

# The formation of granitic pegmatites from the viewpoint of melt and fluid inclusions and new experimental work

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## ABSTRACT

*This paper focuses on critical issues in the formation of pegmatites, and is based mainly on the study of melt and fluid inclusions in minerals, since these provide vital evidence for liquid compositions and phase relations in nature. The development of analytical methods are a prerequisite for the understanding of pegmatite-forming processes, especially for the determination of water concentrations in melt inclusions, as it is now clear that water is a major component in the formation of pegmatites. Furthermore, we can demonstrate that complete miscibility between pegmatite-forming melts and water exist above 700°C and 1 kbar. Hydrothermal anvil cell experiments provide key evidence to support our deductions by demonstrating the contrasting high and low pressure behavior of peralkaline melt fractions.*

**Keywords:** Melt inclusion, fluid inclusion, Raman spectroscopy, HDAC experiments, peralkaline melt fractions.

## INTRODUCTION

Granitic pegmatites are remarkable rocks by virtue of their spectacular appearance, diversity of rare, and in many cases exotic minerals, the extreme enrichment of many rare elements such as Li, Be, B, F, P, Rb, Cs, REE, Nb, Ta, Zr, Hf, U, Th. According to Fersmann (1931) granite pegmatites are crystallization products of residual solutions of granites, which separated during solidification of granite magma. They are characterized by an arranged sequence of mineral associations, by a remarkable size of the individual crystals, by a simultaneous crystallization of different mineral phases, and by an enrichment of highly volatile constituent and diverse elements already mentioned.

Fersmann regards the pegmatite-forming process as part of a continuous physico-chemical process during cooling granitic magmas, starting from magmatic, and proceeding down to hydrothermal temperatures and pressures. Niggli (1920) emphasized the outstanding significance of water as an essential volatile component for the formation of pegmatites. In distinct contrast, other researcher believes that pegmatites are metamorphically or metasomatically generated (Barth, 1962; Gresens, 1967).

In this presentation evidence in favor of the igneous origin of pegmatites are given, based mainly on studies of melt and fluid inclusions, supported by some key experiments using the standard high temperature and pressure techniques, as well as reconnaissance experiments using hydrothermal diamond anvil cell (HDAC). However, we note that liquid-liquid immiscibility produces coexisting conjugate melt pairs with high density and viscosity contrast and the mobile volatile-rich melt phase can act as metasomatic agent over considerable distances.

## RESULTS FROM MELT AND FLUID INCLUSIONS

The study of melt and fluid inclusions provide critical evidence for liquid compositions and phase relations in nature. Progress in the study of the pegmatite genesis is only possible by the combination of classic observations, inclusion research, developing new analytical techniques, and experimental studies of key subsystems. The introduction of the Raman-based

method for the determination of water in small melt inclusions with diameters down to about 5  $\mu\text{m}$  (Thomas, 2000) has proved a very important technology. The development of the “Comparator Technique” greatly simplifies the analytical possibilities of confocal micro-Raman spectroscopy for the determinations of water in glasses and melt inclusions from the ppm level, to over 35 mass%, non-destructively in unexposed inclusions in a mineral matrix (Thomas et al., 2006a; Thomas and Davidson, 2006, 2007; and Thomas et al., 2007). This technique is also particularly important for extremely water-rich melt inclusions typical for pegmatites, which would loose  $\text{H}_2\text{O}$  on exposure.

Re-homogenization experiments on melt inclusions in quartz from a pegmatite in the Variscan tin-tungsten deposit at Ehrenfriedersdorf in the Saxon Erzgebirge, Germany, using the rapid quench technique (Thomas et al., 2000) demonstrate the formation of pseudobinary solvi at relatively low pressure, with bounded liquid-liquid immiscibility and multiple phase separation. Cooling and concomitant fractional crystallization from 700 to 500°C induced development of two immiscible conjugate melts with contrasting properties: an  $\text{H}_2\text{O}$ -poor (type-A) and an  $\text{H}_2\text{O}$ -rich (type-B) melt along the opening solvus (see Thomas et al. 2003, their Fig. 4). Production of two coexisting melts with extremely diverse chemical and physical characters is a very important factor in the evolution of pegmatite-forming melts and solutions (see also Thomas et al., 2006b). Moreover, liquid immiscibility need not be a single event; multiple exsolution events are possible as long as the aluminosilicate melts are  $\text{H}_2\text{O}$  rich. The recognition that three coexisting immiscible liquid phases (Veksler et al., 2002) may, in fact, be stable is an important advance over older, classic concepts of essentially linear pegmatite development. The evidence of such complex melt-melt immiscibility processes, as well as the experimental verifications strongly suggests continuous, as well as discrete processes during the crystallization of pegmatite-forming melts.

