Chemical evolution and origin of the Luumäki gem-beryl pegmatite (SE Finland)

RADOSLAW M. MICHALLIK
Cover photo: Like a puzzle, the different zones of the Luumäki pegmatite only together reveal the key to understand what processes were involved in its formation, leading to gem beryl-bearing pockets.

Author’s address: Radoslaw M. Michallik
Department of Geosciences and Geography
P.O.Box 64
00014 University of Helsinki, Finland
radoslaw.michallik@helsinki.fi

Supervised by: Professor Thomas Wagner
Institute of Applied Mineralogy and Economic Geology
RWTH Aachen University, Germany

Reviewed by: Scientiae Doctor Rainer Thomas
Division of Chemistry and Physics of Earth Materials
Helmholtz-Zentrum Potsdam - Deutsches GeoForschungsZentrum GFZ,
Germany

Reviewed by: Professor Axel Müller
Natural History Museum
University of Oslo, Norway

Opponent: Professor Robert Linnen
Department of Earth Sciences
The University of Western Ontario, Canada

ISSN 1798-7911
http://ethesis.helsinki.fi

Unigrafia
Helsinki 2021
Abstract

The Luumäki gem-beryl bearing pegmatite belongs to the miarolitic pegmatites, a comparatively rare and little studied pegmatite class. However, it is the miarolitic pegmatites that give rise to the scientific hypothesis about the involvement of aqueous fluids during pegmatite formation. The miarolitic cavities with their gem-quality minerals are often accompanied by a surrounding hydrothermally altered halo and this is considered evidence enough for the involvement of a separate aqueous fluid phase. The controversy regarding the involvement of a separate aqueous fluid was renewed in view of recent interpretations of giant crystal growth and graphic granite textures, which are both quite unique for pegmatites. And recent understanding favors a model where pegmatites are being formed by rapid cooling and crystallization from a volatile-rich melt, instead of very slow cooling of an undercooled, water-saturated granite melt.

Some argue that \( \text{H}_2\text{O} \) is essential for reducing the viscosity of granite melts and the element transport to form giant crystals in pegmatites, based on fluid inclusion studies and the water-saturated melt model proposed by Richard Jahns and Wayne Burnham. Recently this model has been redefined by studies on melt and fluid inclusions suggesting a melt-melt immiscibility with subsequent aqueous fluid exsolution, where one melt is haplogranitic and the other more enriched in volatiles, as suggested by Rainer Thomas. Others reason that refining of a melt, similar to the metallurgical process of zone refining, is key for pegmatite consolidation, and a separate \( \text{H}_2\text{O} \) phase plays a minor role if any at all. The proposed model is the constitutional zone refining (CZR) by David London. Both models have in common that the major mineral assemblage of a granitic pegmatite, namely quartz, feldspar and sometimes mica are the products of a haplogranitic melt, whereas more exotic phases, such as beryl, monazite, lepidolithe and tourmaline are the products of a coexisting melt enriched in incompatible elements. The enrichment of these incompatible elements is further advocated by the presence of volatiles such as \( \text{H}_2\text{O}, \text{F}, \text{P} \) and \( \text{B} \) within that coexisting enriched melt.

When pressure, temperature and chemical composition of a cooling melt allow, an aqueous phase can exsolve and interact with the crystalline surroundings, thus contributing to the crystallization of certain phases. This is especially the case in miarolitic pegmatites, in which aqueous separation mostly occurs during the formation of the miarolitic pockets at the end of pegmatite consolidation. The aim of this study was to demonstrate that an aqueous phase separation takes place and to determine at which conditions this event took place.

My study supports the view of a separate aqueous phase in the late stage of pegmatite crystallization and demonstrates that in the case of the Luumäki pegmatite, an aqueous phase separated at the onset of pocket formation at about 380 °C and 1.2 kbar. Furthermore, it is shown that a pegmatite melt is very heterogeneous and within the same pegmatite body one miarolitic pocket can clearly show evidence for a hydrothermally dominated system, while another represents a
magmatic dominated process of formation without clear evidence of the involvement of an aqueous fluid. Also, pegmatite bodies within the same geological framework can differ in their appearance, showing that within a small area of just a few hundred of meters one pegmatite body can show extensive hydrothermal activity whereas the other lacks any evidence of an aqueous fluid separation.

This study also demonstrates that laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) is a powerful tool for in-situ quantitative measurement of fluid inclusion trace element concentrations and is very useful in pegmatite research. The data allowed to verify the magmatic origin of the fluids found by successfully quantifying the halogens Cl, Br and I. The trace element data also show evidence of moderate-saline fluids separating into a low-saline carbonic-aqueous and a high-saline aqueous fluid phase. Although the separation of a moderate-saline aqueous fluid into a carbonic-aqueous phase has been reported earlier, previously such coexisting high-saline brines were considered to originate from highly H₂O-enriched, still water-undersaturated silicate fluids/melts. In view of the results of this study that understanding might have to be reconsidered.

The research of pegmatites and their fluid inclusions is a somewhat complicated endeavor, similar to solving a puzzle, in which most pieces appear very similar to one another, and many more studies need to be conducted to solve such a puzzle. Powerful analytical methods such as in-situ fluid inclusion analysis by means of LA-ICP-MS is a step in the right direction and will hopefully encourage many more to engage in this tedious, yet gratifying search for the bigger picture by looking at the small individual pieces in greater detail as ever before.
Acknowledgements

This study would not have been possible without the support of my supervisor Prof. Thomas Wagner, who had the initial idea for this project, and supported me in gaining the required knowledge and skills where necessary to apply all the methods used for this project. In an equally grateful manner, I also thank Prof. Tapani O. Rämö for his support throughout the years of my studies and the many insightful discussions as well as the many ways in which he takes care of the wellbeing of those responsible for.

The very constructive and educative discussions with Dr. Tobias Fusswinkel as well as his support in LA-ICP-MS analysis and fluid inclusion studies were essential for the successful data acquisition for this study. His knowledge and help in the interpretation of fluid inclusion data is invaluable. His friendship and the many hours spent together outside the project helped to clear my mind for the tasks that lied ahead.

Pasi Heikkilä deserves my special thanks for he is the one, who brought me to the Helsinki University in the first place, where I could start my project as well as develop my skills as electron microprobe operator. His knowledge of the Finnish geology, the Luumäki pegmatite history and mineralogical knowledge cannot be surpassed by any other Finnish geologist.

The support and mentoring by Dr. Jussi S. Heinonen as well as his insight into magma petrology together with his friendship and the valuable time spending together climbing was one of the reasons I did not have too many worries when writing manuscripts or calming the mind for the task of answering reviewer’s constructive criticism.

Many insightful discussions with Dr. Aku Heinonen widened my knowledge and at times the understanding of my project for which I am very thankful. I am looking forward to continuing to work together with such a bright and diligent geologist.

I also want to express my gratitude and thanks for the friendship of our former research group members, Stefan Andersson, Henrik Kalliomäki and Gabriel Berni, who were there to cheer me up and went with me through the difficult times of the project but also through the cheerful moments of the life of a PhD-student.

Without the samples provided by Timo Rönkä, the owner of the Karelia Beryl Oy mining company in Luumäki, and by the Finnish Museum of Natural History as well as by the drill core archive of the Geological Survey of Finland (GTK), this project would have lacked some of the most important puzzle pieces.

I thank the KH Renlund foundation for the financial support of the project throughout 3 years and 9 months, without which this project would not have been possible.

Many of the laboratory tasks would prove to be difficult without the support of our current laboratory stuff, Nikolaos Karampelas, Juhani Virkanen, TujaVaahtojärvi, Hanna Reijola and the already happily retired Helena Korkka, all of which were also my dear co-workers.

Lastly but most importantly and mostly valued is the love and support of my dear wife Heli Michallik, who knows perfectly how to apply gently enough pressure to keep me productive and not give up during difficult times, always calming me down but putting on enough heat so things will get done, one puzzle piece at a time.
“...Dass ich erkenne, was die Welt
Im Innersten zusammenhält. “

“...To understand whatever holds
The world together in its inmost folds.”

- Johann Wolfgang von Goethe (In the play “Faust”)
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List of original publications

This thesis is based on the following publications:


The publications are referred to in the text by their roman numerals.

Author’s contribution to the publications

I:  T. Wagner initiated the idea of the project. R. M. Michallik has conducted the field studies with assistance by T. Wagner. R. M. Michallik has helped to prepare the samples and made the electron microprobe analysis independently. T. Fusswinkel has supported R. M. Michallik with the LA-ICP-MS analysis and data reduction. J. S. Heinonen supported R. M. Michallik with the Rayleigh fractionation modeling. P. Heikkilä and T. Wagner supported R. M. Michallik with interpretation of the geochemical data.

