

**Immiscibility between silicate magmas and brines in the Omsukchan Granite
(NE Russia): melt inclusion probe into magmatic-hydrothermal transition**

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Abstract

Exsolution (unmixing) of volatile-rich phases (fluids, salt and sulphide melts) from cooling and crystallising silicate magmas is critical for element transport from the Earth's interior into atmosphere, hydrosphere, crustal hydrothermal systems, and the formation of orthomagmatic ore deposits. Unmixing is an inherently fugitive phenomenon and melt inclusions (droplets of melt trapped by minerals) provide the most robust evidence of this process. In this study, melt inclusions in phenocrystic and miarolitic quartz were studied to better understand immiscibility in the final stages of cooling of, and volatile exsolution from, granitic magmas, using the tin-bearing Omsukchan Granite (NE Russian) as an example.

Primary magmatic inclusions in quartz phenocrysts (cotectic crystals, crystalline silicate melt, brine- and vapour-rich) demonstrated the coexistence of silicate melt, salt melt/brine, vapour, and emulsions of these, during crystallisation of the granite magma, possibly at the waning stage. Microthermometric experiments, in conjunction with PIXE and other analytical techniques, disclosed extreme heterogeneity in the composition of the non-silicate phases, even in brine globules within the same silicate melt inclusion. We suggest that the observed variability is a consequence of strong chemical heterogeneity in the residual silicate-salt melt system on a local scale, owing to crystallisation, immiscibility and failure of individual phases to re-equilibrate. The possible evolution of non-silicate volatile magmatic phases into more typical "hydrothermal" hypersaline solutions was examined using inclusions in quartz from associated miarolitic cavities.

Keywords: Melt inclusion; Granite; Immiscibility; Fluid; Brine; PIXE

1. Introduction

Volatiles dissolved in aluminosilicate magmas (dominantly H₂O, CO₂, S and Cl) play a fundamental role in magmatic evolution across the compositional spectrum from komatiite to granite, and in the formation of magma related hydrothermal systems. Volatiles have a major control on rheological properties of magmas, crystallisation temperature and sequence. When the volatiles are exsolved from parental magmas, due to the processes of *unmixing* or *immiscibility*, and form a separate volatile-rich phase (fluid), a major change in the element partitioning occurs. It is believed that volatile phases exsolved during the crystallisation of magmas carry significant amounts of metallic elements (e.g., Candela and Holland, 1984; Shinohara, 1994; Webster, 1997; Kamenetsky et al., 1999). If dense, these phases may precipitate in situ (e.g., Fe-Cu-Ni-PGE sulphides); if buoyant, they may enter hydrothermal systems and be responsible for formation of certain types of ore deposits (e.g., W-Sn skarns and greisens, pegmatites, and Cu-Mo-Au porphyries).

For many magmas, the evolution of immiscible volatile phases takes place in the poorly characterised interval between the orthomagmatic and the hydrothermal regimes of magmatic cooling and crystallisation. This interval near the magmatic solidus, referred to as *transitional* with respect to processes and compositions (e.g., Burnham and Ohmoto, 1980), has proved extremely difficult to document and understand, largely because of the transient, reactive nature of volatile phases released during magmatic cooling. Also, igneous petrology has long been segregated from studies of hydrothermal systems; although some overlap always existed in the form of experimental and theoretical studies (e.g., Koster van Groos and Wyllie, 1969; Candela, 1989; Shinohara et al., 1989; Candela, 1991; Cline and Bodnar, 1991; Webster, 1992; Shinohara, 1994; Webster, 1997).

In the case of solidifying felsic magmas, volatile phases are largely exsolved in a temperature window between 850°C and >500°C, which is still remaining virtually “opaque” to geological research. Apart from the problem of how transitional volatile phases eventually acquire the properties of the ore-forming solutions, there are immediate questions about physical state and chemical compositions of late magmatic fluids. These can be answered by employing melt and fluid inclusion research on samples representative of magmatic-hydrothermal transition (see reviews in Roedder, 1984; Roedder, 1992; De Vivo and Frezzotti, 1994; Lowenstern, 1995;

Frezzotti, 2001). Despite the contention that "... interpretation of the inclusion record is commonly ambiguous and difficult, particularly that stage between silicate melt and the hydrous saline melts and aqueous solutions..." (Roedder, 1992), in recent years melt and fluid inclusion approach has become more attractive and gained strength from the use of modern microbeam techniques (e.g., references in Kamenetsky et al., 2002b). In this presentation we aimed the study of inclusions in phenocrystic and miarolitic quartz from the Omsukchan granite (NE Russia) to describe an occurrence of immiscibility between the silicate melt and late magmatic volatile phases, characterise their composition from microthermometric experiments and in situ analysis, and attempt to constrain the physical nature and chemical signature of magmatic derived fluids and their high temperature evolution.

