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

Chapter 1

Statement of the problem

At least as far back as the experimental work of N. L. Bowen and his co-workers, it was recognised that the addition of small amounts of H₂O to silicate melts significantly reduce their liquidus temperatures (e.g. Bowen and Tuttle, 1950). Further, much of the H₂O which can dissolve in silicate melts commonly cannot be incorporated into the formation of hydrous minerals during crystallisation, so during the cooling of magma a volatile-rich immiscible phase(s) may be exsolved (e.g. Burnham, 1967). There is a general, but by no means universal agreement that under some circumstances, these volatile-rich phase(s) may evolve into the hydrothermal fluids responsible for mineralisation (e.g. Gustafson and Hunt, 1975; Henley and McNabb, 1978; Reynolds and Beane, 1985; Hunt, 1991; Hedenquist and Lowenstern, 1994). From both observational and experimental work we have a broad understanding of fluid and melt immiscibility (the Volatile Phase Exsolution (VPE) of Candela (1991)), and the subsequent evolution into hydrothermal fluids (e.g. Shinohara and Hedenquist, 1997). However, we are a long way from understanding these processes in detail. Further progress is hampered by the limited availability of detailed studies of immiscibility, and magmatic / hydrothermal fluid evolution, in natural systems. There is enormous variability in temperature, pressure, major and minor element composition, water content, emplacement and cooling histories between magmatic suites in different tectonic settings. Thus, the limited number of published studies does not provide us with a sufficiently wide base from which to extend our understanding.

To study such problems robust techniques are required to examine processes that occurred at, or near, magmatic temperatures and pressures, after millions of years of subsequent cooling, interactions with various fluids, and eventual exhumation and alteration. The problem is thus two-edged, firstly to devise or extend an existing methodology capable of use wherever possible. Then to use those techniques to investigate in detail examples of melt-phase immiscibility from several different magmatic suites, to characterise the processes of immiscibility, the compositions of these phases, and, where possible, to follow the evolution of such phases into
hydrothermal fluids.

In a general sense, the questions related to immiscibility need to be addressed by the following research:

- Examining the processes of volatile-phase immiscibility in natural magmatic systems, in order to establish, so far as is possible, the physical and chemical controls on these processes, and to compare this with the results from experimental systems.
- Measuring major and minor element concentrations of magmatic phases, particularly volatiles, metals, and ligands in natural magmatic systems, in order to better understand the effect of VPE on the composition of new immiscible phases.
- Exploring the evolution of primary magmatic fluid phases into potentially ore-forming hydrothermal fluids.

These issues need to be studied using techniques that can be applied as widely as possible. However, such techniques must carry certain limitations, as all research techniques do, and this study needs to ascertain those limitations and explore the general applicability of the evolved methodology.

**Rationale for this study**

**The significance of volatile-rich phase immiscibility**

It is possible for magma to differentiate from a low-volatile silicate melt, to a late-stage volatile-rich residual melt, with no phase changes other than crystallisation. However, it is more likely that fluid immiscibility will occur, as the melt reaches volatile saturation and volatile phase(s) exsolve. The processes, continuous up to that point, will suddenly become discontinuous. The newly formed immiscible volatile-rich phase is likely to have significantly different physical properties than the residual magma. It may be less viscous (most volatile phases and some silicate melts), and it may be relatively less dense (aqueous and CO$_2$-rich phases), or more dense (sulphide globules). If the immiscible phases have very different physical characteristics they may separate readily under gravity, unless the melt is too viscous. Thus there will be a discontinuity in the composition of residual melt, and the creation of a new phase, which may separate from the parent melt, selectively removing volatiles. The creation of an immiscible fluid phase is not necessarily a single-step process, since one or more of the immiscible fluid phases may itself undergo immiscible separation as they continue to evolve. For example, a high-salinity magmatic brine resulting from an initial stage of immiscibility may separate into a high-salinity fluid and a low salinity vapour (“boiling”) due to
pressure reduction.

From natural systems, there are a number of types of immiscibility related to volatile saturation:

- silicate melt / high-salinity aqueous fluid
- silicate melt / low-salinity aqueous vapour
- silicate melt / CO$_2$ fluid
- silicate melt / salt melt
- silicate melt / sulphide melt
- high-salinity aqueous fluid / low density vapour (“boiling”)
- aqueous fluid / CO$_2$ fluid
- silicate melt / carbonatite melt

(Roedder, 1984)

Of these, the first two will be the main objects of this study. In addition to the above there are some rare examples of melt/melt immiscibility not related to volatile saturation:

- silicate melt / Fe-rich silicate melt (Philpotts, 1976; Philpotts, 1982; Markl, 2001)
- silicate melt / oxide melt (Roedder, 1984)
- silicate melt / phosphate melt (Roedder, 1984)

Given the abrupt and significant changes to melt composition possible from such processes, fluid immiscibility can exert measurable controls on petrogenesis. However, as the volatile-rich phases are unlikely to survive solidification of the magma unchanged, it can be very difficult to recognise the significance, and even the former presence of fluid immiscibility.

**The significance of volatiles in natural silicate melts**

Volatiles (e.g. H$_2$O, CO$_2$, Cl$^-$, S$^{2-}$ SO$_4^{2-}$, F, B, Li) generally comprise only a small part of magmas, typically 10's - 1000's of ppm in most melts (e.g. Holloway, 1976; Carroll and Rutherford, 1985; Webster, 1997a; Ducea, 1999), except for H$_2$O which can reach 8 wt% in felsic magmas (e.g. Lowenstern, 1994) but is typically 4-6 wt% (e.g. Johnson et al., 1994; Moore et al., 1995, 1998; Holtz et al., 2001). Many volatile elements have low solubilities in silicate melts, which decrease with decreasing temperature and pressure, and most partition readily into any available aqueous fluid. Moreover, most volatiles are incompatible with rock-forming silicates, particularly early crystallising phases, which results in the volatiles concentrating in the late crystallising fractions of a cooling igneous body

Although volatiles are normally minor components of magma, they can exert a
disproportionate control on a variety of petrological processes:

- Reducing the viscosity of a silicate melt, which may in turn affect the efficiency of crystal fractionation (Pichavant, 1981).

- Controlling the solubility of other volatiles; for example, the solubility of H$_2$O in a silicate melt is affected by the concentrations of CO$_2$, Cl$^-$, F, B (among other factors) (e.g. Holtz et al., 1993; Webster, 1997b; Shmulovich and Graham, 1999).

- Controlling the eutectic and cotectic points of other phases in silicate melts, to the extent that the concentrations of volatile elements may determine which phases can, and cannot, crystallise from a given magma, at a given temperature (e.g. Pichavant and Manning, 1984; Pichavant, 1987).

- The presence of one volatile in particular, H$_2$O, promotes crystallisation in a silicate melt or a silicate glass, and significantly decreases the liquidus and viscosities of silicate melts (e.g. Dingwell, 1998, 1999; Bowen and Tuttle, 1950).

- Volatile concentrations (particularly H$_2$O & CO$_2$) may provide the power source for eruptions, in part determining if eruptions are explosive or effusive, or even whether or not a magma vents to the surface (Johnson et al., 1994; Gilbert and Sparks, 1996; Slezin, 2003).

- Metals preferentially partition in volatile-rich phases (e.g. Candela and Holland, 1984; Heinrich et al., 1992; Candela and Piccoli, 1995; Williams et al., 1995), and volatile concentrations in melts may exert controls on metal partitioning (e.g. Keith et al., 1997).

Given that most volatiles are incompatible in silicate melts, at some point during fractionation the volatiles will probably achieve saturation, even with very low concentrations of volatiles in the parental melt. Vapour saturation of magma occurs when the sum of vapour pressures of the individual volatile species exceeds the total confining pressure. If multiple volatile species are present, vapour saturation may occur even though the solubilities of no single species is exceeded (Carroll and Holloway, 1994).

As with fluid immiscibility, the evidence of the original volatile composition of a magma, and its evolution, generally does not survive final solidification. Degassing, in whatever form, removes most volatiles from a melt, and leaves little evidence to recreate the concentrations present during the critical stages of cooling and crystallisation. The aim of this study, to find evidence for fluid immiscibility, and to analyse the compositions of magmatic phases, may go some way to recreate those concentrations in the rock suites under study.
The significance of immiscible aqueous fluid phases

One very important consequence of fluid immiscibility is the potential for the evolution of metal-rich hydrothermal fluids, as metals (in this study particularly Cu, Pb, and Zn) preferentially partition into any available volatile-rich fluid phase. If sufficient volumes of metal-enriched hydrothermal fluids can migrate to a trap site, economic mineralisation may result (e.g. Heinrich et al., 1992; Reyf, 1997). In the absence of such phases, metals will be dispersed throughout the cooled magma as sub-economic traces (e.g. Cline and Bodnar, 1991). The extent of volatile phase exsolution, and its timing relative to crystallisation (Cline and Bodnar, 1991), can strongly affect metal sequestration and transport, and so may have strong economic implications. However, even if no mineralisation occurs, the crystallisation of even a small pluton will produce millions of tons of saline aqueous fluids. These fluids will still interact with wall rocks, potentially producing locally important changes such as Na- or K-metasomatism.

Methodological significance of this study

The end-point of this study is to examine immiscibility processes, and the derivation of hydrothermal fluids in natural systems. The primary investigative method will be melt inclusion studies. Melt inclusion studies are a relatively new, and rapidly progressing field, with consequent rapid expansion of the knowledge base and techniques. Each new study has the potential to aid in this growth, and it is a subsidiary aim of this study to contribute to the development of techniques for the study of glassy, and more complex magmatic inclusions.

A central plank of melt inclusion studies is that un-decrepitated and un-degassed melt inclusions represent a good approximation to the originally trapped magmas. Decrepitation and degassing clearly compromises this position, but need not completely negate it. Some evidence may remain; for example, metal concentrations in decrepitated and degassed melt inclusions at least represent a minimum value. In an ideal world, all melt inclusions would be un-decrepitated and un-degassed, and all studies would have an inexhaustible supply of pristine inclusions to work with. However, in the real world, the largest problem in melt inclusions studies is often obtaining melt inclusions to study. Preservation is so problematic that a researcher typically finds useable melt inclusions, then seeks questions that they can answer. This is almost the reverse of normal practice in geology, which is to begin with the rocks, then seek techniques to extract the desired information. I have previously undertaken a melt inclusion study in the conventional manner, attempting to construct a genetic model for mineralisation at Mt Morgan in Queensland. I personally selected samples in the field from all of the units involved, or
likely to have been involved in mineralising events, and none of them contained any melt inclusions. Thus, the primary requirement for a melt inclusion study is, therefore, rocks in which melt inclusions are present. However, decrepitated and degassed inclusions are invariably present in samples containing melt inclusions, and in many locations they are the only melt inclusions still existing (e.g. Shila, in Peru (Grancea et al., 2002)). The fact that an inclusion is decrepitated and degassed may limit the information that it can provide, but does not necessarily negate all usefulness. For these reasons one aim of this study must be to examine the processes and consequences of decrepitation and degassing, with a view to determining what information, if any, a decrepitated and degassed inclusion can provide. For example:

- Are the traditional petrographic indicators of decrepitation (e.g. Roedder, 1984; Lowenstern, 1995; Frezzotti, 2001) always reliable and adequate?
- Do all melt inclusions in a given sample, or phenocryst, decrepitate and degas in the same way? And to the same extent?
- Does decrepitation and degassing simply remove H2O, and other liquid or vapour phases?
- Are major and minor element concentrations affected? If so, what elements, and to what extent?
- Can the compositional effects of post-trapping degassing be reversed, or at least quantified?

Definitive answers to these questions may- or may not be obtainable, and some answers may be in the negative. Moreover, the potential solutions will depend to some extent on the coexistence (or otherwise) of un-decrepitated and un-degassed inclusions, which provide a “benchmark”, at least for geochemical data. However, I contend that one avenue for expanding the scope of melt inclusion studies is the ability to extract useful and reliable information from less than perfect inclusions. This is particularly so in relation to quartz-hosted melt inclusions, and genetic studies of particular orthomagmatic orebodies, where decrepitated and degassed inclusions are common (sometimes ubiquitous), and the researcher has to work with the rocks available to him.

**Aims of this study**

This study will investigate techniques appropriate to the study of late-stage magmatic processes involving VPE, and the derivation of hydrothermal fluids, in both mineralised and barren systems. Such techniques need to be robust enough to deal with the vagaries of melt inclusion formation and preservation, and thus the limitations and applicability must be examined, in particular:
• The processes and consequences of decrepitation and degassing
• What information can reliably be gained from such inclusions, and
• What methods (if any) can be used to recover geochemical data from decrepitated and degassed inclusions?

As the techniques are devised or improved they will be used to investigate late-stage magmatic processes in mineralised and barren systems, in particular the following issues need to be addressed:

• Immiscibility processes in felsic melts (what kinds of immiscibility occur, eg melt/melt, melt/vapour, and liquid/vapour, and how do they occur?)
• The physical characteristics of immiscible phases, in particular temperature and pressure
• The compositions of immiscible phases
• The effects of immiscibility on the sequestering of metals
• The derivation of hydrothermal fluids from immiscible melt phases

However, these aims are not sequential, results from each stage of research will be used to improve techniques, and thus expand the scope of further investigations.

Why study melt inclusions?

Given that my intention is to study magmatic processes occurring at temperatures of 1000°C or more, occurring in active magma chambers at depths of several kilometres, my proposed methodology requires a detailed description and justification. The path from magma to plutonic rock involves irreversible stages of crystallisation, fractionation, degassing, and perhaps post-magmatic alteration. The composition of a plutonic rock (in particular, its original volatile content) is unlikely to bear any resemblance to the magma from which it derived. Ideally, I would like to be able to study samples of the various magmatic phases trapped in "containers" at the time they formed, and which have subsequently avoided leakage, contamination, or post-magmatic alteration. Perfect closed system "containers" do not exist, but there may be a readily available approximation. Magmatic inclusions trapped in phenocrysts provide the nearest thing to a sample of magmatic phases (within certain limitations) that we are likely to find, and thus are central to this thesis. However, there are certain inherent limitations to the use of magmatic inclusions, and these need to be examined in light of the conditions affecting melt inclusion formation and preservation.
Structure of this thesis

Given a statement of the aims, the proposed research is based largely on magmatic inclusions, and chapter 2 examines the techniques used in this study. Chapter 3 discusses the analytical techniques, their uses, and limitations.

Two case studies contain the bulk of the research in this study, Rio Blanco, Chile, and Okataina, North Island of New Zealand. Each case study begins with a discussion of local and regional geology, to place the study in a geological context. The inclusions in the samples are then described in detail, as are the analyses and the results of experiments performed on the inclusions to better understand them. Each case study finishes with a discussion and conclusions detailing what the inclusions can tell us about conditions at, and prior to their formations. This study is aimed at better understanding of late-stage magmatic processes in mineralised and barren systems, and developing methodologies to do so. This is not a study of rocks per se, rather, what rocks can tell us about the processes involved. Samples used in this study were collected in the field by specialists involved in detailed geological studies of the areas involved, and have been provided with all relevant details, and some whole rock analyses. Samples have been selected that are fresh and unaltered and contain melt inclusions. The latter being the crucial requirement. It is the task of this researcher to extract all possible information relating to late-magmatic processes, to devise or improve a methodology to do so, and to evaluate the potential and limitations of this methodology in the context of the samples available.

With the conclusion of the case studies there follows an evaluation of the research philosophy employed, examining its strengths and weaknesses, particularly in relation to less-than-perfect samples. The individual studies are simply specific cases of general late-stage magmatic processes, of the kind that occurs in numerous other settings, so this study ends by drawing together the common themes and drawing overall conclusions.
Chapter 2: Melt inclusion study techniques

Introduction

The previous chapter gave the aims of this thesis, and explained how a magmatic inclusion study may achieve those aims. This chapter examines the techniques employed in magmatic inclusion studies, and the following chapter discusses the analytical techniques used, before proceeding to the first case study.

A magmatic inclusion study begins with sample selection and preparation, followed by petrographic examination. The purpose of this examination is to understand the types and variations of inclusions present, and to detect compromised inclusions unsuitable for further study. The end point of this work should be a known and described population of inclusions, suitable for analysis.

Melt inclusion studies aim at extracting information regarding magmatic processes, so the cooling and crystallisation experienced by an inclusion invariably cause changes in the inclusion, limiting the researchers ability to draw conclusions. Various experimental techniques have been devised to better approximate the conditions of the inclusion at the time of trapping, and overcoming some of these limitations. These involve heating selected inclusions to their melting temperature or above, in order to homogenise the inclusion and reverse as many post-trapping changes as possible. Homogenisation can also be used to establish the trapping temperature. However, this technique is not without some inherent problems, and all post-trapping changes may not be reversible, and this is discussed. Numerous analytical techniques are available for melt inclusion studies, both on homogenised and un-homogenised inclusions, permitting detailed understanding of their chemistry.

Once collected, the data from experiments on, and analysis of, magmatic inclusions requires interpretation. Events occurring during and after trapping, as well as potential artefacts of homogenisation and analysis, which may affect data interpretation are then reviewed

Sample preparation

The initial screening for magmatic inclusions was usually performed on a 150 μm thick petrographic thin section. As the preferred inclusion size for study is > 50 μm, the standard 30 μm petrographic thin section tends to provide an unrepresentative view of actual magmatic inclusions, and their abundances.

For detailed study purposes, it was usual to prepare epoxy mounts of phenocryst separates. Grainmounts have the advantage that phenocrysts are removed from the
matrix, and several hundred can be placed in a single mount. This can be an important consideration with phenocryst concentrations typically comprising < 10%, and commonly < 5% of a given sample. Removing the matrix from the phenocrysts also makes inclusions easier to see.

Grainmounts were prepared as follows: samples were crushed and sieved into +1mm, 1.0-0.5mm, and 0.5-0.35mm sieve fractions. Sieve fractions > 0.5mm were then separated under a binocular microscope to extract the phenocrysts. Fines were discarded, and the 0.5-0.35mm fraction was only used if the coarser fractions did not contain sufficient phenocrysts. A quantity of phenocrysts was then arranged in rows on a flat surface, and a 25 mm epoxy disk cast over them. The phenocryst-studded side of the grainmount was ground and polished to expose the grains. If needed, exposed phenocrysts could be extracted from the grainmount with a hot needle for further preparation.

Two other forms of preparation were used:
- Individual grainmounts; phenocrysts were individually set in epoxy in the end of an 8 mm brass tube, and polished. This technique is useful where grinding is needed to bring an inclusion closer to the surface, for example in the preparation of PIXE mounts.
- Heating stage wafers; phenocrysts were ground and polished on two sides forming parallel-sided doubly polished wafers, typically 200-600 µm thick, generally somewhat thicker than fluid inclusion wafers.

The latter can be done with individual phenocrysts glued to a glass slide. However, it is generally more efficient to glue a polished epoxy grainmount to a glass side with a soluble glue (phenocryst side down), then cut off the back, leaving a 200-600 µm slice on the slide. This is then polished, the epoxy and phenocryst wafer soaked off the slide with acetone, and the selected phenocrysts removed from the wafer.

Petrographic examination and description

The first step in any magmatic inclusion study must always be a careful petrographic study and description of the samples in question. The petrographic examination should look for:
- Types of inclusions and populations of inclusions present in the sample
- Details of occurrence, and coexistence relationships of those magmatic inclusion populations
- Heterogeneous trapping.
• In-situ immiscibility (ie. post-trapping immiscibility in a homogeneously trapped melt)
• Decrepitated or otherwise compromised inclusions

**Compromised inclusions**

• Several events that a magmatic inclusion may undergo can change its bulk composition, to the extent that it is no longer representative of the melt, as trapped. Coincident with the detailed description of inclusions present, there must be a deliberate search for any signs of compromised inclusions.

However, it is important to note that petrographic examination, by itself, does not guarantee that inclusions are not compromised (ie. that their contents still represent the melt from which they were trapped). Additionally, petrographic indicators may not be obvious. Leakage (whatever the cause), while the inclusion still contains melt, allows decompression and this can result in disproportionately large shrinkage bubbles (Nielsen et al., 1998). However, Lowenstern (1995) suggested the normal range for shrinkage bubbles in felsic melt inclusions is 0.2 - 5 vol%, so what constitutes “disproportionately large” may not be obvious. Likewise, decrepitation cracks that do not extend to the phenocryst edge may not have seriously compromised the inclusion composition; the only effect may be the escape of tiny amounts of material into the cracks.

Some additional techniques are required, both to confirm petrographic indicators of compromised inclusions, and to detect compromised inclusions that either have no petrographic indications, or for which the indicators are equivocal. Placing excessive trust in petrographic indicators has been a problem during this study, and there is evidence that this may be the case in some published studies (e.g. Grancea et al., 2002). I would suggest that this problem might be generally under-recognised.

**Homogenisation**

**Introduction**

Cooling of a magmatic inclusion can generate a wide range of phases, crystallisation of various phases, solidification of melt to a glass, and nucleation of shrinkage bubbles, among other effects. As a result, micron scale inhomogeneity can (and often does) develop within the inclusion. Many analytical techniques used in this study have beam widths of > 5 µm, and some (e.g. LA-ICPMS) have beam widths > 20 µm, so micron-scale inhomogeneity can compromise analytical results. Even where a phase is homogeneous on the scale of the beam width, that phase may not be
representative of the inclusion as a whole. Ideally, such an inclusion should be returned
to a homogeneous state, representative of melt at the moment of trapping, before being
analysed. Within certain limits, this can be achieved by heating the inclusion until all
phase boundaries disappear (homogenisation), then cooling it quickly enough to prevent
the melt recrystallising (quenching). An additional significance of homogenisation is
that in melt inclusions, the temperature at which homogenisation occurs (T_h) can, with
some caution, be taken to represent the temperature at which trapping occurred (T_{trapping}).
Calculating T_{trapping} from T_h for fluid inclusions may require a correction for the trapping
pressure.

Complete melting without bubble disappearance is not homogenisation *per se*,
but it will remove the inhomogeneity, and it may permit conclusions to be drawn about
original composition. However, failure to homogenise implies at least H2O loss.

As homogenisation will play a part in the case studies to follow some details of
experiments as performed at the University of Tasmania are provided.

*Heating stage homogenisation*

Individual phenocrysts are prepared as doubly-polished heating stage wafers
(described on page 9), and experiments are performed on a Linkam TS1500 heating
stage, using an Olympus model BX 60 optical microscope fitted with a CCD camera.
The heating stage contains an electric heating element, capable of heating the sample at
any predetermined rate to 1500°C, and a thermocouple that can record the temperature
with an accuracy of ± 5°C. The heating stage has a circulating-water cooling jacket, and
upper and lower windows, which permits microscopic observation of inclusions during
heating. The water jacket permits rapid cooling at a rate of ≈ 150°C/min or controlled
cooling at any predetermined rate. The water jacket, and air cooling of the windows,
permits the sample to be kept at high temperatures for periods of up to 24 hours without
damage to the microscope. This equipment permits observation of the progress of the
inclusion, to note the order, temperatures, and temperature ranges of any phase changes,
and if homogenisation occurs, to note the homogenisation temperature (T_h). The
disadvantages are that the high viscosity of silicate melts may result in excessively slow
reaction rates, and consequently long observation times (sometimes > 24hours). Also,
magmatic inclusions commonly decrepitate during heating, particularly near the α- to β-
quartz transition (573°C), so the considerable investment in preparation time and
instrument usage for individual grain heating experiments may be lost.
**Bulk homogenisation**

A quantity of quartz phenocrysts (typically a few hundred), or surplus heating stage wafers, were placed in a ceramic crucible in a furnace, and heated to a selected temperature for a specified time. The crucible was then removed from the furnace, and the grains are immediately shaken into a cold, dry, ceramic crucible. This rapidly quenches the grains; I estimate the cooling rate to be \( \approx 800^\circ \text{C}/\text{min} \).

Bulk heating experiments have the advantage that long heating times are not an inconvenience, and large numbers of inclusions can be treated as a single run. This produces large numbers of homogenised inclusions required for statistically valid analyses, at relatively little cost. A preliminary bulk heating can also be used as a screening technique for individual grain heating experiments, since inclusions likely to decrepitate will do so during bulk heating. Additionally, inclusions that show interesting phases after bulk homogenisation can be selected for further experiments.

The lack of optical control means that information is not gathered during heating, and it is rarely possible to establish what a given inclusion looked like prior to heating. An exception to this is the use of surplus heating stage wafers photographed before bulk heating.

In practise, bulk- and individual grain heating experiments are complementary, and the usual practice in this study has been to begin with individual grain experiments to gather \( T_b \) and temperature of other phase transitions. This may be followed by bulk heating experiments, using the results of previous individual grain experiments to set heating parameters, and to obtain large quantities of homogenised inclusions for analysis. Often, this is followed by more individual grain experiments on undecrepitated inclusions from the bulk heating experiments. Particularly inclusions which show immiscible phases, as it is common to find only 3-6 such inclusions from a bulk heating charge of >200 phenocrysts. The aim of homogenisation (by whatever method) is to return the inclusion to a condition approximating its condition at the time of trapping. To do so it must reverse several effects of cooling.

**Potential problems with homogenisation**

**Inclusion leakage**

There are several forms of leakage:

- Diffusion through the host phenocryst.
- Cracks or fractures allowing access to the phenocryst.
The problem common to all of these results from the fact that H$_2$O in a silicate significantly reduces melting temperatures. If an inclusion loses H$_2$O subsequent to trapping, it may prevent the inclusion homogenising at its true trapping temperature, or indeed homogenising at all. Where homogenisation at a reasonable temperature is not possible, it may be assumed that some H$_2$O loss has occurred since trapping; however, the question of what was lost with the H$_2$O remains.

**Experimentally induced diffusive H$_2$O loss**

Diffusion rates are temperature dependent, and elements that have remained in the inclusion, or the host, since the time of trapping, may begin to diffuse in or out of the inclusion, if the temperature is held high enough and for long enough. Experimental evidence (e.g. Danyushevsky et al., 2000) suggests that diffusive re-equilibration can be significant at high temperatures (700-800°C) over relatively short timescales (hours). The solution to this problem is slow heating to lowest temperature consistent with homogenisation. However, as incomplete melting of daughter crystals of the host mineral that have grown on the inclusion walls is difficult to detect visually, care must be taken to avoid underheating. Theoretical work by Qin et al. (1992) suggested that the extent of diffusive re-equilibration should be proportional to inclusion size, so if the composition of one or more elements correlates to inclusion size, there are grounds for suspecting diffusive re-equilibration.

**Fracturing of host during homogenisation**

Fracturing, either due to thermal stress or increased pressure (if there is a volatile phase in the inclusion), can permit escape of volatiles or possible contamination of inclusion by elements in the host, or in the homogenisation environment (e.g. Lowenstern, 1995; Frezzotti, 2001). This problem is particularly significant in quartz phenocrysts near the α- to β-quartz transition (Ghiorso et al., 1979). The sudden 1 vol. % increase at 573°C can cause fracturing, if the heating rate is high enough to build up thermal gradients in the wafer. In this study, this effect was minimised by heating rapidly to 550°C then heating slowly (not more than 10°C per minute) up to 600°C, then resuming heating at the desired rate. Also, bulk heating to 600°C, followed by rapid cooling, was used to eliminate inclusions prone to decrepitation.
Effects that cannot be reversed by homogenisation

Diffusive re-equilibration with the host

A potential problem, particularly while the phenocryst is at an elevated temperature, is diffusive re-equilibration. Elements from both the host and the inclusion may diffuse across the inclusion wall, changing the net composition of the inclusion, and to some degree the host. Given that diffusion rates for specific elements in solids are low at low temperatures, the actual extent of diffusive re-equilibration may be minor, but particularly in cases in which cooling has been prolonged this effect may be considerable.

A second concern is the issue of slow diffusion of volatiles through the crystal lattice of the host. Theoretical studies by Qin et al. (1992) showed that significant and rapid H$_2$O loss is possible under geologically reasonable conditions. Audetat and Gunther (1999) examined this issue in detail with regard to fluid inclusions in quartz, particularly if the inclusion is under stress. Their conclusion was that inclusions can “migrate” in quartz crystals in response to imposed stress fields. Quartz preferentially dissolves on the side of the inclusion under stress and redeposits on the unstressed side. In the process, significant amounts of H$_2$O can be lost from the inclusion. However, the study showed that even where there has been significant H$_2$O loss (up to 30%), the ratios of all other components except H$_2$O and Li remain the same, and there are clear petrographic indicators that show if an inclusion has migrated. Natural diffusive H$_2$O loss will increase the melting temperature of an inclusion, so is usually indicated by excessively high homogenisation temperatures.

