



The formation of peralkaline pegmatitic melt fractions: evidence from melt and fluid inclusion studies

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Abstract Despite extensive studies on granitic pegmatites over more than a century, their origin and genesis – igneous, metamorphic or metasomatic – remain controversial, particularly so for complexly zoned pegmatites. In this contribution we present evidence in favor of an igneous origin and provide insight into the major pegmatite forming processes. Our evidence is based primarily on fluid and melt inclusion studies from several pegmatite occurrences, including the use of experimental and several modern microanalytical techniques. The very existence of silicate melt inclusions in minerals of pegmatites proof their magmatic origin, even though many may be affected by late recrystallization and metasomatism. The experimental results presented herein show that pegmatite forming melts are very H₂O rich, low viscosity, high diffusivity, alkali-rich aluminosilicate melts, that provide excellent transport media for silica, alkalis, and trace elements, and growth media for large crystals. The results also suggest that melt-melt immiscibility processes in H₂O saturated felsic melts may produce peraluminous and peralkaline melt fractions coexisting with volatile dominated phases. It is shown that these processes may play an important role in pegmatite formation and mineralization, because of the fractionation of trace elements and increasing concentrations of the fluxing components. Particular emphasis is given on the characterization of the peralkaline melt fraction and its importance.

Keywords: melt and fluid inclusions, granitic pegmatites, magma immiscibility, peralkaline magma fraction

Resumo Não obstante estudos extensos e seculares em pegmatitos graníticos a sua origem e gênese – ígnea, metamórfica ou metassomática – permanece controversa, particularmente no caso de pegmatitos com zanação complexa. Neste trabalho apresenta-se evidências a favor de uma origem ígnea e discute-se os processos mais importantes envolvidos na sua formação. As evidências apresentadas fundamentam-se no estudo de inclusões fluidas e de fusão em várias ocorrências de pegmatitos, incluindo o uso de trabalhos experimentais e as variadas técnicas analíticas hoje disponíveis. A freqüente observação de inclusões de fusão silicática em minerais de pegmatitos constitui por si prova de sua origem magmática, mesmo que possam ter sido afetados por processos de recristalização e metassomatismo tardios. Os resultados experimentais mostram que, os magmas formadores dos pegmatitos tem baixa viscosidade, elevada difusividade, elevado conteúdo de H₂O, composição aluminossilicática rica em álcalis, características que conferem excelente capacidade para transporte de sílica, álcalis e elementos traço, e qualidade de meio adequado para o crescimento de grandes cristais. Os resultados experimentais sugerem também que processos de imiscibilidade a partir de magma felsico saturado em H₂O, podem gerar frações de fusões respectivamente peralcalina e peraluminosa, e a individualização de frações predominantemente voláteis. Evidencia-se que estes processos desempenham importante papel na formação dos pegmatitos e sua mineralização, devido ao fracionamento de elementos traços e crescente concentração de elementos fluxantes. A caracterização da fração peralcalina e de sua importância são enfatizadas neste trabalho.

Palavras-chave: inclusões fluidas e de fusão, pegmatitos graníticos, imiscibilidade de magmas, fração de magma peralcalino.

FORMATION OF PERALKALINE MELT FRACTIONS In this paper, we demonstrate that strongly peralkaline melt fractions can be formed by fractional crystallization and melt-melt immiscibility in peraluminous, water- and fluorine-rich granites and granite-related pegmatites. Through such processes the initially F and H₂O-rich granite magmas have their residual melt progressively more enriched with volatiles. At saturation, the melt may separate into two immiscible conjugate melt fractions, one of the

fraction shows increasing peraluminosity and the other increasing peralkalinity.

The coexisting melt fractions have strongly differing chemical and physical properties and, due to their high density and viscosity contrast, they will tend to separate readily from each other. The separation of a more mobile phase from the cumulate residuum causes an increase of the peraluminosity of the residuum and of the alkalinity of the mobile phase. Once separated, each melt fraction evolves independently in response to changing T/P/X

conditions and further immiscibility events may occur, each generating its own conjugate pair of melt fractions. The strongly peralkaline melt fractions in particular are very reactive and commonly react until equilibrium is attained. Thus, if the separated peralkaline melt fraction intrudes into the dominantly peraluminous host rock, with which it is in strong disequilibrium, it will react until equilibrium is attained. Consequently, the peralkaline melt fraction is commonly preserved only in the isolated melt and mineral inclusions.

