Crystallization and Differentiation Processes in the Thin Layered Alkali Gabbroic Intrusions of the Ulvö Gabbro Complex, Central Sweden

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ABSTRACT

Fractional crystallization of magma is a commonly invoked mechanism for chemical differentiation in systems that range from volcanoes to entire planets. However, the processes that control separation of crystals and liquids in natural systems remain controversial, since the dynamics of crystallizing magma chambers cannot be studied directly. Currently popular models involve strictly mechanical separation processes e.g., crystal settling and compositional convection. In this thesis, however, it is demonstrated that a disequilibrium process can result in very effective fractional crystallization.

The ~1265 Ma Norra Ulvön Gabbro (NUG) is a ~300 m thick alkali gabbroic saucer-shaped sill in central Sweden that belongs to the Ulvö Gabbro Complex. The NUG is strongly differentiated, displays well developed modal layering, and has not experienced metamorphic alteration. A stratigraphic section through this intrusion has been studied in detail, including major and trace-element whole-rock analysis and *in situ* mineral analysis. Laser-ablation inductively coupled plasma mass spectrometry (LA ICP-MS) has been used to study a wide range of magmatic processes in this intrusion.

Strong stratigraphic variations in major and compatible trace-elements in the NUG were reproduced by a thermodynamically constrained fractional crystallization model. However, in contrast to the predictions of this model, little or no stratigraphic variations of incompatible elements in minerals or whole-rock can be demonstrated. This cannot be explained by any fractional crystallization model that occurs under equilibrium conditions. A trace-element model for diffusive mass transfer between well mixed supernatant liquid and a partially crystallized boundary layer was therefore developed. This model demonstrates that diffusive exchange of compatible elements can be effective, while incompatible elements are decoupled, since the diffusive flux of these elements move in the same direction as the solidification front. *In situ* crystallization on the floor of the intrusion in combination with thermal convection of the supernatant liquid is likely to have resulted in large scale differentiation of this intrusion. Modal layering and erosion-related layering features indicate that convection was an important factor governing the diffusive exchange during the crystallization. The modal layering developed due to fluctuations in the vigor of thermal convection that in turn affected the cooling rate and the nucleation rate of plagioclase relative to olivine and Fe-Ti oxides.

Key words: layered intrusion, fractional crystallization, modal layering, *in situ* crystallization, Ulvö, saucer-shaped sill, post-cumulus, LA ICP-MS.

PREFACE

This thesis is based on the following papers:

I. Character and significance of spectacular layering features in the thin, alkali-basaltic sills of the Ulvö Gabbro Complex, Sweden. Larson SÅ, Hogmalm KJ, Meurer WP. Mineralogy and Petrology 2008;92:427-452.

Hogmalm was responsible for collection and evaluation of geochemical data, made significant contributions to data interpretation, and carried out some field work and writing. Larson carried out fieldwork and writing, Meurer carried out modeling and writing.

II. The Ulvö Gabbro Complex of the 1.27-1.25 Ga Central Scandinavian Dolerite Group (CSDG): Intrusive age, magmatic setting and metamorphic history. Hogmalm KJ, Söderlund U, Larson SÅ, Meurer WP, Hellström FA, Claeson DT. GFF 2006;128:1-6.

Hogmalm planned the project, did field work and was responsible for writing. Hellström identified and selected baddeleyite for analysis. Söderlund carried out the TIMS dating. Larson contributed with field work. All co-authors contributed with discussion.

III. Diffusion-driven decoupling of major and incompatible elements during fractionation in the layered alkali gabbro, Norra Ulvön Gabbro, Sweden. Hogmalm KJ, Meurer WP, Claeson DT, Larson SÅ. Submitted to Journal of Petrology.

Hogmalm carried out planning, field work, collection and interpretation of data, modeling and calculations, and writing. Meurer contributed with planning, field work, calculations of kDs, discussion and some modeling. Claeson contributed with planning, discussion and some trace-element modeling. Larson contributed with planning, field work and discussion.

IV. Development of modal layering by interaction between convection and crystallization, and compaction-controlled enhancement of layering – evidence from the Norra Ulvön Gabbro, Sweden. Hogmalm KJ, Meurer WP, Claeson DT, Larson SÅ. Submitted to Journal of Petrology.

Hogmalm carried out planning, field work, collection and interpretation of data, modeling and calculations, and writing. Meurer contributed with planning, field work, calculations of kDs, and discussion. Claeson contributed with planning, discussion and some writing. Larson contributed with planning, field work and discussion.

V. Using LA-ICPMS mapping and sector zonation to understand growth and trace-element partitioning in sector-zoned clinopyroxene oikocrysts from the Norra Ulvö Gabbro, Sweden. Claeson DT, Meurer WP, Hogmalm KJ, Larson SÅ. Journal of Petrology 2007;48:711-728.

Hogmalm discovered the sector zonation, carried out collection and evaluation of geochemical data and EDS imaging, and was involved in the interpretation of data. Claeson and Meurer were involved in data collection, and carried out data interpretation and writing. Larson contributed with field work and discussion.

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Gustaf Fröding (1860-1911), Gråbergssång

INTRODUCTION

Magma can be found beneath the surface of the Earth and other terrestrial planets and is defined as molten rock (~700-1300ºC) that can contain suspended crystals and gas bubbles. On the Earth, magmas are generated in subduction zones, continental rift zones, mid-oceanic ridges, and hotspots. In these volcanic areas, magma moves to the surface by intruding overlaying rocks and extrudes onto the surface as lava or as explosive eruptions of pyroclastic material. On its way to the surface, magma can accumulate in magma chambers of different size (tens of meters to several kilometers) and shape, where the composition can be modified by fractional crystallization. Fractional crystallization takes place since the crystals that form when magma starts to crystallize have a different composition than the magma. The composition of the magma changes (differentiates) when crystals are separated from it. The separated minerals form cumulate rocks. Due to extensive experimental work during the 20th-century initiated by Bowen (1915, 1919), the thermodynamics of crystallizing magmas is well understood, and given the composition and pressure of the magma one can make accurate predictions of the minerals that will crystallize (Ghiorso & Sack, 1995; Asimow & Ghiorso, 1998). Using this information, we can infer the involvement of fractional crystallization in many magmatic systems. For example, the generation of granitic material, abundant in the Earth continental crust, is likely to be a consequence of fractional crystallization of basaltic magma (Davidson & Arculus, 2005). However, the physical processes that govern separation of crystals and liquid have for obvious reasons never been observed directly in natural systems, and existing models are usually controversial since they are based on observations from either extrusive or intrusive rocks. Volcanic rock sequences mirror the evolution of magma compositions, but provide limited information about physical processes in magma chambers. Intrusive rocks provide records of accumulated crystals, but the liquid evolution is usually poorly constrained. We need to gain a better understanding of crystallization processes in magmatic systems in order to improve our models for large scale differentiation of terrestrial planets, moons and meteorites.

Studies of fossil magma chambers (i.e. igneous rocks), exposed at the surface of the Earth due to uplift and erosion, have provided much of our current understanding of igneous processes in the Earth's interior. A common feature of many of these intrusive bodies is that they are zoned with regard to mineralogy and chemistry, with systematic changes from the contacts, where crystallization started, to the interior, where the last liquid crystallized. This zonation can generally be attributed to changes in the composition of the magma as the intrusion lost heat to the surroundings and started to crystallize (fractional crystallization). In many of these intrusions, small scale (centimeters to meters) oscillations in mineral proportions, called rhythmic or intermittent modal layering have developed, resembling layering in sedimentary rocks (Wager & Brown, 1968). Logically, crystal settling and accumulation, similar to sedimentary processes on the Earth's surface, has been the most widely used model to account for both large scale differentiation and modal layering (Wager & Brown, 1968). However, this model has been challenged on both experimental and observational grounds, in favor of *in situ* crystallization models, where the differentiation takes place by chemical exchange (compositional convection or diffusion) between a solidification front and the magma (Campbell, 1978; McBirney & Noyes, 1979). Development of modal layering during *in situ* crystallization is commonly explained by fractional crystallization in thin stagnant boundary layers, resulting in oscillatory nucleation and growth of minerals (McBirney & Noyes, 1979). The formation of salt-horizons on the bottom of evaporitic basins can serve as an illustrative analogy to *in situ* crystallization processes. Recently, closed-system differentiation models have been questioned altogether (Marsh 2006). Differentiation is instead explained by settling of preexisting crystals (phenocrysts) carried by the intruding magma, and modal layering is attributed to multiple pulses of intruding magma (Marsh, 2006).

