

CHAPTER 4: MELT INCLUSION RECORD OF MAGMATIC IMMISCIBILITY IN CRUSTAL AND MANTLE MAGMAS

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INTRODUCTION

Immiscibility (unmixing of melts and fluids) should be almost inevitable at some point in the evolution of most mantle and crustal magmas during cooling and crystallization. Formation of two immiscible phases “*results in a major geochemical fractionation – all chemical species present, the elements (and their isotopes), and their various compounds, become distributed between these two phases...the compositional divergence between the two phases is...extreme*” (Roedder 2003). The variations in compositions of melts undergoing immiscibility, and physical parameters of their evolution in the plutonic environments, mean that each intrusion should be expected to show differences in the processes of exsolution and compositions of exsolving phases. One of the immiscible phases is universally volatile-rich, and this has important consequences for further magma evolution and geological processes related to it. More specifically, volatile-rich phases generally have significant density and viscosity contrasts with parental silicate magmas, and thus rapid separation of the newly exsolved phases is expected. Further, the exsolution of volatile-rich phases exerts major controls on the chemistry of a magmatic system, particularly on metal partitioning between immiscible melts and fluids, so the volatile phase is highly efficient at sequestering the metals (*e.g.*, Candela 1989, Candela & Piccoli 1995, Williams *et al.* 1995, Heinrich *et al.* 1999, Webster 2004). Magmatic immiscibility and the related formation of volatile-rich melts and fluids are prerequisites for the origin of mineralized hydrothermal solutions that may transport metals to a suitable depositional site. Immiscible separation, however, is not restricted to magmas that form mineralized rocks.

The fugitive nature of magmatic immiscibility involves problems in unraveling physical and chemical characteristics of this fundamental

process. If separation of immiscible phases was efficient, the residual magma should be significantly depleted in incompatible volatiles and metals relative to the parental magma, and reconstructing the original metal and volatile content is extremely difficult. One rapidly developing approach to this problem is the use of melt and fluid inclusions trapped and preserved in magmatic minerals (*e.g.*, Roedder 1992, De Vivo & Frezzotti 1994, Bodnar 1995, Lowenstern 1995, Student & Bodnar 1999, Frezzotti 2001, Kamenetsky *et al.* 2003, Lowenstern 2003 and references therein). Such inclusions provide the closest approximation to samples of continuously evolving (and thus ephemeral) melts and magmatic fluids. Many studies of magmatic inclusions have made possible the recognition of several types of magmatic immiscibility (*e.g.*, between silicate melts, sulfide melts, aqueous and carbonic liquids and vapors, hydrosaline liquids and various combinations of these). For brevity, in this work only those examples from plutonic systems of which the author has first-hand experience will be presented and discussed in detail.

TYPES OF MAGMATIC IMMISCIBILITY

Immiscible silicate melts

Among the reports on silicate-silicate melt immiscibility (*e.g.*, Roedder & Weiblen 1970, De 1974, Dixon & Rutherford 1979, McBirney 1980, Philpotts 1982, Jakobsen *et al.* 2005) only a few are related to mineralized magmatic systems (*e.g.*, pegmatites of the Ehrenfriedersdorf Sn–W deposit, Germany, Thomas *et al.* 2000, the La Copa felsic intrusions within the Rio Blanco Cu–Mo deposit, Chile, Davidson & Kamenetsky 2001, Davidson *et al.* 2005).

Quartz-hosted silicate melt inclusions from the La Copa complex, coexisting within the same grains and growth planes, belong to two contrasting

types: clear rhyolitic glass with one or several shrinkage bubbles, and dark fine-grained crystalline aggregates of feldspar, mica and quartz (Fig. 4-1, Davidson & Kamenetsky 2001, Davidson *et al.* 2005). Dark inclusions may also contain daughter crystals of sphalerite, chalcopyrite, Fe oxides and hydroxides, halite, carbonates and unidentified phases. They are also characterized by a significant and variable amount of fluid components, identified by laser Raman spectroscopy as vapor and liquid H₂O. A common feature of dark inclusions is an associated halo of aqueous vapor-dominated bubbles (< 5 µm) forming a discontinuous rim, which probably formed as a result of post-crystallization decrepitation of inclusions. Decrepitation of seemingly intact large dark inclusions at T~600°C is responsible for their failure to melt and homogenize during heating experiments. Some smaller inclusions show melting at 750–800°C, although complete homogenization (bubble disappearance) was not achieved even at higher temperatures.

Clear evidence of silicate-silicate melt immiscibility in the La Copa samples is observed in inclusions that comprise both clear glass and rounded, commonly spherical, crystalline and amorphous dark masses of dominantly silicate phases with interstitial aqueous fluid (Fig. 4-2). The relative proportions of trapped immiscible melts in such composite inclusions are highly variable, and their compositions are distinctly different (Fig. 4-2). The main difference, as indicated by PIXE

mapping, is elevated metal (Fe, Mn, Cu, Zn, Pb) and alkali element abundances in a volatile-rich silicate melt (Fig. 4-2).

Davidson & Kamenetsky (2001) emphasized that dark silicate melt inclusions, enriched in volatiles and metals, are important to the understanding of late-stage magmatic immiscibility and suggested revisiting the results of other studies on similar inclusions. For example, the melt inclusions from the Lower Bandelier Tuff (Dunbar & Hervig 1992) can be “*strongly devitrified*” and “*darker in color...and some contain clots of crystals*”, and also contain up to 8 wt.% H₂O, in contrast to clear glass inclusions (3–5 wt.% H₂O). It is possible that crystallization of trapped melts was promoted by high H₂O abundances. The interpretation of coexisting volatile-poor, and volatile-rich, silicate melts (melt inclusions) as immiscible liquids at La Copa (Davidson & Kamenetsky 2001) was partly based on the phase diagram derived from homogenization experiments with melt inclusions from the Ehrenfriedersdorf pegmatite (Thomas *et al.* 2000). According to their ground-breaking study, the original H₂O-undersaturated felsic magma separates at a certain temperature into two immiscible liquids, a volatile-poor silicate melt and a volatile-rich silicate melt (or a silicate-bearing fluid). The latter inevitably evolves via one or more consecutive unmixing events into aqueous metal-, salt-rich (“hydrothermal”) fluids with a potential for economic mineralization (see below).

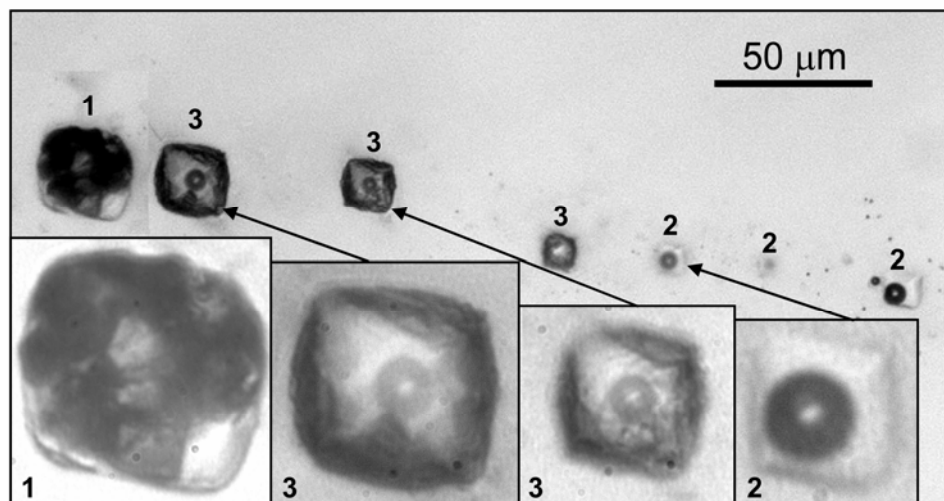


FIG. 4-1. A growth plane in a quartz phenocryst from La Copa complex, Chile (Davidson & Kamenetsky 2006), containing coexisting crystallized silicate melt inclusion (1), glass inclusions (2) and two-phase aqueous fluid inclusions (3). The two-phase aqueous inclusions show Brownian motion of the vapor bubbles, and freeze at low temperature.