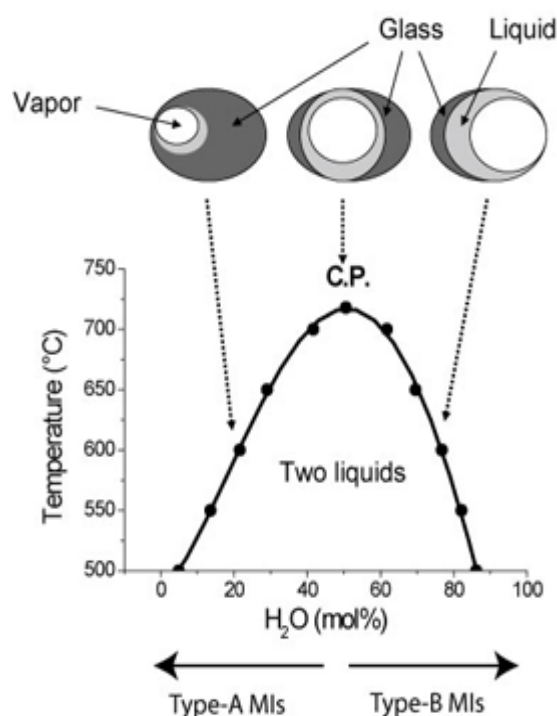


Figure 1. Schematic characteristics of three different types of melt inclusions (type-A, near critical, and type-B) at room temperature (after re-homogenization). The dotted arrows show schematic degrees of filling in relationship to the pseudobinary melt-H₂O system. Solid arrows show the relation to the respective inclusion types (from Thomas *et al.* 2006b)

According to our observation and research on melt inclusions (MI) and fluid inclusions (FI), at least three different mechanisms for generating alkaline melt compositions (or combinations of these) are possible: (i) crystallization and fractionation, for example, of topaz and muscovite, (ii) liquid immiscibility, and (iii) formation of alkali carbonates at high H₂O and CO₂ confining pressures.

Recent observation on simple pegmatites that are composed principally of quartz and feldspar show that many are formed from H₂O- and CO₂-rich peralkaline

aluminosilicate melt fractions and fluids (see Thomas *et al.* 2006a).

Raman spectroscopic studies of FI in quartz from different pegmatites show that nahcolite- and other bicarbonate- (KHCO₃) and carbonate-(Li₂CO₃ and Na₂CO₃)-rich FI are reasonably common. In some instances, the concentrations of bicarbonates and carbonates can achieve relatively high values, e.g., 20-45 mass%. Such inclusions are observed in quartz, feldspar, or beryl in many compositionally simple or complex pegmatites (e.g. Pechtelsgrün/Vogtland, Zwiesel in Eastern Bavaria, Germany; Precambrian pegmatites from the Rønne granite, Denmark; Orlovka, Transbaikalia; Tanco pegmatite, Canada; Naipa and Muiane, Mozambique; Borborema, Brazil and others (Fig. 2).

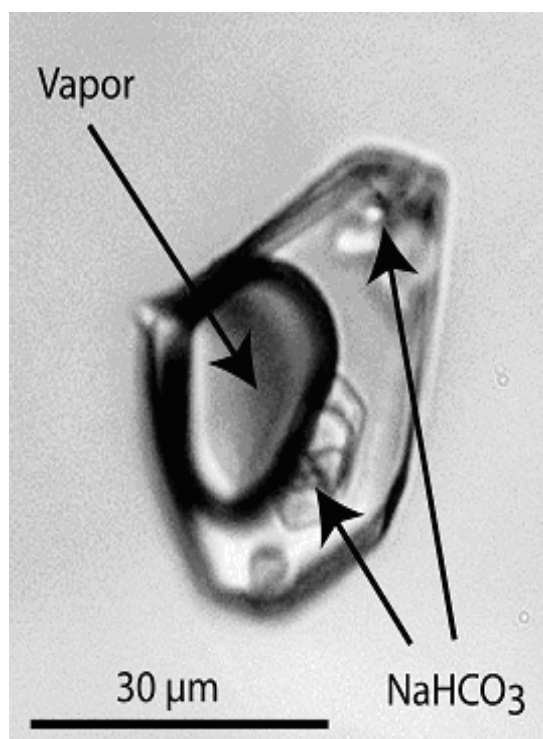
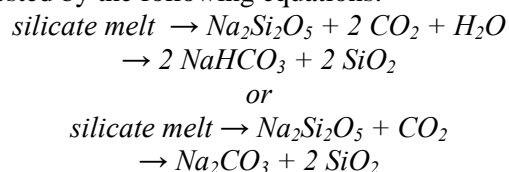


