneity observed in these dispersed phases implies that they not only represent the original size of immiscible globules, but also preserve their original compositions and compositional heterogeneity. Magmatic emulsions, and particularly the volatile-rich globules in them, therefore provide the researcher with a window into the moment of exsolution of aqueous volatile-rich phases.
- Magmatic emulsions are, at best, metastable, and must eventually disperse, and the globules coalesce into large globules of primary magmatic fluid, independently rising in a volatile-poor (or at least less volatile-rich) melt. These large globules of primary magmatic fluid presumably progress to form hydrothermal fluids, such as were trapped in the Don Luis Porphyry or the Omsukchan Granite (Kamenetsky et al., 2003b). Thus, magmatic emulsions are directly parental to hydrothermal fluids.

Primary magmatic fluids

- Aqueous phases occurring within melt inclusions at both Río Blanco and Okataina sample fluids exsolved directly from the magmas, both sampling the composition of individual aliquots, and demonstrating the heterogeneity such aliquots may have during the cooling and crystallisation of magma.
- Exsolved primary magmatic fluid phases range from magmatic vapours, through 1 and 2-phase aqueous liquids, to hypersaline brines and salt-melts.
- In the Don Luis Porphyry, aqueous phases exsolved from the magma are parental to the hydrothermal fluid inclusions found in quartz phenocrysts in the carapace, and provided metals and volatiles to the fluids given off during cooling of magma body. Analyses of melt and fluid inclusions show a progressive enrichment in metals from the silicate-melt, through the magmatic vapour-phase to hypersaline hydrothermal fluids.

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Appendix A

Microprobe Analyses

replicate analyses, permitted total wt% varied between 99.0 - 100.5 wt%, and the

equipment was re-calibrated if values fell outside this, >75% of these analyses were between 99.5 - 100.0 wt%.

 In the table; type, refers to the inclusion type (see abreviations), and host is the phenocryst containing the analysed inclusion (quartz or feldspar). All analyses are given in wt%, truncated to two decimal places, the total is also truncated to two decimal places.

Heating experiments

 The analyses listed here are the results of bulk heating experiments; La Copa Rhyolite - 850°C for 96 hrs, Okataina- NZL1g, to 890°C over 2 hrs, and NZL2d, to 950° C over 3 hrs. All bulk heating experiments were air-quenched, estimated cooling rate \approx 800°C/min (ie. cool enough to touch in ≤ 1 min.). Analyses of heating experiments on CA31 only analysed completely crystal-free glass inclusions. Subsequent analyses were also performed on inclusions containing residual crystals, and these are presented as unaveraged analyses.

Appendix B

Publications

Refereed papers:

- Davidson, P., and Kamenetsky, V. S., 2001, Immiscibility and continuous felsic meltfluid evolution within the Rio Blanco porphyry system, Chile: Evidence from inclusions in magmatic quartz: Economic Geology, v. 96, p. 1921-1929. *The candidate performed the research on which this paper was based, wrote the draft and prepared the illustrations, with the assistance of Dr. Kamenetsky.*
- Kamenetsky, V. S., Davidson, P., Mernagh, T. P., Crawford, A. J., Gemmell, J. B., Portnyagin, M. V., and Shinjo, R., 2002a, Fluid bubbles in melt inclusions and pillow-rim glasses; high-temperature precursors to hydrothermal fluids?: Chemical Geology, v. 183, p. 349-364.

In this paper Dr. Kamenetsky wrote most of the text, and performed the bulk of the research in conjunction with Crawford, A. J., Gemmell, J. B., Portnyagin, M. V., and Shinjo, R., with analytical services provided by Mernagh, T. P. The candidate wrote the inclusion descriptions, and assisted Dr. Kamenetsky writing the text and preparing illustrations.