In this thesis, an attempt has been made to distinguish between these various hypotheses using geochemistry in a well exposed layered gabbroic sill in northeastern Sweden. The use of a novel analytical technique for mineral trace-element analysis, laser-ablation inductively coupled plasma mass spectrometry (LA ICP-MS), provides new insights into processes of crystallization and differentiation of basaltic magma. It is now possible to investigate the chemical evolution of both cumulate rocks and the magmatic liquid from which they crystallized by *in situ* analysis of mineral trace-element composition.

An extended summary of the scope and findings of this thesis with emphasize on general processes, is presented below. For information about the intrusion and more detailed results and discussions of processes, the reader is referred to the published papers and the manuscripts that are included in the thesis below.

METHODS

Textures and mineralogy of igneous rocks can be studied by preparation of thin-sections, which are thin slices of rock (30-100 µm) that can be viewed under an optical microscope. *In situ* analysis of mineral major and trace-element compositions can be performed directly on these thin-sections. Large samples of rock can also be crushed and grinded to a fine powder that can be analyzed for major and trace-elements.

The scanning electron microscope (SEM) is used to investigate major element compositional variation in minerals at a wide range of magnification (~25-10,000x). This instrument scans the surface of a thin-section with a high-energy beam of electrons that knock off electrons from the atoms that make up the minerals, and these electrons can be detected with a back-scattered electron (BSE) detector. The intensity of the BSE signal correlates with the average atomic number (Z), and heavy elements (high atomic number) backscatter electrons more effectively than light elements (low atomic number), and result in a brighter image. Different minerals and chemical zoning in minerals can be distinguished by BSE-imaging since different mineral chemistry results in different average atomic number. Energy dispersive X-ray spectroscopy (EDS) is commonly used in conjunction with a SEM to identify different elements and quantify element concentrations in minerals. The EDS detector analyses X-rays emitted by atoms in minerals that are hit by high energy electrons emitted by the SEM. Atoms in a mineral have unexcited electrons at different energy levels or shells around the nucleus. The electron beam from the SEM excites electron in the inner shells of the atom and ejects them, resulting in an electron hole. An electron from an outer higher-energy shell will immediately fill the hole, and the energy drop between the higher-energy shell and the lower-energy shell is converted to an X-ray. Since each element in the periodic table has a specific atomic structure a unique spectrum of emitted X-rays can be used to identify different atoms in a mineral. The number and energy of the X-rays emitted are measured by the EDS and can be quantified by analysis of mineral standards, to give the major element composition of a mineral.

Major element compositions of whole-rock samples have been analyzed by X-ray fluorescence (XRF), which is similar to the EDS technique. Instead of an electron beam, samples are radiated with high-energy X-rays or gamma rays, resulting in ionization of atoms in the sample. Electrons from higher orbits in the atom fall toward the centre of the ionized atoms which results in the emission of characteristic fluorescent X-rays.

The inductively coupled plasma (ICP) is used to transform atoms into positively charged ions that can be introduced in a mass spectrometer. Plasma is an electrically conductive, hot (10,000 K) gas that can be generated by the interaction of argon gas and a radio-frequency electric current. The plasma is generated when free electrons are introduced in a flow of argon gas, and these electrons interact with an oscillating electromagnetic field and accelerate in different directions at high frequency. The introduced electrons collide with argon atoms at high speed and knock off more electrons, and these new electrons are also accelerated. The process continues until the number of new electrons released by collisions is equal to the number of electrons that recombines with argon ions, and the result is plasma that mainly consists of argon atoms with a small proportion of free electrons and argon ions. The high temperature of the plasma separates the sample into individual atoms which are subsequently ionized by collisions with electrons. The ions from the plasma are focused through a series of cones and lenses into a mass spectrometer, where the ions are separated on the basis of their mass-to-charge ratio. Finally a detector receives an ion signal proportional to the concentration of a sample that can be quantified by calibration with elemental standards. Dissolved whole-rock samples can be introduced in the ICP-MS as aerosols that are formed in a nebulizer equipment. Minerals can be sampled *in situ* in 100 μm thin-sections using high-power laser pulses that evaporate the minerals and create a plume of ablated material that is swept into the plasma by argon carrier gas.

U-Pb isotopic dating of baddeleyite, was performed with by thermal ionization mass spectrometry (TIMS) technique. Chemically purified U- and Pb-rich material is loaded onto a filament which is heated, and during boiling some of the material is ionized. The ions are then focused into an ion beam and passed through a magnetic field to separate them by mass. The relative abundances of U and Pb isotopes can then be measured as isotope ratios. The data must be corrected for mass-dependent fractionation that takes place when the sample is exited.

RESULTS AND DISCUSSION

The Norra Ulvön Gabbro

Differentiation and layering are generally more common in large intrusions (>1 km thick), that cool slowly. Unfortunately this results in significant modification of primary mineralogy, texture and mineral chemistry during late crystallization- and sub-solidus stages (Williams *et al.*, 2006). To avoid this problem I have studied the ~1265 Ma (Paper II) Norra Ulvön Gabbro (NUG; Fig. 1a), one of the intrusions of the Ulvö Gabbro Complex (Fig. 1b), northeastern Sweden.

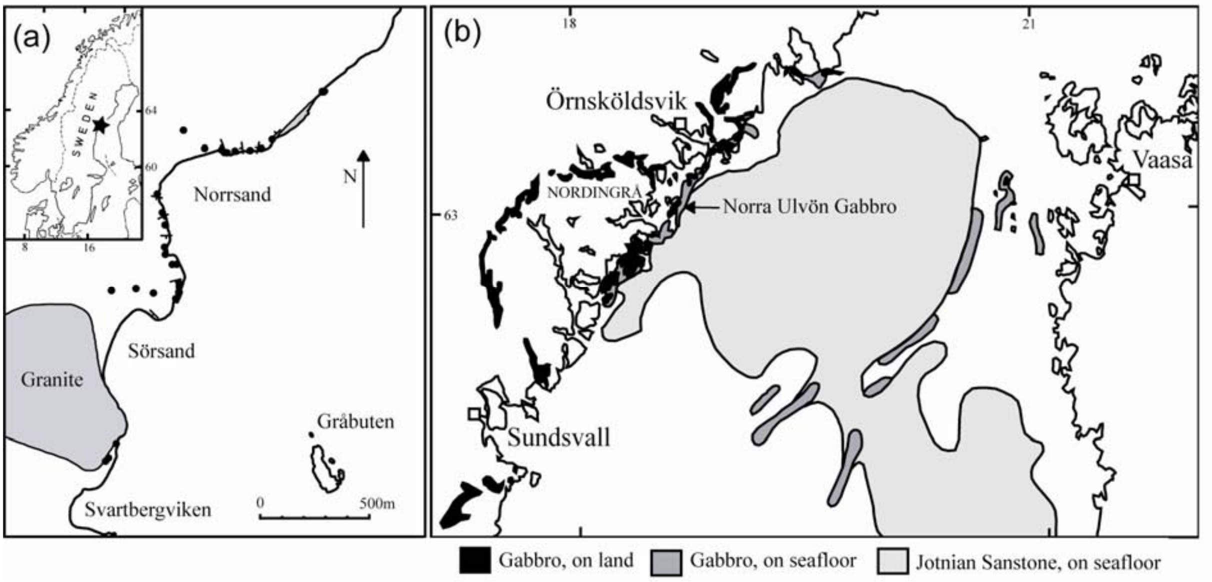

Figure 1. (a) Map showing the main study site on Norra Ulvön, with sample locations (black dots) and orientation of igneous layering. Gray areas represent granitic host rock that constitutes the floor to the north (Norrsand) and roof to the south (Sörsand) (Paper I). (b) Map showing the large circular structures of saucer-shaped mafic sills that constitute the Ulvö Gabbro Complex (modified after Koistinen *et al.*, 2001).

