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**The Influence of Magmatic and Volatile Evolution
upon Lanthanoid Fractionation
within Peralkaline Magmas
(Norra Kärr, Sweden)**

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One volume

Thesis submitted in accordance with the regulations for the degree
of Doctor of Philosophy at the University of Edinburgh

Department of Geology

2019

Abstract

The lanthanoid elements, and in particular the heavier lanthanoids, are essential in the manufacture of advanced technologies due to their unique magnetic, spectral and luminescence properties. However, despite advances in the understanding the behaviour of lanthanoids within chemistry, physics and materials science, the behaviour of these elements within geological systems and in particular the processes by which they become concentrated to form economic ore deposits is still poorly understood.

The southern Swedish Norra Kärr lanthanoid-deposit represents a significant European lanthanoid resource of 0.19 Mt T-LnO, with the principal ore domains exhibiting ore-grades between 0.48 - 0.69 % T-LnO. Despite its economic significance, the formation of the Norra Kärr intrusion and its economic ore bodies is still not fully understood. However, the intrusion represents an ideal locality to study the concentration of lanthanoids within a peralkaline magma due to the presence of an economically important ore resource; a particular bias towards the economically important heavy-[Ln]; and zonation between light and heavy-[Ln] within separate ore domains.

Previous work on the intrusion has primarily focused on analysing the main ore-domains at the expense of other lithologies with the data collected used to develop models for the whole intrusion. This study has analysed the petrology, mineralogy and whole rock geochemical characteristics of all the lithologies of Norra Kärr and placed the intrusion into the wider structural context of deformation within the Baltic shield at the time of emplacement. These new data and interpretations have been used to test the existing models and develop a new model for the emplacement of Norra Kärr; to better contextualise the formation of the ore domains; and to offer a new model for the light-[Ln] vs heavy-[Ln] zonation observed within the ore-body as a whole.

This study has demonstrated that Norra Kärr was emplaced in two magmatic phases, possibly as a series of dyke intrusions; with the first phase magmas more enriched in [Ln] than the second phase magmas. The ore domains developed as a series of cryptic units due to fractionation of the Grennaite-portion of the first magmatic phase. The [Ln]-concentrations were shown to initially increase from the Contact Grennaite to the Pegmatite-Host Grennaite, before enriching in the light-[Ln] and depleting in the heavy-[Ln] as observed in the Crenulated Grennaite. The second phase magmas (Pulaskite-type) display a different mineralogy to the first phase partially due to higher a_{HF} and a more reduced magmatic chemistry. These second phase magmas may have been emplaced due to the effects of ongoing shearing of the intrusion, with the Lakarpite developing its complex chemistry and petrology due to interaction with the still warm Pegmatite-Host Grennaite.

This study has demonstrated that a progressive increase in [Ln] within a melt is possible due to aegirine crystallisation, and that the observed variation in light-[Ln] vs heavy-[Ln] within the ore-domains is due to catapleiite crystallisation. This study has also shown that the volatile evolution within a melt affects the magmatic evolution by dictating the order of Zr-silicate crystallisation. The order of Zr-silicate crystallisation within a magma acts to determine the potential grade of any [Ln]-deposit formed. If eudialyte crystallises first then the ore-grade will decrease with fractionation, whereas if catapleiite crystallises first the grade will increase with a bias towards the light-[Ln].

Lay Summary

The lanthanoid elements (the series of elements between La – Lu) and in particular Tb-Lu, are essential in the manufacture of advanced technologies due to their unique magnetic, spectral and luminescence properties which can enhance and improve the efficiency of low energy lighting, high strength magnets and high-powered lasers. However, the processes by which these elements are concentrated within magmas to form ore deposits is still poorly understood.

Norra Kärr is an economically significant lanthanoid-ore resource in southern Sweden. Despite its economic significance the geological history of the intrusion and the formation of its ore bodies is still not fully understood. However, the rocks at Norra Kärr represent an ideal opportunity to study the concentration of lanthanoids within a peralkaline magma due to the presence of an economically important ore resource; a bias towards the economically more important Tb-Lu elements within the deposit, and an apparent zonation within the rocks between concentrations of 'light-lanthanoids' (La-Gd) and 'heavy-lanthanoids' (Tb-Lu), all of which pose questions as to how the element patterns formed as the magma cooled and crystallised.

This study has analysed all the different rock types at Norra Kärr and developed a geological history for the formation of the intrusion. These new data and interpretations have been used to challenge the existing ideas on how the magmas at Norra Kärr were intruded, cooled and crystallised and which effect this had on the concentrations of lanthanoid elements through time as the liquid magma solidified.

This study has demonstrated that there were two phases of magmatism at Norra Kärr; the first phase magmas (within which lies the ore body) are more enriched in lanthanoids than the second phase magmas. The lanthanoid concentrations were shown to initially increase from the Contact Grennaite to the Pegmatite-Host Grennaite, before enriching in the light-lanthanoids and depleting in the heavy-lanthanoids as observed in the Crenulated Grennaite. The second phase magmas (Pulaskite-type) display a different mineralogy to the first phase partially due to greater effect of fluorine and a more reduced magmatic chemistry. These second phase magmas may have been intruded as a result of ongoing deformation of the intrusion, with the Lakarpite developing its complex chemistry and mineralogy due to interaction with the still warm Pegmatite-Host Grennaite.

This study has demonstrated that it is possible for magmas concentrate lanthanoids due to aegirine crystallisation, and that the observed variation in light-lanthanoids vs heavy-lanthanoids within the ore-domains is due to catapleiite crystallisation. This study has also shown that the volatile evolution (the variation in the concentration of OH, F and Cl) within a magma affects the magmatic evolution by dictating the order of Zr-silicate crystallisation. The order of Zr-silicate crystallisation within a magma acts to determine the potential concentration of any lanthanoid-deposit formed. If eudialyte crystallises first then the ore-grade will decrease with fractionation, whereas if catapleiite crystallises first the grade will increase with a bias towards the light-[Ln].

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I confirm that no part of the material presented in this thesis has previously been submitted by me or any other person for a degree in this or any other university. Where relevant, material from the work of others has been acknowledged.

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Acknowledgements

I firstly thank Mr Magnus Leijd and Mr Johann Berg of Tasman Metals Ltd. for your excellent company in the field and for help in the core-shed. I thank you and the company for providing access to the site and existing data, and for your help with the project.

I gratefully acknowledge receipt of funding from the NERC E3 DTP at Edinburgh University. I very gratefully thank Mr Mike Hall for his work producing such excellent thin sections without which none of this work would have been possible. I sincerely thank Dr Henry Emeleus of Durham University for his insights into alkaline petrology and for showing some initial 'holiday' samples from Norra Kärr so that I knew what I might be up against. I thank Dr Christopher Hayward for his help and training with setting up and operating the EPMA at Edinburgh; it's a joy of a machine to use and I'm very grateful for your time and instruction. I also thank Dr Start Kerns (Bristol), Dr Jon Wade (Oxford) and Dr Phillip Gopon (Oxford) for their training during the NERC EPMA training course and help using the EPMA at the Department of Earth Sciences at Oxford University. I thank Dr Nic Odling for his help and training while collecting the XRF data at Edinburgh, and for the very entertaining chats about geology and gemmology. I thank Dr Christian Schröder at Stirling University for undertaking the Mössbauer analysis and peak fitting. I thank Dr Denis Schlatter for helping with understanding and obtaining the programme for the Self-Organising Map model, a very innovative technique indeed. I thank Professor Fred Worrall of Durham University for his very helpful suggestions and insights into statistical analysis and other observations regarding geochemists and their models. I thank Dr Laetitia Pichevin and Dr Ian Butler for their help and support arranging the LA-ICP-MS analysis and ablation characterisation at Edinburgh; I'm very grateful indeed to you for helping with this at a difficult stage of the project. I thank Professor Tom Andersen of Oslo University for his help setting up the calculations and with drafting the figure for the 3D petrogenetic volatile modelling; I'm very grateful for such interesting conversations on alkaline rocks and the Langesundsfjord, and for your hospitality while visiting the University. I thank Professor Adrian Finch of St Andrews University for his help and advice regarding the biotite modelling, it's a topic which I've been interested in since first learning about Klokken and I hope I've added something useful. I sincerely thank my examiners, Professor Simon Harley of Edinburgh University and Professor Francis Wall of Cambourne School of Mines, for their time, patience and effort examining this thesis, I can only apologise for overdoing it with the mineral pictures and length of the text. Without a doubt your critique has categorically and comprehensively improved the manuscript, my thinking and my work.

Alkaline rocks can be difficult at the best of times and I've very grateful to all the experts with which I've been lucky enough to discuss them with over the years. In particular I thank Professor Godfrey Fitton at Edinburgh for keen insights and for providing Ilímaussaq samples for comparison to clarify my thinking, and Dr Anouk Borst at St Andrews University for helping me back on track several times and for such excellent conversation in St Andrews and at MDSG. I'm also very grateful to Mr Simon Howard for letting me loose on the Royal Edinburgh Museum's (now NMS's) geology collection, looking though an entire catalogue of alkaline rocks was very helpful indeed. I also thank you for letting me loose on the gemmology collection and for your very kind hospitality while visiting Granton.

I am also very grateful to those who've helped expand my geological knowledge during trips abroad. In particular those at Cardiff University: Dr Hannah Stevenson for letting me tag along to Finland and for driving to Lapland and back past all those caravans; Dr Andrew Martin for arranging such an excellent trip to Sweden and for allowing post-IKEA detours to sites of alkaline interest; and to Dr Jamie Price for organising our Balkans adventure to Bulgaria, Serbia and (F.Y.R.) Macedonia. Without you all my shelves would not be groaning quite so much under the weight of Ag, Au, [Ln] + Y, Te-Se, PGE, Fe-oxide, and of course your beloved sulphide bearing rock samples. From Poland I thank Pani Prof Janina Wiszniewska and her group for their hospitality while visiting Moscow, and to Pan Dr Daniel Buczko and Pani Dr Magdalena Musiak-Matek for their hospitality and warm welcome during my time visiting the Polskie Towarzystwo Mineralogiczne and for follow up conversations after.

As I learnt at Durham, the best postgrad students always have something else up their sleeve. In this case I must thank Mr Andrew Fellows and Mrs Miranda Wells at Birmingham City University for not only teaching me gemmology and diamond grading, but also allowing me to teach it back to your innocent students. I hope their knowledge of how to, and how not to, approach analytical techniques and miller indices keep them in good stead. I'm very grateful indeed for the opportunities you've opened up for me by doing so.

My unreserved thanks go of course to those at the North of England Institute of Mining and Mechanical Engineers, in particular Mr Colin Mountford and Mr Derek Newton, for bringing me into the fold and tolerating me trying to turn the Institute into the Royal Chartered membership organisation for science, technology and engineering in the North. I am immeasurably grateful for all of the discussions on mining and otherwise. It's been the best professional development anyone could hope for and I don't think you fully grasp how grateful I am to you all.

I also thank those who have provided good cheer and company over the years. In particular Dr Hannah Rodgers, Dr Rūta Karolytė, and of course Dr Alvilė Kašarinaitė for endless enthusiasm, reassurance and encouragement. I also thank my colleagues at the Cavendish Laboratory at Cambridge for putting up with endless 'rock chat' during the corrections.

I am everlastingly grateful to all at Zespół Pieśni i Tańca Ojczyzna in Edinburgh, especially the Boron's, Pan Dr Stefan, Pan Lech, Pan Rafał and Pan Dr Gabriel, Panna Beata Pietrzak, Pan Robert Mateusz and Pani Dominika Kasolik. I'm very grateful for all that you've done for me, for constructive critiques of grammar, for wonderful events, and most of all for teaching me dances that bring such joy for babcia. Bóg, Honor i Ojczyzna!

As with last time I find myself ending with Durham. I thank the Venerable St Bede for constructive ponderings regarding this manuscript, and for inspiration to try harder and always find more references. I thank all those in Durham University Earth Sciences for the constructive discussions over the years and who cease to be surprised when I appear out of nowhere. I thank all at St Chad's College who years later still welcome me so warmly. Continuing unending gratitude goes to Megumi Chou (now Donworth).

I also thank my parents, my babcia and the rest of the family for endless help, inspiration and support. I got it over the line at last. Cheers!

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Chapter 1

Lanthanoid Deposits: What, Where and Why Norra Kärr?

1.1 Introduction

The lanthanoid elements, and in particular the heavier lanthanoids, are essential in the manufacture of advanced technologies due to their unique magnetic, spectral and luminescence properties. Much of the inorganic chemistry of the lanthanoids is based on the electronic arrangement within 4f electronic orbitals and the 'lanthanoid contraction' this creates. However, despite advances in the understanding lanthanoid chemistry the behaviour and concentration of these elements within geological systems to form economic ore deposits is poorly understood. However, it has been observed that peralkaline intrusions tend to host [Ln]-deposits that are biased towards the economically important heavy-[Ln], with previous geological studies formulating models for these deposits and their host intrusions involving processes of magmatic fractionation and the influence of magmatic volatiles.

Norra Kärr provides an ideal opportunity to study the formation of [Ln]-bearing ore domains within a peralkaline magma due to: the presence of an economically important ore resource; a particular bias towards the economically important heavy-[Ln]; and zonation between light and heavy-[Ln] within separate ore domains. Norra Kärr is still a poorly understood intrusion with studies hampered by a lack of exposed outcrop and the lack of data for all parts of the intrusion.

This study will present new petrological, geochemical and mineralogical data together with interpretations in order to build a model for the formation of all the lithologies at Norra Kärr. This model will in turn inform a more comprehensive ore deposit model for Norra Kärr which will offer an explanation for the light-[Ln] vs heavy-[Ln] zonation observed within the central portion of the intrusion and offer suggestions for future exploration strategies for [Ln]-deposits in the region and also those globally.

1.2 History, Chemistry and Economics of the Lanthanoids

The Lanthanoids form a series of elements which possess either partially filled or filled 4f electronic orbitals and range from atomic numbers 57-71 in the Periodic Table (Cotton 2006). The series does include Lanthanum even though it is more energetically favourable for that element to fill the 5d¹ orbital first rather than the 4f¹. It is this steady filling of the 4f orbitals which accounts for the chemical properties of the Lanthanoids and underlies their use in modern technologies. Significantly, it is the 4f orbital chemistry which differentiates the Lanthanoid elements from the d-block elements.

The Lanthanoids were originally isolated during 1794 – 1945, with several elements isolated from the mineral gadolinite described by Carl Arrhenius from a mine in Ytterby in southern Sweden. Due to the similarity of their chemical properties the Lanthanoids were initially difficult to separate leading to confusion over what they represented within minerals and their place within the Periodic Table.

It is for this reason the Lanthanoids are commonly referred to as 'Rare Earths' (or REE) by geochemists. However, the term 'Rare Earth' is avoided in this study as the Lanthanoids are not 'Rare' as they are crustally more abundant than Au, and the term 'Earth' is actually an old alchemical term for non-metallic substances which are insoluble in water and resistant to heating. The use of the term 'Rare Earths' is also confusing and inaccurate due to the variety of definitions for REE. Scandium and Yttrium have been classed as REE but it is often not clear which elements are being referred to as the terms 'REE', 'REE+Sc', 'REE+Y' and 'REE+Y,Sc' can all meaning the same combination of elements. Some scientists have also included Zr, Hf, U and Th within the term 'REE'. While IUPAC does allow Rare-Earth Metals to encompass Sc, Y and La to Lu inclusive (Thompson et al. 1970), due to the examples above of the unclear use of REE this study will not use the term 'REE' and instead uses the chemically clearer IUPAC notation of 'Ln' referring to the elements La-Lu. A further set of unclear terminology arises between the use of LREE and the HREE (and sometimes the MREE) with geochemists, metallurgists and individual mining organisations often using differing element groupings for each term (sometimes including Sc as an HREE). This study uses the term Light-[Ln] (La-Gd) and Heavy-[Ln] (Tb-Lu) with the division based upon the electronic configuration of the elements ('lights' (La: [Xe] 5d¹ 6s²)-4f⁷, 'heavies' 4f⁸-4f¹⁴).

The explanation for many of the properties of the lanthanoids is that the 4f orbitals penetrate the electronic-[Xe] core of the Lanthanoid atom. Because of this the 4f orbitals cannot overlap with ligand orbitals and therefore they do not significantly participate in bonding, resulting in the electronic spectra and magnetic properties of the elements being essentially unaffected by the ligand environment. An important feature of the lanthanoids is that their physical properties 'overlap' each other. These overlapping properties complicate the separation of individual Lanthanoid elements, especially when the elements are adjacent to each other in the periodic table. However, the regular properties which the Lanthanoids exhibit are also potentially useful for technologies (particularly high strength magnets, high power specific-frequency lasers and low energy lighting technologies) which require the 'fine tuning' of these properties. The controlling factor for the chemical behaviour and industrial application of the lanthanoids is the 'Lanthanide Contraction'. The Lanthanide contraction is a decrease in the radius of the [La³⁺] ion with increase in atomic number from La to Lu. This is caused by the 4f electrons being 'inside' the 5s and 5p orbitals and behaving more like 'core' electrons, leading to properties which are independent of the ligand environment and, as the 5s and 5p electrons are not shielded from the increasing nuclear charge their orbital radius decreases. Though this type of contraction is not unique in the Periodic Table, the lanthanoids display far steadier changes in their properties than any of the other contraction series and this can be seen in the relatively smooth fractionation behaviour. As the primary industrial importance of the [Ln] depends upon their f-block chemistry and the presence of f-orbitals, this study will focus on the development of the La-Lu bearing ore zones.

Lanthanoids are primarily used as additive elements which act to enhance and fine tune the physical properties of a material. For example, [Ln] can be doped along the grain boundaries of magnets allowing magnetic domains to link between grains thereby enhancing the overall magnetic strength and intensity. As such Lanthanoids are only typically required in sparing amounts and due to their highly specific uses the individual market for each element continues to fluctuate as continuous innovation in materials science acts to increase and decrease demand as new technologies are developed and mature. The lanthanoids have become increasingly more essential in technology due

to their enhance properties and coupled with the restricted geography of their geological deposits they have become politically important for countries with advanced manufacturing sectors such as the UK. In 2015 the British Geological Survey classified the lanthanoids as the highest risk metals (BGS 2015) in terms of supply, partially due to the politics of securing metal supply through international trade with other countries, but also due to low recycling rates, a limited number of substitute elements in the event of a supply shortage and issues relating to some sources being related to the mining of the elements as by product metals. While securing the supply of these elements involves addressing political and diplomatic and material science challenges; enhanced geological knowledge of the ore deposits, their formation processes and refinement of exploration strategies, can increase the number of known lanthanoid-deposits worldwide and can aid their development into certified resources thereby reducing resource criticality.

1.3 Geology of [Ln]-Deposits

Geologically, these ‘rare earth’ Lanthanoids are not rare but the term has arisen as it has historically been difficult to chemically separate the [Ln] and hence to either obtain the metals or identify [Ln]-bearing deposits. Recent research and exploration has now shown that [Ln]-deposits form within a variety of geological environments, and a summary of the geological settings of the top fifty-eight most advanced lanthanoid-exploration projects (as of 2017) is given in Table 1.1. The major [Ln]-deposits are predominantly hosted within carbonatites and peralkaline granites and syenites and these are the most targeted deposit-types. With regard to the other deposit-types, laterites are derived from the weathered remains of either carbonatites or peralkaline rocks, while the alluvial deposits are placer deposits of heavy minerals (monazite and xenotime), again formed from carbonatites or peralkaline granites. These examples show just how important these rock types are in forming lanthanoid-deposits and in highlighting the importance of their petrogenetic and ore-forming processes in initially concentrating these elements.

	Number of Occurrences	T-LnO (Mt)	%H-LnO/T-LnO
Carbonatite	25	1.87	0.75
Peralkaline	16	0.71	8.90
Alluvial Deposit	5	0.15	2.68
Vein Hosted	3	2.58	0.76
Black Shale	2	0.02	4.65
Laterite	2	0.10	6.47
Volcaniclastic	2	0.49	34.04
Fault Hosted	1	0.04	2.70
Rhyolite	1	0.03	50.00
Siltstone	1	0.05	6.67

Table 1.1: Number of occurrences of a lanthanoid deposit type along with resource tonnages and %H-LnO enrichment (Technology Metals Review, Ackroyd et al. (2013), Andrews (2016), Ciuculescu et al. (2013), Clow et al. (2011), Comas (2013), Cox et al. (2013), Croll et al. (2015), Dabrowski et al. (2012), Dahlberg (2014), Daigle (2011), Daigle (2012a), Daigle (2012b), Deshamais (2011), Desharnais et al. (2014), Djenchuraeva et al. (2008), Dodd et al. (2014), Druecker et Simpson (2013), Dunn et al. (2009), Egglestone et Sides (2011), Gagnon et al. (2015), Gowans et al. (2014), Hancock et al. (2013), Harmer et Grivas (2011), Harper et al. (2015), Hulse et al. (2013), Jones et Hancox (2012), Koth (2015), Lynas Corp. Ltd. (2015), Orbite Aluminae Inc. (2012), Peak Resources Ltd. (2014), Petersen et Free (2011), Pollard et Mapleson (2013), Puritch et al. (2014), Reed (2013), Robinson et al. (2011), Saucier et al. (2013), Scogings (2014), Short et al. (2015), Workman et al. (2013))

These alkaline rocks make up only a small proportion of rock within the Earth's crust which explains the scarcity of deposits in comparison to other economic minerals. There are also issues exploring for these deposits as there is a lack of understanding of the processes of concentration that have occurred within the deposits. The demand for heavy-[Ln] in particular, has resulted in an increased interest in exploration which has generated a vast amount of new geological data on lanthanoid bearing deposits. When these deposit types are plotted against the tonnage of ore which they contain a specific peralkaline vs carbonatite pattern emerges (Fig. 1.1). As can be seen in Table 1.1 carbonatite occurrences contain far lower %Heavy-LnO/T-LnO values, but larger ore tonnages. From the plot peralkaline rocks appear to display far more enriched %Heavy-LnO values with smaller deposit tonnages (ore bodies are reported from Ilimaussaq which is disproportionally large when compared to the other sites) suggesting that economic Heavy-LnO based deposits are generally smaller. This suggests that the concentration processes for Heavy-LnO favour smaller deposit types, though this observed pattern may equally be due to reporting bias.

Project	Country	T-LnO (Mt)	%H-LnO	Type of Deposit	Main [Ln]-bearing Minerals
Strange Lake (Enriched)	CAN	0.29	21.11	Peralkaline	Allanite, Gittingsite
Norra Kärr	SWE	0.19	19.95	Grennaite	Eudialyte
Strange Lake (Granite)	CAN	4.12	13.47	Peralkaline	Allanite, Gittingsite
Kipawa	CAN	0.11	13.40	Peralkaline	Eudialyte, Mosandrite, Britholite
Tanbreeze (Ilimaussaq)	GRL	28.06	11.20	Peralkaline	Eudialyte
Nechalacho Basal (Thor Lake)	CAN	1.80	6.60	Peralkaline	Monazite, Allanite, Bastnaesite, Synchisite/Parisite, Zircon, Fergusonite
Dubbo	AUS	0.65	6.02	Trachyte	Ancylite, Ca-basnaesite, natroniobite, armstrongite, eudialyte
Kvanefjeld (Ilimaussaq)	GRL	7.37	3.07	Lujavrite	Steenstrupine
Sørensen (Ilimaussaq)	GRL	2.67	2.76	Lujavrite	Steenstrupine
Zone 3 (Ilimaussaq)	GRL	1.11	2.73	Lujavrite	Steenstrupine
Nechalacho Upper (Thor Lake)	CAN	2.35	2.53	Peralkaline	Monazite, Allanite, Bastnaesite, Synchisite/Parisite, Zircon, Fergusonite
Two Tom (Red Wine)	CAN	0.48	1.22	Peralkaline	Monazite

Table 1.2: The most advanced (certified to a NI 43-101 or JORC code standard) peralkaline-rock hosted lanthanoid mining prospects (Hatch 2016 - Technology Metals Review, references in Table 1.1.)

Of the deposits shown in Fig. 1.1 the most similar to Norra Kärr (i.e. other peralkaline intrusions) are shown in Table 1.2 with Fig. 1.2 Shows the chondrite normalised [Ln]-distributions for each of the deposits in Table 1.2. These twelve NI 43-101 certified ore-deposits (as of 2017) are hosted within seven different intrusions with the majority being found along the paleo-shore of the Nuna supercontinent leading Goodenough et al. (2016) to propose that this forms a specific REE-metallogenic province. All of the intrusions appear to have occurred within rift-settings. The mineralogy of the deposits is highly variable, but may represent alteration assemblages, especially at Kipwa (Saucier et al. 2013) and Thor Lake (Ciuculescu et al. 2013) with alteration occurring to a lesser extent at Ilimaussaq (Borst et al. 2016).

There are many aspects (petrology, geochemistry, structure, formation) of these deposits which are not fully understood. This is partly due to the unique nature of each alkaline intrusion and the amount of data available for each deposit.

Figure 1.2: Chondrite normalised [Ln]-concentrations for the most advanced (certified to a NI 43-101 or JORC code standard) peralkaline-rock hosted lanthanoid mining prospects (Hatch 2016 - Technology Metals Review). Note that other peralkaline deposits are more enriched in light-[Ln] than Norra Kärr resulting in a higher heavy-[Ln] vs light-[Ln] character when compared to other deposits.

In comparison to other intrusions the main feature of the ore reserve at Norra Kärr is not that it is 'heavy-[Ln] enriched' but more that it is 'light-[Ln] poor' which suggests that the process of light-[Ln] depletion is perhaps more important in the development of these deposits. However, without a practical understanding of the formation of these intrusions their ore-deposits models for their development are, in some cases, poorly developed leading to issues with exploration strategy, mineral processing, and overall geological theory. Although aspects such as the metallurgy of Norra Kärr lie outside the scope of this study (though this is indirectly linked to the petrological characterisation of the lithologies), this study will attempt to better understand the intrusion and provide models which can aid the exploration and development of peralkaline-hosted lanthanoid-deposits, as well as contribute to a better understanding of alkaline petrogenesis in general.

A note that due to a similar ionic radius Y can substitute for Ho within mineral structures and is included in later [Ln]+Y plots within this thesis to observe whether Y is coupled with Ho. Y is also included as the approximate abundance of the lanthanoids within the crust varies between 83 ppm (Ce) and 0.52 ppm (Tm) (Kaye and Laby 1995), and can lead to larger analytical errors when attempting to measure the heavier [Ln]; Y, however, is more abundant resulting in lower errors during its measurement allowing for a check on heavy-[Ln] concentrations.

1.4 Petrogenesis of Alkaline Rocks

The great lithological and mineralogical diversity of alkaline rocks has attracted the interest of geologists since the birth of geology as a science. A comprehensive petrogenesis of these rocks is still lacking due these rocks having the most extreme compositions of all igneous rocks, and that their petrological, structural and chemical diversity do not allow for easy comparison between occurrences, unlike the detailed studies of layered mafic intrusions (Wooley 2019). However, the growing interest in these rocks for their economic metal deposits (as outlined in section 1.3) has resulted in a wealth of new data on their petrogenesis and evolution being acquired.

Alkaline igneous rocks are silica-undersaturated and have higher concentrations of alkalis ($\text{Na}_2\text{O} + \text{K}_2\text{O}$) than can be accommodated in feldspars alone; the excess appearing as feldspathoids (such as nepheline, leucite, and kalsilite) and as sodic pyroxenes, sodic amphiboles and other alkali-rich phases (Fitton et Upton 1987). 'Alkaline igneous' as a term encompasses plutonic alkaline rocks such as nepheline-syenite, as well as carbonatites, lamprophyres, lamproites and kimberlites. The latter categories of these are dominated by amphiboles and biotites, while Norra Kärr and other peralkaline rocks (greater molar $\text{Na}_2\text{O} + \text{K}_2\text{O}$ than Al_2O_3) are dominated by nephelines and feldspars. As such the evolution of the cooling peralkaline melt follows the nepheline-feldspar portion of the Nepheline–Kalsilite–Quartz ternary, with the behaviour of accumulated H_2O playing an important role in the final evolution of the melt (Hamilton et McKenzie 1965).

Alkaline rocks typically occur within three main tectonic settings, continental rift valleys, intraplate magmatic provinces, and destructive plate boundaries (Fitton et Upton 1987). Continental rift valleys are volumetrically the most important occurrences of alkaline igneous rocks (e.g. the East African Rift), while destructive plate boundaries produce calc-alkaline magmas that tend to become more potassic with time (Fitton et Upton 1987). Alkaline rocks produced by intraplate magmatic provinces tend to not be subject to any obvious tectonic control and have a tendency to undergo repeated phases of alkaline magmatism, e.g. the Kola Peninsula (Kogarko 1987).

Alkaline magmas typically contain high concentrations of alkali metals, Sr, Ba, Pb, [Ln] and the group 3, 4, and 5 transition metals when compared to the concentrations expected of chondritic mantle material. Even the most magnesian alkaline rocks (which must represent near primary magmas) display high concentrations of these elements and as such small-degree partial melting ($< 1\%$) is therefore required. Alkaline intrusions also often contain mantle xenoliths that indicate mantle metasomatism (Fitton et Upton 1987). This combination element enrichment and lithospheric xenoliths indicates that the magmatism is related to an interaction between the asthenosphere and enriched sub-continental lithospheric mantle, with both displaying their own degree of chemical heterogeneity (Fitton et Upton 1987). The concept of mantle metasomatism within the origin of

alkaline magmatism is also attractive as it can explain the high volatile content of the magmas and their mineral assemblages, and indeed the formation of the magmas themselves.

This relationship has been demonstrated by Gudfinnsson et Presnall (2005) who carried out melting experiments involving the garnet lherzolite phase assemblage in the system $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-CO}_2$ (CMAS- CO_2) at 3–8 GPa and 1340°C–1800°C in equilibrium with CO_2 -bearing melts. These experiments showed a continuous gradation in melt composition between carbonatite, kimberlite, melilitite and basalt melts with pressure and temperature. The effect of CO_2 on the solidus in the CMS system is negligible until a pressure of approximately 2.8 GPa is reached at which point the reaction $\text{Fo} + \text{Di} + 2\text{CO}_2 \rightleftharpoons \text{En} + \text{Dol}$ occurs (Moore et Wood 1998) which results in a strong depression in the solidus. The effect of H_2O on the phase relations of the system is small but the effect on melting temperature could be considerable (Gaetani & Grove 1998). Price et al. (2000) reported that the Jericho kimberlite contains 5 to 7 wt % H_2O which is thought to be close to the primary water content of the original magma, while Le Bas (1981) suggested that carbonatites could display similar H_2O contents. As such alkaline melts can be generated at significantly lower temperatures (possibly $\approx 1300^\circ\text{C}$) than comparable magmas in the CMAS- CO_2 system (Gudfinnsson et Presnall 2005).

Different types of alkaline magmatism can often be associated with each other, for instance the Grønneidal-Ika complex contains alkaline syenites and carbonatites with lamprophyres located nearby (Halama et al. 2005). Given the close spatial correlation of differing alkaline magmatism a common origin has been speculated upon. A demonstrated process for this involves immiscibility with the alkaline melt rising from depth before forming a series of sperate magmas via the onset of immiscibility at shallower crustal depths (e.g. Kynicky et al. 2019). These alkaline complexes typically intrude as dykes and/or ring complexes and can display a series of differing lithologies (Woolley 2019). These intrusions can display a range of internal morphologies, with the larger intrusions displaying magmatic layering, e.g. the U-shaped layers at Klokken (Parsons et Butterfield 1981) and display signs of internal deformation, e.g. Lovozero (Féménias et al. 2005). The structural features of peralkaline intrusions will be reviewed and discussed further in relation to Norra Kärr in Chapter 8.

Due to the extreme compositions of the typically volatile bearing alkaline magmas a very wide range of minerals and mineral assemblages can form. Ilímaussaq has approximately 220 mineral species recorded, is the type locality for 27 minerals, and appears to have 9 unique minerals (Petersen 2001). On the Kola peninsula Khibina and Lovozero have over 550 mineral species and are the type locality for over 100 minerals. Most of these rare minerals are sodium titano-, niobo- and zirconosilicates found within pegmatites and hydrothermal veins (Arzamastsev et al. 2008). These minerals can provide a detailed record of magmatic evolution in terms of fractionation (Kogarko 2015), immiscibility (Sørensen et al. 2003), volatile evolution (Andersen et al. 2010), magmatic layering (Hunt et al. 2017) and internal deformation (Féménias et al. 2005).

As alkaline melts are typically enriched in a range of economic elements, particularly the [Ln], they have recently attracted interest in terms of their economic potential (as outlined above). As with other igneous hosted ore-deposits the ore-forming processes are tied to magmatic processes that result in the concentration of key elements and the formation of economic mineralisation, in the case of Norra Kärr the key mineralisation is in the form of eudialyte. Work continues to develop models for the formation of these zones within alkaline intrusions of which this thesis plays a part.

1.4 Discovery and Exploration and Economic Importance of Norra Kärr

Norra Kärr is located on the eastern shore of Lake Vättern in Southern Sweden, approximately 10 km NNE of Gränna. Norra Kärr is approximately 1400 m long by 450 m wide and at least 200 m deep (Tasman Metals NK PFS 2015) and represents a significant lanthanoid resource of 0.19 Mt T-LnO. The central Grennaite lithology is particularly rich in the heavy-[Ln] with reported %T-LnO grades of up to 0.69 %. Overall, the principal ore domains within the host ore-grades between 0.48 - 0.69 % T-LnO. This has made Norra Kärr particularly attractive for exploration and investment, especially as the resource would provide European industry (as of 2015) with a secure 30-year supply of lanthanoid elements.

Norra Kärr was first discovered during regional mapping by the Swedish Geological Survey in 1905, with the first published work on the intrusion authored by Törnebohm in 1906. The next most detailed study after Törnebohm (1906) was by Adamson (1942) who made detailed geological, petrographical and chemical analyses of the intrusion. It was Adamson (1942) who first named the rock types at Norra Kärr, with the different lithologies being named after local settlements, Grennaite (after the town of Gränna), Kaxtorp (after Kaxtorp farm) and Lakarp (after Larkap farm). Pulaskite (after Mount Pułaski in North America) is the only international rock name used. A full description of the lithologies is given in Chapters 2 and 3. A full account of the scientific history of study at Norra Kärr is provided by Sjöqvist (2015).

The first age dates for Norra Kärr were provided by Von Eckermann (1968) with an age of 1020 Ma from a sample of Grennaite. This was revised by Blaxland (1977) to 1580 ± 62 Ma who noted the scatter in the whole-rock data due to isotopic heterogeneity and noted evidence of later isotopic re-equilibration in the mineral separates. The newly accepted age for the intrusion is 1489 ± 8 Ma (Christensson 2013) which is derived from zircon overgrowths within the fenite. This strictly gives an age for the fenitisation of the country rock, but as this is related to the intrusion of the Grennaite this is taken to be the age at which emplacement occurred.

The limited outcrop of the intrusion has until 2010 hampered efforts to properly understand the structure of Norra Kärr. However, exploration drilling carried out by Tasman Metals Ltd. in the early 2010s provided drill core for analysis which yielded a 3D array of cross sections, maps (Fig. 1.3), and chemical data. This data has been used by Axel Sjöqvist (Sjöqvist et al. 2013, Sjöqvist 2015, Sjöqvist et al. 2017) and Petya Atanasova (Atanasova 2017) whose studies predominately focused on the central ore-domains within the Grennaites. This study will go several steps further than those studies conducted by previous modern authors by assessing the evolution of the whole of Norra Kärr rather than focusing in on the previously examined ore-domains. Previous interpretations of Norra Kärr have been limited by being based upon the restricted data available at outcrop, or by the heavy (but understandable) focus on the ore-bearing domains. By aiming to provide a complete overview of the evolution of the intrusion, this study will provide new data interpretations to challenge the previously proposed models of formation. In doing so a new ore-deposit model and exploration strategy will be proposed.

Figure 1.3: Geological map of Norra Kärr. Further detailed description of the intrusion will be given in later chapters. Map courtesy of Tasman Metals based on company mapping and drill core data and interpretation.

1.5 Aims, Objectives and Thesis Layout

The aims of this study are:

- To provide a full assessment of the structural history, petrological relationships and mineral compositions of Norra Kärr and its lithologies.
- To fully assess the major element, trace element and [Ln]-concentration trends within the different units and minerals of Norra Kärr.
- To model the formation of the different lithological units of Norra Kärr and their fractionation trends.
- To provide the most comprehensive model for the formation of Norra Kärr and the zonation of light-[Ln] vs heavy-[Ln] within its ore domains, and to provide suggested future work and economic applications in light of this study.

Currently there is still little data on mineral compositions with few, if any, available plotted data for either mineral or whole rock compositions. This study will utilise a combination of data from the whole rock Tasman Metals dataset and measurements collected by this study to rectify this paucity of data and plotted trends. Models of Norra Kärr have not comprehensively reviewed the place of the intrusion within the whole history of deformation with the Trans-scandinavian Igneous Belt. There is no comprehensive appraisal of the petrology of each of the lithologies, nor of the whole rock major and trace compositions, nor is there a set of mineral data covering all lithologies or the whole range of possible mineral substitutions. There is also no model proposed for either the enrichment of [Ln] within the magmas, nor for the light-[Ln] vs heavy-[Ln] zonation observed within the ore domains. Therefore, by meeting these objectives this study will provide the most comprehensive appraisal of the Norra Kärr intrusion produced to date.

The outline of this thesis is as follows:

- Chapter 2 will detail the pre- and post-intrusion tectonic history of the area hosting Norra Kärr in order to place its intrusion and subsequent development into context. Field relationships will be outlined and new interpretations of core logs and cross-sections will be presented in the form of 3D models. The data from this chapter will be used to aid later discussion of geochemical and mineralogical data.
- Chapter 3 is the first comprehensive description of the petrographical relationships between the minerals within all the lithologies of Norra Kärr. These relationships will be used to construct crystallisation histories for each lithology and to calculate the mineral abundances as well as to draw similarities with the petrography of other alkaline intrusions.
- Chapter 4 presents new, and in some cases the first, analyses SEM and EPMA and LA-ICP-MS analyses of the minerals within the lithologies of Norra Kärr. For many minerals at Norra Kärr

this is the first time their composition has been analysed. The individual mineral species will be classified and their composition trends presented. These trends will be compared to other alkaline intrusions and similarities and differences will be drawn. A qualitative T-fO₂ model for crystallisation at Norra Kärr will be presented based upon the mineral analyses in Chapter 4 and petrological sequence identified in Chapter 3.

- Chapter 5 presents whole rock analyses collected by Tasman Metals and by this study, and will show for the first time the major element evolution of the magmas, an indication of the whole rock redox of the lithologies, the trends in trace element fractionation across the intrusion. A comparison of the whole rock [Ln]-concentrations between the lithologies and with other alkaline intrusions will be made. Geochemical models will be presented to draw conclusions on the formation of the pegmatites, the Lakarpite and the potential for assimilation of the country rock
- Chapter 6 uses the [Ln], Zr and Hf, concentrations for all major minerals present at Norra Kärr to show progressive evolution in whole rock Zr/Hf ratio for the main lithologies in Norra Kärr. The mineral data will be compared with the host whole rock [Ln]-concentrations and the. The data will also be used to calculate the partition coefficients of natural aegirine and be compared to previously reported experimental results
- Chapter 7 presents new models based upon the volatile compositions of minerals analysed in Chapter 5. Models of the minimum percent whole-rock volatile compositions to show the relative evolution of each volatile during crystallisation will be presented. These whole rock trends will be related to modelling of the phase relationships between Zr-silicate minerals in relation to volatile activities, as well as modelling the relative volatile ratio recorded by biotite. The results of the modelling of mineral crystallisation upon the chemistry of the fractionation magma will be used provide a final model for the pattern on [Ln]-enrichment and light-[Ln] vs heavy-[Ln] fractionation pattern observed within the intrusion.
- Chapter 8 will draw together the conclusions reached in the previous chapters. Structural comparisons will be drawn with other alkaline intrusions, and a tentative revised structural history of Norra Kärr along with a summarised model for the emplacement and fractionation of the intrusion and its ore-bearing domains will be presented.
- Chapter 9 will conclude the findings of this thesis and will offer suggestions for future work for improving the exploration of similar ore deposits.

Chapter 2

The Tectonic Setting and Geological Structure of Norra Kärr

2.1 Introduction

It is only since 2011 that the 3D structure of Norra Kärr has been revealed via exploration drilling and an interpretation of its lithological structure has become possible. However, the structural and lithological details are still being refined. This chapter therefore initially focuses on the tectonic history of the area surrounding Norra Kärr in order to fully outline the pre- and post-intrusion events that may have affected its intrusion and development. This will allow a comprehensive later discussion of its intrusive and potential-deformational history. This chapter will then outline the field relationships and 3D structural-modelling of the different lithologies and domains at Norra Kärr in order to provide a background for the later presentation of geochemical data and development of a structural model. Furthermore, comparisons will be drawn with other alkaline-syenite intrusions to show how the features of Norra Kärr relate to other tectonic and intrusive settings.

2.2 Tectonic and Structural History of the Baltic Shield

The geological history of Norra Kärr and the rocks and structures that host it extends back to before 1800 Ma. It is important to note that given the highly recrystallised nature of the rocks, the lack of outcrop exposure in Scandinavia and the extent of time any reconstructions must cover has resulted in a number of controversies and gaps surrounding the geological history of Scandinavia as well as disagreements over terminology which I will outline here. Firstly, there is an ongoing argument about whether the term Svencokarelian (favoured by the Swedish Geological Survey) or Svencofennian (favoured by numerous other authors) should be used to describe the deformation that occurred throughout Scandinavia between 1950 Ma to 1700 Ma. I have chosen to use the term Svencofennian in accordance with Gaál et Gorbatschev (1987) to refer to tectonic events later than the Archean Karelian craton. Secondly, arguments regarding terminology include the Dan-Polonian (a Baltica wide deformation episode introduced by Bogdanova in 2001) vs the Hallandian (an earlier local term to describe the magmatism and metamorphism observed at the same time as the deformation) as well as the timeframes of events they encompass. I have chosen to refer to the initial deformation experienced after 1500 Ma as Dan-Polonian and the later magmatism towards 1400 Ma as Hallandian without adopting a boundary age between them. Thirdly, the Protogine Zone, an area defined as a 'zone of great schistosity', is a term that is a remnant of pre-tectonic Neptunist ideas from the late 1800's that survived by word of mouth amongst Swedish geologists before being officially written down on a map in the 1970's too much confusion (Rodhe 1992). The Protogine Zone appears to be an outdated concept and a term that may or may-not be synonymous with the Svenconorwegian Frontal Deformation Zone (SFDZ), as well as a geographical oddity in that it appears in a slightly different place on the map in each and every publication. Several authors, e.g. Brander 2011, admit that the terms used are the tools that allow for the best answer at the present-time and are very likely to be abandoned, modified or completely renamed in light of new data. A final discussion point is over the terminology used to describe the different tectonic blocks of southern Sweden. The commonly used nomenclature (e.g. Bingen et al. 2008) is shown in Fig. 2.1a, while a new terrane analysis nomenclature as introduced by Andersson (2005) is shown in Fig. 2.1b.

Figure 2.1: (a). Sketch map showing block-units as defined by Bingen et al. (2008); (b). Sketch map showing block-units as defined by Andersen (2005) H-Ro – Hardangervidda-Rogaland, Te – Telemark, B-Li – BambleLillesand, Tr – Tromøy, K-M – Kongsberg-Marstrand, Ra-Ly – Randsfjord-Lygnern, Vn-Hs – Vänern-Halmstad, T-Vt – Trysil-Vättern. The Approximate location of Norra Kärr is marked with the star.

Much of the geological history of southern Sweden was a result of the tectonic conditions along the edge of the Baltic Shield which was part of two supercontinents during the Proterozoic:

- Nuna (1780 to 1400 Ma)
- Rodina (900 to 750 Ma)

Due to subduction along the edge of these continents several orogenic events occurred:

- Sveno-Fennian (1950 to 1700 Ma)
- Gothian (1750 to 1500 Ma)
- Dan-Polonian (1500 to before 1400 Ma) – lower boundary is poorly defined
- Hallandian (after 1500 to 1380 Ma) - upper boundary is poorly defined
- Svenconorwegian (1250 to 900 Ma)

During these events the existing crust was pieced together and then subsequently deformed and metamorphosed under varying pressures and temperatures. The deformation phases associated with the tectonic events will be outlined below.

The Supercontinent of Nuna

The supercontinent of Nuna (Fig. 2.2) existed approximately between 1780 Ma to 1400 Ma (Zhang et al. 2012) and had begun accreting as early as 2100 Ma. During the formation of Nuna the Sveno-Fennian orogeny accreted several arc-systems onto the existing Archean cratons (Nironen 1997) and initiated the formation of what is now the Transscandinavian Igneous Belt (TIB) of southern-Sweden, the host rocks of Norra Kärr.

Figure 2.2: Palaeotectonic continental reconstruction for between 1780 Ma and 1600 Ma (from Phersson et al. 2015). Approximate future location of Norra Kärr is marked with a star on the continent of Nuna.

During the latter part of Nunian history southern Sweden underwent the Gothian Orogen – an extended period of calc-alkaline magmatism related to the continuing subduction along the margin of Nuna (Åhäll et Gower 1997). This has been correlated to be contemporaneous with the Labradorian Orogen occurring at the same time in Canada. Coastal Baltica then experienced the post-orogenic Dan-Polonian Event (Bogdanova 2001) and the Hallandian Event (Brander et al. 2011) (both events are poorly defined with regard to their duration) before the continent of Nuna began to break up

Svencofennian and Gothian Orogenies – Formation of the Transcandinavian Igneous Belt

The Svencofennian Orogeny resulted in the accretion of two volcanic-arc complexes onto the existing Archean Fenno-Scandian crust, thereby forming the earliest TIB crustal blocks – the TIB-1 granitoids - that host the Norra Kärr intrusion. The orogeny occurred after the breakup of an existing Archean craton resulting in the formation of the pre-Svencofennian ocean basin around 1950 Ma. This basin existed for around 40 M.y. before the first island-arc collided with the Archean crust by approximately 1880 Ma along a NW-SE trending subduction zone (Fig. 2.3a; Nironen 1997). The accretion of the second island-arc was more complicated as it approached the new continent from what is now south-east Scandinavia, before accreting onto the continent from a southerly direction to form what is now Southern Sweden.

After these main accretions occurred an easterly-dipping subduction-zone continued to operate along the (present-day) western and southern margin beneath Fenno-scandia (Andersson et al. 2004) resulting in both the emplacement of the TIB-1 granitoids within the Småland-Värmland Belt between approximately 1810 Ma to 1760 Ma, and the continued accretion of smaller crustal fragments, i.e. the Oskarshamn-Jönköping island arc. Around 1760 Ma this northwards subduction ceased leaving only the eastwards subduction occurring (Fig. 2.3b). This stable subduction zone appears to have resulted in a magmatically quiet period lasting between 1760 Ma to 1710 Ma and marked the end of the Svencofennian Orogeny.

Figure 2.3: Sketch showing the proposed palaeotectonic reconstruction of Scandinavia; Left - between 1860 Ma and 1770 Ma; Right - between 1710 Ma and 1660 Ma (from Andersson et al. 2004). Approximate future location of Norra Kärr is marked with a star.

The Gothian Orogeny

The start of the Gothian Orogeny is marked by the shifting of the continental subduction zone from an eastwards directed subduction to a north-eastern subduction direction around 1710 Ma (Andersson et al. 2004). Given that at around the same time the crustal segments of Sarmatia and Volgo-Uralia had collided to form the Eastern European Craton (the ECC) which was approaching Fenno-Scandia and was about to begin accreting to it (Bogdanova et al. 2001), it is likely that this change in subduction orientation is due to the approach of the ECC. The resulting accretion was to form the continent of Baltica.

This change in subduction direction resulted in the reworking of the Transscandinavian Igneous Belt and the emplacement of the TIB-2 and TIB-3 granitoids between 1720 Ma and 1660 Ma. According to the model put forward by Nironen (1997) the TIB magmatism and Revsund magmatism (more mafic in character than the TIB) along the subduction zone, between 1850 Ma and 1650 Ma is not related to extensional collapse and instead is related to a north-south trending marginal rift zone. However, according to Claesson et al. (2001) the crust was in compression until approximately 1700 Ma suggesting that the TIB2 and TIB-3 granitoids were predominantly emplaced in an extensional setting which created N-S and NW-SE trending crustal weak-zones.

Between 1650 Ma and 1510 Ma anorthosite-mangerite-charnockite-granite (AMCG) or 'rapakivi' magmatism occurred within Baltica along pre-existing crustal weak zones that experienced extension (Nironen 1997). The AMCG magmatism suggests that the post-orogenic regime which was in place throughout the 'Gothian Domain' of present-day south-west Sweden, continued to be affected by subduction along the coast of Nuna until approximately 1500 Ma. The degree of

extension along crustal weak zones was enough to result in the emplacement of mafic intrusions (e.g. the Ölme dolerite at 1569 ± 3 Ma, the Åker metabasite at 1562 ± 6 Ma) south of Lake Vättern in what is now termed the Protogine Zone or PZ (Söderlund et al. 2006). Indeed, it appears that the trend of the PZ was a favoured site for magmatism since at least 1692 ± 7 Ma as shown by the emplacement of the Rymmen Gabbro (Claeson 1999).

The exact end point of the Gothian Orogeny is unclear due to the differing tectonic events which occurred across Baltica. Locally, the main collision that occurred within the 'Gothian Domain' of south-west Sweden appears to have happened by 1550 Ma with the domain not experiencing post-orogenic magmatism until 1500 Ma. However, on the crustal scale of Baltica AMCG magmatism had been occurring since 1600 Ma, with 1550 Ma being the start of the collision of Amazonia onto the present-day south-east Baltica (Bogdanova et al. 2001). This began to stress the crust and resulted in a prolonged period of east-west shearing across the continent (e.g. within the West Lithuanian Granulite Domain between 1550 Ma and 1450 Ma), as well as inducing metamorphism, deformation and AMCG magmatism. During this time inherited tectonic fabrics were reactivated and began to shear resulting in compressional and locally extensional tectonic settings across western Baltica. Examples of this can be seen in southern Sweden (Blekinge), on Bomholm and in northern Poland, as well as across Lithuania and Belarus (Bogdanova 2001). As such Bogdanova defined these events as part of the Dan-Polonian (Bogdanova 2001).

The Earlier Dan-Polonian Events – The Genesis of Norra Kärr

The Dan-Polonian duration is poorly defined. It was originally suggested to have happened between 1540 Ma and 1450 Ma (Bogdanova 2001). The period was then redefined to fall between 1500 Ma and 1400 Ma (Bogdanova et al. 2008) bringing the term into conflict with the existing terminology for tectonic events during 1500 Ma to 1400 Ma already covered by the term Hallandian (Hubbard 1975). Despite Möller et al. (2007) suggesting that the term Hallandian should be retained for the events between 1430 Ma to 1380 Ma Brander (2011) suggested that Hallandian should refer to 1470 Ma to 1380 Ma leaving the Dan-Polonian to refer to between 1500 Ma to 1470 Ma.

Post-1500 Ma southern Sweden was experiencing the effects of Dan-Polonian shearing and AMCG magmatism. This effect has been seen in southern Sweden along the Loftahammar-Linköping Deformation Zone (LLDZ) in a reset $^{40}\text{Ar}/^{39}\text{Ar}$ age (reset to ages between approximately 1500 Ma to 1480 Ma) from white mica within the deformation zone, which was also accompanied by Na + Ca alteration (Beunk et al. 2001). This suggests that shear zones and 'alkaline fluids' of some form were active during this time. Furthermore, the idea of hidden AMCG suites below the present surface level is not objected to by a range of authors (Andersson 2004).

In his Licentiate thesis Sjöqvist (2015) discussed the possible regional events around the time Norra Kärr was emplaced (1490 ± 10 Ma - Sjöqvist et al. 2015) and concluded that there was no known suite of magmatic rocks that Norra Kärr could be directly related to. This is due to the greater part of the magmatism between 1500 Ma and 1400 Ma occurring in the younger part of the time period rather than the older. However, given that Norra Kärr *must* have been emplaced at this time, then it *must* have been intruded within the wider context of post-orogenic AMCG magmatism within a deforming craton transmitting 'fluids' along craton-scale deformation zones. The initial model of Bogdanova (2001) leaves open the possibility of localised-extension, thereby creating

accommodation space for magmatism. Bogdanova et al. (2014) reported elevated heating and concurrent NE-SW compression between approximately 1500 Ma and 1450 Ma in the Linderödsåsen horst in Southern Sweden. As the area occupied by the PZ was active during the earlier Gothian Orogeny there must certainly be the potential for it to be reactivated by NE-SW compression concurrent with the E-W Baltica-scale deformation, thereby providing accommodation space for low-volume partial-melts during this time.

The Later Hallandian Event

The degree of magmatism occurring throughout southern Sweden appears to increase (or is more frequently reported/exposed) as we approach 1400 Ma with the Hallandian event being introduced by Hubbard (1975) to cover the emplacement of AMCG magmatism, amphibolite-granulite metamorphism, folding and the deposition of supracrustal rocks. During this time a variety of magmatism occurred and a selection of intrusions are described below.

Čečays et al. (2002) reported on the granitic Stenshuvud (≈ 1460 Ma) and Tågghusa (≈ 1440 Ma) magmatism in Skåne that displays low La/Yb ratios suggesting an upper-crustal melt source involving older (>1850 Ma) material, and concave to almost horizontal HREE trends and a source with a specific composition due to high contents of Cr, Co, Ni and fluorine. Furthermore, the Stenshuvud granites were determined to have crystallised at 13-15 km depth while the Tågghusa granitoids appeared to favour emplacement along the later formed shear zones.

The Eastern Segment of southern Sweden has experienced Hallandian high-temperature metamorphism between 1460 – 1420 (Christoffel et al. 1999; Söderlund et al. 2002; Möller et al. 2007) as recorded by U-Pb ages in zircons that showed the effects of the growth of new crystals, recrystallization, and overgrowth of older crystals, which also coincided with widespread magmatism between 1470 and 1440 Ma (Söderlund et al. 2008). The magmatism, in general, displayed a compositional trend of dolerite intrusions in the northern part of south-west Fenno-Scandia and felsic plutonism in the southern part suggesting that during this time the region was not in an anorogenic tectonic regime (Brander et Söderlund 2009).

By 1455 ± 6 Ma the Jönköping Anorthosite Suite had been emplaced just south-east of Lake Vättern within the current area of the PZ (Brander et Söderlund 2009). By 1450 Ma the rocks of Blekinge Block had been uplifted against the Småland-Blekinge Deformation Zone (SBDZ) and were subsequently intruded by several plutons including the coarse-grained Karlshamn and Eringshoda plutons, the fine-grained Spinkamåla pluton, and the more deformed Vånga pluton (1448 ± 25 Ma – Geisler et Schleicher 2000). All generally dated to around 1450 Ma (Johansson et al. 2015), with smaller plutons of the same age occurring north of the Småland-Blekinge Deformation Zone. Čečays et Benn (2007) demonstrated that the Karlshamn pluton was intruded during a compressional phase and is therefore syn-tectonic.

The Axamo Large Igneous Province

The Axamo LIP (as described by Ernst et al. 2008) occurred at 1410 Ma and are E-W trending dykes of mafic and intermediate character now metamorphosed to amphibolites facies (Bylund et Pisarevsky 2002) and are probably linked to a giant dyke swarm. Åhäll and Connelly (1998) noted that the dykes were orthogonal to the earlier Trond-Göta dykes suggesting that the direction of principal extension had rotated between 1460 Ma and 1410 Ma. Magmatism later than approximately 1400 Ma is thought to have been emplaced within zones of crustal extension (Bogdanova et al. 2014) during the breakup of Nuna.

The Breakup of Nuna – 1400 Ma onwards

The breakup of Nuna resulted in extensional (anorogenic) tectonics across the continent and in southern Sweden including the Torpa granite and the Varberg Charnokite (1380±6 Ma) during a period of 1380 Ma to 1360 Ma (Åhäll et al. 1997). Further magmatism occurred between 1250 Ma to 1200 Ma producing the Hästefjorden suite. Later magmatism included the Protogine Zone LIP, a giant dyke swarm around 1220 Ma in age (Ernst et al. 2008). At 1204 ± 6 Ma the Vaggeryd syenite (along with other syenite bodies) was intruded along the area of the PZ (Jarl 2002). The 1128±51 Ma age of Hf- and F-rich zircon overgrowths within the Vånga pluton implied that the PZ was still active at this point and had 'fluids' flowing through it (Geisler et Schleicher 2000). The paleogeography at the time is shown in Fig. 2.4.

The Supercontinent of Rodina

The supercontinent of Rodina (Fig. 2.5) had begun accreting after 1300 Ma and existed approximately between 900 Ma to 750 Ma (Li et al. 2008) and. The formation of Rodina resulted in the Svenconorwegian Orogeny due to the accretion of Amazonia against Laurentia-Baltica (Cawood et al. 2007). The orogeny is expressed in Scandinavia as four stages; the Arendal Phase, the Agder Phase, the Falkenberg Phase and the Dalane Phase. Svenconorwegian deformation and metamorphism was distributed across most of southern Sweden and may have resulted in deformation along the Protogine Zone within which Norra Kärr lies.

The Sveno-Norwegian Orogeny – Further Deformation along the PZ?

The Svenconorwegian Orogeny has been divided up into several phases by Bingen et al. (2008); these phases are the Arendal Phase (1140 Ma to 1080 Ma, the Agder Phase 1050 Ma to 980 Ma, the Falkenberg Phase (980 Ma to 970 Ma) and the Dalane Phase (970 Ma to 900 Ma) and are outlined below.

The Arendal Phase occurred due to the collision of the Telemarkia and Idefjorden Terranes of southern-Norway that produced an orogenic wedge that included the Bamble and Kongsberg Terranes. This then resulted in crustal thickening, metamorphism and finally thrusting followed by crustal cooling and local basin formation between 1080 Ma and 1050 Ma.

The Agder Phase was the main phase of the Svenconorwegian orogeny and likely resulted from a (possibly oblique) collision between Baltica and Amazonia resulting in crustal thickening within the central part of the orogen and high pressure metamorphism occurring.

Figure 2.4: Palaeotectonic reconstruction of Laurentia and Baltica at 1267 Ma (from Zhao et al. 2004)
The approximate location of Norra Kärr is marked with a star.

Figure 2.5: Palaeotectonic reconstruction of the continent of Rodina at approximately 1000 Ma (from Li et al. 2008). The approximate location of Norra Kärr is marked with a star.

The Delane Phase of the orogeny represents a period of relaxation or gravitational collapse. During this phase the southern part of the Eastern Segment (now a high-grade metamorphic terrane) was exhumed producing domed structures with cores of gneiss. This exhumed material displays E-W trending fold-structures indicating a N-S compression, and overlaps with the formation of steep-N-S-trending normal shear-zones at the front of the orogen (i.e. the protogine zone, however this zone likely has far older origins) and the intrusion of the Blekinge-Dalarna dolerites (a giant-dyke swarm intruded at approximately 946 Ma).

It is unclear to what extent Norra Kärr experienced Svenconorwegian deformation and metamorphism (if at all). Larson et al. (1998) reported the age relations of deformations relative to dated igneous-intrusions (Table 2.1) which suggest that the TIB experienced brittle/ductile deformation in its southern part post 1570 Ma. More severe deformation did occur to the east of the PZ but this was away from Norra Kärr. The Torsby Segment (the northern part of the Eastern Segment) also experienced deformation post 1470 Ma. Therefore, if deformation did not occur during the Hallanidan period then there may be a Svenco-Norwegian component at Norra Kärr.

Post-Svenco-Norwegian History

Southern Sweden was not directly affected by the Caledonian Orogeny (490 – 390 Ma) nor was it affected by the accretion of Pangia (300 Ma) as by that point in time southern Sweden was located within the centre of Laurussia. As such it is unlikely that Norra Kärr experienced any significant deformation post-Svenconorwegian time.

Idefjorden Terrane		Eastern border of Gothian folding	Eastern border of Svenconorwegian penetrative deformation	Torsby Segment	TIB (Norra Kärr)
Lithology and ages	Calc-alkaline, veined orthogneiss [1], 1600 Ma [2]			Alkali-calcic [3] to alkaline granites [2], 1700 Ma [2,4]	Mostly 'A-type granite' c. 1780 Ma [5] and 1700 Ma [6]
Structural characteristics	D1w: Flattening (S1w) mostly strong D2w: Isoclinal folding (F2w)			D1e: Mostly weak (S1e) foliation	
Pre	c. 1200 Ma granites [7,8]			1470 Ma metagabbro [9]	1570 Ma gabbro [10]
Post					
Structural characteristics	D3w: Close-open folding (F3w) D4w: Thrusting of thin sheets (including transposed foliation, local mylonites) D5w: Sub-horizontal folding (F5w) and related lineation			D2e: Open folding (F2e) and related lineation D3e: F3e folding and related lineation	Brittle/ductile heterogeneous foliation and lineation (strongest to the south)

Table 2.1: after Larson et al. (1998), lithologies, ages and structural characteristics for rocks in Värmland, north of Lake Vänern. Keys to references: [1] Connolly & Åhäll (1996), [2] Larson & Cornell (unpubl. data), [3] Lindh & Gorbatshev (1984), [4] Persson et al. (1995), [5] Jarl & Johansson (1988), [6] Heim et al. (1996), [7] Persson (1986), [8] Gorbatshev & Welin (1975), [9] Welin (1994), [10] Wahlgren et al. (1996).

2.3 Tectonic Setting and Emplacement of Norra Kärr

As outlined above the emplacement of Norra Kärr is problematic due the uncertainty regarding the tectonic events occurring between 1550 Ma and 1450 Ma. Available data relating to the geological history of magmatism and deformation relies on the dating of igneous intrusions and the deformations they host. Though the progress made in compiling the data relevant to geological reconstructions across the Fenno-Scandian craton and the Baltic shield has been significant in recent years there is still not enough detailed information to fully understand the history and it is likely that Norra Kärr can provide more evidence of the local cratonic history than the current local cratonic history can tell us about the events at Norra Kärr.

The prolonged-subduction zone along the margin of Nuna should also not be overlooked. The fertilisation of the mantle wedge is an important factor in the formation of magmatic ore deposits during the late Archean and the Proterozoic as well as for the formation of alkaline-rocks (i.e. Maier et al. 2013; Goodenough et al. 2016) and it is likely that this fertilisation played an important part in creating the conditions for the formation of Norra Kärr. Indeed, other F-rich intrusions are found to the south in Skåne. The mantle was also hotter during the Proterozoic and was approximately 1500°C to 1550°C (c.f. 1350°C in the present day, Herzberg et al. 2010; Johnson et al. 2014) and this may have affected how the subduction zone would have operated. In general tectonics during the Archean and Proterozoic and that palaeo-tectonics and the behaviour of the mantle, particularly during subduction, is still a strongly debated issue (i.e. van Hunen et al. 2012).

What is known is that the geological history of the host rocks of Norra Kärr up until 1500 Ma are a result of the accretion of several terranes and a prolonged-subduction zone during the Svenco-Fennian and Gothian Orogenies that produced the majority of the deformation features seen within the surrounding country rock. These events led to large scale N-S trending crustal weaknesses that could act as zones of fluid flow and magmatic intrusion. Rankin (2011) interprets a magnetic map of the area surrounding Norra Kärr to contain several intersecting fault corridors. The stresses during the Dan-Polonian Orogeny resulted in NE-SW compression concurrent with the E-W Baltica-scale deformation. This could have reactivated the existing shear zones thereby providing accommodation space in the crust for low-volume partial-melts during this time.

Magmatism in southern Sweden between 1600 Ma and 1360 Ma is summarised in Fig. 2.6. When compared to this plot Norra Kärr is an outlier relative the period of peak magmatism, however as a low volume melt is it feasible for Norra Kärr to be emplaced within the dating-errors at the start of the felsic magmatism (approximately 1480 Ma).

Figure 2.6: Probability plot of mafic (green) and felsic (red) magmatism in western Fennoscandia. Yellow curve shows the timing of metamorphism mainly concentrated to the southern part of the Eastern Segment. From Brander et Söderland 2009.

2.4 Field Relations and Structure of Norra Kärr

Norra Kärr is located on the south-east shore of Lake Vättern in southern Sweden. The intrusion is covered by extensive vegetation (mostly grasses and pine trees) which has resulted in very poor exposure and has long hampered any proper understanding of the rocks. However, exploration drilling by Tasman Metals Ltd. between 2009-2014 has provided material available for petrological study (see Chapter 3) and has provided new data regarding the subsurface structure. This section outlines both the observed field relationships and the results of 3D modelling of the drill core data completed as part of this thesis using cross-sections provided by Tasman Metals Ltd (further information on these models is given in Appendix 1 (A1.2.1 3D Modelling)). The location and spacing of drill cores used to model the 3D structure of Norra Kärr is given in Fig. 2.7 and shown in 3D in Fig. 2.8. A summary of the lithologies present at Norra Kärr along with the names used by Tasman Metals Ltd., and the corresponding names used in this thesis (along with descriptive lithological names based upon mineralogy) is given in Table 2.2.

2.4.1 The Grennaite Contact with the Växjö Granitoids

The Grennaite (an aegirine-eudialyte- catapleiite nepheline-syenite) is named after the nearby town of Gränna and forms the bulk of the intrusion. It is subdivided into the 'Contact' Grennaite, 'Pegmatite-Host' Grennaite and 'Crenulated' Grennaite, the latter two are described later. The 'contact-domain' is a fine-grained Grennaite variety that lies at the margin of the 500 m wide (E-W) and 1500 m long (N-S) intrusion and is typically up to 100 m thick. Within the Grennaite lies the sheet-like Pulaskite in the north-west section, the pod-like Lakarpite to the south-east and a core of Kaxtorpita at the centre of the intrusion.

Figure 2.7: Geological map of Norra Kärr showing the location and spacing of drill cores (all at approximately 45° dip) drilled by Tasman Metals Ltd. Data courtesy of Tasman Metals Ltd.

Figure 2.8: 3D model showing the distribution of drill cores in relation to the contact between the Norra Kärr intrusion and the Vaxjö Granites (green boundary). View from above.

Tasman	Dobrzański (This Thesis)		Descriptive Lithological Name
Fine-Grained Grennaite	Contact Grennaite		Aeg-Cat-Eud – Nepheline-Syenite
'Pegmatite Domain'	'Pegmatite Domain'	Pegmatite-Host Grennaite	Aeg-Cat-Eud - Nepheline-Syenite
		Pegmatite	Aeg-Cat-Eud - Nepheline-Syenite
Migmatite Domain	Crenulated Grennaite		Aeg-Cat-Eud - Nepheline-Syenite
Kaxtorpite	Kaxtorpite		Aeg-Amp - Syenite
Lakarpite	Lakarpite	Outer Zone	Aeg-Amp-Eud±Cat - Syenite
		Inner Zone	Aeg-Amp-Ros-Fl - Syenite
Pulaskite	Pulaskite	Matrix	Aeg-Amp-Ros-Fl - Syenite
		Enclaves	Aeg-Bt-Amp-Ros-Fl - Syenite

Table 2.2: Summary of lithology names used by Tasman Metals Ltd. and corresponding names used in this thesis along with descriptive lithological names based upon mineralogy. Further petrological description is given in Chapter 3, mineralogical compositions in Chapter 4, and whole-rock compositions and classifications in Chapter 5.

Figure 2.9: Exposure of the fine-grained variety of Grennaite (2 cm coin for scale – centre of the image). [64430N, 14271E, view looking approximately South]

Figure 2.10: Drill core showing the eastern contact between the Växjö Granites (dark country rock – lower 2m of the core) and the Contact Grennaite of Norra Kärr (green with white streaks – upper 3 m of the core) separated by a pale contact zone [NK54 - 153.8m-158.9m]. The appearance of the Contact Grennaite is representative of the bulk of the lithology; foliated and with occasional whiter catapleiite aggregates. Core-box length approximately 1m.

The contact between the Grennaite and the host Våxjö granitoids is seen in the field as a shallow valley which surrounds the intrusion due to weathering along the contact. The Grennaite itself is a light-to-dark-green rock (Fig. 2.9, 2.10), consisting of fine-grained aegirine, feldspar, nepheline, catapleiite and eudialyte and is broadly homogenous in character throughout the lithology.

The eastern contact of Norra Kärr (Fig. 2.11) has been proven to $\approx 320\text{m}$ depth and western contact down to $\approx 100\text{m}$ though both likely extend deeper. Both sides appear to be relatively smooth in shape with the eastern contact appearing to display a uniform dip of $\approx 50^\circ\text{W}$.

When the contact of the intrusion is observed in 3D (Fig. 2.12) the intrusion appears thickest in the centre (approximately $450\text{--}500\text{m}$ wide) before thinning to the north and south. At the southern end of the intrusion the Grennaite thins into two separate sections, the western section is up to 25m thick while the eastern section is up to 50m thick. Both sections are irregular in their morphology and are proven to depths of 25m and 75m respectively. The northern contact of the intrusion has been interpreted to be a straight contact in map view. However, there are no drill holes to prove the contact or its morphology and it may well extend further north with potential for splayed terminations (rather than being 'flat-ended') similar to the southern contact. Norra Kärr may also display a slight sigmoidal shape with the extreme ends orientated more towards NW-SE and the main body of the intrusion orientated slightly more to the NE-SW.

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Figure 2.11: The Grennaite contact of Norra Kärr – view looking southwards.

Figure 2.12: The Grennaite contact of Norra Kärr (green) and the start of the Pegmatite Domain (Red). The volume between these contacts is the 'contact' domain – view looking southwards.

Figure 2.13: Drill core showing the distribution of smaller sheared pegmatite bodies within the fine-grained green 'Pegmatite-Host Grennaite' [NK62 – 192.7m-199.4m]. Core-box length approximately 1m.

Figure 2.14: Drill core showing the textures of massive pegmatite [NK62 – 251.2m-256.9m]. Towards the centre (152.5-153m) the texture changes to very coarse pegmatite, either side coarse euhedral pegmatite extends the size of the 'pod' to an approximate width of 7m. Core-box length approximately 1m.

2.4.2 The Ore Domains – Pegmatitic Grennaite Domain

The 'pegmatite domain' is the term used to denote two different lithologies. The largest by volume is the fine-to-medium grained aegirine-eudialyte- catapleiite nepheline-syenite termed the 'Pegmatite-Host' Grennaite (Fig. 2.13) and a second coarse-grained feldspar-rich lithology termed the true Pegmatites (Fig. 2.14). The boundary between the Contact Grennaite and the Pegmatite-Host Grennaite is defined geochemically as being >299 ppm La which marks the cryptic contact between the non-ore grade Contact Grennaite and the ore-grade 'pegmatite domain'. As a unit this domain hosts up to 0.68% TREO.

In the field and in drill core the Pegmatite-Host Grennaite appears much like the Contact Grennaite though larger eudialyte crystals may be seen especially near the larger pegmatite pods. In many areas the veins of true pegmatitic material can be seen within the Grennaite (Fig. 2.15) occasionally 'pods' consisting of larger masses of coarse feldspar, nepheline, eudialyte and aegirine are seen (Fig. 2.16). Much of this material appears to have been sheared and boudinaged.

In drill core a range of different pegmatite-textures are present. Smaller cm-scale veins consist of coarse cm-scale crystals. Some veins display cm-scale textures of nepheline interstitial to euhedral feldspar and in others feldspar interstitial to euhedral nepheline. Larger m-scale veins display a coarsening inwards texture with subhedral medium-grained nepheline, feldspar, aegirine and eudialyte present on the outer parts of the veins and euhedral coarser-grained nepheline, feldspar, aegirine and eudialyte towards the centre of the pegmatite pod. The abundance of different varieties of pegmatite in drill core varies significantly which has led to classification problems when logging the core on the m-scale. Tasman Metals Ltd. have therefore divided the 'pegmatitic domain' based upon the % of pegmatitic material present within each length of drill core.

The detailed core photos from Tasman Metals Ltd. have allowed a finer scale model of the pegmatite pods to be produced by this study by digitally logging areas that comprise of massive pegmatite (Fig. 2.17) all of which lie within the >299 ppm La boundary (Fig. 2.18). These pods are up to 10's of m's in length and height but only appear to be m's in width. Most pods also appear to connect in some manner. The pegmatite pods do not line up with the supposed 'fold axis' of the intrusion and they are likely primary given the absence of pegmatite bodies in the surrounding country rock, outcrops of which are visible along the coastal road by Lake Vättern. This is unlike in other parts of Scandinavia where intrusive dykes and remelting can be readily observed in road cuttings.

In map view (Fig. 2.7) the pegmatite domain extends predominantly to the western side of Norra Kärr and is slightly thicker towards the north-west of the intrusion. The southern margin of the domain is relatively uniform in shape, while the northern margin separates into two splays.

The domain has been proven to a depth of 327 m (Figs. 2.19, 2.20) though the base has not been observed and likely extends far deeper. The margins of the domain appear to mirror those of the contact with the Växjö granites. The thickness of the domain is variable relative to the margin with the Crenulated Grennaite domain. The thickness is greatest to the north-west of the domain and is thinnest in the eastern part where the domain is absent along the far eastern corner of the Crenulated Grennaite.

Figure 2.15: Outcrop of part of the 'pegmatite domain' displaying courser veins of Pegmatite hosted within finer grained Pegmatite-Host Grennaite (2 cm coin for scale). [64428N, 142685E, view looking approximately East]

Figure 2.16: Outcrop of a cohesive body of pegmatite in the 'pegmatite domain' representative of the thicker pegmatite pods (2 cm coin for scale). [14271N, 64430E, view looking approximately West]

Figure 2.17: 3D model of the pegmatite bodies (grey boundaries) within Norra Kärr and their relationship to the contact of the intrusion (green) and the Crenulated Grennaite (yellow).

Figure 2.18: All assay data points >299 ppm La within Norra Kärr. This marks the cryptic contact between the Contact Grennaite and the 'pegmatite domain' marked by the red boundary. Note the paucity of datapoints within the Contact Grennaite. Contact of the intrusion (green) and the Crenulated Grennaite (yellow).

Figure 2.19: The 3D extent of the cryptic contact (299 ppm La) of the 'pegmatitic domain' (red) in relation to the contact with the country rock (green) and the Crenulated Grennaite (yellow).

Figure 2.20: The 3D extent of the cryptic contact (299 ppm La) of the 'pegmatite domain' within the volume of the Grennaite – view looking along the long axis of Norra Kärr towards the south. Contact with the country rock (green), 'pegmatite domain' (red) and the Crenulated Grennaite (yellow).

