

# Magmatic evolution of topaz-bearing granite stocks within the Wiborg rapakivi granite batholith

Sari Lukkari

*Academic dissertation*

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Front cover : Topaz crystal from the Kymi stockscheider pegmatite, the length of the crystal is 2 cm.  
Photo by Pasi Heikkilä.

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## Abstract

This study brings new insights into the magmatic evolution of natural F-enriched peraluminous granitic systems. The Artjärvi, Säaskjärvi and Kymi granite stocks within the 1.64 Ga Wiborg rapakivi granite batholith have been investigated by petrographic, geochemical, experimental and melt inclusion methods. These stocks represent late-stage leucocratic and weakly peraluminous intrusive phases typical of rapakivi granites worldwide. The Artjärvi and Säaskjärvi stocks are multiphase intrusions in which the most evolved phase is topaz granite. The Kymi stock contains topaz throughout and has a well-developed zoned structure, from the rim to the center: stockscheider pegmatite – equigranular topaz granite – porphyritic topaz granite. Geochemically the topaz granites are enriched in F, Li, Be, Ga, Rb, Sn and Nb and depleted in Mg, Fe, Ti, Ba, Sr, Zr and Eu. The anomalous geochemistry and mineralogy of the topaz granites are essentially magmatic in origin; postmagmatic reactions have only slightly modified the compositions. The Kymi equigranular topaz granite shows the most evolved character, and the topaz granites at Artjärvi and Säaskjärvi resemble the less evolved porphyritic topaz granite of the Kymi stock.

Stockscheiders are found at the roof contacts of the Artjärvi and Kymi stocks. The stockscheider at Artjärvi is composed of biotite-rich schlieren and pegmatite layers parallel to the contact. The schlieren layering is considered to have formed by velocity-gradient sorting mechanism parallel to the flow, which led to the accumulation of mafic minerals along the upper contact of the topaz granite. Cooling and contraction of the topaz granite formed fractures parallel to the roof contact and residual pegmatite magmas were injected along the fractures and formed the pegmatite layers. The zoned structure of the Kymi stock is the result of intrusion of highly evolved residual melt from deeper parts of the magma chamber along the fractured contact between the porphyritic granite crystal mush and country rock. The equigranular topaz granite and marginal pegmatite (stockscheider) crystallized from this evolved melt.

Phase relations of the Kymi equigranular topaz granite have been investigated utilizing crystallization experiments at 100 to 500 MPa as a function of water activity and F content. Fluorite and topaz can crystallize as liquidus phases in F-rich peraluminous systems, but the F content of the melt should exceed 2.5 - 3.0 wt % to facilitate crystallization of topaz. In peraluminous F-bearing melts containing more than 1 wt % F, topaz and muscovite are expected to be the first F-bearing phases to crystallize at high pressure, whereas fluorite and topaz should crystallize first at low pressure.

Overall, the saturation of fluorite and topaz follows the reaction:  $\text{CaAl}_2\text{Si}_2\text{O}_8$  (plagioclase) +  $2[\text{AlF}_3]_{\text{melt}} = \text{CaF}_2$  (fluorite) +  $2\text{Al}_2\text{SiO}_4\text{F}_2$  (topaz). The obtained partition coefficient for F between biotite and glass  $D(\text{F})^{\text{Bt/glass}}$  is 1.89 to 0.80 (average 1.29) and can be used as an empirical fluorimeter to determine the F content of coexisting melts.

In order to study the magmatic evolution of the Kymi stock, crystallized melt inclusions in quartz and topaz grains in the porphyritic and the equigranular topaz granites and the marginal pegmatite were rehomogenized and analyzed. The homogenization conditions for the melt inclusions from the granites were 700 °C, 300 MPa, and 24 h, and for melt inclusions from the pegmatite, 700 °C, 100 MPa, and 24/96 h. The majority of the melt inclusions is chemically similar to the bulk rocks (excluding H<sub>2</sub>O content), but a few melt inclusions in the equigranular granite show clearly higher F and low K<sub>2</sub>O contents (on average 11.6 wt % F, 0.65 wt % K). The melt inclusion compositions indicate coexistence of two melt fractions, a prevailing peraluminous and a very volatile-rich, possibly peralkaline.

Combined petrological, experimental and melt inclusion studies of the Kymi equigranular topaz granite indicate that plagioclase was the liquidus phase at nearly water-saturated (fluid-saturated) conditions and that the F content of the melt was at least 2 wt %. The early crystallization of biotite and the presence of muscovite in crystallization experiments at 200 MPa contrasts with the late-stage crystallization of biotite and the absence of muscovite in the equigranular granite, indicating that crystallization pressure may have been lower than 200 MPa for the granite.



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- I Lukkari, S., 2002. Petrography and geochemistry of the topaz-bearing granite stocks in Artjärvi and Säaskjärvi, western margin of the Wiborg rapakivi granite batholith. *Bulletin of the Geological Society of Finland* 74, Parts 1-2, 115-132.
  
- II Haapala, I. and Lukkari, S., 2005. Petrological and geochemical evolution of the Kymi stock, a topaz granite cupola within the Wiborg rapakivi batholith, Finland. *Lithos* 80, 347-362.
  
- III Lukkari, S. and Holtz, F. 2007. Phase relations of a F-enriched peraluminous granite: an experimental study of the Kymi topaz granite stock, southern Finland. *Contributions to Mineralogy and Petrology* 153, 273-288.
  
- IV Lukkari, S., Thomas, R. and Haapala, I. Magmatic evolution of the Kymi topaz granite stock within the Wiborg rapakivi granite batholith, Finland: a melt inclusion study. *Canadian Mineralogist*, A-type Granite Special Issue, submitted.

For Paper II, S. Lukkari participated in the field work, interpretation of data and preparation of the manuscript. For Papers III and IV, S. Lukkari was responsible for planning and running the experiments, interpreting the data and writing the manuscripts.



# 1. Introduction

The 1.64 Ga Wiborg rapakivi batholith of southeastern Finland consists of several granite varieties ranging from subsolvus hornblende granites to leucocratic, topaz-bearing alkali feldspar granites, and small bodies of contemporaneous mafic rocks (Rämö and Haapala 1995, Haapala and Rämö 1999). The topaz granites are found as small, evolved intrusions within the Wiborg batholith – the Kymi (Haapala and Ojanperä 1972, Haapala and Lukkari 2005), Artjärvi and Säaskjärvi stocks (Lukkari 2002). They are also found within the other Proterozoic rapakivi granite complexes of Finland – the Eurajoki stock (Haapala 1977, 1997), the Suomenniemi batholith (Rämö 1991), and the Ahvenisto complex (Edén 1991). These evolved, geochemically specialized granites represent the late-stage intrusive phases of rapakivi granites and they are often associated with important mineralization (for example, Sn polymetallic deposits in Brazil and Russia, Fe-Cu and Cu-U-Au-Ag deposits in Missouri and South Australia; Haapala 1995).

The origin of the anomalous geochemical character of topaz granites in granite complexes is an intensive debated issue. A few decades ago, several researchers concluded that topaz granites are metasomatic rocks, formed by reactions between post-magmatic fluids and earlier granite (e.g., Beus and Zalachkova 1962, Štemprok 1971). Today, however, a near consensus prevails that these granites are essentially magmatic in origin. The discovery of volcanic and subvolcanic equivalents of topaz granites: ongonites (Kovalenko et al. 1971), topaz-bearing quartz porphyries (Haapala 1977), topaz rhyolites (Congdon and Nash 1988, Christiansen et al. 1986), and macusanites (Pichavant et al. 1988a, 1988b) strongly supports magmatic origin. Several

experimental studies on F-enriched granitic systems (e.g., Manning 1981, Webster et al. 1987, London et al. 1989, Xiong et al. 2002, Lukkari and Holtz 2007) together with recent melt inclusion studies (e.g., Thomas 2000, 2002, Thomas et al. 2003, Webster et al. 2004, Badanina et al. 2004) have shown that magmatic crystallization is the major process for the formation of topaz granites. Studies on topaz granites associated with the Finnish rapakivi granites (Haapala 1977, 1997) also imply that their anomalous geochemistry and mineralogy are magmatic in origin, and that this anomalous character was further enhanced by postmagmatic fluid-rock interaction.

Although previous experimental and melt inclusion studies have shown that topaz granites have crystallized from F-enriched melts and that F has a marked effect on the rheological properties of the melt (decrease in viscosity and density; e.g., Dingwell 1987, Dingwell et al. 1985, 1993), the stability fields of F-bearing minerals and the effects of F on phase relationships in natural systems have remained rather poorly constrained. To improve the situation, I have performed crystallization experiments using a natural equigranular topaz granite from the Kymi stock as starting material. New experimental results on phase relations in peraluminous, F-rich granitic melts relative to water activity, F content and pressure were obtained. The results are used to discuss the role of F in the late-stage crystallization of topaz-bearing rhyolitic melts. The zoned Kymi granite stock is also an excellent target for studying the evolutionary stages of strongly fractionated rapakivi magmas. The magmatic evolution of the Kymi stock was investigated by a melt inclusion study, and a detailed description of the crystallized melt inclusions in the Kymi topaz granites and marginal pegmatite is given. The compositions of the melt inclusions are compared to

whole-rock analyses, and the geochemical evolution of the melt is discussed. This leads to an improved model for the origin of the zoned structure of the Kymi granite stock. The melt compositions yielded by the melt inclusion study have been used as the starting point for the experimental study. Overall, the main purpose of this work is to describe the topaz granites within the classic Wiborg rapakivi granite area and to assess the implications of the petrographical, geochemical, experimental and melt inclusion studies on the Kymi granite stock. The results provide new information on the magmatic evolution

of natural F-enriched granitic systems.

