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Be-daughter minerals in fluid and melt inclusions: implications for the enrichment of Be in granite–pegmatite systems

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Abstract The study of re-homogenized melt inclusions in the same growth planes of quartz of pegmatites genetically linked to the Variscan granite of the Ehrenfriedersdorf complex, Erzgebirge, Germany, by ion microprobe analyses has determined high concentrations of Be, up to 10,000 ppm, in one type of melt inclusion, as well as moderate concentrations in the 100 ppm range in a second type of melt inclusion. Generally, the high Be concentrations are associated with the H₂O- and other volatile-rich type-B melt inclusions, and the lower Be concentration levels are connected to H₂O-poor type-A melt inclusions. Both inclusion types, representing conjugate melt pairs, are formed by a liquid-liquid immiscibility separation process. This extremely strong and very systematic scattering in Be provides insights into the origin of Be concentration and transport mechanisms in pegmatite-forming melts. In this contribution, we present more than 250 new analytical data and show with ion microprobe and fs-LA-ICPMS studies on quenched glasses, as well as with confocal Raman spectroscopy of daughter minerals in unheated melt inclusions, that the concentrations of Be may achieve such extreme levels during melt-melt immiscibility of H₂O-, B-,

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F-, P-, \pm Li-enriched pegmatite-forming magmas. Starting from host granite with about 10 ppm Be, melt inclusions with 10,000 ppm Be correspond to enrichment by a factor of over 1,000. This strong enrichment of Be is the result of processes of fractional crystallization and further enrichment in melt patches of pegmatite bodies due to melt–melt immiscibility at fluid saturation. We also draw additional conclusions regarding the speciation of Be in pegmatiteforming melt systems from investigation of the Be-bearing daughter mineral phases in the most H₂O-rich melt inclusions. In the case of evolved volatile and H₂O-rich pegmatite systems, B, P, and carbonates are important for the enrichment and formation of stable Be complexes.

Keywords Be in pegmatite-forming melts · SIMS · Raman spectroscopy · Melt inclusion · Immiscibility

Introduction

The geochemical behavior of beryllium in magmas is poorly known, especially because of difficulties associated with getting representative, small-scale analyses of natural Bebearing minerals and experimental run products (Charoy 1999). Progress in recent years (e.g., Evensen and London 2002, 2003) has improved our understanding of the behavior of Be in the felsic magmatic processes; however, the decisive processes that lead to enrichment of Be up to ore grade during pegmatitic stages of magma evolution remain elusive. Published solubility experiments and investigations into the stability of Be minerals (Franz and Morteani 1981; Evensen et al. 1999) provided important constraints for compositionally simple granitic melts and suggested that Be re-mobilization leading to mineralization largely involves lower-temperature secondary (non-magmatic) processes, but the species in which form Be is transported and enriched in melts and/or fluids remain speculative (Beus 1966; Kosals 1976).

Recent investigations into fluid and melt inclusions in phenocrysts of evolved felsic magmas have provided important new constraints on the geochemistry of boron and some ore-forming elements (Zn, Sn)-see Rickers et al. (2006). The study of silicate melt inclusions entrapped in quartz of a late-stage, B-, F-, and P-rich pegmatite from Ehrenfriedersdorf, Germany (Webster et al. 1997 and subsequent unpublished data), for example, located extremely volatile-rich melt inclusions containing very high concentrations of Be up to 9,600 ppm. Related, recent research by Zajacz et al. (2008) has also determined elevated Be concentrations in geochemically evolved, felsic melt inclusions from Ehrenfriedersdorf and from the miarolitic granites of the Baveno and Cuasso al Monte intrusions, Italy. Given such high Be concentrations, we should expect crystallized inclusions like these to contain various Be-bearing daughter crystals.

In this work, we review the current understanding of melt inclusions with Be-enriched evolved compositions. We also provide a broadly synthetic model that addresses the roles of fractional crystallization, melt–melt immiscibility, and subsequent hydrothermal processes in the generation and entrapment of Be- and volatile-enriched melt inclusions of felsic and highly differentiated pegmatiteforming magmas.

Brief remarks regarding the type-A and type-B melt inclusion nomenclature

In this study, we use the type-A and type-B nomenclature for melt inclusions according to (Thomas et al. 2000). Type-A inclusions trapped relatively H₂O- and alkali-poor, highly polymerized peraluminous melts. In contrast, type-B inclusions trapped extremely H₂O-, other volatile-component-, and alkali-rich, strongly depolymerized melts. Both inclusion types have strongly divergent compositions and element-partitioning coefficients even though both can be found coexisting in the same growth planes of host phenocrysts (Thomas et al. 2000). These inclusions result from a melt–melt immiscibility event, which induced development of two immiscible conjugate melts with contrasting properties along the opening solvus, due to cooling and concomitant fractional crystallization from 700 to 500° C.

The evolution of these conjugate melt pairs with decreasing temperature is demonstrated by Thomas et al. (2006). Their Fig. 5 shows the behavior of SiO₂, Al₂O₃, the sum of alkalis, F, H₂O, and the bulk density of the generalized SiO₂-Al₂O₃-Na₂O-K₂O-F-H₂O system resulting from extensive electron microprobe and Raman

spectroscopic work on the Zinnwald topaz–albite granite which has many similarities to and bearing on processes occurring at the Ehrenfriedersdorf granite–pegmatite system.