2.4.3 The Ore Domains – Crenulated Grennaite

The Crenulated Grennaite (the ‘migmatite domain’ of Sjöqvist et al. 2013) is a medium-grained variety of the Grennaite variety and is an aegirine-eudialyte- catapleiite nepheline-syenite (Fig. 21). It is the smaller of the two ore domains at Norra Kärr and hosts up to 0.51% TREO. The name derives from the cm-scale crenulation fabric seen within the lithology (see Chapter 3 for further details). The hinges of the tight cm-scale folds display a coarser grain size and comprise of feldspars and nephelines while the limbs are more aegirine rich. The domain has likely developed this texture during deformation due to its courser grain size, while the finer Grennaite-varieties away from the centre of the intrusion developed lineation textures. The Crenulated Grennaite is restricted to a volume inside of the ‘pegmatitic domain’ and there is occasional small bodies of ‘true’ pegmatite material present within the domain. The domain also encloses the Kaxtorpite with which it displays a similar grain-size and strong crenulated-foliation.

In map view the domain appears as an arrow-head shaped body that pinches out to the north (Fig. 2.22). The Crenulated Grennaite has been proven to a depth of ≈ 250 m. The base of the domain can be observed in 3D to dip shallowly to the south until the southern point of the Kaxtorpite whereupon the dip steepens northwards to wrap around the Kaxtorpite before intersecting the surface again just south of the Kaxtorpite (Fig. 2.23). The domain appears to ‘hug’ the contact with the Kaxtorpite; with the thickness between the domain margin with the ‘pegmatitic domain’ and the Kaxtorpite being a relatively uniform thickness on the order of 15-30m.

Figure 2.21: Drill core showing the textures of Crenulated Grennaite (light green) which included deformed Kaxtorpite (dark green) [NK25 – 118.2m-124.8m]. Note the lighter areas dominated by feldspars and feldspathoids. An indication of the crenulated texture can be seen though this is more evident when the core is split in two – see Fig. 3.28 for further details. Core-box length approximately 1m.

Figure 2.22: The 3D extent of the Crenulated Grennaite in relation to the contact (light green) and Kaxtorpite (dark green)– view looking down onto Norra Kärr to the south-west.

Figure 2.23: The 3D extent of the Kaxtorpite within the volume of the Crenulated Grennaite – view looking down onto Norra Kärr.

2.4.4 The Ore Domains – Overall Patterns of Lanthanoid Concentration

A notable feature of Norra Kärr is the zonation in individual lanthanoid concentration throughout the Grennaite domains and the pegmatites and 3D modelling of the deposit (Figs. 2.22, 2.23) clearly shows this zonation. This will be explored further in later chapters (see chapters 4 and 5) however the relationship to the structural units is given here. The patterns in concentration within the Grennaites can be divided up into four zones which are also based upon subtle petrological differences (described further in Chapter 3):

1. The outer fine-grained Contact Grennaite contains the lowest Lanthanoid-contents of the Grennaites (<200 ppm La, <20 ppm Lu) and is not considered ore-grade.
2. The inner Crenulated Grennaite contains higher levels of Light-Lanthanoids (Fig. 2.24) than the other lithologies (e.g. 475-675 ppm La).
3. The inner Pegmatite-Host Grennaite which consists of fine grained-Grennaite with high overall Lanthanoid concentrations (Fig. 2.25). (340-560 ppm La, 18-25 ppm Lu)
4. The 'true' pegmatites within the 'pegmatite domain' which contain the highest overall levels of Lanthanoids (360-615 ppm La, 19-29 ppm Lu). These are enriched in Heavy-Lanthanoids and form large (up to 10m) pod-like bodies.

The Kaxtorpite, Lakarpite and Pulaskite are considered to be non-ore-grade lithologies (<400 ppm La, < 10 ppm Lu).

Figure 2.24: La (ppm) compared to lithology contacts (colour map between 0-2000 ppm La). Higher concentrations of La can be found within the boundary of the Crenulated Grennaite (yellow). View looking onto Norra Kärr west-north-west.

Figure 2.25: Lu (ppm) compared to lithology contacts (colour map between 0-110 ppm Lu). View looking onto Norra Kärr west-north-west.

2.4.5 The Kaxtorpite

The Kaxtorpite (an eckermannite-aegirine-microcline syenite) lies at the centre of Norra Kärr and only extends to a depth of ≈ 200 m. It is named after the nearby Kaxtorp farm. The surface area of the Kaxtorpite is inferred to be approximately 200m long by 250m wide and pinches-out to the north. At outcrop the Kaxtorpite displays a strong-crenulation fabric of aligned amphibole and aegirine (Fig. 2.26). The mineralogy of the Kaxtorpite appears to be homogenous throughout the body and there are cm-scale folds observable in core-section.

The mineralogy of the Kaxtorpite appears to be homogenous throughout the body and there are cm-scale folds observable in core-section. The Kaxtorpite contains phenocrysts of coarse-grained feldspars around which the deformation fabrics wrap. The Kaxtorpite displays a number of differing internal consistencies. The main body of the lithology appear homogeneous throughout, albeit with occasional whips of included Grennaite material (Fig. 2.27). However, towards the contact of the Kaxtorpite and the Crenulated Grennaite the amount of Grennaite material increases (Fig. 2.28) with the Contact Grennaite also containing included portions of the Kaxtorpite (Fig. 2.29). The contact between the Grennaite and Kaxtorpite is often not sharp and displays signs of mingling followed by deformation. In particular Grennaite material becomes incorporated into the crenulation folding of the Kaxtorpite, while within the Crenulated Grennaite the Kaxtorpite becomes similarly deformed and appears to be partially disaggregated. Elsewhere cohesive volumes of Kaxtorpite appear separately within the Crenulated Grennaite (Fig. 2.30) with no obvious connection with the rest of the Kaxtorpite occurrences.

Figure 2.26: Outcrop of Kaxtorpite showing the foliated texture (2 cm coin for scale). [64426N, 14269E, view looking approximately North East]

Figure 2.27: Drill core showing the deformed textures of the main body of the Kaxtorpita (dark green) with some minor Crenulated Grennaite (lighter green) intermingled [NK35 – 7.63m-14.04m]. Note larger white feldspars within the Kaxtorpita (e.g. 18.5m-19m. Core-box length approximately 1m.

Figure 2.28: Drill core showing the deformed textures of Kaxtorpita (dark green) with some Crenulated Grennaite (lighter green) apparently intermingled [NK76 – 34.45m-41.1m]. Note the strongly deformed layers of Grennaite (e.g. between 37.5m-38m), and the apparent inclusion of Kaxtorpita within Grennaite at 39.35m-39.85m. Core-box length approximately 1m.

Figure 2.29: Drill core showing the deformed textures of Crenulated Grennaite (lighter green) and Kaxtorpita (dark green) [NK75 – 102.85m-108.31m]. Core-box length approximately 1m.

Figure 2.30: Drill core showing the folded textures within a section of Kaxtorpites (dark green) and its contact with the Crenulated Grennaite (light green) [NK36 – 131.7m-137.35m]. The deformation texture can be seen highlighted by the lighter feldspars and darker aegirine-amphibole – see Fig. 3.40 for hand specimen details. Core-box length approximately 1m.

In light of these observations, proposed cross-sections of the Kaxtorpites (Fig. 2.34) pose a number of questions. In 3D the Kaxtorpites has a highly irregular contact with the Crenulated Grennaite (Figs. 2.32, 2.33), and potentially the Kaxtorpites extended upwards from the current outcrop and widened out, though any evidence of this has been eroded away. Below outcrop the drill cores intersect smaller masses of Kaxtorpites material within the Crenulated Grennaite which show the diffuse contacts and mingling with the surrounding Grennaite described above. The Kaxtorpites has previously been interpreted to comprise of separate branches; however, based upon the evidence for magmatic mingling and shearing observable in drill core, this model can be reinterpreted as distinct Kaxtorpites ‘rafts’ that have fallen into the Grennaites which produces a single body that deepens towards the west (Fig. 2.23).

This potential model is strengthened by several assumptions made during the drafting of the original cross-sections. Following the ‘fold model’ proposed by Rankin (2011) the Kaxtorpites was interpreted by Tasman Metals Ltd. to be a homogenous body which followed the central axis of the intrusion and fitted to the shape of a folded body. However, this has led to several inconsistencies within the cross-sections.

Firstly, this led to the fitting of Kaxtorpites through areas not logged as such. For example, between 50 m and 100 m along NK10016 there is a section logged as Crenulated Grennaite which has a limb of the Kaxtorpites drawn through it. In within this section of drill core there is only the slightest presence of sheared Kaxtorpites being less than 5% the volume of the core. By removing the interpreted Kaxtorpites from this section a different explanation must be sought for the remaining volumes of Kaxtorpites observed in the drill core.

Secondly, areas described as Kaxtorpites mixed with Grennaite are interpreted as being part of these long limbs of Kaxtorpites. Reinterpreting these areas of Kaxtorpites as distinct volumes within the Crenulated Grennaite leads to a more complex structure being present. The simplest model for such a structure would be one where the main volume of Kaxtorpites within Norra Kärr appears to form an

upside down 'cone' structure surrounded by individual volumes of Kaxtorpite material which have become incorporated (or have possibly formed within, or 'sunk' into) the Crenulated Grennaite. This is potentially supported by drill core observations where there are areas of Kaxtorpite appear mixed into the Grennaite (e.g. Fig. 2.28), and where there are distinct volumes of Kaxtorpite apparently separate from the main Kaxtorpite mass (e.g. the 2m wide volume of Kaxtorpite in Fig. 2.30) and which do not necessarily support the interpretation of a single homogenous structure on a scale of 10s of meters.

Given that this is a less predictable structure it these areas are may well appear more frequently than can currently be confidently shown on the cross-section. This interpretation is difficult to conclusively show due the drill core spacing and limited 3D information which can be derived from the core alone, but it would be a better fit for the information available and would simplify the structure of the cross-sections. This interpretation does not require there to be the extreme degree of folding postulated by the original Rankin (2011) interpretation which is questioned and discussed further later in this thesis (Chapter 8).

Figure 2.31: Reinterpretation of the structure of the Kaxtorpite.

Figure 2.32: The 3D extent of the Kaxtorpite (dark green) in relation to the contact with the country rock (green) The open circles indicate interpreted fallen 'rafts' that have sunk into the Crenulated Grennaite. View looking down onto Norra Kärr towards the south-east.

Figure 2.33: The 3D extent of the Kaxtorpite (dark green) in relation to the Crenulated Grennaite (orange) The open circles indicate interpreted fallen 'rafts' that have sunk into the Crenulated Grennaite. View looking down at onto Norra Kärr to the north-east.

2.4.6 The Lakarpite

The Lakarpite comprises several varieties of arfvedsonite-aegirine-microcline syenite that form several lens or pod type structures in the south-east portion of Norra Kärr almost mirroring the Pulaskite that is present in the north-west of the intrusion. The Lakarpite is named after the nearby Lakarp farm. The famous Norra Kärr ‘discovery outcrop’ (Fig. 2.34) is located at the western contact of a Lakarpite lens and the Grennaite. The Lakarpite hosts deep-purple Fe-rich and comparatively [Ln]-poor eudialyte. In the field the Lakarpite tends to form hummocky ground much like the Pulaskite but is predominantly fine-grained and dark in colour. Its contact within the Grennaite-related rocks appears to display a reaction texture that comprises of non-ore grade coarse grained eudialyte and feldspar crystals.

In drill core the Lakarpite shows a range of mineral assemblages, with the core of the intrusion appearing more like the Pulaskite with abundant fluorite and some rosenbushite (Fig. 2.35), while the contact zones adjoining the Grennaite display a range of eudialyte textures (Fig. 2.35, 2.36). This varying mineralogy is documents in Chapter 3. As shown in Fig. 2.34, there appears to be evidence for some form of hybridisation or mass transfer between the Lakarpite and the Grennaite and this is explored further in Chapter 5.

Figure 2.34: Contact between the darker Lakarpite and the greener Grennaite. The diffuse contact zone between the two lithologies is marked by coarse-grained eudialyte and feldspar (2 cm coin for scale). [64428N, 142703E, the ‘Discovery Outcrop’ view looking approximately North]

The Lakarpite has been proven to a depth of $\approx 280\text{m}$ but is less than 10-20m in thickness (Figs. 2.37, 2.38) and appears to have predominantly intruded the Pegmatite-Host Grennaite. The surface contact of the Lakarpite appears as several 'lens' structures which give the impression of being detached from each other. However, 3D modelling shows that they are the surface expression of a far more complex structure that extends from the north of Norra Kärr down along the eastern margin of the intrusion. This thin sheet appears to wrap and twist along the contact of the pegmatitic domain and in some areas follows the contact between the pegmatitic and contact domains of the Grennaite dipping at a similar angle to the eastern contact of the intrusion.

Figure 2.35: Drill core showing the textures of a section of Lakarpite [NK57 – 102.95m-108.7m]. Note the (western) contact with the Grennaite and the formation of eudialyte (pink) between 103m-103.8m. The rest of the core appears mineralogically unchanged. Core-box length approximately 1m.

Figure 2.36: Drill core showing the textures of a section of Lakarpite [NK57 – 120.17m-125.73m]. This core box represents the eastern side of the Lakarpite to the western one shown in Fig. 2.35. Note that in this case eudialyte (pink) has been able to grow up to 8m into the Lakarpite from the eastern contact with the Grennaite. Core-box length approximately 1m.

Figure 2.37: The 3D extent of the Lakarpite displaying its pod like morphology along the eastern edge of the Norra Kärr closely following the contact with the country rock (green) – view looking south-east.

Figure 2.38: The 3D extent of the Lakarpite – view looking along the long axis of Norra Kärr towards the south.

2.4.7 The Pulaskite

The Pulaskite is a body of arfvedsonite-biotite-aegirine-microcline syenite that forms a sheet in the north-west portion of Norra Kärr. As Pulaskite is an internationally used term it is the only lithology within Norra Kärr not named after a local settlement. This lithology comprises of a feldspar rich matrix and associated enclaves (Fig. 2.39).

At outcrop the Pulaskite is a light cream rock that forms hummocky ground. It contains frequent elongate and deformed enclaves of darker material which appear to indicate primary magmatic mixing-mingling textures. Examination of the orientation of the magmatic structures also suggest that it may be intruding the Grennaite upwards from below the present ground surface (Fig. 2.40) carrying biotite-amphibole rich enclaves with it from deeper down in the intrusion. The Pulaskite appears to have intruded the contact domain of the Grennaite and the contact between the two lithologies is marked by a 3-4 cm thick dark-coloured baked margin (Fig. 2.41). The intrusion of the Pulaskite into the Grennaite has also resulted in the formation of Grennaite xenoliths within the Pulaskite.

The mapped outcrops shown that the main Pulaskite sheet is approximately 800m long and up to 30-40m thick. The Pulaskite displays a number of bifurcating terminations that pinch out at its northern and southern ends. The Pulaskite is proven to a depth of 75m. There are several mapped outcrops that appear to be 30-40m thick lenses but these join up in the subsurface (Figs. 2.42, 2.43). The Pulaskite appears to dip towards the west at approximately 45°.

Figure 2.39: Drill core showing the textures of a section of Pulaskite, with the (eastern) contact with the Grennaite shown within the final metre [NK53 – 30.27m-37m]. Note that the darker portions (e.g. 30.70m-30.80m) are enclaves which appear to have been mildly deformed. Core-box length approximately 1m.

Figure 2.40: Contact between the Pulaskite and the fine-grained Grennaite. The Pulaskite displays numerous dark enclaves. 'G' denotes parts of the Contact Grennaite which have fallen into the Pulaskite, 'E' denoted enclaves from the Pulaskite, 'P' denotes Pulaskite (2 cm coin for scale). [64430N, 142685E, view looking approximately East]

Figure 2.41: Contact between the lighter Pulaskite and the greener Contact Grennaite showing the darker baked margin between the two. The intrusion of the lighter Pulaskite into the Contact Grennaite can also be observed along the margin. (2 cm coin for scale). [64430N, 142685E, view looking approximately East]

Figure 2.42: The 3D extent of the Pulaskite – view looking southwards.

Figure 2.43: The 3D extent of the Pulaskite between the contact with the country rock (green) and the cryptic contact of the 'pegmatite' domain. View looking down onto Norra Kärr.

2.5 Summary of Structure and Tectonics

This chapter has provided a new synthesis of the tectonic history of Norra Kärr and poses a potential interpretation for the structure of the intrusion and further questions about the formation of the lithologies. In particular the intrusion and its ore domains have been modelled in more detail than before and examples of key structures and relationships have been described from observations from the field observations and from drill core. In particular this Chapter has shown that:

- The intrusion of Norra Kärr took place during the Dan-Polonian during a period of wider AMCG magmatism and shearing across Fennoscandia.
- There is a cryptic contact between the Contact Grennaite and the 'pegmatite' domains at 300 ppm La. There is further cryptic zonation between the 'pegmatite domain' and the Crenulated Grennaite. This will be discussed further in Chapter 4.
- The 'pegmatite domain' can be divided into fine-grained Pegmatite-Host Grennaite and 'true' pegmatites which display a range of textural features and can be metres in width. The relationship between the Pegmatites and the Pegmatite-Host Grennaite will be investigated further in Chapter 5.
- The Kaxtorpite has a complex and in places intermingled contact with the Crenulated Grennaite. There are also portions of Kaxtorpite which do not appear to easily connect with the main body of the Kaxtorpite. As such it is possible to instead model the Kaxtorpite as a single magmatic body surrounded by 'rafts' that have sunk into the Grennaite magma. This will be discussed further in Chapter 9.
- The Lakarpite displays a complex 3D structure, with drill cores displaying a potential reactive contact with the Grennaite magma. This will be investigated further in Chapter 5.
- The Pulaskite displays structural features that suggest intrusion occurred upwards relative to the present-day land surface. The Pulaskite also contains sheared enclaves. The relationship between the enclaves and rest of the Pulaskite will be described further in Chapter 4.

Chapter 3

Petrography

3.1 Introduction

This chapter will describe the petrology and petrogenetic sequences of each of the lithologies within the Norra Kärr intrusion. The Norra Kärr samples presented in this study were collected from drill core and were analysed using optical microscopy. Samples from other alkaline intrusions were sourced either from the Grant Institute teaching collection (Edinburgh University) or the geology collection of National Museums Scotland. The first petrological study of Norra Kärr was carried out by Adamson (1944), with modern petrographic work completed by Henig (2012) and Atanasova et al. (2017). However, this work presents the first comprehensive, modern description of the minerals, textures and petrogenetic sequence for all of the rock types at Norra Kärr. The observations presented here will be used as the basis to underpin the analytical and modelling studies presented later in this thesis. Note that a mixture of 30 μm and 100 μm -thick thin-sections have been used resulting in some images displaying minerals with differing orders of interference to that usually expected. Mineral abundances are based upon optical point counting of the minerals within thin sections. The minerals are described in order of crystallisation based upon their cross cutting relationships. On the basis of the structural relationships presented in Chapter 2 and the petrological observations presented here, the lithologies at Norra Kärr (along with the country rock and fenitised contact) will be discussed in the following order:

The Våxjö Granites – These comprise of the mixed and deformed granitoids of the Transscandinavian Igneous Belt (TIB). These rocks form the country rock to the intrusion.

The Fenite – The fenite lies within the Våxjö Granites and forms the contact between the country rock and the Grennaite.

The Grennaite - The Grennaite can be divided into three distinct zones. The Contact Grennaite is the finest grained of the Grennaite varieties and is found at the contact of the intrusion. This grades inwards to the slightly-coarser grained petrographically distinct Pegmatite-Host Grennaite with the geochemical boundary between the two set at 299 ppm La. The Pegmatite-Host Grennaite contains the distinctive coarse grained feldspar rich pegmatites. The final variety is the Crenulated Grennaite which is the coarsest grained of the Grennaites and lies in contact with the Kaxtorp. Together these rocks represent the largest volume of material found at Norra Kärr.

The Kaxtorp – The Kaxtorp forms the structurally highest lithology at Norra Kärr with its base in contact with the Crenulated Grennaite.

The Pulaskite – The Pulaskite occurs as a thin dyke-like body and contains enclaves.

The Lakarp – The Lakarp occurs as dyke-like pods of material with a series of complex petrological zones observed in cross section through the bodies.

3.1.1 Samples and Methodology

All samples listed here and in the rest of this thesis are labelled using the following convention: [NK (Core Number) – (Drillhole Depth in meters)]. Hence [NK62-8] can be read as: Norra Kärr – Drillhole 62 – Sample Depth: 8 m. A full list of the samples used in this study along with a map of their locations is given in Appendix 1.

The mineral abundances stated in each section have been derived from point counting on the slides used in this study and are indicative of the areas sampled. Point counts across multiple slides were then averaged to derive a single figure. For the finer grained Grennaite varieties image-processing software was used on SEM images of the samples in order to arrive at a mineral abundance. The SEM-images of minerals and their associated textures described here are given in Chapter 4 under the relevant mineral. They are not included here as the majority of the minerals, bar eudialyte, do not display zoning or alteration features that can be better observed under SEM than by optical methods.

3.2 Väjö Granitoids (Country Rock) and Fenite

The host rock for Norra Kärr are the Väjö Granitoids which form part of the Transscandinavian Igneous Belt (TIB) (Anderson et al. 2010). This lithology is characterised by large phenocrysts of microcline and an anastomosing foliation as defined by micas (Fig. 3.1).

Fig 3.2 shows the effect of fenitisation upon the Väjö Granites by the Norra Kärr intrusion. The sample displays extensive hematite staining, and in this case also displays a partly mineralised vein.

Figure 3.1: Drill-Core sample from the Väjö Granite [NK62-8]. Note the cm-scale feldspar phenocrysts and anastomosing foliation.

Figure 3.2: Drill-core sample from the Fenite [NK62-16.35]. Note the extensive haematite staining of the sample and the presence of a partly-mineralised vein.

Feldspar

Feldspars occur as cm-scale, subhedral alkali feldspar which exhibits tartan twinning and perthite exsolution (Fig. 3.3). Within the fenite the feldspars also display whiter albite rims.

Biotite

Biotite is present as <1 cm anhedral crystals with a strong light-to-dark brown colour in PPL and a strong single cleavage.

Quartz

Quartz is present as <1 cm anhedral crystals with first order interference colours in XPL.

Haematite

Haematite only occurs within the fenite and is present as <1 cm sized anhedral patches and cm-thick veins (Fig. 3.4).

[NK62-8-XPL]

[NK62-8-PPL]

Figure 3.3: Väjö Granites (30 µm thick section) (left) Feldspars displaying poorly developed tartan-twinning and perthite exsolution, image in PPL; (right) Feldspars, quartz and biotite, image in PPL.

[NK 62-16.35-REF]

[NK62-16.35-PPL]

Figure 3.4: Haematite in the Fenite (30 µm thick section). (left) Haematite patches within a fractured matrix, image in reflected PPL; (right) hematite vein within fenitised country rock, image in PPL.

3.3 The Grennaite and Pegmatites

3.3.1 Contact Grennaite

The Contact Grennaite (Fig. 3.5) is a broadly homogenous rock unit consisting of fine-grained nepheline, feldspar and aegirine with eudialyte and catapleiite being present. The Contact Grennaite is dark green in colour (due to the aegirine content) with <1cm long light-blue catapleiite frequently present. Poikilitic eudialytes are also occasionally present. The Contact Grennaite also includes occasional vein structures.

The Contact Grennaite displays a weak linear fabric which is partly picked-out by the fine-grained minerals but is predominantly observable by the 'smears' of nephelines /feldspars. The larger eudialytes and catapleiites approximately align with the fabric, with the larger poikilitic eudialytes being rimmed with feldspar and displaying weak σ -type structures.

[NK95-53.8]

[NK25-25.9]

Figure. 3.5: Core samples from the Contact Grennaite. Top: [NK95-53.8], left: [NK25-25.9]. In both samples the weak linear fabrics are predominantly picked out by the aegirine and 'smears' of nephelines /feldspars.

Aegirine

Aegirine occurs as the primary phase in all samples and is present as <2mm long anhedral-to-euhedral to- dark-to-light green needles (Fig. 3.6). The crystals display well developed cleavages and cracks and appear unaltered. They exhibit anomalous interference colours in XPL due to their strong body colour. Texturally aegirine can be found enclosed by the feldspar phases.

Catapleiite

Catapleiite occurs as cm-scale irregular masses comprising of <500 µm euhedral needles of catapleiite (Fig. 3.7). These needles display high relief in PPL and 2nd order interference colours in XPL. The masses enclose earlier aegirine and some fine-grained feldspar phases.

Eudialyte

Eudialyte occurs in two textural forms within the Contact Grennaite. The most common texture is as anhedral fine-grained crystals <1 mm in dimension (Fig 3.8-A). The crystals are light pink in PPL and commonly occur attached to aegirine crystals, suggesting the aegirine provided a convenient nucleation site for the eudialyte. The eudialyte does not appear altered, but alteration to catapleiite has been reported within this lithology by Atanasova et al. (2017).

The second eudialyte texture present is mm-scale poikilitic (or potentially 'snowball') eudialyte (Fig. 3.8-B). This texture is comprised of an optically-consistent eudialyte crystal which is anhedral-to-subhedral in shape and contains included aegirine. The eudialyte also displays a potential overgrowth rim which contains rounded felspar and aegirine inclusions.

[NK95-53.8-PPL]

[NK95-53.8-XPL]

Figure 3.6: Anhedral-to-euhedral aegirine crystals enclosed by feldspar (100 µm thick section). (left) – image in PPL; (right) - image in XPL.

[NK25-259-PPL]

[NK25-259-XPL]

Figure 3.7: Masses comprised of euhedral needles of catapleiite (100 µm thick section). (left) – image in PPL; (right) - image in XPL.

[NK32-158.15-PPL]

[NK95-53.8-XPL]

Figure 3.8: A (left) – fine-grained eudialyte crystals enclosing aegirine and enclosed by feldspar. Image in PPL; B (right) –poikilitic eudialyte texture displaying a reaction rim and potential exsolution features. Image in XPL. Both are 100 µm thick sections.

Albite

Albite is predominantly present as <5mm anhedral-to-subhedral crystals (Fig. 3.9). Albite encloses earlier aegirine and eudialyte crystals. The feldspars may display cracks and polysynthetic twinning.

Microcline

Microcline is present as <5 mm anhedral-to-subhedral phenocrysts (Fig. 3.10). It can be distinguished by its distinctive tartan twinning. The microcline phenocrysts enclose earlier aegirine and the crystals are rimmed by <1 mm anhedral Albite crystals with polysynthetic twinning.

Nepheline

Nepheline is present as altered crystals with 'dusty' inclusions (Fig. 3.11). The crystals are anhedral and less than 1 mm in dimension. They enclose earlier aegirine.

Figure 3.9: Anhedral-to-subhedral albite crystals containing enclosing aegirine and eudialyte (100 µm thick section). (left) – image in PPL; (right) - image in XPL.

Figure 3.10: Anhedral-to-subhedral microcline displaying tartan twinning and rimmed by anhedral albite (100 µm thick section). Image in XPL.

Figure 3.11: Anhedral nepheline with dusty alteration features (100 µm thick section). Image in XPL.

3.3.2 Pegmatite Host Grennaite

The 'Pegmatite-Host' Grennaite (Fig. 3.12) consists of a slightly coarser grained variety of the Contact Grennaite. This lithology is broadly homogenous in texture and mineralogy and is dominated by fine-grained nepheline, feldspar and aegirine with eudialyte and catapleiite also present. This lithology comprises the majority of the 'Pegmatite Domain' but within this thesis is treated separately to that of the pegmatites. Veins infilled with catapleiite are also present within the lithology.

The Pegmatite Host Grennaite displays a similar weak linear fabric to that of the Contact Grennaite. Again, the fabric is partly defined by the finer grained minerals as well as well as feldspar 'smears' and the alignment of medium-grained catapleiite. Additionally, deformation fabrics can be observed surrounding blocks of pegmatitic material and evidence of shear within the unit can be observed from the dm-scale disaggregated lens-shaped pegmatite bodies.

[NK53-97.8]

[NK53-269.4]

Figure 3.12: Core samples from the Pegmatite-Host Grennaite. Top: [NK53-97.8], sample hosting cm-scale pegmatite. Left: [NK53-269.4], sample rich in catapleiite lathes.

Aegirine

Aegirine is typically present as <1 cm long euhedral-to-subhedral needle-like crystals, though some coarser grained crystals are present (Fig. 3.13). They display a strong light-dark green colour with some cleavages and cracks. They appear unaltered and exhibit anomalous interference colours in XPL due to their strong body colour. Texturally aegirine can be found enclosed by the feldspar phases.

Catapleiite

Catapleiite is present as primary crystals and as later secondary growths within veins. The primary catapleiite typically occurs as subhedral crystals <1 mm in dimension and are noticeably better formed than in the Contact Grennaite. In PPL the crystals display high relief and are a straw yellow-colour, while in XPL they display 2nd order interference colours in a 30 µm thick section. The crystals show well developed cracks. The catapleiite contains aegirine inclusions and does not appear to have been altered. The secondary catapleiite occurs as cm-sized anhedral crystals which contain numerous inclusions (Fig. 3.14).

Eudialyte

Eudialyte occurs as anhedral crystals <1 mm long (Fig. 3.14) which are typically slightly larger than those observed in the Contact Grennaite. In PPL the crystals display a high relief with a yellowish-pinkish tint. In XPL the crystals display 1st order mottled greys and often exhibit cracks but do not appear altered. The eudialytes contain aegirine inclusions and frequently appear to intergrow with aegirine clusters.

Albite

Albite is predominantly present as <1 cm anhedral-to-subhedral crystals (Fig. 3.14). Albite encloses earlier aegirine, catapleiite and eudialyte crystals. The feldspars may display cracks and polysynthetic twinning.

Nepheline

Nepheline is present as altered crystals with 'dusty' inclusions (Fig. 3.15). Within veins, nepheline crystals are anhedral and less than 1 cm in dimension and can be intergrown with catapleiite.

[NK53-97.8-PPL]

[NK53-97.8-XPL]

Figure 3.13: Euhedral-to-subhedral aegirines (100 µm thick section). (left) – image in PPL; (right) - image in XPL.

[NK53-97.8-PPL]

[NK53-97.8-XPL]

Figure 3.14: Catapleiite and eudialyte (30 µm thick section). (left) – image in PPL; (right) - image in XPL.

[NK53-269.4-PPL]

[NK53-269.4-XPL]

Figure 3.15: Catapleiite and nepheline within a vein structure (30 µm thick section). (left) – image in PPL; (right) - image in XPL.

3.3.3 Pegmatites

The pegmatites (Fig. 3.16) are distinct bodies between several cm's to 10's of m in dimension and are only found within the Pegmatite-Host Grennaite. They are internally variable in texture and grain size (medium-grained pegmatite to the coarse-grained pegmatite) with the larger pegmatites being dominated by nepheline and feldspar. The smaller dm-scale pegmatite 'pods' can either display phenocrysts of feldspar with interstitial nepheline, or phenocrysts of feldspar with interstitial nepheline indicating that the Al-Si ratios of the individual smaller pegmatites may be variable on m-scales. The pegmatites display apparently primary igneous textures, but smaller pegmatites may suffer from disaggregation due to shear. Overall, the pegmatites are dominated by aegirine, purple catapleiite, red eudialyte and feldspars and nephelines. Typically, coarser aegirine grows from the edge of the pegmatite with which catapleiite and eudialyte intergrow. The main fill of the pegmatites is always predominantly feldspar/nepheline. Larger, apparently poikilitic, eudialyte appears within the Pegmatite-Host Grennaite close to the contact larger pegmatite bodies, with the size of these eudialytes decreasing to the background grain-size within a meter of the contact.

[NK53-174.3]

[NK32-131.5]

[NK32-146.9]

Figure 3.16: Core samples of Pegmatite.

Top: [NK53-174.3], medium grained pegmatite.

Middle: [NK32-131.5], deformed and disaggregated pegmatite with nepheline phenocryst.

Bottom: [NK32-146.9], coarser grained pegmatite with feldspar phenocrysts.

Zr-Rich Aegirine

Where present, aegirine with exsolved Zr-rich cores are the earliest formed mineral (Fig. 3.17). The largest occur up to 3-5 mm in size but a range of sizes is observed. In some pegmatite samples aegirines can be up to 3 cm in length. EMPA work by Atanasova (2015) has shown these cores to be exsolved catapleiite. The aegirines are a strong light-dark green and display well-developed cleavages and cracks. Both the crystals and their exsolved cores are subhedral-to-anhedral and may display concentric zoning. The crystals may exhibit strong anomalous interference colours in XPL. The crystals appear unaltered and they are mainly hosted within feldspars, nephelines and eudialytes.

Aegirine

Smaller (<1mm) aegirines, which do not display Zr-rich cores are present within all samples (Fig. 3.18). These tend to be subhedral-to-euhedral and display a strong light-dark green colour with well-developed cleavages and cracks; they appear unaltered. This generation of aegirine is mainly hosted within feldspars, nephelines and eudialytes and may also represent the overgrowths on the primary Zr-rich aegirine.

Catapleiite

Catapleiite occurs as light brown euhedral lathes up to <5mm long and up to 0.5mm thick (Fig. 3.19). They display bright second-to-third order interference colours and well-developed cracks - they appear unaltered. Catapleiite is hosted within eudialyte and feldspars.

[NK62-307.8-PPL]

[NK53-174.3-XPL]

Figure 3.17: Aegirine phenocrysts with exsolved Zr-rich cores within the pegmatite bodies (100 μm thick sections). (left) – aegirine displaying exsolved core and zoned rim, image in XPL; (right) – aegirine displaying complex birefringence colours, image in XPL.

[NK62-307.8-PPL]

[NK62-307.8-XPL]

Figure 3.18: Subhedral-to-euhedral aegirine crystals without Zr-rich cores. (left) aegirine phenocrysts included within eudialyte (centre) and feldspar – image in PPL; (right) aegirine phenocrysts included within catapleiite and feldspar - image in XPL (100 μm thick section).

[NK53-195.8-XPL]

[NK53-174.3-XPL]

Figure 3.19: Euhedral lathes of catapleiite (100 μm thick sections). A (left) - catapleiite within microcline. Image in XPL; B (right) - catapleiite within eudialyte. Image in XPL.

Eudialyte

Eudialyte (strictly-speaking Eudialyte-group Minerals or EGM) occurs as anhedral-to-subhedral crystals up to 5 mm in size. Almost all of the eudialytes observed display patchy cores (Fig. 3.20-A). However, oscillatory zoning is also sometimes present on some samples (Fig. 3.20-B). In 100 μm -thick-sections, eudialyte displays purple to orange colours and any zoning can be clearly seen; in 30 μm -thick-sections eudialyte appears dark-grey in XPL but can still display light-to-dark orange cores. The eudialytes appear to have been altered along radial fractures to an assemblage of light-speckled minerals and/or opaques. The eudialytes frequently host aegirine (Fig. 3.21) but can show multiple relationships with feldspar. In the majority of thin-section observed the feldspars appear to grow around or include the eudialytes. However, on the scale of a hand specimen, it is evident that eudialyte appears to be interstitial to euhedral lathes of feldspar. Apparent reaction rims with feldspar are also observed (Fig. 3.22).

Some observed samples contain eudialyte which appears to have reacted with the feldspathic/nepheline rich melt (Fig. 3.23). These crystals have an irregular shape and highly fractured/granular rims. This texture may have arisen as eudialyte became entrapped in the melt and reacted with it.

[NK25-49.4-XPL]

[NK25-49.4-XPL]

Figure 3.20: Zoned eudialyte crystals (100 μm thick sections). A (left) - Patchy zoning within eudialyte. Alteration can also be seen along the cracks. Image in XPL; B (right) – Oscillatory zoning in eudialyte. The eudialyte also shows alteration along cracks predominantly in the centre of the crystal. Image in XPL.

[NK53-174.3-XPL]

Figure 3.21: Eudialyte enclosing aegirine (30 μm thick section). Image in XPL.

[NK32-146.9-XPL]

Figure 3.22: Altered eudialyte with displaying a potential reaction rim (30 μm thick section). Image in XPL.

[NK47-36.7-PPL]

[NK47-36.7-PPL]

Figure 3.23: Irregularly shaped eudialyte with granular rims hosted within a section of feldspar-rich pegmatite. Both images are in PPL.

Microcline and Albite

Feldspar occurs as both albite and microcline which appear to have co-crystallised. The microcline can be distinguished by its distinctive tartan-twinning while albite displays polysynthetic twins (Fig. 3.24). Both feldspars are anhedral-to-subhedral and can be mm's to cm's in length. Oscillatory zoning or sieve texture are not observed.

Amphibole

Amphibole was observed in only one thin section as a <2 mm long, subhedral light blue crystal (Fig. 3.24). The crystal displays a strong prismatic cleavage and appears unaltered. It is enclosed by altered nepheline.

Nepheline

Nepheline is present either as altered crystals with an aegirine rich phase (Fig. 3.25) or 'dusty' inclusions (Fig. 3.26). The clear crystals are anhedral-to subhedral and less than 3 mm in dimension. The aegirine-rich nepheline is characterised by very-high-aspect-ratio, green needle-like inclusions which are μm 's wide and up to 100's μm 's in length. The needles tend to be aligned in the same orientation (predominantly along the apparent-c-axis of the mineral) but deviations from this are also frequently observed. These crystals may be to be anhedral-to-euhedral and up to 1.5cm in width. They are speckled or mottled interference colours in XPL. Aegirine-rich nepheline commonly forms the cores of larger nepheline crystals and appears to be more altered than the albite or microcline elsewhere in the samples. Texturally the aegirine-rich nepheline encloses the earlier phases of aegirine, catapleiite and eudialyte and is enclosed by albite and microcline.

Metallic Opaques

Metallic opaques are present in some pegmatite samples and are primary crystallisation products rather than alteration (Fig. 3.27). In thin section the metallic opaques are up to 3mm long and are present as needle shaped subhedral crystals. In hand specimen the metallic phases are light grey. They occur within the interstices of the earlier formed minerals.

[NK32-146.9-XPL]

[NK32-146.9-XPL]

Figure 3.24: Anhedral-to-subhedral feldspar phases. A (left) - Microcline exhibiting tartan twinning. Image in XPL (100 μm thick section); B (right) – Microcline enclosing eudialyte (30 μm thick section). Image in XPL.

[NK32-131.5-PPL]

[NK25-49.4-XPL]

Figure 3.25: Anhedral-to-euhedral aegirine-rich nepheline phases. (left) - Aegirine-rich nepheline displaying well developed aegirine-needles. This phase is enclosing catapleiite. Image in PPL; (right) - Aegirine-rich nepheline displaying irregular interference colours (100 μm thick section). Image in XPL.

[NK32-131.5-XPL]

[NK32-74.1-PPL]

Figure 3.26: Anhedral-to subhedral nepheline displaying dusty alteration. Image in XPL (100 μm thick section).

Figure 3.27: Metallic phase enclosed by feldspar and nepheline. Image in PPL.

3.3.4 Crenulated Grennaite

The Crenulated Grennaite (Fig. 3.28) (formerly 'migmatite domain') consists of a medium-grained variety of Grennaite which displays cm-scale crenulation folds. The Crenulated Grennaite is broadly homogenous in both texture and mineralogy and is dominated by aegirine, feldspars and nephelines with eudialyte, catapleiite and occasional pectolite also present.

The larger-scale deformation fabric gradually changes from the weak linear foliation in the surrounding Grennaite to the crenulated fabric shown in the Crenulated Grennaite and Kaxtorpite that comprise the core of the intrusion. There are occasional deformed 'xenoliths' of the Kaxtorpite present as thin slithers within parts of the Crenulated Grennaite.

Figure 3.28: Core sample of Crenulated Grennaite [NK32-69.3].

Aegirine

Aegirine is present as <1mm long needle-like crystals. These crystals are euhedral-to-subhedral and display a strong light-dark green colour with well-developed cleavages and cracks; they appear unaltered. Aegirine is hosted within all other minerals present and, due to its high aspect ratio, it marks out the crenulated fold structures within the rock (Fig. 3.29).

Pectolite

Pectolite is present as 1 mm scale euhedral phenocrysts (Fig. 3.30). In PPL the crystals display a high relief with well-developed cleavages and cracks. The pectolites display smaller included aegirine crystals but also appear to have aegirine crystals grown around them rather than intergrown with them.

Catapleiite

Catapleiite is present as subhedral crystals <1 mm long and <0.5 mm in width (Fig. 3.31). In PPL the crystals display high relief and are a straw yellow-colour, while in XPL they display 2nd order interference colours in a 30 µm thick section. The crystals show well developed cracks. The catapleiite displays aegirine inclusions and does not appear to have been altered.

Eudialyte

Eudialyte occurs as anhedral crystals <1 mm long (Fig. 3.31). In PPL the crystals display a high relief with a yellowish-pinkish tint. In XPL the crystals display 1st order mottled greys and often exhibit cracks but do not appear altered. The eudialytes contain aegirine inclusions and frequently appear to intergrow with aegirine clusters.

[NK32-69.3-PPL]

[NK32-69.3-XPL]

Figure 3.29: Crenulated fold structure as delimited by aegirine needles (100 μm thick section). Aegirine is hosted within all other minerals. (left) - Image in PPL; (right) – Image in XPL.

[NK32-69.3-PPL]

[NK32-69.3-XPL]

Figure 3.30: A euhedral pectolite crystal (100 μm thick section). (left) - Image in PPL; (right) – Image in XPL

[NK82.7.55-PPL]

[NK82.7.55-XPL]

Figure 3.31: Zr-silicate phases. Subhedral catapleiite and anhedral eudialyte (30 μm thick section). (left) - catapleiite and eudialyte displaying high relief. Image in PPL; (right) – catapleiite displaying 2nd order interference colours and eudialyte displaying 1st order interference colours. Image in XPL.

Microcline

Microcline occurs as up to 1 cm long and <5 mm wide subhedral phenocrysts. Microcline can be distinguished by its distinctive tartan-twinning in XPL. Oscillatory zoning or sieve texture are not observed. The microcline phenocrysts display well-developed cracks and enclose finer aegirine crystals (Fig. 3.32). The microcline does not appear altered.

Albite

Albite occurs as <1mm anhedral-to-subhedral elongated crystals. Albite displays some polysynthetic twins and frequently encloses finer aegirine crystals (Fig. 3.33) and does not appear to be altered.

[NK82-7.55-PPL]

[NK82-7.55-XPL]

Figure 3.32: Subhedral phenocrysts of microcline. (left) - Microcline enclosing aegirine. Image in PPL; (right) – Microcline exhibiting tartan twinning. Image in XPL.

[NK32-69.3-PPL]

[NK32-69.3-XPL]

Figure 3.33: Anhedral-to-subhedral crystals of albite enclosing all other phases (100 µm thick section). (left) - Image in PPL; (right) – Image in XPL.

Nepheline

Nepheline occurs as either partially (Fig. 3.34-A) or entirely altered (Fig. 3.34-B) subhedral-to-anhedral crystals up to 3 mm long. Nephelines appear to enclose most of the other minerals present.

[NK32-69.3-PPL]

[NK32-69.3-XPL]

[NK32-69.3-PPL]

[NK32-69.3-XPL]

Figure 3.34: Types of nepheline alteration (100 μ m thick sections). A (top) - Nepheline displaying dusty alteration. (left) Image in PPL; (right) Image in XPL. B (bottom) - Nepheline displaying complete alteration. (left) Image in PPL; (right) Image in XPL

3.3.5 Petrological Overview of the Grennaite Domains

The overall petrogenetic evolution of the Grennaite varieties is shown in Table 3.1. The mineralogy of the Grennaites remains constant (aegirine, catapleiite, eudialyte, feldspars-nephelines) throughout the different varieties described here and follows an evolutionary pattern of aegirine to Zr-silicate and then finally feldspar crystallisation.

Aside from the presence of pectolite in the Crenulated Grennaite the main differences lie within the gradually increasing grain size and textural development of the minerals as well as the development of stronger shear fabrics with increasing proximity to the central Kaxtorpite portion on the intrusion. While further mineralogical trends are described in Chapter 4 and whole-rock trends in Chapter 5, the petrological differences will be expanded upon here.

Contact (2 samples)	Aegirine (10.5%)	Catapleiite (8.4%)	Eudialyte (5.6%)	Feldspar-Nepheline (75.7%)
Pegmatite-Host (2 samples)	Aegirine (28%)	Catapleiite (5%)	Eudialyte (5%)	Feldspar-Nepheline (63%)
Pegmatite (8 samples)	Zr-Aeg/Aeg (14.07%)	Catapleiite (5.44%)	Eudialyte (12.41%)	Amphibole (0.8%) Feldspar / Nepheline (45.84%) / (22.1%)
Crenulated (4 samples)	Aegirine (28%)	Pectolite (3%)	Catapleiite (15%)	Eudialyte (7%) Feldspar-Nepheline (50%)

Table 3.1: Petrogenetic sequence of the Grennaite related rocks.

Variations within the Grennaites

As shown by the field relationships to the other lithologies the Contact Grennaite is likely the first crystallised Grennaite variety; this is further supported by the finest grain size shown of any Grennaite variety. As the volumetrically largest of the Grennaites the crystallisation of minerals here may have the strongest effect on the final chemical trends observed.

Together the Pegmatite-Host Grennaite and the pegmatite bodies comprise one of the two ore domains at Norra Kärr. The Pegmatite-Host Grennaite is texturally similar to the Contact Grennaite with several key differences. It displays coarser grained and more subhedral forms of eudialyte and catapleiite than the Contact Grennaite - which typically displays anhedral interstitial Zr-silicates. It therefore appears that the Pegmatite-Host Grennaite is a more evolved form of the Contact Grennaite and had longer to mature as a lithology. The pegmatites themselves are present as 'pods' of medium-coarse grained pegmatitic material up to 10 m in dimension which are generally vertically to sub-vertically orientated. The grain size of eudialyte is observed to increase with proximity to the pegmatite bodies which indicates that the pegmatites may be inducing a second phase of mineral development on the Pegmatite-Host Grennaite. The relationship between the Pegmatite-Host Grennaite and the Pegmatites will be modelled in Chapter 5.

The Crenulated Grennaite comprises the light-[Ln] enriched ore domain and is texturally different to the other Grennaite varieties as it is coarser and displays folds on the order of up to 5-cm (similar to

the folds seen in the Kaxtorpite). This unit has previously been described as ‘migmatitic’. However, no evidence of melting is seen within the domain and there are no pegmatite bodies associated with it and as such has been renamed in this thesis.

The Grennaite is comparable to other alkaline intrusions in terms of texture and mineralogy, however, there are some differences and retains its own unique petrological character.

d. The Grennaite – and particularly the Crenulated Grennaite – do bear some similarities to the Green Lujavrite of Ílímaussaq (Fig. 3.35) particularly in hand specimen. However, the feldspar content at Norra Kärr appears higher than the Ílímaussaq Lujavrite and so the feldspar-matrix of the fine-grained Grennaite is comparable to part of the Red Wine Complex (Fig. 3.36). However, the Red Wine sample exhibits both amphibole and a different aegirine texture. The Grennaite therefore appear to lie somewhere in between the two lithologies, though like most other alkaline rocks – they are themselves unique.

Figure 3.35: Green Lujavrite from Ílímaussaq displaying similar aegirine textures to Norra Kärr – Image in PPL. [Edinburgh University Collection]

Figure 3.36: Sample from the Red Wine Complex – Image in PPL. [Edinburgh University Collection]

Aegirine Textures

Aegirine exhibits a needle-like texture throughout the Grennaite, progressively becoming coarser towards the central Kaxtorpite (e.g. Figs. 3.6, 3.14, 3.29). However, within the pegmatite bodies several different textures are observed. Not only are the aegirines coarser, two varieties occur with Zr-rich (Fig. 3.17) and Zr-poor (Fig. 3.18) types. The Zr-poor aegirine, though coarser than other aegirine present in Norra Kärr, displays many petrological similarities to the other aegirines within the intrusion and are also comparable to aegirines from the Lujavrite and pegmatites of Ílímaussaq (Fig. 3.37) in terms of texture.

The Zr-rich aegirines are also far coarser than other aegirines in Norra Kärr and commonly display cores of exsolved catapleiite with up to 3.20 wt. % ZrO_2 (Atanasova et al. 2017). Zr-rich aegirine has previously been reported from Ailsa Craig (Harding 1983) with aegirine displaying 1.22 wt. % to 3.15 wt. % ZrO_2 , Cnoc Rhaonastil (Isle of Islay) (Preston et al. 1998) with aegirine displaying 5.30 wt. % ZrO_2 , and from Motzfeldt (Jones et Peckett 1980) with aegirine showing up to 7.0 wt. % ZrO_2 . Curiously, no catapleiite inclusions have been recorded from any of these other localities despite the

higher ZrO₂ contents. Only the Ailsa Craig aegirine exhibit inclusions with these being fluorite. Furthermore, all of the above aegirines (apart from those from Motzfeldt) formed last in the petrogenetic sequence. The question remains as to why catapleiite exsolution appears to have occurred at Norra Kärr and why the cores are so Zr-rich when they were the first formed phase? The latter question could be answered by assuming that the magma was still rich in Zr resulting in Zr-rich aegirine forming as the first phase. This was then followed by a period of co-crystallisation of catapleiite and aegirine. The catapleiite crystallisation would reduce the Zr content of the magma allowing Zr-poor aegirine to then crystallise as both new crystals and as rims on pre-existing Zr-rich crystals, thereby resulting in the observed zonation patterns.

Pectolite

The presence of pectolite within the Crenulated Grennaite (post-aegirine but pre-catapleiite) indicates that during aegirine crystallisation the H₂O activity appears to have been raised to the point at which pectolite was stable. However, the hydrous phase then appears to have switched to the Zr-silicates. Pectolite may therefore represent an intermediate crystallisation step before Zr-silicates become stable and suggest particularly high water contents within the magma at that point in the petrogenetic sequence. Pectolite is common within the Kaxtorpite (see section 3.4) and may suggest some chemical similarity between the formation two lithologies.

Catapleiite and Eudialyte – The role of Volatiles

Water is known to be important in forming Lujavrite-like melts (between 4.3% to 4.5%; Kogarko et al. 1977) and in the case of the Grennaite appears to have led to the formation of the hydrous Zr-silicates of catapleiite and eudialyte. Catapleiite and eudialyte are the main volatile phases within the Grennaite and also display a general coarsening towards the central Kaxtorpite (e.g. Figs. 3.8, 3.14, 3.31). The presence of catapleiite confirms that there was a phase of high H₂O-activity (Andersen et al. 2010) which allowed primary catapleiite to form throughout the fine-grained Grennaite. Sodalite is notably absent from Norra Kärr despite being common within the Lujavrite and Naujaite of Ilímaussaq where Cl is a major rock forming element. Bailey et al. (2001) measured the whole-rock Cl contents as 2–3.5 wt. % Cl (with up to 4.6 wt. % also reported). As such, it is unlikely that the Grennaite ever achieved such a high Cl-concentration and this potentially gives an upper limit to the Cl content.

However, the crystallisation of catapleiite followed by eudialyte (e.g. Fig. 3.19) is a seemingly rare texture. Catapleiite and eudialyte tend to be related via alteration (as is also seen in minor alteration of the Norra Kärr eudialyte) but the combination of phenocrysts of catapleiite and eudialyte appears to have only been reported from Langesund in the Oslo Rift (Fig. 3.38) (Bollingberg et al. 1983; Andersen et al. 2013). Andersen et al. (2010) have calculated a petrogenetic grid in terms of $\log a_{\text{H}_2\text{O}} - \log a_{\text{HF}} - \log a_{\text{Na}_2\text{Si}_2\text{O}_5}$ (where $a_{\text{Na}_2\text{Si}_2\text{O}_5}$ is the activity of Na₂Si₂O₅) and shown that the transition from catapleiite crystallisation to eudialyte crystallisation is due to a reduction in the activity of H₂O. Given the similarity of the textures it is likely that a similar lowering of H₂O activity occurred within the pegmatites likely driven by the crystallisation of OH-rich catapleiite itself. However, this requires further testing as will be carried out in Chapter 7.

Of particular note given the high H₂O activities is the low degree of alteration of the eudialyte within the pegmatites (and the lack of alteration of eudialyte within the fine-grained and Crenulated Grennaite in general) which suggest that the eudialytes were too stable in their surroundings to result in significant alteration beyond that observed in fractures within the crystal. Borst et al. (2016) examined the alteration of eudialyte to catapleiite within the Kakortokites of Ilímaussaq. Unlike at Norra Kärr, there is an increase in the degree of alteration of the eudialyte to catapleiite (Fig. 3.39) with progression through the Kakortokites (black—to-red-to-white) with the catapleiite growing into the eudialyte crystals. However, eudialyte from a Kola intrusion exhibits little alteration suggesting the evolution of Norra Kärr may be more related to that unit from the Kola intrusion than the Kakortokites of Ilímaussaq.

Separate to the generally fine grain-size of catapleiite and eudialyte within the Grennaites, there are portions of the Grennaite which display separate poikilitic eudialytes and catapleiite. One explanation may be that of liquid immiscibility. Textures displaying liquid immiscibility within alkaline plutons are common. ‘Snowballs’ of eudialyte reported at the Toongi deposit in Australia by Spandler et al. (2016), immiscibility textures from extremely agpaitic dykes in the Lujavrite of Ilímaussaq were reported by Markl (2001), while Sorensen et al. (2003) described immiscibility textures up to 15 cm in dimension from the arfvedsonite Lujavrite of Ilímaussaq. In the case of Norra Kärr the poikilitic eudialytes are larger than at Toongi and can be either an agglomeration of eudialyte or contain inclusions of earlier aegirine, and unlike at Ilímaussaq the eudialytes have a more diffuse boundary which is unlikely to indicate a sharp immiscibility boundary.

However, these poikilitic eudialytes observed within the contact Grennaite, and particularly those at the contact of the Lakarpite do appear to represent a separate process from the rest of the solidifying melt and the presence of feldspar rims (subsequently deformed into σ -patterns) is also an unexplained feature when compared to the majority of the fine-grained eudialyte. Furthermore, the coarser eudialytes surrounding Lakarpite do appear to display a composition difference to the rest of the Contact Grennaite eudialytes (see 4.10 - Chapter 4). The explanation may lie in their proximity to the later Lakarpite (and possibly Pulaskite) intrusions whereby the action of heat or intermixing of supercritical-fluids resulted in the formation of these textures. The addition of NaOH or HF to nepheline syenite from Il'menogorsk, Russia, resulted in sub-liquidus immiscible separation into two silicate glasses and the addition of as little as 1 wt. % Cl to melts of Lujavrite from Lovozero also resulted in the formation of two liquids (Yudintsev et al. 1983; Shchekina et al. 1984) and similar processes could have occurred during the later intrusion of the Lakarpite and Pulaskite. For the time being, these textures therefore remain unresolved.

Sulphides

Sulphides are only found within the pegmatites and even then are uncommon. They have previously been described by Kramm et al. (1988) who reported the presence of Pb-Cu-Ag-Bi-sulphides. Sulphides are common within alkaline rocks e.g. Khibiny (Grigorieva et al. 2009) and Gardar (Marks et al. 2003), and sulphide immiscibility has been proposed as model for their presence (Korobeinikov et al. 1998). As the sulphides observed in the pegmatites are enclosed by feldspars and crystallised after all other mineral phases, it is potentially likely that in the last stages of pegmatite crystallisation the melt was dominated by a feldspathic composition which also contained infrequent immiscible sulphide blebs.

Figure 3.37: Ilímaussaq pegmatite sample displaying pegmatitic aegirine (green) within feldspar (white). This texture is commonly observed at the contact of the pegmatites. One-pound coin for scale. NMS Collection.

Figure 3.38: Sample from Langesund exhibiting feldspar (white), amphibole (dark), catapleiite (yellow) and eudialyte (red). Sample size approximately 10cm tall. NMS Collection (photo courtesy of Mr Simon Howard).

Figure 3.39: Eudialyte alteration textures from the Karkortokites of Ilímaussaq and a Kola intrusion. Clockwise from top left: Black Karkortokite displaying unaltered sector zoned eudialyte; Red Karkortokite displaying some initial alteration to catapleiite; White Karkortokite displaying complete alteration to catapleiite; eudialyte from Kola displaying minor alteration. [Edinburgh University Collection]

Feldspar and Nepheline Textures

Sub-cm microcline phenocrysts are observable within the Crenulated Grennaite and bear some resemblance to phenocrysts observed in the Kaxtorpите, again suggesting there are similarities between the two lithologies. There is also a further nepheline phase which is also altered in a similar manner to the Kaxtorpите. From the relationship of the two coexisting feldspars (albite and microcline) the assemblage within the Grennaites appears to be subsolvus indicating that the feldspars crystallised at a temperature <750°C.

The aegirine-rich nepheline appears to be a poorly understood texture. It has previously been described by Retief (1962) who reported similar textures from Pilanesberg, and the texture can also be seen in samples from Kola. Retief (1962) described an association of very fine aegirine microlites within triclinic feldspar orientated along (010); these microlites were not present in the monoclinic feldspars. He suggested that there were two possible origins for the microlites, either exsolution from orthoclase during inversion to microcline or the inclusion of small aegirine-augite crystals and concluded on the basis of crystallographic and experimental evidence that the former hypothesis to be the correct one. This may also be the case at Norra Kärr. However, the texture of the host nepheline is less ordered than the feldspars observed at Pilanesberg.

Deformation Fabrics

An increase in the degree of strain fabrics is evident in a traverse through the Grennaites. In the majority of the Grennaites this is present at a planar near-vertical shear fabric which leads to a degree of mineral alignment. Within the Contact Grennaite feldspar rims around poikilitic eudialyte has been deformed into σ -type structure potentially indicating syn-tectonic shear movements occurred in the latter stages of solidification of Norra Kärr. Deformation fabrics are not seen directly within the pegmatites, but their effects can be observed in the disaggregation of smaller pegmatite bodies.

The crenulation fabrics within the Crenulated Grennaites (and the Kaxtorpите) appear isolated within the core of the intrusion. If a larger tectonic movement was responsible for the crenulations it may be expected that this would be a pervasive fabric throughout the rest of the Grennaites – however this is not present. A larger regional fold structure may be responsible, however evidence for such a structure is not conclusive.

A further explanation may be that the crenulated texture observed may have been caused by folding of the primary magmatic fabric within a syn-tectonic shear-dominated environment and is likely related to the process which formed the shear patterns in the Kaxtorpите. Similar textures can be seen in the Lovozero (Féménias et al. 2005) and Ilímaussaq (Ratschbacher et al. 2015) intrusions as a result of solid-state internal deformation within the large magma chambers. This remains a topic of open enquiry but will be explored further in Chapter 8.

3.4 Kaxtorpite

The Kaxtorpite (Fig. 3.40) is a medium-grained amphibole bearing lithology located in the upper-central portion of Norra Kärr. The Kaxtorpite is broadly homogeneous in both texture and mineralogy. It displays cm-scale crenulation folds similar to the Crenulated Grennaite and with the fold-limbs consisting of intergrown aegirine and amphibole and the inter-fold area dominated by pectolite and feldspars. Coarse-grained microcline phenocrysts are common containing minor aegirine inclusions.

The Kaxtorpite appears to be structurally related to the Grennaite as, structurally, it is located above them and shares a diffuse m-scale contact with the Crenulated Grennaite. This results in there being no obvious contact, rather a zone of diffuse intermingling of material from the Crenulated Grennaite and the Kaxtorpite which can be seen in drill core and in thin section.

Figure 3.40: Core sample of Kaxtorpite [NK57-27.3].

Aegirine

Aegirine is present as typically mm-long subhedral needles. It has a strong light-dark green to straw yellow colour in PPL with the crystals displaying well-developed cracks; they appear unaltered. Aegirine is hosted within all other minerals present and is typically intergrown with blueish amphiboles (Fig. 3.41).

Amphibole

Light blue crystals of amphibole are present either as phenocrysts that are approximately <500 μm in dimension or as mm-long needle-like crystals intergrown with aegirine (Figs. 3.41, 3.42). The amphiboles are a dark-brown colour in XPL. The amphiboles appear to cross cut all other phases apart from aegirine and do not appear to have been altered. The amphiboles will tend to form bands when present as needle-like crystals.

Pectolite

Anhedral-to-euhedral pectolite can be identified by their high relief and well-developed cleavage patterns in observable in PPL (Fig. 3.33). The pectolite typically range in size from 0.5 mm to <2 mm and display 2nd order interference colours in XPL and do not appear to be altered. In some cases the pectolites appear to display mineral inclusions. They are cross-cut by aegirine and amphiboles but appear earlier in the crystallisation sequence than the feldspathic and foid phases.

Microcline

Microcline occurs as up to 2 cm long and 1 cm wide subhedral phenocrysts (Fig. 3.44). Microcline can be distinguished by its distinctive tartan-twinning in XPL. Oscillatory zoning or sieve texture are not observed. The microcline phenocrysts display well-developed cracks and enclose finer aegirine crystals. The microcline does not appear altered.

Albite

Albite occurs as <5 mm long and <1 mm wide crystals that display polysynthetic twinning in XPL (Fig. 3.45). Albite is typically subhedral and does not appear to have been altered.

Nepheline (Altered)

Brown alteration can be found within the aegirine-amphibole mineral bands (Fig. 3.46). This may be altered nepheline. This alteration is anhedral and includes all other minerals present.

[NK25-138-PPL]

[NK25-138-PPL]

Figure 3.41: Subhedral needles of aegirine forming bands within the Kaxtorpite (100 µm thick sections). (left) - bands of intermixed aegirine and amphibole surrounded by feldspar and nepheline – Image in PPL; (right) – Aegirine bands composed of fine crystals - Image in PPL.

[NK25-138-PPL]

[NK25-138-XPL]

Figure 3.42: Amphibole phenocrysts (100 µm thick section). (left) - amphibole displays a light blue colour - Image in PPL; (right) – Amphibole displays blue and brown interference colours - Image in PPL.

[NK57-27.3-PPL]

[NK57-27.3-PPL]

Figure 3.43: Anhedronal pectolite within Kaxtorpite (30 µm thick section). (left) - pectolite displaying well developed cleavage – Image in PPL; (right) – Pectolite displaying 2nd order interference colours - Image in XPL.

[NK25-138-PPL]

[NK25-138-XPL]

Figure 3.44: Phenocryst of Microcline adjacent to albite (100 μm thick section). (Left) - Image in PPL; (right) – Image in XPL.

[NK25-138-PPL]

[NK25-138-XPL]

Figure 3.45: Albite displaying twinning (100 μm thick section). (left) - Image in PPL; (right) — Image in XPL.

[NK25-138-PPL]

[NK53-174.3-XPL]

Figure 3.46: Altered nepheline containing earlier phases (30 μm thick section). (Left) altered nepheline enclosing pyroxene and amphibole - Image in PPL; (right) – altered nepheline containing pyroxene and microcline - Image in XPL.

3.4.1 Petrological Overview of the Kaxtorpite

The petrogenetic sequence of the Kaxtorpite is shown in Table 3.2. This is similar to the other petrogenetic sequences shown by the lithologies of Norra Kärr aside from the presence of pectolite. Amphibole is also present, a mineral absent in the Grennaite with which the Kaxtorpite appears to have mingled with to some extent.

Kaxtorpite (3 Samples)	Aegirine (12.72%)	Amphibole (22.81%)	Pectolite (5.71%)	Microcline-Albite (41.32%)	Nepheline (+Alteration) (23.82%)
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Table 3.2: Petrogenetic sequence of the Kaxtorpite.

The Kaxtorpite displays abundant amphibole (unlike the Crenulated Grennaite with which it is in contact) but shares the same strongly crenulated fabric of cm-scale fold structures. As explored above in section 3.3.5, this crenulation fabric may be due to folding of the primary magmatic fabric within a syn-tectonic shear-dominated environment.

The aegirine within the Kaxtorpite is texturally similar to the other lithologies in the intrusion and intergrows (Fig. 3.43) with the amphibole in a similar manner to the Pulaskite and Lakarpite (see sections 3.4, 3.5). However, the amphibole is texturally different from those lithologies in that it forms elongated needles instead of plates. A further feature of the Kaxtorpite is the presence of large pectolite phenocrysts which enclose the aegirine and amphibole (Fig. 3.43, 3.45). The crystallisation of this pectolite indicates a water rich environment post-amphibole crystallisation. Unlike in the Grennaite there is no hydrous Zr-silicate phase present indicating that pectolite was the only hydrous phase stable at that point in time. Pectolite is also present in the Crenulated Grennaite suggesting a phase of similar conditions within both adjoining lithologies. The presence of the large feldspars show that microcline had time and space to grow and coarsen, possibly co-crystallising with aegirine and early amphiboles. The rest of the Kaxtorpite is rich in albite suggesting this came as a later phase. From the relationship of the two coexisting feldspars (albite and microcline) the assemblage appears subsolvus indicating that the feldspars crystallised at a low temperature (<750°C) similar to the Grennaite.

The Kaxtorpite appears similar in terms of mineralogy and texture to lithologies from the Red Wine Complex of Canada (Fig. 3.47).

Figure 3.47: Thin section from the Red Wine Complex (Canada) displaying a similar texture to the Kaxtorpite. A (left) – image in PPL; B (right) – image in XPL. [Edinburgh University Collection]

3.5 Pulaskite

The Pulaskite is a predominantly feldspathic lithology which forms a dyke-like body on the western side of Norra Kärr. The Pulaskite also contains dark enclaves of material which are rich in amphibole and biotite. The petrological description of the body will therefore be split into two sections; the feldspathic Pulaskite proper (Fig. 3.48) and the enclaves (Fig. 3.49).

The Pulaskite does not appear to be structurally related to the Grennaite or Kaxtorpite, rather it shares similarities in mineralogy and morphology to the Lakarpite. The contact with the Grennaite is sharp and the Pulaskite has resulted in a baked contact with the Grennaite leading to the Grennaite turning a darker colour (Fig. 2.41 – Chapter 2).

Figure 3.48: Core sample of Pulaskite (matrix) [NK53-40.5]. The majority of the minerals are fine-medium grained apart from the coarser grained feldspars. Note in this sample the uncommon coarse-grained amphiboles. There is no distinct fabric within the Pulaskite though evidence of shear along the long axis of Norra Kärr is present.

Figure 3.49: Core sample of Pulaskite containing cm-scale enclaves [NK53-30.8]. Enclaves can be up to dm-scale in size but all appear to show some degree of shear deformation. In this sample three large enclaves of closely packed arginine-amphibole-biotite rich enclaves rimmed by silvery-rozenbushite are visible. The surrounding Pulaskite displays a higher feldspar content and less packed crystals.

3.5.1 Enclaves

The enclaves within the Pulaskite are typically cm- to dm- in dimension and appear in elongated clusters. This may be due either to the deformation or, more likely, due to the original magmatic emplacement with elongation being due to the flow of the magma which has observably deformed the enclaves on an outcrop scale. The centre of the enclaves consists of aegirine, biotite, amphibole and albite along with small crystals of fluorite. There is a large mineralogical and textural contrast between the enclaves and the predominantly feldspar rich Pulaskite which host them.

Aegirine

Aegirine is present as fine euhedral light green needles <1 cm in length (Fig. 3.50). It is included within the amphiboles, biotite and albite and appears to have formed first. The aegirine does not appear altered.

Rosenbushite

Rosenbushite occurs as <1mm long euhedral needles (Fig. 3.51). It is semi-transparent in PPL and tends to form masses of intergrown crystals. It primarily occurs within and along the border of the enclaves. It appears to be enclosed by amphibole.

Biotite

Biotite is present as subhedral phenocrysts <1 mm in dimension (Fig. 3.52). The biotite is a strong brown colour in PPL and displays a well-formed cleavage. In some instances it appears that the biotite displays optical zoning with darker brown cores and dark-green rims. Biotite is typically found within masses of amphibole.

Amphibole

Amphibole is present as subhedral phenocrysts <1 mm in dimension (Fig. 3.53). It is dark blue in PPL and displays well-developed cleavages. In XPL it appears an anomalous blue-green colour and may display optical zoning with darker cores and lighter rims.

[NK53-30.8-PPL]

[NK53-30.8-PPL]

Figure 3.50: Euhedral aegirine needles (100 μm thick sections). (Left) aegirine enclosed by feldspar – Image in PPL; (right) aegirine enclosed by amphibole – Image in PPL.

[NK53-30.8-PPL]

[NK53-30.8-PPL]

Figure 3.51: Euhedral Rosenbushite (30 μm thick section). Image in PPL.

Figure 3.52: Subhedral biotite surrounded by amphibole (30 μm thick sections). Image in PPL.

[NK53-30.8-PPL]

[NK53-30.8-PPL]

Figure 3.53: Subhedral blue-green amphibole (100 μm thick sections). (Left) mm-scale amphibole enclosed by feldspar – Image in PPL; (right) amphibole enclosing aegirine – Image in PPL.

Fluorite

Fluorite is present as anhedral light-purple crystals <500 μm in dimension (Fig. 3.54). It displays cracks and appears unaltered. Texturally the fluorite appears to have formed early enough to be included within albite but is also present in the remaining interstices between the feldspars and also appears to be the latest forming mineral in the paragenetic sequence. This suggests a period of co-crystallisation with albite.

Albite

Albite is present as phenocrysts <1 mm in dimension which display polysynthetic twinning and zoning in XPL (Fig. 3.55). Albite is typically subhedral and does not appear to have been altered. It can display inclusions of fluorite.

[NK53-30.8-PPL]

[NK62-73.9-PPL]

Figure 3.54: Anhedral fluorite (100 μm thick sections). (left) abundant fluorite is present between the individual albite crystals – Image in PPL; (right) fluorite surrounded by earlier aegirine, biotite and amphibole – Image in XPL.

[NK53-30.8-XPL]

[NK53-30.8-XPL]

Figure 3.55: Subhedral albite (100 μm thick sections). (Left) albite displaying polysynthetic twinning and zoning – Image in XPL; (right) fine grained albite crystals which form the matrix of the enclave – Image in XPL.

3.5.2 Pulaskite

The Pulaskite is a white, predominantly feldspathic rock which contains the enclaves described above.

Aegirine

Aegirine is present as subhedral-to-euhedral light green needles. The larger aegirine phenocrysts are <1 cm in length and display well developed cleavages. The smaller aegirine crystals are <500 µm in length and are narrower and more needle-like (Fig. 3.56). Texturally the aegirine appears to have formed first as it is included within the amphiboles, biotites and feldspars. The aegirine does not appear altered.

Amphibole

Amphibole is present as anhedral-to-subhedral dark-blue crystals. The larger amphibole phenocrysts are <2 cm in dimension while the finer crystals are <500 µm in dimension – both varieties enclose aegirine (Fig. 3.57).

Biotite

Biotite is present as anhedral-to-subhedral phenocrysts <2 mm in dimension (Fig. 3.58). The biotite is a strong brown colour in PPL and displays a well formed cleavage. Due to the texture displayed by some biotites it is possible that they have become detached from enclaves and become entrained in the melt – these do not appear altered.

Sphene

Sphene is present as <3 mm long euhedral phenocrysts (Fig. 3.59). It is dark brown in PPL and displays well developed cracks. It encloses aegirine and amphiboles and is enclosed by feldspars and fluorite.

Microcline

Microcline occurs as up to 4 cm long and 2 cm wide subhedral phenocrysts (Fig. 3.60). Microcline can be distinguished by its distinctive tartan-twinning in XPL. Oscillatory zoning or sieve texture are not observed. The microcline phenocrysts display well-developed cracks and enclose finer aegirine crystals. The microcline displays some alteration.

Albite

Albite occurs as <3 mm long and <2 mm wide phenocrysts that display polysynthetic twinning in XPL (Fig. 3.61). Sieve texture is not observed. The albite phenocrysts display well-developed cracks and enclose finer aegirine crystals. Albite is typically subhedral and does not appear to have been altered. Finer grained albite comprises the groundmass of the Pulaskite

Fluorite

Fluorite is present as anhedral light-purple crystals <5 mm in dimension (Fig. 3.62). The fluorites display cracks and well-developed cleavages and appear unaltered. Texturally the fluorite appears to have formed late in the paragenetic sequence as it occurs at grain boundaries and interstices between minerals and is observed enclosing feldspar.

[NK53-297.9-PPL]

[NK53-40.05-PPL]

Figure 3.56: subhedral-to-euhedral aegirine (100 μm thick sections). (left) needles of aegirine enclosed in feldspar— Image in PPL; (right) aegirine phenocrysts enclosed by amphibole – Image in PPL.

[NK53-297.9-PPL]

[NK53-40.05-PPL]

Figure 3.57: Anhedral-to-subhedral dark blue amphibole (100 μm thick sections). (left) a mass of fine-grained amphibole enclosing aegirine –Image in PPL; (right) amphibole phenocryst enclosing aegirine – Image in PPL.

[NK62-73.9-PPL]

[NK95-41.9-PPL]

Figure 3.58: Anhedral-to-subhedral crystals of biotite enclosed by feldspar matrix (100 μm thick section). Image in PPL.

Figure 3.59: Euhedral sphene (100 μm thick section). Image in PPL.

[NK53-297.9-XPL]

[NK53-297.9-XPL]

Figure 3.60: Subhedral phenocrysts of microcline displaying tartan twinning and some alteration (100 μm thick sections). (left) – Image in XPL; (right) – Image in XPL.

[NK53-40.05-XPL]

[NK53-297.9-XPL]

Figure 3.61: Subhedral albite displaying polysynthetic twinning (100 μm thick sections). (left) – Image in XPL; (right) fine grained albite matrix – Image in XPL.

[NK95-41.9-PPL]

[NK95-41.9-PPL]

Figure 3.62: Anhedral fluorite interstitial between feldspars (100 μm thick sections). (left) – Image in PPL; B (right) – Image in PPL.

3.5.3 Contact with the Grennaite

The contact between the Pulaskite and the fine-grained Grennaite (see Fig. 2.41 - Chapter 2) displays several textures not seen elsewhere in either lithology. The Pulaskite displays similar amphibole, biotite and feldspar textures to those described above. However, there is an additional pyroxene texture which exhibits a high relief and light-brown colour in PPL (Fig. 3.63). The crystals form anhedral masses up to 4 mm in dimension and often form needle shaped edges at their margins. The crystals enclose aegirine and amphibole and are enclosed by feldspar.

The margin of the Pulaskite is less than 2 cm thick and is rich in amphibole and feldspars all less than 500 μm in dimension. Subhedral aegirine, up to 1 mm long, is also present. This zone also contains more abundant amphibole than the intruding Pulaskite or the Grennaite indicating high availability of OH^- (Fig. 3.64).

The margin of the Grennaite exhibits a medium grained texture of aegirine, amphibole and altered nepheline (Fig. 3.65). The aegirine is light-to-dark-green in colour and up to 1 mm long with well-developed cleavages. The amphibole is less than 500 μm in dimension.