Figure 2. Nahcolite-rich FI in pegmatite quartz from Pechtelsgrün, Germany

Such bicarbonate- and carbonate-rich FIs (at room temperature, after cooling and decomposition) are probably derived during cooling from primary, high-temperature water-rich silicate melt inclusions, as suggested by the following equations:

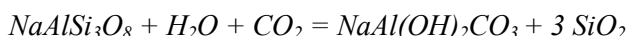
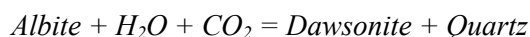


According to the first reaction 30 mass% NaHCO_3 reacts with to 21.5 mass% SiO_2 from the inclusion wall. As an example, in the Zinnwald tin-tungsten deposit we have found such nahcolite-rich fluid inclusions with 5 vol% boromuscovite and ~ 8 vol% SiO_2 crystallized out on the inclusion walls. The calculated bulk composition is given in the Table 1.

| | Mass% |
|-------------------------|-------|
| SiO_2 | 18.6 |
| Al_2O_3 | 2.5 |
| B_2O_3 | 0.8 |
| Na_2O | 7.3 |
| K_2O | 1.0 |
| F | 0.1 |
| CO_2 | 10.3 |
| H_2O | 59.4 |
| Sum | 100.0 |
| ASI | 0.2 |

Table 1 Calculated bulk composition of the nahcolite-rich and boromuscovite-bearing inclusions trapped at magmatic conditions

Inclusions from other simple pegmatites often only contain muscovite and/or dawsonite ($\text{NaAl}(\text{CO}_3)(\text{OH})_2$), beside bicarbonates. The formation of dawsonite during cooling can be explained by the following reactions:



SOME KEY EXPERIMENTS It is known (see Mustart 1972) that sodium disilicate $\text{Na}_2\text{Si}_2\text{O}_5$ is unstable in presence of CO_2 at room temperature, and will tend to decompose to sodium carbonate/bicarbonate and quartz, so we are unlikely to find sodium disilicate in FI at room temperature. Rather, the FI should be Na_2CO_3 - and/or nahcolite-rich, and both are a strong indication of the presence of sodium silicates at magmatic temperatures.

Thus, the finding of carbonates/bi-carbonates in high concentrations in FIs strongly suggests such reactions, and the existence of alkali disilicate melts under magmatic conditions.

These observations are consistent with the experimental results of Koster van Groos & Wyllie (1968) who demonstrated the coexistence of three analogous immiscible liquids in the $\text{NaAlSi}_3\text{O}_8$ - Na_2CO_3 - H_2O system, given suitable conditions of pressure, temperature, and bulk composition.

Recently, we observed CO_2 -rich, type-B inclusions (Fig. 3) characterized by four different phases at room temperature: a peralkaline glass (53 vol%) with 21.9 mass% H_2O , an aqueous liquid phase (22 vol%), a liquid CO_2 phase (25 vol%), and a CO_2 -vapor bubble. The bulk H_2O content is 36.5 mass% and the bulk density is 1.34 g/cm^3 .

Because of the tendency of such inclusions to decrepitate, the homogenization behavior could not be simply studied using conventional microscope heating stages. Therefore, we have performed simple HDAC experiments simulating the behavior of the type-B MIs during heating and cooling.