Inhomogeneous trapping

The assumption that homogenisation will return the contents of an inclusion to approximately its syn-trapping state, rests on the assumption that the material trapped in the inclusion was homogeneous in the first place. If, however, trapping were inhomogeneous, heating to the trapping temperature would not result in homogenisation. Even if homogenisation could be produced, it would require much higher temperatures, and would not provide any useful information. The best defence is careful petrographic examination; co-trapped volatile phases usually appear as larger than normal bubbles, and microphenocrysts should be apparent during optical examination.
Chapter 3: Analytical Techniques

Introduction

The previous chapter dealt with the selection of uncompromised inclusions, and where needed, homogenisation techniques, and their possibilities and difficulties. The analytical techniques used in this study are outlined in this chapter, along with details of the equipment. Additionally, it is important to understand what each analytical technique can, and cannot do, in order to select the best method for a given requirement, and to make sense of the resulting data.

Electron Microprobe

Major element analysis of inclusions in this study was performed on the Cameca SX50 electron microprobe, at the Central Science Laboratory, University of Tasmania. This technique requires inclusions to be exposed, and polished, so samples are either polished thin sections, or more commonly, polished epoxy grainmounts. Unavoidably, this means that liquid or water soluble components are lost prior to analysis.

To avoid alkali diffusion problems, Na and Si concentrations were measured simultaneously, using different spectrometer crystals, before the other elements. The beam current used was 15 nA with a beam diameter of 5 µm. Some experimentation was required to establish these optimum settings, but all the data presented was obtained with these parameters.

Without excessive count times, the detection limits for metals, and most trace elements, is near or above the actual concentrations in the melt inclusions studied, so only major elements are analysed with this system. The system will not readily detect elements lighter than oxygen so H₂O, CO₂, B and Li, which are, or could be in the inclusions, cannot be detected. As light elements in silicate melts (exotic melts excluded) are not expected to amount to more than a few hundred ppm, and CO₂ was not detected by Laser Raman microprobe, the difference between the total oxide wt% and 100% can be taken loosely as the H₂O concentration of the glasses. Repeated analyses of anhydrous host minerals were used throughout this study to test consistency. Totals ranged from 98.8 to 101.2 wt%, with a mean of 100 ± 0.6 wt% (at 1 standard deviation). The oxide wt% deficit is an approximation, but probably good to ≈ 1% (relative), and wherever possible, multiple analyses are made of the same inclusion, and reported as an average.
Electron microscopy

Features in some inclusions are smaller than optical microscope resolution, so very small scale features require the use an electron microscope. This study uses the ElectroScan ESEM2020 (Environmental Scanning Electron Microscope) in the Central Science Laboratory at the University of Tasmania. Samples are either broken phenocrysts with exposed inclusions, selected during hand-picking of phenocrysts for grainmounts, or (rarely) polished sections. To obtain the highest quality image the specimen is given a sub-micron coating of gold. When it is necessary to avoid loss of water-soluble phases, or contamination with alumina polishing compound, polishing with diamond dust and oil is required.

SEM EDS

The ElectroScan ESEM2020 has an Oxford Link Pentafet SATW energy dispersive X-ray detector (EDS system) attached, to obtain X-ray spectra for individual crystals. The EDS system gives the characteristic X-ray spectra for any elements present in the sample, resolution is < 1 µm, but the process is at best semi-quantitative. However, spectra are good enough to permit identification of some minerals, for example the identification of sphalerite by strong S and Zn peaks. Problems typically encountered with EDS spectra include geometric effects created by the 3-dimensional nature of the inclusions. X-ray scattering, and reflection from inclusion walls adds noise to the signal, and the low take-off angle of the detector can make it difficult to obtain reliable spectra for crystals at the bottom of an inclusion. Problems are also created by the need to give the sample a conductive coating, either carbon (best for EDS spectra), or gold (best where good images are required), so the spectra for coating materials are always present in the results.

Laser Raman

A Dilor SuperLabram Laser Raman microprobe at the Australian Geological Survey Organisation, Canberra, was used to identify mineral components of unexposed inclusions. The laser Raman microprobe is useful because it is a non-destructive technique, and can be used on inclusions still embedded in host quartz, overcoming the problem of loss of any aqueous or soluble phases when the inclusion is exposed. The Laser Raman Spectroscope monitors the inelastic scattering of monochromatic visible light, as it interacts with covalent bonds in solids, liquids, and gases. It does not provide information on the specific elements present in a sample, but rather on the way the individual elements are bonded to each other within the sample, which makes the
technique sensitive to the molecular and crystalline structure. As such it can identify covalently bonded minerals, particularly useful in this study in identifying silicate minerals by their crystal structure. It can also detect H$_2$O (liquid, vapour, or chemically bonded) and most gasses, such as CO$_2$, CH$_4$, H$_2$ and N$_2$. However it cannot detect ionic compounds, so it cannot provide any information on the salts which may be present in melt inclusions, and which certainly exist in fluid inclusions. The laser excitation source used was the Ar$^+$ ion at 514 nm, accumulation time varied from 10-60 seconds, and spot size was 1 µm.

**LA-ICPMS**

Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICPMS) was performed using a HP 4500 quadrupole ICPMS with a New Wave Research UP213 ultraviolet ND-YAG laser microprobe (SES-CODES, University of Tasmania). This technique uses a laser beam to ablate material off a prepared sample, inside a sealed chamber. A stream of carrier gas collects the ablated material, and introduced into a Mass Spectrometer, which separates the ions in the plasma by mass, and counts them. This gives an analysis of the ablated material as a ratio of intensities for each atomic mass. The technique is capable of routinely detecting most elements down to a few ppm., and as it is possible to ablate to a depth of several tens of µms, it is possible to analyse inclusions below the surface of the sample. Beam widths are adjustable from 10-200 µm, so it is also possible to ablate entire unexposed inclusions. This is potentially an important advantage, as crystallised or otherwise inhomogeneous inclusions do not need to be homogenised for analysis. LA-ICPMS studies of melt inclusions have shown consistent and repeatable results (e.g. Taylor et al., 1997; Halter et al., 2002) and the technique offers considerable advantages, where applicable.

However the technique has disadvantages; it is destructive of the sample, and data normalisation can be difficult. One analysed element must have been accurately quantified by some other method, prior to LA-ICPMS, in order to normalise the inter-element ratios back to absolute quantities (ppm). For unexposed inclusions estimated concentrations must be used, typically the estimated Na concentration. This can be based on homogenisation temperatures of fluid inclusions; however, there is an assumption that the salinity (expressed as equivalent NaCl wt%), really reflects Na concentration. Since most fluid inclusions contain salts other than NaCl, the NaCl wt% equiv obtained from microthermometry is, at best, an estimate. As an alternative, concentration can be estimated from the measured sizes of halite, relative to the volume of the whole inclusion. Whatever the method used, the errors in these estimates to some extent neutralise the ability to analyse unexposed samples.
PIXE

The Proton Induced X-ray Emission (PIXE) microprobe analyses were performed on the CSIRO-GEMOC Nuclear Microprobe, at North Ryde in Sydney. This technology uses a very high-energy proton beam (3 MeV), focussed to 1.3 µm diameter, to excite the elements in a sample to emit characteristic X-rays and gamma-rays. The beam is raster scanned across the sample, and the emitted X-rays are detected, and used to create an element density map for each element in the sample. This data can then be computer processed to calculate absolute concentrations, using the measured depth and size of the inclusion, excluding anything outside the specified volume, thus disregarding the contribution of elements in the host mineral. It is also possible to specify depth and size parameters of regions within an inclusion, allowing the calculation of absolute concentrations for parts of an inclusion, but the positioning error can become excessive. The PIXE microprobe is capable of simultaneous multi-element analysis of most of the periodic table. Detection limits are around 20 ppm. or better, with an accuracy for saturated aqueous fluids estimated at 30% (Ryan et al., 1999).

This technique is “standardless” in that no prior analysis is need to normalise the data (unlike LA-ICPMS), which is an enormous benefit when analysing unexposed aqueous fluid-bearing inclusions. Also importantly, the technique is non-destructive of intact fluid-bearing inclusions, although interaction with the high-energy particles may cause some phases to break down, or change shape or colour.

However, the technique is not without problems, it requires inclusions to be within 5 µm of the surface of the sample, resulting in extensive sample preparation time (4-5 hours per inclusion). Analyses are very expensive, and data normalisation is not without difficulties.

Data is produced in two forms, element concentration maps, and absolute concentrations; both are used in this study. The element maps give relative concentration for each element over the scanned area, and do not require any assumptions. They are useful in determining the distribution of an element within an inclusion, but provide no quantification. Computer processing the raw data, to extract element concentrations within a specified volume within the sample can obtain absolute concentrations of specific elements. This processing involves a number of assumptions, and some measured parameters, particularly the depth, diameter, and density of the inclusion, and the host composition. Both the assumptions, and errors in the measured parameters effect the accuracy (Ryan et al., 1999).
Introduction

The Río Blanco-Los Bronces Cu-Mo deposit is located in the Andes in central Chile, approximately 70km northeast of Santiago (Fig. 4-1). It is among the largest copper resources in the world (> 50 x 10^6 metric tons of contained Cu), and has major reserves of molybdenum (> 8 x 10^5 metric tons of contained Mo) (Serrano et al., 1996). The deposit consists of a series of mineralised and barren porphyry and breccia complexes, superimposed on a porphyry Cu deposit (Warnaars, 1985). The Los Bronces operation is primarily concerned with a breccia complex on the western side of the deposit, and Río Blanco contains the mineralised porphyry and breccia complexes to the east (Warnaars, 1985).

Towards the end of the magmatic history of Río Blanco-Los Bronces, the Don Luis Porphyry and La Copa volcanic complex (5.3-3.9 Ma) erupted through the northern part of the deposit. All samples in this study are from the Río Blanco section of the deposit, mainly from the La Copa volcanic complex, with the exception of one sample from the Don Luis Porphyry.

Detailed reports on the Río Blanco-Los Bronces Cu-Mo deposit have been published in English by Warnaars (1985), Serrano et al. (1996), and Vargas et al. (1999), and Sr and Nd isotope work has been published by Skewes and Stern (1994, 1996). A detailed fluid inclusion study has recently been published by Skewes et al. (2003), complementing studies in Holmgren et al. (1988) and Vargas et al. (1999). Deckart et al. (2004) have greatly improved the geochronology, providing accurate dates for several porphyry and breccia units, which substantially assists in unravelling the sequence of events at Río Blanco. An unpublished PhD thesis in Spanish (Torros George, 1986) has been written about the La Copa Volcanic complex. Several papers, also in Spanish, written about Río Blanco-Los Bronces are referenced in the papers already mentioned. Dr. David Cooke, Peter Fricken, and Dr Peter Hollings provided the samples used in this study.
Figure 4-1 Map of the west coast of South America, showing the contours of the top of the Benioff Zone above the Nazca plate. Triangles are Quaternary volcanoes on the overriding South American Plate. Filled circles are well-constrained deep focus earthquakes (mainly 525-625 km). The Chilean Flat Slab segment is centered on 30°S and 71°W (Map after Bevis & Isacks (1984)).
It should be noted that the suite of samples studied is spatially associated with, and partly postdates Cu-Mo mineralisation. Deckart et al. (2004) showed that the Don Luis Porphyry was emplaced at the end of the main stage of mineralisation, and the La Copa Rhyolite is post-main stage mineralisation, although certainly responsible for some of the extensive hydrothermal alteration. The fact that the samples are probably late- and post-mineralisation is not a disadvantage, since some rocks will not have been depleted in the metals and ligands required for mineralisation, and the immiscibility processes may have been similar to those nearby that did.

**Fig. 4-2** Modern lithospheric cross-section of the Chilean Flat Slab segment at 30° to 32°S, after Kay et al. (1999). The wedge in the crust is a schematic representation of material added from beneath the Main Cordillera to account for shortening across the Pre-cordillera. The existence of detached lithosphere and mantle blocks is proposed to account for mass balance problems.

**Tectonics**

The whole Pacific coast of Chile is an active subduction zone, with the Nazca Plate subducting at an unusually shallow angle beneath the South American continent (<30° as compared to the more normal >45° (Barazangi and Isacks, 1976; Uyeda, 1987)). In the southern part of the Andean margin (between 28°S and 33°S), there has been further progressive slab flattening (Fig. 4-2), associated with uplift and extensive shortening and thickening of the continental lithosphere, as well as arc and backarc volcanism (Kay and Abbruzzi, 1996). This is now referred to as the flat-slab section of the Chilean subduction zone. It has been suggested (e.g. Bevis and Isacks, 1984; Serrano et al., 1996; Gutscher et al., 2000) that the slab angle decreased in response to the buoyancy of the subducted Juan Fernandez and Nazca Ridges (Fig. 4-1). However,
it should be noted that some authors, such as Von Huene et al. (1997) and Kay et al. (1999) were not convinced of a direct cause and effect with respect to ridge subduction.

Bevis and Isacks (1984) suggested that the boundaries between the flat slab segment, and the flanking Central and Southern Volcanic Zones, are bends rather than tears in the subducting plate (Fig. 4-1). Thus, the change in slab angle is likely to have propagated southwards and eastwards into Chile (in effect, a “bow wave” around the subducting Juan Fernandez Ridge). Three huge Cu-porphyry deposits, Los Pelambres (> 25 x 10^6 tons Cu), Río Blanco-Los Bronces (> 50 x 10^6 tons Cu), and El Teniente (> 70 x 10^6 tons Cu) straddle the boundary between the flat slab segment and the SVZ.

**Geology**

Paleozoic to Mesozoic rocks in southern Chile are discordantly overlain by a strip of Early Tertiary marine to continental volcanic rocks with minor sediments, belonging to the probably time equivalent Pelambres and Coya-Machali Formations. The Pelambres Formation covers a wide time span, from 62 Ma to as young as 28 Ma (Warnaars, 1985). However, Drake et al. (1982) presented evidence for an extensive hiatus in magmatic activity between 56-26 Ma throughout central Chile. Abundant plutonic rocks (Palaeogene and later) intruded the thick pile of Pelambres and Coya-Machali Formation volcanics, including the San Francisco Batholith which forms much of the basement at Río Blanco.

The early Tertiary volcanics were, in turn, discordantly overlain by the Late Oligocene to mainly Miocene andesitic flows and pyroclastics, interbedded with continental sediments (Warnaars, 1985), which Vergara et al. (1988) assigned to the Farellones Formation. The latter authors have given the age of the Farellones Formation as 19.3 - 7.4 Ma on the basis of existing K/Ar dating, noting that the largest volume of extrusive rocks was from the earliest part of this period (18-15 Ma). This overall reduction of magmatism may reflect processes related to the formation of the Chilean flat slab. Progressively, from about 10 Ma to about 4 Ma, there was an extinction of magmatism between 33° and 35°S due to slab flattening (Fig. 4-1), although between 35° and 46°S (the Southern Volcanic Zone) active volcanism has continued unabated to the present (Drake et al., 1982).

Progressive emplacement of components of the San Francisco Batholith occurred between 20.1-7.4 Ma. (Serrano et al., 1996). From about 7.3 Ma to 5.9 Ma (Serrano et al., 1996), a series of mineralised and barren breccias were emplaced explosively into the eastern edge of the San Francisco Batholith, and into the overlying Farellones Formation (Fig. 4-3). This was followed by (and slightly overlapped) the
emplacement of the Late Porphyries between 6.3 and 4.1 Ma (Deckart et al., 2004). Magmatism at Río Blanco was coincident with the southward migration of the southern margin of the flat slab segment. Thickening of the crust is believed to have led to conversion of hydrous amphibole-bearing crust into anhydrous garnet-bearing crust, releasing large volumes of fluid-rich magmas (Kay et al., 1999), consistent with the emplacement of mineralised breccias. Warnaars (1985) noted at least seven distinguishable breccias in the Los Bronces section, and there may be at least four others in the Río Blanco section. Location, matrix, clast composition, types and degrees of mineralisation and alteration can identify each breccia. Some breccia bodies have sharp contacts, but gradational or interfingering contacts are known, for example the Sur Sur and Río Blanco tourmaline breccias.

Fluid inclusion data in Serrano et al. (1996) shows that the early phase of porphyry-Cu mineralisation involved non-boiling fluids, at depths of 3 to > 6km below the paleosurface. Mineralisation in the later tourmaline breccias involved boiling fluids at paleodepths of 1 to > 3km. Fluid inclusion data from the Donoso Breccia suggests paleodepths of as little as a few hundred metres. Extensive unroofing suggests very rapid uplift and consequent erosion during mineralisation. This was followed by a period of relative stability and more normal intrusive and effusive magmatism (the Late Porphyries), before magmatic activity ceased at Río Blanco around 3.9 Ma (Deckart et al., 2004). A degree of temporal and spatial overlap between the (early) mineralised breccias, and the late porphyries, argues for progressive decrease in the proportion of fluids to magma as the crust finished dehydrating. It does not support the notion that the mineralised breccias and late porphyries are in any way separate and unrelated events. Altogether, there is good geochemical, geochronological, and isotopic data evidence for an evolution (progression?) from the San Francisco Batholith, through the mineralised breccias, to the Late Porphyries.

**Late Porphyries**

Beginning at about 6.3 Ma, a series of dacitic to rhyolitic porphyries were intruded into the deposit (Deckart et al., 2004). This overlaps with the emplacement ages of the youngest mineralised breccias, and there is clear evidence of basement rocks (some mineralised) and older breccias, being cut by late porphyries, which are in turn cut by still younger tourmaline breccias (Serrano et al., 1996). Serrano et al. (1996) gave a compilation of K-Ar and $^{39}$Ar-$^{40}$Ar dates, which show that there is a considerable overlap between the mineralised breccias (7.3-4.2 Ma), and the late porphyries (6.3-3.9 Ma).
Figure 4-3  Simplified geological map of the Los Bronces - Río Blanco porphyry copper deposit. The La Copa volcanic complex and Don Luis Porphyry are grouped as Late Porphyries (From Vargas et al. (1999)).
A quartz monzonite porphyry stock dated at 6.3 Ma (Deckart et al., 2004) is probably the first unit of the Late Porphyries. The latest units of the late porphyries are the Don Luis Porphyry (5.23 ± 0.07 Ma), and the La Copa Volcanic Complex (4.03 ± 0.19 Ma) (Deckart et al., 2004).

The La Copa Volcanic Complex

Warnaars (1985) described the La Copa Volcanic Complex as a diatreme, largely based on the steep-sided inverted conical form (Fig. 4-3b). However, the term “complex” is very appropriate. As mapped by Torros George, (1986), the La Copa Volcanic Complex is ≈ 1.5 km wide and 2 km long, and contains 17 mappable units, principally rhyolitic to dacitic intrusives capped by remnants of lavas, with some hydrothermal and contact breccias (autobreccias formed during stock emplacement). Torros George (1986) noted the existence of tuffs in the La Copa complex, and rhyolite flows or domes overlying paleosols. However, the bulk of the complex is thought to be subvolcanic intrusives that have intruded the base of their own volcanic pile. On the western side of the complex is a feature, possibly a Maar, now occupied by La Copa Lake. Many rhyolites, including almost all the samples used in this study, have fragmental textures with a mix of phenocrysts and minor lithic clasts, in a fine-grained matrix. Alteration is sericite-dominated, with local silicification.

The Don Luis Porphyry

Although less complex than the La Copa Volcanic Complex, the Don Luis Porphyry has many similarities (Fig. 4-3b). The form is basically an inverted cone with an oval cross-section, filled with dacite to dacite-latite porphyries and contact breccias. Contacts of the Don Luis Porphyry with surrounding units are generally sharp with minimal alteration. Textures range from aphanitic to feldspar-phyric, often with abundant lithic clasts. The Don Luis Porphyry generally shows moderate sericite alteration; mineralisation is present, but is generally sub-economic.

Mineralisation

Roughly half of the Los Bronces-Río Blanco resource occurs as a porphyry Cu-Mo type deposit with associated potassic alteration zone (Warnaars, 1985), whereas the other half occurs as younger tourmaline-cemented breccia pipes. Both Warnaars (1985) and Serrano et al. (1996) consider the porphyry-style mineralisation to be temporally, spatially, and genetically related to emplacement of both mineralised biotite ± tourmaline ± anhydrite ± micaceous hematite breccias, and quartz monzonite porphyry intrusions on the eastern side of the San Francisco Batholith. Deckart et al. (2004),
largely on the basis of a refined geochronology, suggested that most mineralisation is related to the emplacement of the earliest Late Porphyries (the Quartz Monzonite Porphyry, and the Don Luis Porphyry). However, the emplacement of various units of the La Copa Volcanic Centre contributed to the hydrothermal alteration, if not the mineralisation.

In the mine area chalcopyrite predominates, and bornite, pyrite, and molybdenite are subordinate (Serrano et al., 1996). The potassic alteration zone passes outwards into either actinolite ± magnetite or propylitic chlorite ± epidote. There is a general late stage sericite alteration overprinting the early potassic and propylitic zones.

Sample descriptions

Don Luis Porphyry

Sample 9915 is the only sample from the Don Luis Porphyry used in this study, and is a porphyritic rhyolite, originally containing quartz, feldspar and biotite phenocrysts in a fine-grained groundmass. This sample is the most altered of those studied. Most feldspar is sericitised, and much of the biotite is chloritised. Blocky chalcopyrite and lesser pyrite and magnetite are common (see whole rock analysis, table 6-1). Larger sulphide masses (up to 5 mm) are observed, enclosing quartz and feldspar phenocrysts, and may be clasts of pyritised breccia. Quartz phenocrysts are rounded euhedral forms, but not often fractured. Primary magmatic inclusions are present in the quartz phenocrysts, and apparently secondary fluid inclusions are abundant.

La Copa Volcanic Complex

Intrusive Samples

Samples 9902, 9903, and DC-Rhy1 are porphyritic breccia-textured rhyolites containing quartz, plagioclase, and biotite phenocrysts, with sparse clasts of coarse- and fine-grained volcanics. The phenocrysts are commonly broken euhedra, clasts are angular to sub-rounded, and rare small, blocky, pyrite crystals and twisted biotite laths are present. Quartz phenocrysts show some fracturing, and contain primary magmatic inclusions. There is minor sericite alteration to some feldspar crystals along fractures, but sericite alteration is mainly restricted to the fine-grained groundmass, and secondary fluid inclusions are rare. The whole rock analyses are given in table 6-1
Extrusive Samples

Samples CA30 & CA31

Both samples are breccia-textured glass-bearing rhyolite lavas containing igneous clasts up to 5 cm, and were collected from the Los Bronces side of the La Copa Volcanic Complex. These sample were collected ≈ 50 m. apart, and located immediately above a paleosol; however direct outcrop continuity was not observed. Nevertheless, whole-rock analysis, and the geochemistry of magmatic inclusion populations of the two samples indicate a strong similarity.

The rocks are composed of phenocrysts of plagioclase with minor quartz and biotite, in a groundmass composed of glass (with perlitic cracks) and fine-grained quartz/feldspar. Minor fine-grained opaques are present in the groundmass but not in the glass. The glass / fine-grained groundmass boundary is irregular and scalloped. Some phenocrysts are completely surrounded by glass, and there are “clasts” of fine-grained matrix (with and with out phenocrysts) enclosed in glass. Possible tiny relict pumice clasts occur in the groundmass. There is almost no observable alteration, only minor patchy sericite alteration of the groundmass, and Fe staining.

Sample CA32

This rock was collected immediately above another paleosol and can thus be confidently described as a lava. It was sampled several hundred metres away from the two previous samples, and both the whole-rock analyses and the magmatic inclusion populations suggest that this sample is not from the same flow as CA30 or 31. No continuous exposure linked the two sites and it is not possible to determine stratigraphic relationships.

CA32 is a clast-bearing rhyolite lava with a fine-grained quartz/feldspar groundmass, containing phenocrysts of quartz, plagioclase, and biotite, and dark igneous clasts. Most fine-grained opaques are in the clasts rather than the groundmass. Sericite alteration to the phenocrysts is minor, but is present as patches in the groundmass, as are minor clots of Fe staining.

Sample CA33

Sample CA33 was collected 30 m below CA32 and it cannot be identified as a lava (rather than an intrusive unit) with certainty. However, given the whole-rock data, the presence of glass, and the similarity of magmatic inclusion populations to CA32, the sample is considered to be extrusive. The geochemistry of glass inclusions in both CA32 and CA33 are very similar, but subtly different from CA30 or 31 (Table 6-1).
This suggests that CA32 and CA33 may be from the same lava flow, although CA30 and 31 are different enough to suggest that some time elapsed between their emplacement and that of CA32/33. I infer from the glass compositions (table 6-1, Figs. 6-1, -2, -5, and -6) that the samples should be grouped as CA30, CA31, and CA32/33 with time breaks (and possibly paleosols) between the three groups.

CA33 is a breccia-textured glass-bearing rhyolite containing phenocrysts of plagioclase, quartz, and biotite in a groundmass composed of glass and fine-grained quartz/feldspar. Minor “blobs” of glass with some perlitic cracking and vesicles are present. Most of the phenocrysts are broken. The sample has more blocky opaques than any of the other extrusive samples. As usual there is almost no alteration to the phenocrysts and only a little patchy sericite alteration to the groundmass. Macroscopically, this sample closely resembles CA30, but has less glass and more patchy alteration.
Chapter 5: Description of Magmatic Inclusions

Introduction

The previous chapter examined the geology and tectonics of Río Blanco and the surrounding region, as well as the petrography of the samples. This chapter contains the description of magmatic and fluid inclusions.

To understand the inclusions from Río Blanco, it is first necessary to examine the ways in which they occur in the selected specimens, then make a detailed examination of the appearance of each type of inclusion and their common varieties. The rocks from Río Blanco include intrusive and extrusive samples, and, although the mode of occurrence of inclusions in both types of samples is similar, there are some differences. This chapter examines the occurrence of inclusions, then, for each individual type, describes its characteristics and appearance.

No detailed and widely accepted terminology exists for all possible variations found in magmatic inclusion populations, so it has been necessary to define some new terms for the categories of inclusions found at Río Blanco. A separate glossary is provided (immediately before page 1 of this text), which defines the terminology used in this study, and summarises the inclusion types described below.

The following chapters give details of analyses of the various types of inclusions, and describe experiments performed on the inclusions to improve understanding of the processes involved in their formation. The last chapter of this case study draws together the observations, in a discussion of implications of the Río Blanco inclusions.

Occurrence of inclusions

Primary magmatic inclusions at Río Blanco occur as a random mix of melt inclusions, microphenocrysts, and magmatic vapour inclusions, usually aligned along distinct planes within quartz or feldspar phenocrysts (see diagram 15-1). In many cases these are clearly growth planes (e.g. Fig. 5-1). Individual growth planes may be dominated by a single type of inclusion (Fig. 5-2) or, more commonly, may contain an intimate and random mix of various types of melt inclusions ± microphenocrysts ± vapour inclusions (Fig. 5-3). Moreover, inclusion populations on successive growth planes, in a given phenocryst, show no consistent change between core and rim, which implies only a single generation of primary magmatic inclusions (micro-phenocrysts, melt inclusions, and primary fluid inclusions), being trapped continuously during phenocryst growth.
Diagram 5-1  Representation of melt and fluid inclusions occurrences at Río Blanco. The diagram shows a cross-section of a quartz phenocryst, containing two growth planes decorated with silicate melt and liquid and vapour inclusions (A), all primary. Additionally, several types of vapour-rich 2-phase fluid inclusions are shown, including a cross-cutting trapping plane (B).