II:  R. M. Michallik made the sample preparation, electron microprobe analysis, and the LA-ICP-MS analysis as well as the data reduction independently. Laboratory staff supported R. M. Michallik with loss of ignition measurements. T. Wagner, P. Heikkilä and T. O. Ramö assisted R. M. Michallik with interpretation of the data. P. Heikkilä provided sample material and insightful background information of the Luumäki pegmatite.
III: R. M. Michallik made the sample preparation and microthermometry independently. Raman spectra and LA-ICP-MS measurements as well as data reduction were assisted by T. Fusswinkel. Interpretation of the data was supported by T. Fusswinkel and T. Wagner.

**Abbreviations**

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<thead>
<tr>
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<th>Description</th>
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<tr>
<td>BT</td>
<td>Biotite</td>
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<td>EMPA</td>
<td>Electron microprobe analyser</td>
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<td>FIA</td>
<td>Fluid inclusion assemblage</td>
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<td>FSP</td>
<td>Feldspar</td>
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<td>KFS</td>
<td>Potassium feldspar</td>
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<td>LA-ICP-MS</td>
<td>Laser ablation-inductively coupled plasma-mass spectrometry</td>
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<tr>
<td>LREE</td>
<td>Light rare earth elements</td>
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<td>QTZ</td>
<td>Quartz</td>
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<td>REE</td>
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1 Introduction

Pegmatites are some of the most intriguing igneous rocks found within the Earth’s continental crust. Penetrating the surrounding bedrock formations, they often resemble dikes or veins that differ greatly from their host rock units in composition and structure. While surrounding igneous rocks are generally homogeneous in appearance, pegmatites are very heterogeneous in terms of crystal size and variation of mineral assemblage. Often a fine- to coarse-grained rim is observable, called ‘aplitic granite’ in case of a granitic composition, followed by a gradual coarsening of the grains with individual crystals reaching up to meters in size (Černý 1991; Simmons 2007). The usually observable graphic intergrowth of quartz and alkali feldspar in these coarser zones, is unique to pegmatites. The intergrowth feature of these “fancy rocks” (Jahns 1953) led to the term “pegmatite”, meaning “to make stout or rigid by binding together” (Autenrieth 1958; London 2008).

Although most pegmatites are typically granitic in average composition, the pegmatite veins and dikes commonly contain accessory minerals of exotic chemical compositions, which are often present in colorful shapes and variations, and as already mentioned, at times as large specimens up to several meters in size. Pegmatites are rich in incompatible elements such as Li, Be, B, F, P, Rb, Cs, REEs, Nb, Ta, Zr, Hf, U, Th, just to mention a few (Linnen et al. 2012; Morteani et al. 2000; Sweetapple and Collins 2002). Apart from the appreciation for the beauty and gem-quality, known already in ancient Egypt 2200 BCE (The Precepts of Ptah-Hotep, Horne 1917) and possibly even earlier in human history, many of these minerals are essential in today’s modern technologies. They are used as a source for the glass and ceramic industry, but also increasingly for strategic energy and information technology applications. For these reasons pegmatites and their origin have received particular economic importance in recent decades (Linnen and Cuney 2005; London 1986b; Lyckberg 2006; Simmons 2007).

Geologists ever since wondered about the formation processes of pegmatites and their large and beautiful crystals. Many speculations and ideas emerged throughout the last two centuries, with petrogenetic models ranging from mantle-derived to crustal anatectic, from orthomagmatic to hydrothermal, from intrusive to lateral secretion (London 2008). Only after starting to investigate the crystals themselves, and in particular their crystallization behavior in experiments, their chemical compositions, zonations, fluid and melt inclusions within them, and the small details revealed through geological micro-analysis, speculations were replaced by deductive physical-chemical models (Jahns 1955; Jahns and Burnham 1957, 1958; Fenn 1977; Icenhower and London 1996; London 2008; Tuttle and Bowen 1958). Already since the 1920s a broader picture has started to emerge, leading to a profound understanding of the origin as well as several plausible hypotheses of pegmatite formation (London 2012). In time, thanks to a better understanding of physico-chemical and thermodynamic phase relationships on a microscopic level and advanced analytical tools to investigate the mineral record, two competing models of pegmatite formation were proposed, which are currently the most widely accepted models in the geological community. These two competing models of formation are the ‘Jahns-Burnham model’ proposed by Richard Jahns and Wayne Burnham, and the ‘constitutional zone refining (CZR) in the boundary layer’ approach by David London. The difference in the two models lies in the potential role of a separate aqueous fluid phase during pegmatite consolidation.
1.1 The Jahns-Burnham model for pegmatite petrogenesis

Richard Jahns and Wayne Burnham suggested in 1969 an aqueous fluid-driven transport medium for elemental constituents during pegmatite consolidation. The model was based on the accepted understanding that a pegmatite body is a restricted system, crystallizing in-situ from a magma that is restricted regarding interaction with the surrounding rocks to only exchanging material outwards. In other words, nothing can enter the system from the surrounding rocks, but material from the pegmatite can interact with the host, for example by metasomatism. In the 1950s, Jahns conducted a series of experiments of which only one was published later by Wyllie (1963). These experiments formed the basis for his model of pegmatite formation through water-saturated granitic magmas. Despite the lack of data for distribution coefficients of Na and K in glass and silica melt at that time, Jahns understood that diffusion of these elements through a dry silicate melt would be too slow a process to be solely responsible for the mass transport necessary to grow the giant crystals as found in pegmatites (London 2008). He attributed the transport of the necessary building blocks for the large crystals in pegmatites to a separate coexisting volatile phase in form of a vapor phase or, as he preferred to call it, a supercritical aqueous fluid. Interestingly, despite the lack of data and although describing water as the main component of such a supercritical aqueous fluid, he intuitively did not exclude the possibility of additional “appreciable quantities of dissolved volatile constituents”. He conceded that such volatile constituents, if present, could have an effect on the behavior and transport of elements (Jahns and Burnham 1969). Through his experiments he also acknowledged to some extent the importance of a thermal gradient within the pegmatitic system, although no attention was paid to its role in elemental transport.

The model of an aqueous transport of building blocks or elements is still used today. Some studies suggest the development of graphic granite texture as well as the formation of coarse-grained K-feldspar-quartz intergrowths as the onset of an aqueous fluid separation in pegmatite consolidation (Burnham and Nekvasil 1986; Jahns 1982; Nabelek et al. 2010). Noteworthy are experimental as well as natural system studies of the more complex rare-element pegmatites in the last decades in the effort to understand such possibly involved aqueous fluids in the petrogenesis of pegmatites. These studies describe the solubility of incompatible elements, such as REEs, Y, Zr, Hf, Nb and Ta in the presence of additional volatiles, such as P, F, CO$_2$ and H$_3$BO$_3$ along with H$_2$O, and have led to a much better understanding of the behavior of fluxing elements, their effect on granitic melt systems, mineral/melt partitioning and transport in aqueous fluids (Chakraborty et al. 1993; Evensen and London 2002; Icenhower and London 1995, 1996; Loges et al. 2013; London and Morgan 2005; Migdisov et al. 2009, 2011; Timofeev et al. 2015, 2017).

The understanding of an aqueous transport as a valid explanation of pegmatite forming processes in view of recent fluid and melt inclusion studies has been redefined by Rainer Thomas and colleagues (Thomas 2002; Thomas and Davidson 2013; Thomas et al. 2000, 2009b, 2012). In Thomas’ model the role of an aqueous phase is not responsible for the formation of the main textural features, such as graphic granite intergrowths and different zonation of the pegmatite but plays nevertheless an important role in petrogenetic processes and element transport. The water content in the initial melt can contain up to 25 mass% in peralkaline melts at low pressures up to 2 kbar (Thomas et al.
This water does not exsolve initially into a separate phase but at temperatures below 750 °C a two melt system develops, in which one melt is more peraluminous-granitic in composition (type-A) and the other melt is a more peralkaline supercritical fluid (type-B) enriched in OH⁻, volatiles and exotic components (Thomas et al. 2000, 2019). The initially in the melt dissolved OH⁻ and CO₃⁻ are then dissolved as a hydrothermal fluid (type C) with first H₂O and at slightly lower temperatures also with CO₂, increasing the volume and thus the pressure, forming a very dynamic melt-fluid system (Thomas et al. 2009b). The dynamic melt-fluid system is melt dominated throughout the pegmatite-forming stage down to temperatures around 500 °C, when it changes gradually with decreasing temperature to a hydrothermally dominated system (Thomas et al. 2000).