2. Omsukchan granite intrusive

Porphyritic leucogranites of the Cretaceous Omsukchan massif (Chukotka Peninsula, NE Russia) are located within the Okhotsko-Chukotsky volcanic belt and host economic tin deposits. The depth of intrusion defined from the thickness of overlapping volcanisedimentary host rocks was estimated as 0.7-1.5 km (Sokolov, 1980). The intrusion is a flat top cupola with shallow-dipping flanks, containing three concentric zones of texturally different granites. Mineralisation is localised in the roof of the cupola, within linear zones of metasomatic Na-Fe alteration and quartz-tourmaline veins (Sokolov, 1980). Abundant miarolitic cavities lined with large quartz crystals (to 10 cm) are commonly associated with altered and mineralised granites.

Homogenisation temperatures and salinities of melt and fluid inclusion in quartz and fluorite from granites, miarolitic cavities and metasomatic ore bodies have been previously reported (Naumov and Sokolov, 1981; Kamenetsky et al., 2002b). Temperatures, salinities and compositions were shown to be extremely diverse. To complement the data on inclusions in miarolitic quartz (Kamenetsky et al., 2002b), the emphasis of this study is on a suite of inclusions in quartz phenocrysts.

3. Inclusions in quartz phenocrysts

3.1. Occurrence of inclusions

Coexisting magmatic inclusions in quartz phenocrysts, unaffected by hydrothermal alteration, are aligned along growth planes and syn-crystallisation fractures. There are three main types of inclusions:

(1) Euhedral crystals of feldspar, mica, sphene, magnetite, apatite, zircon etc (i.e., minerals cotectic with quartz and accidentally trapped);

(2) Ovoid to spherical inclusions of magmatic volatile-rich phase that is characterised (at room temperature) by variable proportions of aqueous vapour, liquid and euhedral crystals. The endmembers within this type are represented by essentially vapour (>90 vol%, Fig. 1a) and essentially crystalline (>70 vol%, Figs. 1b,c) inclusions. Optical examination revealed at least nine different mineral species (halite and hematite are tentatively identified) present among solids, and often within a single inclusion. In highly crystalline volatile-rich inclusions (hereafter, brine or salt melt) liquid exists interstitially, and a vapour bubble is deformed.

(3) Variable in shape and size birefringent microcrystalline aggregates of presumably silicate minerals with a misshapen vapour phases filling the spaces between solids, and rare opaque phases (Figs. 1d,e), interpreted to be inclusions of crystallised silicate melt. These are commonly surrounded by radiating fractures and halos of tiny vapour-rich aqueous bubbles, suggesting the melt originally had a high volatile content, which was released during post-entrapment crystallisation and decrepitation of these inclusions (Davidson and Kamenetsky, 2001).

As all types of inclusions occur together it is likely that some consist of heterogeneously trapped combinations of cotectic crystals, silicate melt and aqueous fluids. An example of such composite inclusion (crystallised silicate melt and halite-bearing fluid phase) is shown in Fig. 1f.

3.2. Post-heating occurrence of inclusions

Bulk heating experiments involve heating a quantity of inclusion-bearing quartz phenocrysts in a 1 atm furnace (850-950°C, 20-50 hours) and consequent air quenching. One objective was to identify those inclusions that were trapped at magmatic temperatures and remained uncompromised (unfractured and unsealed). Bulk heating also revealed inclusions that survived temperature-related volume change of host quartz (e.g., α - β quartz transition at ~573°C), and thus were suitable for further microthermometric work. The second aim was to convert crystalline

silicate masses within melt inclusions into homogeneous glass. This, in the case of granitic magmas, usually requires long heating times, and eventually makes heterogeneously trapped phases (e.g., fluid, if present) available for observation and analysis. And finally, immiscible brine and fluid phases, if trapped heterogeneously with silicate melt, can be liberated and further enhanced into larger formations (globules or bubbles) in order to successfully analyse them using microbeam techniques.

The post-heating examination of the Omsukchan granite quartz phenocrysts reveals the presence of small (<10 μm) bubble-free silicate glass inclusions and larger silicate glass inclusions with one or several low-density vapour bubbles and sometimes unmelted silicate and opaque phases (Fig. 2a). Commonly, the bubbles are located in “swellings” on the otherwise rounded surfaces of such inclusions, and this feature is probably due to differential melting and crystallisation within inclusions during heating and “sheltering” by the bubble of the inclusion wall against crystallisation. The majority of silicate glass inclusions contain spherical globules (Figs. 2c-g) composed of microcrystalline material with variable proportions of spherical to deformed dark phase (vapour). The number (from 1-2 to 10's) and sizes (<1 – 15 μm) of globules vary significantly. Commonly in larger inclusions these crystal- and bearing-bearing globules form an emulsion (globules are suspended in the glass “matrix”), and characteristically they are present embedded in the inclusion walls (Figs. 2c,g and 4b) and often without silicate glass, in the host quartz (Figs. 2d,g, and 3). Rarely, silicate melt inclusions contain a single, relatively small (~3.5 vol%) globule, as in the two coexisting inclusions shown in Fig. 2e. Other inclusions show a globule (similar to those described above) rimmed by relatively small volume of the silicate glass (Fig. 2b). And finally, inclusions that contained brine, pre-heating, are present as negative-crystal shaped inclusions of crystalline material and deformed bearing bubble (Figs. 2h,i).