The NUG is a ~300 m thick saucer-shaped, sheet-like intrusion of alkali gabbro that has suffered only minor late-stage modifications (Paper I). The stratigraphy of this intrusion consists of a ~250 m thick floor sequence and a ~50 m thick roof sequence with strong variations in mineralogy and chemistry (Fig. 2) (Paper I). The gabbro also displays well developed rhythmic modal layering. One crucial observation suggests that this intrusion crystallized as a closed-system from a single pulse of magma; the calcium component in plagioclase decreases systematically from the upper and lower margin to the 250 m level, indicating that the magma cooled and crystallized uninterrupted by new major pulses (Fig. 2) (Paper I). Variations in mineral proportions and mineral chemistry in the intrusion can be reproduced with ~70% fractional crystallization of the parental liquid, by thermodynamic modeling (MELTS) (Paper I;

Fig. 10). Therefore, this intrusion provides a natural laboratory for studies of closed-system crystallization and differentiation processes.

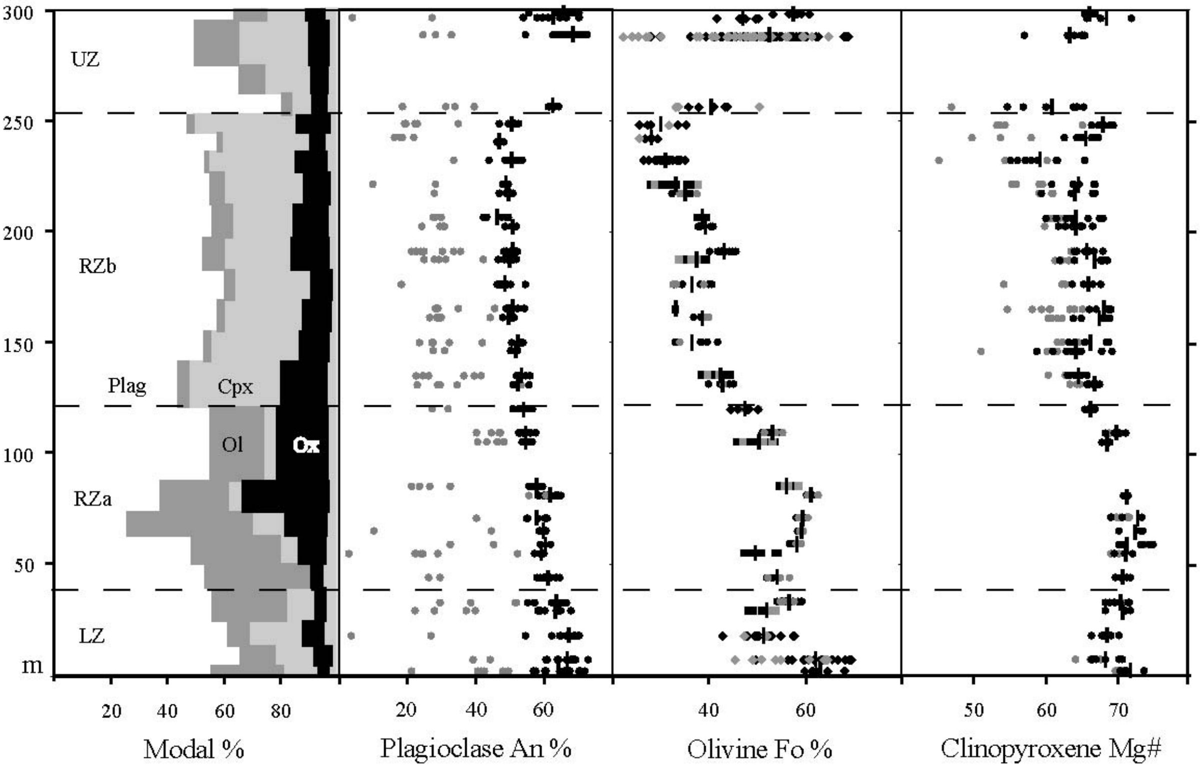

Figure 2. Mineralogical and mineral chemical variations in the stratigraphy through the Norra Ulvön Gabbro indicate a thick floor section and a thin roof section. The variations demonstrate that the intrusion differentiated significantly during the crystallization. UZ = upper zone, RZb = rhythmically layered zone b, RZa = rhythmically layered zone a, LZ = lower zone, Plag = plagioclase, Cpx = clinopyroxene, Ol = olivine, Ox = Fe-Ti oxide.

Evidence for closed-system fractionation

Models where differentiated sills are constructed by fractionation of a single pulse of phenocryst-free magma has recently been questioned by Marsh (2006), who suggests that stratigraphic variations in sills are caused by multiple pulses of magma and settling or flow segregation of phenocrysts. However, based on a review of studies from a large number of sills, Latypov (2003) showed that several features are common for differentiated sills that are more easily explained by *in situ* differentiation processes. The best argument is probably the presence of cryptic layering in I-type sills (i.e., sills with little modal variations) that is especially problematic to explain by open-system models. In light of this controversy, the possibility of recharge, assimilation and the influence of phenocrysts need to be discussed before we can attribute the liquid evolution in the NUG to closed-system fractional crystallization.

Replenishment events can often be seen as reversals in mineral chemical compositions, e.g., an abrupt increase in Mg# or anorthite content at a certain stratigraphic level (Irvine, 1980). The plagioclase compositions in the NUG show a continuous decrease in anorthite composition from the margins to the “Sandwich Horizon” (where the upper and lower solidification frons met), suggesting that the intrusion crystallized without injection of new magmatic pulses. The reversals seen in re-equilibrated olivine and in Fe-Ti oxide crystals, especially at the 50 m level, are probably not caused by changes in the composition of the supernatant liquid. Instead, paper IV shows that the composition of these crystals varies depending on the bulk-rock concentration of incompatible elements. Thus, the compositional reversal is likely an effect of a decrease in the amount of crystallizing interstitial liquid due to compaction. The NUG magma chamber may well have been formed by a series of pulses, but the filling of the chamber must have been completed before any significant crystallization had taken place. Chilled-margin compositions of the UGC intrusions are remarkably uniform (Paper I), suggesting that even though different pulses may have filled the NUG, the initial liquid composition of the intrusion is likely to have been relatively homogenous.

Assimilation of country rock can result in dramatic changes in the composition of basaltic liquid (DePaolo, 1981). There are reports of mixing between gabbro and granitic country rock at intrusion margins, from other parts of the Ulvö Gabbro Complex (Lundqvist *et al.*, 1990). However, there are no field observations indicating that mixing with granitic liquids should have affected the crystallization or the composition of the magma in the NUG. Elements that are usually found at high concentrations in granites, e.g., Zr and Ba can be used as markers for mixing of magmas. Normalizing whole-rock compositions from the interior of the intrusion with the composition of the contact samples reveal that variations in Zr and Ba concentrations are in the same range and correlate with the variation of P_2O_5, which is generally low in granites. This indicates that mixing did not affect this particular intrusion or the chemical evolution.