Prior research on daughter minerals in fluid and melt inclusions

The identification of daughter minerals in fluid and melt inclusions is essential for estimating the bulk composition of the original trapped homogeneous fluid or melt. Such solid phases indicate saturation of the fluid with respect to these phases during cooling (Roedder 1992), so their identification and characterization are of fundamental importance to the study of daughter mineral-bearing fluid and melt inclusions (Burke 2001). The identification of such minerals may not have occurred, in the past, because more traditional analytical techniques such as SEM-EDS and electron microprobe analysis (EMP) cannot detect elements as light as Be and the extremely small size of such minerals renders X-ray analysis difficult, if not impossible. Raman spectroscopy, however, is a very sensitive technique for light elements, which requires minimal sample volume and preparation. In addition, Raman spectroscopy is generally non-destructive and can be used to identify a wide range of minerals (see Downs 2006). Because H₂O is a weak scatterer of Raman radiation, Raman spectra can be obtained from daughter minerals immersed in H₂O (i.e., in aqueous fluid inclusions). Modern confocal Raman microprobes have a lateral resolution of $\sim 1 \ \mu m$ and a depth resolution of $\sim 2 \ \mu m$, which allow confocal spectral measurements from selected regions inside mineral samples, and this enables the characterization of daughter minerals in inclusions. Furthermore, Raman spectra can be derived from dissolved species in solutions; for example, Thomas (2002) identified boric acid in fluid inclusions in quartz, beryl, tourmaline, and cassiterite from different localities (e.g., the tin deposits of Ehrenfriedersdorf, Germany; several granites and pegmatites in the Erzgebirge region, Germany; pegmatites from Elba Island, Italy, Mozambique, Namibia, the Tanco Mine in Canada and others) from tens of % down to 500 ppm boric acid, corresponding to about 90 ppm B. These capabilities also enable in situ studies of speciation changes in solutions at different temperatures and pressures (Schmidt et al. 2005) using microscope-heating stages and/or hydrothermal diamond anvil cells (HDAC).

It has been generally assumed that beryllophosphate minerals (e.g., beryllonite, herderite, and greifensteinite) form mainly in the late stages of the pegmatite crystallization at relatively low temperatures ($\leq 250^{\circ}$ C) and/or often as secondary alteration products (Charoy 1999; Pezzotta et al. 1999; Černá et al. 2002). However, the Be

minerals such as beryl, greifensteinite, herderite, and roscherite have been identified and described from miarolitic cavities in the Variscan granites of the Geyer-Ehrenfriedersdorf region (Slavík 1914; Chukanov et al. 2002; see also Grew et al. 2003). Moreover, in the Sauberg mine near Ehrenfriedersdorf, steeply dipping \leq 10-cm-thick, zirconrich beryl-quartz veins occur in the country rock (see Kumann and Leeder 1994). In addition to secondary and primary fluid inclusions (FI), the quartz and beryl in these rocks contain mostly melt inclusions (MI) with peralkaline bulk chemistry (e.g., type-B MI similar to those described by Thomas et al. 2000) and are definite indications that the formation temperature of these veins ranged from 700 to 600° C.

In large type-B melt inclusions in quartz of the Ehrenfriedersdorf pegmatite as well as in the beryl-quartz veins, we have for this contribution identified hambergite and beryllonite daughter crystals. With trapping temperatures between 700 and 500°C, this observation suggests that these Be minerals in this case are primary and formed at magmatic temperature. The presence of these inclusions implies that such mobile Be- and volatile-rich melt fractions can migrate after separation from granite- and/or pegmatite-forming melts to form separate Be-mineralized veins (Thomas et al. 2006). Other Be-bearing minerals (i.e., Be-phosphates in particular) are very rare constituents of granitic pegmatites and related granites and are mostly found in small miarolitic pockets. In this contribution, we also show that beryllophosphate minerals (e.g., beryllonite [NaBePO₄]) may form as primary phases at the beginning of pegmatite crystallization, and they precipitate at temperatures from 700° down to 500°C. The presence of melts at such low temperatures is the result of the strong enrichments of the melt in H₂O, Li, P, F, Sn, Be, B, and the rare alkali elements Rb and Cs during differentiation. The strong enrichments in volatile components also drive the system to pressure-temperature composition regions that include a solvus where two pegmatite-forming conjugate melts coexist (Thomas et al. 2000, 2003).

In this synthesis, we show that the study of MI offers an answer to the question of why Be-rich minerals form in granite pegmatites in which the granitic bulk-rock samples contain relatively low concentrations of Be. Furthermore, the use of Raman spectroscopy is used to show the form in which Be is coordinated and transported in H_2O -rich type-B melts.

Samples

The samples for this study come from two different types of mineralization in the Variscan granite-pegmatitehydrothermal system of the Ehrenfriedersdorf tin-tungsten deposit in the Erzgebirge, Germany. They include (1) a large pegmatite body and (2) several steeply dipping \leq 10cm-thick, beryl-quartz veins crossing the granites and the country rocks. The age relationship of the pegmatites of (1) to the granites, their style of mineralization and the origin of the pegmatites are presented in several papers (Webster et al. 1997; Thomas et al. 2000, 2003, and 2006; Rickers et al. 2004 and 2006; Romer et al. 2007).

The beryl veins of (2) are from the Sauberg mine near Ehrenfriedersdorf, and they are mainly leek-green beryl crystals (40–60% (vol/vol)) up to 40 mm long with massive quartz. They also contain subordinate albite, muscovite, F-saturated topaz, zircon, cassiterite, fluorite, arsenopyrite, and molybdenite. The coexistence of topaz and fluorite implies according to Dolejš and Baker (2004) a high fluorine activity in the system.

Another sample comes from a small miarolitic cavity (~ 10 cm) in the granite from Wolfsgrün, Eibenstock granite massif, West Erzgebirge. Near the center of this cavity, there are colorless topaz crystals and more rarely small sky-blue beryl crystals. In the topaz of such cavities, there are extremely volatile-rich MI up to 50 µm in diameter. These inclusions contain several Be-bearing daughter mineral phases.

For Raman spectroscopic comparison, a colorless hambergite crystal ($2 \times 2 \times 1.5$ cm) from the Rangkul pegmatite field, eastern Pamirs, Tadzhikistan was used (see Peretyazhko and Zagorsky 1999). This hambergite crystal contains numerous extremely boric acid–rich (up to 70%) primary MI, as well as secondary FI with daughter crystals of boric acid and ramanite-(Cs) (Thomas and Davidson, submitted).

Sample preparation and analytical methods

For the determination of Be in the glass of MI in the phenocrysts, 500-µm-thick doubly polished sample chips were heated to predetermined temperatures (between 600 and 720°C) and held there for 20 h at 1 kbar, then quenched to glass and coexisting liquids using the standard cold-seal pressure technique (see Thomas et al. 2009b). Figure 1a–f show the light-microscopic images of re-homogenized typical type-B MI with a high Be concentration, and Fig. 2 shows type-A and type-B melt inclusions in a single growth zone in beryl from a beryl-quartz vein from the Sauberg mine near Ehrenfriedersdorf.