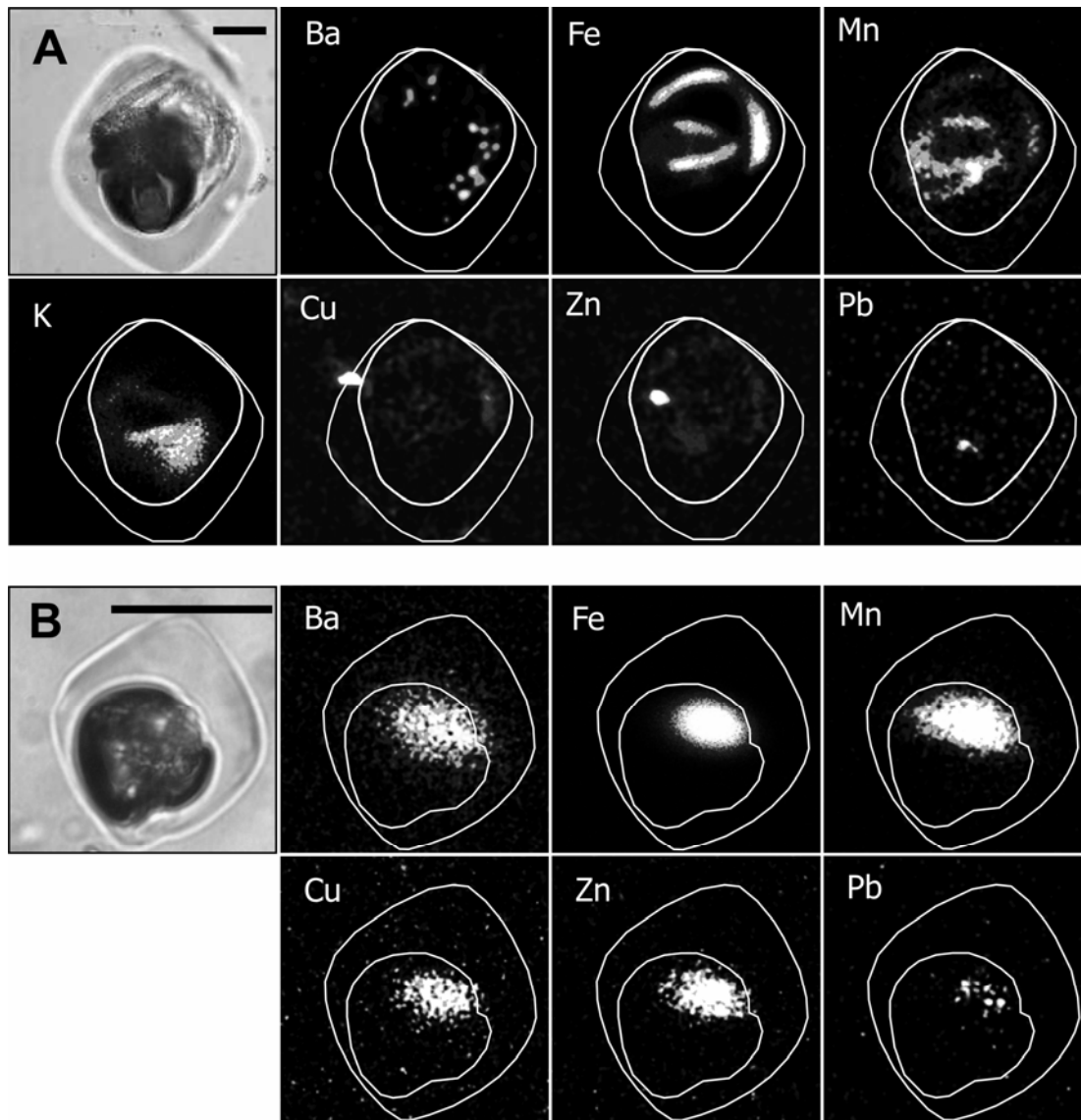


FIG. 4-2. Optical images and proton-induced X-ray emission (PIXE) element maps of quartz-hosted composite inclusions from La Copa complex, Chile (Davidson *et al.* 2005). The inclusions are composed of clear silicate glass and a globule of crystallized volatile-rich melt (dark). Outlines on element maps mark boundaries of inclusions and their volatile-rich silicate globules. Scale bars are 15 μm .

Immiscible silicate melt and aqueous saline fluids

Quartz phenocrysts in felsic intrusive rocks commonly contain numerous aqueous fluid inclusions, but in most cases they are clearly later than the silicate melt inclusions (if present) in the same grains. Trails of secondary aqueous inclusions commonly obliterate any evidence of primary aqueous inclusions, at least presenting a considerable challenge to their confident identification. An unambiguous example of silicate melt and aqueous two-phase fluid inclusions, co-

trapped in the same growth plane, is provided in Fig. 4-1 (after Davidson & Kamenetsky 2006). Notably, the dark silicate melt inclusion in Fig. 4-1 belongs to the volatile-rich type described above. Another example of explicit immiscibility between the silicate melt and magmatic aqueous fluid prior to or simultaneous with quartz crystallization is recorded by Davidson & Kamenetsky (2006) as composite inclusions containing very large numbers of one- or two-phase aqueous bubbles in a silicate glass (microemulsion, Fig. 4-3).

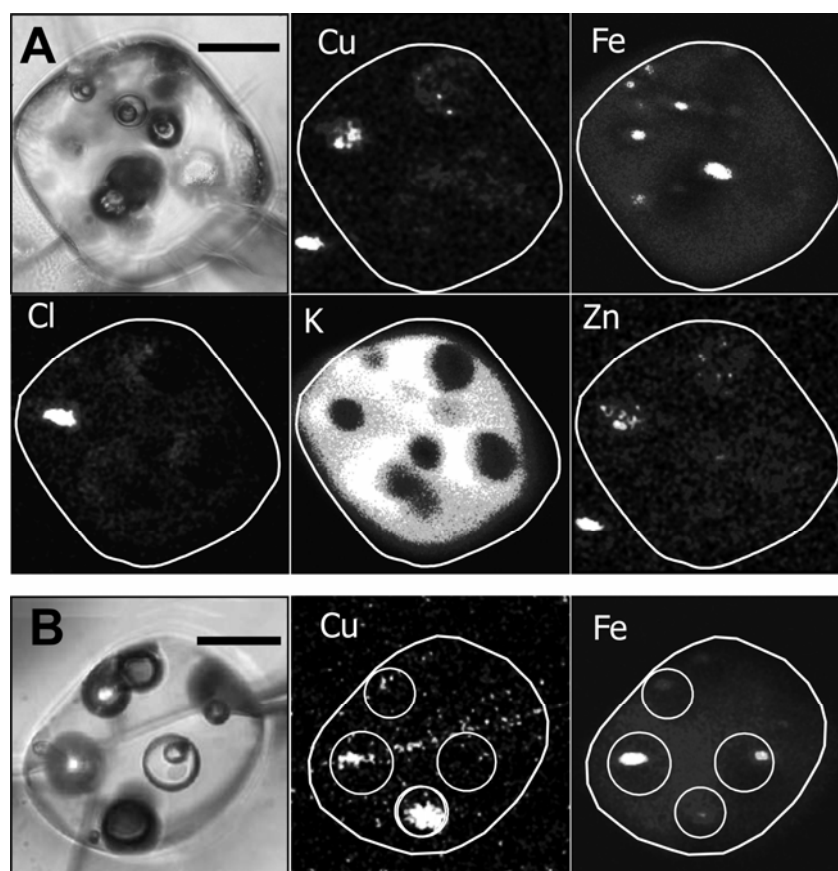


FIG. 4-3. Optical images and proton-induced X-ray emission (PIXE) element maps of quartz-hosted composite inclusions from La Copa complex, Chile (Davidson *et al.* 2005). The inclusions are composed of clear silicate glass and numerous bubbles of aqueous fluid (vapor- and liquid-rich). Outlines on element maps mark boundaries of inclusions and aqueous bubbles (on B). Scale bars are 25 μm .

On the other hand, in cases where crystallization occurs deeper than the magma saturation in H_2O , primary aqueous fluid inclusions are not trapped. Thus, the search for such inclusions in deep-seated plutons can be a futile task. A homogeneous H_2O -undersaturated melt trapped at higher pressure should crystallize and evolve in a closed system (such as within a melt inclusion) towards saturation and immiscibility (Naumov 1979, Roedder 1984, Thomas & Webster 2000). If this is the case, a separate aqueous phase is associated with the silicate content of melt inclusions (Davidson & Kamenetsky 2001, 2006, Davidson *et al.* 2005). Quartz-hosted melt and fluid inclusions from the La Copa magmatic complex, Chile and Taupo Volcanic Zone, New Zealand (thought to be trapped at 2–3 kb pressure according to their high H_2O abundances of up to 7–8 wt.%; Dunbar *et al.* 1989, Dunbar & Kyle 1993, Kamenetsky & Danyushevsky 2005) demonstrate

post-entrapment exsolution of the aqueous fluid.