1.2 The London model for pegmatite petrogenesis

David London and coworkers have performed a series of experiments based on London’s initial studies of fluid inclusions of the Tanco rare-element pegmatite (London 1986b, 1987; London et al. 1987, 1989). These experiments yielded novel results by reproducing zonation, mineralogical fabrics and fractionation trends as observed within natural pegmatites, thus pointing towards the experimentally based argument that pegmatites are crystallizing from a water-undersaturated melt. The processes leading to the reproduction of key features in natural pegmatites in these experiments are disequilibrium growth from metastable supersaturation, fractionation of melt due to increases in fluxes such as B, P and F, and changes in nucleation and growth rates. Undercooling of the pegmatite melt plays a key role in driving pegmatite crystallization and furthermore constrains timescales of pegmatite consolidation to very short times in the range of days to months (London 2008, 2018). London explains the undercooling of pegmatitic melt by several 10s to few 100s of °C with its emplacement away from its source pluton (and the thermal aureole surrounding such) into much cooler host rocks. London thus pinpoints that the onset of pegmatite crystallization occurs at temperatures as low as about 450 °C. When hydrous haplogranites become undercooled by such a high degree, a significant supersaturation as well as delay in nucleation takes place, and alkali feldspar crystal growth rates are at their maximum (Fenn 1977). This leads to the formation of the outer zones and aplitic layers, where the undercooling and supersaturation is most pronounced and unidirectional solidification takes place. Crystallization begins at the margins of the cooling body and follows isothermally the temperature gradient as the pegmatite cools towards its center. The crystal nuclei formed at that solid/melt interface are more prone for survival, and oriented growth towards the inner parts commences.

London (2008) argues that the viscosity of a melt at these conditions is too high to let even aqueous bubbles migrate upwards faster than at a rate of 0.3 mm/yr, and according to his model, solidification of pegmatite bodies takes place rather fast when a hot pegmatite melt intrudes into a much cooler host rock, within only days or months. Thus, convection and aqueous fluids are not an effective means of building block transport. Instead, the formation of the inner zones with coarsening crystals so typical for pegmatite textures is explained by the accumulation of fluxing elements in a boundary layer that follows the temperature gradient. The fluxes lower the viscosity of that layer so that diffusion for a rapid crystal growth is facilitated (London 2009). London suggested a process, commonly known in metallurgy, to be responsible for the accumulation of fluxes
and incompatible elements within such a melt boundary layer; constitutional zone refining (CZR) (London 1992).

In this process, a narrow zone adjacent to the surface of the growing crystal is continuously enriched in excluded components, or in other words, compatible elements are diffused towards the crystal face and incompatible components away from the crystal face, remaining in the boundary layer. Consequently, this layer becomes more and more enriched in the fluxing components and incompatible trace elements not incorporated into the simple rock-forming minerals such as feldspar(s) and quartz, which are the main crystallizing phases during pegmatite consolidation. The bulk melt remains free from backwards diffusion of these fluxes due to its viscosity at the rapid time frame in which pegmatites crystallize. However, the bulk melt continues to diffuse essential building blocks through the boundary layer liquid and promotes the growth of e.g. feldspar(s) and quartz into large and relatively pure crystals that are free from including materials, which are typically observed in pegmatites. Once all the bulk melt is consumed, crystallization occurs from the boundary layer liquid itself, leading to the chemically diverse and exotic mineral assemblages, which are typically found in the innermost zones of natural pegmatite bodies. The formation of the pocket zone, common in shallow miarolitic pegmatites, is attributed to crystallization from such a final boundary layer consisting of a flux-enriched aluminosilicate liquid. Such aluminosilicate liquid, highly enriched in H$_2$O, fluxes, and exotic elements, will initially have a low viscosity, which increases sharply as the fluxes and exotic elements are removed by crystallization of accessory mineral phases. While the fluxes disappear from the liquid, an aqueous fluid is exsolved at the final stages of pocket formation as the remaining aluminosilicate material quenches to a colloidal semisolid, which inverts to clay, thus forming the beautiful gem-quality crystals in clay-filled miarolitic pockets. The exsolved aqueous fluid can then be transported towards the host rock, inducing hydrothermal alteration halos in the contact zone. In this model, the aqueous fluid, if it exsolves, plays only a minor role at the very end of pegmatite consolidation.

1.3 Objective of the study

The scientific debate about pegmatites either forming from H$_2$O-saturated melts or from an H$_2$O-undersaturated melt where the H$_2$O-content has little influence on the formation is still ongoing and unresolved. However, in view of today’s experimental and field evidence, it can be concluded that most of the textural features of pegmatites, such as giant crystals and graphic granite stem from a magmatic dominated process involving a water-undersaturated melt (Fenn 1986; London 2013, 2018). The underlying argument for this conclusion is that geochemical fractionation within a pegmatitic melt by means of an aqueous fluid alone through a highly viscous silica melt cannot reach the required concentrations of incompatible elements in inner pegmatite zones that are necessary for giant crystal growth as well as exotic mineral phase precipitation. It appears however, that there exists field and experimental evidence also for a coexisting aqueous fluid in final pegmatite crystallization stages as shown by fluid inclusion studies (e.g. London 1986a; Maneta and Anderson 2018; Thomas et al. 2009, 2012; Veksler et al. 2002). It is not unlikely that different pegmatites are formed by different petrogenetic processes, especially the still somewhat enigmatic miarolitic pegmatites.

Recent in-situ studies of magmatic-hydrothermal systems in granites with Sn-W deposits, skarn deposits and porphyry intrusions
with Cu-Au-Mo mineralization contributed to a better understanding of their chemical evolution (e.g. Audétat 2019; Klemm et al. 2007, 2008; Rusk et al. 2004; Ulrich et al. 2001; Williams-Jones et al. 2010). Especially laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) has advanced so that quantitative measurements of individual fluid inclusions within their textural context in quartz, and their concentrations of major elements, metals and halogens down to ppm level is possible (Audétat et al. 1998; Fusswinkel et al. 2018; Hammerli et al. 2013; Rauchenstein-Martinek et al. 2014; Ulrich et al. 2001). Utilizing this powerful tool makes it possible to get a new insight into the fluids involved in pegmatite formation and the key processes that control fluid chemistry, fluid phase separation and fluid-rock interaction.

The miarolitic beryl-bearing Luumäki pegmatite is chemically not very complex and with its relatively primitive mineralogical assemblage of mainly K-feldspar, plagioclase, quartz and mica, together with some fluorite, topaz and beryl as the more exotic components, it represents an excellent natural study case for testing models for formation of miarolitic pegmatites. My main objective was to determine whether an aqueous fluid did play a role and if so, at which point in the pegmatite consolidation stage, thus helping to understand better the key processes involved in miarolitic pegmatite forming processes. To address this main objective, geochemical investigation of the magmatic to hydrothermal evolution of the Luumäki system was essential. For instance, the origin of the pegmatite melt was successfully traced back to originate from the rapakivi granite by comparing trace and rare earth elements in different minerals, such as feldspars, mica, quartz, and fluorite. The magmatic evolution of the inner zones of the pegmatite was reconstructed and the data were analyzed for signals indicating the involvement of a hydrothermal fluid. This was addressed by successful fractional crystallization modelling, explaining the incorporation of some incompatible trace elements into K-feldspar, one of the main mineral phases in all pegmatite zones. Furthermore, the chemistry and origin of the fluids involved had to be determined using fluid inclusion studies, in order to understand, whether they are of magmatic or secondary post-magmatic hydrothermal origin.