Papers I and II describe the petrological and geochemical characteristics of the Artjärvi, Säaskjärvi and Kymi granite stocks, and discuss the formation of the stockscheider found in Artjärvi (Paper I) and the origin of the zoned structure of the Kymi stock (Paper II). The results from the crystallization experiments on the Kymi equigranular topaz granite are presented in Paper III, and the composition and significance of the melt inclusions in the Kymi topaz granites and marginal pegmatite are scrutinized in Paper IV.

## 2. Materials and methods

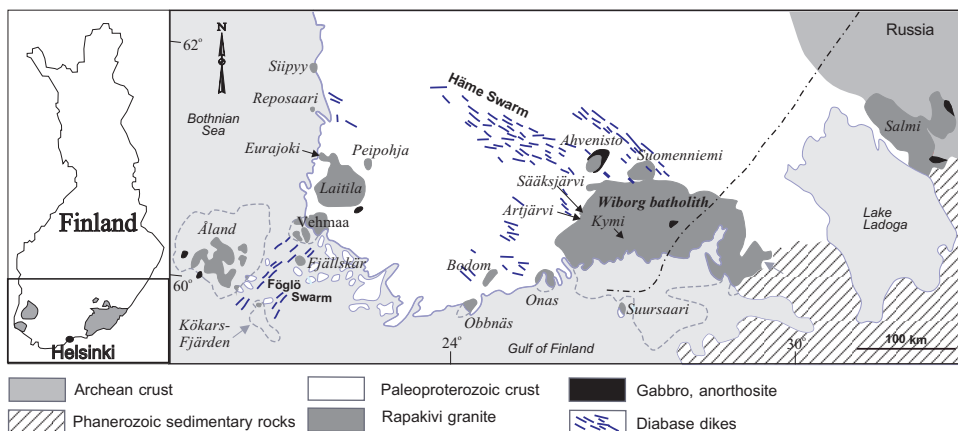
### 2.1. Sampling

The location of the Artjärvi, Säaskjärvi, and Kymi granite stocks within the Wiborg rapakivi batholith and the other topaz granite stocks in Finland are shown in Fig. 1. The lithological map of the Kymi stock with the sample locations for the experimental and melt inclusion studies is shown in Fig. 2. The equigranular topaz granite of the Kymi stock was selected as starting material for crystallization experiments, because it is a prime example of highly evolved, peraluminous F-enriched granite and it is also homogeneous in terms of texture and mineral composition. For the melt inclusion studies, samples were collected from the equigranular and porphyritic granites, as well as from the marginal pegmatite. The equigranular granite samples were collected from a granite quarry in the southwestern part of the stock. The porphyritic granite sample for the melt inclusion study was collected 200 m northward from the quarry, ca. 150 m

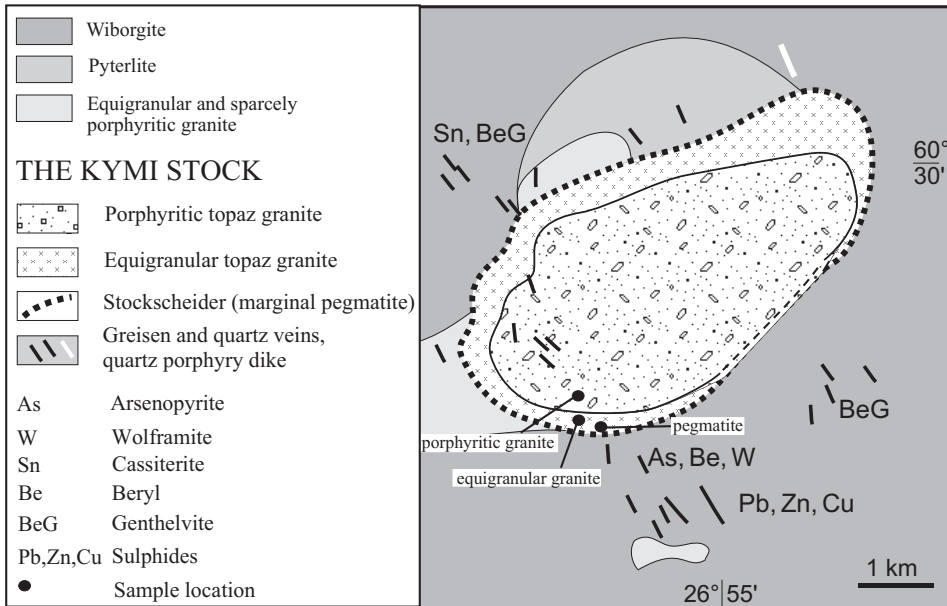
from the contact between the equigranular and porphyritic granites. The samples from the marginal pegmatite were collected from a pegmatite quarry 50 m southeast from the granite quarry (Fig. 2).

### 2.2. Sample preparation

For crystallization experiments, four starting glasses (1.13, 2.12, 3.10, and 5.11 wt % F) were made to study the effect of F on phase relations and crystallization of topaz and fluorite. Powder from the equigranular granite was melted twice in a Pt crucible at 1600 °C and 1 atm for 2.5 h, with grinding in between to obtain a crystal-free, chemically homogeneous starting glass (1.13 wt % F). This was used to prepare a glass with 5.11 wt % F by mixing a 1:2 molar mixture of natural cryolite ( $\text{Na}_3\text{AlF}_6$ ) and anhydrous  $\text{AlF}_3$  powder. The mixture was fused twice in sealed Pt capsules at 1400 °C and 1 atm for 3 h, with grinding in between. The starting glasses with 2.12 wt % and 3.10 wt % F were prepared by mixing the 1.13 wt % F and 5.11 wt % F glass powders. The experi-



**Fig. 1.** A generalized bedrock map of southeastern Fennoscandia showing the localities of the studied topaz-bearing granite stocks (Artjärvi, Säaskjärvi and Kymi) within the Wiborg rapakivi granite batholith and the other topaz granite stocks in Finland. Modified from Rämö and Haapala (2005).



**Fig. 2.** Lithological map of the Kymi topaz granite stock. The sample locations for experimental and melt inclusion studies are marked with black dots. Modified from Haapala and Lukkari.

ments were carried out in sealed Au capsules loaded with anhydrous starting glass powder ( $50 \pm 1$  mg), doubly distilled deionized water and, for  $H_2O$ -undersaturated conditions ( $a_{H_2O} < 1$ ), with silver oxalate ( $Ag_2C_2O_4$ ) as the source of  $CO_2$ . The fluid/silicate ratio was maintained low (10 wt % of fluid) and identical in each sample to avoid changes in the starting glass composition by incongruent dissolution in the fluid phase.

For the melt inclusion homogenization experiments, doubly polished thick sections of quartz and topaz from the granites and pegmatite were prepared. Quartz grains from the porphyritic granite were picked from the groundmass. The thick sections of quartz and topaz containing the melt inclusions were loaded into Au capsules and sealed for the homogenization experiments.

### 2.3. Crystallization experiments

Crystallization experiments with completely molten starting material are the most appropriate method for studying phase relations of F-enriched peraluminous melts. Determination of solidus temperatures from crystallization experiments is, however, difficult, especially at low temperatures. The experiments were performed in externally heated, horizontal cold-seal pressure vessels at 575–760 °C, 100–500 MPa, and 168 h (two samples 216 h), using a solid Ni/NiO buffer to control oxygen fugacity. Two capsules were placed in the same vessel. Heating started from an initial pressure of approximately 50 % of the desired pressure. Quenching was performed isobarically by removing the pressure vessel from the furnace and using a compressed air flux. After the experiments,

the capsules were re-weighted to check for possible leaks.

## **2.4. Melt inclusion homogenization experiments**

Because the melt inclusions in the granites and pegmatite were totally crystalline, it was necessary to rehomogenize the inclusions to a homogeneous, daughter-crystal free glass for the electron microprobe and Raman spectroscopic studies. The homogenization conditions for the melt inclusions were 700 °C, 300 MPa, and 24 h (granite), and 700 °C, 100 MPa, and 24/96 h (pegmatite). To avoid volatile loss during remelting, homogenization was performed under pressure and at temperatures that barely exceeded the trapping temperature. The experiments were conducted in sealed Au capsules with each capsule loaded with small, polished thick-section chips of quartz or topaz. Melt inclusion-bearing quartz grains from the porphyritic granite and pegmatite were homogenized using the conventional hydrothermal rapid-quench technique (Thomas et al. 2000); melt inclusion-bearing quartz and topaz grains from the equigranular granite and pegmatite were homogenized using horizontal cold-seal pressure vessels (Paper IV). In addition, quartz and topaz grains containing melt inclusions from the

granites and pegmatite were homogenized at ambient pressure to obtain compositions of H<sub>2</sub>O-free glass inclusions. These homogenization experiments were performed in a tubular furnace at 900 °C and 20 hours (Thomas 1994). These homogenization methods did not permit direct observation of phase changes during the experiments.