In samples from the La Copa Rhyolite you would find growth planes decorated with silicate melt inclusions (A) (e.g. fig. 5-6) and primary magmatic vapour inclusions (e.g. fig. 5-4) surrounded by haloes of vapour-rich fluid inclusions (shown as dots surrounding melt inclusions). The small fluid inclusions are related to decrepitation of the silicate inclusions, and are thus early secondary inclusions. (C) large, isolated melt inclusions are found outside growth planes (e.g. fig. 5-1). (B) A trapping plane marked by clearly secondary 2-phase liquid/vapour inclusions (e.g. fig. 5-8). (D) less clearly, large, generally liquid-rich two-phase fluid inclusions (e.g. fig. 5-67) can be found in or near growth planes, that can not be connected to secondary trapping...
Fig. 5-1  Photomicrograph of a quartz phenocryst from the La Copa Rhyolite, showing growth plane decorated by micro-phenocrysts, and small crystallised silicate and glass inclusions (lower arrow), and a large isolated glass inclusion (upper arrow).
Sample 9903. Field of view 1 mm. wide

Fig. 5-2 Close-up of a growth plane decorated with crystallised silicate melt inclusions, showing the characteristic parallel alignment of the inclusion axes.
DC-Rhy1. 50µm scalebar

Fig. 5-3 Close-up of a growth plane decorated by crystallised silicate melt and glass inclusions, in a quartz phenocryst from the La Copa Rhyolite. Note the alignment, and close coexistence, of CSMI’s and glass inclusions.
DC-Rhy1. 50µm scalebar

Fig. 5-4 Vapour-rich primary magmatic fluid inclusion, showing the dark, shiny appearance typical of vapour inclusions. There are only minor indications of crystalline material near the top of the inclusion, and this inclusion probably contains < 10% silicates. This inclusion shows the second form of fluid inclusion halo, a “sweat halo”, consisting of tiny vapour-rich fluid inclusions around either end, separated by a narrow band of inclusion-free quartz [Audetat, 1999 #53].
DC-Rhy1. 50µm scalebar

Fig. 5-5 Primary magmatic fluid inclusion (arrowed) in a growth plane with a CSMI. The lower inclusion has the typically inhomogeneous appearance of a CSMI. Strongly developed faceting is apparent in the primary fluid inclusion, for comparison, see the glass inclusion in fig 5-3
9903. 50µm scalebar

Fig. 5-6 A typical CSMI with a decrepitation halo of vapour-rich fluid inclusions. The fluid inclusions are irregular in form, and in a planar array (dipping slightly across the photomicrograph from left to right), centred on the CSMI, suggesting a partly healed decrepitation crack.
9902. 50µm scalebar
The growth planes, and the axis of all inclusions within that plane, are aligned with the host’s principle crystallographic axis. Commonly, magmatic inclusions on a given growth plane are of similar size, and generally small (< 50 µm). Primary fluid inclusions are also observed in trapping planes in Río Blanco phenocrysts, most commonly one-phase vapour inclusions (Fig. 5-4), although rare two-phase liquid-rich inclusions have been found (Fig. 5-5).

Abundant, small, one- and two-phase vapour-rich inclusions (usually < 5µm.) commonly occur in Río Blanco phenocrysts. Typically, these occur in discontinuous haloes around dark melt inclusions (Fig. 5-6), sometimes as clusters around either end (Fig. 5-4), referred to as “sweat haloes” by Audetat and Gunther (1999). This association is presumed to result either from decrepitation of the inclusion, and subsequent partial healing of decrepitation crack(s), and/or loss of fluid during inclusion migration (see Audetat and Gunther, 1999). Both processes probably occur at high temperatures, but after the melt inclusion was trapped, so that such fluid inclusions are arguably pseudosecondary, rather than primary.

The Don Luis Porphyry sample (9915d) contains abundant high-salinity fluid inclusions (unlike the La Copa Rhyolite), but does not contain glass inclusions, which are the abundant in the La Copa Rhyolite. Fluid inclusion morphologies range from equant (Fig. 5-7), and sometimes negative crystal-shaped inclusions (Fig. 5-8), to flat lenticular inclusions with strongly cuspaté margins (Fig. 5-9). Inclusion contents range from hypersaline, liquid+vapour+multiple translucent “salt” phases ± a minor opaque phase, through to two-phase liquid- or vapour-rich fluid inclusions. High-salinity fluid inclusions in sample 9915d can be found in several associations:

- in growth planes with melt inclusions, suggesting they are primary
- in trapping planes without CSMI’s but sometimes with fluid inclusions containing silicates or magmatic minerals. This suggests they are pseudosecondary, since trapping planes with CSMI’s are primary, and the magmatic minerals suggest trapping at (or near) magmatic temperatures.
- in trapping planes that do not contain magmatic minerals in fluid inclusions, and are not growth planes, suggesting their trapping post-dates trapping of melt inclusions, and that they are thus secondary (see diagram 15-1).

Trails of two-phase (L+V) fluid inclusions, either liquid- or vapour-rich, are common in the Don Luis Porphyry, and are also present, although not common, in the La Copa Rhyolite. In the Don Luis Porphyry densely packed trails of large, cuspaté, generally two-phase inclusions appear to overprint an earlier population of hypersaline fluid inclusions, some of which contain high-temperature minerals.
Inclusion types

Glass inclusions

Glass inclusions are characteristically negative crystal-shaped, and contain clear glass with a shrinkage bubble(s) (Figs. 5-10, -11). Occasionally, one or more daughter crystals are observed, typically quartz (Fig. 5-10), and rarely, green amphibole (pyroxene?) fibres (Fig. 5-12). Rare examples of brown glass (Fig. 5-13) have been observed. Large diameter glass inclusions occur (> 100 µ Fig. 5-14), but the typical range is 1-50 µm. Glass inclusions are common on growth planes in the La Copa Rhyolite, coexisting with all other types of primary magmatic inclusions (Fig. 5-15), but they are absent from the Don Luis Porphyry samples.

Although glass inclusions from the La Copa intrusives typically have more or less rounded edges, those from the extrusive units commonly have strongly developed negative-crystal facets, with sharp, prominent ridges where the facets meet (e.g. Fig. 5-16). Strongly facetted glass inclusions tend to be small (typically < 20 µm), and often have decrepitation cracks parallel to the host quartz c-axis, which are rare in normal glass inclusions. Strongly developed facets may be a function of rapid cooling during emplacement of the lavas. Manley (1996) reports a trend from irregular melt inclusions, to well developed negative-crystal shaped inclusions, in rhyolite lava flows with progressively increasing cooling time (Owyhee Plateau, Idaho).

Bubbles in glass inclusions are typically almost spherical, commonly showing a “bull’s-eye” appearance in photomicrographs, due to almost total internal reflection (Fig. 5-10). Large individual crystals within the bubbles are not unusual (Fig. 5-14); analysis and crystal form suggest that these crystals include aluminosilicates and salts. The bubble-fraction (volume of shrinkage bubble(s) as a percentage of the volume of the inclusion) averages 6 % ± 2% (1σ). Bubble volumes were estimated by measuring the cross-sectional area of a bubble in photomicrographs, then calculating the diameter from the area of a circle, then the volume of the sphere from that diameter. Inclusion volumes were obtained by estimating the diameter of a sphere with the same volume as the inclusion, then calculating the volume of the sphere from its diameter. The process is reasonably accurate as the inclusions used were almost spherical well-rounded negative-crystal shapes containing almost spherical bubbles. Accuracy is estimated at ± 5% and errors in bubble and inclusion volume estimates may at least partly cancel each other when calculating bubble-fraction.
Fig. 5-7  Fluid inclusion from the Don Luis Porphyry. The inclusion contains a halite
crystal, brine, a vapour bubble, and an opaque (arrowed, probably chalcopyrite or
magnetite). The inclusion shows the equant form of fluid inclusion, in contrast to the
cuspate form in fig. 5-8
9915. 10µm scalebar

Fig. 5-8  Small, negative-crystal shaped 2-phase liquid-rich fluid inclusion
9915. 50µm scalebar

Fig. 5-9  Large cuspate fluid inclusion from the Don Luis Porphyry. In addition to a
halite crystal (cubic), brine, a vapour bubble, and an opaque (bottom arrow,
chalcopyrite), this inclusion contains a bladed crystal of hematite (top arrow), and a
rounded crystal of sylvite. Trails of hypersaline fluid inclusions from the Don Luis
Porphyry typically contain either cuspate, or equant fluid inclusions (see fig 5-7), but
rarely both.
9915. 50µm scalebar

Fig. 5-10  A typical Río Blanco glass inclusion, hosted in a quartz phenocryst, and
composed of rhyolitic glass with a shrinkage bubble, and a quartz daughter crystal
(arrowed). The “bulls eye” effect is the result of near-total internal refraction, and
obscures the contents of the shrinkage bubble (if any). The volume of the shrinkage
bubble (as a percentage of the total inclusion volume) is typical of Río Blanco glass
inclusions.
9903. 50µm scalebar

Fig. 5-11  A glass inclusion partly exposed by polishing. The shrinkage bubble has been
breached, so does not show the “bulls eye” effect, and is visibly empty.
DC-Rhy1. 50µm scalebar

Fig. 5-12  Multiple-bubble glass inclusion from an intrusive unit of the La Copa
Rhyolite. Green fibrous daughter phases have developed in the glass, some apparently
nucleating on the shrinkage bubbles, others on the inclusion walls. The crystals are too
small to be analysed, but are probably a pyroxene or an amphibole.
9903. 50µm scalebar
Fig. 5-13 Rare example of a brown glass inclusion, in quartz from the La Copa Rhyolite. The inclusion is transected by brown stained zone, probably marking a former decrepitation crack, however, there is a distinct clear zone within 5 µm of the inclusion. The inclusion contains two shrinkage bubbles, and the brown colouration is devitrification, possibly due to ingress of water along the crack.
CA32. 50µm scalebar

Fig. 5-14 Multiple bubble glass inclusion. The total bubble fraction for this inclusion is 8 vol%, which (for Río Blanco glass inclusions) is the mean + 1σ; note the crystals visible in some of the larger bubbles.
DC-Rhy1. 50µm scalebar

Fig. 5-15 Growth plane showing randomly mixed CSMI's and glass inclusions in the La Copa Rhyolite.
9902. 50µm scalebar

Fig. 5-16 Strongly facetted crystallised-glass inclusion from an extrusive unit of the La Copa Rhyolite. Note the prominent, everted boundary between facets, and the green daughter crystals. There is a 30µm long decrepitation crack, parallel to the main axis of the inclusion. Such cracks are rare in glass inclusions in the intrusive units, but more common in the extrusives.
CA30. 25µm scalebar

Fig. 5-17 Glass inclusion with a shrinkage bubble filled with crystalline material. Traces of silicates in shrinkage bubbles (≈ 5 vol%), from the La Copa Rhyolite are common, but such large volumes are unusual.
CA30. 25µm scalebar

Fig. 5-19 Glass inclusion showing extensive post-magmatic alteration. Fuzzy devitrification has begun on the boundaries of the shrinkage bubbles, and appears to have begun propagating into the glass.
DC-Rhy1. 50µm scalebar
The correlations in figures 5-18a, -18b could imply trapping of a homogeneous melt; however, shrinkage bubbles, sensu stricto, should form only a relatively small percentage of a glass inclusion. (Lowenstern, 1995, 2002) suggested a range of 0.1 - 5.0 vol% for shrinkage bubbles in felsic melts, and the measured average from Río Blanco is at the upper end of that range.

![Bubble Fraction distribution, Río Blanco glass inclusions (n=94)](image)

**Fig. 5-18a** Histogram of the bubble-fraction of 94 glass inclusions from Río Blanco; the mean is in the 6 vol% range, but there is considerable spread.

![Inclusion Volume vs Bubble Volume for Río Blanco glass inclusions (n=94)](image)

**Fig. 5-18b** Plot of bubble volume vs the volume of the enclosing glass inclusion. Multiple bubbles (2 - 8) in the same inclusion have been observed (Fig. 5-14), generally in the larger inclusions (> 80 µ). The calculated total bubble fraction for a given multiple bubble glass inclusion is generally within the normal range for a single bubble. This suggests multiple nucleation points, rather than co-trapping of vapour bubbles. Occasional “shrinkage” bubbles in glass inclusions have been observed with bubble-fractions up to 50 vol%, and it is probable that some are actually co-trapped vapour phases (Lowenstern, 1995; Frezzotti, 2001; Lowenstern, 2002).
Examples of inclusions that show definite post-magmatic alteration are uncommon, but range from slightly grey and murky, through to examples showing black dendritic markings (Fig. 5-19), to examples that are almost black, although still with a clearly defined bubble (Fig. 5-20).

Figure 5-21 shows a large glass inclusion that has been exposed on the broken surface of a quartz phenocryst. A distinct parting is obvious between the inclusion and the host quartz (Fig. 5-21b), suggesting that the glass shrank on cooling. Crystalline material occurs in the "shrinkage bubble", and it may be that this inclusion is more properly a composite inclusion, with the bubble partly filled with aluminosilicate crystals.

**Crystallised glass inclusions**

The La Copa extrusive samples shows several types of inclusions that are not observed in the samples of intrusives, including crystallised glass inclusions. Crystallised glass inclusions tend to be small (typically < 20 µm) and are commonly strongly facetted negative crystal-shapes (Fig. 5-22). Typically, they contain a mass of small (≈1 µm), clear and coloured crystals occupying > 20 vol% of the inclusion (Fig. 5-23). Most crystals are translucent, although some are green (amphibole?, Fig. 5-24), red (hematite?, Figs. 5-23, -25), or yellow (Fig. 5-26).

Shrinkage bubbles always occur in crystallised glass inclusions, and are usually deformed (Fig. 5-27), commonly dome-shaped and draped over a mass of daughter crystals (Fig. 5-28), suggesting that crystallisation began before bubble nucleation.

Microprobe analysis shows the crystals to be silicates, with compositions broadly similar to the glass. Variations are typically Na, K, or total Ox wt% values above or below the usual glass range, consistent with a mix of glass and silicate crystals (mainly quartz and feldspar). The analyses do not show any elements in concentrations too large to have been in the original glass, and the crystals are smaller than the large single crystals typical of microphenocryst inclusions. Thus the crystals are assumed to be daughter phases.

Crystallised glass inclusions differ from crystalline silicate melt inclusions (described below), in that they have a distinct shrinkage bubble, appear translucent in transmitted light, and do not contain the highly irregular crystal-lined cavities characteristic of CSMI’s. Likewise, crystallised glass inclusions are not composite inclusions because the crystals appear to be daughter phases.

Very rare examples of trichite-bearing inclusions occur in the extrusive samples from Río Blanco (Figs. 5-29, -30). Trichites are tiny hair-like crystallites that are commonly observed in volcanic glasses, and are interpreted as the product of high degrees of overcooling (Ross, 1962; Sharp et al., 1996).
Fig. 5-20  Pronounced post-magmatic alteration in a multiple-bubble glass inclusion; distinct reaction rims have developed around the shrinkage bubbles. Post-magmatic alteration, such as in figures 5-18 and 5-20, is rare at Río Blanco. DC-Rhy1. 50µm scalebar

Fig. 5-21 (a) Electron photomicrograph of an exposed glass inclusion, (b) close up of the lower part of the same inclusion. Note the distinct parting between the host quartz and the inclusion (arrowed). The shrinkage bubble opens directly into this parting, and is largely filled with crystalline silicates; this inclusion may have had similarities to fig 5-17. Circular features are noted on the surface of the inclusion in 5-20b, which could represent bubbles within the parting. CA31. (a) 50µm scalebar, (b) 25µm scalebar

Fig. 5-22  Crystallised glass inclusion from an extrusive unit of the La Copa Rhyolite, showing characteristically strongly developed facets, and containing a mass of orange/red crystalline silicates. CA30. 25µm scalebar

Fig. 5-23  Crystallised glass inclusion, containing a larger than average amount of crystalline silicates, and a hematite crystal (arrowed). CA33. 50µm scalebar

Fig. 5-24  Crystallised glass inclusion, containing a mass of greenish daughter crystals. CA30. 25µm scalebar
Fig. 5-25  Crystallised glass inclusion, containing a mass of reddish daughter crystals and a deformed shrinkage bubble, apparently deformed by crystallisation of the silicates. CA30. 25µm scalebar

Fig. 5-26 Crystallised glass inclusion, containing yellow and green daughter crystals. CA30. 25µm scalebar

Fig. 5-27 Crystallised glass inclusion, showing a deformed bubble. CA30. 25µm scalebar

Fig. 5-28 Strongly facetted crystallised glass inclusion; note the inverted dome shape of the shrinkage bubble, and the greenish daughter crystals pushing into it. CA30. 25µm scalebar

Fig. 5-29 Glass inclusion containing trichites. These are fine hair-like fibrous crystallites, considered by [Sharp, 1996 #144; Ross, 1962 #143] as resulting from high degrees of over-cooling. CA30. 25µm scalebar

Fig. 5-30 Another example of a glass inclusion containing trichites. CA30. 50µm scalebar
Fig. 5.31 Crystalline silicate melt inclusion, showing the typically inhomogeneous form of CSMI's. The translucent areas are crystalline silicates, and the dark areas are crystal-lined cavities.
9902. 50µm scalebar

Fig. 5.32 A pair of crystalline silicate melt inclusions (CSMI's). CSMI's have a dark, inhomogeneous appearance, and are commonly closely associated with small vapour-rich fluid inclusions, such as those arrowed.
9902. 50µm scalebar

Fig. 5.33 A CSMI exposed by polishing, (a) in reflected light, (b) in transmitted light. Characteristically, CSMI's contain crystalline silicate masses, which appear translucent in transmitted light, and irregular crystal-lined cavities, which appear dark in transmitted light. Note also a small magnetite? lath, possibly a co-trapped microphenocryst (arrowed)
CA30. 50µm scalebar

Fig. 5.34 CSMI's in parallel growth planes, (a) in transmitted light, (b) in reflected light, a close up of the large inclusion exposed by polishing. Note the irregular shape of the crystal-lined cavity, and the brassy chalcopyrite crystal (out of focus).
9902. 50µm scalebars
Crystalline silicate melt inclusions

**Characteristics**

Crystalline silicate melt inclusions (CSMI's) are dark in transmitted light, with pale, rather nebulous areas in irregular zones and patches (Figs. 5-31, -32, -33, and -34). The majority of CSMI’s have a negative-crystal shape, but rounded and irregular angular examples are common. CSMI’s have a very wide size range, from 1 to > 200 µm diameter, most commonly 10-50 µm. When exposed, CSMI’s are found to contain numerous angular, highly irregular cavities, between jagged, crystalline masses (Figs. 5-35, -36). In transmitted light, these cavities show up as black areas, and the crystalline masses as translucent areas. In reflected light, CSMI’s exposed on the broken surfaces of phenocrysts are predominantly white.

The attached SEM images (Figs. 5-35, -36) show that cavities in the inclusions are lined with blocky silicate crystals, primarily feldspars, quartz, and micas. Other images (e.g., Fig. 5-37) show irregular, curved, sheet-like features that are amorphous silicates. Two halite crystals have been identified in CSMI’s by their EDS spectra (e.g. Fig. 5-38). Given that inclusions exposed during polishing have been exposed to water, and that many samples were washed prior to selecting quartz phenocrysts, the few positive identifications of halite should not be taken as representative of its original abundance.

Due to their highly irregular shapes, the percentage of silicates in a given inclusion is impossible to measure accurately, but I estimate that they range from 10% (Fig. 5-38) to 90% (Figs. 5-35, -36); most probably contain > 80% silicate. Laser Raman analysis has failed to detect any liquid water or CO₂ in CSMI’s from the La Copa Rhyolite, and it is presumed that the cavities are filled with low pressure water vapour.

During optical microscope examination of many CSMI’s, either exposed by polishing or broken during sample crushing, small brightly coloured crystals only a few µm in diameter were observed. Figure 5-39 shows a bipyramidal crystal, identified by EDS as sphalerite, platy crystals identified as an iron oxide (possibly hematite), and blocky irregular calcite crystals. Thus, sulphides, oxides, and carbonates are all occasional minor components of CSMI’s.

Melt inclusions resembling Río Blanco CSMI's have been recorded in other studies, for example in the Bishop Tuff (Anderson et al., 1989; Skirius et al., 1990; Dunbar and Hervig, 1992a), and the Lower Bandelier Tuff (Dunbar and Hervig, 1992b). However, the described examples do not include the vapour-rich (low silicate content) CSMI's observed in this study.
Decrepitation features

Unhealed or partly healed decrepitation cracks are a common feature of CSMI’s. Such cracks are always brownish, typically parallel to long axis of the inclusion, and usually do not extend more than one inclusion diameter.

Discontinuous “haloes” of small, vapour-rich, two-phase inclusions are commonly found around large CSMI’s (Fig. 5-41). Some show “sweat haloes” of tiny vapour-rich fluid inclusions, close to the CSMI (Fig. 5-4). In other haloes, rarely extending more than one inclusion diameter beyond the inclusion margin, larger fluid inclusions are found in one or more distinct planes (Fig. 5-6). I interpret these to be decrepitation cracks that filled with exsolved fluids after trapping, and subsequently partly healed (Fig. 5-42). These inclusions are quite different from the large equant 2-phase inclusions (Fig. 5-43) that are demonstrably primary (see below).

"Decrepitation cones" are a dramatic decrepitation feature, consisting of conical arrangements of small (< 3 µm), vapour- and liquid-rich two-phase fluid inclusions, with a large (> 50 µm) CSMI at their apex (Figs. 5-44, -45). The angle of the cone varies from < 90° to > 120°, they always have a CSMI at their apex, and always extend to the phenocrysts edge. I interpret these features as resulting from hydraulic fracturing of the quartz phenocryst, due to the development of significant overpressure as the CSMI’s cooled. Some of the contents of the CSMI extruded into the fracture, which then healed, trapping tiny droplets of fluids as inclusions. They may be considered as large-scale occurrences of the more common decrepitation haloes.

Decrepitation haloes and cones always contain fluid inclusions, are commonly found in direct association with CSMI’s, and do not appear to occur in association with glass inclusions.

Microphenocryst inclusions

The term microphenocryst inclusion is used to cover all inclusions that were solid crystals at the time of trapping. Euhedral microphenocrysts, occasionally with parallel overgrowths, are generally found as individual crystals completely enclosed in the host quartz. However, it is also common to find euhedral microphenocrysts which are attached to, or completely enclosed by CSMI’s (Fig. 5-46), or glass inclusions (Figs. 5-47, -48). Small, irregular clumps of randomly oriented prismatic zircon or apatite crystals are occasionally observed joined by a CSMI (Fig. 5-49). This is probably a surface tension effect, i.e. the CSMI’s acted as collectors for passing solid phases in the melt.
Fig. 5-35  Electron photomicrograph (a) of a CSMI exposed on the surface of a broken quartz phenocryst, (b) close up of the same inclusion. Note the well-formed euhedral feldspar crystals, and the lack of apparent alteration.
9902. (a) 50µm scalebar, (b) 10µm scalebar

Fig. 5-36  Electron photomicrograph (a) an exposed CSMI, (b) close up. The euhedral silicate crystals are feldspar, mica, and quartz.
9902. (a) 50µm scalebar, (b) 10µm scalebar

Fig. 5-37  Electron photomicrograph (a) an exposed silicate-rich CSMI, (b) close up. Some euhedral feldspar crystals are present, but much of the inclusion is filled with curved plates of amorphous silica.
9902. (a) 50µm scalebar, (b) 10µm scalebar
Fig. 5-38  Electron-photomicrograph of a vapour-rich CSMI in a quartz phenocryst. This inclusion contains only a small amount of silicate crystals (< 10%), and a small halite crystal (see attached EDS spectra).
9902. 50µm scalebar

Fig. 5-39  Electron-photomicrograph (a) of a silicate-rich CSMI in a quartz phenocryst, (b) close up of a cluster of non-silicate minerals. This inclusion consists mainly of silicate crystals (> 90%), and small crystals of sphalerite (see attached EDS spectra), magnetite (hematite?) and calcite.
DC-Rhy1. 50µm scalebars

Fig. 5-40  Electron-photomicrograph (a) of a vapour-rich CSMI in a quartz phenocryst, (b) close up. This inclusion contains only minor silicate minerals (≈ 5%), and the host quartz is exposed at the back of the inclusion.
9902. (a) 50µm scalebar, (b) 10µm scalebar
Figure 5-38

EDS spectra for Jan31036

Figure 5-39b

EDS spectra for s3g2-1a

Figure 5-39a

Figure 5-40a

Figure 5-40b
Fig. 5-41  Photomicrograph of a CSMI showing several types of fluid inclusions common to CSMI's.  
9902. 50µm scalebar

Fig. 5-42  CSMI showing common association with elongate vapour-rich fluid inclusions, usually found within one inclusion diameter from the CSMI.  
CA30. 25µm scalebar

Fig. 5-43  A large example of a primary magmatic 2-phase vapour-rich fluid inclusion, from the Don Luis Porphyry, for comparison with the cuspatet vapour inclusions common in some decrepitation haloes.  
9915. 10µm scalebar

Fig. 5-44  Decrepitation cone in a quartz phenocryst from the Don Luis Porphyry, viewed from the side.  A large CSMI occupies the apex of the cone, which is decorated with 2-phase vapour-rich fluid inclusions.  
9915. 50µm scalebar

Fig. 5-45 Overlapping decrepitation cones, (a) viewed from above, (b) close up of fluid inclusions adjacent to the large CSMI in the centre of fig 5-44a.  
9915. 10µm scalebar
Fig. 5-46  Apatite microphenocryst partly encased in a CSMI.  
9903. 50µm scalebar

Fig. 5-47  Apatite microphenocryst partly encased in a glass inclusion; unusually, the shrinkage bubble is wrapped around the apatite crystal, and there is trace devitrification in the glass. This inclusion also show a “sweat halo”, common around CSMI's, but rare with other kinds of magmatic inclusions at Rio Blanco.  
CA31. 50µm scalebar

Fig. 5-48  Exposed glass inclusion containing multiple co-trapped microphenocrysts (a) in reflected light, (b) in transmitted light. In addition to multiple shrinkage bubbles, there are exposed titanomagnetite and apatite crystals, and unexposed zircon crystals.  
DC-Rhy1. 50µm scalebar

Fig. 5-49  A cluster of apatite crystals joined by a CSMI.  
9903. 50µm scalebar

Fig. 5-50  Feldspar microphenocryst, typical of feldspar microphenocrysts from Rio Blanco, ovoid in form and decorated by short, red/brown markings, possibly decrepitation cracks.  
9902. 50µm scalebar
Figure 5-46

Figure 5-47

Figure 5-48a

Figure 5-48b

Figure 5-49

Figure 5-50

Host

Titanomagnetite

Breached shrinkage bubbles

Glass

Apatite

Zircon
**Feldspar**

Feldspar microphenocrysts are the most common microphenocrysts at Río Blanco, and are generally found as clear, oval grains, usually with abundant red-brown surface decorations (Fig. 5-50), and are easily recognised by their lack of shrinkage bubbles. Rare examples show euhedral faces (Fig. 5-51), sometimes decorated with glass inclusions. Feldspar inclusions are typically 5 - 50µ in diameter, and have a fairly consistent aspect ratio of 2:1 (Figs. 5-50, -52). Growth planes generally show alignment of major axes of the coexisting feldspar microphenocrysts, CSMI’s, and glass inclusions.

Feldspar microphenocrysts characteristically have micron-scale red-brown decorations on their surfaces, generally extending up to five µm into the host (Fig. 5-50). More rarely (only seen in sample 9902), large, curved, decrepitation cracks extend outwards up to five inclusion diameters (Fig. 5-52). These decorations are probably decrepitation cracks.

Microprobe analysis of feldspar phenocrysts in the Río Blanco samples indicates a fairly uniform albite-rich composition, approximately Ab75 An20 Or5, consistent with the composition of feldspar phenocrysts in the host rocks. This contrasts strongly with the feldspar analyses from CSMI’s, that range from almost endmember albite to orthoclase, with a wide range of intermediate compositions.

**Other minerals**

Microphenocrysts of zircon typically occur as short lath-shaped crystals, usually with an aspect ratio between 3:1 and 5:1. Parallel overgrowths are common, as are examples of zircon crystals trapped with CSMI’s and glass inclusions (Fig. 5-53).

Microphenocrysts of apatite have been found in several forms, including blocky, equant included crystals with aspect ratios from 1:1 to 3:1 (Fig. 5-54). More commonly, apatite microphenocrysts form, long acicular crystals with aspect ratios up to 100:1 (Fig. 5-55).

Biotite and Fe-Ti oxides are found both in glass inclusions (Figs. 5-56, -57), and as microphenocrysts (Fig. 5-58). Electron microprobe analysis shows that most of the Fe-Ti oxides are magnetite, although often with some hematite component, and Ti-rich lamellae are common.

Inclusions of siderite in quartz phenocrysts are quite rare in the La Copa Rhyolite. Figure 5-59 shows a small transparent inclusion, which has clearly trapped several apatite and titanomagnetite crystals, and which contains small ruby-red hematite crystals. The siderite in this example appears to be primary, and may possibly represent a trapped melt.
**Significant features of microphenocrysts**

Several features of microphenocrysts that are important to note:

- They are compositionally uniform, with stoichiometric compositions for specific minerals (siderite excepted).
- They have euhedral form, with the exception of most feldspar microphenocrysts.
- They show a uniform distribution in all samples and are often found decorating growth planes.
- All euhedral microphenocrysts enclosed in CSMI’s and glass inclusions would have required several orders of magnitude more of their component elements than could be obtained from the glass that surrounds them, so they are clearly not daughter crystals.
- All the minerals found as microphenocrysts also occur as primary macrophenocrysts in the samples (again, siderite excepted).