Considering the potential involvement of phenocrysts, it should first be noted that the rocks of the NUG are medium to fine-grained, with the exception of pegmatitic horizons and bodies (Paper I). The only crystals that reach considerable sizes in the gabbro are interstially grown clinopyroxene oikocrysts. Chilled margins and thin dikes occasionally display porphyritic texture, but there are no observations of olivine and plagioclase crystal sizes >1 mm and the modal abundance of these larger grains is typically <5%. There is no crystal-size population in the gabbro that requires crystal transport from deeper reservoirs. The most convincing argument against phenocryst involvement is that the compositional evolution of the liquid requires plagioclase and Fe-Ti oxide fractional crystallization. Plagioclase phenocrysts are unlikely to have accumulated by gravity due to small density contrasts with the parental liquid, and Fe-Ti oxide did not become a liquidus phase before considerable crystallization of the parental liquid.

Differentiation mechanism

The mechanical differentiation processes; crystal settling, compositional convection and compaction, should theoretically result in trace-element fractionation in accordance with the Rayleigh distillation equation (Paper III; Eq. 1). Elements that are preferentially incorporated in the crystallizing minerals are depleted in the magma, and elements excluded from minerals become enriched in the magma, as the crystallization proceeds. This prediction can be tested in a relatively straightforward manner, since minerals that crystallize in equilibrium with magma incorporate trace-elements proportionally to the composition of the magma, according to mineral-specific partitioning coefficients (kDs) (Blundy & Wood, 2003). This enables us to estimate the trace-element composition of already crystallized magma by analysis of mineral chemistry, and to track liquid trace-element variations during the crystallization. Plagioclase and clinopyroxene crystals are present throughout the NUG intrusion, and they display distinct chemical zoning, indicating that the chemistry of the earliest grown parts of the crystals has been preserved (Paper III & V). In paper III, the most primitive parts of these crystals have been analyzed *in situ* by LA ICP-MS in samples covering the entire stratigraphy. The results demonstrate that the compatible elements (e.g. Sr, Ni and Cr) behaved in accordance with the predictions of the fractional crystallization model (Paper III; Fig. 9). However, the incompatible elements (e.g. Zr, Y, Ba, Ce) remained at nearly constant concentrations in plagioclase and clinopyroxene, indicating that the liquid composition of these elements did not change (Paper III; Fig. 10). Analyses of all mineral phases that crystallized in equilibrium with the supernatant liquid (Paper III; Table 1-4), show that Zr, Y, Ba and Ce elements did in fact behave incompatibly, and they were mainly controlled by late crystallizing accessory phases e.g., baddeleyite and allanite. Bulk-rock analyses throughout the stratigraphy of the intrusion similarly show considerable fractionation of compatible elements, whereas incompatible elements are found at essentially the same concentration as in the chilled margin samples (Paper III; Fig. 7). The implication of these results is that the magma did not primarily differentiate by a mechanical process. Instead, these results can be explained if diffusive exchange was the agent of mass transfer between the supernatant liquid and an inward moving solidification front (Paper III). Diffusion of chemical components in magma is a relatively slow process, but if the supernatant liquid is well mixed and a high degree of crystallinity develops in proximity of the supernatant liquid, diffusive mass transfer of compatible elements from the supernatant liquid to the solidification front can be very effective (Morse, 1986). The decoupling of incompatible elements results from the fact that the diffusive flux of these elements move in the same direction as the solidification front. For the exchange of incompatible elements to take place, the diffusion rate must be more rapid than the advancement of the solidification front. This can only take place over very short distances, which means that the diffusive flux of incompatible elements should be very small, unless the intrusion cools very slowly. Diffusion of incompatible elements is effective on mineral-scales as evident from zoned crystals, but on boundary-layer scales the incompatible elements cannot re-equilibrate with the main magma reservoir and are therefore trapped in the interstitial liquid. Diffusion-driven fractionation results in a much higher partitioning of incompatible elements between solid rock and liquid than expected from the bulk kD for the saturated mineral phases (Paper III; Fig. 11).

Layering mechanism

In situ crystallization at the floor of the intrusion is likely to have dominated the fractionation of the magma (Paper III), but another question is whether the rhythmic modal layering developed as a direct consequence of the *in situ* crystallization. This can be tested since oscillatory nucleation and growth of minerals in boundary layers should result in fluctuations of the magma composition and in mineral chemistry. Plagioclase core trace-element analyses in adjacent felsic (plagioclase-rich) and mafic (olivine- and oxide-rich) layers, revealed no significant differences in major and trace-element compositions (Paper IV; Fig. 7 & Table 3). These results indicate that the composition of the magma remained constant during the development of adjacent felsic and mafic layers, which precludes boundary layer crystallization as the principal mechanism. The development of layering is more likely to be associated with large scale convection of the supernatant liquid, which would explain the lateral extent of the layering (at least 100 m) and occurrences of discordant layering (Fig. 3) (Paper I).

Figure 3. An example of discordant rhythmic layering at Långroudden, north of the Norra Ulvön Gabbro.

However, mechanical sorting of minerals by a convection-related process is inconsistent with frequent observations of mineral grading within layers, with plagioclase-rich bottoms or tops. Plagioclase crystals are less dense than olivine and oxide crystals and the magma, and it is more likely that single plagioclase crystals would float than to accumulate during the crystallization of NUG (Paper IV). Therefore, layering is more likely to have been initiated by fluctuations in the cooling rate at the lower solidification front, caused by variations in the vigor of thermal convection. Periods of strong thermal convection result in increased cooling rates, which in turn should have increased the degree of effective under-cooling at the floor. Higher degrees of under-cooling should lead to more effective nucleation of olivine and oxide, while plagioclase nucleation may be delayed due to sudden super-cooling (Kinzler & Grove, 1985). The mafic layers and mafic parts of graded layers could be the products of disturbances in steady-state crystallization, where strong convective cooling shifts nucleation away from cotectic proportions. The absence of variation in plagioclase chemistry suggests that the convection cannot be accompanied by major variations in the temperature or composition of the supernatant liquid, which is consistent with thermal convection being driven by small temperature differences (<1ºC) in mafic magmas (Martin *et al.*, 1987). Oscillations in the vigor of convection may result from feedback between crystallization and release of latent heat. Periods of strong convective cooling and effective nucleation lead to an increased crystallization rate and release of latent heat, which could result in periodic heating and stabilization of the upper thermal boundary layer, leading to more sluggish convection. Graded layers can, by this model, be explained as the gradual increase or decrease of the effectiveness of convective cooling (Paper IV).

Crystallization processes

Crystallization of basaltic magma chambers is highly complex since it occurs over a wide range of temperatures, involves nucleation and growth of multiple phases, and is dependent on mechanism and rate of cooling. Consequently, the interpretation of the end-product, the igneous rock, remains very difficult. In this thesis, significant progress has been made towards a more quantitative understanding of some of the important questions in igneous petrology, e.g., the development of solidification fronts and the development of ophitic texture. By combining information from mineral zoning, modal abundance and textural observations it has been possible to understand the growth and development of clinopyroxene oikocrysts (Paper V), and to demonstrate a two-stage development of solidification fronts (Paper III).

Growth of oikocrysts

An oikocryst is a large crystal that encloses other smaller crystals (chadacrysts) of different minerals. This relation is usually referred to as poikilitic fabric, and is a common feature in many igneous rocks. Oikocrysts can provide important information about post-cumulus processes because they grow from interstitial liquid between early grown crystals. For instance, the chemical evolution of the interstitial liquid can be studied by *in situ* analysis of the oikocrysts (Meurer & Claeson, 2002). Oikocrysts can also preserve textural relations between chadacrysts, and preserve primary compositions of chadacrysts (Paper IV). However, before we can fully utilize this information we need better constrains on the growth mechanism of oikocrysts. Do oikocrysts nucleate and grow on chadacrysts and fill interstitial spaces like cement in sedimentary rocks or do they grow from the center of interstitial spaces and outwards enclosing chadacrysts?