These experiments provide confirmation for the assumption that such four-phase MI with CO_2 -vapor, liquid CO_2 , H_2O -rich solution and peralkaline silicate glass (Fig. 3) were not formed by heterogeneous trapping – they were trapped as an homogeneous volatile-rich silicate melt. This would also be suggested by relatively constant phase relationships between inclusions.

Heterogeneous trapping should produce randomly variable phase relationships.

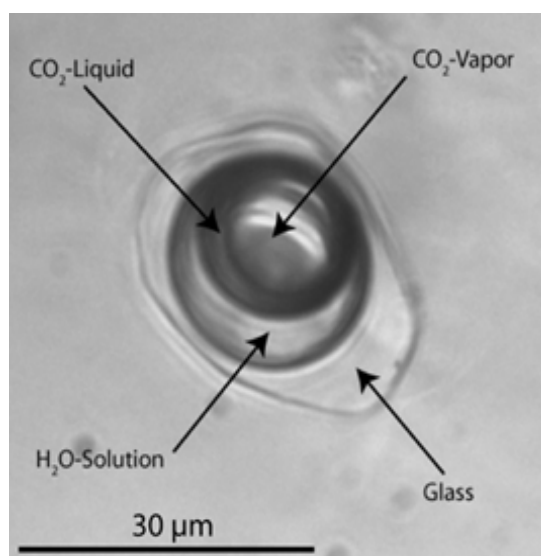


Figure 3. The figure shows a volatile-rich melt inclusion in pegmatite quartz from Zwiesel near Bodenmais, S-Germany. After homogenization at 650°C and a pressure of 3 kbar the homogenous, however, metastable glass decomposes during quenching into four phases. At room-temperature we observe a peralkaline water-rich glass, an aqueous solution as well as liquid and gaseous carbon dioxide. The phases in the inclusion are arranged according density

Based on the observations on natural FI and MI, some hydrothermal diamond-anvil cell (HDAC) experiments (see Bassett 2003) were performed which

show that the H_2O and CO_2 -rich peralkaline MI can be homogenized to a single homogeneous liquid phase at relatively low temperatures (625°C) and pressures (<3 kbar).

Below this temperature three fluid phases coexist: a CO_2 -rich vapor phase, an alkaline carbonate liquid and a small amount of a silicate melt (see Fig. 4).

At re-homogenization experiments on samples from the Borborema pegmatite field we observe

directly the change in speciation from CO_3^{2-} to CO_2 : during cooling and before complete solidification of the melt a CO_2 vapor phase is formed which, by increase of the volume, pushes parts of the melt into the surrounding of the inclusions via micro-cracks, forming a halo of tiny MIs around the "mother" inclusion. This process is similar to the phenomenon of second or resurgent boiling (see Burnham 1979).