Partly crystallized silicate melt inclusions from both localities are occasionally surrounded by swarms of aqueous vapor-rich and two-phase inclusions (Fig. 4-4). These fluids either heal fractures radiating from silicate melt inclusions, or decorate what appear to be oriented structural defects (dislocations, channels) in the quartz (Fig. 4-4). The spatial association of a “parental” silicate melt inclusion with systematically aligned aqueous inclusions, in conjunction with their elongated, commonly tubular shapes (Fig. 4-4), suggests the host quartz may have experienced hydraulic fracturing, caused by fluid overpressure within the silicate melt. The build-up of fluid pressure was a result of the melt crystallization, saturation in volatiles, immiscible separation of a fluid phase, and also possibly the compaction of host phenocrysts at the α – β quartz transition.

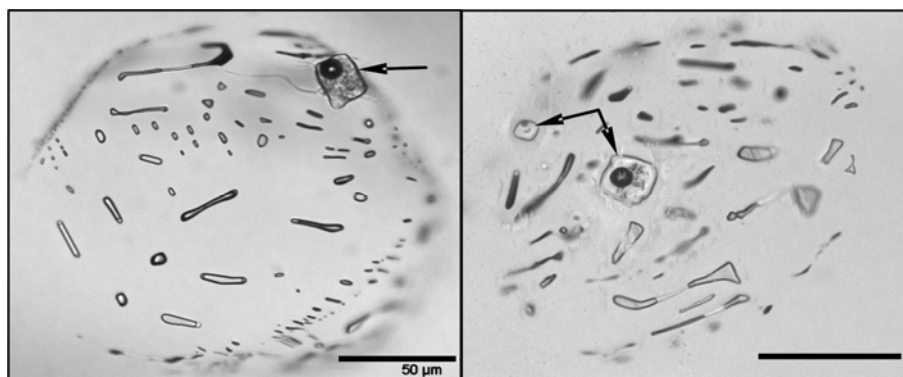


FIG. 4-4. Systematic distribution of aqueous fluid inclusions around crystallized silicate melt inclusions (shown by arrows) in quartz from the Taupo Volcanic Zone (New Zealand). Scale bars are 50 μm .

Glass inclusions from the La Copa and Taupo Volcanic Zone contain aqueous vapor, aqueous liquid, or both (Fig. 4-4, 5), sometimes with cubic chloride crystals (Fig. 4-5C, D). Bubbles of an aqueous liquid typically have spherical shape, although in the case of the La Copa samples some bubbles appear to be plastically deformed in a contracting glass (Fig. 4-5A, B). Microthermometric experiments on one- and two-phase aqueous bubbles from the La Copa samples (Davidson & Kamenetsky 2006) confirmed that these bubbles contain an aqueous liquid, since they freeze into a mass of ice crystals at temperatures below -40°C . The salinities of aqueous fluids, estimated using the data of Bodnar & Vityk (1994), range from 13–17 wt.% NaCl eq. in liquid-phase bubbles, to ≥ 40 wt.% NaCl eq. in bubbles containing salt precipitates.

Dense aqueous fluid bubbles in melt inclusions have been observed in plagioclase and quartz from andesites and rhyolites in Slovakia, the western Carpathians and central Tien Shan (Naumov *et al.* 1992, 1994, 1996). This implies that they may not be unusual, and should be looked for in other instances. Aqueous one-phase liquid bubbles in silicate glass are likely to be a metastability phenomenon, reflecting the surface tension effects in very small containers. At certain bubble volumes, for a given composition and density, fluid “*will remain stretched indefinitely (i.e., without nucleation of a bubble), as the stable configuration*” (Roedder 1984). In other words, the fluids may increase their average inter-molecular distances, rather than nucleate a bubble. It should be noted that the nucleation of vapor phase inside a homogeneous liquid bubble occurs sometimes during heating and freezing experiments and during PIXE or Raman measurements (Fig. 4-5D). But the

fact that, in some cases, the bubbles spontaneously return to a single liquid state means that in this specific situation the “stretched” configuration is actually more stable.

Samples of most pristine magmatic fluids, formed in a closed system of their parental melt (melt inclusion), have demonstrable quantities of chlorine and metals. The compositions of glass-hosted aqueous bubbles, apart from observed chloride crystals (Fig. 4-5C, D) and moderate chlorine content, are characterized by elevated concentrations (1–3 orders of magnitude with respect to silicate glasses) of Cu, Zn and Fe (Fig. 4, Davidson & Kamenetsky 2006) and Cu and Ag (Kamenetsky & Danyushevsky 2005), but at present this enrichment is not expressed in absolute terms. Our preliminary data indicate that metals are indeed sequestered from the silicate melt into *in situ* exsolved aqueous bubbles, and that compositional diversity of immiscible fluids can occur at very fine scales.

Immiscible silicate melt and hydrosaline liquids/salt melts

Exsolution of a moderately saline aqueous fluid from a silicate melt, and its later separation into vapor and brine fluids, has been a cornerstone of the orthomagmatic model (*e.g.*, Burnham 1979). Magmas are also capable of direct exsolution of highly concentrated chloride liquids (brine, salt melt, or hydrosaline fluid; see definitions in Halter & Webster 2004) together with low density aqueous vapors (*e.g.*, Cline & Bodnar 1994, Shinohara 1994, Bodnar 1995). It has been demonstrated that the initial melt composition puts strong constraints on “*the type of volatile phase that exsolves*” and “*the relative timing of volatile phase exsolution*” (Webster 2004). Given the existing evidence, a

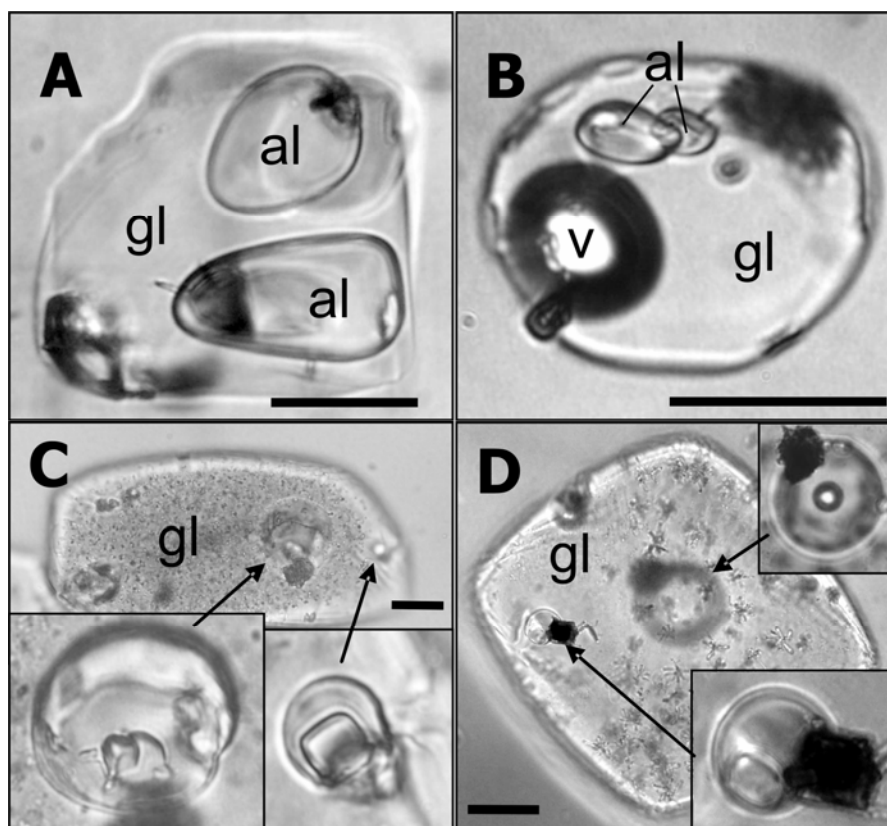


FIG. 4-5. Aqueous globules in quartz-hosted silicate melt inclusions (Davidson & Kamenetsky 2006) from La Copa complex, Chile (A, B) and Taupo Volcanic Zone, New Zealand (C, D). Single-phase aqueous liquid bubbles have elliptical, “deformed” (A, B) or spherical shapes (C, D). Salt crystals are commonly present inside aqueous liquid (C, D). Note that the vapor phase in Fig. 5D (upper close-up) only appeared after laser Raman analysis, prior to this it was single phase aqueous liquid. **gl** – silicate glass, **al** – aqueous liquid, **v** – vapor. Scale bars are 20 μm .

continuum from high-density salt melts to low-density aqueous vapors, coexisting with each other and with their “parental” silicate magma, occurs in nature (*e.g.*, Roedder & Coombs 1967, Reyf & Bazheyev 1977, Reyf 1984, 1997, Solovova *et al.* 1991, Frezzotti 1992, Roedder 1992, Solovova *et al.* 1992, De Vivo & Frezzotti 1994, Lowenstern 1994, De Vivo *et al.* 1995, Kamenetsky *et al.* 1999). Quartz-hosted inclusions from the La Copa magmatic complex, Chile (Davidson *et al.* 2005, Davidson & Kamenetsky 2006), mineralized Omsukchan granite, NE Russia (Kamenetsky *et al.* 2004b), dacitic porphyries from the Bajo de la Alumbrera deposit, Argentina (Harris *et al.* 2003, 2004), granite clasts in the Gawler Craton rhyolites, South Australia, and Panguna Cu–Au porphyry deposits, Bougainville Island, Papua New Guinea, are used below to confirm common silicate melt – salt melt immiscibility in plutonic felsic systems.