Thus, these crystals have characteristics demonstrating that they are microphenocrysts, and which can be used to distinguish them from melt inclusions, even when they have been trapped inside melt inclusions.

**Fluid inclusions**

**La Copa Volcanic Complex**

**Primary fluid inclusions**

**Vapour-rich fluid inclusions**

Typically, primary vapour-dominated fluid inclusions are very dark, slightly rounded, negative crystal-shaped inclusions (Fig. 5-60), commonly around 50μ diameter, although they range from 20-100 μ. In transmitted light, vapour-rich fluid inclusions show a range of appearances. Some are completely black with a shiny surface (Fig. 5-61), which, when exposed at the surface, are seen as smooth-walled negative crystal-shaped cavities. Other examples of vapour-rich fluid inclusions have a matt black colour in transmitted light, but with clear crystalline areas around the rim (Fig. 5-62). When exposed at the surface, they consist of a central cavity with a small amount of silicates (< 10 vol %) (see Fig. 5-38). Rare halite crystals occur in this type of inclusion (Fig. 5-38).

Figure 5-63 shows an inclusion that may be an example of a composite of silicate glass and magmatic vapour; the photomicrograph shows a small arc of co-trapped glass, demonstrating that the inclusion is magmatic.
Fig. 5-51 An unusual euhedral feldspar microphenocryst, most of the facets having trapped glass inclusions with shrinkage bubbles.
CA32. 50µm scalebar

Fig. 5-52 Ovoid feldspar microphenocryst with clearly developed decrepitation cracks. The microphenocryst itself contains an apatite microphenocryst (arrowed)
9902. 50µm scalebar

Fig. 5-53 Zircon microphenocryst enclosed in a glass inclusion, with multiple shrinkage bubbles (arrowed)
9903. 50µm scalebar

Fig. 5-54 Twinned apatite microphenocryst, in quartz.
CA31. 25µm scalebar

Fig. 5-55 Acicular apatite microphenocrysts, joined by a small glass inclusion.
9902. 50µm scalebar

Fig. 5-56 Biotite microphenocryst enclosed in a glass inclusion; note the shrinkage bubble nucleated on the crystal.
CA30. 25µm scalebar
Fig. 5-57 Exposed glass inclusion containing a Ti-magnetite microphenocryst.  
DC-Rhy1. 50µm scalebar

Fig. 5-58 Titanomagnetite microphenocryst in quartz, showing exsolution lamellae of a Ti-rich phase, and three small apatite crystals on the edge of the microphenocryst.  
9902. 50µm scalebar

Fig. 5-59 Siderite microphenocryst (a) in transmitted light, (b) in reflected light. This inclusion encloses apatite and hematite microphenocrysts.  
9902. 25µm scalebar

Fig. 5-60 (a) Vapour-rich primary magmatic fluid inclusion, (b) as in (a) but re-focused. This inclusion shows the uniform, shiny, dark appearance typical of primary vapour inclusions at Río Blanco, and is the result of almost total internal reflection. In (b) a single crystal can be seen (arrowed) which appears to be the only solid contents of the inclusion.  
CA30. 50µm scalebar
Figure 5-57

Host

Titanomagnetite

Breached shrinkage

Figure 5-58

Host

quartz

Titanomagnetite

Apatite

Figure 5-59a

P15-0028

Figure 5-59b

P06-0016

Figure 5-60a

P06-0047

Figure 5-60b

P06-0048

Host

Hematite

Siderite

Apatite

P29-0001

P29-0002
Fig. 5-61  Another vapour-rich primary magmatic fluid inclusion (a), re-focused (b). In rare primary vapour-rich inclusions it is possible to focus the microscope to eliminate the internal reflection. In (b) it can be seen that the only contents of this inclusion are rosettes of tiny silicate crystals, and a single hematite? crystal (arrowed). It appears that the solid contents of this inclusion amount to only a few percent of the total.
CA30. 25µm scalebar

Fig. 5-62  Probable vapour-rich primary fluid inclusion. Crystalline silicates can be seen around the edge of this inclusion, but its appearance is not as inhomogeneous as typical CSMI's (eg the CSMI in fig 5-63). If exposed, this inclusion would probably resemble fig 5-37.
9915. 50µm scalebar

Fig. 5-63  Composite inclusion, containing magmatic vapour and a small rim of glass (arrowed)
DC-Rhy1. 50µm scalebar

Fig. 5-64  Primary magmatic 2-phase fluid-rich inclusions in a growth plane, showing 3 fluid inclusion and a CSMI. The fluid inclusions are liquid-rich 2-phase inclusions, with strongly faceted negative-crystal shapes.
9902. 50µm scalebars

Fig. 5-65  A primary magmatic 2-phase fluid-rich inclusion and CSMI, in a growth plane parallel to fig 5-64.
9902. 50µm scalebars
Liquid-rich fluid inclusions
Rare examples of two-phase, primary, liquid-rich fluid inclusions have been positively identified at Río Blanco (Figs. 5-64, -65). Water is confirmed by laser Raman microprobe analysis, but the inclusions do not contain other components that can be identified in the Raman spectra, i.e. no detectable CO₂, NH₄, aluminosilicates, etc. Similar inclusions have been reported in several Russian papers (Naumov et al., 1992; 1994; 1996), but are otherwise rare in the literature. In figure 5-64, the trail of H₂O-only inclusions occurs on a definite growth plane, and the inclusions are crystallographically aligned with adjacent CSMI’s, including one in the same growth plane. There is no evidence of cracks or fractures through which these inclusions may have leaked. The absence of aluminosilicate crystals in these inclusions provides additional evidence that they are not re-filled vapour inclusions, since primary magmatic vapour inclusions always contain at least traces of aluminosilicate crystals. Apart from the strongly developed faceting (Fig. 5-65), there is little to differentiate primary 2-phase fluid inclusions from glass inclusions, so it is possible that other examples have been overlooked, and they may not be as rare as it appears.

**Primary/pseudosecondary fluid inclusions**

As previously noted, the La Copa Rhyolite samples do not contain high-salinity fluid inclusions, but do show abundant two-phase fluid inclusions (usually vapour-rich), commonly in direct association with CSMI’s. Many are very small, vapour-rich inclusions, usually found clustered around the ends of CSMI’s (Fig. 5-66), resembling the “sweat haloes” referred to in Audetat and Gunther (1999). Larger and more elongate examples are found in decrepitation cones (Fig. 5-45), and may be up to 15 µm long and 5 µm in diameter (Fig. 5-67). Such inclusions typically contain < 10 vol% liquid. The small size and smaller liquid volume make microthermometry almost impossible, but halite crystals are not observed in such inclusions, so the aqueous liquid must have salinity less than required for halite saturation. Another type of vapour-rich fluid inclusion, most commonly found within two inclusion diameters of a CSMI (Figs. 5-6, 5-42), typically, have irregular outlines, and may be up to 25 µm in longest dimension, but appear to be no more than a few µm thick. Characteristically they have << 10 vol% liquid, and appear transparent in transmitted light. From their appearance, it seems likely that this type of inclusion represent partly-healed decrepitation cracks.

All the inclusions thus far described are directly associated with CSMI’s, and appear related to in situ decrepitation, presumably during cooling of the host quartz, and thus are arguably pseudosecondary.
However, a distinct population of larger, elongate 2-phase vapour-rich inclusions exist, not directly associated with CSMI’s, and which occurs in growth planes (Fig. 5-67). Such inclusions do not occur in trails crosscutting growth planes, and when found in growth planes they are widely dispersed and generally have their long axis parallel to the growth plane. Such vapour-rich 2-phase fluid inclusions are probably primary.

**Secondary fluid inclusions**

Obviously secondary fluid inclusions are not particularly common in the La Copa samples (intrusives or extrusives), but are recognised by their occurrence in distinct trails, which crosscut growth planes. Typically, such inclusions are flat liquid-rich two-phase fluid inclusions (with cuspatate margins), not found in close association with CSMI’s. Trails of secondary vapour-rich fluid inclusions are rare, and trails with hypersaline fluid inclusions have not been found in the La Copa samples.

**Don Luis Porphyry**

**High salinity fluid inclusions**

Only the Don Luis Porphyry sample shows abundant halite-bearing fluid inclusions. Some of these inclusions are flat lenticular shapes with scalloped and embayed margins (Fig. 5-68), and are aligned in planes that cut the phenocrysts. Rounded, globular halite-bearing inclusions are also observed (Figs. 5-7, 5-69); however, both types rarely coexist in the same trapping plane. Trapping planes containing the more globular forms also typically host silicate-rich and magmatic crystal-bearing fluid inclusions (discussed below).

High-salinity fluid inclusions contain an aqueous liquid (brine), a vapour bubble, several clear, blocky crystals (halite + several other salts), and commonly one or more opaque crystal (Fig. 5-69). Clear acicular crystals and ruby-red bladed hematite crystal are observed in some inclusions, as are highly birefringent anhydrite crystals (Fig. 5-68). The number of phases in each inclusion ranges from 3 to 10. High-salinity fluid inclusions are found in phenocrysts from the Don Luis Porphyry with coexisting CSMI, and microphenocryst inclusions, but they are not found coexisting with glass inclusions. Vapour-rich hypersaline fluid inclusions are rare (Figs. 5-70, -71).

Among the high-salinity fluid inclusions present in the Don Luis Porphyry sample (9915d), several types occur that might be interpreted (on purely petrographic grounds) to be magmatic, rather than hydrothermal in origin.
Fig. 5-66  CSMI showing a typical “sweat halo” of tiny vapour-rich fluid inclusions.  
9915. 50µm scalebar

Fig. 5-67  A primary vapour-rich 2-phase fluid inclusion; this inclusion is much larger and more regular in form than decrepitation-related vapour-rich fluid inclusions, and is not associated with a CSMI.  
CA30. 25µm scalebar

Fig. 5-68  Large, cuspate hypersaline fluid inclusions; the inclusions in figure 5-9 are from this trapping plane, which does not appear to be a growth plane. In addition to halite, sylvite, hematite, and opaque phases (including chalcopyrite and magnetite), one of the inclusions contains an anhydrite crystal (arrowed)  
9915. 50µm scalebar

Fig. 5-69  Equant hypersaline fluid inclusion containing halite, brine, and a vapour-bubble, with an opaque phase, probably chalcopyrite. Generally, inclusions with this form are not found in the same trapping planes as cuspate fluid inclusions (eg fig 5-66)  
9915. 25µm scalebar

Fig. 5-70  Vapour-rich hypersaline fluid inclusion.  
9915. 10µm scalebar

Fig. 5-71  Vapour-rich hypersaline fluid inclusion.  
9915. 10µm scalebar
Anhydrite
Fig. 5-72  Hypersaline fluid inclusion containing an apatite microphenocryst (arrowed),
with a halite crystal, a small opaque phase, brine, and a vapour-bubble
9915. 10µm scalebar

Fig. 5-73  Hypersaline fluid inclusion containing an zircon microphenocryst
9915. 50µm scalebar

Fig. 5-74  Hypersaline fluid inclusion containing an elongate crystalline mass of
feldspar (arrowed), in addition to halite, chalcopyrite, brine, and a vapour-bubble
9915. 10µm scalebar

Fig. 5-75  CSMI containing H₂O, and an anhydrite crystal (arrowed)
9915. 50µm scalebar

Fig. 5-76  Apatite microphenocryst enclosing a 2-phase liquid-rich fluid inclusion
(arrowed)
9915. 50µm scalebar (inset 10µm scalebar)

Fig. 5-77  Irregular cuspate 2-phase liquid-rich fluid inclusion.
9915. 10µm scalebar
High-salinity inclusions that contain microphenocrysts of magmatic minerals, eitherapatite (Fig. 5-72) or zircon (Fig. 5-73) represents the first type. Phenocrysts of apatite and zircon are clean euhedral crystals, not attached to, or embedded in the host crystal. They show no signs of damage or adhering matrix, and the normal complement of "salt" crystals, brine, and a vapour bubble occupy the remaining space.

A second type of inferred magmatic fluid inclusion is represented by silicate-rich hypersaline fluid inclusions containing silicate daughter phases (typically feldspar or mica), in addition to the brine+vapour bubble+salts ± opaque phases. As an example, figure 5-74 shows a fluid inclusion containing a cluster of strongly birefringent, clear, intergrown crystals, that give a weak laser Raman spectra for plagioclase.

CSMI’s containing significant amounts of H₂O and soluble salts are found in the Don Luis Porphyry, which may form the other end of the silicate-fluid inclusion continuum. They are dark and inhomogeneous (Fig. 5-75), typical of CSMI's, but Laser Raman microprobe analysis proves the existence of liquid water and anhydrite crystals, neither of which are found in CSMI's from the La Copa Rhyolite.

Another example of an apparently magmatic fluid inclusion is a two-phase liquid-rich fluid inclusion inside an apatite microphenocryst, in a quartz phenocryst from the Don Luis Porphyry (Fig. 5-76). Trapping of a primary fluid during the growth of an apatite microphenocryst strongly implies the existence of an aqueous phase at magmatic temperatures.

**Low-salinity fluid inclusions**

Liquid- and (less commonly) vapour-rich two-phase fluid inclusions are found in the Don Luis Porphyry, generally as flat, lenticular shapes, often with scalloped and embayed margins (Fig. 5-77). A given trapping plane generally contains hypersaline or vapour-rich fluid inclusions, but not both.

**Fluid inclusion summary**

The La Copa Rhyolite inclusion population includes primary magmatic fluid inclusions, mainly vapour-rich, but with minor 2-phase vapour- and liquid-rich examples. There are abundant (arguably pseudosecondary) vapour-rich fluid inclusions associated with the decrepitation of CSMI’s, and only rare secondary 2-phase liquid-rich inclusions.

The Don Luis Porphyry contains rare, generally vapour-rich, primary magmatic fluid inclusions. However, it has an abundant population of hypersaline, and 2-phase, liquid- and vapour-rich fluid inclusions.
These are predominantly secondary in origin, although there is evidence that some contain magmatic minerals (zircon, apatite, and feldspar), and are presumed to be pseudosecondary (i.e., trapped at magmatic or near magmatic temperatures).

**Composite inclusions**

In this study, the term composite inclusion refers to inclusions that contain clearly defined areas of two or more types of material, which also occur as separate inclusions. By interpretation, they represent inhomogeneous trapping of coexisting, and, at the time of trapping, necessarily immiscible components of the magmatic system. Typically they consist of clear glass (with or without the shrinkage bubbles and daughter crystals typical of glass inclusions), with clearly defined globules of:

- crystallised silicate melt (Fig. 5-78)
- primary magmatic aqueous fluid
  - high-density (now liquid) (Fig. 5-79)
  - low-density (now vapour) (Figs. 5-80, 81)
- microphenocrysts (Fig. 5-82)

Composites of these components in crystallised silicate melt (CSMI's) probably exist, but are generally not visible due to the dark, inhomogeneous nature of crystalline silicate melt inclusions. In the following chapters I infer their existence, on the basis of analytical and experimental data, but they are not apparent visually.

**Composites of glass and crystallised silicate melt**

Composite inclusions have similar sizes and shapes to glass inclusions, and the characteristic features are the presence of rounded, often spherical globule(s) with a dark inhomogeneous appearance (Fig. 5-83). Large silicate crystals sometimes project from this globule. The glass sometimes contains a shrinkage bubble, and rare examples have been found in which multiple shrinkage bubbles have nucleated in the glass (Fig. 5-84). When exposed by polishing, the globular mass is found to contain an intergrown mass of tiny silicate crystals (Fig. 5-83a), with all the components of a CSMI (see page 41). Characteristically, the proportion of glass and CSMI material varies between inclusions, with a range from inclusions with a globule of CSMI material only a little bigger than the shrinkage bubble (Fig. 5-83), to inclusions in which only a small arc of glass is visible (Fig. 5-63).

Composite inclusions are found in all La Copa samples in intimate coexistence with CSMI's and glass inclusions, including on the same growth planes. However, composite inclusions are rare, typically << 1% of the combined CSMI and glass inclusion populations.
Fig. 5-78  Brown glass inclusion with a large crystalline mass penetrating the shrinkage bubble.
CA32. 50µm scalebar

Fig. 5-79  Two composite inclusions, containing glass and aqueous globules, some of which also contain crystalline phases, from extrusive units of the La Copa Rhyolite.
CA30. 10µm scalebar

Fig. 5-80  Composite photomicrograph of three adjacent multiple-bubble glass inclusions in the same growth plane. As the line of inclusions dips into the sample, each inclusion has a different focal depth, so three photomicrographs (P29-0053, -0054, and -0055) have been combined in their correct positions.
CA30. 50µm scalebar

Fig. 5-81  Glass inclusion containing a large number of tiny bubbles, interpreted as having trapped a magmatic emulsion of melt and vapour bubbles.
CA. 25µm scalebar

Fig. 5-82  Composite inclusion containing an apatite microphenocryst, green amphibole? daughter crystals, and a muscovite crystal.
DC-Rhy1. 50µm scalebar
Figure 5-78

Figure 5-79

Figure 5-80

Figure 5-81

Figure 5-82

Apatite

Muscovite

P30-0023

P28-0013

P29-0053, -0054, -0055

P28-0028

P16-0045
Fig. 5-83  Exposed composite inclusion containing glass and crystalline silicate melt (a) in reflected light, (b) in transmitted light. In this example the crystalline silicate melt is only slightly larger than a normal shrinkage bubble.  
9903. 50µm scalebar

Fig. 5-84  Composite inclusion containing glass and crystalline silicate melt; in this example the crystalline silicate melt is much larger than a normal shrinkage bubble, and two shrinkage bubbles can be seen in the glass.  
9903. 50µm scalebar

Fig. 5-85  Composite inclusion containing glass and a globule of aqueous liquid; additionally, two other aqueous globules in this inclusion are out of focus. Note traces of crystalline precipitates on the globule walls.  
CA30. 50µm scalebar

Fig. 5-86  Composite inclusion in a feldspar phenocryst, containing glass and three globules of aqueous liquid; crystalline precipitates are apparent on the globule walls.  
CA30. 25µm scalebar

Fig. 5-87  Composite inclusion containing glass and a globule of aqueous liquid; in this example, the globule also contains a vapour bubble and a large proportion of crystalline precipitates.  
CA30. 25µm scalebar
Fig. 5-88 Composite inclusion containing glass and a two-phase aqueous globule.
CA30. 25µm scalebar

Fig. 5-89 In this composite inclusion two single-phase aqueous globules occur in glass with a large shrinkage bubble. The two globules are deformed in parallel, although the shrinkage bubble is not affected.
CA30. 25µm scalebar

Fig. 5-90 A composite inclusion, interpreted to be a magmatic emulsion inclusion, containing a random mix of vapour-bubbles and liquid-rich globules. Some of the aqueous globules also contain crystalline precipitates.
CA30. 25µm scalebar

Fig. 5-91 Another magmatic emulsion inclusion, this one containing a larger number of smaller globules.
CA30. 25µm scalebar

Fig. 5-92 Exposed magmatic emulsion inclusion (a) in reflected light, (b) in transmitted light. This example shows an uneven distribution of globules, which are crowded to one side of the inclusion.
CA30. 25µm scalebar
**Composites of glass and primary magmatic aqueous fluids**

Composite inclusions of this type (e.g. Fig. 5-85) are found only in the extrusive samples of the La Copa Rhyolite. Composite inclusions of glass and primary magmatic aqueous fluids are characteristically rounded negative crystal-shaped inclusions, typically 20-100 µm in diameter. The glass is clear, and has the same composition as normal glass inclusions (see table 6-4). Daughter crystals are rare, but trapped microphenocrysts are common.

The primary magmatic fluid occurs as distinct, clearly defined rounded bubbles or globules containing one of more of the following:

- liquid water (Fig. 5-86)
- liquid water + “salts” (Fig. 5-87)
- two-phase liquid+vapour (Fig. 5-88)
- water vapour (Shrinkage bubbles?) (Fig. 5-80)

Characteristically, the volume of globules or bubbles relative to the total volume of the inclusion varies widely between inclusions, as does the number of globules or bubbles of each phase. Vapour or shrinkage bubbles in this type of composite inclusion are typically almost spherical, although the one- and two-phase liquid-filled globules are commonly elongate, appearing to be deformed or stretched. Examples are noted (Fig. 5-89) in which multiple clear globules in close proximity, within the same inclusion, appeared to be deformed in parallel. This suggests plastic deformation of melt and the enclosed aqueous globules, with subsequent nucleation of the shrinkage bubble.

The presence of multiple globules in such composite inclusions is common (Fig. 5-80), and ranges up to examples of emulsion textures (Figs. 5-90, -91, and -92). As with other inclusions of this type, a diverse range of combinations of globules exists, including all possible combinations of liquid water, liquid water + “salts”, two-phase liquid+vapour, and vapour only.

**General characteristics of composite inclusions**

The volume ratio of two components of composite inclusions varies widely between inclusions. Indeed, a continuous gradation exists between inclusions in which glass is the dominant component, and those in which it is the minor component.

A clear and distinct boundary occurs between the components of composite inclusions, and one components retains a globular form indicative of co-trapping from a melt, rather than post trapping crystallisation (c.f. crystallised glass inclusions).

Multiple bubbles or globules may be present in the same composite inclusion, sometimes of the same types, sometimes with a range of different types.
Chapter 6: Analytical Results

Introduction

Having described the occurrence of inclusions present in the Río Blanco samples, this chapter examines their geochemistry, beginning with details of the whole rock analysis to provide the endpoint in the evolution of the Río Blanco magmas. Analytical data for melt inclusions provides a glimpse of the starting point, in so far as melt inclusions can sample parental magmas. The analytical data is presented in order of inclusion type to enable a better understanding of the inclusions, for which only optical descriptions have thus far been provided.

Whole Rock Analyses

The samples used in this study are fresh quartz + feldspar ± biotite-phyric rhyolites (Table 6-1), as described in chapter 4. Minor sericite alteration is present (predominantly in the groundmass), although the Don Luis Porphyry sample also contains minor pyrite and chalcopyrite. Loss on ignition varies between 1.56 and 5.28 wt%, and results from secondary effects (the presence of pyrite and post-magmatic alteration). To allow for alteration effects, Table 6-2 presents the major element data recalculated to 100 wt% (zero LOI, with recalculation of Fe in the pyritic sample).

Figure 6-1 shows that the recalculated data divides neatly into three sub-sets. The sample from the Don Luis Porphyry is distinct from the La Copa samples, most notably having a slightly lower SiO₂ and a higher Fe₂O₃ (tot) (even allowing for recalculation to remove Fe in sulphides). The CaO content is significantly lower; however, the total alkali content is almost identical to the other samples (table 6-2). This difference in composition is consistent with the fact that the Don Luis Porphyry is younger than, and spatially distinct from, the La Copa Rhyolite. However, Warnaars (1985, and Serrano et al. (1996) considered the Don Luis Porphyry to be co-magmatic with the La Copa Volcanic complex.
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</tr>
</tbody>
</table>

Table 6-1 Whole rock analyses for the Rio Blanco samples. All major element analyses by XRF, in Ox wt%, all trace element data by XRD, in ppm; analyses performed at the University of Tasmania. Analyses of La Copa extrusive samples CA30-33 courtesy of Pete Hollings. All blank entries we un-analysed or below detection limit.
Table 6-2. Rio Blanco whole rock analyses, recalculated to 100% wt%, no LOI, no sulphur, Total Fe recalculated to remove pyrite where present.

<table>
<thead>
<tr>
<th>Ident</th>
<th>Location</th>
<th>DC-Rhy1</th>
<th>9902</th>
<th>CA30</th>
<th>CA31</th>
<th>CA32</th>
<th>CA33</th>
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<tr>
<td></td>
<td>Don Luis</td>
<td>La Copa</td>
<td>La Copa</td>
<td>La Copa</td>
<td>La Copa</td>
<td>La Copa</td>
<td>La Copa</td>
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<tr>
<td></td>
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<tr>
<td>SiO₂</td>
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<td>70.78</td>
<td>70.59</td>
<td>70.90</td>
<td>71.13</td>
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<tr>
<td>TiO₂</td>
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<td>0.18</td>
<td>0.19</td>
<td>0.21</td>
<td>0.20</td>
<td>0.25</td>
<td>0.21</td>
</tr>
<tr>
<td>Al₂O₃</td>
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<td>15.91</td>
<td>16.09</td>
<td>16.72</td>
<td>16.97</td>
<td>16.75</td>
<td>16.48</td>
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<tr>
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<td>1.41</td>
<td>1.58</td>
<td>1.62</td>
<td>1.35</td>
</tr>
<tr>
<td>MnO</td>
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<td>0.02</td>
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<td>0.04</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>MgO</td>
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<td>0.42</td>
<td>0.48</td>
<td>0.44</td>
<td>0.67</td>
<td>0.63</td>
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<td>CaO</td>
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<td>2.35</td>
<td>2.26</td>
<td>2.27</td>
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<tr>
<td>K₂O</td>
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<td>3.59</td>
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<tr>
<td>Na₂O</td>
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<td>4.93</td>
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<td>P₂O₅</td>
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<td>0.07</td>
<td>0.07</td>
<td>0.08</td>
<td>0.09</td>
<td>0.08</td>
</tr>
<tr>
<td>Total Alkalis</td>
<td>9.55</td>
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<td>9.98</td>
<td>10.33</td>
<td>9.89</td>
<td>9.73</td>
<td>10.21</td>
</tr>
</tbody>
</table>

In figure 6-1, both La Copa intrusive samples are distinct from the four La Copa extrusive samples, but they are clearly on the same linear trend in SiO₂ v Al₂O₃. For comparison, average compositions of La Copa K- and Na-feldspars are included, and it can be seen that the trend for all La Copa samples passes through the value for quartz and average feldspar compositions. This data suggests that all La Copa samples are broadly co-magmatic, and that the intrusive samples could be derived from the extrusive composition by minor feldspar fractionation or accumulation of 1-2% quartz.

When K₂O is plotted against SiO₂ (Fig. 6-2), samples CA30 and 31 trend towards the average Na-feldspar, and CA32 and 33 trend towards the average K-feldspar. The exact stratigraphic connections between the four extrusive samples were not available in the field (see chapter 4). Samples CA30 and 31 were found above the same paleosol, and CA32 and 33 in the same region as each other, but without continuous exposure. The compositional similarity of CA30/31 and CA32/33 supports the contention that CA30/31 represent a flow or flows in one sequence, CA32/33 representing a flow or flows in another, very closely related sequence. The two groups could have resulted from selective Na- or K-feldspar fractionation from the same melt. This is also observed in the analyses of magmatic inclusion glasses, described below.
analyses $\text{Al}_2\text{O}_3$ vs $\text{SiO}_2$ of samples used in the Rio Blanco case study (recalculated to 100 Ox wt%, and sulphide-free). Also shown are the average High-K and Low-K feldspar composition for La Copa feldspars.

$\text{K}_2\text{O}$ vs $\text{SiO}_2$ (recalculated to 100 Ox wt%). Also shown are the average High-K and Low-K feldspar composition for La Copa feldspars.
Glass inclusions

Microprobe Analyses

Figure 6-3 indicates a positive correlation between total wt% vs SiO$_2$ content in glass inclusions. Within the limitations of the technique, the total wt% deficit (100 - total Ox wt%) indicates the water content of the glass, which may be as high as 5.5 wt% in some inclusions. To examine this issue, figure 6-4 plots Al$_2$O$_3$ against SiO$_2$ for the glass inclusions, both raw data, and recalculated to 100 wt%. The raw data shows a wide and irregular spread, whereas the recalculated data defines a more restricted spread, and shows a linear trend that is parallel to the trend for whole rock analyses. This suggests that current inclusion compositions reflect the parental melt composition ± a variable amount of H$_2$O. This may represent pre-trapping degassing of the magma, but the random distribution of high- and low-H$_2$O inclusions, even in the same growth plane, and the failure of Río Blanco glass inclusions to homogenise (see next chapter), suggest decrepitation of the inclusions and subsequent degassing. Given this problem, all further plots use data recalculated to anhydrous.

Excluding obvious microphenocryst phases, glass inclusions may contain clear, and more rarely green, daughter crystals. In all cases in which glass inclusions with daughter phases were analysed by electron microprobe, the glass was within the normal range for Río Blanco inclusion glasses, although sometimes tending to the lower end of the range in FeO, CaO, or MgO where coloured daughter phases were present. Clear daughter crystals were the only ones large enough to be analysed, and were always found to be quartz.