2 Geological setting

The Luumäki pegmatite system, consisting of at least two pegmatite bodies, is located about 25 km west-southwest of the town of Lappeenranta in the Luumäki district on the small island of Kännätsalo in SE-Finland (Fig. 1). The granitic pegmatites are situated within the locus classicus late Paleoproterozoic Wiborg rapakivi granite batholith. The Wiborg batholith is an anorogenic (A-type) granite complex that intruded into the Paleoproterozoic Svecofennian metamorphic basement rocks and is composed of several granitic units (Rämö and Haapala 2005). The main unit of this batholith is the wiborgite granite with its typical ovoid-shaped K-feldspar up to several cm in size mantled by a few mm thick plagioclase (oligoclase) within an interstitial matrix composed of mainly quartz, feldspar, biotite, hornblende, fluorite and oxides (Rämö and Haapala 1995, 2005). Other smaller granitic units within the Wiborg batholith are dark wiborgite, pyterlite and equigranular granite. The difference between wiborgite and dark wiborgite is that the latter has additionally plagioclase megacrysts but less alkali feldspar megacrysts. The pyterlite units lack mainly hornblende and contain instead biotite as a ferromagnesian mineral, and the plagioclase mantles around the K-feldspar ovoids are not as frequent as in
Figure 1. Geological map of the Luumäki pegmatite system as reconstructed from field mapping, drill core logging and GPR radar as well as previous exposure on the surface. (A) Position of the Luumäki pegmatite within the NE-flank of the Wiborg rapakivi batholith in SE Finland. (B) Position of the beryl bearing Luumäki N and the barren Luumäki S outcrops relative to each other. (C) Luumäki N outcrop with previously exposed quartz core and miarolitic pockets. Core sample locations as well as surface sample sites are shown. (D) Cross section (along line A-B) showing the interpretation of the geometry and pegmatite zones. Modified from Lahti and Kinnunen (1993), and Michallik et al. (2017, 2019, 2020).
wiborgite and dark wiborgite units. Equigranular granite units lack the development of K-feldspar ovoids and are found mainly at the periphery of the batholith (Rämö and Haapala 2005). The youngest units of the Wiborg batholith are leucocratic topaz-bearing alkali feldspar granites often containing miarolitic cavities in their upper parts, and pegmatite zones such as the Kymi topaz granite stock and the Eurajoki stock (Berni et al. 2017; Haapala 1995, 1997; Haapala and Lukkari 2005; Lukkari and Holtz 2007). Pegmatites are rare within the rapakivi granites, with some pegmatites containing gem-quality smoky quartz, topaz and beryl (Lyckberg 2006). The rapakivi granites, when compared to other granitic suites are enriched in Si, K, Rb, Ga, Zr, Hf, Th, U, Zn, and REEs with a relative enrichment in LREE, a negative Eu-anomaly and high Fe/Mg, K/Na and Rb/Sr ratios (Haapala and Lukkari 2005; Rämö and Haapala 1995, 2005).

The Wiborg rapakivi batholith in SE-Finland is late Paleoproterozoic in age with a minimum duration of magmatism at 1642-1630 Ma (Rämö et al. 2014; see also Vaasjoki et al. 1991). However, more recent studies distinguish between the age of the ovoids and the interstitial matrix based on U-Pb age determination in zircons with the youngest age regarded as the final crystallization age (from zircons within the interstitial matrix) to be at a weighted mean of 1628 ± 2.5 Ma (Heinonen et al. 2016a, 2016b). In comparison, dating of the Luumäki pegmatite by the U-Pb method on monazite from the inner zone resulted in an age of 1628 ± 4 Ma (Rämö and Lahti 2008).

The Luumäki pegmatite system is exposed in two pegmatite outcrops at the surface (Fig. 1B). The larger pegmatite is referred to as Luumäki N (north) and is about 30 m wide at its thickest exposure and about 80 m long, slightly dipping to the SE at a shallow angle. This larger body shows abundant miarolitic pockets up to several meters in size (Fig. 2A). It has been actively mined since 1982 with several operational interruptions and is currently operated by the company Karelia Beryl Oy (Lyckberg 2006). Most of the inner zones and the quartz core have been already mined out. Documentation of the pegmatite has been carried out in 2007 by the Geological Survey of Finland (GTK) by means of 16 diamond drill cores, which are stored at the GTK drill core archive. The pegmatite has been described as belonging to the topaz-beryl type from the niobium-yttrium-fluorine (NYF) family of the miarolitic rare-element pegmatite class (Černý and Ercit 2005; Lahti and Kinnunen 1993). The smaller body is referred to as the barren Luumäki S (south) pegmatite and is about 250 m to the south and about 6 m in diameter at the surface outcrop (Fig. 2D). The Luumäki S pegmatite lacks visible miarolitic cavities and no mining operation is carried out at this site. Both pegmatite bodies show well developed zones, which are an equigranular border zone, graphic-granite wall zone, very coarse-grained intermediate zone, and quartz core zone (Lahti and Kinnunen 1993). The transition between the host rock and the border zone is gradual with an up to few tens of cm wide change from the ovoid dominated host rock rapakivi granite in some places directly into the wall zone (Fig. 2B), but mainly into an equigranular granite zone, which then gradually develops into the graphic granite wall zone.

The mineral composition of the Luumäki pegmatite is relatively primitive with the main components being quartz, K-feldspar, albite, biotite, and within the intermediate zone accessory topaz, fluorite, and magmatic common beryl. Miarolitic cavities are found mainly in the inner zones and the quartz core zone, and consist of euhedral to hypidiomorphic smoky quartz, gem-beryl (heliodor) and some K-feldspar embedded in a mixture of reddish
clay minerals and quartz. One distinct miarolitic pocket has been also reported from the periphery of the pegmatite close to the host rock rapakivi granite. Aggregates of two micas together with plagioclase and quartz have been found from the barren Luumäki S pegmatite.

Geologically, the Luumäki pegmatite system is somewhat similar to the Volynian pegmatite system located near the town of Volodarsk-Volynski in Ukraine, which is also a gem beryl-bearing pegmatite system situated within a Proterozoic rapakivi-like granite bedrock (Lyckberg et al. 2009). However, the Volynian pegmatite system is much more complex and extensive in comparison to the two Luumäki pegmatites, with numerous pegmatites and pegmatite clusters. In these pegmatite clusters the rich chamber-type pegmatites, containing single giant pockets with gem mineralization, are typically situated in a contact zone between the granite and adjacent mafic rocks. In comparison, the Luumäki pegmatite system, consisting of only two pegmatite bodies found thus far, is situated entirely within the surrounding rapakivi granite and contains several smaller gem mineral-bearing pockets. These distinct differences make a direct comparison between both systems difficult, particularly because no modern mineralogical, geochemical and fluid inclusion studies of the Volodarsk-Volynski system are available.

3 Sampling and methods

3.1 Sampling

Samples of the different pegmatite zones as well as the surrounding host rapakivi granite were collected during two field campaigns in 2013 and 2014. The second field campaign was conducted after exposing new parts of the pegmatite when the open pit mine has been further extended to the
SE by the mining company. Samples were also taken from the 16 drill cores stored at the GTK. In addition, gem-beryl samples have been provided by the mine owner Mr. Timo Rönkä. Magmatic common beryl samples were obtained from the Museum of Natural History, Helsinki University. Several gem-beryl samples from the first gem-beryl bearing pockets found in the 1990s as well as some magmatic common beryl samples were acquired from the private collection of Mr. Pasi Heikkilä.

3.2 Trace element analysis
Chemical analysis of the minerals feldspar, biotite, quartz, fluorite and beryl have been carried out at the Mineralogical Laboratory of the Department of Geosciences and Geography at the Helsinki University. The major and minor element analysis for feldspars, biotite and beryl was performed with a JEOL JXA-8600 Superprobe modernized with the SAMx software package. Standard analytical conditions of 15kV and 15nA were used with a focused beam for the feldspars and beryl measurements, and a 10 microns defocused beam for biotite analysis. The average of a triplet measurement few 10s of microns apart was used as internal standard for the subsequent laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) analysis. This triplet measurement with the electron microprobe analyzer (EMPA) was performed to ensure the homogeneity of the sample at the impact of the up to 120 micrometer large laser beam spot. LA-ICP-MS measurements were conducted using the Coherent GeoLas MV 193 nm laser-ablation system coupled to an Agilent 7900s ICP mass spectrometer. The detailed setup of the instruments and measurement methods is described in papers I and II. As internal standard for quantification of the trace element results for the minerals feldspar, biotite and beryl, the Al concentrations as determined by EMPA analysis were used. For quartz and fluorite, the ideal stoichiometry of SiO$_2$ and CaF$_2$ was assumed.