Primary magmatic inclusions in quartz phenocrysts are aligned along growth planes and

syn-crystallization fractures, and belong to three main types: syngenetic crystals (*e.g.*, feldspar, mica, apatite, zircon), glassy or crystallized silicate melt, and non-silicate volatile-rich phases. Crystallized silicate melt inclusions are commonly surrounded by radiating fractures and halos of tiny vapor-rich aqueous bubbles (Fig. 4-4), suggesting the melt originally had a high volatile content, which was released during post-entrapment crystallization and decrepitation of these inclusions. Volatile-rich inclusions are much more common than silicate melt inclusions and characterized by round to negative crystal shapes and relatively small size (typically $<15 \mu\text{m}$). They contain variable proportions of aqueous vapor, liquid and non-silicate crystals, ranging from essentially vapor to dominantly crystalline end-members (Fig. 4-6). Composite inclusions, consisting of trapped combinations of cotectic crystals, silicate melt and aqueous saline fluids (Figs. 4-5A, B, 7), are also common.

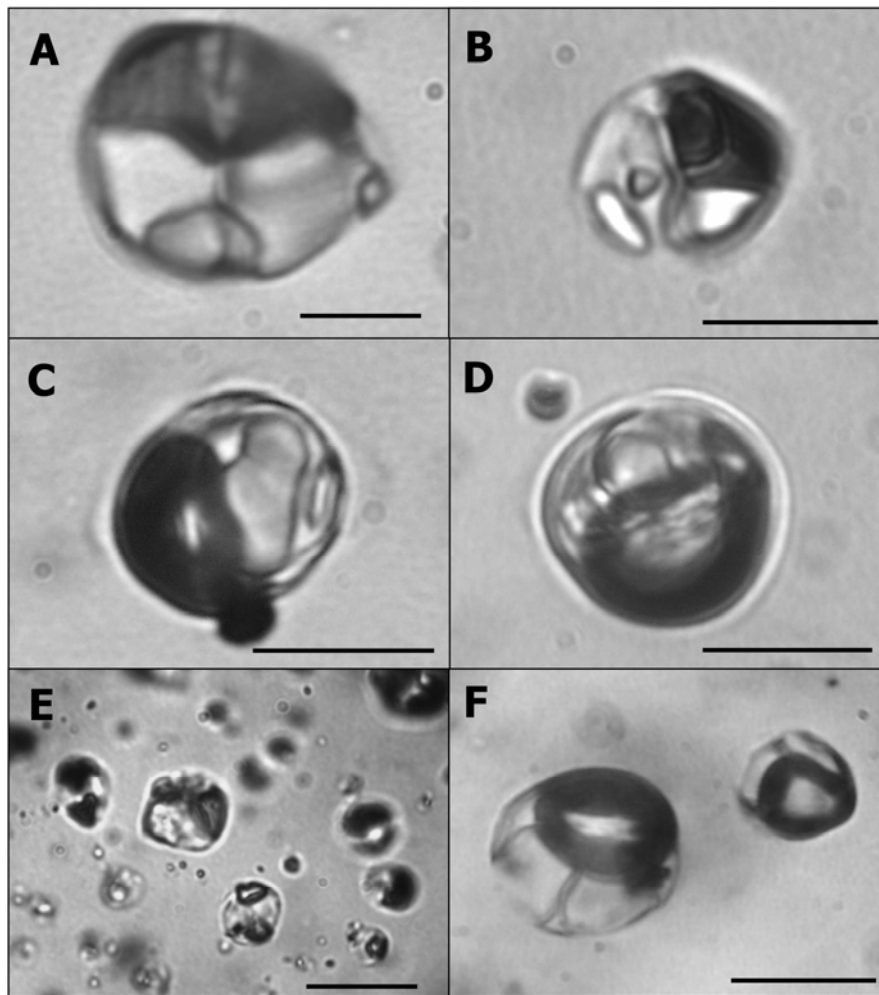


FIG. 4-6. Magmatic inclusions of crystallized hydrosaline liquid from the Gawler Craton, South Australia granites (A, B), Omsukchan granite, NE Russia (C, D), Mt. Vesuvius endoskarn (E) and Panguna porphyry, PNG. Note a large-sized vapor bubble (dark) in all inclusions. Host minerals are quartz (A-D, F) and sanidine (E). Scale bars are 20 μm .

Co-trapping of silicate melt with hydrosaline liquid is most evident in the inclusions that escaped post-trapping crystallization of their silicate melt component (*i.e.*, glass; Fig. 4-7B-D). However, in most cases fine-grained crystalline silicate masses inside composite inclusions obscure evidence of non-silicate phases that are present. Heating such inclusions and subsequent quenching (Kamenetsky *et al.* 2003) are used to make heterogeneously trapped non-silicate phases available for observation and analysis. After heating, melt inclusions consist of clear silicate glass and spherical globules of salt melt (Fig. 4-7E-H). Globules are crowded with microcrystals of chlorides (\pm anhydrite \pm magnetite \pm chalcopyrite) and always contain a significant quantity (up to 50 vol.%) of a spherical to deformed

vapor phase (Fig. 4-7B-H). The number (from 1–2 to 100's) and sizes ($<1\text{--}15\text{ }\mu\text{m}$) of globules vary significantly even in neighboring inclusions. Commonly in larger composite inclusions these crystal- and vapor-bearing globules form an emulsion (globules are suspended in the glass “matrix”, Fig. 4-7E-H). This presents a clear case of magmatic immiscibility in which at least two liquids were stable simultaneously during quartz growth. The size of the trapped continuous silicate melt phase is random, depending on the size of the growth irregularities on the surface of the host crystal (Roedder 1984), whereas the size of the trapped globules is suggested to be representative of the actual size of dispersed salt melt phase at the time of immiscibility, and before coalescence (Reyf 1984).