Ion microprobe analysis

The concentrations of Be in the silicate glass of the MI were determined by secondary ion microscopy (SIMS)



Fig. 1 Optical photomicrographs of type-B melt inclusions in pegmatite quartz from Ehrenfriedersdorf, Germany. **a** shows a type-B melt inclusion in pegmatite quartz from Ehrenfriedersdorf after re-homogenization at 700°C and 1 kbar: *G* glass, *L* water- and H_3BO_3 -rich solution, *V* vapor. The *black spot* in the liquid phase is sassolite with graphite dust (similar to Fig. 1d in Thomas et al. 2000 or Fig. 4a in Thomas 2002). **b** An exposed type-B melt inclusion, the two *circular marks* in the glass (*G*) are a result of the EMP measurements. Open cavity (*V*) was filled with exsolved liquid, vapor

and water-soluble phases produced during quenching—and is now empty. **c**–**f** representative type-B melt inclusions in beryl from a beryl–quartz vein from the Sauberg mine near Ehrenfriedersdorf, re-homogenized at 700°C and 1 kbar. Under the microscope, the glass can be only recognized with great difficulty because of the slight difference in the refractive index of the glass and the beryl host. The photos were taken using contrast enhancing by "Black Shading" and oblique incident illumination

using a Cameca IMS-3f at the Woods Hole Oceanographic Institution. The glasses of each MI were analyzed 5 times each in one or two surface locations. The samples were analyzed at 12.5 keV and approximately 1-nA beam current with a focused beam that was typically $\geq 15 \ \mu m$ in diameter; the count times for Be were 10 s. Only highenergy secondary ions with excess kinetic energies in the 78 ± 20 eV range were analyzed in order to minimize the effects of mass interferences and reduce matrix effects potentially involving the bulk glasses. The MI glasses are variably enriched in F, B, P, and Al, and one of our Be standard glasses (i.e., the Macusani obsidian) is also enriched in these components. Thus, we conclude that the SIMS analyses of the MI were not adversely influenced by their P-, Al-, and F-rich bulk matrices and that the reported Be concentrations are accurate within precision quoted by Webster and Duffield (1994). Additional details are given in Webster et al. (1997) and the cited references therein.

Micro-Raman spectroscopy

Raman spectra were recorded with a Jobin-Yvon LabRam HR800 spectrometer (grating: 1,800 and 2,400 g/mm), equipped with an Olympus optical microscope and a longworking-distance LMPlanFI 100×/0.80 objective. We used the 514- and 488-nm excitation of a Coherent Ar⁺ laser Model Innova 70C, a power of 200 mW (about 10 mW on sample), at a resolution ≤ 0.6 cm⁻¹. For the study in the low-frequency range, we used the notch as well as edge filters. Each unpolarized spectrum represents the accumulation of six acquisitions of 20 s each. The spectra were collected at a constant laboratory temperature (20°C) with a Peltier-cooled CCD detector $(-70^{\circ}C)$, and the positions of the Raman bands were controlled and eventually corrected using the principal plasma lines in the Argon laser (see Craig and Levin 1979). The differences between the recommended and measured positions of the plasma lines



Fig. 2 Optical photomicrographs of a beryl sample from the berylquartz veins from the Sauberg mine near Ehrenfriedersdorf, Germany, showing both type-A and type-B melt inclusion types in the immediate vicinity of a single growth zone, re-homogenized at 700°C and 1kbar. All *dark spherical spots* are type-B melt inclusions (volatile-rich), which are the most abundant type in the sample. The bright inclusions in the upper third of the overview photo are all type-A melt inclusions, note the inhomogeneous distribution of type-A and type-B inclusions on a mm scale suggesting the beginning of coalescence of melt into progressively larger melt pools. The *upper photo* (*A1*) shows a close-up from the growth zone with predominant type-A melt inclusions. The *lower two photos* (*B1* and *B2*) represent typical type-B melt inclusions (labeled as in the overview photo). *G* glass, *L* water-rich solution, *V* vapor

in the fingerprint spectral region are not larger than 0.6 cm^{-1} using a pinhole aperture of 100 μ m.

NIR femtosecond laser ablation-inductively coupled plasma-mass spectrometry (fs-LA-ICPMS)

Some MI in quartz of the Ehrenfriedersdorf and Greifenstein granite were analyzed for Be and 26 other elements using NIR femtosecond laser ablation-inductively coupled plasma-mass spectrometry at the University of Toulouse, France. A detailed description of the technique used is given in Borisova et al. (2008).

In the present study, we use only the obtained data for Be (see Tables 3 and 4). The complete results of the trace element determinations of MI in granites and pegmatites from the Erzgebirge region are presented in Borisova et al. (in preparation).

Results

Pegmatite and beryl veins from Ehrenfriedersdorf

Characteristically, the type-A MI contain berlinite [AlPO₄] and topaz, and the type-B MI contain topaz and the phosphates including amblygonite [LiAl(PO₄)(F,OH)], lacroixite [NaAl(PO₄)F], triplite [(Mn^{2+} , Fe²⁺, Mg, Ca)₂(PO₄)(F,OH)], and herderite [CaBePO₄(F,OH)]. This information is summarized by Rickers et al. (2006) and Thomas et al. (2006) in their overviews of the daughter minerals in MI and fluid inclusions in pegmatite quartz from Ehrenfriedersdorf. Much of this information was determined with confocal micro-Raman spectroscopy.