3.3. Heating stage experiments with melt and brine inclusions

Heating stage experiments were performed to observe, document (e.g., photographing or video recording) and register temperature of phase transformations (such as melting, homogenisation, crystallisation etc) inside individual inclusions. A

Linkam TS1500 heating stage with TMS 94 temperature control unit and an Olympus BX51 microscope with a DP11 digital camera were used. Heating/cooling rates (from 5 to 100°C/min) were varied when required for more efficient documentation. All grains were first bulk heated in the furnace and quenched (see above). Heating stage studies targeted spherical globules inside clear silicate glass, and also those trapped in quartz with no silicate glass around them.

Examples of experiments with spherical globules present in the silicate glass are given in Fig. 4. Several subsequent heating runs for each inclusion showed consistent results. Although, the behaviour of all globules studied was very similar, the temperatures of phase transformations in different samples varied. The following general observations were made for spherical globules during heating (Fig. 4):

(1) They remain constant in size, do not change their position with respect to silicate phase (melt), and do not mix with silicate melt even at temperatures exceeding liquidus (900-1100°C);

(2) The first visible changes occur at 120-190°C. These include movement and re-arrangement of solids and vapour bubble, enhancement of phase boundaries, and the appearance of new phases;

(3) The vapour phase acquires spherical shape at 250-350°C, and the boundaries between solid phases become invisible;

(4) In some inclusions vapour bubbles disappear at 420-510°C, and then renucleate at ~580°C. In other globules there is no large change in the bubble size until the quartz transition temperature (~573°C), in some cases bubbles increase significantly, up to almost the size of the globule;

(5) Melting of solid phase(s) becomes noticeable at >600°C and is seen as appearance of liquid (melt) surrounding a cubic crystal;

(6) Heating above 630°C results in rapid decrease of the bubble and crystal(s), with complete melting occurring at 670-735°C. At these temperatures the liquid in globules has lower refractive index and low viscosity than silicate melt;

(7) Vapour bubbles shrink and move randomly and rapidly, until final disappearance at 790-935°C;

(8) At the temperature of bubble homogenisation an elongate prismatic brownish crystal, possibly formed as a result of reaction between salt and silicate melt, may remain on the globule-silicate melt interface (Fig. 4a).

It is worth noting that, irrespective of their size, the above phase transformations take place almost simultaneously in all entrapped globules within an individual silicate melt inclusion. This may suggest similar compositions and entrapment conditions. The observed differences between globules in different inclusions can be tentatively attributed to the effects of internal pressure.

A record of typical heating experiment with a glass-free, spherical inclusion embedded in quartz is shown in Fig. 5. In this case, a clear cubic crystal melted at 630°C, and the melting of a brownish elongate crystal and homogenisation into liquid occurred at 890°C. The melting and homogenisation temperatures can vary by 100-150°C for several tens inclusions studied, even for those within same quartz phenocryst.

4. Inclusions in miarolitic quartz

Miarolitic cavities within the Omsukchan granite are filled with euhedral quartz crystals that contain numerous populations of inclusions, mainly aligned along syn-crystallisation fractures and more rarely along the growth planes. The majority of inclusions are crystallised saline aqueous solutions (brines), with some vapour-rich inclusions. Silicate melt inclusions have not been recorded. The earlier studies of brine inclusions in the Omsukchan miarolitic quartz (Naumov and Sokolov, 1981; Kamenetsky et al., 2002b) recorded their large size (to 300 μm), high homogenisation temperatures (to 840°C), and diverse and often metal-enriched chemical compositions. We emphasise the significance of miarolitic brine inclusions for this study is in that they probably represent a magmatic volatile phase that separated from the residual melt at the brink of its solidification. Therefore, they can compliment the results for the fluids exsolved earlier, and trapped as brine globules in phenocrystic quartz. Moreover, the exceptionally large size of miarolitic brine inclusions makes it possible to better document assemblage of daughter minerals, and phase transformation during heating.

4.1. Inclusion paragenesis

The fact that multiphase brine inclusions belong to the crosscutting trapping planes, and thus to the different trapping events (Roedder, 1979), calls for

development of criteria for recognition of “assemblages” or “texturally coeval” groups of inclusions. In the following two examples we present descriptions and measurements of phase proportions for inclusions that coexist within a section of the trapping plane (between cross-cutting fractures, Figs. 6a,d), and thus are considered to be trapped simultaneously as a homogeneous solution.