In the NUG, clinopyroxene crystals grow as large spherical oikocrysts (up to 5 cm in diameter) enclosing plagioclase, olivine and oxide chadacrysts (Paper I). These clinopyroxene crystals display an unusual feature called sector zonation, which means that the different crystal growth-sectors have different chemical compositions (Fig. 4) (Paper V).

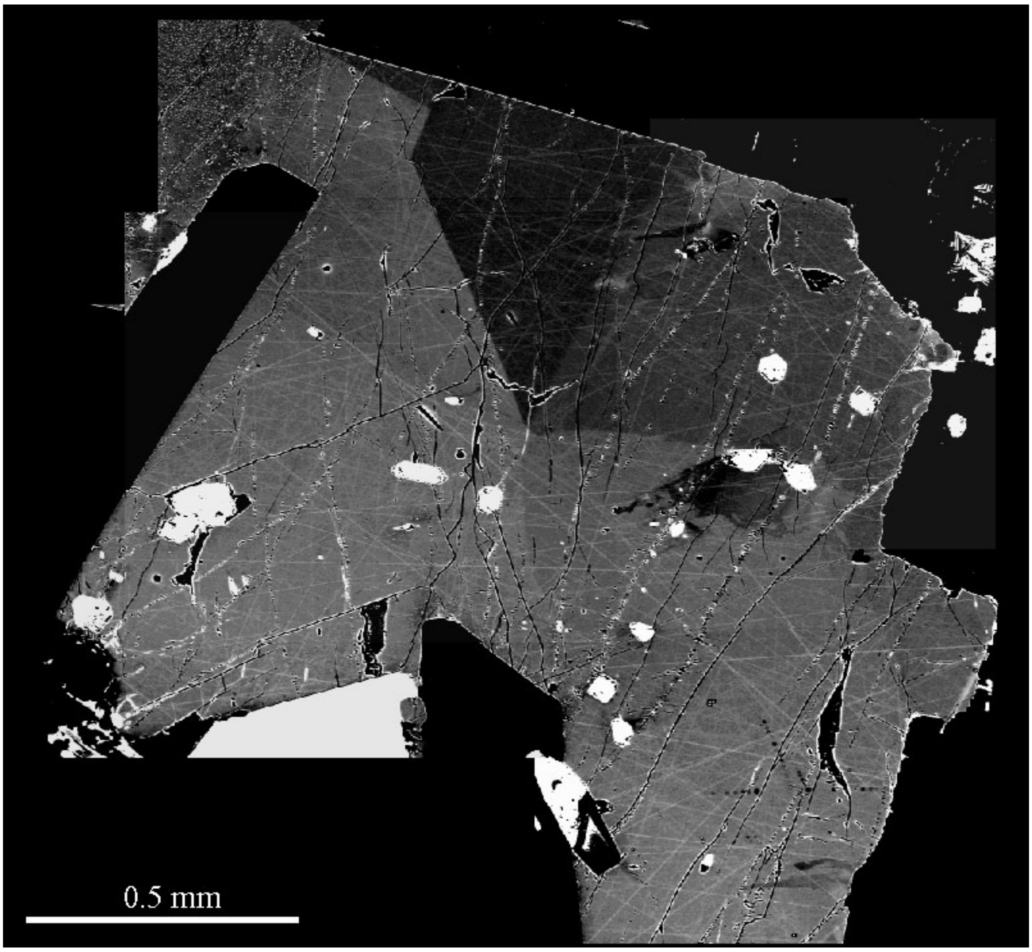

Figure 4. A sector-zoned domain within a clinopyroxene oikocryst from the lower zone in the Norra Ulvön Gabbro.

Boundaries between different growth sectors can be observed in thin-sections by optical microscopy or by SEM. Triple junctions where three different sectors meet can be very useful, since they define the location in the crystal where crystal growth started (Paper V; Fig. 11). Interestingly, oikocrysts in the NUG display several triple junctions within a single large crystal, and these junctions are always found in the center of domains between chadacrysts (Paper V; Fig. 10). These observations rule out the possibility that growth started from a single point in the center of the oikocryst with growth continuing outward around chadacrysts. Instead, the only reasonable explanation is that the oikocrysts initially grew with a branching morphology i.e., skeletal crystals grew outwards into adjoining interstitial spaces. Continued growth took place on skeletal crystals and filled the interstitial domains from the center and out (Paper V). Sector zonation is usually associated with rapid crystal growth and is more common in extrusive rocks, suggesting that the oikocrysts in NUG grew rapidly. Rapid growth would explain why the initial growth took place as skeletal crystals (cf. Faure *et al.*, 2003). The rapid crystallization of clinopyroxene could be explained by a high degree of super saturation. That oikocrysts grew from center of domains is also supported by the fact that the most evolved clinopyroxene compositions, i.e. where the last liquid is likely to have crystallized, is found adjacent to chadacrysts (Paper V).

Solidification fronts

When a magma chamber cools, the bulk of the crystallization is likely to take place in solidification fronts at the margins of the intrusion (Marsh, 1996). A solidification front is a zone between magma and fully crystallized rock with a mixture of crystals and liquid. Nucleation in a solidification front is much easier than nucleation in the rest of the magma for two reasons; 1. nucleation that takes place on other crystals requires lower degree of super-cooling (Kirkpatrick, 1977; Dowty, 1980), 2. local super-saturation near crystals can lead to nucleation if the magma is multiply saturated (simultaneous crystallization of several minerals) (Marsh, 1996), since crystallization of one mineral leads to enrichment of chemical components suitable for another mineral. Crystallization in solidification fronts releases latent heat, and cooling and crystallization are balanced in a way that only a very low degree of super-cooling occurs (Brandeis & Jaupart, 1987). This super-cooling is not likely to be sufficient for homogeneous nucleation in the interior of the magma chamber (Campbell, 1978).

However, the thickness of the solidification fronts is a controversial issue (e.g., Holness *et al.*, 2009; McBirney *et al.*, 2009). Marsh (1996) considers solidification fronts to be very thick and that the degree of crystallinity increases almost linearly from the supernatant liquid to the margin of the intrusion. Morse (1986) on the other hand, advocates a very thin solidification front on the scale of centimeters to meters. Both views are physically realistic, but the actual result is highly dependent on nucleation and growth functions, which are poorly constrained for natural conditions and cooling rates. An increased understanding of the characteristics of solidification fronts is clearly needed.

Plagioclase is a very useful mineral since it was one of the first minerals that saturated in the NUG parental liquid and continued to crystallize until the rock was fully crystallized (Paper I). Plagioclase is a solid-solution between a Ca-component (anorthite) and a Na-component (albite), and the proportion of the end-members is controlled by the temperature and composition of the magma. Solid-state diffusion of the end-member components is very slow in plagioclase (Cherniak, 2003), so no re-equilibration was possible on the timescale it took to cool the intrusion to the closure temperature of plagioclase. The plagioclase crystals in the NUG tend to be strongly zoned (Fig. 5), with cores that have high anorthite content, followed by rims with a progressive decrease in anorthite content away from the core (Paper I).