Critical to the understanding of pegmatite formation is the observation that the primary coexisting melt fractions produced by liquid-liquid immiscibility have different physical and chemical properties, and by

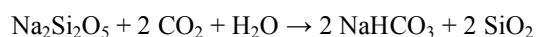
evolution along the two branches of the solvus boundary these different melts are characterized by an increase of the chemical contrast – increasing of the peraluminosity (type-A melt) versus increasing the peralkalinity (type-B melt) with cooling (Thomas et al., 2006c). The two principal immiscible conjugate melts are also characterized by strong differences in the wetting behavior and melt structure – highly polymerized peraluminous melts versus strongly depolymerized peralkaline melts. We also note strong differences in the enrichment of incompatible elements in the different melt fractions formed by immiscibility. As an example, zircons crystallized from peraluminous type-A melt, and peralkaline type-B melt fractions from an Ehrenfriedersdorf pegmatite show great differences in the major and trace element substitution, e.g., 2.4 vs. 15.1 mass% HfO<sub>2</sub>, respectively (Thomas et al., 2006c; Romer et al., 2007). Such immiscible melt fractions also have strong viscosity and density contrasts and can be efficiently separated from each other under gravity, or pressure filtration. Together, it can be seen that pegmatite formation involves at least two immiscible and radically different melts, and this observation is basic to understanding pegmatite crystallization.

Another important observation is the formation of melt emulsions. An emulsion is a heterogeneous system, consisting of at least two immiscible phases, one of which is dispersed in the form of droplets in the other. Generally, emulsions are unstable with respect to their component bulk phases, although the phases are in chemical equilibrium with any coexisting crystals. If there is a difference between the density of the dispersed and continuous phases, then under the influence of gravity, separation occurs. Since the phases also have pronounced differences in major and minor element concentration such a process of separation can produce an equivalent disconnect between the compositions of the new phases, which can explain the crystallization of extremely divergent mineral phases in very close proximity. However, separation of immiscible phases need not be complete, depending on the precise emplacement / cooling conditions, variable degrees of separation are possible, and these add further complexity to pegmatite formation. Rapid cooling may inhibit separation, but the low viscosity of the peralkaline melts may also make complete separation from the place of origin possible. In the Ehrenfriedersdorf granite-pegmatite system we noted small (up to 10 cm width) sub-vertical veins in the granite host, mainly composed of beryl and quartz containing only peralkaline type-B melt inclusions, in addition to CO<sub>2</sub>, CH<sub>4</sub>, and H<sub>2</sub>-rich high temperature fluid inclusions. We interpret this volatile-rich melt as a type-B melt separated near the solvus crest (see Figure 1 in Thomas et al., 2006c) at high temperatures around 700°C coming from a deeper region in the granite batholith. Another type-B melt also found in the Ehrenfriedersdorf pegmatite, was a melt fraction formed at low temperature near 600°: an F-poor, strongly peralkaline pegmatite-forming melt crystallizing

nepheline. Such crystals or corroded remnants up to 500 µm in size were found in pegmatite quartz and potassium feldspar. Coexisting melt inclusions show the strongly peralkaline character of this melt fraction, having an ASI of 0.42. Normally, due to the intense greisenization common in the final stages of many such systems, most evidence of the action of a former peralkaline fluid or melt are removed more or less completely. Therefore, the pegmatites and melt inclusions are often the only remnants of the melt-melt immiscibility in granite systems, and are thus critical to our understanding.

Recent observation on simple pegmatites composed principally of quartz and feldspar show that many are formed from H<sub>2</sub>O- and CO<sub>2</sub>-rich peralkaline aluminosilicate melts and fluids (Thomas et al. 2006b) as indicated by daughter minerals in fluid inclusions such as nahcolite, zabuyelite [Li<sub>2</sub>CO<sub>3</sub>], dawsonite (see Sirbescu and Nabelek, 2003a and b) and others, demonstrating high concentrations of alkalis and carbonates in water-rich melts at high temperatures. Such inclusions are observed in quartz and feldspar in many compositionally simple pegmatites (e.g., Pechtelsgrün/Vogtland, Zwiesel in Eastern Bavaria, Germany; Precambrian pegmatites from the Rønne granite, Denmark and others). Such bicarbonate- and carbonate-rich Fls (at room temperature, after cooling and decomposition) are probably derived from primary, high-temperature water- and carbonate-rich silicate melt inclusions, as suggested by the following equation:

Carbonate-rich silicate melt →



According to this reaction 30 mass% NaHCO<sub>3</sub> (we have often found equally high concentrations in such inclusions) corresponds to 21.5 mass% SiO<sub>2</sub>, which is deposited on the inclusion wall, and transform the primary water-rich melt inclusion into an apparent fluid inclusion.