The first example concerns a simple case of the four-phase (liquid + vapour bubble + cubic crystal (halite?) + opaque crystal) inclusions. Despite significantly variable size (7-180 μm) thirty-two measured inclusions in this plane (Figs. 6a-c) have nearly constant volumes of vapour bubble and cubic mineral relative to the volume of inclusion ($0.127\pm 10\%$ and $0.043\pm 15\%$, respectively). In the second example (Figs. 6d-f) thirty-four multiphase (liquid + vapour bubble + 3 to 6 crystals) inclusions of different size (13-120 μm) show similar and constant bubble/inclusion volume ratios ($0.127\pm 12\%$) that in this case seem to be characteristic of homogeneous trapping of aqueous saline fluids. Daughter minerals are typically euhedral, although crystalline aggregates are also present, and show a variety of crystal forms and optical properties, including colour, relief and birefringence (Kamenetsky et al., 2002b). Different appearance of the assemblages of daughter crystals as well as their different compositions (confirmed by laser Raman spectroscopy, Kamenetsky et al., 2002b), is likely to reflect divergent post-entrapment crystallisation paths for individual inclusions. Moreover, even at room temperature the content of multiphase inclusions is metastable and prone to spontaneous recrystallisation followed by changes in a number, shape and volume ratios of phases (Fig. 7, see also Lowenstern, 1994). This makes it problematic to distinguish between multiphase inclusions belonging to different trapping events.

4.2. Heating stage experiments with multiphase inclusions

Due to their small size, the behaviour of spherical brine globules in quartz phenocrysts during heating is not fully discernible (Fig. 5). However, as the formation of miarolitic quartz immediately postdated quartz phenocrysts, the microthermometry of larger miarolitic multiphase inclusions can be cautiously used to characterise earlier granitic brines.

As expected from the variable appearance of inclusions at room temperature (e.g., Figs. 6e,f), the melting behaviour even in those that seemingly belong to the same trapping plane, is also distinct. The summary of general features is as follows (Fig. 8). Most crystals in the multiphase inclusions dissolve below 300-350°C. The first crystal usually melts at 55-60°C, the second – at 130-150°C, the third and fourth disappear at 250-300°C. The large isotropic phase with low relief and cubic shape (presumably halite) melts at 300-625°C (554°C in the example in Fig. 8a). Breakdown of some birefringent phases at $T \sim 400^\circ\text{C}$ results in the formation of dispersed dark particles (photo at 390°C in Fig. 8c) that coalesce into semi-transparent aggregate of high relief prismatic crystals (photo at 554°C in Fig. 8a and photo at 398°C in Fig. 8c). These newly formed phase(s) starts to melt at 620-630°C, but usually persists to much higher temperatures ($\sim 800^\circ\text{C}$). Bubbles dissolve at variable temperatures from 380 to 840°C. In the example shown (Fig. 8a) a bubble first disappeared at 480°C, then re-appeared at 593°C (just above the temperature of quartz transition), and disappeared again at 618°C. Relatively large inclusions ($>50 \mu\text{m}$) often decrepitate at temperatures below complete homogenisation (photo at 650°C in Fig. 8b; note that an aggregate of crystals is still present) with the inclusion content expelled at the grain surface through a fracture. Quenching of the inclusions results in formation of aggregates of prismatic crystals at $<250^\circ\text{C}$ that almost fill the inclusion (Fig. 8d), whereas slow cooling produces a large cubic crystal (halite?) at $<420^\circ\text{C}$, followed by spontaneous crystallisation of prismatic birefringent crystals at $<200^\circ\text{C}$ (Fig. 8e).

5. Composition of globules and brine inclusions

Low temperatures of the first and final melting in the globular inclusions in quartz phenocrysts and multiphase inclusions in miarolitic quartz, the low viscosity of their content inferred from heating runs (Figs. 4, 5 and 8), and the presence of aqueous bearing and liquid are suggestive of essentially non-silicate, volatile-rich compositions for these inclusions. Furthermore, the presence of cubic daughter crystals indicates a significant chloride component. Due to their low viscosity chloride-rich aqueous fluids and melts (as well as other non-silicate melts) are not quenchable into homogeneous phase (glass). Consequently, at room temperatures the studied inclusions contain aggregates of crystals, a large volume vapour bubble(s) and interstitial aqueous solution (e.g., Figs. 2h,i and 8d,e). There are many difficulties in

calculating bulk inclusion composition based on the compositions of individual phases and their mass proportions, most immediately, loss of aqueous and gaseous components when such inclusions are exposed. Additionally, the solid content of inclusions is hygroscopic. The analytical methods applied in this case (scanning electron and nuclear microscopy) were partly successful in detecting some elements present and their abundances, although quantitative analysis of fluid and brine inclusions, especially their volatile components, is still under development.

Commonly, inclusions close to the surface of host grains decrepitate during heating and emptied their contents on to the surface (Figs. 8b and 9). We used a scanning electron microscope (Electroskan ESEM2020 equipped with a Link Pentafet SATW energy dispersive X-ray detector, University of Tasmania) to estimate the composition of crystalline and amorphous phases deposited on the surface of host quartz as a result of evaporation of the ejecta from decrepitated (bursting) non-silicate inclusions (Fig. 9). Although the ejecta is heterogeneous in phase and chemical composition, it is typically characterised by the dominance of Na, S, Fe, Ca, and Mn. Potassium and Zn are minor components, whereas Cl and Cu are completely missing from the X-ray spectra (Fig. 9). Because some elements are more volatile than others (Cl and Cu in this case) the quantification of the bulk inclusion composition using this method is not possible.