[NK-Pulaskite-Grennaite Contact-PPL]

[NK-Pulaskite-Grennaite Contact-PPL]

Figure 3.63: Light brown, high relief pyroxene (30 μm thick section). (Left) as part of a mass of amphibole – Image in PPL; (right) a mineral mass of the pyroxene potentially displaying a quench texture – Image in XPL.

[NK-Pulaskite-Grennaite Contact-PPL]

Figure 3.64: Margin of the Pulaskite in contact with the Grennaite (30 μm thick section). Image in PPL.

[NK-Pulaskite-Grennaite Contact-PPL]

Figure 3.65: Margin of the Grennaite in contact with the Pulaskite (30 μm thick section). Image in PPL.

3.5.3 Petrological Overview of the Pulaskite

The petrogenetic sequence of the Pulaskite and the enclaves is shown in Table 3.3. The Pulaskite displays very different textures to the surrounding Grennaite and appears to have intruded into the Grennaite while the latter was partially solid. This resulted in the chilling textures seen at the Pulaskite margin and in the baking and alteration textures observed at the Grennaite margin (Fig. 2.41 – Chapter 2). The presence of the enclaves further supports the hypothesis of intrusion from below the present surface due to both the observed field relationships and the observed textural differences between the enclaves and their Pulaskite host.

Pulaskite (3 Samples)	Aegirine (19%)	Sphene (1%)	Biotite (13%)	Amphibole (14%)	Fluorite (3%)	Feldspar (47%)
Enclaves (1 Sample)	Aegirine (16.3%)	Ros (2.5%)	Biotite (7.05%)	Amphibole (41.92%)	Fluorite (12%)	Feldspar (20.63%)

Table 3.3: Petrogenetic sequence of the Pulaskite and the enclaves.

The aegirine within the enclaves is more euhedral and needle-like compared to aegirine elsewhere in Norra Kärr. The amphibole is generally finer-grained than the biotite; while the matrix of the enclaves consists of albite displaying occasional oscillatory zoning with no microcline present. Fluorite is also more abundant within the enclaves than in the Pulaskite.

The body of the Pulaskite displays far coarser textures than the enclaves and predominantly consists of albite with microcline phenocrysts. Aegirine commonly intergrows with amphibole and it is possible that some of these masses are derived from crystal transfer from the enclaves into the Pulaskite via disaggregated enclaves. A separate intergrowth texture is seen in particularly feldspathic parts of the Pulaskite which lack enclaves. This texture consists of mm-scale pyroxene and cm-scale amphibole and may be related to the feldspathic nature of the surrounding magma forcing the crystals to coarsen due to the difficulty of nucleating further aegirine and amphibole. This texture has also been observed within the sodalite-bearing portions of Lujavrite at Ilímaussaq (Fig. 3.66).

Figure 3.66: Lujavrite from Ilímaussaq displaying a similar texture to the Pulaskite (see Fig. 3.56). A (left) – image in PPL; B (right) – image in XPL

The difference in texture and the petrogenetic sequences displayed by the enclaves and the body of the Pulaskite suggests that the enclaves formed in a mush from initial crystallisation of the magma. This must have depleted the melt in Fe, Mg and some volatiles and enriched the remaining melt in feldspar-component. This melt also reached an appreciable F-content as indicated by the fluorite content. The oscillatory zoning of albite within the enclaves and lack of such textures in the body of the Pulaskite shows that there was a varying availability of chemical components in the enclaves compared to a steady fractionation trend in the body of the Pulaskite. The lack of glass also shows that the mush and the Pulaskite were at similar temperatures, hence no 'chilling' effects, and the transfer of crystals from the enclaves into the Pulaskite indicates that there was no great rheological difference between the two magmas (Zhang et al. 2015). The feldspathic magma then appears to have intruded into the Grennaite entraining the mush as it ascended leading to disaggregation. This indicates that the Norra Kärr body extends deeper than the current drilling has observed with there likely being a larger magma chamber below at depth where the magma continued to fractionate after the initial emplacement of the Grennaite. However, the lack of a gravity anomaly shown by Norra Kärr and the evidence of shearing may indicate that this magma chamber was sheared away at some point in the history of the intrusion.

The textures displayed by fluorite appear complex in the Pulaskite. There is evidence from the presence of small (<50 µm) fluorite crystals in microcline that fluorite may have begun to co-crystallise with the feldspars. As the 'dry' feldspar phases continued to crystallise the magma would have become further enriched in volatiles which would then become concentrated in melt along the grain boundaries of the feldspars. These melt pockets could then have begun to grow before crystallising fluorite and becoming trapped as the lithology solidified. Furthermore, the relationship of the two coexisting feldspars (albite and microcline) shows that the assemblage can be considered as subsolvus indicating that the feldspars crystallised at a low temperature (<750°C) similar to the Grennaite varieties and the Kaxtorpite showing that this process would be happening as the last stages of crystallisation. The presence of microcline phenocrysts suggests that in the body of the Pulaskite microcline was the first forming feldspar phase and had time to grow and coarsen with albite forming the matrix.

3.6 Lakarpite

The Lakarpite is a predominantly feldspathic lithology which forms a series of deformed pods in a dyke-like morphology on the eastern side of Norra Kärr (Figs. 2.37, 2.38 – Chapter 2). The Lakarpite does not appear to be structurally related to the Grennaite or Kaxtorpите instead sharing a comparable structural shape with the Pulaskite though the mineralogy of the different bodies does vary. The contact with the Pegmatite-Host Grennaite appears highly variable and diffuse, potentially indicating a degree of interaction between the two different magmas.

The Lakarpite is mineralogically complex and can be divided into a core zone and a contact zone depending upon the presence of rosenbushite/fluorite or eudialyte. Each zone displays at least two differing petrological textures which will be described below. The petrological description of each phase within the Lakarpite will be outlined for all the varieties together in order to highlight the differences and similarities in both mineralogy and texture.

‘Core’ Zone

The core zone is comprised of ‘Pulaskite-type’ textures (Fig. 3.67) and ‘Core-type’ textures (Fig. 3.68). The ‘Pulaskite-type’ Lakarpite displays many mineralogical and textural similarities with the Pulaskite (described in Section 3.5) and it is possible that the two are magmatically related. This variety includes a biotite-bearing offshoot of the Lakarpite which is located between the contact of the Grennaite and the country rock (Växjö Granite). The ‘core’-Lakarpite exhibits a similar mineralogy to the Pulaskite-type Lakarpite but with more abundant amphibole and rosenbushite. Some weak shear fabrics can be observed in both lithologies.

Figure 3.67: Core sample of Pulaskite-type Lakarpite [NK28-64.4]. Note high biotite content and large feldspar lathes.

Figure 3.68: Core sample of Core-type Lakarpite [NK57-116.7]. Note masses of silvery rosenbushite.

'Contact' Zone

The contact zone is comprised of the two eudialyte bearing 'Zr-rich core' (Fig. 3.69) and 'Zr-rich' (Fig. 3.70) types. The 'Zr-rich core' Lakarpite has been defined on the bases of its mineralogical and textural similarities with the 'core'-Lakarpite, but also on its eudialyte and higher Zr content (see Chapter 5). The 'Zr-rich' Lakarpite is defined by the presence of large eudialyte crystals and a dark-green variety of amphibole – this is in contrast with the dark-light blue varieties found in the other Lakarpite varieties.

Figure 3.69: Core sample of Zr-rich core type Lakarpite [NK57-126.5]. The sample comes from the contact zone with the Contact Grennaite and contains xenoliths of Grennaite. While the mineralogy tends to be a courser version of the core zone, eudialyte is also present and tends to be light-pink and amorphous in texture.

Figure 3.70: Core sample of Zr-rich type Lakarpite [NK33-226.5]. The mineralogy tends to be courser than the core zone of the Lakarpite with eudialyte present as well-formed crystals. Catapleiite may also be present.

3.6.1 Lakarpite Zones

Aegirine

Aegirine appears to be the first formed phase in all of the Lakarpite varieties and it is texturally enclosed by all other phases (Fig. 3.71). None of the aegirine appear altered.

In the Pulaskite-type Lakarpite the aegirine is subhedral-to-euhedral and is typically less than 500 μm long. The crystals are light-to-dark green in PPL and display some cracks. The aegirine occurs either as individual crystals or in 'masses' along with biotite. These masses can be up to several millimetres in dimension.

In the Core-Lakarpite the aegirine is subhedral-to-euhedral and are less than 1 mm long. The crystals are light-to-dark green in PPL and display some cracks. The aegirine occurs either as individual crystals or in 'masses' along with dark-blue amphibole. These masses can be up to several millimetres in dimension. A further pyroxene is present within this zone as <1 mm subhedral-to-euhedral high-relief crystals similar to those observed in the Crenulated domain and the Kaxtorpite.

In the Zr-rich Core-Lakarpite aegirine is subhedral and <1 mm in dimension. It is light-to-dark green in PPL and displays well developed cracks. The aegirine is commonly found in 'masses' along with dark-blue amphibole.

In the Zr-rich Lakarpite aegirine occurs as elongate subhedral-to-euhedral crystals <1 mm long. The aegirine forms masses several millimetres in length. These masses are rimmed by dark-green amphibole.

Figure 3.71: Subhedral-to-euhedral aegirine: Pulaskite-type (lower-left) ; Core-type (lower-right) ; Zr-rich-core (upper-left) ; Zr-rich-type (upper-right). All images in PPL.

Amphibole

Amphibole is present within all the Lakarpite varieties (Fig. 3.72). The amphiboles present within each variety vary in texture and colour and are commonly observed enclosing the earlier-formed aegirine.

In the Pulaskite-type Lakarpite the amphibole is dark-to-light blue in PPL and is typically <500 μm in dimension. The amphibole is anhedral in shape and is present either as individual crystals or in masses including aegirine. These masses can be up to several millimetres in size and typically lack a defined shape.

In the core-Lakarpite, the amphibole is dark-to-light blue in PPL and is typically <500 μm in dimension. The amphibole anhedral-to-euhedral in shape and often displays characteristic 120° crystal faces. Amphibole is present in either individual crystals or in masses along with aegirine. These masses can be up to several millimetres in dimension and are typically elongate in shape.

In the Zr-rich core Lakarpite the amphibole is dark-blue in PPL and is typically <500 μm in dimension. The amphibole anhedral-to-subhedral in shape and is present as individual crystals or in masses along with aegirine. These masses can be up to several millimetres in dimension.

In the Zr-rich Lakarpite amphibole is dark-green in PPL and is typically <1 mm in dimension. The amphibole is anhedral-to-euhedral in shape and often displays characteristic 120° crystal faces. Amphibole is present either as individual crystals or as a rim around aegirine masses with some interstitial amphibole present in the masses as well.

[NK57-126.5-PPL]

[NK33-226.5-PPL]

[NK28-64.4-PPL]

[NK57-107.3-PPL]

Figure 3.72: Anhedral-to-euhedral amphiboles: Pulaskite-type (lower-left); Core-type (lower-right); Zr-rich-core (upper-left); Zr-rich-type (upper-right). All images in PPL.

Sphene

Sphene is present as mm-long euhedral phenocrysts in the Core -type Lakarpite (Fig. 3.72). It is light yellow in PPL and displays well developed cracks. It encloses aegirine and rosenbushite and is enclosed by feldspars and fluorite.

Biotite

Biotite is only present within the Pulaskite-type Lakarpite found at the contact of Norra Kärr. There biotite occurs as anhedral-to-subhedral crystals <1 mm in dimension (Fig 3.73). The biotite is a strong light-to-dark brown colour in PPL and does not appear altered.

Fluorite

Fluorite is only present in the Pulaskite-type Lakarpite and the core-Lakarpite (Fig. 3.74). In the Pulaskite-type Lakarpite, fluorite is present as light-to-dark purple anhedral masses <3 mm in dimension. Texturally the fluorite appears to be enclosing feldspar.

In the core-Lakarpite, fluorite is present as light-to-dark purple anhedral crystals <500 μm in dimension. Texturally the fluorite appears to be enclosed by feldspar.

Figure 3.73: Biotite enclosing aegirine and enclosed by later feldspar phases (100 μm thick sections). (Left) biotite enclosing aegirine – image in PPL; (right) within feldspar matrix – image in XPL.

Figure 3.74: Anhedral purple fluorite. (left) late-stage fluorite enclosed by feldspar – image in PPL; (right) fluorite enclosed within feldspar phenocrysts – image in PPL.

Zr-Silicate Phases – Rosenbushite, Eudialyte and Catapleiite

Zr-silicate phases are present in all Lakarpite varieties except the Pulaskite-type, and commonly enclose earlier aegirine and amphibole (Fig. 3.75).

Rosenbushite can be present in the Pulaskite-type and core-Lakarpite as <2 mm long pale coloured needles. These display a high relief in PPL. Texturally the crystals appear later than in the aegirine and amphiboles and are themselves enclosed by the feldspar phases. Eudialyte is present in the Zr-rich core Lakarpite as anhedral-to-subhedral phenocrysts <5 mm in dimension. The crystals display high relief and a weak-pink colour in PPL. The crystals exhibit a granular texture and enclose aegirine and amphibole. In the Zr-rich Lakarpite both eudialyte and catapleiite are present. The eudialyte occurs as anhedral-to-euhedral phenocrysts <2 cm in dimension. The crystals display high relief and a weak-pink colour in PPL. In XPL the crystals exhibit irregular zoning with higher interference colours towards the core of the crystals while the rims display lower order-colours. The eudialytes appear to have been altered along radial fractures to an assemblage of light-speckled minerals and/or opaques. The eudialytes can host aegirine and amphibole when grown around the aegirine-amphibole masses or alternatively may not contain any included minerals when hosted by feldspars. Catapleiite is present as <3 mm long and 0.5 mm wide euhedral crystals which are light brown in PPL. They display bright third-order interference colours and appear unaltered.

Figure 3.75: Zr-silicate phases: Core-type (lower-right and left – images in PPL) Lakarpite displays needles of rosenbushite enclosed by feldspar; Zr-rich-core (upper-left – image in PPL) displays granular eudialyte; Zr-rich-type (upper-right – image in XPL) displays catapleiite and eudialyte (100 µm thick section).

Microcline

Microcline is present within all the Lakarpite varieties apart from the Zr-rich Lakarpite. Microcline typically forms mm-to-cm scale phenocrysts which commonly enclose other minerals (Fig. 3.76).

In the Pulaskite-type Lakarpite, microcline is present as subhedral phenocrysts <5mm in dimension. It can be distinguished by its distinctive tartan-twinning in XPL. Oscillatory zoning or sieve texture are not observed. The microcline phenocrysts display well-developed cracks and enclose finer aegirine crystals. The microcline does not appear altered.

In the core-Lakarpite, microcline is present as subhedral phenocrysts <1 cm in dimension. Once again, microcline can be distinguished by its distinctive tartan-twinning in XPL. Oscillatory zoning or sieve texture are not observed. The microcline phenocrysts display well-developed cracks and enclose smaller albite phenocrysts which are up to 2-to-3 mm in length. The microcline does not appear altered.

In the Zr-rich core Lakarpite, microcline is present as subhedral phenocrysts <2 cm in dimension and is distinguished by its distinctive tartan-twinning in XPL. Oscillatory zoning or sieve texture are not observed. The microcline phenocrysts display well-developed cracks and enclose earlier formed minerals. The microcline does not appear altered.

[NK57-126.5-XPL]

[NK28-64.4-XPL]

Figure 3.76: Microclines displaying tartan twinning and inclusions of albite (100 µm thick sections): Pulaskite-type (lower-left) ; Core-type (lower-right) ; Zr-rich-core (upper-left). All images in XPL.

[NK57-116.7-XPL]

Albite

Albite is present in all Lakarpite varieties and can be present as both a phenocryst and groundmass phase (Fig. 3.77).

In the Pulaskite-type Lakarpite albite is present as <1 mm subhedral crystals and typically forms rounded anhedral crystals <500 µm in dimension. Albite displays polysynthetic twinning in XPL and cracks can be observed in the larger crystals. Albite encloses all other phases within the lithology. This lithology may also display a 'crush texture' indicating a brittle deformation phase. The albite appears unaltered.

In the core-Lakarpite albite occurs as <1 mm subhedral crystals and typically forms rounded-to-angular anhedral-to-subhedral crystals <500 µm in dimension. Albite displays polysynthetic twinning in XPL and does not appear to be altered. Albite appears to enclose all other phases within the lithology.

In the Zr-rich core Lakarpite, albite is present as <2 mm subhedral phenocrysts and rounded-to-angular anhedral-to-subhedral crystals <500 µm in dimension. Albite displays polysynthetic twinning in XPL and does not appear to be altered.

In the Zr-rich Lakarpite, albite is present as anhedral phenocrysts <1 mm in dimension. Albite displays polysynthetic twinning in XPL and does not appear to be altered. Albite is enclosed by other feldspar phases.

Figure 3.77: Anhedral-to-subhedral albite: Pulaskite-type (lower-left) and the Core-type (lower-right) exhibit an albite matrix; Zr-rich-core (upper-left) and Zr-rich-type (upper-right) display albite phenocrysts (100 µm thick sections). All images in XPL.

Nepheline

Nepheline is only present within the Zr-rich Lakarpite and there it is present as either aegirine-rich nepheline (Fig. 3.78) or clear nepheline (Fig. 3.79).

Aegirine-rich nepheline is present as less than 4 mm long anhedral-to-subhedral crystals. These nephelines display cores with very-high-aspect-ratio green needle-like inclusions which are μm 's wide and up to 100's μm 's in length. The needles tend to be aligned in the same orientation (predominantly along the c-axis of the mineral) but deviations from this are also frequently observed. The nephelines themselves display speckled or mottled interference colours in XPL. Clear Nepheline is present as less than 4 mm long anhedral-to-subhedral crystals. The nephelines display low relief in PPL and exhibit 'dusty' altered cores. Texturally they appear to be the last formed phase and enclose all other minerals.

Figure 3.78: Anhedral-to-subhedral aegirine-rich feldspar. (left) Aegirine-rich feldspar displaying anomalous interference colours – image in XPL; (right) aegirine-rich feldspar enclosed by nepheline and growing against aegirine and eudialyte – image in PPL.

Figure 3.79: Nepheline displaying dusty cores (100 μm thick section). (left) nepheline enclosing aegirine and growing against eudialyte – image in XPL; (right) nepheline enclosing aegirine and eudialyte – image in XPL.

3.6.2 Contact with the Grennaite

The contact between the Lakarpite and the Grennaite displays evidence of potential ‘baking’ and metasomatism. The contact is characterised by being dark in colour and displaying anhedral eudialyte which appears to have overgrown an otherwise recognisable fine-grained Grennaite fabric of aegirine and albite.

These eudialytes are typically <2 cm in dimension and are anhedral displaying a ‘blob’ like texture which crosscuts an earlier Grennaite foliation. Fig. 3.80 shows a eudialyte with a blackened core and a pink rim. Within the core of the eudialyte there is aegirine and albite. The albite also occurs in drusy pockets which also contain inclusion free eudialyte (Fig. 3.81).

['Discovery Outcrop']

['Discovery Outcrop']

Figure 3.80: ‘blob’ like eudialyte displaying a blackened core and pink rim. (left)– image in PPL; (right)– image in XPL

['Discovery Outcrop']

['Discovery Outcrop']

Figure 3.81: Albite and eudialyte within drusy pockets within the blackened core. (left)– image in PPL; (right)– image in XPL

3.6.3 Petrological Overview and Petrogenetic Sequence of the Lakarpite

The Lakarpite displays a very different texture to the surrounding Grennaite and also varies in texture internally. The Lakarpite can be described in terms of different zones and as each zone displays a slightly differing mineralogy, it is likely that the Lakarpite is evolving as a body in response to intruding into the Grennaite. The field relations suggest that the Grennaite was still ductile at the time of Lakarpite intrusion and this can also be seen in the textures along the contact of the Lakarpite which potentially show that there was chemical interaction between the two bodies of magma, as well as potential metasomatism of the Grennaite (e.g. Fig. 3.68). Overall, the Lakarpite is the most mineralogically diverse lithology at Norra Kärr. A summarised petrogenetic sequence is shown in Table 3.4.

Lakarpite Type	1 st Phase					Last Phase
Pulaskite (3 samples)	Aegirine (20.13%)	Biotite (2.38%)	Amphibole (19.3%)	Fluorite (2%)	Feldspar-Nepheline (57.06%)	
Core (1 sample)	Aegirine (14.5%)	Sphene (0.76%)	Amphibole (14.5%)	Rosenbushite (9.54%)	Fluorite (1%)	Feldspar-Nepheline (60.68%)
Core-Zr (1 sample)	Aegirine (6.88%)	Amphibole (18.11%)	Eudialyte (8.69%)	Feldspar-Nepheline (67.24%)		
Zr-rich (1 sample)	Aegirine (9.42%)	Amphibole (13.77%)	Eudialyte (52.9%)	Catapleiite (2.17)	Albite (13.04%)	Nepheline (8.7%)

Table 3.4: Petrogenetic sequence of the Lakarpite varieties

Aegirine is present within all the Lakarpite types but there are relatively few textural changes throughout the body. The most notable feature is that the aegirine becomes less euhedral the further from the core-zones it is and increasingly tends to form ‘masses’ of crystals. These phenocrysts may also represent remnant phenocrysts from earlier crystallisation and may have become entrained within the melt. Biotite is only present in the Pulaskite-type Lakarpite, while amphibole is present in all Lakarpite varieties. This potentially indicates that a transition from a biotite dominated assemblage to an amphibole dominated one occurs with distance from the core due to changing chemical conditions.

Fluorite is only present in the core zones of the Lakarpite suggesting that F⁻ activities were higher in the later stages of the melt. Texturally the both the Pulaskite-type Lakarpite and the core-Lakarpite contain fluorite which crystallised before the microcline phase. The Pulaskite-type contains abundant fluorite which also appears to form late stage melt pockets within the albite portions of the lithology indicating a high F⁻ activity at this stage of crystallisation. However, the core-Lakarpite not only displays lower abundances of fluorite but also displays rosenbushite which appears to have crystallised at the same petrogenetic stage as the fluorite. This suggests that the HF activity had dropped but also that fluorite saturation was briefly achieved. A drop in HF activity would also promote the crystallisation of rosenbushite over that of fluorite (Andersen et al. 2010). This will be modelled further in Chapter 7.

Fluorite and rosenbushite are not present in the Zr-enriched zones, instead the Zr-silicate phases are eudialyte in the Zr-enriched-core zone and eudialyte and catapleiite in the Zr-rich-contact zone of the Lakarpite. Zr-content is not enough to dictate the phases formed; i.e. a higher concentration of Zr would result in a greater abundance of any given phase. Instead the HF^- activity has to fall sufficiently to allow eudialyte to crystallise (Andersen et al. 2010). Furthermore, the presence of catapleiite in the Zr-rich zone shows that the OH-activity is also increasing (Andersen et al. 2010). Texturally the eudialyte in the Zr-enriched-core zone is ragged and granular suggesting that it was difficult for the mineral to grow. This is in contrast with the Zr-rich-contact zone which displays some euhedral eudialyte suggesting the mineral had space to grow freely in equilibrium within the melt.

The feldspar phases within the Pulaskite-, core- and Zr-rich-core zones show a similar trend to the Kaxtorpite and the Pulaskite, with cm-sized phenocrysts of microcline surrounded by a matrix of albite. This suggests initial microcline crystallisation and coarsening before the co-crystallisation of albite. Furthermore, from the relationship of the two coexisting feldspars (albite and microcline) the assemblage can be considered as subsolvus indicating that the feldspars crystallised at a low temperature ($<650^\circ\text{C}$). This is in common with the rest of the lithologies at Norra Kärr.

The presence of nepheline in the Zr-rich Lakarpite type may also show a potential interaction with the surrounding Grennaite whereby the magma has been formed to crystallise nepheline due to the diffusion of alkali components into the Lakarpite zone.

3.7 Overall Petrogenetic Sequence for Norra Kärr

The petrogenetic history of Norra Kärr is surprisingly consistent across lithologies, for an intrusion with such a diverse mineralogy. Table 3.5 shows a summarised account of all the petrogenetic sequences identified. In all cases aegirine (or a Zr-rich variant) crystallises first. Within the silica suite biotite or amphibole then crystallises. This is followed by the crystallisation of the Zr-silicate phases some of which contain the main ore horizons at Norra Kärr, with the exclusion of the Kaxtorpite which does not appear to contain a Zr-silicate or fluorite phase. The final phases are either microcline phenocrysts with an albite matrix or solely albite. Furthermore, the subsolvus textures displayed by all microcline-albite assemblages indicate that, at a late stage, all of the different magma types behaved in a similar way and had cooled to similar temperatures (i.e. <650°C).

This consistency shows that the different magmas at Norra Kärr actually appear closely related to each other. Arguably this petrological sequence shows that the magma evolves through a Fe-dominated phase (aegirine), continuing through a phase of Zr- and volatile-dominated crystallisation (eudialyte/fluorite) ending with a phase of Al- dominated crystallisation (feldspars).

Lithology		1 st Phase					Last Phase		
Grennaïtes	Contact	Aeg				Cat-Eud		Mc-Ab	Nep
	Peg-Host	Aeg				Cat-Eud		Ab-Mc	Nep
	Pegmatite	Zr-Aeg	Aeg			Cat-Eud	Amp	Ab-Mc	Nep
	Crenulated	Aeg		Pec		Cat-Eud		Mc-Ab	Nep
Kaxtorpite		Aeg		Amp	Pec			Mc-Ab	Nep
Pulaskite	Pulaskite	Aeg	Sp	Bt	Amp	Fl		Mc-Ab	
	Enclaves	Aeg	Ros	Bt	Amp	Fl		Ab	
Lakarpite	‘Pulaskite’	Aeg		Bt	Amp	Fl		Mc-Ab	
	‘Core’	Aeg	Sp	Ros	Amp	Ros-Fl		Mc-Ab	
	‘Core-Zr’	Aeg			Amp	Eud		Mc-Ab	
	‘Zr-rich’	Aeg			Amp	Eud-Cat		Ab	Nep

Table 3.5: Summary of each petrogenetic sequence at Norra Kärr. Aeg - Aegirine, Zr-Aeg – Zr-rich Aegirine, Amp – Amphibole, Pec – Pectolite, Sp -Sphene, Ros – Rosenbushite, Bt – Biotite, Cat – Catapleiite, Eud – Eudialyte, Mc- Microcline, Ab – Albite, Nep – Nepheline.

The petrology outlined here poses a number of questions that will be outlined further in later chapters. That there is an unusual order of zircon-silicate mineral crystallisation appears significant given the zonation of [Ln] within the Grennaïte hosted ore-domains and this will be explored further in Chapter 7.

The origin of the pegmatites within the Pegmatite-Host Grennaite will be explored further in Chapter 5 in through whole-rock modelling to determine their origin given that they display a feldspar rich nature similar to the Pulaskite but display a similar mineralogy to the Pegmatite-Host.

The complexity of the Lakarpite in terms of its mineralogy will be explored in terms of its whole-rock composition and the influence of volatiles on its mineralogy and evolution and how this places it structurally within the intrusion in Chapter 7.

Further trends in mineral chemistry will be outlined in Chapter 4 and whole-rock trends will be explored in light of this in Chapter 5. Further modelling based upon mineral abundance and the petrogenetic sequence will be presented in Chapters 6 and 7.

3.8 Petrological Conclusions

This petrological study has provided a modern analysis, interpretation and comparison of the lithologies at Norra Kärr. In particular this study has shown that:

- While many of the textures exhibited by the minerals within Norra Kärr are comparable to other alkaline intrusions (e.g. Ilímaussaq, Red Wine and the Kola intrusions) Norra Kärr not only shows its own unique petrological character but also a remarkable mineralogical diversity within a small volume of magma.
- The magma at Norra Kärr appears to have evolved through a Fe-dominated phase, followed by a Zr and volatile dominated phase and finally an Al (feldspathic) dominated phase. Further, the similar petrogenetic histories and the subsolvus feldspar textures throughout the intrusion indicate that almost all of the magmas cooled and evolved in a similar manner.
- The Zr and volatile dominated phase produced different phases (eudialyte, catapleiite, rosenbushite, fluorite) in such an order that may depend upon fluctuations in $\log a_{\text{H}_2\text{O}}$ and $\log a_{\text{HF}}$, as observed in other alkaline intrusions, with the evolution of the Lakarpite being particularly complex. This will be further examined in Chapter 7.
- The ore bearing eudialyte phases only display minor alteration features indicating that the pattern of [Ln] throughout the Grennaites is primary in nature with any secondary alteration processes unlikely to have occurred.
- The presence of enclaves in the Pulaskite indicate the presence of a deeper source of fractionating alkaline magma.
- The intrusion appears to have been subject to some deformation which has produced mineral defined shear fabrics and deformation of enclaves, which likely occurred while the cooling magma was still ductile.

Chapter 4

Mineralogy

4.1 Introduction

Previous EPMA and SEM-EDS work on Norra Kärr is limited to two previous studies. Sjöqvist et al. (2013) focused on eudialytes from the 'pegmatite domain' the Crenulated Grennaite and the Lakarpite. Atanasova et al. (2017) collected data on the pyroxenes, eudialytes, feldspars and catapleiites from the Grennaite; with Atanasova et al. (2015) having previously only focused on developing an analytical EPMA method using a single crystal of eudialyte. This chapter presents a far broader set of EPMA data than has previously been presented for the major minerals within the renamed and subdivided lithologies presented in Chapters 2,3 and 4. Representative [Ln]-concentration profiles for eudialyte will also be presented and comparisons with the chemical zonation observed within eudialyte crystals via SEM and EPMA mapping will be given. This data is then compared to other alkaline intrusions and conclusions made regarding the evolution of major elements and volatiles within each magmatic phase, along with a tentative reconstruction of the T-fO₂ path taken by the evolving magma is presented.

4.2 Methods and Statistical Analysis

Data was collected using SEM-EDS, EPMA and LA-ICP-MS. Further details of the analytical methodologies used are given in Appendix 1.

The EPMA data collected was statistically tested across different slides using the Levene Test for equal variance in order to determine if the data collected for a given lithology showed significant heterogeneity or not. In very nearly all cases this test was satisfied ($\alpha > 0.05$) with the data collected showing that the mineral chemistry was consistent throughout each lithology.

A further test for normality was applied using the Anderson-Darling test. This showed that the analyses for each mineral were variable in whether or not the Wt% oxide analyses were normally distributed. As such the Wt% oxide values are reported with $\pm$ being the interquartile range rather than using a standard deviation.

4.3 Aegirine – Aegirine-Augite

A total of 251 EPMA and 2547 LA-ICP-MS analyses of pyroxene were collected. Aegirine is present throughout the intrusion with Aegirine-Augite present within the Pulaskite and core Lakarpite zones.

4.3.1 SEM-EDS Petrology

All pyroxenes within Norra Kärr are broadly similar in size and texture throughout the different lithologies, being up to several mm in length and displaying a needle-like habit; BSE-SEM images are given in Fig. 4.1. Aegirine – Aegirine-Augite is the first forming mineral in all lithologies and intergrowth textures between needle-shaped aegirine and amphibole are commonly seen. However, there are unique textures within some lithologies. The Pegmatites display coarse aegirines with Zr-rich cores displaying catapleiite exsolution (Atanasova et al. 2017) which display bright spots in BSE-SEM. Fig. 4.1 also shows that aegirines within the Kaxtorpite, the inner zones of the Lakarpite and the Pulaskite display brighter cores and darker rims. Andersen et al. (2017) described this texture as common in Pilanesberg and ascribed it to the inner cores of the aegirines containing higher concentrations of Zr.

4.3.2 Substitutions

Pyroxenes follow the structural formula:

W = Ca, Na,
X = Mg, Fe²⁺, Mn, Ni, Li,
Y = Al, Fe³⁺, Cr, Ti,
Z = Al, Si

The main substitutions in alkali pyroxenes are based upon the transition between Ca and Na with the redox state of Fe playing an important role in the M1 site which it also shares with Mg. Mn can also substitute into the M1 site but is typically not a main mineral forming element. A summary of the representative mineral compositions from EPMA and calculated formulae of the pyroxenes is given in Table 4.1. The Fe²⁺ and Fe³⁺ contents presented later in this section were calculated using the stoichiometric cation charge balance for each analysis. Trace element concentrations from LA-ICP-MS given in Table 4.2, and chondrite normalised values in Table 4.3.

Ca vs Na (Fig. 4.2) is shown to display trends in W-site substitution. Overall, the aegirines are Na-rich, with minor Ca-substitutions present within the Pulaskite and the core-Lakarpite zones. Ti vs Fe (Fig. 4.3) and Mn vs Fe (Fig. 4.4) show that the Fe content predominantly plots above 0.7 a.p.f.u., with the which is dependent upon the abundance of Ti, Mn and Mg (Table 4.1). While there is a spread in the data for the Grennaite, the Kaxtorpite and Pulaskite tend to show the most Fe-substitution while the Pegmatites show the least. Fig. 4.3 shows most analyses plot below 0.02 a.p.f.u. Ti, with the exception of the core-Lakarpite zones and in particular the Kaxtorpite. Fig. 4.4 shows that the majority of aegirine analyses display low Mn abundance.

Figure 4.1: BSE-SEM images of Aegirine from different lithologies in Norra Kärr. Red scale bar is equal to 100 μm. NK code number refer to core and depth sampled. The majority of aegirines, do not show any zoning in the BSE-images; only aegirines from the Kaxtorpite, the inner zones of the Lakarpite and the Pulaskite display brighter cores and darker rims. The aegirines from the pegmatite display brighter spots due to catapleiite exsolution.

	Grennaite			Gren Peg			Pegmatite			Crenulated			Kaxtorpite			Lakarpite-Pul		
n=	20			21			26			26			47			9		
SiO ₂	53.83	+	0.33	53.35	+	0.63	52.78	+	0.36	53.02	+	1.03	52.94	+	0.38	52.86	+	0.20
		-	0.95		-	0.67		-	0.36		-	0.34		-	0.69		-	0.28
TiO ₂	0.12	+	0.05	0.16	+	0.03	0.26	+	0.08	0.35	+	0.06	1.87	+	0.38	1.19	+	0.17
		-	0.01		-	0.02		-	0.03		-	0.03		-	0.15		-	0.48
Al ₂ O ₃	5.87	+	0.78	2.28	+	3.42	1.78	+	0.19	2.83	+	2.90	2.67	+	1.73	2.20	+	0.24
		-	0.55		-	0.61		-	0.23		-	0.73		-	0.43		-	0.30
Fe ₂ O ₃	25.31	+	1.34	30.46	+	1.10	31.49	+	0.55	28.99	+	1.39	26.04	+	1.13	28.44	+	0.44
		-	0.70		-	6.21		-	0.33		-	4.13		-	2.44		-	0.92
MnO	0.10	+	0.02	0.11	+	0.02	0.17	+	0.03	0.17	+	0.02	0.29	+	0.11	0.33	+	0.02
		-	0.02		-	0.02		-	0.02		-	0.02		-	0.08		-	0.04
MgO	0.12	+	0.05	0.16	+	0.01	0.27	+	0.02	0.25	+	0.03	1.23	+	0.21	1.21	+	0.35
		-	0.01		-	0.03		-	0.03		-	0.04		-	0.14		-	0.02
CaO	0.62	+	0.11	0.68	+	0.06	0.95	+	0.07	0.40	+	0.02	1.33	+	0.33	2.93	+	0.64
		-	0.12		-	0.09		-	0.07		-	0.04		-	0.23		-	0.45
Na ₂ O	13.83	+	0.25	13.84	+	0.23	13.34	+	0.28	13.95	+	0.27	13.08	+	0.37	12.38	+	0.31
		-	0.25		-	0.16		-	0.21		-	0.23		-	0.25		-	0.18
K ₂ O	1.26	+	2.08	0.01	+	0.00	b.d.l.	+	b.d.l.	0.01	+	0.00	0.03	+	0.00	0.03	+	0.00
		-	0.62		-	0.00		-	b.d.l.		-	0.00		-	0.02		-	0.00
Total	101.06			101.04			101.04			99.96			99.48			101.58		
Si	1.950			1.946			1.936			1.951			1.943			1.929		
Al	0.241			0.098			0.077			0.123			0.116			0.095		
Ti	0.003			0.004			0.007			0.010			0.052			0.032		
Fe ³⁺	0.785			0.928			0.959			0.890			0.783			0.849		
Mg	0.000			0.000			0.000			0.000			0.000			0.013		
Fe ²⁺	0.003			0.003			0.005			0.005			0.009			0.010		
Mn	0.007			0.009			0.015			0.014			0.068			0.066		
Na	0.025			0.026			0.037			0.016			0.053			0.115		
Ca	0.985			0.982			0.954			0.989			0.940			0.880		
K	0.000			0.000			0.000			0.000			0.000			0.000		

Table 4.1 (continued on next page)

Lakarpite-Core			Lakarpite-Zr-Core			Lakarpite-Zr			Lakarpite-Gren			Pulaskite			Pulaskite-Enclaves			
21			10			30			2			25			14			n=
52.83	+	0.41	51.02	+	1.02	50.97	+	0.24	52.31	+	0.21	52.37	+	0.19	52.32	+	0.45	SiO ₂
	-	0.25		-	1.48		-	0.10		-	0.21		-	0.49		-	4.41	
1.31	+	0.13	0.11	+	0.11	0.35	+	0.08	0.35	+	0.09	0.28	+	0.15	0.41	+	0.15	TiO ₂
	-	0.61		-	0.01		-	0.06		-	0.09		-	0.07		-	0.11	
2.12	+	0.37	2.30	+	0.22	1.92	+	0.55	2.05	+	0.27	1.74	+	0.41	2.23	+	2.25	Al ₂ O ₃
	-	0.45		-	0.20		-	0.21		-	0.27		-	0.28		-	0.10	
27.69	+	0.65	19.51	+	6.80	29.53	+	0.32	18.04	+	5.76	26.66	+	1.24	27.33	+	0.48	Fe ₂ O ₃
	-	0.59		-	0.78		-	0.42		-	5.76		-	3.04		-	3.53	
0.27	+	0.04	1.02	+	0.05	0.24	+	0.04	0.70	+	0.26	0.77	+	0.17	0.40	+	0.09	MnO
	-	0.01		-	0.62		-	0.04		-	0.26		-	0.43		-	0.02	
1.48	+	0.27	7.19	+	0.10	0.37	+	0.08	0.67	+	0.00	2.04	+	0.26	1.72	+	0.14	MgO
	-	0.23		-	5.04		-	0.04		-	0.00		-	1.10		-	0.09	
2.78	+	0.71	0.21	+	0.27	1.20	+	0.17	5.97	+	2.11	6.40	+	1.02	4.33	+	0.95	CaO
	-	1.06		-	0.06		-	0.20		-	2.11		-	4.14		-	0.21	
12.43	+	0.36	9.46	+	3.04	12.89	+	0.18	13.55	+	0.46	10.27	+	2.07	11.46	+	0.26	Na ₂ O
	-	0.93		-	0.11		-	0.19		-	0.46		-	0.47		-	0.45	
0.02	+	2.27	2.33	+	0.07	0.00	+	0.01	0.12	+	0.00	0.01	+	0.01	0.01	+	0.01	K ₂ O
	-	0.01		-	0.03		-	0.01		-	0.00		-	0.01		-	0.00	
100.92			93.15			97.47			93.75			100.55			100.21			Total
1.940			1.994			1.933			1.946			1.939			1.938			Si
0.092			0.105			0.086			0.113			0.076			0.097			Al
0.036			0.003			0.010			0.015			0.008			0.011			Ti
0.818			0.608			0.934			0.858			0.708			0.767			Fe ³⁺
0.047			0.000			0.000			0.054			0.089			0.071			Mg
0.008			0.033			0.008			0.006			0.022			0.013			Fe ²⁺
0.081			0.410			0.021			0.037			0.112			0.097			Mn
0.108			0.008			0.049			0.069			0.246			0.180			Na
0.884			0.706			0.945			0.903			0.738			0.820			Ca
0.000			0.112			0.000			0.000			0.000			0.000			K

Table 4.1: Representative EPMA analyses and calculated compositions of pyroxene from Norra Kärr. Calculated on the basis of 6 oxygens and normalised to 4 cations.

	Contact Grennaite			Pegmatite-Host Grennaite			Pegmatites			Crenulated Grennaite			Kaxtorpite			Lakarpite- Pulaskite		
n =	137			185			917			373			219			23		
Y	1.35	+	1.33	8.91	+	4.30	6.09	+	25.11	1.88	+	25.07	2.80	+	1.58	0.00	+	0.02
		-	0.80		-	2.88		-	3.37		-	0.99		-	0.88		-	0.00
La	0.62	+	0.36	3.44	+	2.94	5.11	+	41.62	2.67	+	20.36	15.24	+	7.34	5.33	+	3.71
		-	0.29		-	1.77		-	3.68		-	1.87		-	5.09		-	3.20
Ce	1.05	+	0.34	8.84	+	4.37	4.63	+	5.56	4.91	+	36.48	20.18	+	9.56	8.72	+	5.73
		-	0.29		-	2.66		-	3.92		-	2.78		-	4.74		-	4.73
Pr	0.10	+	0.11	1.29	+	0.68	1.26	+	0.55	0.50	+	3.66	1.69	+	0.97	0.32	+	0.28
		-	0.07		-	0.52		-	0.42		-	0.26		-	0.69		-	0.32
Nd	0.44	+	0.44	5.61	+	2.73	4.50	+	3.41	1.71	+	12.36	5.19	+	4.28	b.d.l.	+	0.55
		-	0.41		-	3.53		-	4.18		-	0.80		-	3.39		-	b.d.l.
Sm	b.d.l.	+	0.14	b.d.l.	+	0.99	1.27	+	0.78	b.d.l.	+	0.97	b.d.l.	+	b.d.l.	b.d.l.	+	b.d.l.
		-	b.d.l.		-	b.d.l.		-	0.41		-	b.d.l.		-	b.d.l.		-	b.d.l.
Eu	b.d.l.	+	b.d.l.	b.d.l.	+	b.d.l.	0.13	+	0.22	b.d.l.	+	b.d.l.	b.d.l.	+	b.d.l.	b.d.l.	+	b.d.l.
		-	b.d.l.		-	b.d.l.		-	0.06		-	b.d.l.		-	b.d.l.		-	b.d.l.
Gd	b.d.l.	+	b.d.l.	b.d.l.	+	0.46	0.65	+	1.13	b.d.l.	+	0.44	b.d.l.	+	b.d.l.	b.d.l.	+	b.d.l.
		-	b.d.l.		-	b.d.l.		-	0.59		-	b.d.l.		-	b.d.l.		-	b.d.l.
Tb	b.d.l.	+	0.04	b.d.l.	+	0.15	0.18	+	0.32	b.d.l.	+	0.17	b.d.l.	+	b.d.l.	b.d.l.	+	b.d.l.
		-	b.d.l.		-	b.d.l.		-	0.10		-	b.d.l.		-	b.d.l.		-	b.d.l.
Dy	0.01	+	0.42	0.08	+	0.93	0.69	+	2.26	b.d.l.	+	1.58	b.d.l.	+	b.d.l.	b.d.l.	+	b.d.l.
		-	0.01		-	0.08		-	0.46		-	b.d.l.		-	b.d.l.		-	b.d.l.
Ho	b.d.l.	+	0.10	0.02	+	0.23	0.31	+	0.91	b.d.l.	+	0.52	b.d.l.	+	b.d.l.	b.d.l.	+	b.d.l.
		-	b.d.l.		-	0.02		-	0.19		-	b.d.l.		-	b.d.l.		-	b.d.l.
Er	0.11	+	0.26	0.47	+	0.85	1.06	+	2.11	0.02	+	1.54	b.d.l.	+	b.d.l.	b.d.l.	+	b.d.l.
		-	0.11		-	0.47		-	0.59		-	0.02		-	b.d.l.		-	b.d.l.
Tm	b.d.l.	+	b.d.l.	0.10	+	0.22	0.28	+	0.89	b.d.l.	+	b.d.l.	b.d.l.	+	b.d.l.	b.d.l.	+	b.d.l.
		-	b.d.l.		-	0.10		-	0.15		-	b.d.l.		-	b.d.l.		-	b.d.l.
Yb	1.05	+	0.54	4.55	+	1.61	3.91	+	4.11	0.59	+	3.38	b.d.l.	+	b.d.l.	b.d.l.	+	b.d.l.
		-	0.46		-	1.92		-	2.20		-	0.50		-	b.d.l.		-	b.d.l.
Lu	0.27	+	0.10	1.27	+	0.51	1.27	+	1.40	0.14	+	0.60	b.d.l.	+	b.d.l.	b.d.l.	+	b.d.l.
		-	0.12		-	0.46		-	0.43		-	0.14		-	b.d.l.		-	b.d.l.

Table 4.2 (continued on next page)

Lakarpite-Core			Lakarpite-Zr-Core			Lakarpite-Zr			Pulaskite			Pulaskite (Enclave)			n
226			109			48			215			95			=
17.24	+	24.72	5.65	+	1.97	10.78	+	4.53	77.52	+	18.60	56.96	+	66.46	Y
	-	4.82		-	1.37		-	1.77		-	22.54		-	40.64	
76.99	+	57.14	b.d.l.	+	5.53	1.94	+	2.35	6.30	+	10.42	166.62	+	686.62	La
	-	27.83		-	b.d.l.		-	0.87		-	3.73		-	135.12	
130.01	+	227.88	1.64	+	19.40	10.82	+	2.44	23.33	+	19.84	376.55	+	848.55	Ce
	-	52.18		-	1.04		-	1.50		-	7.68		-	310.79	
13.06	+	23.77	b.d.l.	+	1.58	2.02	+	0.59	4.50	+	2.11	35.64	+	82.52	Pr
	-	5.26		-	b.d.l.		-	0.47		-	1.49		-	31.18	
40.12	+	72.84	b.d.l.	+	5.91	11.02	+	5.27	24.92	+	11.44	117.84	+	194.12	Nd
	-	16.71		-	b.d.l.		-	4.05		-	7.75		-	102.20	
4.25	+	10.44	b.d.l.	+	0.22	0.92	+	2.62	6.66	+	4.50	18.11	+	27.02	Sm
	-	3.49		-	b.d.l.		-	0.92		-	4.46		-	18.11	
0.12	+	2.20	b.d.l.	+	b.d.l.	b.d.l.	+	b.d.l.	b.d.l.	+	b.d.l.	0.85	+	3.24	Eu
	-	0.12		-	b.d.l.		-	b.d.l.		-	b.d.l.		-	0.85	
2.03	+	6.86	b.d.l.	+	b.d.l.	0.52	+	3.64	5.30	+	5.48	10.08	+	17.85	Gd
	-	1.95		-	b.d.l.		-	0.52		-	3.63		-	10.08	
0.10	+	1.65	b.d.l.	+	b.d.l.	b.d.l.	+	b.d.l.	0.42	+	1.22	1.19	+	3.49	Tb
	-	0.10		-	b.d.l.		-	b.d.l.		-	0.42		-	1.19	
1.26	+	4.52	b.d.l.	+	b.d.l.	0.25	+	2.32	10.22	+	5.38	8.38	+	13.24	Dy
	-	1.26		-	b.d.l.		-	0.25		-	5.20		-	8.38	
0.05	+	2.57	b.d.l.	+	b.d.l.	b.d.l.	+	0.04	2.29	+	1.13	1.03	+	2.20	Ho
	-	0.05		-	b.d.l.		-	b.d.l.		-	1.06		-	1.03	
b.d.l.	+	0.20	b.d.l.	+	b.d.l.	1.52	+	1.18	16.14	+	6.36	0.45	+	4.55	Er
	-	b.d.l.		-	b.d.l.		-	1.22		-	5.06		-	0.45	
b.d.l.	+	b.d.l.	b.d.l.	+	b.d.l.	b.d.l.	+	b.d.l.	4.09	+	1.43	b.d.l.	+	0.01	Tm
	-	b.d.l.		-	b.d.l.		-	b.d.l.		-	1.74		-	b.d.l.	
b.d.l.	+	b.d.l.	b.d.l.	+	0.86	7.81	+	4.40	68.79	+	42.00	3.27	+	3.46	Yb
	-	b.d.l.		-	b.d.l.		-	2.35		-	14.00		-	3.27	
b.d.l.	+	b.d.l.	0.06	+	0.37	1.85	+	0.53	16.74	+	7.00	0.59	+	0.87	Lu
	-	b.d.l.		-	0.06		-	0.57		-	3.38		-	0.59	

Table 4.2: Representative LA-ICP-MS analyses for [Ln] and Y concentrations (ppm) within pyroxenes from Norra Kärr.

	Contact Grennaite	Peg-Host Grennaite	Pegmatite	Crenulated Grennaite	Kaxtorpite	Lakarpite- Pulaskite	Lakarpite- Core	Lakarpite- ZrCore	Lakarpite- Zr	Pulaskite	Pulaskite -Enclave	
n=	137	185	917	373	219	23	226	109	48	244	215	n=
Y	0.64	4.24	2.90	0.89	1.33	b.d.l.	8.21	2.69	5.13	36.91	27.12	Y
La	1.68	9.37	13.94	7.28	41.52	14.51	209.78	b.d.l.	5.28	17.15	454.02	La
Ce	1.09	9.24	4.84	5.13	21.09	9.11	135.85	1.71	11.30	24.38	393.46	Ce
Pr	0.74	9.41	9.19	3.64	12.37	2.35	95.35	b.d.l.	14.78	32.82	260.18	Pr
Nd	0.62	7.90	6.33	2.40	7.30	b.d.l.	56.42	b.d.l.	15.49	35.05	165.74	Nd
Sm	b.d.l.	b.d.l.	5.50	b.d.l.	b.d.l.	b.d.l.	18.38	b.d.l.	3.97	28.83	78.41	Sm
Eu	b.d.l.	b.d.l.	1.51	b.d.l.	b.d.l.	b.d.l.	1.34	b.d.l.	b.d.l.	b.d.l.	9.78	Eu
Gd	b.d.l.	b.d.l.	2.11	b.d.l.	b.d.l.	b.d.l.	6.64	b.d.l.	1.69	17.32	32.94	Gd
Tb	b.d.l.	b.d.l.	3.18	b.d.l.	b.d.l.	b.d.l.	1.75	b.d.l.	b.d.l.	7.17	20.50	Tb
Dy	0.03	0.22	1.80	b.d.l.	b.d.l.	b.d.l.	3.31	b.d.l.	0.66	26.82	22.00	Dy
Ho	b.d.l.	0.23	3.69	b.d.l.	b.d.l.	b.d.l.	0.54	b.d.l.	b.d.l.	26.87	12.05	Ho
Er	0.46	1.90	4.27	0.09	b.d.l.	b.d.l.	b.d.l.	b.d.l.	6.10	64.83	1.83	Er
Tm	b.d.l.	2.92	8.00	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	114.86	b.d.l.	Tm
Yb	4.22	18.33	15.76	2.36	b.d.l.	b.d.l.	b.d.l.	b.d.l.	31.49	277.39	13.17	Yb
Lu	7.14	33.21	33.28	3.62	b.d.l.	b.d.l.	b.d.l.	1.48	48.60	439.45	15.38	Lu

Table 4.3: Representative LA-ICP-MS analyses for [Ln] and Y concentrations (ppm) within pyroxene from Norra Kärr normalised to chondrite (Taylor & McLennan 1985).

Figure 4.2: Ca vs Na plot for pyroxenes from Norra Kärr.

Figure 4.3: Ti vs Fe plot for pyroxenes from Norra Kärr.

Figure 4.4: Mn vs Fe plot for pyroxene from Norra Kärr.

Figure 4.5: Calculated Fe^{2+} vs Fe^{3+} plot for pyroxene from Norra Kärr.

Fig. 4.5 shows the calculated Fe^{2+} vs Fe^{3+} for each of the Aegirine analyses. The majority of analyses show that iron is present solely as Fe^{3+} though some analyses do contain up to 0.2 a.p.f.u. Fe^{2+} with the majority of these Fe^{2+} -bearing Aegirines being located in the Kaxtorpite and Pulaskite

The ternary plots in Fig. 4.5 shows further variations in the composition of the pyroxenes. On an alkali pyroxene discrimination diagram (Fig. 4.6-A) though the majority of the analyses fall within the aegirine field two trends may be seen within the data. The Grennaite and the Kaxtorpite show trend which lies below Quad_{10} and between $\text{Aeg}_{100}\text{Jd}_0$ and $\text{Aeg}_{50}\text{Jd}_{50}$, while the Pulaskite and Lakarpite lie along a trend between aegirine and aegirine-augite. This suggests that two fractionation trends are observable within the first phase and second phase magmas. Similarly, the Na-Ca-Fe plot (Fig. 4.6-B) again shows that the pyroxenes are predominantly Na and Fe bearing matching the standard aegirine composition, with a trend of slight Ca enrichment within pyroxenes from the Pulaskite. On the Aeg-Hed-Di plot (Fig. 4.6-C) the data potentially indicates two separate evolutionary paths. It is difficult to place the trend along which the Grennaite lie due to several trends meeting at the Aegirine-endmember, but they do not stray beyond that of Motzfelt. The Pulaskite, Lakarpite and Kaxtorpite lie along a similar trend to Lovozero and Katzenbuckel. The discrepancy between the Grennaite and the Kaxtorpite trends may be due to fractionation resulting in differing magma compositions either side of the phonolite minimum (see Chapter 4).

Figure 4.6: Aegirine ternary plots: (A)-Top Left – Jd-Aeg-CMF Plot; (B) – Top Right – Di-Hed-Aeg Plot; (C) – Bottom Left – Ca-Fe-Na Plot, (D) –Bottom Right – Trends in pyroxene evolution in other alkaline intrusions. Katzenbuckel, SW Germany (Mann et al., 2006); Murun, Siberia (Mitchell and Vladykin, 1996); Lovozero, Kola Peninsula (Korobeinikov and Laajoki, 1994); Eastern Uganda (Taylor and King, 1967); Fen, Norway, acmitic trend (Mitchell, 1980); Alnö (Vuorinen et al. 2005); Grønnedal-Ika (Marks et al. 2004); South Qôroq, South Greenland (Stephenson, 1972); Motzfeldt, South Greenland (Schönenberger and Markl, 2008); North Qôroq, South Greenland (Coulson, 2003); Puklen (Marks et al. 2004); Ilímaussaq, South Greenland (Larsen, 1976). ΔFMQ trends (Marks et al. 2008, Wu et al. 2016).

4.3.3 Trace Elements

The chondrite normalised plot of the aegirines is given in Fig. 4.7 and 4.8. The Contact Grennaite shows a pattern with a trend towards enrichment in the heavy-[Ln] (Tb upwards). Aegirine from the Pegmatite-Host Grennaite shows a similar [Ln]-pattern with an overall enrichment in [Ln]. The aegirine from the Crenulated Grennaite exhibits a similar [Ln]-pattern to that of the Contact Grennaite, though richer in light-[Ln] and poorer in heavy-[Ln]. Y and Ho appear to be decoupled within these analyses.

These patterns may well reflect the overall evolution of the Grennaites suggesting that the [Ln]-concentrations within the different zones of Grennaite magma were already changing by the time that aegirine started to crystallise within each zone. These patterns therefore potentially show the change in magma chemistry in relation to a steadily moving crystallisation front within the chamber; with the Contact Grennaite representing an 'initial' magma composition, the Pegmatite-Host Grennaite showing an overall enrichment in [Ln] within the magma and the final Crenulated Grennaite reflecting the final bias towards light-[Ln] over heavy-[Ln].

The aegirine from the pegmatites appears to be a more enriched version of the Pegmatite-Host Grennaite, displaying a full U-shaped pattern with more enrichment towards La and Lu and corresponding Y-Ho. This Aegirine can also consistently display up to 1 Wt% Zr (with up to 6 Wt% recorded in some analyses close to exsolved zones). Aegirine from the Kaxtorpите displays enriched levels of light-[Ln] with the heavy-[Ln] below detection.

The aegirines from the second phase of intrusion (Fig. 4.8) generally show higher overall [Ln]-concentrations than the first phase, and again exhibit U-shaped patterns. Aegirine within the Pulaskite appears to exhibit either a bias towards La or Lu, where aegirine from the enclaves is more light-[Ln] rich whereas the matrix aegirine is more heavy-[Ln] rich.

Figure 4.7: [Ln]-concentrations normalised to chondrite for aegirine from the Grennaites, Pegmatites and Kaxtorpите.

Figure 4.8: [Ln]-concentrations normalised to chondrite for aegirine from the Lakarpite and Pulaskite.

4.3.4 Aegirine Summary

The pyroxene content of Norra Kärr can be divided into the more abundant dark-green needle-shaped aegirines (with some component of aegirine-augite). In BSE-SEM images the cores of some aegirines are brighter than the rims, a texture commonly observed within Pilanesberg and ascribed by Andersen et al. (2017) to the inner cores of the aegirines containing higher concentrations of Zr. This is corroborated by Wt% Zr concentrations detected by LA-ICP-MS within aegirines from the Pegmatites. Overall, the compositions of the aegirines tend to be homogenous, displaying similar Na, Fe and Mn compositions. Variations in Ca and Ti are shown by aegirines from the Pulaskite and Lakarpite. In particular, the inner zones of the Lakarpite exhibit higher Ti than the outer Lakarpite zones. This effect may be due to the reaction of the Lakarpite contact with the Pegmatite-Host Grennaite. Trace element analysis shows that Y appears to be decoupled from Ho abundance, and that the U-shaped [Ln]-patterns within aegirines may be recording a crystallisation front within the Grennaites.

The compositions of the pyroxenes plotted in Fig. 4.6-D can be used to give an approximate indication of the oxidation state of the magma (Marks et al. 2008, Wu et al. 2016). Assessing the trends the analyses in Fig. 4.6-C fit with is difficult due to the highly evolved nature of the complex, but the data approximately lies between that of Motzfelt and Lovozero and Katzenbuckel suggesting that the oxygen fugacity of the magmas was approximately between FMQ +1 / -2 at the time of aegirine crystallisation.

4.4 Amphiboles

A total of 312 EPMA and 1920 LA-ICP-MS analyses of amphibole were collected. As yet no modern analyses have been published for the amphiboles of Norra Kärr. All the silica-rich lithologies are amphibole bearing with only one occurrence of amphibole in a pegmatite recorded thus far. A summary of the petrology is given below. It should be noted that amphibole should only accommodate eight Si atoms – however due to the complexity of amphiboles within alkaline systems it is generally accepted that totals can be higher due to certain elements (such as the lanthanoids) not being routinely measured (e.g. Vartiainen and Woolley 1976). The Kaxtorpite analyses do display particularly high Si-contents and this is likely due to appreciable amounts of Li which was not analysed at the time but has been previously reported by Deer et al. (1997). Analyses from Norra Kärr will be compared to those from Lovozero (Féménias et al. 2005), Mont St Hilaire Syenites (Shilling et al. (2011), Strange Lake (Segel et al. 2017), Pilanesberg (Andersen et al. 2017, Andersen et al. 2018) and Ilímaussaq (Augite-Syenite – Marks et Markl 2001, Kakortokite – Lindhuber et al. 2015).

4.4.1 SEM-EDS Petrology

Amphibole is found within the Kaxtorpite, Lakarpite and Pulaskite and is typically intergrown with aegirine. In the Kaxtorpite and Lakarpite it is the second forming mineral after aegirine; in Pulaskite it is the third forming mineral after aegirine and then biotite. In the Kaxtorpite amphibole forms elongated needles which enclose aegirine while being enclosed by pectolite. A coarse amphibole texture can be seen in some feldspathic rich parts of the Pulaskite. Amphibole is present in the core, Zr-core, and Zr-rich Lakarpite varieties with biotite being present in the Pulaskite-type Lakarpite. An amphibole was also found within a sample of pegmatite as a light blue subhedral crystal. None of the amphiboles appear to display zoning in BSE-SEM images (Fig. 4.9).

Figure 4.9: BSE-SEM images of amphibole from different lithologies in Norra Kärr. Red scale bar is equal to 100 μm . The amphiboles do not show any zoning in the BSE-images.

4.4.2 Substitutions

Amphiboles follow the structural formula:

Where:

A = Na, K,

B = Ca, Na, Mn,

C = Mg, Fe³⁺, Fe²⁺, Al, Ti, Mn, Cr, Li, Zn,

T = Si, Al,

OH = OH, F, Cl, O

(Deer et al. 1997)

Leake et al. (1997) classified amphiboles which display $(Ca+Na)_{[B]} \geq 1$ using ^[4]Al or Si content, Na_B (Fig. 4.10) and $(Na+K)_{[A]}$ (Fig. 4.11, the excess A-site occupancy is likely due to unanalysed Zn or Li). The summary of mean amphibole compositions is given in Table 4.4 (with trace element concentrations from LA-ICP-MS given in Table 4.5, and chondrite normalised values in Table 4.6). The major element analyses show that all amphiboles from Norra Kärr display $(Ca+Na)_{[B]} \geq 1$ and:

1. Have Si contents greater than 7,
2. Display $Na_{[B]} > 1.5$,
3. Display full $(Na+K)_{[A]}$ sites,

This classifies all the amphibole analyses as sodic-amphiboles field and they form part of the Eckermannite-Arfvedsonite series. This series is further classified using $Mg/(Mg+Fe^{2+})$ vs $Fe^{3+}/(Fe^{3+}+[6]Al)$ shown in Fig. 4.12, where the Fe²⁺ and Fe³⁺ contents of the amphiboles were modelled using a charge balance method. The amphiboles from the Kaxtorp and the single amphibole from the Pegmatites all lie close to the Ferro-Eckermannite - Arfvedsonite field. Indeed, Norra Kärr is the type locality for Eckermannite and was first described there by Adamson (1942, 1944). All other amphiboles are predominantly Arfvedsonites with some analyses plotting in the Magnesio-Arfvedsonite field. The inner two petrological zones of the Lakarpite plot close to the amphiboles from the Pulaskite and its enclaves. With the outer two petrological zones plotting further away.

Fig. 4.10 shows the variation in Si and Na_[B] for Norra Kärr and other alkaline intrusions with the Kaxtorp and Pegmatite amphiboles being the most evolved of the amphiboles from Norra Kärr. The amphiboles from the Pulaskite and its enclaves are the least evolved of the amphiboles and may show two different compositional trends. The Lakarpite amphiboles are intermediate between the other lithologies. In comparison to other alkaline intrusions, the Norra Kärr amphiboles fit the fractionation trend observed within the Foyaite of Pilanesberg. The Kaxtorp and Pegmatite amphiboles are similar only to the most fractionated amphiboles within the Pilanesberg Foyaite, while the Lakarpite amphiboles are similar to amphiboles from the Strange Lake intrusion. The Pulaskite and enclaves are similar to the Ilímaussaq Kakortokites and amphiboles from Lovozero, while amphiboles from the feldspar-rich positions of the Pulaskite share more affinity with the syenites of Mont St Hilaire than those from the enclaves. None of the amphiboles from Norra Kärr show similarities with the amphiboles from the Augite-Syenite of Ilímaussaq.

Figure 4.10: $\text{Na}_{[\text{B}]}$ vs Si for Norra Kärr amphiboles compared to amphiboles from other intrusions.

Figure 4.11: Na_A+K_A boxplot for amphiboles from Norra Kärr.

Figure 4.12: Classification plot for alkali ($\text{Na}_A+\text{K}_A > 0.5$) amphiboles from Norra Kärr.

	Pegmatite			Kaxtorpite			Lak-(P)			Lak-(Core)		
n=	5			124			11			28		
SiO ₂	57.19	+	0.16	56.26	+	0.61	53.27	+	0.20	53.69	+	0.44
		-	0.40		-	0.63		-	0.41		-	0.32
TiO ₂	0.13	+	0.002	0.26	+	0.04	0.49	+	0.36	0.47	+	0.10
		-	0.02		-	0.04		-	0.09		-	0.06
Al ₂ O ₃	7.40	+	0.15	6.52	+	0.45	1.56	+	0.06	1.56	+	0.24
		-	0.22		-	0.44		-	0.10		-	0.11
Li ₂ O	0.60	+	-	1.00	+	-	0.60	+	-	0.60	+	-
		-	-		-	-		-	-		-	-
FeO	12.96	+	0.20	8.91	+	0.54	17.74	+	3.65	18.76	+	0.21
		-	0.32		-	0.45		-	0.36		-	0.38
MnO	0.80	+	0.05	0.53	+	0.03	0.78	+	0.07	0.90	+	0.27
		-	0.07		-	0.05		-	0.24		-	0.06
MgO	6.20	+	0.07	9.34	+	0.17	9.27	+	0.18	9.18	+	0.17
		-	0.13		-	0.15		-	3.52		-	0.33
CaO	b.d.l.	+	0.06	0.13	+	0.03	1.47	+	2.05	1.00	+	0.20
		-	b.d.l.		-	0.03		-	0.32		-	0.17
Na ₂ O	9.86	+	0.03	9.81	+	0.15	8.77	+	0.67	8.87	+	0.18
		-	0.28		-	0.14		-	0.28		-	0.17
K ₂ O	2.46	+	0.10	2.46	+	0.07	2.35	+	0.17	2.40	+	0.11
		-	0.14		-	0.08		-	1.20		-	0.09
F	2.95	+	0.07	2.45	+	0.13	1.69	+	0.11	2.14	+	0.11
		-	0.02		-	0.11		-	0.87		-	0.03
Cl	b.d.l.	+	-	b.d.l.	+	-	b.d.l.	+	-	b.d.l.	+	-
		-	-		-	-		-	-		-	-
Total	97.61			95.23			96.29			97.44		
T-site												
Si	7.992			7.927			7.895			7.862		
Al[IV]	0.008			0.073			0.105			0.138		
Ti	0.000			0.000			0.000			0.000		
ΣT	8.000			8.000			8.000			8.000		
C-site												
AlVI	1.199			0.999			0.139			0.152		
Ti	0.014			0.028			0.054			0.052		
Li	0.336			0.566			0.357			0.353		
Mg	1.295			1.957			2.051			2.000		
Fe	1.501			1.054			2.197			2.286		
Mn	0.095			0.063			0.099			0.111		
ΣC	4.440			4.667			4.898			4.955		
ΣC-5	-0.560			-0.333			-0.102			-0.045		
B-site												
Ca	0.000			0.019			0.236			0.159		
Na	2.000			1.981			1.764			1.841		
ΣB	2.000			2.000			2.000			2.000		
A-site												
Na	0.663			0.704			0.686			0.677		
K	0.435			0.439			0.445			0.447		
ΣA	1.098			1.143			1.130			1.124		
X-site												
F	1.298			1.092			0.801			0.989		
Cl	0.000			0.000			0.000			0.000		
OH*	0.702			0.908			1.199			1.011		

Table 4.4 (continued on next page)

Lak-(Zr-Core)			Lak-(Zr-Rich)			Pulaskite			Pul-Enclave			n=
23			50			5			66			
55.30	+	0.20	52.00	+	1.19	48.82	+	0.29	49.22	+	0.38	SiO ₂
	-	0.38		-	0.43		-	0.27		-	0.78	
0.11	+	0.01	0.18	+	0.05	0.45	+	0.07	0.39	+	0.06	TiO ₂
	-	0.002		-	0.01		-	0.08		-	0.05	
2.50	+	0.12	1.83	+	0.14	3.38	+	0.04	2.22	+	0.27	Al ₂ O ₃
	-	0.26		-	0.13		-	0.19		-	0.17	
0.60	+	-	0.60	+	-	0.60	+	-	0.60	+	-	Li ₂ O
	-	-		-	-		-	-		-	-	
17.76	+	0.23	20.02	+	0.42	26.67	+	0.72	19.97	+	0.24	FeO
	-	0.27		-	0.27		-	1.08		-	0.23	
1.02	+	0.06	1.54	+	0.09	3.99	+	0.07	1.60	+	0.09	MnO
	-	1.02		-	0.07		-	0.19		-	0.09	
7.21	+	0.04	6.68	+	0.13	1.85	+	0.06	7.99	+	0.27	MgO
	-	0.09		-	0.18		-	0.01		-	0.10	
0.16	+	0.05	0.35	+	0.08	0.62	+	0.09	2.07	+	0.25	CaO
	-	0.02		-	0.02		-	0.002		-	0.22	
9.42	+	0.09	8.95	+	0.06	8.48	+	0.24	7.95	+	0.08	Na ₂ O
	-	0.14		-	0.08		-	0.55		-	0.12	
2.33	+	0.05	2.42	+	0.11	2.44	+	0.47	2.17	+	0.11	K ₂ O
	-	0.03		-	0.08		-	0.11		-	0.16	
2.45	+	0.23	1.73	+	0.16	1.08	+	0.09	1.30	+	0.10	F
	-	2.45		-	0.08		-	0.001		-	0.07	
b.d.l.	+	-	b.d.l.	+	-	b.d.l.	+	-	b.d.l.	+	-	Cl
	-	-		-	-		-	-		-	-	
96.40			94.57			97.29			94.17			Total
												T-site
8.076			7.948			7.508			7.491			Si
-0.076			0.052			0.492			0.392			Al[IV]
0.000			0.000			0.000			0.044			Ti
8.000			8.000			8.000			7.927			ΣT
												C-site
0.522			0.301			0.128			0.000			AlVI
0.012			0.021			0.052			0.000			Ti
0.357			0.368			0.371			0.367			Li
1.585			1.507			0.424			1.813			Mg
2.197			2.552			3.430			2.542			Fe
0.125			0.201			0.520			0.206			Mn
4.798			4.949			4.925			4.928			ΣC
-0.202			-0.051			-0.075			-0.072			ΣC-5
												B-site
0.025			0.057			0.102			0.338			Ca
1.975			1.943			1.898			1.662			Na
2.000			2.000			2.000			2.000			ΣB
												A-site
0.725			0.703			0.661			0.693			Na
0.438			0.469			0.474			0.420			K
1.163			1.172			1.136			1.114			ΣA
												X-site
1.125			0.835			0.527			0.626			F
0.000			0.000			0.000			0.000			Cl
0.875			1.164			1.473			1.373			OH*

Table 4.4: Representative EPMA analyses and calculated compositions of amphibole from Norra Kärr. Li₂O values are those used to model the charge balance within each analysis. Calculated so the total cations is never >16. Note the need Fe³⁺ for charge balance and that the total A site often is >1 and the C-site is often <5, indicating the omission of an element during analysis. *Data derived via calculation.

	Kaxtorpite			Lak-(P)			Lak-(Core)			Lak-(Zr-Core)			Lak-(Zr-Rich)			Pulaskite			Pul-Enclave			n =
	406			427			299			101			124			306			257			n =
Y	6.16	+	15.80	0.11	+	0.29	4.61	+	4.72	3.31	+	1.63	10.79	+	7.05	91.36	+	34.70	13.33	+	22.32	Y
		-	5.10		-	0.11		-	1.72		-	1.20		-	3.83		-	21.36		-	5.15	
La	9.00	+	32.43	0.60	+	2.24	30.23	+	15.09	0.42	+	3.41	b.d.l.	+	1.33	30.77	+	19.40	15.97	+	39.74	La
		-	8.55		-	0.47		-	14.89		-	0.42	b.d.l.	-	b.d.l.		-	9.09		-	10.19	
Ce	22.48	+	61.37	1.17	+	3.11	75.69	+	39.28	2.35	+	12.02	5.41	+	1.72	81.39	+	32.48	37.58	+	87.41	Ce
		-	18.51		-	0.79		-	36.10		-	1.62		-	2.04		-	24.59		-	21.26	
Pr	1.07	+	6.06	b.d.l.	+	0.24	7.56	+	4.15	0.02	+	1.06	0.55	+	0.64	11.01	+	3.86	2.69	+	8.47	Pr
		-	1.07		-	b.d.l.		-	3.86		-	0.02		-	0.48		-	3.29		-	2.69	
Nd	1.40	+	16.28	b.d.l.	+	0.71	24.58	+	16.62	b.d.l.	+	3.17	2.26	+	3.37	28.88	+	9.95	8.26	+	28.89	Nd
		-	1.40		-	b.d.l.		-	13.21		-	b.d.l.		-	1.94		-	10.59		-	8.26	
Sm	b.d.l.	+	0.02	b.d.l.	+	b.d.l.	3.11	+	2.75	b.d.l.	+	0.30	b.d.l.	+	0.02	b.d.l.	+	4.18	b.d.l.	+	4.79	Sm
		-	b.d.l.		-	b.d.l.		-	2.08		-	b.d.l.		-	b.d.l.		-	b.d.l.		-	b.d.l.	
Eu	b.d.l.	+	b.d.l.	b.d.l.	+	b.d.l.	0.06	+	0.28	b.d.l.	+	b.d.l.	b.d.l.	+	b.d.l.	b.d.l.	+	b.d.l.	b.d.l.	+	0.21	Eu
		-	b.d.l.		-	b.d.l.		-	0.06		-	b.d.l.		-	b.d.l.		-	b.d.l.		-	b.d.l.	
Gd	b.d.l.	+	0.35	b.d.l.	+	b.d.l.	1.43	+	1.88	b.d.l.	+	b.d.l.	b.d.l.	+	b.d.l.	1.49	+	3.51	b.d.l.	+	3.73	Gd
		-	b.d.l.		-	b.d.l.		-	1.17		-	b.d.l.		-	b.d.l.		-	1.49		-	b.d.l.	
Tb	b.d.l.	+	0.25	b.d.l.	+	b.d.l.	0.09	+	0.29	b.d.l.	+	b.d.l.	b.d.l.	+	b.d.l.	0.90	+	0.68	b.d.l.	+	0.78	Tb
		-	b.d.l.		-	b.d.l.		-	0.09		-	b.d.l.		-	b.d.l.		-	0.69		-	b.d.l.	
Dy	b.d.l.	+	1.90	b.d.l.	+	b.d.l.	0.64	+	1.16	b.d.l.	+	0.30	b.d.l.	+	0.70	6.66	+	4.69	0.87	+	3.55	Dy
		-	b.d.l.		-	b.d.l.		-	0.60		-	b.d.l.		-	b.d.l.		-	2.20		-	0.87	
Ho	b.d.l.	+	b.d.l.	b.d.l.	+	b.d.l.	b.d.l.	+	0.20	b.d.l.	+	0.01	b.d.l.	+	0.01	1.74	+	1.62	b.d.l.	+	0.68	Ho
		-	b.d.l.		-	b.d.l.		-	b.d.l.		-	b.d.l.		-	b.d.l.		-	1.08		-	b.d.l.	
Er	b.d.l.	+	0.87	b.d.l.	+	b.d.l.	b.d.l.	+	0.02	b.d.l.	+	b.d.l.	1.30	+	1.23	5.91	+	16.18	0.09	+	1.46	Er
		-	b.d.l.		-	b.d.l.		-	b.d.l.		-	b.d.l.		-	0.79		-	2.52		-	0.09	
Tm	b.d.l.	+	b.d.l.	b.d.l.	+	b.d.l.	b.d.l.	+	b.d.l.	b.d.l.	+	b.d.l.	b.d.l.	+	b.d.l.	b.d.l.	+	6.71	b.d.l.	+	0.01	Tm
		-	b.d.l.		-	b.d.l.		-	b.d.l.		-	b.d.l.		-	b.d.l.		-	b.d.l.		-	b.d.l.	
Yb	b.d.l.	+	0.78	b.d.l.	+	b.d.l.	b.d.l.	+	b.d.l.	b.d.l.	+	0.35	9.85	+	4.54	22.83	+	92.07	1.35	+	2.25	Yb
		-	b.d.l.		-	b.d.l.		-	b.d.l.		-	b.d.l.		-	2.60		-	7.23		-	1.04	
Lu	b.d.l.	+	b.d.l.	b.d.l.	+	b.d.l.	b.d.l.	+	b.d.l.	b.d.l.	+	0.22	2.44	+	0.98	8.89	+	16.91	0.22	+	0.31	Lu
		-	b.d.l.		-	b.d.l.		-	b.d.l.		-	b.d.l.		-	0.87		-	3.21		-	0.22	

Table 4.5: Representative LA-ICP-MS analyses for [Ln] and Y concentrations (ppm) within amphibole from Norra Kärr.