## **2.5. Analytical techniques**

After the melt inclusion homogenization experiments, the sections were polished until the homogenized glass inclusions in the quartz and topaz grains were exposed. They, and the run products of the crystallization experiments, were examined by optical microscope, scanning electron microscopy, electron microprobe, and X-ray powder diffractometry (only the experimental run products). Mineral phases, composition of the glasses from the crystallization experiments, and compositions of the homogenized melt inclusions were analyzed by electron microprobe (detailed analytical conditions for the microprobe analyses are given in Papers III and IV). Water concentrations of some of the melt inclusions and some mineral identifications were determined by confocal Raman spectroscopy following the method of Thomas (2000) and Thomas et al. (2006).

### 3. Petrography and geochemistry

#### 3.1. Topaz granites

The Artjärvi and Säaskjärvi granite stocks are multiphase rapakivi granite intrusions with topaz granite as the most evolved intrusive phase. The Artjärvi stock (Fig. 3) is composed of porphyritic and equigranular biotite granite and equigranular topaz granite, and the Säaskjärvi stock (Fig. 4) comprises equigranular biotite granite and porphyritic topaz granite. The Kymi stock consist of two types of topaz granites – a porphyritic granite at the centre and an equigranular granite at the margin and the stock is rimmed by a pegmatitic zone, stockscheider. The topaz granites of the three granite stocks differ in texture, mineral composition and geochemical characteristics from the more primitive “normal” rapakivi granites within the Wiborg rapakivi granite batholith. Plagioclase-mantled alkali feldspar megacrysts (i.e., the rapakivi texture sensu

lato) are absent. In terms of modal composition, the topaz granites from Kymi are monzogranites (albite grains considered as “plagioclase”) and from Artjärvi and Säaskjärvi syenogranites. Detailed petrographic and geochemical descriptions of the granites are given in Papers I and II.

The equigranular topaz granites at Kymi and Artjärvi are homogeneous and fine- to medium-grained. The main minerals are quartz, perthitic alkali feldspar, and plagioclase; biotite and topaz are ubiquitous minor constituents. Accessory minerals include fluorite, monazite, bastnäsite, columbite, molybdenite, anatase and apatite. Quartz is found as early euhedral phenocrystic quartz and late interstitial quartz. Alkali feldspar is string, vein, or patch perthite. Topaz is found mainly as primary anhedral to subhedral grains, but a significant fraction of topaz is found as small secondary grains in plagioclase. The equigranular topaz granite at Kymi has significantly higher topaz content than the topaz granite at Artjärvi.

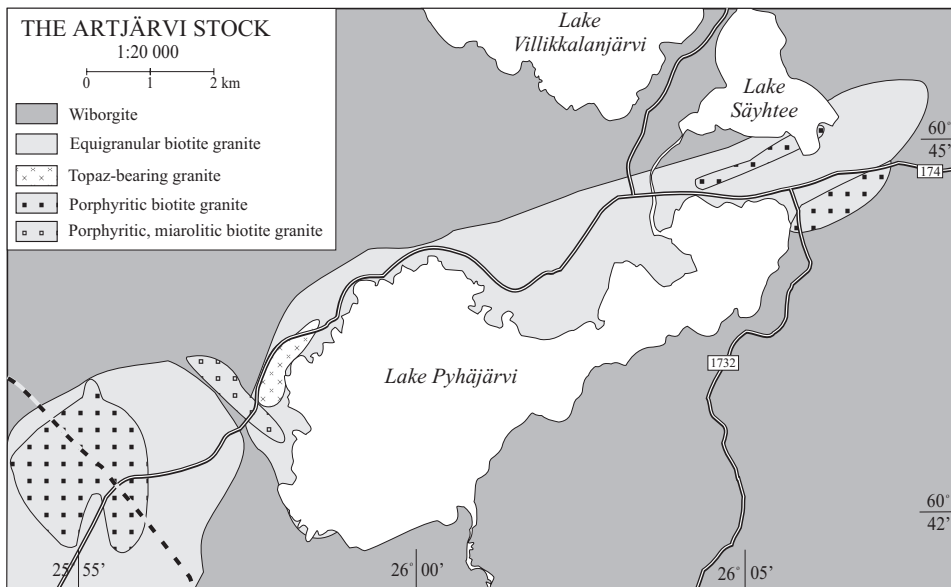
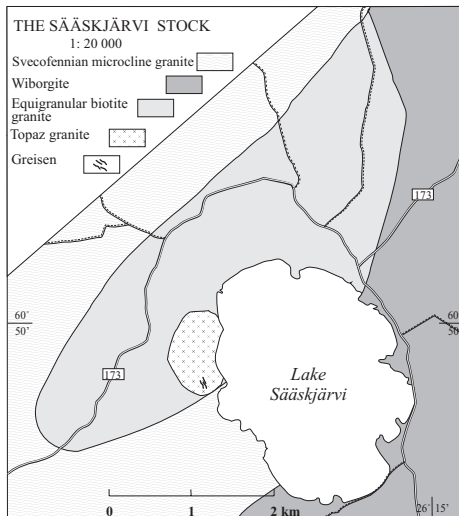


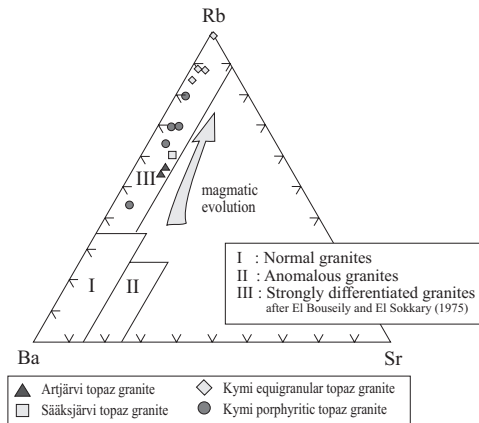
Fig. 3. Lithological map of the Artjärvi granite stock. Modified from Lukkari (2002).

The topaz granites at Sääskjärvi and in the inner part of the Kymi stock are porphyritic with euhedral alkali feldspar megacrysts together with drop quartz in a medium- to fine-grained groundmass. The porphyritic topaz granites show a weak local orientation, and the abundance and size of the megacrysts vary. The groundmass is composed of alkali feldspar (string or vein perthite), plagioclase and quartz. Well-preserved plagioclase is zoned with oligoclase cores and albitic margins, whereas plagioclase grains containing small secondary inclusions of sericite, topaz, fluorite, and quartz (induced by de-anorthitization) are albite throughout. Biotite and topaz are the minor constituents. Topaz is found both as a magmatic mineral and as small, secondary grains replacing plagioclase. Characteristic accessory minerals include fluorite, zircon, anatase, ilmenite, columbite, monazite, thorite, molybdenite and apatite.

The topaz granites show evidence of postmagmatic reactions (exsolution and minor recrystallization of the alkali feldspar,



**Fig. 4.** Lithological map of the Sääskjärvi granite stock. Modified from Lukkari (2002).



**Fig. 5.** Rb-Ba-Sr diagram (after El Bouseily and El Sökkary, 1975) showing the highly evolved character of the topaz granites from the Artjärvi, Sääskjärvi, and Kymi stocks.

alteration of dark mica to chlorite and plagioclase to topaz, fluorite, and muscovite) and the equigranular granite of the Kymi stock appears to have undergone the strongest subsolidus reactions.

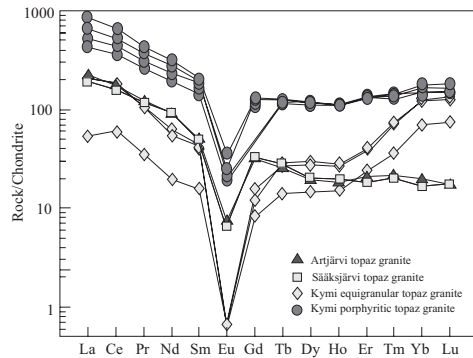
The topaz granites are mainly peraluminous with A/CNK of 0.89 to 1.16 (in average 1.05), rich in F (up to 1.66 wt % F in the equigranular granite of the Kymi stock), and low in Mg, Fe, and Ti. The trace element composition is characterized by anomalously high Li, Be, Ga, Rb, Sn, and Nb and by unusually low Ba, Sr, and Zr concentrations as well as by a strong negative Eu-anomaly. The evolved character of these chemically specialized granites is displayed in Figs. 5 and 6. In the Rb-Sr-Ba diagram (Fig. 5), the topaz granites from all three stocks plot invariably within the field of strongly differentiated granites. The Kymi equigranular granite shows the most evolved character, while the topaz granites at Artjärvi and Sääskjärvi resemble the porphyritic granite of the Kymi stock. The REE patterns (Fig. 6) show deep negative Eu anomalies:  $Eu_N / Eu^*_N$  is 0.2 to 0.1 in the Kymi porphyritic

granite, 0.2 in the Artjärvi and Säaskjärvi granites and 0.1 to 0.0 in the Kymi equigranular granite. This suggests extreme crystal fractionation or preferential partitioning of  $\text{Eu}^{2+}$  in an aqueous fluid phase coexisting with the melt (see Irber 1999), and is thus compatible with petrographic observations. In the Kymi stock local miarolitic cavities, pegmatite-lined druses and mineral alteration, as well as associated mineralized hydrothermal veins and altered fracture zones indicate fluid saturation and fluid loss during late- and postmagmatic stages.