3.3 Fluid inclusion studies
Fluid inclusion studies were performed at the Mineralogical Laboratory of the Department of Geosciences and Geography at the Helsinki University. Petrographic description of fluid inclusion assemblages (FIA) has been done on doubly polished thick sections using a standard research transmitted light microscope. Microthermometric data of individual fluid inclusions has been collected with the Leica DM2500P petrographic microscope equipped with a Linkam THMSG-600 cooling-heating stage. Trace element data has been obtained by means of LA-ICP-MS using a small volume cell originally developed at ETH Zürich for maximizing the intensity signal and reducing the limit of detection (LOD). The first tens of micrometres prior to the measurement of an individual fluid inclusion have been pre-drilled starting with the smallest beam diameter and gradually increased to the right diameter for the final ablation to minimize depth to diameter ratio errors of the signal (Guillong and Pettke 2012). The triple-halogen analysis of Br, Cl and in particular I was quantified by the novel approach of Fusswinkel et al. (2018) following the standardization method as described by Seo et al. (2011). Microthermometric data were calculated into densities and proportions of NaCl, KCl and CaCl$_2$ as obtained from the LA-ICP-MS data. These proportions were used for more accurate salinity calculations with the Pitzer thermodynamic model as described in Leisen et al. (2012b) for the aqueous fluid inclusions, thus improving the quality of quantifying trace element concentration data. Composition as well as densities for the carbonic-aqueous inclusions and high-saline aqueous fluid inclusions were calculated by means of calculation software.
from Bakker (1997, 2003) and halite dissolution temperatures (Bodnar and Vittyk 1994), respectively. A more detailed description of instrumentation setup and method is described in paper III.

4 Review of original papers

4.1 Paper I
This paper summarizes the petrographic observations and the chemical compositions of the main minerals feldspar, quartz, biotite and fluorite throughout the zones of the pegmatite and the host rapakivi granite. The geometry and geology of the pegmatite has been established based on field work, drill core logging and ground penetrating radar. The pegmatite body was thus identified as being irregular in appearance with 30 m at its maximum width, slightly dipping towards SE. Continuing towards this direction some 250 m away another smaller, chemically similar pegmatite is exposed. Chemical element and trace element analysis was performed by electron microprobe and subsequent LA-ICP-MS analysis. The results show a continuous enrichment in incompatible elements, particularly Rb, Cs and Tl in K-feldspar from the host rock and throughout the pegmatite zones. REE concentrations in plagioclase give evidence of a change to more oxidized conditions by reversing the Eu-anomaly from negative to positive towards the evolved inner zones of the pegmatite, consistent with the abundant observation of hematite in late-stage mineral assemblages. The elements Rb and Cs in K-feldspar proved to be good markers to trace the chemical evolution of the pegmatite and Rayleigh fractional crystallization modeling. Using these elements has shown that the crystallization of the pegmatite prior to miarolitic pocket formation can be well explained with magmatic crystallization. However, the sudden change in K-feldspar chemistry after more than 90% of the pegmatite has already crystallized is an indication for a separation of an oxidizing aqueous fluid during miarolitic pocket formation. Mineral trace element data for the host rock rapakivi and the Luumäki pegmatite, together with field observations as well as previously published geochronological data demonstrate that the Luumäki pegmatite is derived from the residual melt of the rapakivi granite, thus representing the final fraction of the batholith melt to crystallize, and defining the Luumäki pegmatite as an intragranitic pegmatite.

4.2 Paper II
In this paper the focus is put on the chemical composition of the beryl from the Luumäki pegmatite. Samples from the magmatic common beryl of the intermediate zone as well as gem-beryl from the different miarolitic pockets were analyzed by means of electron microprobe and subsequent LA-ICP-MS analysis. Field observations show that beryl saturation was reached very late in the Luumäki pegmatite with magmatic beryl found only in the innermost zones close to the contact with the quartz core. Gem-beryl has been found in two geologically different miarolitic pocket locations, one in the inner parts of the pegmatite at the border between the intermediate zone and the quartz core, close to the magmatic beryl occurrences, and the other some 20 m away close to the pegmatite border with the host rock rapakivi. Although both miarolitic gem-beryl crystals are similar in appearance, differences are clearly seen in their chemical trace element compositions. The trace element chemistry of gem-beryl from the miarolitic pockets close to the quartz core correlate with the magmatic beryl showing a common trend in the concentrations of trace elements such as Sc, Fe, Ga and Cs. These beryls have been interpreted
as stage I gem-beryl formed from a magmatic dominated liquid, highly enriched in volatile, incompatible and fluxing elements. Gem-beryl from the peripheral miarolitic pockets close to the host rock rapakivi are chemically disconnected from any magmatic trend and enriched in Na and Li, show abundant fluid inclusions and are texturally associated to the K-feldspars with anomalous trace element compositions (see paper I), which deter from the magmatic trend. Water in beryl has been measured by means of loss of ignition and determined to 1.6 wt%. These beryls are interpreted as stage II gem-beryl formed by a hydrothermal fluid dominated system. Miarolitic pocket formation thus can be the result of both processes, a silica-melt and hydrothermal-fluid dominated one, indicating heterogeneity of the pegmatite melt within the same pegmatite body and the involvement of hydrothermal fluids in the late pegmatite consolidation process.

4.3 Paper III
The third paper focuses on fluid inclusion studies from quartz samples and two miarolitic gem-beryl samples mainly from the miarolitic pockets, which represent the final consolidation processes of the pegmatite. Petrography studies of all samples were followed by microthermometry, qualitative Raman spectroscopy and quantitative LA-ICP-MS analysis of trace element compositions of the fluid inclusion assemblages in quartz. Four main assemblages of fluid types could be identified. Type I and type II are moderate-saline aqueous fluids, type III are low-saline aqueous-carbonic fluids, and type IV are high-saline aqueous fluids. Type I and II differ in their total homogenization temperatures and slightly in trace element concentrations as well as in the range of their salinity. Type I inclusions are found as secondary inclusions in the massive quartz of the pegmatite at the transition to pocket quartz, whereas type II is found in all pocket smoky quartz samples and the pocket beryl samples. Type III and IV occur mainly as secondary inclusions in all quartz samples, and even coexist on the same fluid inclusion trails. The trace element data shows that fluids of type I, III and IV have a linear trend with the aqueous carbonic type III being depleted in element concentrations, the high-saline type IV enriched in element concentrations, and type I plotting in between on the same trend. Type II fluids, although similar to type I fluids, are decoupled from this trend. All fluids have in common that they are of magmatic origin, as proven by their trace element chemistry, in particular their halogen ratios. This textural and geochemical findings lead to the conclusion that fluid saturation of the pegmatite magma occurred at the onset of pocket formation with type I fluid being the earliest fluid that exsolved and subsequently separated into an aqueous-carbonic type III and high-saline type IV fluid, followed by type II fluid, which was present during the pocket mineral assemblage crystallization. P-T estimates for type I and type II fluid exsolution based on calculated fluid densities yield 380 ± 80 °C and 1.2 ± 0.7 kbar.

5 Discussion
The involvement of a separate hydrothermal fluid in pegmatite crystallization has been the subject of an ongoing controversial debate since the beginning of pegmatite research in the early 20th century. Field studies of pegmatites have been interpreted as showing clear evidence for the involvement of an aqueous fluid but also as having originated from a water-undersaturated melt with only post-emplacement hydrothermal overprints. Many fluid inclusion studies on pegmatites suggest aqueous fluids being present during pegmatite consolidation (e.g. Beurlen et al. 2001; Sirbescu and Nabelek 2003; Thomas et
al. 2000; Trumbull 1995). The Ehrenfriedersdorf pegmatite in the Erzgebirge, SE Germany, is an example of extensive and highly detailed fluid and melt inclusion studies (Borisova et al. 2012; Seltmann et al. 1995; Thomas et al. 2003, 2009b; Webster et al. 1997; Zajacz et al. 2008) in which two types of melt inclusions along with aqueous fluids have been observed. The study of such inclusions led to the concept of a highly water-rich silicate melt/fluid phase and the concept of melt-melt immiscibility. The water-rich silicate melt/fluid, named so to describe its melt-like and aqueous-like properties, exists initially as one phase above a certain critical point in the pressure-temperature field and once it cools down below the solidus and even further, it separates into a haplogranitic melt, a volatile-rich melt and a hydrothermal fluid (Thomas et al. 2019). Such hydrothermal fluid is then trapped as primary fluids in the pegmatite forming quartz, often along with two coexisting melts (Thomas et al. 2003, 2009b).

An example for the difficulty of interpreting fluid inclusions is the well studied Tanco pegmatite (Černý et al. 1996). It was first being reported as containing primary saline-aqueous and secondary aqueous-carbonic fluid inclusions, but subsequently all aqueous fluid inclusions have been interpreted as secondary in origin and the crystal-rich high-saline aqueous inclusions have been interpreted as bulk-melt and later re-interpreted as boundary-layer liquids without any separate aqueous fluid being involved (London 1986a, 2008; Thomas et al. 1988). In London’s model the argument put forward is that a boundary layer, similar to experiments on haplogranite, is capable of dissolving large amounts of H$_2$O while it is enriched in other volatile forming elements such as F, B, P (Chakraborty et al. 1993; Holtz et al. 1993; London 2008; Taylor et al. 1979). This in tum means that in the case of miarolitic pegmatites only after crystallizing most of the boundary layer medium, at the very end of pocket formation, its chemical composition can change to the point that an aqueous phase may be liberated (London 2013). Excessively salt-rich inclusions are seen as hydrous salt melts and not as originating from aqueous fluids (London 2008).