	Kaxtorpite	Lak-(P)	Lak-(Core)	Lak-(Zr-Core)	Lak-(Zr-Rich)	Pulaskite	Pul-Enclave	
n =	406	427	299	101	124	306	257	n =
Y	2.93	0.05	2.20	1.58	5.14	43.50	6.35	Y
La	24.53	1.62	82.38	1.13	b.d.l.	83.84	43.51	La
Ce	23.49	1.22	79.09	2.45	5.65	85.04	39.27	Ce
Pr	7.84	b.d.l.	55.17	0.11	3.99	80.40	19.66	Pr
Nd	1.97	b.d.l.	34.58	b.d.l.	3.17	40.62	11.61	Nd
Sm	b.d.l.	b.d.l.	13.48	b.d.l.	b.d.l.	b.d.l.	b.d.l.	Sm
Eu	b.d.l.	b.d.l.	0.69	b.d.l.	b.d.l.	b.d.l.	b.d.l.	Eu
Gd	b.d.l.	b.d.l.	4.69	b.d.l.	b.d.l.	4.86	b.d.l.	Gd
Tb	b.d.l.	b.d.l.	1.51	b.d.l.	b.d.l.	15.54	b.d.l.	Tb
Dy	b.d.l.	b.d.l.	1.67	b.d.l.	b.d.l.	17.48	2.30	Dy
Ho	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	20.49	b.d.l.	Ho
Er	b.d.l.	b.d.l.	b.d.l.	b.d.l.	5.23	23.73	0.38	Er
Tm	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	Tm
Yb	b.d.l.	b.d.l.	b.d.l.	b.d.l.	39.73	92.04	5.43	Yb
Lu	b.d.l.	b.d.l.	b.d.l.	b.d.l.	64.11	233.39	5.72	Lu

Table 4.6: Representative LA-ICP-MS analyses for [Ln] and Y concentrations (ppm) within amphibole from Norra Kärr normalised to chondrite (Taylor & McLennan 1985).

The main substitutes in Arfvedsonite are $\text{Mg} \rightleftharpoons \text{Fe}^{2+}$ and $\text{Al} \rightleftharpoons \text{Fe}^{3+}$, while Eckermannite displays $\text{Fe}^{3+} + [\text{M}3]\text{Li} = \text{Mg} + [\text{M}3]\text{Mg}$ (Deer et al. 1997). In addition to these Müller-Lorch et al. (2007) investigated the amphiboles within the Ilímaussaq complex and showed that the following substitutions were also important:

A number of these substitutions, along with others, will be investigated below.

A plot of K vs Na shows that the amphiboles lie along a linear trend around 0.4 to 0.6 a.p.f.u. with no great deviation in K concentration (Fig. 4.13). There is variation in Na content with the Kaxtorpite and Pegmatite amphiboles displaying the highest Na contents and the Pulaskite the Lowest Na contents. The Lakarpite exhibits a gradation between these compositions. Müller-Lorch et al. (2007) noted that based on observations from Ilímaussaq a linear pattern in K indicates that no hydrous-supercritical-phase exsolved from the magma suggesting that the formation of the amphiboles was by magmatic processes alone. Had a hydrous-phase been present any Na would partition into it forming a supercritical-hydrosaline phase leading to an increase in K in the amphiboles. Müller-Lorch et al. (2007) did show that the production of a supercritical-hydrosaline phase was a process that occurred within late-stage pegmatites at Ilímaussaq, however the K variation occurred in a distinct trend over >0.4 K atoms per formula unit which is not observed here. Compared to other intrusions the Norra Kärr amphiboles display similar compositions to those from Lovozero, the Mont St Hilare syenite, the Pilanesberg Foyites and the Kakortokite of Ilímaussaq. In terms of alkalinity they plot near to amphiboles from Strange Lake but display slightly higher K-contents. They do not have an affinity with the Aegirine-Syenite of Ilímaussaq which displays far lower Na contents.

On a Ca vs $\text{Na}_{[\text{A}]}$ plot Ca can be seen to be decreasing from the enclaves to the Kaxtorpite (Fig. 4.14). In general, there is an increase in Na and a decrease in Ca from the Pulaskite enclaves, through the Lakarpite and into the Kaxtorpite and Pegmatites. This suggests that the enclaves are the most primitive of the second-phase magmas, whereas the amphiboles in the first phase display little difference in composition. Compared to other intrusions the Norra Kärr amphiboles plot at the end of the Ca vs Na fractionation sequence, and match well with amphiboles from Lovozero, the Mont St. Hilare syenite, the Pilanesberg Foyites and the Kakortokite of Ilímaussaq and in this case those from Strange Lake. Again, there is no affinity with the Aegirine-Syenite of Ilímaussaq.

A plot of Ca vs Si shows that the Norra Kärr amphiboles are at the end of the fractionation trend (Fig. 4.15). Much like K vs Na, the Kaxtorpite and Pegmatite amphiboles are the most evolved, and the Pulaskite and Enclave amphiboles are the least evolved. The Lakarpite amphiboles are intermediate to the other analyses. Compared to other alkaline intrusions the Pulaskite and enclaves are similar to those from the Pilanesberg Foyites and the Kakortokite of Ilímaussaq. The most evolved amphiboles match compositions from Strange Lake.

Figure 4.13: K vs Na for Norra Kärr amphiboles compared to amphiboles from other intrusions.

Figure 4.14: Ca vs Na+K for Norra Kärr amphiboles compared to amphiboles from other intrusions.

Figure 4.15: Ca vs Si for Norra Kärr amphiboles compared to trends from other intrusions.

On an $\text{Al}^{[\text{VI}]}$ vs Si plot the amphiboles at Norra Kärr are located at the end of fractionation trend (Fig. 4.16) with the T-site is saturated with Si, leaving all Al in the lattice calculated to be in the C-site as $\text{Al}^{[\text{VI}]}$. Despite this, amphiboles from the Kaxtorp and Pegmatites display far higher $\text{Al}^{[\text{VI}]}$ than amphiboles from other lithologies at Norra Kärr and other alkaline intrusions. The Pulaskite and enclaves display the least evolved compositions, with the Lakarpite exhibiting intermediate compositions. Amphiboles from other intrusions display similar $\text{Al}^{[\text{VI}]}$ contents (apart from the Augite-Syenite of Ilímaussaq which instead contains between 1-2 a.p.f.u. $\text{Al}^{[\text{VI}]}$) with the Pulaskite and Enclave amphiboles being similar to those of Lovozero and the Kakaortokites of Ilímaussaq, and the Lakarpite being comparable to the Strange Lake amphiboles and those from the latter stages of fractionation in the Pilanesberg Foyite. As such, amphiboles from the Kaxtorp and Pegmatites appear to be distinctive in their composition relative to the known major alkaline intrusions.

Müller-Lorch et al. (2007) identified that $(\text{Na,K}) + \text{Si} \rightleftharpoons \text{Ca} + \text{Al}$ to be the most significant substitution within amphiboles during fractionation in Ilímaussaq. Fig. 4.17 shows this substitution for amphiboles from Norra Kärr and other alkaline intrusions. For Norra Kärr the pattern can be explained by a combination of higher Si and Na contents (K is typically 0.5 a.p.f.u.) and variation in $\text{Al}^{[\text{VI}]}$ due to the low Ca contents (0.5 a.p.f.u.). Similarities with other intrusions are the same as those described for Fig. 4.16 above.

Fig. 4.18-a shows the Na-Fe-Mg ternary plot for Norra Kärr amphiboles. Amphiboles on this plot tend to show either a variation in Mg-Fe or Fe-Na. Norra Kärr appears to display a Fe-Na trend (similar to the Fe-Na trend observed within the pyroxene data) within each lithology, though the lithologies are separated by differing Mg/Fe values. This suggests that each lithology has its own starting Mg/Fe variation which then evolved towards a more Na rich composition.

The only other alkaline intrusions to show similar trends are Strange Lake and the Ilímaussaq Kakortokites (Fig. 4.18-b). These rocks display similar Fe/Na compositions but far lower Mg-contents than Norra Kärr. In contrast, Lovozero, the Pilanesberg Foyites, Mont St Hilaire and the Augite-Syenite of Ilímaussaq all show variation in Mg-Fe instead. This can be seen on a Fe vs Mg plot (Fig. 4.19) where the overall trend within amphibole compositions is broadly linear. Norra Kärr amphiboles do not appear to greatly-vary in their Fe or Mg compositions. The Kaxtorp exhibits some of the highest Mg-contents and lowest-Fe contents which are matched by the low Fe-content of the pegmatite amphibole. There is some minor variation internally within the different Lakarpite varieties with a trend of decreasing Mg and increasing Fe by 1 a.p.f.u. each. The Pulaskite and enclaves display a compositional variation, with the enclaves displaying a more Mg-rich composition, and the amphiboles within the feldspar-rich portion of the Pulaskite are more Fe-rich. However, it appears that the Mg content of each lithology does not vary enough to affect the Na-Fe-Mg ternary plot (Fig. 4.18-b). While the both Strange Lake and the Ilímaussaq Kakortokites display similar Na/Fe ratios on the Na-Fe-Mg ternary, they exhibit far higher Fe contents than Norra Kärr; while the other intrusions display more similar amphibole compositions, including the Augite-Syenite of Ilímaussaq.

Figure 4.16: Al^{VI} vs Si for Norra Kärr amphiboles compared to amphiboles from other intrusions.

Figure 4.17: $Ca+Al^{VI}$ vs $Na+K+Si$ for Norra Kärr amphiboles compared to other intrusions.

Figure 4.18: Ternary plot of Na-Fe-Mg for: (a) Norra Kärr amphiboles, (b) amphiboles from other intrusions (all data from Norra Kärr in grey for comparison).

Figure 4.19: Fe_{Total} vs Mg for Norra Kärr amphiboles compared to amphiboles from other intrusions.

Figure 4.20: Ti vs $Mg/(Fe+Mg)$ for Norra Kärr amphiboles compared to amphiboles from other intrusions.

Figure 4.21: Mn vs Fe_{Total} for Norra Kärr amphiboles compared to amphiboles from other intrusions.

Fig. 4.20 shows the variation in Ti vs $Mg/(Fe+Mg)$. The Kaxtorpite and the outer Lakarpite varieties vary in $Mg/(Fe+Mg)$ by approximately 0.2, while greater variation is seen in the Pulaskite and the inner zone of the Lakarpite (the Pulaskite-type Lakarpite). There is little variation in Ti content, with only the Pulaskite enclaves showing variations >0.1 . There does appear to be a slight decrease in Ti from the inner two zones of the Lakarpite to the outer two zones. Amphiboles from Norra Kärr exhibit lower concentrations of Ti compared to other alkaline intrusions. Amphiboles from Mont St Hilaire, Pilanesberg Foyites and the Augite Syenite of Ilímaussaq show Ti concentrations up to 0.5 a.p.f.u..

On a Mn vs Fe plot (Fig. 4.21) the Norra Kärr amphiboles exhibit low concentrations of Mn, with the Kaxtorpite displaying the lowest Mn-content and the Pulaskite displaying the highest Mn-contents. The Lakarpite varieties show intermediate compositions to these. This pattern is converse to the trend in Mn/Fe observed in the whole-rock data which shows that the Pulaskite having the lowest MnO concentrations while the Kaxtorpite has the highest concentrations. Compared to other alkaline intrusions the Norra Kärr amphiboles plot on a near identical trend to the Pilanesberg Foyites. This trend also overlaps with amphiboles from Lovozero. The Ilímaussaq amphiboles plot on a separate trend with lower Mn values, with the compositions of amphiboles from Strange Lake overlapping with the Ilímaussaq Kakortokites. The Mount St Hilaire amphiboles from a separate trend with higher Mn concentrations.

Fig. 4.22 shows the variation in Fe^{2+} and Fe^{3+} for the amphiboles as derived from charge balance calculations. The amphiboles from the Kaxtorpite and Pegmatites consistently display the lowest Fe^{2+} values, with the Pulaskite and Lakarpite marking a separate trend. The amphiboles within the feldspathic matrix of the Pulaskite appear to be more Fe^{2+} -rich than those from the enclaves. Marks and Markl (2003) identified that the amphiboles of an agpaitic dyke rock connected to the Ilímaussaq intrusion showed that a substitution of Si for Al is charge balanced by the exchange of Fe^{2+} for Fe^{3+} . However, as the T-site of the amphiboles is nearly entirely occupied by Si there is little to no substitution of Si by Al^{IV} . This leads to any variations in Fe^{3+} being due to the oxygen fugacity of the magma rather than due to its role in charge balancing any substitutions in the T-site. Here the Kaxtorpite, Pegmatites and the Pulaskite Enclaves indicate more oxidised compositions vs the more reduced Lakarpite composition.

These patterns reflect the ranges of whole rock- Fe^{2+}/Fe^{3+} presented later in Chapter 5 (see grey markers in Fig. 4.22). As amphibole is the mineral which displays the widest variation in Fe^{2+}/Fe^{3+} it is likely that the overall redox of the rocks is being displayed by the amphibole content.

Figure 4.22: Calculated Fe^{3+} vs Fe^{2+} for Norra Kärr amphiboles.

Figure 4.23: F vs $\text{Mg}/(\text{Fe}+\text{Mg})$ for Norra Kärr amphiboles compared to other intrusions.

4.4.3 Volatile Content of the Amphiboles

Fig. 4.53 shows the range of F in relation to $\text{Mg}/(\text{Fe}/\text{Mg})$, with Figs. 4.24 and 4.25 showing the measured wt% F contents of the Norra Kärr lithologies and from other alkaline intrusions. The Pulaskite and Lakarpite amphiboles appear more fractionated than the Kaxtorpite, with the Kaxtorpite displaying consistently higher F contents than the Pulaskite. The Norra Kärr amphiboles match a similar trend to those of the Pilanesberg Foyites and are similar in F content to those from Strange Lake; amphiboles from the major alkaline intrusions also exhibit the very low Cl contents observed at Norra Kärr.

Figure 4.24: Boxplots for the wt% F content of amphiboles from Norra Kärr.

Figure 4.25: Boxplots for the wt% F content of amphiboles from other alkaline intrusions. The amphiboles from Norra Kärr are particularly F-rich when compared to those from other intrusions.

4.4.4 Trace Elements

Similar to the aegirines, the analysed amphiboles generally display relatively flat [Ln]-profiles apart from a bias towards light-[Ln] (Fig. 4.26).

Figure 4.26: Median [Ln]-concentrations for Norra Kärr amphibole normalised to chondrite. The plot shows a relatively flat profile with only a slight preference for light-[Ln].

4.4.5 Amphibole Summary

Like other many other amphiboles from alkaline intrusions amphiboles from Norra Kärr are sodic in composition and appear to display restricted individual fractionation trends. They match the range of Na and K compositions of other alkaline amphiboles and are at the more fractionated end of the Ca-fractionation sequence (low Ca contents). Further the overall pattern of Na and K shows that there was no separate hydrous-supercritical phase present during amphibole crystallisation unlike at the later stages of Ilímaussaq. On a Na-Mg-Fe ternary the amphiboles from other intrusions show Mg-Fe fractionation series; in contrast the Norra Kärr amphiboles display a more limited range of compositions. Restricted variations in composition are also shown by Fe, Mg, Ti and Mn, with the Norra Kärr amphiboles having particularly low Ti contents compared with amphiboles from other intrusions. In terms of volatile content all the amphiboles from Norra Kärr are F-rich, unlike most other alkaline intrusions which are OH-rich.

Compositionally the Norra Kärr amphiboles are most similar to the more amphiboles from the Pilanesberg Foyites and plot on top of Pilanesberg fractionation trends (e.g. Mn). They are also similar to amphiboles from Lovozero and the Ilímaussaq Kakortokites (in contrast with the Ilímaussaq Augite-Syenite whose amphiboles are only similar to Norra Kärr in terms of K vs Na). The

Kakortokites formed late in the Ilímaussaq fractionation series and show rhythmic layering which is absent at Norra Kärr. The compositional similarities may therefore relate to similarities in the overall fractionation stage of the magma as also shown by their bearing little relation to the Augite-Syenite which was one of the earlier units at Ilímaussaq. Amphiboles from Norra Kärr only share some similarities with those from Strange Lake and Mont St Hilaire in terms of Ca, Al and Si content. Notably, while the Strange Lake amphiboles are far more evolved in terms of Mg/Fe+Mg they are the only amphiboles that significantly overlap with Norra Kärr in terms of F content.

Sundis (1945) has previously reported up to 0.59 wt% ZnO and 1.15 wt% Li₂O with amphiboles from the Kaxtorp. Hence, unanalysed Zn may be responsible for the issue of excess Na+K in the A-site, and missing cations in the C-site for the composition calculations. As Li₂O could not be measured via EPMA it was modelled using 0.6 Wt% Li₂O, 1 Wt% Li₂O for the Kaxtorp (0.34 – 0.56 Li a.p.f.u.) in order to reach a charge balanced solution. In comparison, Siegel et al. (2017) reported that amphiboles from Strange Lake contain between 0.06-0.11 a.p.f.u. Zn and between 0.15-0.74 a.p.f.u. Li. Siegel et al. (2017) ascribed the concentration of Zn and Li within the magma as being due to initially high magmatic concentrations and incompatibility with the minerals forming within the melt. Where the Zn did decrease within amphiboles this was due to other Zn-bearing phases crystallising from the melt. As such the high levels of Li and Zn within the Kaxtorp amphiboles is likely due to the first magmatic phase at Norra Kärr being initially rich in the elements which were then progressively enriched in the remaining melt due to the Grennaites containing no Zn- or Li bearing phases.

Overall, the amphibole compositions show that the magmas at Norra Kärr are highly fractionated. However, each lithology does not appear to exhibit an amphibole fractionation trend suggesting that fractionation during crystallisation was restricted and as such the amphiboles appear to show only a snapshot of their surrounding chemical compositions. Amphiboles from the Kaxtorp and Pegmatites tend to overlap in or display similar compositions (although the Kaxtorp has higher Mg/(Fe+Mg) than the Pegmatites) suggesting that the two lithologies may be chemically related, supporting the evidence presented in Chapter 4 for both lithologies being part of a single intrusive phase. Similarly, the Pulaskite and Lakarpite amphiboles display similar compositions supporting a relationship based upon a second magmatic phase of intrusion. The feldspathic and enclave portions of the Pulaskite have similar compositions supporting their relationship. The amphiboles within the Lakarpite indicate internal differences within the lithology. The inner Lakarpite zones showing compositions similar to the Pulaskite, while the outer Lakarpite zones tend to plot closer to the compositions of the Kaxtorp and the Pegmatite amphiboles.

The Fe²⁺/Fe³⁺ ratio of a magma is controlled in part by the fO₂ (Siegel et al. 2017) and may have been recorded by the amphibole composition. A lack of chemical zoning within the amphiboles potentially points to 'static' fO₂ early on in the fractionation sequence, and the lack of evidence for an exsolved hydrous supercritical-fluid suggests that the magma was not degassing its volatile content to the extent of affecting the fO₂ physically. However, the Fe²⁺ and Fe³⁺ are also affected by substitutions in the C-site and by the concentration of volatiles; and it has also been shown that in peralkaline igneous systems, high concentrations of F⁻ and OH⁻ in the melt allow more Fe³⁺ to be present at a given fO₂ (Birkett et al., 1996; Giehl et al., 2013). While there do appear to be different trends in Fe²⁺ and Fe³⁺ at Norra Kärr between the Kaxtorp and Pegmatites and the Pulaskite and Lakarpite, further work would be required to show whether the amphiboles may have recorded a primary difference in magmatic Fe²⁺ and Fe³⁺.

4.5 Pectolite

A total of 15 EPMA and 230 LA-ICP-MS analyses of pectolite were collected. Pectolite is only present within the Crenulated Grennaite and the Kaxtorpite. A summary of the petrology is given below, with major element analyses given in Table 4.7, trace element concentrations from LA-ICP-MS are given in Table 4.8, and chondrite normalised values in Table 4.9.

4.5.1 SEM-EDS Petrology

Pectolite is identifiable in BSE-SEM images as coarse anhedral crystals displaying strong cleavage planes (Fig. 4.27).

Figure 4.27: BSE-SEM images of pectolite. Red scale bar is equal to 100 μm .

4.5.2 Substitutions

Pectolite follows the structural formula:

(Deer et al. 1997)

The main substitutions are between Ca and Mn with the Mn variety being Schizolite. Fig. 4.28 shows that pectolites from the Kaxtorpite are close to the Ca-endmember composition while those from the Crenulated Grennaite are of intermediate Ca-Mn composition (likely marshallussmanite but further structural work would be required to confirm this).

Pectolite typically forms as a primary mineral during the later magmatic stages in alkaline intrusions (Deer et al. 1997, Anderson et al. 2018). This appears to be the case at Norra Kärr, with the pectolite being texturally later than aegirine/aegirine-amphibole crystallisation with large crystals being observed within the later forming Crenulated Grennaite and the Kaxtorpite. The higher Mn content within the pectolite from the Crenulated Grennaite is likely due to the increase in Mn due to fractionation of the Grennaite. The formation of OH-rich pectolite in the Kaxtorpite likely indicates a decrease in F-activities due to F-rich amphibole crystallisation pushing the system to a higher H_2O activity. It may also have formed as a sink for the remaining Ca within the magma due to the lack of fluorite with which to form fluorite.

Pectolite of a similar Ca-Mn composition to that from the Crenulated Grennaite is also found within the green foyites of Pilanesberg, however, pectolite from the Kaxtorpite displays no relation to that from Pilanesberg as it is far more Ca-rich.

Crenulated				Kaxtorpите			
n=	5			10			n=
SiO ₂	51.67	+	0.31	53.50	+	0.11	SiO ₂
		-	0.64		-	0.13	
FeO	0.82	+	0.01	0.36	+	0.05	FeO
		-	0.13		-	0.04	
MnO	18.85	+	0.26	3.41	+	0.60	MnO
		-	0.003		-	0.15	
MgO	0.08	+	0.0001	b.d.l.	+	b.d.l.	MgO
		-	0.01		-	b.d.l.	
CaO	15.76	+	0.05	30.47	+	0.36	CaO
		-	0.08		-	0.48	
Na ₂ O	8.98	+	0.01	9.31	+	0.09	Na ₂ O
		-	0.05		-	0.06	
Total	96.17			97.06			Total
<i>Number of ions on the basis of 8 O and 1 OH</i>							
Si	3.012			2.993			Si
Fe	0.041			0.017			Fe
Mn	0.938			0.161			Mn
Mg	0.007			0.000			Mg
Ca	0.985			1.834			Ca
Na	1.010			1.013			Na

Table 4.7: Representative EPMA analyses and calculated compositions of Pectolite from Norra Kärr. OH is assumed to fill the X-site to total 1.

Figure 4.28: Mn vs Ca for Pectolites from Norra Kärr and the Pilansberg Foyites.

Crenulated				Kaxtorpите			
n =	37			193			n =
Y	6389.66	+	396.00	41.20	+	29.77	Y
		-	552.55		-	14.16	
La	280.90	+	31.23	41.56	+	56.84	La
		-	35.37		-	19.79	
Ce	1387.92	+	138.33	69.35	+	72.22	Ce
		-	190.60		-	43.01	
Pr	274.55	+	30.88	17.44	+	16.49	Pr
		-	35.15		-	9.61	
Nd	1320.70	+	234.81	34.83	+	29.37	Nd
		-	126.48		-	20.82	
Sm	486.64	+	48.47	12.16	+	8.32	Sm
		-	58.98		-	7.34	
Eu	56.17	+	5.20	4.68	+	2.39	Eu
		-	4.14		-	2.49	
Gd	658.02	+	61.38	24.23	+	10.95	Gd
		-	83.25		-	13.39	
Tb	131.82	+	11.80	9.36	+	4.03	Tb
		-	17.17		-	4.51	
Dy	1019.45	+	67.34	80.96	+	32.55	Dy
		-	176.64		-	38.24	
Ho	280.74	+	36.05	21.71	+	8.64	Ho
		-	40.46		-	8.76	
Er	975.86	+	184.13	72.70	+	32.31	Er
		-	101.66		-	34.21	
Tm	141.95	+	30.73	10.98	+	5.03	Tm
		-	17.80		-	3.73	
Yb	1447.70	+	194.82	85.20	+	40.22	Yb
		-	213.19		-	39.87	
Lu	167.34	+	34.86	12.34	+	4.76	Lu
		-	20.24		-	4.26	

Table 4.8: Representative LA-ICP-MS analyses for Y and [Ln] for Pectolites from Norra Kärr.

Crenulated		Kaxtorpите	
n=	37	193	n=
Y	3042.7	19.6	Y
La	765.4	113.2	La
Ce	1450.3	72.5	Ce
Pr	2004.0	127.3	Pr
Nd	1857.5	49.0	Nd
Sm	2106.7	52.7	Sm
Eu	645.6	53.8	Eu
Gd	2150.4	79.2	Gd
Tb	2272.8	161.3	Tb
Dy	2675.7	212.5	Dy
Ho	3299.0	255.1	Ho
Er	3919.1	291.9	Er
Tm	3987.5	308.5	Tm
Yb	5837.5	343.5	Yb
Lu	4392.1	324.0	Lu

Table 4.9: Representative LA-ICP-MS analyses for Y and [Ln] from for Pectolites from Norra Kärr normalised to chondrite (Taylor & McLennan 1985).

4.5.3 Trace Elements

The [Ln]-plot for pectolite (Fig. 4.29) shows that in both the Crenulated Grennaite and the Kaxtorpite the mineral displays a bias towards the heavy-[Ln]. Y is coupled with Ho in the pectolite from Crenulated Grennaite but not in those from the Kaxtorpite.

The pectolite from the Crenulated Grennaite displays far higher [Ln] concentrations than pectolite from the Kaxtorpite, as can be seen in the whole-rock-[Ln] patterns for these lithologies. The pectolites do have a stronger bias towards the heavy-[Ln] than seen in the whole-rock patterns; however, they do not have a strong influence on the whole-rock composition given that pectolite makes up <5% of the minerology of the lithologies.

Figure 4.29: Y and [Ln]-concentrations for Norra Kärr pectolite normalised to chondrite.

4.6 Rosenbushite

A total of 9 EPMA and 340 LA-ICP-MS analyses of rosenbushite were collected. As yet no modern analyses have been published for the rosenbushite at Norra Kärr. Rosenbushite is only present within the core of the Lakarpite, and within and around the edge Pulaskite enclaves. A summary of the petrology is given below. Major element analyses are given in Table 4.10, trace element concentrations from LA-ICP-MS given in Table 4.11, and chondrite normalised values in Table 4.12.

4.6.1 SEM-EDS Petrology

Rosenbushite is identifiable in BSE-SEM images as bright needle-shaped crystals (Fig. 4.30). Rosenbushite typically forms masses of needles. These masses are smaller within the Lakarpite than the Pulaskite.

Figure 4.30: BSE-SEM images of rosenbushite. Red scale bar is equal to 100 μm .

4.6.2 Substitutions

Rosenbushite follows the structural formula:

Where:

X = OH, F, Cl, O

(Deer et al. 1997)

The main substitutions are between Zr and Ti. There appears to be little compositional difference between rosenbushites from Norra Kärr. In terms of Ti vs Zr (Fig. 4.31) and Na vs Ca (Fig. 4.32) rosenbushites from Norra Kärr are richer in Ti and Ca but display similar Wt% F to rosenbushites from the Langesundsford (Andersen et al. 2010) (Fig. 4.33). Overall rosenbushite shows that F and Ti were dominant in the Norra Kärr magmas system at the time of crystallisation.

7.1-Lak(P)				7.2-Lak(Core)			
n=		3			6		n=
SiO ₂	32.55	+	0.95	32.17	+	0.00	SiO ₂
		-	0.27		-	0.00	
ZrO ₂	8.26	+	0.04	11.59	+	0.00	ZrO ₂
		-	1.01		-	0.00	
HfO ₂	0.15	+	0.00	0.18	+	0.00	HfO ₂
		-	0.01		-	0.00	
TiO ₂	12.38	+	1.21	11.70	+	0.00	TiO ₂
		-	0.53		-	0.00	
[Ln] ₂ O ₃ *	1.00	+	0.00	1.07	+	0.00	[Ln] ₂ O ₃ *
		-	0.00		-	0.00	
CaO	30.46	+	0.70	30.74	+	0.00	CaO
		-	0.53		-	0.00	
Na ₂ O	7.60	+	0.34	8.71	+	0.00	Na ₂ O
		-	0.24		-	0.00	
F	7.45	+	0.33	8.46	+	0.00	F
		-	0.15		-	0.00	
-O=(F,Cl)	3.14	+	0.14	3.56	+	0.00	-O=(F,Cl)
		-	0.06		-	0.00	
Total		96.71		101.06			Total
<i>Numbers of ions on the basis of 9 (O,OH,F) or 6 cations</i>							
Si		2.085		2.012			Si
Ti		0.590		0.547			Ti
Zr		0.254		0.346			Zr
Hf		0.003		0.003			Hf
[Ln]*		0.026		0.030			[Ln]*
Na		0.933		1.060			Na
Ca		2.090		2.015			Ca
F		1.488		1.646			F
O ²⁻ *		0.732		0.582			O ²⁻ *
OH ⁻ *		0.236		0.226			OH ⁻ *

Table 4.10: Representative EPMA analyses and calculated compositions of Rosenbushite from Norra Kärr. Cl was analysed but was b.d.l.. Bulk [Ln] concentrations were derived from LA-ICP-MS analysis on a suite of Rosenbushite from each lithology. *Data derived via calculation.

Lakarpite-Pul				Lakarpite-Core			Pulaskite-Enclaves		
n =	162			131			47		n =
La	213.62	+	155.04	276.91	+	75.85	850.38	+	197.18
		-	97.07		-	60.37		-	394.42
Ce	507.49	+	404.34	776.93	+	205.96	1635.01	+	537.88
		-	210.18		-	203.63		-	685.78
Pr	202.63	+	491.72	211.54	+	807.48	254.19	+	115.32
		-	114.94		-	112.85		-	110.15
Nd	2103.17	+	1687.76	3189.76	+	1122.72	944.91	+	287.22
		-	1474.12		-	2664.07		-	375.88
Sm	785.89	+	377.04	821.32	+	134.85	585.42	+	369.88
		-	337.81		-	162.20		-	195.56
Eu	127.50	+	72.85	146.44	+	23.97	56.28	+	18.46
		-	47.34		-	30.93		-	20.17
Gd	898.87	+	402.10	821.26	+	77.23	608.97	+	171.63
		-	368.68		-	189.60		-	189.23
Tb	222.47	+	99.74	187.22	+	23.88	143.97	+	39.42
		-	85.97		-	39.30		-	47.96
Dy	1574.25	+	584.68	1219.20	+	157.32	1179.54	+	457.11
		-	546.60		-	308.24		-	315.91
Ho	358.68	+	133.09	264.57	+	40.20	286.03	+	95.16
		-	133.47		-	63.21		-	80.92
Er	832.81	+	235.87	599.77	+	110.72	1194.73	+	292.90
		-	311.82		-	167.17		-	404.25
Tm	109.95	+	35.02	88.64	+	16.84	179.36	+	61.39
		-	40.68		-	35.06		-	74.19
Yb	609.82	+	213.16	545.91	+	125.86	1319.08	+	420.27
		-	215.28		-	228.39		-	452.04
Lu	76.73	+	26.90	68.34	+	12.70	167.34	+	34.55
		-	28.58		-	26.60		-	56.14

Table 4.11: Representative LA-ICP-MS analyses for Y and [Ln] concentrations (ppm) within Rosenbushite from Norra Kärr.

Lakarpite-Pul		Lakarpite-Core		Pulaskite-Enclaves	
n=	162	131	47	n=	
La	582	755	2317	La	
Ce	530	812	1708	Ce	
Pr	1479	1544	1855	Pr	
Nd	2958	4486	1329	Nd	
Sm	3402	3555	2534	Sm	
Eu	1466	1683	647	Eu	
Gd	2937	2684	1990	Gd	
Tb	3836	3228	2482	Tb	
Dy	4132	3200	3096	Dy	
Ho	4215	3109	3361	Ho	
Er	3345	2409	4798	Er	
Tm	3088	2490	5038	Tm	
Yb	2459	2201	5319	Yb	
Lu	2014	1794	4392	Lu	

Table 4.12: Representative LA-ICP-MS analyses for [Ln] and Y concentrations (ppm) within Rosenbushite from Norra Kärr normalised to chondrite (Taylor & McLennan 1985).

Figure 4.31: Ti vs Zr for Rosenbushite from Norra Kärr and the Langesundsfjord.

Figure 4.32: Na vs Ca for Rosenbushite from Norra Kärr and the Langesundsfjord.

Figure 4.33: Wt% F vs Zr for Rosenbushite from Norra Kärr and the Langesundsfjord.

4.6.3 Trace Elements

The [Ln]-plot for rosenbushite (Fig. 4.34) shows relatively 'flat' [Ln]-patterns. Rosenbushite from the Lakapite displays an unturned U-shaped pattern, while rosenbushite from the Pulaskite enclaves appears to be slightly more enriched in the heavy-[Ln] than the Light-[Ln]. All display Eu-anomalies. These patterns suggest that rosenbushite fractionation is not able to significantly alter the [Ln]-patterns of lithologies but is a major [Ln]-bearing mineral reducing the overall concentration of the elements within the melt.

Figure 4.34: [Ln]-concentrations for Norra Kärr rosenbushite normalised to chondrite. The plot shows a relatively flat profile with only a slight preference for heavy-[Ln].

4.7 Sphene

A total of 37 EPMA and 240 LA-ICP-MS analyses of sphene were collected. As yet no modern analyses have been published for the sphene at Norra Kärr. Sphene is present within Pulaskite and Lakarpite

4.7.1 SEM-EDS Petrology

Sphene is present as euhedral-to-subhedral crystals within the Pulaskite and Lakarpite. It shows little to no zoning in BSE (Fig. 4.35)

Figure 4.35: BSE-SEM images of sphene. Red scale bar is equal to 100 μm .

4.7.2 Substitutions

Sphene follows the structural formula:

Where:

X = OH, F, Cl, O

(Deer et al. 1997)

The representative analysis for the sphene from the Pulaskite is shown in Tables 4.13, with trace element concentrations from LA-ICP-MS given in Table 4.14, and chondrite normalised values in Table 4.15. The main substitutions for sphene lie within the X-site. Along with rosenbushite, sphene is the main Ca-bearing mineral within the Pulaskite. Ca does substitute for Na (Deer et al. 1997) a substitution observed in sphenes from the Saima (Wu et al. 2016) and Pilanesberg (Andersen et al. 2017) intrusions, but not within the Ca-dominated sphenes from Norra Kärr (Fig. 4.36) despite the Pulaskite being richer in bulk rock Na_2O than CaO . Norra Kärr sphene also shows lower amounts to Ti than sphene from the Saima and Pilanesberg intrusions (Fig. 4.37).

4.7.3 Trace Elements

The [Ln]-plot for sphene (Fig. 4.38) shows that Y and Ho appear to be coupled within the samples analysed, and a [Ln] profile biased towards the light-[Ln] particularly with regards to the sphene in the Pulaskite. This suggests that sphene fractionation is able to significantly bias later lithologies towards enrichment in the heavy-[Ln]. However, sphene is in very low abundance (<1%) within the Lakarpite and Pulaskite which both show restricted fractionation profiles and slight enrichment in the light-[Ln]. Therefore, sphene crystallisation within the magma is unlikely to have been significant prior to emplacement.

Pulaskite			
n=	37		
SiO ₂	29.07	+	0.18
		-	0.08
TiO ₂	36.74	+	0.16
		-	0.09
[Ln] ₂ O ₃ *	4.82	+	0.00
		-	0.00
Y ₂ O ₃ *	0.43	+	0.00
		-	0.00
Al ₂ O ₃	1.21	+	0.06
		-	0.06
FeO	1.43	+	0.04
		-	0.05
MnO	0.18	+	0.02
		-	0.01
MgO	0.01	+	0.01
		-	0.01
CaO	27.78	+	0.17
		-	0.12
Na ₂ O	0.03	+	0.01
		-	0.01
K ₂ O	b.d.l.	+	0.01
		-	b.d.l.
F	0.37	+	0.05
		-	0.05
-O=(F,Cl)	0.15	+	0.02
		-	0.02
Total	101.91		
<i>Numbers of ions on the basis of 4 cations</i>			
Si	0.92		
Al	0.05		
Fe	0.11		
Ti	0.88		
Mg	0.00		
Mn	0.00		
Na	0.00		
[Ln]*	0.09		
Y*	0.01		
Ca	0.94		
K	0.00		
F	0.04		
O ²⁻ *	0.65		
OH*	0.12		

Table 4.13: Representative EPMA analysis and calculated compositions of Sphene from Norra Kärr. Cl was analysed but was b.d.l.. Y and [Ln] concentrations were derived from LA-ICP-MS analysis on a suite of Rosenbushite from each lithology.

Lakarpite-Pulaskite				Lakarpite-Core			Pulaskite			
n =	34			49			157			n =
Y	0.06	+	10.78	48.31	+	10.16	3383.45	+	1902.38	Y
		-	0.06		-	25.61		-	333.08	
La	1.20	+	0.56	974.82	+	131.55	7053.25	+	1124.75	La
		-	1.20		-	628.29		-	964.33	
Ce	3.22	+	19.65	1493.67	+	970.41	18634.42	+	6830.49	Ce
		-	2.76		-	1344.30		-	2814.45	
Pr	b.d.l.	+	0.26	201.33	+	28.65	2231.22	+	1041.53	Pr
		-	b.d.l.		-	114.71		-	347.05	
Nd	b.d.l.	+	1.29	594.61	+	84.46	7711.33	+	7157.93	Nd
		-	b.d.l.		-	301.83		-	1277.77	
Sm	b.d.l.	+	b.d.l.	57.99	+	16.98	1203.55	+	1118.67	Sm
		-	b.d.l.		-	24.24		-	197.18	
Eu	b.d.l.	+	b.d.l.	8.07	+	0.73	295.02	+	46.71	Eu
		-	b.d.l.		-	4.85		-	24.40	
Gd	b.d.l.	+	b.d.l.	24.63	+	6.41	1044.37	+	864.43	Gd
		-	b.d.l.		-	11.47		-	133.09	
Tb	b.d.l.	+	b.d.l.	2.69	+	0.70	126.56	+	86.72	Tb
		-	b.d.l.		-	0.84		-	19.45	
Dy	b.d.l.	+	b.d.l.	12.67	+	3.11	667.64	+	415.51	Dy
		-	b.d.l.		-	5.97		-	98.72	
Ho	b.d.l.	+	b.d.l.	1.08	+	0.62	127.39	+	81.37	Ho
		-	b.d.l.		-	0.41		-	14.40	
Er	b.d.l.	+	b.d.l.	0.55	+	0.63	408.81	+	246.66	Er
		-	b.d.l.		-	0.55		-	56.22	
Tm	b.d.l.	+	b.d.l.	b.d.l.	+	b.d.l.	57.01	+	35.07	Tm
		-	b.d.l.		-	b.d.l.		-	9.11	
Yb	b.d.l.	+	b.d.l.	b.d.l.	+	b.d.l.	480.71	+	266.73	Yb
		-	b.d.l.		-	b.d.l.		-	77.89	
Lu	b.d.l.	+	b.d.l.	b.d.l.	+	b.d.l.	68.48	+	25.29	Lu
		-	b.d.l.		-	b.d.l.		-	14.12	

Table 4.14: Representative LA-ICP-MS analyses for Y and [Ln] concentrations (ppm) within Sphene from Norra Kärr.

NK57-116.7 (LAK-P)		NK57-107.3 (LAK-C)		NK62-94.3 (Pul-En)	
n=	34	49	157	n=	
Y	0.03	23.00	1611.17	Y	
La	3.26	2656.19	19218.66	La	
Ce	3.37	1560.78	19471.70	Ce	
Pr	b.d.l.	1469.54	16286.28	Pr	
Nd	b.d.l.	836.31	10845.75	Nd	
Sm	b.d.l.	251.04	5210.19	Sm	
Eu	b.d.l.	92.80	3391.09	Eu	
Gd	b.d.l.	80.49	3412.98	Gd	
Tb	b.d.l.	46.32	2182.03	Tb	
Dy	b.d.l.	33.24	1752.35	Dy	
Ho	b.d.l.	12.69	1496.89	Ho	
Er	b.d.l.	2.21	1641.80	Er	
Tm	b.d.l.	b.d.l.	1601.54	Tm	
Yb	b.d.l.	b.d.l.	1938.35	Yb	
Lu	b.d.l.	b.d.l.	1797.32	Lu	

Table 4.15: Representative LA-ICP-MS analyses for Y and [Ln] concentrations (ppm) within Sphene from Norra Kärr normalised to chondrite (Taylor & McLennan 1985).

Figure 4.36: Na vs Ca for Sphene from Norra Kärr compared with Saima and Pilanesberg intrusions.

Figure 4.37: Na vs Ti for Sphene from Norra Kärr and the Saima and Pilanesberg intrusions.

Figure 4.38: [Ln]-concentrations for Norra Kärr sphene normalised to chondrite. The plot shows a profile biased towards the light-[Ln].

4.8 Biotite

A total of 114 EPMA and 381 LA-ICP-MS analyses of biotite were collected. As yet no modern analyses have been published for the biotite's of Norra Kärr. Biotite is only present within the Pulaskite and the Pulaskite-zone of the Lakarpite. A summary of the petrology is given below. Analyses from Norra Kärr will be compared to those from Pilanesberg (White Foyite – Andersen et al. 2017), Mont St Hilaire Syenites (Shilling et al. (2011) and Ilímaussaq (Augite-Syenite – Marks et al. 2001, Schönerberger et al. 2006).

4.8.1 SEM-EDS Petrology

Biotite is similar in size and texture throughout the Pulaskite and Lakarpite consisting of anhedral-to-subhedral phenocrysts <2 mm in dimension that can display optical zoning and well-developed cleavage. In the Pulaskite biotite forms after aegirine but before any of the amphibole phases. Biotite is integral to the enclaves in the Pulaskite and examples of biotite which appear to have detached from the enclaves are also seen. In the Lakarpite amphibole is absent when biotite is present. Fig. 4.39 shows BSE-SEM images for biotite within lithologies throughout the intrusion. None display any signs of cryptic zonation suggesting that all the EPMA analyses collected represent the homogenous composition of the crystals.

Figure 4.39: BSE-SEM images of Biotite from different lithologies in Norra Kärr. Red scale bar is equal to 100 μ m.

4.8.2 Substitutions

Biotite follows the general mica structural formula:

A = K, Na, Ca, (interlayer cations)

R = Al, Mg, Fe²⁺, Fe³⁺, Li, Ti, Mn²⁺, Mn³⁺, Zn, Cr, V, Na (octahedral layer cation)

T = Si, Al, Fe³⁺, Be, B (tetrahedral layer cation)

X = OH, F, Cl, O,

With the main biotite substitutions occurring as: $K(Mg, Fe^{2+})_{3-x}Al_x[Al_{1+x}Si_{3-x}O_{10}](X)_2$

(Deer et al. 1997)

The main element substitutions within biotite that will be outlined here are between Ca, Na, and K within the A-site, Mg, Fe, Mn, Ti within the R-Site and Si and Al in the T-site. Representative biotite compositions are presented in Table 4.16, trace element concentrations from LA-ICP-MS given in Table 4.17 and chondrite normalised values in Table 4.18.

Figure 4.40: Structural classification grid for micas from Norra Kärr.

Figure 4.41: Biotite classification grid for Norra Kärr biotite and those from other intrusions.

Lak-(P)				Pulaskite			Pul-Enclave			
n=	10			71			33			n=
SiO ₂	41.39	+	0.24	38.34	+	1.02	38.32	+	0.19	SiO ₂
		-	0.14		-	6.33		-	0.33	
Al ₂ O ₃	10.47	+	0.18	10.67	+	0.19	10.51	+	0.07	Al ₂ O ₃
		-	0.15		-	0.17		-	0.12	
TiO ₂	1.45	+	0.02	0.88	+	0.25	1.36	+	0.03	TiO ₂
		-	0.01		-	0.29		-	0.03	
FeO	14.92	+	0.13	19.45	+	0.66	20.37	+	0.24	FeO
		-	0.23		-	0.65		-	0.24	
MnO	2.26	+	0.05	0.66	+	0.66	1.59	+	0.03	MnO
		-	0.01		-	0.03		-	0.03	
MgO	12.95	+	0.13	11.91	+	1.03	10.10	+	0.08	MgO
		-	0.07		-	1.16		-	0.21	
CaO	0.01	+	0.01	0.05	+	0.06	0.05	+	0.03	CaO
		-	0.0005		-	0.03		-	0.01	
Na ₂ O	0.08	+	0.02	0.09	+	0.02	0.13	+	0.01	Na ₂ O
		-	0.08		-	0.02		-	0.01	
K ₂ O	10.26	+	0.06	9.62	+	0.46	9.80	+	0.06	K ₂ O
		-	0.09		-	0.92		-	0.12	
F	2.39	+	0.07	1.10	+	0.27	1.33	+	0.10	F
		-	0.08		-	0.21		-	0.07	
Cl	b.d.l.	+	b.d.l.	0.003	+	0.004	0.005	+	0.003	Cl
		-	b.d.l.		-	0.003		-	0.002	
O=F,Cl	1.007	+	0.029	0.462	+	0.004	0.560	+	0.003	O=F,Cl
		-	0.034		-	0.089		-	0.026	
Total	95.18			92.31			93.01			Total

Numbers of ions on the basis of 12 (O,OH,F) or 22 positive charges

Si	3.08	2.97	3.03	Si
Al ^[IV]	0.92	1.00	0.97	Al ^[IV]
Fe ³⁺	0.00	0.03	0.00	Fe ³⁺
ΣT	4.00	4.01	4.00	ΣT
Al ^[VI]	0.00	0.00	0.00	Al ^[VI]
Ti	0.08	0.05	0.08	Ti
Fe ³⁺	0.55	0.29	0.33	Fe ³⁺
Fe ²⁺	0.38	0.97	1.02	Fe ²⁺
Mn	0.14	0.05	0.11	Mn
Mg	1.44	1.41	1.18	Mg
ΣR	2.59	2.78	2.72	ΣR
Ca	0.00	0.00	0.00	Ca
Na	0.01	0.02	0.02	Na
K	0.97	0.97	0.97	K
ΣA	0.98	1.00	1.00	ΣA
F	0.56	0.32	0.33	F
Cl	0.00	0.00	0.00	Cl
O ²⁻ _{calc}	0.73	0.85	0.83	O ²⁻ _{calc}
OH _{calc}	0.71	0.82	0.83	OH _{calc}
ΣX	2.00	2.00	2.00	ΣX

Table 4.16: Representative EPMA analyses and calculated compositions of Biotite from Norra Kärr.

Pulaskite				Pulaskite-Enclave			
n =	309			72			n =
Y	2.76	+	4.66	0.86	+	38.07	Y
		-	2.70		-	0.86	
La	b.d.l.	+	b.d.l.	2.39	+	6.13	La
		-	b.d.l.		-	2.39	
Ce	b.d.l.	+	2.08	14.22	+	21.57	Ce
		-	b.d.l.		-	12.87	
Pr	b.d.l.	+	b.d.l.	b.d.l.	+	1.69	Pr
		-	b.d.l.		-	b.d.l.	
Nd	b.d.l.	+	b.d.l.	b.d.l.	+	8.39	Nd
		-	b.d.l.		-	b.d.l.	
Sm	b.d.l.	+	b.d.l.	b.d.l.	+	b.d.l.	Sm
		-	b.d.l.		-	b.d.l.	
Eu	b.d.l.	+	b.d.l.	b.d.l.	+	b.d.l.	Eu
		-	b.d.l.		-	b.d.l.	
Gd	b.d.l.	+	b.d.l.	b.d.l.	+	b.d.l.	Gd
		-	b.d.l.		-	b.d.l.	
Tb	b.d.l.	+	b.d.l.	b.d.l.	+	1.56	Tb
		-	b.d.l.		-	b.d.l.	
Dy	b.d.l.	+	b.d.l.	b.d.l.	+	21.43	Dy
		-	b.d.l.		-	b.d.l.	
Ho	b.d.l.	+	b.d.l.	b.d.l.	+	3.47	Ho
		-	b.d.l.		-	b.d.l.	
Er	b.d.l.	+	b.d.l.	b.d.l.	+	25.33	Er
		-	b.d.l.		-	b.d.l.	
Tm	b.d.l.	+	b.d.l.	b.d.l.	+	b.d.l.	Tm
		-	b.d.l.		-	b.d.l.	
Yb	b.d.l.	+	b.d.l.	b.d.l.	+	24.76	Yb
		-	b.d.l.		-	b.d.l.	
Lu	b.d.l.	+	b.d.l.	b.d.l.	+	1.77	Lu
		-	b.d.l.		-	b.d.l.	

Table 4.17: Representative LA-ICP-MS analyses for Y and [Ln] concentrations (ppm) within Biotite from Norra Kärr.

Pulaskite		Pulaskite-Enclave	
309		72	
Y	1.32	0.41	Y
La	b.d.l.	6.52	La
Ce	b.d.l.	14.85	Ce
Pr	b.d.l.	b.d.l.	Pr
Nd	b.d.l.	b.d.l.	Nd
Sm	b.d.l.	b.d.l.	Sm
Eu	b.d.l.	b.d.l.	Eu
Gd	b.d.l.	b.d.l.	Gd
Tb	b.d.l.	b.d.l.	Tb
Dy	b.d.l.	b.d.l.	Dy
Ho	b.d.l.	b.d.l.	Ho
Er	b.d.l.	b.d.l.	Er
Tm	b.d.l.	b.d.l.	Tm
Yb	b.d.l.	b.d.l.	Yb
Lu	b.d.l.	b.d.l.	Lu

Table 4.18: Representative LA-ICP-MS analyses for Y and [Ln] concentrations (ppm) within Biotite from Norra Kärr normalised to chondrite (Taylor & McLennan 1985).

Fig. 4.41 shows that all of the micas analysed are true micas with almost all cations in the A-site being A^+ rather than A^{2+} cations. This is due to the lack of Ca within the minerals with the A-site being predominately filled by K^+ . The micas are approximately all trioctahedral due to having >2.5 cations in the R-site. This site is predominantly filled with Fe and Mg. Biotites from the Augite-Syenite of Ilímaussaq, the White Foyite of Pilanesberg and the Syenite of Mont St Hilaire all plot in the same position as the main set of Norra Kärr analyses.

Biotites from Norra Kärr lie between the Phlogopite and Annite fields (Fig. 4.41). Biotite from the Lakarpite appears to be entirely Phlogopite, while the Pulaskite matrix and enclaves straddle the classification line. The Norra Kärr biotites appear to be less evolved than biotite from other alkaline intrusions, with the majority of biotites from Ilímaussaq, Pilanesberg and Mont St Hilaire being richer in Fe and classifying as annites and siderophyllites.

Fig. 4.24 shows the variation in K and Na within the A-site. All Norra Kärr biotites are richer in K than Na, and this matches the compositional trend observed in biotite from other alkaline intrusions. On an Al^{IV} vs Si plot (Fig. 4.43) the Lakarpite and Pulaskite enclaves display the highest Si contents, while the Pulaskite matrix displays lower Si and higher Al. As this is the major substitution in the T-Site a linear trend is formed, and this is matched by the biotites from other alkaline intrusions which display some overlap with the compositions of the Norra Kärr biotites.

Figs. 4.44 and 4.45 show Ti and Mn vs $Mg/(Fe+Mg)$. As in Fig. 4.41 these plots show that Lakarpite contains the most magnesian-biotite with the Pulaskite slightly richer in Fe. The Norra Kärr biotites all display low Ti contents (<0.2 a.p.f.u.) whereas more the evolved biotite from other alkaline intrusions display higher Ti contents, with the Augite-Syenite of Ilímaussaq containing up to 0.4 a.p.f.u. Ti. The pattern of Mn content is different, with the the Ilímaussaq Augite-Syenite displaying low Mn concentrations and Pilansberg and Norra Kärr displaying higher Mn contents.

Figure 4.42: K vs Na for Norra Kärr biotite and biotites from other alkaline intrusions.

● Pil-WhiteFoy ▲ MSH-Syenite ◆ Ilímaussaq-AugSy ◆ Lakarpite-(P) ■ Pulaskite ■ Pulaskite-Enclave

Figure 4.43: Al^{IV} vs Si for Norra Kärr biotite and biotite from other alkaline intrusions.

● Pil-WhiteFoy ▲ MSH-Syenite ◆ Ilímaussaq-AugSy ◆ Lakarpite-(P) ■ Pulaskite ■ Pulaskite-Enclave

Figure 4.44: Ti vs $Mg/(Fe+Mg)$ for Norra Kärr biotite and biotite from other alkaline intrusions.

● Pil-WhiteFoy ▲ MSH-Syenite ◆ Ilímaussaq-AugSy ◆ Lakarpite-(P) ■ Pulaskite ■ Pulaskite-Enclave

Figure 4.45: Mn vs $Mg/(Fe+Mg)$ for Norra Kärr biotite and biotite from other alkaline intrusions.

4.8.3 Volatile Content of the Biotites

The wt% F content of the Norra Kärr biotites is shown in Fig. 4.46, with the biotite of the inner Lakarpite zone displaying higher (by approximately 1 wt%) F content than the Pulaskite and its enclaves. The Norra Kärr biotites appear to be particularly F rich when compared to biotite from the Augite-Syenite of Ilímaussaq, the White Foyite of Pilanesberg and the Syenite of Mont St Hilaire. There appears to be little to no Cl⁻ present in the X-sites.

Figure 4.46: Wt% F for Norra Kärr biotites and biotite from other alkaline intrusions.

4.8.4 Trace Elements

LA-ICP-MS was used to analyse the biotite's from the Pulaskite and its enclaves for their trace element concentrations which revealed little to no detectable [Ln] or Y. This may be due in part to poor laser-coupling with the minerals analysed but is also indicative of the inherently very low [Ln] and Y concentrations that are typically displayed by true micas due to the lack of an appropriate position for [Ln] in the mineral structure (Deer et al. 1997).

4.8.5 Biotite Summary

In contrast with biotite from other alkaline intrusions the Norra Kärr biotite's do not show a trend in fractionation and instead cluster around the Phlogopite-Annite compositional boundary. In terms of $\text{Mg}/(\text{Fe}+\text{Mg})$ the biotite's also show a lack of a fractionation trend and are less evolved than biotite from other alkaline intrusions. Therefore, the Norra Kärr biotite's appear to show only a snapshot of their surrounding chemical compositions. This is not-surprising given that biotite is only present within the smaller Lakarpite and Pulaskite dyke-intrusions and which do not appear to show much fractionation. The lack of a variation in composition shows that the feldspathic and enclave portions of the Pulaskite are also likely to be related.

The biotite's are low in Ca and Na and are instead removing K from the melt. In terms of mean whole-rock $\text{Na}_2\text{O}/\text{K}_2\text{O}$ the Pulaskite displays a ratio of 1.5. As earlier phases are rich in Na over K this restricts the ability of the biotite's to form a fractionation series in Na as shown by other alkaline intrusions. The biotite's are also low in Ti despite the Pulaskite having a bulk rock mean of 0.4 Wt% TiO_2 . This may be due to earlier sphene crystallisation. Comparatively the Norra Kärr biotite's have higher Mn than the Augite-Syenite of Ilímaussaq but lower overall Mn than Pilanesberg. The Augite-Syenite was one of the earlier intrusive phases in Ilímaussaq, while the White Foyite from Pilanesberg had time to fractionate. The Norra Kärr biotite's may therefore represent a magma more fractionated than the earlier Ilímaussaq magmas and closer to the original composition of the White Foyite which then did not have the opportunity to fractionate further.

In terms of volatile content, the biotite's are more F-rich than other alkaline intrusions, with the Lakarpite displaying particularly high F-concentrations. Biotite growth at this point would also reduce the OH^- content of the remaining magma potentially leading to higher activities of F^- and the crystallisation of fluorite later in the petrological sequence.

4.9 Catapleiite

A total of 51 EPMA and 879 LA-ICP-MS analyses of catapleiite were collected across more lithologies than had previously been analysed. Catapleiite is prevalent throughout the Grennaite where it is the first forming Zr-Silicate phase. A second generation of Catapleiite is present in veins within the Pegmatite-Host Grennaite, and as a product of eudialyte alteration.

4.9.1 SEM-EDS Petrology

Catapleiite is present throughout the Grennaite-related rocks in several textural forms and is the first forming Zr-silicate in all Grennaite lithologies. Catapleiite is best developed in the pegmatites as mm-long euhedral crystals; a smaller anhedral variety is found within the Crenulated Domain and in the fine-grained Grennaite it is present as cm-scale irregular masses. Two forms were identified in the Pegmatitic Domain Grennaite, one as anhedral crystals similar but smaller than the crenulated domain, and a second aggregate texture found near analcime veins. Catapleiite is also present in the Zr-Lakarpite where it forms euhedral crystals enclosed by feldspar. Fig. 4.47 shows BSE-SEM images for the catapleiites within lithologies throughout the intrusion. None display any signs of cryptic zonation suggesting at all the EPMA and LA-ICP-MS analyses collected represent the homogenous composition of the crystals.

4.9.2 Substitutions

Catapleiite follows the structural formula:

Where:

A = Na₀₋₂, Ca

The main substitution in catapleiite is based upon the transition between Ca and Na. Representative mineral compositions from EPMA are shown in Table 4.19, with trace element concentrations from LA-ICP-MS given in Table 4.20 and chondrite normalised values in Table 4.21.

4.9.3 Catapleiite Summary

Catapleiite is the first forming Zr-silicate phase in the Grennaite and shows a distinct trend of decreasing Na and increasing Ca with fractionation (Fig. 4.48). This matches the overall major element trends discussed in Chapter 4. Within the Grennaite the bulk Na₂O-content of the magma decreases by ≈1 wt% during fractionation and there is an increase in CaO by ≈2 wt% between the Contact Grennaite and the Crenulated Grennaite. The catapleiite from the Contact Grennaite show the highest Na contents and represents the start of the fractionation trend.

The catapleiite analysed from the Pegmatite-Host Grennaite came from near the contact with the Contact Grennaite (the Na-rich variety) and close to the core of the Pegmatite-Host Grennaite (the Na-poorer variety) thereby showing an internal fractionation trend. The catapleiite from the contact of the Lakarpite match with those from the core of the Pegmatite-Host Grennaite supporting the chemical connection/reaction between the two lithologies discussed in Chapter 4.

Figure 4.47: BSE-SEM images of Catapleiite from different lithologies in Norra Kärr. Red scale bar is equal to 100 μm . Note the cross-cutting relationships between the earlier catapleiite and later eudialyte within the Grennaite. Secondary catapleiite is found within a vein within the Peg-Host Grennaite and the Lakarpite (Cat-Alt).

	Grennaite			Gren-Vein			Gren Peg			Pegmatite			Crenulated			Lakarpite-Zr		
n=	14			3			12			10			7			5		
SiO ₂	43.65	+	0.25	43.72	+	0.03	43.34	+	0.14	43.43	+	0.45	42.88	+	0.22	42.96	+	0.11
		-	0.37		-	0.20		-	0.24		-	0.21		-	0.31		-	0.01
Na ₂ O	14.49	+	0.27	14.90	+	0.15	11.68	+	2.98	14.00	+	0.05	7.47	+	0.26	12.07	+	0.43
		-	0.33		-	0.09		-	0.29		-	0.23		-	0.16		-	0.68
CaO	0.43	+	0.15	0.16	+	0.04	3.99	+	0.51	1.29	+	0.40	7.66	+	0.04	3.96	+	0.25
		-	0.22		-	0.02		-	3.38		-	0.40		-	0.18		-	0.26
ZrO ₂	32.19	+	0.72	31.32	+	0.21	31.71	+	0.44	29.52	+	1.04	31.72	+	0.22	31.72	+	0.35
		-	0.61		-	0.17		-	0.49		-	0.49		-	0.18		-	0.32
HfO ₂	0.70	+	0.06	0.58	+	0.03	0.53	+	0.03	0.54	+	0.04	0.47	+	0.01	0.49	+	0.03
		-	0.08		-	0.03		-	0.03		-	0.01		-	0.04		-	0.00
Y ₂ O ₃	0.07	+	0.05	0.15	+	0.04	0.18	+	0.03	0.21	+	0.01	0.03	+	0.01	0.13	+	0.00
		-	0.00		-	0.00		-	0.05		-	0.03		-	0.00		-	0.06
F	0.32	+	0.41	0.16	+	0.05	1.14	+	0.15	0.42	+	-	0.77	+	0.12	1.33	+	0.09
		-	0.12		-	0.00		-	0.39		-	-		-	0.32		-	0.07
Total	91.97			90.93			92.52			89.39			91.01			92.66		
<i>Number of ions on the basis of 6 cations</i>																		
Si	2.96			2.97			3.01			3.01			3.16			2.99		
Na	1.92			1.96			1.58			1.87			1.09			1.62		
Ca	0.03			0.01			0.30			0.10			0.60			0.29		
Zr	1.07			1.04			1.07			0.99			1.14			1.08		
Hf	0.01			0.01			0.01			0.01			0.01			0.01		
F	0.00			0.00			0.00			0.00			0.00			0.00		

Table 4.19: Representative EPMA analyses and calculated compositions of Catapleiite from Norra Kärr. Cl was not analysed.

	Contact Grennaite		Pegmatite-Host Grennaite (Vein)		Pegmatite-Host Grennaite		Pegmatite		Crenulated Grennaite	
n=	132		20		33		508		186	
Y	1247.46	+ 372.94 - 378.29	683.76	+ 726.28 - 156.82	861.38	+ 31.06 - 470.34	1335.78	+ 273.09 - 175.82	271.94	+ 1843.81 - 54.69
La	0.80	+ 2.95 - 0.47	171.44	+ 362.29 - 56.62	0.65	+ 0.36 - 0.28	4.02	+ 4.98 - 2.73	35.11	+ 2511.19 - 28.17
Ce	2.92	+ 9.41 - 0.99	362.17	+ 824.13 - 85.60	1.96	+ 0.50 - 0.56	7.81	+ 8.82 - 5.03	56.84	+ 5639.65 - 45.81
Pr	0.34	+ 0.50 - 0.15	56.68	+ 112.36 - 10.86	0.29	+ 0.07 - 0.07	0.91	+ 0.98 - 0.47	6.56	+ 764.82 - 5.25
Nd	2.47	+ 2.36 - 0.67	280.51	+ 547.43 - 53.81	2.49	+ 0.63 - 0.47	5.72	+ 3.08 - 1.84	20.85	+ 3447.76 - 15.95
Sm	3.73	+ 1.27 - 0.80	92.26	+ 186.85 - 20.74	2.93	+ 0.43 - 0.31	6.78	+ 1.54 - 1.34	4.34	+ 758.86 - 2.46
Eu	0.51	+ 0.68 - 0.17	12.16	+ 18.68 - 3.19	0.61	+ 0.04 - 0.06	1.43	+ 0.38 - 0.35	0.69	+ 63.87 - 0.40
Gd	17.62	+ 5.59 - 5.94	109.41	+ 212.59 - 26.05	12.45	+ 0.93 - 0.85	27.75	+ 7.29 - 5.96	6.38	+ 745.01 - 1.79
Tb	8.69	+ 1.79 - 2.94	23.23	+ 41.49 - 5.08	4.89	+ 0.54 - 0.33	11.61	+ 2.38 - 2.20	1.86	+ 133.21 - 0.33
Dy	117.91	+ 37.03 - 34.63	191.90	+ 292.29 - 33.65	60.73	+ 5.66 - 6.01	129.89	+ 24.29 - 26.17	20.23	+ 992.63 - 3.22
Ho	52.59	+ 15.35 - 16.39	47.82	+ 58.15 - 8.91	22.14	+ 2.14 - 1.62	47.07	+ 9.94 - 7.39	7.31	+ 227.68 - 1.23
Er	227.80	+ 91.22 - 55.67	168.92	+ 170.05 - 24.47	106.11	+ 12.37 - 4.26	186.69	+ 43.85 - 49.00	34.74	+ 775.03 - 5.50
Tm	51.53	+ 16.23 - 10.62	33.97	+ 26.30 - 3.58	27.83	+ 1.71 - 1.63	36.23	+ 7.05 - 5.76	7.77	+ 118.61 - 1.29
Yb	618.28	+ 167.95 - 109.16	319.72	+ 157.57 - 34.15	298.41	+ 25.53 - 15.13	311.27	+ 103.55 - 87.12	88.93	+ 849.50 - 12.37
Lu	58.12	+ 11.83 - 8.94	32.54	+ 15.78 - 2.35	36.08	+ 1.92 - 1.46	34.74	+ 9.62 - 8.44	10.05	+ 105.68 - 1.47

Table 4.20: Representative LA-ICP-MS analyses for Y and [Ln] concentrations (ppm) within Catapleiite from Norra Kärr.

	Contact Grennaite	Pegmatite-Host Grennaite	Pegmatite-Host Grennaite (Vein)	Pegmatite	Crenulated Grennaite	
	132	20	33	152	508	
Y	594.0	325.6	410.2	636.1	120.5	Y
La	2.2	467.1	1.8	11.0	44.8	La
Ce	3.0	378.4	2.0	8.2	30.5	Ce
Pr	2.5	413.7	2.1	6.6	24.7	Pr
Nd	3.5	394.5	3.5	8.0	18.8	Nd
Sm	16.1	399.4	12.7	29.4	12.1	Sm
Eu	5.8	139.8	7.0	16.5	5.3	Eu
Gd	57.6	357.6	40.7	90.7	17.5	Gd
Tb	149.9	400.5	84.2	200.2	29.4	Tb
Dy	309.5	503.7	159.4	340.9	49.3	Dy
Ho	618.0	561.9	260.1	553.1	79.7	Ho
Er	914.9	678.4	426.1	749.8	129.7	Er
Tm	1447.4	954.1	781.8	1017.6	200.7	Tm
Yb	2493.1	1289.2	1203.2	1255.1	336.2	Yb
Lu	1525.4	854.1	947.0	911.7	248.0	Lu

Table 4.21: Representative LA-ICP-MS analyses for Y and [Ln] concentrations (ppm) within Catapleiite from Norra Kärr normalised to chondrite (Taylor & McLennan 1985).

Figure 4.48: Ca vs Na substitution in Catapleite from Norra Kärr compared to catapleite from other intrusions.

Figure 4.49: Hf vs Zr substitution in Catapleite from Norra Kärr compared to catapleite from other intrusions.

The catapleite from the Crenulated Grennaite represent the most fractionated end of the fractionation trend and display the highest Ca-contents of any of the analysed varieties. A similar trend is seen in terms of Hf vs Zr (Fig. 4.49). The Contact Grennaite displays the highest Hf concentrations, which decrease with fractionation towards the Crenulated Grennaite. This is despite Hf not showing a similar trend in the whole-rock data. While the dominant volatile within catapleite is crystal-bound H₂O, up to ≈1 Wt% F was detected.

The LA-ICP-MS show that catapleiite has a general bias towards the heavy-[Ln] (Fig. 4.50). The Contact Grennaite has the most heavy-enriched catapleiite, followed by the Pegmatite-Host Grennaite and the Pegmatites. The Pegmatite-Host Grennaite also appears more enriched in [Ln] overall. A later generation of catapleiite from a vein within the Pegmatite-Host Grennaite shows a [Ln]-pattern similar to the Contact Grennaite but less [Ln]-rich. The Crenulated Grennaite catapleiite shows the lowest [Ln]-concentrations with a slight enrichment in the light-[Ln] along with the heavy-[Ln]. Due to the abundance of catapleiite within the ore bearing first phase of intrusion and its ability to sequester appreciable [Ln] (particularly the heavy-[Ln]) it may play a role in altering the [Ln] concentrations of the magma as progressive fractionation occurs within the chamber.

Figure 4.50: [Ln]-concentrations for Norra Kärr catapleiite normalised to chondrite. The plot shows a relatively flat profile with only a preference for heavy-[Ln].

Comparison with Other Catapleiite Occurrences

Catapleiite in Norra Kärr is notable for forming prior to eudialyte in contrast to other alkaline intrusions (Deer et al. 1997). Frequently catapleiite is reported as a secondary alteration mineral which typically replaces eudialyte (e.g. Borst et al. 2016). Andersen et al. (2010) outlined that an elevated sodium concentration in the magma was needed to stabilise minerals such as Na-catapleiite in nepheline syenite, a situation that appears to be present within Norra Kärr. Little analytical compositions data is available for catapleiite compositions despite several studies of the mineral. However, Andersen et al. (2010) and Wu et al. (2015) did provide analyses from the Langesundsfjord alkaline-pegmatites (Oslo Rift) and the Saima alkaline intrusion (Liaodong Peninsula) respectively. There are both primary and secondary catapleiite within the Saima intrusion, with the primary varieties (plotted in Fig. 4.48) forming within a lujavrite. These catapleiite are similar in composition to the Contact Grennaites and formed within an assemblage similar to the Grennaites (albeit with the inclusion of minor titanite and biotite). The catapleiite from the Langesundsfjord formed within several pegmatites spread over an area of several kilometres. However, a similar fractionation trend is observed at Norra Kärr over a far smaller area.

4.10 Eudialyte

A total of 102 EPMA and 2432 LA-ICP-MS analyses of eudialyte were collected across all textural varieties of Grennaite, the pegmatites, and the outer eudialyte-bearing zones of the Lakarpite.

4.10.1 SEM-EDS Petrology

Eudialyte is present throughout the Grennaite-related rocks and is also found in the Zr-rich portions of the Lakarpite. The largest eudialytes are found in the pegmatites with smaller anhedral eudialyte present in the Crenulated Domain and the Grennaite in the pegmatitic Domain. In the fine-grained Grennaite eudialyte is present as two textural forms. The most common texture is as anhedral fine-grained crystals but mm-scale ‘snowball’ eudialyte is also present. In the Zr-rich-core Lakarpite eudialyte is present as granular anhedral phenocrysts. In the Zr-rich Lakarpite eudialyte is present as larger subhedral phenocrysts. BSE-SEM images of these textures are presented in Fig. 4.51.

4.10.2 Substitutions

Eudialyte follows the structural formula:

Where:

N(1–5) = Na, H₃O⁺, K, Sr, [Ln], Ba, Mn, Ca,

M(1) = Ca, Mn, [Ln], Na, Sr, Fe,

M(2) = Fe, Mn, Na, Zr, Ta, Ti, K, Ba, H₃O⁺,

M(3) and M(4) = Si, S, Nb, Ti, W, Na, Al

Z = Zr, Ti, or Nb,

θ = O, OH, or H₂O,

X(1) and X(2) = Cl, F, H₂O, OH, CO₃, SO₄, AlO₄, MnO₄,

Rastsvetaeva (2007)

The main substitutions within eudialyte are Na ⇌ K, Fe ⇌ Mn, Ca ⇌ [Ln] and Zr ⇌ Ti ⇌ Nb (Deer et al. 1997, Borst et al. 2018). These analyses will be compared with others reported for eudialyte from the Langesundsfjord (Andersen et al. 2010), Pilanesberg (Andersen et al. 2018) and Ilímaussaq (Pfaff et al. 2008, Lindhuber et al. 2015, Hunt et al. 2017). Major element analyses are given in Table 4.22, trace element concentrations from LA-ICP-MS given in Table 4.23, and chondrite normalised values in Table 4.24.

Contact

Peg-Host

Pegmatite

Crenulated

Figure 4.51 (continued on next page)

Lakarpite-Zr-Core

Lakarpite Zr-Rich

Discovery Outcrop

Figure 4.51: BSE-SEM images of eudialyte from Norra Kärr. Red scale bar is equal to 100 μm . Contact Grennaite: Eudialytes showing complex core textures with accompanying rims; Pegmatite-Host Grennaite: Eudialytes displaying complex cores but no evident rims; Pegmatites: Eudialytes showing fractured and altered cores with oscillatory rims evident; Crenulated Grennaite: Eudialytes displaying fractured and altered cores; Lakarpite-Zr-Core: Eudialytes from the innermost of the outer-two petrological zones of the Lakarpite showing multiple inclusions and little internal texture; Lakarpite-Zr-Rich: Eudialyte from the outermost petrological zone of the Lakarpite displaying alteration along cracks and catapleiite overgrowths; Discovery Outcrop: A eudialyte showing patchy globular texture (left) and a trigonal core (right).