### 3.2. Marginal pegmatites

Marginal pegmatites, stockscheiders (“stock separators”), are typically associated with the roof contacts of topaz granite cupolas (e.g., Breiter et al. 2005, Frindt and Haapala 2004). Stockscheiders are also found in the upper contact zones of the Artjärvi and Kymi topaz granites.

At Artjärvi, the contact between the topaz granite and equigranular biotite granite is marked by a 3-m-wide layered pegmatite zone consisting of fine-grained topaz granite and numerous pegmatite layers parallel to the contact (Paper I). The upper contact of the topaz granite is characterized by parallel, fine-scale schlieren layering showing grading in the proportions of mafic silicates. Generally, the layers have sharp bases and transitional upper parts, but in the uppermost layer, the amount of the mafic minerals decreases downwards from the upper contact. The dark layers are enriched in biotite, plagioclase, zircon, and apatite compared to the host topaz granite. Biotite occurs as crystals aligned parallel to the layering. Euhedral plagioclase crystals are found as accumulations in the dark layers with interstitial quartz and alkali feldspar. The pegmatite layers cut the fine-scale layering and the topaz granite, and locally bifurcate. They are homogeneous with no internal layering;



**Fig. 6.** Chondrite-normalized (Boynnton, 1984) REE patterns of the topaz granites from the Artjärvi, Säaskjärvi, and Kymi stocks.

in a few layers, fan-shaped alkali feldspar crystals show directional growth away from the upper contact. Besides alkali feldspar, the pegmatite layers contain quartz, plagioclase, and biotite as main minerals, and topaz, zircon, fluorite, ilmenite, and apatite as accessory minerals. The pegmatite layers have graphic quartz-alkali feldspar and quartz-plagioclase intergrowths.

Whole-rock composition shows that the principal chemical differences between the granite, pegmatite, and biotite-rich layers are controlled by mineral proportions. Pegmatite layers show slight enrichment in  $\text{K}_2\text{O}$  and Rb and depletion in  $\text{CaO}$ ,  $\text{Fe}_2\text{O}_3^{\text{tot}}$ ,  $\text{TiO}_2$  and  $\text{P}_2\text{O}_5$  compared with granite layers, probably because of the enrichment of alkali feldspar and depletion of mafic accessory minerals such as biotite and apatite. Biotite-rich layers in the upper part of the stockscheider clearly differ from the granite and pegmatite layers. They are enriched in  $\text{CaO}$ ,  $\text{Fe}_2\text{O}_3^{\text{tot}}$ ,  $\text{TiO}_2$ ,  $\text{P}_2\text{O}_5$ , Zr, Ba, La, Ce and Nd, and slightly depleted in  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$  and  $\text{SiO}_2$ , owing to the relative abundances of plagioclase, biotite, zircon, and apatite.

At Kymi, the contact between the equigranular topaz granite and the surrounding rapakivi granite is characterized



by a 2-4 m wide, heterogeneous pegmatite zone consisting of massive pegmatite and coarse pegmatite pockets or druses in the massive pegmatite and equigranular granite (Paper II). Some aplite-pegmatite dikes cut the country rock (wiborgite) in the immediate vicinity of the contact and parallel to it. The main minerals in the stockscheider are alkali feldspar, quartz, albite, biotite, and topaz. Accessory minerals include muscovite,

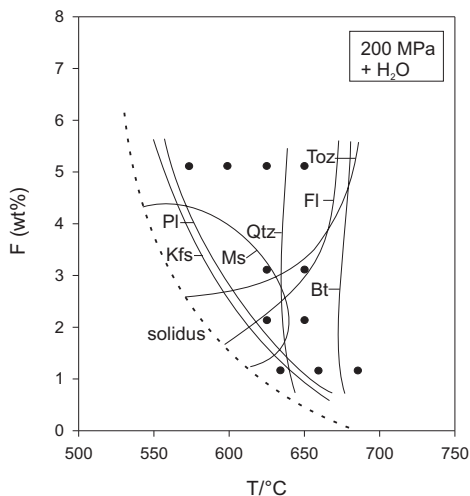
fluorite, tourmaline, monazite, bastnaesite, arsenopyrite, molybdenite, beryl, columbite, cassiterite, and plumbomicrolite. The stockscheider thus belongs to the NYF pegmatites of Černý and Ercit (2005). A characteristic textural feature of the massive stockscheider pegmatite is a dendritic growth of biotite perpendicular to the country rock contact toward the interior of the stock.

## 4. Experimental results on Kymi granite stock

### 4.1. Crystallization experiments

Phase relations of F-rich Kymi equigranular topaz granite have been investigated experimentally as a function of water activity and F content at 100 to 500 MPa (Paper III). The crystalline phases of the run products include all naturally occurring main mineral phases (quartz, alkali feldspar, plagioclase, biotite, fluorite and topaz) plus muscovite. In addition, glass and fluid phase were present in all experiments. The experimental results show that F has a significant effect on the phase relations and the composition of the melt and mineral phases.

The phase relations for the four studied systems (initial F content of 1.13, 2.12, 3.10, and 5.11 wt %) at 200 MPa are presented in Fig. 4a-d of Paper III. The results show that biotite is the only F-bearing phase present in the system with the initial F content of 1.13 wt %. With increasing bulk F content, first fluorite and then topaz are observed in the run products. Topaz crystallizes only when F content of the melt exceeds 2.5 - 3 wt %. Alkali feldspar crystallizes close to the solidus at all water activities and bulk F contents. Muscovite is only observed in compositions with bulk F contents of 2.12 and 3.10 wt %. The only system in which all four F-bearing phases (biotite, muscovite, fluorite and topaz) are present is 3.10 wt % F. For this composition, the crystallization sequence varies strongly as a function of water activity: at low  $a_{H_2O}$ , plagioclase crystallizes as a liquidus phase and fluorite, topaz, and muscovite near solidus, whereas in water saturated conditions, plagioclase crystallizes near solidus and biotite, fluorite, and topaz (crystallize) near the liquidus. In the 5.11 wt % F system, topaz crystallizes as liquidus mineral and is followed first by



**Fig. 7.** Phase relations as a function of temperature and F content of the melt at 200 MPa and water saturation. Experiments are marked with black dots. Mineral abbreviations (Kretz, 1983): Bt-biotite, Fl-fluorite, Kfs-alkali feldspar, Ms-muscovite, Pl-plagioclase, Qtz-quartz, Toz-topaz.

fluorite and biotite, then quartz. The stability fields of feldspars are strongly shifted to low temperatures. The effect of F on the phase relations at 200 MPa and water saturated conditions is presented in Fig. 7. Stability fields of fluorite and topaz increase with increasing fluorine content of the melt, while the crystallization temperatures of plagioclase and alkali feldspar decrease with increasing F. The stability fields of quartz and biotite do not change significantly, and the stability of muscovite at 200 MPa is restricted to compositions between 1-5 wt % bulk F.

The compositions of experimental plagioclases ( $An_1 - An_{23}$ ) differ from the compositions of natural plagioclase of the Kymi equigranular topaz granite ( $An \sim 2$ ). Furthermore, the experiments show that the An content of plagioclase decreases with increasing bulk F content of the melt. This can be explained by the crystallization of increasing amounts of fluorite with increas-

ing amount of F in the bulk composition, leading to residual melts almost devoid of Ca. Another possible explanation is a back-reaction of plagioclase, and is discussed later. Also, the composition of biotite is influenced by the F content of the melt. The F content of biotite is proportional to the bulk F content of the melt, so that the calculated partition coefficient for F between biotite and glass ( $D(F)^{Bt/glass}$ ) varies from 0.80 to 1.89 (1.29 on average), and decreases with increasing F content and aluminosity of the glass. Increasing bulk F content of the system increases the F but decreases the Ca content in the residual melt. Furthermore, the A/CNK increases with increasing F content of the melt, and is interpreted to be related to the high F content of melts saturated with fluorite (Paper III).