Comparison with whole rock composition

Figure 6-4 also provides a comparison between the magmatic inclusion glass compositions, and the whole rock analyses. It can be seen that the whole rock analyses and the magmatic inclusion glass compositions (recalculated to 100 wt%), all lie on the same linear trend, and figure 6-1 demonstrated that the trend for the whole rock analyses lies between average feldspar and quartz compositions. This is consistent with the view that the magmatic inclusion glass compositions reflect the parental melt composition. The current whole rock composition of the samples could be explained either by selective addition of feldspar or the selective removal of silica from the melt, as the fresh, almost unaltered nature of the samples argues against post-crystallisation silica leaching.
Fig. 6-3 Microprobe analyses of all glass inclusions from the La Copa Rhyolite. Each point represents the average of 2-5 spot analyses in the same inclusion; thus each point is one inclusion. Solid symbols are extrusive samples, hollow symbols are intrusives.

Fig. 6-4 All microprobe analyses of La Copa Rhyolite glass inclusions (black crosses), with the same data recalculated to 100 wt% (red crosses), and whole-rock compositions (also recalculated).
Comparison between samples

The analyses of glass inclusions show relatively little variation between samples on different oxide/oxide plots, as would be expected given that the samples are co-magmatic. However, some small but consistent differences exist, both between the intrusive and extrusive samples, and between different extrusive samples. For example, in figure 6-5 the intrusive samples show a wider range of values of both total alkalis and silica, whereas the extrusive samples tend to cluster at one end of that range. Likewise, some minor variation occurs between glass inclusion compositions from the extrusive samples, with those in samples CA30 and CA31 having distinct, if slightly overlapping fields, and those in samples CA32 and CA33 are also distinct. For example, in figure 6-5 CA30/CA31 and CA32/CA33 show parallel and partly overlapping fields in the Al₂O₃ v SiO₂ plot. However, all three show a parallel trend, and in figure 6-6 the three groups show slightly differing Na/K values. Similar trends are observed in the whole-rock analyses, and support the contention that melt inclusion compositions reflect parental melt compositions, and that slightly differing degrees of plagioclase fractionation (within a co-magmatic group) could produce the observed variations.

Crystalline silicate melt inclusions

CSMI’s consist of µm-scale silicate crystal masses + interstitial liquid/vapour, and this inhomogeneity produces significant analytical difficulties. ESEM imaging shows that CSMI’s contain silicate crystal clumps that are typically inhomogeneous on a µm scale (Figs. 5-36, -39). However, in order to minimise alkali diffusion during analysis, a minimum microprobe beam of 5µm diameter is needed. Thus, any microprobe data from unheated CSMI’s is generally an average of multiple crystals. Heating experiments, aimed at melting and homogenising such inclusions, is the only method likely to provide bulk compositions for CSMI’s, and this is examined in the next chapter. The most useful technique for analysing CSMI’s is the PIXE microprobe, which can produce element concentration maps with a sub-micron resolution.

Figure 6-7 gives some typical microprobe analyses of a crystalline silicate melt inclusion, with an average glass analysis for reference. The analyses of CSMI’s suggest a variable mix of Na- and K-feldspars with quartz, and also show the extent of inhomogeneity within a single CSMI.
Microprobe analyses of glass inclusions, recalculated to 100 wt%. Also shown are the whole rock analyses for all Rio Blanco samples (recalculated). Solid symbols are La Copa extrusive samples, hollow symbols are intrusives.

Fig. 6-6 Microprobe analyses of glass inclusions, recalculated to 100 wt%. Solid symbols are La Copa extrusive samples, hollow symbols are intrusives.
**Fig. 6-7a** Individual microprobe analyses within a CSMI, for comparison, the average glass composition from the same sample (with 1 standard deviation) is included.

<table>
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<th>Analysis</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>average glass (9902)</th>
<th>stdev</th>
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<td>65.73</td>
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<td>MgO</td>
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<td>0.00</td>
<td>0.01</td>
<td>0.01</td>
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<td>0.01</td>
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<td>0.35</td>
<td>0.23</td>
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<td>0.05</td>
<td>0.02</td>
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<td>0.00</td>
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<td>0.00</td>
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<tr>
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<td>96.48</td>
<td>98.60</td>
<td>96.36</td>
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</tr>
</tbody>
</table>

**Fig. 6-7b** Photomicrograph showing the location of the individual analysis in the table in 6-7a, with the outline of the exposed part of this inclusion overlaid. Left, reflected light, right, transmitted light, sample 9902, 50 µm scalebar

The scanning electron microscope with EDS provides a limited capacity for qualitative analysis of µm scale targets. EDS analysis of the silicate component of CSMI’s simply confirms the presence of aluminosilicates with variable Na/K values, consistent with microprobe analysis. However, this technique has demonstrated the presence of µm scale crystals of halite, sulphides (sphalerite), oxides (magnetite), and carbonates (calcite), in the crystal-lined cavities between the silicate crystal clusters (see Figs. 5-38, -39). Although such crystals are relatively rare, they may hold significant amounts of metals. This point may be relevant when considering the results of LA-ICPMS analyses.
As might be expected from the ESEM images of CSMI’s, laser Raman microprobe analysis of such inclusions shows the presence of mixed Na & K-feldspars as well as muscovite mica. The inclusions studied by this method were all hosted in quartz phenocrysts, which makes detection of quartz in CSMI’s impossible. In addition to feldspars and mica, at least six phases (probably silicates) have been analysed that have unidentifiable Raman spectra (personal communications, Terry Mernagh, Laser Raman Laboratory Manager, GeoScience Australia). These spectra (Figs. 6-8, -9) are not within the known range for feldspars or micas, and do not correspond to any published reference spectra for known minerals. Since the unidentified spectra are observed from several different inclusions, in different samples, it seems that the spectra represent real minerals. Electron microprobe analysis of inclusions known, from laser Raman analysis, to contain the unidentified minerals, show only the typical Na/K-bearing aluminosilicates. It thus seems likely that the six unidentified phases are silicates, but whether the phases represent stable minerals that have not yet been identified, known minerals for which there are, as yet, no reference spectra, or whether they represent metastable phases, remains problematic.

The proportions of silicate crystals and vapour-filled interstitial cavities in CSMI’s show a very wide range (e.g. Figs. 5-37, 38), so, for convenience, the CSMI’s in this section are referred to as either silicate-rich or silicate-poor. PIXE element concentration maps are included for BM36a (Fig. 6-10), BM36b (Fig. 6-11), BM18 (Fig. 6-12), BM34 (Fig. 6-13), BM31 (Fig. 6-14), BM35 (Fig. 6-15), BM32 (Fig. 6-16), BM36c (Fig. 6-17), and BM33 (Fig. 6-18). These are presented in order of apparent silicate content, from silicate-rich to silicate-poor (ie. vapour-rich). Table 6-3 gives the results of PIXE analyses in this study, as absolute concentrations.

In the element concentration maps for most CSMI’s, Ba, Zr, and Rb show the best correspondence to the outline of the inclusion, particularly silicate-rich inclusions (e.g. Fig 6-10). This suggests that the lithophile elements (e.g. Cs, Ba, Rb, Zr, and Sr) occur as a solid solution in all silicate phases, consistent with LA-ICPMS data.

PIXE element maps for CSMI’s representing the vapour-rich end of the CSMI’s spectrum (e.g. Figs 6-16, -17) typically show no element with a complete correspondence to the outline of that inclusion, and show very pronounced inhomogeneity in the distribution of Ca, K, and Fe. It is known from electron microscope imaging, electron microprobe analysis, and laser Raman spectroscopy, that the silicate component of CSMI’s is an intimate but random mix of Na- and K-feldspars, mica, and quartz. In vapour-rich CSMI’s like those shown in figures 5-38, -39, the silicate crystals are spread more or less thinly on the inclusion walls. The pattern observed in the Ca, K, and Fe element maps might represent random
clumping of crystalline phases bearing these elements, and quartz which does not. This random clumping may also be present in silicate-rich CSMI’s like Fig 6-10, but with a greater thickness of silicates; the pattern occupies much of the inclusion. The Fe and Mn element maps show a strong correspondence, suggesting Fe and Mn are interchangeably substituted in the same mineral phase(s).

The distribution of the metals, Cu, Pb, and Zn (sometimes in conjunction with Br, Cr, Fe, Rb, and Sr) is quite variable. In many inclusions these elements show a general correspondence to the outline of the inclusion, implying distribution as a low concentration solid solution in the silicates (Figs. 6-10, -18). In other cases (e.g. Fig. 6-17), Cu ± Zn ± Pb show as small distinct bright spots, suggesting small metal-rich crystals, possibly sulphides. A third pattern is seen in figure 6-13 in which bright spots are observed in Br, Cr, Cu, Fe, Pb, Rb, Sr, and Zn, which correspond to zero concentrations in the As and S element maps. The latter observation suggests that these are not sulphides. Microphenocryst of Fe-Ti oxides, apatite, and zircon are common in the Río Blanco rocks, and figure 6-13 may represent a microphenocryst co-trapped with the silicate melt.

Some CSMI’s from the Don Luis Porphyry show features not observed in the La Copa Rhyolite. Figure 6-19 shows the PIXE map of one such inclusion, in which laser Raman analysis (see Fig. 6-32) disclosed the presence of feldspar, muscovite, and chalcopyrite, and the only example of an anhydrite crystal found in a CSMI. As is typical, the Rb image corresponds most closely to the inclusion outline, and the non-corresponding images of K, Ca, and Fe are typical of CSMI’s, excluding the Ca bright spot corresponding to the large anhydrite crystal.

An initial, purely qualitative LA-ICPMS analysis was performed in March 2000, on a small number of CSMI’s, in part to examine the feasibility of using LA-ICPMS to analyse CSMI’s. Figure 6-20 gives the result of one such analysis, and reveals the presence of metals (e.g. Cu, Zn, Pb, Sb, Ag) which are at concentrations below the detection limit for the electron microprobe. Ablation of the magmatic inclusion silicate component shows consistent ratios of lithophile elements (e.g. Cs, Ba, Rb, and Sr) throughout the inclusion. Boron concentrations are well above background values and correlate with the abundance of lithophile elements (e.g. Cs, Ba, Rb, and Sr) in the silicate contents of CSMI’s. The spectra obtained demonstrated that Cu behaves differently to all other chalcophile and lithophile elements, in that its concentration peaks at the moment the inclusion is breached by the laser, though individual, minor Cu spikes were detected throughout the ablation process.
Figure 6-8  Photomicrograph of a CSMI in a quartz phenocryst; with associated Laser Raman spectra. PD49 shows unknown mineral #2, PD51 shows unknown mineral #1, the arrows mark the characteristic spectra for the unknown minerals, the other lines are quartz. Sample 9902, 50 µm scalebar

Figure 6-9  Photomicrograph of a type-2 inclusion in a quartz phenocryst from sample 9902, La Copa intrusives; with associated Laser Raman spectra. PD52 shows unknown #5, PD53 shows unknown #1.
Figure 6-10  PIXE microprobe element maps for inclusion BM36a, a silicate-rich CSMI. BM36a appears to be the most silicate-rich CSMI analysed by PIXE in this study. The Zr image shows the close correspondence with the outline of this inclusion, typical of Rb, Sr, and Zr in Rio Blanco CSMI's. There are strong concentrations of Ba, Ca, K, Fe, and Mn, but the highest concentrations do not correspond either with the outline of the inclusion, or with each other. Cu and Zn are above background concentrations in this inclusion, but do not show any obvious correspondence with any other elements. Sample 9903. 10µm scalebar
Note to PIXE images: Twenty nine PIXE analyses are presented in the study, and a standard format will be used for all. Each set of images begins with a photomicrograph showing the inclusion in question, in a frame corresponding (in size and position) to the accompanying PIXE element maps. Outlines, representing the inclusion, sometimes also phases within that inclusion, are overlain on selected images to aid comparison. The element concentration maps are false-colour images produced from the analysis, one element per image, with an intensity scale from highest- (white) to lowest-concentration (black), a false-colour relative intensity scale is included on most pages. The concentrations for each element are normalised to the highest and lowest concentration in that image, and thus con-
Figure 6-11  BM36b, a silicate-rich CSMI, although with two large, presumably vapour-filled bubbles. Again, Zr shows the best correspondence to the outline of the inclusion. The lower bubble appears as a low concentration on all other maps, although the upper bubble corresponds to higher concentrations of Ca and Fe, along with a large fraction of the Cu, Pb, and Zn.
Sample 9903. 10µm scalebar

Figure 6-12  BM18, a silicate-rich CSMI from the Don Luis Porphyry. The Cl image shows no correspondence with the outline of the inclusion, typical of PIXE images of CSMI's from Río Blanco. However, some other Don Luis Porphyry silicate inclusions (eg fig 6-44) do show Cl-enrichments.
Sample 9915. 10µm scalebar
Figure 6-13  BM34, a CSMI mid-way between silicate-rich (eg BM36a) and vapour-rich CSMI's (eg BM36c). The linear concentration of Ba, Mn, Zn (arrowed in the Ba image) is outside the inclusion, and is probably contamination in a crack. The small, strong concentration in Br, Cu, Fe, Pb, Rb, and Zn (arrowed in the Br image) is inside the inclusion, and may be a co-trapped microphenocryst, note the zero concentration in the As image (arrowed) corresponding to the same phase. Rb shows a reasonable correspondence with the outline of the inclusion, but all other elements are sparsely and irregularly distributed.

Sample 9902. 25µm scalebar

Figure 6-14  BM31, the image suggests that the silicate-component is predominantly distributed on the right-hand side of the inclusion, corresponding to the highest concentrations of K and Fe. Note that the K and Ca concentrations do not correspond. The dark area in the photomicrograph is probably a vapour-filled, crystal-lined cavity (see fig 5-39, -39).

Sample 9902. 10µm scalebar
Fig 6-13

25 µm

As  Ba  Br

Ca  Cu  Fe

Mn  Pb  Rb  Zn

Fig 6-14

10 µm

As  Ba  Ca

Cu  Fe  K

Mn  Rb  Sr  Zn  Zr

Min.  Relative intensity  Max.
Figure 6-15 BM35, vapour-rich CSMI, note the general correspondence between the translucent areas in the photomicrograph, and the highest K concentrations. The element maps for Br, Cu, Fe, Pb, Rb, Sr, and Zn, show a small area with high concentrations, apparently corresponding to a small microphenocryst (arrowed).
Sample 9903. 25µm scalebar

Figure 6-16 BM32, a very vapour-rich CSMI. No element corresponds to the whole inclusion, even Rb, suggesting only a very minor silicate content. The bright spot in the Zr image may be a zircon microphenocryst below the inclusion.
Sample 9902. 25µm scalebar
Figure 6-17 BM36c, a typical vapour-rich CSMI; only Sr shows a general correspondence to the outline of the inclusion.
Sample 9903. 25µm scalebar

Figure 6-18 BM33, the most vapour-rich CSMI analysed in this study; arguably this inclusion is a primary magmatic vapour inclusion. No element corresponds to the whole inclusion, and even Rb only corresponds to the K image.
Sample 9903. 25µm scalebar
Fig 6-17

Min. Relative intensity Max.

Fig 6-18

Min. Relative intensity Max.
Figure 6-19  BM21c, a CSMI containing several components of a hypersaline fluid inclusion. Laser Raman microprobe analysis show a chalcopyrite microphenocryst (arrow in the Cu image), and a large anhydrite crystal (arrow in the Ca image), as well as liquid $\text{H}_2\text{O}$. As in previous CSMI's (eg fig 6-10, 6-12) Rb has the closest correspondence to the inclusion outline, whereas K, Mn, and Fe are randomly distributed within the inclusion.

Sample 9915. 25$\mu$m scalebar

Fig. 6-20  Selected laser ablation-ICPMS data (B, Cu, Zn, Rb, and Cs) from a CSMI (~80 $\mu$m) enclosed in quartz. The X-axis shows elapsed time from the beginning of ablation, and the Y-axis shows the spectrometer signal for each mass in counts per second. At $\approx$ 6 seconds, this particular inclusion was breached by the laser, from $\approx$ 6 - 75 seconds material within the inclusion was ablated, at $\approx$ 75 seconds the laser burned through the inclusion. Note the correlation between Rb, B, and Cs, the explosive release of Cu as soon as the inclusion was breached, and the presence of minor Zn and Cu spikes possibly corresponding to single micron-sized daughter sulfides.
Fig 6-19

![Image of elemental mapping](image1)

Fig 6-20

![Graph of raw LA-ICP-MS data for sample BM3 g7-1](image2)
Table 6-3. PIXE microprobe analysis of fluid inclusions from the Don Luis Porphyry, and melt inclusions from the La Copa Rhyolite. Analyses performed on the CSIRO-GEMOC Nuclear Microprobe, at North Ryde in Sydney, data processed to give concentrations in ppm, td = no analysis because the inclusion was too deep, na = not analyzed.

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<th>Fluid inclusions Cl K Ca Mn Fe Cu Zn Ga As Br Rb Sr Zr Ba Pb</th>
<th>Composite inclusions</th>
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<th>Glass + liquid</th>
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</tbody>
</table>
This suggests that Cu is mainly concentrated in an interstitial vapour- or liquid-phase, or lines the vapour-filled cavities, and is expelled early in the ablation. The small, random peaks during ablation of the silicate part of the inclusion, possibly correspond to tiny sulfide crystals previously described (Fig 5-39).

**Composite inclusions**

**Composites of glass and crystalline silicates**

Table 6-4 shows the average of three spot analyses performed on the glass component of a composite inclusion, with the averaged analyses of other glass inclusions from the same sample. It can be seen that the glass in the composite inclusion is very similar to the overall average for glass inclusions in the sample, and well within the range of such inclusions.

<table>
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<th>Stdev</th>
<th>Min</th>
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<td>75.70</td>
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<td>1.53</td>
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<tr>
<td>TiO₂</td>
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<td>0.08</td>
<td>0.06</td>
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<tr>
<td>Al₂O₃</td>
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<td>14.61</td>
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<tr>
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<td>0.05</td>
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<td>96.41</td>
<td>95.60</td>
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Table 6-4  Electron microprobe analyses of a composite inclusion containing glass and crystalline silicates, average of three analyses. The inclusion is from sample 9902, and is shown in figure 5-83. For comparison the maximum, mean, 1σ, and minimum values for all glass inclusions in the same sample.

Typically, laser Raman analysis of CSMI's from the La Copa Rhyolite disclose the presence of feldspars (of various compositions), and muscovite. Some CSMI's from the Don Luis Porphyry have been shown to contain anhydrite, chalcopyrite, and hematite. Anhydrite has never been identified in CSMI's from the La Copa Rhyolite, although chalcopyrite and hematite have.
Figure 6-21  BM41, a composite inclusion containing glass, a shrinkage bubble, and crystalline silicates on the right-hand side of the shrinkage bubble. Sr shows the best correspondence to the inclusion (outline removed to show contrast), and Ba, Ca, and K, show good correspondence to the glass, consistent with the analyses of glass inclusions. In contrast, the area of crystalline silicates shows high concentrations of metals (Cu, Fe, Mn, Pb, and Zn), and as low concentrations of As, Ca, and Cl. The shrinkage bubble is poorly represented in the element maps, being visible only as a region of low concentrations in the As, Ca, and Cl images, extending beyond the patch of crystalline silicates, but not visible on the images for the metals. These images show that the glass, shrinkage bubble, and crystalline silicates all have discrete composition, even if it is not possible to separate out absolute concentrations for each phase.
Sample 9902. 25µm scalebar

Figure 6-22  BM42a, also a composite inclusion containing glass, a shrinkage bubble, and crystalline silicates. Note that the crystalline silicate phase is proportionately larger than in fig 6-21, consistent with inhomogeneous trapping. The element map for Si is included, and the shrinkage bubble appears as a low-concentration zone. The distribution of metals (Cu, Fe, Mn, Pb, and Zn), and Ba, are contained in the shrinkage bubble, but restricted to the upper edge. This suggests a crystalline silicate phase within, but discrete from, the shrinkage bubble.
Sample 9902. 10µm scalebar
Figure 6-23  BM45a, a rare example of a composite? inclusion containing crystallised glass, a shrinkage bubble, and an opaque phase. A probable microphenocryst (strong metal concentration, and zero As) is attached to the shrinkage bubble (arrow on the photomicrograph). Most of the Cl is concentrated in a globule phase wrapped around the shrinkage bubble (brine?). Zn, Fe, and to a lesser extent Cu are also contained in an area of crystalline glass (arrowed in the Fe image).
Sample 9903. 50µm scalebar

Figure 6-24  PD1, a composite inclusion containing glass, a shrinkage bubble, and crystalline silicates. Metal concentrations in this inclusion are apparently low, but there is a small bright spot in the Zn image, which could be a micron-scale sphalerite crystal, as observed in fig 5-39.
Sample 9903. 25µm scalebar
PIXE element maps for four composite glass and crystalline silicate inclusions are presented, BM41 (Fig. 6-21), BM42a (Fig. 6-22), BM45a (Fig. 6-23), and PD1 (Fig. 6-24), figure 6-21 is characteristic. The bulk of this inclusion is glass, with a small globule of crystalline silicates attached to the shrinkage bubble. The PIXE element maps show an overlapping pattern of Ca, K, Rb, and Sr, corresponding to the silicate glass, suggesting they occur as a solid solution in the glass. The shrinkage bubble is apparent only as an area of low concentration in the Ca and Rb element maps. The dark globule of crystalline silicates shows a quite different pattern from that of the glass, or the shrinkage bubble, notably, with distinct concentrations of Cu, Fe, Ge, Mn, Pb, and Zn. These metals are concentrated in an arc on the edge of the shrinkage bubble, corresponding well to the globule visible in the photomicrograph. The highest concentrations of Fe and Mn are associated with the dark globule, but lower concentrations correspond to the inclusion outline, consistent with the presence of Fe and Mn in the electron microprobe analyses of melt inclusion glass. The crystalline silicate globule shows as zero concentrations in the Ca, Cl, and As element maps.

Figure 6-22, shows a similar inclusion, also with enhanced concentrations of metals in a small area of the inclusion, except that the elevated concentrations of Ba, Cu, Fe, Ge, Mn, Pb, and Zn are within the area occupied by the bubble, but are concentrated in the upper half. This observation is important, as it suggests that the shrinkage bubble and the crystalline silicate melt globule have joined, but the globule has retained its integrity, even if it is no longer distinct in the photomicrograph.

The PIXE microprobe can provide element concentration maps for each element with sub-micron resolution, making it a most useful tool for studying CSMI's. However, normalising the data to give absolute concentrations involves considerable difficulties, and attempts to extract concentration data for individual phases (often < 10 µm dia), or other regions within magmatic inclusions, has proved unsuccessful. However, PIXE element concentration maps show the differing element patterns of glass and crystalline silicates, and show that the crystalline silicates contain the bulk of the metals.

**Composites of glass and primary magmatic fluid**

Laser Raman microprobe analysis of inclusions that are composites of glass and globules of aqueous fluid discloses only the spectra for free water, with no detectable CO₂, N₂, NH₄, or other gaseous phases. None of the crystalline precipitates analysed gave a Raman signature, and are probably ionic salts of some kind (or quartz?).

The PIXE element maps for three composite inclusions containing glass and globules of aqueous liquids are presented, BM28 (Fig. 6-25), BM47 (Fig. 6-26), and BM48 (Fig. 6-27).
In such inclusions, the glass component typically has uniform concentration of Ca, K, Fe, Mn, Rb, and Sr, suggesting a solid solution of these elements. Cu and Zn are present as diffuse low concentrations corresponding to the glass, but most of the Cu (Fig. 6-26) and Zn (Figs. 6-26, -27) corresponds to the location of bubbles. In figure 6-27, Cl intensity shows some correspondence with Cu and Zn, possibly both are present as soluble chloride complexes. However, the Cl signal attenuates rapidly with depth, and Cu and Zn signals from deeper in the inclusion do not show any distinct correspondence. The distribution of Fe is also inhomogeneous; in addition to Fe in the glass, PIXE maps of composite glass and aqueous fluid inclusions often show small Fe bright spots within the bubbles. Figure 6-25a shows a close up of one bubble in such an inclusion, and it can be seen that the Fe signature corresponds to a tiny opaque phase (magnetite?), in an area of clear crystalline precipitates. No Cl bright spot corresponds to the precipitate; however rapid attenuation of the Cl signal with depth may be masking it.

**Fluid Inclusions**

**Primary magmatic fluid inclusions**

Figure 6-28 shows the PIXE analysis for an unambiguous primary magmatic vapour-rich fluid inclusion. However, the silicate content of some CSMI's (e.g. BM33, Fig. 6-18), as indicated by their very low K + Ca concentrations (table 6-3), is low, and is comparable with vapour inclusions (c/f Fig. 5-40). It can be seen in Figure 6-28 that the inclusion contains almost no silicate material, only a small cluster of crystals in the top right hand corner. The element map for Rb does not correspond to the whole inclusion (as it does in CSMI’s); the only correspondence is with the crystalline mass, the rest of the inclusion being effectively a hole in the quartz host. The crystalline mass has two components, one containing K, Fe, and Mn, may be a silicate. The other, with strong concentrations of As, Br, Cu, Pb, and curiously Sr, may be a sulphide, given the very high Pb concentration (43000 ppm, table 6-3), possibly galena. Zn and Rb appear evenly distributed between the two phases.