- Kamenetsky, V. S., De Vivo, B., Naumov, V. B., Kamenetsky, M. B., Mernagh, T. P., van Achterbergh, E., Ryan, C. G., and Davidson, P., 2003a, Magmatic inclusions in the search for natural silicate-salt melt immiscibility: methodology and examples, in De Vivo, B., and Bodnar, R. J., eds., Melt inclusions: methods, applications and problems. Developments in Volcanology: 5. Melt inclusions in volcanic systems: methods, applications and problems, p. 65-82. Elsevier, Amsterdam..
- Kamenetsky, V. S., Naumov, V. B., Davidson, P., Achterbergh, E. v., and Ryan, C. G., 2003b, Immiscibility between silicate magmas and brines in the Omsukchan Granite (NE Russia): melt inclusion probe into magmatic-hydrothermal transition: (in press).
- Kamenetsky, V. S., van Achterbergh, E., Ryan, C. G., Naumov, V. B., Mernagh, T. P., and Davidson, P., 2002b, Extreme chemical heterogeneity of granite-derived hydrothermal fluids; an example from inclusions in a single crystal of miarolitic quartz: Geology, v. 30, p. 459-462.

In these papers Dr. Kamenetsky wrote the text, and performed the bulk of the research in conjunction with De Vivo, B., and Naumov, V. B., with analytical services provided by Mernagh, T. P., van Achterbergh, E., and Ryan, C. G. The candidate assisted Dr. Kamenetsky writing the text and preparing illustrations.

Abstracts

15th Australian Geological Convention, Sydney

Oral Presentation:

Melt inclusion studies of immiscible hydrosaline magmatic fluids: the first stage of hydrothermal fluids?, Paul Davidson, Vadim Kamenetsky: In Skilbeck, C. G. and Hubble, T. C. T. (eds), 2002; Understanding Planet Earth; Search for a sustainable future. Abstracts of the $15th$ Australian Geological Convention, University of Technology, Sydney, NSW, Australia. July 3-7 2000, No. 59, p118

16th Australian Geological Convention, Adelaide

Oral Presentation:

Magmatic fluids coexisting with felsic melts: An example from Rio Blanco, Chile. Paul Davidson, Vadim Kamenetsky, Pete Hollings, Dave Cooke, Peter Frikken: In Preiss, V. P. (ed), 2002, Geoscience 2002; Expanding Horizons. Abstracts of the 16th Australian Geological Convention, Adelaide Convention Centre, Adelaide, SA, Australia. July 1-5 2002, No. 67, p 205

Poster Presentation:

Volatile phase exsolution - how it happens in nature? An insight from rhyolitic magmatic inclusions, Taupo Volcanic Zone, New Zealand. Paul Davidson, Vadim S. Kamenetsky, Sharon Allen: In Preiss, V. P. (ed), 2002, Geoscience 2002; Expanding Horizons. Abstracts of the 16th Australian Geological Convention, Adelaide Convention Centre, Adelaide, SA, Australia. July 1-5 2002, No. 67, p 80

Giant Ore Deposit Workshop, Hobart

Poster Presentation:

Magmatic fluids coexisting with felsic melts: An example from Rio Blanco, Chile. Paul Davidson, Vadim Kamenetsky, Peter Hollings, David R. Cooke, Peter Frikken: In Stewart, A. L., Agnew, M. W., and Cooke, D. R. (eds) Giant Ore Deposit Workshop Hobart Centre for Ore Deposit Research p 9-11

2002 Goldschmidt Conference, Davos, Switzerland

Poster Presentation:

Magmatic fluids coexisting with felsic melts: An example from Rio Blanco, Chile. Paul Davidson, Vadim Kamenetsky, Pete Hollings, Dave Cooke, Peter Frikken: In Podosek, F. A. Goldschmidt 2002, Davos, Geochimica et Cosmochimica Acta, 1, p A169

The candidate performed the research on which these seminars ware based, wrote the abstracts and text, and prepared the illustrations and visual presentations, with the assistance of Dr. Kamenetsky. Sharon Allen, Pete Hollings, Dave Cooke, and Peter Frikken provided samples and geological information on Okataina and Río Blanco. All oral presentations and posters were presented by the candidate, except the poster for the 2002 Goldschmidt Conference, which was created by the candidate, but presented by Dr. Kamenetsky.