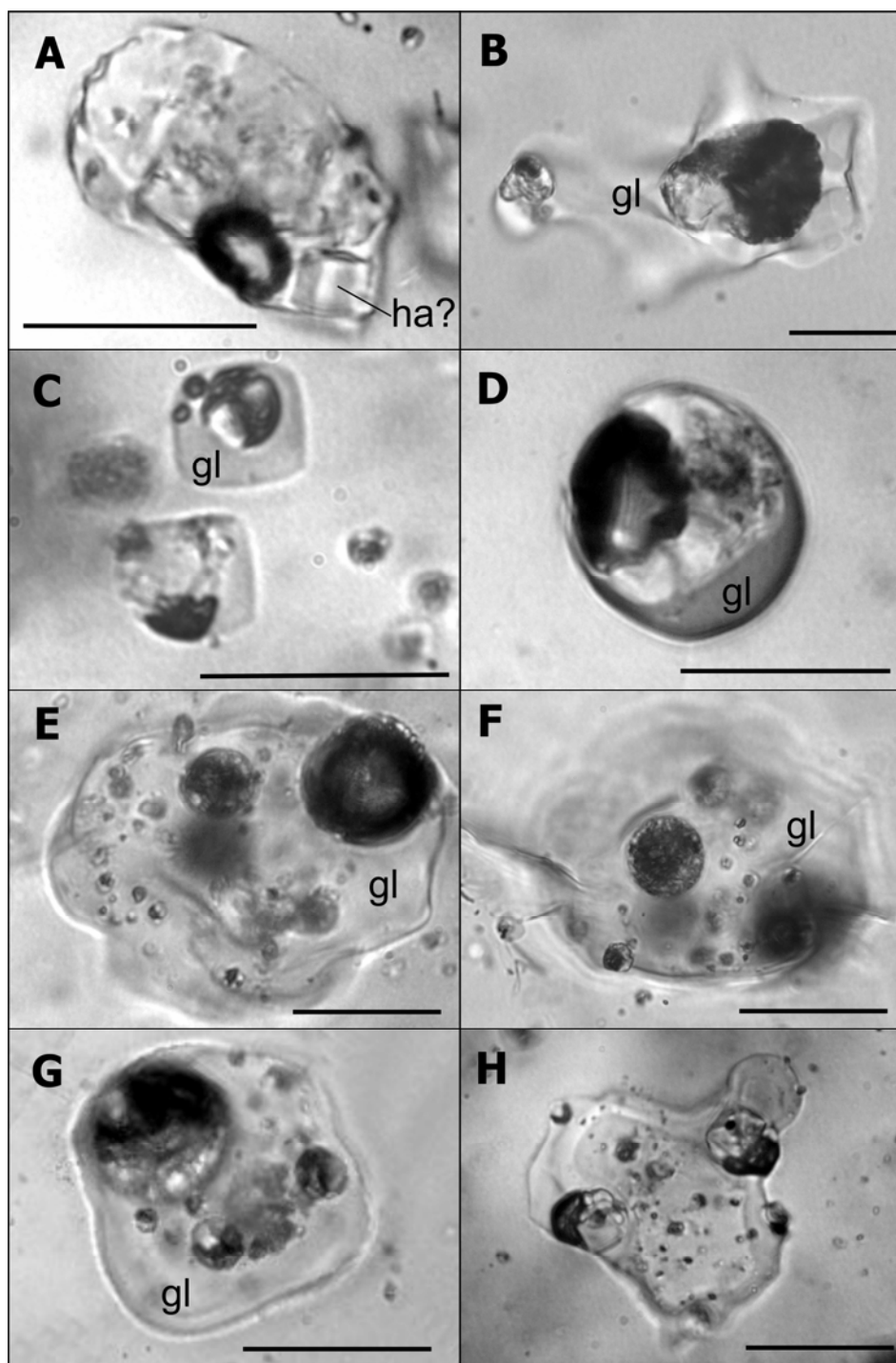


FIG. 4-7. Magmatic inclusions composed of silicate melt (crystallized and glassy - **gl**) and heterogeneously trapped hydrosaline liquid from the Omsukchan granite, NE Russia (A, E, F), Gawler Craton, South Australia granites (B), Mt Vesuvius endoskarn (C, D), La Copa complex, Chile (G) and Bajo de la Alumbrera porphyry, Argentina. Note cubic crystal, possibly halite (**ha?**), associated with aqueous fluid in the lower right corner of the inclusion in (A). Numerous spherical globules of dominantly chloride composition suspended in the silicate glass matrix (“microemulsion” in E-H) were observed only after heating (800-850°C) and partial homogenization of the silicate content of these inclusions. Host minerals are quartz (A, B, E-H) and sanidine (C, D). Scale bars are 20 μm .

Morphologically similar hydrosaline globules hosted in quartz (Fig. 4-6) and co-trapped with the silicate melt (Fig. 4-7) are confirmed to be compositionally alike by microthermometric experiments and microbeam analyses (Harris *et al.* 2003, 2004, Kamenetsky *et al.* 2004b). The globules are all metal- (1000's–10000's ppm) and chloride-rich (Fig. 4-8), although the element abundances and ratios vary significantly, even for co-trapped globules (Kamenetsky *et al.* 2004b). Compositional variability among hydrosaline globules suggests strong fractionation of most elements between immiscible liquids and the disequilibrium character of exsolution. The latter means that if immiscibility is a continuous process in highly evolved magmatic systems, the components of a dispersed hydrosaline phase must have varying composition, because of the variability of diffusion rates for different elements. In the residual granitic system, where crystallization and immiscibility drive chemical fractionation to the extreme, chemical disequilibrium may occur on very small spatial and temporal scales, and is maintained by slow element diffusion and delayed mixing in a relatively cold, viscous and strongly crystalline environment.

Identification of immiscible silicate melts and hydrosaline liquids is the first important step in linking typical aluminosilicate magmas and typical hydrothermal chloride solutions. For example, zoned quartz phenocrysts from the mineralized Panguna porphyries, Papua-New Guinea, show systematic distribution of magmatic inclusions from the dominantly silicate melt in the cores to domin-

antly aqueous saline fluid inclusions in the rims (Fig. 4-9). Another example from the Bajo de la Alumbrera porphyry records silicate and salt melt inclusions occurring together within quartz phenocrysts, as well as mineralized (chalcopyrite, bornite) quartz veins (Fig. 4-7H; Harris *et al.* 2003, 2004). The hydrosaline liquid inclusions in the vein quartz were interpreted to be the most primitive and copper-rich ore fluids identified to date, exsolved from the crystallizing melt at ~100 MPa. These inclusions appear to represent a “broth” of the silicate melt and hydrosaline metal-enriched fluids, characteristic of the magmatic to hydrothermal transition that is a prerequisite to the formation of economic deposits.

Immiscible silicate melt and carbonic (CO₂, carbonate) fluids

Natural and experimental carbonate-silicate systems show almost ubiquitous evidence of multiphase liquid/fluid immiscibility involving different silicate and carbonate melts; as well as CO₂ fluid and chloride, sulfate and phosphate phases (see reviews in Roedder 1994, Frezzotti 2001, Lowenstern 2001, Kamenetsky *et al.* 2002a, Veksler 2004, Panina 2005). Compelling evidence for this type of immiscibility comes from the studies of melt and fluid inclusions in diamonds, peridotite xenoliths, alkaline intrusive complexes, and carbonatites. In contrast to widespread occurrence of the silicate-CO₂-carbonate immiscibility in mantle-derived rocks and magmas, this type of unmixing in the silicic crustal magmas is by far less pronounced (see reviews in De Vivo & Frezzotti

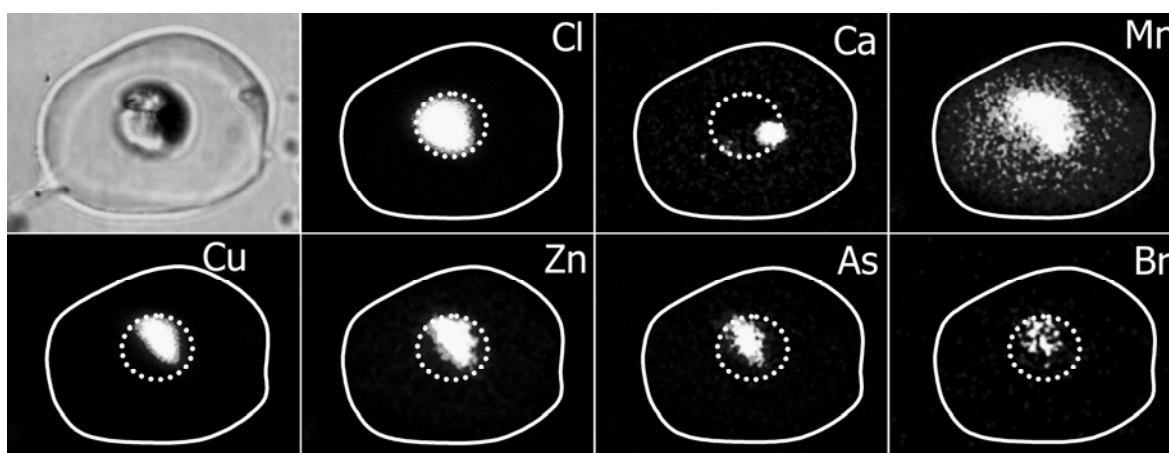


FIG. 4-8. Optical image and proton-induced X-ray emission (PIXE) element maps of a heated composite inclusion in quartz from the Omsukchan granite, NE Russia (Kamenetsky *et al.* 2004). The inclusion is composed of clear silicate glass and a heterogeneously trapped globule of hydrosaline liquid. Outlines on element maps mark boundaries of the inclusion and the globule. Inclusion size is ~25 μm .