**Hypersaline fluid inclusions**

As mentioned in the technique section (chapter 3, page 18), the laser Raman microprobe is ineffective when examining ionic compounds, such as chlorides. However, anhydrite, chalcopyrite, and hematite have been identified in several hypersaline fluid inclusions (Figs. 6-29, -30).
Figure 6-25  BM28, a composite melt inclusion in a feldspar phenocryst, containing glass and aqueous globules (a), closeup of the right-hand globule (b). Seven, touching, adjacent single-phase aqueous globules form a line in the glass inclusion; similar linear arrays of liquid-filled globules, or single-phase aqueous globules, have been observed in other melt inclusions from Río Blanco. Removing host contributions for inclusions in feldspar is difficult, but some evidence is available. The shrinkage bubble (lower right, out of focus) does not show up on the element maps, and most of the aqueous globules show up mainly as a low concentration region in the K image. However, two of the globules (#1 and #5 from the right) contain strong concentrations of Fe, which correspond to a cluster of transparent crystals, and a single opaque phase, in the close up of globule #1 (fig 6-25a).
Sample CA31. (a) 25µm scalebar, (b) 10µm scalebar

Figure 6-26  BM48, multiple aqueous globules in a composite glass inclusion. Individual globules show most clearly as “holes” in the K, and Si images. Metals (Fe, Cu, Zn) and Cl are concentrated unevenly in some of the bubbles, although others show no obvious concentrations. Note the concentrations of Cl, Cu and Zn in one of the bubbles (arrowed); Fe is concentrated in several bubbles, possibly corresponding to tiny opaque phases (magnetite?) visible in some of the globules. Cl (as brine) may be more widespread than the images suggest, as the secondary x-rays produced by Cl attenuate badly passing through even a few µm of glass. The high-Cl bubble is the un-breached globule closest to the surface.
Sample CA31. 25µm scalebar
Figure 6-25

Figure 6-25a, close-up

Figure 6-26
Figure 6-27  BM47, another composite inclusion containing glass and multiple aqueous globules. One of the bubbles contains a concentration of Cu distributed evenly through out the bubble, implying Cu in solution. In contrast, the Fe-rich bubbles contain 1- or 2-phase aqueous liquid, with small opaque phases (arrowed). Inhomogeneity is common in such inclusions, with coexisting bubbles of vapour, and 1- or 2-phase liquids, with inhomogeneous concentrations of metals.
Sample CA31. 25µm scalebar

Figure 6-28  BM43, a primary magmatic vapour inclusion. Just visible in the upper left-hand corner of the inclusion is a small crystalline cluster, which appears to be the only solid contents of this inclusion. It has two parts; adjacent to the inclusion wall is a small area with strong Br, Cu, Pb, Zn, Rb, and Sr, but no Fe, Ca, or K. The larger part shows strong concentrations of Fe, Mn, K, Zn, and traces of Cu. The Pb concentration of the inclusion is exceptionally high (43,000 ppm) suggesting that the smaller phase is a Pb-bearing phase (galena?), while the larger phase could be a Fe-bearing silicate.
Sample DC-Rhy-1. 25µm scalebar
**Fig 6-27**

![Figure 6-27](image)

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**Fig 6-28**

![Figure 6-28](image)

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Figure 6-29  Minerals identified by laser Raman microprobe, in inclusions from the Don Luis Porphyry. A trail of cuspatc hypersaline fluid inclusions, containing hematite, chalcopyrite, and anhydrite. Sample 9915. 50µm scalebar

Figure 6-30  An elongate hypersaline fluid inclusions, containing chalcopyrite, and anhydrite. Sample 9915. 50µm scalebar

Figure 6-31  An implied high-temperature hypersaline fluid inclusion, containing chalcopyrite, magnetite, and a feldspar, the spectra of which most closely matches orthoclase. Sample 9915. 25µm scalebar

Figure 6-32  CSMI containing anhydrite, chalcopyrite, muscovite, and a feldspar, the spectra of which most suggests an alkali-feldspar. Sample 9915. 25µm scalebar

Figure 6-33  A similar CSMI, with muscovite and feldspars, probably plagioclase and an alkali-feldspar. Sample 9915. 25µm scalebar

Figure 6-34  A hypersaline fluid inclusion, prior to LA-ICPMS analysis, although otherwise similar to other hypersaline fluid inclusions; the analysis showed 3 wt% Al, suggesting feldspars. Sample 9915. 25µm scalebar
Figure 6-35  BM15, a large, cuspat, hypersaline fluid inclusion in a quartz phenocryst from the Don Luis Porphyry. The inclusion contains a halite crystal (arrow in the Cl image), an anhydrite crystal (arrow in the Ca image), a chalcopyrite crystal (arrows in the photomicrograph and the Cu image). Apart from the chalcopyrite crystal, substantial amounts of metal are in solution. The outline of the inclusion has been omitted in many of the images to show the strong contrast between the inclusion and the host quartz. Sample 9915. 25µm scalebar

Figure 6-36  BM15b, a small equant fluid inclusion in the same phenocryst as fig 6-35, but not in the same trapping plane. There is an anhydrite crystal under the bubble, and the opaque phase (arrowed) appears to be magnetite or hematite. Sample 9915. 25µm scalebar
Figure 6-37  BM16b, another small equant fluid inclusion, containing a disproportionately large anhydrite crystal (c/f fig 6-35). The inhomogeneity apparent in the relative size of phases in different inclusions is reflected in the absolute concentration data (table 6-3).
Sample 9915. 10µm scalebar

Figure 6-38  BM17, a cuspate hypersaline fluid inclusion. The bright spot visible in the As and Ca images may correspond to the acicular (apatite?) phase, but may also be an unidentified transparent hexagonal phase just visible beneath it. The bright spots on the Sr and Ti images are probably microphenocrysts outside, and below the fluid inclusion.
Sample 9915. 10µm scalebar
Figure 6-39  BM21a, a small, but exceptionally metal-rich fluid inclusion (9,000 ppm Cu, 2700 ppm Zn, table 6-3). The small opaque phases are probably chalcopyrite, but the Cu, Zn, and Pb images show these elements are distributed throughout the inclusion.
Sample 9915. 10µm scalebar

Figure 6-40  BM21b, a small equant hypersaline fluid inclusion.
Sample 9915. 10µm scalebar
Figure 6-41  BM7b, another large cuspatc hypersaline fluid inclusion. The apparent low Cl concentrations in fig 6-40 and 6-41 are artefacts, due to the excessive depth of the inclusions.
Sample 9915. 50µm scalebar

Figure 6-42  BM7a. Most of the Cu present in this inclusion is located in two opaque phases under the edge of the vapour-bubble.
Sample 9915. 25µm scalebar
Figure 6-43 BM16, hypersaline fluid inclusion containing feldspar. Laser Raman microprobe analysis disclosed the presence of a chalcopyrite microphenocryst (arrow in the photomicrograph), a small magnetite microphenocryst (arrow in the Fe image), and a cigar-shaped cluster of feldspar crystals (arrow in the K image) Sample 9915. 25µm scalebar
In addition, muscovite, and an alkali feldspar, has been identified in an inferred hypersaline high-temperature inclusion (Figs. 6-31, -32). None of the bubbles examined show any trace of gases.

PIXE element maps are presented for hypersaline fluid inclusions: BM15 (Fig. 6-35), BM15b (Fig. 6-36), BM16b (Fig. 6-37), BM17 (Fig. 6-38), BM21a (Fig. 6-39), BM21b (Fig. 6-40), BM7b (Fig. 6-41), BM7b (Fig. 6-42), and BM16 (Fig. 6-43). Reduction of the raw data has produced an estimate of absolute concentration, calculated for the whole inclusion; this data is presented in table 6-3. The data show wide and apparently random variation in element ratios between inclusions.

Ideally, LA-ICPMS should be performed on inclusions for which microthermometric analyses are available, as this provides the best estimate of Na concentration, which can be used as the internal standard. Unfortunately, LA-ICPMS analysis of fluid inclusions became available only late in this study, and while still “bedding down” the system. The internal standard problem was addressed by the use of microthermometric data on visually similar inclusions from the same sample, but not the same inclusions, which largely had decrepitated during microthermometric experiments. Additionally, microscope measurement of inclusions and contained halite crystals, and subsequent calculation of inclusion/halite crystal volume ratios were used as a check on the estimated salinity. The internal standard problem means that, for successful analysis, the conversion to ppm concentrations gives an estimated cumulative error of 20-30 % relative (similar to PIXE analysis). The data produced from this work is given both in relative percentage of each element, with respect to the total analysed for that inclusion, and as absolute ppm concentrations. Of the two, the relative percentages are more reliable, but absolute concentrations are needed to compare inclusions, even if the data has a sizeable error component. With the above caveat, LA-ICPMS analysis has provided useful data; Table 6-5 gives the relative percentages of elements in a selection of Río Blanco fluid inclusions, and table 6-6 gives the same analyses in ppm.

The element concentrations for hypersaline fluid inclusions, both PIXE and LA-ICPMS, show a wide and generally random variation between elements; in particular, the most abundant elements (Na, Cl and K) show no apparent relationship. Copper and Zn concentrations are high, with averages of 2280 and 1584 ppm. respectively, but with maximum values of 7169 and 5899 ppm. One unusual result of the analyses is a single inclusion (Fig. 6-34) which contains 5.64 % Al. Aluminium was absent in most inclusions and was only analysed for in one session; its presence in one hypersaline inclusion may indicate the presence of feldspar, as indicated by other analytical methods in one other inclusion (Fig. 6-43).
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**Min** 209 23000 11653 5017 3204 74 114 114 114 116 136 147 121 | 121

**2-phase**
Table 6-6  LA-ICPMS analysis of fluid inclusions from the Don Luis Porphyry. Analyses given as percentages of the total contents, blank entries not analysed, or below detection limit.

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Mean 0.39  38.00  30.58  17.07  11.97  0.6337  0.3519  0.2567  0.3135  0.0640  0.0808  0.1531  1.4065  0.0020  0.0051
stdev 0.14  7.68   6.77   1.35   2.38   0.1482  0.1638  0.1871  0.2214  0.0195  0.0258  0.0517  0.7720  0.0017  0.0036
Min  0.18  27.29  22.40  10.01  5.66   0.0740  0.1725  0.1519  0.1616  0.0199  0.0287  0.0775  0.7656  0.0008  0.0025
**Summary**

Analyses by several different techniques have shown that Río Blanco CSMI's and glass inclusions differ widely in their physical characteristics, but not in major element composition. Some variation in metal concentration is apparent, but appears to relate to the percentage of vapour present in CSMI's, possibly in the form of oxide and sulphide crystals in cavities in CSMI's, which may have precipitated from the vapour-phase after crystallisation of silicates.

Composite inclusions show characteristic differences between the co-trapped phases. In comparison to the enclosing glass, crystallised silicate and aqueous fluid globules show sharp compositional boundaries for some elements. In particular, Cu, Zn, Cl, and to a lesser extent Fe, show a distinct preference for the globules. The absolute amounts of metals involved are not large, but globule boundaries (or phases within them) are distinctively marked in element concentration maps.

Fluid inclusions show distinctly inhomogeneous compositions, with generally high metal concentrations. It will be an issue for the discussion chapter to consider the connection between the increasingly metal-rich phases coexisting with the silicate melt, and the extremely metal-rich late-stage fluid inclusions.
Chapter 7: Experimental Results

Introduction

After introductions, which deal with the specific details of the techniques used, The descriptions and results of experiments performed on the inclusions are presented in two sections, homogenisation experiments on silicate inclusions, and microthermometry on fluid (or fluid-bearing) inclusions. Experiments were performed on Río Blanco inclusions to:

- obtain homogenised inclusions for microprobe analysis,
- estimate trapping temperatures for melt and fluid inclusions, and
- investigate the behaviour of inclusions at magmatic temperatures.

The results are given in order of inclusion type.

Homogenisation experiments

Glass inclusions

- Individual heating experiments

Introduction

Homogenisation experiments on individual inclusions under microscope observation (chapter 2, page 12) were performed to estimate trapping temperatures, and to provide optimum parameters for bulk heating experiments. As the inclusions often decrepitated near the \( \alpha \) to \( \beta \) quartz transition temperature (573°C), normal procedure was to heat rapidly to 550°C (typically 100°C/min.), then slowly to 600°C (typically 10°C/min.), then more rapidly to the temperatures of interest. As set up for my experiments, the LINKAM TS1500 heating stage quenches from 900°C to room temperature in 4-5 minutes, giving a maximum quenching rate of 3-4°C/sec. As it was possible to watch the inclusion as it quenched, it was established that this quenching rate was fast enough to prevent nucleation of daughter crystals, but not fast enough to consistently prevent nucleation of shrinkage bubbles.
Results

Heating experiments with glass inclusions typically begin by a darkening of the inclusion between 350-450°C (Fig. 7-1c). This is followed by the formation (or perhaps separation) of an apparently liquid phase between 600-700°C (Fig. 7-1e). Between 700-750°C the contents of the dark zone coalesced into one or more droplets, and sometimes merged with the shrinkage bubble (Figs. 7-1f, -1g). Within this temperature range, small shrinkage bubbles nucleated in some inclusions. Heating to temperatures as high as 1000°C, and holding inclusions at 850°C for up to 4 hours, failed to homogenise any glass inclusion, or even to coalesce bubbles in multiple-bubble inclusions (e.g. Fig. 7-1j).

Heating experiments on a crystalline glass inclusion (Figure 7-1) show progressive melting of the crystallised part of the inclusion beginning at 400°C, but still not complete after 3 hours at 900°C. Even bulk heating is not enough to produce complete melting in crystalline glass inclusions.

Failure to homogenise may be due to one of four reasons:

1. Insufficient time being allowed for homogenisation of viscous silicate melts,
2. Inhomogeneous trapping; if a liquid/vapour phase was inhomogeneously trapped with the melt, the combined inclusion would have a T_h above that of the glass,
3. Diffusive re-equilibration of water, and
4. Decrepitation of the inclusions, and consequent degassing.

Glass inclusions from Okataina, that have similar major element chemistry to Río Blanco glass inclusions (eg. Tables 6-1, 12-1, 12-2), homogenise completely at temperatures of 800 - 900°C, so there would seem to be no problem in the length of the Río Blanco experiments. Inhomogeneous trapping may have affected a proportion of cases, but the relatively constant bubble fraction of ≈ 6 vol% (± 2 vol%, 1σ) implies homogeneous trapping. Diffusive H₂O loss, possibly due to prolonged cooling in a sub-volcanic intrusion is possible, but in chapter 10 it will be shown that this has not occurred appreciably in the Okataina glass inclusions. Given the ubiquitous decrepitation of coexisting CSMI's, it seems likely that decrepitation, and consequent degassing, is the most probable cause of failure of glass inclusions to homogenise. If this loss occurred while the inclusion still contained a melt, it could also explain the larger than expected shrinkage bubbles in glass inclusions, (≈ 6 vol% for Río Blanco, against an estimated range for felsic glass inclusions generally of 0.2-5.0 vol% (Lowenstern, 1995)). Likewise, if degassing had proceeded to completion (for the particular temperature and pressure conditions) it could also explain the relative uniformity of the bubble-fraction.
Crystalline silicate melt inclusions

Río Blanco inclusions

- Individual heating experiments

  Heating experiments on large (> 10 µm) CSMI’s have largely failed to produce homogenisation at any temperature (up to 1100°C) and in any practical timeframe (< 5 hours). Homogenisation of small CSMI’s (< 10 µm) was noted at temperatures between 820-850 °C (Fig. 7-2), as was partial melting of occasional larger inclusions (Fig. 7-3). However, even partial melting was not common.

- Bulk heating experiments

Introduction

  CSMI’s are characteristically crystallised and inhomogeneous on a µm-scale, and heating experiments provide the only method of obtaining a homogeneous composition for analysis. On the basis of individual grain experiments (Figs. 7-2, -3) it became clear that melting times for CSMI’s were excessive. Homogenisation did occur in some small CSMI’s (< 10 µm) at temperatures as low as 823°C. However, in larger inclusions, temperatures up to 1000°C, over several hours, did not result in homogenisation, and rarely produced full melting. To achieve much longer heating cycles than was possible with the heating stage, bulk heating techniques were employed. A quantity of quartz or feldspar grains was placed in a ceramic crucible; this was heated in a box furnace to a chosen temperature, and left at this temperature for a specified time. By experiment, the optimum parameters were found to be 850°C for 96 hours. Details of this technique are given on page 12. Subsequent microscopic examination showed that fracturing due to thermal stress was minor. The grains were then prepared as grainmounts (see page 9).

  It is not possible to determine the pre- and post-heating composition for a given inclusion. However, the inclusions coexisted randomly in the samples, and the same analytical techniques and protocols were employed for all analyses, so it may be assumed that the analysed inclusions represent samples of the same populations, pre- and post-heating.
Figure 7-1 Crystallised glass inclusion in a quartz phenocryst from sample CA31, an extrusive rhyolite from the La Copa Volcanic Complex.  (a) The inclusion at room temperature, a crystalline mass occupies the left-hand end of this inclusion, (b) at 400°C the inclusion had visibly darkened, (d, e, f,) the darkened zone progressively melted and merged, (g) finally merging with the shrinkage bubble at 750°C, (h, i, j) holding at this temperature failed to completely melt the crystalline component, or to coalesce all the shrinkage bubbles.

CA31. 25µm scalebar
Fig. 7-1
Figure 7-2  Homogenisation of a CSMI in quartz, in a growth plane decorated with abundant similar inclusions. Photomicrographs in the top row show heating to 820°C, with homogenisation at 825°C, upon cooling the bubble re-nucleated, and repeated cycling gave a consistent homogenisation temperature of 823°C. CA31. Field of view 30 x 30 µm.

Figure 7-3  Individual grain homogenisation experiment, CSMI in a quartz phenocryst. (a) the inclusion at room temperature, (b) by 500°C the inclusion showed loss of internal phase boundaries, (c, d) at 750°C extensive melting can be seen, and vapour-filled cavities have begun to merge. (e, f) previous experiments with similar inclusions had shown that complete melting in similar inclusions did not always occur at temperatures as high as 1000°C, so this inclusion was held a lower temperature to see if extra time would achieve homogenisation. After 2 hrs most of the phases had melted (g), but at 3 hrs only an opaque phase remained (arrowed), but homogenisation had not occurred (h) the inclusion cooled to room temperature without any phase changes. CA31. 25µm scalebar
**Results**

Even under the extreme experimental conditions used, complete melting (e.g. Fig. 7-4) was not always achieved, and residual crystals of a feldspar-like composition were found in a significant percentage of inclusions (Figs. 7-5, -6). The positioning of shrinkage bubbles in embayments in the inclusion margin (Figs. 7-4, -6b) is probably the result of the shrinkage bubble locally protecting the inclusion wall against re-crystallisation of quartz. The technique may have resulted in overheating of inclusions (see discussion, page 14) and this needs to be taken into account when interpreting the results. Additionally, since the process was not undertaken with any optical control, it was not possible to determine which inclusions began as glass, and which as CSMI’s, except when surplus heating stage wafers were used (Figs. 7-6, -7).

Figure 7-8 plots Al₂O₃ vs SiO₂ for sample CA31 (recalculated to 100 wt%). The heated inclusions plot on a coherent trend, between feldspar and quartz compositions, with a considerable overlap; however a number of inclusions show higher SiO₂ than any unheated glass inclusions. Danyushevsky et al., (2000) and Lowenstern (1995) have shown that diffusive H₂O loss is rapid at high temperatures, and particularly so if overheating occurs during an experiment. To test for experimentally induced H₂O loss, the un-recalculated data is plotted in figure 7-9. This shows that most of the homogenised inclusions lie on a trend line towards 100 wt% (ie anhydrous) and thus must be presumed to have lost significant H₂O. However, a group of inclusions, which plotted as high-silica in Fig. 7-9, show the same implied H₂O concentration as the un-heated glass inclusions.

The possibility of melting of quartz from inclusion walls must also be considered. If these inclusions have incorporated some host quartz via melting, then plots not showing silica, e.g. Na vs K should show a dilution effect, but no change in the K:Na ratio. That is, the glasses show a 5% increase in silica over unheated inclusions from the same sample; if this resulted from dilution by melted host, than all other elements would be reduced proportionally. Figure 7-10 shows a Na₂O vs K₂O plot for the same samples, and it can be seen that some heating experiment glasses, and the unheated glasses, overlap in the Na vs K plot, arguing against incorporation of silica, at least in these inclusions. On the other hand the high-silica inclusions show a distinct trend, too large to be consistent with simple dilution by 5% melting of the host. Better evidence for this is provided by the bulk heating experiment on CA33. Figure 7-11 plots Al₂O₃ vs SiO₂, and figure 7-12 plots Na₂O vs K₂O; the drop in Na₂O content is up to 50%, and could not be the result of a 5% dilution by melted host quartz.
Fig. 7-8  Bulk heating experiment results, sample CA31 La Copa extrusives. Each point represents the average of 2-5 spot analyses in the same inclusion. Open diamonds are homogeneous glass inclusions (post heating), solid diamonds are inclusions with > 77.7 wt% SiO₂, arbitrarily described as “high-Silica”, dots are glass inclusions (unheated) from sample CA31, squares are the average K- and Na-feldspars.

Fig. 7-9  Bulk heating experiment results, sample CA31, original data, not recalculated to 100 wt%. Each point represents one inclusion. Open diamonds symbols are homogeneous glass inclusions (post heating), solid diamonds are the same inclusions described as high-silica in Fig. 7-9. Dots are unheated glass inclusions from the same sample.

Figure 7-4  A completely melted CSMI, from a bulk heating experiment, 850°C for 96 hrs. The apparent projection of the shrinkage bubble into the host quartz is probably an artefact, caused by the bubble locally “armouring” the inclusion wall against melting and recrystallisation.
Figure 7-5  A partly melted CSMI, from a bulk heating experiment, 850°C for 96 hrs. Note the residual crystalline mass; electron microprobe analysis shows similar residual crystalline material to have a variable aluminosilicate composition, similar to feldspar.

Figure 7-6  Bulk heating experiment on a CSMI in a surplus heating stage wafer (a) before heating, (b) after heating. During heating the inclusion has changed shape slightly, but the volume remains the same; residual crystals remain after heating to 850°C for 96 hrs.

Figure 7-7  Bulk heating experiment on a crystallised glass inclusion in a surplus heating stage wafer (a) before heating, (b) after heating. During heating the inclusion has changed shape slightly, but the volume remains the same; no residual crystals remain after heating.
experiment results, sample CA31. Open diamonds are homogeneous glass inclusions (post heating), solid diamonds are the inclusions described as “high-silica” in Fig. 7-9, solid circles are unheated glass inclusions from the same sample.

Fig. 7-11 Bulk heating experiment results, sample CA33 La Copa extrusives. Each point represents the average of 2-5 spot analyses in the same inclusion, thus each point represents one inclusion. Diamonds are homogeneous glass inclusions (post heating), solid circles are unheated glass inclusions from the same sample.
Fig. 7-12  Bulk heating experiment results, sample CA33. Diamonds are homogeneous glass inclusions (post heating); dots are unheated glass inclusions from the same sample.

The origin of the “high-silica” compositions is uncertain, but it could be explained by a significant, but variable loss of alkalis, from a starting composition similar to the unheated glass. Indeed figure 7-10 suggests two separate alkali loss trends in sample CA31, starting from different high- and low-silica compositions. However, only a single trend is apparent in sample CA33.

Thus, the “high-silica” heated inclusions represent a population of inclusions, different to the glass inclusions, which have not lost H$_2$O, or acquired significant SiO$_2$ by melting of the host, during the experiments. Since the only silicate inclusions in the samples were CSMI's and glass inclusions, it may be presumed that these “high-silica” inclusions represent melted (but not homogenised) CSMI's. However, it should be stressed that only heated inclusions that were homogeneous after heating have been plotted in figures 7-8 to -12; most CSMI's still retained residual feldspar (e.g. Figs. 7-4, -5, & -6). If these inclusions had completely melted, then the compositions would have been pushed towards feldspar compositions (Fig. 7-8), in some cases to even more SiO$_2$-poor compositions than the unheated glass inclusions. So, it seems that glass inclusion compositions are simply a sub-set of CSMI compositions, and that some CSMI compositions could be derived from “glass” compositions by variable alkali loss.
Don Luis Porphyry inclusions

- Bulk heating experiments

Introduction

Two features of CSMI’s from the Don Luis Porphyry suggested that they differed from CSMI’s from the La Copa Volcanic Complex:

- Laser Raman microprobe studies showed that some CSMI’s from the Don Luis Porphyry contained liquid water, and large crystals of minerals not found in inclusions from the La Copa Rhyolite, for example the anhydrite crystal shown in figure 6-43.
- Petrographic observation and microthermometric study of sample 9915 suggested an apparently continuous gradation from CSMI’s, through various hypersaline fluid inclusions containing “magmatic” minerals, to hypersaline and 2-phase fluid inclusions.

Bulk heating experiments were performed in order to homogenise these CSMI’s for comparison. The technique used was the same as bulk heating experiments on Río Blanco CSMI’s, except that the maximum temperature (850°C) was held for 48 hours, rather than 96 hours. Given the risk of diffusive water loss from the inclusions during prolonged heating, a shorter time frame was selected. It was observed that 48 hours produced results from Don Luis Porphyry samples, comparable with 96 hours for the La Copa Rhyolite samples.

Results

Most CSMI’s less than 20 µm in diameter, and some larger, melted more or less completely. However, larger inclusions more commonly retained 5-80% residual feldspar crystals (Fig. 7-13), as did most CSMI’s from the La Copa Rhyolite (Figs. 7-5, -6). In all cases one or more shrinkage bubbles occurred in the inclusion, having very variable bubble-fractions (estimated range of 5-80 vol%). In the majority of inclusions the bubbles were a single vapour phase. However, some contained multiphase bubbles, ranging from 2-phase vapour dominated (Fig. 7-14), to bubbles containing abundant clear “salts” with vapour and a small amount of liquid (Figs. 7-15, -16), the inclusions resembling salt-melt inclusions (Kamenetsky et al., 2003a). Apparently similar salt-melt globules have been produced during homogenisation of CSMI’s by M-L. Frezzotti (see Frezzotti (1992) Fig. 3, page 25), and (Kamenetsky et al., 2003b).
Many fluid inclusions decrepitated during heating; others were found that showed only salt phases and a vapour bubble, but no liquid water (Fig. 7-15b). During preparation for PIXE microprobe analysis, fracturing of the quartz above the inclusion was noted during polishing. A similar effect was noted when preparing unheated composite inclusions containing glass+aqueous liquid in quartz phenocrysts, but not composite inclusions in feldspar. Also, a crack was observed propagating into a salt-rich bubble in the inclusion pictured in figure 7-16, which caused sudden decompression of the bubble and complete vaporisation of the liquid phase. These suggest that the contents of the melted inclusion were under considerable pressure. Subsequent laser Raman spectroscopy has shown that the crystalline material in these bubbles contains anhydrite, suggesting a chloride/sulphate-melt, rather than strictly salt-melt. PIXE microprobe images for two such inclusions (Figs. 7-18, -19) both show that the globules show very strong concentrations of metals (Cu, Zn, and Fe), as well as Cl, Br, and As.

Laser Raman spectroscopy demonstrated that the opaque phase in these inclusions is magnetite, and the presence of disordered carbon in the bubbles. Both anhydrite and magnetite have been confirmed in CSMI’s and halite-bearing fluid inclusions in the same samples. Re-filling of cavities in CSMI’s by post-magmatic brine cannot be completely discounted, given the abundance of hypersaline fluid inclusions in the sample, but the fact that the chloride/sulphate-melt globules are under pressure suggests they are primary.

The bulk heating experiments on CSMI’s from the Don Luis Porphyry confirm the presence of H₂O, anhydrite, and unidentified chlorides (probably at least NaCl and KCl) in some CSMI’s from this sample. This confirms the laser Raman data, and distinguishes silicate-rich CSMI’s in the Don Luis Porphyry (which have significant amounts of “salts”) from silicate-rich CSMI’s in the La Copa samples (which do not).

**Microthermometry**

**Introduction**

A LINKAM THMS 600 fluid inclusion stage with liquid nitrogen cooling (effective range +600°C to -100°C), and a LINKAM TS1500 heating stage (effective range 20°C to 1500°C) under an Olympus BX 60 microscope were used in the microthermometric experiments. Standard microthermometric techniques were used (e.g. Roedder, 1984).
Figure 7-13  A partly melted CSMI from the Don Luis Porphyry, 850°C for 48 hrs, still containing a residual crystalline mass.
9915. 10µm scalebar

Figure 7-14 Two-phase aqueous globule in a partly melted CSMI.
9915. 10µm scalebar

Figure 7-15 Partly melted CSMI from the Don Luis Porphyry, (a) containing multiphase salt-melt globules, (b) close up of the hypersaline fluid inclusion in the upper left of (a). Arrows point to the largest of the salt-melt globules.
9915. (a) 25µm scalebar, (b) 10µm scalebar

Figure 7-16 Partly melted CSMI, showing numerous multiphase salt-melt globules, arrows point to the largest of the salt-melt globules.
9915. 25µm scalebar

Figure 7-17 A large CSMI and numerous fluid inclusions in a quartz phenocryst from the Don Luis Porphyry. Inset: close up of a fluid inclusion containing a halite crystal that occupies ~95% of the inclusion.
9915. 50 µm scalebar, inset 25µm scalebar
Figure 7-18  PD2, partly homogenised CSMI from heating experiments on samples from the Don Luis Porphyry. The large globule is composed of re-crystallised salt-melt, and contains most of the metals (Cu, Fe, Pb, and Zn) as well as most of the As, Br, Cl, and Sr in the inclusion. The glass component contains a uniform distribution of Ca, K, Fe, and Rb, corresponding to the outline of the inclusion, as is noted in the glass in composite inclusions (eg figs 6-21, -22).
Sample 9915. 25µm scalebar

Figure 7-19  PD3, another partly homogenised CSMI. In this example several of the smaller globules (arrowed) can be shown to have similar composition to the large salt-melt globule, and to the salt-melt globule in fig 7-18. The inclusion is the same one shown in fig 7-16.
Sample 9915. 25µm scalebar
Each experiment was repeated 2-4 times, and homogenisation temperatures with
variation > ± 5°C and final ice melting temperatures with variation > ± 0.2°C were
discarded. The usual repeatability was homogenisation temperatures, ± 2°C and final
ice melting temperatures, ± 0.1°C.

Don Luis Porphyry

Multi-phase inclusions

The multi-phase inclusions used in these experiments contained liquid + vapour
+ one or more solid phases. A single solid phase was probably halite, but multiple solid
phases may have included halite, sylvite, anhydrite, and other, unidentified, minerals.
Final homogenisation of these inclusions was by both halite- and bubble-disappearance,
but predominantly by halite disappearance (= 60 % of hypersaline fluid inclusions), with
an average of 462°C (1σ = 54°C). (Table 7-1, Fig. 7-20). The bubble disappearance
data has a very wide range, and rather irregular distribution, with an average of 385°C
(79°C, 1σ).

Table 7-1. Summary of homogenisation temperatures of fluid inclusions from
sample 9915. The maximum recommended operating temperature for the Linkam
THMS 600 stage is 600°C; a small number of inclusions were noted that retained a
small amount of halite at 600°C, and homogenisation is presumed to be by halite
disappearance at 600-650°C.

<table>
<thead>
<tr>
<th>Homogenisation by:</th>
<th>Multi-phase inclusions</th>
<th>2-phase inclusions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Halite disappearance</td>
<td>Bubble disappearance</td>
</tr>
<tr>
<td>T_h,max.</td>
<td>600°C</td>
<td>600°C</td>
</tr>
<tr>
<td>T_h,mean</td>
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<td>385°C</td>
</tr>
<tr>
<td>1 std dev</td>
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<td>T_h,min.</td>
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<tr>
<td>T_h,mean - 1 std dev</td>
<td>408°C</td>
<td>306°C</td>
</tr>
</tbody>
</table>

Table 7-1. Summary of homogenisation temperatures of fluid inclusions from
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disappearance at 600-650°C.