Careful screening of the type-B MI with Raman spectroscopy detected two other Be daughter phase minerals: beryllonite [NaBePO₄] and hambergite [Be₂BO₃(OH,F)], and this represents the first observation of these minerals in samples of the Ehrenfriedersdorf region. Tables 1 and 2 give the main Raman frequencies (in cm^{-1}) of these phases together with other reference data, and Figs. 3 and 4 present the Raman spectra of both mineral phases. Both Be minerals (2-5% (vol/vol)) in the MI have Raman spectra that are identical to spectra obtained on natural macroscopic crystals of beryllonite and hambergite, which were studied for comparison. In particular, the Raman spectra of beryllonite show two strong bands at 1,012 and 1,055 cm^{-1} and a couple of weak bands at lower frequencies (e.g., 138, 432, and 547 cm^{-1}). Hambergite is characterized by a sharp and very strong Raman band at about 150 cm^{-1} and other strong bands at 988 cm^{-1} and 3,402 cm^{-1} . Even very small hambergite daughter crystals ($\sim 1 \mu m$) in inclusions (corresponding to about 5×10^{-13} g Be), buried deeply in the beryl matrix, clearly show the 150 cm^{-1} Raman band in addition to the strong beryl bands at 684 and $1,067 \text{ cm}^{-1}$.

Importantly, these Be-bearing phases are not found in the coexisting type-A inclusions. By implication, there was a different Be partitioning between the coexisting relatively H_2O - and alkali-poor, peraluminous melts (Type-A inclusions) and the extremely H_2O -, other volatile-component-, and alkali-rich peralkaline melts (type-B inclusions).

Miarolitic cavity in granite from Wolfsgrün

With Raman spectroscopy, we have identified the following daughter mineral phases in type-B MI (see Downs 2006): sassolite $[H_3BO_3]$ (5% (vol/vol)), elpasolite $[K_2NaAlF_6]$,

Table 1 Main Raman frequencies (in cm⁻¹) of the daughter mineral phase beryllonite in quartz together with reference data of beryllonite from the RRUFF project (Downs 2006)

| Beryllonite from Ehrenfriedersdorf | Quartz host | RRUFF no. R060299 | RRUFF no. R060552 | RRUFF no. R070249 |
|---------------------------------------|----------------|----------------------|----------------------|----------------------|
| 138.6 | 126.2 | 138.4 | 138.4 | _ |
| 161.2 | | 161.1 | 161.5 | (163.0) |
| | 206.0 | | | |
| (355.9) | 354.3 | 353.9 | 354.4 | 354.4 |
| 432.6 | | 432.5 | 432.0 | _ |
| (465.0) | 463.5 | 466.2 | 465.3 | 466.2 |
| 547.9 | | 547.7 | 547.2 | 546.2 |
| 1,012.3 | | 1,011.5 | 1,010.5 | 1,011.0 |
| 1,055.5 | (1,061) | 1,054.9 | 1,054.4 | 1,047.2 |
| | (1,081.5) | | | 1,065.5 |

The bold numbers are the strongest Raman bands and the numbers in the brackets are very weak

| Table 2 Main Ramanfrequencies (in cm^{-1}) of thedaughter mineral phasehambergite together withreference data from naturalhambergite crystals | Hambergite from Ehrenfriedersdorf in beryl | Pamir (c axis)* | Pamir (⊥c axis)* | RRUFF no. R050603 ^a | RRUFF no. R050672 ^a |
|---|---|----------------------|---------------------|-----------------------------------|-----------------------------------|
| | (104.0) | (106.6) | | | |
| | 123.3 | | | 122.4 | 136.4 |
| * From the Rangkul pegmatite field, eastern Pamirs, Tadzhikistan | 146.9 | 149.0 | | | |
| | 154.4 | 157.4 | 150.8 | 155.7 | 154.7 |
| | | | (159.0) | | |
| ^a RRUFF: see Downs (2006) | 269.8 | 269.2 | | 267.5 | 267.5 |
| The bold numbers are the strongest Raman bands, and the numbers in the brackets are very | | 287.1 | | | |
| | | 398.3 | (401.2) | | |
| | 987.5 | 989.0 | 988.4 | 986.8 | 986.3 |
| The bands at about 155 cm ^{-1} , 988 cm ^{-1} , and 3,400 cm ^{-1} show extensive intensity | 3,403.3 | 3,402.4 | 3,420 | | |
| | 3,468.6 | 3,467.7 | 3,481.5 | | |
| | | 3,595.4 | 3,600.4 | | |
| changes depending upon the sample orientation | | (3,664.2) | 3,665.3 | | |

cryolite $[Na_3AlF_6]$, and cryolithionite $[Na_3Li_3Al_2F_{12}]$ (0.5% each (vol/vol)), ramanite-Cs [CsB₅O₈ · 4 H₂O], bertrantite [Be₄Si₂O₇(OH)₂], beryl [Be₃Al₂Si₆O₁₈], phenacite [Be₂SiO₄], and euclase [BeAlSiO₄(OH)] (1% each (vol/ vol)). The volume estimation of each Be mineral is very conservative, which gives a computed beryllium content of these inclusions as about 10,000 ppm. However, it could as much as be fourfold higher. Despite high boron concentrations, no hambergite formed in these inclusions. Again, these Be-bearing phases are not found in the coexisting type-A MI.

Hambergite crystals from the Rangkul pegmatite field, eastern Pamirs, Tadzhikistan

The hambergite crystals contain many boric acid-rich primary MI and secondary FI. The primary MI are mainly sassolite (up to 70% (g/g)), and the secondary fluid inclusions contain daughter crystals of sassolite, ramanite-(Cs), and NaHCO₃ (see Thomas et al. 2008). From this daughter mineral paragenesis, it follows that hambergite and therefore the Be are very soluble at higher temperatures in alkali-borate-rich solutions (see Fig. 5).

Interpretation of analytical results

The analytical results from the Ehrenfriedersdorf pegmatite and host granite provide an opportunity to examine the progress in Be concentrations in the various stages of evolution of this complex system. Here, the MIs represent various stages of evolution of a highly evolved granite melt system that finally gave rise to granite-related Sn-W mineralization in this region.