Experimental studies as well show that both possibilities may exist, pegmatite-like products with water-undersaturated melt were formed in some experiments, but the exsolution of an aqueous fluid occurred in others (Bartels et al. 2011; London 1999; Maneta and Anderson 2018; Veksler et al. 2002). Therefore, straightforward interpretation of the aqueous fluid has become complicated. Some researchers favoring the water-undersaturated hypothesis argue that the aqueous fluid trapped in fluid inclusions represent later secondary overprints, which are not related to the pegmatite forming episode. Others reason that field observation, salinity, and the concentration of certain elements in the fluid inclusions are sufficient evidence for the magmatic origin of the fluids involved (e.g., Fuertes-Fuente et al. 2000; London et al. 2012; Smith 1953; Thomas et al. 2000, 2009a). The difficulty with field studies is therefore to determine whether the observed aqueous fluid in fluid inclusions is of magmatic origin or if it represents a later hydrothermal overprinting event. This makes fluid inclusion studies combined with mineral trace element studies and textural geological observations essential for unraveling the puzzle of pegmatite formation and the processes involved.

### 5.1 Indirect evidence for aqueous fluid exsolution from mineral trace element data

The Luumäki pegmatite system with its simple mineralogical composition represents a good target to investigate the involvement of aqueous
fluids within a miarolitic pegmatite system. It consists of two exposed pegmatite bodies, and both are chemically similar with the exception that the larger pegmatite body has abundant miarolitic pockets and a hydrothermal alteration halo up to a few meters in thickness penetrating into the host rock rapakivi granite (Fig. 1D), thus demonstrating an event where aqueous fluid exsolved from the pegmatite melt. Despite the evidence of fluid inclusions in minerals such as gem-quality beryl and smoky quartz from the miarolitic pockets, and the hydrothermal alteration aureole that penetrates several meters into the host rock granite, the magmatic origin of the fluids involved needs to be demonstrated in order to determine when a separate aqueous fluid phase was liberated during the crystallization history of the Luumäki pegmatite. In this study this problem was approached somewhat indirectly, by not focusing on the fluid inclusions initially but on the mineralogy and geochemistry of the Luumäki pegmatite and its origin. By proving that the Luumäki pegmatite is the product of residual melts of the rapakivi granite batholith it could initially be concluded that any aqueous fluid within the pegmatite has the potential for being of magmatic origin and should therefore show a similar geochemical fingerprint as granitic fluids.

The evidence for the Luumäki pegmatite having originated from the host rock rapakivi granite has been proven by field observations and geochemical properties of the minerals in combination with pre-existing geochronological data (Michallik et al. 2017). Already the field observation of a gradual change from the rapakivi host rock to the border zone and further to the wall zone as well as the lack of any sharp contact or aplitic contact led to the initial interpretation that the pegmatite body did not intrude into the rapakivi granite but instead represents the residual melt of the Wiborg batholith itself (Fig. 2B). This led to the decision to analyze the minerals of the host rock rapakivi granite in addition to minerals from the different zones of the pegmatite. The data show a geochemical link between the host rock and the pegmatite body. This is clearly seen in fluorite, plagioclase and K-feldspar, and the concentrations of trace elements such as Rb, Cs, Tl and the REEs in these minerals (Fig. 3). Fluorite shows the same pattern and range of REE concentrations in the same order from the altered contact zone that is within the host rock, the border zone and the wall zone (Fig. 3D). Although abundant, unfortunately no fluorites from the fresh rapakivi granite have been found in the studied thick sections. Trace element concentrations in plagioclase also show a similar pattern and concentration range for the detected REEs between the rapakivi host rock and the different zones of the pegmatite with a reverse in the Eu-anomaly within the inner zones (Fig. 3E and F). The anorthite component of plagioclase shows a continuous decrease from the rapakivi granite to the innermost zones of the pegmatite, as expected (Cameron et al. 1949; Černý 1994; Michallik et al. 2017). In case of K-feldspar, trace element patterns from minerals of the surrounding host rock mark the lowest concentrations of Rb, Cs, and Tl at the onset of the trend, and the concentrations systematically increase up to K-feldspar from the miarolitic pockets, where they are decoupled from the continuous trend seen throughout the other zones of the pegmatite (Fig. 3A and C). This decoupled trend has been interpreted as a major change in petrological processes, likely representing the change of the pegmatite system from a melt-dominated to a fluid and melt dominated one during pocket formation (Michallik et al. 2017). The elements Rb and Cs have been used to calculate (using Rayleigh fractionation) the volume of initial pegmatite magma that had to crystallize prior to such enrichment, as these
elements are good proxies in K-feldspar for tracing magmatic evolution (Icenhower and London 1996; London 2008). The result of more than 90 vol% of melt required to crystallize prior to the pocket formation as indicated through the decoupled enrichment in these elements is reasonable and in good agreement with the observed proportions of the different zones of the pegmatite.

The Rb vs K/Rb variation is noteworthy, where the concentrations from the host rock rapakivi interstitial K-feldspar lie on the same trend as feldspar from the pegmatite zones, whereas concentrations in K-feldspar from within ovoids of the rapakivi granite are slightly distinct (Fig. 3B). It was an unsurprising coincidence then that a recent paper published on the age of the rapakivi granite host rock based on age determination from in-situ zircon grains extracted from the ovoids as well as from the...
interstitial matrix gave further evidence for the Luumäki pegmatite originating from the host rock rapakivi granite itself. In this recent study different crystallization ages were determined with a youngest, final crystallization age for the Wiborg rapakivi batholith from the interstitial matrix zircons at $1628 \pm 2.5$ Ma (Heinonen et al. 2016a, 2016b). This age is well within the error of the previously reported age for the Luumäki pegmatite of $1628 \pm 4$ Ma, as determined using the U-Pb system of monazite (Rämö and Lahti 2008). The remarkable similarity in age of the matrix of the host rock rapakivi granite and the pegmatite, combined with the similarity and continuity in trace element patterns, was thus interpreted as evidence for the Luumäki pegmatite to originate from its host rock, the Wiborg granite batholith. Further consideration of water-content in beryl as an independent geothermobarometer (Pankrath and Langer 2002), along with published constraints on pressure of formation of the rapakivi batholith, in combination with the calculated densities of the studied fluid inclusions, suggest a pressure and temperature of formation for the miarolitic Luumäki pegmatite at $380 \pm 80$ °C and $1.2 \pm 0.7$ kbar (Michallik et al. 2020). The Luumäki pegmatite is an intragranitic pegmatite and these estimates of crystallization pressure are therefore also applicable for constraining the crystallization pressure of the Wiborg batholith itself. They are in good agreement with previously suggested pressures of below 1.9 - 2 kbar (Heinonen et al. 2020; Lukkari and Holtz 2007).

5.2 Indirect evidence for aqueous fluid exsolution from beryl trace element data

The Luumäki pegmatite represents an example of early, not highly evolved pegmatites, as is commonly the case with beryl-bearing pegmatites that show no enrichment in Li-bearing or other exotic phases (Černý and Ercit 2005; London and Evensen 2003). The Be concentration in pegmatites needs to reach a certain threshold for beryllium minerals to crystallize. London and Evensen (2002) showed that if an original granite melt would contain only 6 ppm Be it would be sufficient to enrich the initial pegmatite melt to concentrations of about 35 ppm in order to be able to form beryl bearing pegmatites via fractional crystallization. According to this model beryl would crystallize when the pegmatite melt itself would reach concentrations of about 205 ppm Be. This required concentration is based on an average Be content of some beryl-rich pegmatites (London 2008). A straightforward Rayleigh calculation using the same partition coefficients for Be as London and Evensen (2002) for the rapakivi and Luumäki pegmatite bulk mineral assemblage with an initial rapakivi melt containing 8 ppm Be (as reported by Haapala 1988) would reach the required 35 ppm after about 92% of granite crystallized. The difference to London’s model is that he assumed a pegmatite body outside the source granitic melt, and suggested multiple episodes of fractionation and extraction of melt each time after 75% of crystallization, due to high viscosity of the silicate liquid hardly moving within a mostly crystalline body. Because this is not the case for the Luumäki pegmatite as it remained within its source rapakivi granite melt, it is likely that the initial pegmatite melt started with even higher Be concentrations. Assuming a slightly higher starting composition of about 45 ppm Be after 95% of the rapakivi melt crystallized, whether this occurred by multiple episodes of melt extraction or not, the required composition of 205 ppm within the pegmatite melt would be reached after about 85% of the pegmatite crystallized, and beryl crystallization would commence. This is what can be well observed in the Luumäki pegmatite with the common
magmatic beryl initially appearing within the late intermediate zone of the pegmatite, close to the quartz core after more than 80% of the pegmatite crystallized. Beryl in gem-quality is then found within the subsequently formed miarolitic pockets.