Using the tables in Bodnar and Vityk (1994), the final T_h of 461°C implies an
average salinity of 56 wt% NaCl_{equiv} and a range of 48 - 61 wt% NaCl_{equiv} (at 1σ). Given
the good repeatability for the homogenisation experiments, and a general
correspondence between T_h and the percentage of crystals seen in the inclusion, the wide
spread in the data seems to be real. A slight discrepancy between the data for
homogenisation by halite disappearance and homogenisation by bubble disappearance is apparent. Although there is extensive overlap, the average is higher for halite disappearance, with a tighter spread (Table 7-1, Fig. 7-20). It is possible that there are two separate, but overlapping populations of hypersaline fluid inclusions, one higher temperature, homogenising by halite disappearance, the other slightly lower in temperature, homogenising mainly by bubble disappearance. However, both Vargas et al. (1999), Skewes et al. (2003) report both types of homogenisation in the same fluid inclusion population, and the apparent discrepancy is not large.

Homogenisation temperatures can also provide some estimate of trapping temperatures, if the fluid inclusions represent trapping in a 2-phase assemblage (ie boiling). In that case the homogenisation temperatures approximate the trapping temperatures. However, the petrographic evidence for a boiling assemblage in the hypersaline fluid inclusions from the Don Luis Porphyry is equivocal. The strict test for a boiling assemblage is the occurrence of liquid- and vapour-rich fluid inclusions randomly arranged in the same trapping plane (Roedder, 1984). This is difficult to satisfy in the samples used, as the trapping planes are commonly several hundred µms thick and cross and anastomose irregularly.

![Homogenisation Temperatures](image)

**Fig. 7-20** Histograms of the distribution of homogenisation temperatures by halite dissolution and by bubble disappearance for hypersaline fluid inclusions from sample 9915

Another approach to this question is to ask whether the fluid could have been sub-critical at the time of trapping, on the basis of estimated depth of formation. A
paleodepth of $< 2$ km is estimated from fluid inclusions in mineralised breccias at Río Blanco (Holmgren et al., 1988; Vargas et al., 1999), in units adjacent to, but slightly older than the La Copa Rhyolite. More recently, Skewes et al. (2003) published fluid inclusion data from the Donoso breccia, which is also slightly older than the Don Luis Porphyry, and located $\approx 1$ km to the east, in the Los Bronces section of the property. Here crystallisation pressures were estimated at $\geq 1$ kbar. Although insufficient geological evidence exists to give a precise paleodepth of crystallisation of quartz in the Don Luis Porphyry samples, it seems reasonable to estimate a trapping pressure of 0.5 Kbar, with an upper limit of $\approx 1$ kbar.

Experimental work by Knight and Bodnar (1989) has shown that 30 wt% NaCl solutions have a critical pressure of 1.574 kbars at 820°C. Modelling by Shinohara (1994), based in part on the work of Knight and Bodnar (1989), has suggested that rhyolitic magmas exsolving fluids at depths less than 5.2 km. (1.3 kbars lithostatic pressure) must do so in the subcritical region (L+V, L+V+Halite in a high-salinity system). On the pressure correction tables for 40 wt% NaCl, from Bodnar and Vityk (1994), the critical temperature/pressure curve for homogenisation temperatures greater than 500°C is always greater than 0.5 kbars. While acknowledging the risk in using pressure corrections with salinities above those on which the tables were calculated (50-60 wt% NaCl$_{equiv}$ in the Don Luis Porphyry), the absence of experimentally verified tables leaves little choice.

Additional evidence for sub-critical conditions is provided by the occurrence of fluid inclusions containing $> 95$ wt% halite (Fig. 7-17). Roedder (1984) and Campbell et al. (2001) noted that such inclusions have been observed, but are only possible if the solution was oversaturated with respect to NaCl at the time of trapping, ie. the halite had already crystallised when trapped.

Thus, the evidence suggests that the Don Luis Porphyry hypersaline fluid inclusions were trapped under sub-critical conditions, and the $T_b$ for these inclusions is a reasonable approximation to $T_{trapping}$.

**2-phase inclusions**

If the primary and pseudosecondary fluid inclusions for the Don Luis Porphyry were trapped in a boiling assemblage (L+V±Halite), it follows that the 2-phase fluid inclusions were probably also from a boiling assemblage. Homogenisation in the 2-phase inclusions was by bubble disappearance, with an average of 292°C ($\pm 22°C, 1\sigma$), and a range of 260-360°C. The final ice melting temperatures have a range of -0.6°C to -2.7°C with an average of -1.4 °C (0.7°C, 1σ). Due to the difficulty of observing ice formation and melting in low salinity inclusions (particularly those with a large vapour
phase), the final ice melting temperature data-set is not large, but the average final ice melting temperature of -1.4°C implies a salinity of 2.5 wt% NaCl$_{equiv}$. The combination of low-salinity, and lower $T_h$ values than for multi-phase inclusions, could imply meteoric fluid rather than magmatic. However, Skewes et al. (2003) argued from stable isotope data that little, or no, meteoric fluids were involved in the formation of similar 2-phase fluid inclusions in the Donoso Breccia, favouring mixing and condensing of magmatic vapours. In this study, vapour-rich multiphase inclusions were noted (Figs. 5-70, 71), and some homogenisation temperatures for multiphase inclusions are actually lower than any of the 2-phase inclusions. Thus the vapour-rich multiphase inclusions, and at least some 2-phase inclusions, appear to be coeval with the hypersaline inclusions. Although not conclusive, my data suggests that the 2-phase inclusions are magmatic, rather than meteoric fluids.

**Summary of the microthermometry**

The microthermometric data for fluid inclusions from the Don Luis Porphyry demonstrates trapping of fluid inclusions, beginning with hypersaline inclusions at >600°C to (rarely) < 200°C, overlapping with trapping of 2-phase inclusions from 360°C to 260°C. The fluids trapped in the hypersaline fluid inclusions were magmatic, and there may also have been magmatic fluid in the 2-phase inclusions. Trapping generally occurred under sub-critical conditions (ie “boiling”), although the random distribution of fluid inclusions, and the paucity of obvious trapping planes, means that paragenetic controls are insufficient to rule out episodes of supercritical “non-boiling” conditions. However, the slight discrepancy between the homogenisation by halite- and bubble-disappearance could hint at periodic “non-boiling” conditions.

The above data on inclusions from the Don Luis Porphyry can be compared to that obtained by Skewes et al. (2003) from the Donoso breccia pipe in the Los Bronces section of the deposit. Skewes et al. (2003) found evidence for the formation of one of the latest mineralised breccias (slightly older than the Don Luis Porphyry) by magmatic fluids, with almost no significant input of meteoric water. These authors reported evidence of two distinct fluids; both were high-temperature and high-salinity, one was a non-boiling high-pressure fluid, and the other coexisting high-salinity liquid and low-salinity vapour, suggesting low pressure, boiling, solutions. These two fluids coexisted in the same samples and were interpreted to have trapped fluids cycling between boiling and non-boiling as the brecciation and mineralisation occurred. Hypersaline multiphase fluid inclusions had $T_h$ values of 244 - 668°C and salinities between 31.6 and 56.7 wt% NaCl$_{equiv}$ although some hypersaline fluid inclusions did not homogenise at 690°C (the upper limit of their heating stage).
Liquid-rich fluid inclusions had $T_h$ values of 173-448°C, and limited data on vapour-rich fluid inclusions showed $T_h$ values of 330-550°C, with salinities between 2.6 and 24.9 wt% NaCl$_{equiv}$.

**Composite inclusions of glass+primary magmatic fluid**

During microthermometry on composite inclusions of this type, metastable vapour bubbles appeared and disappeared randomly during freeze/thaw cycles in some aqueous globules (Figs. 7-21, 7-22), and positive final ice melting temperatures ($T_m$) were measured. The captions to figures 7-21 and 7-22 detail the metastability observed during two specific series of microthermometric experiments, on initially single-phase aqueous globules. In some cases, after a random number of freeze/thaw cycles a bubble nucleated upon melting of the ice. If the experiment stopped at that point, the bubble would spontaneously disappear at some random time after nucleation. In some cases it was < 1hr, and in other cases > 6hours, but less than a few days, although in no case was the bubble disappearance actually observed. During any subsequent freezing of an inclusion with a metastable bubble, the bubble disappeared during freezing but usually reappeared when the ice melted. Roedder (1984) described four types of metastability, all involving two-phase (L+V) inclusions that metastably **failed to nucleate a bubble** for some random time (usually < 6hours) after unfreezing. However, in the Río Blanco composite inclusions the “stable” state is a single-phase aqueous liquid, and the “metastable” state is a two-phase (L+V) fluid. Thus metastable bubble nucleation has occurred, rather than a metastable failure to nucleate.

Two examples of positive final ice melting temperature ($T_m$) were noted, one with a final ice melting temperature of +0.7°C and one of +0.8°C. The stage was recalibrated against synthetic fluid inclusions to be certain of these temperatures. Roedder (1984) noted that in most cases of metastability the true $T_m$ is usually less than 10°C below the apparent $T_m$, and often only a few degrees, but it is impossible to be certain.

Most final ice melting temperature data for single-phase aqueous globules in composite inclusions falls in the range 0.0°C to -1.5°C. Given that metastability was noted only in this type of bubble, it seems likely that the actual $T_m$ for these inclusions is lower by an unknown amount. Additionally, a smaller number of clear bubbles had much lower $T_m$’s, in the range -5 to -14°C, primarily -9 to -14°C. Using the data of Bodnar and Vityk (1994), the lower freezing point depression temperatures suggest salinities of 0-2.5 wt% NaCl$_{equiv}$, and the higher freezing point depression temperatures suggest salinities of 13-17 wt% NaCl$_{equiv}$ (Fig. 7-23).
Figure 7-21  Microthermometric experiments on a clear bubble type-C inclusion in a quartz phenocryst from a La Copa extrusive sample. The sequence is: (a) at the end of one freeze/thaw cycle a vapour bubble appeared spontaneously in the clear bubble, (b) the inclusion froze at -35°C as before, and is shown here with ice still present at -0.7°C and (e) at 0°C (final ice melting temperature = +0.8°C), (d) an hour later, after experiments with other inclusions in the grain, it was noted that the bubble had disappeared, (e) the inclusion still froze at the same temperature (shown here at -31.6°C), (f) and is shown here with ice still present at +0.7°C (final ice melting temperature still = +0.8°C)
Figure 7-22  Microthermometric experiments on a clear bubble type-C inclusion in a quartz phenocryst from a La Copa extrusive sample. The sequence is: (a) at the beginning of the experiment the large clear bubble showed only a single liquid phase, (b) the inclusion snap froze at -38°C (shown here as a mass of tiny ice crystals at -47.8°C) and had a final ice melting temperature of +0.7 °C, after three freeze/thaw cycles a vapour bubble appeared and the experiment was terminated, (c) 6 hrs later the bubble had spontaneously disappeared and the experiment was resumed on the same inclusion, shown here with ice still present at -0.5°C (final ice melting temperature still +0.7°C), (d) after one more freeze/thaw cycle the vapour bubble spontaneously reappeared in the clear bubble and was still present when the experiments finished, (e) one week later the experiment was resumed and it was found that the bubble had spontaneously disappeared, inclusion shown here at room temperature, (f) and is shown here with ice still present at -0.2°C (final ice melting temperature still +0.7°C).
Given the fact that clear bubble inclusions almost inevitably decrepitated at
temperatures of less than 250°C, no data is available to estimate trapping temperatures
or pressures.

As described in chapter 5, some aqueous globules contain crystalline
precipitates and a Fe-rich opaque. Microthermometric data shows salinities of
precipitate-free bubbles up to 17 wt% NaCl\textsubscript{equiv}, but with no data available for
precipitate-bearing clear bubbles. Given the immiscibility effects noted in the low
salinity inclusions, and the presence of precipitates in some clear bubbles, it seems
likely that the actual range of salinities for these presumably primary magmatic fluids is
9 to \approx 40 wt% NaCl\textsubscript{equiv}.

![Fig. 7-23 Histograms of the
distribution of freezing point
depression temperatures for aqueous
fluids in clear bubble inclusions from
Rio Blanco extrusive samples.](image)

Conclusions from the analytical and experimental work

Combining the petrographic observations from chapter 5 with the analytical and
experimental results discussed in this chapter, it is possible to draw the following
general conclusions:

**Current whole rock composition**

- The intrusive and extrusive compositions from the La Copa Rhyolite are consistent
  with differentiation by fractionation. The current whole rock compositions can be
  obtained from the parental melt (as inferred from the magmatic inclusions), either
  by addition of Na- or K-feldspar, or removal of a few percent of quartz from the
  same parental melt.
- The extrusive samples have fractionated more than the intrusive samples.
Glass inclusions

- The wide variation in the current water content of melt inclusion glasses (as inferred from totals of microprobe analyses) predominantly reflects extensive (indeed almost universal) decrepitation and degassing, even though petrographic evidence of decrepitation is usually lacking (excepting the large shrinkage bubbles).
- The absence of detectable amounts of CO₂ in the inclusions suggests differentiation and degassing at shallow depths.

Crystalline silicate melt inclusions

- CSMI's consist of a variable mix of:
  - intimately mixed Na- and K- feldspars, quartz, and muscovite, with other as yet unidentified silicates
  - a vapour-dominated aqueous phase, with an unknown, but possibly significant salinity
- Silicate-dominated (>80 % silicate), and silicate-poor (<20 % silicate) endmembers are known from ESEM studies, and intermediate stages are inferred from petrographic observations. The K concentration of an inclusion is a good indicator of the relative proportion of silicate.
- CSMI’s contain slightly elevated levels of metals (Cu, Pb, and Zn), relative to the coexisting glass inclusions, and the concentration of metals appears to correlate with the percentage of vapour-phase in the inclusion.
- CSMI’s show a wider range of compositions than coexisting glass inclusions.
  - CSMI's that can be completely melted contain consistently more SiO₂ and less, but variable Na and K, suggesting derivation from compositions similar to glass inclusions by variable loss of alkalis.
  - CSMI's that cannot be completely melted probably have compositions similar to glass
- The trapping temperature of CSMI’s appears to be 825°C.
- CSMI's from the Don Luis Porphyry (but not the La Copa Rhyolite) show the presence of anhydrite, and chalcopyrite, in addition to the silicate minerals found in CSMI's from the La Copa Rhyolite.
- Heating experiments on Don Luis Porphyry CSMI's demonstrate very high concentrations of chlorides and sulphates not found in La Copa Rhyolite CSMI's.
Composite inclusions

Glass + Crystalline silicates

- The glass in this type of composite inclusion is compositionally identical to coexisting glass inclusions.
- The dark crystalline silicate globules noted in this type of composite inclusion have all the components of, and correspond to the composition of, CSMI's.
- Analytical data shows that the discrete bodies of glass and crystalline silicates have sharply defined boundaries and different compositions, carrying the greater amount of metals (probably as metal-rich precipitates from the original magmatic vapour).

Glass+primary magmatic fluids

- The glass in this type of inclusion is also identical to coexisting glass inclusions.
- The fluid in globules in this type of composite inclusion is of moderate to high salinity, up to 13-17 wt% NaCl-equiv (proved) and possibly > 35 wt% NaCl-equiv (if the clear crystals are precipitated salts).
- Metastability effects noted in the single-phase aqueous globules are not consistent with those observed in low-temperature fluid inclusions, and there is evidence that the globules are under pressure. Both points suggest they are primary, rather than post-magmatic refilling, confirming the petrographic evidence (chapter 5)

Fluid Inclusions

There is an apparently continuous range from CSMI's, to multiphase hypersaline fluid inclusions and vapour-dominated fluid inclusions in the Don Luis Porphyry sample.

Hypersaline, magmatic mineral-bearing inclusions

- Trapping of rare apatite and zircon phenocrysts in fluid inclusions, and the presence of silicate minerals in hypersaline fluid inclusions, imply trapping of the fluid inclusion at (or near) magmatic temperatures.

Hypersaline fluid inclusions

- Characteristically, hypersaline fluid inclusions in the Don Luis Porphyry show high trapping temperatures (340-620°C) and high salinities (43 - 73 wt%, average 53 wt% NaCl-equiv)
- Microthermometric analyses suggest that trapping may have occurred in the sub-critical region, from a two-, and possibly three-phase liquid (liquid+vapour ± halite)
Low salinity fluid inclusions

- Two-phase fluid inclusions from the Don Luis Porphyry demonstrate low- to medium-trapping temperatures (280-400°C), and low salinities (average 2.5 wt% NaCl_{equiv}).
Chapter 8: Discussion and Conclusions

Discussion

Introduction

This chapter summarises my observations on immiscibility processes in the Río Blanco magma chamber, as illustrated by the observed magmatic inclusions, and concludes the Río Blanco case study. On the basis of the inclusion descriptions, phase compositions, and experimental evidence it is now possible to model immiscibility processes at Río Blanco.

Volatile phase exsolution from silicate magmas involves two related sets of features; the physical characteristics involved in the formation and separation of the phases, and the composition of those phases. With this in mind, this chapter begins with consideration of the melts, which subsequently underwent immiscible phase separation, and the phases evolved, followed by the evidence for the physical nature of volatile phase exsolution. This discussion closes with an examination of the chemical consequences of that separation, both on the newly exsolved phases, and in the wider sense of mineralisation potential.

Melts represented by Río Blanco melt inclusions

Crystalline silicate melt inclusions

The following lines of evidence demonstrate that CSMI’s represent a discrete melt, rather than accidental trapping of other phases (glass, microphenocrysts, or magmatic vapour), or post-trapping alteration or devitrification of a pre-existing phase:

- The felted masses of tiny silicate crystals seen in CSMI’s (Figs 5-35, -36, -37) do not resemble trapped crystals (microphenocryst inclusions), common in the host phenocrysts, as well as in glass inclusions (Fig 5-48). Microphenocrysts are generally large (> 10µm), single, euhedral crystals. Intergrown clusters of silicate crystals are not observed as microphenocrysts at Río Blanco.
- Crystal aggregates in CSMI’s always show micron-scale compositional inhomogeneity; in contrast, microphenocrysts are compositionally uniform, and show stoichiometric compositions for the particular phenocrystic mineral.
- Devitrification involves the sub-solidus reorganisation of silicate glass; the electron microscope images of crystalline aggregates with open-space filling textures suggest crystallisation from a melt, not devitrification.
- Electron microprobe studies show that the crystalline masses do not contain chlorite, clays, or other common alteration minerals observed at Río Blanco, which argues against post-magmatic alteration.
- Microprobe analysis of feldspar phenocrysts in the Río Blanco samples indicates a fairly uniform albite-rich composition, approximately Ab75 An20 Or5. This contrasts strongly with the feldspar analyses from CSMI’s, that range from almost endmember albite to orthoclase, with a wide range of intermediate compositions.
- Heating experiments with CSMI’s demonstrated at least partial, and often complete melting of their crystalline contents at temperatures of 650-850°C, and homogenisation (in small inclusions) at 825°C. Trapped microphenocrysts must have already been crystalline at magmatic temperatures (>850°C).
- CSMI’s show an irregular distribution of crystal-lined cavities (e.g. Figs. 5-35, 36), without any indication of a shrinkage bubble. This implies that crystallisation of the silicate melt occurred before a shrinkage bubble had the opportunity to form. Glass inclusions with obvious signs of post-magmatic alteration (e.g. Figs. 5-19, -20) are rare, but do exist at Río Blanco, and unlike CSMI’s all have shrinkage bubbles.

The inhomogeneous, recrystallised nature of CSMI’s, and their endemic decrepitation, makes any estimate of original volatile content impossible. However, several lines of evidence suggest that CSMI’s originally had a high volatile content (primarily H2O).

- The common occurrence of haloes of aqueous inclusions, and decrepitation cracks, around CSMI’s (e.g. Fig 5-4, -6), and the occurrence of decrepitation cones (e.g. Fig. 5-44), are indicators of an initially volatile-rich nature.
- The cavities in CSMI’s are lined with sharply faceted quartz, feldspar, mica, and rare halite (Fig. 5-38), sulphide, oxide, and carbonate crystals (Fig. 5-39). This crystallinity implies growth in an aqueous medium (liquid or vapour) in an open space.
- LA ICPMS data for a CSMI from sample 9915 shows the presence of Cu concentrated in a phase that was expelled immediately the inclusion was breached, implying the Cu was concentrated in the cavities of CSMI (either dissolved, or more probably precipitated out on the cavity walls). This is also consistent with the view that Cu will strongly partition into a liquid phase (e.g. Candela and Holland, 1984), and growing evidence for preferential partitioning into vapour, rather than a coexisting aqueous liquid (Heinrich et al., 1992). This is also indicative of the existence of a volatile-rich phase.
Taken together, the preceding lines of evidence demonstrate that CSMI’s do indeed represent a melt present in the Río Blanco magma, and, although exact H₂O analyses are not obtainable, it is reasonable to suppose that the trapped phase was volatile-rich.

**Glass inclusions**

Microprobe analyses demonstrate that glass inclusions from Río Blanco have consistently low H₂O concentrations, with an average 3.81 wt% H₂O ± 0.83 (1σ), but with a range of 0-5.5 wt% (Fig. 6-3). Río Blanco glass inclusions also have large shrinkage bubbles, with an average bubble fraction of 6 (± 2 vol% at 1σ) (c/f, the estimated normal range of 0.2 to 5.0 vol% in Lowenstern (1995)). Additionally, although Río Blanco glass inclusions will melt, they will not homogenise. In the Okataina case study, and in the literature generally (e.g. Lowenstern, 1995), large shrinkage bubbles and homogenisation at unrealistic temperatures (typically > 1000°C), is taken to imply that the inclusion in question has decrepitated and leaked, lack of direct petrographic evidence not withstanding. This is because decrepitation above the glass transition temperature reduces the pressure of the trapped melt, causing the shrinkage bubble to expand, and fluids (typically H₂O vapour) to leak out before the crack has time to heal. Analysis of glass inclusions, and melted (although not homogenised) CSMI's (Figs. 7-10, to -13), demonstrates that CSMI's and glass inclusions have overlapping compositions. Glass inclusions appear to have a more restricted range, but the compositions of at least some CSMI's could be derived from glass compositions by variable loss of alkali components. Thus, it appears both Río Blanco CSMI's and glass inclusions have decrepitated and degassed, possibly from the same (or at least similar) volatile-rich melts. To explain the difference we need to focus on the conditions at the time of decrepitation.

**Decrepitation and degassing in Río Blanco melt inclusions**

Although CSMI's and glass inclusions are decrepitated and degassed, possibly from the same melt, both types coexist randomly and intimately in the same growth planes. This apparent anomaly can be explained by considering the circumstances under which decrepitation can occur. If an inclusion decrepitates at high temperature, the inclusion may be fluid enough to exsolve (and lose) a large percentage of its H₂O. However, if the inclusion is close to the glass transition temperature, it may be sufficiently viscous to restrict H₂O loss despite the pressure loss. Likewise, if the inclusion decrepitates without any great reduction in external pressure (e.g. the approximately isobaric cooling of phenocrysts within the Río Blanco intrusion), there will be little pressure gradient to force the H₂O out of the breached inclusion. Thus, the
The coexistence of CSMI’s and glass inclusions could be a function of the circumstances of decrepitation (temperature and pressure) for an individual inclusion, rather than differences in the initial composition.

**Aqueous magmatic fluid phase**

*Co-existence of silicate melts and aqueous magmatic fluids*

Composite inclusions containing a globule (or globules) of 1- or 2-phase aqueous liquid, in a silicate glass having a similar composition to other glass inclusions, are observed in the Rio Blanco samples known to be lavas. Two explanations of these inclusions are possible; either they represent inhomogeneous trapping of a coexisting aqueous fluid phase, or, more prosaically, they could simply be post-magmatic refilling of breached shrinkage bubbles.

- Most examples of such composite inclusions show no sign of cracks or fractures through which fluids could have gained ingress. Although not conclusive, this does argue against post-magmatic re-filling.

- Microthermometry, and the presence of translucent crystals of an unidentified crystalline precipitate in some clear globules (Figs. 5-87, 6-25), suggest a variable but sometimes high salinity ($9 - \approx 40\text{wt}\% \text{NaCl}_{\text{equiv}}$). These elevated salinities imply magmatic rather than meteoric origin, and also argue against post-emplacement refilling.

- The presence of aqueous fluid-only primary magmatic inclusions in the samples, commonly vapour phase (Figs. 5-61, -62, -63), but more rarely liquid (Figs. 5-64, -65), implies a discrete aqueous fluid phase in the magma.

- In many cases the aqueous globules in composite inclusions demonstrate signs of plastic deformation, consistent with pre- or syn-trapping deformation of melt containing a globule(s) of another phase (Fig. 5-89). Shrinkage bubbles, on the other hand, are typically almost spherical, even in inclusions with deformed clear bubbles. Shrinkage bubbles are a post-trapping phenomenon, when any deformation to the melt should have finished. Also, it seems improbable to suggest selective refilling of deformed bubbles only, and this supports inhomogeneous trapping.

The above lines of evidence support the contention that there was a coexisting aqueous phase in the Rio Blanco magma, which was occasionally trapped in melt inclusions. However, the nature of the aqueous inclusions presents some problems. In many composite inclusions the fluid exists, at room temperature, as a single-phase aqueous liquid (with a variable proportion of dissolved components). It is commonly observed that single-phase liquid fluid inclusions are of low temperature ($< 100^\circ\text{C}$) origin (e.g. Roedder, 1984). However, Roedder (1984, page 292) demonstrated that it is
possible for inclusions formed at higher temperatures to fail to nucleate a bubble on cooling. During microthermometric experiments on composite inclusions of glass + aqueous fluid from the La Copa extrusives (e.g. Figs. 7-21, -22), nucleation of metastable bubbles, and the existence of metastably superheated ice (i.e. final ice melting temperatures greater than 0°C) were observed. It thus appears that the existence of single-phase aqueous globules is itself a metastable effect. Although a detailed explanation for the metastable single-phase fluids remains elusive, it should be noted that similar inclusions have been found and described in the Russian literature. A series of papers in the 1990’s (Naumov et al., 1992, 1994, 1996) described aqueous fluid-only inclusions, and 1- and 2-phase aqueous globules in glass inclusions in felsic rocks from various parts of the Soviet Union. Their descriptions and photomicrographs have a strong resemblance to the primary magmatic aqueous fluid-bearing inclusions from the Río Blanco extrusives. Other examples are described by Prokofiev et al. (1999) from the Banska Stiavnica precious- and base metal deposit, Slovakia. Similar metastable single-phase aqueous fluids are also noted in the Okataina case study (chapter 10).

**Immiscibility of silicate melts and aqueous magmatic fluids**

Roedder (1984) proposed a simple but convincing test of immiscibility; namely, the existence of a population of magmatic inclusions showing trapping of variable proportions of the supposed immiscible phases. Variable phase relations are important, since post-trapping exsolution/crystallisation of a phase will tend to produce a constant phase ratio (Frezzotti et al., 1994; Kamenetsky et al., 2003a), whereas accidental trapping, by definition, will not. Roedder’s test can also be applied in the case of composite inclusions of glass + aqueous fluids. Figures 5-85 to 5-89, and 8-1, -2 demonstrate the widely variable phase ratios within composite inclusions containing fluid bubbles. These widely varying phase ratios strongly support the contention that the aqueous fluid was immiscible with respect to the silicate melt.

The only other alternative is that the aqueous fluids exsolved post-trapping (e.g. Naumov et al., 1996). However, to dissolve such large amounts of H₂O in a silicate melt would require enormous pressure, in some inclusions > 10 kbars (e.g. Manning, 1994; Mysen and Acton, 1999; Bureau and Keppler, 1999; Newton and Manning, 2000; Mysen and Wheeler, 2000). The available geological evidence does not support pressures in excess of 1 kbar, and probably considerably less. Naumov et al. (1996) proposed a geological overpressuring event to explain similar inclusions found in andesites from Slovakia. There is no evidence of such an event at Río Blanco, making it difficult to support post-trapping exsolution as a source of the aqueous fluid.
The coexistence of silicate melt and aqueous fluids demonstrated in this study, is consistent with evidence of immiscibility observed, or inferred, in other studies, for example Roedder and Coombs ((1967) additional data Webster and Rebbert (2001)), Frezzotti (1992), De Vivo and Frezzotti (1994), Lowenstern (1994), and De Vivo et al. (1995).