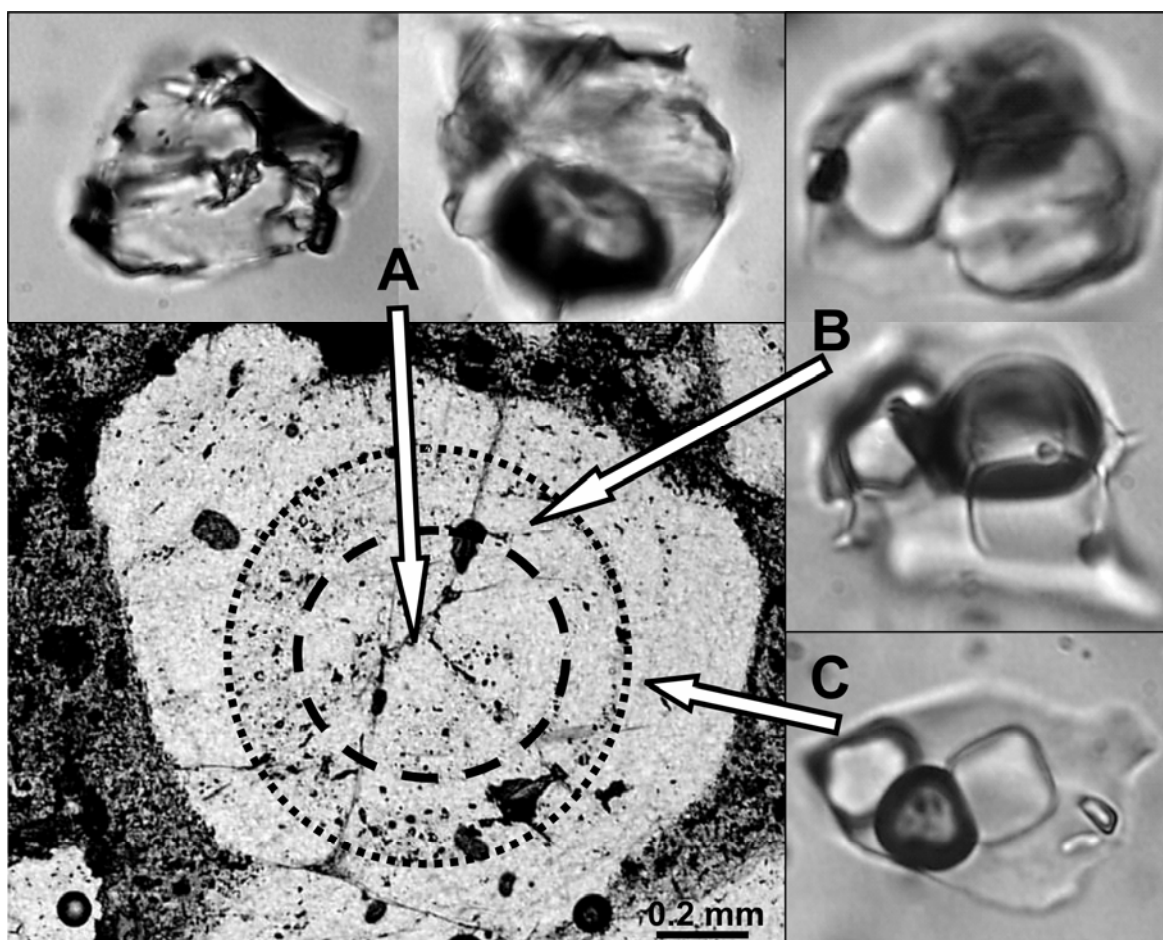


FIG. 4-9. Zoned quartz phenocryst in the Panguna porphyry, PNG and its magmatic inclusions present in different growth zones. The phenocryst core is dominated by crystallized silicate melt inclusions (A). The magmatic-hydrothermal transition is recorded in increasing numbers of hydrosaline (B) and brine fluid (C) inclusions towards the phenocrysts rims. Inclusion sizes are ~20-25 μm .

1994, Lowenstern 2001). The data available to the author show coexistence of silicate melt and dense CO_2 fluid (Fig. 4-10) among magmatic inclusions in quartz from granitic clasts in the Gawler Craton rhyolites, South Australia and the Timbarra granite, New England Fold Belt, East Australia (Mustard *et al.* 2003, 2006), and in the silicate phenocrysts from rocks forming marginal parts of the Mt. Vesuvius magma chamber (Fulignati *et al.* 2001). The latter example offers an opportunity to study fluids involved in magma-wall rock reactions.

The CO_2 -rich composition of granite-derived magmatic fluids is of particular importance in genetic modeling of intrusion-related deposits of Au (*e.g.*, Timbarra) and lithophile elements (*e.g.*, Fe-Cu-Au-U-REE mineralization in the eastern Gawler Craton). Melt inclusion studies performed on a composite 250 Ma I-type granite pluton

hosting the Timbarra Au deposit (Mustard *et al.* 2003, 2006) showed that metal enrichment occurred as a result of crystal fractionation (enrichment factors: 40 for Au, 5–20 for Mo, W, Bi, As and Sb, and 1–3 for Zn, Pb and Cu). Individual inclusions of the crystallized silicate melt in the most fractionated Timbarra rocks contain daughter ore minerals (gold, senarmontite (Sb_2O_3), scheelite (CaWO_4), wulfenite (PbMoO_4), molybdenite (MoS_2), sphalerite (ZnS) and stibnite (Sb_2S_3)). Importantly, magmatic inclusions do not record immiscibility between the silicate melt and Cl-bearing fluids; instead the magmatic fluids are CO_2 -rich (Fig. 4-10A) with up to 12.6% N_2 and 1.2% CH_4 . Such chemically “inert” fluids were largely responsible for preferential partitioning of metals into the silicate melt, and thus crystallization-related metal enrichment in the residual magmas (Mustard *et al.* 2006).

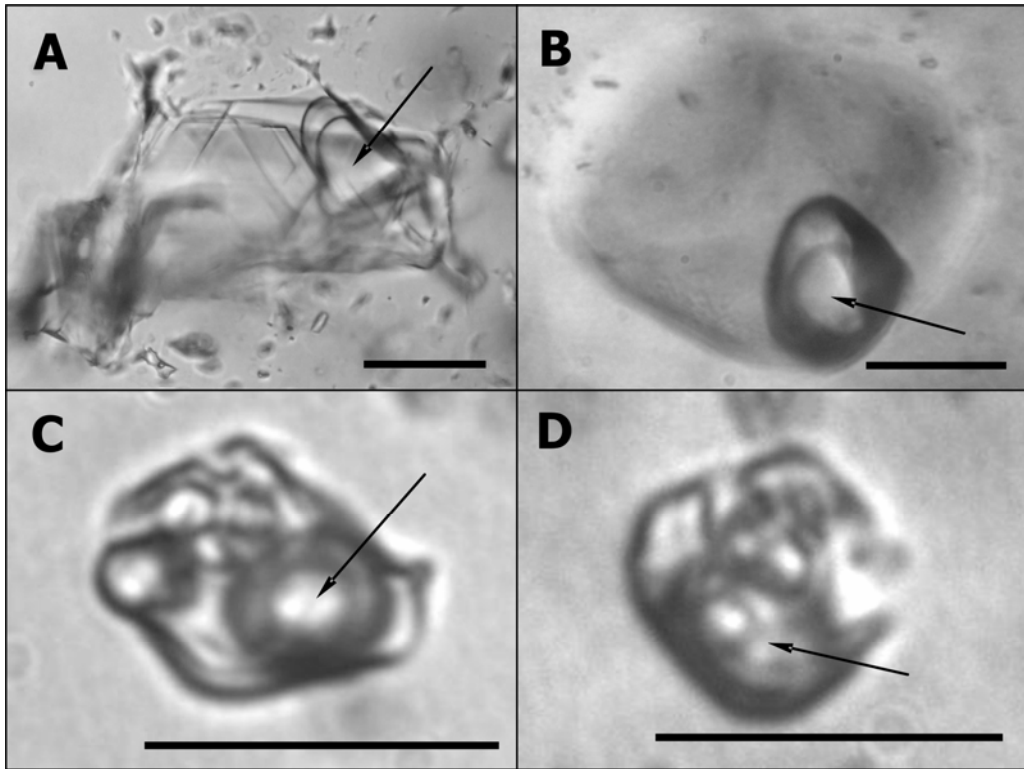


FIG. 4-10. Magmatic inclusions composed of silicate melt (crystallized and glassy) and high-density CO₂ fluid (shown by arrows) from Timbarra granite, New England Fold Belt, East Australia (A), Mt. Vesuvius endoskarn (B), and Gawler Craton, South Australia granites (C, D). Host minerals are quartz (A, C, D) and nepheline (B). Scale bars are 10 μ m.