Grennaite				Gren-Peg			Pegmatite			Crenulated		
n=	12			13			35			20		
SiO ₂	48.29	+	0.28	48.72	+	0.26	48.08	+	0.52	48.56	+	0.22
		-	0.47		-	1.47		-	0.48		-	0.32
TiO ₂	0.21	+	0.01	0.27	+	0.00	0.18	+	0.01	0.20	+	0.03
		-	0.00		-	0.00		-	0.04		-	0.01
ZrO ₂	12.53	+	0.57	12.65	+	0.21	12.31	+	0.40	11.85	+	0.40
		-	1.25		-	0.26		-	0.56		-	1.29
HfO ₂	0.36	+	0.01	0.36	+	0.01	0.29	+	0.02	0.26	+	0.01
		-	0.02		-	0.02		-	0.03		-	0.02
Nb ₂ O ₅	0.67	+	0.30	0.62	+	0.11	0.84	+	0.19	0.75	+	0.08
		-	0.18		-	0.06		-	0.10		-	0.11
Ta ₂ O ₅	0.21	+	0.03	0.13	+	0.00	0.15	+	0.01	0.15	+	0.00
		-	0.03		-	0.00		-	0.02		-	0.00
Al ₂ O ₃	0.33	+	0.05	0.21	+	0.06	0.34	+	0.04	0.19	+	0.01
		-	0.06		-	0.01		-	0.05		-	0.01
Y ₂ O ₃	2.45	+	0.00	4.34	+	0.06	2.54	+	0.76	1.84	+	1.50
		-	0.00		-	0.00		-	0.00		-	0.00
[Ln] ₂ O ₃	4.90	+	0.00	5.01	+	0.14	4.32	+	1.91	6.27	+	2.68
		-	0.00		-	0.00		-	0.00		-	0.02
FeO	2.14	+	0.57	3.16	+	0.13	2.86	+	0.21	0.85	+	0.06
		-	0.11		-	0.48		-	0.13		-	0.04
MnO	1.83	+	0.15	1.65	+	0.20	2.10	+	0.13	4.56	+	0.24
		-	0.13		-	0.05		-	0.16		-	0.14
MgO	b.d.l.	+	-	0.01	+	0.00	0.01	+	0.00	0.02	+	0.00
		-	-		-	0.00		-	0.00		-	0.00
CaO	8.63	+	0.49	7.84	+	0.07	7.13	+	0.30	5.32	+	0.09
		-	0.20		-	0.76		-	0.24		-	0.13
Na ₂ O	14.47	+	0.08	14.40	+	0.29	13.97	+	0.39	11.05	+	0.42
		-	0.58		-	0.94		-	0.37		-	0.40
K ₂ O	0.24	+	0.12	0.18	+	0.32	0.35	+	0.26	0.71	+	0.06
		-	0.04		-	0.01		-	0.03		-	0.03
F	0.19	+	0.07	0.12	+	0.03	0.26	+	0.03	0.16	+	0.02
		-	0.01		-	0.02		-	0.05		-	0.02
Cl	0.64	+	0.21	0.29	+	0.16	0.40	+	0.04	0.38	+	0.02
		-	0.27		-	0.01		-	0.03		-	0.07
-O=F,Cl	0.18	+	0.07	0.10	+	0.01	0.10	+	0.01	0.11	+	0.03
		-	0.06		-	0.04		-	0.01		-	0.02
Total	97.91			99.86			96.04			93.00		
<i>Numbers of ions on the basis of 76 (O,OH,F,Cl)</i>												
Si	25.360			25.375			25.570			25.974		
Ti	0.082			0.109			0.072			0.080		
Zr	3.223			3.240			3.184			3.061		
Hf	0.055			0.054			0.044			0.040		
Nb	0.171			0.148			0.195			0.177		
Ta	0.031			0.019			0.021			0.023		
Al	0.204			0.127			0.211			0.120		
Y	0.687			1.204			0.728			0.537		
[Ln]	1.566			1.524			1.529			2.585		
Fe	0.947			1.376			1.272			0.386		
Mn	0.812			0.730			0.948			2.056		
Mg	b.d.l.			0.007			0.007			0.013		
Ca	4.858			4.359			4.060			3.012		
Na	14.723			14.531			14.392			11.338		
K	0.158			0.122			0.236			0.485		
F	0.313			0.193			0.427			0.261		
Cl	0.586			0.252			0.361			0.333		
OH _{Calc}	1.414			1.748			1.639			1.667		

Table 4.22 (continued on next page)

Zr-Core			Zr			Discovery			
9			10			3			n=
47.06	+	2.14	48.02	+	0.31	50.89	+	0.03	SiO ₂
	-	0.42		-	0.08		-	0.25	
0.18	+	0.01	0.20	+	0.02	b.d.l	+	-	TiO ₂
	-	0.01		-	0.02		-	-	
11.75	+	0.16	12.61	+	0.24	10.43	+	0.13	ZrO ₂
	-	1.62		-	2.09		-	0.34	
0.29	+	0.01	0.27	+	0.01	0.23	+	0.00	HfO ₂
	-	0.01		-	0.02		-	0.01	
0.89	+	0.12	0.96	+	0.04	0.30	+	0.02	Nb ₂ O ₅
	-	0.23		-	0.24		-	0.03	
b.d.l	+	-	b.d.l	+	-	b.d.l	+	-	Ta ₂ O ₅
	-	-		-	-		-	-	
0.10	+	0.02	0.25	+	0.09	0.08	+	0.00	Al ₂ O ₃
	-	0.01		-	0.04		-	0.00	
0.00	+	0.00	4.67	+	0.00	7.57	+	0.00	Y ₂ O ₃
	-	0.00		-	0.00		-	0.00	
1.45	+	0.00	6.86	+	0.00	6.34	+	0.00	[Ln] ₂ O ₃
	-	0.00		-	0.00		-	0.00	
3.44	+	0.12	3.27	+	0.08	5.98	+	0.00	FeO
	-	0.21		-	0.06		-	0.00	
2.15	+	0.17	2.34	+	0.17	1.29	+	0.01	MnO
	-	0.09		-	0.12		-	0.03	
0.01	+	0.00	0.02	+	0.00	0.01	+	0.00	MgO
	-	0.00		-	0.00		-	0.00	
8.54	+	0.04	7.47	+	0.06	10.66	+	0.08	CaO
	-	0.07		-	0.16		-	0.01	
14.22	+	0.09	13.58	+	0.12	13.92	+	0.00	Na ₂ O
	-	0.17		-	0.12		-	0.09	
0.17	+	0.03	0.41	+	0.04	0.32	+	0.24	K ₂ O
	-	0.01		-	0.03		-	0.07	
0.13	+	0.01	0.25	+	0.01	b.d.l	+	-	F
	-	0.02		-	0.02		-	-	
0.36	+	0.00	0.28	+	0.02	0.43	+	0.00	Cl
	-	0.01		-	0.01		-	0.01	
0.13	+	0.01	0.16	+	0.01	0.10	+	0.00	-O=F,Cl
	-	0.04		-	0.07		-	0.00	
90.61			101.33			108.34			Total
26.558			24.960			24.744			Si
0.073			0.078			b.d.l.			Ti
3.094			3.196			2.482			Zr
0.047			0.041			0.031			Hf
0.201			0.230			0.065			Nb
b.d.l.			b.d.l.			b.d.l.			Ta
0.064			0.153			0.043			Al
0.000			1.291			1.964			Y
0.325			2.127			2.090			[Ln]
1.570			1.433			2.440			Fe
1.015			1.029			0.531			Mn
0.007			0.013			0.007			Mg
5.096			4.173			5.573			Ca
15.291			13.735			13.164			Na
0.117			0.274			0.199			K
0.205			0.405			b.d.l.			F
0.331			0.255			0.352			Cl
1.669			1.745			1.648			OH _{Calc}

Table 4.22: Representative EPMA analyses and calculated compositions of Eudialyte from Norra Kärr. OH calculated to fill an X-site of 2.

n =	Grennaite		Gren-Peg		Pegmatite		Crenulated	
	122		183		1016		375	
Y	19306.94	+ 5515.98 - 4985.93	34672.61	+ 3118.77 - 1785.06	20018.70	+ 11881.15 - 4179.01	20326.81	+ 5433.36 - 12004.73
La	5595.69	+ 1669.61 - 1566.58	4373.85	+ 1740.84 - 545.82	5290.83	+ 1474.72 - 1316.74	11938.06	+ 1890.52 - 6348.88
Ce	8713.19	+ 2572.69 - 2115.34	8413.49	+ 2123.81 - 698.88	9057.03	+ 1699.38 - 1407.67	23565.33	+ 3827.93 - 13661.13
Pr	1200.60	+ 371.58 - 289.83	1344.94	+ 193.76 - 146.36	1143.34	+ 312.91 - 136.81	3229.64	+ 466.16 - 1766.21
Nd	5396.70	+ 1774.20 - 1074.69	7231.26	+ 1116.25 - 572.49	5174.71	+ 1875.34 - 627.99	14196.42	+ 2111.99 - 8056.30
Sm	2003.30	+ 568.31 - 473.62	2484.53	+ 257.15 - 142.87	1788.25	+ 462.61 - 334.29	3221.34	+ 442.41 - 1659.85
Eu	231.48	+ 52.44 - 48.52	283.58	+ 23.58 - 19.28	200.11	+ 57.24 - 39.69	300.44	+ 40.69 - 144.36
Gd	2716.66	+ 774.76 - 674.05	3156.84	+ 272.63 - 216.65	2577.87	+ 343.96 - 518.23	3128.64	+ 451.97 - 1597.24
Tb	612.36	+ 167.83 - 127.21	690.02	+ 62.78 - 45.52	538.96	+ 92.42 - 71.16	522.55	+ 80.62 - 278.73
Dy	4470.53	+ 1268.48 - 1051.57	5419.62	+ 761.53 - 433.74	3846.95	+ 1354.40 - 375.62	3489.38	+ 472.76 - 1870.22
Ho	1151.30	+ 376.72 - 258.56	1253.83	+ 146.78 - 115.49	881.31	+ 324.01 - 94.36	720.70	+ 140.99 - 375.00
Er	3990.35	+ 970.17 - 1120.16	3985.78	+ 538.45 - 494.40	2683.30	+ 1177.15 - 409.52	2021.39	+ 520.71 - 948.62
Tm	630.82	+ 183.44 - 149.82	670.98	+ 60.55 - 54.15	422.08	+ 164.89 - 59.49	338.97	+ 65.54 - 169.89
Yb	4674.53	+ 1533.18 - 1323.55	4230.16	+ 600.66 - 561.62	2854.58	+ 1244.18 - 465.56	2240.05	+ 701.12 - 961.73
Lu	492.56	+ 139.07 - 139.53	512.97	+ 37.84 - 40.92	309.95	+ 94.14 - 58.25	248.09	+ 53.09 - 124.88

Table 4.23 (continued on next page)

Lak-Zr-Core			Lak-Zr			Discovery			
192			423			121			n =
5.00	+	1.06	36802.36	+	1628.64	59603.54	+	5242.88	Y
	-	1.06		-	1009.74		-	50332.10	
288.56	+	88.80	7683.70	+	1172.60	7434.96	+	1311.86	La
	-	58.74		-	964.31		-	982.14	
725.49	+	183.43	11697.00	+	1377.27	14023.19	+	1210.65	Ce
	-	145.36		-	1230.85		-	1274.47	
87.66	+	41.06	1675.82	+	173.45	2001.42	+	174.57	Pr
	-	20.42		-	145.05		-	164.20	
424.35	+	160.53	9261.08	+	902.74	9259.04	+	656.62	Nd
	-	101.21		-	731.26		-	828.51	
2115.54	+	329.48	3195.59	+	132.38	865.83	+	165.33	Sm
	-	498.97		-	121.48		-	119.84	
279.34	+	37.46	367.65	+	19.24	118.56	+	22.11	Eu
	-	70.07		-	15.61		-	14.18	
2351.43	+	331.56	4056.72	+	132.71	3682.74	+	320.39	Gd
	-	534.04		-	118.59		-	228.01	
619.57	+	89.12	920.82	+	29.28	772.44	+	39.79	Tb
	-	130.22		-	32.33		-	77.78	
651.81	+	2814.71	6740.54	+	450.16	6812.18	+	402.91	Dy
	-	257.78		-	366.21		-	465.13	
860.80	+	160.10	1537.52	+	68.44	1142.29	+	85.21	Ho
	-	210.49		-	98.23		-	88.12	
1976.75	+	378.15	4745.38	+	288.57	3448.99	+	250.10	Er
	-	418.22		-	312.80		-	271.37	
288.05	+	50.26	785.39	+	47.80	490.27	+	39.50	Tm
	-	63.35		-	78.38		-	47.38	
1652.06	+	290.00	5387.83	+	353.46	3500.26	+	261.34	Yb
	-	346.76		-	499.77		-	188.66	
199.31	+	27.67	568.37	+	33.15	379.27	+	23.47	Lu
	-	45.01		-	63.85		-	28.43	

Table 4.23: Representative LA-ICP-MS analyses for Y and [Ln] concentrations (ppm) within Eudialyte from Norra Kärr.

	Grennaite	Gren-Peg	Pegmatite	Crenulated	Lak-Zr-Core	Lak-Zr	Discovery	
	122	183	1016	375	192	423	121	
Y	9193.8	16510.8	9532.7	9679.4	2.4	17524.9	28382.6	Y
La	15247.1	11917.8	14416.4	32528.8	786.3	20936.5	20258.8	La
Ce	9104.7	8791.5	9464.0	24624.2	758.1	12222.6	14653.3	Ce
Pr	8763.5	9817.1	8345.5	23574.0	639.9	12232.3	14608.9	Pr
Nd	7590.3	10170.5	7278.1	19966.8	596.8	13025.4	13022.6	Nd
Sm	8672.3	10755.5	7741.3	13945.2	9158.2	13833.7	3748.2	Sm
Eu	2660.7	3259.6	2300.1	3453.4	3210.8	4225.8	1362.7	Eu
Gd	8878.0	10316.5	8424.4	10224.3	7684.4	13257.2	12035.1	Gd
Tb	10558.0	11896.9	9292.4	9009.4	10682.3	15876.2	13318.0	Tb
Dy	11733.7	14224.7	10097.0	9158.5	1710.8	17691.7	17879.7	Dy
Ho	13528.8	14733.6	10356.1	8468.9	10115.1	18067.2	13422.9	Ho
Er	16025.5	16007.1	10776.3	8118.0	7938.7	19057.8	13851.4	Er
Tm	17719.7	18847.7	11856.2	9521.7	8091.2	22061.4	13771.7	Tm
Yb	18848.9	17057.1	11510.4	9032.4	6661.5	21725.1	14113.9	Yb
Lu	12928.1	13463.8	8135.3	6511.6	5231.2	14918.0	9954.6	Lu

Table 4.24: Representative LA-ICP-MS analyses for Y and [Ln] concentrations (ppm) within Eudialyte from Norra Kärr normalised to chondrite (Taylor & McLennan 1985).

Figure 4.52: K vs Na for Norra Kärr eudialytes compared to eudialyte from other intrusions.

Figure 4.53: Mn vs Fe for Norra Kärr eudialytes compared to eudialyte from other intrusions.

Figure 4.54: [Ln+Ce+Nd] vs Ca for Norra Kärr eudialytes compared to eudialyte from other intrusions.

The Na-K substitution (Fig. 4.52) shows that the majority of eudialytes from Norra Kärr display a restricted trend in Na-concentration. However, earlier Grennaite-Host Grennaite show low-concentrations of K and higher-Na, while those from the Crenulated Grennaite show higher concentrations of K supporting the whole-rock trend shown in Chapter 4. The pegmatites display wider spread of K and Na values than the Grennaites and have the highest K concentrations. The eudialytes within the outer two petrological zones of the Lakarpite plot within the field of the earlier Grennaite varieties.

Compared to other alkaline intrusions the Norra Kärr eudialytes display high Na- and K-contents. The earlier Grennaites display similar Na and K concentrations to the Kakortokites of Ilímaussaq while the Crenulated Grennaite and the Pegmatites have similar Na-concentrations and higher K-concentrations, with the pattern of K-enrichment being similar to that of the Green Foyaite at Pilanesberg.

Norra Kärr has two distinct groups of eudialyte in terms of Fe vs Mn (Fig. 4.53). The first group shows increasing Fe concentrations from the Contact Grennaite into the Pegmatite-Host Grennaite and the Pegmatites. The highest Fe concentrations are shown by the outer two petrological zones of the Lakarpite which also display slightly higher Mn concentrations than the early Grennaite varieties. The second group of eudialyte is only observed in the Crenulated Grennaite and shows very high Mn contents and low Fe content. This matches the major element pattern seen in Chapter 4 with Initially increasing Fe in the earlier Grennaites followed by a decrease to the Crenulated Grennaite and an overall trend of increasing Mn concentrations.

Overall Norra Kärr displays lower Fe concentrations compared to other alkaline intrusions. The eudialytes in the earlier Grennaites display similar Mn contents to Langesundsford and Ilímaussaq eudialytes, with a particular similarity with the eudialytes within the Aegirine Lujavrites of Ilímaussaq. The Mn content of eudialyte within the Crenulated Grennaites is only matched by Pilanesberg, with the Green Foyite displaying a strong Fe-Mn fractionation trend matched by the fractionation trend also shown at Norra Kärr between the Pegmatite-Host Grennaites and the Crenulated Grennaites.

A similar trend to Mn vs Fe is observed in a plot of La+Ce+Nd vs Ca. The eudialytes again split into two groups with the earlier Grennaites displaying lower Light-[Ln] contents than eudialytes from the Crenulated Grennaite. Within the Ca-[Ln] substitution there is a progressive increase in [Ln] and a corresponding decrease in Ca with fractionation within the Grennaites. Again, the outer two petrological zones of the Lakarpite have compositions similar to the Pegmatite-Host Grennaite.

Eudialytes from Norra Kärr display broadly similar Light-[Ln] contents to other alkaline intrusions, with the earlier Grennaites again broadly matching the composition of eudialytes from the Aegirine Lujavrite from Ilímaussaq. However, the eudialytes from the Crenulated domain display the highest Light-[Ln] contents of any of the other alkaline intrusion and some of the lowest Ca contents in Fig. 4.54.

Figure 4.55: [La+Ce+Nd] vs Mn/(Fe+Mn) for Norra Kärr eudialytes compared to eudialyte from other intrusions.

Figure 4.56: Nb vs Zr for Norra Kärr eudialytes compared to eudialyte from other intrusions.

Figure 4.57: Fitted Mössbauer spectra for eudialyte within a whole-rock sample from a Norra Kärr pegmatite showing the reflectance peaks for the iron sites (Fe^{2+}).

Both Figs. 4.53 and 4.54 show distinctive nearly linear trends, and when La+Ce+Nd is plotted vs Mn/Fe+Mn a further overall trend of Light-[Ln] enrichment with fractionation emerges (Fig. 4.55). Here the Contact and Pegmatite-Host Grennaite lie at a similar point along the fractionation trend with the Pegmatite-Host Grennaite displaying enrichment in [Ln]. The Pegmatites and outer two petrological zones of the Lakarpite also overlap in this field. The eudialytes from the Crenulated Grennaite show the greatest fractionation and the greatest enrichment in Light-[Ln].

Compared to other alkaline intrusions Norra Kärr appears to be more evolved than Langesundsfjord and the Karkortokites of Ilímaussaq but again broadly similar to the Aegirine Lujavrite. In particular the Norra Kärr eudialytes appear to follow a similar evolutionary trend as the Green Foyite of Pilanesberg. There is little variation with respect to the Zr-Nb substitution within the Z-site. This is similar to the other alkaline intrusions in Fig. 4.56.

4.10.3 Mössbauer and the Hydration State of Eudialyte

The redox of eudialyte was measured using Mössbauer and modelled using an amphibole spectrum (Fig. 4.57) which shows that the Fe is present as Fe^{2+} within eudialyte. Schilling et al. (2011) state that $\text{Fe}^{3+}/\Sigma\text{Fe}$ within eudialyte is not controlled by the oxygen fugacity of the melt but by the hydration state of the eudialyte itself - with more hydrated eudialyte displaying higher Fe^{3+} contents. The high (calculated) OH^- content shown in Table 4.22 appears to contradict this as these eudialytes are all particularly OH^- rich suggesting further work is required to constrain this effect. The volatile content of the eudialytes is explored below.

4.10.4 Volatile Content

Volatiles within eudialyte are located within an O-site and an X-site. The -O-site is dominated by OH⁻ and crystal bound H₂O, whereas the X-site allows several different volatiles to enter and substitute. Figs. 4.58 and 4.59 are boxplots wt% F⁻ and Cl⁻. Eudialyte from Norra Kärr displays typically displays between 0.2 wt% and 0.5 wt% Cl, with eudialyte from the contact Grennaite displaying a greater range between 0.3 wt% and 1 wt%. With fractionation from the Contact Grennaite to the Crenulated Grennaite the range of wt% Cl narrows, with the Pegmatites displaying slightly higher wt% Cl than the Pegmatite-Host Grennaite. Eudialyte shows a more restricted range in terms of wt% F and lie between 0.1 wt% F to 0.3 wt% F. The contact Grennaite displays the highest wt% F of the Grennaites, and again the Pegmatites have a greater volatile content than the surrounding Pegmatite-Host Grennaite. The higher concentrations of both Cl and F in the Pegmatites than the surrounding Grennaite may support them being formed from later stage melt as the surrounding lithologies crystallised.

In comparison to other alkaline intrusions eudialytes from Norra Kärr typically display lower wt% Cl contents but approximately the same wt% F content. However, despite both Cl and F being present within eudialytes, F was not analysed Eudialytes from Ilímaussaq by Pfaff et al. 2008, Lindhuber et al. 2015 and Hunt et al. 2017. This shows the importance of analysing for a range of volatile species when studying eudialyte rather than just focusing in on Cl⁻ alone.

Figure 4.58: Boxplot of wt% Cl for eudialytes from Norra Kärr and other alkaline intrusions.

Figure 4.59: Boxplot of wt% F for eudialytes from Norra Kärr and other alkaline intrusions.

4.10.5 Trace Elements in Eudialyte

The [Ln]-patterns of the eudialyte (Fig. 4.60, 4.61) broadly match the patterns seen within the whole rock analyses. As eudialyte is the only mineral capable of removing high concentrations of [Ln] from the melt the patterns presented likely represent the final composition of the local melt at the time of crystallisation.

Eudialyte from the Contact Grennaite is broadly flat with a broad heavy-[Ln] enrichment. The Pegmatite-Host eudialyte also has a broad heavy-[Ln] enrichment. This [Ln]-pattern also overlaps with the average eudialyte composition of the Zr-Rich Lakarpite zone which provides further evidence of interaction between the two lithologies. In all of these cases Y and Ho concentrations are also coupled. The Zr-Core Lakarpite, however, shows far lower [Ln]-concentrations and displays a near flat [Ln]-pattern, potentially as it is closer to the [Ln]-poor core of the Lakarpite. Y is also significantly less abundant and is not coupled with Ho in the Zr-Core Lakarpite.

Eudialyte from the Grennaite side of the well-known 'discovery outcrop' at Norra Kärr (see Fig. 2.34 – Chapter 2) manifests a similar overlapping pattern to that of the Pegmatite-Host Grennaite and Zr-Rich Lakarpite, though Y and Ho are not coupled in eudialyte from the 'discovery outcrop'.

Eudialyte from the pegmatites show an intermediate [Ln]-pattern with similar La-Sm concentrations as the Contact and Pegmatite-Host Grennaites, but dissimilar Gd-Lu concentrations more akin to the Crenulated Grennaite. Y and Ho are coupled within the Pegmatites.

The Crenulated Grennaite eudialyte demonstrates a strong enrichment in the light-[Ln] and heavy-[Ln] concentrations similar to that of the pegmatite. The slight bias towards heavy-[Ln] observed within eudialyte from the earlier Grennaites may, along with catapleiite crystallisation, result in an overall enrichment in light-[Ln] within the magma.

Figure 4.60: Y and [Ln]-concentrations for Norra Kärr eudialyte from the first phase of intrusion normalised to chondrite. In general the plot shows a relatively flat profile with only a slight preference for heavy-[Ln] with the exception of eudialyte from the Crenulated Grennaite.

Figure 4.61: Y and [Ln]-concentrations for Norra Kärr eudialyte formed due to the second phase of intrusion (with the Pegmatite-Host Grennaite eudialytes for comparison) normalised to chondrite. The plot shows a relatively flat profile with only a slight preference for heavy-[Ln].

4.10.6 Element Maps and [Ln]-Profiles

Multiple maps of eudialyte from each lithology were obtained using SEM-EDS and EMPA; maps displaying characteristic features are presented here. Each figure groups the elements according to common substitutions (outlined in a.p.f.u. plots in section 4.10.2) and by alteration and volatile content, with the maps presented in order of increasing fractionation. Maps of the Lakarpite eudialytes do not show visible chemical zoning and are not shown.

Fig. 4.62 shows the element maps for a eudialyte from the Contact Grennaite. In a BSE image the crystal shows a dark patchy core and a bright rim. The core is correlated with higher Si and Fe contents, while the rim is richer in Mn and Cl. Within the core of the crystal there is some patchy Mn and K zoning while Ca and Na are distributed relatively evenly throughout the core and rim of the crystal. Fig. 4.63 shows the element maps for a eudialyte from the Pegmatite-Host Grennaite. In a BSE image the crystal displays a patchy core surrounding a trigonal-shaped centre. There does not appear to be a well-developed rim to the crystal. Less variation is seen in this crystal than in Fig. 4.62. All elements apart from K and Al are patchily distributed throughout the whole crystal. However, K is present in higher concentrations in the core of the crystal and Al is present in a crack within the mineral.

Figs. 4.64 and 4.65 show the element maps of eudialytes from the Pegmatites. In a BSE image the crystal in Fig. 4.64 displays a patchy core and zoned rims (see also 'Pegmatite' Fig. 4.51). This crystal displays a core which is richer in Si and Zr, and a rim richer in Ca, Mn, Na and Cl and [Ln]. Fe is evenly distributed throughout the crystal, apart from in the altered cracks within the crystal where it is in higher concentrations along with elevated levels of Ca, Zr, Al and [Ln]. K is also higher in the zones around the cracks where it has substituted for Na. The crystal in Fig. 4.65 shows much the same pattern in BSE and in terms of element distribution. The core is rich in Si, Zr, while the rim is richer in Ti, Ca, Mn and Cl which display repeating patterns that also align with the optical zoning seen in Chapter 3 (Fig. 3.20-B). Cracks are enriched in Fe, Zr, Ca and Al, with the same Na/K replacement observed in the areas around the cracks.

Contact: NK32-158.15

Figure 4.62: SEM-EDS element map for a eudialyte from the Contact Grennaite. Note elevated Mn and Cl within the rim of the crystal.

Pegmatite-Host: NK53-269.3

Figure 4.63: SEM-EDS element map for a eudialyte from the Pegmatite-Host Grennaite.

Pegmatite: NK25-49.4

Figure 4.64: EPMA element map for a eudialyte from the Pegmatites. Note the strongly zoned nature of the crystal and the minor alteration along internal cracks.

Pegmatite: NK25-49.4

Figure 4.65: SEM-EDS element map for a eudialyte from the Pegmatites. Note the multiple rims highlighted by Mn, Zr and Ca, along with the minor alteration along internal cracks.

Crenulated: NK82-7.55

Figure 4.66: SEM-EDS element map for a eudialyte from the Crenulated Grennaite.

Fig. 4.66 shows the element maps of a eudialyte from the Crenulated Grennaite. In BSE there does not appear to be a well-developed rim. The crystal displays reasonably evenly distributed Si, Zr, Fe, Na, K, Cl and [Ln]. There is some patchy variation in Mn, while Ca shows a distinct pattern in concentration and appears to be enriched with proximity to cracks within the crystal. These cracks display a distinct Al alteration.

Overall, each eudialyte shows a core rich in Si and Zr (the main structural elements in eudialyte) with some crystals from the Contact Grennaite and Pegmatites displaying rims enriched in Mn, Cl and in the case of the Pegmatites [Ln]. This suggests that as the crystals grew, the environment around them changed as recorded by the progressive increase in Mn and Cl concentrations along with the lighter-[Ln] such as Ce. The eudialytes from the Pegmatites and the Crenulated Grennaite also exhibits Al alteration along cracks within the crystal which also have enhanced concentrations of Zr, Ca and [Ln]. It is likely that these have been altered to catapleiite during late stages of crystallisation. However, unlike eudialytes from Ilímaussaq (Borst et al. 2016) the Norra Kärr eudialytes display very low levels of alteration suggesting the crystals were in equilibrium with their environment for some time after.

Figs. 4.67 – 4.70 show the representative profiles for light-[Ln] and heavy-[Ln] concentrations across representative profiles of analysed eudialytes from the Grennaite at Norra Kärr. Of course, these profiles only provide a restricted sample of the numerous eudialyte crystals that are present within each lithology at Norra Kärr. All profiles have been smoothed using a three-point moving average. As shown in Appendix 1 – Fig. A.1.3 the width of the ablation trench is too large in relation to the zoning seen in BSE images within the finer grained eudialytes to accurately resolve each discrete zone. As such these profiles can only offer an indication of the chemical variation within the crystals. In the majority of the profiles the trends in [Ln] concentration match up for both the light-[Ln] and the heavy-[Ln]. It is likely that the variation in [Ln] is caused by the changes in the major element composition of the crystals.

Eudialyte from the Contact Grennaite and Pegmatite-Host Grennaite both show complex internal zoning in BSE. This can potentially be seen in eudialyte from the Contact Grennaite (Fig. 4.67) where there is some variation in [Ln] across the crystal, with higher concentration in the centre and rims of the crystal. This is less evident in eudialyte from the Pegmatite Host Grennaite (Fig. 4.68) but there does appear to be a slight difference in relative La vs Lu concentrations with Lu being relatively higher in one half of the crystal. Eudialyte from the Crenulated Grennaite (Fig. 4.69) also shows an uneven distribution of [Ln] with one side of the crystal showing lower concentrations of [Ln] than the other, and a noticeable dip in [Ln] abundance between the rim and core of the crystal on one side. Eudialyte from the pegmatites shows optical and BSE variation from the core of the crystal towards the rim. To some extent this is observable in Fig. 4.70 with the core being higher in [Ln] before decreasing towards the rim of the crystal where the [Ln] concentrations begin to increase.

Figure 4.67: [Ln] profile through a fine-grained eudialyte crystal from the Contact Grennaite [NK32-158.15] showing highly variable internal concentrations of [Ln]. Step size 10µm.

Figure 4.68: [Ln] profile through a fine-grained eudialyte crystal from the Pegmatite-Host Grennaite [NK53-97.8] showing uneven distribution of [Ln] and a slight heavy-[Ln] enrichment to one side. Step size 10 μ m.

Figure 4.69: [Ln] profile through a fine-grained eudialyte crystal from the Crenulated Grennaite [NK32-69.3] showing uneven distribution of [Ln]. Step size 10 μ m.

Figure 4.70: [Ln] profile through a coarse-grained eudialyte within the Pegmatites [NK25-49.4]. Step size 10 μ m. The core of the crystal to the left of the plot with the rim on the right.

4.10.7 Eudialyte Summary

Eudialyte is the second forming Zr-silicate after catapleiite, and predominantly provides information about the evolution of the Grennaite. The eudialyte crystals appear to have had a complex growth history as evidenced by the composite textures seen within BSE images. Most eudialytes have a central core that is richer in Si and Zr which is followed by a Mn and Cl rich rim in the Contact Grennaite and a more complex zoned rim in the Pegmatites.

Chemically the eudialytes can be split into two groups; a first less evolved group consists of the earlier Grennaite varieties, the Pegmatites and the outer two zones of the Lakarpite. The second group consists of the more evolved eudialytes from the Crenulated Grennaite. Together the eudialytes show that there has been a pattern of increasing fractionation in terms of Na and K; Mn/(Fe+Mn) and Light-[Ln] content from the Contact Grennaite to the Crenulated Grennaite which matches the pattern observed in the whole-rock data. Both the Pegmatites and the eudialytes from the Lakarpite show little variation from the chemistry of the eudialytes from the Pegmatite-Host Grennaite. The eudialytes show that the predominate volatile within the Grennaites was OH⁻ and they also show a pattern of decreasing Cl⁻ with fractionation, albeit one which appear to locally increase at the rims of some eudialytes.

Many of the trends shown by eudialytes from Norra Kärr are seen within other alkaline intrusions and specifically the Green Foyite of Pilanesberg. The eudialytes do not appear to be similar to those from Langesundsfjord, and with respect to Ilímaussaq they bear little in common with the Kakortokites but do share some similar chemistry with the Aegirine Lujavrite. Both the Green Foyite and Aegirine Lujavrite have similar mineralogy's though the Green Foyite shows a wider degree of fractionation which Norra Kärr appears to match.

4.11 Fluorite

Fluorite is present within the inner zones of the Lakarpite and the Pulaskite and its enclaves. BSE-SEM images show that the fluorite extends along cracks within the feldspars and does display some brighter minerals around its boundary (Fig. 4.71).

Figure 4.71: BSE-SEM images of fluorite from the Pulaskite-type Lakarpite, and the Pulaskite. Red scale bar is equal to 100 μm . In both images the fluorites predominately surrounded by feldspars.

While most fluorite appears to have crystallised before the feldspar phases, there are instances of co-crystallisation with feldspars particularly within the Pulaskite. While the Lakarpite and Pulaskite contain 2.279 Wt.% and 2.316 Wt.% CaO respectively (Chapter 4) the concentration of Ca was seemingly never high enough to react with F in the melt until the latter stages. Ca could have been enriched within the melt by the earlier crystallisation of Ca-poor pyroxenes, biotites and amphiboles as only rosenbushite contains appreciable concentrations of Ca but this is a comparatively minor phase within the lithologies. Furthermore, earlier amphiboles within the Pulaskite contain appreciable F contents which may have reduced the activity of F^- in the melt. However, the final onset of dry alkali-feldspar crystallisation may have resulted in the required conditions being met for fluorite crystallisation.

4.12 Microcline, Albite and Nepheline

A total of 265 feldspar and 53 nepheline analyses were collected. Only alkali-feldspars have been observed. These minerals are prevalent throughout the Norra Kärr where they are the last forming phase or found within the Pulaskite where they may co-crystallise with fluorite.

4.12.1 SEM-EDS Petrology

Feldspars and foids are the last phases to crystallise from the magma. Microcline typically forms larger subhedral-phenocrysts up to 5 cm long and always displays tartan twinning. Albite is typically anhedral to subhedral to anhedral crystals less than 5mm in dimension. Aegirine-rich feldspar occurs in the pegmatites and the Zr-rich Lakarpite and is a microcline containing inclusions of aegirine aligned along the c-axis. Nepheline is typically less than 5-mm in dimension and is typically altered. There does not appear to be any zoning present within the BSE images (Fig. 4.72).

Fig. 4.72: BSE-SEM images of feldspars and nepheline from different lithologies within Norra Kärr. Red scale bar is equal to 100 μm .

4.12.2 Substitutions

Feldspars and Nephelines follow the structural formulae:

(Deer et al. 1997)

The main substitutions in alkali feldspars are dominated by K and Na within the M site.

Representative EPMA analyses are given below for Albite (Table 4.25) Orthoclase (Table 4.26) and Nepheline (Table 4.27). The feldspar compositions are plotted on the feldspar ternary (Fig. 4.73) and both the nepheline and feldspar compositions are plotted in on the Qz-Nep-Kal ternary (Fig. 4.74).

Albite	Con.	P.-H.	Peg.	Cren.	Kax.	L-Core	L-ZrCore	Pul.	Pul.-En.
n=	20	14	4	1	34	19	8	21	20
SiO ₂	68.96	68.63	69.19	68.42	68.78	69.03	68.82	68.60	66.16
Al ₂ O ₃	19.44	15.97	18.92	18.10	19.17	19.13	18.93	19.14	19.17
Na ₂ O	12.31	12.29	12.02	12.38	12.05	12.10	12.13	12.10	12.08
K ₂ O	0.06	0.09	0.08	0.09	0.09	0.10	0.13	0.11	0.12
CaO	0.09	0.04	b.d.l.	0.11	0.01	0.01	0.01	0.01	0.02
FeO	0.11	0.19	0.08	0.44	0.05	0.07	0.04	0.03	0.11
MnO	0.04	b.d.l.	b.d.l.	0.01	0.01	0.02	b.d.l.	b.d.l.	0.02
MgO	b.d.l.	0.005	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.01	0.002
TiO ₂	0.04	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.01	b.d.l.	b.d.l.	b.d.l.
Si	2.97	3.07	3.01	2.99	2.99	2.99	3.00	2.99	2.94
Al	0.99	0.84	0.97	0.93	0.98	0.98	0.97	0.98	1.00
Na	1.03	1.07	1.01	1.05	1.02	1.02	1.02	1.02	1.04
K	0.00	0.01	0.00	0.01	0.01	0.01	0.01	0.01	0.01
Ca	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00
Fe	0.00	0.01	0.00	0.01	0.00	0.00	0.00	0.00	0.00
Mg	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ti	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table 4.25: Representative EPMA analyses and calculated (on the basis of 8 O) compositions of Albite from Norra Kärr.

Orthoclase	Con.	P.-H.	Peg.	Cren.	Kax.	L-Pul	L-Core	L-ZrCore	Pul.	Pul.-En.
n=	1	4	6	6	26	7	1	16	16	41
SiO ₂	65.13	64.00	65.15	63.82	63.27	64.36	64.34	64.15	64.50	62.20
Al ₂ O ₃	18.69	14.63	17.98	16.36	18.15	17.81	16.54	17.92	18.16	18.39
Na ₂ O	0.37	0.36	0.55	0.32	0.35	0.46	0.40	0.39	0.37	0.40
K ₂ O	16.73	16.62	16.17	16.67	16.61	16.39	16.16	16.43	16.60	16.54
CaO	b.d.l.	0.03	0.01	0.01	0.01	0.02	b.d.l.	0.01	0.01	0.001
FeO	0.19	b.d.l.	0.07	b.d.l.	0.19	0.10	0.05	0.02	0.11	0.14
MnO	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.01	b.d.l.	b.d.l.	b.d.l.	0.01	0.01
MgO	b.d.l.	0.003	b.d.l.	b.d.l.	0.01	b.d.l.	b.d.l.	b.d.l.	0.005	b.d.l.
TiO ₂	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.02	b.d.l.	b.d.l.	b.d.l.	0.04	0.01
Si	2.98	3.10	3.01	3.04	2.96	3.00	3.06	3.00	2.99	2.94
Al	1.01	0.84	0.98	0.92	1.00	0.98	0.93	0.99	0.99	1.02
Na	0.03	0.03	0.05	0.03	0.03	0.04	0.04	0.04	0.03	0.04
K	0.98	1.03	0.95	1.01	0.99	0.97	0.98	0.98	0.98	1.00
Ca	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe	0.01	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00
Mg	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ti	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table 4.26: Representative EPMA analyses and calculated (on the basis of 8 O) compositions of Orthoclase from Norra Kärr.

Nephelines n=	Con. 3	P.-H. 6	Peg. 11	Cren. 17	Kax. 9	L-ZrRich 6	Pul. 1
SiO ₂	42.28	47.51	46.69	47.65	42.63	47.72	43.38
Al ₂ O ₃	34.69	25.69	26.65	24.84	33.10	25.72	30.42
Na ₂ O	16.63	16.54	15.66	16.24	12.04	16.16	16.56
K ₂ O	7.01	7.72	6.96	2.29	7.07	0.01	6.25
CaO	b.d.l.	0.04	0.05	0.04	0.31	0.03	b.d.l.
FeO	0.30	0.09	0.08	0.06	0.35	0.24	0.26
MnO	b.d.l.	b.d.l.	0.02	0.25	0.01	b.d.l.	b.d.l.
MgO	b.d.l.	0.01	0.03	0.18	0.005	0.002	b.d.l.
TiO ₂	b.d.l.	b.d.l.	0.01	b.d.l.	0.01	b.d.l.	b.d.l.
Si	1.02	1.19	1.19	1.28	1.12	1.31	1.09
Al	0.98	0.76	0.80	0.78	1.02	0.83	0.90
Na	0.78	0.80	0.78	0.84	0.61	0.86	0.81
K	0.22	0.25	0.23	0.08	0.24	0.00	0.20
Ca	0.00	0.00	0.00	0.00	0.01	0.00	0.00
Fe	0.01	0.00	0.00	0.00	0.01	0.00	0.00
Mg	0.00	0.00	0.00	0.01	0.00	0.00	0.00
Mn	0.00	0.00	0.00	0.01	0.00	0.00	0.00
Ti	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table 4.27: Representative EPMA analyses and calculated (on the basis of 4 O) compositions of Nepheline from Norra Kärr.

Figure 4.73: Feldspar ternary. The majority of feldspar analysis lie at the end-members of Ab and Or. After Fuhrman et Lindsley (1988)

Figure 4.74: Qz-Nep-Kal ternary under 5 kbar [$P(\text{H}_2\text{O}) = P(\text{Total})$] (after Zhang and MacKenzie 1984) Norra Kärr feldspar and nepheline analyses plotted. Feldspars plot as end-members, while nephelines lie close to the nepheline eutectic.

Figs. 4.73 and 4.74 show that the feldspars predominantly crystallised as two pure end-members of albite and K-feldspar. Fig. 4.74 also shows that nephelines lie close to the eutectic points of the Qz-Nep-Kal triangle indicating low temperatures of crystallisation. The presence of larger microclines within the trachytic units, and particularly within the Xactorpit, suggests that feldspars were co-crystallising alongside earlier aegirine (below at most 800°C) and were able to grow into cm-scale broadly euhedral crystals before the magma achieved a crystal load high enough to prevent further growth. The later albite displays a more subhedral-to-anhedral texture suggesting that it crystallised at the same time – potentially on the eutectic. The presence of the two populations of pure end-member feldspars indicates that the pressure conditions were at least 5 kbar.

While there is evidence of earlier co-crystallisation, feldspar and nepheline appear to be the last forming phases in the petrological sequence. Almost pure feldspar end-member compositions have also been reported in lujavrites of Ilímaussaq (Markl et al. 2001), who showed that the crystallisation temperature of the lujavrites was between 350°C–400°C. This suggests that residual crystallisation could have continued down to such temperatures in Norra Kärr too, with the presence of tartan twinning within microclines also indicating that a degree of low temperature recrystallisation had occurred (Mitchell et Platt 1982). Woolley et. al (1996) explained the presence of fine-aegirine needles within nephelines from nepheline syenites in Malawi as being due to the exsolution of the Fe content within the nepheline, potentially aided by deformation. As shown by Table 4.27, several nephelines display an appreciable trace Fe content, which could explain the presence of the aegirine needles within the aegirine-rich variety of nepheline.

4.13 Discussion

The mineralogy and petrology of the two magmatic phases at Norra Kärr are unique to this intrusion; however, reasonable comparisons can be made with other alkaline intrusions. In this section the overall comparisons will be made with other alkaline intrusions allowing the trends in mineral chemistry to be placed into context. An overview of magmatic evolution and a tentative T-fO₂ history will be proposed (Figs. 4.75-4.77).

4.13.1 Comparison with other Alkaline Intrusions

Each mineral within Norra Kärr broadly displays its own unique composition, however, comparisons with other alkaline intrusions can be broadly made. Due to the overlapping nature of aegirine evolution trends between intrusions the pyroxenes are not a useful comparator but in general the aegirines from Norra Kärr lie between Motzfelt and Lovozero-Katzenbuckel showing that they did not follow the same trend as seen in Ilímaussaq.

The amphiboles provide a better comparator, overall being most similar to amphiboles from Pilanesberg. They also show some similarities with Lovozero and the kakortokites of Ilímaussaq, the latter being in the later forming stages of Ilímaussaq indicating the highly fractionated nature of the Norra Kärr melt. However, the amphiboles are also some of the least evolved in terms of Mg/(Fe+Mg) but display the highest F concentration of any intrusion bar Strange Lake (with which they show differences in composition in terms of minor substitutable structural elements). The amphiboles also show overall restricted fractionation trends.

Sphene displays higher fluorine concentrations than the Saima and Pilanesberg intrusions. Norra Kärr rosebushites are compositionally different to those from Langesundsfjord but display similar fluorine contents. Biotite displays similarities to the white foyites of Pilanesberg, but like the Norra Kärr amphiboles the biotites show a restricted fractionation range and display the least evolved compositions when compared to biotites from Pilanesberg, Mont St Hilaire and Ilímaussaq.

Catapleiite compositions are closest to Langesundsfjord (unlike the rosenbushites). The eudialytes however, display the closest similarities to eudialytes from the Green Foyite of Pilanesberg (while retaining some minor similarities with eudialytes from the Aegirine-Lujavrite of Ilímaussaq).

Overall, it appears that Norra Kärr is most similar (but certainly not identical) to the Pilanesberg intrusion, with the first phase of intrusion being similar to the Green Foyites, and the second phase of intrusion being similar to the White Foyites.

4.13.2 Mineral Evolution Trends in Mineral Chemistry and Possible T-fO₂ Path

Norra Kärr appears to consist of two phases of intrusion: the first phase being the Grennaites and the Kaxtorpite, and the second phase the Lakarpite and Pulaskite. However, the Grennaites are phonolitic while the Kaxtorpite, Lakarpite and Pulaskite are trachytic (Chapter 5 – Fig 5.1) and as such display differing evolutionary paths.

Initial Aegirine Crystallisation (All Lithologies)

The aegirines of the Grennaite and the Kaxtorpite all lie along an Aeg-Jd trend and represent highly fractionated aegirine compositions throughout the first phase of intrusion irrespective of the whole rock trends in Na and Fe. The magma is sufficiently concentrated in Zr to result in Zr-rich cores within some aegirines.

Separately, the aegirine/aegirine-augites within the Lakarpite and Pulaskite lie along the Aeg-Quad trend and represent a fractionation sequence towards the aegirine endmember from a more Ca-Fe-Mg rich endmember. In particular, the inner zones of the Lakarpite appears to be less evolved than the outer zones; pyroxenes from the Pulaskite are particularly less evolved in terms of Ca.

Due to the compositional similarities with Pilanesberg the redox trends and chemographic grids identified and developed by Andersen et al. (2017, 2018) can be used to approximately understand some of the processes occurring at Norra Kärr. Aegirine begins to crystallise in the system $\text{SiO}_2\text{-Fe}_2\text{O}_3\text{-Na}_2\text{O-SiO}_2$ at around 950°C to 850°C (Bowen et al. 1930) and the data from the Norra Kärr aegirines indicates that the starting $f\text{O}_2$ of the first and second phase magmas at Norra Kärr lie between FMQ +1 and -2. This matches the model produced for Pilanesberg by Andersen et al. (2017; Figure 9) and is replicated in Fig. 4.77. The crystallisation of Fe^{3+} -Aegirine results in the $f\text{O}_2$ of the lithologies to start to fall. While Martel et al. (2013) have shown that Amp+Ox are stable at temperatures 900°C -700°C, it is likely that conditions were too oxidising to support amphibole leading to ‘amphibole breakdown’ and the freeing up of F within the melts (Deer et al. 1997, Scailliet & Macdonald 2001).

Biotite-and Sphene (Trachytes)

Biotite and sphene are only present within the Lakarpite and Pulaskite. The appearance of sphene at approximately 825°C (Martel et al. 2013) likely results in ending Aegirine-Augite crystallisation as sphene removes any available Ca from the melt. Biotite compositions indicate that the second phase magmas may represent less evolved magma compositions due to the higher Mg content. The biotite's are rich in K but show low Ti compositions possibly as a result of earlier sphene crystallisation. All biotite's display an OH rich composition.

The biotite stability field lies just below FMQ = 0 and extends to IW = 0, being intersected upon a fall in temperature at static $f\text{O}_2$ or at a decreasing $f\text{O}_2$. The difference in whether biotite appears at all in the fractionation sequence is dependent upon the activity of H_2O (Andersen et al. 2018). A higher activity results in the formation of biotite over amphibole with the crystallisation of F-rich amphibole within peralkaline magmas more dependent upon temperature and low $f\text{O}_2$ (Scailliet & Macdonald 2001) than water availability. As such the Pulaskite and core of the Lakarpite appear to have been ‘wet’ enough for biotite crystallisation, unlike the outer zones of the Lakarpite.

At this time the Grennaite (phonolites - no biotite) and Kaxtorpite (trachyte – no biotite) are likely following a trend between FMQ 0 -+1 (above the Biotite-Aegirine line – Fig. 4.77) and/or do not have a high enough water activity for biotite. However, the core-Lakarpite and Pulaskite will be progressing beneath this line which could provide an explanation for the difference in mineralogy between the Kaxtorpite and the Pulaskite-Lakarpite despite all three lithologies displaying broadly similar major element chemistries.

Amphibole and Coarse Microcline (Trachytes)

Aside from an amphibole in the Pegmatites, amphibole is restricted to the trachytic lithologies. Amphibole in the Kaxtorpite is present as Eckermannite-Arfvedsonite. All amphiboles lie at the end of the alkali-amphibole fractionation series indicating the highly evolved nature of the first magmatic phase. However, in terms of $Mg/(Fe+Mg)$ the amphiboles of the first intrusive phase could be considered less evolved than the second intrusive phase. The Kaxtorpite amphiboles are richer in Mg than the Fe-rich amphibole of the pegmatite. The F-rich nature of the Kaxtorpite amphiboles also indicate a high F-activity. Subsequent to amphibole, Ca and Mn rich pectolite crystallises within the Kaxtorpite. This may indicate that the F-activity is reducing favouring the formation of pectolite over fluorite as a sink for the remaining Ca within the magma.

The amphiboles within the second intrusive phase are predominantly arfvedsonites with those from the Pulaskite and the inner zones of the Lakarpite less evolved than those from the outer Lakarpite zones which plot closer to the compositions matching amphiboles from the first intrusive phase. The Lakarpite amphiboles are richer in Fe, while the Pulaskite amphiboles are richer in Ca, Mg and Ti. Both sets of amphiboles display similar concentrations of K and Mn. The Pulaskite is less F-rich than the Lakarpite, possibly due to earlier forming F-rich rosenbushite. Overall, the amphiboles appear to be indicating restricted fractionation sequences.

As discussed above, the crystallisation of F-rich amphibole within peralkaline magmas is more dependent upon temperature and low fO_2 than water availability. Amphibole may thus begin to crystallise due to the fO_2 of the magma having become more reduced due to aegirine formation or due to having fallen in temperature to below 700°C. The redox range for riebeckite-arfvedsonite is shown in Fig. 4.77 cutting across the redox-buffer systems. The solidus of the magma will already have been suppressed by the presence of water and fluorine, but also by a low fO_2 (Scaillet & Macdonald 2001). As such any amphibole crystallisation at this stage may continue to lower the solidus due to the removal of Fe^{3+} from the melt.

At this stage coarse subhedral phenocrysts of microcline are abundant within the trachyte magmas. This often contain small inclusions of aegirine but are otherwise clear. Given the presence of pure microcline and albite later in the sequence ('two-feldspars' – Fig. 4.74) it is likely that the solvus has been suppressed either by lithostatic or volatile pressure. As such, the crystallisation of larger microcline phenocrysts could begin around 700°C and need not disturb or enclose other coeval phases due to the low degree (<30%-40%) of previously solidified crystals within the melt.

Zr-Silicate Formation

The pattern of Zr-silicates within the two intrusive phases is very different. Within the Grennaite the first forming phase, catapleiite, is present throughout the Grennaite and shows a steady increase in Ca with fractionation through the Contact – Pegmatite-Host – Crenulated Grennaite fractionation sequence, which also matches the pattern observed in the whole-rock data. This may be due to the crystallisation of aegirine which does not remove Ca from the melt. Water activities are also high enough during this stage of crystallisation to crystallise catapleiite over eudialyte. The second forming Zr-silicate, eudialyte, shows that with fractionation from the Contact-to-Crenulated Grennaite there is an increase in K (with a decrease in Na), Mn and Light-[Ln] (with some minor increase in Fe midway through the sequence), which all match the observed whole-rock

patterns. Both K and Mn are not major constituents of aegirine and could be concentrated by its earlier crystallisation. They could also be concentrated by eudialyte fractionation due to preferential removal of Na and Fe. Ca, however, appears to decrease in concentration within the eudialytes. This may be due either to the dominance of the Light-[Ln] – Ca substitution, or due to Ca being less available due to catapleiite crystallisation. However, residual Ca still seems to be present post-eudialyte crystallisation as shown by the Ca-, K-, Al-alteration observed along altered fractures within the eudialytes. The higher concentrations of Al at this stage may also result in Al-rich rims around pyroxenes as observed by Atanasova et al. (2017). The eudialyte also becomes lower in F overall, however Cl is concentrated at the later stages of eudialyte crystallisation shown by higher concentrations in the crystal rims.

The Lakarpite and Pulaskite show a different pattern. The next phase to crystallise after amphibole in the Pulaskite is fluorite, which appears to co-crystallise interstitially with feldspar. This may have been driven by earlier minerals (sphene, biotite, amphibole) removing OH from the melt leading to rising F concentrations. This can also be observed in the Pulaskite-type Lakarpite. Within the core-type Lakarpite the crystallisation of F-rich amphiboles was followed by rosenbushite and fluorite crystallisation, suggesting that the magma was originally F-rich and became more so during fractionation. Within the outer Lakarpite zones OH-rich eudialyte was able to crystallise with mineral compositions similar to the eudialytes that crystallised within the contact and Pegmatite-Host Grennaite. Catapleiite is also present within the Zr-Rich Lakarpite; it displays a similar composition to catapleiite from the Pegmatite-Host Grennaite and displays a high OH-content.

Within Pilanesberg the crystallisation of amphibole took place at roughly the same stage that Zr became incompatible in pyroxene and began to form its own mineral (approximately 625°C). In the case of Norra Kärr the first Zr-silicate formed within the Grennaite is catapleiite which suggests that a_{H_2O} was elevated at this stage. In the case of the Pulaskite, the presence of rosenbushite suggests a_{HF} was dominant. Andersen et al. (2010) used chemigraphic grids to understand the variations in Nds, OH and F activity that drove the crystallisation of different Zr-silicate phases. This will be explored further in Chapter 7 along with the pattern of Zr-mineral crystallisation within the Lakarpite.

Two-Feldspar and Nepheline Crystallisation (All Lithologies)

While coarse microclines were able to form above 600°C, once the solvus was reached two feldspars began to crystallise filling the remaining 60% of the volume of the lithologies lithology; co-crystallising with nepheline at a suppressed solidus temperature close to the nepheline eutectic point of the Qz-Nep-Kal ternary using up the remaining Al within the melt.

Figure 4.75: Crystallisation stages for the Grennaite and the Kaxtorpite showing trends in mineral composition for each stage. Due to the spatial relationship of the different units it is likely that each stage occurred at different times for each separate unit.

Figure 4.76: Crystallisation stages for the Pulaskite and Lakarpite showing trends in mineral composition. Note that crystallisation happened later in time than in Fig. 4.75, with the Pulaskite possibly intruding the Contact Grennaite after it had significantly crystallised (perhaps by 625°C) while the Lakarpite intruded into the Pegmatite-Host Grennaite while it was still hot (possibly between 700°C - 625°C).

Figure 4.77: Temperature-oxygen fugacity diagram after Andersen et al. (2017) with and approximate for T- fO_2 cooling path for Norra Kärr marked in red. The Norra Kärr magmas approximately follow the Bt-Aeg line within the limits of FMQ = +1 to -2 as shown by aegirine evolution trends, before following the arfvedsonite-richterite trend during amphibole crystallisation as the magmatic temperature decreases. Zr became incompatible within Pilanesberg pyroxenes at approximately 625°C triggering the crystallisation of separate Zr-silicate phases. The predominate phase crystallising during cooling is given at the base of the figure. The buffer curves (HM: Hematite-Magnetite, QFM: Quartz-Fayalite-Magnetite in a silica saturated system, MW: Magnetite-Wüstite, IW: Iron-Wüstite) are calculated at 1 kbar according to Frost (1991). Andersen et al. (2017) calculated the aegirine-biotite coexistence line at 1 atmosphere at unit activities of $Na_2Si_2O_5$, $NaFeSi_2O_6$, $KFe_3AlSi_3O_{10}(OH)_2$ and H_2O using thermodynamic data from the HSC Chemistry database. Stability limits for ferro-richterite of compositions $NaNaCaFe_4MgSi_8O_{22}(OH)_2$ and $NaNaCaFe_5Si_8O_{22}(OH)_2$ were from experimental data by Charles (1977). The approximate limit for coexisting arfvedsonite and aegirine at $a_{H_2O} = 1$ is based on experimental data of Ernst (1962), and the maximum fO_2 limit for coexistence of aegirine and aenigmatite at variable $a_{Na_2Si_2O_5}$ on estimates by Nicholls and Carmichael (1969). The temperature range for the solidus of agpaiteic magmas in the Ilímaussaq complex is based on experimental data from Piotrowski and Edgar (1970) and Sood and Edgar (1970) and petrological modelling by Markl et al. (2001), the T- fO_2 path for agpaiteic magmas in the Ilímaussaq Complex is also from Markl et al. (2001). Aegirine and ferro-richterite stability limits are not univariant but depend on other activity parameters according to Andersen et al. (2017). Arrows on the aegirine-biotite and aegirine-arfvedsonite curves show direction of displacement caused by reducing an activity of specified components below unity.

4.14 Conclusions

This chapter has shown that the minerals within Norra Kärr further highlight the whole rock trends within each magmatic phase in terms of the major element chemistry discussed in Chapter 4, as well as showing that:

- Aegirine displays two compositional trends, Aeg-Jd within the first intrusive phase (Grennaite and Kaxtorpite) and Quad-Aeg within the second intrusive phase (Lakarpite and Pulaskite). The aegirines also indicate a starting fO_2 within the initial magma of FMQ +1 to -2.
- Biotite displays OH^- -rich compositions and records restricted fractionation within the Pulaskite and Lakarpite.
- Amphiboles and Biotite are the main recorder of redox within the lithologies at Norra Kärr with the Fe^{3+} amphiboles rich in the first intrusive phase (Kaxtorpite) and Fe^{2+} -rich within the second intrusive phase (Lakarpite and Pulaskite). Amphibole also records restricted fractionation by the lithologies.
- The compositions of catapleiite and eudialyte indicate progressive fractionation from the Contact Grennaite inwards to the Crenulated Grennaite as shown by trends in Ca, Mn and Light-[Ln] which also match the trends seen within whole-rock data (Chapter 4). Eudialyte shows progressive increase in OH^- and decrease in F. The Ca trend within catapleiite is likely driven by aegirine crystallisation, while the trends within the eudialyte are a combination of aegirine and catapleiite.
- SEM-EDS-maps of eudialyte display localised increases in Mn within the rims and suggesting interstitial melt evolution. Within the pegmatites multiple repeating rims suggest fluctuating melt compositions. Minor Al, K and Ca alteration is also observed suggesting enriched concentrations within the residual melt.
- The compositions of catapleiite and eudialyte within the Lakarpite are similar to those from the Pegmatite-Host Grennaite suggesting interaction between the Grennaite and the outer zone of the Lakarpite.
- Feldspars all plot as pure end member compositions while nepheline compositions are close to the eutectic point, both indicating low temperatures in the latter stages of crystallisation within the intrusion.
- Overall the mineral compositions displayed within Norra Kärr show the most similarities to compositions from the Pilanesberg alkaline intrusion, with the first phase of intrusion being similar to the Green Foyites, and the second phase of intrusion being similar to the White Foyites - albeit with both phases of intrusion displaying more restricted fractionation trends than observed at Pilanesberg.

Chapter 5

Whole Rock Geochemistry

5.1 Introduction

To date there has been no published assessment of the whole-rock major and trace element geochemistry of Norra Kärr. While Sjöqvist et al. (2013) did present a limited whole-rock major-element dataset this was limited to a brief overview summary. This chapter will build upon the structural and petrological features identified in the preceding Chapters to derive the most robust model for the intrusion presented so-far. The data presented will be a mixture of the data collected by Tasman Metals Ltd. during their exploration drilling campaign and data collected at the University of Edinburgh.

5.2 Analytical Methodology

The whole-rock data presented in this chapter is a mixture of that obtained from Tasman Metals Ltd or from analysis at the University of Edinburgh. The Tasman dataset was sorted to remove any lithology mixtures (e.g. assays containing both Pegmatite and Grennaite lithologies). These were removed from the dataset to ensure only geochemical comparisons between individual lithologies could be carried out. The total number of datapoints for each dataset is shown in Table 5.1. Analysis of the two datasets showed that the datasets are comparable. The analytical methods for each dataset are outlined below. Data collected at Edinburgh is given in Appendix 4.

	Lithology	Grennaite	Gren-Peg	Pegmatite	Crenulated	Kaxtorpite	Lakarpite	Pulaskite
TAS	Major (N =)	78	61	43	29	18	20	10
TAS	Trace (N =)	2695	228	1128	1494	461	285	279
EDI	Major (N =)	5	5	5	5	5	5	8
EDI	Trace (N =)	5	5	5	5	5	5	8

Table 5.1: Total number of major and trace element analyses available from the Tasman Metals (TAS) and Edinburgh (EDI) datasets.

5.2.1 Statistical Techniques

Analysis of Variance (ANOVA)

ANOVA is a statistical method that tests the hypothesis that the means of two or more populations are equal and is based upon using variances to determine whether the means are different. The test works by comparing the variance between group means versus the variance within groups as a way of determining whether the groups are all part of one larger population or separate populations with different characteristics. The null hypothesis states that all population means (factor level means) are equal while the alternative hypothesis states that at least one is different

In this study ANOVA was used to identify whether a given element or oxide had the same mean across all lithologies at Norra Kärr. The output showed whether the means were equal (which would indicate a commonality across lithologies) or if they were not equal and if so whether they could be grouped together. The groups produced were ranked from A (the highest mean) to a letter depending on the number of groups present. Some elements showed means that overlap with two groups and as such would be labelled with both letter groups, e.g. B/C.

This method was able to highlight where elemental concentrations were strategically significantly different or common between lithologies from which conclusions could be drawn regarding the processes at work, rather than simply assessing trends by eye alone.

Self-Organising Map (SOM) Analysis

A Self Organising Map (SOM) is an unsupervised neural network able to group together similar components and separate dissimilar components within a database. A particular strength of the method is finding unusual co-occurring associations of attribute values within a database and can identify linkages between data items based on common features. The result is a series of images or 'maps' which shows patterns based upon common features (Kohonen 1982, Kohonen 2001).

This technique has been used to analyse exploration datasets to search for elements that match with occurrences of target elements (Schlatter 2014) and has been used as a way of data mining to assist with the analysis of disparate and complex datasets.

In this study SOM was used to identify correlations between lithologies and trace elements. The patterns produced enabled the division of elements into separate grouping to explore differences between different lithological groups. The strength of the method is that it allows an independent way of correlating the geochemical dataset rather than relying on subjective comparison of plotted datasets.

5.3 Major Element Geochemistry

This section will outline the whole-rock major element geochemistry of the lithologies at Norra Kärr. An overview of the fractionation trends will be given along with Harker plots for the major elements. Ternary and further fractionation plots will then be presented.

5.3.1 Whole-Rock TAS and Relationship to the Qz- Nep-Kal Eutectic

The alkali vs silica (TAS) plot for Norra Kärr is shown in Fig. 5.1 alongside a plot of whole-rock Qz- Nep-Kal eutectic ternary diagram in Fig. 5.2.

Both plots clearly show that the lithologies lie either side of the Al-Or/Nep eutectic (the phonolite minimum). The TAS plot shows that the ore-bearing Grennaite lies within the phonolite field while the Kaxtorpite and Pulaskite lie within the Trachyte field similar to the patterns observed at other alkaline complexes (e.g. the Brazilian alkaline rocks of São Paulo: Enrich et al. 2005). The Lakarpite behaves separately and appears to plot in both regions.

The Qz- Nep-Kal plot shows that the Kaxtorpite and Pulaskite and the Lakarpite plot within the feldspar dominated field of the triangle. In contrast to the TAS plot the Lakarpite behaves similarly the Kaxtorpite and Pulaskite plotting in only one region of the ternary. The Grennaite all plot within the nepheline field with the Contact Grennaite plotting further up the thermodynamic gradient than the Crenulated Grennaite. The Pegmatites plot in a scattergun pattern alongside the other data.

Figure 5.1: Total Alkali-Silica plot for whole-Rock compositions plots for the lithologies at Norra Kärr.

The Nep-Qz-Kal triangle also indicates that the lithologies are far richer in Al than Si. When wt% Al_2O_3 vs wt% SiO_2 is plotted on a Harker plot (Fig. 5.2) it is observed that the two rock suites can be effectively divided by plotting vs Al_2O_3 with 15 wt% Al_2O_3 being a useful dividing line. Harker plots are typically understood as showing increasing fractionation with increasing wt% SiO_2 . However, as shown by the trends towards the eutectic in the Qz-Nep-Kal triangle plot, this would be incorrect for Norra Kärr as the more silica-rich lithologies (Kaxtorpite, Lakarpite and Pulaskite) appear to show increasing fractionation with decreasing wt% SiO_2 . Plotting vs wt% SiO_2 also results in an overlap of the two fractionation trends due to an overlap in wt% SiO_2 concentrations. Therefore, the following Harker plots are plotted vs wt% Al_2O_3 as this best shows the fractionation trends and suitably discriminates both suites of rocks (Phonolitic and Trachytic) from each other.

Figure 5.2: Qz-Nep-Kal ternary under 5 kbar [$P(\text{H}_2\text{O}) = P(\text{Total})$] (after Zhang and MacKenzie 1984). Whole-rock compositions of the lithologies at Norra Kärr plotted. The 5 kbar plot was chosen on the basis of the pressure conditions required for the sub-solvus feldspar outlined in Chapters 3 and 4.

5.3.2 Harker Plots

As described above the majority of the Harker plots described below are plotted vs Al_2O_3 . A statistical analysis of the major element geochemical data using ANOVA is displayed in Table 5.2 and outlined in the description of each element.

Silica (SiO_2) – All the lithologies present display an overlap in wt% SiO_2 with the Pulaskite, Kaxtorpite and Lakarpite displaying higher concentrations. This pattern is likely due to the trend in magmatic fractionation as dictated by the Nep-Qz-Kal eutectic ternary (Fig. 5.1). The Contact Grennaite and the Pegmatite-Host Grennaite share means suggesting little change in evolution. Compared to the Contact Grennaite the Crenulated Grennaite is enriched in silica and the Pegmatites are depleted in silica. This suggests that the Crenulated Grennaite has been affected by nepheline crystallisation while the Pegmatites were affected by a separate process. The higher silica contents of the Kaxtorpite and Pulaskite may indicate an element of crystal accumulation.

Alumina (Al_2O_3) - The alumina concentrations divide the Grennaites from the other lithologies along a line of ≈ 16 wt% Al_2O_3 with the Kaxtorpite, Lakarpite and Pulaskite being the least enriched in alumina (Fig. 5.3). The Contact Grennaite is the most alumina rich of the Grennaite followed by the Crenulated Grennaite. It is likely that this trend is controlled by the aluminosilicate (nepheline/feldspar) crystallisation.

Zirconium (Zr) – There is a sharp contrast between the phonolitic and trachytic suites in terms of Zr content with the latter containing significantly lower (< 5000 ppm) Zr concentrations than the Grennaites (Fig. 5.4). Overall the Zr-content of the phonolites display an increase towards the phonolite eutectic. The Contact Grennaite and the Crenulated Grennaite display equivalent means whereas the Pegmatite-Host Grennaite and Pegmatites display the highest means. This fractionation pattern is likely controlled by Zr-Silicate crystallisation.

Alkalis (Na_2O and K_2O) - Overall the phonolites exhibit a higher alkali content than the trachytes with the Grennaites appearing to display reasonably constant alkali concentrations (Fig. 5.5). However, there are individual differences between the wt% Na_2O and K_2O contents. The Na_2O content is highest in the Contact Grennaite and lowest in Crenulated Grennaite. The K_2O content behaves differently with lower means displayed by the Contact Grennaite and the higher means displayed by the Crenulated Grennaite and the Pegmatites. This alkali pattern suggests that Na_2O is decreasing with fractionation (potentially due to both aegirine and nepheline crystallisation) while K_2O is increasing with fractionation.

Iron (Fe_2O_3) - The bulk iron content is reported as Fe_2O_3 (Fig 5.6). The Contact Grennaite displays the lowest iron content followed by the Crenulated Grennaite with the Pegmatite-Host and Pegmatites displaying the highest concentrations. This trend is likely controlled by the Aegirine crystallisation. Additionally, the Lakarpite shares a mean with the Pegmatites potentially indicating a relationship between the two lithologies.

Figure 5.3: wt% Al_2O_3 vs wt% SiO_2 for the lithologies at Norra Kärr.

Figure 5.4: Zr (ppm) vs wt% Al_2O_3 for the lithologies at Norra Kärr.

Figure 5.5: Sum wt% Na_2O and wt% K_2O vs wt% Al_2O_3 for the lithologies at Norra Kärr.

Figure 5.7: Bulk-rock Area% redox states for iron within each of the Norra Kärr lithologies as calculated from Mössbauer data. The limited dataset requires extrapolation of the data to be treated with caution.

Mössbauer spectrometry was carried out on several samples from across Norra Kärr to investigate the redox state of Fe within each lithology. The results were calculated as %area of Fe^{3+} and Fe^{2+} for each whole-rock spectra with the results given in Fig. 5.7. The pattern which emerges is that the Grennaite and the Kaxtorpite are particularly Fe^{3+} rich, as opposed to the Pulaskite and Lakarpite which are richer in Fe^{2+} . Part of this will be due to the abundance of Fe^{3+} -bearing aegirine (typically up to 1/3 of the mineral content of the lithologies) with the other part of the spectrum due to the presence of amphibole and its varying $\text{Fe}^{3+}/\text{Fe}^{2+}$ contents with an increase in Fe^{2+} required to charge balance the amphibole structure (Deer et al. 1997). This mineralogical effect is shown particularly strongly in the Pulaskite where there is abundant aegirine-amphibole-biotite in the enclaves, but more aegirine-amphibole in the feldspar rich matrix resulting in a spectrum of $\text{Fe}^{3+}/\text{Fe}^{2+}$ contents. The difference in the Lakarpite points may be due to different processes occurring between the core

and contact of the Lakarpite though it is likely that in a larger dataset there would be some overlap. The elevated Fe^{2+} contents within the pegmatites are due to Fe^{2+} in eudialyte.

Though only one analysis was obtained for each lithological zone, data from Chapter 4 show that there is a restricted compositional spread in the mineral chemistry and it may be unlikely that the data will diverge far from the analytical points presented. As was also shown in Chapter 4 - 4.4.2 the calculated $\text{Fe}^{3+}/\text{Fe}^{2+}$ contents do show that the Kaxtorpite amphiboles have lower calculated Fe^{2+} than the Pulaskite amphiboles. On this basis there appears to be some difference between the Grennaite and Kaxtorpite, and the Pulaskite and Lakarpite on the grounds of Fe-redox as shown by their mineral content.

Magnesia (MgO) – The mean magnesia content is higher in the Kaxtorpite and Pulaskite than the Grennaite by approximately 1 wt% with the Grennaite displaying an inherently low concentration of MgO. There is an evident decrease in MgO with fractionation within the trachytic-magmas (Fig. 5.8). This may be due to crystallisation of amphiboles within these lithologies. Given that the trachytic and phonolitic magmas each internally share the statically same mean it is likely that the concentration of MgO is inherent to each magmatic type.

Figure 5.8: wt% MgO vs wt% Al_2O_3 for the lithologies at Norra Kärr.

Figure 5.9: wt% CaO vs wt% Al_2O_3 for the lithologies at Norra Kärr.

Lime (CaO) - Despite there being an apparent spread of the data (Fig. 5.9) all lithologies share the same statistical mean suggesting that the low CaO concentration is a feature of the Norra Kärr alkaline magmatic system as a whole due to earlier fractionation lower in the crust.

Titania (TiO₂) - Titania contents are significantly higher in the trachyte's than the phonolites with the Kaxtorpite and Pulaskite sharing the highest means overall. The decrease in wt% TiO₂ with fractionation (Fig. 5.10) within the trachyte's likely due to amphibole fractionation. The contact and Pegmatite-Host Grennaite display the lowest concentrations of the phonolites with the Crenulated Grennaite displaying the highest concentrations.

Manganese (MnO) - Manganese contents are highest in first phase of magmatism with an increase in MnO content from the Contact Grennaite through the Pegmatite-Host Grennaite and the highest concentrations in the Crenulated Grennaite and Kaxtorpite which suggests a pattern of increasing magmatic fractionation through the series (Fig. 5.11).

Phosphorus (P₂O₅) - The trachyte's display higher phosphorus contents than the phonolites (Fig. 5.12). Much like the MgO content the trachytes and the phonolites both display their own statically same mean.

	Grennaite	Grennaite-Peg	Pegmatite	Crenulated	Kaxtorpite	Lakarpite	Pulaskite
N	78	56	32	25	17	19	8
wt% SiO ₂	56.086 B/C	56.070 B/C	54.692 C	56.889 B	60.292 A	57.626 B	61.743 A
wt% Al ₂ O ₃	18.013 A	16.476 C	16.602 B/C	17.584 A/B	13.762 E	14.203 D/E	15.925 B/C/D
Zr (ppm)	11374 B	15248 A	15741 A	10363 B	2384 C	10360 B	2063 C
wt% Na ₂ O	11.122 A	11.148 A	10.212 B	9.988 B/C	8.851 B/C	9.754 C	7.16 D
wt% K ₂ O	3.655 C/D	3.316 C/D	4.248 A/B	3.796 A/B/C	3.003 D	3.615 B/C/D	4.715 A
wt% Fe ₂ O ₃	5.093 C	6.641 A	5.934 A/B	5.049 B/C	4.36 C	6.836 A	4.289 C
wt% MgO	0.1313 B	0.1816 B	0.3078 B	0.2544 B	1.498 A	1.299 A	1.17 A
wt% CaO	1.212 A	1.049 A	1.747 A	1.658 A	2.616 A	2.279 A	2.316 A
wt% TiO ₂	0.0599 C	0.0638 C	0.0772 B/C	0.074 B	0.467 A	0.193 B	0.4 A
wt% MnO	0.119 D	0.206 C	0.268 B/C	0.336 B	0.583 A	0.481 A	0.159 C/D
wt% P ₂ O ₅	0.0196 B	0.00196 B	0.00188 B	0.0016 B	0.0994 A	0.0468 A/B	0.1463 A

Table 5.2: One-Way ANOVA analysis of major element concentrations for each of the lithologies at Norra Kärr. The factor was each lithology while the response was each element. All numbers are means, all letters are the groupings with the means decreasing in values from A onwards.

5.3.3 Alkalinity, Al-Saturation and Fractionation Plots

When the whole-rock data is plotted to show alkalinity vs aluminosity almost all analyses plot below the peralkaline field (Fig. 5.13). This is despite Norra Kärr displaying petrological assemblages that can be classified as Low to Medium Agpaitic (using the classification of Khomyakov 1995) which is usually reserved only for peralkaline rocks (as defined by Sørensen 1974). The debate surrounding the use of agpaitic is still ongoing (e.g. Marks et Markl 2017) and will not be discussed further here apart from briefly highlighting of the inconsistency in the terminology. The majority of the lithologies at Norra Kärr are peraluminous with only the Kaxtorpite and Lakarpite (along with a minority of Grennaite analysis) plotting in the metaluminous field. The range in peralkalinity and aluminosity is comparable to that observed in other major alkaline intrusions (Fig. 5.14). The ranges for each of the lithologies at Norra Kärr are shown in Fig. 5.15.