Before conducting SIMS measurements for Be in the MI glasses, the bulk compositions of the inclusion glasses were determined with electron microprobe techniques, and the



Fig. 3 Raman spectra of beryllonite in melt inclusions in quartz from the Ehrenfriedersdorf pegmatite, Germany; see text for description. The *bands* labeled with 206Qu and 464Qu are bands of the quartz host at the frequency positions 206 and 464 cm⁻¹, respectively



Fig. 4 Raman spectra of hambergite in melt inclusions in quartz and beryl from the beryl veins in the Ehrenfriedersdorf Sauberg mine, Germany. The *bands* labeled with 686Brl and 1070Brl are bands of the beryl host at the frequency positions 686 and $1,070 \text{ cm}^{-1}$, respectively

results (as well as summaries of the analytical methods) are given in Webster et al. (1997) and Thomas et al. (2003). Tables 3 and 4 present the results of the Be determinations of MI hosted by quartz of the Ehrenfriedersdorf pegmatite together with Be analyses of whole rocks (granite and pegmatite). Also, included are SIMS data, data from LA-ICPMS studies at the ETH Zürich (Zajacz 2007), fs-LA-ICPMS (Borisova et al., in preparation) and estimated concentrations of Be based on the volumes of the Be daughter minerals in inclusions. Data for the topaz–albite– granite from Zinnwald, Germany, are also given for comparison.

Hösel (1994) analyzed four different granite phases A to D, representing the evolution from a more simple (A) to the most evolved type (D). Regarding Be only, we would note minor variation between them, suggesting Be enrichment



Fig. 5 Optical photomicrographs of a typical secondary fluid inclusion in a hambergite crystal from the Rangkul pegmatite field, eastern Pamirs, Tadzhikistan, with sassolite, ramanite-(Cs), and nahcolite daughter crystals, showing that hambergite is highly soluble in an alkali-borate-rich solution, and that Cs is also enriched to a very high level in the secondary fluid. The upper photomicrograph is in dark field illumination to highlight the extreme birefringence characteristic of the B-rich daughter phases

post-dates granite formation. The Ehrenfriedersdorf granites contain 8.3 ± 2.5 ppm Be (Hösel 1994) and is nearby constant, independent from the evolution stage, signified by the granite phases A to D. After magmatic fractionation, some MI in granite contain a maximum of 40 ppm Be. This represents an approximately fourfold enrichment of Be. Beryllonite and herderite were found in the P-rich pegmatite, and hambergite was only found in type-B MI in quartz of the beryl-rich quartz veins that cross the Ehrenfriedersdorf granite and country rock and contain mostly type-B MI in quartz and beryl. Accordingly, we interpret these veins to have formed from silicate-rich hydrous melts.

In comparison with the whole-rock granite values $(8.3 \pm 2.5 \text{ ppm Be}, \text{Hösel 1994})$, the MI data show clearly that Be is enriched in pegmatite-forming melts by factors of about 17 to 60 for type-A and 150 to 750 for type-B melts. In melts that represent the solvus crest, the Be enrichments relative to the Be in the bulk rock are 1,000-fold. The sequestration of Be between the conjugate melt pairs differs by a maximum factor of about 12. Such strong enrichment of Be in glass of the type-B MI is consistent with the observation of Be-bearing daughter minerals such as beryllonite and hambergite in the unheated MI.

| Sample | Type-A MI (ppm Be) | Type-B MI (ppm Be) | Partition coefficients | | |
|---------------------------------|--------------------------------|-------------------------|---|---------------------------------|--------------------------------|
| | | | $\overline{D_{\mathrm{Be}}^{\mathrm{melt}-A/\mathrm{granite}}}$ | $D_{ m Be}^{ m melt-B/granite}$ | $D_{ m Be}^{ m melt-B/melt-A}$ |
| Ehrenfriedersdorf | | | | | |
| Granites A, B, C, D, whole-rock | 8.3 ± 2.5 (135) | | | | |
| Granite A, B, MI | 13 (1)* | | 1.57 | | |
| | 9.5 ± 4.0 (10)** | | 1.14 | | |
| Granite, C, MI | 40 (1)* | | 4.82 | | |
| | 49 ± 13 (12)** | | 5.90 | | |
| Granite D, MI | 135 ± 28 (7)** | | 16.3 | | |
| Pegmatite, whole-rock | 3 (1)* | | 0.36 | | |
| Pegmatite, MI | 152 ± 23 (4)** | $7,000 \pm 1,800$ (35) | 18.3 | 843 | 72.5-22.4 |
| | 312 ± 46 (10)** | 11,025 (5) ^a | 37.6 | 1,328 | |
| Pegmatite, MI | 142 ± 76 (17)* | 1,234 (2)* | 17.1 | 148.7 | 8.7 |
| Pegmatite, MI | 492 (2)* | 6,120 (2)* | 59.3 | 737.4 | 12.4 |
| Pegmatite, MI ^d | 2,000-5,000 (10) ^b | | 240-600 | | 1 |
| Beryl-vein ^d | 4,500–11,250 (10) ^c | | 540-1,355 | | 1 |
| Zinnwald | | | | | |
| Granite, whole-rock | 7.3 (1) | | | | |
| Granite, early MI | 18 (3) | | 2.5 | | |
| Topaz-albite-granite, MI | 118 (1)* | 670 (2)* | 16.2 | 91.8 | 5.7 |

Table 3 Be concentrations in the whole rock and in melt inclusionsin quartz from the granite-pegmatite system Ehrenfriedersdorf,Germany, determined with ion microprobe, NIR femtosecond laser

ablation-inductively coupled plasma-mass spectrometry or estimated from daughter crystal volume and different partition coefficients

Data from the evolved topaz–albite–granite from Zinnwald, Germany, are given for comparison. In the Ehrenfriedersdorf region, there are 4 different granite phases A to D, representing the evolution from a more simple (A) to the most evolved granite (D) according to Hösel (1994) We used only those melt inclusions for which a clear assignment to the inclusion type was possible (type-A vs. type-B MI's) (*n*) number of determinations/estimations. Melt inclusions in quartz were re-homogenized; all other inclusions were not refused prior to analysis

* In the melt inclusion glass (SIMS data); ** (fs-LA-ICPMS)

^a Be concentration estimated from the beryllonite daughter crystal volume: $3.1 \pm 0.8\%$ (vol/vol) in type-B MI's

^b Be concentration estimated from the beryllonite daughter crystal volume; 2% (vol/vol) beryllonite corresponds to about 2,000 ppm Be (inclusion density: 2.0 g/cm³)

^c Be concentration estimated from the hambergite daughter crystal volume; 2% (vol/vol) hambergite corresponds to about 4,500 ppm Be (inclusion density: 2.0 g/cm³)

^d Note that at the critical point, the differences between the type-A and type-B melts disappear

Beryllium reaches its highest concentrations of 1,200 up to 11,250 ppm, and these Be levels result in the formation of phosphates such as beryllonite and herderite during system cooling and crystallization. Two % (vol/vol) beryllonite corresponds to about 2,000 ppm Be. Interestingly, the unheated type-B melt inclusions in quartz and beryl in the veins contain hambergite daughter crystals, and these crystals represent a minimum volume of 2% that corresponds to about 4,500 ppm Be in the inclusions.