The experiments at 650 °C show that the stabilities of muscovite and fluorite are pressure dependent (Fig. 8 in Paper III). At 100 MPa (for a given F content) muscovite is not present, but is stable at higher pressures. The stability field of muscovite is shifted to higher pressures in F-rich systems (e.g., at 400 MPa, ~5 wt % F, 650 °C). Fluorite, on the contrary, is stable at low pressure but topaz stability is probably not strongly dependent on pressure. Thus, for a given bulk composition and F content, topaz and muscovite will be the first F-bearing phases to crystallize in peraluminous melts at high pressures, whereas fluorite and topaz are expected to be the first F-bearing phases at low pressures (Paper III).

## 4.2. Melt inclusion experiments

Melt inclusions from the granites and pegmatite of the Kymi stock provide compositional information of the melt from which the host minerals (quartz and topaz) have crystallized. In this study, homogenization of the melt inclusions was performed under

pressure, to seal their volatile content during the experiment. The results obtained from the melt inclusion study are presented in Paper IV.

The granites and pegmatite of the Kymi stock contain two coexisting types of melt inclusions that differ in volatile content: volatile-poor (type A) and volatile-rich (type B). In addition, the granites contain large melt inclusions with low F, Cl and FeO contents, and the equigranular granite small melt inclusions with high F content. The low-F melt inclusions in the granites are interpreted to have formed during the rehomogenization (Paper IV), and therefore the compositions of this type of melt inclusions are not discussed further. Some of the unheated melt inclusions in quartz from the equigranular granite contained crystals of  $LiAlF_4$ , topaz and cryolite ( $Na_3AlF_6$ ), topaz and cryolite are found also as solid aggregates in quartz. Coexisting melt and topaz inclusions are abundant in all phases of the Kymi stock, especially in the pegmatite. Many melt inclusions in the porphyritic granite contain small crystals of muscovite. This is unexpected, because muscovite is absent as a magmatic mineral in the porphyritic granite. Some fluid inclusions in topaz from the pegmatite contain zabuyelite ( $Li_2CO_3$ ) daughter crystals.

Average melt inclusion compositions from the granites and pegmatite and the whole-rock compositions of the Kymi stock are presented in Table 1. All melt inclusions are volatile-rich. The type B melt inclusions are remarkably rich in  $H_2O$  (up to 29 wt % in melt inclusions from pegmatite), and some melt inclusions from the equigranular granite are extremely F-enriched (up to 14.5 wt % F). Melt inclusions from the equigranular granite have notably lower  $H_2O$  concentration than those from the porphyritic granite and pegmatite (Table 1). The average F contents of the melt inclusions are

0.9 wt % from the porphyritic granite (1.11 wt % in whole rock), 1.9 wt % and 11.6 wt % (the high-F type) from the equigranular granite (1.66 wt % in whole rock), and 1.3 wt % from the pegmatite. In general, melt inclusions (especially the high-F type) are depleted in K and Ca, and enriched in Sn compared to the whole-rock (Table 1). They are predominantly peraluminous like the whole-rocks; few melt inclusions from the granites show weakly peralkaline compositions. The high-F melt inclusions from the

equigranular granite are strongly peraluminous, mainly because of the very low K contents. Melt inclusions from the pegmatite are enriched in Rb compared to those from the equigranular granite, and the melt inclusions from the equigranular granite are depleted in Rb compared to the whole rock. The normative compositions of the melt inclusions plot into the field of 1-2 wt % F, obtained from the experiments on the Kymi equigranular granite at 200 MPa (Paper IV).

**Table 1.** Average compositions of melt inclusions in quartz from the granites and pegmatite of the Kymi topaz granite stock and of the bulk rocks of the parental granites

Sample	Porphyritic granite	Porphyritic granite	Equigranular granite	Equigranular granite	Equigranular granite*	Pegmatite
	Whole rock	Melt inclusions	Whole rock	Melt inclusions	Melt inclusions, high-F	Melt inclusions
SiO <sub>2</sub>	74.30	69.56 ± 1.46	73.70	73.19 ± 1.00	68.51 ± 2.94	69.62 ± 1.59
Al <sub>2</sub> O <sub>3</sub>	12.40	12.10 ± 1.04	14.70	12.73 ± 0.48	16.61 ± 1.98	13.41 ± 0.61
Na <sub>2</sub> O	2.73	3.69 ± 0.32	4.01	4.05 ± 0.30	3.88 ± 1.04	3.55 ± 0.30
K <sub>2</sub> O	5.03	3.78 ± 0.31	4.60	3.94 ± 0.62	0.65 ± 0.43	3.91 ± 0.49
CaO	1.61	0.47 ± 0.22	0.90	0.20 ± 0.05	0.10 ± 0.14	0.23 ± 0.15
FeO	1.6	n.a.	0.50	n.a.	n.a.	n.a.
Fe <sub>2</sub> O <sub>3</sub>	0.80	n.a.	0.42	n.a.	n.a.	n.a.
FeO <sub>tot</sub>	n.a.	0.34 ± 0.11	n.a.	0.07 ± 0.08	0.57 ± 0.80	0.62 ± 0.43
MgO	0.02	0.01 ± 0.02	0.00	0.01 ± 0.01	d.l.	0.01 ± 0.01
MnO	0.01	0.04 ± 0.05	0.01	0.01 ± 0.01	0.03 ± 0.06	0.07 ± 0.04
TiO <sub>2</sub>	0.13	0.01 ± 0.01	0.04	0.01 ± 0.01	d.l.	0.01 ± 0.01
Sn (ppm)	29	79 ± 85	10	33 ± 27	154 ± 122	239 ± 298
P <sub>2</sub> O <sub>5</sub>	0.01	0.02 ± 0.03	0.01	0.02	0.02 ± 0.02	0.01 ± 0.01
Cl	0.02	0.17 ± 0.07	0.01	0.01 ± 0.01	0.50 ± 0.11	0.20 ± 0.09
F	1.11	0.93 ± 0.32	1.66	1.88 ± 0.49	11.61 ± 3.33	1.31 ± 0.39
Rb (ppm)	641	n.a.	990	588 ± 232	692 ± 96	1574 ± 369
H <sub>2</sub> O <sup>a</sup>	0.80	10.18 ± 1.25	0.3	4.76 ± 1.10	2.96 ± 2.45	7.87 ± 1.65
H <sub>2</sub> O <sup>b</sup>	n.a.	10.72 ± 0.56	n.a.	n.a.	n.a.	11.6 ± 0.13
Total <sup>c</sup>	100.00	100.78	99.40	100.23	97.72	100.59
A/CNK <sup>d</sup>	0.96	1.10 ± 0.13	1.11	1.13 ± 0.12	2.45 ± 0.87	1.29 ± 0.12
Q	39.9	36.1	33.6	37.6	-	41.5
Ab	26.3	34.6	36.9	37.1	-	31.5
Or	33.9	29.3	29.6	25.3	-	27.0

All analyses (except marked with \*) are corrected as a function of H<sub>2</sub>O content of melt (R<sup>2</sup>=0.9 for Na<sub>2</sub>O and K<sub>2</sub>O). Water is added and the analyses are recalculated to sum of 100 %.

n.a.= not analyzed, d.l.= under detection limit.

<sup>a</sup>H<sub>2</sub>O by subtracting the oxide sum (in wt %) of electron microprobe analysis from 100 %.

<sup>b</sup>H<sub>2</sub>O Determined by confocal Raman spectroscopy, 9 samples, 3 measurements from each.

<sup>c</sup>Sum corrected for F and Cl.

<sup>d</sup>Molecular Al<sub>2</sub>O<sub>3</sub>/(CaO+Na<sub>2</sub>O+K<sub>2</sub>O).

\*rehomogenized at 1 atm pressure.

## 5. Origin of topaz granites within the Wiborg rapakivi granite batholith

### 5.1. Artjärvi and Säaskjärvi stocks

Petrographic and geochemical studies of the Artjärvi and Säaskjärvi granite stocks (Paper I) show that these granites are evolved multiphase rapakivi granite intrusions with an order of emplacement of (1) porphyritic biotite granite, (2) even-grained biotite granite, and (3) topaz granite. Major and trace element chemistry shows that the general evolution trends go from porphyritic biotite granite through even-grained biotite granite to topaz granite at Artjärvi and from even-grained biotite granite to topaz granite at Säaskjärvi. The topaz granites from Artjärvi and Säaskjärvi show petrographic and geochemical features similar to those of other topaz granites in Finland (Haapala 1977a, 1997, Haapala and Lukkari 2005, Rämö 1991, Edén 1991). The petrographic and geochemical results also allow discussion about the origin of the layered marginal pegmatite at the upper contact of the topaz granite at Artjärvi. The pegmatite is considered to have formed in two steps (Fig. 11 in Paper I). First, the schlieren layering of the stockscheider formed by the velocity-gradient flow sorting mechanism (Tobish et al. 1997). Narrowing of the magma chamber produced an increase in flow velocity, which may have caused mafic cumulates to accumulate underneath the overhang and along the walls. Most of the accumulation was associated with upward vertical flow, but accumulation also took place under horizontal flow conditions. At Artjärvi, the presence of biotite crystals oriented parallel to the schlieren layers indicates accumulation during subhorizontal flow along the hanging wall contact. Subsequently, the cooling and contraction of the topaz granite formed frac-

tures parallel to the roof contact and residual pegmatite magmas were injected along fractures to form pegmatite layers.