The chemical relation between the common magmatic beryl from the intermediate zone and the later formed gem-quality beryl from the miarolitic pockets and a possible concurrent aqueous fluid was investigated by means of beryl trace element chemistry. The question of when an aqueous fluid exsolved from the pegmatite melt was already addressed in the Rayleigh fractionation model of Rb and Cs in K-feldspar, showing that at the onset of fluid separation most of the pegmatite must have been already crystallized (Michallik et al. 2017). Thus, it puts the phase separation between the residual melt and a potential aqueous fluid into the late stage of pegmatite consolidation during the miarolitic pocket formation episode. This conclusion is further supported by the trace element data of gem-quality beryl from various miarolitic pockets of the pegmatite. Interestingly, two types of miarolitic pockets have been found, one type within the core part of the pegmatite body, at the border between the core quartz and the intermediate zone, in the vicinity of large magmatic beryl minerals up to a meter in size. Such position of miarolitic pockets between the core quartz and the feldspathic intermediate zone is in agreement with experiments for water-undersaturated flux-bearing silicate liquids (London et al. 1989). However, the other type of miarolitic gem-beryl bearing pockets has been found at the periphery of the pegmatite close to the contact with the surrounding host rock rapakivi granite, which shows the extensive hydrothermal alteration halo described as contact zone (Fig. 1).

Although both pockets are similar in their mineral assemblage, the trace-element data of the gem-beryls show that they are clearly different,

![Figure 4](image_url)

**Figure 4.** Selected minor and trace element distribution in magmatic and miarolitic gem-quality beryl from the Luumäki N pegmatite showing the grouping of beryl compositions into two distinct groups (group 1 and group 2). (A) Fe vs. Li diagram (B) Ga vs. Li diagram. (C) Mn vs Li diagram. (D) Sc vs Li diagram. See text for further discussion. Modified from Michallik et al. (2019).
leading to the conclusion that the two types have been formed by two distinct processes, one magmatic dominated (Stage I gem-beryl) and the other hydrothermally dominated (Stage II gem-beryl). This is evident from the textural context of the different pockets and from the different geochemical trends observed between the magmatic beryl, and the gem-beryl. Stage I gem-beryl from miarolitic pockets within the intermediate zone, close to the magmatic common beryl shows a similar range and continuous trend for the concentrations of trace elements such as Li, Fe, Ga, Mn and Sc together with the magmatic beryl from the intermediate zone, as represented by group 1 (Fig. 4). In contrast, the stage II gem-beryl shows elevated values of Li and generally a depletion in all other metals and is compositionally decoupled from the magmatic beryl. Moreover, it shows chemical similarities to hydrothermally altered magmatic beryl samples and both form a trend represented by group 2 (Fig. 4). The miarolitic pocket with the stage II gem-beryl is texturally associated with the K-feldspar that is decoupled from the magmatic trend (Michallik et al. 2017) as well as the hydrothermally altered contact aureole within the host rock. This observation, together with the abundance of fluid inclusions within the stage II gem-beryls is indicative of a later crystallization of this beryl, when the residual pegmatite liquid was already more depleted in such elements and experienced a major chemical change interpreted here as the shift to a system dominated by melt-fluid coexistence (Michallik et al. 2019).

5.3 Direct evidence for aqueous fluid exsolution from fluid inclusion major and trace element data

The mineral trace element data have led to the conclusions that 1) the Luumäki pegmatite has originated from the last batches of rapakivi granitic melt and 2) that fluid exsolution occurred during the last stage of pegmatite formation. Based on these results and interpretations, the final part of the research has focused on investigating the fluid inclusions found in quartz and beryl.

The study of the fluid inclusions itself confirms the magmatic origin of the fluids and defines the point in time of aqueous fluid exsolution in the pegmatite crystallization history more precisely. Microthermometry and trace element data of fluid inclusions in the minerals quartz as well as limited data from the gem-beryl show the involvement of four types of fluids and their time sequence and relation to one another (Michallik et al. 2020). Two types of aqueous fluids are similar, having moderate salinity, but show different homogenization temperatures, a third type is low-salinity aqueous-carbonic and the fourth one is high-salinity aqueous. The textural context of these fluids confirms that the moderate-salinity aqueous fluid with the higher homogenization temperature of 380 °C was the first fluid to exsolve (type I), as it is found only on trails outside the pockets up to the border between the core quartz and the pocket quartz, but it does not penetrate into the pocket quartz (Fig. 5B). This demonstrates that the type I fluid must have exolved prior to the onset of pocket mineral crystallization. The second moderate-salinity aqueous fluid (type II) with homogenization temperatures of about 280 °C is often found on growth zones and in recrystallization zones within the pocket quartz (Fig. 5A and C) and gem-beryl. Thus, the type II fluid must have coexisted together with the medium from which the pocket material crystallized. The low-salinity aqueous-carbonic (type III) and the high-salinity aqueous fluids (type IV) are found within the pocket quartz as well as outside the pockets on secondary features of quartz (Fig. 5A and B). These were the last fluids involved in the process of pegmatite crystallization. Based on the textural context...
of the fluid types together with the already indicated drastic trace element changes of pocket minerals such as K-feldspar and beryl, it has been concluded that fluid exsolution occurred at the onset of pocket formation.

It was then demonstrated that the aqueous fluids are of magmatic origin by trace element analysis of in-situ fluid inclusions found in smoky quartz from the miarolitic pockets within the core zone. This has been accomplished by successfully measuring the concentrations of Cl, Br, and I. The concentration of these halogens and especially their Br/Cl and I/Cl ratios in magmatic-hydrothermal fluids may be modified by fluid-mixing, seawater evaporation, dissolution and precipitation of halite, but remains mostly unaffected by fluid-rock interaction processes (Banks et al. 2000a, 2000b; Fusswinkel et al. 2018; Hammerli et al. 2014; Kendrick et al. 2007). The studied fluid inclusions all have Br/Cl and
I/Cl ratios that reflect a felsic melt source, affected by processes such as precipitation of halite due to extensive fluid boiling and partitioning between melt and exsolving fluid (Böhlke and Irwin 1992; Bureau et al. 2016; Hovland et al. 2006; Kesler et al. 1995; Lukanin 2015; Scott et al. 2017).

In the corresponding I/Cl vs. Br/Cl diagram, all four types of aqueous fluids plot in the range of bulk crust and granitic fluid concentrations, and distinctly away from other surface, continental shield or metamorphic fluids (Fig. 6).

Interestingly, the concentrations of various elements for the early type I fluids are situated in between on a trend together with aqueous-carbonic type III fluids and the high-salinity type IV fluids (Fig. 7). This led to the conclusion that the low-salinity aqueous-carbonic fluids as well as aqueous high-salinity brines within the pegmatite, similar to previously reported ones (London 1986a; Sirbescu and Nabelek 2003), are the product of phase separation of a magmatic aqueous fluid into two separate fluids. The moderate salinity in type I and type II fluids, the distribution of elements such as Cu and S into the aqueous-carbonic type III but alkali, alkaline earth and transition metal elements into the high-salinity type IV fluids, combined with the evidence of the triple halogen ratios, prove that all four types of fluids are magmatic in origin (Iveson et al. 2019; Kokh et al. 2017; Michallik et al. 2020).