By more extensive fractionation and formation of pegmatite-forming melts, we observe further enrichments of Be by factors of about 240 to 600. We interpret these to represent the pegmatite-forming melts formed near the crest of the type-A and type-B melt solvus. The highest enrichment of Be by factors of about 540 to 1,400 is reached in the volatilerich, beryl-forming melts. Plotting these data into a Rayleigh fractional diagram shows that Be in the Ehrenfriedersdorf granite-pegmatite system is largely incompatible up to the onset of melt-melt immiscibility.

The incompatibility of Be in volatile-rich, highly evolved melt fractions can also be seen from the daughter mineral assemblage in volatile-rich melt inclusions in topaz from the miarolitic cavity in the Eibenstock granite. Here, the last melt portion is extremely enriched in F as indicated by the host mineral and the mineral phases elpasolite, cryolite, and cryolithionite as well as highly enriched in Be as indicated by the Be minerals bertrandite, beryl, phenacite, and euclase. This corresponds to about 10,000 ppm Be or more in these melt fractions.

One possible interpretation for the very high Be enrichment (Tables 3, 4) is that these Be minerals may have crystallized in the melt and been accidentally trapped in MI during the crystal growth. If this had occurred, then the amount of co-trapped phase should be completely

Table 4 Assignment of the determined or estimated Be concentrations to the assessed temperatures using the samples and data on the basis of the plot of boron versus water concentration in conjugate type-A and type-B melt inclusions in pegmatite quartz from the Ehrenfriedersdorf, Germany, complex (Thomas et al. 2003) and new data (see Table 3)

| Temperature (°C) | Beryllium (ppm) | | | | |
|---------------------|------------------------|----|---------------------------|----|--|
| | Type-A melt inclusions | n | Type-B melt inclusions | п | |
| 600 | 142 ± 76 | 10 | 1,234 | 2 | |
| 640 | 152 ± 23 | 4 | 6,120 | 2 | |
| 650 | 312 ± 46 | 10 | $7,000 \pm 1,800$ | 35 | |
| 680 | 492 | 2 | | | |
| 700 | | | 11,025 | 5 | |
| 712 | 2,000 | 5 | | | |
| 712 | 4,500 | 5 | 11,250 | 5 | |
| 720 | 5,000* | | | 5 | |

n number of determinations

* At the solvus crest, the difference between type-A and type-B melts disappear

random, from 100% to 0%, and any value between. However, a plot of the frequency distribution of the volume of daughter beryllonite in inclusions in one quartz crystal of the Ehrenfriedersdorf pegmatite gives a mean, from 40 inclusions, of $3.1 \pm 0.8\%$ (vol/vol). This consistency demands that the Be-bearing phases are daughter phases, not co-trapped phases (e.g., Roedder 1984). Moreover, homogenization experiments, some under visual control, were conducted to establish estimated trapping temperatures, and bulk homogenization experiments were not performed at higher temperatures, so it is improbable that any co-trapped phases would have melted during homogenizations. Additionally, if Be mineral crystals did co-exist in the melt, they should also be trapped in the host as crystal inclusions, and detailed studies of the Ehrenfriedersdorf pegmatite have failed to find any of these Be-enriched minerals included in phenocrysts, although crystal inclusions of topaz, for example, are common. This also indicates that as high as the Be concentrations were in the Ehrenfriedersdorf melts, they were still at or below Be solubility under the conditions of MI trapping.

One example in which accidental co-trapping may have occurred involves random co-trapping of type-A and type-B melts in the same MI. That this has occurred in the Ehrenfriedersdorf pegmatite can be shown by the range of glass/fluid ratios previously described. Although the great majority of inclusions are type-A or type-B, there are a few examples of intermediate values which show that some cotrapping occurred, but also that it can be identified when it does.



Fig. 6 Plot of the beryllium content in type-A and type-B melt inclusions in the Ehrenfriedersdorf, Germany, pegmatite quartz versus temperature (see Table 4). Shown are the two boundary lines corresponding to the both different inclusion types. The differences between the type-A and type-B melts disappear in the critical region. The field (A + B) corresponds to an immiscibility gap. Inclusions trapped in this field should show a large scatter in the Be data between both boundary cases

Furthermore, Table 3 also shows a great difference of the Be concentration in the conjugate type-A and type-B melt inclusions. The difference is largest at lower temperatures, but near the critical point the differences between the type-A and type-B melts disappear (see Fig. 6). This behavior is qualitatively similar to those of boric acid and Rb in the Ehrenfriedersdorf pegmatite system (Thomas et al. 2003 and Rickers et al. 2006). The Be concentration is temperature dependent and traces the boundaries of the pseudobinary immiscibility field nicely. If this distribution mode is ignored, then the concentration data of Be seem chaotic.

Taken together, the problems of changing solubilities during cooling, co-trapping of random proportions of coexisting immiscible melts/fluids, often poor control of exact trapping temperatures for individual analyzed MI (rather than maximum trapping temperatures for selected MI populations), and melt/melt, melt/fluid, and melt/rock interactions during pegmatite magma evolution should cause broad dispersion and apparently chaotic compositional variations in large MI populations. Some apparently chaotic metal concentrations in MI from pegmatites have been reported (Audétat et al. 2008; London and Evensen 2002). However, with precise controls on the trapping temperatures of individual MI (and thus the exact point in the magmas evolution) and allowance for co-trapping of multiple conjugate immiscible fluids, consistent data sets can be recognized from the apparently chaotic variations and applied to the interpretation of complex evolving and vigorously interacting magmatic systems.