The distribution and abundance of elements heavier than Cl within unopened inclusions were studied by the proton-induced X-ray emission method (PIXE) using the CSIRO-GEMOC Nuclear Microprobe (e.g., Ryan et al., 2001a; Ryan et al., 2001b). The PIXE data on the multiphase inclusions in miarolitic quartz, reported earlier (Kamenetsky et al., 2002b), have demonstrated significant concentrations of Cl (up to 50 wt%), K, Fe and Pb (up to 20 wt%), Ca (up to 6 wt%), Mn and Zn (up to 3 wt%), and Cu, As, Br, Rb, Sr and Sn (up to 1000-3000 ppm). The concentrations of individual elements were 20-90 times higher in the high-salinity (50 wt% Cl) crystal-rich inclusions compared to the low-salinity (5 wt% Cl) liquid-rich type. Given the highly variable element ratios in these inclusions a conclusion was made that the granite-derived aqueous saline fluids (brines), if represented by quartz-hosted inclusions, were extremely heterogeneous in composition at the time of quartz growth (Kamenetsky et al., 2002b). These results are complemented in this study by the PIXE element images and concentrations obtained from the spherical brine globules in quartz phenocrysts (Fig. 10 and Table 1). It appears that both types of spherical

globules (i.e. trapped with silicate melt and included in quartz) have the same geochemical signature. They are enriched in Cl (and probably Na, not analysed by PIXE), K, Fe, Cu, and to a lesser extent in Ca, Mn, Zn and Pb. Even elements with concentrations of several hundred ppm (Se, As, and Br) are regarded here as highly enriched relative to average crustal abundance, and granitic magmas, in particular.

The partitioning of a number of analysed elements between co-trapped silicate melt and globules is shown in Fig. 10. The intensity of secondary X-rays for a given element depends on the concentration, density, and depth from the surface. For example, in Fig. 10a the signal from Cl (a relatively light element with low energy X-rays) was strongly attenuated for a deep-seated globule, whereas the intensities of a Cu signal for this, and the shallow globule are comparable. Attenuation of low energy X-rays and uncertainties in the inclusion geometry, depth and density increase the error in the calculated concentrations. However, these uncertainties can be reduced if the ratios of elements of similar mass (and with similar X-ray energy), such as Fe and Mn, Cu and Zn, As and Se, etc are used. The reliability of element ratios, analysed by PIXE, is independently confirmed by the laser ablation ICPMS analyses of fluid inclusions (L. Danyushevsky, pers. comm.).

A number of the element ratios for two globules enclosed within a single silicate melt inclusion (Fig. 10a) are noticeably different (Table 1). Although there exists broad chemical similarity for pairs of spatially associated brine globules in the same quartz phenocryst (Fig. 10c, Table 1, sample DK1-8, pairs of inclusions B - C, and D - E as shown in Fig. 3), the average element ratios for each pair of inclusions are significantly different. Furthermore, the comparison between all analysed brine globules in quartz phenocrysts show considerable variability (>25%) in many element ratios (Table 1).

Tin was detected in brine inclusions in miarolitic quartz in relatively high amounts (up to 1700 ppm). Tin resides in minute crystalline phases that are possibly not cassiterite, as other elements (Cl ± As ± Mn ± Ca) are also present (Fig. 11 and figure 3D from Kamenetsky et al., 2002b).

6. Discussion and conclusions

6.1. Evidence for immiscibility

Since the pioneering work on the immiscibility between silicate melts and dense saline fluids in the Ascension Island granites (Roedder and Coombs, 1967), only a few studies of intrusive samples have elaborated on the problem of exsolution of brines/ salt melts from, and coexistence with, deep-seated felsic magmas. Specifically, the unambiguous records of the silicate and salt melts co-trapping in a single composite inclusions provided by the studies of the Mariktikan granite intrusion, Buryatia, Russia (Reyf and Bazheyev, 1977), Monte Genis leucogranite, Sardinia, Italy (Frezzotti, 1992) and felsic xenoliths from Ventotene Island, Italy (De Vivo et al., 1995). The reasons for apparent lack of more widespread evidence for the silicate melt – brine (salt melt) immiscibility have been previously discussed (Roedder, 1984; Roedder, 1992), and we concur that the presence of dispersed, essentially non-silicate phases in the silicate magma is, to certain extent, disadvantageous for the trapping of silicate melt inclusions. However, we consider the “human factor” more important, for many years these inclusions have not been recognised in quartz from intrusive rocks and “typically hydrothermal” quartz veins. Given the results of this study, we suggest that the application of heating and quenching to several hundred quartz grains should be routinely used to identify the presence of the silicate glass (with or without shrinkage bubbles and heterogeneously trapped volatile-rich phases), otherwise obscured by post-entrapment processes. In the case of quartz phenocrysts from the Omsukchan granite this technique revealed a clear case of immiscibility with at least two liquids simultaneously present during quartz growth, with a meniscus between them. This is best demonstrated by the emulsion textures of many inclusions, in which multiple brine globules (i.e., the dispersed phase) are randomly distributed within silicate glass (Figs. 2c-g) that at the time of trapping was a continuous melt phase from which quartz phenocrysts crystallised. The size of the trapped continuous melt phase is random, largely depending on the size of the growth irregularities on the surface of the host mineral (Roedder, 1984), whereas the size of the trapped dispersed phase is representative of the actual size of emulsion (Reyf, 1984). In other words, the size of the salt melt globules present in the silicate melt inclusions (<1 – 15 μm ; Figs. 2c-g) is characteristic of the size of natural dispersed phase at the time of immiscibility and before the coalescence.