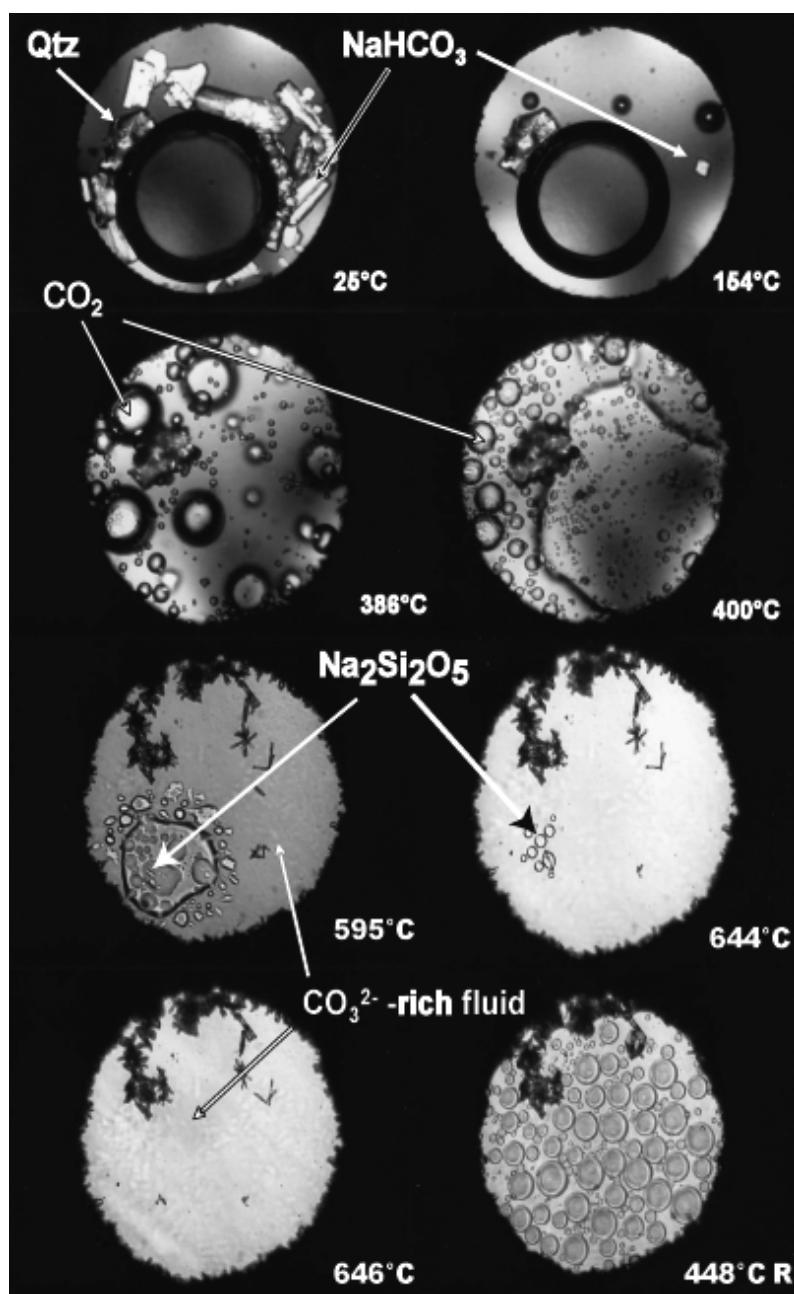


Figure 4. Photos of a HDAC experiment in the $\text{SiO}_2\text{-NaHCO}_3\text{-H}_2\text{O-CO}_2$ system – view into the sample chamber at different temperatures: Start conditions at 25°C (the sample chamber – formed by a Re gasket 0.05 mm thick with a hole of 0.300 mm in diameter placed between the diamond anvils – is filled with a small piece of a quartz crystal + nahcolite + nahcolite saturated solution + vapor bubble). The temperature of the nahcolite melting (T_m) is 154°C , corresponding to about 30 mass% NaHCO_3 . At about 386°C abundant CO_2 is released according to the reaction $2 \text{NaHCO}_3 \rightarrow \text{Na}_2\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O}$. A second carbonate-rich liquid phase forms at 400°C . This phase consumes quartz; all quartz is solved at 480°C , and forms an aqueous Na-disilicate fluid with a carbonate-rich fluid. The Na-disilicate fluid dissolves completely at 646°C into the liquid phase. Upon cooling to 448°C this homogeneous solution separates suddenly into two liquid phases. CO_2 is completely complexed up to this temperature. Gaseous CO_2 is only formed at temperatures lower than 400°C , above this temperature CO_2 is completely contained as carbonate/bicarbonate complexes. The needlelike crystals are rhenates/Re-oxides formed from the Re gasket

CONCLUSIONS The current studies on MI and FI demonstrate that as well as highly fluxed silicate

melts with high concentration of H_2O , F, Cl, B, and P, peralkaline melt fractions rich in H_2O and CO_2 can



also produce pegmatite-forming melts (see Thomas *et al.* 2006b). The low viscosity of the homogeneous fluid at about 650°C is demonstrated by the high mobility of small opaque Re-phases observed under the microscope during the HDAC experiments. The fast Brownian movement in the hydrothermal diamond anvil cell is a very good means of visualizing

this important fluid/melt property (see Thomas *et al.* 2006b).

Furthermore, the HDAC experiments show clearly that a silicate melt is completely soluble in a water-rich solution, demonstrating that there is a continuous transition between the two extremes (Roedder 1984).

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