Discussion

London (2008) has suggested that exotic MI compositions like those of this study may represent entrapment of boundary layer melt, rather than the pegmatite melt composition generally. However, in our view, this effect, if present, is negligible, and we have presented several lines of evidence to that effect. The MI found in pegmatites contain very high concentrations of H₂O; volatiles such as F, B, P, and Li; and alkali carbonates and bicarbonates. Estimates imply viscosities of from 10^3 to as low as 3 Pa.s. (Audétat and Keppler 2004; Thomas et al. 2006), and the high concentrations of other volatiles and carbonates suggest even lower viscosities. At such low viscosities, the diffusion rates of all elements should produce a tendency for elements to diffuse in or out of the region so rapidly as to produce a negligible boundary layer effect. Moreover, at such low viscosities, convection and even gravitational instability and turbulence due to bubble rise should significantly disrupt any incipient boundary layers. Another factor in the boundary layer effect is the compatibility of a given element in a particular mineral. If the element is crystal compatible, then it will be selectively depleted in the boundary layer, and if incompatible it will be enriched, thus any boundary layer effect should be dependent on the mineral in which the inclusion occurs. We and other authors have found similar type-A and type-B MI in quartz, topaz, beryl, K-feldspar, and tourmaline in many different pegmatites from around the world (see Table 1 in Thomas and Davidson 2008) which would seem to be solid evidence that such melt fractions are not a boundary layer effect. Thus, the evidence supports the view that MI compositions in pegmatite minerals reflect the pegmatiteforming magma and also some of the various phases and immiscible conjugate melt pairs that may be present in it (see also Thomas et al. 2009a and b). This provides a basis from which to consider Be concentrations in pegmatiteforming melts.

Be concentrations in evolving melts

A basis from which to assess the evolution of Be concentrations in pegmatites data on Be concentrations in granites is needed. Published data show the presence of tens, up to hundreds of ppm Be in granitic whole-rock samples. Förster and Rhede (2006) found up to 54 ppm Be in the late-Variscan Be–Ta-rich granite of Seiffen (eastern Erzgebirge, Germany), and Charoy (1999) determined a value of 303 ± 58 ppm Be in five Beauvoir, France, granite samples. Moreover, Evensen and London (2002) report up to 130 ppm Be in evolved facies of cordierite-free granitic rocks. Furthermore, their model for the ascent and evolution of granitic magmas indicates that cordierite-free, highly differentiated melts may dissolve up to 70 ppm Be. This model does not, however, account for simultaneous extensive enrichments in volatile and fluxing components as the residual fractions of melt become increasingly enriched in Be and that is a key issue addressed in the samples of the present study.

The presence of highly elevated abundances of Be in natural silicate glasses is well demonstrated. Clearly, some silicate melts are capable of dissolving high concentrations of Be. Silicate MI from Ehrenfriedersdorf, Germany, contain up to 9,600 ppm Be; for example, MI from Zinnwald, Germany, contain up to 670 ppm Be (Webster et al. 2004). Zajacz (2007) measured a mean of 570 ± 150 ppm Be (n = 22) with LA-ICPMS in unheated type-A MI entrapped in pegmatitic quartz from Mt. Malosa in the Chilwa alkaline province in Malawi. There, he found a type-B MI with 1,723 ppm Be. Clearly, some silicate melts are capable of dissolving high concentrations of Be.

These data are consistent with the Be concentrations of experimentally generated silicate glasses (Evensen et al. 1999); this study measured up to $\sim 1,450$ ppm Be (4,016 ppm BeO) in the silicate glasses and determined that, in general, high Be concentrations were stabilized by elevated temperature and low peraluminosity of the melts. It also observed that the maximum concentrations of the incompatible element, Be, in silicate magmas are limited by beryl crystallization and that the most Be-enriched abundances of their glasses correlate with the presence of elevated Li, B, P, and F in some of their experimental charges. One point that, however, should be noted here is that the melts used in Evensen et al. (1999) were synthetic compositions and not always equivalent to those of the chemically complex Ehrenfriedersdorf MI and the other MI in this study. Thus, we would not expect exactly the same behavior of Be between their experimental work and our results from natural MI. In consequence, the Be contents of the most extremely Be-enriched MI may be much higher than those measured in the experiments of Evensen et al. (1999).

B-, F-, P-, \pm Li-enriched magmas during extended fractional crystallization and late-stage melt-melt immiscibility will facilitate even greater Be enrichments in the comparatively H₂O-rich melt fractions represented by type-B MI. At the beginning of the melt-dominated pegmatite stage, after about 80% crystallization, the Be concentrations of residual F-, P-, and Li-rich silicate melt may be as high as 4,000 ppm as was predicted by Evensen and London (2002). Subsequent separation of H₂O-enriched melt from silicate-dominated melt involves elevated enrichment factors that favor the former melt, and this process may lead to extreme Be concentrations. We assume that the observation of Evensen et al. (1999), i.e., that the temperature of beryl saturation in felsic liquids is a strong function of the concentrations of F, B, Li, and P, becomes increasingly significant as the abundances of these fluxing components continue to increase to the most extensive levels of magma evolution that precede final crystallization. The data of Tables 3 and 4 indicate that Be is sequestered preferentially into the water-rich melt phase (i.e., those melt fractions represented by the type-B MI) during melt-melt immiscibility processes, and this is consistent with the observation of nearly 11,000 ppm Be in type-B MI trapped near the two-melt solvus crest in the pegmatite from Ehrenfriedersdorf, Germany. It is at such high Be concentrations that type-A and type-B inclusions should contain Be minerals as daughter phases, and this is consistent with the presence of beryllonite and hambergite in some Ehrenfriedersdorf MI.

The low-water, high-silica (type-A) MI also contain elevated Be. The MI from Ehrenfriedersdorf and Zinnwald, Germany, contain ca. 100–1,000 ppm Be. Similarly, 2,300 ppm Be was determined in brine inclusions in pegmatite quartz from the Yermakovka F–Be deposit, Transbaikalia (Reyf and Ishkov 1999).