### 5.2. Experimental constrains on the evolution of F-rich peraluminous melts

Stability of fluorite and topaz and the composition of the coexisting melt phase are determined in the crystallization experiments to discuss the solubility of F in natural silicate melts (Paper III). In addition, determination of compositions of melt inclusions from the topaz granites and pegmatite of the Kymi stock enables discussion about the late-stage evolution of F-enriched peraluminous melts (Paper IV).

The experimental study on the equigranular topaz granite of the Kymi stock (Paper III) confirms that fluorite and topaz can crystallize as magmatic liquidus phases in F-rich peraluminous systems in accordance with studies by Price et al. (1999), Xiong et al. (1999), and Veksler and Thomas (2002). This study shows that the main parameters controlling the stability of fluorite ( $\text{CaF}_2$ ) are the F and Ca contents of the melt. At conditions in which plagioclase crystallizes as a liquidus phase (low water activity and moderate F content), crystallization of plagioclase consumes Ca from the melt and thus displaces the crystallization of fluorite near to solidus temperatures. With increasing F content of the melt, the thermal stabilities of fluorite and topaz increase at the expense of plagioclase stability. Decrease of CaO with increasing F content of the melt is also shown in the melt inclusion experiments (Paper IV).

The crystallization experiments show that the F content of the melt increases with increasing amount of F in the bulk system, despite the crystallization of F-bearing minerals such as topaz and fluorite (Paper III). Thus, the crystallization of fluorite that con-

sumes Ca from the residual melt does not buffer the F content of melts in natural systems. This is partly due to either the increasing A/CNK with ongoing crystallization in residual melts and to the preferential association of F with excess aluminum in silicate melts (e.g., Manning 1981, Webster et al. 1997), or the association of F with excess Al and Ca (Dolejš and Baker 2006). Hence, the F content of a melt saturated with fluorite increases with increasing A/CNK. The positive correlation between F and A/CNK is not shown clearly in the melt inclusion compositions; only the high-F melt inclusions from the equigranular granite are strongly peraluminous (Paper IV).

The majority of the melt inclusions from the Kymi topaz granites show only similar F contents than the whole rock granites (Table 1). However, the occurrence of cryolite and topaz clusters in quartz grains and unheated quartz-hosted melt inclusions, and the presence of high-F melt inclusions in the equigranular granite strongly favor the presence of an extremely F-enriched melt during the crystallization of quartz. The simultaneous entrapment of topaz crystals and melt inclusions in quartz shows that the melt was saturated with topaz during the crystallization of quartz. According to the experimental study (Paper III), the F content of the melt should exceed 2.5-3.0 wt % for the crystallization of topaz to take place. However, the results of the crystallization experiments (Paper III) do not allow discussion of the extremely F and H<sub>2</sub>O -rich character of the melt.

The whole-rock and melt inclusion compositions, as well as the glass composition of the crystallization experiments, are mainly peraluminous. However, there are some indirect indications that may suggest the idea of melt separation and formation of a peralkaline melt fraction at the final stages of crystallization (see Thomas et al. 2000, 2005, 2006). The coexistence of the two

types of melt inclusions (type-A and type-B) in quartz from all three phases of the Kymi stock might represent the two immiscible melt fractions, the very high concentrations of H<sub>2</sub>O in type-B melt inclusions (up to 29 wt %) are possible only in peralkaline silicate melts at such low pressures (Mustart 1972). Clusters of cryolite and topaz in unheated quartz from equigranular granite could be remnants of conserved and isolated peralkaline melt batches. However, more fluid and melt inclusion research is required to determine the possible role of liquid immiscibility at the final stages of the crystallization of the Kymi granite stock.

### **5.3. Modeling the crystallization of the Kymi equigranular granite**

Combined petrographic, geochemical, experimental and melt inclusion studies are a powerful tool in reconstructing the magmatic evolution of the Kymi topaz granite stock. The good correspondence between the whole-rock composition of the equigranular granite (Paper II) and the melt compositions obtained from the melt inclusion study (Paper IV) proves that the chosen starting material for the crystallization experiments (Paper III) was indeed representative. Petrographic, geochemical, and mineral chemical studies (Haapala and Ojanperä 1972, Rieder et al. 1996, Elliott 2001, Haapala and Lukkari 2005) indicate that the equigranular topaz granite of the Kymi stock crystallized quite rapidly under low pressure and fluid-saturated conditions, and that the crystallization may have started at ~ 660 – 610 °C or even below. Petrographic observations imply that plagioclase was the first main mineral to crystallize, and was followed by early quartz, topaz, alkali feldspar / biotite, fluorite, and late quartz.

Combined petrological and experimental studies of the equigranular topaz granite

indicate that plagioclase was the liquidus phase at nearly water-saturated (fluid-saturated) conditions and that the F content of the melt was ~2 - 3 wt % at the beginning of crystallization. The melt inclusion analyses of Paper IV show that the early quartz crystals crystallized from a melt containing an average of 1.9 wt % F and 4.8 wt % H<sub>2</sub>O (Table 1). Using the average partition coefficient  $[D(F)]^{Bt/glass} = 1.29$  obtained from the crystallization experiments (Paper III), the mean F content of natural biotite (3.92 wt %) indicates that these minerals were in equilibrium with melts containing about 3 wt % F (assuming that biotite composition was not affected by subsolidus reactions). Furthermore, the presence of topaz in the equigranular granite indicates that the F content of the melt was somewhat greater than 2.1 wt %. As a result of crystallization of anhydrous, F-free minerals during the first crystallization stage (plagioclase and quartz), the F content of the residual melt was high enough (~3 wt %) for the crystallization of topaz and fluorite. Finally, close to the solidus temperature, alkali feldspar and quartz crystallized.

In the crystallization experiments at 200 MPa, biotite and muscovite crystallized near to the liquidus temperature at the conditions described above. Petrographic observations from the equigranular granite, however, suggest that biotite crystallized after quartz and topaz, whereas muscovite is absent as a magmatic mineral. The study by Webster et al. (1987) shows that the thermal stability of biotite increases with increasing pressure. The crystallization experiments in this study (Paper III) show that the stability of muscovite is shifted to higher pressures in F-rich systems. Thus, the early crystallization of biotite and the presence of muscovite at 200 MPa, indicate that the equigranular granite may have crystallized at a pressure lower than 200 MPa. The presence

of muscovite as daughter crystals in the melt inclusions from the porphyritic granite of the Kymi stock and, absent in the equigranular granite may therefore be explained by crystallization during the homogenization procedure at a homogenization pressure (300 MPa) higher than the trapping pressure (Paper IV).

Taking into account the compositional difference between the natural and experimental plagioclase (An<sub>2</sub> and An<sub>1-23</sub>, respectively) and the decrease of An content of the plagioclase with increasing F content of the melt, a new reaction for the saturation of fluorite and topaz is presented (Paper III). This reaction, CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub> (plagioclase) + 2[AlF<sub>3</sub>] = CaF<sub>2</sub> (fluorite) + 2Al<sub>2</sub>SiO<sub>4</sub>F<sub>2</sub> (topaz), is modified from a reaction proposed by Dolejš and Barker (2004) for metaluminous systems to be more appropriate for peraluminous systems. The reaction shows that the An component of plagioclase is consumed by the formation of F-bearing phases. The back-reaction probably started under super-solidus conditions when F, dissolved in the melt or in the coexisting fluid phase, reacted with plagioclase. Considering that aqueous (F-bearing) fluids can penetrate minerals along microcracks much easier than silicate melts, which have a higher viscosity than fluids, and that fluid-saturation was reached early in the crystallization sequence (see above), the transport of elements via fluids may have been determinant for the back reaction of plagioclase, even at magmatic stages. The melt inclusion study confirms the presence of an extremely volatile rich melt fraction during the crystallization of the equigranular granite (Paper IV). In contrast, the presence of quartz, topaz, and fluorite (± sericite) as very small grains in the natural, turbid plagioclase (albite) strongly suggests that the densely packed inclusions are not magmatic, but were formed by the back-reaction of primary Ca-bearing plagioclase

(oligoclase). The formation of nearly pure albite by interaction between F-bearing fluid and oligoclase may also have continued at the subsolidus stage (see Haapala 1997). Field observations from the Kymi stock and the absence of very low An plagioclase in highly evolved volcanic rocks with compositions similar to the granites of Kymi (Christiansen et al. 2007) confirm the mobilization of the fluid phase. Mirolitic cavities and pegmatite-lined druses in the stock-scheider and in the contact zone between the porphyritic and equigranular granite suggest that much of the crystallization took place under fluid-saturated conditions. The hydrothermal greisen and quartz veins and altered fracture zones further suggest vigorous fluid loss (Paper II).