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**Figure 6.** Molar Br/Cl, Br/I and I/Cl ratios of all four types of fluid inclusion assemblages from the Luumäki pegmatite compared to data for different crustal fluids. The grey thick line marked SET represents the seawater evaporation trajectory (Fehn et al. 2000), and data for seawater (red star) and the grey mantle field were adopted from Kendrick et al. (2013, 2017). Data for the grey S-type granite field were taken from Böhlke and Irwin (1992), Irwin and Roedder (1995), Banks et al. (2000a, 2000b), and Seo et al. (2011). Data for the bulk crust composition were taken from Krauskopf and Bird (1995). Source of other data: Variscan veins from Ireland from Meere and Banks (1997); Canadian shield brines from Frape and Fritz (1987) and Bottomley et al. (2005); St. Austell Granite, Salton Sea, Creede epithermal deposit, Orogenic Au in Alleghany from Böhlke and Irwin (1992); Sandstone-hosted Pb-Zn deposits from Kendrick et al. (2005). Figure adapted from Michallik et al. (2020) and modified from Fusswinkel et al. (2018).
Pegmatite melts, in particular of granitic composition, differ from the typical granitic melts in that they are highly enriched in what are usually incompatible elements. These enriched pegmatitic melts represent the last residual melts of larger magma bodies and it is commonly accepted that such enrichment from the source granitic melt can be achieved when the melt is enriched in volatile components such as $\text{H}_2\text{O}$, $\text{P}$, $\text{B}$ and $\text{F}$ (Chakraborty et al. 1993; Holtz et al. 1993; London 2008; Taylor et al. 1979). These volatiles remain initially dissolved in the melt as it cools down, aiding the concentration of incompatible elements through complexation and hindering crystallization of the melt at its solidus temperature, and further below that temperature (Fenn 1977; London 1999, 2009). The melt becomes then undercooled and whether it penetrates into cooler regions or remains within its original cooling source pluton, it experiences a thermal gradient from its cooling margins into the hotter core (London 2008). Along this gradient, crystallization commences in what some explain as crystallization through a boundary layer, further enriched in volatiles and incompatible elements (London 1992), and others as melt-melt immiscibility through a highly water-rich silicate fluid/melt (Thomas et al. 2019). In both models important building blocks of minerals are easily diffusing to the crystal surface from the granitic melt and incompatible ones away from it, further concentrating them in the residual volatile-rich melt. And in both models the result of crystallization of the main pegmatite body is a fairly haplogranitic composition of quartz, K-feldspar, albite and often biotite or micas with gradual incorporation of incompatible elements into the crystal structure. The residual volatile-rich melt is then responsible for the crystallization of more evolved exotic minerals such as beryl, topaz, fluorite, monazite, tourmaline and others at the late stages of pegmatite consolidation. It

5.4 Implications for pegmatite formation processes

Figure 7. Bivariate plots of selected trace element concentrations from all four types of fluid inclusion assemblages. Note the alignment of type II, type III, and type IV fluid data on the same trend (dotted line). (A) Rb vs. K. (B) Rb vs. Mn. (C) Rb vs. Cs. (D) Rb vs. Zn. See text for further discussion. Figure modified from Michallik et al. (2020).
seems that both models are describing one and the same magmatic dominated petrologic process of two compositionally distinct melts coexisting during pegmatite formation. When pressure, temperature and enrichment in volatiles of the volatile-rich melt are favorable, an aqueous fluid phase separates from the melt. This is the case in miarolitic pegmatites, as the miaroles themselves together with accompanying hydrothermal alteration halos are evidence of such separation processes and the subsequent interaction of an aqueous fluid with the surrounding host rock.

The observations and data from the Luumäki pegmatite system support both cases, one of aqueous fluid exsolution, in that the larger pegmatite body (Luumäki N) shows both, the meter-sized miarolitic pockets as well as an extensive hydrothermal alteration halo and evidence for fluid phase exsolution from fluid inclusions; whereas the smaller pegmatite body (Luumäki S) lacks any miarolitic cavities, larger biotite agglomerates or hydrothermal overprints of the minerals and thus did not experience any aqueous fluid exsolution. The Luumäki S pegmatite has, however, small aggregates of medium- to coarse-sized biotite and muscovite together with feldspar and quartz, indicative of crystallization from a volatile-rich fractionated melt that remained water-undersaturated. The close proximity of both pegmatite bodies (they are only about 250 meters apart) and their geochemical fingerprint are indicative of both originating from the same source, yet their initial water content must have been different to begin with. This shows that pegmatite bodies of the same origin and within the same geological framework can show evidence for both models of crystallization, one where an aqueous fluid exsolves from the melt and one where the melt remains water-undersaturated throughout.

Moreover, even within the same pegmatite body one miarolitic pocket shows products that can be easily explained by crystallization from a volatile-rich melt such as the boundary layer with little evidence of the involvement of aqueous fluids. This is seen in the beryl-bearing pockets from the inner zones of the Luumäki pegmatite with beryls embedded in reddish fine-grained jasper and the continuous trend in trace elements between common magmatic beryl and miarolitic gem-beryl. In contrast, the peripheral miarolitic pockets have an extensive hydrothermal alteration halo and the gem-beryl is embedded in more loose reddish clay, showing a discontinued trend and depletion in trace elements, but high enrichment in Li when compared to the magmatic common beryl. Interestingly, this is what is to be expected when an aqueous vapor phase exsolves, since the partition coefficient for most incompatible elements such as Li favors melt over vapor compared to vapor/melt partition coefficients of major components, for which it may be higher (London et al. 1988), thus aiding their incorporation into the crystallizing phase. The study conducted by London et al. (1988) on the Macusani glass states, however, that these experimental partitioning coefficients may apply only to peraluminous, differentiated and Cl-poor granitic systems at slightly higher temperatures of about 700 °C. In contrast, the exsolved aqueous fluids in the Luumäki pegmatite show significant concentrations in Cl as well as most measured elements and exsolved at much lower temperatures of around 380 °C.

Of particular interest is the evidence of a further phase separation of the aqueous fluid itself into a high-salinity aqueous and a low-salinity aqueous-carbonic fluid. Aqueous high-salinity fluids have been previously seen as evidence of a water-rich silica melt/fluid, excluding the possibility to originate from any aqueous fluid separation (London 1986a, 2008; Sirbescu and Nabelek 2003). In view of the results of this study this interpretation may need to be reconsidered.
The high-salinity aqueous brine in the Luumäki pegmatite does not represent neither a separate melt nor a boundary layer fluid but does originate from an already exsolved aqueous intermediate-salinity fluid. It should not be surprising that if an aqueous fluid exsolves from a final boundary layer melt highly enriched in incompatible elements, or as others prefer to call it, from a silica melt/fluid, then the resulting elemental concentrations in the aqueous fluid should be high as well. Despite a partitioning coefficient favoring melt over vapor, a distribution into the aqueous fluid of only e.g. 10% of a ten times more enriched melt is still a ten times higher concentration within such an exsolved fluid than from a typical haplogranitic melt, thus eventually leading to high-salinity aqueous fluids as observed in the Luumäki pegmatite. The original moderate-salinity aqueous type I fluid, from which the high-salinity type IV fluids together with the aqueous-carbonic type III fluids originate, clearly exsolved earlier than the latter two. Hence, the alternative interpretation that the moderate-salinity type I and the aqueous-carbonic type III fluids originate from the high-salinity type IV fluid, representing a silica melt/fluid, is not possible based on textural and petrographic grounds. Another point to consider is that if high-salinity brines are evidence for a water-rich silica fluid, which did not separate any aqueous fluid, then such inclusions should be present also in the quartz from the final melt agglomerates of the Luumäki S pegmatite, which is not the case.

6 Conclusions and suggestions for future studies

It is undisputed that miarolitic pegmatites carry evidence of aqueous fluid exsolution and this study further supports this view. It places the exsolution of an aqueous fluid at the onset of miarolitic pocket formation. Prior to the pocket formation, the Luumäki pegmatite crystallized from a water-undersaturated melt. The temperature at which the melt became water saturated and an aqueous fluid exsolved is about 380 °C ± 80 °C, thus lower than the temperatures for which currently vapor/melt or aqueous fluid/melt partitioning coefficients are available. It would be of great interest to conduct further experimental studies to determine vapor/melt partitioning coefficients at such low temperatures to understand better the significance of these supercritical aqueous fluids in element transport. Furthermore, the CO₂-H₂O-NaCl system in combination with siderophile and lithophile elements should be experimentally investigated, in order to determine under which conditions as well as metal concentrations a separation into carbonic-aqueous and high-saline aqueous fluids takes place.

The models of pegmatite consolidation as proposed by David London and Rainer Thomas are both applicable in case of the Luumäki pegmatite and represent different pathways of pegmatite crystallization depending on the P-T-X conditions. As shown in this study, in certain circumstances both processes might play a key role in the formation of late stage pocket-mineralization (Michallik et al. 2019), indicating that pegmatite melts can be locally very heterogeneous. The key parameter for the exsolution of an aqueous fluid phase during pegmatite formation, and for the timing when such an aqueous phase would separate from the silica melt during the pegmatite consolidation is the initial H₂O-content of the pegmatite melt. Thus, further studies of the initial water-content in natural pegmatite systems as well as experimental studies are of importance to understand better, at which pressure, temperature and volatile concentrations a fluid phase will exsolve.
References


Course Series 37, pp. 169-206.