Although heterogeneous trapping of immiscible volatile-rich (brine) and volatile-poor (silicate melt) phases, as shown by the emulsion textures, is most

common in the case of the Omsukchan melt inclusions, some inclusions may still represent homogeneous trapping of either silicate or salt melt “endmembers” (Figs. 2a,h,i and 3). As the number of brine inclusions with no traces of the continuous phase exceeds the number of homogeneous silicate glass inclusions by several orders of magnitude, we conclude that the trapping of the discontinuous brine phase is preferred, possibly because of better wetting properties (Roedder, 1984). Endmember phases present in variable proportions within a single two-phase inclusions (Figs. 2b-g) further advocate heterogeneous trapping, especially when the amount of brine is relatively large (>20%). In cases with only a small proportion of brine (Fig. 2e), heterogeneous trapping is less certain because in situ immiscibility is at least possible.

The temperatures of phase transformations and homogenisation within quartz-hosted inclusions recorded in this study (Figs. 4, 5 and 8; see also Naumov and Sokolov, 1981), although important in generally supporting the presence of essentially non-silicate components in the granitic magma at >650-700°C, are not applicable to direct quantification of crystallisation temperatures. This is due largely to several unknown parameters controlling internal pressure, and thus experimental temperatures. The most important are the compressibility of silicate and salt melts (e.g., Roedder and Bodnar, 1980) and their effect on each other in the case of heterogeneously trapped inclusions, the effects of α - β quartz transition and related microfracturing.

6.2. Compositions of immiscible non-silicate phases

Based on the phase composition of inclusions in quartz phenocrysts in the Omsukchan granite, the crystallising system consisted of at least silicate melt, saline fluid (brine) and low-density vapour (Figs. 1-3). We interpreted these phases as formed due to immiscibility of the precursor granitic magma that happened before or during quartz crystallisation. As in many other studies our data is not sufficient to resolve whether there was an immiscible fluid of moderate salinity from which vapour and brine formed (Burnham, 1979), or whether vapour and brine were exsolved directly from the magma (e.g., Cline and Bodnar, 1994; Shinohara, 1994; Bodnar, 1995). What remains certain is that two non-silicate, volatile-rich phases (i.e., brine and vapour) have been coexisting with each other and with the silicate melt, possibly over significant temperature interval. This provides the most compelling support for

the idea that "...granite is only an intermediate stage on a long evolutionary line of melt to 'fluid' compositions. Crystallisation of volatile-bearing granitic magmas can result in a wide range of fluid compositions, at various P, T, and degrees of crystallisation" (Roedder, 1984).

In our study a wide range of "fluid" compositions, as sampled by brine globules in phenocrystic quartz, is also recorded, despite a limited number of analyses (Table 1). The globules are all metal-rich chloride complexes (Fig. 10, Table 1), although the element abundances and ratios vary significantly, even for co-trapped brine globules (Figs. 4a and 10a). There may be numerous reasons for this, e.g., exsolution of globules (now co-trapped) from different magma batches. But the most immediate is an extreme fractionation of most elements between immiscible silicate melt and non-silicate "fluids" and the disequilibrium character of exsolution. The latter means that if immiscibility is a continuous process, the components of dispersed phase must have varying composition because of relatively slow diffusion rates. Here we regard disequilibrium as a scale-dependent phenomenon, especially in the residual granitic system, where crystallisation and immiscibility drive chemical fractionation to the extreme. In practice, two adjacent immiscible brine globules formed consecutively, sample melts of significantly different compositions due to progressive depletion in elements compatible with a brine, by the earlier nucleated globule. But as diffusion rates vary for different elements, even the element ratios in adjacent, consecutively formed globules may be expected to fluctuate (Fig. 10a, Table 1).