#### **5.4. Origin of the zoned structure of the Kymi granite stock**

This thesis presents two models for the formation of the zoned structure of the Kymi granite stock (Papers II and IV). Based on petrographic, mineralogical and geochemical studies, Haapala and Lukkari (2005) concluded that the zoned structure of the Kymi topaz granite stock is a result of differentiation and convection within the magma chamber and upward flow of the residual melt along the sloping contacts (model 2, Paper II), rather than a result of an intrusion of highly evolved residual melt from the

deeper part of the chamber along the fractured contact between the porphyritic granite and the country rock (model 1, Paper II). However, new field observations together with results obtained from the melt inclusion study (Paper IV) lead to reconsideration of the development of the zoned structure, and the model 1 is considered more compatible (Paper IV).

According to the improved model (Paper IV), the crystallization of the Kymi stock started with solidification of the porphyritic granite against the country rock. As the crystallization of the porphyritic granite proceeded, a zone of highly evolved granite magma was accumulated in the carapace of the magma chamber, between the porphyritic granite and the country-rock rapakivi granites, and led to crystallization of the equigranular granite and pegmatite. The opening of the contact between the porphyritic granite crystal mush and the country-rock rapakivi granites may have been related to repeated shallow sub-surface cauldron subsidence (cf. Vormaa 1976, Selonen et al. 2005) or simple gravitational sinking of a semisolid porphyritic granite block deeper into the magma chamber. The new magma rose from the inner or lower parts of the chamber and fractionated further during upwelling along the walls of the chamber, and possibly also along fractures through the porphyritic granite.



## 6. Conclusions

The following conclusions can be made based on the petrographic, geochemical, experimental and melt inclusion studies of the Artjärvi, Säaskjärvi, and Kymi granite stocks within the classic Wiborg rapakivi granite batholith:

1. The anomalous geochemistry and mineralogy of the topaz granites are essentially magmatic in origin; postmagmatic reactions have only slightly modified the compositions. The Kymi equigranular topaz granite shows the most evolved character, and the topaz granites at Artjärvi and Säaskjärvi resemble the porphyritic topaz granite of the Kymi stock.

2. The stockscheider at the roof contact of the Artjärvi stock is considered to have formed in two steps: (a) The schlieren layering of the stockscheider has formed by velocity-gradient sorting mechanism parallel to the flow, which led to accumulation of mafic minerals along the upper contact of the topaz granite, (b) cooling and contraction of the topaz granite formed fractures parallel to the roof contact and the residual pegmatite magmas were injected along the fractures to form the pegmatite layers.

3. Crystallization experiments show that with increasing F content of the melt, the thermal stabilities of fluorite and topaz increase at the expense of plagioclase stability. Increasing F concentrations in the melt seem to have had a minor or no effect on the crystallization temperatures of quartz and biotite. The stability field of muscovite is restricted to compositions with more than 1.1 wt % and less than 5.1 wt % bulk F at 200MPa.

4. The reaction modeling the formation of fluorite and topaz,  $\text{CaAl}_2\text{Si}_2\text{O}_8$  (plagioclase) +  $2[\text{AlF}_3] = \text{CaF}_2$  (fluorite) +  $2\text{Al}_2\text{SiO}_4\text{F}_2$

(topaz), implies that the An component of plagioclase is consumed by the formation of the F-bearing phases. Thus, the formation of topaz and fluorite may occur at magmatic stages, simultaneously with the back-reaction of plagioclase.

5. The stability of muscovite and fluorite is pressure dependent, while the stability of topaz is probably not strongly dependent on pressure. In peraluminous, F-bearing melts containing more than 1 wt % F, topaz and muscovite are expected to be the first F-bearing phases to crystallize at high pressure, fluorite and topaz at low pressure.

6. The majority of the melt inclusions from the Kymi stock show similar F concentrations as the whole rocks. The occurrence of clusters of cryolite and topaz in unheated melt inclusions and as solid inclusions in the equigranular granite and the presence of the high-F melt inclusions in the equigranular granite indicate extremely high concentrations of F in the melt.

7. The crystallization of the equigranular topaz granite started with plagioclase at nearly water-saturated (fluid-saturated) conditions and F content of the melt of ~2 - 3 wt %. The early crystallization of biotite and the presence of muscovite in the crystallization experiments at 200 MPa, in contrast with late-stage crystallization of biotite and the absence of muscovite in the natural assemblage, indicate that crystallization pressure may have been lower than 200 MPa for the granite.

8. The zoned structure of the Kymi stock is interpreted to be a result of intrusion of highly evolved residual melt from deeper parts of the magma chamber along the fractured contact between the porphyritic granite crystal mush and the country rock. The equigranular granite and pegmatite crystallized from this melt or its derivatives.

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## 8. References

- Badanina, E.V., Veksler, I.V., Thomas, R., Syr-  
itso, L.F., Trumbull, R.B., 2004. Magmatic  
evolution of Li-F, rare-metal granites: a case  
study of melt inclusions in the Khangilay  
complex, Eastern Transbaikalia (Russia).  
*Chemical Geology* 210, 113-133.
- Beus, A.A., Zalachkova, N.E., 1964. Post-mag-  
matic high temperature metasomatic proces-  
ses in granitic rocks. *International Geology  
Review* 6, 668-681.
- Boynnton, W.V., 1984. Cosmochemistry of the  
Rare Earth Elements: Meteorite studies. In:  
Henderson P. (Editor), *Rare earth element  
geochemistry*, Elsevier, Amsterdam, Ox-  
ford, New York, Tokyo, 63-114.
- Breiter, K., Müller, A., Leichmann, J., Gabašová,  
A., 2005. Textural and chemical evolution  
of fractionated granitic system: the Podlesí  
stock, Czech Republic. *Lithos* 80, 323-345.
- Christiansen, E.H., Burt, D.M., Sheridan, M.F.,  
Wilson, R.T., 1983. The petrogenesis of to-  
paz rhyolites from the western United States.  
*Contributions to Mineralogy and Petrology*  
83, 16-30
- Christiansen, E.H., Haapala, I., Hart, G.L., 2007.  
Are Cenozoic topaz rhyolites the erupted  
equivalents of Proterozoic rapakivi gran-  
ites? Examples from the western United  
States and Finland. *Lithos* doi:10.1016/  
j.lithos.2007.01.010.
- Černý, P., Ercit, T.S., 2005. The classification of  
granitic pegmatites revisited. *Can Miner.* 43,  
2005-2026.
- Congdon, R.D., Nash, W.P., 1991. Eruptive  
pegmatite magma: rhyolite of the Honey-  
comb Hills, Utah. *American Mineralogist*  
76, 1261-1278.
- Dingwell, D.B., 1987. Melt viscosities in the sys-  
tem  $\text{NaAlSi}_3\text{O}_8\text{-H}_2\text{O-F}_2\text{O}_{-1}$ . In: Mysen B.O.  
(ed) *Magmatic processes: Physicochemical  
principles*. Geochemical Soc Special Publi-  
cation 1, 423-433.
- Dingwell, D.B., Scarfe, C.M., Cronin, D.J., 1985.  
The effect of fluorine on viscosities in the  
system  $\text{Na}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2$ : implications for  
phonolites, trachytes and rhyolites. *Ameri-  
can Mineralogist* 70, 80-87.
- Dingwell, D.B., Knoche, R., Webb, S.L., 1993.  
The effect of F on the density of haplogranite  
melt. *American Mineralogist* 78, 325-330.
- Dolejš, D., Baker, D.R., 2004. Thermody-  
namic analysis of the system  $\text{Na}_2\text{O-K}_2\text{O-  
CaO-AL}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O-F}_2\text{O}_{-1}$ : Stability of  
fluorine-bearing minerals in felsic igneous  
suites. *Contributions to Mineralogy and Pe-  
trology* 146, 762-778.
- Dolejš, D., Baker, D.R., 2006. Fluorite solubility  
in hydrous haplogranitic melts at 100 MPa.  
*Chemical Geology* 225, 40-60.
- Edén, P. 1991. A specialized topaz-bearing rap-  
pakivi granite and associated mineralized  
greisen in the Ahvenisto complex, SE Fin-  
land. *Bulletin of the Geological Society of  
Finland* 63, 25-40.
- El Bouseily, A.M., El Sökkary, A.A., 1975. The  
relation between Rb, Ba, and Sr in granitic  
rocks. *Chemical Geology* 16, 207-219.
- Elliott, B., 2001. Crystallization conditions of the  
Wiborg rapakivi batholith, SE Finland: An  
evaluation of amphibole and biotite mineral  
chemistry. *Mineralogy and Petrology* 72,  
305-324.
- Frindt, S., Haapala, I., 2004. Anorogenic Gross  
Spitzkoppe granite stock in central western  
Namibia: Part II. Structures and textures  
indicating crystallization from undercooled  
melt. *American Mineralogist* 89, 857-866.
- Haapala, I., 1977. Petrography and geochemis-  
try of the Eurajoki stock; a rapakivi-granite  
complex with greisen-type mineralization in  
southwestern Finland. *Geological Survey of  
Finland, Bulletin* 286.
- Haapala, I. 1995. Metallogeny of the rapakivi  
granites. *Mineralogy and Petrology* 54, 149-  
160.
- Haapala, I. 1997. Magmatic and postmagmatic  
processes in tin-mineralized granites: topaz-  
bearing leucogranite in the Eurajoki rapakivi  
granite stock, Finland. *Journal of Petrology*  
38, 1645-1659.
- Haapala, I., Ojanperä, P., 1972. Genthelvitte-bear-  
ing greisens in southern Finland. *Geological  
Survey of Finland, Bulletin* 259
- Haapala, I., Rämö, O.T., 1999. Rapakivi gran-  
ites and related rocks: An introduction. In:  
I. Haapala, O.T. Rämö (Eds.), *Rapakivi  
granites and related rocks*. *Precambrian Re-  
search* 95, 1-7.
- Haapala, I., Lukkari, S., 2005. Petrological and  
geochemical evolution of the Kymi stock, a