Figure 5.13: Whole-rock alkalinity vs aluminosity plot for the lithologies at Norra Kärr.

Figure 5.14: Average whole-rock alkalinity vs aluminosity plot other alkaline intrusions. Pilanesberg - Elburg et Cawthorn (2017), Khibina and Lovozero - Kramm et Kogarko (1994), Ilímaussaq - Bailey (2006)

Figure 5.15: Left – Range of peralkalinites; Right – Range of Aluminium Saturation Index (ASI)

Fig. 5.16 shows plots of other commonly used discriminant fractionation ratios. Fig. 5.16a shows the Mn/(Fe+Mn) ratio. This plot shows that the Contact Grennaite is the least evolved of the Grennaites and the Crenulated Grennaite is likely the most evolved with the Kaxtorpite even more so. Fig. 5.16b shows the K/Rb ratio. This has been shown by Blevin (2004) and Xianwu et al. (2009) to discriminate highly fractionated melts as Rb is progressively enriched in residual melts relative to K. From this ratio the Crenulated Grennaite can be observed to be the most fractionated of the Grennaites. The Pulaskite is the least fractionated of all the magmas.

Figure 5.16: (a) Left – Range of Mn/(Fe+Mn) ratios; (b) Right – Range K/Rb ratios.

5.3.4 Ternary Plots

The ternary diagrams in Fig. 5.17 were plotted to examine potential fractionation paths. Fig. 5.17a (AFM plot) shows that all the magmas present at Norra Kärr plot within the 'calc-alkaline' field and appear to be at the very end of the fractionation sequence. While the Kaxtorpite and Pulaskite show little variation within the plot, the Grennaite appears to show a trend of increasing Fe thereby going 'backwards' along the fractionation trends usually shown by this plot. This is likely due to the crystallisation of alkali-rich minerals during the Grennaite evolution. Fig. 5.17b (NKC plot) shows that the magmas were particularly Na-rich and evolved towards higher Na-concentrations. The Kaxtorpite is more Na-rich than the Pulaskite which is relatively more enriched in K. The Grennaite shows a more complex trend. The Contact Grennaite is predominantly very Ca-poor while the Crenulated and Pegmatite-Host Grennaite are slightly richer in Ca. The Crenulated Grennaite then shows a Na-Ca trend while the Pegmatite-Host Grennaite shows a Na-K trend which is also shown by the Pegmatites. Fig. 5.17c was plotted to show the effect of the petrological crystallisation sequence (Fe-Zr-Al) observed in Chapter 3. The Kaxtorpite and Pulaskite show very low Zr-contents and are richer in Al than Fe. The Grennaite is also richer in Al than Fe, with the Crenulated Grennaite showing higher Al and lower Zr than the Pegmatite-Host Grennaite which shows higher Fe and higher Zr. All variations are likely petrologically controlled with higher Zr resulting in more abundant eudialyte/catapleiite and the Al/Fe being dependent upon the proportions of Aegirine to Feldspars present in the rock.

Figure 5.17: Ternary plots for whole-rock data from Norra Kärr. (a) - top-left: AFM plot, (b) - top-right: NKC plot, (c) - bottom-left: AZF plot.

5.3.5 Fenite

The fenite around Norra Kärr can be visibly identified by the presence of haematite staining. Figs. 5.18 and 5.19 show the extent of chemical alteration of the fenite zone relative to the surrounding Vaxjö Granite. Except for a significant decrease in silica and increases in alumina and soda there is little significant change in the major element chemistry. In terms of available trace element chemistry there has been a decrease in Sr content and minor increases in Sn, Ga, Pb, Hf and Nb, and larger increases in Y, Rb and Zn (though the latter are still less than 0.01 wt%).

Figure 5.18: Difference in the mean wt% major element concentration between the Vaxjö Granite and Fenite (based upon n=5 for each lithology).

Figure 5.19: Difference in mean trace element concentrations (ppm) between Vaxjö Granite and Fenite (based upon n=5 for each lithology).

5.3.6 Major Element Summary

Like other alkaline complexes (e.g. Enrich et al. 2005) the evolution of the Norra Kärr magmas (particularly the Al_2O_3 content) appear to be controlled by evolution towards the phonolite minimum and the nepheline eutectic on the Nep-Qz-Kal ternary. As shown by the AFM ternary the magmatic system overall is highly fractionated (likely following the alkaline trend) with the magmas being overall richer in Na when compared to K or Ca. The limited Fe^{3+} - Fe^{2+} data also potentially show evidence for two magmas, the first intrusive phase being one with a predominantly Fe^{3+} -mineralogy (the Grennaite and Kaxtorpite) and the second phase being one with a mineral assemblage richer in Fe^{2+} due to the presence of amphibole and biotite (the Pulaskite and Lakarpite).

In comparison to other alkaline intrusions Norra Kärr compares similarly in the pattern of peralkalinity and aluminosity. Interestingly Norra Kärr appears more enriched in Zr than other alkaline intrusions (Fig. 5.20). While Zr concentrations within the Pulaskite, Kaxtorpite and less fractionated Contact Grennaite are similar for the majority of lithologies from other intrusions, only the Ledig Foyaite from Pilanesberg and the Kakortokites from Ilímaussaq (all means above 5000 ppm Zr) come close to the Norra Kärr Grennaite. Only the Red Kakortokites (with a mean of 20100 ppm Zr) match the Pegmatites and Pegmatite-Host Grennaite in Zr concentration.

Figure 5.20: Whole-rock Zr (ppm) vs Al_2O_3 (wt%) for other alkaline intrusions compared to Norra Kärr.

The low CaO content is the same across all lithologies suggesting that this is a characteristic of all magma at Norra Kärr, likely caused by earlier fractionation of Ca-bearing minerals along the calc-alkaline trend. Notably MgO , TiO_2 , and P_2O_5 are concentrated as a function of whether the magma is phonolitic or trachytic (with higher concentrations in the latter).

The Grennaite shows several major elements fractionation trends. The Contact Grennaite shows the highest Na_2O content and lowest K_2O content, while the Crenulated Grennaite shows the lowest Na_2O content and highest K_2O content suggesting decreasing Na and increasing K with fractionation. MnO displays a slightly stronger fractionation trend than TiO_2 and when plotted as a function of $\text{Mn}/(\text{Mn}+\text{Fe})$ shows a trend of increasing fractionation from the Contact Grennaite towards the

Crenulated Grennaite. This trend remains even though the Pegmatite-Host Grennaite displays a Fe_2O_3 content by 1% higher than the Contact or Crenulated Grennaites. Furthermore, the Kaxtorpite displays the highest Mn/(Mn+Fe) ratios despite being a trachytic-type magma unlike the phonolite-type Grennaites. This fractionation trend is also supported by the K/Rb ratio which also shows fractionation from the Contact towards the Crenulated Grennaites.

Overall, the majority of major element fractionation trends show that of the different Grennaite varieties the Contact Grennaite is the least fractionated and the Crenulated Grennaite the most fractionated (the Pegmatite-Host Grennaite being intermediate). There are problems with this as the Zr and Fe_2O_3 concentrations are highest in the Pegmatite-Host Grennaite suggesting a more complex fractionation pattern for these elements. For instance, on a K/Rb vs Zr is plot (Fig. 5.21) the overall trend in Grennaite fractionation suggests that there is an increase in Zr from the contact towards to central portions of Norra Kärr which then decreases with further fractionation towards the Crenulated Grennaites. A similar trend in changing Zr concentrations with fractionation has previously been reported by Markl et al. (2001) within pyroxenes from Ilímaussaq.

Figure 5.21: Whole-rock K/Rb ratios vs Zr (ppm).

5.4 Trace Element Geochemistry

The exploration dataset provided by Tasman Metals includes analyses of 21 trace elements plus the 14 lanthanoids (Table 5.3) and a total of 137,970 data points. This provided an excellent opportunity to make a statistically significant analysis of the pattern of trace elements within the lithologies. In order to fully analyse the dataset Self Organising Map (SOM) analysis was used to ‘map’ the relationships between the concentration of each element in order to highlight geochemical trends. This modelling was used to support the relationships observed within boxplots of the trace element data and traditional comparisons of ‘geochemical pairs’.

Geochemical Pairs

Geochemical pairs can be used to see if the behaviour between a pair of elements with similar ionic charges, radii and electronegativities changes during magmatic fractionation. Based upon the elements available this study considered the behaviour of, Nb, Ta, Hf, Zr, Pb, Ni, Co, Mn and Fe. Cr vs Ni; Co, Fe, Mn; Ti vs Ag and Mn vs V could not be plotted due to a lack of statistically useable data due to the low concentrations present or a lack of analyses available for major elements.

Group I	Rb, Cs,
Group II	Sr, Ba,
Transition Metals	V, Cr, Co, Ni, Cu, Y, Zr, Nb, Mo, Hf, Ta, W,
Metalloids	Zn, Ga, Sn, Tl, Pb,
Lanthanoids	La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu
Actinoids	Th, U,

Table 5.3: ‘Trace’ elements available in the Tasman Metals dataset.

5.4.1 Self-Organising Map (SOM) Analysis

A bulk SOM of the geochemical data from Norra Kärr was calculated using the SOM Toolbox 2.0 code by Alhoniemi et al. (2002). This initial SOM model was run with a dataset containing (n= 9689 data entries, 232,536 data points), with eighteen elements run in the model alongside six-lanthanoid elements (Figs. 5.22, 5.23). La and Sm represented the light-[Ln], Ho and Lu represented the heavy-[Ln] and Eu and Ce were included to model any potential difference due to the Eu^{2+} and Ce^{4+} states. Three patterns emerged from the model: (1) a pattern where elements were sorted to the bottom and right-hand side of the U-matrix; (2) where elements were sorted to the middle left and bottom of the u-matrix and (3) where elements were sorted to the top of the u-matrix. Pattern (1) correlated more with the light-[Ln] and included Cs, Ga, Pb, Rb, Sn and Tl. Pattern (2) correlated more with the heavy-[Ln] and included Hf, Nb, Ta, W, Y and Zr. Pattern (3) represented elements not strongly associated with the lanthanoids and included Ba, Cr, Sr, Th, U and Zn (Figs. 5.22, 5.23). The individual elements in the geochemical dataset were then interpreted for each rock type based upon these three groupings. This was carried out by using plotting boxplots of the data for each of the lithologies present at Norra Kärr. The commonalities and differences between the elemental concentrations for each rock type are discussed below.

Figure 5.22: SOM analysis for the whole assay data set for the rocks of Norra Kärr.

Figure 5.23: SOM analysis summary. U-Matrix represents the overall pattern of correlation. (1) Represents the pattern of light-[Ln] correlation, (2) the pattern for heavy-[Ln] correlation and (3) for not correlation with the [Ln]. Yellow is the highest correlation, green medium correlation and blue the lowest correlation.

Pattern (1) correlated more with the Light-[Ln] (Cs, Ga, Pb, Rb, Sn, Tl)

Rb, Cs, Ga, Tl, Sn, Pb were shown by SOM analysis to correlate with the light-[Ln]. One-way ANOVA analysis highlighted that in almost all cases the highest mean concentrations of any of these elements is exhibited by the Crenulated Grennaite (Table 4, Fig. 5.24).

	Grennaite	Grennaite-Peg	Pegmatite	Crenulated	Kaxtorpite	Lakarpite	Pulaskite
N	2923	2691	1128	1434	461	285	279
Rb	272.155 C/D	275.66 C	352.05 B	419.94 A	259.66 D	255.82 D	226.79 E
Cs	4.0594 D	6.720 C	7.04 C	26.224 A	13.67 B	3.428 D	4.86 C/D
Ga	80.445 D	92.734 B	87.905 C	100.522 A	77.557 E	59.24 F	48.573 G
Tl	0.9973 B	0.99610 B	0.981 B	1.2529 A	0.9345 B/C	0.6211 D	0.8254 C
Sn	57.757 B	113.171 A	112.59 A	114.273 A	40.56 C	46.8 C	27.247 D
Pb	75.05 D	345.97 B	611.8 A	332.88 B	156.65 C	203.9 C	74.96 D

Table 5.4: ANOVA analysis for Rb, Cs, Ga, Tl, Sn, Pb concentrations across the lithologies at Norra Kärr.

Rb and particularly Cs are enriched within the Crenulated Grennaite. Fig. 5.25 shows that Cs is at a low concentration across the range of lithologies but shows a sharp spike in concentration in the crenulated Grennaite close to the eutectic point of the phonolite minimum (around 16 wt.% Al₂O₃) which indicated that the Crenulated Grennaite is highly evolved. The pattern displayed in Fig. 5.25 is also observed for Rb concentrations. Both elements have been shown experimentally to be highly incompatible in feldspars (Icehower et London 1996), this results in their concentration in latter differentiated Grennaite melts due to more compatible elements being taken up by feldspars first.

Ga is known to substitute for Al (Peucat et al. 2007) and Fe³⁺ (Bailey et al. 2001) in minerals. Fig. 5.26 shows that Ga concentrations are higher in the Grennaite-lithologies and the Kaxtorpite (>60 ppm) with the Crenulated Grennaite displaying a similar spike in Ga concentrations to the Cs and Rb plots. Trends in Ga concentration are likely to be mirroring trends in magmatic evolution. The contact Grennaite appears to evolve along a line of 80 ppm Ga with the Crenulated Grennaite exhibiting a spike close to the phonolite minimum. The Pegmatite-host Grennaite appears to mirror the scatter in Ga concentrations shown by the Pegmatites potentially indicating a different evolutionary history.

In the case of Tl it is likely that as there are such low concentrations of this element any variations observed are unlikely to be significant. However, Tl does show higher concentrations in the first intrusive phase (the Grennaite-related lithologies) than the second intrusive phase (Lakarpite/Pulaskite).

Sn displays a wide variation in concentration throughout the Grennaite-related rocks. When plotted vs Ga (Fig. 5.27) Sn displays higher concentrations in the Crenulated Grennaite and the Pegmatites. Sn tends to partition into later stage magmas (Audétat et al. 2000) again suggesting these lithologies are the most fractionated. Pb is highest in concentration in the Pegmatites but is included here as it significantly higher in concentration in the ore-domains than within any other lithology.

Figure 5.24: Boxplots showing the concentrations of Rb, Cs, Ga, Tl, Sn, Pb concentrations across the lithologies at Norra Kärr.

Figure 5.25: Cs (ppm) vs Wt% Al₂O₃

Figure 5.26: Ga (ppm) vs Wt% Al₂O₃

Figure 5.27: Ga (ppm) vs Sn (ppm)

Pattern (2) Correlate more with the Heavy-[Ln] (Zr, Hf, Nb, Ta, Y, W)

Zr, Hf, Nb, Ta, Y, W were shown by SOM analysis to correlate with the heavy-[Ln]. One-way ANOVA analysis highlights that in all cases the highest mean concentrations of any of these elements is displayed by the Pegmatites with the host-Pegmatite Grennaite displaying the second highest mean concentrations in all cases (Table 5.5). The boxplots in Fig. 5.28 show similar patterns in relative concentration across the lithologies with only W not showing a visibly discernible trend (this is, however, picked out by the ANOVA analysis). Variations in W concentration have been shown by Bailey et al. (2001) to be due to eudialyte fractionation. The Grennaite and Crenulated Grennaite tend to display the next highest mean concentrations.

The Kaxtorpите and Pulaskite the share means that are statistically similar and also display the lowest concentrations of the pattern 2 elements. It is possible that the low concentration of the pattern 2 elements is due to factors relating to the formation of each original batch of magma (both lithologies are on the trachyte side of the phonolite-minimum) rather than co-evolution.

The Lakarpite displays a wider range in concentration of pattern 2 elements than any other lithology. It exhibits statistically similar mean concentrations of Nb and W in comparison to the host-Pegmatite Grennaite and concentrations of Zr, Hf, Ta and Y intermediate between the Grennaite-lithologies and the Kaxtorpите and Pulaskite. This may support the hypothesis that the Lakarpite magma ‘reacted’ with the Grennaite-lithologies preferentially taking in Nb and W over other elements in this group.

	Grennaite	Grennaite-Peg	Pegmatite	Crenulated	Kaxtorpите	Lakarpite	Pulaskite
N	2923	2691	1128	1434	461	285	279
Zr	10830.6	14496.3	15922	10828.7	2993.1	8906	3549
	C	B	A	C	E	D	E
Hf	260.95	307.82	329.92	240.43	67.67	195.76	84.49
	C	B	A	D	F	E	F
Nb	200.9	438.77	507.57	282	133.39	433.4	106.85
	D	B	A	C	E	B	E
Ta	20.188	25.590	30.475	19.385	6.595	25.12	7.568
	D	B	A	D	E	C	E
Y	899.81	1750.56	2048.3	1174.34	360.6	1488.1	388.3
	E	B	A	D	F	C	F
W	3.2101	4.0821	4.5062	3.2608	0.9631	4.26	1.133
	C	B	A	C	D	A/B	D

Table 5.5: ANOVA analysis for Zr, Hf, Nb, Ta, Y, W concentrations across the lithologies at Norra Kärr.

Figure 5.28: Boxplots showing the concentrations of Zr, Hf, Nb, Ta, Y, W concentrations across the lithologies at Norra Kärr.

Pattern (3) Elements not strongly associated with [Ln]

Sr, Ba, U, Th, V, Cr, Co, Ni, Zn were shown by SOM analysis not to correlate with any [Ln] enrichment. Further one-way ANOVA analysis showed that these elements are predominantly associated with the Pulaskite and Lakarpite with the highest mean concentration observed in the Kaxtorpite. The lowest mean concentrations (Table 5.6) are found in the Grennaite-related rocks within which the highest means are observed within the Crenulated Grennaite. The pattern of Sr and Ba (Fig. 5.29) may be due to the fractionation of K-feldspar within each magma matching the pattern of K/Rb fractionation (Fig. 5.16b). Of note are the U and Th patterns which appear to be inverse and have yet to be correlated with specific minerals to explain their pattern. V, Cr, Co, Ni and Zn display broadly similar patterns of distribution. Flohr et Ross (1990) grouped V, Cr and Co together as elements that can be found in early formed minerals in syenites and particularly in Na-amphiboles (Flohr 1994). Bailey et al. (2001) pointed to higher concentrations of Co in the Ilímaussaq Karkortokites due to scavenging by arfvedsonite which resulted in lower concentrations of Co in the residual magmas. This suggests that if the Kaxtorpite and Grennaite magmas were coexisting then the Kaxtorpite would be able to scavenge the V, Co, Ni and Zn of the Grennaites thereby producing the observed pattern. Cr is least affected by this, while Zn is the most affected. Sundius (1945) reported that an Ekermannite (the amphibole within the Kaxtorpite – see Chapter 4) contained 0.59 wt% ZnO strongly suggesting that amphibole had scavenged the available Zn. The Lakarpite and Pulaskite are also amphibole (and biotite) bearing lithologies which could similarly host these elements leading to the concentrations observed in the second magmatic phase. Li was not included in the SOM analysis due to fewer available datapoints but is included here as it is very closely associated to the Kaxtorpite.

	Grennaite	Grennaite-Peg	Pegmatite	Crenulated	Kaxtorpite	Lakarpite	Pulaskite
N	2923	2691	1128	1434	461	285	279
Sr	60.45 E	104.66 D	161.29 C	160.93 C	233.32 A	192.34 B	238.02 A
Ba	90.17 D	79.67 D	114.5 C	123.88 C	423.5 B	403.7 B	614.9 A
U	6.2067 F	11.8666 C/D	12.474 C	18.825 B	24.432 A	10.952 D/E	9.987 E
Th	5.0863 D	5.4288 D	5.8013 D	10.244 C	63.44 A	23.14 B	27.664 B
V	2.0349 E	1.7137 E	1.703 E	3.013 D	50.97 A	36.47 C	45.29 B
Cr	46.506 C	34.110 E	36.776 D/E	37.512 D	70.85 A/B	66.33 B	76.59 A
Co	0.1299 E	0.2069 E	0.2419 E	0.6977 D	8.02 A	5.385 C	6.648 B
Ni	0.9863 C	0.6384 C	0.594 C	1.0139 C	10.525 A	9.418 B	8.380 B
Zn	103.616 E	81.701 F	103.7 E	135.75 D	1356.8 A	409.9 B	328.62 C
N	1	0	15	5	2	2	3
Li	98.50 B		132.2 B	106.92 B	960.00 A	161.8 B	158.8 B

Table 5.6: ANOVA analysis for V, Cr, Co, Ni, Sr, Ba, U, Th, Zn and Li concentrations across the lithologies at Norra Kärr.

Figure 5.29: Boxplots showing the concentrations of Sr, Ba, U, Th, V, Cr, Co, Ni, Zn and Li concentrations across the lithologies at Norra Kärr.

5.4.2 Geochemical Pairs

The plots and statistical data for Nb vs Ta, Zr vs Hf, Nb vs Zr, Nb vs Hf, Pb vs Zr, Ni vs Co, Mn vs Fe are presented in Appendix 5 with the key points summarised here.

Nb-Ta and Zr-Hf both plot as linear trends showing the element pairs are following the same trend. On a Nb/Ta vs Zr/Hf plot there is a limited spread of data for Norra Kärr as a whole (Fig. 5.30).

On a Nb vs Zr plot (Fig. 5.31) the nesting of the Grennaite within each other can be observed. Here the Contact Grennaite shows a wide spread of Nb-Zr concentrations, the Pegmatite-Host Grennaite shows elevated Nb-Zr values to that of the Contact Grennaite, while the Crenulated Grennaite displays a more restricted range of Nb-Zr values which are overall higher than the Contact Grennaite. The Pegmatites display Nb-Zr values that overlap with the Pegmatite-Host Grennaite suggesting there is a relationship between the two.

This suggests that there is some form of fractionation occurring, in this case it Nb-bearing eudialyte would likely be the cause of this. Zr-bearing mineral fractionation would move the magmas towards the left of the plots (possibly caused by aegirine or aegirine-catapleiite crystallisation) which may explain the higher-Nb concentrations of the Pegmatite-Host Grennaite. Further fractionation by Nb-bearing eudialyte would then result in the depleted Nb observed within the Crenulated Grennaite. The wide spread of the pegmatites may be the result of input of fractionated melt from both the Pegmatite-Host and Contact Grennaites.

On a plot of Ni/Co two trends appear, one with lower Ni concentrations, and a second with higher Ni (Fig. 5.32). The lower Ni/Co corresponds to the Pulaskite and Kaxtorp and overlaps with the Grennaites. However, the higher Ni/Co trend appears to overlap only with some limited analyses from the Grennaites. This trend and its relationship to the drill core and petrology is explored further in Fig. 5.33.

Figure 5.30: Nb/Ta vs Zr/Hf plot showing all data available for the main rock types at Norra Kärr.

Figure 5.31: Nb / Zr plot showing all data available for the Grennaites at Norra Kärr.

Figure 5.32: Nb/Ta vs Zr/Hf plot showing all data available for the main rock types at Norra Kärr.

5.4.3 Trace Element Summary

The trace elements at Norra Kärr can be divided into three main groups using SOM analysis, each group in turn relates to different portions of the Norra Kärr intrusion and its evolution. Zr, Hf, Nb, Ta, Y and W have been shown to correlate with the Pegmatite-Host Grennaite with slightly higher concentrations observed in the Pegmatites. These elements are particularly associated with eudialyte of which Zr, Hf, Nb and Ta are part of the essential structure. Y is readily taken up by eudialyte while W has been detected in eudialytes from Mont St Hilaire (Johnsen et al. 1999) and up to several hundred ppm W in eudialytes from Ilímaussaq (Bailey et al. 2001). Pb does not entirely fit the pattern shown but is also particularly enriched in the pegmatites (mean of 612 ppm). Pb may also be concentrated into the eudialytes with Wu et al. 2010 reporting up to several hundred ppm Pb in eudialytes from a range of alkaline intrusions. Cs, Ga, Rb and Sn have been shown to correlate with the Crenulated Grennaites. This may be indicative of the latter stages of feldspar fractionation as Rb and Cs are incompatible in feldspars and become enriched in later stage melts. The remaining assayed elements (Sr, Ba, U, Th, V, Cr, Co, Ni, Zn) all have their highest concentrations in the Kaxtorpite or Pulaskite. The Ga plot (Fig. 5.26) shows that there are Ga concentrations of ≈ 80 ppm across the Grennaites and the Kaxtorpite, with the Pulaskite at lower Ga concentrations. also support the hypothesis that these lithologies are derived from the same magmatic phase.

The data from the plots of 'geochemical pairs' show several interesting features. The Nb/Ta and Zr/Hf pairs both display positive linear trends suggesting that the geochemistry of these pairs is behaving as expected. This is shown in the Nb/Ta vs Zr/Hf plot as a concentrated overlap of points. Nb/Zr appears to show the evolutionary path of the Grennaites and Pegmatites. A similar pattern appears to be shown by Pb and Zr (as also seen in the SOM analysis) and is also likely due to fractionation within the Grennaites possibly driven by eudialyte crystallisation. The Mn/Fe plots further display the Mn/(Fe+Mn) fractionation trend shown by Fig. 5.16a. Here the relationship between the Crenulated Grennaite and the Kaxtorpite can be observed as both lithologies lie between 20,000 – 40,000 ppm Fe and have vertical trends in Mn enrichment. The evolutionary trend between the different Grennaite varieties can also be seen in the increasing concentrations of Mn.

The Ni/Co plot shows the most variation within the Lakarpite with two trends observed. This suggests that there is some form of mineral or possibly redox process occurring within the Lakarpite. When Ni/Co is matched to petrological data the eudialyte rich zones coincide with both an increase in Zr concentration and Co with a corresponding decrease in Ni (Fig. 5.33). This may have been caused by some degree of mass-transfer from the Grennaite into which the Lakarpite intruded. Some degree of 'mixing' is supported by an increase in Zr (along with Hf, Nb, Ta, Y and W as shown in the boxplots in Fig. 5.28) which may explain the formation of a number of separate petrological zones within the Lakarpite. This will be explored further in section 5.6.6.

Figure 5.33: Element concentrations and Ni/Co ratios in a drill core cross-section of the Lakarpite. See map in Chapter 2 (Fig. 2.7).

A further aspect to consider is the effect of lithium and fluorine upon the system. Dolejš et Baker (2007 a,b) investigated the compositional limits of fluoride–silicate melt immiscibility in the system $K_2O-Na_2O-Al_2O_3-SiO_2-F_2O-H_2O$ and found that the miscibility gap was restricted to very high F contents and could not be reached by haplogranite (Qz-Al-Or) compositions that crystallise cryolite and topaz. However, Gramenitskiy and Shchekina (1994) and Gramenitskiy et al. (2005) demonstrated that the region of liquid immiscibility greatly expands in Li-bearing compositions where unmixing has been observed at much lower F contents and in the presence of liquidus silicates. The experiments of Veksler et al. (2012) confirmed the strong effect of Li; all of the fluoride–silicate starting mixtures were Li-rich and the miscibility gap observed in the experiments extended to less than 4 wt.% F on the silicate side. In contrast to other alkali metals Li is strongly concentrated in the immiscible fluoride liquid whereupon it decreases the liquidus temperature by suppressing crystallization of cryolite, topaz and other F-rich solids. It is also important in that unlike Ca and other alkaline earth elements Li does not form refractory fluorides.

Fluorine is observed in the form of a common anion at Norra Kärr within mineral phases; coupled with appreciable Li content in the Kaxtorpите (see mineral tabulations in Chapter 4) it is possible that Norra Kärr has evolved from an F-rich melt which (aided by the presence of Li) was able to separate into a series of immiscible F-enriched melts. The F-immiscibility within the Fe^{3+} -dominated Grennaite which forms the first magmatic phase may then have led to the immiscible-separation of the Kaxtorpите from the Grennaite. Veksler et al. (2012) also showed that fluoride-silicate melts separate better than the other systems studied due to the lower viscosity of the silicate melts produced – therefore this process could therefore further aid the separation of the melts. A series of immiscible-unmixing's of this sort would be likely to have resulted in preferential element fractionation between the first and second stage magmas and between the Kaxtorpите and the Grennaite as shown by the SOM analysis.

5.5 Lanthanoid Concentrations

The lanthanoid patterns for each of the lithologies at Norra Kärr, normalised to chondrite (Taylor and McLeannan 1985), are plotted below (Fig. 5.34) with the ANOVA means presented in Table 5.7. Overall, each lithology exhibits a negative Eu anomaly and Light-[Ln] enrichment. Y and Ho are coupled within the Kaxtorpите, Pulaskite and the Contact Grennaite, but are uncoupled in the other lithologies.

Figure 5.34: Median Y and [Ln] concentrations relative to chondrite for all lithologies at Norra Kärr. Ranges for the data are not shown here due to overlap but are plotted in Figures 5.35 – 5.38.

5.5.1 The Grennaite-Related Lithologies

The first phase of intrusion comprises the Grennaites (Contact, Pegmatite-Host and Crenulated) and the Kaxtorpите. Fig. 5.35 shows the lanthanoid patterns for the Grennaite rocks. The Contact Grennaite has the lowest concentrations of La-Sm of the Grennaites while the Pegmatite-Host and Crenulated Grennaite display overlapping concentrations albeit with the Crenulated Grennaite slightly more enriched in La-Sm overall. A different pattern is observed from Gd-Lu with the Pegmatite-Host being the most enriched and the Contact and Crenulated Grennaite displaying overlapping concentrations. On the basis of field relationships these lithologies were intruded as the first batch of magma and may have evolved in a sequence from each other.

Fig. 5.36 shows the Lanthanoid-pattern for the Crenulated Grennaite and the Kaxtorpите. These lithologies are part of the first magmatic phase, lie adjacent to each together in the field and display shared geochemical and petrological characteristics. While the Kaxtorpите displays lower [Ln] concentrations both lithologies plot with the same shape (which is also different to the other Grennaite) which may support a further geochemical similarity between the two rock types.

Figure 5.35: Median and upper and lower quartile ranges for the lanthanoid concentration (relative to chondrite) for the Grennaite-lithologies at Norra Kärr.

Figure 5.36: Median and upper and lower quartile ranges for the lanthanoid concentration (relative to chondrite) for the Crenulated Grennaite and the Kaxtorpite at Norra Kärr.

Figure 5.37: Median and upper and lower quartile ranges for the lanthanoid concentration (relative to chondrite) for the Pegmatite-Host Grennaite and the Pegmatites at Norra Kärr.

Figure 5.38: Median and upper and lower quartile ranges for the lanthanoid concentration (relative to chondrite) for the Pegmatite-Host Grennaite and the Pulaskite and Lakarpite at Norra Kärr.

5.5.2 The Relationship of the Pegmatites to the Pegmatite-Host Grennaite

The pegmatites at Norra Kärr are restricted to the Pegmatite-Host Grennaite and are not observed in the Contact or Crenulated Grennaite despite being these lithologies being adjacent to the Pegmatite-Host Grennaite. When the lanthanoid-patterns of the Pegmatite-Host Grennaite and the pegmatites are compared (Fig. 5.37) the shapes are very nearly identical with the pegmatites being slightly more enriched in the [Ln] than the Pegmatite-Host Grennaite. This suggests that the Pegmatite-Host Grennaite has acted as a control on the concentration of [Ln] within the pegmatites with the process through which the pegmatites formed appears to have enriched the pegmatites relative to their host rocks.

5.5.3 The Relationship of the Lakarpite to the Grennaite and Pulaskite

Based on field evidence and geochemistry the Lakarpite and Pulaskite form a second phase of magmatism at Norra Kärr. However, from the petrological evidence presented in Chapter 3 and geochemical evidence presented in this Chapter the Lakarpite can be understood as a very complex intrusive body. Furthermore, the Lakarpite displays a complex [Ln]-pattern with the upper quartile matching Lanthanoid concentrations of the upper bound of the pegmatites and the lower quartile lying within the Pulaskite field (Fig. 5.38). These patterns show that the Lakarpite appears to display characteristics of both the Pulaskite and the central portion of the Grennaite (the Pegmatite-Host and Crenulated Grennaites). This suggests that a Pulaskite-type magma may have intruded into the central portion of the Grennaite and becoming modified chemically and petrologically in the process.

5.5.4 Lanthanoid Summary

The lanthanoid plots show several trends within the intrusion. All plots show a negative Eu anomaly which typically indicates earlier feldspar fractionation during ascent through the crust. Within the Grennaites the Contact Grennaite (the earliest Grennaite) shows a 'flat' [Ln] pattern. Relative to this the Pegmatite-Host and Crenulated Grennaites are significantly more enriched in La-Sm, and the Pegmatite-Host Grennaite more enriched in Gd-Lu, than the Contact Grennaite. The Pegmatites are only slightly more enriched than the Pegmatite-Host Grennaite. Interestingly, the Kaxtorpite displays a similar though less [Ln] enriched) pattern to the Crenulated Grennaite. The Lakarpite appears to show an intermediate affinity between the Pulaskite and the Pegmatite-Host Grennaite.

When compared to the Ilímaussaq intrusion the Norra Kärr Pulaskite compares well to the Foyaite and Pulaskite of the third phase of Ilímaussaq magmatism (Fig. 5.39). When the Grennaites and Kaxtorpite are compared to the Lujavrites and Kakortokites (Fig. 5.40) they follow similar patterns in Gd-Lu as all these lithologies. However, the Arfvedsonite- and Medium-Coarse- Lujavrites along with the Red- and White- Karkortokites all display higher La-Sm concentrations (only the Aegirine- Lujavrite and Black Karkortokite have comparable La-Sm concentrations to the Norra Kärr rocks). When the Kaxtorpite is compared to the other amphibole bearing lithologies at Ilímaussaq (Fig. 5.41) the same pattern of similar Gd-Lu concentrations and enriched La-Sm concentrations is seen with only the Black Karkortokite displaying a similar [Ln] pattern. Overall it appears that, relative to Ilímaussaq, Norra Kärr is not enriched in heavy-[Ln] but is depleted in light-[Ln].

Figure 5.39: Norra Kärr Pulaskite compared to selected lithologies from Ilímaussaq.

Figure 5.40: Norra Kärr Grennaite compared to selected lithologies from Ilímaussaq.

Figure 5.41: Norra Kärr Kaxtorpite compared to selected amp-bearing lithologies from Ilímaussaq.

	Grennaite	Grennaite-Peg	Pegmatite	Crenulated	Kaxtorpite	Lakarpite	Pulaskite
N	2695	228	1128	1434	461	285	279
La	161.15 E	457.47 C	494.3 B	547.8 A	350.4 D	440.3 C	170.35 E
Ce	357.24 D	1024.8 B	1147.8 A	1127.1 A	573.6 C	966.9 B	343.35 D
Pr	47.82 E	133.02 B/C	152.11 A	135.97 B	63.33 D	123.49 C	42.65 E
Nd	198.7 C	524.7 B	631.78 A	500.88 B	215.88 C	493.0 B	160.77 D
Sm	61.85 D	138.21 B	182.83 A	115.77 C	42.89 E	133.90 B	38.10 E
Eu	8.36 D	16.77 B	22.46 A	13.46 C	5.47 E	16.69 B	5.16 E
Gd	78.29 D	152.13 B	204.18 A	120.22 C	42.81 E	150.01 B	41.82 E
Tb	17.75 D	30.67 B	41.72 A	23.50 C	7.8 E	30.97 B	8.47 E
Dy	130.88 D	207.84 B	282.80 A	159.28 C	50.82 E	214.2 B	58.44 E
Ho	31.34 D	47.24 B	62.47 A	35.8 C	11.179 E	48.12 B	13.26 E
Er	103.24 D	144.62 B	191.22 A	112.47 C	34.997 E	148.45 B	41.58 E
Tm	16.66 D	22.35 B	29.19 A	17.59 C	5.31 E	22.58 B	6.48 E
Yb	105.99 C	138.11 B	178.49 A	110.19 C	32.904 D	138.25 B	40.89 D
Lu	15.15 C	19.12 B	24.33 A	15.30 C	4.623 D	19.07 B	5.74 D

Table 5.7: ANOVA analysis for [Ln] concentrations across the lithologies at Norra Kärr.

5.6 Whole-Rock Geochemical Models

So far this thesis has outlined aspects of the petrological, mineralogical and geochemical trends present at Norra Kärr. This section utilises the data presented earlier in this chapter (along with mineral data from Chapter 4) to investigate these trends further, in particular:

1. Is there evidence for assimilation of the country rock by the Grennaite magma as shown within the [Ln] concentrations (5.6.2).
2. From which lithology could the feldspar-rich Pegmatite have been derived, are they related to the Pegmatite- Host Grennaite or from the feldspar-rich Pulaskite (5.6.3)
3. Which minerals are responsible for the enrichment of Zr, [Ln] and the overall evolution of the Grennaites (5.6.4).
4. What could be the role of volatiles within the formation of the Kaxtorpite (5.6.5)
5. Can the Lakarpite can be produced via the mixing of the Pulaskite magma with the Pegmatite-Host magma (5.6.6)

5.6.1 Variability of Elements

Partition coefficients (K_D) are frequently unavailable for elements within alkaline magmas and their constituent minerals. In order to examine the relative order of compatibility within the magmas at Norra Kärr the variability of each element was calculated following Eq. 5.1 (Schiano et al. 1993):

$$V_{\alpha} = \frac{\sigma(\alpha)}{\bar{\alpha}}$$

Equation 5.1 (Janoušek et al. 2016)

Where:

α = The selected Chemical Element

V_{α} = Variability of element α

$\sigma(\alpha)$ = Standard Deviation of α

$\bar{\alpha}$ = Mean concentration of α

The largest changes in elemental concentration are for elements with K_D values very different from 1. Eq. 5.1 describes the correlation between K_D and the variability of the dataset (the less compatible an element is the higher the variability and vice versa).

Fig. 5.42 shows the calculated variabilities for elements within each lithology at Norra Kärr. The most incompatible elements (those with the highest variabilities) are elements like V, Ba, Pb which are found in latter stages of Grennaite fractionation. Variability within the Grennaites shows a marked

decrease from W onwards due to the remaining elements being compatible within the mineral assemblages. Elements within the trachyte lithologies (Kaxtorpite, Pulaskite and Lakarpite) show less variability overall. Ga is the least variable element of all lithologies likely due to its tendency to readily substitute into Al-bearing minerals.

This study had no access to other full exploration datasets and so the relative variability of these elements between different intrusions cannot be fully assessed. However, were such datasets available it would be possible to track the relative variability of elements between intrusions (which may be due to the source of melting source and the crystallising assemblage) and comparative differences made between different magmas of the order of element compatibility.

Lithology	n=
Contact Grennaite	2695
Pegmatite-Host Grennaite	228
Pegmatites	1128
Crenulated Grennaite	1434
Kaxtorpite	461
Lakarpite	285
Pulaskite	279

Table 5.8: Number of data points used for each element used in the calculation of element variability for each lithology.

Figure 5.42: Calculated variability of elements within each lithology in Norra Kärr arranged in general order of decreasing variability.

5.6.2 Mixing of Host Väjö Granite and Grennaite

In order to test the influence of assimilation of the country rock on the [Ln]-content a mixing model using Eq. 5.2 was calculated with the results displayed in Fig. 5.43. The country rock was taken to be the Väjö granite and the assimilating magma taken as the Pegmatite-Host Grennaite which makes up the bulk of the Norra Kärr intrusion.

$$C_M = f_1 C_1 + (1 - f_1) C_2$$

Equation 5.2 (Janoušek et al. 2016)

Where:

C_M = Composition of the mixed magma

C_n = Endmember composition of a magma or solid rock

f_1 = Proportion of endmember 1 in the mixture

The model shows that the Pegmatite-Host Grennaite would have had to have mixed with 20%-40% of the country rock to produce a similar heavy-[Ln] pattern to the Contact Grennaite, and between 60%-to-80% of the country rock to produce a similar light-[Ln] pattern. It is not possible to reproduce the median Contact Grennaite composition through mixing. Given the low temperature of the magma (<850°C) and a lack of petrological evidence for melting or assimilation of the country rock it is unlikely that mixing with the country rock was involved in forming the [Ln]-concentrations of the Contact Grennaite.

Fig. 5.44 Further shows that that the Contact Grennaite plots away from the mixing line between the Väjö Granites and the Pegmatite-Host Grennaite, with the Contact Grennaite exhibiting a higher heavy-[Ln] content. This could be explained by the greater enrichment in light-[Ln] over heavy-[Ln] within the Fenite relative to the Väjö Granites as seen in the whole rock data (Fig. 5.45).

Figure 5.43: Results of a mixing model for the Väjö Granite and the Pegmatite-Host Grennaite.

Figure 5.44: Results of a mixing model for the Växjö Granite and the Pegmatite-Host Grennaite, with the whole rock composition of the Fenite and Contact Grennaite also shown. The mixing line steps in increments of 10%.

Figure 5.45: Whole rock chondrite normalised [Ln]-patterns for the Växjö Granite, Fenite and the Contact Grennaite. Note the higher enrichment in the light-[Ln] over heavy-[Ln] in the Fenite.

5.6.3 Generation of the Pegmatites

The pegmatites appear to display a similar stockwork-like morphology as the pegmatite veins observable in the Lovozero intrusion (i.e. Arzamastsev et al. 2008) while also appearing to be more feldspar and nepheline rich than the surrounding Grennaite. This suggests that the pegmatites may be derived from either the feldspar-rich Pulaskite intruding as a stockwork, or by forming in a stockwork-like pattern as shearing opened up areas of lower stress within the cooling (and increasingly viscous) Pegmatite-Host Grennaite magma, allowing residual fractionated liquids to form a 'stockwork' of pegmatite bodies.

Fig. 5.46 shows a plot of Zr (a compatible element within the melt as evidenced by Zr-silicate saturation) vs Pb (a typically incompatible element) in order to examine the trends in fractionation. The strong overlap between the Pegmatites and the Pegmatite-Host Grennaite shows that it is unlikely that there has been an input from the Pulaskite, and further shows that restricted fractionation occurred between the Pegmatite-Host Grennaite and the Pegmatites otherwise there would be a more widespread trend in decreasing Zr.

This plot, along with Fig. 5.21 that showed that the Pegmatites and the Pegmatite-Host Grennaite display similar K/Rb ratios, suggests that the Pegmatites are solely derived from Pegmatite-Host Grennaite; their formation likely involving the segregation of this residual melt from the existing Grennaite mush under dilation to form the observed pegmatite lenses.

Figure 5.46: Plot to show the behaviour of compatible Zr vs incompatible Pb within the Pegmatites, the Pegmatite-Host Grennaite and the Pulaskite.

5.6.4 Grennaite Fractionation and Ore-Enrichment

In order to show which minerals are predominantly responsible for the major and trace element fractionation within the Grennaites Figs. 5.47 to 5.50 were plotted along with the median compositions of minerals from Norra Kärr.

Fig. 5.47 and 5.48 show the effect of mineral crystallisation upon the Fe_2O_3 , Al_2O_3 , and La within the Grennaites. Fig. 5.47 Shows that the shallow compositional trend of the Contact Grennaite can be matched to progressive crystallisation of nepheline. The later Grennaite varieties and the Pegmatites display a steeper compositional trend seemingly indicating a progressive change from nepheline dominated to aegirine dominated fractionation. Fig. 5.48 shows that nepheline crystallisation may have some effect on increasing the La content within the Contact Grennaite, however the later lithologies appear to display more influence from aegirine and catapleiite/eudialyte fractionation.

Fig. 5.49 shows that the trend in Zr and La are initially controlled within the Contact Grennaite by aegirine and then by the co-crystallisation of aegirine and catapleiite. Later lithologies are also controlled by co-crystallisation of aegirine and catapleiite/eudialyte. Nepheline and feldspar crystallisation does not appear to play a role in fractionating these two elements.

Fig. 5.50 shows again that initial aegirine fractionation within the Contact Grennaite increases the La and Lu concentrations within the magmas. This then transitions to co-crystallisation of aegirine and catapleiite with the Pegmatite-Host and Crenulated Grennaites potentially showing evidence of being influenced by aegirine- eudialyte (and possibly nepheline-and feldspar crystallisation as well) leading to a drop in Lu concentrations. Unlike Fig. 5.49 nepheline and feldspar do appear to play a role in raising [Ln] but cannot be responsible alone for the difference observed in La vs Lu within the later Crenulated Grennaite.

The point at which catapleiite crystallisation transitions to eudialyte crystallisation can be observed as a change in slope in the data at approximately 500 ppm La. This second stage of fractionation potentially provides the process by which the light-[Ln] enrichment in the steadily fractionating Grennaite magmas occurred.

Overall, the progressive changes in overall magma chemistry appears to be predominately driven by a trend in initial nepheline crystallisation moving towards feldspar fractionation as seen within the Nep-Qz-Kal ternary. The co-crystallisation of aegirine and catapleiite appears to be the main factor in concentrating Zr and La within the Grennaites, with the final trend in the enrichment of light-[Ln] over heavy-[Ln] within the Crenulated Grennaite being due to catapleiite crystallisation of and/or the co-crystallisation of nepheline/feldspar and Zr-silicates in the later stages of fractionation.

Figure 5.47: Wt% Fe_2O_3 vs Al_2O_3 plotted with the compositions of the main fractioning minerals. Note that the fractionation trend broadly aligns along the tie lines for aegirine and nepheline.

Figure 5.48: La (ppm) vs Wt% Al_2O_3 plotted with the compositions of the main fractioning minerals. Note that the fractionation trend broadly aligns along the tie line between nepheline and feldspar but that these minerals do not broadly show a process for fractioning La.

Figure 5.49: Zr (ppm) vs La (ppm) plotted with the compositions of the main fractioning minerals. Note that the fractionation trend broadly aligns across the aegirine-catapleiite tie line. Aeg-Cat-Felds/Neph and Aeg-Eud-Felds/Neph triangular-tie-lines shown for illustration alongside the calculated cumulate produced for each triangle from observations of mineral abundance.

Figure 5.50: Zr (ppm) vs La (ppm) plotted with the compositions of the main fractioning minerals. Note that the fractionation trend broadly aligns along the aegirine-catapleiite tie line, with a downwards trend in Lu at approximately 500 ppm La.

5.6.5 Kaxtorpite Fractionation

Given that the Kaxtorpite and the Grennaite appear to have intruded as part of the same initial magmatic phase but lie either side of the phonolite minimum it is possible that the initial magma immiscibility separated soon after intrusion. This hypothesis can only be fully tested experimentally, however a close relationship with the Grennaites can be shown via:

1. A diffuse intermingled boundary between the Kaxtorpite and the Crenulated Grennaite,
2. Similarities in trace element composition (i.e. Cs, V) with the Crenulated Grennaite including a similar (albeit less concentrated) [Ln]-pattern (Fig. 5.36),
3. Similar field relationships, morphology and mineralogy between the Kaxtorpite and the Crenulated Grennaite to that observed at the Yastrebets intrusion between a lower nepheline syenite and an upper amphibole rich cap.

A significant compositional difference between the Grennaites and the Kaxtorpite is their volatile budgets (Chapter 4). The evolution of the Grennaites and the Kaxtorpite is difficult to model as accurate original volumes for the Grennaite and the Kaxtorpite are not available due to erosion of the Kaxtorpite and the top of the Norra Kärr chamber, as well as the unproven depths to which the Grennaites extend.

However, if the total volatile budget for each lithology within the first intrusive phase (as calculated from the mineral data in Chapter 4) is used as the original volatile content of the magma then an approximate bulk K_D for the Grennaites and the Kaxtorpite can be tentatively calculated. The results are shown in Table 5.9.

	1 st Phase (%)	K_D Σ Grennaites	K_D Kaxtorpite
F	0.16	0.04	0.96
Cl	0.02	1.00	0.00
<i>OHcalc</i>	<i>0.90</i>	<i>0.93</i>	<i>0.07</i>

Table 5.9: Approximate bulk K_D for volatile species within the Grennaites and the Kaxtorpite.

The results show that the Kaxtorpite has a greater affinity for F than the Grennaites, while the Grennaite have a greater affinity for Cl and OH than the Kaxtorpite. However, whether the distribution of volatiles within the chamber is driving the differences in magmatic composition and potentially magmatic immiscibility is yet to be examined and would require experimental evidence based upon these natural systems.

5.6.6 Formation of the Lakarpite Zones Through Mixing

In order to test if the outer zone of the Lakarpite was formed due to the mixing of the Pegmatite-Host Grennaite and a Pulaskite-type intrusive body a mixing model using Eq. 5.2 was calculated with the results shown in Fig. 5.51. A further model, Fig. 5.52, was calculated which compared the mixing of an evolved Pegmatite-Host Grennaite which has fractionated 20% Aegirine with a Pulaskite-type intrusive body.

The model in Fig. 5.51 shows that it is possible to generate a median Lakarpite composition with 70%-to-90% mixing of a Pulaskite and Pegmatite-Host magma. Specifically, with 70% mixing the heavy-[Ln] pattern (Gd-Lu) is matched, with between 80%-to-90% mixing required for the light-[Ln] pattern to be matched. The model in Fig. 5.52 shows that with 50% to 60% mixing the heavy-[Ln] pattern (Gd-Lu) is matched, and with between 60%-to-70% mixing the light-[Ln] pattern is matched.

These mixing ratios are feasible due to the low width and high surface area of the Lakarpite dyke as well as the low volumes of material affected. It should be noted that the lower quartile of Lakarpite [Ln]-concentrations matches the median Pulaskite composition thereby requiring no mixing. This indicates that a range of degrees of mixing or mass transfer took place from an original Pulaskite-type magma to a more evolved eudialyte-bearing Lakarpite composition.

However, the upper quartile for the Lakarpite is more enriched in [Ln] than the upper quartile of the unfractionated Pegmatite-Host Grennaite. It is likely that the Lakarpite intruded once the Pegmatite-Host Grennaite had cooled enough to be sufficiently viscous to support the dyke structure; as such these higher [Ln] contents may indicate leaching of elements during a later stage of Grennaite fractionation (e.g. post aegirine – Fig. 5.52 - and perhaps catapleiite crystallisation). This is supported by the separate petrological zonation within the Lakarpite, suggesting physical mixing of crystals was unlikely to have occurred and rather a mixing of evolved magmatic liquids diffusing and mixing from the Pegmatite-Host Grennaite into the Lakarpite likely occurred.

Furthermore, Fig. 5.53 shows that the Lakarpite lies off of the direct mixing line and displays an enrichment in the light-[Ln]. This could be tied to interactions with the increasingly light-[Ln] rich composition of the remaining Grennaite magma as shown by whole rock and eudialyte compositions.

Figure 5.51: Results of a mixing model between the Pulaskite and the Pegmatite-Host Grennaite.

Figure 5.52: Results of a mixing model between the Pulaskite and the Pegmatite-Host Grennaite which has undergone aegirine crystallisation.

Figure 5.53: Results of a mixing model between the Pulaskite and the Pegmatite-Host Grennaite, with the whole rock composition of the Lakarpite also shown (25th, 50th and 75th quartile compositions). The mixing line steps in increments of 10%. All compositions are normalised to Chondrite (Taylor & McLeannan 1985). A (top) results for the mixing of the un-fractionated whole-rock Pegmatite-Host Grennaite; B (bottom) results for the mixing of the Aegirine-fractionated whole-rock Pegmatite-Host Grennaite composition.

5.7 Geochemical Discussion

While Norra Kärr has displays its own unique magmatic features it does display similarities to other alkaline intrusions in terms of its composition on a TAS plot and displaying a low CaO content. Like other highly fractionated alkaline intrusions which lie along the AFM alkaline-trend Norra Kärr's overall fractionation pattern (especially in terms of Si and Al) is controlled by the Nep-Qz-Kal eutectic diagram. Within these trends the Norra Kärr magmas are Na-dominated with the trachyte's magmas far richer in MgO and P₂O₅ than the phonolite magmas.

The data presented here, combined with field-relationships, petrography and major- and trace-element analysis, appear to show that two intrusive phases occurred at Norra Kärr. The first phase consisted of a phonolite magma which formed the Grennaite, and possibly also differentiated into the Kaxtorp, with a predominantly Fe³⁺-mineral assemblage. The second phase consisted of trachytic magma which formed the Pulaskite with a Fe²⁺-bearing assemblage, and which also formed the intrusion that was to become the Lakarp. Further trends seen in the major, trace and lanthanoid concentrations will be outlined below and are summarised in Figs. 5.54, 5.55, 5.56.

5.7.1 Phase 1 Magmas: Grennaite and Kaxtorp

The Grennaite is divided into three petrological and geochemical zones: the Contact Grennaite, the Pegmatite Host Grennaite (which hosts the Pegmatites) and the Crenulated Grennaite. Several element trends suggest that this is the order in which the Grennaite crystallised (Fig. 4.53). Further details are given for each of the Grennaite varieties below, but overall the main factor in concentrating Zr and La within the Grennaite (as shown by modelling) is the co-crystallisation of aegirine and catapleiite, with the final trend in the enrichment of light-[Ln] over heavy-[Ln] within the Crenulated Grennaite being due to catapleiite crystallisation and/or the co-crystallisation of nepheline/feldspar and Zr-silicates in the later stages of fractionation.

The first trend is shown by variations in Na₂O and K₂O. All magmas at Norra Kärr are rich in sodium, with the contact Grennaite displaying the highest Na₂O concentrations. As fractionation progresses through the sequence the Na₂O decreases and K₂O increases towards the Crenulated Grennaite. This trend is repeated on a smaller scale by changes in TiO₂ and MnO concentrations and is also shown by K/Rb and Mn/Fe+Mn ratios. In all cases the Contact Grennaite appears to be the least fractionated of the three varieties of Grennaite, while also displaying the lowest [Ln] concentrations of any of the Grennaites. As catapleiite appears more abundant than eudialyte this may have resulted in a 'depletion' in [Ln] relative to the other Grennaites.

The second most fractionated Grennaite (in terms of major element trends) is the Pegmatite-Host Grennaite. This Grennaite variety displays the highest concentrations of Zr, Hf, Nb and Ta (along with Y and W) of any of the Grennaites. This Grennaite is also more enriched in [Ln] and particularly in La-Sm than the Contact Grennaite. As these trace elements are associated with eudialyte this suggests that eudialyte crystallisation was important at this stage of fractionation. When compared to the K/Rb vs Zr plot there is a spike in the Zr at this stage of fractionation. This suggests that if the K/Rb is a true indicator of the fractionation trend then the remaining magma must have become depleted in Zr, Hf, Nb and Ta at this stage due to eudialyte crystallisation.

Figure 5.54: Summary of element fractionation patterns within the first (phonolitic) magmatic phase.

Figure 5.55: Summary of the second (trachytic) magmatic phase.

The pegmatites are geochemically closely related to the Pegmatite-Host Grennaite and display similar or slightly enriched element concentrations along with a similar (but more enriched) [Ln] pattern. Field relationships show that the pegmatites are intimately related to their host rocks and are not found in the Contact or Crenulated Grennaites. The geochemical data, along with the field relationships, show that the Pegmatites formed from the Pegmatite-Host Grennaite and preferentially enriched themselves in [Ln] and other elements relative to their host rocks. As such they appear to be solely derived from low-degree fractionated residual melts from Pegmatite-Host Grennaite rather than having a relationship with the Pulaskite.

The Crenulated Grennaite is the most fractionated (in terms of major element trends) and displays the highest concentrations of Rb, Cs, Ga and Sn. Increases in Rb and Cs and Ga are related to feldspar fractionation and are most concentrated in late-stage magmas. Relative to the Pegmatite-Host Grennaite the Crenulated Grennaite is depleted in Gd-Lu and enriched in La, Ce and Pr. This may indicate that eudialyte crystallisation within the Pegmatite-Host Grennaite removed Gd-Lu from the melt suggesting a eudialyte control on the light-[Ln] to heavy-[Ln] distribution between these two petrologically different ore-domains.

The Kaxtorpite can be grouped with the Grennaites on the basis of geochemical evidence, which can be supported by the field-relationships between the adjacent lithologies and some shared petrological and structural features. Geochemically the Kaxtorpite displays the high Ga concentrations similar to the Grennaites, as well as displaying high V and Cs concentrations which are also observed in the Crenulated Grennaite. The specific feature of the Kaxtorpite is its uniquely high Li concentrations which are not seen elsewhere at Norra Kärr (Table 4.6). These Li concentrations in particular mark the Kaxtorpite out as separate from the other trachyte magmas (the Lakarpite and Pulaskite) and also provide an explanation for its formation. As discussed in 5.4.3 Li expands the region of silicate immiscibility, suggesting that the Kaxtorpite may have separated to the top of the first intrusive magmatic phase as a separate trachyte lithology. In doing so V, Cs and [Ln] were transferred between the Kaxtorpite and Crenulated Grennaite leading to a similar shaped [Ln]-pattern seen between the two lithologies. As shown from calculations the Kaxtorpite has a higher affinity for fluorine than the Grennaites which are richer in OH and Cl. However, whether this precipitated or resulted from magmatic immiscibility within the first phase intrusion is yet to be examined and would require experimental evidence.

5.7.2 Phase 2 Magmas: Pulaskite and Lakarpite

The geochemistry of the Pulaskite and Lakarpite appear to indicate a second magmatic phase at Norra Kärr (Fig. 4.53). The Pulaskite displays a distinct major element chemistry; a trachyte magma low in Zr, Fe₂O₃ and alkalis, but high in MgO, TiO₂ and P₂O₅. It also appears to be the least fractionated of the magmas in terms of K/Rb. The Pulaskite is also high in V, Co, Ni and Zn and displays the lowest [Ln] concentrations of any magma at Norra Kärr. On this basis it is likely to be the least fractionated magma and the last to intrude. This is also supported by the presence of very enclaves within the Pulaskite body.

The Lakarpite, however, displays a highly varied major element chemistry that is both similar to the Pulaskite and the Grennaite. The same is true for the trace elements, with far higher Zr, Hf, Nb, Ta Y and W concentrations, and lower Ni concentrations, than the other trachyte's thereby displaying a greater affinity to the Pegmatite-Host Grennaite into which the Lakarpite intruded. Further, this change in Ni concentration relative to Co has led to two trends in Ni/Co which can be mapped through cross-sections of the Lakarpite (lower ratios in the centre and higher at the contact with the Pegmatite-Host Grennaite) which is inverse to the trend seen in Zr concentration.

The [Ln] concentrations within the Lakarpite also appear to indicate an affinity for both the Pulaskite (shown in the core zones of the Lakarpite which also display a similar petrology to the Pulaskite) and the Pegmatite-Host Grennaite (shown at the contact of the Lakarpite within which there is an abundance of eudialyte and some catapleiite similar to the Grennaite petrology). As such the cause of these different chemical and petrological trends may therefore be related to a mixing/assimilation/redox-reaction between the Lakarpite (a Pulaskite magma) and the Pegmatite-Host Grennaite. Indeed, modelling shows that it is possible to generate the different zones of the Lakarpite through mixing the Pulaskite with the Pegmatite-Host Grennaite, though the process is likely more complex than direct physical mixing of magmatic liquids and are likely driven by mass transfer processes. The Lakarpite also appears to record the later stage light-[Ln] enrichment of the Grennaite magmas.

Despite the Lakarpite and Pulaskite both starting out as the same type of magma with both intruding into the Grennaite, only the Lakarpite become chemically altered. This suggests that the Lakarpite intruded into the still 'reactive' (or hot) Pegmatite-Host Grennaite, whereas the Pulaskite intruded into the 'unreactive' Contact Grennaite. This may indicate that either the Lakarpite intruded first and the Pulaskite second, or different parts of the magma chamber where cooler/less reactive than others at the same time. In this case both rock-types are likely later dyke intrusions into the level of the magma-chamber that seen in outcrop, something that is supported by field-relationships between the Pulaskite and Lakarpite and the Grennaite.

Figure 5.56: Summary of the models presented within this chapter: 1 – Lack of mixing between the Grennaite and the Vaxjö (5.6.2); 2 – Formation of Pegmatites from concentrated Pegmatite-Host Grennaite magma (5.6.3); 3 – Trends in whole-rock Z and La/Lu driven by aegirine and aegirine-catapleiite crystallisation (5.6.4); 4 – Volatile fractionation within the first phase magma (5.6.5); 5 – Formation of the Lakarpite zones due to mass transfer between a magma of Pulaskite composition and the fractionated Pegmatite-Host Grennaite liquid (5.6.6).

5.8 Geochemical Conclusions

This chapter has provided a new synthesis of the major and trace element data from Norra Kärr. In particular the order of intrusion crystallisation of the different lithologies has been proposed, and models have been presented to as supporting evidence for the processes that generated the Pegmatites, the Lakarpite and the observed pattern the progressive enrichment of light-[Ln] observed within the Grennaites. This Chapter has shown that:

- On the basis of the geochemical patterns presented here, (major element, trace elements and SOM correlations) there is evidence that there are two distinct intrusive phases at Norra Kärr, with the phonolitic Grennaites (and likely also Kaxtorp) intruded first, followed by a second phase of trachytic magma which formed the Lakarpite and Pulaskite. This can be supported by the field relationships in Chapter 2, and the difference in petrology and mineralogy as shown in Chapters 3 and 4.
- Overall the Norra Kärr magmas are comparable to other alkaline intrusions in terms of where they plot on a TAS plot and Nep-Qz-Kal and AFM ternary's and display consistently low CaO contents across the two magmatic phases.

- The likely order of Grennaite crystallisation is the Contact, then Pegmatite-Host, then Crenulated. This leads to an initial enrichment in [Ln] followed by a depletion in heavy-[Ln] along with Zr, Hf, Nb and Ta.
- The Pegmatites are chemically similar to the Pegmatite-Host Grennaite and are likely to have separated from their host Grennaite as a fractionated residue producing a slightly enriched chemical signature.
- The Kaxtorpite has a significantly higher Li content suggesting it may have been able to form an immiscible trachytic melt during the first magmatic phase. The Kaxtorpite has a higher affinity for fluorine than the Grennaites which are richer in OH and Cl. However, whether this precipitated or resulted from magmatic immiscibility within the first phase intrusion is yet to be examined and would require experimental evidence.
- It is possible to generate the different zones of the Lakarpite through mixing the Pulaskite with the Pegmatite-Host Grennaite, though the process is likely more complex than direct physical mixing of magmatic liquids. The Lakarpite also records the later stage light-Ln enrichment of the Grennaite magmas.
- Overall it appears that, relative to Ilímaussaq, Norra Kärr is not enriched in heavy-[Ln] but is depleted in light-[Ln] suggesting that fractionation deeper in the system is responsible for the overall [Ln] concentrations; local fractional crystallisation within the centre of the chamber is therefore responsible for more subtle variations.
- The Grennaite does not appear to have mixed with the Våxjö Granite, but there may well have been a loss of light-[Ln] to the fenite from the Contact Grennaite.
- Modelling shows that aegirine is primarily responsible for enriching the magmas in Zr; and that aegirine-catapleiite co-crystallisation will enrich the magmas in [Ln]. Catapleiite crystallisation may also be able to enrich light-[Ln] over heavy-[Ln] within the melts.

Chapter 6

Mineral and Whole-Rock [Ln], Zr and Hf Evolution

6.1 Introduction

In this chapter new LA-ICP-MS data will be presented to show the variation in [Ln]-concentration and Zr/Hf throughout the fractionation sequence of each lithology. This chapter builds upon the petrological data (Chapter 3) and mineralogical data (Chapter 4) and whole rock data (Chapter 5) previously presented. Chondrite normalised plots will be presented to show the pattern of [Ln]-concentration within the minerals of Norra Kärr and initial conclusions will be drawn as to how this affects progressive [Ln]-fractionation trends. Calculated K_d values for aegirine are presented and compared to the experimental results presented by Beard (2018). Whole rock and mineral Zr/Hf ratios are presented to initially model the progressive fractionation of Zr and Hf within the Grennaite and compared to work by Kogarko (2015) for the Lovozero intrusion. Further modelling of both Zr/Hf ratios will be presented here, with additional [Ln]-fraction modelling in Chapter 7.

6.2 Whole Rock vs Mineral [Ln] and Y Concentrations

This section will present the average concentrations of the lanthanoids (normalised to chondrite) within the minerals of Norra Kärr as obtained by LA-ICP-MS analysis.

Figs. 6.1 – 6.5 Show the chondrite normalised concentrations for eudialyte and catapleiite plotted (on separate axes) alongside the chondrite normalised whole rock compositions. This shows that the average [Ln]-concentrations within eudialyte approximately match the [Ln]-patterns shown by the whole rock data. This suggests that the eudialyte are recording the final composition of the magma at the stage they crystallised within the chamber. Compared to eudialyte the catapleiites are orders of magnitude less enriched in [Ln], however they all display an observable bias towards the heavy-[Ln] potentially influencing the evolution of the melt towards a more light-[Ln] enriched composition.

Figure 6.1: Chondrite normalised whole-rock [Ln]-concentrations for the Contact Grennaite along with aegirine, catapleiite and eudialyte.

Figure 6.2: Chondrite normalised whole-rock [Ln]-concentrations for the Pegmatite-Host Grennaite along with aegirine, catapleiite and eudialyte. Modal proportions given in brackets.

Figure 6.3: Chondrite normalised whole-rock [Ln]-concentrations for the Crenulated Grennaite along with aegirine, catapleiite and eudialyte. Modal proportions given in brackets.

Figure 6.4: Chondrite normalised whole-rock [Ln]-concentrations for the Pegmatites along with eudialyte and catapleiite. Modal proportions given in brackets.

Figure 6.5: Chondrite normalised whole-rock [Ln]-concentrations for the Zr-Lakarpite Contact Grennaite along with aegirine and eudialyte. Modal proportions given in brackets.

6.3 Calculated relative K_d for Aegirine ([Ln] and Y)

Published distribution coefficients for alkaline systems show a large range of values (Marks et al. 2004). As such approximate distribution coefficient (K_d) values for Norra Kärr were calculated for aegirine within each lithology. Aegirine is the first forming phase within each of the magmas and the whole rock composition is assumed to be the original starting melt composition. While it is reasonable to assume the whole rock values to be indicative of the starting melt composition for the Kaxtorpites and Pegmatites, it is likely that due to progressive fractionation with the Grennaite lithologies these starting concentrations will vary. This also effects the K_d values for Eu due to earlier feldspar crystallisation.

Fig. 6.6 shows the calculated K_d values for the first phase of intrusion. The Pegmatites show the most complete trend and indicate a preference for heavy-[Ln]. The Grennaite lithologies all show similar trends, with low K_d for mid-range [Ln], and slightly higher K_d for the heavier-[Ln] than the lighter-[Ln]. Aegirine from the Kaxtorpites shows higher K_d values for the light-[Ln] but there is limited data to show the trend in the heavy-[Ln].

The Pulaskite (Fig. 6.7) demonstrates two differing K_d trends between the enclaves and the matrix. The enclaves have higher K_d values for the light-[Ln] which would lead to an increase in heavy-[Ln] within the melt. The matrix has an affinity for the heavy-[Ln] effectively balancing out the [Ln]-contents within the lithology. The Lakarpite aegirines (Fig. 6.8) show a range of K_d values with the inner zone aegirines displaying higher affinity for the lighter-[Ln], whereas the outer zone aegirines display a similar pattern to the Grennaite aegirines with lower affinities for the mid-range and higher affinities for heavier-[Ln] than the lighter-[Ln].

Figure 6.6: K_d for aegirines from the first phase of intrusion.

Figure 6.7: K_d for aegirines from the Pulaskite.

Figure 6.8: K_d for aegirines from the Lakarpite.

Beard (2018) calculated K_d values for experimentally grown aegirine and reported that the K_d values for [Ln] varied as a function of Aeg-content within the pyroxene (Fig. 6.9). The K_d values presented here display similar patterns with his experimental data with the high-aegirines of the Grennaites showing the similar trends in higher K_d values for the heavy-[Ln]. The aegirines within the second phase of intrusion display slightly higher K_d values for the light-[Ln] that match the calculations by Beard (2018) for the lower Aeg-contents that these crystals display (section 4.3.2 – Chapter 4). However, despite following the same patterns the K_d values presented here are lower than those calculated by Beard (2018). This could be analytical issue with poor coupling with aegirine or could alternatively be explained by the influence of the fluorine within the Grennaite melt which would result in a suppression of the K_d values for aegirine (Beard 2018).

Modelling by Beard (2018) showed that aegirine crystallisation under ‘dry’ (feldspar rich magma) oxidising (FMQ +1) conditions (as may be found within the Grennaites) results in steady enrichment in light-[Ln] (La) over heavy-[Ln] (Sm). With the Grennaites crystallising up to 30% aegirine this may well result in some degree of enrichment in light-[Ln] that is recorded by the eudialytes.

Figure 6.9: D values for Cpx/Glass from Beard (2018).

6.4 Mineral and Whole-Rock Zr/Hf Ratios

The average concentration of Zr (ppm), Hf (ppm) and Zr/Hf values for the minerals at Norra Kärr is given in Table 6.1, with the whole rock values given for comparison in Table 6.2.

Figs 6.10 shows the Hf and Zr for aegirine which show a linear spread of overlapping Hf and Zr concentrations despite differences in whole rock Zr and Hf.

Fig. 6.11 shows the division in Zr and Hf for pectolites, with the Kaxtorpite displaying lower concentrations than the Crenulated Grennaite.

The Hf and Zr concentrations within amphiboles (Fig. 6.12) show that the Kaxtorpite and Lakarpite have the lowest Zr and Hf concentrations while the Pulaskite and Pulaskite Enclaves display higher concentrations with a greater spread in the data. Sphene (Fig. 6.13), Rosenbushite (Fig. 6.14) and Biotite (Fig. 6.15) also show a spread in data points for the Pulaskite and Pulaskite Enclaves which further indicate differences in trace element composition for those minerals.

Catapleiite (Fig. 6.16) shows a spread of data points with no distinct trend shown, due to Zr (and by extension Hf) being a key element within the mineral formula. Eudialyte compositions (Fig. 6.17), with the exception of the Zr-Core Lakarpite, lie along a linear trend with the majority of the data plotting around 9 Wt% and 14 Wt% Zr. Lesser Zr concentrations may relate to alteration zones.

Table 6.1 shows the average mineral Zr/Hf ratios. Within the Grennaite the Zr/Hf ratio increases within aegirine indicating that aegirine may be removing relatively more Hf than Zr from the melt. The Zr/Hf ratio falls from catapleiite to eudialyte with the catapleiite potentially removing relatively more Zr than Hf from the melt.

There is also a general trend of the Contact Grennaite displaying the lowest mineral Zr/Hf ratios, followed by the Crenulated Grennaite, while the Pegmatite-Host Grennaite displays the highest mineral values. This is also seen within the whole rock Zr/Hf for the Grennaite (the Pegmatites have the highest Zr/Hf of all the lithologies) which increases from the Contact Grennaite to the Pegmatite-Host Grennaite before lowering slightly to the Crenulated Grennaite.

This extent to which mineral fractionation may affect Zr/Hf will be tested later in this chapter using the Zr and Hf concentrations presented here. These values, alongside the [Ln]-concentration presented earlier, will also be used to further model the evolution of the ore-bearing Grennaite magma.

Aegirine	n =	Zr			Hf			n =	Zr/Hf		
Contact Grennaite	137	311.8	+	194.4	17.3	+	10.2	137	18.7	+	2.8
			-	57.7		-	3.4			-	1.7
Pegmatite-Host Grennaite	185	3841.4	+	1030.8	113.5	+	25.0	185	36.3	+	3.5
			-	589.0		-	14.1			-	8.6
Pegmatite	917	2614.5	+	3536.0	88.9	+	56.6	917	27.8	+	1879.9
			-	1079.5		-	86.2			-	4.3
Crenulated Grennaite	373	752.4	+	2826.2	30.8	+	82.6	373	25.3	+	4.8
			-	291.3		-	11.1			-	2.5
Kaxtorpite	219	2100.5	+	543.7	67.8	+	21.2	219	31.1	+	3.3
			-	335.0		-	11.2			-	3.0
Lakarpite (Pulaskite-Core)	23	2243.4	+	1903.5	90.5	+	46.8	23	33.1	+	8.1
			-	476.0		-	48.6			-	6.5
Lakarpite (Core)	226	13322.4	+	2383.1	522.7	+	115.9	226	27.3	+	7.1
			-	9879.5		-	430.1			-	3.4
Lakarpite (Zr-Core)	109	2794.9	+	3307.3	51.5	+	37.9	109	63.1	+	13.9
			-	362.2		-	14.4			-	9.8
Lakarpite (Zr-Rich)	48	5481.3	+	254.6	166.4	+	11.9	48	31.9	+	2.5
			-	649.8		-	13.4			-	2.3
Pulaskite	215	12404.0	+	2379.3	391.4	+	223.7	215	29.9	+	4.9
			-	1320.8		-	46.8			-	4.2
Pulaskite (Enclaves)	95	27352.6	+	2780.3	590.2	+	140.0	95	44.9	+	7.1
			-	25387.6		-	582.7			-	3.4

Amphibole		Zr			Hf			n=	Zr/Hf		
Kaxtorpite	406	146.1	+	308.6	5.0	+	8.3	406	27.9	+	16.5
			-	59.7		-	2.8			-	5.9
Lakarpite (Pulaskite-Core)	427	517.5	+	698.1	17.5	+	30.8	427	29.0	+	8.5
			-	75.6		-	5.1			-	4.5
Lakarpite (Core)	299	665.3	+	79.1	18.3	+	4.7	299	38.1	+	9.7
			-	76.6		-	3.9			-	7.6
Lakarpite (Zr-Core)	101	1682.7	+	301.0	25.7	+	10.0	92	70.0	+	21.1
			-	314.4		-	8.4			-	16.6
Lakarpite (Zr-Rich)	124	2023.1	+	370.7	52.2	+	11.6	123	38.5	+	3.4
			-	520.4		-	14.9			-	3.2
Pulaskite	306	8.9	+	10352.5	1041.2	+	414.7	306	35.0	+	2.9
			-	4.8		-	678.1			-	5.0
Pulaskite (Enclaves)	257	6450.3	+	2696.7	204.1	+	41.4	240	35.9	+	6.9
			-	2052.7		-	36.4			-	11.9

Pec	n=	Zr			Hf			n=	Zr/Hf		
Crenulated Grennaite	37	1933.6	+	143.8	46.1	+	5.5	37	42.1	+	2.81
			-	200.6		-	8.9			-	1.66
Kaxtorpite	193	116.7	+	142.3	2.3	+	6.5	192	47.5	+	14.14
			-	60.5		-	1.3			-	18.13

Catapleiite	n=	Zr			Hf			n=	Zr/Hf		
Contact Grennaite	132	230841.9	+	85612.1	6531.9	+	504.5	97	35.3	+	13.6
			-	197518.5		-	334.0			-	8.6
Pegmatite-Host Grennaite	20	217373.8	+	86277.2	3190.5	+	294.2	20	75.7	+	16.8
			-	46202.7		-	179.5			-	16.1
Pegmatite-Host Grennaite (Vein)	33	230841.9	+	9338.0	4810.5	+	231.2	33	47.7	+	5.5
			-	8900.0		-	237.2			-	4.0
Pegmatite	508	230841.9	+	53410.9	4691.5	+	601.0	338	50.6	+	15.8
			-	40811.9		-	830.1			-	11.7
Crenulated Grennaite	152	230841.9	+	143371.3	4976.0	+	582.1	135	47.3	+	28.6
			-	79452.3		-	317.5			-	18.6

Eudialyte	n=	Zr			Hf			n=	Zr/Hf		
Contact Grennaite	122	106637.7	+	42328.6	3746.3	+	992.0	122	29.4	+	1.9
			-	36460.7		-	941.4			-	2.1
Pegmatite-Host Grennaite	183	135620.7	+	20037.8	3712.5	+	553.1	183	38.8	+	7.5
			-	35153.5		-	667.9			-	5.4
Pegmatite	1016	81836.8	+	202593.8	2251.8	+	403.1	1016	47.9	+	7.5
			-	16523.3		-	241.7			-	8.6
Crenulated Grennaite	375	123176.7	+	219449.0	2603.3	+	868.4	375	40.9	+	12.3
			-	40299.6		-	628.5			-	6.0
Lakarpite (Zr-Core)	192	93993.5	+	22774.3	10008.7	+	1516.6	191	9.1	+	1.7
			-	30596.3		-	2139.1			-	1.4
Lakarpite (Zr-Rich)	423	138210.5	+	10435.4	3969.7	+	132.2	423	35.7	+	1.5
			-	18968.5		-	168.6			-	1.2
'Discovery Outcrop'	121	183216.6	+	16583.7	4708.9	+	233.9	121	36.5	+	2.4
			-	10870.0		-	301.2			-	1.8

Biotite		Zr			Hf				Zr/Hf		
Pulaskite	309	6.6	+	10.5	0.00	+	0.0	23	43.5	+	115.1
			-	3.9		-	0.0			-	21.1
Pulaskite (Enclaves)	72	0.0	+	3609.6	0.00	+	283.4	28	28.3	+	2.0
			-	0.0		-	0.0			-	4.6

Rosenbushite		Zr			Hf			Zr/Hf			
Lakarpite (Pulaskite-Core)	162	69611.0	+	3229.3	1639.7	+	678.4	5	68.5	+	0.069
			-	3832.6		-	257.1			-	4.165
Lakarpite (Core)	131	51374.5	+	8107.4	2883.2	+	347.6	13	83.9	+	25.160
			-	11563.6		-	780.3			-	42.560
Pulaskite (Enclaves)	47	74241.3	+	26117.7	2786.5	+	1232.9	17	706.887	+	78.076
			-	31906.2		-	2621.0			-	52.421

Sphene		Zr			Hf			Zr/Hf			
Lakarpite (Pulaskite-Core)	34	358.0	+	53.6	5.2	+	6.9	20	50.0	+	84.6
			-	246.7		-	5.2			-	18.4
Lakarpite (Core)	49	2813.8	+	3379.6	160.3	+	264.3	49	16.1	+	7.3
			-	1502.3		-	110.8			-	1.0
Pulaskite (Enclaves)	157	1254.0	+	184.4	104.6	+	20.4	157	11.8	+	0.9
			-	104.2		-	11.7			-	0.7

Table 6.1: Zr (ppm), Hf (ppm) and Zr/Hf ratios for minerals from Norra Kärr.