Immiscible non-silicate melts

Cooling, crystallization and unmixing of silicate magmas inevitably results in the exhaustion of the aluminosilicate components, and separation of essentially non-silicate volatile-rich phases from the aluminosilicate solids at, and below, the silicate magma solidus. Very little is known about these residual phases, especially in the plutonic environment, because they are highly fugitive and reactive in nature, and prone to chemical modifications via boiling, mixing, crystallization and interaction with wall-rocks. Unmixing of these residual non-silicate phases into compositionally more simple components is expected, based on experimental and melt inclusion studies (*e.g.*, Panina 2005, and references therein), and a variety of rocks (different carbonatites, skarns and pegmatites) and styles of alteration and mineralization can be genetically linked to ephemeral, still hypothetical, syn- and post-magmatic fluids and melts. Examples below from the endoskarn samples of Mt. Vesuvius (Fulignati *et al.* 2001, 2005); miarolitic quartz in the Omsukchan

granite, NE Russia (Kamenetsky *et al.* 2002b, 2004b) and Udachnaya East pipe kimberlite, Siberia (Kamenetsky *et al.* 2004a, 2006) demonstrate the role of heating experiments with melt inclusions in deciphering immiscibility processes in deep-seated carbonate-chloride liquids.

Multiphase melt inclusions in nepheline from the endoskarn xenoliths of the A.D. 472 Mt. Vesuvius eruption, representing the magma chamber – carbonate wall-rock interface, are composed of Na–Ca carbonates, Na–K chlorides and minor Ca- and Na–K sulfates and Fe–Cu–Zn–Pb sulfides (Fulignati *et al.* 2001). On heating at 1 atm. they show complete melting of daughter crystals at 800–830°C, followed by vapor-bubble homogenization between 860 and 885 °C, although some solids (possibly heterogeneously trapped silicates) may persist up to higher temperatures. Cooling of homogenized inclusions always results in immiscibility between two clear liquids (Fig. 4-11) at ~670–700°C. One new melt forms either a single spherical globule around a vapor bubble (Fig. 4-11A) or several globules that later coalesce

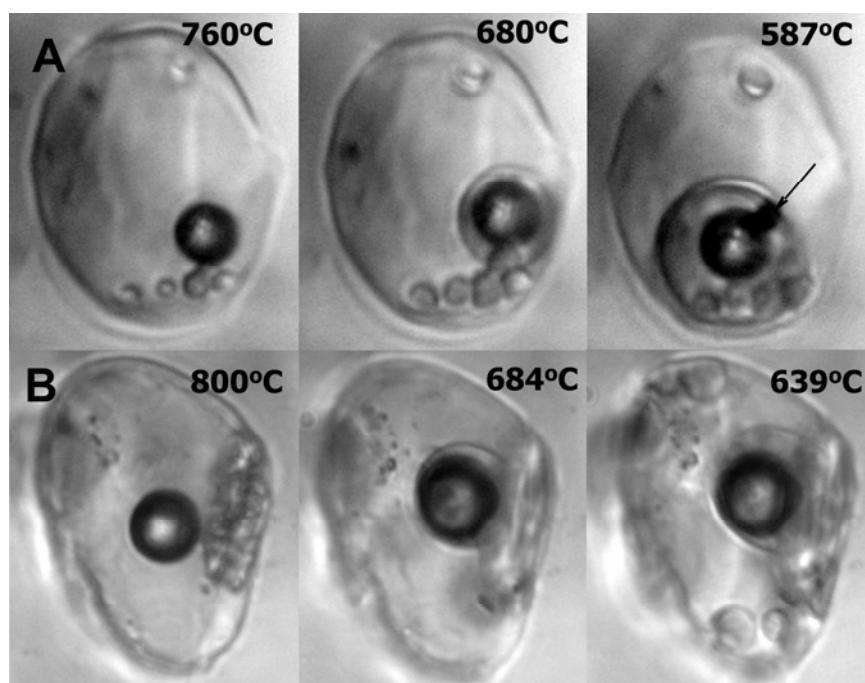


FIG. 4-11. Photomicrographs illustrating cooling behavior of carbonate-chloride melt inclusions in nepheline from the Mt. Vesuvius endoskarn (Fulignati *et al.* 2001). Note formation and increase in size of a single (A) or multiple (B) globules of immiscible chloride melt. The arrow points to a sulfide globule formed at the carbonate-chloride meniscus. Inclusion sizes are ~30-35 μm .

(Fig. 4-11B). Repeated heating and cooling of the same inclusion show that the immiscibility is reversible at a constant temperature (~670-700°C). Below 550°C spontaneous crystallization within the two unmixed liquids obscures original phase boundaries and deforms the vapor bubble. These inclusions were interpreted to reflect compositions formed as a result of interactions between high-temperature, magmatic-derived hydrosaline liquids and carbonate country rocks. The liquids they represent are important in transferring elements into skarn environments, and the observed carbonate-chloride melt immiscibility, if it occurs in nature, can account for specific metasomatic reactions (carbonate-related and chloride-related) and mineral assemblages in the ore deposits.

Miarolitic quartz from the tin-mineralized Omsukchan granite intrusion, NE Russia, contains several populations of spectacular inclusions of crystallized hydrosaline liquids (Kamenetsky *et al.* 2002b, 2004b). The daughter phase assemblage in these inclusions is, without doubt, the most complex that an investigator may come across. Cubic, pseudocubic, hexagonal, pyramidal, and prismatic crystals are common, as well as minerals with high relief and birefringence. However, there is no order

or pattern to the alignment of the crystals and no clear relationships between the shape, color (except for hematite plates), birefringence, and relief of crystals. Even at room temperature, the contents of these inclusions are metastable and prone to spontaneous recrystallization followed by changes in the number, shape and volume ratios of phases. In addition to common halite, sylvite and hematite, at least 10 different solids have been distinguished by Raman spectroscopy. Most of them exhibited very intense OH-stretching bands between 3400 and 3450 cm^{-1} , however, the overall Raman spectra do not correspond to those of the common minerals. No carbonate, sulfate, phosphate, nitrate, or borate bands were observed in these spectra, but antarcticite ($\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$) and Sn chloride (possibly abhurite $\text{Sn}_3\text{O}(\text{OH})_2\text{Cl}_2$) have been tentatively identified. The PIXE analysis of these inclusions showed significant Br, Fe, Mn, Zn and Pb enrichment, associated with individual daughter crystals (Kamenetsky *et al.* 2002b), and the LA-ICP-MS analysis confirmed that Cl is the major anion. Kamenetsky *et al.* (2002b) suggested that the inclusions are largely composed of complex hydrous chlorides.

The inclusions in miarolitic quartz homogenize (except for a few newly formed tiny crystals) into liquid at 550–650°C. On cooling they remain homogeneous for ~100–150°C below homogenization temperature, and then undergo spontaneous unmixing into at least two liquids and nucleation of several vapor bubbles (Fig. 4-12). At the onset of immiscibility one liquid forms worm-like segregations that float freely in the matrix of another liquid, change their shape and size continuously, until they finally coalesce at ~320–350°C (Fig. 4-12). With further cooling the boundary between two liquids (colloids?) fades out, and spontaneous changes in the phase composition (possibly coagulation of gels) in both phases occurs within a few degrees at 120–140°C.

Multiphase melt inclusions in the groundmass olivine from the Udachnaya East kimberlite consist of three principal components – calcite, Na–K–Ca carbonate and Na–K chloride minerals (Golovin *et al.* 2003, Kamenetsky *et al.* 2004a, 2006). Other daughter phases, such as olivine, phlogopite-tetraferriphlogopite, Fe–Ti–Cr oxides, aphthitalite ($K_3Na(SO_4)_2$) and djerfisherite ($K_6(Fe,Ni,Cu)_{24}S_{26}Cl$), are present in subordinate abundances. Homogenization of these inclusions occurs by vapor bubble disappearance at 660–760°C. Cooling to 610–580°C results in a spontaneous process in which inclusions acquire a ‘foggy’ appearance but only momentarily. This process can best be described as the formation of an emulsion, i.e. microglobules of one liquid in another (*i.e.*, melt immiscibility). Microglobules coalesce immediately into larger, elongate, sausage-like globules (Fig. 4-13B). The neighboring globules (“boudins”) are subparallel, and are grouped into

regularly aligned formations with a common angle of ~75–80° (Fig. 4-13B). A resemblance to the skeletal or spinifex texture is evident for several seconds, after which the original “pinch-and-swell structure” pulls apart giving rise to individual blebs of melt. The latter coalesce and become more spherical with time or further cooling (Fig. 4-13C). The immiscible phases are recognized as carbonate- and chloride-dominated, respectively, on the basis that these minerals are dominantly present in the unheated melt inclusions.