- topaz granite cupola within the Wiborg rapakivi batholith, Finland. *Lithos* 80, 347-362.
- Irber, W., 1999. The lanthanide tetrad effect and its correlation with K/Rb, Eu/Eu\*, Sr/Eu, Y/Ho, and Zr/Hf of evolving peraluminous granite suites. *Geochimica et Cosmochimica Acta* 63, 439-508.
- Kovalenko, V.I., Kuzmin, M.I., Antipin, V.S., Petrov, L.L., 1971. Topaz-bearing quartz keratophyre (ongonite), a new variety of subvolcanic igneous dike rocks. *Doklady Akademii Nauk SSSR, Earth Science Section* 199, 132-135.
- Kretz, R., 1983. Symbols for rock-forming minerals. *American Mineralogist* 68, 277-279.
- London, D., Morgan, G.B., Hervig, R.L., 1989. Vapor-undersaturated experiments with Macusani glass + H<sub>2</sub>O at 200 MPa and the internal differentiation of granitic pegmatites. *Contributions to Mineralogy and Petrology* 102, 1-17.
- Lukkari, S., 2002. Petrography and geochemistry of the topaz-bearing granite stocks in Artjärvi and Säaskjärvi, western margin of the Wiborg rapakivi granite batholith. *Bulletin of the Geological Society of Finland* 74, 115-132.
- Lukkari, S. Holtz, F., 2007. Phase relations of a F-enriched peraluminous granite: An experimental study of the Kymi topaz granite stock, southern Finland. *Contributions to Mineralogy and Petrology* 153, 273-288.
- Manning, D.A.C., 1981. The effect of fluorine on liquidus phase relationships in the system Qz-Ab-Or with excess water at 1 kb. *Contributions to Mineralogy and Petrology* 76, 206-215.
- Mustart, D.A., 1972. Phase relations in the peralkaline portion of the system Na<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-H<sub>2</sub>O. PhD thesis, Stanford University, USA, 187 pp.
- Pichavant, M., Kontak, D.J., Herrera, J.V., Clark, A.H., 1988a. The Miocene-Pliocene Macusani volcanics, SE Peru I. Mineralogy and magmatic evolution of a two-mica aluminosilicate-bearing ignimbrite suite. *Contributions to Mineralogy and Petrology* 100, 300-324.
- Pichavant, M., Kontak, D.J., Briquieu, L., Herrera, J.V., Clark, A.H. 1988b. The Miocene-Pliocene Macusani volcanics, SE Peru II. Geochemistry and origin of a felsic peraluminous magma. *Contributions to Mineralogy and Petrology* 100, 325-338.
- Price, J.D., Hogan, J.P., Gilbert, M.C., London, D., Morgan, G.B., 1999. Experimental study of titanite-fluorite equilibria in the A-type Mount Scott Granite: Implications for assessing F contents of felsic magma. *Geology* 27, 951-954.
- Rämö, O.T. 1991. Petrogenesis of the Proterozoic rapakivi granites and related basic rocks of southeastern Fennoscandia: Nd and Pb isotopic and general geochemical constraints. *Geological Survey of Finland, Bulletin* 355, 161p.
- Rämö, O.T., Haapala, I., 1995. One hundred years of rapakivi granite. *Mineralogy and Petrology* 52, 129-185.
- Rämö, O.T., Haapala, I., 2005. Rapakivi granites. In: Lehtinen, M., Nurmi, P.A., Rämö, O.T. (Eds.), *Precambrian Geology of Finland - Key to the Evolution of the Fennoscandian shield. Developments in Precambrian Geology, Volume 14.* Elsevier, Amsterdam, 553-562.
- Rieder, M., Haapala, I., Povondra, P., 1996. Mineralogy of dark mica from the Wiborg rapakivi batholith, southeastern Finland. *European Journal of Mineralogy* 8, 593-605.
- Selonen, O., Ehlers, C., Luodes, H., Lerssi, J., 2005. The Vehmaa rapakivi granite batholith – an assemblage of successive intrusions indicating a piston-type collapsing centre. *Bulletin of the Geological Society of Finland* 77, 65-70.
- Štemprock, M., 1971. Petrochemical features of tin-bearing granites in the Krushne hory Mts., Czechoslovakia. *Society of Mining Geologists of Japan, Special Issue* 2, 112-118.
- Thomas, R., 1994. Estimation of water content of granitic melts from inclusion data. In: *Metallogeny of Collisional Orogens* In: Seltmann, Kämpf, Möller, (Eds). *Czech Geological Survey, Prague*, 224-229.
- Thomas, R., 2000. Determination of water contents of granitic melt inclusions by confocal laser Raman microprobe spectroscopy. *American Mineralogist* 85, 868-872.
- Thomas, R., 2002. Determination of the H<sub>3</sub>BO<sub>3</sub> concentration in fluid and melt inclusions in granite pegmatites by laser Raman micro-

- probe spectroscopy. *American Mineralogist* 87, 56-68.
- Thomas, R., Webster, J.D., Heinrich, W., 2000. Melt inclusions in pegmatite quartz: complete miscibility between silicate melts and hydrous fluids at low pressure. *Contributions to Mineralogy and Petrology* 139, 394-401.
- Thomas, R., Förster, H.-J., Heinrich, W. 2003. The behavior of boron in a peraluminous granite-pegmatite system and associated hydrothermal solution: a melt and fluid-inclusion study. *Contributions to Mineralogy and Petrology* 144, 457-472
- Thomas, R., Förster, H.-J., Rickers, K., Webster, J.D., 2005. Formation of extremely F-rich hydrous melt fractions and hydrothermal fluids during differentiation of highly evolved tin-granite magmas: a melt/fluid-inclusion study. *Contributions to Mineralogy and Petrology* 148, 582-601.
- Thomas, R., Webster, J.D., Rhede, D., Seifert, W., Rickers, K., Förster, H.-J., Heinrich, W., Davidson, P., 2006. The transition from peraluminous to peralkaline granitic melts: Evidence from melt inclusions and accessory minerals. *Lithos* 91, 137-149.
- Tobish, O.T., McNulty, B.A., Vernon, R.H., 1997. Microgranitoid enclave swarms in granitic plutons, central Sierra Nevada, California. *Lithos* 40, 321-339.
- Veksler, I.V., Thomas, R., 2002. An experimental study of B-, P- and F-rich synthetic granite pegmatite at 0.1 and 0.2 GPa. *Contributions to Mineralogy and Petrology* 143, 673-683.
- Vorma, A., 1976. On the petrochemistry of rapakivi granites with special reference to the Laitila massif, southwestern Finland. *Geological Survey of Finland, Bulletin* 285, 1-98.
- Webster, J.D., Holloway, J.R., Hervig, R.L., 1987. Phase equilibria of a Be, U and F-enriched vitrophyre from Spor Mountain, Utah. *Geochim Cosmochim Acta* 51, 389-402.
- Webster, J.D., Thomas, R., Rhede, D., Förster, H.-J., Seltman, R., 1997. Melt inclusions in quartz from an evolved peraluminous pegmatite: Geochemical evidence for strong tin enrichment in fluorine-rich and phosphorus-rich residual liquidus. *Geochim Cosmochim Acta* 61, 2589-2604.
- Webster, J., Thomas, R., Förster, H.-J., Seltmann, R., Tappen, C., 2004. Geochemical evolution of halogen-enriched granite magmas and mineralizing fluids of the Zinnwald tungsten mining district, Erzgebirge, Germany. *Mineralium Deposita* 39, 452-472.
- Xiong, X.-L., Zhao, Z.-H., Zhu, J.-C., Rao, B., 1999. Phase relations in albite granite-H<sub>2</sub>O-HF system and their petrogenetic applications. *Geochemical Journal* 33, 199-214.
- Xiong, X.-L., Rao, B., Chen, F.-R., Zhu, J.-C., Zhao, Z.-H., 2002. Crystallization and melting experiments of a fluorine-rich leucogranite from the Xianghualing Pluton, south China, at 150 MPa and H<sub>2</sub>O-saturated conditions. *Journal of Asian Earth Sciences* 21, 175-188.