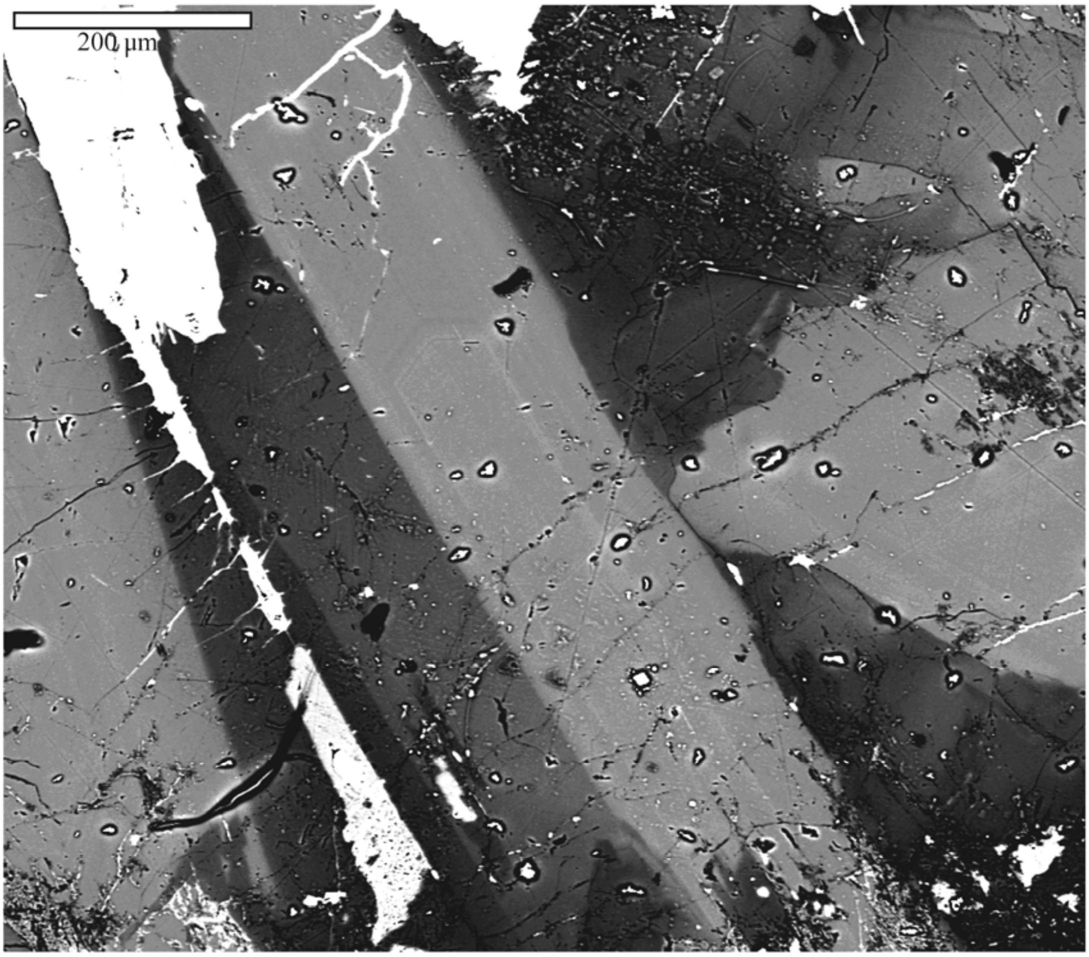

Figure 5. An example of a strongly zoned plagioclase crystal from the lower zone in the Norra Ulvön Gabbro.

This information can be quantified by SEM-EDS point-counting on thin-sections, which makes it possible to link the anorthite content to modal proportion of plagioclase (Paper III). Plotting the anorthite content against modal proportion provides the distribution of core versus rim, and is also a convenient way of studying chemical variations within these groups (Paper III; Fig. 8d). In a sample from the 78 m stratigraphic level, analyses of cores make up ~50% of the total modal proportion of plagioclase, and the anorthite content decreases linearly from ~60% to ~53% in the cores in a plot versus modal proportion (Paper III, Fig. 8d). The most anorthite-rich plagioclase probably grew in equilibrium with the supernatant liquid, but the decrease in anorthite content suggests that the continued growth of plagioclase core was affected by fractional crystallization of interstitial liquid. This could have taken place if the growth of plagioclase core occurred in a relatively thin zone at the edge of the solidification front. The decrease in anorthite could represent an increase in the distance from the supernatant liquid where diffusive exchange with the supernatant was less effective and the liquid cooled and experienced fractional crystallization. The data presented in paper III indicates that ~50% of the plagioclase growth took place by more or less effective diffusive exchange with the supernatant liquid. This in turn implies that the thickness of the zone of core growth must be on the scale of millimeters, assuming experimentally determined diffusion rates (Paper III).

In the rims of plagioclase crystals, the anorthite content decreases much more rapidly from 53% to 1% anorthite over 50% crystallization. It is likely that growth of rims started when the interstitial liquid was no longer buffered by exchange with the supernatant liquid, and the interstitial liquid had to undergo fractional crystallization for further growth to take place. This means that crystallization of rim material must have occurred over a larger range of temperature, suggesting that the increases in crystallinity progressed more slowly during this stage of development of the solidification front. The implications are that the thickness of the solidification front increases when crystals grow from interstitial liquid only (Paper III).

In paper III, it is suggested that the solidification fronts in the NUG developed during two main stages. During the first growth stage diffusive exchange with the supernatant liquid resulted in rapid growth of crystals in a thin boundary layer. When the maximum diffusive length scale was exceeded the growth became much slower, and a thick solidification front developed.

Post-cumulus processes

Processes that occur in the interior of solidification fronts, without influence from the supernatant liquid, are commonly referred to as post-cumulus processes. Compaction, late stage mineral growth and re-equilibration of mineral compositions are important processes included in this category. Since a relatively high porosity (~50%) remains after the first adcumulus growth stage, compaction of the floor solidification front under its on weight is possible. Compaction is the most likely explanation for the weak enrichment of incompatible elements in whole-rock analyses of samples from the "Sandwich Horizon", where the upper and lower solidification fronts met. The slightly lower content of incompatible elements in the lower part of rhythmically layered series (RZa) rocks is probably also a consequence of compaction (Paper III). It can also be demonstrated that compaction can result in enhancement of modal layering (Paper IV). Mafic layers in RZa have much lower content of incompatible elements in whole-rock analyses and more primitive olivine and Fe-Ti oxide composition than the felsic layers. This implies that less interstitial liquid crystallized in the mafic layers, but this is likely not a result of primary accumulation. The modal abundance of interstially grown clinopyroxene (oikocrysts) is higher in the mafic layers than in the felsic layers, suggesting that the expulsion of interstitial liquid occurred after the growth of interstitial clinopyroxene (Paper IV). Compaction after the growth of clinopyroxene is also supported by smaller sizes of oikocrysts in mafic layers than in felsic layers. The equidimensional crystal shape of olivine and Fe-Ti oxide and the absence of a rigid plagioclase framework in the mafic layers suggest that mafic layers with a low initial modal abundance of plagioclase compact more easily than felsic layers. Plagioclase components were expulsed from the compacting mafic layers since there are few available crystals of plagioclase where continued post-cumulus growth could have taken place (Paper IV).

Diffusive re-equilibration of mineral trace-element content

Solid-state diffusion of major elements can be fairly rapid in olivine and Fe-Ti oxides, and the effect of diffusion on trace-element compositions has been investigated in paper IV. Olivine and Fe-Ti oxides have more primitive compositions (higher Ni, Cr and lower REE, Zr and Nb) when enclosed in clinopyroxene oikocrysts (Paper IV), suggesting that the growth of the oikocrysts enclosed the olivines and oxide crystals, and protected them from re-equilibration with evolving interstitial liquid since diffusion in clinopyroxene is very slow (Cherniak, 1998). This suggests that the much higher content of incompatible elements in olivine and oxide crystals outside oikocrysts is a result of rapid diffusion of high-field strength elements (HFSE) in these minerals. Olivine crystals in samples collected less than 10 m from the contacts are zoned in both major and incompatible elements (Fig. 6), suggesting that the cooling was too rapid for diffusion to be effective.