		Zr (ppm)			Hf (ppm)			Zr/Hf		
Vaxjo Granite	366.50		+	134.50	9.25	+	3.20	39.17	+	2.01
			-	57.50		-	1.15		-	2.80
Fenite	2015.00		+	2167.50	48.65	+	56.60	42.09	+	2.72
			-	967.50		-	25.15		-	2.63
Contact Grennaite	10400.00		+	2500.00	252.00	+	48.50	40.89	+	2.40
			-	1620.00		-	30.00		-	2.04
Pegmatite-Host Grennaite	14000.00		+	2200.00	295.00	+	53.00	47.24	+	2.25
			-	1700.00		-	40.00		-	2.24
Pegmatites	15500.00		+	2700.00	319.50	+	65.50	48.35	+	3.21
			-	2200.00		-	51.50		-	2.49
Crenulated Grennaites	10900.00		+	1000.00	238.00	+	21.00	44.98	+	2.39
			-	1240.00		-	18.00		-	2.21
Kaxtorpite	2630.00		+	1060.00	60.00	+	24.80	42.87	+	1.94
			-	1070.00		-	22.80		-	1.84
Lakarpite	8610.00		+	5690.00	186.00	+	126.00	45.89	+	2.97
			-	6470.00		-	145.20		-	3.39
Pulaskite	3530.00		+	1150.00	85.90	+	23.85	41.58	+	1.45
			-	1510.00		-	37.95		-	1.25

Table 6.2: Whole rock Zr (ppm), Hf (ppm) and Zr/Hf ratios for the country rock, fenite and each lithology at Norra Kärr.

Figure 6.10: Hf vs Zr for aegirines from Norra Kärr.

Figure 6.11: Hf vs Zr for pectolite from Norra Kärr.

Figure 6.12: Hf vs Zr for amphiboles from Norra Kärr.

Figure 6.13: Hf vs Zr for sphene from Norra Kärr.

Figure 6.14: Hf vs Zr for rosenbushites from Norra Kärr.

Figure 6.15: Hf vs Zr for biotites from Norra Kärr.

Figure 6.16: Hf vs Zr for catapleiites from Norra Kärr.

Figure 6.17: Hf vs Zr for eudialytes from Norra Kärr.

6.4.1 Mineral and Whole Rock Zr/Hf Comparison

An increase in whole rock Zr/Hf has been shown to act as an indicator of increasing fractionation within alkaline complexes of Ilímaussaq (Bailey et al. 2001), Lovozero (Kogarko 2015) and the Kugda Massif (Kogarko 2019). In particular, Kogarko showed that at Lovozero and Kugda the increase is due to the higher K_D of Hf within the minerals and in particular aegirine (which comprises up to 30% of the crystal volume of Lovozero).

Figure 6.18: Average whole rock Hf (ppm) and Zr (ppm) for the lithologies at Norra Kärr.

At Norra Kärr the whole rock Zr/Hf within the Grennaite does not follow such a simple pattern of increasing whole rock Zr/Hf (Table 6.2, Fig. 6.18). The Contact Grennaite has the lowest whole rock Zr/Hf ratio (40.89) increasing to 45.01 within the Pegmatite-Host Grennaite (and increasing further to 48.35 within the pegmatites) before falling to 44.98 in the Crenulated Grennaite. The low Zr/Hf of the Contact Grennaite may be due to: the primary magma composition; loss of Zr and Hf by mineral fractionation; or, due to the loss of Zr and Hf to the fenite. The fenite itself is between 681 to 3816 ppm enriched in Zr (and 14 to 96 ppm enriched in Hf) compared to the country rock (Vaxjö Granite) indicating that these elements must have been derived from the intruded magma. (c.f. the Pegmatite-Host Grennaite which is approximately 3500 ppm richer in Zr, and approximately 41 ppm richer in Hf, than the Contact Grennaite).

Of the minerals present in both intrusions, the aegirine, amphibole and eudialyte from Lovozero (Kogarko 2015) compare favourably in terms of average Zr/Hf ratios for those minerals from the Grennaite and Kaxtorpите Norra Kärr. Lovozero appears to have higher K_d values for Zr and Hf in aegirine than Norra Kärr (Table 6.3) but given the similar ratio between the K_d values for Zr and Hf, Norra Kärr should still follow a similar trend of increasing Zr/Hf enrichment as observed at Lovozero.

Lithology	$K_d(\text{Zr})$		$K_d(\text{Hf})$	
Contact Grennaite	0.03	+ 0.04	0.07	+ 0.09
		- 0.03		- 0.06
Pegmatite-Host Grennaite	0.27	+ 0.30	0.49	+ 0.40
		- 0.26		- 0.39
Pegmatites	0.17	+ 0.34	0.28	+ 0.38
		- 0.12		- 0.01
Crenulated Grennaite	0.07	+ 0.30	0.13	+ 0.44
		- 0.05		- 0.09
Lovozero	0.39	+ -	0.58	+ -
		- -		- -

Table 6.3: K_d for Zr and Hf in Aegirine.

Fig. 6.19 shows the pattern of mineral Zr/Hf in order of mineral fractionation for the Grennaite. While there is some overlap between the minerals, the Zr/Hf ratio of aegirine and catapleiite display Zr/Hf that increases from the Contact Grennaite and then decreases through Pegmatite-Host, then Pegmatites, to Crenulated Grennaite indication preferential uptake of Hf over Zr within the minerals. Eudialyte shows a minor difference with Zr/Hf increasing through the Grennaite with the Pegmatites, however, as eudialyte is the both the last forming Zr-silicate and a major Zr-sink its Zr/Hf pattern may be recording a steady increase in Zr within the remaining fractionated melt.

Figure 6.19: Pattern of mineral Zr/Hf ratios within the Grennaite.

Due to the small size of Norra Kärr, evidence of the magma being at the end of magmatic fractionation series (section 5.3.4 -Chapter 5), and evidence of a restricted fractionation pattern shown by the aegirines (section 4.3.2 -Chapter 4) within the Grennaite; it is therefore reasonable to assume that the Grennaite magma was intruded as a single magmatic phase which subsequently underwent fractionation. Consequently, the major initial process controlling Zr and Hf fractionation until Zr-saturation is due to the pyroxene fractionation which forms approximately 30% of the crystallisation product of the magma.

Fig. 6.20 summarises the pattern of mineral Zr/Hf in order of mineral fractionation for the second phase of intrusion. Compared to the Grennaite the aegirines have slightly higher, and the eudialytes slightly lower, Zr/Hf ratios. In general, all the minerals within the second phase lithologies display similar Zr/Hf ratios

Figure 6.20: Pattern of mineral Zr/Hf ratios within the second phase of intrusion.

6.4.2 Whole Rock Zr/Hf Ratios via Fractionation

To test the influence of mineral crystallisation upon the whole rock Zr/Hf ratio a batch crystallisation model using Eq. 6.1 was calculated:

$$C_L = \frac{C_0}{K_D + F(1 - K_D)}$$

Equation 6.1 (Janoušek et al. 2016)

Where:

C_L = Concentration of an element in the fractionated liquid,

C_0 = Starting concentration of an element in a liquid at each fraction step,

K_D = Derived partition coefficient for an element at each mineral fractionation step,

F = Melt fraction,

The model utilised the whole rock composition as C_0 for step 1 in all calculations. The K_D for the first fractionating mineral was calculated by dividing the concentration of an element within the mineral by the whole rock composition. For the second step the K_D was calculated by dividing the concentration of an element within the mineral by the calculated C_L for step 1. This was repeated for subsequent steps. The F for each step is calculated by subtracting the percent mineral abundance of the modelled mineral for that step from 1, with subsequent steps subtracting from the previously calculated F . The modelling used the average Zr and Hf concentrations presented in Chapter 6, with F calculated using mineral abundance data from Chapter 3.

Figure 6.21: Modelled trends in the evolution of whole rock Zr and Hf within the fractionating Grennaite magmas. Sequence Aeg>Cat>Eud>End.

Figure 6.22: Modelled trends in the evolution of whole rock Zr/Hf ratio within the fractionating Grennaite magmas. Sequence Aeg>Cat>Eud>End.

The model for Zr/Hf (Fig. 6.21, 6.22) show that the initial fractionation of aegirine does increase the Zr/Hf ratio of the remaining magma. Within the Contact Grennaite subsequent catapleiite and eudialyte crystallisation also tends to increase the Zr/Hf ratio. This could therefore allow the remaining magma (from which the Pegmatite-Host and Crenulated Grennaite, as well as the Pegmatites formed) to have increased its Zr/Hf ratio matching the observed pattern in the whole rock data. The initial Zr/Hf ratio of the Pegmatite closely matches that of the Pegmatite-Host

Grennaite suggesting that that two lithologies are closely related. However, with increasing fractionation the Zr/Hf of the Pegmatites increases while the Pegmatite-Host Grennaite decreases, with the difference likely occurring due to the Zr/Hf ratio of the catapleiite affecting the model; catapleiite from both the Pegmatite-Host and Crenulated Grennaite have Zr/Hf ratios >60 with the Pegmatites and Contact Grennaite <45. The decrease in Zr/Hf within the Pegmatite-Host Grennaite caused by catapleiite appears to reduce the ratio and may well be the cause of the lower initial Zr/Hf ratio observed in the Crenulated Grennaite. Any differences may alternatively be due to concentration of fractionated magma from the Pegmatite-Host Grennaite into the Pegmatites themselves.

6.5 Discussion

Despite the issues with the absolute [Ln]-concentrations due to poor ablation of some of the silicate minerals, this data does provide reliable relative [Ln]-patterns and approximate absolute concentrations. Comparison with the whole rock [Ln]-concentrations (section 6.2) shows that eudialyte matches the whole rock pattern. This is partly due to eudialyte being the main [Ln]-bearing mineral in each lithology, but the pattern also suggests that the eudialyte is recoding the [Ln]-pattern of the magma at its time of crystallisation thereby showing the progressive trends in in [Ln]-enrichment and depletion within the first-phase magma as the Grennaites fractionate. These patterns are likely to have been affected by the preceding minerals with catapleiite generally showing a preference for the heavy-[Ln] with a slight enrichment towards La relative to Eu. Aegirine shows flatter patterns than catapleiite but again shows a slight preference for the heavy-[Ln] with an accompanying slight enrichment towards La relative to Eu. This overall trend in heavy-[Ln] depletion can be observed within the eudialyte patterns which show an enrichment in all [Ln] during fractionation between the Contact Grennaite and the Pegmatite-Host Grennaite before a further increase in light-[Ln] and decrease in heavy-[Ln]. Within the pegmatite finer details are observable with the pegmatite aegirine removing's less than expected amounts of Tb-Tm which potentially expresses itself as a later enrichment in Tb-Tm observed within the pegmatite eudialytes. The importance of the sequence of catapleiite-eudialyte crystallisation on the overall magmatic composition will be modelled further in Chapter 7 in light of further Zr-silicate modelling presented in section 7.2.

The calculated K_d values using the data presented in this chapter (section 6.3) compare well to the experimentally derived K_d values of Beard (2018). In particular the Grennaites approximately match the experimental K_d patterns for 'high' aegirine ($Aeg_{>50}$) with higher values for the heavy-[Ln]. However, Beard (2018) used artificial glasses within his K_d experiments with the natural samples used from Tenerife displaying significantly different whole rock [Ln]-concentrations to the unique patterns displayed by Norra Kärr. The unique compositions of the evolving magmas may explain why aegirine from the Kaxtorp and Pualskite-Enclaves also shows higher K_d values for the light-[Ln] similar to mid-aegirine, while the Pulaskite matrix matches the heavy-[Ln] pattern similar to high-aegirine with both indicating that the local magmatic composition may influence the K_d values to some extent. The calculated K_d values may have been further altered by the presence of fluorine within the Grennaite magmas (as inferred from eudialyte compositions in Chapter 4 and the high concentration of fluorine within the Kaxtorp) the presence of which was shown by Beard (2018) to suppress the K_d values within experiments. The presence of fluorine may also explain the lower than

expected K_d values for Zr and Hf within aegirine which would be predicted to be approximately between 1 and 3 – with this study calculating them to be <1 . Beard (2018) proposed that the initial enrichment in heavy-[Ln] within peralkaline magmas was due to the fractionation of moderately sodic pyroxenes deeper down within a fractionating alkaline system, with later highly-sodic pyroxenes (aegirine) leading to a strong enrichment of heavy-[Ln] within the aegirine cumulate phases thereby increasing light-[Ln] within the residual melt. This supports previous evidence to suggest the highly fractionated nature of Norra Kärr (see Chapters 4 and 5) with the intrusion representing this latter stage of aegirine cumulate crystallisation resulting in progressive light-[Ln] enrichment, with the Pulaskite-Enclaves potentially being evidence of the latter stages of this process.

The Zr/Hf ratios presented in the chapter show that the whole rock Zr/Hf ratio within Norra Kärr does appear to vary to some limited degree (Fig. 6.23), by progressively increasing with fractionation from the Contact Grennaite to the Pegmatite-Host Grennaite before decreasing with fractionation towards the Crenulated Grennaite (the pegmatites show higher Zr/Hf values than the Pegmatite-Host Grennaite). This could be due to aegirine displaying higher K_d values for Hf than Zr resulting in a progressive increase in Zr over Hf during fractionation – an effect that has also been observed by Kogarko (2015) within the Lovozero intrusion. The mineral Zr/Hf ratios appear to show that it is possible that aegirine crystallisation is driving the initial increase in Zr/Hf with later Zr-silicate crystallisation driving the decrease of Zr/Hf towards the Crenulated Grennaite, as shown by modelling presented earlier in Chapter 5.

Figure 6.23: Summary of the whole rock and mineral Zr/Hf ratios, along with mineral [Ln]-patterns from Chapter 4. The progressive change in eudialyte [Ln]-concentration from heavy-enriched to light-enriched is shown. The pattern in whole rock Zr/Hf is also shown along with the Zr/Hf ratio of the fenite.

6.6 Conclusions

This chapter has presented new concentration data for Zr, Hf and [Ln] for the minerals at Norra Kärr. This chapter has shown that:

- Aegirine tends to be richer in the heavy-[Ln] overall with only a slight enrichment in the light-[Ln].
- The K_d values calculated for aegirine at Norra Kärr match the same trends in K_d as observed in aegirines produced experimentally by Beard (2018).
- Catapleiite tends to be enriched in the heavy-[Ln].
- The observed trend in whole rock Zr/Hf ratios are able to be modelled through a mixture of aegirine and catapleiite fractionation.
- [Ln]-concentrations in eudialyte match the same pattern observed in the whole rock [Ln]-concentrations, suggesting the eudialyte is recording the final stage composition of the magma.
- Calculated K_d values for Zr and Hf for aegirine suggest that aegirine crystallisation may be able to increase the whole rock Zr/Hf ratio with the Zr-silicate minerals (particularly catapleiite) able to reduce it during further fractionation.
- It is possible that loss of Zr and Hf to the fenite may also have reduced the mineral Zr/Hf values observed within the Contact Grennaite.

Chapter 7

Volatile Modelling

7.1 Introduction

Of all the minerals at Norra Kärr the Zr-silicate phases display the widest range of mineral species and chemical compositions (as shown in Chapters 3, 4 and 6) with eudialyte being the main ore bearing phase. Throughout Norra Kärr the Zr-silicates lie in the middle of the standard petrological sequence of 'aegirine – Zr-Silicate – feldspar' crystallisation (Chapter 3), with subtle differences in the mineral species, petrology, abundance and potentially being linked to the degree of ore-mineralisation found through the intrusion. Modelling of Zr-silicates by Andersen et al. (2010) showed that eudialyte, catapleiite and other phases are affected by the activity of OH^- , HF^- and alkalinity of a magma, allowing a relative comparison of evolving volatile conditions within a melt to be understood from the order of phase crystallisation. This chapter will focus on modelling the relationships between the main Zr-silicate phases in Norra Kärr using the same method as Andersen et al. (2010). To constrain the activity of HF within the Lakarpite/Pulaskite a model using biotite developed by Finch et al. (1995) will be applied to biotites from Norra Kärr and other alkaline intrusions. A tentative model of Wt% abundance for Cl, F and $\text{OH}/\text{H}_2\text{O}$ based upon a model by Stock et al. (2016) within each lithology at Norra Kärr will also be presented.

7.2 Zirconium Silicate Phase Modelling

A method of modelling the evolution of mineral phases within alkaline intrusions using chemographic grid was first developed by Andersen et al. (2010) for the activities of H_2O , HF and 'Nds' within the alkaline magmas. This method was later used by Borst et al. (2016) for modelling the activities of H_2O , CaO and 'Nds' within the Ílímaussaq intrusion, and by Andersen et al. (2017, 2018) for modelling activities of H_2O , fO_2 and 'Nds' within the white and green foyites of Pilanesberg. The model presented here was developed with help from Prof. Tom Andersen (University of Oslo) using an Excel spreadsheet developed by Prof. Andersen with the resulting 3D equations plotted using AutoCAD. Textural relationships between the Zr-silicate phases have already been presented earlier in Chapter 3 from optical microscopy, and additional observations in Chapter 4 from SEM images; these are summarised in Table 7.1. Fluorite is included to indicate when the fluorite saturation level is reached. The mineral compositions used in this modelling were presented in Chapter 4.

These models are unique to the intrusions that they describe, hence the model shown in Fig. 7.1 is specific to Norra Kärr in that the mineral assemblages shown are the ones produced by the composition of the Norra Kärr magmas at approximately 5 kbar pressure (as derived from the feldspar and nepheline plots in Chapter 4). These models are able to show the broader trends within alkaline intrusions as they describe the compositional relationships between the minerals independent of pressure and temperature. However, as the models show all phases present independent of their crystallisation temperature they should not be interpreted separately from any petrological evidence.

	Lithology	Primary	Alteration
1 st Phase	Contact Grennaite	Catapleiite, Eudialyte	
	Peg-Host Grennaite	Catapleiite, Eudialyte	
	Pegmatite Grennaite	Catapleiite, Eudialyte	Eudialyte → Catapleiite
	Crenulated Grennaite	Catapleiite, Eudialyte	Eudialyte → Catapleiite
2 nd Phase	Lakarpite -Pulaskite	Fluorite	
	Lakarpite -Core	Rosenbushite, Fluorite	
	Lakarpite -Core-Zr	Eudialyte	
	Lakarpite -Zr-rich	Eudialyte, Catapleiite	Eudialyte → Catapleiite
	Pulaskite Matrix	Rosenbushite, Fluorite	
	Pulaskite Enclaves	Rosenbushite, Fluorite	

Table 7.1: Summary of the primary and secondary Zr-silicate assemblages within each lithology at Norra Kärr.

		NaO _{0.5}	KO _{0.5}	CaO	FeO	FeO _{1.5}	LnO _{1.5}	ZrO ₂	TiO ₂	NbO _{2.5}	AlO _{1.5}	SiO ₂	HO _{0.5}	FO _{-0.5}	ClO _{-0.5}
<i>Major Minerals</i>															
Aegirine	Aeg	1.0	0.0	0.0	0.0	1.0	0.0	0.0	0.0	0.0	0.0	2.0	0.0	0.0	0.0
Albite	Ab	1.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.0	3.0	0.0	0.0	0.0
Microcline	Kf	0.0	1.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.0	3.0	0.0	0.0	0.0
Nepheline	Ne	3.0	1.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	4.0	4.0	0.0	0.0	0.0
<i>Zr-Silicates</i>															
Zircon	Zrc	0.0	0.0	0.0	0.0	0.0	0.0	1.0	0.0	0.0	0.0	1.0	0.0	0.0	0.0
Zr-Aegirine	ZrAeg	1.0	0.0	0.0	0.0	0.5	0.0	0.5	0.0	0.0	0.0	2.0	0.0	0.0	0.0
Catapleiite	Cat	1.6	0.0	0.2	0.0	0.0	0.0	1.0	0.0	0.0	0.0	2.9	4.0	0.0	0.0
Eudialyte	Eud	13.9	0.2	4.2	1.2	0.0	2.8	3.2	0.1	0.2	0.1	25.4	1.3	0.3	0.4
Rosenbushite	Ros	1.0	0.0	2.0	0.0	0.0	0.0	0.3	0.6	0.0	0.0	2.0	1.8	0.2	0.0
<i>Fluorite</i>															
Fluorite	Flu	0.00	0.00	1.00	0.00	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.00	0.00
<i>Components in Melt</i>															
Na ₂ Si ₂ O ₅	Nds	2.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	2.0	0.0	0.0	0.0
	H ₂ O	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	2.0	0.0	0.0
	HF	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.0	1.0	0.0
	HCl	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.0	0.0	1.0
<i>Externally Buffered Components</i>															
	CaO	0.0	0.0	1.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	TiO ₂	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.0	0.0	0.0	0.0	0.0	0.0	0.0
	Nb ₂ O ₅	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	2.0	0.0	0.0	0.0	0.0	0.0
	Ln ₂ O ₃	0.0	0.0	0.0	0.0	0.0	2.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	O ₂	0.0	0.0	0.0	-4.0	4.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

Table 7.2: Composition (in moles per formula unit) of phases and species used in the petrogenetic modelling. Note that the HO_{0.5} values are derived from the calculated values OH⁻ which have not been independently determined.

Andersen et al. (2010) proposed that the relationships between the main rock forming minerals within an alkaline rock are related to the magma by a series of mineral-melt reactions influenced by temperature, pressure, oxygen fugacity, activities of volatile species (e.g. water and halogens), and the peralkalinity of the melt. A full description of the method used here is given by Andersen et al. (2010) and is partly summarised below.

It assumes that crystallisation occurs at constant pressure and temperature within the model in order to assess the relative variation in a_{Nds} (where Nds = $\text{Na}_2\text{Si}_2\text{O}_5$, Andersen et Sørensen 2005), a_{HF} and $a_{\text{H}_2\text{O}}$. These three variables define a 3D chemical potential or log activity space in which a petrogenetic grid can be constructed from observed mineral assemblages and compositions using the Schreinemaker's method (Zen 1966, White et al., 2008). The model uses: $\text{NaO}_{0.5}$, $\text{KO}_{0.5}$, CaO , FeO , $\text{FeO}_{1.5}$, $\text{LnO}_{1.5} + \text{YO}_{1.5}$, ZrO_2 , TiO_2 , $\text{NbO}_{2.5}$, $\text{AlO}_{1.5}$, SiO_2 , $\text{HO}_{0.5}$, $\text{FO}_{0.5}$, $\text{ClO}_{0.5}$. Stoichiometric endmember compositions for microcline, albite and nepheline were used in the model calculations with the compositions of other phases given in Table 7.2. Chlorine is only of interest for reactions involving eudialyte and is omitted from the grid as the other phases can be modelled between OH-F endmembers. In general, the activity of Cl will increase the stability of eudialyte at the expense of rosenbushite; the maximum attainable a_{Cl} of a nepheline syenite magma being demonstrated by the presence of sodalite – a mineral absent in Norra Kärr. Instead, the presence of fluorite indicates the highest possible activity of fluorine (or HF) suggesting this volatile is more important. This is also supported by the predominantly F-rich X-site compositions of volatile bearing minerals (see Chapter 4). Andersen et al. (2010) note that the fluorite saturation reaction is independent of which zirconium silicate minerals are stable and is governed by a combination of $\text{NaO}_{0.5}$, $\text{KO}_{0.5}$, CaO , FeO , $\text{AlO}_{1.5}$, SiO_2 , $\text{HO}_{0.5}$, $\text{FO}_{0.5}$. The equation of a plane in an orthogonal, 3D coordinate system with log a_{Nds} , log $a_{\text{H}_2\text{O}}$ and log a_{HF} as axes is described using:

$$n_{\text{Nds}} \log a_{\text{Nds}} + n_{\text{H}_2\text{O}} \log a_{\text{H}_2\text{O}} + n_{\text{HF}} \log a_{\text{HF}} = \text{constant}$$

Equation 7.1

Although the right-hand side of the equation (and hence the absolute coordinates of the plane) remains unconstrained, its orientation in activity space is uniquely given by the ratios of the stoichiometric coefficients; for example, the slope of the intersection of a plane with a section parallel with the log a_{Nds} and log a_{HF} axes is given by $-n_{\text{Nds}}/n_{\text{HF}}$, and similar for the slopes in the projections defined by the two other combinations of orthogonal axes. Andersen et al. (2010) stress that any modelling using this method is semiquantitative. Therefore, the 3D petrogenetic grid shown in Fig 7.1 is internally consistent and does give a true representation of the relative slopes of the divariant planes and univariant lines in 3D log activity space, along with the relative positions of the stability volumes of the single Zr-silicate minerals. However, no information is provided on the absolute values of component activities, and the relative sizes of the divariant fields and the stability volumes of single phases are arbitrary. Any quantitative calibration of petrogenetic grids produced by this method would require experimental data on critical mineral assemblages, and/or thermodynamic data on the zirconium silicate minerals and on components in the volatile-bearing silicate melt, none of which is available (Andersen et al. 2010). However, modelling of a_{HF} using a method developed by Finch et al. (1995) using biotite compositions will be presented in section 7.3 along with modelling of the evolution of the whole rock volatile contents through time in section 7.4, in order to give an indication relative volatile evolution in relation to the petrogenetic grid produced here (Fig. 7.1).

Figure 7.1: 3D view of the petrogenetic grid for the Zr-Silicate minerals at Norra Kärr in $\log a_{\text{Nds}} - \log a_{\text{H}_2\text{O}} - \log a_{\text{HF}}$ space showing the phase stability fields at, and immediately below, the fluorite saturation surface. The equations describing the boundaries for each volume are given in Table 7.3.

Zircon-Volume

Zrc-AegZr 0.50 Zrc + 0.50 Aeg + 0.25 Nds = 1.00 ZrAeg

Zrc-Cat 1.10 Zrc + 0.08 Ab + 0.03 Kf + 0.20 CaO + 2.00 H₂O + 0.85 Nds = 1.00 Cat + 0.03 Ne

Zr-Aegirine Volume

AegZr-Zrc 2.00 ZrAeg = 1.00 Zrc + 1 Aeg + 0.5 Nds

AegZr-Eud 6.40 ZrAeg + 2.53 Ab + 1.18 Kf + 4.10 CaO + 0.10 TiO₂ + 0.10 Nb₂O₅ + 1.30 Ln₂O₃
+ 0.45 H₂O + 4.80 Nds + 0.30 HF + 0.40 HCl = 1.00 Eud + 0.88 Ne + 2.2 Aeg + 0.25 O₂

AegZr-Cat 2.20 ZrAeg + 0.08 Ab + 0.03 Kf + 0.20 CaO + 2.00 H₂O + 0.30 Nds = 1.00 Cat + 0.03 Ne
+ 1.1 Aeg

Catapleiite-Volume

Cat-Zrc 0.91 Cat + 0.02 Ne = 1.00 Zrc + 0.07 Ab + 0.02 Kf + 0.18 CaO + 1.82 H₂O + 0.77 Nds

Cat-AegZr 0.45 Cat + 0.01 Ne + 0.50 Aeg = 1.00 ZrAeg + 0.03 Ab + 0.01 Kf + 0.09 CaO + 0.91 H₂O
+ 0.14 Nds

Cat-Eud 2.91 Cat + 2.31 Ab + 1.10 Kf + 1.00 Aeg + 3.52 CaO + 0.10 TiO₂ + 0.10 Nb₂O₅ + 1.30 Ln₂O₃
+ 3.93 Nds + 0.30 HF + 0.40 HCl = 1.00 Eud + 0.8 Ne + 5.37 H₂O + 0.25 O₂

Cat-Ros 0.27 Cat + 0.24 Ab + 0.08 Kf + 2.05 CaO + 0.60 TiO₂ + 0.27 Nds + 1.60 HF = 1.00 Ros
+ 0.08 Ne + 1.25 H₂O

Eudialyte Volume

Eud-Cat 0.34 Eud + 0.28 Ne + 1.85 H₂O + 0.09 O₂ = 1.00 Cat + 0.79 Ab + 0.38 Kf + 0.34 Aeg
+ 1.21 CaO + 0.03 TiO₂ + 0.03 Nb₂O₅ + 0.45 Ln₂O₃ + 1.35 Nds + 0.1 HF + 0.14 HCl

Eud-Ros 0.09 Eud + 0.03 Ab + 1.72 CaO + 0.59 TiO₂ + 1.57 HF + 0.02 O₂ = 1.00 Ros + 0.01 Ne
+ 0.02 Kf + 0.09 Aeg + 0.01 Nb₂O₅ + 0.12 Ln₂O₃ + 0.74 H₂O + 0.1 Nds + 0.04 HCl

Eud-ZrAeg 0.16 Eud + 0.14 Ne + 0.34 Aeg + 0.04 O₂ = 1.00 ZrAeg + 0.39 Ab + 0.18 Kf + 0.64 CaO
+ 0.02 TiO₂ + 0.02 Nb₂O₅ + 0.2 Ln₂O₃ + 0.07 H₂O + 0.75 Nds + 0.05 HF + 0.06 HCl

Rosenbushite Volume

Ros-Eud 10.67 Ros + 0.06 Ne + 0.24 Kf + 1.00 Aeg + 0.10 Nb₂O₅ + 1.30 Ln₂O₃ + 7.92 H₂O
+ 1.07 Nds + 0.40 HCl = 1.00 Eud + 0.27 Ab + 18.3 CaO + 6.3 TiO₂ + 16.77 HF + 0.25 O₂

Ros-Cat 3.67 Ros + 0.30 Ne + 4.57 H₂O = 1.00 Cat + 0.89 Ab + 0.3 Kf + 7.5 CaO + 2.2 TiO₂
+ 0.98 Nds + 5.87 HF

*Table 7.3: Divariant mineral reactions between zr-silicate minerals, major minerals and melt.
Compositions of the minerals and their abbreviations are given in Table 7.2.*

7.2.1 Petrogenetic Modelling Summary

The petrogenetic grid shown in Fig. 7.1 Can be used to understand the relative changes in the volatile evolution of a_{H_2O} and a_{HF} activities, the two major volatile species identified within the X-sites of the minerals analysed in Chapter 4, within the magmas at Norra Kärr. Chapter 4 has shown that each of the different species of Zr-silicates contain differing degrees of overall lanthanoid concentrations as well as patterns in chondrite normalised [Ln]-spider-plots which may in turn affect the pattern of [Ln]-ore concentrations with magmatic evolution.

Grennaites

The Grennaites all display a pattern of catapleiite followed by eudialyte crystallisation. This indicates that the magma had a high initial a_{H_2O} which must have declined during magmatic evolution in order to allow later eudialyte crystallisation. This decrease in a_{H_2O} may have been caused by loss of H_2O to the fenite or due to extensive catapleiite crystallisation within the Grennaites. In terms of the [Ln] budget of the magma, the initial dominance of a_{H_2O} within the melt resulted in the crystallisation of the Catapleiite which preferentially removes heavy-[Ln] (Chapter 4) from the magma. This may then have increased the concentration of light-[Ln] within the remaining melt forming the observed pattern of light-[Ln] enrichment over heavy-[Ln] within the Grennaites. Later alteration of eudialyte to catapleiite, particularly within the pegmatites and Crenulated Grennaite, indicates a return to higher a_{H_2O} possibly due to extensive nepheline and feldspar crystallisation.

Lakarpite

The different phases within each zone of the Lakarpite indicates a complex evolutionary history for volatiles within this lithology. The fluorite bearing Pulaskite-type Lakarpite indicates F-saturation in the core of the lithology. The Core-type Lakarpite starts less saturated in F leading to initial Rosenbushite crystallisation followed by increasing a_{HF} leading to fluorite crystallisation. The outer Lakarpite zones initially crystallise eudialyte indicating still lower initial a_{HF} near the contact of the Lakarpite with the Pegmatite-Host Grennaite. For the outermost Lakarpite zone the crystallisation of eudialyte followed by catapleiite indicates not only a low a_{HF} but increasing a_{H_2O} , which is also accompanied by minor alteration of eudialyte to catapleiite.

Pulaskite

Both the matrix and enclaves of the Pulaskite crystallise rosenbushite before fluorite indicating initially F-undersaturated conditions with increasing a_{HF} through time. This is also demonstrated by the rim of rosenbushite around the edge of the enclaves suggesting a 'contact zone' of rosenbushite forming due to potential 'degassing' of the increasingly F-rich enclaves.

7.3 Effect of Zr-silicate crystallisation order on [Ln] Concentrations

The order of Zr-silicate crystallisation in Norra Kärr within the ore-bearing Grennaite is catapleiite followed by eudialyte as shown in Chapters 3, 4 and 5. Modelling in this chapter has shown that this is due to higher initial $a_{\text{H}_2\text{O}}$ within the Grennaite magma. However, other studies have shown that a more common pattern observed in alkaline intrusions is eudialyte followed by catapleiite. Both patterns were modelled in order to observe the effect of the order of Zr-silicate crystallisation on the concentration or depletion of [Ln]. To test the influence of the order of Zr-silicate crystallisation upon the whole rock La/Lu ratio a batch crystallisation model was calculated using Eq. 7.1

$$C_L = \frac{C_0}{K_D + F(1 - K_D)}$$

Equation 7.1 (Janoušek et al. 2016)

Where:

C_L = Concentration of an element in the fractionated liquid,

C_0 = Starting concentration of an element in a liquid at each fraction step,

K_D = Derived partition coefficient for an element at each mineral fractionation step,

F = Melt fraction,

The model utilised the whole rock composition as C_0 for step 1 in all calculations. The K_D for the first fractionating mineral was calculated by dividing the concentration of an element within the mineral by the whole rock composition. For the second step the K_D was calculated by dividing the concentration of an element within the mineral by the calculated C_L for step 1. This was repeated for subsequent steps. The F for each step is calculated by subtracting the percent mineral abundance of the modelled mineral for that step from 1, with subsequent steps subtracting from the previously calculated F . The modelling used the average element concentration data presented in Chapter 4, with F calculated using mineral abundance data from Chapter 3.

The model for Norra Kärr (Fig. 7.2) involved aegirine crystallisation followed by catapleiite then eudialyte with the Zr-silicates representing a trend of decreasing $a_{\text{H}_2\text{O}}$ within the Grennaite magma. This model demonstrates that in all cases aegirine crystallisation results in an increase in both La and Lu, while eudialyte crystallisation results in a decrease in La and Lu. Catapleiite crystallisation, however, leads to a decrease in Lu and an increase in La. Consequently, catapleiite is the factor in the enrichment of subsequent magmas in the light-[Ln] over the heavy-[Ln]. This potentially explains the observed pattern in light-[Ln] enrichment over heavy-[Ln] within the whole-rock and eudialyte data.

When the Zr-silicate pattern is reversed (representing a trend of increasing $a_{\text{H}_2\text{O}}$ within an alkaline magma) a pattern of overall depletion of [Ln] is observed (Fig. 7.3). While aegirine crystallisation leads to an initial increase in La and Lu within the magma, the onset of eudialyte crystallisation reduces both the La and Lu concentrations within the remaining magma with the subsequent catapleiite crystallisation unable to reverse the trend.

These models support the work of Beard (2018) in showing that aegirine will increase the overall [Ln] content of a magma. Additionally, they also show that the order of Zr-silicate crystallisation within the magmatic fractionation sequence (as dictated by the trend in volatile evolution within a magma) has an influence on the lanthanoid fractionation pattern within an alkaline magma.

Figure 7.2: Fractionation model for Aegirine-Catapleiite-Eudialyte crystallisation within a magma of decreasing a_{H_2O} (Norra Kärr type). Note the enrichment of light-[Ln] over heavy-[Ln] due to catapleiite crystallisation.

Figure 7.3: Fractionation model for Aegirine-Eudialyte-Catapleiite crystallisation within a magma of increasing a_{H_2O} . Note the overall depletion of [Ln] within the magmas due to eudialyte crystallisation.

7.4 Biotite Modelling

Fluorine is a common component within alkaline magmas, with the substitution of OH⁻ for F⁻ commonly occurring within biotite. This substitution can give an approximate estimate of the log(*f*_{H₂O}/*f*_{HF}) conditions of a magma at the time of biotite formation, though McCreath (2009) notes that due to the possibility of low temperature substitution the volatile contents of biotites may not necessarily be preserved.

Halogen-exchange within biotite is affected by the activity of volatiles within a melt of a given temperature, the site occupation of cations within octahedral sites and any later alteration processes. A further outline of the halogen-hydroxyl exchange in biotite is given by Munoz et Ludington (1974). All biotite samples presented here are unaltered; however, the compositions of the natural Norra Kärr biotites do not allow for an absolute determination of fugacity. In particular the experimentally derived halogen-hydroxyl exchange constants given below are for pure OH-F substitution with biotite; in the case of Norra Kärr the biotites show calculated Fe³⁺ contents up to 0.8 a.p.f.u. resulting in the oxidizing coupled substitution Fe²⁺ + OH⁻ ⇌ Fe³⁺ + O²⁻ (Finch et al. 1995) which allows the introduction of oxide ions (calculated O²⁻ contents up to 0.93 a.p.f.u.) into the X-site. The OH content of the biotites was also not independently determined and has been calculated via a charge balance method as part of the mineral formulae calculation. As such the method described below does not provide absolute estimates of fugacity but it is useful indicator of the relative fugacity's between samples (McCreath (2009) in this case the Lakarpite, and the Pulaskite and its enclaves, which are all inferred to have equilibrated over similar temperatures.

The experimentally derived halogen-hydroxyl exchange equilibrium constants for biotites (Table 7.4, Munoz et Ludington 1974) allow the calculation of (H₂O)/*f*(HF) for biotites that lie along Mg-Fe and OH-F compositional trends using the methods defined by Gunow et al. (1980).

Composition	Log K
Phlogopite	2100/T + 1.523
Annite	2100/T + 0.416
Siderophyllite	2100/T + 0.200

Table 7.4: Exchange equilibrium constants for halogen-hydroxyl exchange in biotites (Equilibrium constants defined by Munoz and Ludington (1974; 1977) for fluid pressures of 1 or 2 kbar over a temperature range of 673-1000 K).

Assuming ideal mixing this can be written for the phlogopite end member as Eq. 7.2:

$$\log K = \frac{2100}{T} + 1.523X_{Mg} + 0.416X_{Fe} = \log \left[\frac{X_F}{X_{OH}} \right]^{biotite} + \log \left[\frac{f_{H_2O}}{f_{HF}} \right]^{fluid}$$

Equation 7.2

Where:

X_{Mg} = Mg/(Mg+Fe) in the octahedral site

X_{Fe} = Fe/(Fe+Mg) in the octahedral site

This can then be rearranged to calculate the fugacity ratio in equilibrium with biotite analyses (Munoz 1984, McCreath 2009). This equation (Eq. 7.3) was used to model the results presented in section 7.3.2 at the inferred crystallisation temperature of 700°C.

$$\log \left[\frac{f_{H_2O}}{f_{HF}} \right]^{fluid} = \frac{2100}{T} + 1.523X_{Mg} + 0.416X_{Fe} - \log \left[\frac{X_F}{X_{OH}} \right]^{biotite}$$

Equation 7.3

7.4.1 F-Fe avoidance within Norra Kärr Biotites

Similar to biotites from other alkaline intrusions the F-content decreases with increasing Fe/(Fe+Mg) following the general rule of F-Fe avoidance (Rosenberg et Foit 1977) within biotites. Following the approach of Finch et al. (1995) a ‘maximum fluorine line’ can be fitted to a biotite dataset with the slope of the line indicating the relative F-content of the surrounding magma at the time of crystallisation; steeper slopes indicate both higher inferred F-contents and higher degrees of ‘Short Range Order’ within the octahedral layer of the biotites (McCreath 2009). Mason (1992) stated that if Fe-F avoidance controls F-partitioning within biotites, ordered micas will accommodate more F than disordered ones at the same F fugacity. This leads to ‘Mason Maximum Fluorine Line’ which shows the amount of F-substitution in biotite under conditions of complete Fe-OH order and Mg-F order.

Fig. 7.4 shows that the Lakarpite lies approximately along the ‘Mason Maximum Fluorine Line’ and therefore appears to follow the theoretical limits of F-substitutions and a high degree of Fe-OH and Mg-F order. The Pulaskite and its enclaves cluster together at a lower Wt% F on the trends for South Qôroq and Klokken intrusions. Fig. 7.5 shows additional biotite datasets used as compositional comparisons in Chapter 4. Again, the biotite from the Pulaskite displays similar F-contents to the White Foyite of Pilanesberg as well as some similarity with Mont Saint Hilaire.

Figure 7.4: Plot of $\text{Fe}/(\text{Fe}+\text{Mg})$ vs Wt% F for biotite analyses from Norra Kärr and the 'maximum fluorine lines' for Gardar intrusions after Finch et al. (1995).

Figure 7.5: Plot of $\text{Fe}/(\text{Fe}+\text{Mg})$ vs Wt% F for biotite analyses from the Augite-Syenite of Ilimaussaq, the White Foyite of Pilanesberg and the Syenite of Mont Saint Hilare, along with the 'maximum fluorine lines' for Gardar intrusions after Finch et al. (1995). Norra Kärr is comparable with both Pilanesberg and Mont Saint Hilare, while the Augite Syenite of Ilimaussaq shows far higher F-contents (similar to Igdlersfigsalik) than the other intrusions.

7.4.2 Biotite $\log(f_{\text{H}_2\text{O}}/f_{\text{HF}})$ Equilibrium Conditions at Norra Kärr

Using equation 7.3 lines of equilibrium for biotites at a given temperature value for different $\log(f_{\text{H}_2\text{O}}/f_{\text{HF}})$ values can be plotted. The limitations of this ‘Munoz’ model have previously been highlighted by Gunow et al. (1980) and Finch et al. (1995) including issues with octahedral site ordering, the degree of mixing of F⁻ and OH⁻ within the crystal structure, and interaction with separate supercritical-fluid phases. However, in the case of the Lakarpite, the biotites lie close to the ideal ‘Mason maximum fluorine line’ indicating good ordering and there is no evidence for the crystals being altered by later supercritical-fluids. Furthermore, analyses presented in Chapter 4 show Cl is absent within the Norra Kärr biotites hence there is no interference from the Cl-OH exchange system, and the biotites also crystallised within a restricted volume and did not have time to show fractionation trends (Chapter 4).

Fig. 7.6 shows the results of this modelling for the Norra Kärr biotites with the temperature set to 700°C based upon the T- $f\text{O}_2$ model (Fig. 4.77) presented in Chapter 4. This shows that the biotites from the Pulaskite-type Lakarpite and the Pulaskite enclaves lie along the same equilibrium line of 3.65 $\log(f_{\text{H}_2\text{O}}/f_{\text{HF}})$. The biotites from the Pulaskite matrix deviate from this approaching 3.9 $\log(f_{\text{H}_2\text{O}}/f_{\text{HF}})$. This suggests that the amount of H₂O within the melt is higher than within the enclaves. Alternatively, these biotites are equilibrated to a crystallisation temperature different to the other lithologies.

Figure 7.6: Plot of $\text{Fe}/(\text{Fe}+\text{Mg})$ versus Wt.% F for biotites from Norra Kärr. Continuous curves illustrate the theoretical composition of micas in equilibrium with a stated $\log(f_{\text{H}_2\text{O}}/f_{\text{HF}})$ for a temperature of 700°C.

7.5 Petrological Modelling

The previously presented modelling method of Andersen et al. (2010) does not provide any qualitative calibration of petrographic grids produced, nor does the biotite modelling method used by McCreath (2009) provide absolute estimates of volatile fugacity. However, the compositions of the lithologies may be able offer a minimum constraint upon the amount of volatiles required to produce the conditions within the previous models. Stock et al. (2016) presented a MELTS model used to calculate the point at which volatile saturation was achieved within the Camp Flegri volcanic system; however, MELTS does not work for highly alkaline systems nor are properties of the Zr-silicates suitably constrained for these models. However, a qualitative model using the same parameters (% crystallisation, temperature, % volatile content) as Stock et al. (2016) can be produced using the results and models presented in Chapters 3 and 4.

Here the mineral abundance within the samples presented in Chapter 3 are used to represent the degree of progressive crystallisation of melt and order of mineral crystallisation. The approximate temperature of crystallisation for each phase is given by the T-fO₂ model (Fig. 4.77 in Chapter 4) with the percentage volatile content of the remaining melt calculated using the mineral compositions presented in Chapter 4. For each model the percentage volatile content for each mineral was calculated by dividing the Mr of each volatile phase by the Mr of the host mineral. This was then multiplied by the mineral abundance, with the sum of all of the volatile contents taken as the minimum percentage volatile content of the lithology. Each step of the model involved removing the volume of a mineral and its volatile content (in order of crystallisation) from the total volume and volatile content of the model with the remaining volatile content divided by the remaining volume. The assumptions used in this modelling are that these models represent a closed system with all the volatiles contained within mineral phases. In reality, the percentage of volatiles contained within each lithology may well be greater than shown in the models, but they can provide an internally consistent set of results that can be used to compare the minimum volatile content of each lithology.

7.5.1 Grennaïtes and Pegmatites

The models show that the most significant volatile within the Grennaïtes and the Pegmatites is OH⁻ (Figs. 7.7 – 7.10). With fractionation through the Grennaïtes the OH⁻ content appears to increase. This is due to the high OH⁻ content of catapleiite with the overall OH⁻ content of these lithologies dependent upon the abundance of catapleiite. Aegirine crystallisation plays a relatively unimportant role in concentrating OH⁻ in comparison to the onset of feldspar and nepheline crystallisation. The OH⁻ of the Grennaïtes is significantly decreased during catapleiite crystallisation (between 40% to 60% at the onset of catapleiite crystallisation), with eudialyte removing a further 1.2wt% of OH⁻ from the remaining melt. This supports the models presented in 7.2 where, at the onset of Zr-saturation, the aH₂O activity has been driven high enough by feldspar and nepheline crystallisation to result in the preferential formation of catapleiite over eudialyte. The presence of eudialyte being altered to catapleiite within the pegmatites and Crenulated Grennaïte indicates that there are still some residual volatiles present as the magma cooled post-eudialyte crystallisation.

Figure 7.7: Petrological model for the minimum volatiles present within the Contact Grennaite.

Figure 7.8: Petrological model for the minimum volatiles present within the Peg-Host Grennaite.

Figure 7.9: Petrological model for the minimum volatiles present within the Crenulated Grennaite.

Figure 7.10: Petrological model for the minimum volatiles present within the Pegmatites.

The presence of Pectolite within the Crenulated Grennaite is likely due to an elevated OH^- content forcing a hydrous mineral to form before Zr-saturation in aegirine is achieved. Once Zr-saturation is achieved then the system would switch to catapleiite crystallisation in order to reduce the aH_2O .

The pegmatites (Fig. 7.10) display a higher OH^- content than the Pegmatite-Host Grennaite, however, the drop in OH^- by only 30% during catapleiite crystallisation suggests that the pegmatites were consistently closer to the catapleiite-eudialyte tie-line than the Grennaites were during their evolution.

7.5.2 Kaxtorpite

In contrast to the Grennaites the Kaxtorpite (Fig. 7.11) displays lower OH^- contents but a far higher F⁻ content. This is due to the presence of F-rich amphibole which is the sole major volatile bearing phase within the Kaxtorpite. As previously discussed in Chapters 4 and 5 this may indicate the migration of fluorine towards the top of the Grennaites during the first phase of intrusion is a similar manner to the amphibole cap observed at Yastribets (Kogarko et al. 1995 – see Chapter 8 for cross-section comparison). As the amphibole represents the entire F-content of the lithology it appears that fluorite saturation was never reached. Pectolite forms after the amphibole due to the increase in OH^- content, however as there isn't enough Zr for catapleiite formation it is not replaced as in the Grennaites and persists until the latter stage of crystallisation.

Figure 7.11: Petrological model for the minimum volatiles present within the Kaxtorpite.

7.5.3 Lakaprite

The model presented in Fig 7.1 indicates that the Lakaprite is predominantly dominated by a trend in F-activity. This can be seen as a steady decrease in F-content as shown within Figs. 7.12- 7.15.

The most central zone of the Lakaprite (the Pulaskite-type Lakaprite) displays a higher F-content than OH-content, leading to fluorite saturation once the OH/F ratio has reached 0. The Core-type Lakaprite starts with a higher OH content than then Pulaskite-type with the first forming Zr-silicate being rosenbushite. The rosenbushite field within the petrogenetic grid (Fig. 7.1) shows that this lithology is below fluorite saturation but above the field for eudialyte crystallising, though the temperature is possibly still too high for eudialyte crystallisation or saturation within the melt. Rosebushite is not abundant enough to significantly effect the OH⁻ abundance given the continued crystallisation of anhydrous phases (aegirine and feldspars), however amphibole is and reduces the remaining OH⁻ budget of the melt along with increasing the F⁻ content and leading to F-saturation in the latter stages of crystallisation.

The outer zones of the Lakaprite also show initial OH⁻ contents higher than the F-contents. Within the Zr-rich core Lakaprite this leads to the first forming Zr-silicate phase being eudialyte. The outermost zone of the Lakaprite (the Zr-rich Lakaprite) shows increasing OH/F ratios during crystallisation until the onset of eudialyte crystallisation which consumes F and Cl leading to catapleiite crystallisation.

All models support the patterns indicated for the Lakaprite by the petrogenetic grid of a decrease in F-activity from the core of the Lakaprite outwards and the start of a trend towards an OH-dominated trend.

Figure 7.12: Petrological model for the minimum volatiles present within the Pulaskite-type Lakaprite.

Figure 7.13: Petrological model for the minimum volatiles present within the Core-type Lakarpite.

Figure 7.14: Petrological model for the minimum volatiles present within the Zr-Core-type Lakarpite.

Figure 7.15: Petrological model for the minimum volatiles present within the Zr-Lakapite.

7.5.4 Pulaskite

The models presented in Figs 7.16 and 7.17 show that the Pulaskite, much like the Lakarpite, is predominantly influenced by a fluorine trend. The models also show the enclaves appear to be more F-rich than the matrix. The slightly higher initial OH/F ratio in the matrix of 0.42 (vs 0.20 in the enclaves) supports the pattern shown by the biotite models which indicate that the biotites within the Pulaskite matrix indicate an environment slightly higher in OH-than is shown by the enclaves.

The enclaves began crystallising rosenbushite at an OH/F ratio of 0.33 and the matrix at 0.19, similar to the Pulaskite-type Lakarpite (OH/F = 0.37). Only when fluorine is the only volatile present does fluorite saturation appear to be reached.

Figure 7.16: Petrological model for the minimum volatiles present within the Pulaskite enclaves.

Figure 7.17: Petrological model for the minimum volatiles present within the Pulaskite matrix.

7.6 Discussion

The models presented in this chapter have used the petrological sequence and mineral chemistry presented in earlier chapters to show that the order of Zr-silicate crystallisation is related to the volatile content of the magma with attempts made to relate this to $\log(f\text{H}_2\text{O}/f\text{HF})$ ratios and approximate minimum OH/F ratios for each lithology. The only other published petrogenetic grid comparable to the mineralogy of Norra Kärr is Anderson et al. (2010) and Borst et al. (2016) which showed the same relationships between eudialyte and catapleiite (an $a_{\text{H}_2\text{O}}$ trend) and eudialyte-rosenbushite-fluorite (an a_{HF} trend). This order of Zr-silicate crystallisation also affects the concentration of [Ln] within the melt and may provide a model for the enrichment and fractionation of [Ln] within the ore domains at Norra Kärr.

First Intrusive Phase

The petrogenetic modelling shows that the Grennaite is dominated by a OH^- trend with catapleiite forming first, thereby reducing the initial OH^- content leading to later eudialyte crystallisation. The petrological models support this with OH^- contents being far higher than the other volatile species at the onset of catapleiite crystallisation, with eudialyte crystallising only the OH/F ratio has significantly dropped (usually <25). As shown in Chapter 4 eudialyte is capable of removing high concentrations of [Ln] from a melt, whereas catapleiite removes lower concentrations of [Ln] overall with a preference for the heavy-[Ln] in general. The effect of catapleiite followed by eudialyte crystallisation (and vice versa) on the [Ln] content of the magmas was modelled in 7.3 and showed that while the initial aegirine crystallisation was able to increase the overall [Ln] content of the magma, it is the order of Zr-silicate crystallisation (catapleiite then eudialyte) which sequesters the heavy-[Ln] and pushes the fractionating magma to become enriched in the light-[Ln]. This could therefore explain how the deeper and less fractionated Pegmatite-Host Grennaite became enriched in heavy-[Ln], with eh residual melt (the Crenulated Grennaite) being enriched in light-[Ln].

These models also show that aegirine and feldspar crystallisation is able to raise the volatile content by up to 5-times depending upon the initial level of OH^- and the degree of crystallisation. The models assume closed crystallisation, whereas it is likely that at this point the cooling magma will be losing volatiles to the surrounding environment. In the case of the Contact Grennaite volatiles will be lost to both the fenite and the Pegmatite-Host Grennaite as well as the crystallising minerals. Any volatiles remaining within the melt at the onset of feldspar crystallisation would also be lost. This loss of volatiles from earlier lithologies can be seen in the raised starting volatile compositions of the Crenulated Grennaite and the Pegmatites relative to the Pegmatite-Host Grennaite.

The Xaxtopite shows higher F^- and lower OH^- contents in contrast to the Grennaites despite being part of the same phase of intrusion. The only F-bearing phase within the Grennaites is eudialyte, with aegirine and feldspars being dry and catapleiite being water-rich. Any fluorine that was initially within the Grennaites could end up being concentrated within the remaining melt at the top of the chamber along with the remaining fractionating Grennaite magma; with the amphiboles acting as a 'sponge' collecting the remaining elements and volatiles (Chapters 4,5).

Figure 7.18: Summary of the a_{H_2O} and a_{HF} trends at Norra Kärr along with minimum initial OH/F and ratios for each lithology and the calculated $\log(fa_{H_2O}/fa_{HF})$ values for biotites.

Second Intrusive Phase

The petrogenetic modelling shows that the second phase magmas tend to follow a trend in varying HF⁻, with the petrological modelling confirming that the second phase magmas tend to display higher initial F-concentrations that evolve with fractionation. The Pulaskite enclaves and the Pulaskite-type Lakarp both contain biotite which was modelled to have crystallised in equilibrium with a magma displaying a $\log(fH_2O/fHF)$ of 3.65, with the Pulaskite matrix biotites being in equilibrium with a magma 3.9 $\log(fH_2O/fHF)$ indicating slightly higher concentrations of OH⁻ within the melt. These latter conditions are supported by the petrological modelling with the Pulaskite matrix having a starting OH/F ratio of 0.4 and the enclaves a ratio of 0.2.

In both the enclaves and matrix, the Pulaskite initially crystallises rosenbushite before fluorite indicating initially F-undersaturated conditions with increasing F-activity through time. Here amphibole appears able to increase the amount of F within the melt while rosenbushite act to

remove it. Fluorite is modelled as co-crystallising towards the end of feldspar formation with fluorite-saturation occurring post amphibole formation with the fluorite removing what remains of the F-content of the magma with any excess fluorine either being expelled from the enclaves (potentially leading to the formation of the rosenbushite rim observed around the enclaves as the fluorine mixes with the relatively OH⁻ matrix magma lowering the HF⁻ activity) or being trapped within the feldspar matrix.

The Lakarpite modelling shows that the inner zones follow a F⁻-trend (Fl-Ros-Eud) while the outermost zone follows an OH⁻-trend. The inner Pulaskite-type Lakarpite starts with a magma displaying a log(fH₂O/fHF) of 3.65 (as calculated from the biotite compositions) with an initial OH/F ratio of 0.37, eventually crystallising fluorite. The Core-type and Zr-Core-type Lakarpite have higher initial OH/F ratios of 0.3 and 2.34 respectively. However, the F—content of the core-type is high

enough to keep the OH/F ratio low enough to crystallise rosenbushite, while the Zr-core-type has a higher relative OH⁻ content resulting in eudialyte forming. The Zr-Lakarpite has the highest initial OH/F ratio of 5.54 resulting in the crystallisation of eudialyte. The eudialyte then removes the F⁻ content of the magma resulting in the OH/F ratio increasing leading to catapleiite crystallisation. These trends could have been caused by volatile loss during crystallisation but as discussed in Chapters 4 and 5, the outer zone of the Lakarpite appears to have reacted with the Pegmatite-Host Grennaite resulting in higher Zr and OH⁻ contents than expected.

7.7 Conclusions

This chapter has presented a series of models to model the relationship between the petrological sequence observed at Norra Kärr and the trends in magmatic volatile evolution. This data has been used to model the change in [Ln] content within the magma due to differing orders of Zr-silicate crystallisation due to differing volatile evolution paths. This chapter has shown that:

- The Grennaite was initially water rich and crystallised catapleiite. This reduced the $a_{\text{H}_2\text{O}}$ leading to later eudialyte crystallisation.
- The trend of catapleiite then eudialyte crystallisation is able to generate the overall light-[Ln] enrichment observed within the Grennaite at Norra Kärr, a process only possible in a magma with a decreasing $a_{\text{H}_2\text{O}}$. If a magma is increasing in $a_{\text{H}_2\text{O}}$, then the consequential trend of eudialyte then catapleiite crystallisation results in a process of overall [Ln]-depletion.
- The petrological models have shown a trend in increasing OH/F ratios within the Grennaite following previously identified trends in progressive Grennaite fractionation.
- The Kaxtorpite has a higher F⁻ content than the Grennaite with the volatile content of the lithology hosted within the amphibole contents.
- The Lakarpite and Pulaskite predominantly demonstrate a trend in changing a_{HF} . This is shown by the trend in fluorite, rosenbushite and eudialyte crystallisation.

- The outer Zr-Lakarpite zone also exhibits a trend in $a_{\text{H}_2\text{O}}$ leading to later catapleiite crystallisation.
- The Pulaskite enclaves display rosenbushite rich rims, likely indicating F-degassing from the enclaves and meeting the OH^- richer matrix magma.
- Modelling of biotite compositions have shown that the Pulaskite-enclave and Pulaskite-type Lakarpite magmas both equilibrated at $\log(f\text{H}_2\text{O}/f\text{HF})$ of 3.65, with the Pulaskite matrix biotites in equilibrium with a magma 4.9 $\log(f\text{H}_2\text{O}/f\text{HF})$ indicating slightly higher OH^- contents.
- Petrological modelling indicates a trend of increasing OH/F ratios from the central zones of the Lakarpite to the outer zones.

Chapter 8

Summary Structural, Emplacement and Fractionation Models

8.1 Introduction

This thesis presents the most comprehensive study of Norra Kärr and its comparison with other alkaline intrusions to date. However, the whole story of the Norra Kärr intrusion is not yet fully told. Further explanation of the morphology of the intrusion and its development is stymied by the erosion of the top of the chamber and the lack of deeper drilling which would likely provide evidence for the source of the enclaves observed within the Pulaskite. However, the exploration dataset provided by Tasman Metals Ltd. has provided an opportunity to develop a new set of models for the structural emplacement, trends in magmatic evolution and development of [Ln]-fractionation trends. This chapter will summarise the general features of the intruding magmas; present a new working hypothesis the emplacement and deformation of Norra Kärr, summarise the main mineral trends within the lithologies and finally present an ore-deposit model and summary intrusive and evolution model for Norra Kärr.

8.2 Overview of Magmatic Intrusion and Fractionation

8.2.1 New Lithological Divisions in light of this Study

On the basis of the newly acquired data, this study has renamed and subdivided the lithologies at Norra Kärr to better highlight the structural (Chapter 2), geochemical (Chapter 5) and petrological (Chapter 3) differences between different units. The outer Grennaite unit is now the Contact Grennaite defined as containing being <299 ppm La; the 'pegmatite domain' is now the Pegmatite-Host Grennaite with the Pegmatites treated separately to mark them as structurally distinct within the unit despite the similar mineralogy (but differing) petrology shown by the Pegmatite-Host Grennaite to the other Grennaite units. The 'migmatite' domain is now the Crenulated Grennaite removing the genetic term 'migmatite' as the unit displays a crenulated deformation fabric with no evidence of remelting present.

The shape of the Kaxtorpite has been reinterpreted to show the separate volumes of Kaxtorpite intersected by drill cores do not necessarily indicate a connected relationship to the rest of the body higher up in the chamber; instead, they appear to represent fallen rafts of material sinking into the Grennaite (Chapter 2.4.3). The Lakarpite has been subdivided into different petrological and geochemical zones in order to highlight important chemical, petrological and mineralogical differences within the intrusive body; the Pulaskite is now recognised as being comprised of a matrix of feldspar rich material containing distinct enclaves. These new divisions and names serve to better highlight the cryptic variation occurring within the different units of the intrusion allowing improved conclusions to be made regarding their formation.

8.2.2 Initial Magmatic Emplacement

Evidence from whole rock geochemistry has shown that Norra Kärr intruded as an already highly fractionated set of magmas (Chapter 5.3.4) that lie at the far end of fractionation on an AFM ternary

and on a TAS plot where they lie either side of the phonolite minimum (Chapter 5.3.1). The age of these magmas has been determined by Sjöqvist et al. (2017) from U-Pb date from zircon to be 1.49 ± 0.01 Ga, with zircon in the unfenitised Väckjö Granite dated at 1.79 ± 0.01 Ga reflecting the intrusion of the TIB-1 granites of the Transscandinavian Igneous Belt. Sjöqvist et al. (2017) also reported xenocrysts within the Norra Kärr magmas that show the existence of Svecofennian and TIB crustal material beneath the intrusion and indicate an Archaean component in the basement rocks.

The intruded magmas appear to have intruded in two magmatic phases. The evidence for this is shown by the field relationships, petrology, and whole-rock compositions (Chapters 2, 3, 4, 5) which show that the Lakarpite and Pulaskite do not appear to be related to the original magmatic phase of the Grennaite as proposed by Rankin (2011). Rankin thought the Lakarpite to be a magmatic channel structure; however a study of the major and trace element geochemistry, petrology, mineralogy of the Lakarpite has shown that the Lakarpite is not geochemically related to the Grennaite or Kaxtorp - nor does it match observed channels from basaltic (i.e. Otanmäki) or alkaline (i.e. Klokken) intrusions - and instead displays a reaction contact due to a form of mixing with the evolved Pegmatite-Host Grennaite (Chapter 5.6.6) which suggests a later separate intrusive phase. This second magmatic phase is also supported by the field relationships that show that the Pulaskite intruded into the Contact Grennaite by the presence of xenoliths of Grennaite within the Pulaskite near the contact between the two lithologies (Chapter 2.4.7), as well as the enclaves appearing to be intruding upwards from the current land surface. This evidence feeds into the revised structural model presented later in this chapter (section 8.3) and possibly indicates that Norra Kärr can best be interpreted as a dyke-structure rather than a deformed sill.

8.2.3 Intrusion and Fractionation of the First Magmatic Phase

The initial intrusion of Norra Kärr resulted in the crystallisation of the Contact Grennaite and the fenitisation of the country rock (the Väckjö Granites) as described by Christensson (2013) and Sjöqvist et al. (2017). This fenitisation may have resulted in lower light-[Ln] and Zr concentrations within the Contact Grennaite (Chapter 5.3.5). Despite evidence for the loss of some elements to the fenite the Contact Grennaite represents the most primary of all the Grennaite compositions (Chapter 5.4). This is supported by geochemical modelling (Chapter 5.6.2) which shows that it is unlikely that assimilation played a role in the formation of the Contact Grennaite as this would require up to 80% mixing between the Pegmatite-Host Grennaite and the Väckjö Granites to achieve. The petrological trend within the Grennaites is one of increasing grain size and a more euhedral texture for all minerals present with increases occurring through the Pegmatite-Host Grennaite and into the Crenulated Grennaite.

This formation sequence is supported geochemically through element fractionation patterns (Chapter 5) as well as fractionation trends observed within catapleiite (Ca vs Na) and eudialyte (Light-[Ln] vs Ca). The trend is shown particularly well on a plot of whole rock K/Rb vs Zr which also shows that the Pegmatites are intimately related to the Pegmatite-Host Grennaite. This is supported by geochemical modelling (Chapter 5.6.3) indicating that the pegmatites are not significantly different in whole rock composition (as shown by whole rock Zr vs Pb) but do show enrichment in some elements (K, Zr, Hf, Nb, Ta, Y, W, Pb, Sr, Ba - Chapter 5.4) relative to the Pegmatite-Host Grennaite. This suggests that the pegmatites formed from a slightly more concentrated (but not fractionated) version of the Pegmatite-Host Grennaite magma. Their 3D structure and feldspar rich

nature may give the impression they could be connected to the second phase magmas (i.e. the feldspar rich Pulaskite), but this is ruled out by the geochemical modelling (Chapter 5.6.3) with their formation possibly due to continuing shearing of the Pegmatite-Host Grennaite as a model for their formation. By following the sequence of Grennaite fractionation (Contact, Pegmatite-Host, Crenulated) the evolution of the magmatic [Ln]-content can be followed. The Grennaites have previously been by Sjöqvist et al. (2013) and Atanasova et al. (2017) who both predominantly focussed on the trends in eudialyte, and this study supports the overall [Ln] concentrations observed in their mineral analyses. This thesis shows that as fractionation progressed the [Ln]-concentrations steadily increased from the Contact into the Pegmatite-Host before depleting in heavy-[Ln] and enriching in light-[Ln] into the Crenulated Grennaite. This led to the formation of the economic Grennaite units of the Pegmatite-Host Grennaite and pegmatites which are biased towards the heavy-[Ln] and the Crenulated Grennaite which is biased towards the light-[Ln]. A potential model for this [Ln] enrichment and the heavy-[Ln] vs light-[Ln] bias within different Grennaite units (based upon the modelling in Chapter 7.2) will be presented later in this chapter (section 8.5).

8.2.4 Intrusion and Fractionation of the Second Magmatic Phase

While the Grennaites are the most fractionated lithologies the Pulaskite is the least fractionated in terms of K/Rb. Based upon field relationships the Pulaskite intruded after the Contact Grennaite had cooled enough to allow blocks of Grennaite to fall into the Pulaskite, while the Lakarpite intruded while the Pegmatite-Host Grennaite was still warm enough to generate a reaction contact. While temperatures would have varied within the Grennaite from the contact inwards it is still likely that the Lakarpite was intruded first and the Pulaskite second due to the larger volume of the Pulaskite and the presence of enclaves tapping a deeper structure compared to the smaller volume of intruded Lakarpite. The Pulaskite appears to be the more primitive of the two lithologies with enclaves dominated by Fe²⁺-rich minerals which may indicate the presence of a cumulate mush in a deeper chamber. The Lakarpite is more complicated and can be divided into an inner zone of a composition and petrology akin to the Pulaskite, and an outer zone display a different petrology and mineralogy which is richer in Zr and [Ln]. The different petrological zones also display differing ratios in Ni/Co. These differences can be explained via geochemical modelling (Chapter 5.6.6) as a result of some form of mixing or reaction between the Pegmatite-Host Grennaite and an original magma with a Pulaskite composition. This reinterpretation of the Lakarpite as a dyke that subsequently developed an outer reaction zone solves the problem as to what the lithology represented (an issue during the original core logging) due to is varying petrology, mineralogy and geochemistry but also strong similarity to the Pulaskite.

8.2.5 Possible Later Metamorphic Effects

Atanasova et al. (2017) also reported the possibility of metamorphic overprinting of the intrusion at 400°C –550°C during the greenschist facies Sveconorwegian–Grenvillian orogeny. However, the modelling cited could overlap with late-magmatic temperatures, and the Al-rich rims of pyroxenes could also be due to late magmatic processes similar to those in Ilímaussaq (Marks et Markl 2003) Where Al in the rim of the pyroxenes may be due to the later activity of a Na-rich and oxidising residual melt or fluid phase. As such, any metamorphic effects on the intrusions would require their own independent age dates to confirm them as separate from any late-magmatic processes.

8.3 Potential Structural Reinterpretation of Norra Kärr

Rankin (2011) provided a consultancy report on the structural geology of Norra Kärr which was written before further geochemical and petrological studies took place. In light of a paucity of structural measurements in some areas of the intrusion and the new interpretations of the magmatic features presented in this thesis, this structural interpretation merits reappraisal.

Rankin (2011) presents a range of structural measurements in his report, but also may have misinterpreted the magmatic structure of Norra Kärr based upon the limited outcrop available. Specifically, there are two key features used to justify the younging directions within the intrusion which led to the model of a sill with the Lakarpite at the bottom. The magmatic arguments are:

1. Opposing younging directions inferred from a 10's-cm scale structure within the Grennaite interpreted as a magmatic channel structure near the contact between the Grennaite and the country rock.
2. The Lakarpite is interpreted as a magmatic channel structure eroding into the eastern portion of the Grennaite, thus placing the Pulaskite at the top of the intrusion.

Starting from an initial model of a sill a series of deformations are described. However, there is a lack of data-points for some lineations, something understandable given the lack of outcrop. The presence of an S2 foliation in the centre of the 'fold' (i.e. within the Kaxtorpите) is not necessarily conclusive as the original S0 magmatic layering described does not necessarily have to be in the same orientation in the centre of the intrusion as it is at the contact; a feature observed within other intrusions which display U-shaped primary internal layering (e.g. Klokken, Yastrebits). As such there is the potential for the three measurements of L2 lineations and nine measurements of S2 foliations to have been overinterpreted in light of the earlier assumption regarding the magmatic processes, and the 'bedding' (here magmatic-layering) - cleavage relationship is not sufficiently clear. While presence of a synform at Norra Kärr is not necessarily ruled out, it is also not required by the data so far presented.

The relationship between the regional fold structures observed in the area and the Norra Kärr intrusive is also not clear. The Västana Granites had accreted as a result of a N-S to NNE-SSW trending subduction zone between 1860 Ma -1660 Ma which may explain the regional N-S to NNE-SSW elliptical fold trends observed by Rankin in the regional magnetic data. There is also only evidence for brittle/ductile heterogeneous foliation and lineation in the area of Norra Kärr post 1570 Ma (likely due to regional shear allowing extensional systems and shear zones to form that crosscut earlier folding features) unlike the definite open folding and lineation seen to the west of Norra Kärr on the other side of the Protogine Zone (Chapter 2.2). The regional folding trends that Rankin ascribes to causing a D2 deformation at Norra Kärr, may therefore pre-date Norra Kärr by several hundred Ma. However, a more evident deformation regime is the dextral shear system observed by Rankin to the south of Norra Kärr, and for which there is the regional evidence to support this system being contemporaneous with the intrusion (Chapter 2.2).

The current model for Norra Kärr states that it was intruded as a sill and subsequently deformed during regional folding into a synformal structure. However, a synform is not necessarily required by the data presented, nor can the age of the regional folding observed be definitively said to post-date the intrusion of Norra Kärr. The data and observations within this thesis also questions the starting magmatic model, and as such a new interpretation of the evidence is discussed below.

Norra Kärr appears to have been intruded in two phases. The first phase involves the Grennaite which developed internal U-shaped cryptic layering (Chapter 2.4.4), and the formation of the Kaxtorpite which appears to mingle downwards into the Grennaite (Chapter 2.4.5). This phase can be interpreted to have intruded upwards on the basis of several lines of evidence.