The fate of extremely Be-rich melts

It follows from these data, from the presence of beryllonite and hambergite as daughter phases in these inclusions, and from the low calculated viscosities of such volatile-rich residual melts (Thomas and Webster 2000; Thomas et al. 2006) that such H₂O- and Be-rich, highly mobile media are capable of moving over long distances through the host rock. Such fluids and H₂O-rich type-B melts are very mobile and can move away from the source of the formation along veins and channelways or along grain boundaries. Such reactive fluids and melts should act as agents of metasomatism. In addition, the Be concentration is so high that Be minerals such as beryl precipitate directly from the mineral-forming silicate-rich fluid or extremely H₂O-rich melt.

In the case of the B-, P-, and F-rich pegmatite systems, such as those at Ehrenfriedersdorf, the homogeneous type-B melts are not stable during subsequent cooling. Upon cooling from about 700°C down to room temperature, such H₂O-rich melts separate into their component minerals and fluids, which are more stable at lower temperatures. They decompose to a stable assemblage of mineral phases including quartz, feldspar, mica, and alkali phosphates such as beryllonite and herderite and others—all contained within the relict MI. The first phases that are formed are

molecular H₂O and, for example, boric acid, then the mineral phases orthoclase and topaz, and later other minerals including phosphates and fluorides. During this essentially fractional crystallization process, quartz is deposited on the inclusion wall (becoming indistinguishable against the host quartz phenocryst), and this forces the existing fluid and crystal phases into the center of the inclusion, producing the appearance of a fluid inclusion (see Thomas et al. 2006, 2008, Thomas and Davidson 2008). During trapping of the type-B MI in topaz of Wolfsgrün, the activity of silica is higher than that of the Ehrenfriedersdorf case, and the phosphorus concentration is low. Here, during cooling, the Be minerals crystallized in the order euclase, beryl, phenacite, and bertrandite and not as phosphates or borates. There are two different mechanisms for such high enrichment of Be: (1) extreme levels of crystal-liquid fractionation (~99% solidified) or alternatively (2) via melt-melt immiscibility (see Dolejš and Baker 2007a and b). The observed inclusion assemblage is more consistent with the second mechanism.

Moreover, as was shown by Thomas et al. (2006), the overall chemistry of the host granite has a dominantly peraluminous character, but it also must contain melts with strongly peralkaline composition given the peralkaline character of the type-B MI. The preservation of this peralkaline geochemistry is relatively rare because of overprinting by late-stage pneumatolytic alteration.

Short remarks on the speciation of beryllium

According to Černý (2002), substantial gaps in our knowledge in understanding the mineralogy of Be remain to be filled, namely in the speciation of Be in evolved, volatile-rich granite pegmatites. From our observation, Be is favorably enriched in the H₂O- and volatile-rich type-B melts. In the case of the very P-and F-rich melt system of the Ehrenfriedersdorf pegmatite, Be forms stable phosphates: beryllonite [NaBePO₄] and herderite [CaBe(PO₄)F] after decomposition of the H₂O-rich melt during cooling. In extremely F- and B-rich systems (e.g., beryl-quartz veins from Ehrenfriedersdorf, and miarolitic cavities from Wolfsgrün in the Eibenstock granite massif), Be forms hambergite [Be₂BO₃(OH, F)] and/or beryl [Be₃Al₂Si₆O₁₈], phenakite [Be₂SiO₄], and euclase [BeAlSiO₄(OH)] as stable compounds. In extremely B-rich melt patches (e.g., the Rangkul pegmatite field), hambergite crystallized directly from the melt at high temperatures. In the melt quenched at 600°C, we directly determined the complex $[BeF_2]^{2-}$ with Raman spectroscopy (Thomas and Davidson, submitted). In the same paper, we also show that in H₂O- and B-rich systems at high temperatures, Be is highly mobile as Be(OH)₂-forming bromellite [BeO] on cooling, which is maybe an intermediate phase.

In carbonate/bicarbonate-rich pegmatite-forming melt systems (Thomas et al. 2006), Be can form complex compounds of the type $M_2[Be(CO_3)_2]$ (M = Li, Na, K, Rb, Cs) together with alkali tetrafluoroberyllates. As an example, $K_2[Be(CO_3)_2]$ is readily soluble in H_2O and should go into the volatile-, carbonate-, and H_2O -rich melt fraction. The high contents of CO₂ and CO₃²⁻ in type-B MI in large beryl crystals from Orlovka in the Khangilay complex, Eastern Transbaikalia (Russia), make the existence of Be-carbonate complexes likely (Thomas et al. 2009a).

However, for a more complex understanding of the geochemical behavior of Be during magmatic-pegmatitic evolution, more studies on the solubility and stability of complex compounds of Be at various temperatures and pressures, especially including HDAC experiments combined with spectroscopic studies, are necessary.

Conclusions

This study suggests that melt–melt immiscibility processes in H₂O-saturated felsic melts may be an important factor not only in pegmatite formation, but in the partitioning and transportation of Be. Furthermore, the trapping of portions of these different phases as melt or fluid inclusions provides us with small but very informative samples of these fluids. The identification of daughter minerals and volatile concentrations in fluid and melt inclusions is essential for estimating the bulk and trace-element composition of the original trapped homogeneous fluids or melts. The Raman microprobe is a useful tool in this approach particularly for light components such as Be, B, OH⁻, or H₂O. However, utilization of this information requires a detailed understanding of what melts were trapped and at which stage of magmatic evolution the trapping occurred.

Melt inclusion evidence presented herein shows that Be can become extremely concentrated especially in the pegmatite-forming H₂O-rich melt fractions during extended fractional crystallization of evolved granite magmas and during late-stage melt-melt immiscibility. Furthermore, melt-melt immiscibility in residual magmas already enriched by fractionation is the critical factor in this most extreme enrichment. We have demonstrated that such enrichments in Be can be much higher than previously considered (e.g., >10,000 ppm Be). Such enrichments are needed to explain ore-grade concentrations of beryl in pegmatites and the occasional occurrences of giant beryl crystals (>1 m diameter) in some of these pegmatites.

Other factors are also important in the rather exotic compositions of immiscible melt fractions, including very high concentrations of B, which is a key mean for the accumulation of Be, due to the formation of stable Be–B complexes.

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