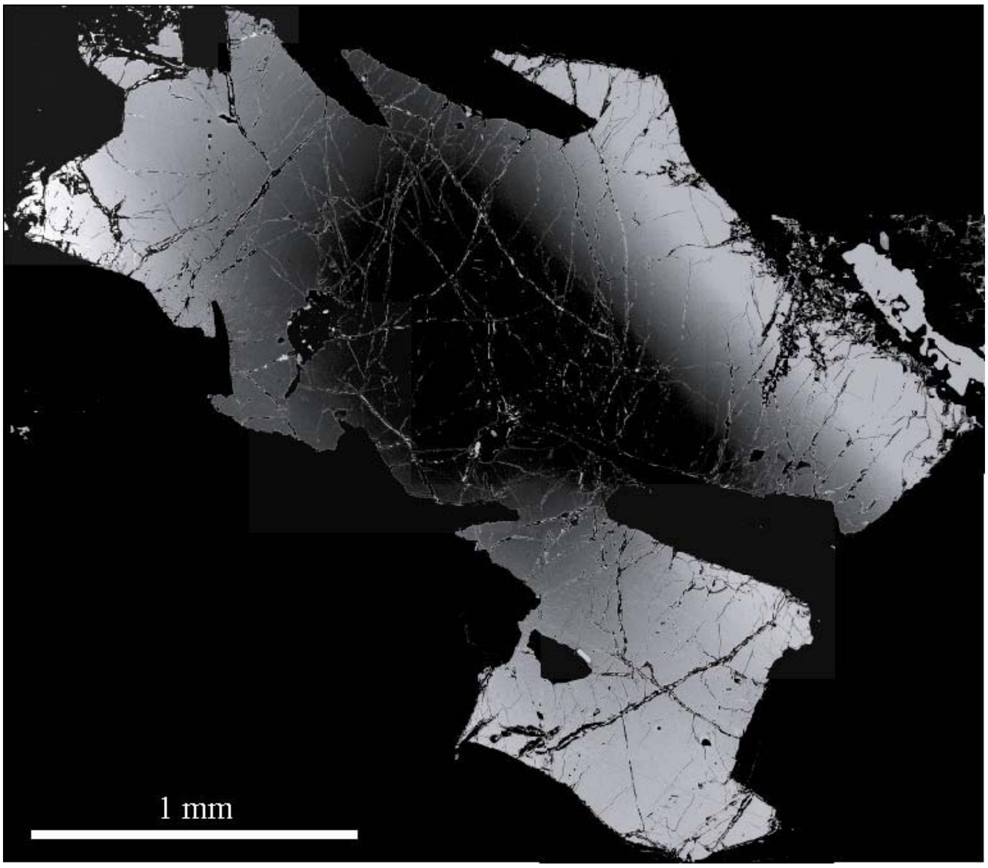

Figure 6. A strongly zoned olivine crystal in a sample collected close to the lower contact in the Norra Ulvön Gabbro.

Olivine crystals in samples taken further away from the contacts are unzoned, indicating that they have undergone re-equilibration, even concerning the incompatible elements. This indicates that the diffusion rate of +3 and +4 ions is almost as fast as diffusion of cations, which is supported by recently published experimental data on REE diffusion in olivines (Spandler *et al.*, 2007). These observations support that the difference in olivine and Fe-Ti oxide compositions between felsic and mafic layers was a result of a difference in the amount of crystallizing interstitial liquid between the layers, and not an effect of a primary layer-forming mechanism (Paper IV).

The re-equilibration of olivines makes them unsuitable for estimating the composition of the supernatant liquid, but the trace-element composition of olivines can instead be used to investigate the evolution of the interstitial liquid. The chemical variation between different olivine crystals in a set of samples in central RZa is likely to represents re-equilibration with interstitial liquid at various stages of the crystallization (Paper IV; Fig. 4 & 10). There is a systematic spatial variation in the chemistry of olivine crystals in the thin-sections that indicates that individual crystals re-equilibrated with the local composition of the interstitial liquid. The increase in Y and decrease in Ni in the olivines are the results of fractional crystallization of the interstitial liquid. The most primitive olivines, enclosed by oikocrysts, were in equilibrium with a liquid similar to the parental liquid. Interestingly, the decrease in Ni is very small in comparison to the strong increase in Y. This implies that the Ni content in olivine was buffered by exchange with the supernatant liquid, whereas Y increased as would be expected from fractional crystallization of the interstitial liquid. These relations are predicted by the model for diffusion-driven fractionation, presented in paper III.

IMPLICATIONS

Some problems with existing models for differentiated sills

Most differentiated mafic sills are characterized by a floor sequence that is ~5-7 times thicker than the roof sequence (Jaupart & Tait, 1995; Latypov, 2003). Systematic stratigraphic variations in mineralogy and mineral chemistry in these intrusions indicate that the composition of the supernatant liquid changed significantly, and that the liquidus temperature dropped several hundred degrees during the crystallization. This is usually true even for intrusions that show little variations in mineral modal proportions or major elements, which can, nevertheless, have strong cryptic variations in mineral chemistry (Latypov, 2003). Accumulation of crystals on the floor of intrusions has historically been the most popular model to explain the thick floor sequence and the differentiation of intrusions (Wager & Brown, 1968). This popularity steams from the simplicity of the model, and also since the image of the magma chamber as a sedimentary system feels so familiar. However, in this thesis, clear evidence against the involvement of crystal settling in the differentiation and the development of modal layering in the NUG is presented. These findings may appear to be controversial, but when experimental results are considered, settling of crystals formed in place in a magma chamber seems more and more unlikely. Crystallization experiments show that nucleation of minerals in basaltic liquids takes place on surfaces of experimental equipment or on existing crystals exclusively (Pupier *et al.*, 2008), which is obviously not conducive to sinking and floating of crystals. More troubling, partially crystallized magma develops yield-strength or high viscosity that prevents crystals to move relative to magma unless they are unrealistically dense or large (McBirney & Noyes, 1979; Mangan & Marsh, 1992). Further, plagioclase is usually less dense than basaltic liquid, which rule out a simple settling mechanism for one of the major minerals formed during crystallization of mafic intrusions (Murase & McBirney, 1973). These results have led some workers to invoke settling of phenocrysts carried by the intruding magma as the main mechanism for differentiation of sills (Marsh, 1996; Marsh, 2006). This is a more realistic mechanism since the yield-strength of the magma is weak close to the liquidus temperature and in some cases there is strong field evidence in support of this model (Marsh, 1996). The phenocrysts origin from erosion of solidification fronts in conduits and magma chambers deeper in the crust (Marsh, 1996), or by homogenous nucleation that could occur during rapid pressure release and degassing when magma is transported to the shallower crustal levels (Brophy, 2009). However, there are many intrusions where settling of phenocrysts fail to account for the gradual chemical and mineralogical variations, e.g., when plagioclase fractionation is required to explain chemical variations. Also, settling of phenocrysts is likely to result in punctuated fractionation (Marsh, 1996), rather than the gradual fractionation observed in the NUG (Paper I) and other differentiated sills (Latypov, 2003). Settling of phenocrysts may be important in some magmatic systems, but there must be other processes operating during the crystallization that result in separation of crystals and liquid.