Although it is expected that coalescence of immiscible volatile-rich phases may reduce chemical variability, however, we anticipate that different batches of magmatic "fluids" have different histories in transit to miarolitic cavities (in effect fluid chambers) where they accumulate. If this is the case, discrete batches of fluids, following a rock-dominated chemical path (e.g., Heinrich, 1990), are prone to modifications caused by interaction with a granite (solid rocks and residual magma pockets). Moreover, implied unmixing of the fluids due to boiling or effervescence, cooling and related crystallisation, and mixing of fluid batches with each other and possibly external fluids can be responsible for even greater fluid variability, and the change of primary magmatic geochemical signature, as observed in inclusions trapped by miarolitic quartz (Table 1; see also Kamenetsky et al., 2002b). Although some element ratios remain relatively constant for brine inclusions in earlier phenocrystic quartz, and later miarolitic quartz, the concentration of Cu and proportion of Cu to

other metals decrease dramatically in miarolitic brines (from wt% to hundreds of ppm, Table 1; Kamenetsky et al., 2002b). Such discontinuous evolution of the fluid and the absence of Cu mineralisation in the Omsukchan granite pose the question whether magmatic fluids in passage to miarolitic cavities experienced separation and loss of vapour-rich phase in which Cu strongly partitions (e.g., Lowenstern et al., 1991; Heinrich et al., 1992; Lowenstern, 1993; Heinrich et al., 1999; Kamenetsky et al., 2002a)? Other questions also arise, one is the fate of other economic metals (e.g., Pb and Zn) that are present in significant amount in brine inclusions but did not form mineralisation. Similarly, despite strong influx of iron during metasomatism of the Omsukchan granite (Sokolov, 1980), Fe sulphides are virtually absent, implying the lack of sulphur in the system.

In conclusion we emphasise that “...formation and evolution of the many different types of immiscible fluids is complex ...but (interpretations) may be of great value in understanding magmatic processes and the resultant ore deposits.” (Roedder, 1992), and thus the research into evolution of truly magmatic fluids to hydrothermal solutions is timely important and will require an international multidisciplinary effort.

Acknowledgements

We are grateful to David Steele for help with the electron microscopy. This paper has benefited from discussions with R. Bodnar, C. Heinrich, J. Lowenstern, T. Sushchevskaya, and J. Webster. The research was supported by the Australian Research Fellowship and the Centre for Ore Deposit Research (University of Tasmania) grants to V.S. Kamenetsky and Russian Foundation for Basic Research grant 01-05-64109 to V.B. Naumov.

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Figure captions

Fig. 1. Magmatic inclusions in quartz phenocrysts. (a) coexisting vapour-rich (dark bubbles) and multiphase brine inclusions; (b, c) multiphase, crystal-rich brine inclusions; (d-f) silicate melt inclusions consisting of birefringent material of different crystallinity, opaques, vapour phases (dark) and sometimes non-silicate minerals. Note cubic crystal, possibly halite, in the lower right corner of the inclusion in (f). Scale bars are 20 μm .

Fig. 2. Magmatic inclusions in quartz phenocrysts after bulk heating and quenching (see text for details), except in (g) photographed at $\sim 850^\circ\text{C}$. (a) silicate glass with shrinkage bubble; (b) composite inclusions consisting of a spherical brine globule and a relatively small amount of silicate glass; (c-g) variable proportions of coexisting brine globules and silicate glass in individual inclusions. Note emulsion texture in (c, f, and g), and the presence of similar brine globules in the host quartz around these inclusions in (d and g). (h, i) microcrystalline structure and deformed vapour phase (dark) of rapidly quenched brine inclusions. Scale bars are 10 μm . Compositions of globules in coexisting inclusions in (e) are in the Table 1 (# 3 and #4); PIXE element maps for DK1-7A are shown in Fig. 10b.

Fig. 3. Spherical and ovoid inclusions of brine in a single quartz phenocryst (positions are circled). Inclusion size is $\sim 10\text{-}12$ μm . Compositions of inclusions are in the Table 1 (# 5-8); PIXE element maps for DK1-8E are shown in Fig. 10c.

Fig. 4. Phase transformations in spherical brine globules, co-trapped with silicate melt, during heating stage experiments. Scale bars are 15 μm . Compositions of brine globules in the inclusion in (a) are in the Table 1 (# 1 and #2); their PIXE element maps are shown in Fig. 10a.

Fig. 5. Phase transformations in the spherical brine globule, entrapped in quartz phenocryst (no silicate glass present), during a heating stage experiment. Scale bar is 15 μm .

Fig. 6. Multiphase inclusions of aqueous saline fluid within trapping planes in miarolitic quartz. Crosscutting planes are shown by arrows in (a, d). (b, c) and (e, f) representative coexisting inclusions from the trapping planes shown in (a) and (c), respectively (in labelled circles). Similar inclusions were reported by Kamenetsky et al., 2002.

Fig. 7. Metastable nature of multiphase brine inclusions in miarolitic quartz, shown by spontaneous recrystallisation of daughter crystals at room temperature. Photographs of inclusions are taken: (b) 270 days after (a), and (d) 188 days after (c). Similar inclusions were reported by Kamenetsky et al., 2002.