Remarkable textures, observed in kimberlitic melt inclusions at the exact moment of melt unmixing (Fig. 4-13B), are governed by the carbonate crystallographic properties. Similar textures, but on a much larger scale, are recognized in the round chloride-carbonate segregations (nodules, 5–30 cm across) in the same kimberlite rocks. The nodules are composed of regularly interspersed layers (sheets) of carbonates and chlorides (Fig. 4-13D). The groups of aligned carbonate sheets make up larger (2–2.5 cm) formations that appear as isosceles triangles in cross-sections or as rhombohedra in three dimensions. The surfaces of individual carbonate sheets are locally flat, but more typically bumpy, or boudin-like. The thickness of boudins rarely exceeds 1–1.5 mm, and symmetrical zoning is visible at the cross sections of inflated parts. Sugary aggregates of chlorides appear to fill in the intra-sheet spaces and cracks in the carbonates. The chlorides are dominated by halite, whereas round and amoeboid blebs of sylvite in halite often show textures reminiscent of liquid immiscibility rather than unmixing of solid solution (Kamenetsky *et al.* 2006).

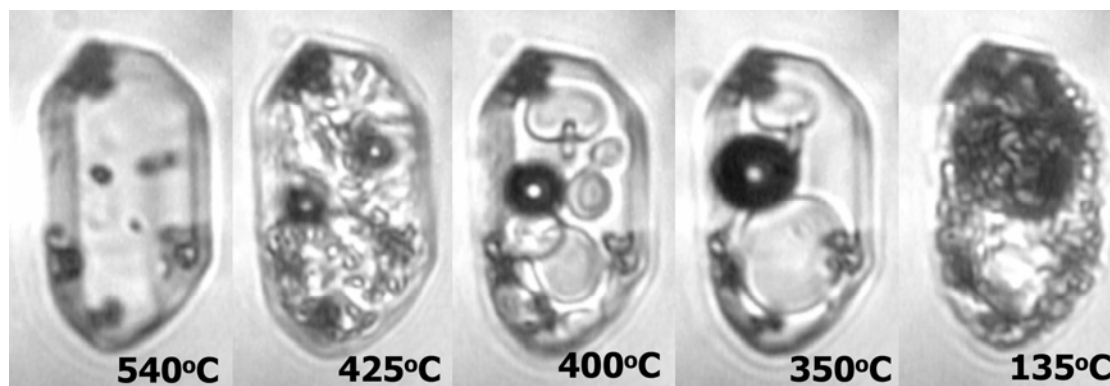


FIG. 4-12. Photomicrographs showing cooling behavior of a hydrosaline fluid inclusion in miarolitic quartz from the Omsukchan granite (NE Russia). This and other co-trapped inclusions homogenize at ~550°C and remain homogeneous on cooling until immiscibility occurs at ~425°C. See text for details. Inclusion size is 50 μ m.

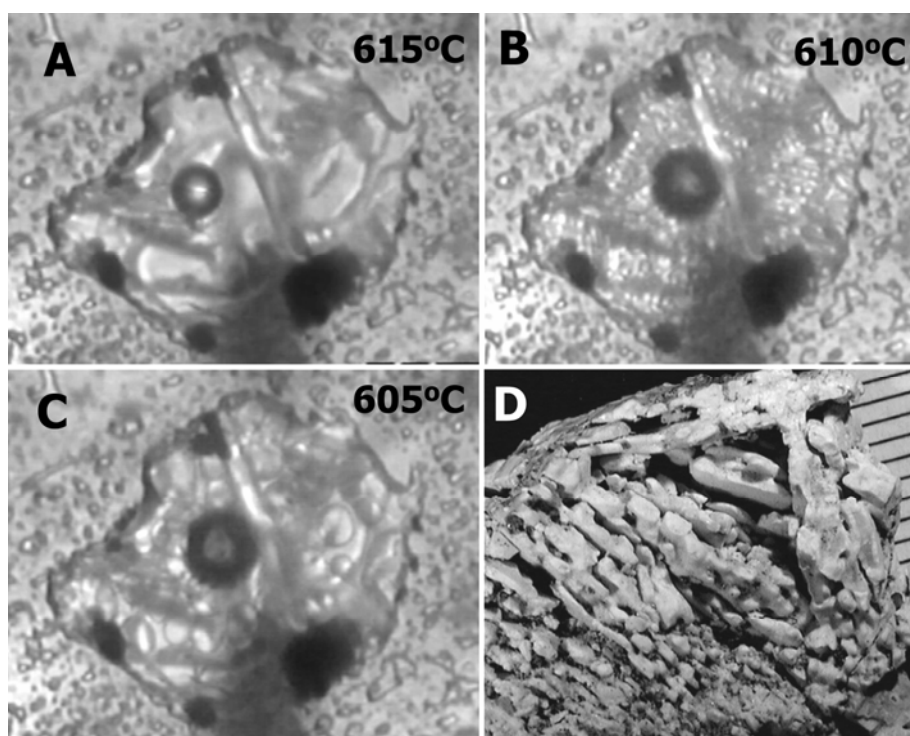


FIG. 4-13. Photomicrographs demonstrating carbonate-chloride immiscibility in an olivine-hosted melt inclusion (A-C) and residual melt pocket (“nodule”) from the Udachnaya East kimberlite, Siberia (Kamenetsky *et al.* 2006). Note textural similarity between olivine-hosted melt inclusion at the moment of immiscibility (B) and chloride-carbonate nodule (D). See text for details. Inclusion size is 50 μm .

The presence of similar textures in olivine-hosted melt inclusions at $\sim 600^\circ\text{C}$ and chloride-carbonate nodules in the kimberlite groundmass (Fig. 4-13) is the first record of unambiguous chloride-carbonate melt immiscibility in mantle-derived magmas. The preservation of magmatic immiscibility among residual non-silicate components of the original kimberlite magma correlates well with the enrichment of the Udachnaya East kimberlite in alkali elements and chlorine (2.3–3.2 wt.% Cl, 2.6–3.7 wt.% Na, and 1.6–2.0 wt.% K). Such enrichment is inherited from the kimberlite parental/primary magma, and it can be responsible for kimberlite’s low liquidus temperatures, low viscosities, and rapid ascent, as well as potential catalytic effects on the growth of diamonds. Under mantle conditions, the chloride- and carbonate-rich kimberlite would be highly volatile, mobile, reactive, and capable of pervasively percolating and wetting ambient peridotite. Thus, such kimberlite magmas, kimberlite-derived chloride-carbonate melts, and their immiscible products, may play a previously unrecognized role as potent metasomatic agents in both mantle and crust.

CONCLUSIONS

Immiscible magmatic liquids and vapors trapped as melt and fluid inclusions in phenocrysts are the closest approximation of naturally exsolved volatile-rich phases. Such inclusions can be used as a natural experimental laboratory to model volatile phase exsolution from cooling and crystallizing magmas (a proxy for some large-scale magma chamber processes, such as sequestering of metals and degassing), and thus may make possible quantification of partitioning of metals and volatiles.

Since magmatic immiscibility and consequent separation of a volatile-rich phase from a cooling silicate magma is a keystone of the orthomagmatic models of ore formation, more insights into late magmatic–early hydrothermal processes and phases are required. If we are to apply melt/fluid inclusion studies to unravel the details of immiscibility event(s), then the choice of samples becomes critical. Apart from technical problems (*e.g.*, presence of phenocrysts, availability and preservation of inclusions) we face a dilemma, which rocks are most suitable for such a study? At first glance, the choice of rocks spatially and

temporally related to mineralization (*e.g.*, host intrusions) seems most attractive, because such rocks are interpreted as originating from magmas that supplied the volatiles and ore-forming elements. However, if this viewpoint is correct, such rocks (and likely their melt inclusions) must be depleted in volatiles and metals relative to the precursor (parental) magma. Moreover, in such rocks the magmatic signature is commonly overprinted by later hydrothermal events. On the other hand, rocks cogenetic with those having a demonstrated direct relationship to mineralization, but without a proven link of their own, may be a case in which the evolution from silicate magmas to mineralizing fluids has not gone to completion. By studying examples in which immiscibility does not go all the way to ore formation, it should be possible to use the melt/fluid inclusion approach to record consecutive “snapshots” of the immiscibility processes and production of immiscible phases. The first occurrence of immiscibility in magmas appears to be most important in the magmatic-hydrothermal transition, and thus our studies of magmatic immiscibility should be primarily directed towards recognition of coexisting silicate melt and essentially non-silicate melts or fluids.

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