The pioneers who studied the Skaergaard (Wager, 1963) and the Stillwater (Hess, 1939) intrusions recognized that some process acted to buffer the composition of the interstitial liquid since interstitially grown minerals lacked compositional zoning in some cumulates. They explained these observations by diffusive exchange with the supernatant liquid, and the process was called adcumulus growth. More recent studies have questioned the effectiveness of diffusive exchange, and adcumulus growth has instead been attributed to convective exchange of supernatant liquid and interstitial liquid (Tait & Jaupart, 1996). The density difference between the interstitial liquid and supernatant liquid that develops when the interstitial liquid undergoes fractional crystallization is thought to be the driving force behind this convection. This process, generally referred to as compositional convection, has recently been suggested as an important mechanism in the fractionation of basaltic sills (Latypov, 2003). However, in many mafic intrusions compositional convection is not a viable mechanism since the density of the interstitial liquid increases during fractionation. For instance, according to MELTS, the density of the NUG liquid increases with fractionation until Fe-Ti oxide saturates. Another problem is that the density difference between the supernatant liquid and the interstitial liquid should be very small when adcumulus growth produces unzoned or weakly zoned crystals. The composition of the interstitial liquid cannot change without affecting the chemistry of the growing crystals. In my view it is unlikely that a density difference that develops during growth of unzoned crystals is sufficient to initiate convection in the interior of the solidification front, especially if the yield-strength of the interstitial liquid is considered.

There exists compelling evidence for upward migration of interstitial liquid due to compaction of crystal mushes in systems that range from large layered intrusions (Meurer & Boudreau, 1998b), differentiated sills (Shirley, 1987), to thick lava flows (Boudreau & Philpotts, 2002). Compaction is probably involved in the formation of adcumulates and the extraction of very evolved interstitial liquid from cumulates in large layered intrusions (Meurer & Boudreau, 1998a). However, the effect of compaction on major elements should be relatively small in mafic sills since the advancement of the solidification front is likely to be more rapid than the rate of compaction. The migration of interstitial liquid in sills may never reach the supernatant liquid and is only moved upward in the solidification front until the Sandwich Horizon is reached. This migration leads to enrichment of incompatible elements in bulk rock samples, but should not to any major extent, affect the composition of the supernatant liquid.

Differentiation of mafic sills by diffusion-driven fractionation

Becker (1897a, b) was the first to propose that magma could undergo fractional crystallization by *in situ* crystallization on the margins of a convecting magma chamber, similar to precipitation of salts from solutions in chemistry laboratories. Hess (1956) suggested that *in situ* fractional crystallization governed by thermal convection and diffusive mass transfer was the principal mechanism of differentiation in the Palisades sill, and Wager and Brown (1968) inferred the involvement of this process in many other differentiated sills. Campbell (1978) and McBirney and Noyes (1979) questioned the effectiveness of crystal settling on the basis of experimental studies and field observations from the Skaergaard and the Jimberlana intrusions. These studies also pointed to the importance of *in situ* crystallization, and diffusion was considered the key chemical exchange mechanism between a convecting supernatant liquid and crystallizing cumulate rocks. *In situ* crystallization has since continued to be an important concept in igneous petrology, but compositional convection has been the favored process of mass exchange. Morse (1986, 2002) is one of few workers that has continued to advocate the importance of diffusive exchange in the formation of some cumulate rocks. The results in this thesis again points toward the importance of diffusion in crystallization and differentiation of basaltic magma, and below I discuss the general importance of diffusion and *in situ* crystallization in mafic sills.

It is fairly well established that the bulk of the crystallization of sills takes place *in situ* in solidification fronts that grow inward from the floor and the roof (Marsh, 2006). However, *in situ* crystallization without some form of chemical exchange with the supernatant liquid does not result in intrusion-scale differentiation, and chemical evolution will be restricted to fractional crystallization of the interstitial liquid. The closed-system fractionation observed in the NUG and other differentiated sills, ultimately depends on mixing of the supernatant liquid by vigorous thermal or possibly compositional convection. There is simply no way around it; without convection, no internal differentiation. To initiate vigorous thermal convection at the roof of a sheet-like intrusion, the thermal gradient required for convection must be smaller than the super-cooling required for nucleation (Worster *et al.*, 1990). The exact kinetic super-cooling associated with heterogeneous nucleation in basaltic liquids is not well constrained, but it is not unreasonable to assume that it is greater than the ~0.3°C (over 0.5 m) that is required to initiate thermal convection in a 300 m thick basaltic intrusion, obtained by applying fluid mechanic equations by Martin *et al.* (1987). Thermal convection would explain the thin roof zone in sills, since a high heat flux through the roof counteracts crystallization, and internal convective cooling would promote crystallization of a thick floor sequence (Worster *et al.*, 1990). In the NUG, the well developed modal layering is a strong evidence for convective movement in the magma chamber. The absence of modal layering in most other differentiated sills does not exclude thermal convection, but may indicate that the vigor of the convection fluctuated less than in the NUG.

If the supernatant liquid is kept well mixed by thermal convection, diffusive exchange of high and low temperature components between the solidification front and the supernatant liquid can result in large scale fractionation of the intrusion. However, the effectiveness of the diffusive exchange depends on how much of the crystallization that takes place before the maximum diffusion length scale is exceeded. Crystallization of thick solidification fronts should result in negligible fractionation since little of the crystallization takes place in equilibrium with the supernatant liquid. A very thin solidification front, on the other hand, can result in perfect fractional crystallization of the supernatant liquid since all of the crystallization can occur under equilibrium conditions. Basically, crystal growth in equilibrium with the supernatant liquid requires that nucleation in the solidification front is suppressed, so that there is time available for diffusive exchange. Crystallization in the interior of intrusions is likely to progress in balance between cooling and release of latent heat of crystallization. Growth of minerals requires lower degree of under-cooling than nucleation of minerals, and if crystallization progress very close to the equilibrium temperature, growth can occur while nucleation is suppressed (Brandeis *et al.*, 1984; Brandeis & Jaupart, 1987). The cooling rate also influences nucleation since slow cooling conditions decrease the nucleation rate (Cashman, 1993; Pupier *et al.*, 2008), while the effect on growth rate tends to be small. This indicates that the effectiveness of diffusion-driven fractionation would depend on the size of intrusions, and would be most influential in very large intrusions that crystallize slowly.

Differentiation of mafic sills by *in situ* crystallization coupled with thermal-convection and diffusive exchange has not previously been demonstrated quantitatively. This does, however, not exclude the possibility that diffusion-driven fractional crystallization could be involved in the differentiation of other sills than the NUG. To be able to identify this process, good control over the chemical evolution of both the supernatant liquid and the cumulate rocks must be established. *In situ* analysis of mineral trace-element composition is required for reliable estimation of the composition of the supernatant liquid, and to my knowledge, this has previously not been done throughout the stratigraphy of an entire sill. Further, to preserve evidence for diffusion-driven fractionation, the intrusion should not have undergone post-cumulus compaction to any greater extent, since this would disturb the primary distribution of incompatible elements in whole-rock samples. A constant concentration of incompatible elements in cumulus minerals would still point to the involvement of diffusion.

In spite of the current lack of mineral trace-element data from other differentiated sills, diffusion-driven fractional crystallization can explain a number of observations that existing models can not. Plagioclase fractionation can occur by *in situ* fractional crystallization even though the density of plagioclase is lower than that of most mafic liquids. *In situ* fractional crystallization can readily account for cryptic chemical variations in the so called I-type sill that lacks signs of crystal accumulation. In contrast to compositional convection, fractionation by diffusion is possible even when the density of the interstitial liquid increases during fractionation, e.g., in most tholeiitic intrusions. However, diffusion-driven fractionation cannot explain the accumulation of highly evolved liquid frequently observed at Sandwich Horizons in many mafic sills (Marsh, 2002). Compaction of the lower solidification front or migration of interstitial liquid into tears in the upper solidification front, must also be involved (Marsh, 2002). However, this is by no means contradictory to the involvement of diffusion during primary differentiation of mafic magmas. Additional work, analytical as well as theoretical, is required before the model of fractional crystallization developed in this thesis can be extended to other differentiated sills. However, results presented herein support Hess's hypothesis (1956) that diffusion and *in situ* crystallization are important processes during the differentiation of thin sills, and of layered intrusions in general as proposed by Campbell (1978).

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