An important corollary of this is a pressure increase inside such melt inclusions as a natural consequence of crystallization and cooling. Partial decrepitation of the inclusion may occur and a part of the melt or fluid may be squeezed out the inclusion, sometimes seen as a halo of tiny melt inclusions around the “mother inclusion”. Sometimes the pressure increase is as large as the inclusions are destroyed completely, especially at speciation changes at temperatures near the α-β transition of quartz, forming fish-bone muster trails of fluid inclusions, very typical in pegmatite quartz from the Borborema pegmatite field in Brazil (Beurlen, H., personal communication).

#### **REMARKS ON THE FORMATION OF GRAPHIC TEXTURES IN PEGMATITES**

Graphic-textured zones are very characteristic of most pegmatites, except for stockscheider pegmatites, and typically have very simple mineralogy, even in complex

pegmatites. Since most minerals in graphic quartz-feldspar intergrowths are very poor in primary melt and fluid inclusions the origin and genesis of this important part of the granitic pegmatites remain controversial (cf. London, 2005). However, very water-rich melt inclusions were found for the first time in graphic pegmatite quartz from Königshain, eastern Germany (Thomas et al., 2006b) showing that, at least here, liquid-liquid immiscibility is also an important step in pegmatite formation. Since then, these observations have been made at other pegmatites (Malkhan/Transbaikalia or Brandberg-Amis Complex/Namibia). Furthermore, these observations demonstrate that at the beginning of the pegmatite crystallization water is already an essential volatile component and that in relatively high concentrations. More details of the processes have come to light during the study of melt inclusions in quartz and feldspar in a Tertiary graphic pegmatite from the Island of Elba, Italy. Here, we observed evidence of all of the constituents of pegmatites, which are not normally found in graphic textured pegmatite (including highly water soluble Rb and Cs pentaborates), located along grain boundaries, elongated channels or tubes that form an interconnected geometry on which parts of the melt or fluid phases migrate away from the place of formation of graphic granite. The rare presence of these otherwise unpreserved structures show conclusively that such easily destroyed structures are already present at the first stage of pegmatite crystallization. Moreover, finding of such phases suggest that we need to look to finer-scale processes to complete our picture of pegmatite formation.

Thus we need to ask why stockscheider pegmatites do not show graphic textures? This is not a simple problem, but we would suggest that equilibrium versus non-equilibrium crystallization is a possible answer. Another possibility is a fundamental difference in the mineral-forming media at the start of crystallization: water-poor silicate melt in the case of graphic textures, versus extremely water-rich melt in the case of stockscheider pegmatites, since these may represent volatile migration into the apical parts of intrusions (cf. Oelsner, 1952).

#### NEW EXPERIMENTAL WORK

In addition to the ground-breaking studies of the meaning of the observed pseudobinary solvi for pegmatite genesis (see Thomas et al., 2000), an important focus of our work is understanding the formation and meaning of peralkaline melt fractions rich in water and CO<sub>2</sub>, which can also produce pegmatite-forming melts lacking significant amounts of other volatiles such as fluorine and boron. Here the key model is the simple peralkaline system NaHCO<sub>3</sub>-SiO<sub>2</sub>-H<sub>2</sub>O, and HDAC experiments and Raman studies on this system show clearly that their behavior is strongly pressure dependent. At high pressure a bicarbonate-rich solution can rise up from the lower crust to higher level without any reaction with the wall-rocks, and then at

low pressure these originally inert fluids transform into highly reactive fluids by the formation of sodium hydroxide, which vigorously reacts with the mostly peraluminous surrounding rocks.

These results imply that the peralkaline melt fractions have a greater importance than previously assumed. The significance of peralkaline silicate melts has been demonstrated by Mustart (1972): “addition of any amount of sodium disilicate to ab – w melts, results in development of some quantity of feldspar-saturated liquid containing 15 wt% H<sub>2</sub>O at 700°C, 21 wt% at 600°C, and up to 43 wt% H<sub>2</sub>O at 530°C. The precise amount of liquid produced depends on the amount of excess alkali silicate added.” Recently, in an experimental study, Preston et al. (2003) investigated the composition of the fluids in equilibrium with silica-undersaturated alkaline magmas in the model system Al<sub>2</sub>O<sub>3</sub>-Na<sub>2</sub>O-SiO<sub>2</sub>-H<sub>2</sub>O at 850°C and 1 kbar. The fluids in this study contain 40-50 mass% dissolved solids (SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and Na<sub>2</sub>O). The fluid and melt define a single solvus surface. The authors show that such fluids are capable of converting a granite to a nepheline normative composition (nepheline syenite) at low fluid:rock ratios. We would suggest such peralkaline melts and/or fluids are responsible for the metasomatic and greisenization effects noted in the final stages of pegmatite formation, and in areas distal to the pegmatite.

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