Fig. 8. Phase transformations in multiphase brine globules during heating stage experiments in miarolitic quartz. (b) decrepitated inclusion shown in (a). (d, e) Rapidly ($\sim 100^\circ\text{C}/\text{min}$) and slowly ($5^\circ\text{C}/\text{min}$) cooled inclusion shown in (c). Inclusion sizes are ~ 60 μm . Similar inclusions were reported by Kamenetsky et al., 2002.

Fig. 9. Scanning electron photomicrographs and representative EDS spectrum of polymineral aggregates crystallised on the surface of miarolitic quartz, from ejected contents of decrepitated during experimental heating brine inclusions. Elevated abundances of Si in the spectrum are from host quartz.

Fig. 10. Optical images and PIXE element maps of heated inclusions of silicate glass and brine (a, b) and unheated brine inclusion (c) in quartz phenocrysts. Mapping was performed using a 0.3–0.7 nA beam of 3 MeV protons focused into an $\sim 2 \mu\text{m}$ beam spot with a CSIRO-GEMOC nuclear microprobe (Ryan et al., 2001a, 2001b). Legend shown in lower-right image of (c) indicates relative intensity (and, thus, concentration). Colour scale in each element image is normalised to its own maximum. Outlines on element maps mark boundaries of inclusions and brine globules. Corresponding compositions are given in Table 1: #1 and #2 for shallow and deeper globules, respectively upper and lower globules in (a); #3 for a globule in (b) and #8 for inclusion in (c).

Fig. 11. Scanning electron photomicrograph of a broken surface of miarolitic quartz and an EDS spectrum of the crystal in the cavity of the exposed (presumably) brine inclusion.

Table 1. Compositions and selected element ratios of individual spherical brine globules in quartz phenocrysts, and average composition of multiphase saline fluid inclusions in miarolitic quartz, analysed by nuclear microprobe (PIXE).

	1	2	3	4	5	6	7	8	9	10
Cl (wt%)	54	15	43	53	7	12	24	12	25	17
K (wt%)	nq	nq	nq	nq	1.6	2.9	5.0	2.9	5.4	5.0
Ca (wt%)	0.53	0.78	2.68	0.90	0.90	1.88	1.51	0.88	1.3	1.4
Mn (wt%)	0.71	0.73	1.17	1.05	0.76	1.35	2.06	1.24	1.0	0.7
Fe (wt%)	nq	nq	nq	nq	4.04	7.38	19.32	7.89	5.4	4.1
Cu (wt%)	3.71	6.02	15.44	22.2	2.47	3.61	2.90	1.31	0.024	0.020
Zn (wt%)	0.49	0.48	0.43	0.47	0.48	0.82	1.34	0.80	0.50	0.36
As (ppm)	1216	467	4298	6552	1155	2026	281	161	226	276
Se (ppm)	1201	301	1426	3834	<46	<98	<99	63	bdl	
Br (ppm)	1079	1454	900	800	590	1040	1301	786	472	329
Rb (ppm)	2046	<667	3483	3622	510	1773	3264	1184	807	713
Sr (ppm)	970	<728	<463	3286	399	590	869	427	253	144
Pb (ppm)	4677	3407	1727	2301	2055	3720	7107	4777	2415	1842
Fe/Cu					1.64	2.05	6.66	6.00	263	158
Mn/Zn	1.46	1.53	2.73	2.23	1.59	1.65	1.54	1.55	2.1	0.6
Zn/Pb	1.04	1.41	2.47	2.04	2.33	2.20	1.88	1.67	2.3	1.2
Cu/Zn	7.59	12.5	36.1	47.3	5.16	4.41	2.17	1.65	0.07	0.10
K/Ca					1.77	1.56	3.33	3.33	5.7	4.4
As/Br	1.13	0.32	4.78	8.19	1.96	1.95	0.22	0.20	0.52	0.42
Pb/Br	4.33	2.34	1.92	2.88	3.48	3.58	5.46	6.08	5.5	3.2
Mn/Br	6.59	5.04	12.9	13.1	12.9	13.0	15.8	15.7	23	9
Cu/As	30.5	128.9	35.9	33.9	21.4	17.8	103.3	81.6	2.1	2.1

(1-4) - spherical brine globules co-trapped with silicate melt: (1) and (2) – shallow and deeper globules, respectively, sample DK1-5 (Figs. 4a and 10a); (3) and (4) – globules in coexisting silicate melt inclusions, labelled DK1-7A and DK1-7B, respectively, in Fig. 2e (see Fig. 10b for PIXE maps of DK1-7A). (5-8) - spherical brine globules hosted in a single quartz phenocryst, labelled DK1-8 B, C, D, E in Fig. 3 (see Fig. 10b for PIXE maps of DK1-8E). (9, 10) – average composition and standard deviation for twenty-nine inclusions in miarolitic quartz (Kamenetsky et al., 2002).

The concentrations were calculated by assuming a bulk density of 1.5 g/cm³, except (3) and (4) for which a bulk density of 2.0 g/cm³ was used. PIXE analytical parameters are given in the caption to Fig. 10.

nq – not quantified due to uncertainties caused by the presence of these elements in the host silicate glass; bdl – below detection limit.