Physical characteristics of volatile phase exsolution

The exsolution of aqueous fluids at Río Blanco

A proposed mechanism

The volatile-rich magmas at Río Blanco, could, by continued cooling become sufficiently supersaturated to force exsolution of an aqueous phase. In practice (e.g. Proussevitch and Sahagian, 1998), this occurs as minute aqueous-phase bubbles (or globules) located on suitable bubble nuclei. If sufficient nuclei exist, it should be possible for exsolution to form a magmatic emulsion, ie. an intimate mixture of bubbles and melt, having properties resembling a discrete phase, different from those of bubbles or melt individually (e.g. Proussevitch et al., 1993). In a magmatic emulsion consisting of melt, and aqueous liquid or vapour, there will be a strong density/viscosity contrast between the components. It has previously been shown that exsolution of a volatile phase from the Río Blanco magma occurred at subcritical pressures. Modelling by Shinohara (1994) suggests that at a depth of 5.2 km (1.3 kbar lithostatic pressure), any exsolved volatile phase should be divided into:

- 1 wt% water with a salinity of 55 wt% NaCl and
- 99 wt% vapour with a salinity of 3.2 wt% NaCl.

At lower pressure the percentage of water increases by a few percent, with an increase in salinity. If bubble nuclei are sufficiently abundant, it should be possible to produce an emulsion of melt+vapour+brine (but dominantly melt+vapour). The generation of such an emulsion would result in vapour bubbles (and rare brine globules) surrounded by walls of melt, which would chill to glass if cooled quickly enough. This is exactly what is observed in magmatic emulsion inclusions (e.g. Figs. 5-80, -81, and -90, -91, -92).

It is difficult to make quantitative estimates of the physical properties of Río Blanco magmatic emulsions on the basis of existing experimental work. The viscosity of vapour emulsions in rhyolitic melts is known to be strongly dependent on H₂O content of the melt (Bagdassarov and Dingwell, 1992; Proussevitch and Sahagian, 1998;
Lejeune et al., 1999), melt composition and temperature (Lejeune et al., 1999), and bubble fraction (Bagdassarov and Dingwell, 1992; Proussevitch et al., 1993; Proussevitch and Sahagian, 1998), although less dependent on pressure (Bagdassarov and Dingwell, 1992). Since the available experimental work was carried out on a wide range of starting compositions, usually involving more or less rapid decompression, only a few points can be made. As the bubble fraction of an emulsion increases to 25%, the emulsion viscosity (due only to the presence of bubbles) will decrease by around one order of magnitude over the bubble-free melt (Bagdassarov and Dingwell, 1992). With a bubble fraction between 25% and 73%, the emulsion viscosity would probably change little. With a bubble fraction > 73% (the formal definition of a magmatic foam), the viscosity should decrease rapidly (Proussevitch et al., 1993).

Experimental work also provides some estimate of the stability of such bubble emulsions. Modelling in Shinohara et al. (1995), using an arbitrary bubble fraction of 20%, a typical magma viscosity of $10^7$ Pa s, and the model of Proussevitch et al. (1993), suggests that magmatic emulsions would be stable for > 1 year. Based on a quartz crystallisation rate in the order of $10^{-8}$ cm/s$^{-1}$ for a supercooled granite magma (Swanson and Fenn, 1986), a quartz phenocryst could grow > 3 mm in the same period.

Although conditions in the Río Blanco magma were not identical to the experimental conditions of Swanson and Fenn (1986), or Proussevitch et al. (1993), these calculations suggest that trapping of samples of a volatile-rich magmatic emulsion is probably feasible, given the stability of magmatic emulsions and growth rates of quartz crystals. The appearance of inclusions such as those in figure 8-1 strongly implies trapping of a magmatic emulsion, and is consistent with the theoretical, and experimental data, which suggests that such emulsions may be sufficiently stable to be trapped as magmatic emulsion inclusions.

The formation of magmatic emulsions would also have consequences for the compositions of the phases, as partitioning between melt and coexisting liquid- and vapour-phases would control the compositions of the new phases. This would be true for major elements, such as alkalis (Sakuyama and Kushiro, 1979; Frank et al., 2003), as well as metals (Candela and Piccoli, 1995).

Glass inclusions that have clearly trapped magmatic emulsions (e.g. Fig. 5-90) are found in lavas from Río Blanco, where quenching may have preserved them. Such inclusions have not been observed in the Río Blanco intrusives, but CSMI's which may represent crystallised equivalents (Figs. 5-36, -37) are present. These vapour-rich CSMI's may be magmatic emulsion inclusions, in which the fine-scale structures were destroyed by crystallisation. Such inclusions contain relatively small amounts of silicates, and must have contained a large, but variable proportion of magmatic vapour.
However, magmatic emulsions are unstable in the long term, and should begin to disrupt under the influence of gravity and continued bubble growth (Proussevitch et al., 1993). Bubbles continue to grow by exsolution from the bubble walls, expelling inter-bubble melt (syneresis), and coalescing with adjacent bubbles. The rate of this process is dependent on bubble-size, and begins slowly, speeding up only when the bubbles pass a critical size (Proussevitch et al., 1993). The critical bubble size is dependent on several factors, such as melt viscosity and the volume fraction of bubbles, being most rapid in magmatic foams (bubble fraction > 73%). There would be a progressive evolution from magmatic emulsions (Figs. 8-1, -2), to foam (Figs. 8-3, -6), to single discrete vapour bubbles (Fig. 8-4). Just such an evolution can be traced in the various types of magmatic emulsion inclusions found in the Río Blanco extrusives, giving a “snapshot” of this brief, transient process.

As previously noted, obvious magmatic emulsion inclusions (e.g. Fig. 8-1) are not found in the La Copa Rhyolite intrusives; however, composite inclusions containing glass and crystalline silicates are (e.g. Fig. 8-5). Magmatic emulsions must eventually be disrupted by syneresis, into discrete liquid and melt phases. If a magmatic inclusion such as (Fig. 8-1), were to begin post-trapping coalescence of the bubbles, the result could be an inclusion with a large shrinkage bubble, containing crystalline silicates, and much of the metal in the inclusion, which would have partitioned into the vapour-phase. The composite inclusion in figure 8-5 fits this description, and many of the PIXE images of composite inclusions suggest significant vapour components. The apparent absence of magmatic emulsion inclusions could be a function of cooling rates, with magmatic emulsions in the intrusive rocks having sufficient time for the bubbles to begin coalescing.

Although the discussion thus far has concentrated on vapour bubbles in the magmatic emulsions, modelling by Shinohara (1994) suggests that a typical rhyolitic magma at 1.2 kbar, 1 wt% of any exsolved aqueous fluid should be liquid with a salinity of 55 wt% NaCl, and at 0.5 kbar 4 wt% of any aqueous fluid should be liquid with a salinity of 72 wt% NaCl. Also, condensation of the vapour phase ± mixing with the brine phase should produce a range of aqueous fluids at magmatic temperature. Fluids with a similar range of salinities are observed in the composite inclusions of glass+aqueous liquid (Fig. 8-1). Indeed melt inclusions at Río Blanco contain an excellent record of the phases coexisting in the magma, melt (now CSMI's and glass inclusions), magmatic emulsions, and magmatic vapour and brine bubbles.
Fig. 8-1  A composite inclusion, interpreted to be a magmatic emulsion inclusion, containing a random mix of vapour-bubbles and liquid-rich globules. Some of the aqueous globules also contain crystalline precipitates.
CA30. 25µm scalebar

Fig. 8-2  Composite inclusion containing glass and a globule of aqueous liquid, in this example the globule also contains a vapour bubble and a large proportion of crystalline precipitates
CA30. 25µm scalebar

Fig. 8-3  Glass inclusion containing multiple large bubbles, so tightly packed that they deform each other (the definition of a foam [Proussevitch, 1993 #168])
CA30. 50µm scalebar

Fig. 8-4  Composite inclusion, containing magmatic vapour and a small rim of glass (arrowed)
DC-Rhy1. 50µm scalebar

Fig. 8-5  Composite inclusion containing glass + crystalline silicates; closeup of the inclusion in figure 6-22 (PIXE element maps). Almost all of the Cu, Pb, Zn, Fe, Mn and Ba in this inclusion are found in the bubble, above the white line, the rest of the bubble is only an area of low concentration in the Ca and K images (corresponding to the glass).
Sample 9902. 10µm scalebar
Fig. 8-6  Electron-photomicrograph of a foam inclusion, hosted in quartz, and composed largely of bubbles separated by thin walls of silicate glass. Most of the material inside the bubbles is silicate dust introduced when the phenocryst was broken, rather than in-situ crystals. Compare to the photomicrograph in fig 8-3
CA30. 50µm scalebar

Fig 8-7  Electron-photomicrograph of two CSMI's, hosted in quartz, demonstrating the range of silicate contents possible for CSMI's. Left \(\approx\) 90% silicates, right < 10% silicates
Both 9902. 50µm scalebars
The derivation of aqueous fluids in the Don Luis Porphyry

In contrast to the samples sourced from the La Copa Volcanic Complex, the Don Luis Porphyry sample contains a large population of coexisting primary silicate, and pseudosecondary silicate+hypersaline fluid, and hypersaline fluid inclusions. These partly overlap with populations of secondary hypersaline and 2-phase fluid inclusions trapped at progressively lower temperatures. Given the decrepitation problems, homogenisation temperatures for silicate inclusions are not known, but melting temperatures > 800°C have been obtained, and trapping temperatures may be similar to the \( T_h \) of 825°C obtained for CSMI's in the La Copa Rhyolite. There is no method for estimating trapping temperatures for fluid inclusions containing magmatic minerals, but they must be > 650°C, as some hypersaline inclusions have homogenisation temperatures as high as 650°C. Given these temperatures, it seems reasonable to infer that many inclusions in the Don Luis Porphyry were formed at magmatic temperatures, trapping fluids circulating around the growing phenocrysts, and continued to do so down to \( \approx 200°C \).

In heating experiments on Don Luis Porphyry CSMI's, globules of hypersaline brine and chloride/sulphate melts were observed in some inclusions after quenching. Thus, significant amounts of \( H_2O \), chlorides, and sulphates were present in some CSMI's from the Don Luis Porphyry, a point confirmed by the observation of anhydrite crystals in CSMI's from the Don Luis Porphyry, but not from the La Copa samples.

To explain the similarities and differences between inclusion populations of the La Copa, and Don Luis Porphyry samples, I propose a model for the crystallisation of the Río Blanco magmas. The starting point for this model is a gradually crystallising volatile-rich silicate magma. Crystal fractionation progressively enhances the volatile concentration of the magma, eventually forcing \( H_2O \) oversaturation. This produces an unmixing event, and exsolution of an immiscible phase rich in \( H_2O \), salts, volatiles, metals and other incompatible elements, forming (at least temporarily) a magmatic emulsion. Quartz crystallising at such times traps melt inclusions, with or without magmatic emulsion inclusions (only well preserved by quenching in the La Copa extrusives).

Eventually, the vast majority of the silicate melt in the magma chamber is consumed, and at this point, the La Copa Rhyolite and Don Luis Porphyry diverged. The residual, low-viscosity, extremely volatile-rich melt, along with exsolved aqueous fluids, migrated upwards, collecting in roof cupolas, or in pockets under the crystallisation front. The La Copa Rhyolite is represented by the silicate melt, and the Don Luis Porphyry represents a pocket of very late stage residual melt.
These pockets will continue crystallising silicates and become even more highly enriched in H$_2$O, salts, volatiles, and incompatible elements. Phenocrysts growing at this time will trap very volatile-rich melts, and coexisting hypersaline fluids. At some point the melt will have become rheologically solid, and begun to deform under the influence of (among other things) tectonic deformation, and contraction due to cooling. This will progressively fracture the phenocrysts, and permit the trapping of fluid inclusions, showing a progressive reduction in trapping temperatures, and a progression from pseudosecondary to secondary. At the upper end of this temperature range, microphenocryst such as apatite and zircon could be trapped in fluid inclusions (Figs. 5-72, to -75). At lower temperatures (but still $\approx$ magmatic) pseudosecondary hypersaline fluid inclusions would be trapped, and at still lower temperatures, below the complete crystallisation of the magma, secondary hypersaline and 2-phase inclusions. The endpoint of silicate crystallisation will be hydrothermal fluids, which may escape and continue evolving towards ore-formation, or dissipate into the country rocks without mineralisation.

In this model, the crystallised magma would contain inclusions of silicate melt, and exsolved aqueous fluids (dominantly magmatic vapours if the exsolution occurred under sub-critical pressures), and all inclusions would be primary. Magmatic emulsions could be trapped if quartz growth was rapid enough, although preservation of magmatic emulsion textures would require suitable conditions. Metal concentrations in magmatic inclusions would be low, except in vapour and vapour-rich inclusions. Such a pattern is observed in the La Copa Rhyolite (intrusives and extrusives).

In contrast, rocks produced from pockets of residual melt would contain similar primary melt- and vapour-inclusions (in inherited phenocrysts), but would also contain silicate melt inclusions containing increasingly high concentrations of volatiles, grading into hypersaline fluid inclusions. Trapping would likewise grade from primary, through pseudo-secondary, to secondary, as the system cooled and the phenocrysts fractured. Metals would be partitioned preferentially into the residual melts in such pockets, and their abundance would increase considerably over the parental magma (potentially, even approaching ore-grade). This is the pattern observed in the Don Luis Porphyry.

**Compositional consequences of volatile phase exsolution**

The immiscible separation of volatile-rich phases from silicate melts is both driven by composition (ie volatile concentrations), and has potentially profound effects on the compositions of the new phases. There is excellent fine-scale evidence of physical processes involved at Rio Blanco (e.g. magmatic emulsion inclusions), but the endemic decrepitation presents some problems and limitations. Bulk heating
experiments suggest CSMI's and glass inclusions sample similar (if not identical) melts. Glass inclusions range from 0-5.5 wt% H₂O, and lie on what I infer to be a degassing trend from melts with > 5.5 wt% H₂O. The compositions of some CSMI's could be derived from glass-like melts with variable alkali loss (predominantly Na), although other CSMI's appear to show compositions overlapping with glass. Major element compositions (excluding H₂O, Na, and to a lesser extent K) appear to be unaffected by decrepitation, except for a relative upgrading by selective removal of other components. The effects on metal concentrations are unclear. However, PIXE data shows that crystalline silicate globules in composite inclusions show higher metal concentrations than coexisting glass. With these caveats in mind, the analytical data for Río Blanco melt inclusions (including inclusions experimentally re-melted) can provide insights into the compositional consequences of immiscibility and volatile phase exsolution.

### Fractionation of metals from the Río Blanco magma

The CSMI's which have been subjected to PIXE analysis were, in part, selected to show a range from silicate-rich to silicate-poor (Fig. 8-7). In transmitted light the silicate component of a CSMI appears transparent, whereas the vapour-filled cavities appear black. The photomicrographs accompanying the PIXE element maps of CSMI's (Figs. 6-10 to -19) show a wide variation in colour density, and subjectively, I rank them from bm36a (silicate-rich) to bm36c (silicate-poor, and thus vapour-rich). Of the elements analysed, K, Ca, Ba, Fe, and Mn are most likely to be incorporated into the silicate component of a CSMI. In practice, the potassium concentration most closely corresponds to the previously mentioned subjective ranking of CSMI's (see Table 8-1).

<table>
<thead>
<tr>
<th>CSMI's</th>
<th>K</th>
<th>Ca</th>
<th>Mn</th>
<th>Fe</th>
<th>Cu</th>
<th>Zn</th>
<th>Rb</th>
<th>Sr</th>
<th>Zr</th>
<th>Ba</th>
<th>Pb</th>
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<tr>
<td>bm36a</td>
<td>73342</td>
<td>7903</td>
<td>362</td>
<td>5233</td>
<td>22</td>
<td>46</td>
<td>bd.</td>
<td>bd.</td>
<td>bd.</td>
<td>2350</td>
<td>bd.</td>
</tr>
<tr>
<td>bm36b</td>
<td>72611</td>
<td>4110</td>
<td>332</td>
<td>5483</td>
<td>40</td>
<td>45</td>
<td>bd.</td>
<td>bd.</td>
<td>bd.</td>
<td>2553</td>
<td>bd.</td>
</tr>
<tr>
<td>bm18</td>
<td>71953</td>
<td>2366</td>
<td>485</td>
<td>10601</td>
<td>55</td>
<td>96</td>
<td>332</td>
<td>362</td>
<td>274</td>
<td>3645</td>
<td>bd.</td>
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<tr>
<td>bm34</td>
<td>45005</td>
<td>2937</td>
<td>617</td>
<td>11342</td>
<td>85</td>
<td>79</td>
<td>237</td>
<td>175</td>
<td>5031</td>
<td>1368</td>
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<tr>
<td>bm31</td>
<td>21147</td>
<td>6145</td>
<td>301</td>
<td>4565</td>
<td>44</td>
<td>63</td>
<td>bd.</td>
<td>215</td>
<td>bd.</td>
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<tr>
<td>bm35</td>
<td>15427</td>
<td>3214</td>
<td>527</td>
<td>10056</td>
<td>48</td>
<td>59</td>
<td>136</td>
<td>172</td>
<td>930</td>
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<tr>
<td>bm32</td>
<td>td</td>
<td>td</td>
<td>431</td>
<td>5979</td>
<td>73</td>
<td>92</td>
<td>243</td>
<td>219</td>
<td>346</td>
<td>2224</td>
<td>bd.</td>
</tr>
<tr>
<td>bm36c</td>
<td>7628</td>
<td>1266</td>
<td>bd.</td>
<td>1541</td>
<td>76</td>
<td>28</td>
<td>bd.</td>
<td>123</td>
<td>&lt;50</td>
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<td>Vapour-rich fluid inclusions</td>
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<td>579</td>
<td>141</td>
<td>17940</td>
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</tbody>
</table>

Table 8-1 PIXE element analysis of Río Blanco CSMI's and vapour inclusion, ranked subjectively by decreasing silicate content (from bm36a to bm43); data is a sub-set of Table 6-3.
There is an order of magnitude reduction in the K concentration between bm36a and bm36c, which would be consistent with a reduction from 90% to 10% silicates. Such a reduction can be seen between the two CSMI's in figure 8-7. There is considerable variation between K, Ca, Ba, Fe, and Mn, and to take account of this K/Mn has been selected as another suitable proxy for silicate concentration. When the ratios of Cu and Zn against K and Fe, are plotted against the apparent silicate content (Fig 8-8), K concentration (Fig 8-9), and against K/Mn (Fig. 8-10), there appears to be a general inverse correlation between Cu and Zn concentration, and the percentage of silicates in the inclusion (using K and K/Mn as proxies for silicates).

Efforts to extract absolute concentration data from individual phases in composite inclusions has been largely unsuccessful, due to the small size of these phases, and the difficulty of measuring their position, and volume, in three dimensions. Table 6-3 details the calculated element concentrations for the inclusions (melt, composite, and fluid) analysed by PIXE microprobe. To obtain compositions for the glass component in composite inclusions, data from cylindrical volumes of the inclusions, selected as being free of any bubbles or globules, were processed as if they were discrete inclusions (table 6-3). The trend towards preferential partitioning of Cu and Zn into volatile phases is suggested by data from bm48, a composite inclusion with multiple aqueous globules in glass.

Fig 8-8 Ratios of Cu/K, Zn/K, Cu/Fe, and Zn/Fe for CSMI's ranked by their apparent silicate content (see text); 1 is the most vapour-rich, 8 is the most silicate-rich. Concentrations are from PIXE analysis, Table 6-3.
Fig 8-9  Ratios of Cu/K, Zn/K, Cu/Fe, and Zn/Fe for CSMI's vs K concentration. Data by PIXE analysis, Table 6-3.

Fig 8-10  Ratios of Cu/K, Zn/K, Cu/Fe, and Zn/Fe for CSMI's vs K/Mn. Data by PIXE analysis, Table 6-3.
The Cu and Zn concentrations for the whole inclusion (164 ppm, and 141 ppm respectively) are higher than any CSMI, but their concentration in a cylinder of the inclusion containing only glass are normal for CSMI's (34 and 62 ppm respectively). This is consistent with the PIXE element maps, which show that the metals are concentrated in the aqueous globules.

In summary, the PIXE data demonstrates preferential partitioning of Cu and Zn into the vapour-phase in silicate melt inclusions, and into the aqueous globules trapped in composite melt inclusions. This is consistent with experimental evidence (e.g. Heinrich et al., 1992; Candela and Piccoli, 1995; Williams et al., 1995) that Cu partitions strongly from silicate melts into coexisting liquid or vapour phases, and with melt inclusion studies (e.g. Lowenstern et al., 1991; Kamenetsky et al., 2002a) that show high concentrations of Cu in vapour-rich cavities in melt inclusions.

**Fractionation of metals in the Río Blanco fluid phases**

In addition to the PIXE analysis of silicate melt inclusions from the La Copa Rhyolite, there are also analyses (both PIXE and LA-ICPMS) for fluid inclusions from the Don Luis Porphyry. The change in ratios between bm36a and bm36c is distinct, and there is a general progression between them, albeit, with a few discrepancies such as the high Zn concentrations in bm18 and the low concentration in bm38, and the very low Mn concentration in bm36c. The absolute amounts of metals are not large, 22-85 ppm Cu, 28-96 ppm Zn, but consistently Cu and Zn favour the vapour-rich CSMI's, suggesting they were preferentially partitioned from the melt into the vapour phase. This trend may also be suggested by the vapour inclusion (bm43, table 6-3), which has four times as much Cu and a little more Zn than any of the CSMI's, with half the K and Ca of the most vapour-rich CSMI (bm36c).

Figures 8-11 to 8-13 show plots of Fe, Cu, and Pb concentrations against K/Mn (used as a proxy for silicates in CSMI's). Similar plots against Ca/Mn give similar results (e.g. Fig. 8-14). In all cases, the silicate inclusions show a wide spread in K/Mn, and near constant Fe, Cu, and Pb, whereas the metals show high concentrations at very low K/Mn. The spread in K/Mn for silicate inclusions has already been related to a corresponding decrease in silicate concentration (from high K/Mn and high silicate concentration, to low K/Mn and high vapour content). This is consistent with the occurrence of the single vapour inclusion (Figs. 8-8, -9, and -10), between the field for silicate inclusions (but at the vapour-rich end) and the field for fluid inclusions. The one exception is Pb against K/Mn, there is only limited data for Pb in silicate inclusions, but, on a log plot the increase in Pb is not very pronounced, except for the puzzling presence of 46000 ppm of Pb in a vapour inclusion (probably a µm-scale galena crystal).
Fig 8-11  Cu vs K/Mn, for CSMI's, vapour, and hypersaline fluid inclusions, data by PIXE analysis (Table 6-3) and LA-ICPMS (Table 6-5, -6)

Fig 8-12  Fe vs K/Mn, for CSMI's, vapour, and hypersaline fluid inclusions, data by PIXE analysis (Table 6-3) and LA-ICPMS (Table 6-5, -6)
Fig 8-13  Pb vs K/Mn, for CSMI's, vapour, and hypersaline fluid inclusions, data by PIXE analysis (Table 6-3) and LA-ICPMS (Table 6-5, -6)

Fig 8-14  Cu vs Ca/Mn, for CSMI's, vapour, and hypersaline fluid inclusions, data by PIXE analysis (Table 6-3) and LA-ICPMS (Table 6-5, -6)
Extreme inhomogeneity in fluid inclusion compositions was reported in Kamenetsky et al. (2002b), and will be further discussed in chapter 13, but the trend from silicate-rich, to vapour-rich CSMI's, through vapour-inclusions, to hypersaline fluid inclusions is one of increasing metal concentration, most importantly Cu, Zn, and to a lesser extent Pb.

It needs to be noted that the fluid inclusions and CSMI's are not in the same samples. However, the whole-rock compositions of the La Copa Rhyolite and Don Luis Porphyry are similar, as both units are co-magmatic (Warnaars, 1985; Vargas et al., 1999; Skewes et al., 2003; Deckart et al., 2004), and CSMI's and primary magmatic vapour inclusions are common in both. It has already been suggested that the La Copa Rhyolite and Don Luis Porphyry, respectively, represent the bulk parental melt, and a very late stage residue from a similar melt. The overall trend to increasing metal concentration, with decreasing K, Ca, Ba, Rb, and Mn (previously shown to be proxies for silicate in CSMI's) is a potential link between separate magma bodies evolving over time in the same system.

These results are consistent with experimental work (e.g., Candela and Holland, 1984; Candela and Piccoli, 1995) which show strong partitioning of metals from silicate melts into coexisting aqueous phases. Moreover, the results are comparable with studies of the Mole Granite, Australia (Heinrich et al., 1992), which demonstrate preferential partitioning from magmatic brines into coexisting vapour phases.

**Consequences for metallogenesis**

High concentrations of Cu, Pb, Zn, As, Br, SO$_3^-$ and Cl, were present in the Don Luis Porphyry, at least during trapping of some CSMI's, and in the fluids trapped as hypersaline fluid inclusions. Some of this excess of volatiles and metals could have resulted from magma with initially higher concentrations; however, most can be traced to concentration by mixing and condensing of volatile and metal-rich aqueous phase. Given that most CSMI's melted during the heating experiments did not show chloride/sulphate globules, it may suggest that most CSMI's trapped only moderately volatile-rich melts, and that some CSMI's (showing high concentrations of chlorides and sulphates) trapped very volatile-rich melt. The most reasonable explanation for such a progressive concentration is that the very volatile-rich CSMI's represent inclusions trapped during the later stages of concentration of the aqueous phase. This suggests that any increased metallogenic potential results from late-stage concentration, rather than an inherently more metal-rich (ie “fertile”) magma.

The La Copa inclusions show only minor evidence of trapping of an exsolved phase (dominantly vapour-rich). In contrast, the abundance of hypersaline fluid
inclusions in the Don Luis Porphyry suggests that the phenocrysts, from at least 850-350°C, were in contact with hypersaline metal-rich fluids. If fluids escaping from a cooling magma (e.g. the La Copa Rhyolite) ponded near a chamber roof, cooling and condensing of magmatic vapours would result in the formation of hypersaline magmatic fluids, and possibly their trapping as fluid inclusions. I suggest that the La Copa Rhyolite inclusion population is consistent with exsolution of hydrothermal fluids, and their subsequent migration out of the sampled area. If any mineralisation had resulted, it would either occur in the roof rocks (subsequently removed by erosion) or in the wall rocks surrounding the La Copa Rhyolite. This may be borne out by the discovery of porphyry-style Cu-Mo mineralisation in the country rock surrounding the La Copa Rhyolite pipe (unpublished communication, CODELCO), and the observation that no mineralisation has yet been found with the La Copa Rhyolite. The Don Luis Porphyry inclusions also show exsolution of hydrothermal fluids, but also suggest ponding (plus mixing and condensing) of fluids generated at some as yet unexposed depth. This is support by the weakly mineralised and hydrothermally altered nature of the Don Luis Porphyry, and the presence of sulphides (pyrite and chalcopyrite) in the sample analysed. The contrasting melt and fluid inclusion populations of the Don Luis Porphyry and La Copa Rhyolite may be vectors to areas suitable for ore-formation, and therefore, may have exploration significance.

Conclusions

Study of magmatic inclusions in the Río Blanco samples demonstrate the existence of a volatile-rich melt at Río Blanco. They have also sampled an immiscible, volatile-rich melt fraction almost at the moment of its formation via exsolution from the magma, and in rare cases may follow the progressive disruption of the magmatic emulsion into discrete liquid and vapour phases coexisting with the Río Blanco magma. Further, I have demonstrated that although CSMI's do not homogenise, they are amenable to study by advanced, whole-inclusion analytical techniques such as LA-ICPMS and the PIXE microprobe. Thus, we have available for study the earliest stage of the evolution of hydrothermal fluids at Río Blanco, during which much (if not all) of the volatile and metal component that could be sequestered, was sequestered. This study has shown that CSMI's do trap samples of melt no more compromised than coexisting glass inclusions, and thus capable of providing useful evidence of immiscibility. If this was unique to Río Blanco this discovery would still be significant. However, there is reason to believe that CSMI's are present, although unrecognised, in other intrusive bodies.
The samples from the Don Luis Porphyry demonstrate a slightly different process, perhaps one representative of the final stage of cooling in the margins of any Río Blanco intrusion. Here, a body containing only volatile-rich melts unmixed to form abundant hypersaline brine and vapour bubbles. These denser brines, probably resulting from the much more volatile-enriched environment in the upper level of the Don Luis Porphyry, correspond to the hydrothermal fluids found in fluid inclusions in porphyry orebodies.