Such U-shaped cryptic variation has been documented in the Klokken intrusion from Gardar (Fig. 8.1-A) which displays a well-developed internal morphology consisting of inward dipping layered structures symmetrical about the focus of the intrusion that have been shown to still display their original orientations (Upton 1960, Parsons et Butterfield 1981). Cryptic variation is displayed by near continuous variation in Fe/(Fe+Mg) and an increase in Mn within pyroxenes, olivine and biotite and a decrease in the proportion of plagioclase feldspar through the evolution of the intrusion (Parsons 1979). The Norra Kärr Grennaite is similar in that there are observable petrological differences alongside the mineral and whole-rock cryptic variations, and these appear to map out U-shaped volumes within the intrusion. This is also observed in smaller alkaline intrusions, such as Yastrebet (Fig. 8.1-B) – a small nearly-oval alkaline intrusion less than 2 km long and 4 km² in area. Yastrebet is morphologically comparable to Norra Kärr in several ways. The syenites have been divided into the: fine-grained outer contact syenites, the medium-grained riebeckite syenites of the main series, the coarse-grained and pegmatitic quartz syenites of the central core, and syenites of the upper laminated group. On top of the grain size comparison there is cryptic layering upwards through the central main laminated core of the intrusion as seen by an increase in alkalinity of the pyroxenes and amphiboles, a decrease in the silica content of biotite and an increase in the K content of the feldspars. Cryptic layering also seen from the contact inwards with alkaline pyroxenes and amphiboles not observed in the contact regions (Kogarko et al. 1995). There is also some rhythmic layering displayed by alternating leucocratic and mesocratic syenites with melanocratic (or extremely melanocratic) schlieren-like segregations composed of clinopyroxene, amphibole and, biotite occurring more readily. Furthermore, Yastrebet also displays an amphibole-rich caps (the riebeckite syenite) and such features are also observed in other alkaline intrusions. The Kaxtorpite may well be one such ‘cap’ indicating that it is sitting at the top of the intrusion. The Kaxtorpite’s wavy contact with the Crenulated Grennaite may have involved some aspect of deformation but does not require a regional-scale fold to explain it. Indeed, a fold cannot explain the areas of isolated Kaxtorpite which may indicate ‘rafts’ of material that have fallen into the Grennaite (Chapter 2.4.5).

The pegmatites within the Grennaite also add to the structural evidence. In Rankin’s model they lie along the axial plane of the ‘fold’. In the 3D modelling presented in Chapter 2 the larger pegmatite bodies do appear to be semi-vertical follow the central N-S axis of the intrusion. However, a greater degree of deformation may be expected within them if a folding event had occurred, whereas in drill core the larger pegmatites appear to be relatively undeformed internally. Some smaller pegmatites can be observed to display evidence of boudinage with others showing evidence of cm-scale folding, and mineral stain shadows being observed elsewhere in the intrusion. However, a fold structure is not necessarily required to produce these fabrics either and the deformation observed could instead be produced by strike-slip shear processes as have been observed in pegmatites in northern Scotland. Indeed, the process of shear within a still ductile magmatic intrusion may even aid the formation of the pegmatites by creating accommodation space for fractionated melt to accumulated within the cooling crystal mush. Such a process would be able to account for the trends in element enrichment observed within the whole-rock compositions of the pegmatite (Chapter 5.4).

Figure 8.1: Examples of the internal morphologies of alkaline intrusions. Left (A) - Cross-section through the Klokken alkaline complex. After Parsons et Butterfield (1981). Right (B) - Cross-section through the Yastrebits alkaline complex. After Kogarko et al. (1995).

Putting together the observations at Norra Kärr alongside these comparisons shows that the U-shaped cryptic and petrological changes are commonly seen in alkaline stocks and dykes, and amphibole-rich caps can be a common feature of these intrusions. Rankin's first key piece of magmatic-based younging evidence, the single 'channel' feature at the contact of the Grennaite, is also not convincing to determine a single younging direction for the whole of the intrusion as it instead this could be a feature of side-wall crystallisation and crystal slumping downwards into the chamber. As such the first phase of intrusion could be interpreted as a dyke-like body which intruded upwards and crystallised in a manner similar to Yastrebits or Klokken. If the sill model is ruled out and the cryptic variation in Norra Kärr was originally U-shaped then the fold model becomes difficult to reconcile with what is actually observed. The same goes for the observed morphology of the Kaxtorpite.

The second phase of intrusion, the Lakarpite and Pulaskite, offer further insights into the structure of the intrusion. Rankin's second key piece of evidence for the fold model is the Lakarpite representing a horizontal magmatic 'channel' structure. However, this thesis interprets the Lakarpite to be an intrusive Pulaskite-type body which has been altered by magmatic mass-transfer processes (Chapter 5.6.6). Furthermore, it also appears to thin toward the present surface (as seen in cross section) implying that it has intruded 'upwards' towards the present surface level.

Rankin (2011) also described the Pulaskite as 'agmatitic' (a migmatite with a breccia-like structure) when the lithology actually appears to be the result of a primary magmatic process (Chapter 2.4.7),

and the 'breccia' disaggregated enclaves of material (Chapter 3.5). The Pulaskite (which appears related to the intrusion of the Lakarpite) displays evidence of these enclaves rising 'upwards', and Grennaite xenoliths falling 'downwards' from below the present surface level. While both lithologies display evidence of weak shearing (e.g. the elongate deformation within the Pulaskite enclaves) there is no known evidence of folding within the unit. While both lithologies could have been intruded horizontally and developed similar internal features in a sill rather than an upwards intruding dyke, these features do tie well with the general orientations of the cryptic, petrological and structural features observed during the first phase of intrusion and do not rule out a dyke-style emplacement model. Furthermore, the lack of evidence for folding and abundant evidence of some degree of N-S shear appear to support the regional shear rather than fold-based model.

Shear has been noted to affect other alkaline intrusions, with two examples are given below, the relatively undeformed Gardar Rift of Southern Greenland and the shear-zone dominated Eastern Ghats, India. Shear is noted from the Gardar where intrusions are frequently elliptical in cross-section and occur at the intersections of regional dyke swarms and regularly spaced sinistral wrench-fault systems (Stephenson 1976). Stephenson (1976) also showed that the dominant movement along major Gardar faults is strike-slip with plenty of evidence for fault movement being contemporaneous with magmatic activity, with Emeleus et al. (1970) showing that dykes were intruded shortly after the emplacement of the major intrusions and it is likely that the rocks of the South Qôroq Centre were still hot during the faulting and intrusion, with the dykes (e.g. those at Igdlertfigssalik) displaying deflection morphologies similar to those observed along ductile shear zones. These large-scale sinistral fault zones acted as channels for ascending magmas throughout the Gardar period and led to the high-level cylindrical ring-intrusions being emplaced. The fault zones then resulted in the more or less continuous movement that created ductile shear zones within the hot intrusions. The intrusions then deformed so as to give elliptical cross-sections but did not develop internal fabrics (i.e. a $\max \gamma$ of 1.2). The time relationships in the province between faults, major intrusions and dykes are best illustrated by the South Qôroq Centre (Fig. 8.2), which was brittle enough to allow the emplacement of a dyke swarm yet subsequently suffered ductile deformation together with the dykes. Away from the intrusions, deformation is entirely by brittle fracture and the amount of fault movement correlates well with the sum of brittle and ductile movement within the intrusions. The magnitude of deformation appears to have been greatest along the northern fault systems and decreased southwards.

Similarly, Bhattacharya et al. (2004) describe the alkaline syenite complex of Koraput in the Eastern Ghats belt that is on a smaller scale to Gardar but has undergone more intense deformation. It is 4 km long and up to 0.75 km wide and has intruded into deformed metapelitic granulites that display rootless folds. Here, the intrusion is bounded by two sets of mylonitic foliation that are observed within the dominant NE orientated shear planes. These the stretching lineations (cross-cut by the intrusion) indicate sinistral strike slip. Microstructures indicate a reverse-fault sense of movement; possibly representing a Reidel shear. There are also upright folds on mesoscopic scale presumably the result of some sub-horizontal compression related to the emplacement of the alkaline magma. Koraput displays magmatic foliation with the parallel alignment of mafic minerals in nepheline syenite, compositional banding and parallel alignment of feldspars in perthite syenite all of which are consistently NE trending and dip steeply SE. These structures therefore indicate the passage of magma along the dominant shear planes.

Figure 8.2: Progressive stages in the development of the South Qôroq and Igdlérfigssalik Centres modelled as a stack of cards: A, Circular South Qôroq cut by a dyke swarm and the circular Igdlérfigssalik Centre; B, a 4 km wide shear zone cuts the northern part of the South Qôroq; C, a shear zone affects both intrusions; D, brittle fracture along the two major faults produces a final outline comparable to the mapped intrusions. After Stephenson (1976).

Figure 8.3: Model for the emplacement of Koraput: A, dominant and subsidiary shear zone develop; B, sinistral-top normal fault sense of movement along the dominant shear zone and reverse along the subsidiary shear zone produces a gap; C, sigmoidal gap is filled with the alkaline intrusion (red); D, schematic map of the alkaline complex. After Bhattacharya et Kar (2004).

The combined effect of movement on these shear planes is a sygmoidal gap with maximum width along the strike of the subsidiary, NW trending shear plane (Fig. 8.3). The shape and orientation of the alkaline body perfectly matches with this sygmoidal gap and hence can be considered to have been emplaced in a pull-apart structure along a NW-trending Reidel shear. Bhattacharya et Kar (2004) state that the emplacement of the Koraput alkaline complex in a pull-apart structure is consistent with the transcurrent shear zone cavity opening model of Hutton (1988) and similar to those reported for the Donegal granite in Ireland (Hutton 1982) and the Mortagne granite in France (Guineberteau et al. 1987).

Both examples show that syn-magmatic shear process can not only create accommodation space for alkaline intrusions but can also affect their shape and internal fabrics. In the case of the Norra Kärr the evidence from the pegmatite deformation fabrics, the Pulaskite enclaves and the shear zone described by Rankin that shear was an important process in the formation of the intrusion. Norra Kärr also displays a slight sigmodal shape (similar to Koraput), however, further structural and exploration work is required to determine the exact shape of the intrusion in their regard. Similarly, while Rankin (2011) did identify several structural trends in the TIB country rock surrounding Norra Kärr (Fig. 8.4) there is a lack of data to back up the cross-cutting relationships and age dates for these structures. While it is possible to link the intrusion and deformation of Norra Kärr to local shear zones and broader N-S deformation it is more difficult to give a complete history of deformational processes in the local area and further work is required to finalise any model.

Figure 8.4: Interpretation of major structures within the TIB country rock surrounding the Norra Kärr intrusion (green with red outline). After Rankin (2011).

This thesis has shown that the initial assumptions made by Rankin (2011) about the magmatic model are either incorrect or are not unique to a sill-based model. Furthermore Rankin (2011) does not provide a summary sketch of the initial sill model, but in either potential ‘sill’ morphology problems are posed. If Norra Kärr started as a sill with the Pulaskite on top and Lakarpite at the base, then there are problems as to how the U-shaped cryptic and petrological zonation patterns could have formed, and how the Kaxtorpite could have crystallised vertically. If the sill originally started with the Kaxtorpite at the top and Lakarpite and Pulaskite at the base (as in Fig. 8.4) then an isoclinal fold would be required which may preserve and accentuate the cryptic layering and Kaxtorpite features, but which would also set up parasitic folds with hinges aligned to the N-S axis. These are not observed at outcrop and there is not enough structural data provided to identify a systematic switch in E-W vergence in the foliations. There also does not appear to be a regional scale folding event that could facilitate the formation of such a fold. What is observable is abundant evidence of shear within the intrusion.

Starting with the model that the Kaxtorpite represents an amphibole rich cap with portions ‘fallen’ into the Grennaite from the present surface, that the U-shaped cryptic layering is caused by inwards crystallisation of the Grennaite from the contact, and the relatively undeformed Pulaskite and Lakarpite intruded up towards the present surface; the simplest model would be that Norra Kärr intruded as a dyke-like structure. This is further supported by the northern end of the intrusion being shallower and the southern end deeper, with the southern end showing potential as being the feeder system to the rest of the intrusion. As the structural measurements provided by Rankin (2011) do not exclusively rule out a fold, the foliations observed and the boudinaged and folded pegmatites (and even the formation of accommodation space for the intrusion) could instead be explained via the effects of regional shear. Furthermore, the evidence for a contemporaneous regional shear-regime and Rankin’s observations of a nearby shear zone would provide a mechanism for this.

Consequently, an alternative and competing working hypothesis based on the model of a dyke emplaced during syn-tectonic shearing is proposed. A new model is presented below in Fig. 8.5, and a new set of deformations starting from a dyke rather than a sill is given in Table 8.1. As mentioned above, further detailed structural work is required to complete the model which should be able to incorporate or challenge the evidence and ideas presented in this thesis.

Model from Rankin (2011)		New Structural Model	
	Norra Kärr intruded as a sill		Norra Kärr intruded as a dyke
D1	N-S/NE-SW compression and shear	D1	Deformation along NE-SW trending shear zone
S1	Sub-parallel magmatic layering	F1	Potential syn-magmatic folding of pegmatite
F1	Folds in pegmatite	S1	Vertical N-S fabric related to shearing
D2	Regional elliptical E-W compression		
F2	Intrusion folded to present shape		
S2	Foliation related to F2 folding		
D3	E-W kink folds due to N-S compression	D2	E-W kink folds due to N-S compression
S3	Crenulation of S1/S2 fabrics	S2	Crenulation of S1 fabric
F3	E-W trending folding along the contact of NK	F2	E-W trending folding along the contact of NK
		D3	W-rotation of NK along basin bounding faults

Table 8.1: Summary of the sequence of deformation events in the newly proposed structural model as compared to the model proposed by Rankin (2011).

Figure 8.5: A comparison between the model proposed by Rankin (2011) and this thesis.

D0 - Intrusion

Rankin (2011) describes Norra Kärr as lying within a NNE- trending structural corridor within the TIB. The TIB itself is dominated by a significant NW- to WNW-trending structural grain that includes folding and domal granitoid morphology, and anastomosing shear and fault zones. Locally the NNE structural corridor includes a N-S to NNE-trending elliptical folding of the TIB; anastomosing N- to NNE-trending fault / shear zones within the TIB, associated with variable demagnetisation and local E-W shear zones.

The characteristics of the NNE structural-corridor (potentially part of the Protogine Zone) suggest that could have acted as the primary deep-crustal or mantle-tapping conduit for emplacement of Norra Kärr. The pervasive NW- to WNW- structural grain within the TIB suggests that the emplacement locus for Norra Kärr was coincident with intersection of the NNE structural corridor with part of the deep-crustal NW-SE fault or shear zone. This role is supported by the presence of other syenites bodies and fennitised granite and gneiss bodies along a N-S structural corridor to the south of Norra Kärr.

Norra Kärr is an N-S trending intrusive body within this NNE structural corridor and is modelled here as intruding as a dyke. The north and south ends of the intrusion curve away from the main trend of the body in a potential σ -structure. Norra Kärr dips west and this may be the result of fault movement as part of the later Vattern basin (D3). Evidence for these larger scale basin-bounding fault structures that are part of Vättern Graben and can be seen in the centre of nearby Gränna. To the east and west of Norra Kärr lie granites that are part of the TIB.

D1 - Indications of Syn-Magmatic Shear

Evidence of syn-magmatic shear is pervasive throughout the intrusion and Rankin (2011) shows that there is an E-W to NE-SW shear zone south of Norra Kärr that is associated with a significant zone of demagnetisation within the host TIB due to haematite alteration of magnetite within the shear zone associated this with N-S to NE-SW compression. When these observations are combined they could represent a single syn-magmatic deformation event along a sinistral shear zone with an oblique element. This could therefore result in the formation of the fabrics seen in the Crenulated Grennaite and the Kaxtorpite.

Rankin (2011) also highlights small (cm) scale folds within the pegmatites as part of the S1 fabric, and states that these folds have fold-axes that are highly variable due to later folding. However, following the dyke model then the orientations of these axes are dependent upon the orientation of pegmatite development within the shearing Pegmatite-Host Grennaite and these folds could have been a result of syn-tectonic shear.

The effect of shearing may also extend to the intrusion of the Lakarpite and Pulaskite. If enough deformation had occurred to disturb the lower magma chamber or to create a stress field that promoted the intrusion of these dykes then the second phase of intrusion could be considered as related to the syn-deformational processes.

D2 – E-W- Kink Folds Due to N-S Compression

Rankin (2011) stated a D3 deformation phase involving a weak-to-moderate N-S compressive deformation which formed localised kink folding of earlier fabrics and at the regional scale and suggests that this deformation event also produced rapid changes seen in drill core and produced

local box-folding. This phase affected little else apart from the shape of the intrusion. It is possible that the timing of this deformation was pre-800 Ma after which time the crust was in extension which would form the Vättern Graben (Månsson 1996). This may have occurred due to N-S compression or shearing once Norra Kärr had crystallised.

D3 - W-rotation along basin bounding faults

The Vättern Graben began to form before 800 Ma with later regional extension resulting in the formation of a half-graben (Månsson 1996). Later Permian rifting reactivated the ductile fabric of the basement rocks resulting in the present day 100 m deep trench under Lake Vättern. An example of these reactivated faults can be seen in the cliff face in the centre of Gränna. The half-graben follows the west side of the 'Protogine Zone' and resulted in the formation of faults along the zone. These can also be seen on the gravity map interpreted by Rankin (2011). This may have acted to tilt Norra Kärr to the west.

8.4 Petrological and Mineralogical Trends

Within this structural framework of larger scale intrusive events a series of other more local petrological, mineralogical, geochemical and volatile evolutionary trends were occurring. Petrological observations have shown that the overall evolutionary trend within the magmas is to crystallise aegirine as the first mineral phase and feldspars and nepheline as the last mineral phase (Chapter 3). Within the second intrusive phase biotite, sphene, rosenbushite and amphibole crystallise as intermediate minerals in the sequence, while catapleiite and eudialyte crystallised as intermediate phases within the Grennaite. These overall petrological trends indicate that the different magmas were following similar fractionation trends of being initially Fe-dominated, progressing through a phase of Zr-saturation and then finally Al-dominated crystallisation. On top of this sequence their chemistry and volatile content was also causing differences in the intermediate crystallising mineral species (Chapters 4, 7).

Aegirine is the first forming phase and as such records the initial chemical composition of the magmas as well as the initial magmatic redox conditions. Aegirine displays two compositional trends that support the evidence for two phases of magmatism; an Aeg-Jd trend within the Grennaite and Kaxtorpite, and an Aeg-Quad trend within the Lakarpite and Pulaskite (Chapter 5). Comparison with other aegirine fractionation trends indicates that the starting magmas at Norra Kärr had a redox of +1 to -2 FMQ and that the magmas lie at the end of a longer fractionation trend (Chapter 5). Aegirine is also responsible for increasing the overall Zr content of the Grennaite magmas as well as slightly enriching the magmas in [Ln] overall (Chapter 8). The amphiboles indicate that the magmas are at the end of a fractionation sequence and that there was little internal fractionation of the Kaxtorpite, Lakarpite and Pulaskite magmas during their crystallisation; perhaps due to the restricted volume of magma involved. The amphiboles compositions also show a similarity between the Kaxtorpite and the Pegmatites (Chapter 4.4), as well as showing that the inner Lakarpite has an affinity to the Pulaskite while the outer Lakarpite displays compositions intermediate to the Kaxtorpite and Pulaskite. This again provides further evidence for two separate magmatic phases and of the Lakarpite reaction with the Grennaite. The amphiboles also indicate that no separate supercritical fluid phase was present during their crystallisation. They are particularly F-rich with the majority of the fluorine content of the first magmatic phase hosted within the Kaxtorpite as opposed to the OH-rich Grennaite (Chapter 5).

Within the second magmatic phase the intermediate minerals other than amphibole are sphene, rosenbushite, biotite and fluorite. The biotite displays both a primitive composition and indicates a lack of internal fractionation within the Lakarpite and Pulaskite. Biotite is particularly OH-rich with modelling indicating higher a_{H_2O} within the feldspar-rich matrix than within the enclaves (Chapter 7). The relationship between rosenbushite crystallising before fluorite indicates a trend of increasing a_{HF} with crystallisation of an already F-rich magma. This trend is also observed within the inner zone of the Lakarpite; however, overall the Lakarpite indicates a trend in decreasing a_{HF} as a sequence of fluorite-rosenbushite-eudialyte is observed from the core zone outwards, with the trend switching to increasing a_{H_2O} with the occurrence of catapleiite in the outermost Lakarpite zone (Chapter 7). This is likely due to a combination of a loss of F to the Grennaite during intrusions and the hybridisation between the Grennaite and the Lakarpite along the contact between the two lithologies.

The intermediate minerals within the Grennaite are catapleiite and eudialyte and it is significant that they form in that order thereby indicating a trend in decreasing a_{H_2O} within the magma during crystallisation (Chapter 7). Zr-silicates begin to crystallise once Zr-saturation is reached within the magmas and this likely occurred when aegirine was still crystallising. Evidence for this can be best observed within the coarse grained aegirine from the pegmatites as the point at which the Zr-rich core transitions to a Zr-poor rim at the beginning of catapleiite crystallisation (Chapters 3, 5). Catapleiite records the fractionation of the Grennaite in its Ca vs Na content, while eudialyte records a similar fractionation trend in light-[Ln] vs Ca. Eudialyte also appears to have had a complex crystallisation history as observed in the zoned crystals visible in SEM images (chapter 5) that display Zr and Si rich cores and Mn and Cl rich rims. The crystallisation of aegirine and the Zr-silicates influences the whole rock Zr/Hf ratio and produces the observed pattern of increasing in Zr/Hf towards the Pegmatite-Host Grennaite followed by a decrease towards the Crenulated Grennaite (Chapter 8). However, local variations within the Contact Grennaite and the Pegmatites may be due to loss of Zr to the fenite and earlier Zr-silicate crystallisation within the Pegmatite-Host Grennaite respectively. Aegirine and importantly catapleiite crystallisation also played a role in effecting light- and heavy-[Ln] concentrations within the magma (section 8.5)

Feldspar and nepheline also show that the magmas crystallised at a low temperature near the eutectic at 650°C. These minerals also played a significant role in driving the overall magmatic evolution of the magmas with a trend of increasing feldspar over nepheline crystallisation observed both petrologically and in geochemical modelling (Chapter 4.12).

8.5 Ore Deposit Model

While it is likely that the first phase magma was already rich in [Ln], this does not directly explain the variation in light-[Ln] and heavy-[Ln] observed within the Grennaite at Norra Kärr. The process for forming this zonation can be explained via a combination of magmatic and volatile evolution within the Grennaite melt. As the Grennaite magma cooled it progressed through the stages of aegirine crystallisation, Zr-saturation and feldspar-nepheline crystallisation. Aegirine crystallisation was able to raise Zr concentrations along with limited increases in [Ln] concentrations, however, a far larger effect on La/Lu fractionation was due to subsequent catapleiite crystallisation before the ore-bearing eudialyte formed. The effect of combined aegirine and catapleiite crystallisation acted to further enrich the [Ln]-concentrations within the magma but also began to remove heavy-[Ln] from the melt. When catapleiite crystallisation became dominant more heavy-[Ln] were removed from

the melt than light-[Ln]; thereby resulting in an overall increase in the concentration of light-[Ln] within the remaining liquid. This sequence of events can explain how the [Ln]-concentrations were raised from the Contact Grennaite to the Pegmatite-Host Grennaite, and then how heavy-[Ln] were removed and light-[Ln] concentrated in order to produce the light-[Ln] enriched Crenulated Grennaite. This scenario of events was only possible due to the magmatic volatile evolution from an initially high $a_{\text{H}_2\text{O}}$ capable of crystallising catapleiite, to a lower $a_{\text{H}_2\text{O}}$ that switched the magma to eudialyte crystallisation. Had the magma initially had an $a_{\text{H}_2\text{O}}$ low enough to initially crystallise eudialyte then the overall [Ln]-concentrations would have plummeted in the magma due to being removed by the eudialyte. This could not have produced the [Ln]-trends observed, nor would there have been such a dramatic enrichment in in [Ln] within the central Grennaite ore domains.

8.6 Summary Magmatic Model

The first magmatic phase at Norra Kärr was intruded as a melt already enriched in [Ln], though depleted in light-[Ln] in comparison to other alkaline intrusions (e.g. Ilímaussaq). The original magma was likely to have been a low degree partial melt derived from a fertilised mantle wedge formed during the Svenco-Fennian and Gothian orogenies. The magma then began to ascend through the crust during the Dan-Polonian deformation of Baltica ultimately ending up within a shear zone and emplacing a now highly fractionated magma as a dyke-like structure. The first magmatic was already rich in [Ln], likely due to a combination of the fertilised mantle wedge, magmatic immiscibility and preceding aegirine crystallisation acting to further enrich the melt in [Ln].

At a point just before intrusion the magma may have immiscibly separated into an oxidised OH-rich phase which was emplaced first (the Grennaites and Kaxtorpite) and a F-rich second phase that remained at depth and formed a cumulate mush for a longer period (the proto Pulaskite magma). It was into this first magmatic phase that the [Ln] were particularly concentrated.

From the evidence presented in this thesis the Grennaites then began to fractionate with the Kaxtorpite potentially immiscibly separating and forming an F-rich amphibole cap to the intrusion. As the Grennaites fractionated, aegirine and catapleiite crystallisation enriched the overall [Ln]-content of the magma, with catapleiite crystallisation responsible for particularly enriching the fractionating melt in light-[Ln] producing the whole rock [Ln]-zonation observed within the intrusion. The pegmatites formed from the Pegmatite-Host Grennaite most likely as the magma became increasingly viscous and the remaining melt concentrated the original composition with little compositional fractionation occurring. The pegmatites may also have been aided in their formation by the development of areas of lower strain due to ongoing shearing within the increasingly viscous magma as the host shear zone continued to deform.

This continuing deformation may have then resulted in the intrusion of the Lakarpite into the eastern side of the cooling Pegmatite-Host Grennaite, with the consequent formation of the diffuse reaction contact between the Lakarpite and the Grennaites. The Pulaskite then intruded into the western portion of the Contact Grennaite, during which it disturbed the crystal mush from the lower portion of the chamber and brought it upwards as enclaves. The intrusion continued to cool and subsequently underwent N-S compression forming kink folds, and later on westerly rotation due to the opening of the Vättern graben.

Chapter 9

Conclusions and Economic Applications

9.1 Introduction

Providing an explanation for the formation of Norra Kärr and the development of light-[Ln] vs heavy-[Ln] zonation with the ore domains is important in order to improve the understanding of alkaline systems and is central to developing practical exploration strategies for [Ln]-deposits. This Chapter summarises the conclusions of this study, provides suggestions for future work and discusses the economic applicability of the study in relation to syenite hosted [Ln]-deposits.

9.2 Summary of Aims and Objectives

The aims of this study and the chapters in which they were addressed is given below:

1. To provide a full assessment of the structural history, petrological relationships and mineral compositions of Norra Kärr and its lithologies.

The structural history and field relationships were addressed in Chapter 2, providing a structural framework for data presented later. The petrological relationships and the mineral crystallisation sequence was addressed in Chapter 3 based upon optical observations; these results were used in later chapters to model the fractionation trends in relation to the crystallisation sequence. The wt% composition and mineral zonation from EPMA and SEM analysis of the minerals within all the lithologies of Norra Kärr were presented in Chapter 4 along with the ppm concentration of [Ln] presented from LA-ICP-MS.

2. To fully assess the major element, trace element and [Ln]-concentration trends within the different units and minerals of Norra Kärr.

The major element, trace element and [Ln]-concentration trends were addressed in Chapters 4, 5 and 6. The trends in volatile evolution were addressed in Chapters 4 and 7.

3. To model the formation of the different lithological units of Norra Kärr and their fractionation trends.

The formation of the different lithological units was modelled in Chapters 5, 6 and 7, with the fractionation trends in whole rock Zr/Hf addressed in Chapters 5 and 6 with the effect of mineral crystallisation also modelled in Chapter 7.

4. To provide the most comprehensive model for the formation of Norra Kärr and the zonation of light-[Ln] vs heavy-[Ln] within its ore domains, and to provide suggested future work and economic applications in light of this study.

Models for the structural and magmatic evolution of the intrusion were presented in Chapters 5, 6 and 7 along with an ore deposit model in Chapter 8 accounting for the development of the distribution of light-[Ln] vs heavy-[Ln] within the ore domains. Suggestions for further work and the economic applicability of this study are given later in this chapter (sections 9.4 and 9.5).

9.3 Findings and Conclusions

9.3.1 Structural History and Field Relationships

Chapter 2 summarised the tectonic history of Norra Kärr, outlined the field relationships of the units present within the intrusion and provided comparisons with the internal structure of other alkaline intrusions. The chapter introduced a new lithological nomenclature and subdivisions of the different units to better highlight their cryptic and petrological variations. This chapter showed that the Kaxtorpite can be better modelled as separate rafts of material sloughing off of an amphibole-rich cap; that the Pegmatite show a distinct 3D 'stockwork-like' structure; that the Lakarpite exhibits a potential reactive contact; and that the Pulaskite displays a sharp contact with the orientation of internal enclaves suggesting intrusion upwards from beneath the present land surface.

- From a new synthesis of the tectonic history of the area, Norra Kärr can be shown to have formed in an environment of syn-tectonic shear that was potentially able to tap low partial melts from a fertilised mantle wedge formed during the earlier Svenco-Fennian and Gothian Orogenies. It is also unlikely that Norra Kärr underwent any later isoclinal folding as only brittle/ductile heterogeneous foliation and lineation occurred in the TIB post-1570 Ma.

9.3.2 Petrology

The petrographical study in Chapter 3 provided the relationships between minerals within all lithologies at Norra Kärr and established the crystallisation sequence present within each subdivided unit. This highlighted the subtle petrological changes shown by the progressive Grennaite fractionation as well as the petrological differences between the different zones within the Lakarpite. The fabrics displayed by the different lithologies indicated the varying influence of shear upon different parts of the intrusion. While many of the petrographic textures exhibited by the minerals at Norra Kärr are comparable to other alkaline intrusions, the intrusion represents its own unique petrological character alongside a remarkable range of mineralogical and textural diversity.

- The magma at Norra Kärr appears to have evolved through a Fe-dominated phase (aegirine), followed by a Zr and volatile dominated phase and finally an Al (feldspathic) dominated phase. Further, the similar petrogenetic histories and the subsolvus feldspar textures throughout the intrusion indicate that almost all of the magmas cooled and evolved in a similar manner.
- The Zr and volatile dominated phase produced different phases (eudialyte, catapleiite, rosenbushite, fluorite) in such an order that may indicate the evolution of $a_{\text{H}_2\text{O}}$ and a_{HF} within the different magmas with the evolution of the Lakarpite being particularly complex.

9.3.3 Whole Rock Major, Trace and Lanthanoid Element Concentrations

The whole rock data presented in Chapter 5 significantly highlighted the presence of two separate phases of intrusion as showed by whole rock redox measurements and supported by field relationships and petrological evidence presented earlier. The first phase magma (the Grennaite and Kaxtorpite) shows a series of major and trace element patterns indicating that the Grennaite crystallised sequentially to form the Contact Grennaite, the Pegmatite-Host Grennaite, and finally the Crenulated Grennaite. Using this sequence the evolution of [Ln] within the fractionating Grennaite magma can be shown to be initially concentrated overall in [Ln] (Contact to Pegmatite-Host) before being depleted in heavy-[Ln] and enriched in light-[Ln]. Overall it appears that Norra Kärr is not enriched in heavy-[Ln] but is depleted in light-[Ln] suggesting that fractionation deeper in the system is responsible for the initial magmatic concentrations with local fractional crystallisation within the centre of the chamber responsible for the subtle cryptic variations. The second phase magmas (the Lakarpite and Pulaskite) appear to be less fractionated than the first phase, with the Lakarpite appearing to exhibit a Pulaskite-type core which changes to a more complex composition with proximity to its contact with the Pegmatite-Host Grennaite.

- Based upon field relationships, petrological differences and whole rock geochemistry, Norra Kärr can be understood to have been emplaced in at least two phases; the first phase being the more oxidised Grennaite and Kaxtorpite, the second phase being the more reduced Lakarpite and Pulaskite.
- The Norra Kärr magmas are both highly fractionated alkaline magmas lying at the end of the AFM and TAS fractionation trends. The magmas plot either side of the Phonolite minimum and their evolution is controlled by the Nep-Qz-Kal eutectic phase diagram.
- The sequence of Grennaite fractionation is Contact Grennaite, then the Pegmatite-Host Grennaite (with an overall increase in [Ln]), and finally the Crenulated Grennaite (with a depletion in heavy-[Ln] and an enrichment in light-[Ln]).
- The Lakarpite displays evidence of chemical/redox reaction with the Pegmatite-Host magma leading to the formation of diffuse chemical and petrological zones.

9.3.4 Mineral Composition and Zoning

Chapter 4 presented the mineral compositions and BSE-SEM textures of minerals from all the lithological units of Norra Kärr, along with EPMA/SEM-EDS maps of eudialyte from all units where it is present. Each of the minerals within the intrusion evidenced a separate part of the magmatic history. Aegirine compositions support the presence of two chemically different magmatic phases and indicate an initial magmatic fO_2 of FMQ +1 to -2 for both magmas. Compositional trends in both eudialyte and catapleiite support the Grennaite fractionation sequence presented in Chapter 5. Element maps of eudialyte also indicate the complex history of each individual eudialyte crystal which typically display Zr and Si rich cores and Mn and Cl rich rims. The compositions of amphibole and biotite both suggest that there was limited fractionation within the Kaxtorp, Pulaskite and Lakarp. The amphibole compositions also show that the pegmatites and the Kaxtorp are compositionally similar to each other, while the Lakarp exhibits a range of composition between the Kaxtorp and the Pulaskite supporting the presence of a reaction or mixing zone. While the final stage of feldspar and nepheline crystallisation occurred near the respective eutectic points of the Qz-Nep-Kal ternary thereby indicating low temperature crystallisation within both magmatic phases. Overall the mineral compositions from Norra Kärr are most similar (but certainly not identical) to the Pilanesberg intrusion, with the first phase of intrusion being similar to the Green Foyites, and the second phase of intrusion being similar to the White Foyites. These measurements presented in Chapter 4 also allowed for the development of a redox model for crystallisation within the two magmatic phases based upon that produced by Andersen et al. (2017) for Pilanesberg. This model showed that the difference in a_{H_2O} between the two magmatic phases could explain their differing mineralogies and that Zr-silicate saturation likely occurred at approximately 625°C.

- The initial magmatic fO_2 was FMQ +1 to -2. The pattern of mineral crystallisation that followed was partly influenced by the differences in a_{H_2O} and the a_{Nd} within each magma.
- Mineral compositions support: the presence of two magmatic phases; the sequence of Grennaite crystallisation presented in Chapter 5; the presence of a Lakarp reaction contact; that the Pulaskite is the least evolved of any of the Norra Kärr lithologies.
- Both nepheline and end member feldspar compositions indicate that the magmas crystallised at low temperatures near the respective feldspar and feldspathoid eutectics.
- The minerals from Norra Kärr display similarities to those from the Pilanesberg intrusion, with the first phase of intrusion being similar to the Green Foyites, and the second phase of intrusion being similar to the White Foyites.

9.3.5 Mineral [Ln]-Comparisons and Zr/Hf Ratios

Chapters 4 and 6 presented ppm concentrations of [Ln] alongside the whole-rock data and Zr and Hf concentrations from minerals from all lithologies from Norra Kärr. This data showed that of all the minerals eudialyte shows the closest match to the final whole rock [Ln]-pattern and appears to be recording the final [Ln]-composition of the fractionated melt. Catapleiite and aegirine generally show a preference for heavy-[Ln] over light-[Ln]. Calculated K_D values for aegirine match K_D values shown by aegirines produced experimentally by Beard (2018) thereby supporting his study. The data also allowed examination of the evolution of whole rock Zr/Hf ratios within the Grennaite through examination of mineral Zr/Hf ratios for each of the cryptic Grennaite units with aegirine playing a role in increasing the Zr/Hf ratio supporting a study by Kogarko (2016) which determined that aegirine crystallisation increased the Zr/Hf ratios with progressive magmatic fractionation in Lovozero.

- Aegirine and catapleiite are biased towards removing heavy-[Ln] from the melt, while eudialyte appears to record the overall [Ln]-pattern of a magma at the point at which it crystallises out due to the strong incorporation of all [Ln].
- Natural aegirine from Norra Kärr display similar K_D values for [Ln] as experimental aegirine supporting the experimental evidence that aegirine plays a role in enriching [Ln] within alkaline magmatic ore deposits.
- Aegirine is also able to increase the whole rock Zr/Hf ratio due to preferential uptake of Hf over Zr as previously shown for Lovozero. However, catapleiite tends to reduce the Zr/Hf ratio.

9.3.6 Volatile Modelling

The models presented in Chapter 7 show that each of the magmatic phases has its own trend in volatile evolution. The first magmatic phase was dominated by an initially high a_{H_2O} which then decreased resulting in catapleiite followed by eudialyte crystallisation. The second magmatic phase was dominated by an initially high a_{HF} leading to crystallisation of fluorite and rosenbushite. The Lakarpite exhibits a more complex history of volatile evolution with the core dominated by lower OH/F ratios (as indicated by the presence of fluorite and rosenbushite) and the outer zones dominated by a switch to increasing OH/F ratios (as evidenced by eudialyte and catapleiite crystallisation).

- The first magmatic phase is dominated by high a_{H_2O} while the second phase shows high a_{HF} . The whole rock volatile actives may be better understood in terms variation in OH/F and OH/Cl ratios.
- Aegirine is able to raise the volatile content by 10%-40% within the lithologies during closed crystallisation; a process which could drive the volatile evolution within the Grennaite.
- Modelling of biotite compositions have shown that the $\log(f_{H_2O}/f_{HF})$ was between 3.65-4.9

9.3.7 Geochemical Modelling

The results of the geochemical models in Chapter 5 further highlighted the complex evolution of Norra Kärr. Assimilation of the country rock was not a significant process during crystallisation, instead loss of elements to the fenite appears to be a more important factor on the final composition of the Contact Grennaite. The pegmatites can be shown to have formed from the Pegmatite-Host Grennaite due to the expulsion of concentrated liquid from the increasingly viscous host magma due to syn-tectonic shearing, a process supported by field relationships and whole rock and mineral chemistry (Chapters 3, 4, 5). The progressive compositional zonation Lakarpite can be shown to have formed through the interaction ('mixing') of a Pulaskite-type magma as it intruded into the still warm Pegmatite-Host Grennaite. The main driver of element fractionation is the order of mineral crystallisation. within the Grennaites aegirine crystallisation increases the Zr/Hf ratio and [Ln] content of the magma; subsequent catapleiite crystallisation results in a lowering of the magmatic Zr/Hf ratio but increases the La/Lu ratio while eudialyte acts to significantly remove [Ln] from the melt (though this order of Zr-silicate crystallisation is controlled by the trend in volatile evolution within the magma). The final stage of feldspar crystallisation drives the magma towards the eutectic composition on the Nep-Qz-Kal ternary.

- Modelling shows that aegirine is primarily responsible for enriching the magmas in Zr; and that aegirine-catapleiite co-crystallisation can also enrich the magmas in [Ln]. Catapleiite crystallisation is also able to enrich light-[Ln] over heavy-[Ln] within the melts.
- The trend of catapleiite then eudialyte crystallisation is able to generate the overall light-[Ln] enrichment observed within the Grennaites at Norra Kärr, a process only possible in a magma with a decreasing a_{H_2O} . If a magma is increasing in a_{H_2O} , then the resulting trend of eudialyte then catapleiite crystallisation results in a process of overall [Ln]-depletion.

9.3.8 Summary Models

A summary and synthesis of the of the models presented in this thesis were given in Chapter 8. These include the new lithological divisions for the intrusions, along with models for the emplacement and magmatic fractionation together with an overall ore deposit model. A reassessment of the model for the structural evolution of the intrusion was proposed in light of the new data involving intrusion as a dyke along an active shear zone. Many textures within the intrusion can be identified as being due to syn-magmatic shear without the need for a fold.

1. Norra Kärr represents a highly fractionated alkaline magma derived from partial melting of a fertilised mantle wedge developed between 1.8 Ga and 1.6 Ga. This magma may have been emplaced as a series of dykes in two magmatic stages within an active shear zone. This shear zone remained active post emplacement resulting in syn-magmatic deformation features developing within the intrusion.
2. The ore domains formed due to mineral-driven fractionation of an initially [Ln]-enriched melt. This fractionation was dependent upon the magmatic volatile activity causing catapleiite to form before eudialyte thereby driving the variation in La/Lu within the melt.

9.4 Recommendation for Future Work

This study has accounted for the overall structure and evolution of Norra Kärr and presented new models for its emplacement and fractionation, along with an ore deposit model which takes into account the variation in light-[Ln] vs heavy-[Ln] observed within the Grennaite. Suggestions for further exploratory, experimental and modelling work in light of the results presented in this thesis are given below:

1. Experimental evidence is required to further understand the relationship between the Grennaite (Green Foyite type) and Pulaskite (White Foyite type) magmas and whether there is the potential for these liquids to be generated through magmatic immiscibility. This would provide answers as to how the Grennaites become preferentially enriched and if element partitioning between the two liquids played a role.
2. The ternary phase diagram of Fe-Zr-Al could be experimentally derived in relation to redox and differing volatile contents as this system represents the evolutionary path of the Norra Kärr magmas.
3. The effect of aegirine crystallisation has been shown to raise the Zr/Hf ratio of a magma and enrich it in [Ln]. This effect could be modelled in relation to other alkaline magmas.
4. The effect on element enrichment and depletion within magmas can be modelled in relation to Zr-Silicate phase stability which is controlled by the relative activity of differing volatiles.
5. The process of forming an amphibole-rich cap to alkaline intrusions (the Kaxtorpite) from a Grennaite magma is not understood. Experimental evidence could provide answers as to the possible mechanism driving the element and volatile partitioning observed between the Grennaites and the Kaxtorpite.
6. The interaction between the Pulaskite and Grennaite magmas generated the Lakarpite. Experiments could seek to replicate this interaction and identify the redox effects and element partitioning which occurred.
7. Further exploratory drilling to deeper depths at Norra Kärr and of outcropping fennites elsewhere in the region should give a better understanding of the lower and upper parts of the chamber respectively.

9.5 Economic Considerations

Further Exploration at Norra Kärr

The ore resource model at Norra Kärr should be revisited to take into account the newly proposed structural model. It is possible that the Pegmatite-Host Grennaite may extend to a deeper depth and at a different location to that currently inferred by using the 'fold-model'. In light of the 'dyke-model' it may therefore be more voluminous. To fully test the dyke-model of emplacement drilling should be carried out to test the new model with the prediction that the Pegmatite-Host Grennaite extends to deeper depths at the southern end of the intrusion, and that the Pulaskite-type magmatic dykes would be encountered along with a potential second chamber at depth marking the deepest vertical extent of the ore body (assuming that it has not been sheared away by tectonic movement).

The regional exploration model could also be revised in light of this and could focus on exploring along the shear zones rather than targeting fold structures. Any outcrops of fenite should be mapped in relation to the surrounding structures. Initial drilling of targets may initially hit amphibole rich Kaxtorpite-like lithologies with the ore bearing domains hidden deeper below these caps.

General Exploration for Nepheline syenite hosted [Ln]-deposits

An exploration problem encountered at Norra Kärr was that it did not appear on gravity or magnetic surveys as if displayed similar geophysical characteristics as the surrounding Våxjö granites which comprise the country rock. Other nepheline-syenite hosted [Ln]-deposits are found in similar tectonic, structural and lithological environments. While the individual structural history of other granite provinces needs to be taken into account, it is suggested that exploration take place along and around known and inferred shear zones which may be detected by magnetic surveys; especially if the shear zones have been heatatised.

Once a prospective syenite or fenite has been found then initial drilling must be undertaken to the fullest vertical extent otherwise the depth of the prospective body would not be proven thus hampering efforts to construct an incontestable structural model and hence a reliable resource estimate.

An appreciation of the importance of the Zr-silicate phases in relation to the inferred structure of a prospective deposit must be made as this can inform a later drilling campaign with the Zr-silicate being used as an exploration tool. If the pattern of Zr-silicates is understood then ore-bodies can be better conceptualised. For instance, if an uneconomic catapleiite bearing unit is intersected by drilling and its place within the overall structure of the intrusive body is known then drilling could then target an area where a more residual part of the intrusion could lie or elsewhere in the intrusion where eudialyte would be predicted to have crystallised.

9.6 Final Comments

The aim of the project was to better understand the structural history, petrological relationships and mineral compositions of Norra Kärr and its lithologies, and to provide models for the evolution of the intrusion which account for the formation of the ore-bearing domains and the observed light-[Ln] vs heavy-[Ln] zonation within them.

This study has demonstrated through analysis and modelling that Norra Kärr was emplaced in two magmatic phases as a series of dyke intrusions. While the specific mechanisms of magmatic evolution and potential immiscibility or separation are not fully understood before the point at which Norra Kärr intruded, the first phase magmas were initially more enriched in [Ln] than the second phase magmas. The process by which the Kaxtorpite formed from the first magmatic phase is unknown but the development of amphibole caps above Grennaite (or other lithologies such as lujavrite or syenite) appears to be a common process.

This study has shown that the ore domains developed as a series of cryptic units within the Grennaites due to fractionation of the Grennaite-portion of the first magmatic phase. This progressive fractionation is displayed by subtle changes in petrography, mineralogy and through major and trace element patterns. The [Ln]-concentrations were shown to initially increase from the Contact Grennaite to the Pegmatite-Host Grennaite, before enriching in the light-[Ln] and depleting in the heavy-[Ln] as observed in the Crenulated Grennaite.

The second phase magmas (Pulaskite-type) display a different mineralogy to the first phase partially due to higher a_{HF} and a more reduced magmatic chemistry. These second phase magmas may have been emplaced due to the effects of ongoing shearing of the intrusion, with the Lakarpite developing its complex chemistry and petrology due to interaction with the still warm Pegmatite-Host Grennaite.

This study has demonstrated that a progressive increase in [Ln] within a melt is possible due to aegirine crystallisation and that the observed variation in light-[Ln] vs heavy-[Ln] within the ore-domains is due to catapleiite crystallisation. This study has also shown that the volatile evolution within a melt affects the magmatic evolution by dictating the order of Zr-silicate crystallisation. This order of Zr-silicate crystallisation acts to determine the potential grade of a deposit. If eudialyte crystallises first then the grade will decrease with fractionation, whereas if catapleiite crystallises first then the grade will increase with a bias towards the light-[Ln].

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APPENDIX 1 – Samples and Analytical Methods

A1.1 Samples

The full list of samples used in this study is given below in Table A1.1. Access to core samples and the filed site was kindly granted by Tasman Metals Ltd. Core locations are given in Fig. A1.1.

Lithology	Sample	Method Used			
		EPMA	LA-ICP-MS	XRF	Möss
Contact Grennaite	NK25-25.9	X		X	
Contact Grennaite	NK28-15.6			X	
Contact Grennaite	NK32-158.15	X	X	X	
Contact Grennaite	NK-47-139.00				X
Contact Grennaite	NK53-271.9			X	
Contact Grennaite	NK95-53.8	X		X	
Pegmatite-Host Grennaite	NK53-97.8	X	X		
Pegmatite-Host Grennaite	NK33-185.7			X	
Pegmatite-Host Grennaite	NK33-46.6			X	
Pegmatite-Host Grennaite	NK53-213.7			X	
Pegmatite-Host Grennaite	NK53-269.3	X	X		X
Pegmatite-Host Grennaite	NK62-122.3			X	
Pegmatite-Host Grennaite	NK95-181.1			X	
Pegmatite	NK25-49.4	X	X	X	
Pegmatite	NK32-131.5				
Pegmatite	NK32-146.9	X		X	
Pegmatite	NK33-204.65			X	
Pegmatite	NK46-36.7		X		
Pegmatite	NK53-174.3	X	X	X	
Pegmatite	NK53-230	X	X		
Pegmatite	NK-53-30.80				X
Pegmatite	NK62-173.2	X	X		
Pegmatite	NK62-207.2			X	
Crenulated Grennaite	NK82-7.55	X	X	X	
Crenulated Grennaite	NK32-69.30	X	X	X	
Crenulated Grennaite	NK25-146.2			X	X
Crenulated Grennaite	NK33-143.4			X	
Crenulated Grennaite	NK57-57.90			X	
Kaxtorpite	NK57-49.2	X		X	X
Kaxtorpite	NK25-138	X	X	X	
Kaxtorpite	NK33-139.1			X	
Kaxtorpite	NK57-10.70	X		X	
Kaxtorpite	NK57-27.30	X		X	
Lakarpite (Pulaskite-Type)	NK28-64.4	X		X	
Lakarpite (Pulaskite-Type)	NK57-116.7	X	X	X	
Lakarpite-(Core-Type)	NK57-107.3	X	X	X	

Lakarpite-(Core-Type)	NK-57-110.90				X
Lakarpite (Zr-Core-Type)	NK57-126.5	X	X	X	
Lakarpite (Zr-Rich-Type)	NK33-226.5	X	X	X	
Lakarpite (Zr-Rich-Type)	NK-62-317.08				X
Lakarpite (Zr-Rich-Type)	NK57-103.15	X			
Discovery Outcrop Sample	DISCOVERY	X	X		
Pulaskite	NK53-30.80	X	X		X
Pulaskite	NK53-297.9	X		X	
Pulaskite	NK62-73.6			X	
Pulaskite	NK62-73.9	X	X	X	
Pulaskite	NK95-37			X	
Pulaskite	NK95-41.9	X	X		
Pulaskite (Enclave Sample)	NK53-40.05	X	X	X	
Pulaskite (Enclave Sample)	NK62-86.3			X	
Pulaskite (Enclave Sample)	NK62-94.3	X	X		X
Pulaskite (Enclave Sample)	NK95-37			X	
Pulaskite (Enclave Sample)	NK95-41.9			X	

Table A1.1: List of Samples analysed in this thesis.

A1.2 Methods

The data for this thesis was collected using SEM, EPMA, Mössbauer spectroscopy and LA-ICP-MS using the methods described below.

A1.2.1 3D Modelling

3D modelling of the intrusion as presented in Chapter 2 was carried out in Edinburgh using Midland MOVE 2015.1. The base data (borehole data, map and cross-sections) were provided by Tasman Metals Ltd. and had been produced by Magnus Leijd and Johan Berg. Modelling at Edinburgh took this data and inputted into Midland MOVE and hand picked the horizons to create the model. Further work involved interpreting drill core images provided by Tasman Metals Ltd. to create a model of the Pegmatite horizons and possible 3D structure of the Kaxtorpite.

A1.2.2 Scanning Electron Microscopy (SEM-EDS)

SEM images were collected at Edinburgh University using a Carl Zeiss SIGMA HD VP Field Emission SEM. Secondary-Electron imaging utilised a SIGMA In-lens detector; Backscatter-Electron imaging utilised a 4-quadrant solid-state angle-selective backscatter (AsB) detector. Images were collected at 20 KeV and 70 µm aperture size.

A1.2.3 Electron Probe Micro-Analysis (EPMA)

EPMA data were collected at the Department of Earth Sciences at the University of Oxford using a CAMECA SX-5 FE electron microprobe, and at Edinburgh University using a CAMECA SX100 electron microprobe with a tungsten source. The beam settings for amphibole analysis was 15 KeV with a beam size of 10 µm. The standards used are listed in Table A1.2 below. La concentrations were also collected using EPMA and used as a check against the [Ln]-concentrations collected by LA-ICP-MS.

Figure A1.1: Map of the locations of drill cores sampled for this study. All drill holes dip at approximately 45° East, or for NK12082 - 45°south. Ticks along drill cores represent 25m intervals.

Element	Peak	Standard	Crystal	Sin θ	Wt%	I (nA)	HV
F	Ka	BaF2	TAP	71219	21.67	20	15
Fe	Ka	Andradite	LLIF	48080	20.37	20	15
Mn	Ka	Mn	LLIF	52186	100	20	15
Al	Ka	Albite	TAP	32458	10.34	20	15
Na	Ka	Albite	TAP	46267	8.61	20	15
Mg	Ka	MgO	TAP	38437	60.303	20	15
K	Ka	Orthoclase	PET	42758	13.44	20	15
Ca	Ka	Wollastonite	PET	38385	34.312	20	15
Cl	Ka	BaFCl	LPET	54050	18.48	-0.001	15
Ti	Ka	TiO2	LPET	31413	59.93	20	15
Si	Ka	Albite	TAP	27742	32.03	20	15

Table A1.2: Standards used during electron microprobe analysis of the Norra Kärr minerals.

A1.2.4 Mössbauer Spectroscopy

Mössbauer spectroscopy was undertaken at the University of Stirling to study the mineralogical composition of iron-bearing phases within each lithology. Eight samples were selected for analysis. Two from the Grennaite (one each from the northern and southern ends) were chosen to assess the overall homogeneity of the volumetrically larger Grennaite. Two samples were chosen from the Lakarpite (one from the inner Zr-poor zones and one from the outer Zr-rich zones) in order to assess any change in redox from the core to the contact of the Lakarpite intrusion. Samples were taken from halved core and ground using an agate pestle and mortar to a fine (<1 mm) powder in order to homogenise the coarser grained lithologies and to eliminate orientation effects during the Mössbauer analysis. These ground whole-rock samples were then sent to the Stirling Mössbauer Lab and a subsample of the material was then analysed. Samples were analysed with a miniaturized Mössbauer spectrometer MIMOS II (Klingelhöfer et al., 2003). Mössbauer spectra were collected at room temperature in backscattering geometry with a ^{57}Co in Rh matrix radiation source in constant acceleration mode. Spectra were calibrated against a measurement of $\alpha\text{-Fe(0)}$ foil (25- μm thickness) at room temperature. All spectrum fitting was carried out by Dr Christian Schröder at Stirling University. The analysis allowed for the bulk spectra of each mineral to be isolated and for the % Fe^{2+} and Fe^{3+} to be calculated.

A1.2.5 X-Ray Fluorescence Analysis

The majority of the whole-rock data was provided under NDA by Tasman Metals Ltd. Additional data was collected in Edinburgh. The analytical methods used for both sets of data are given below.

Data from Tasman Metals

Chemical data was collected from ICP-MS and XRF analysis bulk samples from crushed drill core. After recovery of the drill-core samples the cores were sent to the ALS Chemex laboratory in Sweden where it was cut into halves and subdivided into 2 m lengths. The half of the core to be used in the assay was then dried at 110-120°C and then crushed with either an oscillating jawcrusher or a roll crusher. A 250 g subsample of the homogenised crushed material was then obtained using a riffle splitter. This 250 g sample was then pulverised using a ring mill to a grain size of <75 μm .

Approximately 10-15 g of the pulverised sample was then analysed independently of Tasman Metals Ltd. by the ALS Chemex assay laboratory in Vancouver using the 'ME-MS81' method. A prepared 0.2 g sample was added to lithium metaborate flux (0.90 g), mixed well and fused in a furnace at 1000°C. The resulting melt was then cooled and dissolved in 100 mL of a solution containing 0.635 mol dm⁻³ HNO₃ and 1.332 mol dm⁻³ HCl. The resultant solution was then analysed by ICP-MS. Zirconium rich samples which exceeded the reporting limit of the ME-MS81 method (> 1%) were further assayed by XRF method 'ME-XRF10'. About 55 percent of the samples were re-analysed for Zr.

Data Collected at Edinburgh

Prior to XRF sample preparation, all samples were crushed to <50 µm grain size.

Powder pellets for major-element XRF: 8g ± 0.1g of crushed sample was mixed with 0.4 mL (8 'drops') of 2% PVA binder solution. The sample was then placed into an Al-pellet-cup and placed into an X-Press Automatic Press. The samples was pressed at 8-tonnes for 2 minutes with a 20 second release time.

Glass discs for trace-element XRF: Crushed samples were dried in an oven at 110°C for two hours. 0.95g (±0.01g) of sample was then placed into a Pt-Au crucible (assayed at 95%/5% Pt/Au content) which was then transferred to a 1100°C furnace for 20 minutes and covered with Pt-lids. The samples were then removed and reweighed in order to calculate the loss on ignition. Johnson and Matthey Spectroflux 105 (47% Li₂B₄O₇, 37% Li₂O, 16% of La₂O₃) was then added in a ratio of 1:5 sample:flux ratio. This mixture was fused at 1100°C furnace for 20 minutes then cooled at r.t.p. to form a glass. The sample was reweighed and additional flux added to return the sample to the 1:5 sample:flux ratio. The sample was then fused for a second time over a Meker-burner and homogenised. A glass disc was created by pouring the melt onto a graphite plate heated to 220°C on a hotplate and left to anneal at that temperature for 10 minutes. The discs were then transferred to a 110°C hotplate and for 10 minutes. The Pt/Au crucibles were subsequently cleaned using warm 6M HCl.

Samples were analysed for selected major and trace elements at the School of GeoSciences University of Edinburgh, using a Philips PW2404 wavelength dispersive sequential X-ray spectrometer fitted with an Rh anode end window X-ray tube. The XRF spectrometer was calibrated for major and trace element analysis using international standard samples. The concentrations for Nb and Zr are given by Jochum et al. (1990) with all other elements listed in Govindaraju (1994).

A1.2.6 LA-ICP-MS

Methods and Blank Correction

All LA-ICP-MS data was collected at the University of Edinburgh using a nu-instruments ATTOM high-resolution ICP-MS attached to an EXCIMER Laser ATLEX-LR-I(HV-SSP) (manufactured by ATL Lasertechnik GmbH). The software used for processing the ICP data was NuQuant version 1.0X AttoLab V2.11. Further information on the plasma settings within the ICP-MS are given in Table A1.3, and laser settings in Table A1.4. The isotopes monitored during analysis were: Fe⁵⁶, Y⁸⁹, Zr⁹¹, La¹³⁹, Ce¹⁴⁰, Pr¹⁴¹, Nd¹⁴⁶, Sm¹⁴⁷, Eu¹⁵³, Gd¹⁵⁷, Tb¹⁵⁹, Dy¹⁶³, Ho¹⁶⁵, Er¹⁶⁶, Tm¹⁶⁹, Yb¹⁷², Lu¹⁷⁵, Hf¹⁷⁸. The data was then processed by applying a blank correction. This was carried out by removing any analyses with

counts below five times the mean standard deviation of the starting blank analyses for each session. A drift correction was applied to these corrected counts by dividing them by a conversion factor calculated from the drift in counts obtained from the NIST 610 and NIST 612 standards.

Laser Ablation Pit Analysis

This study used NIST 610 and 612 glasses and a natural basalt standard BCR-2G. The concentrations of elements within the NIST glasses is reported by Pearce et al. (1997) and BCR-2G by the GeoReM database (Jochum et al. 2005). SEM images (Fig. A1.2) were collected to determine the backscatter contrast of the material and the morphology of the ablation trenches. The NIST glasses exhibit a homogenous backscatter response with all trenches observed within the NIST glasses displaying steep sided vertical edges and little sputtered material. To examine the depths of the pits the sections were angled at 42° within an SEM. The depth of the pits in NIST 610 are 11.86 µm and 14.77 µm (Fig. A1.2) and in NIST 612 9.21 µm, 12.82 µm and 16.83 µm (Fig. A1.2). The BCR-2G displays some heterogeneity in backscatter images; SE images show steep sided vertical edges but also evidence of unablated sputtered material.

Plasma Control		
Coolant: 13 L/min	RF Set Value: 1300	Ar Pressure: 52.1 PSI
Auxiliary: 0.9 L/min	Vac Cap Lightning Position: 2200	He Pressure: 1 PSI
Nebuliser: 30.1 PSI	Vac Cap Running Position: 2042	Air Pressure: 54.8 PSI
RF Forward Power: 1300 W		
RF Reflected Power: 6 W		
Ion Optics		
Source	Analyser	Detector
Acceleration: 5990	ESA Plates: 193.180	Multiple HT: -2977
Extraction: 2270	Vertical Deflector: 0	Discriminator: 0.353
Source V1: 44	Vertical Focus: 0	Dead Time: 11
Source H1: 57	Quad 1: 4	IC Deflector 1: -222
Focus: 4270	Quad 2: -11	IC Deflector 2: -183
Source V2: -65	Fast Scan Deflector: 0	Beam into Faraday: 240
Source H2: -17		Attenuation 1: 3
Transfer V: 0		Attenuation 2: -171
Transfer H:0		Attenuation 3: 177

Table A1.3: Plasma and ion-optics settings for the ICP-MS.

Laser Status	
Laser gas: ArF	Carrier Gas: He
Rep Rate: 15Hz	Energy Setpoint 3 mJ
Laser Energy: 50.1%	Pressure 6093 mbar
Aperture Slit: 100um x 100um	Voltage 0.99 Kv

Table A1.4: Instrument settings for the laser ablation system.

Figure A1.3 shows representative laser ablation pits within minerals from Norra Kärr. Ablation within aegirines typically results in a clean trench without sputtered edges. Ablation within feldspars typically results in a shallow trench indicating that the laser may not be coupling well with the material. Eudialyte and catapleiite ablate well with visible decrepitation occurring during analysis. The trenches within eudialyte have clean steep-sided edges. Trenches can include raised aegirine inclusions which appear to be unablated. Amphibole appears to ablate well but can display shallower trenches with occasional sputtering. Biotite does not appear to ablate well with sputter trails along the edges of the trenches often visible.

Figure A1.2: Laser ablation pits generated within the ablation standards used in this study. Red scale bar is equal to 100 μm.

Figure A1.3: Representative laser ablation pits generated within minerals from Norra Kärr. Red scale bar is equal to 100 μm. Note the variation in trench morphology across different minerals in the sample of Crenulated Grennaite.

EPMA Comparison

Fe And Zr were used as internal major element standards for the silicate and Zr-silicate minerals respectively. When compared to the EPMA data collected in Chapter 5 the drift-corrected LA-ICP-MS data for the silicate minerals showed lower than expected Fe, while the Zr-silicates displayed slightly higher than expected Zr. The ICP-MS detection programme resulted in some results with attenuated Fe and Zr values requiring careful sorting of the drift-corrected data. The silicate minerals were corrected using the ppm Fe content obtained via EPMA, while the Zr-silicates were corrected using Zr (eudialyte was corrected using both Fe and Zr due to higher concentrations of both elements). LA-ICP-MS analysis of experimentally grown aegirines by Beard (2018) also required a major element correction with Al being chosen in that case.

EPMA analysis could only provide reliable concentrations of La with the other Lanthanoids in either too low concentration or falling under a too high detection limit. The typical range of detection limits for La within silicate minerals ranged from 5-250 ppm La therefore the reported values may be selecting only the upper end of the actual range of La-concentrations. Other even numbered [Ln] could be detected with EPMA (particularly within eudialyte) but a full [Ln]-pattern could not be obtained.

When the La (ppm) concentrations obtained via EPMA are compared to those obtained via LA-ICP-MS, the latter technique appears to broadly underreport the [Ln] concentrations within the silicate minerals (Fig. A1.4). Within the aegirine, amphibole, and biotite concentrations of La are around 100-200 ppm lower than would be expected from EPMA. [Ln]-concentrations were within the feldspars were not detected by LA-ICP-MS, though this may be due to the ablation trenches being shallower due to the laser not coupling well with the material. However, the La concentrations obtained by LA-ICP-MS for the eudialyte reasonably match those obtained via EPMA. This suggests that the analyses of the Zr-silicates can be treated with confidence as reasonably accurately reflecting the [Ln]-makeup of the minerals. As the Zr-silicates play more of a role in the concentration of [Ln] and are several orders of magnitude more enriched in [Ln] than the silicates, any issues with the silicate analyses can be discounted as while the absolute numbers may be lower the relative patterns are likely to remain the same. This highlights the issues of using the same ablation setup for both Zr-silicate and silicate materials.

La (ppm) within silicate minerals as measured by EPMA. Not that the detection limit for La ranges from 50-250 ppm.

La (ppm) within silicate minerals as measured by LA-ICP-MS.

La (ppm) within rosenbushite and eudialyte minerals as measured by EPMA.

La (ppm) within rosenbushite and eudialyte minerals as measured by LA-ICP-MS.

Figure A1.4: *La (ppm) concentrations for minerals from Norra Kärr obtained via EPMA and LA-ICP-MS.*

APPENDIX 2 - NK Mineral Data (EPMA)

See Electronic Appendix

Electronic data tables for Aegirine, Amphibole, Pectolite, Rosenbushite, Sphene, Biotite, Catapleiite, Eudialyte, and Feldspars and Nephelines.

APPENDIX 3 - NK Mineral Data (LA-ICP-MS)

See Electronic Appendix

Electronic data tables for Aegirine, Amphibole, Pectolite, Rosenbushite, Sphene, Biotite, Catapleiite and Eudialyte.

APPENDIX 4 - NK Whole Rock Data (XRF)

See Electronic Appendix

Electronic data tables for whole-rock XRF analyses collected at Edinburgh.

APPENDIX 5 - Geochemical Pairs: Further Plots and Statistics

The abbreviations below are used in the statistical tables within this Appendix.

c – intercept on y-axis

m – gradient

$R^2(\%)$ – Explained variation / Total variation (0% indicates the model explains none of the variability, 100% indicates that the model explains all the variability of the response data around its mean.)

$R^2\text{-(adj)}(\%)$ - indicates how well terms fit a curve or line adjusted for the number of terms in a model.

S - the standard error of the regression

Niobium vs Tantalum

Fig. A5.1 shows the Nb/Ta values of main rock types at Norra Kärr. Overall there is a positive linear trend in the data suggesting that this geochemical pair is behaving as expected within a fractionating system. Individual rock plots are given in Fig. A5.2 and the statistical fit of the data in Table A5.1. The Grennaite and the Crenulated Grennaite show similar spreads of data as do the Kaxtorpите and Pulaskite. The Lakarpite and Pegmatite Domain display the largest ranges of Nb/Ta but both also display very tight statistical fits.

Figure A5.1: Nb vs Ta plot showing all data available for the main rock types at Norra Kärr.

Lithology	c	m	S	$R^2(\%)$	$R^2\text{-(adj)}(\%)$
Grennaite	-0.59	9.53	27.85	83.1	83.1
Grennaite-Peg	186.8	6.84	51.799	50.9	50.7
Pegmatite	160.2	11.4	116.24	62.1	62.1
Crenulated	44.79	12.24	68.28	39.3	39.3
Kaxtorpите	40.66	14.06	44.58	58.7	58.6
Lakarpite	64.54	14.69	127.13	88.4	88.3
Pulaskite	10.42	12.74	18.38	91.4	91.4

Table A5.1: Statistics by rock type for Nb vs Ta

Figure A5.2: Nb vs Ta plots for the main lithologies at Norra Kärr.

Zirconium vs Hafnium

Fig. A5.3 shows the Zr/Hf values of the main rock types at Norra Kärr. Overall there is a positive linear trend in the data suggesting that this geochemical pair is behaving as expected within a fractionating system. Individual rock plots are given in Fig. A5.4 and the statistical fit of the data in Table A5.2. The Grennaite, Lakarpite and Crenulated and Pegmatitic domains all display similar Zr/Hf ranges with the Kaxtorpите and Pulaskite displaying lower ranges. All data sets display good statistical fits and all appear to display close Zr/Hf ratios.

Figure A5.3: Zr vs Hf plot showing all data available for the main rock types at Norra Kärr.

Lithology	c	m	S	R ² (%)	R ² -(adj)(%)
Grennaite	37.91	0.0207	18.98	94.3	94.3
Grennaite-Peg	21.26	0.0208	38.74	54.6	54.4
Pegmatite	-1.41	0.0208	35.33	87.1	87.1
Crenulated	43.66	0.018	17.54	83.1	83.1
Kaxtorpите	5.45	0.0207	8.699	96.2	96.2
Lakarpite	-1.198	0.022	20.88	98.1	98.1
Pulaskite	1.696	0.023	5.86	98.6	98.6

Table A5.2: Statistics by rock type for Zr vs Hf

Figure A5.4: Hf vs Zr plots for the main lithologies at Norra Kärr.

Niobium vs Zirconium

Fig. A5.5 shows the Nb/Zr values of the main rock types at Norra Kärr. Individual rock plots are given in Fig. A5.6 and the statistical fit of the data in Table A5.3. Overall the behaviour of the Kaxtorp, Lakarp and Pulaskite is different to the Grennaite-related rocks. The former group all display different ranges in Nb/Zr values but they all exhibit straight line fits to the data. The Grennaite-related rocks however all display a wider spread of data with an initial increase in Nb concentration occurring and then declining with increasing Zr concentration. This suggests that there is some form of fractionation occurring, in this case it Nb-bearing eudialyte would likely be the cause of this. Zr-bearing mineral fractionation would move the magmas towards the left of the plots (likely caused by aegirine or aegirine-catapleiite crystallisation) which may explain the higher-Nb concentrations of the Pegmatite-Host Grennaite. Further fractionation by Nb-bearing eudialyte would then result in the depleted Nb observed within the Crenulated Grennaite. The wide spread of the pegmatites may be the result of input of fractionated melt from both the Pegmatite-Host and Contact Grennaites.

Figure A5.5: Nb vs Zr plot showing all data available for the main rock types at Norra Kärr.

Lithology	c	m	S	R ² (%)	R ² -(adj)(%)
Grennaite	54.89	0.00016	26.51	0.1	0.0
Grennaite-Peg	182.1	0.015	67.02	17.8	17.5
Pegmatite	387.5	0.007	185.899	3.1	3.1
Crenulated	48.7	0.022	74.57	27.7	27.6
Kaxtorp	47.62	0.287	33.56	76.6	76.6
Lakarp	-33.33	0.052	123.78	89	89
Pulaskite	17.23	0.025	33.95	70.8	70.7

Table A5.3: Statistics by rock type for Nb vs Zr

Figure A5.6: Nb vs Zr plots for the main lithologies at Norra Kärr.

Niobium vs Hafnium

Fig. A5.7. shows the Nb/Hf values of the main rock types at Norra Kärr. Individual rock plots are given in Fig. A5.8 and the statistical fit of the data in Table A5.4. Overall the patterns observed are similar to that of Nb/Zr.

Figure A5.7: Nb vs Hf plot showing all data available for the main rock types at Norra Kärr.

Lithology	c	M	S	R ² (%)	R ² -(adj)(%)
Grennaite	78.91	0.42	59.16	23.8	23.8
Grennaite-Peg	258.6	0.399	70.28	9.6	9.2
Pegmatite	400.1	0.33	186.13	2.9	2.8
Crenulated	105	0.74	81.86	12.8	12.8
Kaxtorpите	45.87	1.29	37.97	70.1	70
Lakarpите	-25.25	2.34	125.34	88.7	88.7
Pulaskite	16.01	1.08	33.92	70.9	70.8

Table A5.4: Statistics by rock type for Nb vs Hf

Figure A5.8: Nb vs Hf plots for the main lithologies at Norra Kärr.

Lead vs Zirconium

Fig. A5.9 shows the Pb / Zr values of the main rock types at Norra Kärr. Individual rock plots are given in Fig. A5.10 and the statistical fit of the data in Table A5.5. Overall the pattern amongst all of the rock types is broadly similar with the pattern of Pb concentration being reasonably symmetrically distributed either side of a mid-point of peak Pb concentration (albeit with some skewness towards lower Zr values). Similar patterns are seen for Pb/Hf and Pb/Nb.

Eudialyte is known to be Pb-bearing, so again a similar set of mineral-driven fractionations to Nb/Zr may well be happening here. The spike in Pb within the Crenulated Grennaite is similar to the spike in Cs and Ga (Figs. 5.25, 5.26) and is indicative of later stage concentration of these elements by earlier fractionation, and then continued fractionation within the Crenulated Grennaite itself.

Figure A5.9: Pb vs Zr plot showing all data available for the main rock types at Norra Kärr.

Lithology	c	m	S	R ² (%)	R ² -(adj)(%)
Grennaite	6.82	0.0052	69.58	7.1	7.1
Grennaite-Peg	239.3	-0.00082	162.9	0	0
Pegmatite	988.5	-0.024	614.4	2.8	2.8
Crenulated	334.9	-0.0002	214.51	0	0
Kaxtorp	64.1	0.031	135.598	18.9	18.9
Lakarp	13.44	0.021	260.64	23.3	23
Pulaskite	39.97	0.010	69.85	8	7.7

Table A5.5: Statistics by rock type for Pb vs Zr.

Figure A5.10: Pb vs Zr plots for the main lithologies at Norra Kärr.

Nickel vs Cobalt

Fig. A5.11 shows the Ni / Co values of the main rock types at Norra Kärr. Within the data there appears to be three different patterns. The Pulaskite and the Kaxtorpite both display straight line trends (with the Lakarpite partially following this trend as well); the Crenulated Grennaite and the Lakarpite both display two separate trends and the Grennaite and Pegmatite display low concentrations of both Ni and Co. Individual rock plots are given in Fig. A5.12 and the statistical fit of the data in Table A5.6.

Figure A5.11: Ni vs Co plot showing all data available for the main rock types at Norra Kärr.

Lithology	c	m	S	R ² (%)	R ² -(adj)(%)
Grennaite	-2.636	2.24	5.47	13.4	13.4
Grennaite-Peg	-4.018	1.58	2.3	12.8	12.5
Pegmatite	-3.91	0.84	3.37	2.6	2.5
Crenulated	-3.698	0.8817	4.7369	4.6	4.5
Kaxtorpite	-2.719	1.582	5.98952	55.8	55.7
Lakarpite	-2.052	1.806	10.4118	26.2	26.2
Pulaskite	-5.761	1.952	5.69966	64.8	64.8

TableA5.6: Statistics by rock type for Ni vs Co.

Figure A5.12: Ni vs Co plots for the main lithologies at Norra Kärr.

Manganese vs Iron

Fig. A5.13 shows the Mn/Fe values of the main rock types at Norra Kärr. Individual rock plots are given in Fig. A5.14 and the statistical fit of the data in Table A5.7. Each rock type seems to display a different pattern. The Grennaite and Pegmatite both have reasonably flat patterns with the Pegmatite showing higher concentration of Mn, this is likely indicating straightforward magmatic fractionation processes. The spikes in Mn within the Crenulated Grennaite and the Kaxtorpите may well be due to them representing the later fractionated liquids within the first magmatic phase at Norra Kärr. The Pulaskite displays a restricted range of Mn/Fe while the Lakarpite displays a linear trend with high Mn/Fe values possibly related to mass transfer with the Grennaites.

Figure A5.13: Mn vs Fe plot showing all data available for the main rock types at Norra Kärr.

Lithology	c	m	S	R ² (%)	R ² -(adj)(%)
Grennaite	176.3	0.019	211.756	42.3	41.5
Grennaite-Peg	5981	-0.098	167.73	87	82.7
Pegmatite	1442	0.015	754.17	6.5	4.3
Crenulated	-2448	0.014	857.72	30.3	27.7
Kaxtorpите	-591	0.17	2941.18	7	1.2
Lakarpite	-1615	0.11	895.399	77	75.7
Pulaskite	-841	0.06996	480.88	27.9	18.9

Table A5.7: Statistics by rock type for Nb vs Zr.

Figure A5.14: Mn vs Fe plots for the main lithologies at Norra Kärr.